

Molecular Physics Division Fachverband Molekülphysik (MO)

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Overview of Invited Talks and Sessions

(Lecture rooms f102 and f142; Poster Empore Lichthof)

Invited Talks

MO 7.1	Tue	11:00–11:30	f102	Monitoring ultrafast excited-state intramolecular proton transfer by ultrafast electronic and fluorescence spectroscopy — ●ANDREAS STEINBACHER, PRAMOD KUMAR VERMA, FREDERICO KOCH, ALEXANDER SCHMIEDEL, PATRICK NUERNBERGER, TOBIAS BRIXNER
MO 9.1	Tue	14:30–15:00	f102	Structural investigations on a linear depsipeptide and cyclopeptides by combined IR/UV spectroscopy: Importance of dispersion interactions — ANKE STAMM, DOMINIC BERNHARD, ●MARKUS GERHARDS
MO 15.1	Thu	11:00–11:30	f102	Imaging of an autoionizing resonance using time-, energy- and angular-resolved photoelectron spectroscopy. — MARTIN ECKSTEIN, CHUNG-HSIN YANG, FABIO FRASSETTO, LUCA POLETTI, GIUSEPPE SANSONE, MARC J. J. VRAKKING, ●OLEG KORNILOV
MO 16.1	Thu	11:00–11:30	f142	Vibrational spectra, structures, and chemical bonding of silicon hydride cluster cations — ●OTTO DOPFER
MO 16.2	Thu	11:30–12:00	f142	Far-infrared spectroscopy of metal cluster rare-gas complexes — DAVID YUBERO VALDIVIELSO, VALERY CHERNY, DENNIS PALAGIN, JOOST M. BAKKER, ●ANDRÉ FIELICKE
MO 21.1	Fri	11:00–11:30	f142	Rotational state thermometry of hydroxyl anions at the Cryogenic Storage Ring (CSR) — ●CHRISTIAN MEYER, ARNO BECKER, KLAUS BLAUM, CHRISTIAN BREITENFELDT, SEBASTIAN GEORGE, JÜRGEN GÖCK, MANFRED GRIESER, FLORIAN GRUSSIE, PHILIPP HERWIG, JONAS KARTHEIN, CLAUDE KRANTZ, HOLGER KRECKEL, SUNIL KUMAR, JORRIT LION, SVENJA LOHMANN, PREETI M. MISHRA, OLDŘICH NOVOTNÝ, AODH P. O'CONNOR, ROLAND REPNOW, KAIJA SPRUCK, STEFAN SCHIPPERS, DIRK SCHWALM, LUTZ SCHWEIKHARD, STEPHEN VOGEL, ROBERT VON HAHN, ANDREAS WOLF
MO 21.6	Fri	12:30–13:00	f142	Infrared Spectroscopy of mass/charge selected biomolecules in liquid helium droplets — ●GERT VON HELDEN

Invited talks of the joint symposium SYAD

See SYAD for the full program of the symposium.

SYAD 1.1	Tue	11:00–11:30	e415	Artificial gauge fields and topology with ultracold atoms in optical lattices — ●MONIKA AIDELSBURGER
SYAD 1.2	Tue	11:30–12:00	e415	Many-body physics with impurities in ultracold quantum gases — ●FABIAN GRUSDT
SYAD 1.3	Tue	12:00–12:30	e415	How to determine the handedness of single molecules — ●MARTIN PITZER
SYAD 1.4	Tue	12:30–13:00	e415	Quantum systems under gravitational time dilation — ●MAGDALENA ZYCH

Invited talks of the joint symposium SYML

See SYML for the full program of the symposium.

SYML 1.1	Wed	11:00–11:30	e415	Laboratory studies of interstellar molecules: from the first molecules to complex organics in space — ●HOLGER KRECKEL
SYML 1.2	Wed	11:30–12:00	e415	Detecting astrophysically relevant ions in laboratory and space — ●STEPHAN SCHLEMMER
SYML 1.3	Wed	12:00–12:30	e415	Interstellar ice - a hot topic — ●HAROLD LINNARTZ
SYML 1.4	Wed	12:30–13:00	e415	Exoplanets: The Thorny Path to Habitable Conditions — ●MANUEL GÜDEL
SYML 2.1	Wed	14:30–15:00	e415	Physics with keV Ion Beams in the Cryogenic Storage Ring CSR — ●ANDREAS WOLF
SYML 2.3	Wed	15:15–15:45	e415	A generalized theory for rovibrational motion in cold, extremely floppy molecules — ●HANNO SCHMIEDT, PER JENSEN, STEPHAN SCHLEMMER
SYML 2.6	Wed	16:15–16:45	e415	Lead-cluster investigations at ClusterTrap — STEPHAN KÖNIG, PAUL FISCHER, GERRIT MARX, ●LUTZ SCHWEIKHARD, MARKUS WOLFRAM, ALBERT VASS

Invited talks of the joint symposium SYBO

See SYBO for the full program of the symposium.

SYBO 1.1	Thu	11:00–11:30	e415	Recent advances of Optical Coherence Tomography — ●WOLFGANG DREXLER
SYBO 1.2	Thu	11:30–12:00	e415	Vortex-beams for precise and gentle dissection in refractive corneal surgery — ●ALFRED VOGEL, SEBASTIAN FREIDANK, NORBERT LINZ
SYBO 1.3	Thu	12:00–12:30	e415	Structured Illumination and the Analysis of Single Molecules in Cells — ●RAINER HEINTZMANN
SYBO 1.4	Thu	12:30–13:00	e415	Biophotonics - a potential solution to unmet medical needs!? — ●JUERGEN POPP
SYBO 2.1	Thu	14:30–15:00	e415	Smart and multimodal light sheet microscopy — ●JAN HUISKEN
SYBO 2.2	Thu	15:00–15:30	e415	Laser Applications at the Cochlea: Imaging and Stimulation — ●ALEXANDER HEISTERKAMP, NICOLE KALLWEIT, PETER BAUMHOFF, ALEXANDER KRUEGER, NADINE TINNE, HEIKO MEYER, ANDREJ KRAL, HANNES MAIER, TAMMO RIPKEN
SYBO 2.3	Thu	15:30–16:00	e415	Sculpted light landscapes for optical micro-manipulation — CHRISTINA ALPMANN, ALVARO BARROSO PENA, EILEEN OTTE, KATHRIN DIECKMANN, ●CORNELIA DENZ
SYBO 2.4	Thu	16:00–16:30	e415	Optogenetics: Lighting Up the Brain — ●GERO MIESENBOECK

Sessions

MO 1.1–1.8	Mon	11:00–13:00	f102	Quantum Control and Femtosecond Spectroscopy 1
MO 2.1–2.6	Mon	11:00–12:30	f142	Collisions, Energy transfer and ab initio Modelling
MO 3.1–3.8	Mon	14:30–16:30	f102	Electronic Spectroscopy 1
MO 4.1–4.6	Mon	14:30–16:00	f142	Cold Molecules & Helium Droplets 1
MO 5.1–5.7	Mon	17:00–18:45	f107	Atomic clusters I (with A)
MO 6.1–6.10	Mon	16:30–19:00	Empore Lichthof	Posters 1: Novelties in Molecular Physics: Femtosecond Spectroscopy
MO 7.1–7.7	Tue	11:00–13:00	f102	Femtosecond Spectroscopy 2
MO 8.1–8.8	Tue	11:00–13:00	f142	Experimental Techniques
MO 9.1–9.7	Tue	14:30–16:30	f102	Biomolecules and Photochemistry
MO 10.1–10.8	Tue	14:30–16:30	f107	Atomic clusters II (with A)
MO 11.1–11.19	Tue	16:30–19:00	Empore Lichthof	Posters 2: Novelties in Molecular Physics: Femtosecond Spectroscopy, Quantum Control, Electronic Spectroscopy, Biomolecules and Photochemistry
MO 12.1–12.4	Wed	11:00–13:00	e415	Symposium SYML: From First Molecules to Life (with MS)
MO 13.1–13.6	Wed	14:30–16:45	e415	Symposium SYML: Molecules and Ions in Isolation (with MS)

MO 14.1–14.22	Wed	16:30–19:00	Empore Lichthof	Posters 3: Novelties in Molecular Physics: Theory of Molecular Dynamics, Collisions and Energy Transfer, and Experimental Techniques
MO 15.1–15.8	Thu	11:00–13:15	f102	Femtosecond Spectroscopy 3
MO 16.1–16.7	Thu	11:00–13:15	f142	Molecular Clusters
MO 17.1–17.6	Thu	14:30–16:00	f102	Electronic Spectroscopy 2
MO 18.1–18.7	Thu	14:30–16:15	f142	The Modelling of Molecular Dynamics
MO 19.1–19.30	Thu	16:30–19:00	Empore Lichthof	Posters 4: Novelties in Molecular Physics: Femtosecond Spectroscopy, Molecular Clusters, Cold Molecules and Helium Droplets
MO 20.1–20.8	Fri	11:00–13:00	f102	Femtosecond Spectroscopy 4
MO 21.1–21.6	Fri	11:00–13:00	f142	Cold Molecules & Helium Droplets 2

Annual General Meeting of the Molecular Physics Division

Wednesday 13:00–13:30 e415

MO 1: Quantum Control and Femtosecond Spectroscopy 1

Time: Monday 11:00–13:00

Location: f102

MO 1.1 Mon 11:00 f102

Controlling the ultrafast relaxation dynamics of uracil: A theoretical study — ●DANIEL KEEFER¹, SEBASTIAN THALLMAIR¹, SPIRIDOULA MATSIKA², and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, LMU München — ²Department of Chemistry, Temple University, Philadelphia, USA

The RNA nucleobase Uracil exhibits ultrafast relaxation dynamics after optical excitation to the second electronically excited state S2 (first bright state) [1]. With the constantly increasing capabilities of experimental pulse shaping techniques at hand, it is an obvious question how the dynamics of such a biologically relevant molecule can be influenced. We will give theoretical insights on this issue by designing laser pulses with the help of quantum optimal control theory (OCT).

The 2D potential energy surface for the S2 state of Uracil exhibits a double well structure and contains a conical intersection (CoIn) seam. After excitation to the S2 state, the nuclear wave packet evolves via a local minimum to the CoIn seam, and subsequently relaxes to the S1 state. This relaxation process happens on the femtosecond timescale. We optimized laser pulses to influence the ultrafast dynamics in two extreme ways: One goal was to directly steer the wave packet to the conical intersection seam, and thereby to shorten the time for relaxation to the ground state. Another optimization aim was to keep the wave packet in the S2 state as long as possible by trapping it in the local minimum and potentially prevent relaxation via the CoIn seam.

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

MO 1.2 Mon 11:15 f102

Rydberg contributions in angular dependent strong field ionization — ●ROBERT SIEMERING¹, BETHANY JOCHIM², MOHAMMAD ZOHRABI², ALEKSEY VOZNYUK⁴, JACOB MAHOWALD⁴, DYLAN SCHMITZ⁴, KELSIE BETSCH², BEN BERRY², TRAVIS SEVERT², NORA KLING^{2,3}, TIM BURWITZ⁴, KEVIN CARNES², MATTHIAS KLING^{2,3}, ITZIK BEN-ITZHAK², ERIC WELLS⁴, and REGINA DE VIVIE-RIEDLE¹ — ¹Ludwig-Maximilians-Universität, München, Germany — ²J.R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, KS 66506 USA — ³Max Planck Institute of Quantum Optics, Garching, Germany — ⁴Department of Physics, Augustana University, Sioux Falls, SD 57197 USA

Much of our intuition about strong-field processes is built upon studies of diatomic molecules which have electronic states that are relatively well separated in energy. In polyatomic molecules, however, the electronic states are closer together, leading to more complex dynamics. We investigate experimentally and theoretically the strong-field ionization followed by hydrogen elimination for the hydrocarbon series C₂D₂, C₂D₄, and C₂D₆. Our findings suggest that one has to take into account the shape of the field dressed orbitals rather than the field free orbitals in order to interpret the experimental measurements. The Rydberg character contribution to these field dressed orbitals in strong-field ionization has to be considered to explain the photofragment angular distribution. This improved understanding can facilitate efforts at image-based strong-field coherent control.

MO 1.3 Mon 11:30 f102

Controlling the dynamics of chemical reactions with tailored laser fields — ●ROBERT SIEMERING¹, MATTHIAS KÜBEL², CHRISTIAN BURGER², NORA KLING², HUI LI², BORIS BERGUES², ALI ALNASAR³, ITZIK BEN-ITZHAK⁴, MATTHIAS KLING², and REGINA DE VIVIE-RIEDLE¹ — ¹Ludwig-Maximilians-Universität, München, Germany — ²Max Planck Institute of Quantum Optics, Garching, Germany — ³Physics Department, American University of Sharjah, POB26666, Sharjah, UAE — ⁴J.R. Macdonald Laboratory, Physics Department, Kansas-State University, Manhattan, KS66506, USA

The rearrangement of hydrocarbon bonds is a ubiquitous process in chemical reactions related to biology, combustion, and catalysis. Thus, the ability to control the movement of nuclei with tailored light within a hydrocarbon molecule holds promise for far-reaching applications. We demonstrate by experiment and theory the steering of deprotonation from symmetric acetylene molecules and of hydrogen migration in simple hydrocarbons, namely acetylene and allene, using waveform-controlled, few-cycle laser pulses. The rearrangement dynamics are monitored using coincident 3D momentum imaging spectroscopy, and

described with a quantum-dynamical model. Our observations reveal that the underlying control mechanism is due to the manipulation of the phases in a vibrational wavepacket by the intense off-resonant laser field. This mechanism permits control over the directionality of chemical reactions via vibrational excitation on timescales defined by the subcycle evolution of the laser waveform.

MO 1.4 Mon 11:45 f102

Nuclear spin coherence in the positively charged Nitrogen-Vacancy center in diamond — ●HELMUT FEDDER¹, SINA BURK¹, MATTHIAS PFENDER¹, NABEEL ASLAM¹, SEBASTIAN ZAISER¹, PHILIPP NEUMANN¹, ANDREJ DENISENKO¹, PATRICK SIMON², JOSÉ GARRIDO², MARTIN STUTZMANN², MARCUS DOHERTY³, NEIL MANSON³, AUDRIUS ALKAUSKAS⁴, and JÖRG WRACHTRUP¹ — ¹3. Physikalisches Institut, Uni Stuttgart — ²Walter Schottky Institut, TU München — ³Australian National University, Canberra, Australia — ⁴Center for Physical Sciences and Technology, Lithuania

Electron and nuclear spins associated with point defects in semiconductors are promising systems for solid state quantum technologies with applications in quantum information processing and quantum sensing. In a typical quantum register architecture, an electron spin is used as an ancilla for readout and control, whereas nuclear spins serve as register qubits [1-2]. Flip-flop processes of the electron spin limit the nuclear spin coherence time. This limitation can be overcome by controlling the defect's ionization state. Here we increase the coherence time of the ¹⁴N nuclear spin associated with the Nitrogen-Vacancy center in diamond by controlling its charge state. We exploit planar double junction diodes fabricated by surface transfer doping with hydrogen [3] to rapidly switch the charge state from NV⁻ (S=1) to NV⁺ (S=0). We verify the NV⁺ state by nuclear magnetic resonance and demonstrate the enhancement of the ¹⁴N coherence time. [1] Saeedi et al., *Science* **342**, 830 (2013). [2] P.C. Maurer et al., *Science* **336**, 1283 (2012). [3] M. Hauf et al., *Nano Lett.* **14**, 2359 (2014)

MO 1.5 Mon 12:00 f102

Femtosecond dynamics of isolated radicals in the gas phase — ●ANJA ROEDER¹, LIONEL POISSON², and INGO FISCHER¹ — ¹University of Wuerzburg, Am Hubland Süd 97074 Wuerzburg, Germany — ²EA, Laboratoire Francis Perrin-Bât 522 91191 Gif-sur-Yvette, France

Radicals are important intermediates in combustion processes and in the formation of polyaromatic hydrocarbons (PAHs), a precursor to soot. The benzyl radicals were produced from nitrite precursors via pyrolysis and subsequently expanded in a molecular beam. Using femtosecond pump-probe spectroscopy the lifetimes of their excited states were examined via photoelectron spectroscopy and mass spectroscopy. The benzyl radical was excited in the D5 state using 266 nm and ionized with either a 800 nm or the BBO-doubled 400 nm probe pulse. The dynamics of the D5-state was examined using time-resolved mass spectra and time-resolved photoelectron spectra. The results obtained can be understood in framework of the calculations performed by the group of R. Mitric (Wuerzburg), in which the initial populated D5 state decays quickly via the D4 to the D3 state (short time constant), which decays more slowly to the D1 state (long time constant).

Acknowledgements: Roland Mitric

MO 1.6 Mon 12:15 f102

Time-resolved Circular Dichroism Spectroscopy of Hemoglobin — ●HEIKO HILDENBRAND, ANDREAS STEINBACHER, FEDERICO KOCH, MARCO SCHMID, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Circular dichroism (CD) is a common technique to analyze chiral samples. However, the typically utilized long optical path lengths, high concentrations, and long integration times in the steady state are not suitable for ultrafast spectroscopy. Hence, only few chirality-sensitive spectroscopic approaches in the liquid phase are known in the literature [1].

Here, we present broadband time-resolved CD spectroscopy which is based on a setup capable of mirroring an arbitrary polarization state of an ultrashort laser pulse. Hence, by passing a broadband probe pulse through this setup we can switch between opposite handedness on a shot-to-shot basis to detect pump-induced CD changes. To demon-

strate the capabilities of this approach we investigated the early photochemistry of oxygenated hemoglobin and myoglobin by time-resolved circular dichroism and transient absorption spectroscopy in the visible spectral region, since the spectrometer is also capable of acquiring both signals simultaneously.

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

MO 1.7 Mon 12:30 f102

Capturing Charge Transfer Dynamics at Dye - Semiconductor Interfaces by Means of Ultrafast XUV Photoelectron Spectroscopy — ●MARIO BORGWARDT¹, MARTIN WILKE¹, LEONE SPICCIA², KATHRIN M. LANGE³, IGOR YU. KIYAN¹, and EMAD F. AZIZ¹ — ¹Institute of Methods for Material Development, Helmholtz-Zentrum Berlin, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany — ²School of Chemistry and ARC Centre of Excellence for Electromaterials Science (ACES), Monash University, Clayton 3800, VIC, Australia — ³Institute of Solar Fuels, Helmholtz-Zentrum Berlin, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany

We present time-resolved XUV photoelectron spectroscopy as a tool to investigate the ultrafast charge transfer processes at the interface between Ru polypyridyl complexes and various semiconductor nanoparticles. To monitor the electron density distribution among the ground as well as the excited states at the interface XUV light from high-order harmonic generation is used as a probe after exposure with a pump laser pulse in the visible wavelength range. With this approach, we identified for the first time directly the absolute binding energies of the involved charge-transfer states and could provide a comprehensive characterization of the analyzed interfaces. [1] The advantage of studying simultaneously injection kinetics and the electronic structure will

be discussed and an outlook for future applications of this method in view of other promising energy related materials will be presented.

[1] Borgwardt, M. et al. *J. Phys. Chem. C* 2015, 119 (17), 9099-9107.

MO 1.8 Mon 12:45 f102

Wavelength dependence of Photoelectron Circular Dichroism in Femtosecond Multiphoton Ionization — ●ALEXANDER KASTNER, STEFANIE ZÜLLIGHOVEN, TOM RING, CRISTIAN SARPE, CHRISTIAN LUX, ARNE SENFLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

The asymmetry of photoelectron angular distributions (PADs) from randomly oriented enantiomers of chiral molecules in the ionization with circularly polarized light arises in forward/backward direction with respect to the light propagation. This effect was termed Photoelectron Circular Dichroism (PECD) and so far investigated using synchrotron radiation [1]. We observed highly structured asymmetries in the range of $\pm 10\%$ on bicyclic Ketones [2, 3]. Due to the multi photon ionization (MPI), high order Legendre polynomials appear in the measured PADs. In the case of Resonance Enhanced MPI (REMPI) using femtosecond laser pulses, the observed Legendre polynomial distribution is determined through the intermediate resonance and can be influenced by the laser wavelength. In this contribution we show our recent findings on wavelength dependence of the PECD effect of bicyclic Ketones.

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

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

[3] C. Lux et al., *Chem. Phys. Chem*, DOI: 10.1002/cphc.200 (2015)

MO 2: Collisions, Energy transfer and ab initio Modelling

Time: Monday 11:00–12:30

Location: f142

MO 2.1 Mon 11:00 f142

Studying competing reaction pathways in $F^- + CH_3I$ using 3D velocity map imaging — ●TIM MICHAELSEN, EDUARDO CARRASCOSA, JENNIFER MEYER, BJÖRN BASTIAN, MARTIN STEI, and ROLAND WESTER — University of Innsbruck, Austria

We study ion-molecule reactions in a kinematically complete way using velocity map imaging in a crossed-beam setup [1,2]. A major focus of our group are substitution reactions of halide anions with methyl halides. Due to a fruitful collaboration between theory and experiments a lot of insight into the mechanics of these S_N2 reactions was gained [3]. Beyond these, at sufficiently high collisional energies and entrance geometries other reaction channels become available and we will focus on these here. Specifically, we present in this talk the reaction of $F^- + CH_3I$ where we observed three additional reaction pathways: the proton transfer forming CH_2I^- , the formation of IF^- via halogen abstraction and first evidence of a $[FHI]^-$ product ion [4].

Furthermore we report on the latest results on a study of the transition between predominantly substitution (S_N2) driven reactions to elimination (E2) driven ones. This was realized by measuring the energy and angle differential cross sections for reactions between different halide ions (Cl^- , F^-) and methyl halides of subsequent degree of methylation at multiple collision energies.

[1] J. Mikosch et al., *Science* 319, 183 (2008) [2] S. Trippel, et al., *PRL* 110, 163201 (2013) [3] R. Otto et al., *Nat. Chem.* 4.7 534 (2012) [4] E. Carrascosa et al., submitted to *JPC* (2015)

MO 2.2 Mon 11:15 f142

Incoherent photoelectron scattering in above threshold ionization of dense media — ●MARTIN WILKE, RUBA AL-OBAYDI, IGOR YU. KIYAN, and EMAD F. AZIZ — Institute for Methods for Material Development and Joint Ultrafast Dynamics Lab in Solutions and at Interfaces (JULiq) at Helmholtz-Zentrum Berlin, and Freie Universität Berlin, FB Physik, Berlin, Germany

We report on how the typical cutoff laws of fast electron emission by high-intensity ionization processes of single molecules as above-threshold ionization (ATI) and high-order ATI (HATI) can be substantially violated by laser-assisted electron scattering (LAES) on neighboring molecules. Such collective effects occur during the ionization process on the time scale of few laser cycles (40 fs at 1300 nm) in dense media. Above a certain density threshold electron heating by inelastic

scattering even dominates the fast photoelectron emission by strong laser fields. Recording photoemission spectra in UHV and providing gas densities of a few millibars and liquids as target is enabled by the liquid micro-jet technique. A study of strong field ionization for different densities and solvents in gas and liquid phase was performed and supported by numerical calculations.

MO 2.3 Mon 11:30 f142

Autofragmentation of rovibrational excited metal dimer anions — ●JÜRGEN GÖCK¹, ARNO BECKER¹, KLAUS BLAUM¹, CHRISTIAN BREITENFELDT^{1,2}, SEBASTIAN GEORGE¹, 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, OLDRICH NOVOTNY¹, AODH P. O'CONNOR¹, ROLAND REPNOW¹, KAIJA SPRUCK^{1,3}, STEFAN SCHIPPERS³, DIRK SCHWALM^{1,4}, 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 — ⁴Weizmann Institute of Science, Rehovot 76100, Israel

The autofragmentation of Co_2^- and Ag_2^- ions was investigated over times up to 1000 s in the Cryogenic Storage Ring (CSR) [1] at the MPIK. The 35 m circumference electrostatic storage ring is operated at cryogenic temperature using liquid helium as cooling agent. The cryogenic environment of below 10 K leading to a residual gas pressure of lower than 10^{-13} mbar room temperature equivalent offers perfect conditions for background-free gas phase spectroscopy experiments. The rovibrationally excited anions were produced in a metal ion sputter source, accelerated to 60 keV and stored in the CSR. The neutral and charged fragments of the reaction $X_2^s \rightarrow X^- + X$ were recorded by micro channel plate based detectors [2]. Results and analysis will be presented. A coincidence signal from auto dissociation of the anions was observed as function of the storage time up to 1000 s. The non-exponential nature of the decay will be presented and compared to earlier short-time measurements [3]. [1] R. von Hahn et al., *Nucl. Instrum. Meth. B* 269, 2871 (2011) - [2] K. Spruck et al., *Rev. Sci. Instrum.* 86, 023303 (2015) - [3] J. Fedor et al., *Phys. Rev. Lett.* 94, 113201 (2005)

MO 2.4 Mon 11:45 f142

Theoretical Photoelectron Spectroscopy: Unravelling Ultrafast Spin-Crossover Transitions — ●GILBERT GRELL¹, SERGEY I. BOKAREV¹, SAADULLAH G. AZIZ², and OLIVER KÜHN¹ — ¹Universität Rostock, Institut f. Physik, Albert Einstein Straße 23-24, 18059 Rostock, DE — ²King Abdulaziz University, Chemistry Department, Faculty of Science, 21589 Jeddah, Saudi Arabia

Recently, we have demonstrated the ability of the RASSCF/RASSI method together with a Dyson orbital formalism to accurately predict the L-edge photoelectron spectra (PES) of aqueous transition metal complexes [1]. Key features of this methodology are the account for the multiconfigurational character (RASSCF), the inclusion of spin-orbit coupling (RASSI), as well as the accurate numerical evaluation of the PES intensities. This contribution focuses on the application of the protocol to interpret VIS pump / XUV photoelectron probe experiments that regard the spin-crossover (SCO) transitions on $[\text{Fe}(\text{bpy})_3]^{2+}$. We will provide a clear understanding of the actual SCO pathway, thus closing the open questions that arise from contradicting experimental results [2-4].

We acknowledge financial support by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah (Grant No. D-003-435), and the DFG (Grant No. KU952/10-1)

- [1] Grell et al., J. Chem. Phys. 143, 074104 (2015)
- [2] Zhang et al., Nat. 509, 345 (2014)
- [3] Auböck and Chergui, Nat. Chem. 7, 629 (2015)
- [4] Sousa et al., Chem. Eur. J. 19, 17541 (2013)

MO 2.5 Mon 12:00 f142

Natural extension of Hartree-Fock through extremal 1-fermion information — ●CARLOS L. BENAVIDES-RIVEROS — Martin-Luther-Universität Halle-Wittenberg, 06120 Halle (Saale), Germany

Fermionic natural occupation numbers (NON) do not only obey Pauli's exclusion principle but are even stronger restricted by so-called generalized Pauli constraints. Whenever given NON lie on the boundary of the allowed region the corresponding N-fermion quantum state has a significantly simpler structure. By employing this structure a variational optimization method for few fermion ground states is elaborated.

We quantitatively confirm its high accuracy for systems with the vector of NON in a small distance to the boundary of the polytope. In particular, we derive an upper bound on the error of the correlation energy given by the ratio of the distance to the boundary of the polytope and the distance of the vector of NON to the Hartree-Fock point. As a consequence, the proposed method is the computationally cheapest covering the leading order correlations for systems exhibiting the recently found quasipinning phenomenon. Moreover, these geometric insights shed some light on the concept of active spaces, correlation energy, frozen electrons and virtual orbitals.

MO 2.6 Mon 12:15 f142

Mechanism of Forward and Backward Scattering and Modification of the Polanyi rule for reaction $\text{A}+\text{BC}\rightarrow\text{AB}+\text{C}$ and $\text{AC}+\text{B}$ — ●VICTOR WEI-KEH CHAO — Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 80778, Taiwan, R.O.China — Group 1101, State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P.R.China — Victor Basic Res. Labor. e.V. 33602 Bielefeld, Germany

The Polanyi rule - The reactive cross sections can be enhanced with transl. and vibr. prepared BC on the early and late barrier PESs, respectively, has contributed immensely over 60 years. Results of $\text{H}+\text{FCl}(\text{v},\text{j})\rightarrow\text{HF}+\text{Cl}$ and $\text{HCl}+\text{F}$ at $E_{\text{rel}}=0.5\text{-}20$ kcal/mol show, considerations of 1. Mass combination of A, B and C, 2. Width and steepness of the entrance channel, 3. Space on the barrier top, are necessary. The entrance channel is very steep and narrow (For HCl is ca.3 times wider), and barrier top for HF (For HCl is ca.5 times wider) is very small compared with the bond length of FCl, whatever cause both transl. and vibr. enhancement on the early barrier PESs. Appearance of max. of curvature $\sigma_{\text{AB-VBC}}$ can be similarly explained. The forward and backward scattering mechanism can also be clarified. The nascent, light AB (HF) and heavy C (Cl) will be forwards and backwards scattered, respectively, on the barrier top because of the exoergicity and mass ratio $\text{AB}/\text{C} < 1$; heavy AC (HCl) and light B (F) backwards and forwards, with $\text{AC}/\text{B} > 1$. Support of financial aids by Section 11, DICP, CAS (KF-2013-01, KF-2014-01), and VBR are acknowledged.

MO 3: Electronic Spectroscopy 1

Time: Monday 14:30–16:30

Location: f102

MO 3.1 Mon 14:30 f102

Theoretical soft X-ray spectroscopy from time correlation functions — ●SVEN KARSTEN, SERGEY BOKAREV, SERGEI IVANOV, and OLIVER KÜHN — Institut für Physik, Universität Rostock, Rostock

Soft X-ray spectroscopy can reveal element-specific information about the electronic structure of an absorbing atom and its interactions with the local environment. The interpretation of experimental X-ray spectra requires a detailed theoretical consideration of the core-excited electronic states. Conventionally, the electronic spectra are obtained via single point calculations combined with phenomenological broadening. A more realistic account of vibrational and environmental effects is commonly provided by an incoherent sampling of molecular dynamics (MD) trajectories. However, this completely neglects nuclear dynamical correlations. In the present contribution such correlations are included via a rigorous reformulation of X-ray absorption spectra (XAS) and resonant inelastic X-ray scattering spectra (RIXS) in terms of transition dipole correlation functions. The time evolution is provided by ground state (ab initio) MD simulations. Performing DFT or RASSCF static point calculations for each MD snapshot yields, upon tracing the entire manifold of relevant electronic levels, all necessary ingredients. The success of the proposed methodology is exemplified for oxygen K-edge XAS and RIXS of bulk water which provides insight into H-bond dynamics.

MO 3.2 Mon 14:45 f102

Electronic Spectra of 2- and 3-Tolunitrile in the Gas Phase — ●FELIX GMEREK, JOSEFIN WILKE, MARTIN WILKE, BENJAMIN STUHLMANN, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Düsseldorf, Germany

The electronic structures of tolunitriles find considerable interest, be-

cause they are prototypes for small aromatic push-pull systems containing an electron pushing methyl-group and an electron pulling nitrile-group.

Therefore, we investigated the structure of 2- and 3-tolunitrile by combining the results of single vibronic level fluorescence (SVLF) spectroscopy^[1] and rotationally resolved laser induced fluorescence (HRLIF) spectroscopy^[2], which allows us to determine the structural changes upon electronic excitation, *via* a combined Franck-Condon/rotational constants fit with unique accuracy.

Additionally, the torsional barriers of the methyl groups, determined *via* SVLF and HRLIF spectroscopy, respectively, have been used as a probe for the structural changes upon electronic excitation for both molecules.

[1] J. A. Ruiz-Santoyo, J. Wilke, M. Wilke, J. T. Yi, D.W. Pratt, M. Schmitt, L. Álvarez-Valtierra, JCP, 2015, submitted

[2] F. Gmerek, B. Stuhlmann, L. Álvarez-Valtierra, D. W. Pratt, M. Schmitt, JCP, 2015, submitted

MO 3.3 Mon 15:00 f102

Electronic Stark measurements with rotationally resolved laser induced fluorescence spectroscopy — ●JOSEFIN WILKE, MARTIN WILKE, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

High resolution laser induced fluorescence spectroscopy can be used to assign the electronic nature of electronically excited singlet states to be 1L_a and 1L_b states in the nomenclature of Platt. Therefore, several molecular parameters like the orientation of the transition dipole moment, the changes of the bond lengths, or the frontier orbital contribution upon excitation are needed to determine the electronic nature. Also the permanent electric dipole moment of the ground and the first excited states can be used for the assignment, because the 1L_a state

has a larger permanent dipole moment than the unpolar 1L_b state. Therefore, a homogeneous electric field is needed, which lifts up the M degeneracy by the Stark effect. By changing the polarization of the excitation light from parallel to perpendicular related to the orientation of the electric field different field configurations which are linked to the selection rules $\Delta M=0$ and $\Delta M=\pm 1$ can be measured. In this talk recent results for the permanent dipole moments of planar substituted indoles will be presented.

MO 3.4 Mon 15:15 f102

Experimental study of the conformational space of a neurotransmitter: Serotonin — ●MARTIN WILKE¹, JOSEFIN WILKE¹, CHRISTIAN BRAND², and MICHAEL SCHMITT¹ — ¹Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf — ²Faculty of Physics, University of Vienna, Austria

The conformational space of the neurotransmitter serotonin (5-hydroxytryptamine) has been studied in the ground and the first electronically excited state, using a combination of rotationally resolved electronic spectroscopy and *ab initio* theory. On the basis of the rotational constants, the excited state life times and the orientations of the transition dipole moments four conformers can be assigned. Furthermore a characteristic change of 230 cm^{-1} was observed experimentally between the excitation energies of the Gpy(out)/*anti* and Gpy(out)/*syn* conformer. Changing the orientation of the ethyl amine side chain towards the Phenyl moiety leads to an increase of the excitation energy. Several reasons for this behaviour are discussed and an incremental system for the prediction of excitation energies of doubly substituted indoles is presented.

MO 3.5 Mon 15:30 f102

Observation of 3-methoxyphenol rotational isomers via high resolution laser induced fluorescence spectroscopy — ●MICHAEL SCHNEIDER, JOSEFIN WILKE, MARTIN WILKE, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

Three of four possible 3-methoxyphenol isomers have been studied via high resolution laser induced fluorescence spectroscopy. By means of evolutionary algorithms the molecular parameters of the measured spectra of different isomers were determined. With the aid of CC2/cc-pVTZ *ab initio* calculated structures the measured isomers were matched to one of the possible rotational isomers. The assignments agree with the results of microwave spectroscopy of other research groups. Furthermore, the transition dipole moment orientation were determined and the electronic origins of the isomers of 3-methoxyphenol and its parent molecules anisole and phenol were compared.

MO 3.6 Mon 15:45 f102

Fluorescence measurements from x-ray irradiated liquid water — ANDREAS HANS¹, ANDRÉ KNIE¹, ●CHRISTIAN OZGA¹, ROBERT SEIDEL², PHILIPP SCHMIDT¹, XAVER HOLZAPFEL¹, MARVIN POHL², PETR SLAVÍČEK³, BERND WINTER², and ARNO EHRESMANN¹ — ¹Institut für Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany — ²Helmholtz-Zentrum für Materialien und Energie, Albert-Einstein-Straße 15, 12489 Berlin, Germany — ³Department of Physical Chemistry, University of Chemistry and Technology, Technická 5, 16628 Prague, Czech Republic

The investigation of the decay dynamics of liquids and solutions after x-ray irradiation became accessible in recent years owing to the tremendous progress in liquid microjet techniques. This method meets the

high vacuum conditions required for experiments using x-ray excitation at synchrotron radiation facilities. Mainly via electron spectroscopy, several non-local de-excitation processes and intermolecular interaction mechanisms were identified. Their role in radiation biology is currently lively discussed. However, the detection of charged particles as a probe for decay mechanisms is constrained due to their short escape length in dense media. We present a complementary experimental method in which fluorescence detection is used to investigate reaction products after excitation of liquid microjets with synchrotron radiation. This approach is especially beneficial to track neutral and long-living species.

MO 3.7 Mon 16:00 f102

TD-DFTB analysis of time- and geometry-dependent excitonic couplings in PTCDI crystals — ●PER-ARNO PLÖTZ¹, JÖRG MEGOW², THOMAS NIEHAUS³, and OLIVER KÜHN¹ — ¹Institut für Physik, Universität Rostock, Germany — ²Institut für Chemie, Universität Potsdam, Germany — ³Institut Lumière Matière, Université Claude Bernard Lyon 1, France

Polarisation effects on chromophores and their influence to the excitonic coupling are simulated for a PTCDI (perylene-tetracarboxylic-diimide) crystal [1], whose thin films are possible building blocks for optoelectronics. Starting from a classical MD trajectory Frenkel exciton parameters are calculated, i.e. the monomeric transition energies as well as the Coulomb couplings between the on-site transitions. The efficient TBFE [2] method making use of tight-binding-based density functional theory in the linear response formulation (TD-DFTB) [3] is capable not only to follow the specific inter- but also the intramolecular structural changes in a thermal environment, distinguishing it from other methods computing the Coulomb coupling with fixed transition charges. Thus the calculation of the spectral density from a classical trajectory is possible. Its analysis provides the key to assign optical properties to specific vibrational modes.

[1] J. Megow et al., J. Phys. Chem. C, 2015, 119, 5747-5751.

[2] P.-A. Plötz et al., J. Chem. Phys., 2014, 140, 174101.

[3] T. A. Niehaus et al., Phys. Rev. B, 2001, 63, 085108.

MO 3.8 Mon 16:15 f102

IR/UV Ion Dip Spectroscopy of the Phenyl Radical and Propargyl Radical Self-Reaction — ●PHILIPP CONSTANTINIDIS¹, HANS-CHRISTIAN SCHMITT¹, FLORIAN HIRSCH¹, INGO FISCHER¹, BIN YAN², ARGHYA DEY², and ANOUK M. RIJS² — ¹University of Würzburg, Institute of Physical and Theoretical Chemistry, Am Hubland, D-97074 Würzburg, Germany — ²Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7-c, 6525 ED Nijmegen, The Netherlands

It is a major concern of combustion research to elucidate the growth mechanisms of polycyclic aromatic hydrocarbons (PAHs), which occur as products of incomplete combustion. Due to their carcinogenic and pollutant nature, efforts are directed towards their prevention.

Our group applies IR/UV ion dip spectroscopy combined with free jet technique to investigate the intermediates and reaction products formed by pyrolytically generated hydrocarbon radicals in a high-temperature flow reactor. The mass-selected IR spectra contain both mass and structural information of the observed species, which allow identification of isomers. As intense tunable IR radiation is needed for this type of experiment, the measurements are performed with the free electron laser FELIX in Nijmegen.

Subject of our study is the self-reaction of propargyl and phenyl radicals, which are assumed to be important components of PAH formation.

MO 4: Cold Molecules & Helium Droplets 1

Time: Monday 14:30–16:00

Location: f142

MO 4.1 Mon 14:30 f142

Optimized-focusing injector for single-particle coherent diffractive x-ray imaging — ●NILS ROTH^{1,3}, TIM OSSENBRÜGGEN¹, BERND LIENAU³, DANIEL HORKE^{1,2}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²The Hamburg Center for Ultrafast Imaging, University of Hamburg, Germany — ³Department of Physics, University of Hamburg, Germany

Atomic resolution single-particle coherent diffractive imaging requires reproducible particles to build up a 3D molecular image [1]. Current experiments are limited by the inefficient delivery of particles and correspondingly low hit-rates, i.e., poor usage of sample and x-ray photons. We are developing a controllable and efficient vaporization and aerodynamic lens [2] system to provide tightly focused beams of nanoparticles and biological systems, which will efficiently be guided to the interaction point. Here, we present detailed numerical simulations, as well as experimental characterization, of such particle injection.

tors. Using in-vacuum microscopes and light scattering we are able to determine the size of the produced particle beam. The distribution of gas from nozzles and particle injectors is studied quantitatively using plasma-formation imaging. This yields an accurate pressure-distribution map, important for benchmarking simulations. The increased hit-rate achieved in such a setup will make "molecular-movie" experiments more likely.

- [1] Barty et al., *Annu. Rev. Phys. Chem.* **64** 415-435 (2013),
 [2] Lui et al., *Aerosol Sci. Technol.* **22** 293-313 (1995a)

MO 4.2 Mon 14:45 f142

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

Diffractive imaging of aligned and oriented molecules in the gas phase is a promising tool to unravel ultrafast molecular dynamics [1,2], such as internal rearrangement processes or photofragmentation. We present an experimental approach to strongly align molecules at full repetition rate of free-electron lasers [3]. The molecules were non-adiabatically aligned with a chirped laser pulses (pulse duration 94 ps) provided by the available in-house Ti:Sapphire laser system at the Coherent X-ray Imaging (CXI) beamline at the Linac Coherent Light Source (LCLS). We report on the current status of the photon data analysis and discuss prospects for future experiments. This work was carried out in a collaboration with the spokespersons F. Wang, J. Küpper, P. Bucksbaum, and H. Chapman. The collaboration consists of CFEL, PULSE, LCLS, European XFEL, Aarhus University, Kansas State University, Stanford University, and Uppsala University. Use of the LCLS, SLAC national accelerator laboratory, is supported by the US Department of Energy, Office of Science, and Office of Basic Energy Sciences.

- [1] *Phys. Rev. Lett.* **112**(8), 083002 (2014) [2] *Annu. Rev. Phys. Chem.*, **64**(1), 415-435 (2013) [3] *J. Phys. B.* **48**(20), 204002 (2015)

MO 4.3 Mon 15:00 f142

X-ray photophysics of gas-phase molecules and clusters — ●THOMAS KIERSPEL^{1,2}, SEBASTIAN TRIPPEL¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²The Hamburg Center for Ultrafast Imaging, University of Hamburg, Germany — ³Department of Physics, University of Hamburg, Germany

Properties of atoms and molecules strongly dependent on their environment. Hydrogen bonds are of universal importance in chemistry and biochemistry and it is, therefore, highly desirable to bridge the gap between isolated and solvated molecules.

We present photophysics and charge redistribution on indole, the chromophore of the amino acid tryptophan, and separated indole-water₁ clusters [1], i.e., indole 'solvated' by a single water molecule, upon side-specific 1s ionization of indole's N atom. The species were spatially separated by the use of strong inhomogeneously electric fields prior the interaction zone. Photoelectrons and ionic fragments were recorded in coincidence with a double-sided velocity map imaging (VMI) spectrometer. Indications for charge and proton or hydrogen transfer were observed. Results will be discussed based on the fragmentation channels of the different species and the 3D reconstruction of the molecule's orientation.

This work was carried out in a collaboration with DESY and Kansas State University. The experiment was conducted at the Variable Polarization XUV Beamline P04 of PETRA III at DESY.

- [1] Trippel et al., *Phys. Rev. A.* **86**, 033202 (2012)

MO 4.4 Mon 15:15 f142

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

We present a new method for internal-state thermometry of guided polyatomic molecules. Bright beams of polar molecules are produced by a cryogenic buffer-gas cell and extracted by electrostatic guiding [1]. Their rotational-state distribution is probed via RF-resonant depletion spectroscopy. With the help of a complete trajectory simulation, resolving the guiding efficiency for all the thermally populated states, we are able to determine the internal temperature in the buffer-gas cell based on the RF depletion spectroscopy. This thermometry method is demonstrated for various regimes of buffer-gas cooling, beam formation, and for molecular species of different sizes, e.g., CH₃F and CF₃CCH. The results provide strong evidence that the collisional relaxation rate for rotational degrees of freedom is larger than for motional ones. In addition, the relaxation rates for states with different *K*-quantum number appear to be different.

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

MO 4.5 Mon 15:30 f142

Direct cooling of polar molecules to sub-millikelvin temperatures — ●ALEXANDER PREHN, MARTIN IBRÜGGER, ROSA GLÖCKNER, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

Applications of ultracold ($T < 1$ mK) polar molecules including ultracold chemistry, quantum simulation, and high-precision spectroscopy exploit the rich internal level structure and the electric dipole moment of the molecules. The desired use of chemically diverse species requires development of direct cooling methods. However, a versatile technique to cool molecules to the ultracold regime has been lacking.

Here, we present direct cooling of formaldehyde (H₂CO) to the microkelvin regime [1]. Our approach, optoelectrical Sisyphus cooling, which was first demonstrated with methyl fluoride (CH₃F) [2], provides a simple dissipative cooling method applicable to a variety of electrically trapped dipolar molecules. By reducing the temperature by three orders of magnitude and increasing the phase-space density by a factor of $\sim 10^4$ we generate an ensemble of about $3 \cdot 10^5$ molecules with a temperature of about 420 μ K. In addition to producing a record-large ensemble of ultracold molecules, we have good control over the internal molecular state: the molecules in the prepared ensemble populate a single rotational state with more than 80% purity.

- [1] A. Prehn et al., arXiv:1511.09427 (2015).
 [2] M. Zeppenfeld et al., *Nature* **491**, 570 (2012).

MO 4.6 Mon 15:45 f142

Feasibility of microwave manipulation and Stark deceleration of polyatomic asymmetric molecules — ●JACK B. GRANEK¹, SIMON MERZ¹, DAVID PATTERSON², THOMAS BETZ¹, and MELANIE SCHNELL¹ — ¹Max-Planck-Institut für Struktur und Dynamik der Materie, Luruper Chaussee 149, 22761 Hamburg, Germany — ²Harvard University, Department of Physics, Cambridge, USA

Motion manipulation of large molecules or ground-state molecules requires methods that are compatible with high-field-seeking states. In inhomogeneous fields, molecules in high-field-seeking states experience a force towards the field maxima. However, true 3D field maxima cannot be realized in free space with static fields alone so time-dependent fields are required. In previous experiments, focusing and deceleration of ammonia molecules was achieved [1]. Ammonia was considered, to a good approximation, an isolated two-level system. We have performed numerical calculations to predict and develop microwave manipulation experiments for polyatomic asymmetric molecules. This approach goes beyond the two-level approximation often employed for simpler molecules, e.g. NH₃ and acetonitrile [2], and is more broadly applicable. Trajectory simulations were carried out to predict microwave focusing measurements using a cylindrically symmetric microwave resonator. We also explore the potential for the Stark deceleration of specific rotational states of similarly complex systems that are low-field seeking up to a certain electric field strength.

- [1] S. Merz et al., *Phys. Rev. A* **85**, 063411 (2012).
 [2] S. Spieler et al., *Mol. Phys.* **111**, 1823-1834 (2013).

MO 5: Atomic clusters I (with A)

Time: Monday 17:00–18:45

Location: f107

MO 5.1 Mon 17:00 f107

Time-resolved luminescence detection from noble gas clusters after photon excitation — ●ANDREAS HANS¹, PHILIPP SCHMIDT¹, FLORIAN WIEGANDT², CHRISTIAN OZGA¹, XAVER HOLZAPFEL¹, TILL JAHNKE², MARTIN PITZER¹, UWE HERGENHAHN³, REINHARD DÖRNER², ARNO EHRESMANN¹, and ANDRÉ KNIE¹ — ¹Institut für Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel — ²Institut für Kernphysik, J.W. Goethe Universität, Max-von-Laue-Straße 1, 60438 Frankfurt — ³Leibniz-Institut für Oberflächenmodifizierung e.V., Permoserstraße 15, 04318 Leipzig

Fluorescence spectrometry is a powerful technique to investigate the electronic structure and decay mechanisms of atomic clusters. In these clusters the lifetimes of excited states can deviate significantly from those in the atomic case. It was shown that time-resolved detection enables an efficient discrimination of cluster and monomer signal [1]. This way features can be separated, even if they overlap in excitation energy or emission wavelength. The lifetimes of excited states can give further information about the nature of the emission mechanism, e.g. emission from excitonic states, from evaporated atoms, or due to radiative charge transfer. We illustrate the experimental technique of time-resolved fluorescence spectrometry upon excitation by synchrotron radiation and present results from experiment on neon and argon clusters.

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

MO 5.2 Mon 17:15 f107

The X-Ray Movie Camera: filming exploding xenon clusters by using a novel XUV imaging setup — ●MARIO SAUPPE¹, LEONIE FLÜCKIGER^{2,1}, KATHARINA KOLATZKI¹, BRUNO LANGBEHN¹, MARIA MÜLLER¹, BJÖRN SENFFLEBEN¹, ANATOLI ULMER¹, JAN-NIS ZIMBALSKI¹, JULIAN ZIMMERMANN¹, TOBIAS ZIMMERMANN¹, TAIS GORKHOVER^{1,3}, CHRISTOPH BOSTEDT^{4,3}, CÉDRIC BOMME⁵, STEFAN DÜSTERER⁵, BENJAMIN ERK⁵, MARION KUHLMANN⁵, DANIEL ROLLES^{6,5}, DIMITRIOS ROMPOTIS⁵, ROLF TREUSCH⁵, TORSTEN FEIGL⁷, THOMAS MÖLLER¹, and DANIELA RUPP¹ — ¹TU Berlin — ²La Trobe University, Melbourne — ³SLAC — ⁴Argonne National Laboratory, Northwestern University, Chicago — ⁵DESY — ⁶Kansas State University — ⁷optiX fab

From the first theoretical concepts on, the development of x-ray free electron lasers has been accompanied by the vision of the “molecular movie”. Here we present a very recently performed XUV pump-probe experiment at the free-electron laser FLASH, using a novel two-detector setup for capturing “two-frame movies”. While the scattering image on the first detector shows the intact single xenon cluster, delivering information about initial size, shape and exposed intensity, the second detector images the same cluster at a later stage. The new, permanently at FLASH installed, multilayer based split and delay stage DESC was used to study the light induced dynamics in large xenon clusters up to the longest possible delay of 650 ps.

MO 5.3 Mon 17:30 f107

Influence of wavelength and pulse duration on single-shot x-ray diffraction patterns from non-spherical nanoparticles — ●KATHARINA SANDER¹, CHRISTIAN PELTZ¹, CHARLES VARIN², STEFAN SCHEEL¹, THOMAS BRABEC² und THOMAS FENNEL¹ — ¹Institute of Physics, University of Rostock — ²Institute of Physics, University of Ottawa

The availability of intense femtosecond x-ray laser pulses from FELs has made it possible to visualize the structure and dynamics of nano-systems via single-shot diffractive imaging. It has been demonstrated that such experiments can be conducted on single free clusters to measure their size as well as their three-dimensional shape and orientation [1]. To model the corresponding diffraction patterns we use a microscopic model based on the discrete dipole approximation (DDA) [2]. We introduce a complex scaling DDA (CSDDA) and study single-shot x-ray diffraction patterns from non-spherical, absorbing nanotargets in the limit of linear response [3]. We employed the method to the scattering by icosahedral silver clusters and compare the scattering pattern for soft and hard x-ray radiation. Our results confirm that 3D structure information is only accessible for long wavelength, i.e. with soft x-ray pulses, but remains visible even for attosecond pulse durations for which the interference fringes vanish.

- [1] I. Barke *et al.*, *Nat. Comm.* **6**, 6187, (2015)
 [2] E. M. Purcell *et al.*, *Astrophysical Journal* **186**, 705-714, (1973)
 [3] K. Sander *et al.*, *J. Phys. B* **48**, 204004 (2015)

MO 5.4 Mon 17:45 f107

Interatomic coulombic decay (ICD) in He nanodroplets — ●MYKOLA SHCHERBININ¹, AARON LAFORGE¹, SAI SMRUTI SAMANTARAY², VANDANA SHARMA³, ROBERT RICHTER⁴, and MARCEL MUDRICH¹ — ¹University of Freiburg - Faculty of Mathematics and Physics, Freiburg, Germany — ²Indian Institute of Technology - Dept. of Physics, Chennai, India — ³Indian Institute of Technology, Department of Physics, Ordnance Factory Estate, India — ⁴Elettra - Sincrotrone Trieste, Basovizza, Trieste, Italy

ICD is an important relaxation process for electronically excited atoms which are weakly bound in molecules and clusters [1]. While ICD has been observed in van der Waals clusters containing Ne, Ar, and Xe before, for He, ICD has so far been studied only for the He dimer [2]. We present a synchrotron study of ICD induced in He nanodroplets by simultaneously ionizing and exciting one He atom of the droplet in a shakeup process. Subsequent transfer of internal energy to the neighbouring atoms leads to the formation of He⁺ atomic ions as well as small He_n⁺ cluster ions, which we observe in electron-ion-ion coincidence. The corresponding photoelectron as well as ion kinetic energy spectra reveal the details of the ICD and subsequent fragmentation processes.

- [1] L. S. Cederbaum *et al.*, *Phys. Rev. Lett.* **79**, 4778 (1997) [2] T. Havermeier *et al.*, *Phys. Rev. Lett.* **104**, 133401 (2010)

MO 5.5 Mon 18:00 f107

Control of NIR avalanching in clusters by XUV-driven seed electrons — ●BERND SCHÜTTE^{1,2}, MATHIAS ARBEITER³, ALEXANDRE MERMILOD-BLONDIN¹, MARC VRAKING¹, THOMAS FENNEL³, and ARNAUD ROUZÉE¹ — ¹Max-Born-Institut Berlin, Germany — ²Imperial College London, UK — ³Universität Rostock, Germany

The interaction of intense NIR laser pulses with clusters induces highly nonlinear dynamics on attosecond to nanosecond timescales. Recently, we made progress in understanding the relaxation dynamics of clusters in the picosecond to nanosecond range, where electron-ion recombination [1] and correlated electronic decay [2] play an important role.

Novel experimental approaches are required in order to gain access to the ionization dynamics on an attosecond to femtosecond timescale. Here we report on a method, in which cluster ionization is ignited by generating a few (< 10) seed electrons using an XUV pulse. The clusters become strongly ionized (charges up to Ar⁴⁺ are observed) by a time-delayed NIR laser pulse at an intensity of 3×10^{12} W/cm². This is far below the tunnel ionization threshold and corresponds to a ponderomotive potential of only 170 meV. The results are explained by avalanching via efficient inverse bremsstrahlung and electron impact ionization, as well as by resonant absorption of laser energy [3]. In the future, we will apply our concept in order to time-resolve the strong-field ionization of solid-density targets with attosecond resolution.

- [1] B. Schütte *et al.*, *Phys. Rev. Lett.* **112**, 253401 (2014).
 [2] B. Schütte *et al.*, *Nat. Commun.* **6**, 8596 (2015).
 [3] B. Schütte *et al.*, arXiv:1509.03250 (2015).

MO 5.6 Mon 18:15 f107

Ionization avalanching in clusters ignited by extreme-ultraviolet driven seed electrons — ●MATHIAS ARBEITER¹, BERND SCHÜTTE², ALEXANDRE MERMILOD-BLONDIN³, MARC J. J. VRAKING³, ARNAUD ROUZÉE³, and THOMAS FENNEL¹ — ¹University of Rostock, Germany — ²Imperial College London, United Kingdom — ³Max-Born-Institut, Berlin, Germany

Nanoplasma formation in rare-gas clusters under intense near-infrared (NIR) fields is triggered by atomic tunnel ionization. Subsequently, the ionization dynamics is dominated by impact ionization avalanching, efficient heating via inverse Bremsstrahlung (IBS), and resonant collective plasmon excitation. This ionization ignition, however, requires high intensities to reach the tunnelling threshold [1].

Recent experiments show that a few photo-activated seed electrons from an additional weak XUV pulse allow the control of ionization avalanching [2]. In this two-color scenario, highly charged ion emission occurs at NIR intensities far below the tunnel ionization thresh-

old and is switched by the XUV field. We studied the XUV-induced nanoplasma formation as well as its subsequent NIR-driven evolution by molecular dynamics simulations. We find that avalanching starts with even very few seed electrons and that resonance effects are crucial to explain the observed ion emission. Further, our results support that the XUV-NIR scenario might enable the so far unprecedented investigation of IBS at low ponderomotive potentials.

- [1] Rose-Petruck et al., *Phys. Rev. A* 55:1182 (1997).
 [2] B. Schütte et al., arXiv:1509.03250 (2015)

MO 5.7 Mon 18:30 f107

Cluster size determination of clusters by fluorescence spectrometry — ●XAVIER HOLZAPFEL¹, ANDREAS HANS¹, PHILIPP SCHMIDT¹, FLORIAN WIEGANDT², LTAIEF BEN LTAIEF¹, PHILIPP REISS¹, REINHARD DÖRNER², ARNO EHRESMANN¹, and ANDRÉ KNIE¹ — ¹University of Kassel, Institute of Physics and Center of Interdisciplinary Nanostructure Science and Technology (CINSaT), D-34132

Kassel, Germany — ²Institute of Nuclear Physics, J. W. Goethe University, D-60438 Frankfurt, Germany

Clusters are finite aggregates and cover the gap between molecular and condensed matter physics and are thus used to study microscopic phenomena for many decades [1]. Rare gas clusters are created randomly by supersonic expansion and a scaling law is widely applied to express the mean cluster size of the distribution [2]. Different experiments report deviations between calculated and measured mean cluster size and further investigations are necessary for quantification [3]. Resonant excitation of outer valence electrons in rare gas clusters by synchrotron radiation yield characteristic informations in the resulting fluorescence yield about the mean cluster size. In the ongoing contribution we present a novel way of cluster size determination of clusters by photon induced fluorescence spectrometry (PIFS) [4].

- [1] J. Jortner: *Z. Phys. D* 24, 247 (1992). [2] U. Buck et al.: *J. Chem. Phys.* 105, 5408 (1996). [3] H. Bergersen et al.: *PCCP* 8, 1891 (2006). [4] A. Knie et al.: *New Journal of Physics* 16, 102002 (2014).

MO 6: Posters 1: Novelties in Molecular Physics: Femtosecond Spectroscopy

Time: Monday 16:30–19:00

Location: Empore Lichthof

MO 6.1 Mon 16:30 Empore Lichthof

Vibrational and vibronic coherences in the two dimensional spectroscopy of coupled electron-nuclear motion — ●JULIAN ALBERT¹, MIRJAM FALGE¹, SANDRA GOMEZ², IGNACIO SOLA², HEIKO HILDENBRAND¹, and VOLKER ENGEL¹ — ¹Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Campus Nord, 97074 Würzburg, Germany — ²Departamento de Química Física, Universidad Complutense, 28040 Madrid, Spain

We theoretically investigate the photon-echo spectroscopy of coupled electron-nuclear quantum dynamics [1]. Two situations are treated. In the first case, the Born-Oppenheimer (adiabatic) approximation holds. It is then possible to interpret the two-dimensional (2D) spectra in terms of vibrational motion taking place in different electronic states. In particular, pure vibrational coherences which are related to oscillations in the time-dependent third-order polarization can be identified. This concept fails in the second case, where strong non-adiabatic coupling leads to the breakdown of the Born-Oppenheimer-approximation. Then the 2D-spectra reveal a complicated vibronic structure and vibrational coherences cannot be disentangled from the electronic motion.

- [1] J. Albert, M. Falge, S. Gomez, I. R. Sola, H. Hildenbrand, V. Engel, *J. Chem. Phys.* 143, 041102 (2015)

MO 6.2 Mon 16:30 Empore Lichthof

Two-dimensional femtosecond optical spectroscopy of trapping dynamics in a charge-transfer process — ●MARTIN KESS and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Campus Nord, Emil-Fischer-Str. 42, 97074 Würzburg, Germany

We study charge-transfer dynamics monitored by two-dimensional (2D) optical spectroscopy. The often used model consisting of two coupled diabatic electronic states in a single reaction coordinate is used to demonstrate the relation between the vibronic dynamics and the 2D-spectra. Within the employed wave-function approach, dissipation is included via a quantum-jump algorithm with explicit treatment of dephasing. States with long lifetimes which decay slowly due to the interaction with the environment are identified. Using filtered Fourier transforms it is shown that the population of these trap states can be monitored as a function of energy and time.

MO 6.3 Mon 16:30 Empore Lichthof

Theoretical analysis of exciton annihilation in Squaraine-Squaraine Copolymers — ●KILLIAN HADER¹, CHRISTOPH LAMBERT², VOLKHARD MAY³, and VOLKER ENGEL¹ — ¹Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Campus Nord, 97074 Würzburg, Germany — ²Universität Würzburg, Institut für Organische Chemie, Am Hubland, 97074 Würzburg, Germany — ³Institut für Physik, Humboldt Universität, Newtonstr. 15, D-12489 Berlin, Germany

We use a microscopic model [1] to describe exciton annihilation processes in Squaraine-Squaraine Copolymers. Transient absorption traces measured at different laser powers exhibit an unusual time-dependence [2]. The analysis shows that, at shorter times, exciton-

exciton annihilation, being effective through the laser excitation of next-neighbor building blocks, determines the excited state decay. At later times, excitations being localized on units which are not directly connected remain so that diffusion or smaller long range interactions are the rate-limiting step leading to a slower decay.

- [1] V. May, *J. Chem. Phys.* 140, 054103 (2014) [2] S. F. Völker, A. Schmiedel, M. Holzapfel, K. Renziehausen, V. Engel, C. Lambert, *J. Phys. Chem. C*, 118, 17467 (2014)

MO 6.4 Mon 16:30 Empore Lichthof

Sub-One Per Cent Enantiomeric Excess Sensitivity using Femtosecond Photoelectron Circular Dichroism — ALEXANDER KASTNER, CHRISTIAN LUX, TOM RING, ●STEFANIE ZÜLLIGHOVEN, CRISTIAN SARPE, ARNE SENFTLEBEN, and THOMAS BAUMERT — University of Kassel, Institute of Physics and Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

Photoelectron circular dichroism (PECD) is investigated experimentally on chiral specimen with a varying amount of enantiomeric excess (e.e.). As a prototype we measure and analyze the photoelectron angular distribution from randomly oriented fenchone molecules in the gas phase resulting from ionization with circularly polarized femtosecond laser pulses. The quantification of these measurements shows a linear dependence with respect to e.e.. In addition, a distinction of differences in the e.e. (denoted as detection limit) below one per cent for nearly enantiopure samples as well as for almost racemates is demonstrated. In combination with a reference the assignment of absolute e.e. values is possible. The present measurement time is a few minutes but can be reduced further. This table-top laser-based approach facilitates a widespread implementation in chiral analysis.

MO 6.5 Mon 16:30 Empore Lichthof

Mass-selective Circular Dichroism after Femtosecond Laser Ionization — ●TOM RING, ALEXANDER KASTNER, STEFANIE ZÜLLIGHOVEN, TOBIAS GRABSCH, CRISTIAN SARPE, CHRISTIAN LUX, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel

Multi Photon Ionization grants access to Circular Dichroism (CD) with circularly polarized laser pulses. The analysis via time of flight mass spectra provides a mass-selective tool to distinguish chiral molecules in the gas phase.[1,2] Hence, mixtures of chiral molecules as well as CD effects on fragments can be investigated.

Introducing a twin mass peak setup allows circumventing shot-to-shot fluctuations in laser pulse intensity, gas density or ion detection. Two foci with a small spatial displacement result in time-separated mass spectra; a change in helicity from focus to focus implements a self-referencing system. The in-line optical setup allows to make use of femtosecond laser pulses, whose broad bandwidth promises new possibilities in chiral control. Besides the advantages of this setup we present first results on different chiral molecules.

- [1] Titze et al.: *ChemPhysChem* 2014, 15, 2762-2767
 [2] Horsch et al.: *Chirality* 2012, 24, 684-690

MO 6.6 Mon 16:30 Empore Lichthof

Time-Resolved XUV-induced Electron Solvation Dynamics in Water Clusters — ●RUPERT MICHIELS¹, AARON LAFORGE¹, CARLO CALLEGARI², MARCEL DRABBELS³, PAOLA FINETTI², OKSANA PLEKAN², KEVIN C. PRINCE², STEFANO STRANGES⁴, MATTHIAS BOHLEN¹, MYKOLA SHCHERBININ¹, and FRANK STIENKEMEIER¹ — ¹Universität Freiburg, Germany — ²Elettra-Sincrotrone, Trieste, Italy — ³EPFL Lausanne, Switzerland — ⁴University of Rome, Italy

The solvation of electrons in aqueous solutions plays a nearly ubiquitous role in biological and chemical systems although a fundamental understanding of its properties (e.g. solvation time, binding energies, solvation shells, and binding motifs) has yet to be fully attained. Here, we report on solvated water clusters induced by XUV ionization followed by electron recapture. The binding energies of the solvated electron were measured in a pump-probe scheme as a function of cluster size in which we found solvation times in the femtosecond to picosecond range.

MO 6.7 Mon 16:30 Empore Lichthof

Deactivation of photo-excited Berenil — ●LENA GRIMMELSMANN, CHRISTIAN SPIES, and PATRICK NUERNBERGER — Physical Chemistry II, Ruhr-University Bochum, Universitätsstraße 150, 44801 Bochum

Berenil is an aromatic diamidin consisting of two amidinophenyl units which are linked by a triazene bridge. It binds well to several molecules, e.g. it can serve as a DNA minor groove binder. The steady-state photochemical behavior of Berenil was analyzed already, but no measurements addressing the dynamical behavior have been performed up to now. We have done steady-state absorption and fluorescence measurements, as well as time-resolved measurements via femtosecond fluorescence upconversion. The fluorescence quantum yield of Berenil in different solvents is very low. The reason is the notable fast decay of the excited-state, which has a lifetime of about 400 fs. Possibly, a rapid internal conversion due to an intramolecular rotation is the reason for the ultrafast decay.

We want to verify the assumption of the fast rotation by binding of Berenil to trypsin and to G-quadruplex DNA to prevent or decelerate the rotation. A slower fluorescence decay when Berenil is bound can be an evidence for the hindered rotation. As a further approach, investigations of unbound berenil in solvents with different viscosities are performed to analyze the environmental impact on the photo-induced dynamics and hence on the fluorescence lifetime.

MO 6.8 Mon 16:30 Empore Lichthof

Femtosecond Photoelectron and Transient Grating Spectroscopy in the Extreme Ultraviolet Domain — ANDREA BATTISTONI¹, JAKOB GRILJ^{1,2}, MARKUS KOCH^{1,3}, EMILY F. SISTRUNK^{1,4}, THOMAS J. A. WOLF¹, and ●MARKUS GÜHR^{1,5} — ¹PULSE, SLAC National Accelerator Laboratory and Stanford University, 94025 Menlo Park, CA, USA — ²EPFL, Lausanne, CH 1015,

Switzerland — ³Experimental Physics, Graz University of Technology, A-8010 Graz, Austria — ⁴Lawrence Livermore National Laboratory, Livermore, CA 94550, USA — ⁵Physik und Astronomie, Universität Potsdam, 14476 Potsdam, Germany

We present ultrafast photoelectron [1] and transient grating spectroscopy [2] using extreme ultraviolet (EUV) pulses from a laser source based on high harmonic generation. For the molecular photoelectron spectroscopy, we compare one-photon to multi-photon probing demonstrating the importance of intermediate resonances in the transient decay [3]. For the transient gratings, we show how broadband EUV continua allow us to distinguish acoustic and electronic effects in a solid VO₂ sample with a light induced insulator-to-metal transition. Permanent gratings, matched to the period of the transient, facilitate heterodyne detection of the (weak) nonlinear response of VO₂ [4].

[1] M. Koch et al., J. Photoelectr. Spectr. Rel. Phen. **197**, 22 (2014)[2] E. Sistrunk et al., Optics Express **24**, 4340 (2015)[3] M. Koch et al., Phys. Rev. A **91**, 031403 (2015)[4] J. Grilj et al., Photonics **2**, 392 (2015)

MO 6.9 Mon 16:30 Empore Lichthof

Laser-based THz-field-driven XUV streak camera for time resolved measurements of angular energy distribution of electrons — ●RANKE MARTIN, KARIMI FAWAD, PFAU MARKUS, DIMITRIOU ANASTASIOS, and FRÜHLING ULRIKE — Institut für Experimentalphysik, Universität Hamburg

In this work, we present a novel setup for the study of femtosecond (fs) dynamics in atoms and molecules with the use of a terahertz (THz) -field-driven extreme ultraviolet (XUV) streak camera. High-harmonic generated XUV pulses are synchronized and superimposed with intense single-cycle THz pulses in a gas target. The XUV pulses are used to excite and ionize atoms or molecules. The resulting electrons are accelerated by the electric THz field which directly relates the change of the momentum to the THz vector potential. The kinetic energies of the electrons are measured fully angle resolved by a new velocity map imaging (VMI) spectrometer. The intense THz pulses are generated with a tilted pulse front setup of near infrared laser pulses by means of optical rectification in a nonlinear crystal.

MO 6.10 Mon 16:30 Empore Lichthof

Vibronic spectra of homo- and hetero-dimer aggregates — ●JOHANNES WEHNER, MARTIN KESS, and VOLKER ENGEL — Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Campus Nord, 97074 Würzburg, Germany

We calculate two-dimensional photon-echo spectra of molecular dimers employing different wave-function based approaches. Calculations using perturbative, non-perturbative and phase-cycling methods are compared. The differences in spectra obtained for homodimers and heterodimers are investigated. The two-dimensional spectra are discussed by comparing purely electronic level systems with their vibronic counterparts. In particular, the effect of orientational averaging is addressed.

MO 7: Femtosecond Spectroscopy 2

Time: Tuesday 11:00–13:00

Location: f102

Invited Talk

MO 7.1 Tue 11:00 f102

Monitoring ultrafast excited-state intramolecular proton transfer by ultrafast electronic and fluorescence spectroscopy — ●ANDREAS STEINBACHER¹, PRAMOD KUMAR VERMA², FREDERICO KOCH¹, ALEXANDER SCHMIEDEL³, PATRICK NUERNBERGER⁴, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Korea University, Seoul 136-701, Republic of Korea — ³Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ⁴Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany

Excited-state intramolecular proton transfer (ESIPT) is one of the most successful models for understanding complex proton transfer dynamics. In general, ESIPT is an ultrafast process occurring on a subpicosecond time scale. Hence, we employ transient absorption from the deep-UV to the visible spectral region and fluorescence upconversion

to investigate the photoinduced ESIPT dynamics in β -diketones. Electronic excitation in the UV is followed by ultrafast proton transfer to form a vibrationally hot tautomeric species. Further relaxation steps are determined by the actual symmetry of the investigated β -diketone and also by the solvent environment. Here, we address both issues by comparing the results for symmetric and unsymmetric β -diketones in various solvents. Depending on the actual molecular system, photoisomerization reactions and even ground-state intramolecular proton transfer could be observed.

MO 7.2 Tue 11:30 f102

Pursuing Primary Processes of Diphenylcarbene in Binary Solvent Mixtures — ●JOHANNES KNORR¹, PANDIAN SOKKAR², SEBASTIAN SCHOTT³, PAOLO COSTA⁴, WOLFRAM SANDER⁴, ELSA SÁNCHEZ-GARCÍA², and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr — ³Institut für Physikalische und Theoretische Chemie,

Am Hubland, Universität Würzburg, 97074 Würzburg — ⁴Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

The ultrafast reaction dynamics of carbenes in solution are governed by intersystem crossings, intermolecular proton uptake, or concerted reactions with the solvent. In this study, we combine quantum mechanics/molecular mechanics calculations and broadband femtosecond transient absorption spectroscopy applied to diphenylcarbene, and unravel the underlying dynamics and reaction mechanisms that take place in binary solvent mixtures at room temperature. The results show that a competition between the reaction pathways occurs that not only depends on the solvent molecule near-by but also on its interaction with other solvent molecules. In-depth analysis of the solvation dynamics and the amount of nascent intermediates corroborates the importance of a hydrogen-bonded complex with a protic solvent molecule, in striking analogy to complexes found at cryogenic temperatures [1].

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

MO 7.3 Tue 11:45 f102

A ps time-resolved study of NI, Me-NI and NDCA — ●HANS-CHRISTIAN SCHMITT, THIEMO GERBICH, INGO FISCHER, JENS PETERSEN, and ROLAND MITRIC — Insitute for Physical and Theoretical Chemistry, University of Würzburg, Germany

In a molecular beam experiment we investigated the excited state dynamics of isolated Naphthalimide (NI), N-Methyl-Naphthalimide (Me-NI) and 1,8-Naphthalic anhydride (NDCA).

Our ps-laser system allowed us to probe different vibronic states with a resolution of 20 cm⁻¹. Hereby we found an interesting dependence of the decay time from the excitation energy. In NDCA the lifetime drops from 1.2 ns at the origin of the S₁ to 30 ps at an excess energy of 800 cm⁻¹. In NI and Me-NI the lifetimes are nearly constant at around 10-17 ps. The experiments were accompanied by surface hopping dynamics simulations that give detailed insights into the occurring photochemical processes. These are a fast internal conversion via a conical intersection and intersystem crossing which compete as deactivation processes.

MO 7.4 Tue 12:00 f102

Two-Dimensional Electronic Spectroscopy Can Fully Characterize the Population Transfer in Molecular Systems — ●JAKUB DOSTÁL¹, BARBORA BENEŠOVÁ², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Department of Mathematics, University of Würzburg, Emil-Fischer-Straße 40, 97074 Würzburg

Excitation energy transfer (EET) in complex systems often proceeds through series of intermediate states. One of the goals of time-resolved spectroscopy is to identify the spectral signatures of all of them in the acquired experimental data and to characterize the energy transfer scheme between them. It is well known that in the case of transient absorption (TA) spectra such a decomposition can be ambiguous even if many simplifying considerations (such as described below) are taken. The systematic decomposition of coherent 2D spectra has not been investigated to date.

Here we show that the unique retrieval of the complete set of rate constants and TA spectra of all states is possible by simultaneously fitting the 2D spectrum and absorption spectrum. An efficient implementation of the fitting routine is proposed. We focus on the ideal case of a system with well separated spectral bands, with no dark states present and with EET strictly governed by a set of linear rate equations of the first order. We also assume that the spectra of the intermediate states are not linearly dependent. This represents a theoretical basis for quantitative analysis of EET in experimental 2D spectra.

MO 7.5 Tue 12:15 f102

Quantum chemical studies of pyrene: long known molecule, new insights — ●MATTHIAS K. ROOS, TERESA KÜBLBÖCK, SEBASTIAN REITER, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Pyrene, an intensively studied molecule especially known for its excimers, is used today as a fluorescence marker. Yet, the microscopic mechanism accounting for its photophysics is still rather unclear. It is experimentally known that after excitation to the S₂ (L_a) ultrafast relaxation to the S₁ (L_b) occurs followed by fluorescence or excimer formation.

We studied pyrene with quantum chemical methods including TD-DFT and CASSCF in the gas phase and in solution (PCM). With this, we optimized minima for the L_a and L_b state and simulated absorption spectra that are in excellent agreement with the experimental ones. We also located a conical intersection between the S₂ and S₁ near the excited states minima enabling the ultrafast relaxation. In addition, an explanation is presented for the difference in oscillator strength between L_a and L_b without considering the symmetry of the molecule.

Furthermore, we investigated possible structures for the pyrene excimer. Minima are located on the S₁ and S₂ surface that differ in the rotation angle between the pyrene moieties. Hirayama's rule is confirmed that excimers for bridged pyrenes should exist especially for a propyl bridge. For the first time, we can present optimized structures for such bridged excimers already suggested in the literature.

MO 7.6 Tue 12:30 f102

Detection of multiple-quantum coherences in dilute samples — ●LUKAS BRUDER, MARCEL BINZ, ULRICH BANGERT, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, 79104 Freiburg

Multidimensional spectroscopy allows efficient isolation and detection of multiple-quantum coherences (MQCs). MQC signals have been used to explore higher-lying molecular states and many-body phenomena in various systems. Detecting such higher order effects usually requires particularly sensitive methods. We present a simple approach based on quasi-continuous phase modulation which allows efficient isolation of MQC signals in a collinear two-pulse experiment [1]. We demonstrate the detection of multiphoton quantum beats in atomic vapors and supersonic doped helium droplet beams. Furthermore, collective resonances up to the 5th order are observed, which is surprising considering the low density in our samples. The origin of these features is currently investigated. Our approach can readily be extended to higher dimensional spectroscopy. Moreover, it may facilitate coherent time-resolved spectroscopy in the XUV spectral range.

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

MO 7.7 Tue 12:45 f102

Ultrafast Dynamics of Vibrational Relaxation of Pseudohalides in Liquid-to-Supercritical Water. A Critical Test of Fermi's Golden Rule — ●JEANNINE GLEIM, DENIS CZURLOK, JÖRG LINDNER, and PETER VÖHRINGER — Institut für Physikalische und Theoretische Chemie, Universität Bonn

In recent years, the vibrational spectroscopy of pseudohalide anions in condensed media has attracted much attention. They were studied in the context of dynamical solute-solvent interactions and vibrational energy relaxation (VER) in hydrogen-bonded liquids like water.

Here, the stretching vibration of ¹⁵N-labelled thiocyanate, selenocyanate and azide anions in aqueous solution were studied with Fourier-Transform IR-spectroscopy (FTIR) as well as femtosecond IR-pump-probe spectroscopy (fs-IR-PP). All experiments were carried out under isobaric conditions at a pressure of 500 bar over a wide temperature range covering the liquid and supercritical phases of water.

Relaxation rate constants were determined from the decay of the *v* = 1 excited state absorption. In all studied cases, the temperature dependencies of the relaxation rate constants are similar. However, the relaxation pathways differ. While the relaxation of thiocyanate and selenocyanate follow the VET pathway, that of azide follows a combination of both, the IVR and VET pathways. The results are interpreted in terms of Fermi's Golden Rule and a resonant VET from the solute's stretching mode to the combination tone of the bending and librational modes of water.

MO 8: Experimental Techniques

Time: Tuesday 11:00–13:00

Location: f142

MO 8.1 Tue 11:00 f142

Toward electron diffraction off controlled molecules — ●NELE L. M. MÜLLER¹, SEBASTIAN TRIPPEL¹, KAROL DŁUGOŁĘCKI¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²The Hamburg Center for Ultrafast Imaging, Hamburg — ³Department of Physics, University of Hamburg

The aim of this work is to investigate the structure and intrinsic dynamics of small molecules in the gas-phase by electron diffraction. Controlling the molecules' state and spatial orientation will allow to enhance the information retrieved from diffraction data, such as bond length and angles [1]. This contribution details the setup consisting of an electron gun and a controlled-molecules apparatus [2,3,4]. It allows for laser- and electron-interaction with the state-selected and laser-aligned molecules. Apart from recording electron diffraction patterns, the new setup allows for imaging the spatial orientation of molecules through ion Velocity-Map Imaging. Characterizing experiments and electron diffraction data of isotropic gas-phase samples will be presented.

- [1] Hensley, Yang, Centurion, *Phys. Rev. Lett.* **109**, 133202 (2012)
 [2] Müller, Trippel, Długołęcki, Küpper, *J. Phys. B* **48**, 244001 (2015)
 [3] Trippel, Mullins, Müller, Kienitz, Długołęcki, Küpper, *Mol. Phys.* **111**, 1738 (2013)
 [4] Chang, Horke, Trippel, Küpper, *Int. Rev. Phys. Chem.* **34**, 557 (2015)

MO 8.2 Tue 11:15 f142

Optical cell transfection platform — ●HANS GEORG BREUNIG¹, ANA BATISTA², AISADA UCHUGONOVA^{1,2}, and KARSTEN KÖNIG^{1,2} — ¹JenLab GmbH, Science Park 2, 66123 Saarbrücken, Germany and Schillerstr. 1, 07745 Jena, Germany — ²Department of Biophotonics and Laser Technology, Saarland University, 66123 Saarbrücken, Germany

Cells can be transfected by transient laser-induced perforation of the cell membrane which allows foreign genetic material to enter the cell interior. This method (optoporation) has emerged as a powerful non-invasive and highly efficient cell-transfection technique. We present an experimental platform based on a modified multiphoton laser scanning microscope employing a femtosecond laser, beam shaping, and custom-made control software for computer-automated cell optoporation. The software evaluates the image contrast due to cell contours, automatically designates cell locations for laser illumination, centres those locations in the laser focus (Gaussian or Bessel beam profile), and executes the illumination. By software-controlled meandering of the sample stage, in principle all cells in a typical cell culture dish can be targeted without further user interaction. For an illumination duration of 100 ms, 7-8 positions on different cells can be targeted every second. Ultra-short fs pulses are in particular efficient for the optoporation due to underlying multiphoton absorption processes. The experimental capabilities of the setup are illustrated in experiments with Chinese hamster ovary cells. Furthermore, the influence of laser characteristics on the optoporation efficiency is discussed.

MO 8.3 Tue 11:30 f142

Piezo-electric detection of a pulsed supersonic beam — ●WOLFGANG CHRISTEN¹, PAUL SAFTIEN¹, and KARSTEN LANGE² — ¹Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin — ²Sensor- und Lasertechnik, Schulstr. 15, 15366 Neuenhagen

Supersonic molecular beams obtained by the adiabatic expansion of a gas under high pressure into vacuum constitute a powerful and versatile technique in modern physics, with applications in analytical chemistry, cluster science, metrology, optical spectroscopy, quantum physics, and surface science. Accordingly, various techniques have been developed for beam detection, with each method providing characteristic features.

Here we report on the development of a piezo-electric based detection of pulsed supersonic beams in an ultrahigh vacuum environment. Key benefits of this technique are a fast detector response and the fact that no ionisation is required. Besides characteristic features of the detection we present first experimental results for supersonic beams of helium, argon, and carbon dioxide, in a wide range of source conditions (source pressures between 5 and 120 bar, source temperatures between –40 and 110 °C).

MO 8.4 Tue 11:45 f142

Enhancement of CARS signal via tailored probing in spectral focusing — ●LUKAS BRÜCKNER, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-chemisches Institut, Universität Heidelberg, Germany

In the framework of coherent anti-Stokes Raman scattering (CARS), applying the same chirp to pump and Stokes frequencies allows for focusing most of the spectral amplitude into one specific Raman line. Here, a novel approach for spectral focusing using a broadband oscillator in combination with a pulse shaper controlling phase and amplitude is presented. The flexibility of the single-beam setup allows for variable and fast adjustment of the instantaneous bandwidth to the linewidths of different Raman levels throughout the spectrum. Furthermore, by identifying the frequencies acting as pump, Stokes and probe, the high degree of control can be exploited in order to specifically and independently tailor the spectral region acting only as probe to achieve the highest signal intensity. While maintaining optimal excitation of the vibrational coherence, a significant increase in comparison with usual spectral focusing schemes is readily obtained without even nearly maxing out the applicable power of the probe before photo-damage can be observed. The signal improvement and contrast is demonstrated by imaging the lipid distribution of human skin tissue.

- [1] L. Brückner, T. Buckup and M. Motzkus, *Opt. Lett.* **22**, 5204-5207 (2015)

MO 8.5 Tue 12:00 f142

Investigation of the chemical enhancement contribution to SERS using a Kretschmann arrangement — ●FAEZEH MOHAGHEGH, ALIREZA MAZAHARI TEHRANI, and ARNULF MATERNY — Physics and Earth Sciences, Jacobs University Bremen, Campus Ring 1, 28759 Bremen

The fundamental enhancement mechanisms of SERS are the so-called electromagnetic enhancement (EM) caused by surface plasmon polaritons (SPPs) and a chemical enhancement (CE) resulting from the change of the molecule' electronic structure when adsorbed on the metal surface.

In our work, we use a Kretschmann arrangement (KC), which allows for the study of the SERS effect using reproducible flat metal surfaces as SERS substrates. Dye molecules are used as adsorbates. The experiment has been optimized to achieve reproducible conditions. Within the experiment a decaying behavior of the Raman line intensities has been observed and analyzed. SERS spectra were obtained excluding the contribution of this deactivation process for different angles of incidence of the exciting laser beam. The Raman deactivation rate was found to be different for different vibrational modes where high-energy vibrations showed slower decay than the group of low-energy modes. The variation of the surface plasmon excitation in the thin silver film coated onto the prism surface of the KC resulted in drastically different relative enhancements of the different Raman modes pointing to a dominating contribution of the chemical enhancement mechanism in the single-layer SERS experiment.

MO 8.6 Tue 12:15 f142

A new laser desorption source for controlled molecule imaging — ●NICOLE TESCHMIT¹, DANIEL HORKE¹, KAROL DŁUGOŁĘCKI¹, DANIEL GUSA¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²The Hamburg Center for Ultrafast Imaging, Hamburg — ³Department of Physics, University of Hamburg

Control methodologies for neutral molecules allow for, e.g., the separation of different conformers, the alignment and orientation of molecules in space, and the separation of different quantum states or clusters, by using static and/or dynamic electric fields [1]. Such controlled molecules are ideal targets to gain structural and dynamic information with Coulomb explosion and diffractive imaging measurements [2].

Here, we present a new laser-desorption setup for the production of very cold molecules that will allow for the above mentioned control experiments. Large biological molecules will be vaporized and, subsequently, cooled by entrainment in supersonic noble gas beams. We present characterisation measurements of the created molecular beam and a quantitative comparison to other vaporisation methods such as

laser induced acoustic desorption and thermal vaporisation.

- [1] Y.-P. Chang et al, *Int. Rev. Phys. Chem.* 34, 557 (2015)
 [2] J. Küpper et al, *Phys. Rev. Lett.* 112, 083002 (2014)

MO 8.7 Tue 12:30 f142

The Structure of Water under Extreme Conditions — ●HENDRIK VONDRACEK, LUKAS KNAKE, and MARTINA HAVENITH — Ruhr-Universität Bochum, LS Physikalische Chemie II, Bochum, Deutschland.

Studies of water under extreme conditions (high and low temperatures, extreme pressures) are of particular scientific interest. Understanding the properties of water under extreme conditions is not only a fundamental prerequisite for a better understanding of geological and biological processes and the exploitation of various technical applications, but is also widely believed to be fundamental for a deeper understanding of the structure of water under ambient conditions.¹ Under high pressures and temperatures to the supercritical regime, the structure of water and the hydrogen bond network show peculiar features, e.g. clustering.²

THz spectroscopy is an ideal tool to study the structural properties of water as it allows for a direct study of the intermolecular hydrogen-bond network. The principle of this spectroscopic technique and specific experimental challenges will be explained. Furthermore, first results of spectroscopic measurements of water under high pressure conditions will be presented.

- [1] A. Nilsson, L.G.M. Pettersson - Perspective on the structure of liquid water - *Chem. Phys.*, 389,1-34 (2011). [2] Q. Sun, Q. Wang and D. Ding - Hydrogen Bonded Networks in Supercritical Water - *J.*

Phys. Chem. B, 118, 11253-11258 (2014).

MO 8.8 Tue 12:45 f142

High resolution IR-spectroscopy based on Synchrotron radiation — ●PIA KUTZER¹, OLIVIER PIRALI², and THOMAS GIESEN¹ — ¹Universität Kassel, Institut für Physik, Heinrich-Plett Str. 40, D-34132 — ²Société civile Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin - BP 48, F-91192 Gif Sur Yvette Cedex

The AILES beam line at SOLEIL Synchrotron facility is dedicated to a spectral range between 8 and 1500 cm⁻¹ with a maximum resolution of 0.0008 cm⁻¹. Together with a multi-pass White cell this allows high resolution Fourier transform spectroscopy with a long absorption pathlength up to 150 m with a very sufficient sensitivity.

This spectrometer is very useful for studies on stable molecules like eg. Dimethyl-Ether (DME) as well as for instable radicals. Especially its use for investigation of astrophysical molecules is of relevance in the interpretation of astrophysical spectra.

Here we present our results on astrophysically relevant DME isotopologues as well as on Tert-butyl-Phosphor-di-Bromide (PBr-tBu) a chiral molecule which has been studied for the first time by means of spectroscopy.

We recorded first infrared broadband spectra of PBr-tBu in the region of 100 cm⁻¹ to 650 cm⁻¹ at AILES beamline and also high resolution broadband spectra of singly and doubly ¹³C substituted DME in the region of 70 cm⁻¹ to 500 cm⁻¹.

Here we show our results on the vibrational bands of PBr-tBu and also on the C-O-C bending mode of DME isotopologues.

MO 9: Biomolecules and Photochemistry

Time: Tuesday 14:30–16:30

Location: f102

Invited Talk

MO 9.1 Tue 14:30 f102

Structural investigations on a linear depsipeptide and cyclopeptides by combined IR/UV spectroscopy: Importance of dispersion interactions — ANKE STAMM, DOMINIC BERNHARD, and ●MARKUS GERHARDS — TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern

Depsipeptides as a special subclass of peptides contain at least one ester bond replacing a peptide bond which gives rise to a different folding behavior compared to an ordinary peptide. For a better understanding of their biological activity on a molecular level, knowledge on the structure of the isolated depsipeptides is of importance. As a first model system investigated in a molecular beam experiment we have chosen cyclohexylcarbonyl-glycine-lactate-2-anisidine (CyCO-Gly-Lac-NH-PhOMe; abbrev.MOC). MOC represents a linear depsipeptide whose structural investigation should give basic insights into preferred conformations of isolated depsipeptides. The system contains both an aromatic phenyl ring and an aliphatic cyclohexyl ring which interact via CH/π dispersion interactions. This structure is only stable if dispersion is taken into account. An experimental analysis on the depsipeptide as well as on cyclopeptides is performed by application of mass- and isomer-selective combined double and triple resonance IR/UV methods in a molecular beam. In order to assign structures, DFT calculations including dispersion corrections were performed and compared with the experimental IR spectra.

MO 9.2 Tue 15:00 f102

Multiphoton microscopy for corneal pathologies diagnosis — ●ANA BATISTA^{1,2}, HANS GEORG BREUNIG^{1,3}, AISADA UCHUGONOVA¹, BERTHOLD SEITZ⁴, ANTÓNIO MIGUEL MORGADO^{2,5}, and KARSTEN KÖNIG^{1,3} — ¹Department of Biophotonics and Laser Technology, Saarbrücken, Germany — ²Institute for Biomedical Imaging and Life Sciences, Coimbra, Portugal — ³JenLab GmbH, Jena, Germany — ⁴Department of Ophthalmology, University of Saarland, Medical Center, Homburg/Saar, Germany — ⁵Department of Physics, Coimbra, Portugal

The diagnosis of corneal pathologies may be improved by multiphoton microscopy (MPM), which provides 3D imaging of the cornea with subcellular resolution, and information on tissue morphology and cells' metabolism. Here, we report on the use of MPM for ex-vivo characterization of non-pathological human corneas and evaluation of structural and metabolic changes due to pathology. A 5D multiphoton micro-

scope with high spatial, temporal, and spectral resolutions was used for image acquisition.

All layers of the human cornea were characterized ex-vivo based on their autofluorescence and SHG. The autofluorescence lifetime of the metabolic co-factors NAD(P)H and flavins was used to assess the cells' metabolic state. Corneal samples with different pathologies showed significant differences in the metabolism of corneal epithelial cells. Different collagen fibrils structural organizations as well as autofluorescence lifetimes were observed in the corneal stroma of pathological samples. Discrimination between different pathologies was also feasible.

MO 9.3 Tue 15:15 f102

Time-resolved XUV photoelectron spectroscopy of organic molecules in solution — ●JOHAN HUMMERT, GEERT REITSMA, IASON KATECHIS, MARTIN ECKSTEIN, and OLEG KORNILOV — Max Born Institut Berlin, Germany

The characteristics and function of biologically relevant molecules are often controlled by their environment, i.e. an aqueous solution or a protein. To investigate this interaction it is therefore imperative to study electronic structure and dynamics of molecules in solution. For this purpose we implement time-resolved photoelectron spectroscopy which can provide information unaccessible with techniques like transient absorption spectroscopy.

We combine our time delay compensating XUV monochromator [1] with the liquid jet technique [2]. This enables us to probe molecular electronic states with a single XUV photon of tunable energy in the range of 10 to 50 eV. With a tunable excitation wavelength (TOPAS) and a demonstrated time resolution of 40fs our setup is promising for investigation of diverse organic molecules in multiple solvents.

In first experiments we resolve the electronic ground states of water soluble molecules, investigating the shift of the ionization potential due to solvation. We further observe changes of the photoelectron spectrum of liquid water upon exposure to 400 nm light.

- [1] Eckstein et. al., *JPCL* 6, (2015): 419-25
 [2] Faubel et. al., *JCP* 106, (1997): 9013-31

MO 9.4 Tue 15:30 f102

High-resolution study of the smallest sugar dimer: Interplay of hydrogen bonds in the glycolaldehyde dimer — ●SABRINA ZINN^{1,2,3}, CHRIS MEDCRAFT¹, THOMAS BETZ¹, and MELANIE SCHNELL^{1,2,3} — ¹Max Planck Institute for the Structure

and Dynamics of Matter, Hamburg, Germany — ²Center for Free-Electron Laser Science, Hamburg, Germany — ³The Hamburg Centre for Ultrafast Imaging, Hamburg, Germany

The aggregation of glycolaldehyde was studied in a conformer-selective manner using high-resolution rotational spectroscopy in the gas-phase. Glycolaldehyde is formally the smallest sugar molecule, as it contains an aldehyde- and a hydroxy-group and was the first and so far the only sugar found in space. On this model system, we reveal hydrogen bond selectivity that guides the molecular recognition of carbohydrates in nature, in agreement with previous FTIR measurements.

In the high-resolution spectrum we assigned the rotational spectra of two stable dimer conformers. The lowest energy conformer reveals C_2 symmetry by forming two intermolecular hydrogen bonds and by giving up the rather strong intramolecular hydrogen bond. In addition, we assigned all of its singly ¹³C- and ¹⁸O- substituted species in natural abundance allowing us to determine the precise structure of this conformer. Predicting a precise structure of a weakly bound complex using quantum chemical calculations is still challenging, even for a small complex like the glycolaldehyde dimer. That is why an experimental determination of the structure is highly important to get precise information about the interplay of intermolecular interactions.

MO 9.5 Tue 15:45 f102

Molecular structure and chirality decrypted by rotational spectroscopy — ●SÉRGIO R. DOMINGOS¹, CRISTÓBAL PÉREZ¹, DAVID SCHMITZ¹, ANNA KRIN¹, AMANDA STEBER¹, DAVID PATTERSON², and MELANIE SCHNELL¹ — ¹Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany — ²Physics Department, Harvard University, Cambridge MA, United States

The ability to determine the conformation and handedness of chiral molecules is crucial in establishing how molecular structure and biological activity are related. Thus, fast and reliable methods that can analyze chiral mixtures are of utmost importance and are increasing in demand in chemical and pharmaceutical sciences. Chiral analysis using broadband rotational spectroscopy has been recently demonstrated [1] and is paving the way towards becoming an established analytical tool for chirality detection: radiation associated with a loop of three dipole-allowed rotational transitions is emitted exactly out of phase by molecules of opposite chirality, thus providing a direct signal of molecular chirality. The double-resonance scheme with two orthogonally-polarized transient electromagnetic fields results in the emission of microwave radiation along a third, mutually-orthogonal polarization, which we detect. The phase information encoded in the microwave field reveals the sign of the dipole-moment triple-product. Due to its resonant nature, microwave three-wave-mixing is developing into a probe of chirality with unprecedented conformer-selective capabilities. Recent studies on terpenes will be presented and discussed.

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

MO 10: Atomic clusters II (with A)

Time: Tuesday 14:30–16:30

Location: f107

MO 10.1 Tue 14:30 f107

Laser-induced delayed electron emission of Co_4^- clusters — ●CHRISTIAN BREITENFELDT^{1,2}, KLAUS BLAUM², SEBASTIAN GEORGE², JÜRGEN GÖCK², JONAS KARTHEIN², THOMAS KOLLING³, CHRISTIAN MEYER², JENNIFER MOHRBACH³, GEREON NIEDNER-SCHATTEBURG³, LUTZ SCHWEIKHARD¹, and ANDREAS WOLF² — ¹Institut für Physik, Ernst-Moritz-Arndt Universität, Felix-Hausdorff-Str. 6, 17487 Greifswald, Germany — ²Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ³Fachbereich Chemie, Universität Kaiserslautern, 67663 Kaiserslautern, Germany

The Cryogenic Trap for Fast ion beams CTF located at the Max-Planck-Institute for nuclear physics is an electrostatic ion beam trap setup for the study of dynamical processes of stored ion beams. A tunable optical parametric oscillator laser is used to induce delayed electron detachment, monitored by the rate of neutralized particles leaving the trap region as a function of time after laser excitation. By comparing the count rates after laser excitation at various photon energies ranging from 0.95 eV to 1.88 eV and different storage times the ions' internal energy distribution can be reconstructed. Two types of ion sources have been used to produce Co_4^- : First, a caesium ion

MO 9.6 Tue 16:00 f102

The Photodissociation of the Ortho-Xylyl Radical, C₈H₉, Investigated by Velocity Map Imaging — ●KAI PACHNER and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland Süd, 97074 Würzburg, Deutschland

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

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

MO 9.7 Tue 16:15 f102

Tracking chemical reactions with time-resolved sulfur-1s spectroscopy: Light induced radical formation and isomerization of 4-Methylbenzenethiol in the liquid phase — MIGUEL OCHMANN¹, ●INGA VON AHNEN¹, AMY CORDONES-HAHN², ABID HUSSAIN¹, JAE HYUK LEE², KIRYONG HONG^{2,3}, KATRIN ADAMCZYK¹, TAE KYU KIM³, ROBERT W. SCHONLEIN², ORIOL VENDRELL¹, and NILS HUSE¹ — ¹Department of Physics, University of Hamburg and Max Planck Institute for the Structure and Dynamics of Matter, Center for Free Electron Laser Science, Hamburg, Germany — ²Ultrafast X-ray Science Lab, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, USA — ³Department of Chemistry and Chemistry Institute of Functional Materials, Pusan National University, Busan, South Korea

Sulfur analogues to alcohols (R-SH) are abundant in nature and their chemistry is similar to alcohols. Recent results on the model system 4-methylbenzenethiol from transient absorption spectroscopy indicate sulfur radical generation upon UV excitation and formation of another species which eludes identification by optical spectroscopy. It was theorized that the hydrogen atom attaches to the aromatic ring. We used transient Sulfur-1s spectroscopy as a new element-specific probe of transient electronic and molecular structure. Two induced absorption peaks below the ground-state bleach clearly indicate formation of two new sulfur-species. Using TDDFT calculations we identified the thio-radical and a thione isomer with the photoejected hydrogen atom attached to the aromatic ring.

sputter source, known to produce ro-vibrationally excited ions at temperatures of more than 1000 K, and second, a laser vaporization source with helium expansion to produce ions with ro-vibrational excitation levels corresponding to low temperatures. The cooling and heating process of Co_4^- has been observed.

MO 10.2 Tue 14:45 f107

Quantum Monte Carlo study of Mg-doped droplets of helium-4 at zero temperature — ●YAROSLAV LUTSYSHYN and DIETER BAUER — Institut für Physik, Universität Rostock, 18051 Rostock, Germany

Mg-doped helium droplets are believed to have an observable metastable state in which the alkali atoms remain separated by a considerable distance, thus forming so-called "atomic foam". The exact nature of such a state is not well understood. We study the long-distance interaction induced between a pair of Mg atoms due to the confinement effects in the superfluid. We will present quantum Monte Carlo results for the effective interaction of the dopants.

MO 10.3 Tue 15:00 f107

Slow electrons from intense NIR laser-cluster interactions —

•B. SCHÜTTE^{1,2}, M. ARBEITER³, T. FENNEL³, A. I. KULEFF⁴, J. LAHL^{5,6}, T. OELZE⁵, M. KRUKUNOVA⁵, D. R. AUSTIN¹, C. STRÜBER¹, P. YE¹, M. J. J. VRAKING², J. P. MARANGOS¹, and A. ROUZÉE² — ¹Imperial College London, UK — ²Max-Born-Institut Berlin, Germany — ³Universität Rostock, Germany — ⁴Universität Heidelberg, Germany — ⁵TU Berlin, Germany — ⁶Lund University, Sweden

Clusters in intense NIR fields absorb laser energy extremely efficiently, resulting in the observation of keV electrons. Here we report on a surprisingly dominant contribution of slow electrons with kinetic energies < 2 eV following the ionization of rare-gas clusters by NIR pulses ($I = 5 \times 10^{14}$ W/cm²). Our THz streaking results reveal that these electrons are emitted with a significant delay in the picosecond to nanosecond range. We show that the emission of slow electrons can be expected from correlated electronic decay (CED) [1], which may involve autoionization processes [2]. In comparison to CED, where one electron relaxes from a Rydberg state to the ground state and transfers its excess energy to a nearby electron [1], the rates of intra-Rydberg CED processes can be orders of magnitude larger, and are associated with slow-electron emission. Our results may be the key to explaining the emission of highly charged ions from clusters that are observed in spite of the very efficient recombination of ions and electrons [3].

[1] B. Schütte *et al.*, Nat. Commun. **6**, 8596 (2015).

[2] B. Schütte *et al.*, Phys. Rev. Lett. **114**, 123002 (2015).

[3] B. Schütte *et al.*, Phys. Rev. Lett. **112**, 253401 (2014).

MO 10.4 Tue 15:15 f107

Photo excitation of size and charge-state selected multi-anionic aluminum clusters — •MARKUS WOLFRAM¹, STEPHAN KÖNIG¹, FRANKLIN MARTINEZ², GERRIT MARX¹, LUTZ SCHWEIKHARD¹ und ALBERT VASS¹ — ¹Felix-Hausdorff-Straße 6, Institut für Physik, Greifswald, Deutschland — ²University of Rostock, Germany

Studies of photo excited di-anionic gold clusters indicated that in addition to the well known competing mechanisms of electron detachment and cluster fragmentation the simultaneous emission of two electrons is another possible decay channel. However, in this case the neutral product cluster was no longer stored in the Penning trap and therefore could not be detected. In the meantime, by simultaneously storing cluster anions and electrons the production of gold and aluminum cluster anions of up to the sixth and tenth charge state, respectively, has been achieved. Furthermore, the experimental procedures for cluster preparation have been refined using the SWIFT (Stored Waveform Inverse Fourier Transform) technique. Thus, it is now possible to investigate the photo-induced decay pathways of stored anionic clusters as a function of cluster size n and charge state z beyond the dianions. After preliminary experiments with Nd:YAG laser beams, it is planned to extend the available photon energies by use of an OPO laser. In this contribution the recent modifications of the experimental setup and first results on the photo excitation of size and charge-state selected multi-anionic aluminum clusters will be presented. The project is funded by the Collaborative Research Center (SFB) 652

MO 10.5 Tue 15:30 f107

Energetic Highly-charged Ion Emission from Laser-induced Coulomb Explosion of Silver Clusters — •DZMITRY KOMAR, JOSEF TIGGESBÄUMKER, and KARL-HEINZ MEIWES-BROER — Universität Rostock, Institut fuer Physik, Albert-Einstein-Str. 24, D-18059 Rostock

Silver nanoparticles of about 4000 atoms are exposed to intense 130 fs optical single and double laser pulses (in the range 10^{13} - 10^{14} W/cm²). The detection system includes a newly developed momentum spectrometer which operates similar to a classical Thomson parabola spectrometer. However, the new setup features practically underground free measurement which allows for a huge dynamic range, an improved energy resolution and a significantly enhanced transmission. Charged resolved energy ion spectra from the laser-exposed Coulomb explosion of small silver clusters have been recorded. Under single laser pulse excitation conditions, multiply charged ions Ag q^+ (up to $q=12$) with energies exceeding 14 keV have been detected. Optical delay studies show the impact of nanoplasmonic oscillations on the ionization dynamics which reflects in the ion charge states as well as the recoil energies. Under optimal pump-probe conditions, i.e. when the Mie-frequency of the expanding nanoplasma matches the laser-nanoparticle resonance, significantly higher charge states (up to $q=19$) and more energetic ions (up to 300 keV) are observed. The collective electron motion most pronounced at the plasmon resonance has an impact on

the angular emission distribution of the ions. Especially the highly charged ions are predominantly emitted along the laser polarization axis.

MO 10.6 Tue 15:45 f107

Slow electrons from direct photoionization in clusters — •ABRAHAM CAMACHO GARIBAY, ULF SAALMANN, and JAN-MICHAEL ROST — MPI-PKS, Dresden

Sequential ionization of clusters by intense XFEL pulses is known to give a broad plateau like photoelectron spectrum. For sufficiently high charge states, the coulomb potential can be deep enough to trap the outgoing photoelectron, giving rise to a nanoplasma (an effect known as frustrated ionization). This nanoplasma eventually thermalizes and evaporates, giving rise to a high peak near zero. We have found that this high peak is formed not only by evaporating plasma electrons, but it also has a component from directly emitted photoelectrons that naturally arises during the transition between the sequential ionization regime into the frustrated ionization one. We have found that this effect can be explained in a simple way by noting that plasma electrons do not increase the system charge, which requires a small modification in the probability of electron emission as a function of position. By making a simple approximation it is possible to obtain an analytical formula with good agreement with the results obtained by means of molecular dynamics simulations.

MO 10.7 Tue 16:00 f107

Surface composition of free mixed NaCl/Na₂SO₄ nanoscale aerosols — •BURKHARD LANGER, EGILL ANTONSSON, CHRISTOPHER RASCHPICHLER, DMITRY MARCHENKO, and ECKART RÜHL — Physikalische Chemie, Freie Universität Berlin

Nanoscale NaCl/Na₂SO₄ aerosols ($d \approx 70$ nm) serve as a model for marine salt aerosols. The crystallization process of droplets of such binary salt solutions was measured using synchrotron radiation from BESSY II by photoelectron spectroscopy, which is particularly surface sensitive. Intensities of the chlorine $2p$ and the sulfur $2p$ lines in photoelectron spectra taken at a photon energy of 270 eV are compared for different mixing ratios of the salts. This allows us to determine the chemical surface composition of free, mixed NaCl/Na₂SO₄ aerosols grown by drying aqueous saline droplets. It turns out that the ratio of the surface constituents deviates significantly from the mixing ratio in the aqueous solution, whereby the minority species in droplets are increasingly found on the surface of the solid mixed aerosols. This result can be explained by the nucleation process during crystallization, in which each of the two salts produces its own pure crystal nuclei rather than crystallizing together. The variation of the surface ion concentration as a function of the mixing ratio in the droplets, as observed here for nanoscale aerosols, is in contrast to earlier findings suggesting a core-shell structure of mixed salt aerosols that are in the micron range [1].

[1] Z. Ge *et al.*, J. Colloid Interface Sci. **183**, 68-77 (1996).

MO 10.8 Tue 16:15 f107

Assigning cluster size and laser intensity specific features to single cluster ion spectra — •M. MÜLLER¹, M. SAUPPE¹, A. ULMER¹, B. LANGBEHN¹, Y. OVCHARENKO¹, L. FLÜCKIGER¹, S. TOLEIKIS², H. HÖPPNER², S. STEPHAN², T. GORKHOVER¹, J.-P. MÜLLER¹, D. RUPP¹, and T. MÖLLER¹ — ¹TU Berlin, Hardenbergstr. 36, 10623 Berlin — ²DESY, Notkestr. 85, 22607, Hamburg

Intense laser-cluster interaction results in nanoplasma formation which is a topic of current interest. Due to the finite size of clusters and their availability in the gas phase, no energy can dissipate into surroundings. An inherent difficulty in the analysis of most experimental results of laser-cluster interaction has been the convolution of the cluster size distribution and focal density distribution. Single-shot-single-particle experiments avoid averaging over the two mentioned distributions and allows for uncovering a large variety of individual processes. We present results from an experiment at the Free-Electron Laser FLASH (Hamburg, Germany) with a strong NIR and XUV-FEL source available at the same time. The ion-time-of-flight (TOF) spectra from clusters induced by intense and short NIR laser pulses taken in the single-shot-single-particle mode exhibit features depending either mainly on the laser intensity or the cluster size. For the latter we will compare our results with the size distribution derived from the FEL induced diffraction patterns. These assignments will be relevant for all kinds of single cluster experiments using optical lasers.

MO 11: Posters 2: Novelties in Molecular Physics: Femtosecond Spectroscopy, Quantum Control, Electronic Spectroscopy, Biomolecules and Photochemistry

Time: Tuesday 16:30–19:00

Location: Empore Lichthof

MO 11.1 Tue 16:30 Empore Lichthof
Relaxation and dissociation dynamics of XUV induced wavepackets in polyatomic molecules — ●GEERT REITSMA, MARTIN GALBRAITH, LORENZ DRESCHER, JOHAN HUMMERT, MARC VRAKING, OLEG KORNILOV, and JOCHEN MIKOSCH — Max-Born-Institut, Berlin, Germany

The combination of ultrafast science with advanced spectroscopic techniques, like mass spectrometry, velocity map imaging, and transient absorption spectroscopy, offers an excellent opportunity to gain knowledge on relaxation and dissociation dynamics in polyatomic molecules. However, in ultrafast science, one always has to reach a compromise between the optimal spectral and the optimal temporal resolution. At the same time this also triggers an intriguing question: To which extent does the coherence of the excitation process influence the molecular response? To address this question, we employ two HHG beamlines: one attosecond beamline providing <5fs time resolution with an intrinsically broad spectrum, and one monochromator beamline providing a 300 meV spectral resolution with a 30fs time-resolution. The attosecond beamline was used to measure photodissociation timescales of methyl iodine and iodobenzene by means of transient absorption spectroscopy, mainly making use of the broad spectrum of the ultrashort XUV-pulses. We measured non-adiabatic relaxation timescales of electron-correlation states in benzene and polycyclic aromatic hydrocarbons by means of time-resolved mass spectrometry. The monochromator beamline will be employed to obtain complementary data for selected harmonics.

MO 11.2 Tue 16:30 Empore Lichthof
Investigation of the transient absorption of the adsorbate in contact with different metallic surfaces — ●ALIREZA MAZAHERI TEHRANI, FAEZEH MOHAGHEGH, and ARNULF MATERNY — Physics and Earth Sciences, Jacobs University Bremen, Campus Ring 1, 28759 Bremen

The interactions of molecules adsorbed on metal surfaces with surface plasmon polaritons are of great importance for spectroscopic applications, such as surface enhanced Raman spectroscopy (SERS). So far, experimental SERS investigations have mostly been performed in the frequency domain using continuous wave lasers. This way, although the results are quite interesting concerning applications, they mostly fail to nicely address the underlying physical concepts and mechanisms of SERS. Time-resolved experiments, however, would help us to gain a better understanding of the underlying energy transfer mechanisms involved in surface enhanced spectroscopy due to different time scale characteristics of the adsorbate in various configurations. In this work we investigate the transient absorption of the adsorbate in contact with different metallic surfaces. Surface plasmons polaritons are excited with a femtosecond laser pulse (Pump) adjusted to the ground state absorption. Dynamic information of the system can then be probed by another time-delayed femtosecond laser pulse, which can freely be adjusted to other excited states of adsorbates or to the ground state absorption. This experiment provides us with a much deeper insight into the energy transfer mechanisms between SPPs and molecules.

MO 11.3 Tue 16:30 Empore Lichthof
Direct Observation of Excited State Chirality in Formic Acid — YAN YANG¹, HARAMRIT K. GILL¹, ●MARTIN PITZER^{1,2}, MAXSIM KUNITSKI¹, TILL JAHNKE¹, REINHARD DÖRNER¹, and MARKUS SCHÖFFLER¹ — ¹Institut für Kernphysik, Goethe-Universität Frankfurt am Main — ²Experimentalphysik IV, Universität Kassel

In this contribution, we present first results on a laser-induced excitation of the planar molecule formic acid (HCOOH) into a chiral excited state. As the energy barrier between the left-handed and right-handed forms (enantiomers) is generally lower in excited states than for chiral molecules in the ground state, the tunneling between the two enantiomers is expected to occur on timescales observable in a pump-probe setup. Measuring the tunneling time can help to detect a possible effect of parity violation in chiral molecules [1]. Formic acid molecules are among the most simple examples with a chiral π^* state [2]. Excitation into this state is accomplished by a femtosecond laser pulse and the handedness is probed by Coulomb Explosion Imaging, using a COLTRIMS-setup (Cold Target Recoil Ion Momentum Spectroscopy)

[3,4]. Different excitation energies and pump-probe schemes are employed in order to investigate the temporal behaviour of the excited molecule.

- [1] R. Berger, Phys. Chem. Chem. Phys. 5 (2003), 12-17
- [2] T.L. Ng and S. Bell, J. Mol. Spec. 50 (1974), 166-181
- [3] M. Pitzer, et al., Science 341 (2013), 1096-1100
- [4] R. Dörner, et al., Phys. Rep., 330 (2000), 95-192

MO 11.4 Tue 16:30 Empore Lichthof
Collinear two-dimensional spectroscopy via fluorescence detection with shot-to-shot phase cycling — ●SIMON DRAEGER¹, SEBASTIAN ROEDING¹, JAKUB DOSTÁL¹, ANDREAS STEINBACHER¹, PATRICK NUERNBERGER², and TOBIAS BRIKNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Physikalische Chemie II, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum

Coherent multidimensional spectroscopy is a powerful tool to study electronic couplings and coherences of molecular systems. We present a novel all-collinear setup to perform pulse-shaper-assisted two-dimensional electronic spectroscopy with fluorescence detection. The variation of the interpulse delays and their relative phases (phase cycling) is performed shot-to-shot with a pulse shaper (Dazzler, Fastlite) with 1 kHz rate, enabling a rapid data acquisition. We show data of a 4-pulse excitation of cresyl violet in the liquid phase and compare it with data acquired in the non-collinear BOXCAR geometry. With the applied acquisition scheme, rephasing and non-rephasing contributions can be extracted from one single measurement session via phase cycling.

MO 11.5 Tue 16:30 Empore Lichthof
Photoinduced processes of bilins in solution and as protein-bound cofactor — ●DANIEL MUSCHOL¹, MAXIMILIAN THEISS¹, PATRICK SINGER¹, NICOLE FRANKENBERG-DINKEL², TILMAN LAMPARTER³, and ROLF DILLER¹ — ¹Dept. of Physics — ²Dept. of Biology, Univ. Kaiserslautern, 67663 Kaiserslautern, Germany — ³Botanical Inst., Karlsruhe Inst. of Techn., 76131 Karlsruhe, Germany

Bilins are linear tetrapyrroles with rich and diverse photochemistry in solution, involving C-C single- and double-bond isomerization of one or several of the pyrrole-pyrrole methine bridges. When bound as cofactor to plant phytochrome proteins they serve as chromophores for a photoinduced signal cascade enabling red-light sensing and a variety of essential biological processes, such as seed germination, shade avoidance and photomorphogenesis. In the bound form protein-chromophore interaction restricts the potentially possible degrees of freedom and guides the excited electronic state dynamics along a complex reaction coordinate involving both chromophore as well as protein contributions, including H-bond networks and protein bound water molecules. For a better understanding of these mechanisms for molecular reaction control we study the primary photochemistry of the bilins biliverdin (BV), phycocyanobilin (PCB) and bilirubin (BR) in solution and of the BV-binding bathy-phytochromes Agp2 (*Agrobacterium fabrum*) and PaBphP (*Pseudomonas aeruginosa*) employing fs transient absorption in the UV/Vis and mid-IR spectral region. In particular, Agp2 shows strongly pH dependent primary reaction kinetics suggesting excited state proton transfer processes.

MO 11.6 Tue 16:30 Empore Lichthof
Robust control of molecular excitation using GDD-TOD-shaped femtosecond laser pulses — ●HENDRIKE BRAUN¹, TIM BAYER², CRISTIAN SARPE¹, MATTHIAS WOLLENHAUPT², and THOMAS BAUMERT¹ — ¹Universität Kassel, Institut für Physik und CINSaT, 34132 Kassel, Germany — ²Carl von Ossietzky Universität Oldenburg, Institut für Physik, 26129 Oldenburg, Germany

We report on adiabatic population control in molecules using intense shaped femtosecond laser pulses. The laser pulses employed are spectrally phase-shaped using a combination of second and third order dispersion [1]. The resulting pulses offer a variety of different temporal amplitude and phase shapes to optimally adapt to the laser-induced intramolecular excitation dynamics [2,3]. Third order dispersion (TOD) results in temporally asymmetric pulses featuring gentle slopes as well

as rapidly varying amplitude profiles. Group delay dispersion (GDD) provides time-dependent frequency sweeps being essential for adiabatic control scenarios [4]. In our experiments we investigate the interaction of GDD-TOD-shaped pulses with potassium molecules serving as a prototype system for coherent control scenarios. We support our experimental studies by quantum dynamics simulations in order to model the interaction processes and extract the quantum control mechanisms at play.

- [1] J. Schneider *et al.*, Phys. Chem. Chem. Phys. **13**, 8733 (2011)
 [2] H. Braun *et al.*, J. Phys. B **47**, 124015 (2014)
 [3] T. Bayer *et al.*, Adv. Chem. Physics, accepted
 [4] N. Vitanov *et al.*, Annu. Rev. Phys. Chem. **52**, 763 (2001)

MO 11.7 Tue 16:30 Empore Lichthof

Optimisation of strong laser field-free alignment using tailored light fields — ●EVANGELOS THOMAS KARAMATSKOS^{1,2}, TERRY MULLINS¹, SEBASTIAN TRIPPEL¹, ROSARIO GONZÁLEZ-FÉREZ³, ARNAUD ROUZÉE⁴, and JOCHEN KÜPPER^{1,2,5} — ¹Center for Free-Electron Laser Science, DESY — ²Department of Physics, University of Hamburg — ³Instituto Carlos I, Universidad de Granada — ⁴Max Born Institute, Berlin — ⁵The Hamburg Center for Ultrafast Imaging, University of Hamburg

Laser induced electron diffraction and molecular frame photoelectron angular distribution measurements have emerged as potential new techniques for imaging molecular structure and dynamics. Control over the rotational motion of molecules represents the first step towards this goal. Here, we present a combined theoretical and experimental effort to optimise the degree of laser field-free alignment of molecules in the gas phase. We start by solving the time-dependent Schrödinger equation for a rigid rotor in interaction with a non-resonant laser field and a static electric field [2] and use an iterative learning-loop algorithm to determine the ideal pulse shape that optimises the degree of alignment. These calculations serve as a guide to complement the experiments where the temporal profile of the alignment laser pulse is optimally tailored using a spatial light modulator in a feedback loop, using the same evolutionary strategies as in the simulations. We discuss the simulation results and the experimental realization on the example of the linear molecule OCS. [1] Stapelfeldt *et al.*, Rev. Mod. Phys. **75**, 543 (2003) [2] Omiste *et al.*, J. Chem. Phys. **135**, 064310 (2011)

MO 11.8 Tue 16:30 Empore Lichthof

Cavity-controlled ultracold chemistry — ●TOBIAS KAMPSCHULTE¹, ANDREAS KÖHN², and JOHANNES HECKER DENSCHLAG¹ — ¹Inst. f. Quantenmaterie, Universität Ulm — ²Inst. f. Theoretische Chemie, Universität Stuttgart

Ultracold molecules can be formed from ultracold atoms by photoassociation involving a spontaneous emission process, resulting in a number of final states. Here we want to use strong coupling to an optical cavity to selectively enhance the creation of a certain final state. During this process, a photon will be emitted into the cavity mode which can be detected. A collective enhancement of the effect would enable “superradiant chemistry”. Furthermore, we propose using the cavity as a non-destructive detector for ultracold molecules, i.e. by avoiding photon scattering. Finally, we present realistic parameters for cavities and how to integrate them into an existing cold-atom setup.

MO 11.9 Tue 16:30 Empore Lichthof

Strong-field ionization of HD molecules with two-color laser pulses — ●YONGHAO MI, NICOLAS CAMUS, MARTIN LAUX, LUTZ FECHNER, ROBERT MOSHAMMER, and THOMAS PFEIFER — Max-Planck-Institute for Nuclear Physics

Single and double ionization of HD molecules as well as fragmentation and Coulomb-explosion in strong two-color laser pulses (800 nm + 400 nm) have been studied utilizing a reaction-microscope. Asymmetries in the emission directions of both electrons and ions are analyzed as a function of the relative phase between the two fields and differences between the various fragmentation-channels are discussed in terms of possible ionization pathways.

MO 11.10 Tue 16:30 Empore Lichthof

Non-adiabatic dynamics and Dynamic Stark Effect: Wave-packet confinement and induced photon emission in alkali halides. — ●SIMONA SCHEIT¹, YASUKI ARASAKI², YUTA MIZUNO², and KAZUO TAKATSUKA² — ¹Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg — ²Department of Basic Science, Graduate School of Arts and Sciences, University of

Tokyo, Komaba, 153-8902, Tokyo, Japan

The two lowest Sigma states of alkali halides with their characteristic avoided crossing can be diabaticized in such a way that the two resulting diabatic states are those of minimum and maximum intrinsic dipole moment. Taking as example the LiF molecule it will be shown that, by shining a strong continuous non-resonant driving field in the visible, the non-adiabatic dynamics can be controlled by exploiting the Dynamic Stark Effect in such a way that the nuclear wave packet is trapped in the region of the crossing. The result is a back and forth transition between diabatic states of very different intrinsic dipole moments, with consequent fast oscillations in the molecular dipole moment resulting in the emission of dipole radiation with characteristic high harmonics structure. The effect of molecular rotation on the photoemission spectrum will be investigated, as well as the mechanism of wave-packet confinement, which leads to a complete suppression of photodissociation.

MO 11.11 Tue 16:30 Empore Lichthof

Angle-resolved spectroscopy of electron emissions by chiral molecules — ●JAN DREISMANN and STEFAN SCHIPPERS — AG Atom- und Molekülphysik, Justus-Liebig-Universität Gießen

Chirality of molecules is of essential importance to their effect in chemical reactions. The understanding of the importance of chiral molecules in biology and medicine is growing. However the physical properties of chiral systems are not well-known until now. There are many open questions like the chirality’s influence on the molecules’ atomic structure and electron dynamics. Interactions of polarized photons or electrons with chiral molecules can give insights in this unknown physics.

An electron spectrometer ESA-22 with angular resolution is used for analysis of electrons from these reactions. Electrons emitted in the spectrometers scattering plane pass electrostatic electrodes for energy separation and then are detected on 22 channel-electron-multipliers. Changes to the existing setup had to be made for using an molecular gas target and an electron beam instead of a photon beam.

We present first experimental spectra of Methyl lactate ($C_4H_8O_3$) taken after the refurbishments. Electron impact on this molecule leads to fragmentation thus we observe angle resolved Auger spectra for the main components oxygen and carbon.

MO 11.12 Tue 16:30 Empore Lichthof

Study of the self-reaction products of propargyl radicals via IR/UV ion-dip-spectroscopy — ●FLORIAN HIRSCH¹, PHILIPP CONSTANTINIDIS¹, INGO FISCHER¹, and ARGHYA DEY² — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Department of Molecular and Laser Physics, Institute for Molecules and Materials, Radboud University Nijmegen, 6525 AJ Nijmegen, Netherlands

The self-reaction products of propargyl radicals produced by flash pyrolysis have been studied by ion-dip-spectroscopy in a free jet. On the basis of the high stability of these radicals, it has been assumed for years that they might play an important role in the formation of polycyclic aromatic hydrocarbons (PAHs) and consequently soot.

The spectroscopic method utilized in this study is capable of providing mass selective infrared spectra, which can be used for unambiguous identification of the formed molecules. The radicals have been generated by flash pyrolysis from the bromide precursor and ionized at fixed wavelengths between 263 - 275 nm. A tunable free electron laser provided infrared radiation in the range of 550 - 1750 cm⁻¹. Subsequent analysis of the differences in ion signals, with and without infrared excitation, resulted in the sought after infrared spectra. Eventually comparison with theoretical and experimental data was performed for identification of the various reaction products.

This poster will provide a fundamental overview of methodology and results of this study, executed at the Free Electron Laser for Infrared eXperiments (FELIX) (Nijmegen, Netherlands).

MO 11.13 Tue 16:30 Empore Lichthof

Why Did Nobody Report on Single-Molecule Experiments on FMO Yet? — ●ALEXANDER LÖHNER¹, KHURAM ASHRAF², RICHARD COGDELL², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV and Bayreuth Institute of Macromolecular Research (BIMF), University of Bayreuth, Germany — ²Institute of Molecular, Cell & Systems Biology, College of Medical Veterinary and Life Sciences, University of Glasgow, United Kingdom

In green-sulfur bacteria sunlight is absorbed by chlorosomes and transferred to the RC via the Fenna-Matthews-Olson (FMO) complex.

FMO consists of three monomers each accommodating eight BChl a molecules, and was the first pigment-protein complex for which the structure has been determined with atomic resolution [1]. Since then this complex has been the subject of numerous studies both experimentally and theoretically.

Here we report about fluorescence-excitation spectroscopy as well as emission spectroscopy from individual FMO complexes at low temperatures. It appears that the FMO complexes are subjected to very fast spectral fluctuations resulting in spectra that resemble those from ensembles that were recorded under the same experimental conditions. In other words, on the time scales that are experimentally accessible by single-molecule techniques the FMO complex features an ergodic behaviour.

[1] Fenna, Matthews, Nature 258 (1975), 573

MO 11.14 Tue 16:30 Empore Lichthof

Investigation of synergetic effects on the photophysics of functional molecules in solvent mixtures — ●CHRISTIAN SPIES, CLAUDIO BEAKOVIĆ, BASTIAN GEISSLER, and PATRICK NUERNBERGER — Ruhr-University Bochum, Physical Chemistry II, Bochum, Germany

Several molecules are well known for their solvent-dependent photochromism, for instance spiropyrans can usually be switched by UV-light to a merocyanine form which absorbs in the visible spectral region. [1,2] The absorption wavelength, as well as the thermal ground-state relaxation rate into the spiro-form, shows synergetic effects in some solvent mixtures. [3,4] A synergetic effect causes a property of the solute to be higher or lower compared to each of the neat solvents. In this contribution we employ a systematic approach to analyze this kind of behavior in more detail to disclose which solvent and solute parameters are important for a synergetic effect to emerge. Steady-state as well as ultrafast time-resolved measurements in different solvent mixtures shed light on the interactions and dynamics in solution. It turns out that the occurrence of synergetic effects depends on a complex interplay between solvent-solvent and solvent-solute interactions. [1] J.B. Flannery, J. Am. Chem. Soc. 90 (1968), 5660. [2] C. Lenoble et al., J. Phys. Chem. 90 (1986), 62. [3] P. Jacques, Chem. Phys. Lett. 171 (1990), 353. [4] M. Rosés et al., J. Chem. Soc., Perkin Trans. 8 (1995), 1607.

MO 11.15 Tue 16:30 Empore Lichthof

Time-resolved fluorescence of 2-dimensional crystals of LH2 complexes — ●INGA ELVERS¹, PU QIAN², NEIL HUNTER², RICHARD HILDNER¹, and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Department of Molecular Biology and Biotechnology, University of Sheffield, Sheffield S10 2TN, United Kingdom

We investigate the fluorescence kinetics and energy transport properties of artificially arranged arrays of light-harvesting2 (LH2) complexes. The LH2 complexes were extracted from the purple bacterium *Rba. sphaeroides* and crystallised into 2-dimensional sheet-like or tubular crystals using a lipid from *E. Coli*. Employing a versatile streak-camera setup, we investigate the fluorescence kinetics of these arrays as a function of the excitation fluence and the repetition rate. We find that the lifetime of both samples are significantly shorter with respect to samples consisting of isolated LH2 complexes. Furthermore, the fluorescence decays of the arrays strongly depend on the variation of the excitation fluence and the repetition rate. These observations indicate the occurrence of exciton-exciton annihilation processes and allows to study the energy transfer dynamics within these arrays.

MO 11.16 Tue 16:30 Empore Lichthof

Design of an Experimental Setup for Optical Gating with Single Molecules — ●JOHANNES MAIER¹, TINA WELLER², MUKUNDAN THELAKKAT², MARTTI PÄRS¹, and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV and Bayreuth Institute of Macromolecular Research (BIMF), University of Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, Germany

Photochromic molecules can be interconverted between two metastable states by light [1-3]. We synthesized a triad consisting of a photochromic unit (Dithienylperfluorocyclopentene, DCP) and two highly fluorescent chromophores (Perylene Bisimide, PBI) and monitored the PBI fluorescence intensity as a function of the state of the DCP. To ensure sufficiently long observation times for the study of individual triads we had to achieve both an enhanced photostability and an improvement of the light collection optics. The former was accomplished by performing the experiments at cryogenic temperatures, and for the latter we resorted to solid immersion lens (SIL) optics [4], which yielded

an enhancement of the light collection efficiency by a factor of 1.8 with respect to the situation without the SIL. In first experiments we demonstrate distinctive changes of the fluorescence intensity emitted from individual triads triggered by changing the state of the DCP.

[1] Hirshberg: C. R. Hebd. Seances Acad. Sci. 1950, 231, 903 [2] Pärs, Hofmann, Willinger, Bauer, Thelakkat, Köhler: Angew. Chem. Int. Ed. 50 (2011), 11405 [3] Pärs, Gräf, Bauer, Thelakkat, Köhler: APL 103(2013), 221115 [4] Jasny, Sepiol, Irgartinger, Traber, Renn, Wild: Rev. Sci. Instrum. 67(1996), 1425

MO 11.17 Tue 16:30 Empore Lichthof

A molecular movie of Interatomic Coulombic Decay in NeKr — ●FLORIAN TRINTER¹, TSVETA MITEVA², MIRIAM WELLER¹, SEBASTIAN ALBRECHT¹, ALEXANDER HARTUNG¹, MARTIN RICHTER¹, JOSHUA WILLIAMS¹, AVERELL GATTON³, BISHWANATH GAIRE³, THORSTEN WEBER³, JAMES SARTOR⁴, ALLEN LANDERS⁴, BEN BERRY⁵, VASIL STUMPF², KIRILL GOKHBERG², REINHARD DÖRNER¹, and TILL JAHNKE¹ — ¹Institut für Kernphysik, Goethe-Universität, 60348 Frankfurt am Main, Germany — ²Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany — ³Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, California 94720, USA — ⁴Department of Physics, Auburn University, Auburn, Alabama 36849, USA — ⁵J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA

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

MO 11.18 Tue 16:30 Empore Lichthof

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

Time-resolved (TR) infrared experiments enable the investigation of chemical reactions, photochemical/-physical processes and their kinetic traces. With the step-scan technique we are able to identify electronically excited states and excited state structures by comparison with theoretical results from quantum chemical calculations. Here we present the first TR step-scan FTIR measurements on a dimetallic Cu(I)-NHETPHOS-complex in a KBr matrix. These complexes which are developed for emitter material in OLEDs are a very promising substitute for currently used Ir-complexes. We show the capabilities of step-scan FTIR measurements as well as femtosecond transient absorption and reflection measurements in a KBr matrix and thin films. Time-resolved IR spectra of electronically excited states have been obtained and in combination with quantum chemical calculations we could characterize the molecular structure of the electronic T₁-state (with a lifetime of about 2 μs). Wavelength and temperature dependent measurements have been performed to gain detailed information about the excited state processes and deactivation mechanisms.

MO 11.19 Tue 16:30 Empore Lichthof

A setup for time- and frequency resolved kinetic terahertz absorption spectroscopy using temperature jumps — ●CLAUDIUS HOBERG — Ruhr-Universität Bochum

The constant rearrangement of hydrogen bonds in the water network occurs on picosecond timescales having their spectral signatures in the THz frequencies. Solvents like salts and biomolecules are known to alter these picosecond motions of the hydrogen bond network. By using temperature jumps we induce non-equilibrium conditions in samples and monitor the kinetic response of the hydrogen bond network. The time-domain THz setup utilizes direct digitization of signals, rapid scanning techniques together with a temperature controlled sample cell. The setup provides a time resolution of 0.5 μs in the spectral range between 0.3 and 2.5 THz and a dynamic range of about 70 dB.

MO 12: Symposium SYML: From First Molecules to Life (with MS)

Time: Wednesday 11:00–13:00

Location: e415

Invited Talk MO 12.1 Wed 11:00 e415
Laboratory studies of interstellar molecules: from the first molecules to complex organics in space — ●HOLGER KRECKEL — Max-Planck-Institut für Kernphysik, Heidelberg, Germany

Modern telescopes have detected more than 180 different molecules, bearing witness to a surprisingly rich interstellar chemistry network that operates efficiently at extremely low densities and temperatures. The key to the molecular complexity in the gas phase are reactions between molecular ions and neutral atoms and molecules, as this class of reaction is often exothermic and barrier-less and therefore proceeds even in low-temperature environments. However, many of the key interstellar species are highly reactive under terrestrial conditions and thus difficult to study in the laboratory.

I will report on laboratory studies that simulate the formation of molecular hydrogen in the early universe and describe the merged beams technique that allows for the determination of energy-resolved rate coefficients for interstellar applications. Furthermore, I will introduce the planned neutral-ion collision setup at the Cryogenic Storage Ring (CSR) of the Max Planck Institute for Nuclear Physics (Heidelberg). This new experimental development aims at the study of ion-neutral collisions relevant for the formation of key species like water and complex organic molecules, under true interstellar conditions.

Invited Talk MO 12.2 Wed 11:30 e415
Detecting astrophysically relevant ions in laboratory and space — ●STEPHAN SCHLEMMER — 1. Physikalisches Institut, Universität zu Köln

Ions play a pivotal role in the astrophysics of the interstellar medium as they are readily formed by cosmic ray ionisation. They are also key species to understand the physics and chemistry of many other environments. Today's radio telescopes like the Atacama Large Millimeter Array (ALMA) and the airborne observatory SOFIA are sensitive enough to detect those species in space. In fact, many molecules and in particular some ions are first detected in space. However, laboratory spectra are missing as they are difficult to record due to their transient, i.e. highly reactive, nature. In recent years various meth-

ods of action spectroscopy have been developed in our group to overcome these limitations. In all cases changes in the rate of chemical reactions are imposed by excitation of the parent, mass selected ion. Recording the product formation in ion traps as a function of the excitation frequency results in the respective molecular spectra. Examples include mid-resolution vibrational, as well as high-resolution ro-vibrational and pure rotational spectra. In this presentation the methods are introduced and recent examples related to astrophysical searches in the radio frequency range will be discussed.

Invited Talk MO 12.3 Wed 12:00 e415
Interstellar ice - a hot topic — ●HAROLD LINNARTZ — Leiden Observatory, University Leiden

The talk reviews laboratory based studies of interstellar ice analogues. The physical and chemical processes at play upon UV irradiation and atom bombardment are discussed. It is shown how water and complex organics - building blocks of life - form in the solid state and how photodesorption rates help to understand the formation of planets.

Invited Talk MO 12.4 Wed 12:30 e415
Exoplanets: The Thorny Path to Habitable Conditions — ●MANUEL GÜDEL — Dept. Astrophysics, University of Vienna

Habitable conditions on planetary surfaces evolve as a consequence of complex interactions between the host star, the planet itself, and a variety of solid bodies in interplanetary space. The long journey toward habitability begins in the protoplanetary disk, the birthplace of planets; here, important molecules such as water and organics form, but also protoplanetary bodies grow and eventually accrete gas envelopes from the disk. At later stages, outgassing and colliding smaller bodies begin to form a secondary atmosphere with important molecular ingredients such as nitrogen, carbon dioxide and water. Meanwhile, the evolving stellar conditions, in particular stellar high-energy radiation and ionized winds, influence the evolution of the atmosphere, potentially leading to its severe erosion. In this presentation, I will describe the intricate interplay between these factors and discuss conditions that need to be met before a planet can become habitable.

MO 13: Symposium SYML: Molecules and Ions in Isolation (with MS)

Time: Wednesday 14:30–16:45

Location: e415

Invited Talk MO 13.1 Wed 14:30 e415
Physics with keV Ion Beams in the Cryogenic Storage Ring CSR — ●ANDREAS WOLF — Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany

As a cryogenic electrostatic storage ring, the CSR offers long-time storage for ion beams with energies in the multi-keV regime. The first operation [1] showed that the 35 m diam. electrostatic lattice of the ring could be successfully realized and operated at 6 K and at a residual gas density of $< 100 \text{ cm}^{-3}$. Beam storage times reached about 10 min or more for 60 keV ion beams in the studied range of mass numbers 16–218. With this, a new tool emerges for studying internal properties and fragmentation reactions of many types of complex gas-phase ions, both anions and cations. Moreover, the ring is designed for electron cooling, presently being implemented. We discuss the experimental perspectives of this facility and of long-time stored, phase-space cooled keV ion beams more generally.

[1] S. Vogel *et al.*, this Spring Meeting, MS Division.

First Cold Operation of the Cryogenic Storage Ring (CSR) — ●STEPHEN VOGEL¹, ARNO BECKER¹, KLAUS BLAUM¹, CHRISTIAN BREITENFELDT^{1,2}, SEBASTIAN GEORGE¹, JÜRGEN GÖCK¹, MANFRED GRIESER¹, FLORIAN GRUSSIE¹, 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, KAJA SPRUCK^{1,3}, STEFAN SCHIPPERS³, DIRK SCHWALM^{1,4}, LUTZ SCHWEIKHARD², ROBERT VON HAHN¹, and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, 69117 Heidel-

berg, Germany — ²Institut für Physik, Ernst-Moritz-Arndt Universität Greifswald, 17487 Greifswald, Germany — ³Institut für Atom- und Molekülphysik, Justus-Liebig-Universität Gießen, 35392 Gießen, Germany — ⁴Weizmann Institute of Science, Rehovot 76100, Israel

CSR is an electrostatic storage ring for ions of $< 300 \text{ keV}$ per unit charge kinetic energy. The ion beam optics and vacuum chambers of the 35-m circumference ring can be cryogenically cooled. The ring was cooled down with 4-K liquid He in 28 cryopumping units, starting from near 10^{-10} mbar vacuum at 300 K. Ion beams of 60–90 keV were stored for species including Ar^+ , OH^- , CH^+ , C_2^- , CO_2^- , Ag_2^- and Co_3^- . With the cold ring, extensive non-destructive beam diagnostics were performed including Schottky-noise and beam-position detection. Beam lifetimes up to 2500 s were measured by laser photodetachment. Inelastic collisions of the stored ions with rest gas molecules were nearly undetectable, indicating $< 100 \text{ cm}^{-3}$ rest-gas density (corresponding to $< 10^{-14}$ mbar pressure at 300 K). Rotational cooling of OH^- ions to $> 95\%$ in $J = 0$ was shown by near-threshold photodetachment.

Invited Talk MO 13.3 Wed 15:15 e415
A generalized theory for rovibrational motion in cold, extremely floppy molecules — ●HANNO SCHMIEDT¹, PER JENSEN², and STEPHAN SCHLEMMER¹ — ¹I. Physikalisches Institut, Universität zu Köln — ²Physikalische und Theoretische Chemie, Bergische Universität Wuppertal

We present a fundamentally new theory of the non-separable [1] rotational and vibrational motion in the class of extremely floppy molecules, with a special focus on its most prominent member, protonated methane (CH_5^+). Based on the molecular symmetry, we find the rotation group in *five* dimensions, $O(5)$, to be the underlying dy-

namical group. For protonated methane, it is now possible to predict for the very first time (i) energy levels in a zero-order approximation, (ii) dipole selection rules, and (iii) branching rules for the still valid three-dimensional angular momentum quantum number. Additionally, a classification of the eigenstates of the O(5) theory in the finite molecular symmetry group can be established.

Most astonishing, two new quantum numbers are identified to be the basis of the new theory. In this talk, we will show its very first application to experimental data, published only recently [2], and show how they fit surprisingly well within the zero-order approximation.

[1] Schmiedt, H., Schlemmer, S., Jensen, P., *J. Chem. Phys.* **143** (15), 154302 (2015)

[2] Asvany, O., Yamada, K.M.T., Brünken, S., Popatov, A., Schlemmer S., *Science* **347**, 1346-1349 (2015)

MO 13.4 Wed 15:45 e415

Control of small water clusters — •HELEN BIEKER^{1,2}, DANIEL HORKE^{1,2}, DANIEL GUSA¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY — ²The Hamburg Center for Ultrafast Imaging, University of Hamburg — ³Department of Physics, University of Hamburg

To unravel the microscopic details of intermolecular interactions in water, we prepare controlled samples of size- and isomer-selected water clusters. The spatial separation of neutral molecules can be achieved using inhomogeneous electric fields, allowing us to create pure samples of individual structural isomers or of size-selected 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 and subsequent dispersion of the various clusters in strong electric fields, extending previous studies [2]. Future experiments aim at utilizing x-ray and electron diffractive imaging to study the structures and the ultrafast dissociation/fragmentation dynamics of these polymolecular systems.

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

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

MO 13.5 Wed 16:00 e415

Chiral rotational spectroscopy — •ROBERT CAMERON^{1,2}, JÖRG GÖTTE^{1,2}, and STEPHEN BARNETT² — ¹Max-Planck-Institut für Physik komplexer Systeme, Dresden, Deutschland — ²School of Physics and Astronomy, University of Glasgow, Glasgow, UK

We present a new technique for the rotational spectroscopy of chiral molecules which enables the determination of individual components $G'_{XX}, G'_{YY}, G'_{ZZ}, A_{X,YZ}, A_{Y,ZX}$ and $A_{Z,XY}$ of the optical activity polarisability. Knowledge of these components fully characterises the enantiomeric constitution of a molecule. Our method gives an incisive signal for molecules with multiple chiral centres and even if the various stereoisomers of the chiral molecule are in a racemic mixture.

The necessary requirements on which our technique is based can also be found in space, which is why our method can also be exploited in the search for the molecular chirality in the interstellar medium, which, if found, could explain the existence of the biological homochirality of life as we know it.

Invited Talk MO 13.6 Wed 16:15 e415

Lead-cluster investigations at ClusterTrap — STEPHAN KÖNIG, PAUL FISCHER, GERRIT MARX, •LUTZ SCHWEIKHARD, MARKUS WOLFRAM, and ALBERT VASS — Institut für Physik, Universität Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald

During the last couple of years the Penning-trap setup ClusterTrap has been further extended and used for studies of the production and properties of poly-anionic metal clusters, focusing mainly on the elements gold and aluminum. Recent experiments reached out to further elements including lead. As before, the lead clusters were exposed to an "electron bath": Mono-anionic lead clusters were produced in a laser vaporization source and were transferred and captured in the trap; by shooting primary electrons axially through the trap, argon buffer-gas atoms are ionized. The argon cations immediately leave the trap while the secondary electrons stay stored and can attach to the clusters - provided they overcome the repulsing Coulomb barrier. The measurements as a function of cluster size yield the appearance sizes for doubly and triply charged anionic clusters. In addition, and unlike the other clusters, the lead clusters show distinct dissociation patterns, with very prominent peaks at the (monoanionic) dodecamer and in particular the decamer. These clusters are also dominant in photodissociation spectra of larger mono-anions and apparently also of the dianions. The experiments are still ongoing and will be extended with respect to further charge states, including cationic species.

MO 14: Posters 3: Novelties in Molecular Physics: Theory of Molecular Dynamics, Collisions and Energy Transfer, and Experimental Techniques

Time: Wednesday 16:30–19:00

Location: Empore Lichthof

MO 14.1 Wed 16:30 Empore Lichthof

Quantum dynamics and electronic effects in ion-molecule interactions in cold traps — •IBROKHIM ISKANDAROV, FABIO CARELLI, FRANCESCO GIANTURCO, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria

Until a few years ago, studies of cold reactive processes in hybrid-traps have been restricted to atomic ions and neutral atoms. The ion-neutral hybrid-trapping technique has been recently extended to also probe cold reactive collisions of sympathetically cooled molecular ions by their interaction with laser cooled atomic ions [1]. By choosing N_2^+ molecules and Rb atoms as a system, they can reveal very important features about the interaction forces between molecular ions and atoms.

Inelastic collisions with neutral buffer gas have been shown to represent an effective way to cool the internal molecular degrees of freedom and going beyond the translational cooling [2]. This approach rests on the fact that in the framework of the neutral buffer gas cooling scheme, the rotational molecular temperature can be tuned to a value lower than the translational one. We are currently computationally probing this effect in case of interaction of MgH^+ with He as a buffer gas.

[1] F. Hall and S. Willitsch, *Phys. Rev. Lett.* **109**, 233202 (2012).

[2] P.F. Staunum, K. Højbjerg, P.S. Skyt, A.K. Hansen, M. Drewsen, *Nature Physics* **6**, 271 (2010).

MO 14.2 Wed 16:30 Empore Lichthof

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

The purpose of this work is a first comparison of two methods describing a coupled electron-nuclear dynamics: the purely quantum mechanical ansatz NEMol and the TD-DFT based Ehrenfest dynamics. For this purpose the dynamics of (Z)-3-aminoacrolein in the electronic ground state was analyzed. Using different quantum chemical methods the potential profile of tautomerism was calculated and the critical points of the reaction were identified to set up one-dimensional potential energy surfaces along the reaction. We introduce a novel form of the NEMol ansatz which is formulated for a single electronic state. This modified NEMol ansatz was used to calculate the dynamics of the tautomerism using the one-dimensional potential energy surfaces. The TD-DFT based Ehrenfest dynamics was investigated for a single trajectory. The comparison between the NEMol ansatz and the TD-DFT Ehrenfest dynamics is so far limited due to the difference in dimensionality. Therefore the first steps for a one-dimensional TD-DFT Ehrenfest dynamics are presented. Comparing the TD-DFT Ehrenfest trajectory with a semi classical trajectory shows that the electron dynamics has an influence on the motion of the nuclei even for this very simple reaction in the electronic ground state.

MO 14.3 Wed 16:30 Empore Lichthof

Ab initio calculations of the Ion feature in X-ray Thomson scattering — KAI-UWE PLAGEMANN¹, HANNES RÜTER¹, THOMAS BORNATH¹, •MOHAMMED SHIHAB^{1,2}, MICHAEL P. DESJARLAIS³, CARSTEN FORTMANN⁴, SIEGFRIED H. GLENZER⁵, and RONALD REDMER¹ — ¹Institut für Physik, Universität Rostock — ²Physics Department, Tanta University, Egypt — ³SNL, Albuquerque, USA — ⁴QuantumWise A/S, 2100 Copenhagen, Denmark — ⁵SLAC, Menlo Park, CA 94025, USA

Warm dense matter of solid-like densities and temperatures of several eV is relevant for planetary interiors and inertial confinement fusion experiments. A versatile and reliable tool to probe such extreme states of matter is X-ray Thomson scattering (XRTS) from which information about plasma parameters like electron density, electron temperature and mean ionization state can be inferred directly from the dynamic structure factor [1]. An important contribution to the dynamic structure factor is the ion feature [4] which describes elastic scattering of X-rays off electrons. We apply an ab initio method for the calculation of the form factor of bound electrons, the slope of the screening cloud of free electrons, and the ion-ion structure factor in warm dense beryllium. With the presented method we can calculate the ion feature from first principles [5]. These results will facilitate a better understanding of X-ray scattering in warm dense matter and an accurate measurement of ion temperatures which would allow determining non-equilibrium conditions, e.g., along shock propagation.

MO 14.4 Wed 16:30 Empore Lichthof

Ab initio calculations of the Ion feature in X-ray Thomson scattering — KAI-UWE PLAGEMANN¹, HANNES RÜTER¹, THOMAS BORNATH¹, •MOHAMMED SHIHAB^{1,2}, MICHAEL P. DESJARLAIS³, CARSTEN FORTMANN⁴, SIEGFRIED H. GLENZER⁵, and RONALD REDMER¹ — ¹Institut für Physik, Universität Rostock, Germany — ²Physics Department, Tanta University, Egypt — ³SNL, Albuquerque, USA — ⁴QuantumWise A/S, 2100 Copenhagen, Denmark — ⁵SLAC, Menlo Park, CA 94025, USA

Warm dense matter of solid-like densities and temperatures of several eV is relevant for planetary interiors and inertial confinement fusion experiments. A versatile and reliable tool to probe such extreme states of matter is X-ray Thomson scattering (XRTS) from which information about plasma parameters can be inferred directly from the dynamic structure factor [1]. An important contribution to the dynamic structure factor is the ion feature [2] which describes elastic scattering of X-rays off electrons. We apply an ab initio method for the calculation of the form factor of bound electrons, the slope of the screening cloud of free electrons, and the ion-ion structure factor in warm dense beryllium. With the presented method we can calculate the ion feature from first principles [3]. These results will facilitate a better understanding of X-ray scattering in warm dense matter and an accurate measurement of ion temperatures which would allow determining non-equilibrium conditions, e.g., along shock propagation. [1] Glenzer and Redmer, *Rev. Mod. Phys.*, 81(2009). [2] Chihara, *J. Phys.: Condens. Matter*, 12(2000). [3] K.-U. Plagemann et al., *Phys. Rev. E* 92(2015).

MO 14.5 Wed 16:30 Empore Lichthof

Charge transfer reactions with Ar⁺ in its ground state — TIM MICHAELSEN, •BJÖRN BASTIAN, ATILAY AYASLI, JENNIFER MEYER, EDUARDO CARRASCOSA, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria

The crossed-beam technique has become the method of choice for the analysis of reaction dynamics [1] as it allows to precisely assess the complete kinematics of both reactants and products. In the last decade, it could be extended from neutral partners to ion neutral reactions [2]. The combination with three-dimensional velocity map imaging has allowed us to obtain energy- and angle-differential cross sections for the Ar⁺+N₂ charge transfer reaction [3], opposing previous experimental results and in agreement with theoretical predictions [4]. Recently, a radio-frequency ion trap has been added to our setup that allows to achieve an improved energy resolution of the ion beam and, more notably, quenching of reactant ions to their ground state.

Here, we present the status of experiments that aim for fully state-to-state resolved differential cross sections of the charge transfer reaction involving the Ar⁺ ground state into the different vibrational levels of the N₂⁺ product. Further, reactions with other neutral partners as O₂ and CO will be considered.

[1] Y. T. Lee. *Science* **236** (4803), 793 (1987). [2] J. Mikosch et al. *Phys. Chem. Chem. Phys.* **8**, 2990 (2006). [3] S. Trippel et al. *Phys. Rev. Lett.* **110**, 163201 (2013). [4] R. Candori et al. *J. Chem. Phys.* **115**, 8888 (2001).

MO 14.6 Wed 16:30 Empore Lichthof

Toward ion-neutral collision measurements at the CSR — •ELISABETH A. GUERIN, FLORIAN GRUSSIE, AODH P. O'CONNOR, and HOLGER KRECKEL — Max-Planck-Institut für Kernphysik, Heidelberg

To date, almost 200 molecules have been detected in the interstellar medium or circumstellar shells, including relatively complex organic molecules. It has become clear that two-body ion-neutral collisions play a critical role in the formation of molecules in the interstellar medium. However, with temperatures in interstellar clouds typically ranging from 10 to 100 K, the exact pathways and time scales of chemical reactions under these conditions are still poorly studied. In particular, thermal rate coefficients at relevant conditions have not been experimentally established for most ion-neutral reactions.

Simulating such reactions in a laboratory environment is one goal for the Cryogenic Storage Ring (CSR) located at the Max Planck Institute for Nuclear Physics in Heidelberg. Cooled ions (~10K) stored in the ring will be merged with a neutral atomic beam at a tunable center of mass collision energy. Reaction rate coefficients can be determined by measuring particle fluxes, beam overlap and the production rate of reaction products. The storage ring itself has been successfully commissioned in the summer of 2015 with the experimental vacuum chambers reaching temperatures below 10K. In the neutral beam setup, neutral particles will be created by photodetachment of a negative ion beam (kinetic energy up to 300 keV) which for this purpose is crossed with a continuous wave high-power diode laser (2 kW) operating at 808 nm.

MO 14.7 Wed 16:30 Empore Lichthof

First experiments with the Cologne Chirped Pulse FTMW Spectrometer — •MARIUS HERMANN¹, CHRISTIAN ENDRES², ALEXEY POTAPOV¹, and STEPHAN SCHLEMMER¹ — ¹I. Physikalisches Institut, Universität zu Köln, Zùlpicher Strasse 77, 50937 Köln, Germany — ²present address: Max Planck Institute for extraterrestrial Physics, Giessenbachstrasse 1, 85748 Garching, Germany

Detection of complex molecules in space strongly relies on the ability to reproduce and precisely measure their spectra in the laboratory [1, 2]. With the recent advancements in semiconductor development and the ability to have fast and high frequency amplifiers and detectors available the chirped pulse Fourier transform microwave techniques has been widely tested and established [3]. Having the ability to polarize a molecular ensemble and study its free induction decay and its collision behaviour within short measuring times promises to improve our understanding of molecular collisions in space.

Here we report and present our set-up of a chirped pulse Fourier transform microwave spectrometer. Utilizing a short waveguide molecular gas cell on a cold head we hope to be able to measure and characterize pure rotational transition data on many complex molecules in the frequency range of 2-26.5 GHz using a 5 GHz arbitrary waveform generator. Preliminary measurements on ammonia as a proof of concept were taken and are presented as a benchmark for sensitivity.

[1] A. Belloche et. al, *A&A* (2013).

[2] Müller, H. S. P. et. al, *A&A* (2001)

[3] Brown, G. G., *Review of Scientific Instruments* (2008)

MO 14.8 Wed 16:30 Empore Lichthof

The low-energy electron cooler for the Cryogenic Storage Ring (CSR) — •PATRICK WILHELM, KLAUS BLAUM, CLAUDE KRANTZ, JORRIT LION, SVENJA LOHMANN, OLDŘICH NOVOTNÝ, STEPHEN VOGEL, and ANDREAS WOLF — Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Deutschland

In the recently commissioned Cryogenic Storage Ring CSR, molecular ions are stored for hundreds to thousands of seconds in a low temperature radiation field with a mean temperature below 10 K. By this, stored ionic molecules and clusters can undergo radiative relaxation down toward their ro-vibrational ground-state. Measurements probing fundamental molecular and cluster dynamics can be performed with good internal state definition. For phase-space cooling and for high-precision electron-ion reaction experiments, a low-energy velocity-matched merged electron beam device is set up for the cryogenic environment. Cold electrons are produced by a GaAs photocathode setup at 300 K. The merging of the electrons with the stored ion beam is realized by a cryogenic magnetic guiding field created by a set of solenoids, toroids and racetrack coils made from high-temperature superconductors. The CSR electron cooler is designed to achieve an average kinetic electron beam energy of as low as 1 eV at a thermal energy spread

of about 1 meV. The manufacturing process of the cooler system is completed; implementation in the storage ring and commissioning are planned for the first half of 2016.

MO 14.9 Wed 16:30 Empore Lichthof
Mesophase Behaviour of Binary Mixtures of Symmetric Ester-Type Banana-Shaped Compounds — ●MIROSLAV CVETINOV¹, MAJA STOJANOVIĆ¹, DUŠANKA OBADOVIĆ², ANIKO VAJDA³, KATALIN FODOR-CSORBA³, NANDOR EBER³, NEMANJA TRIŠOVIĆ⁴, and JELENA ANTANASIJEVIĆ⁴ — ¹University of Novi Sad, Faculty of Sciences, Department of Physics, Novi Sad, Serbia — ²University of Novi Sad, Faculty of Education, Sombor, Serbia, — ³Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary — ⁴University of Belgrade, Faculty of Chemistry, Belgrade

We have investigated three binary mixtures composed of two symmetric ester-type banana-shaped compounds. Compound I is 2,6-bis[2-(4-ethanoyloxyphenyl)ethenyl]pyridine, which is banana-shaped mesogen expressing banana B1 mesophase at high temperature range. Compound II, 1,3-phenylene-bis[4'-(9-decenyloxy)benzoyloxy] benzoate, doesn't exhibit any mesophase in cooling down to its crystallization temperature. The occurring mesophases have been identified by their optical textures and by the means of X-Ray diffraction. Molecular models were prepared using RM1 model of semi-empirical quantum chemistry. At the concentration of 27wt% of compound II, there is apparent lowering of B1 mesophase temperature range in respect to the pure compound I. Yet, at the concentration of 36wt% of compound II, the mixture lost its mesogenic character. Hence, mixing two classic banana-shaped compounds is viable way to attain mesophase range closer to the room temperature.

MO 14.10 Wed 16:30 Empore Lichthof
High-resolution spectroscopy on the hyperfine structure of small aluminum bearing molecules — ●BJÖRN WASSMUTH¹, ALEXANDER BREIER¹, THOMAS F. GIESEN¹, and JÜRGEN GAUSS² — ¹Institut für Physik, Universität Kassel, 34132 Kassel, Germany — ²Institut für Physikalische Chemie, Universität Mainz, 55099 Mainz, Germany

An advanced method of producing metal-containing small molecules in the gas phase is based on laser ablation technique. The vaporized gas phase products can be investigated by means of millimeter/submillimeter-wave spectroscopy or by using high-resolution spectrometers in the visible frequency range. The experimental investigation is guided by high-level quantum chemical calculations performed at Mainz.

These experimental methods have been applied to measure AIO and ALS produced by laser ablation of solid aluminum and a dilution of N₂O (2%) or H₂S (7%) in helium. The adiabatically expanding gas mixture is probed by monochromatic radiation in the frequency range up to 400 GHz. Measurements reveal the hyperfine structure of both linear molecules to follow Hund's case $b_{\beta S}$ coupling due to the nuclear spin of aluminum. With the present measurements new highly accurate line positions for future observations and more accurate molecular parameters are available.

MO 14.11 Wed 16:30 Empore Lichthof
Laserbasierte XUV Quelle mit Monochromator für zeitaufgelöste Molekülspektroskopie — ●MARKUS PFAU, MARTIN RANKE, FAWAD KARIMI, ANASTASIOS DIMITRIOU und ULRIKE FRÜHLING — Institut für Experimentalphysik, Universität Hamburg

Für die Untersuchung der Elektronendynamik in Molekülen sind Femtosekunden Lichtpulse mit Photonenergien im Spektralbereich von Vakuumultraviolett bis hin zum weichen Röntgenbereich notwendig. Eine Möglichkeit zur Erzeugung dieser Photonen ist die Nutzung der höheren Harmonischen eines Laserstrahls. Da die Harmonischen kollinear über einen breiten Spektralbereich emittiert werden, ist eine spektrale Trennung nötig.

Wir berichten hier über ein Experiment zur Erzeugung intensiver hoher Harmonischer im XUV Bereich und einem Gittermonochromator zur Trennung der Harmonischen, welcher zum Einen eine hohe Transmission aufweist und zum Anderen die Pulslänge von ca. 35 fs nicht wesentlich vergrößert. Außerdem wird ein experimenteller Aufbau zur zeitaufgelösten Molekülspektroskopie vorgestellt.

MO 14.12 Wed 16:30 Empore Lichthof
Laser absorption spectroscopy of iodine: 915 nm to 985 nm in

a single scan — ●CHRISTIAN NÖLLEKE, STEPHAN FALKE, CHRISTOPH RAAB, and RUDOLF NEUHAUS — TOPTICA Photonics AG, Lochhamer Schlag 19, Gräfelfing/München, Germany

Iodine gas cells serve as frequency reference for lasers thanks to the good understanding of their rich molecular spectrum. This is particularly true for the wavelength range 500 nm to 900 nm, where the theoretical model of the B-X system and experimental findings agree on a level of a few MHz. Hence, iodine cells provide frequency references with a line spacing of typically a few GHz only.

In order to extend this knowledge towards longer wavelengths, a deeper understanding of the A-X system of iodine is required. Recent developments in laser technology enable high-resolution spectroscopy with unprecedented ease. In this work, we record absorption spectra with a 75 cm long iodine cell, in which vapor pressure and temperature of the molecular gas is controlled independently. We utilize the vast mode-hop-free tuning range of the DLC CTL developed within our company to investigate the distribution of observable molecular lines as well as their signal-to-noise ratio in the range 915 nm to 985 nm. Moreover, for selected lines, we perform at saturation absorption spectroscopy using the fine-tuning of the laser. This experiment is an important step towards a detailed theoretical model of the A-X system and hence a good frequency reference in this range.

MO 14.13 Wed 16:30 Empore Lichthof
Detection system for dissociative recombination studies at the Cryogenic Storage Ring — ●SUNNY SAURABH¹, ARNO BECKER¹, CLAUDE KRANTZ¹, OLDŘICH NOVOTNÝ¹, STEFAN SCHIPPERS², KAIJA SPRUCK², XAVIER URBAIN³, STEPHEN VOGEL¹, and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, D-69117 Heidelberg, Germany — ²Institut für Atom- und Molekülphysik, Justus-Liebig-Universität Gießen, 35392 Gießen, Germany — ³Université Catholique de Louvain B-1348 Louvain-la-Neuve, Belgium

Dissociative recombination (DR) is an important destruction and neutralization process in plasma environments, such as the interstellar medium. DR reaction rates, product channels and product excitation states are important parameters for describing such environments. Based on this DR reaction dynamics can be understood as well. We are planning to perform DR experiments in cold environment below 10 K for the first time in our newly commissioned Cryogenic Storage Ring at MPIK. In a configuration of merged electron and ion beams, neutral products form and leave the ion beam orbit. To collect these products a large-area, MCP-based neutral particle detector is used. The detector provides relative temporal information on neutral products in \sim ns time scale. A fast \sim 1 kHz frame-rate CMOS camera viewing the phosphor screen anode will allow us to correlate this temporal information with the product impact positions on the detector surface on event-to-event basis. For this purpose, a new data acquisition system to control the detector, the timing, and the collision energy between the electron and ion beams for DR rate measurements is under development.

MO 14.14 Wed 16:30 Empore Lichthof
Investigation of 1-Phenylethanol with Circular Dichroism - Resonance-enhanced Multiphoton Ionization (CD-REMPI) in the Gas Phase — ●JÖRN LEPPELMEIER, ARAS KARTOUZIAN, ULRICH BOESL, and ULRICH HEIZ — Lehrstuhl für Physikalische Chemie, Technische Universität München, Germany

The Circular Dichroism - Resonance-enhanced Multiphoton Ionization (CD-REMPI) provides a three dimensional discrimination methode for the investigation of chiral molecules in the gas phase. Beside the already two dimensional combination of mass selectivity given by a Time Of Flight - Mass Spectrometer (TOF-MS) together with wavelength selectivity due to Resonance-enhanced Multiphoton Ionization (REMPI), an enantioselective component is added by utilizing the Circular Dichroism (CD) effect. Therefore, within the REMPI process the resonance excitation of the studied molecules is initialized by circularly instead of linearly polarized light. Thus, CD-REMPI allows fast enantiosensitive gas phase studies of chiral molecules without the requirement of previous sample preparation. These are ideal conditions e.g. for the detection of product species coming from stereoselective catalysis reactions.

With our contribution we want to demonstrate the sensitivity of the CD-REMPI technique with enantiomeric excess measurements regarding the asymmetry factor g of 1-Phenylethanol by using the Twin-Peak methode [1].

[1] C. Logé and U. Boesl, ChemPhysChem, 12 (2011) 1940-1947

MO 14.15 Wed 16:30 Empore Lichthof

ion-ion coincidence imaging using an in-vacuum pixel detector — ●JINGMING LONG¹, FEDERICO FURCH¹, JUDITH DURÁ¹, ANTON TREMSIN², CLAUD-PETER SCHULZ¹, ARNAUD ROUZÉE¹, and MARC VRAKKING¹ — ¹Max Born Institute for Nonlinear Optics and Short Pulses Spectroscopy, Max Born Straße 2A, 12353, Berlin, Germany — ²Space Sciences Laboratory, University of California at Berkeley, Berkeley CA 94720, USA

The ionization and fragmentation of molecules by intense laser fields has been the subject of intense research for decades. Two main experimental techniques developed to record the momentum distribution of the charged particles generated from strong field ionization are widely used: the velocity map imaging and the 3D coincidence imaging. The full 3D momentum vectors of all participating fragments can be measured in coincidence using a reaction microscope (REMI) or a cold target recoil ion momentum spectrometer (COLTRIMS).

Recently, we have implemented a new in vacuum pixel detector, the so-called Timepix, as a replacement of traditional delay line anodes. This new 3D detector has been tested for ion-ion coincidence experiments showing the possibility to reach sub-pixel spatial resolution (<55 μm) and a 25 ps temporal resolution, at a 1 kHz frame readout rate. Combined with a high repetition rate (400 kHz) laser, our ion-ion coincidence imaging spectrometer can achieve an event rate faster than 10^4 ion events per second, and can be a powerful tool in studies of ultrafast nuclear dynamics in strong laser fields.

MO 14.16 Wed 16:30 Empore Lichthof

A novel technique to study time-resolved structural imaging of transition state dynamics — ●KATRIN REININGER, FRIEDRICH FREYSE, and JOCHEN MIKOSCH — Max-Born-Institute, Berlin

Progress in time-resolving transition state dynamics of bimolecular chemical reactions has been very limited due to the start-time dilemma and the absence of a significant probe mechanism, which gives insight into the structural dynamics.

We are developing a novel probe that images, one molecule at a time, the time-dependent spatial structure of individual transition states. For this we combine two modern techniques of molecular physics: (i) Reaction precursors are prepared as small clusters of ions and neutral molecules which serve as starting point for inducing transition state dynamics by photodissociation of a chromophore. The relative collision energy is tunable by varying the photodissociation wavelength. (ii) Coulomb Explosion Imaging, induced by short and intense infrared laser pulses combined with full coincidence detection of the resulting positively charged fragments will then be used to follow the dynamics and ultimately to reconstruct the evolving spatial molecular structure.

We will present the experimental setup and its characterisation. First experiments on controlling vibrations in a diatomic molecule will be shown. To increase the repetition rate, the implementation of an Electrostatic Ion Beam Trap to recycle the ion target is investigated.

MO 14.17 Wed 16:30 Empore Lichthof

Multiplex Detection of Homodyne Nonlinear Time-Resolved Signals for Multimodal Spectroscopy — ●ANDREAS LUDWIG, TAKESHI MIKI, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität, D-69120 Heidelberg, Germany

The goal of Multimodal Time-Resolved Spectroscopy is the combination of multiple time-resolved signals to understand complex molecular dynamics. Spectral resolution of such signals is a fundamental aspect because signal contributions in different techniques appear at different detection wavelengths. While detection at kHz rates of (self-) heterodyne signals, like those of transient absorption, is nowadays straightforward, the same is not true for weak homodyne signals. In this work, we have implemented a detection setup based on a spectrometer and kHz CCD. The setup covers the spectral range from 450 to 700nm with a resolution of about 1nm. Readout rates of up to 1.5kHz can be achieved. Synchronizing the CCD detector readout to the laser as well as to the scanning of optical delay stages enables shot-to-shot detection. The setup is benchmarked by detecting spectrally resolved third- and fifth-order techniques like degenerate four-wave mixing, pump-four wave mixing and 2D Raman at 1kHz readout rates. Dephasing of vibrational coherence in the excited state and coupling between different modes is demonstrated for different organic molecules in solution.

MO 14.18 Wed 16:30 Empore Lichthof

Spectral focusing with flexible shaped laser pulses for chemical imaging — ●LUKAS BRÜCKNER, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Universität Hei-

delberg, Germany

Due to the high degree of control, the implementation of spectral focusing into a single-beam CARS setup containing a pulse shaper has several advantages over usual multi-beam setups and opens up new possibilities. We show in simulation and experiment how the flexible adjustment of the spectral focusing phase makes it possible to address and optimize multiple important parameters for imaging and microspectroscopy. The effect of the applied chirp on the spectral resolution and the possibility of dividing the spectrum into pump, Stokes and probe frequencies in order to allow for time-delaying the probe for background-free imaging are shown. In addition, their amplitudes can be independently adjusted and certain spectral regions completely suppressed to prevent biological samples from photo damage. The possibility of using a transform-limited probe also greatly increases the signal levels of simultaneously detected SHG and TPEF-signals in multimodal imaging. Furthermore, the applicability of the concept to a broad spectral range from the fingerprint region to the CH-vibrations around 3000 wavenumbers is shown

[1] J. Rehinder, L. Brückner, A. Wipfler, T. Buckup, and M. Motzkus, *Opt. Express* 22, 28790 (2014)

[2] L. Brückner, T. Buckup and M. Motzkus, *Opt. Lett.* 22, 5204-5207 (2015)

MO 14.19 Wed 16:30 Empore Lichthof

Unique inherent property of seawater promotes the SERS detection in femtomolar range — RAHSHA HASSANEIN, ●PATRICE DONFACK, BERND VON DER KAMMER, and ARNULF MATERNY — Physics and Earth Sciences, Jacobs University Bremen, Campus Ring 1, 28759 Bremen

Surface-enhanced Raman spectroscopy (SERS) has been used extensively in order to overcome the inherent weakness of the Raman signal when detecting substances at very low concentrations. Underwater sensing is becoming an emerging and yet rather challenging field. Since often only traces of substances have to be detected, SERS is the only way to obtain vibrational data. Complex SERS substrates have been tested for this application. In this contribution, we will demonstrate that colloidal SERS substrates in solution when added to sea water yields extremely high enhancement factors. Using such a straightforward approach leads to the enhancement of the Raman signal of crystal violet in sea water, which enabled us to detect concentrations as low as femtomolar.

MO 14.20 Wed 16:30 Empore Lichthof

Raman Spectroscopy for the Characterization of Milk Properties — ●MAXIMILIAN SCHALLWIG¹, PATRICE DONFACK¹, FAEZEH MOHAGHEGH¹, RALF ZINK², NADINE GEBERS², and ARNULF MATERNY¹ — ¹Physics and Earth Sciences, Jacobs University Bremen, Campus Ring 1, 28759 Bremen — ²DMK Deutsches Milchkontor GmbH, Flughafenallee 17, 28199 Bremen

Raman spectroscopy yields molecular fingerprints in form of unique vibrational spectra. Therefore, it is a useful technique also for analytical purposes. Raman spectra obtained from systems like natural food of plant or animal origin are rather complex due to the superposition of spectra from different components. Still the spectra can be used to extract information about essential nutrients, but also contaminations, adulterations and deterioration. In the present study, we have used Raman spectroscopy in combination with statistical evaluation techniques like principal component analysis and linear regression in order to analyse milk and milk products. We show that different important parameters can be determined like fat contents, saturation degree etc. Raman spectroscopy has proven to be a valuable tool for the fast and non-invasive characterization of these samples.

MO 14.21 Wed 16:30 Empore Lichthof

Polarization Rotation IMPACT-FT-MW Spectrometer — ●DENNIS WACHSMUTH and JENS-UWE GRABOW — Institut für Physikalische Chemie, Leibniz Universität Hannover, Callinstr. 3A, Hannover, Deutschland

As has been previously shown, the in-phase/quadrature phase modulation passage-acquired coherence technique (IMPACT) Fourier-transform microwave (FT-MW) spectrometer delivers broadband capabilities at highest spectral resolution.

Nevertheless due to specific details in the electronic setup the applicable maximum polarization power was limited. Hence less polar molecules were difficult to measure.

In a novel approach this disadvantage could be circumvented by use of

the polarization direction of the microwave radiation. The setup prevails the high spectral resolution but increases the sensitivity dramatically while allowing the utilisation of very high power tube amplifiers. In this contribution we present the novel apparatus in detail as well as experimental results obtained with the modified spectrometer.

MO 14.22 Wed 16:30 Empore Lichthof

Optical focusing of isolated particles for diffractive imaging experiments — ●SALAH AWEL^{1,2}, RICK KIRIAN⁴, JOCHEN KÜPPER^{1,2,3} und HENRY CHAPMAN^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY — ²The Hamburg Center for Ultrafast Imaging, University of Hamburg, — ³Department of Physics, University of Hamburg — ⁴Arizona State University, Tempe

The short, intense, and coherent x-ray pulses produced by x-ray free-electron lasers (XFELs) have lead to major advances in macromolecular structure determination. Single-particle imaging is among the new

paradigm to emerge consists of directing a stream of randomly oriented bioparticles across the focus of the XFEL beam so that high-resolution 3D structure can be constructed from diffraction patterns of multiple identical particles. Presently, the difficulty of efficiently delivering bioparticles to a sub-micrometer x-ray focus is a limiting factor. For a 100 nm x-ray focus, current sample delivery efficiencies (fraction of particles intercepted by an x-ray pulse) are on the order of 10^{-7} on average, and hit fractions (fraction of x-ray pulses intercepting a particle) are below 0.1%. In order to mitigate this problem, we are developing techniques for guiding aerosolized nanoparticles to the X-ray focus with specially shaped laser illumination [1]. Our current experiments aim at transversely confining streams of aerosolized particles as they exit an aerosol injector with a counter-propagating "hollow" quasi-Bessel beam, using radiation pressure and thermal (photophoretic) forces [2].

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

[2] Eckerskorn et al., *Phys. Rev. Applied* (accepted 29 Oct. 2015).

MO 15: Femtosecond Spectroscopy 3

Time: Thursday 11:00–13:15

Location: f102

Invited Talk

MO 15.1 Thu 11:00 f102

Imaging of an autoionizing resonance using time-, energy- and angular-resolved photoelectron spectroscopy. — MARTIN ECKSTEIN¹, CHUNG-HSIN YANG¹, FABIO FRASSETTO², LUCA POLETTO², GIUSEPPE SANSONE³, MARC J. J. VRAKING¹, and ●OLEG KORNILOV¹ — ¹Max-Born-Institute, Berlin, Germany — ²CNR-IFN, Padova, Italy — ³Politecnico, Milan, Italy

One of the prominent examples of multielectron dynamics is the atomic and molecular autoionization - emission of an electron from an electronically excited system. Such processes typically happen on time-scales of few tens of femtoseconds and requires time-resolved methods with excellent resolution. Here we investigate autoionizing Rydberg states of molecular nitrogen using time-, energy- and angular-resolved photoelectron spectroscopy employing a recently constructed time delay compensating XUV monochromator [1]. Probing the autoionizing resonance with an IR pulse upon the XUV excitation we observe, that angular distributions of the emitted electron depend on time, which indicates the presence of two coupled states forming the resonance. One of the states has a lifetime of 14 fs, while the lifetime of the other is too short to be detected. Such combination of short and long-lived states is similar to the effect of interference stabilization known in the field of laser-induced interactions and suggests that useful analogies exist between the latter and the field of multielectron dynamics. [1] Eckstein et. al., *J. Phys. Chem. Lett.* **6**, 419 (2015)

MO 15.2 Thu 11:30 f102

Photoelectron circular dichroism observed in the above-threshold ionization signal from chiral molecules with femtosecond laser pulses — CHRISTIAN LUX¹, ●ARNE SENFTLEBEN¹, CRISTIAN SARPE¹, MATTHIAS WOLLENHAUPT², and THOMAS BAUMERT¹ — ¹Institut für Physik und CINSA², Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel — ²Institut für Physik, Carl von Ossietzky Universität Oldenburg, Carl-von-Ossietzky-Straße 9-11, 26129 Oldenburg

Photoelectron circular dichroism (PECD) is investigated experimentally as a function of the number of absorbed circularly polarized photons. Three structurally different chiral molecules yet showing similar absorption spectra are studied. They are isotropically distributed in the gas phase and ionized with femtosecond laser pulses. We measure and analyze the photoelectron angular distribution of threshold electrons ionized with three photons and compare them to those of above-threshold (ATI) electrons ionized with four photons. Additionally to an increase in high even order Legendre polynomials the coefficients of the high odd order Legendre polynomials rise with increasing photon number. Consequently, the ATI electrons also carry the chirality signature. All investigated chiral molecules reveal an individual set of coefficients for the threshold and ATI signatures despite their similarities in chemical structure. The presented data set can serve as a guideline for theoretical modelling of the interaction of circularly polarized light with chiral molecules in the multiphoton regime.

MO 15.3 Thu 11:45 f102

VUV-induced dissociation of H₂O studied by single-shot au-

tocorrelation — ●ARNE BAUMANN¹, DIMITRIOS ROMPOTIS¹, OLIVER SCHEPP¹, MAREK WIELAND^{1,2,3}, and MARKUS DRESCHER^{1,2,3} — ¹Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — ²The Hamburg Centre for Ultrafast Imaging (CUI), Luruper Chaussee 149, 22761 Hamburg, Germany — ³Centre for Free-Electron-Laser Science (CFEL), Luruper Chaussee 149, 22761 Hamburg, Germany

The femtosecond dissociation dynamics of the water molecule upon excitation into the $\tilde{A}(^1B_1)$ state have been studied by a single-shot autocorrelation pump-probe experiment in the vacuum ultraviolet spectral range. The scheme is based on wave-front splitting of intense Ti:Sa fifth harmonic pulses at 161.8 nm and a colliding pulse geometry, mapping the temporal delay onto a spatial coordinate. This dramatically decreases acquisition time compared to traditional delay-scanning approaches, increasing the statistical precision of the measurement.

Isotope substitution has been utilized to study the primary and secondary kinetic isotope effects on the reaction dynamics of this prototypical over-the-barrier dissociation reaction. Depending on the degree of hydrogen substitution the observed dynamics take place in 10 ± 2 fs and less.

MO 15.4 Thu 12:00 f102

Second order interferometric gas-phase autocorrelation in the VUV — ●OLIVER SCHEPP¹, ARNE BAUMANN¹, THOMAS GEBERT^{1,2,3}, DIMITRIOS ROMPOTIS¹, MAREK WIELAND^{1,2,3}, and MARKUS DRESCHER^{1,2,3} — ¹Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — ²The Hamburg Centre for Ultrafast Imaging (CUI), Luruper Chaussee 149, 22761 Hamburg, Germany — ³Centre for Free-Electron-Laser Science, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

We studied the ultrafast photodissociation dynamics of molecules in an VUV-pump VUV-probe scheme using a Michelson-type all-reflective interferometric autocorrelator realized with two moveable interdigitated reflective gratings. An imaging time-of-flight spectrometer is used for separating ions formed in different diffraction orders in the focal plane. In the setup, 18 fs VUV pulses centered at 161.8 nm are created in a variable-length gas cell driven by a Ti:Sa laser and spectrally selected for driving non-resonant two-photon ionization processes. With the fringe-resolved 2nd order autocorrelation in Kr the pulse duration of the VUV pulses was determined. With well-characterized VUV pulses, photo-reaction dynamics of molecular gas targets like O₂ are studied.

MO 15.5 Thu 12:15 f102

Optimizing sparse sampling patterns for 2D electronic spectroscopy using an evolutionary algorithm — ●SEBASTIAN ROEDING¹, NIKITA KLIMOVICH^{1,2}, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Department of Physics, The University of Texas at Austin, Austin, Texas 78712, USA

Recent implementations of coherent two-dimensional (2D) electronic spectroscopy have shown that this technique is not limited to samples

in solution. By detecting emitted photoelectrons from a surface [1] or as a photocurrent in a semiconductor nanostructure [2] it became possible to acquire 2D spectra of various types of samples. However, these time-domain experiments suffer from the vast amount of acquisition steps necessary.

We use the paradigm of compressed sensing [3] to reduce the density of sampling points. We employ an evolutionary algorithm to find the best sampling matrix for a data set at a given population time and show how this matrix can be used to measure the same sample at other population times. Furthermore, we discuss the possibility to represent the data on a periodic von Neumann lattice [4] which will be a transform domain with increased sparsity and should further improve signal reconstruction.

- [1] Aeschlimann et al., *Science* 333, 6050 (2011)
 [2] Nardin et al., *Opt. Express* 21, 28617 (2013)
 [3] Donoho, *IEEE Trans. Inf. Theory* 52 (4), 1289 (2006)
 [4] Dimler et al., *New J. Phys.* 11, 105052 (2009)

MO 15.6 Thu 12:30 f102

Femtosecond oxygen K-edge absorption spectroscopy of thymine — T. J. A. WOLF¹, R. HEILEMANN MYHRE^{1,2}, H. KOCH^{1,2}, A. BATTISTONI¹, N. BERRAH³, P. H. BUCKSBAUM¹, R. COFFEE⁴, S. CORIANI⁵, G. COSLOVIC⁴, J. CRYAN¹, R. FEIFEL⁶, K. GAFFNEY¹, J. GRILJ⁷, T. MARTINEZ^{1,8}, S. MIYABE¹, S. MÖLLER⁴, M. MUCKE⁹, A. NATAN¹, R. OBAID³, T. OSIPOV⁴, O. PLEKAN¹⁰, A. SAGE³, R. SQUIBB⁶, S. WANG¹, and ●M. GÜHR^{1,11} — ¹PULSE, SLAC National Accelerator Laboratory and Stanford University, USA — ²Chemistry Dept., NTNU, Trondheim, Norway — ³Physics Dept., University of Connecticut, Storrs USA — ⁴LCLS, SLAC National Accelerator Laboratory, USA — ⁵Chemistry Dept., Università di Trieste, Italy — ⁶Physics Dept., Gotheborg University, Sweden — ⁷LSU, EPFL, Lausanne, Switzerland — ⁸Chemistry Dept., Stanford University, USA — ⁹Physics Dept., Uppsala University, Sweden — ¹⁰Sincrotrone Elettra, Trieste, Italy — ¹¹Physics and Astronomy, Universität Potsdam, Germany

We show first results of ultrafast soft x-ray absorption spectroscopy in the gas phase. After ultraviolet excitation to the $\pi\pi^*$ state, the nucleobase thymine undergoes internal conversion to the $n\pi^*$ and electronic ground state. We probe this nonadiabatic process using resonant absorption at the oxygen K-edge. We identify a UV induced bleach of the initially unoccupied π^* states around 531 eV in the absorption spectrum. In addition, we observe an entirely UV generated absorption feature about 4.5 eV lower than the π^* resonances, which we assign to a molecular nonadiabatic relaxation channel.

MO 15.7 Thu 12:45 f102

Temporal resolution in noisy-pulse transient absorption spectroscopy — ●KRISTINA MEYER¹, NIKLAS MÜLLER¹, ZUOYE LIU^{1,2}, and THOMAS PFEIFER¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²School of Nuclear Science and Technology, Lanzhou University, 730000 Lanzhou, China

Pump-probe experiments with deuterium molecules using Free-Electron-Laser (FEL) pulses revealed molecular dynamics on time scales shorter than the average pulse duration [1]. This enhanced temporal resolution was explained by the partially coherent nature of the FEL pulses [2] and a temporal correlation between the pump and probe pulses. The average spectrum of the FEL pulses provides a coherence time much shorter than the average pulse duration, which is the ultimate limit of temporal resolution instead of the average duration of the noisy, fluctuating pulse shape. Here, we demonstrate the generalization of this noisy-pulse concept to time-resolved spectroscopy in complex systems in the liquid phase. Using a pulse shaper we generated partially coherent laser pulses in the visible to near-infrared range and performed transient-absorption measurements in a solution of the dye IR144 in methanol. Features occurring on time scales (~ 60 fs) shorter than the average pulse duration (300 fs) could be identified in the measured absorption spectra. Thus, we demonstrate the universality of the concept of achieving a temporal resolution beyond the average pulse duration with statistically fluctuating pulses. [1] Y. Jiang et al., *PRA* 81, 051402(R) (2010), [2] K. Meyer et al., *PRL* 108, 098302 (2012)

MO 15.8 Thu 13:00 f102

Diffraction imaging of a molecular rotational wavepacket with femtosecond MeV electron pulses — J. YANG¹, ●M. GÜHR^{2,3}, TH. VECCHIONE², M. S. ROBINSON¹, R. LI², N. HARTMANN², X. SHEN², R. COFFEE², J. CORBETT², A. FRY², K. GAFFNEY², T. GORKHOVER², C. HAST², K. JOBE², I. MAKASYUK², A. REID², J.S. ROBINSON², S. VETTER², F. WANG², S. WEATHERSBY², C. YONEDA², M. CENTURION¹, and X. WANG² — ¹Physics Dept., University of Nebraska, Lincoln, USA — ²SLAC National Accelerator Laboratory, Menlo Park, USA — ³Physics and Astronomy, Universität Potsdam, Germany

We captured the rotational wavepacket dynamics of nonadiabatically laser-aligned nitrogen molecules with a combination of 100 fs root-mean-squared (RMS) temporal resolution and sub-Angstrom spatial resolution that makes it possible to resolve the position of the nuclei within the molecule. In addition, the diffraction patterns reveal the angular distribution of the molecules, which changes from prolate (aligned) to oblate (anti-aligned) in 300 fs. Our results demonstrate a significant and important step towards making atomically resolved movies of molecular reactions.

MO 16: Molecular Clusters

Time: Thursday 11:00–13:15

Location: f142

Invited Talk

MO 16.1 Thu 11:00 f142

Vibrational spectra, structures, and chemical bonding of silicon hydride cluster cations — ●OTTO DOPFER — Institut für Optik und Atomare Physik, TU Berlin

Silanes and their derivatives and ions are fundamental species in a variety of chemical disciplines. In contrast to hydrocarbon ions ($C_xH_y^+$), almost no information is available for the corresponding $Si_xH_y^+$ cations. Here, IR spectra of $Si_xH_y^+$ cations produced in a supersonic plasma molecular beam expansion of SiH_4 are inferred from photodissociation of cold Ne and Ar complexes obtained in a tandem quadrupole mass spectrometer coupled to an electron impact ionization source and an octopole ion trap. In addition, the clusters are characterized in their ground electronic states by quantum chemical calculations to investigate the effects of ionization and Ar/Ne complexation on their geometric, vibrational, and electronic structure [1-3]. We present initial results for $Si_2H_6^+$, $Si_2H_7^+$ and $Si_3H_8^+$, which have complex potential energy surfaces, with low-energy isomers featuring unusual three-center two-electron (3c-2e) bonding. The IR spectrum of disilanium, $Si_2H_7^+$, a fully H-passivated Si_2 core with a Si-H-Si bridge is described by a 3c-2e bond. The excess proton in the Si-H-Si bridge generates three additional fundamentals, which provide the fingerprint of the 3c-2e bond. New results on protonated silanols will be presented.

- [1] Savoca, George, Langer, Dopfer, *PCCP* 15, 2774 (2013). [2] Savoca, Langer, Dopfer, *Angewandte Chemie* 125, 1376 (2013). [3] George, Savoca, Dopfer, *Chem. Eur. J.* 19 45 (2013).

Invited Talk

MO 16.2 Thu 11:30 f142

Far-infrared spectroscopy of metal cluster rare-gas complexes — DAVID YUBERO VALDIVIELSO¹, VALERY CHERNY², DENNIS PALAGIN³, JOOST M. BAKKER², and ●ANDRÉ FIELICKE¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany — ²FELIX Laboratory, Faculty of Science, Radboud University Nijmegen, The Netherlands — ³Physical & Theoretical Chemistry Laboratory, University of Oxford, UK

Multiple photon dissociation spectroscopy in the far-infrared [1] is used to obtain vibrational spectra of transition metal clusters in the gas phase. More precisely, weakly bound complexes of the clusters with rare-gas atoms are irradiated with monochromatic light from an IR Free Electron Laser and their wavelength-dependent depletion is used as probe for the absorption process. Experimental far-IR spectra are typically recorded in the $85-500\text{cm}^{-1}$ region to cover the range of the structure-specific vibrational fundamentals, i.e., the finger-print range, for the metal clusters. Comparison with calculated vibrational spectra obtained, for instance, by using DFT methods, allows for structural assignments. I will present recent results for Ar solvation complexes of

the cobalt cation, where by comparison with results from density functional theory calculations we identify distorted square, square pyramidal, and octahedral structures for $CoAr_4^+$, $CoAr_5^+$, and $CoAr_6^+$, respectively. $CoAr_5^+$ is a particularly interesting case as it appears to undergo rapid dynamics which finds its expression in a broad vibrational lineshape. A second example are the structures of binary cobalt-manganese clusters.

[1] A. Fielicke et al., Phys.Rev.Lett. 93 (2004) 023401.

MO 16.3 Thu 12:00 f142

Fluorescence lifetime reduction of organic semiconductors attached to the surface of solid neon cluster — ●SHARAREH IZADNIA, MARKUS MÜLLER, AARON LAFORGE, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

The collective emission of coherent light is a fundamental process in quantum mechanics. The resulting radiation leads to effects such as superradiance. One particularly fascinating manifestation of superradiance is the process of spontaneous coherent emission of light by an ensemble of identical excited atoms, which was initially predicted by Dicke [1]. Superradiance has been observed almost universally in weakly interacting systems such as hot dense gases [2]. Here, we report the experimental observation of fluorescence lifetime reduction of tetracene by directly tuning the number of molecules attached to the surface of neon clusters and excitation laser power. For average intermolecular distances greater than 33 Å, we attribute the reduction in fluorescence lifetime to Dicke superradiance [3], while for smaller intermolecular distances, additional lifetime reduction occurs due to the onset of non-radiative de-excitation (e.g. singlet fission).

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

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

[3] M. Müller, S. Izadnia, S. M. Vlaming, A. Eisfeld, A. LaForge and F. Stienkemeier. Phys. Rev. B 92, 121408(R) (2015)

MO 16.4 Thu 12:15 f142

Spectroscopy and Kinetics on Metal Cluster Surfaces: The Fe/N₂, Co/N₂ and Ni/N₂ systems — ●SEBASTIAN DILLINGER, JENNIFER MOHRBACH, ANNIKA STEINER, and GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie and Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany

We present kinetic data of N₂ adsorption on isolated cationic Fe/Co/Ni clusters in combination with Infrared (Multi) Photon Dissociation (IR(M)PD) spectra of the cluster adsorbate complexes at cryo temperatures. We will display and discuss the cluster size range of n=7-20. We find metal, cluster size and adsorbate number dependent effects in the IR(M)PD spectra as well as in the kinetic data: Trends and exceptions superpose. For our experiments we utilized a unique tandem cryo trap setup at 12 K to 26 K.

MO 16.5 Thu 12:30 f142

X-ray Magnetic Circular Dichroism of Heteronuclear Complexes in Isolation — ●JOACHIM HEWER¹, MATTHIAS TOMBERS¹, JOHANNES LANG¹, GEREON NIEDNER-SCHATTEBURG¹, and TOBIAS LAU² — ¹Fachbereich Chemie und Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, Germany — ²Helmholtz-Zentrum Berlin Materialien und Energie, BESSY II, Berlin, Germany
We applied synchrotron based X-ray magnetic Circular dichroism

(XMCD) spectroscopy to ligand stabilized $[Mn_2LnL_x]^+$ complexes (Ln = Nd, Eu, Gd, Dy, Lu; L = organic ligands) when isolated as individual ions under cryo conditions. Such investigations allow for a magnetic characterization of these complexes void of any surface or packing effects. The element selectivity of the XMCD technique allows to determine the contribution of the individual metals to the total magnetic moment of the molecules. Furthermore, sum rule analysis of the recorded XMCD spectra allows to decompose the total magnetic moment into its spin and orbital contributions. The variation of the incorporated lanthanoid ions is at the center of interest and interpretation.

MO 16.6 Thu 12:45 f142

Tuning the optical properties of diamondoids through plasmonics — ●ANDRE KNECHT¹, TOBIAS ZIMMERMANN¹, ANDREA MERLI¹, MERLE RÖHR², JENS PETERSEN², ROLAND MITRIC², THOMAS MÖLLER¹, and TORBJÖRN RANDE¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg

Diamondoids, subnanometer-sized carbon-cages, show interesting properties like negative electron affinity and intrinsic photoluminescence in the UV regime [1,2]. The feasibility of functionalization, as well as the size and shape selectivity of the diamondoids, gives rise to numerous possibilities to tune their optical properties. Hence, these molecular diamonds are ideal to investigate a size regime where a transition from molecular to bulk-like optical properties takes place.

Moreover, diamondoid properties can be modified through adsorption on metal surfaces [2]. Adjusting the local environment of diamondoids through the proximity of metal clusters, we can tune the metal plasmon resonance to the radiative transitions of the diamondoid [3]. To investigate these plasmon resonance coupling effects, we use ion yield spectroscopy. First ion yield spectra of Au-adamantanethiol-hybrids show significant changes in the UV absorption cross section and represent an important step towards the systematic development of novel nanoscopic plasmonic hybrid systems.

[1] R. Richter, et al., Phys. Chem. Chem. Phys. 17.6 (2015): 4739-4749. [2] W. Clay, et al., Nano letters 9.1 (2008): 57-61. [3] P. Anger, et al., Phys. Rev. Lett. 96, 113002 (2006).

MO 16.7 Thu 13:00 f142

Theoretical investigations to photophysical properties of mono-, di- and trimetallic gold complexes — ●FABIAN DIETRICH¹, ANNEKEN GRÜN¹, SIMON P. WALG², MERVE CAYIR KÜÇÜKDİSLİ², WERNER R. THIEL², and MARKUS GERHARDS¹ — ¹Physikalische und Theoretische Chemie, TU Kaiserslautern — ²Anorganische Chemie, TU Kaiserslautern

A set of Au complexes with pyrimidinylpyridine(NH(CH₂)₂PPh₂) as well as bispyrimidinylpyridine-(NH(CH₂)₂PPh₂)₂ ligands are investigated since they are of great interest in synthesis due to their catalytic activity. Quantum chemical calculations are performed for the explanation of experimental spectra. We use time dependent density functional theory (TD-DFT) to compute UV/Vis-spectra. The influence of different solvents is taken into account by the application of the polarized continuum model (PCM). The comparison with UV/Vis-measurements show the strengths of TD-DFT calculation in such cases where excitations are localized on π -systems and no charge transfers have to be taken into account. The metal induced shifts are represented well. Both experimental and theoretical spectra are investigated under the issue of cooperativity which will be quantified.

MO 17: Electronic Spectroscopy 2

Time: Thursday 14:30–16:00

Location: f102

MO 17.1 Thu 14:30 f102

Molecular-Frame Photoelectron Imaging of Controlled Complex Molecules — ●JOSS WIESE¹, SEBASTIAN TRIPPEL¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²The Hamburg Center for Ultrafast Imaging, Hamburg — ³Department of Physics, University of Hamburg

Since chemical function arises from the interplay amongst valence electrons, a view at the evolution of the highest occupied molecular orbitals (HOMOs) during a chemical reaction promises direct insight into the fundamentals of chemistry. Therefore, we employ tomographic photo-

electron imaging of spatially controlled complex molecules strong-field ionised by intense near-infrared laser pulses [1]. Reconstructed static three-dimensional photoelectron distributions in molecular-frame velocity space of indole and its water complex will be presented. These allow for the observation of the molecules' electron density distributions, photoelectron kinetic energies, and off-molecular-plane emission angles in 3D. The experimentally retrieved observables are discussed employing an extended strong-field approximation model. Those three observables provide a close glimpse at the laser-distorted HOMO potential surfaces of the investigated molecules in the gas phase and yield

access to their changes in polarisability and dipole moment upon ionisation. Furthermore, the direct comparison of indole and its water complex allows inspection of the nature of hydrogen bonding in heteroaromatic biomolecules.

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

MO 17.2 Thu 14:45 f102

Collective excitations and their impact on plasmon-induced double photoemission from fullerenes — MICHAEL SCHÜLER¹, YAROSLAV PAVLYUKH¹, PAOLA BOLOGNESI², LORENZO AVALDI², and ●JAMAL BERAKDAR¹ — ¹Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle, Germany — ²CNR-ISM, Area della Ricerca di Roma 1, CP10, 00016 Monterotondo Scalo, Italy

The correlated release of an electron pair from a sample upon absorbing one photon, called double photoemission (DPE), is a process that is particularly sensitive to the effective electron-electron interaction. As a prototypical example we consider the C₆₀ molecule. We analyse its strongly pronounced collective many-body excitations (plasmons) using ab initio calculations based on the time-dependent density-functional theory (TDDFT). Utilizing the nonnegative matrix factorization method, the individual plasmon modes are isolated and characterized by their multipolar and spatial distribution of the associated charge-density oscillations. This allows to construct a new model for the density-density response function and the effective electron-electron interaction that accurately describes typical experiments such as electron-energy loss spectroscopy (EELS). Using our model parameterization of screened interaction and further ab initio calculations, we compute the electron-pair coincidence spectrum of C₆₀. Both theory and experiment underpin the new features arising from the dynamically screened interaction mediating the effective electron-electron interaction and thus endorse DPE as a powerful tool for tracing electron pair correlations in complex many-body systems.

MO 17.3 Thu 15:00 f102

Multimodal Time-Resolved Spectroscopy of Vibrational Coherence and Population Dynamics in the Excited State — ●TAKESHI MIKI, MARCUS MOTZKUS, and TIAGO BUCKUP — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

The interpretation of dynamics in the excited states of molecules often challenges time-resolved spectroscopy in particular due to spectrally overlapping contributions as well as ultrafast optical signals. Multimodal Time-Resolved Spectroscopy combines multiple time-resolved signals to disentangle and map complex molecular dynamics. In this work we exploit two different time-resolved spectroscopies, transient absorption (TA) spectroscopy and pump-degenerate four wave mixing (pump-DFWM) spectroscopy, to map the interplay between population and vibrational coherence dynamics. An algorithm is developed to globally fit the whole spectrally resolved data of both methods. A kinetic model is developed via global target analysis of the TA data, which is further refined by exploiting the very sensitive homodyne signal of pump-DFWM spectroscopy. This way, time decay constants of electronic states, frequency and phase of vibrational molecular modes, and transition dipole moments of excited state transitions can be obtained under the assumption of a unified molecular model. This is applied (i) to disentangle the vibrationally modulated from the not vibrationally modulated stimulated emission and (ii) to determine specific vibrational frequencies and their origin during the deactivation of electronic states. The method is applied to prototype organic molecules.

MO 17.4 Thu 15:15 f102

Investigations on the isolated diphenyl ether-methanol complex by combined IR/UV spectroscopy in the electronically excited and the ionic state — ●DOMINIC BERNHARD¹, ANKE STAMM¹, FABIAN DIETRICH¹, CHRISTOF HOLZER², WILLEM KLOPPER², and MARKUS GERHARDS¹ — ¹Fachbereich Chemie, TU Kaiserslautern — ²Institut für Physikalische Chemie, KIT

Dispersion interactions are ubiquitous regarding intermolecular interactions. Their relative contributions strongly vary depending on the

investigated system and the theoretical prediction of these contributions is challenging. Diphenyl ether represents a system with competing docking sites for methanol: the ether oxygen atom as a well-known hydrogen bond acceptor and the two phenyl rings as dispersion energy donors can lead to π binding. Interestingly, both calculated binding motifs are predicted to be almost equally stable, requiring an experimental verification. Therefore, we investigated the diphenyl ether-methanol complex in molecular beam experiments using IR/UV and IR/IR/UV spectroscopy in the electronic ground state (S₀), the electronically excited state (S₁) and the ionic ground state (D₀). In the S₀ state the OH $\cdots\pi$ type structure is dominating, whereas the slightly less stable OH \cdots O isomer is far less abundant (cooperation with the groups of Prof. Martin Suhm, University of Göttingen and PD Melanie Schnell, MPSD Hamburg). This talk will be focussed on the results for the S₁ and D₀ state. In the S₁ state different isomers are discussed and compared with theory. A structural rearrangement takes place in the D₀ state due to electrostatic effects.

MO 17.5 Thu 15:30 f102

A Flatjet System for Soft X-Ray Spectroscopy in the Liquid Phase — ●MARIA EKIMOVA¹, WILSON QUEVEDO², MANFRED FAUBEL³, PHILIPPE WERNET², and ERIK NIBBERING¹ — ¹Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Berlin, Germany — ²Institute for Methods and Instrumentation for Synchrotron Radiation Research, HZB, Berlin, Germany — ³Max Planck Institute for Dynamics and Self-Organization, Goettingen, Germany

Recent progress in soft-X-ray absorption spectroscopy (XAS) has led to new insights into the local molecular interactions in liquid water, alcohols and in solutions. The methods used to measure XAS typically involve either standing sample cells with silicon nitride (Si₃N₄) membranes or single liquid jets. Signal contribution of the Si₃N₄ membrane, or possible radiation damage may complicate the sample cell approach. Single liquid jets on the other hand have limited diameter, preventing a proper XAS measurement in transmission mode. Here, we present [1] a *free-windows* flatjet system as a new approach to perform solution-phase soft X-ray spectroscopy directly in transmission mode. The collision of two single jets with a diameter of 50 μ m under an impact angle of 48° leads to double sheet formation, of which the first sheet is 6 mm long, 1 mm wide and with a thickness of 1.4-3 μ m. We demonstrate the feasibility of N and O K-edge transmission XAS of salt solutions. Our results pave the way of using liquid flatjets both in steady-state and ultrafast soft X-ray spectroscopy.

References:

[1] M. Ekimova et al., *Struct.Dyn.* **2**, 054301 (2015)

MO 17.6 Thu 15:45 f102

Laser-induced acoustic desorption of large molecules via tape-drive method — ●ZHIPENG HUANG^{1,3}, DANIEL A. HORKE^{1,2}, MATTHIAS SCHUST¹, TIM OSSENBRÜGGEN¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Center for Ultrafast Imaging, University of Hamburg — ³Department of Physics, University of Hamburg

By dispersing molecular beams with strong electric fields, we can routinely produce pure samples of individual conformers or clusters according to their quantum state. Selected molecules can be further controlled using alignment and orientation by laser and static electric fields [1]. We are currently working towards extending these techniques to much large molecules and systems.

Laser-induced acoustic desorption (LIAD) is a promising technique for gentle and efficient preparation of large intact neutral molecules in the gas-phase [2]. Here we demonstrate our newly set-up LIAD source, designed for prolonged measurement times through automatic sample replenishment. Molecules are sprayed onto a long 10 μ m tantalum foil band that is irradiated from the backside by a third harmonic Nd:YAG laser (355 nm). The induced shockwave travels through the foil and desorbs molecules from the frontside of the foil. We present results and characterizations of the source, and discuss its potential for applications in x-ray or electron diffraction imaging.

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

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

MO 18: The Modelling of Molecular Dynamics

Time: Thursday 14:30–16:15

Location: f142

MO 18.1 Thu 14:30 f142

Caldeira-Leggett Model Description of Condensed Phase Vibrational Spectroscopy — ●FABIAN GOTTWALD, SERGEI D. IVANOV, and OLIVER KÜHN — Institut für Physik, Universität Rostock, Rostock

Formulating a rigorous system-bath partitioning approach remains an open issue. In this context the popular Caldeira-Leggett (CL) model enables simple modeling of system-bath interactions via spectral density functions. For parametrizing spectral densities we propose a Fourier-based method that outperforms existing time-domain methods [1]. Moreover, the widely used rigid bond method turns out to be inappropriate and leads to a systematic overestimation of relaxation times, unless the system under study is indeed of CL form. The validity of the CL model for describing anharmonic dynamics of real systems is often taken for granted. It is shown that such a use does not pass the self-consistency check for a broad class of solute-solvent systems, unless the system part of the potential is effectively harmonic [2]. The check is performed by comparing the spectra resulting from the corresponding generalized Langevin dynamics with their counterparts from explicit classical molecular dynamics. Although there exist systems that can be mapped onto the CL model, no a priori criteria are found and the ultimate verdict is provided by the self-consistency check only.

[1] F. Gottwald, S. Karsten, S. D. Ivanov, O. Kühn. *J. Chem. Phys.* **142**, 244110 (2015).

[2] F. Gottwald, S. D. Ivanov, O. Kühn. *J. Phys. Chem. Lett.* **6**, 2722 (2015).

MO 18.2 Thu 14:45 f142

Unraveling the Quantum State Mixing of Excitonic and Vibronic Excitations in the Dynamics of Molecular Aggregates

— ●MARCO SCHRÖTER¹, TÖNU PULLERITS², and OLIVER KÜHN¹ — ¹Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany — ²Chemical Physics, Lund University, Box 124, 22100 Lund, Sweden

One possible source of coherent oscillations observed in two-dimensional electronic spectroscopy experiments is the quantum state mixing (QSM) of electronic and vibronic excitations in molecular aggregates. In the present contribution the signatures of Coulomb coupling induced QSM between excitonic and vibronic excitations in the dynamics of a model aggregate are discussed. To this end numerically exact dissipative exciton dynamics calculations applying the hierarchy equations of motion (HEOM) method are performed. A Fourier analysis of the coherent oscillations in the population dynamics after an initial excitation of the highest exciton state is supplemented by exciton-vibronic structure calculations employing direct diagonalization [1]. This allows us to unravel the origin of the oscillations and to obtain insights on the general influence of QSM on the dynamics as a function of Coulomb and vibronic coupling strengths [2].

[1] M. Schröter et al., *Physics Reports* 567, 1 (2015)

[2] M. Schröter et al., *Annalen der Physik* 527, 536 (2015)

MO 18.3 Thu 15:00 f142

Using vibrational dynamics in complex time to investigate the isotope dependence of High-Harmonic Generation in H₂

— MANFRED LEIN and ●MARC RUHMANN — Institut für Theoretische Physik and Centre for Quantum Engineering and Space-Time Research (QUEST), Leibniz Universität Hannover, Appelstraße 2, 30167 Hannover, Germany

High-Harmonic generation takes place when an atom or molecule is subject to a strong laser field. It is commonly understood as a sequence of ionization, electron excursion and recombination. In the quantum mechanical strong-field approximation (SFA), the times of ionization and recombination, which are real in a classical model, are complex numbers.

In (small) molecules such as H₂, the harmonic intensity is approximately proportional to the modulus squared of the vibrational autocorrelation acquired over the electron excursion time. This provides a link between harmonic spectra and vibrational dynamics and explains why heavier isotopes produce more intense radiation.

Here we investigate the ratio of harmonics from D₂/H₂ by evolving the nuclear wave packets in complex time as given by the SFA. We consider, on the one hand, a reduced-dimensional model where we

compare with exact solutions of the TDSE, on the other hand, a three-dimensional model including orientation averaging. We find, for both short and long trajectories, the ratio to be generally lower compared to the classical times and with a different qualitative shape.

MO 18.4 Thu 15:15 f142

Wie hängen Elektronenimpulsverteilungen aus Ionisation von Molekülen in linear und zirkular polarisierten Laserpulsen zusammen? — ●SIMON BRENNKECKE und MANFRED LEIN — Institut für Theoretische Physik, Appelstraße 2, 30167 Hannover

Für ausgerichtete symmetrische Moleküle wie z.B. homonukleare zweiatomige Moleküle vergleichen wir die Ionisation in linear und zirkular polarisierten starken Laserfeldern. Innerhalb der Strong-Field Approximation zeigen wir, dass die Winkelverteilung der Elektronen bei zirkularem Laserfeld im Grenzfall kleiner Frequenzen und kleiner Feldstärke bis auf eine Drehung um 90° gleich der Orientierungsabhängigkeit des Signals in Feldrichtung bei linearem Feld wird. Dies gilt, wenn die Laserpulse genügend lang sind. Für den Fall von H₂⁺ demonstrieren wir dies durch explizites Auswerten der Theorie. Die numerische Lösung der zeitabhängigen Schrödingergleichung zeigt den Effekt ebenfalls. Für realistische Laserparameter ist die Modulationstiefe der Winkelabhängigkeit beim zirkularen Feld größer als beim linearen Feld, sofern das σ_g-Grundzustandsorbital betrachtet wird. Bei vorhandenen Knotenebenen kann hingegen die zirkulare Modulationstiefe geringer als beim linearen Feld ausfallen.

MO 18.5 Thu 15:30 f142

Tuning the nonradiative lifetime via excitonic interaction — ●ALAN CELESTINO and ALEXANDER EISFELD — MPIP/KS, Dresden, Germany

Nonradiative electronic transitions are typical in many molecules. These transitions can occur in the pico- or even femtosecond scale. For being able to occur so rapidly, nonradiative transitions can also suppress the slower spontaneous emission in certain molecules. For these molecules, controlling the nonradiative lifetime equals controlling the lifetime of an electronic excitation. Depending on the application in mind one would like to make this lifetime longer or shorter. Aggregated molecules interact and both their radiative and nonradiative lifetimes are in general changed by this interaction. In the present work we study the influence of transition dipole-dipole interaction (excitonic interaction) between molecules on their nonradiative lifetime. As an example, we consider the dynamics of Frenkel excitons in a homodimer. The monomer is a two electronic level system coupled to nuclear vibrations. We consider the nonradiative channel to be well localized in the nuclear space. We calculate numerically the nonradiative lifetime of the dimer for different excitonic interaction strengths, positions of the nonradiative coupling and nuclear relaxation times. Using a Born-Oppenheimer approximation in the dimer level, we obtain the relevant dimeric potential surfaces. By using them, we can explain the direction of the changes in lifetime induced by excitonic interaction depending on the nonradiative channel position. For strong excitonic interaction, we can quantitatively predict the nonradiative lifetime.

MO 18.6 Thu 15:45 f142

Molecular quantum dynamics coupled with classical molecular dynamics of the solvent environment — ●FLORIAN ROTT¹, SEBASTIAN THALLMAIR^{1,2}, JULIUS ZAULECK¹, and REGINA DE VIVIER-RIEDLE¹ — ¹Department Chemie, LMU München — ²LS für BioMolekulare Optik, LMU München

Recently, we introduced a new method combining quantum dynamics (QD) and classical molecular dynamics (MD) to model the influence of an explicit solvent environment on the QD of molecular reactions [1]. In this QD/MD approach we extract solvent potentials from MD trajectories by evaluating a set of different snapshots. The solvent potentials are included in the Hamiltonian used for the QD calculations. Using this method we were able to describe the photochemical bond cleavage of diphenylmethylphosphonium ions in solution.

So far, the solvent molecules have been frozen and no feedback from the QD system to the MD system has been included. We will present an extension of the method where both systems are propagated at the same time. Using the Ehrenfest method, we will show how the interactions between the quantum system and the classical

cal MD system are calculated. We demonstrate our method for the photoinduced dynamics of ICN in liquid argon and present first results.

[1] S. Thallmair, J. P. P. Zauleck, R. de Vivie-Riedle, *J. Chem. Theory Comput.* **11**, 1987 (2015).

MO 18.7 Thu 16:00 f142

Resonant inelastic X-ray Scattering (RIXS) Studies of Hydrogen-Bonded Cyano-Groups at the Nitrogen K-edge — ●ABID HUSSAIN¹, S. SCHRECK⁴, P. WERNET⁴, A. FHLISCH⁴, O. VENDRELL², and NILS HUSE^{1,3} — ¹MPSD,CFEL, Luruper Chaussee 149, 22761 Hamburg, Germany — ²CFEL, DESY Notkestraße 85, 22607 Hamburg, Germany. — ³INF, University of Hamburg, Jungiusstraße 11, 20355 Hamburg, Germany. — ⁴Institute for Methods and Instrumentation in Synchrotron Radiation Research, Helmholtz-Zentrum Berlin

To probe the influence of hydrogen bonding on the electronic structure of the nitrogen atoms in cyano-groups, acetonitrile and acetonitrile-water mixtures have been investigated using X-ray absorption spectroscopy and Resonant Inelastic X-ray Scattering (RIXS). We employed first principles restricted active space self-consistent field (RASSCF) calculations in order to interpret experimental electronic structure probes via nitrogen core-level transitions. In the current study, we elucidate with highest chemical specificity the relative involvement of different molecular orbitals (MO). These calculations give explicit access to each electronic state with the extracted information allowing to assign the dominant transitions in the X-ray absorption spectrum, and unearthing the electronic character of every final valence excitation resulting from RIXS at a specific incident photon energy. Our theoretical results are in very good agreement with experimental spectra, highlighting the sensitivity of RIXS even for weak interactions.

MO 19: Posters 4: Novelties in Molecular Physics: Femtosecond Spectroscopy, Molecular Clusters, Cold Molecules and Helium Droplets

Time: Thursday 16:30–19:00

Location: Empore Lichthof

MO 19.1 Thu 16:30 Empore Lichthof

Time-Dependent Modeling of the Ionization Dynamics in Chiral Molecules — ●MESSAN AFANDE¹, BEHNAM NIKOBAKHT², R. ESTEBAN GOETZ¹, TIMUR ISAEV², ROBERT BERGER², and CHRISTIANE P. KOCH¹ — ¹Theoretische Physik, Universität Kassel, Kassel, Germany — ²Theoretische Chemie, Phillips-Universität Marburg, Marburg, Germany

Experiments based on femtosecond polarized laser pulse excitation of chiral molecules reveal a circular dichroism in the measured photoelectron signal. The observed dichroism is used to get insight into the dynamics of chiral molecules, in particular, in the characterization of the handedness of such molecules. A combination of *ab initio* calculations with a single center expansion reproduces the experimental results semi-quantitatively. Here, this theoretical framework is extended to a time-dependent approach. This allows the study of dynamical effects, including the dependence on the pulse parameters such as chirps. The time-dependent study aims at a better understanding of the dynamics in the ionization process of chiral molecules. Here, we present the time-dependent modeling approach and first results.

MO 19.2 Thu 16:30 Empore Lichthof

Pump-Probe Experiments in a Collinear Phase Modulation Scheme Using a Low Repetition Rate Laser System — ●MARCEL BINZ, LUKAS BRUDER, ULRICH BANGERT, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Germany

Recently various active and passive stabilization methods have been developed to facilitate coherent time-resolved spectroscopy in the visible and ultra violet spectral region. Among these, the phase modulation approach of the Marcus group [1] has proven to be particularly sensitive and very versatile. The drawback of this method is however the need of a high repetition rate laser system ($\gtrsim 200\text{kHz}$) which is not available in many labs. Recently, we have successfully implemented this technique with amplified fs laser pulses at 5kHz repetition rate. Performing electronic wave packet interferometry of dilute atomic vapors we could confirm an excellent SNR. This is surprising since the average laser power in these experiments is factor 800 lower than in previous experiments with 80MHz repetition rate. Moreover, we found that phase-synchronous undersampling can be readily performed with the phase modulation scheme allowing to use even lower repetition rate lasers.

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

MO 19.3 Thu 16:30 Empore Lichthof

Heterodyne-detected Sum Frequency Generation Spectroscopy of Polyacrylic Acid at the Air/Water- Interface — ●PATRICK BALZEROWSKI², KONRAD K. MEISTER¹, JAN VERSLUIS¹, and HUIB J. BAKKER¹ — ¹FOM-Institute for Atomic and Molecular Physics AMOLF, Amsterdam, The Netherlands — ²Institute for Physical Chemistry II, Ruhr-Universität Bochum, Bochum, Germany Here we present our findings on the conformational and hydration be-

havior of polyacrylic acid (PAA) at the air/water interface studied by heterodyne-detected vibrational sum frequency generation spectroscopy (HDVSFG). The amount of adsorption at the water/air interface and the influence of PAA on the water structure at the interface are found to be highly dependent on the degree of ionization (acid dissociation) of the carboxylic acid groups. At a low degree of ionization PAA is surface active and the spectral features suggest that PAA remains in a dense packing arrangement with intrachain hydrogen bonds. The HDVSFG spectra clearly show that the interfacial water molecules have a net orientation with their OH groups pointing towards the surface. Increasing the ionization degree of the carboxylic acid groups leads to an increase of the negative charge and to a break-up of the intrachain hydrogen bonds. This increase in negative charge comes along with an increase of the VSFG signal of the interfacial water molecules due to their enhanced orientation. At ionization degrees of $\alpha > 0.203$ PAA loses its enhanced surface propensity and is well desolved in the bulk. Changing the ionic strength of the solution by addition of NaCl is observed to lead to a recurrence of PAA to the interface.

MO 19.4 Thu 16:30 Empore Lichthof

Accurate ultra-broadband prism-based amplitude and phase-shaping in the visible — ●PHILIPP HILLMANN, ALEXANDER KASTNER, JENS KÖHLER, CRISTIAN SARPE, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CIN-SaT, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

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

Supercontinua exceeding one octave are a prerequisite to generate few-cycle light pulses in the temporal domain. Combining supercontinuum generation spanning from the ultraviolet to near-infrared spectral region with high-throughput prism based pulse shaping [3] opens up the possibility to temporally steer wavepacket dynamics on the sub-cycle timescale expanding the technique to a broader range of electronic systems.

We present the current status of our setup for ultra-broadband amplitude and phase shaping of femtosecond laser pulses characterized by transient grating frequency resolved optical gating.

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

[2] M. Wollenhaupt *et al.*, *JPPA* **180**, 248-255 (2006)

[3] T. Binhammer *et al.*, *IEEE* **41** (12), 1552-1557 (2006)

MO 19.5 Thu 16:30 Empore Lichthof

Excited state dynamics of dimetallic $[\text{Ag}_2(\text{dcpm})_2]^{2+}$ in gas- and solution phase — ●FLORIAN BÄPPLER¹, SEBASTIAN KRUPPA², CHRISTOPH RIEHN², and ROLF DILLER¹ — ¹Dept. of Physics, — ²Dept. of Chemistry, Univ. Kaiserslautern, 67663 Germany

$[\text{Ag}_2(\text{dcpm})_2]^{2+}$ (dcpm = bis(dicyclohexylphosphanyl)) is a prototype

example for luminescent binuclear Ag(I) complexes exhibiting interesting photophysical and photochemical properties. Due to the absence of ligand-centered UV-chromophores it serves as a good model system for the investigation of argentophilic metal-metal interactions [1]. Here, we investigate the excited state dynamics of $[\text{Ag}_2(\text{dcpm})_2]^{2+}$ in parallel in gas phase by fs transient photofragmentation [2], and in solution (CH_3CN) by fs transient absorption [2] at room temperature. Surprisingly, both methods reveal similar deactivation kinetics, characterized by a triple exponential decay (1, 10 and 350 ps) after excitation of the silver-centered $^1\text{MC}(d\sigma^*-\rho\sigma)$ state at 260 nm. This suggests similar excited state deactivation processes in gas- and solution phase and consequently little influence of solvent (CH_3CN) molecules. In particular, fast exciplex formation $[[\text{Ag}_2(\text{dcpm})_2]^{2+}/\text{CH}_3\text{CN}]^*$ as suggested [3] for an analog Au_2 -complex can be excluded as essential component of the reaction coordinate, although it could occur concomitantly as a side effect in solution. Consequences for the interplay between photophysics and complex-solvent interaction are discussed.

[1] Schmidbauer et al., *Angew. Chem. Int. Ed.* 2015, 54, 746-784.

[2] Imanbaev et al., *Chemical Physics* 2014, 442, 53-61.

[3] Ma et al., *Chemistry-A European Journal* 2015, 21, 13888-13893.

MO 19.6 Thu 16:30 Empore Lichthof

Ultrafast studies on luminescent mono- and dinuclear copper(I)-complexes in solid and liquid phase — ●MERTEN GRUPE¹, FLORIAN BÄPPLER¹, FABIAN DIETRICH², DANIEL VOLZ³, STEFAN BRÄSE⁴, ROLF DILLER¹, and MARKUS GERHARDS² — ¹Dept. of Physics, TU Kaiserslautern, 67663 Kaiserslautern — ²Dept. of Chem., TU Kaiserslautern, 67663 Kaiserslautern — ³Cynora GmbH, 76646 Bruchsal — ⁴Dept. of Org. Chem., KIT, 76131 Karlsruhe

The efficiency of luminescence in copper-complexes is controlled by several photoinduced intra- and intermolecular processes, such as molecular flattening, intersystem crossing, solvation etc. For the elucidation of the underlying photophysics we employed femtosecond UV/Vis transient absorption (TA) as well as transient reflectivity (TR) spectroscopy and DFT calculations on luminescent mono-^[1] and dinuclear^[2] copper(I)-complexes. The results allow a rigorous comparison of the respective ultrafast dynamics in solution and solid phase, possibly controlled by metal-metal cooperativity. Together with the investigations of [3] fundamental kinetics of homo- and heteroleptic mononuclear copper(I)-complexes can be contrasted.

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

[2] D. Volz et al. *Chem. Mater.*, 2013, 25, 3414-3426

[3] M. Iwamura et al. *Acc. chem. res.*, 2015, 48, 782-791

MO 19.7 Thu 16:30 Empore Lichthof

Ultrafast Ionization and Fragmentation Dynamics of Chlorinated Silane Derivatives — ●INA HALFPAP, CLARA ADELE VON RANDOW, EGILL ANTONSSON, CHRISTOPHER RASCHPICHLER, and ECKART RÜHL — Physical Chemistry, Freie Universität Berlin, Takustr. 3, 14195 Berlin

The femtosecond pump-probe technique is known to be a suitable approach to study molecular strong-field ionization processes in the time domain. To follow specific fragmentation pathways, mass spectrometry is the most suitable approach. The fragmentation dynamics of highly excited molecular neutrals and ions can be affected by dynamic resonances, where the wavepacket motion on ionic potential energy surfaces plays a crucial role.

We present recent results on the ionization and fragmentation dynamics of trichloromethylsilane (SiCl_3CH_3), dichlorodimethylsilane ($\text{SiCl}_2(\text{CH}_3)_2$), and chloro-trimethylsilane ($\text{SiCl}(\text{CH}_3)_3$) investigated by a one-color 804 nm femtosecond pump-probe experiment recording the ion yields of fragment ions. The intense pump pulse (250 μJ /pulse) is used to ionize the sample molecules which is followed by a time delayed less intense probe pulse (70 μJ /pulse). This leads to additional fragmentation of the parent and fragment ions. The yields of parent and fragment ions show broad dynamic resonances with maxima in a range of $\Delta t = 0.5$ ps. The experimental findings are explained in terms of dynamic ionic resonances leading to an enhanced dissociation of the parent ions as well as some fragment ions.

MO 19.8 Thu 16:30 Empore Lichthof

Photophysics and Photochemistry of a Dinuclear Pt-Pt Complex and its Trinuclear Ag-Pt-Pt Derivative Studied by Femtosecond Time-Resolved UV/Vis Spectroscopy in Solution — ●FABIAN RUPP¹, LIEDY FLORIAN¹, SEBASTIAN V. KRUPPA², CHRISTOPH RIEHN², and ROLF DILLER¹ — ¹Dept. of Physics, TU Kaiserslautern — ²Dept. of Chemistry, TU Kaiserslautern, 67663

Kaiserslautern, Germany

Metal-metal interactions are crucial for the design and application of multinuclear transition metal complexes in new electronic devices or chemical catalysis. In a comparative study we investigated the photophysical and photochemical properties of the model compound tetrakis- μ -pyrophosphitodiplatinate(II) (PtPOP) and its Ag-derivative (AgPtPOP) in solution by fs time-resolved UV/Vis spectroscopy. Whereas PtPOP possesses a strong absorption band in the electronic ground state at 369 nm, the band is shifted to 398 nm for AgPtPOP, allowing selective photoexcitation. PtPOP excited states dynamics such as vibrational cooling, intersystem crossing, coherent wave packet dynamics [1] and electron detachment [2] have been studied intensively. On these grounds the influence of the added Ag^+ on the molecular dynamics is deduced in particular via wave packet oscillation period and dephasing time. This also allows to characterize the shapes of the potential energy surfaces of the electronic ground and first excited singlet state, respectively.

[1] R. van der Veen et al., *JACS*, 2011, **133**, 305

[2] S. V. Kruppa et al., *Int. J. Mass. Spec.*, 2015, accepted

MO 19.9 Thu 16:30 Empore Lichthof

Effect of alkyl chain length on the ultrafast vibrational dynamics of C-H stretching in 1-alkyl-3methylimidazolium ionic liquids — MEHDI M. KAZEMI, MAHESH NAMBOODIRI, JOHANNES KIEFER, and ●ARNULF MATERNY — Physics and Earth Sciences, Jacobs University Bremen, Campus Ring 1, 28759 Bremen

Femtosecond time-resolved coherent anti-Stokes Raman scattering (fs-CARS) is used to study the ultrafast vibrational dynamics in ionic liquids (ILs). The effect of increasing the alkyl chain length, n , in 1-alkyl-3methylimidazolium bis-(trifluoromethylsulfonate)imide ($\text{C}_n\text{C1ImTFSI}$ $n=6,8,10,12$) ionic liquid on the vibrational dynamics of C-H stretching is studied. The high frequency C-H stretching modes 2800-3000 cm^{-1} are excited and probed by the fs-CARS excitation around 3000 cm^{-1} . The results show that the vibrational dynamics of the ILs depends more on the viscosity than the hydrogen bonding as the alkyl chain length increases.

MO 19.10 Thu 16:30 Empore Lichthof

Structural Dynamics of Intercalated Water in Graphene Oxide — ●AMUL SHINDE^{1,2}, KATRIN ADAMCZYK^{1,2}, ANDREAS ROSSO², R. J. DWAYNE MILLER^{2,3}, and NILS HUSE^{1,2} — ¹Institut für Nanostruktur- und Festkörperphysik, Universität Hamburg, 20355 Hamburg, Germany — ²Max Planck Institut für Struktur und Dynamik der Materie, 22761 Hamburg, Germany — ³Departments of Chemistry and Physics, University of Toronto, Toronto, Ontario, Canada M5S 3H6

The effects of nanoconfinement on the structural dynamics of water is of fundamental scientific importance in both natural and engineered environments. Here we present an experimental investigation of intercalated water in graphene oxide (GO) using ultrafast infrared spectroscopy. The water organization in a fluctuating network of intermolecular hydrogen bonds is different to bulk water due to the decreased symmetry and new interactions with GO functional groups. We discuss the structural response of this network to energy input and address the implications for the mechanical properties of multilayered composite materials like GO.

MO 19.11 Thu 16:30 Empore Lichthof

IR spectroscopy on anionic and cationic, two- and three-centred, isolated nickel-ethanol clusters — ●DANIEL BELLAIRE¹, MARKUS BECHERER¹, FABIAN DIETRICH¹, ADAM KUBAS², KARIN FINK², and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern — ²Karlsruhe Institute of Technology, Institute of Nanotechnology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen

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

culations.

Specifically, anionic and cationic $Ni_m(\text{ethanol})_n^{+/-}$ ($m=2,3$; $n=1-3$) clusters are spectroscopically investigated and explored by the aforementioned methods. A strong OH bond activation is observed in the anionic cases. The results give insight both into the structure and reactivity of the nickel aggregates.

MO 19.12 Thu 16:30 Empore Lichthof

Automated size determination of single clusters from x-ray scattering images — ●ALEXANDER NELDE¹, BRUNO LANGBEHN¹, MARIA MÜLLER¹, DANIELA RUPP¹, MARIO SAUPE¹, ANATOLI ULMER¹, THOMAS MÖLLER¹, and NINA ROHRINGER² — ¹TU Berlin — ²Max Planck Institute for the Physics of Complex Systems

Short wavelength Free-electron lasers (FELs) allow imaging of individual nano particles in free flight. In laser-cluster interaction studies, single-cluster imaging can be used to sort the single-shot measurement of reaction products (e.g. ions, electrons) by cluster size. The large data sets require automated analysis, often challenging due to detector geometries and noisy background signal. An automated size determination algorithm based on Mie-fits will be presented and the measured size distribution from large xenon clusters imaged at the FLASH FEL will be discussed.

MO 19.13 Thu 16:30 Empore Lichthof

Optical properties of thionized diamondoids — ●TOBIAS ZIMMERMANN¹, THERESA HÖHNE¹, ANDRE KNECHT¹, ROBERT RICHTER¹, ANDREY A FOKIN², PETER R SCHREINER², THOMAS MÖLLER¹, and TORBJÖRN RANDE¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin — ²Institut für Organische Chemie, Justus-Liebig-Universität Giessen

Diamondoids, perfectly size- and shape-selectable sp^3 -hybridized carbon nanoparticles, exhibit intrinsic UV luminescence. It was shown through size- and shape-dependent studies that pristine diamondoids offer detailed insight into luminescence properties of large molecules [1]. However, so far no gas phase luminescence has been observed for diamondoids functionalized with foreign atoms. Recently, it has been predicted that thionization could alter the optical gaps for such particles to the VIS/IR spectral regime [2]. While adamantane-2-thione, the smallest member of the series, is known to show phosphorescence in solution [3], a broader selection of different sized thionized diamondoids could be successfully synthesized just recently. To probe luminescence in the gas phase and the effect of the particle size as well as thionization order, we investigated the electronic structure of this series in a combined study with synchrotron radiation and an OPO laser system.

[1] R. Richter *et al.*, *Phys. Chem. Chem. Phys.* **17**, 4739 (2015).

[2] M. Vörös *et al.*, *Phys. Rev. Lett.* **108**, 267401 (2012).

[3] K. J. Falk *et al.*, *J. Am. Chem. Soc.* **111**, 6518 (1989).

MO 19.14 Thu 16:30 Empore Lichthof

A setup for studying correlation effects in poly-anionic metal clusters by photoelectron spectroscopy — ●MADLEN MÜLLER¹, FRANKLIN MARTINEZ², GERRIT MARX¹, PATRICE OELSSNER², SLAWOMIR SKRUSZEWICZ², JOSEF TIGGESBÄUMKER², ROBERT WOLF³, KARL-HEINZ MEIWES-BROER², and LUTZ SCHWEIKHARD¹ — ¹Ernst-Moritz-Arndt-Universität, Greifswald, Deutschland — ²Universität Rostock, Rostock, Deutschland — ³Max-Planck-Institut für Kernphysik, Heidelberg, Deutschland

Photoelectron spectroscopy experiments provide insight into the electronic structure of atomic clusters. In the case of multiply negatively charged clusters, electron affinities and Coulomb barriers can be probed by varying the photon energy. In addition, poly-anionic metal clusters serve as model systems for electron-correlation phenomena. A setup is presented, which combines a radio-frequency ion trap, used for cluster-size selection, with a velocity-map imaging and a magnetic-bottle time-of-flight electron spectrometer. As a first test, measurements on mono-anionic fullerenes with respect to the first electron affinity, thermionic electron emission and the photoelectron angular distribution of the excess electron are conducted by the use of UV nanosecond pulses. The investigations will be extended to poly-anionic metal clusters, in the future. As higher charge states are only observed for larger cluster sizes, the enhanced requirements on the mass resolving power will be matched by a multi-reflection time-of-flight mass-separator. The project is funded by the Collaborative Research Center (SFB) 652.

MO 19.15 Thu 16:30 Empore Lichthof

Characterization of pulsed nozzles for production of atomic

and molecular clusters — ●MATTHIAS BOHLEN, JONAS GRZE-SIAK, AARON LAForge, RUPERT MICHIELS, NICOLAS RENDLER, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg

Pulsed nozzles in general offer many advantages over continuous beams such as higher droplet densities and reduced gas load. We use a home-built pulsed nozzle, developed in cooperation with CRUCS Center at UBC, Vancouver, that produces gas pulses down to 20 μs duration at repetition rates up to several hundred Hz. Investigations of power consumption and other properties are presented. A rich variety of applications, that include the production of water and ammonia clusters, is discussed as well as the characterization of the influence of multiple source parameters on the cluster size distribution.

Additionally, we have recently introduced a new method for doping clusters by laser ablation [1]. Here, we present the results from characterization of the laser ablation setup. In particular, it was shown that pulsed nozzles produce beams of both doped and seeded laser ablated material.

[1] R. Katzy, M. Singer, S. Izadnia, A.C. LaForge, F. Stienkemeier; *Rev. Sci. Instrum.*, in press

MO 19.16 Thu 16:30 Empore Lichthof

Infrared Laser Spectroscopy of Organic Radicals and their Bimolecular Complexes — ●DANIEL LEICHT, MATIN KAUFMANN, RAFFAEL SCHWAN, DANIEL HABIG, GERHARD SCHWAAB, and MARTINA HAVENITH — Ruhr-Universität Bochum, Bochum, Germany

Organic radicals are known to be important intermediates in many reactions e.g. in combustion, explosives and tropospheric chemistry. Using the technique of helium nanodroplet infrared spectroscopy we study organic radicals including but not limited to the allyl and benzyl radicals. The helium droplet environment enables us to not only study the bare radicals but also their bimolecular complexes with other small molecules (i.e. water, hydrochloric acid, oxygen, nitric oxide). In the case of water and HCl we observe the formation of H-bonds to the radicals' π -systems; these H-bonded complexes can be viewed as the exit channel of the hydrogen abstraction reaction by either Cl atoms or OH radicals from the corresponding organic compound. Open-shell species, such as oxygen and nitric oxide, however, chemically react with the organic radicals to form e.g. peroxy species. The spectroscopic observation of these organic radicals and their complexes therefore helps us to better understand their formation and reactivity.

MO 19.17 Thu 16:30 Empore Lichthof

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

The mixed alkali-alkaline earth molecules have recently attracted the interest of the scientific community due to possible applications in the field of cold and ultracold molecules. The combination of alkaline and alkaline earth atoms leads to molecules which have permanent electric and magnetic dipole moments and thus offer manipulation of their states by external fields. Several ab initio calculations have been published on various combinations of a group IA and a group IIA atom from which one expects $2^2\Sigma^+ - 2^2\Sigma^+$ transitions in the near infrared. Experimentally, not so much is known about the molecular electronic states. We have successfully recorded the near infrared spectrum of LiSr. The molecules were created in a heatpipe and their thermal emission was recorded via a high resolution Fourier transform spectrometer. The assignment of the dense spectrum was facilitated by tuning a diode laser to a molecular line of the emission spectrum, resulting in the observation of P-R-doublets and a simple vibrational progression. We used the rotational constants from ab initio-calculations for a first guess of the rotational quantum numbers. Then we proceeded to take into account more transition lines from higher rotational and vibrational levels. Perturbations due to couplings between the $2^2\Sigma^+$ state and the $1^2\Pi$ state have been observed and will be used to investigate the $2^2\Sigma_{1/2}^+ - 1^2\Pi_{1/2}$ and $2^2\Sigma_{1/2}^+ - 1^2\Pi_{3/2}$ couplings.

We will report on the status of the investigations.

MO 19.18 Thu 16:30 Empore Lichthof

Modeling of superradiance in molecular systems — ●DAVID W. SCHÖNLEBER and ALEXANDER EISFELD — Max-Planck-Institut für Physik komplexer Systeme, 01187 Dresden

We study superradiance in molecular systems in a setup similar to the one used in recent experiments [1]. In molecular systems, an excited

electronic state can decay into different vibrational states of the electronic ground state, which are subject to relaxation. We employ a simple three-level model to analyze the effect of vibrational relaxation, as well as effects of aggregate geometry, on the visibility of superradiance.

[1] Phys. Rev. B **92**, 121408(R) (2015)

MO 19.19 Thu 16:30 Empore Lichthof
Thermalization of OH⁻ in Multipole RF-Ion Traps with cold He, H₂ and HD as buffer gas — ●GERHARD EGGER, SEUNGHYUN LEE, OLGA LAKHMANSKAYA, ERIC ENDRES, DANIEL HAUSER, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Österreich

High order multipole ion traps are a versatile tool for performing spectroscopy on cold molecular ions and analyzing cold ion-neutral reaction dynamics with astrophysical relevance. In contrast to a Paul trap, the linear 22-pole trap features a large field free region [1]. Cooling is achieved by collisions with neutral buffer gas, thermalizing the kinetic temperature as well as the internal degrees of freedom which works well for many ion species. Furthermore, the temperature can be tuned from several Kelvin to room temperature, which enables temperature dependent measurements of reactions. With rotationally resolved near threshold photodetachment of OH⁻ the rotational temperature can be determined [2].

Interestingly, below 20 K the rotational temperature does not decrease linearly any more even though the trap temperature is reduced [2]. This can not easily be explained by the known heating effects. Therefore further measurements at different temperatures have been performed. Clearly seeing the effect in He buffer gas we performed corresponding measurements also in H₂ and HD. These results will be presented.

[1] R. Wester, J. Phys. B **42**, 154001 (2009) [2] R. Otto et al, Phys. Chem. Chem. Phys. **15**, 612 (2013)

MO 19.20 Thu 16:30 Empore Lichthof
Cold Penning-Reactions using a Li-MOT — ●JONAS GRZESIAK, FRANK STIENKEMEIER, and MARCEL MÜDRICH — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg i.Br.

Cold reactive scattering, especially in merged beams, has recently attracted wide attention.[1] Our setup for measuring elastic scattering of cold atoms and molecules originating from a rotating nozzle and atoms trapped in a Li-MOT has been extended for investigating reactive scattering. To this end we use a pulsed supersonic and cryogenic source with different homemade discharge units to provide an intense and cold beam of metastable rare gas atoms. We discuss the optimization of the metastable source as well as first results on cold Penning reactions of the pulsed beam atoms with the ultracold Li-atoms from the MOT. A detailed study of the possible extension of our setup combining the rotating nozzle with the pulsed source in a merged beams experiment is given.

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

MO 19.21 Thu 16:30 Empore Lichthof
Implementation of a Cryogenic Multipole Ion Trap for THz Spectroscopy of Molecular Systems — ●LENA REMMERS, MORITZ FISCHER, STEFFEN SPIELER, KATHARINA GEISTLINGER, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck

Spectroscopy of rovibrational transitions by continuous THz radiation is a promising approach to unravel the structure and dynamics of weakly bound systems. In our group a new setup combining an electro-spray ionization source and a cryogenic multipole ion trap is being built. This approach provides access to intact macromolecules in the gas phase with positive or negative charge. These are focused and guided by means of an ion funnel and a quadrupole ion guide. By use of a quadrupole mass selector the ions are selectively loaded into the 16-pole trap. The cryogenic trap provides a possibility for ground-state preparation of trapped ions via buffergas cooling. This setup will be used to perform rotational spectroscopy of the target molecular ion using a THz radiation source (based on difference frequency mixing of two near infrared diode lasers) and an additional IR-Laser entering the trap perpendicular to the ion path. Here we report on the status and characteristics of this experiment and on latest results on trapping ions and clusters. First experiments are planned on small OH⁻(H₂O)_n and H₃O⁺(H₂O)_n clusters.

MO 19.22 Thu 16:30 Empore Lichthof
Towards Highly Sensitive Detection of Cold Formaldehyde via Laser-Induced Fluorescence — ●ERICH DOBLER, MARTIN IBRÜGGER, ALEXANDER PREHN, ROSA GLÖCKNER, SOTIR CHERVENKOV, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Due to their rich internal structure and the long-range dipole-dipole interaction, cold polar molecules offer many exciting applications ranging from many-body physics to quantum information science. For such experiments, a highly sensitive detection technique to observe even smallest numbers of molecules is essential.

For this purpose, we implement a detection scheme based on laser-induced fluorescence (LIF) for formaldehyde (H₂CO), the molecule currently under investigation in our optoelectrical cooling experiment [1,2]. Successful detection of H₂CO via LIF has already been shown [3] and, moreover, this technique also allows state-selective measurements. We present the setup and the results from absorption and LIF spectroscopy from the \tilde{X}^1A_1 electronic ground state to the 4^1 vibrational manifold of the \tilde{A}^1A_2 excited state of formaldehyde. Those measurements are performed as a first step towards the realization of a LIF-based detection of ultracold molecules.

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

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

[3] E. R. Hudson *et al.*, Phys. Rev. A **73**, 063404 (2006).

MO 19.23 Thu 16:30 Empore Lichthof
Mixed-field orientation of molecules without rotational symmetry: time-dependent analysis — ●LINDA V. THESING¹, ROSARIO GONZÁLEZ-FÉREZ², and JOCHEN KÜPPER^{1,3,4} — ¹Center for Free-Electron Laser Science, DESY — ²Instituto Carlos I, Universidad de Granada — ³The Hamburg Center for Ultrafast Imaging, University of Hamburg — ⁴Department of Physics, University of Hamburg

We theoretically investigate the rotational dynamics of molecules without rotational symmetry in combined non-resonant laser fields and static electric fields. It was experimentally demonstrated that asymmetric top molecules with a permanent dipole moment non parallel to any principal axis of polarizability can be 3D aligned and orientated using elliptically polarized laser pulses in combination with weak dc electric fields [1]. A theoretical analysis assuming adiabatic behavior was not able to explain these findings accurately [1]. Here, we solve the time-dependent Schrödinger equation for different field configurations for 6-chloropyridazine-3-carbonitrile (CPC) as an example molecule in order to study the influence of nonadiabatic phenomena that have previously been shown to play an important role for mixed field orientation dynamics [2].

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

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

MO 19.24 Thu 16:30 Empore Lichthof
A Novel Scheme for Slowing Molecules — ●MAURICE PETZOLD, MIRCO SIERCKE, PAUL KAEBERT, PHILIPP GERSEMA, and SILKE OSPELKAUS — Institut für Quantenoptik, Leibniz Universität Hannover

Current efforts to directly cool molecules to degeneracy are largely limited by the flux of slow molecules available in experiments. While slowing methods for molecules have been available for a long time, they have not been able to achieve efficiencies comparable to methods used for atoms. In this poster, we present our ideas for novel slowing methods of molecules. We propose a novel scheme based on radiative forces to slow down molecules to trappable velocities. The magneto-optical scheme is continuous and provides compression of the 1D-velocity distribution. We give detailed calculations of the forces obtained for the case of SrF and give estimates for the expected flux of cold molecules. To demonstrate the feasibility of our approach, we report on progress on applying our method to a thermal beam of Potassium atoms.

MO 19.25 Thu 16:30 Empore Lichthof
Stopping intense beams of internally cold molecules via centrifugal forces — ●XING WU, THOMAS GANTNER, MARTIN ZEPPENFELD, SOTIR CHERVENKOV, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching, Germany

Cryogenic buffer-gas cooling produces intense beams of cold molecules [1][2]. It offers a versatile source for studying collision dynamics and reaction pathways in the cold regime, and a variety of other appli-

cations. In order to be trapped and further cooled [3], these cold molecular beams still need to be decelerated. Here, we demonstrate that intense and continuous beams of electrically guided molecules produced by a cryogenic buffer-gas cell [2], can be brought to a halt by the centrifugal force in a rotating frame [4]. In addition, our RF-resonant depletion detection shows that up to 90% rotational-state purity can be achieved in the so-produced cold molecular beams. In combination with complete trajectory simulations which resolve the guiding efficiency for different states, it allows us to determine the internal temperature of these buffer-gas cooled molecules.

- [1] J. D. Weinstein *et al.*, *Nature* **395**, 148 (1998)
- [2] L.D. van Buuren *et al.*, *Phys. Rev. Lett.* **102**, 033001 (2009)
- [3] M. Zeppenfeld *et al.*, *Nature* **491**, 570 (2012)
- [4] S. Chervenkov *et al.*, *Phys. Rev. Lett.* **112**, 013001 (2014)

MO 19.26 Thu 16:30 Empore Lichthof

Infrared spectroscopy of trimethylamine N-oxide in helium droplets — ●RAFFAEL SCHWAN, MATIN KAUFMANN, DANIEL LEICHT, GERHARD SCHWAAB, and MARTINA HAVENITH — Ruhr-University Bochum, Germany

Helium nanodroplet spectroscopy is a well-established experimental technique to investigate reactive species like radicals or ions as well as weakly bound aggregates. Due to the ambient temperature of 0.37 K of the helium droplets only the ro-vibrational ground state of the investigated species is populated, which simplifies the observed infrared spectrum. Since helium droplets are superfluid, embedded molecules can still rotate freely.

Trimethylamine N-oxide (TMAO) is a naturally occurring osmolyte and plays an important role in the stabilization of proteins. Recent results using THz spectroscopy show the formation of TMAO-water aggregates involving 3-4 water molecules which are bound strongly to TMAO via hydrogen bonding [1].

First infrared spectra of the isolated TMAO molecule in helium droplets were obtained. For a distinct assignment of the spectral features mass-selective measurements were used. Future measurements aim to observe the stepwise formation of TMAO-water aggregates in helium droplets by characterizing the aggregates based on their infrared spectra and corresponding *ab initio* calculations.

- [1] Knake, L., Schwaab, G., Kartaschew, K., Havenith, M. (2015). *The Journal of Physical Chemistry B*, 119(43), 13842-13851.

MO 19.27 Thu 16:30 Empore Lichthof

Characterization of Microstructured Electric Trap for Optoelectrical Cooling of Polar Molecules — ●MARTIN IBRÜGGER, ALEXANDER PREHN, ROSA GLÖCKNER, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

Due to their rich internal level structure, polar molecules offer a wide range of exciting applications such as quantum simulation and controlled chemistry. However, many applications rely on long interaction times and localization, thus requiring trapping of the molecules. In our approach the trap consists of a pair of microstructured capacitor plates [1] creating a box-like potential. With this configuration we achieve record-long lifetimes for polar polyatomic molecules and dramatically reduce Stark broadening, therefore providing the optimal environment for optoelectrical Sisyphus cooling.

Here we investigate the properties of our trap with cooled formaldehyde [2]. We find $1/e$ trap decay times of up to one minute and confirm via Stark spectroscopy [3] the box-like potential. A homogeneous offset field inside the trap allows us to spectroscopically resolve transitions between single M sublevels of different rotational states. This enables us to control the rotational state and prepare the molecules in single M sublevels by optical pumping [4].

- [1] B.G.U. Englert *et al.*, *Phys. Rev. Lett.* **107**, 263003 (2011).
- [2] A. Prehn *et al.*, arXiv:1511.09427 (2015).
- [3] R. Glöckner *et al.*, *New J. Phys.* **17**, 055022 (2015).
- [4] R. Glöckner *et al.*, arXiv:1511.07360 (2015).

MO 19.28 Thu 16:30 Empore Lichthof

Micro Solvation of Glycine — ●MATIN KAUFMANN, RAFFAEL SCHWAN, DANIEL LEICHT, DEVENDRA MANI, GERHARD SCHWAAB, and MARTINA HAVENITH — Lehrstuhl für Physikalische Chemie II, Ruhr-Universität Bochum

Glycine is the smallest amino acid and serves as a model system for the interaction of amino acids and water. In the gas phase, glycine is in its neutral form, while in crystal structure and aqueous solution it occurs as a zwitterion.

Theoretical [1] and experimental [2] studies on the micro solvation of glycine have been carried out, however, no unambiguous statement was made on the number of water molecules needed to transition from hydrogen bonded structures involving the neutral form of glycine to structures involving the zwitterionic form of glycine.

The helium nanodroplet isolation technique is established as a way to stabilize molecular aggregates and reactive species, making them accessible to spectroscopic studies. Infrared spectra of glycine in complexes with an increasing number of water molecules are recorded and the observed transitions are assigned utilizing *ab initio* calculations for most of the viable structures.

- [1] S. M. Bachrach, *J. Phys. Chem. A* 2008, 112, 3722
- [2] R. Ramaekers, *J. Chem. Phys.* 2004, 120, 4182

MO 19.29 Thu 16:30 Empore Lichthof

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

We demonstrate the use of very strong static electric fields to improve the well-known techniques to state-select molecules in the electric deflector and for mixed-field orientation [1]. These are important methods to provide ideal samples for molecular-frame imaging of molecular dynamics in the gas phase [2]. For the state selection we developed a Stark deflector with a two-rod geometry, similar to [3]. Experimental results confirm a stronger deflection and better state separation than previous Stark deflectors. In mixed-field orientation a strong static electric field avoids nonadiabatic effects [4]. Therefore, we extended the idea of a two plate velocity map imaging spectrometer [5] to allow for strong electric fields up to 22 kV/cm. We will present its use in alignment and orientation experiments and disentangle the rotational motion of molecules in combined strong electric fields and laser pulses.

- [1] Chang *et al.*, *Int. Rev. Phys. Chem.* 34, 557 (2015)
- [2] Holmegaard *et al.*, *Nat. Phys.* 6, 428 (2010)
- [3] Stefanov *et al.*, *Meas. Sci. Technol.* 19, 055801 (2008)
- [4] Nielsen *et al.*, *Phys. Rev. Lett.* 108, 193001 (2012)
- [5] Papadakis and Kitsopoulos, *Rev. Sci. Instr.* 77, 083101 (2006)

MO 19.30 Thu 16:30 Empore Lichthof

Charge Transfer in hetero-molecular organic Van der Waals complexes — ●ALEXANDER RUF and FRANK STIENKEMEIER — University of Freiburg, Freiburg, Germany

Charge transfer between excitonic states determines the functionality of many technological and biological systems. Despite their great importance and the extensive previous research the details of the complex quantum mechanical dynamics are still not clearly understood and interpretation of experimental data and simulations is not unequivocal. Single isolated hetero-molecular complexes can serve as an ideal model system to isolate specific effects promoting charge and energy transfer. For this purpose helium nano droplets offer unique properties in respect of complex formation, preparation of initial quantum states, control of environmental interactions and applicability of spectroscopic techniques. An outline of the anticipated experimental approaches to study charge transfer dynamics in model systems is given.

MO 20: Femtosecond Spectroscopy 4

Time: Friday 11:00–13:00

Location: f102

MO 20.1 Fri 11:00 f102

The primary photochemical processes of a ferracyclobutadiene in liquid solution studied by ultrafast mid-infrared spectroscopy — ●BORIS WEZISLA, JÖRG LINDNER, and PETER VÖHRINGER — University of Bonn

Metallacyclobutadienes belong to a class of molecules, which are of particular interest in modern catalysis, since they have been shown to be key intermediates in alkyne metathesis. These reactions are important tools in the synthesis of complex molecules, drugs, and polymers. Our group recently communicated laser flash photolysis experiments combined with time-resolved Fourier-transform infrared spectroscopy of a pseudo-square-pyramidal ferracyclobutadiene (FeCBD). This study focused on the timescale of nanoseconds to milliseconds, and found a primary cleavage of an equatorial carbonyl ligand, which is subsequently replaced by the solvent molecule within the time resolution.

Here, we expand this study by exploring the primary processes leading to the formation of this solvent species after excitation of metal-to-CO CT states with 355 nm or 266 nm laser pulses. The ensuing photochemical processes are detected in a time- and frequency-resolved manner using femtosecond mid-infrared (fs-MIR) spectroscopy in the carbonyl stretching region (1900–2100 cm^{-1}). The spectro-temporal evolution of the transient signal reveals that the primary events are complete within 300 ps. The primary quantum yield for the formation of a FeCBD featuring a solvent molecule in the equatorial binding site is found to be less than 20%. The results are discussed in terms of TD-DFT and extensive modeling of the time-dependent mid-IR response.

MO 20.2 Fri 11:15 f102

XUV Transient Absorption Spectroscopy of Photochemical Reactions — ●LORENZ DRESCHER, MARTIN GALBRAITH, GEERT REITSMA, JUDITH DURA, OLEG KORNILOV, SERGUEI PATCHKOVSKII, MARC VRAKING, and JOCHEN MIKOSCH — Max-Born-Institut, Berlin, Germany

Transitions of atomic core orbitals into unoccupied molecular valence orbitals offer a site-specific view of chemical binding [1]. Spectrally, such resonant transitions are located just below the inner-shell ionization edges. Recent advances in generation of XUV pulses from High Harmonic Generation (HHG) allow to probe such molecular core-to-valence transitions in transient absorption spectroscopy at ultrafast time resolution in a tabletop setup [2]. In our experiment, methyl iodide and iodobenzene photodissociations have been excited by 266 nm femtosecond laser pulses and the transient absorption spectra at the 4d-pre-edge of iodide have been measured using quasi-continuous XUV spectra from HHG driven by sub-6 fs NIR pulses. Our results show the rearrangement of the valence shell after excitation and how the electronic states involved in photodissociation differ for iodobenzene and methyl iodide molecules.

[1] J. Stöhr, *NEXAFS Spectroscopy*, Springer (1992)

[2] Attar et al., *JCP* 141, 164308 (2014)

MO 20.3 Fri 11:30 f102

Calculation of 2D electronic spectra using a stochastic Schrödinger equation approach — ●PANPAN ZHANG and ALEXANDER EISFELD — MPIPES Dresden

The hierarchy of pure states (HOPS) [1] is a powerful approach to calculate the dynamics of an open quantum system using stochastic trajectories. We show that HOPS can be used in combination with phase cycling methods [2] to calculate two-dimensional electronic spectra.

[1] D. Suess et al; *Phys. Rev. Lett.* 113, 150402 (2014)

[2] P. Tian et al; *Science*. 300, 1553 (2003)

MO 20.4 Fri 11:45 f102

Nonperturbative calculation of phase-modulated wave packet interferometry — ●ZENGZHAO LI and ALEXANDER EISFELD — Max-Planck-Institute for the Physics of Complex Systems, Noethnitzer Str. 38, 01187 Dresden, Germany

Recent phase-modulated wave packet interferometry experiments on gases of alkaline atoms showed signals from states where multiple atoms are excited simultaneously [*Phys. Rev. A* 92, 052412 (2015)]. To shed light on the origin of these signals, we solve the Schrödinger equation for this system numerically and in addition using perturbation theory. Our calculations indicate that these signals can arise even

from non-interacting atoms.

MO 20.5 Fri 12:00 f102

Quantum dynamics of molecular reactions in an explicit solvent cage — ●SEBASTIAN THALLMAIR^{1,2}, JULIUS ZAULECK¹, and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, LMU München — ²LS für BioMolekulare Optik, LMU München

Solvents are a crucial factor in every day chemistry. Additionally to electrostatic effects, dynamic solvent effects can emerge during ultrafast reactions with large amplitude molecular motion. We showed their importance for the photochemical bond cleavage of diphenylmethylphosphonium ions in solution [1] which is a common way to generate highly reactive carbocations.

Recently, we developed a new method combining quantum dynamics (QD) and classical molecular dynamics (MD) to model the influence of an explicit solvent environment on the QD of molecular reactions [2]. In this QD/MD approach, we extract the solvent potential from the MD trajectories by evaluating a set of different snapshots. Each solvent arrangement is taken into account individually and its potential is included in the Hamiltonian used for the QD calculations. The solute Hamiltonian is set up in specially designed reactive coordinates and the potential energy surfaces are evaluated at the ONIOM/CASSCF(10,10)/M06-2X level of theory. The solvent cage hinders the free dissociation and guides the molecular wave packet to the conical intersection which is not accessible in the gas phase. There the experimentally observed diphenylmethyl cations are formed.

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

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

MO 20.6 Fri 12:15 f102

Ultrafast vibrational dynamics of solvated protons — ●FABIAN DAHMS, RENE COSTARD, ERIK T. J. NIBBERING, and THOMAS EL-SAESSER — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2a, 12489 Berlin, Germany

Over the past decades, the nature of the hydrated proton has been subject of intense study. The key roles of hydrated protons in aqueous proton transport (known as the von Grothaus mechanism), in aqueous acid-base chemistry and in proton pump membrane proteins are indisputable, yet the interconverting mechanisms and related structures such as Zundel and Eigen cations have remained elusive. With one and two color mid-infrared pump-probe spectroscopy in a range from 1500 cm^{-1} up to 3700 cm^{-1} , we determine the absorption bands' nature and the intrinsic vibrational lifetimes of Zundel cations on a femtosecond time scale. The extensive experimental results allow for following the energy flow and redistribution after vibrational excitation. Moreover, we gain new information about the origin of the broad Zundel absorption continuum.

MO 20.7 Fri 12:30 f102

Photocleavage of coumarin dimers studied by UV ultrafast transient absorption spectroscopy — ●MAN JIANG, TIAGO BUCKUP, and MARKUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität, D- 69120 Heidelberg, Germany

The photoinduced cleavage of a coumarin dimer into its two monomers is a promising mechanism for laser controlled medical applications, like the release of pharmaceutical drugs for on-demand in-vivo treatment. In order to understand the underlying dynamics of the cleavage reaction in detail and develop strategies for an increase of the reaction efficiency, UV transient absorption spectroscopy was applied to a typical coumarin dimer, 2-methylallylcarboxy-dicoumarin (linker 2). Linker 2 has an intact lactone ring structure and leads to a symmetric cleavage yielding the sole monomer product. Exciting the dimer with ultrashort pulses at 280 nm with 30 fs pulse duration, we were able to explore the precise time-scale of coumarin monomers formation and to determine the quantum yield of the dimer splitting. A branched kinetic model was developed which describes the formation of monomer and relaxation dynamics to the ground state with the corresponding rate constants. The branching ratio between the two pathways is about 1:2. Furthermore, the dependence of the dynamics of the cleavage reaction on the dimer side group substitution will be discussed.

MO 20.8 Fri 12:45 f102

Imaging molecular dynamics in I₂ by strong-field ionization — ●FLORIAN BACH, FELIX BRAUSSE, FARUK KREČINIĆ, ARNAUD ROUZÉE, HANS-HERMANN RITZE, and MARC VRAKING — Max-Born-Institut, Berlin, Germany

We investigated the dissociating wave packet dynamics in I₂ molecules following excitation by a 710 nm, 50 fs, pump laser pulse into the A state. The molecular motion was mapped into the photoelectron and photoion momentum distributions resulting from strong-field ioniza-

tion by a 1300 nm probe laser pulse. Both momentum distributions were recorded with a velocity map imaging spectrometer (VMIS). The kinetic energy distribution of the I⁺ fragments shows a clear signature of the dissociating wave packet motion induced by the pump laser pulse. We observe as well a modification of the angular distribution of the high kinetic energy photoelectrons that result from laser induced electron rescattering with the time delay between the two pulses that we assign to the change of the internuclear distance of the molecule.

MO 21: Cold Molecules & Helium Droplets 2

Time: Friday 11:00–13:00

Location: f142

Invited Talk

MO 21.1 Fri 11:00 f142

Rotational state thermometry of hydroxyl anions at the Cryogenic Storage Ring (CSR) — ●CHRISTIAN MEYER¹, ARNO BECKER¹, KLAUS BLAUM¹, CHRISTIAN BREITENFELDT^{1,2}, SEBASTIAN GEORGE¹, JÜRGEN GÖCK¹, MANFRED GRIESER¹, FLORIAN GRUSSI¹, PHILIPP HERWIG¹, JONAS KARTHEIN¹, CLAUDE KRANTZ¹, HOLGER KRECKEL¹, SUNIL KUMAR¹, JORRIT LION¹, SVENJA LOHMANN¹, PREETI M. MISHRA¹, OLDŘICH NOVOTNÝ¹, AODH P. O'CONNOR¹, ROLAND REPNOW¹, KAJA SPRUCK^{1,3}, STEFAN SCHIPPERS³, DIRK SCHWALM^{1,4}, LUTZ SCHWEIKHARD², STEPHEN VOGEL¹, ROBERT VON HAHN¹, and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — ²Institut für Physik, Ernst-Moritz-Arndt Universität Greifswald, 17487 Greifswald, Germany — ³Institut für Atom- und Molekülphysik, Justus-Liebig-Universität Gießen, 35392 Gießen, Germany — ⁴Weizmann Institute of Science, Rehovot 76100, Israel

The population of rotational states in a beam of OH⁻ ions stored in the CSR [1] was monitored for up to 1200 s using near-threshold photodetachment spectroscopy, similar to previous ion trap studies [2]. In the 35 m circumference electrostatic storage ring operated at around 10 K vacuum chamber temperature, storage times of the order of 1 hour for 60 keV ion beams were recently demonstrated. By photodetachment spectroscopy the evolution of level populations in J=2, 1 and 0 could be derived. Equilibrium populations over 95% in J=0 were reached.

[1] R. von Hahn *et al.*, Nucl. Instr. Meth. B 269, 2871 (2011)

[2] R. Otto *et al.*, Phys. Chem. Chem. Phys. 15, 612 (2013)

MO 21.2 Fri 11:30 f142

The Cryofuge: Deceleration of buffer-gas-cooled polar molecules — ●THOMAS GANTNER, XING WU, SOTIR CHERVENKOV, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

We present a general technique to produce an intense, continuous, guided beam of rotationally and motionally cold molecules. The molecules are first cooled in a cryogenic buffer gas cell [1] and then extracted and guided by an electrostatic quadrupole guide [2] to the centrifuge decelerator [3]. There, they are slowed down by employing the centrifugal force in a rotating quadrupole guide. Finally, they are detected by a quadrupole mass spectrometer. We demonstrate the deceleration of various molecules (CH₃F and CF₃CCH), achieving fluxes of about 10¹⁰ molecules/s with internal-state purity above 90% at velocities below 20 m/s by varying the settings of the buffer gas cell as well as the centrifuge rotation frequency.

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

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

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

MO 21.3 Fri 11:45 f142

Toward multi-MW continuous-wave intracavity power lasers for the alignment of molecules — ●BASTIAN DEPPE^{1,2,3,4}, GÜNTER HUBER^{1,2,3}, CHRISTIAN KRÄNKEL^{1,3}, and JOCHEN KÜPPER^{2,3,4} — ¹Institut für Laser-Physik, Universität Hamburg — ²Department of Physics, University of Hamburg — ³Centre for Ultrafast Imaging, University of Hamburg — ⁴Center for Free-Electron Laser Science, DESY, Hamburg

We are setting up a CW thin disk laser with high finesse to align molecules for pump-probe experiments at X-ray light sources with arbitrary repetition rates. A resonator internal focus of $\omega_0 = 25 \mu\text{m}$ will provide intensities in excess of 10 GW/cm², sufficient for the continuous adiabatic alignment of molecules. Recently we demonstrated more

than 130 kW of intracavity power at only 60 W of pump power with a pump spot diameter of 1.2 mm using Yb:YAG as the gain medium [1]. This result gives rise to a further scaling of the intracavity power by nearly two orders of magnitude into the multi-MW-range by pumping with the same intensity onto a pump spot diameter in the cm-scale utilized in state-of-the-art commercial thin disk lasers. In our presentation we will discuss the progress of our research in this respect and discuss different resonator configurations, different ytterbium-doped gain materials, the effects of additional required intracavity optics and polarization elements, as well as the challenges connected to in-vacuum operation of the laser.

[1] Deppe, Huber, Kränkel, Küpper, Opt. Exp. 23, 28491 (2015)

MO 21.4 Fri 12:00 f142

Light induced collapse of magnesium foam in helium droplets investigated by photoelectron spectroscopy — ●LEV KAZAK, JOSEF TIGGESBÄUMKER, and KARL-HEINZ MEIWES-BROER — Institute of Physics, University of Rostock, Albert-Einstein-Str. 24, 18059 Rostock, Germany

Recent investigation shows, that magnesium atoms embedded in helium droplets exist in metastable network of single atoms surrounded by the layer of helium atoms, called foam. The resonant two-photon ionization (R2PI) of Mg atom doped helium droplet reveals a narrow peak blue-shifted relative to atomic transition at $\lambda=279$ nm. For droplet containing more than one Mg atom, additional peak at $\lambda=282$ nm appears. This feature is presented irrespective to the cluster size (up to Mg₂₀). It suggests that before the absorption of the photon, single magnesium atoms are dissolved within the droplets, with interatomic Mg-Mg distance about 10 Å. Here we are using photoelectron spectroscopy to reveal the electronic structure of Mg complexes. The magnesium aggregate are probed by R2PI in vicinity of 31P10-31So transition in the wavelength region 276-284 nm. Complex photoelectron spectra arise when more than one magnesium atom is present in the droplet. Additionally, peaks, which corresponds to highly excited atoms appears, indicating a possible relaxation of the metastable structure. The photoelectron spectra at different doping conditions will be discussed.

MO 21.5 Fri 12:15 f142

Imaging desorption dynamics of rubidium atoms attached to helium nanodroplets — ●JOHANNES VON VANGEROW¹, ANTONIO LEAL², MANUEL BARRANCO^{2,3}, NADINE HALBERSTADT³, FRANÇOIS COPPENS³, MARTÍ PI², FRANK STIENKEMEIER¹, and MARCEL MUDRICH¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany — ²Departament ECM, Facultat de Física, and IN²UB, Universitat de Barcelona. Diagonal 645, 08028 Barcelona, Spain — ³Laboratoire des Collisions, Agrégats, Réactivité, IRSAMC, UMR 5589, CNRS et Université Paul Sabatier-Toulouse 3, 118 route de Narbonne, F-31062 Toulouse Cedex 09, France

This contribution will focus on photo-induced dynamics of rubidium (Rb) atoms attached to the surface of quantumfluid helium nanodroplets. A femtosecond (fs) pump-probe sequence is initiated by resonant excitation to droplet perturbed states correlating to the Rb 6p and 5p atomic orbitals. Subsequently, a fs probe pulse ionises the Rb atom and velocity map ion and electron images are recorded. Depending on excitation wavelength and pump-probe delay, dynamics involving either desorption or submersion as well as formation of Rb⁺He_n = 1, 2 complexes are observed. The experimental results will be discussed and compared to simulations based on time dependent density functional theory.

Invited Talk

MO 21.6 Fri 12:30 f142

Infrared Spectroscopy of mass/charge selected biomolecules in liquid helium droplets — ●GERT VON HELDEN — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Mass-to-charge selected ions are accumulated in an ion trap and picked

up by a traversing beam of helium droplets. The doped droplets are probed by light from the Fritz-Haber-Institut Free-Electron-Laser (FHI-FEL) and IR spectra of the embedded species are recorded. Results for several types of biological molecules ranging from peptides to proteins and carbohydrates will be presented.