

## Molecular Physics Division Fachverband Molekülphysik (MO)

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### Overview of Invited Talks and Sessions

(Lecture halls f102 and f142; Poster Empore Lichthof)

#### Invited Talks

MO 1.1	Mon	11:00–11:30	f102	<b>Infrared Spectroscopy of <math>\text{HHe}_n^+</math> and <math>\text{DHe}_n^+</math> Complexes</b> — ●OSKAR ASVANY, STEPHAN SCHLEMMER
MO 3.1	Mon	14:00–14:30	f102	<b>Enantio-selective controllability of asymmetric top molecules</b> — ●MONIKA LEIBSCHER, EUGENIO POZZOLI, MARIO SIGALOTTI, UGO BOSCAIN, CHRISTIANE P. KOCH
MO 4.1	Mon	14:00–14:30	f142	<b>Structure and dynamics of gas phase metal clusters</b> — ●BERND VON ISSENDORFF
MO 14.1	Wed	14:00–14:30	f142	<b>Elucidating transition metal clusters and complexes in cryo isolation</b> — ●GEREON NIEDNER-SCHATTEBURG
MO 14.2	Wed	14:30–15:00	f142	<b>Rotational Studies of (chiral) Molecules/Complexes in Jets (&amp; Flames)</b> — ●JENS-UWE GRABOW
MO 21.1	Fri	14:00–14:30	f142	<b>Laboratory experiments as tool to understand the infrared sky at high spectral resolution</b> — ●GUIDO W. FUCHS

#### Invited talks of the joint symposium SYCU

See SYCU for the full program of the symposium.

SYCU 1.1	Mon	11:00–11:30	e415	<b>Photoelectron circular dichroism in the light of resonance enhanced multi-photon ionization</b> — ●THOMAS BAUMERT
SYCU 1.2	Mon	11:30–12:00	e415	<b>New strategies for controlled chirality from the rovibrational dynamics of molecules</b> — ●ANDREY YACHMENEV
SYCU 1.3	Mon	12:00–12:30	e415	<b>Time-dependency in Photoelectron Circular Dichroism: from femtosecond scale to attosecond</b> — ●VALERIE BLANCHET
SYCU 1.4	Mon	12:30–13:00	e415	<b>Synthetic chiral light for efficient control of chiral light-matter interaction</b> — ●DAVID AYUSO, OFER NEUFELD, ANDRES F. ORDONEZ, PIERO DECLEVA, GAVRIEL LERNER, OREN COHEN, MISHA IVANOV, OLGA SMIRNOVA

#### Invited talks of the joint symposium SYAI

See SYAI for the full program of the symposium.

SYAI 1.1	Mon	14:00–14:30	e415	<b>Atom interferometry and its applications for gravity sensing</b> — ●FRANCK PEREIRA DOS SANTOS, LUC ABSIL, ROMAIN CALDANI, XIAOBING DENG, ROMAIN KARCHER, SÉBASTIEN MERLET, RAPHAËL PICCON, SUMIT SARKAR
SYAI 1.2	Mon	14:30–15:00	e415	<b>Atom interferometry for advanced geodesy and gravitational wave observation</b> — ●PHILIPPE BOUYER
SYAI 1.3	Mon	15:00–15:30	e415	<b>Fundamental physics with atom interferometry</b> — ●PAUL HAMILTON
SYAI 1.4	Mon	15:30–16:00	e415	<b>Atoms and molecules interacting with light</b> — ●LUCIA HACKERMÜLLER

**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	<b>Electron Pulse Control with Terahertz Fields</b> — ●DOMINIK EHBERGER
SYAD 1.2	Tue	11:30–12:00	e415	<b>Laser-Based High-Voltage Metrology with ppm Accuracy</b> — ●KRISTIAN KÖNIG, CHRISTOPHER GEPPERT, PHILLIP IMGAM, JÖRG KRÄMER, BERNHARD MAASS, JOHANN MEISNER, ERNST OTTEN, STEPHAN PASSON, TIM RATAJCZYK, JOHANNES ULLMANN, WILFRIED NÖRTERSCHÄUSER
SYAD 1.3	Tue	12:00–12:30	e415	<b>Structured singular light fields</b> — ●EILEEN OTTE
SYAD 1.4	Tue	12:30–13:00	e415	<b>Coherent Coupling of a Single Molecule to a Fabry-Perot Microcavity</b> — ●DAQING WANG

**Invited talks of the joint symposium SYQL**

See SYQL for the full program of the symposium.

SYQL 1.1	Thu	11:00–11:30	e415	<b>The unity of physics: the beauty and power of spectroscopy</b> — ●PAUL JULIENNE
SYQL 1.2	Thu	11:30–12:00	e415	<b>Using spectroscopy to explore the Rb<sub>2</sub> molecule and its formation</b> — ●JOHANNES HECKER DENSCHLAG
SYQL 1.3	Thu	12:00–12:30	e415	<b>Cold molecules: a chemistry kitchen for physicists</b> — ●OLIVIER DULIEU
SYQL 1.4	Thu	12:30–13:00	e415	<b>The birth of a degenerate Fermi gas of molecules</b> — ●JUN YE

**Invited talks of the joint symposium SYCM**

See SYCM for the full program of the symposium.

SYCM 1.1	Fri	11:00–11:30	e415	<b>Trapped Laser-cooled Molecules for Quantum Simulation, Particle Physics, and Collisions</b> — ●JOHN DOYLE
SYCM 1.2	Fri	11:30–12:00	e415	<b>Cold polyatomic molecules</b> — ●GERHARD REMPE
SYCM 1.3	Fri	12:00–12:30	e415	<b>Collisions between laser-cooled molecules and atoms</b> — ●MICHAEL TARBUTT
SYCM 1.4	Fri	12:30–13:00	e415	<b>Collisions between cold molecules in a superconducting magnetic trap</b> — ●EDVARDAS NAREVICIUS

**Sessions**

MO 1.1–1.8	Mon	11:00–13:15	f102	<b>Clusters I (joint session MO/A)</b>
MO 2.1–2.7	Mon	14:00–16:15	a320	<b>Atomic Clusters (joint session A/MO)</b>
MO 3.1–3.9	Mon	14:00–16:30	f102	<b>Chiral Molecules</b>
MO 4.1–4.9	Mon	14:00–16:30	f142	<b>Electronic Spectroscopy I</b>
MO 5.1–5.18	Mon	17:00–19:00	Empore Lichthof	<b>MO Poster 1</b>
MO 6.1–6.10	Tue	14:00–16:30	f102	<b>Electronic Spectroscopy II</b>
MO 7.1–7.7	Tue	14:00–15:45	f142	<b>Clusters II (joint session MO/A)</b>
MO 8.1–8.16	Tue	17:00–19:00	Empore Lichthof	<b>MO Poster 2</b>
MO 9.1–9.8	Wed	11:00–13:00	f102	<b>Femtosecond Spectroscopy I</b>
MO 10.1–10.10	Wed	11:00–13:30	f142	<b>Collisions and Reactions</b>
MO 11	Wed	13:30–14:00	f142	<b>Annual General Meeting</b>
MO 12.1–12.1	Wed	13:10–13:55	f303	<b>Lunch talk: German Research Foundation (DFG) (joint session A/K/P/MO/MS/Q)</b>
MO 13.1–13.5	Wed	14:00–15:15	f102	<b>Cold Molecules (joint session MO/Q)</b>
MO 14.1–14.8	Wed	14:00–16:30	f142	<b>Vibrational and Rotational Spectroscopy</b>
MO 15.1–15.17	Wed	17:00–19:00	Empore Lichthof	<b>MO Poster 3</b>
MO 16.1–16.9	Thu	14:00–16:15	f102	<b>Femtosecond Spectroscopy II</b>
MO 17.1–17.8	Thu	14:00–16:00	f142	<b>Theory</b>
MO 18.1–18.6	Thu	14:00–15:45	f442	<b>Cold Molecules II (joint session Q/MO)</b>
MO 19.1–19.23	Thu	17:00–19:00	Empore Lichthof	<b>MO Poster 4</b>
MO 20.1–20.8	Fri	14:00–16:00	f102	<b>Control (joint session MO/Q)</b>
MO 21.1–21.7	Fri	14:00–16:00	f142	<b>Astrophysics and Ions</b>

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

Wednesday 13:30–14:00 f142

## MO 1: Clusters I (joint session MO/A)

Time: Monday 11:00–13:15

Location: f102

## Invited Talk

MO 1.1 Mon 11:00 f102

**Infrared Spectroscopy of  $\text{HHe}_n^+$  and  $\text{DHe}_n^+$  Complexes** — ●OSKAR ASVANY and STEPHAN SCHLEMMER — I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, Köln

The combination of a cryogenic ion-trap machine, operated at 4.7 K, with the free-electron-laser FELIX allowed the first experimental characterization of the antisymmetric stretch ( $\nu_3$ ) and bending ( $\nu_2$ ) fundamentals of the linear He-X<sup>+</sup>-He (X=H, D) cores of the in situ prepared  $\text{HHe}_n^+$  and  $\text{DHe}_n^+$  complexes for  $n = 3 - 6$ . The found band origins, at around 1290  $\text{cm}^{-1}$  for  $\nu_3$  and around 850  $\text{cm}^{-1}$  for  $\nu_2$  (for  $\text{HHe}_n^+$ ), are fully supported by first-principles quantum-chemical computations. These results are consistent with structures for the species with  $n = 3$  and 6 being of T-shaped  $C_{2v}$  and of  $D_{4h}$  symmetry, respectively, while the species with  $n = 4$  are suggested to exhibit interesting dynamical phenomena related to large-amplitude motions. Future high-resolution measurements will give detailed insight into the structure of these fundamental complexes.

MO 1.2 Mon 11:30 f102

**Photon-energy dependent ionisation of isolated Xenon atoms**

— THOMAS BAUMANN<sup>1</sup>, REBECCA BOLL<sup>1</sup>, MARKUS ILCHEN<sup>1</sup>, JOAKIM LAKSMAN<sup>1</sup>, TOMMASO MAZZA<sup>1</sup>, MICHAEL MEYER<sup>1</sup>, VALERIA MUSIC<sup>1</sup>, DANIEL RIVAS<sup>1</sup>, ●ALJOSCHA RÖRIG<sup>1</sup>, SVITOZAR SERKEZ<sup>1</sup>, PHILIPP SCHMIDT<sup>1</sup>, SERGEY USENKO<sup>1</sup>, JULIA SCHÄFER<sup>2</sup>, ROBIN SANTRA<sup>2</sup>, SANG-KIL SON<sup>2</sup>, SHASHANK PATHAK<sup>3</sup>, DANIEL ROLLES<sup>3</sup>, and BENJAMIN ERK<sup>4</sup> — <sup>1</sup>European XFEL GmbH, Schenefeld, Germany — <sup>2</sup>Center for Free-Electron Laser Science (CFEL), Hamburg, Germany — <sup>3</sup>Kansas State University, Manhattan, USA — <sup>4</sup>Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany

In October 2019 we investigated the photon-energy-dependence of the ionisation process of isolated Xenon atoms exposed to extremely intense soft X-ray radiation at the European XFEL free-electron laser in Schenefeld, Germany. We were able to tune the photon energy over a wide range (700 eV - 3000 eV) while maintaining constant high pulse energy of several millijoule. As a function of photon energy, we detected distinct variations of the ion yield in certain charge state regions due to non-linear effects, and extreme-charge states up to +42 of Xenon. These variations are the result of transient resonances that increase the photoionisation cross section at certain charge states and photon energies, as the binding energies in the atomic orbitals shift as a result of increasing charge state during a single FEL pulse. The experimentally obtained data is in good accordance with the calculated charge state distributions, thus allowing us a detailed insight into the transient electronic structure of highly excited atoms.

MO 1.3 Mon 11:45 f102

**Oscillations in immiscible liquids due to persistent currents**

— ●FREDERIC FOLZ, AYOUB ELYAAGOUBI, ALBRECHT OTT, and GIOVANNA MORIGI — Universität des Saarlandes

Absorption spectroscopy exhibits a noisy absorption pattern in samples of colloidal gold at marginal stability [1]. This might be the signature of an oscillatory behavior. Here, we discuss a theoretical model that traces these oscillations back to agglomeration and sedimentation processes, given a persistent influx of molecules. We analyse the results in relation to the experimental findings.

[1] Experiments carried out by Ayoub Elyaagoubi in the group of Prof. Ott at Saarland University, unpublished

MO 1.4 Mon 12:00 f102

**Geometry and Stability of Small Cationic Silicon Carbide Clusters**

— ●ROBERT RADLOFF, LARS DAHLÖF, KAI POLLW, KARIM AHMED SAROUKH, MARKO FÖRSTEL, and OTTO DOPFER — Technische Universität Berlin, Institut für Optik und Atomare Physik, Germany

Ejecta of carbon-rich stars contribute significantly to interstellar dust. The emitted particles are generally hot and consist of single atoms or ions. With increasing distance from the star, this matter cools down and starts to condense, eventually forming first molecules and creating a rich chemistry. Observations suggest not only small molecules like SiC [1], Si<sub>2</sub>C [2], SiC<sub>2</sub> [3], etc. to be present in the circumstellar environment of carbon-rich stars but also solid silicon carbide grains [4]. Up to now, it has remained unclear how these dust grains are created.

It seems likely that they form from small SiC molecules via condensation but no intermediates have been detected so far.

In this contribution we present the energetic, geometric, and optical properties of small cationic silicon carbide clusters obtained via photodissociation spectroscopy, mass spectrometry, and quantum chemical calculations. We show the first optical spectrum of a silicon carbide cation and present hitherto unreported fragmentation channels and ground state geometries of several cationic silicon carbide clusters.

[1] J. Cernicharo et. al., *Astrophys. J. Lett.* **341**, L25 (1989)

[2] J. Cernicharo et. al., *Astrophys. J. Lett.* **806**, L3 (2015)

[3] P. Thaddeus et. al., *Astrophys. J. Lett.* **283**, L45-48 (1984)

[4] R. Treffers and M. Cohen, *Astrophys. J.* **188**, 545-552 (1974)

MO 1.5 Mon 12:15 f102

**N<sub>2</sub> activation on size selected Tantalum clusters investigated by cryo kinetics and IR spectroscopy**

— ●MATTHIAS P. KLEIN<sup>1</sup>, DANIELA V. FRIES<sup>1</sup>, ANNIKA STEINER<sup>1</sup>, HELMUT SCHWARZ<sup>2</sup>, and GEREON NIEDNER-SCHATTEBURG<sup>1</sup> — <sup>1</sup>Fachbereich Chemie und Forschungszentrum OPTIMAS, TU Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern — <sup>2</sup>Institut für Chemie, Technische Universität Berlin, 10623 Berlin

Catalytic N<sub>2</sub> activation by active transition metal surfaces is one of the most important industrial processes. For a thorough understanding of the activation steps, we need suitable model systems. By means of cryo IR-PD spectroscopy and cryo adsorption kinetics supported by DFT modelling, we are able to investigate the vibrational and kinetic behavior of various transition-metal-cluster-N<sub>2</sub>/H<sub>2</sub> complexes (Fe, Co, Ni, Rh, Ru) and gain information about reaction precursors and intermediates. Small tantalum clusters have shown to activate N<sub>2</sub> dissociatively and even support the formation of ammonia. We chose to examine the Ta<sub>4</sub><sup>+</sup> and Ta<sub>5</sub><sup>+</sup> clusters in more detail. We observe a rearrangement of the adsorbate shell and activated N<sub>2</sub> upon stepwise N<sub>2</sub> adsorption. In the Ta<sub>4</sub><sup>+</sup> case, the adsorption kinetics suggest a complex dynamics for large adsorption shells. A pseudo-first-order kinetic fit fails in this case. In contrast, the adsorption kinetics of the Ta<sub>5</sub> cluster are reproducible by such a fit. IR bands represent a range from weakly bound N<sub>2</sub> to actual N<sub>2</sub> activation precursors.

MO 1.6 Mon 12:30 f102

**Optimizing Aerodynamic Lens Geometries for Gold Nanoparticle Beams**

— ●LENA WORBS<sup>1,2</sup>, JANNIK LÜBKE<sup>1,2,3</sup>, ARMANDO ESTILLORE<sup>1</sup>, AMIT K. SAMANTA<sup>1</sup>, LOURDU XAVIER PAULRAJ<sup>1</sup>, KARTIK AYYER<sup>1,4</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — <sup>2</sup>Fachbereich Physik, Universität Hamburg — <sup>3</sup>Center for Ultrafast Imaging, Hamburg — <sup>4</sup>Max Planck Institute for the Structure and Dynamics of Matter, Hamburg

Coherent diffractive imaging at free-electron lasers promises to allow the reconstruction of the three-dimensional molecular structures of isolated particles at atomic resolution [1]. However, because of the typically low signal to noise ratio, this requires the collection of a large amount of diffraction patterns. Since every intercepted particle is destroyed by the intense x-ray pulse, a new and preferably identical sample particle has to be delivered into every pulse. One delivery technique is an aerodynamic lens stack (ALS), providing collimated or focused beams of nanoparticles. With the aid of numerical simulations we optimized the geometry of an ALS to produce high-density beams of nanoparticles, e.g., gold nanoparticles. Here, we present the simulation result for an optimized ALS and its experimental characterization using novel laser-based particle detection techniques [2]. We also show an application of ALS for XFEL experiments on gold nanoparticles.

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

[2] L. Worbs, et al., *Opt. Expr.*, arXiv:1909.08922 [physics.optics]

MO 1.7 Mon 12:45 f102

**Chemical dynamics in Argon clusters induced by intense x-rays**

— ●ZOLTAN JUREK<sup>1,2</sup>, YOSHIKI KUMAGAI<sup>3</sup>, HIRONOBU FUKUZAWA<sup>3,4</sup>, SANG-KIL SON<sup>1,2</sup>, BEATA ZIAJA<sup>1,2,5</sup>, ROBIN SANTRA<sup>1,2,6</sup>, and KIYOSHI UEDA<sup>3,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron, Notkestrasse 85, 22607 Hamburg, Germany — <sup>2</sup>The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22671 Hamburg, Germany — <sup>3</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,

Sendai 980-8577, Japan — <sup>4</sup>RIKEN SPring-8 Center, Sayo, Hyogo 679-5148, Japan — <sup>5</sup>Institute of Nuclear Physics, PAS, Radzikowskiego 152, 31-342, Krakow, Poland — <sup>6</sup>Department of Physics, University of Hamburg, Jungiusstrasse 9, 20355 Hamburg, Germany

In this talk, we focus on the dynamics of rare gas clusters exposed to ultrashort X-ray Free Electron Lasers (XFELs) pulses of intermediate x-ray fluence. In this fluence regime the system is only partially ionized. Therefore, chemical properties of the sample may still play an important role in shaping the ionization dynamics beside the emerging Coulomb forces. As a result, complex fragmentation of the cluster can occur. We show signatures of chemical effects in spectroscopy observables, and present our theoretical simulations, unraveling the time evolution of irradiated Ar clusters in detail [1]. This study addresses a regime that is a very common scenario at current XFEL experiments. [1] Y. Kumagai et al, Phys. Rev. Lett. 120, 223201 (2018)

MO 1.8 Mon 13:00 f102

**The role of water in the photophysics of indole** — •LANHAI HE<sup>1</sup>, MELBY JOHNY<sup>1,2</sup>, THOMAS KIERSPEL<sup>1,2</sup>, JOLIUN ONVLEE<sup>1,2</sup>, BERND WINTER<sup>4</sup>, SEBASTIAN TRIPPEL<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup>

— <sup>1</sup>Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — <sup>2</sup>Center for Ultrafast Imaging, Universität Hamburg — <sup>3</sup>Department of Physics, Universität Hamburg — <sup>4</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Hydrogen bonds play an important role in biological processes and proteins, e.g., protein folding and molecular recognition. The influence of water in complex systems, such as a protein, can only be explained if the cluster formation and the breaking of the micro-solvated molecular clusters itself is understood. We studied the photo-fragmentation of indole and indole-water<sub>1</sub> upon x-ray absorption, which triggers inner-shell ionization from nitrogen and carbon (1s) orbitals. The generated ions and electrons were measured with an angle-resolved coincidence detection scheme, and the results revealed fragmentation-pathway-dependent electron spectra, linking the structural fragmentation dynamics to different electronic excitations. On the other hand, the photoelectron spectrum of an aqueous indole-water solution has been measured through x-ray ionization of indole in a liquid microjet. Analyzing the chemical shifts for the characteristic photoelectron spectra, the hydration of indole in water solutions is about to be identified.

## MO 2: Atomic Clusters (joint session A/MO)

Time: Monday 14:00–16:15

Location: a320

### Invited Talk

MO 2.1 Mon 14:00 a320

**Time-resolved X-ray Imaging of Anisotropic Nanoplasma Expansion** — •CHRISTIAN PELTZ<sup>1</sup>, CHRISTOPH BOSTEDT<sup>2</sup>, MATHIAS KLING<sup>3</sup>, THOMAS BRABEC<sup>4</sup>, ECKART RUEHL<sup>5</sup>, ARTEM RUDENKO<sup>6</sup>, TAIS GORKHOVER<sup>7</sup>, and THOMAS FENNEL<sup>1</sup> — <sup>1</sup>Institute of Physics, University of Rostock, Germany — <sup>2</sup>Paul Scherrer Institute, Villigen, Switzerland — <sup>3</sup>Faculty of Physics, LMU Munich, Germany — <sup>4</sup>Department of Physics and Centre for Photonics Research, University of Ottawa, Canada — <sup>5</sup>Physical Chemistry, FU Berlin, Germany — <sup>6</sup>Department of Physics, Kansas-State University, USA — <sup>7</sup>LCLS, SLAC National Accelerator Laboratory, Menlo Park, USA

We investigate the time-dependent evolution of laser-heated solid-density nanoparticles via coherent diffractive x-ray imaging, theoretically and experimentally. Our microscopic particle-in-cell calculations for R = 25 nm hydrogen clusters reveal that infrared laser excitation induces continuous ion ablation on the cluster surface. This process generates an anisotropic nanoplasma expansion that can be accurately described by a simple self-similar radial density profile. Its time evolution can be reconstructed precisely by fitting the time-resolved scattering images using a simplified scattering model in Born approximation [1]. Here we present the first successful high resolution reconstruction of corresponding experimental results, obtained at the LCLS facility with SiO<sub>2</sub> nanoparticles (D=120 nm), giving unprecedented insight into the spatio-temporal evolution of the nanoplasma expansion.

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

### Invited Talk

MO 2.2 Mon 14:30 a320

**Imaging anisotropic dynamics in superfluid helium nanodroplets** — •B. LANGBEHN<sup>1</sup>, K. SANDER<sup>2</sup>, Y. OVCHARENKO<sup>1,3</sup>, C. PELTZ<sup>2</sup>, A. CLARK<sup>4</sup>, M. CORENO<sup>5</sup>, R. CUCINI<sup>6</sup>, A. DEMIDOVICH<sup>6</sup>, M. DRABELLS<sup>4</sup>, P. FINETTI<sup>6</sup>, M. DI FRAIA<sup>6,5</sup>, L. GIANNESI<sup>6</sup>, C. GRAZIOLI<sup>5</sup>, D. IABLONSKY<sup>7</sup>, A. C. LAForge<sup>8</sup>, T. NISHIYAMA<sup>9</sup>, V. OLIVER ÁLVAREZ DE LARA<sup>4</sup>, P. PISERI<sup>10</sup>, O. PLEKAN<sup>6</sup>, K. UEDA<sup>7</sup>, J. ZIMMERMANN<sup>1,11</sup>, K. C. PRINCE<sup>6,12</sup>, F. STIENKEMEIER<sup>8</sup>, C. CALLEGARI<sup>6,5</sup>, T. FENNEL<sup>2,11</sup>, D. RUPP<sup>1,11,13</sup>, and T. MÖLLER<sup>1</sup> — <sup>1</sup>TU Berlin — <sup>2</sup>Univ. Rostock — <sup>3</sup>European XFEL — <sup>4</sup>EPFL Lausanne — <sup>5</sup>ISM-CNR Trieste — <sup>6</sup>Elettra-Sincrotrone Trieste — <sup>7</sup>Tohoku Univ. Sendai — <sup>8</sup>Univ. Freiburg — <sup>9</sup>Kyoto Univ. — <sup>10</sup>Univ. di Milano — <sup>11</sup>MBI Berlin — <sup>12</sup>Swinburne Univ. of Tech. — <sup>13</sup>ETH Zürich

Intense short-wavelength light pulses from free-electron lasers (FELs) enable the study of the structure and dynamics of nanometer-sized particles in the gas phase using coherent diffraction imaging methods. In our experiment, we explored the light induced dynamics of xenon doped helium nanodroplets. We used intense near-infrared pulses to ignite a nanoplasma inside the droplets. After a variable time delay of up to 800 ps, we imaged the dynamics triggered by the nanoplasma using extreme ultraviolet pulses from the FERMI FEL. The recorded

scattering patterns exhibit pronounced directionalities that can be attributed to anisotropic changes of the droplet surface. A possible connection of these directed dynamics to the droplet's vortex structure will be discussed.

MO 2.3 Mon 15:00 a320

**Setup and characterization of a helium liquid jet for diffraction experiments** — •K. KOLATZKI<sup>1,2</sup>, R. M. P. TANYAG<sup>2</sup>, G. NOFFZ<sup>2</sup>, A. ULMER<sup>2</sup>, T. MÖLLER<sup>2</sup>, and D. RUPP<sup>1,3</sup> — <sup>1</sup>LFKP, ETH Zurich, Switzerland — <sup>2</sup>IOAP, TU Berlin — <sup>3</sup>Max-Born-Institut Berlin

When conducting coherent diffractive imaging experiments at XUV and X-ray facilities with atomic clusters as targets, it is desirable that these targets are constant in size and spacing. Large helium droplets produced via Rayleigh-type breakup of a liquid jet meet these requirements: Compared to other types of clusters or droplets, they can exhibit very narrow size distributions and even spacing. Helium droplets also have a simple electronic structure, show interesting properties like superfluidity and can be used as a cooling matrix for embedded atoms and molecules.

Recently, we have constructed and characterized a source for a helium liquid jet and subsequent droplets, which is available for user experiments at the European XFEL's SQS endstation. Via shadowgraphy methods, we have analyzed the jet's shape and the droplet size distributions. Results from these measurements and an improved setup will be presented.

MO 2.4 Mon 15:15 a320

**Solvation and desorption dynamics of Cs atoms attached to He nanodroplets** — •NICOLAS RENDLER, AUDREY SCOGNAMIGLIO, LUKAS BRUDER, KATRIN DULITZ, and FRANK STIENKEMEIER — University of Freiburg, Freiburg, Germany

Despite the low perturbative environment provided by the superfluidity of helium nanodroplets, excited or charged dopants can be strongly affected by the surrounding helium atoms. Numerous processes can be triggered by the electronic excitation and ionization of the dopant. For example, the repulsive electron-He interaction can result in the ejection of electronically excited dopants [1] which can be accompanied by electronic relaxation induced by the He environment [2]. In some cases, pairwise He-dopant interaction can also lead to the formation of He-dopant exciplexes [2,3]. Desorption dynamics, electronic relaxation as well as exciplex formation, strongly depend on the dopant species and still lack a complete understanding. We present an experimental study of the desorption dynamics of photo-excited Cs atoms attached to He nanodroplets using femtosecond pump-probe spectroscopy in combination with velocity-map imaging detection.

[1] M. Mudrich, F. Stienkemeier, Int. Rev. Phys. Chem. 33, 301-339, (2014).

[2] E. Loginov, M. Drabbels, J. Phys. Chem. A 111, 7504-7515, (2007).

[3] J. von Vangerow et al., *J. Phys. Chem. Lett.* **8** (1), 307-312, (2017).

MO 2.5 Mon 15:30 a320

**Coherent diffractive imaging of excited state population dynamics in a helium droplet** — ●BJÖRN KRUSE<sup>1</sup>, BENJAMIN LIEWEHR<sup>1</sup>, CHRISTIAN PELTZ<sup>1</sup>, and THOMAS FENNEL<sup>1,2</sup> — <sup>1</sup>Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23, D-18059 Rostock — <sup>2</sup>Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, D-12489 Berlin

Coherent diffractive imaging (CDI) of isolated helium nanodroplets has been successfully demonstrated with a lab-based HHG source [1] operating in the vicinity of the 1s - 2p transition of helium. To reconstruct the shape and orientation of nanoparticles, CDI experiments have so far been analyzed in terms of a classical linear response description [2]. However, for high intensities and especially for resonant excitation, population dynamics of bound electrons and stimulated emissions may become important, violating the assumptions underlying a linear description. To what extent and how nonlinear processes influence CDI scattering images is currently largely unknown. In our theoretical analysis, we describe the quantum-mechanical few-level bound state dynamics using a density matrix formalism and incorporate this into a 3D Maxwell solver based on the finite-difference time-domain method (FDTD). We discuss the spatio-temporal population dynamics and its impact on scattering images.

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

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

MO 2.6 Mon 15:45 a320

**Development of core-level binding energies of mass-selected lead clusters** — ●KLARA RASPE<sup>1</sup>, NORMAN IWE<sup>1</sup>, FABIAN BÄR<sup>2</sup>, KARIMAN ELSHIMI<sup>2</sup>, SIMON DOLD<sup>2</sup>, FRANKLIN MARTINEZ<sup>1</sup>, STEFFEN PALUTKE<sup>3</sup>, MARION KUHLMANN<sup>3</sup>, SVEN TOLEIKIS<sup>3</sup>, JOSEF TIGGESBÄUMKER<sup>1</sup>, BERND VON ISSENDORFF<sup>2</sup>, and KARL-HEINZ MEIWES-BROER<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany — <sup>2</sup>Fakultät für Physik, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Ger-

many — <sup>3</sup>Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg, Germany

The high photon flux and the photon energies of several tens of eV as delivered by FLASH allow to conduct core-level photoemission studies on size-selected metal clusters in the gas phase. Interesting aspects are phenomena like core-hole screening and the subsequent dynamics triggered by the core electron emission. However, probing these nanometer-sized targets requires the preparation of a sufficiently high target density in the FEL interaction region. This condition is met by an experimental setup, which includes a high-current cluster source, a quadrupole mass filter and a radio-frequency ion trap. Photoelectron spectra of lead cluster anions have been recorded in the size range of  $N = 3$  up to 50 atoms. The spectra show a size-dependent shift of the binding energies of the 5d electrons towards the bulk work function, which is compared to the metallic sphere model.

MO 2.7 Mon 16:00 a320

**Coulomb interaction in the photoemission of polyanionic silver clusters** — ●NORMAN IWE<sup>1</sup>, FRANKLIN MARTINEZ<sup>1</sup>, MADLEN MÜLLER<sup>2</sup>, KLARA RASPE<sup>1</sup>, LUTZ SCHWEIKHARD<sup>2</sup>, JOSEF TIGGESBÄUMKER<sup>1</sup>, and KARL-HEINZ MEIWES-BROER<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Rostock, Rostock, Deutschland — <sup>2</sup>Institut für Physik, Universität Greifswald, Greifswald, Deutschland

Multiply negatively charged, nano-sized particles are characterized by a barrier potential, given by the Coulomb interaction between the excess electrons. In order to extract details of this barrier with unprecedented quality, photoelectron spectroscopy is combined with tunable laser pulse excitation. The emitted photoelectron interacts with the remaining negatively charged system, which leads to a specific Coulomb cut-off in the photoelectron spectra, as known from molecular polyanions.

In this contribution, we present experimental spectra of mass- and charge-selected silver clusters,  $Ag_{800}^{z-}$  ( $z=2-6$ ), which show a characteristic dependence on the laser wavelength. The photoelectron spectra are qualitatively described by electrons coming from a Fermi distribution in a jellium-like potential, while direct emission as well as tunneling through the Coulomb barrier are taken into account.

## MO 3: Chiral Molecules

Time: Monday 14:00–16:30

Location: f102

### Invited Talk

MO 3.1 Mon 14:00 f102

**Enantio-selective controllability of asymmetric top molecules** — ●MONIKA LEIBSCHER<sup>1</sup>, EUGENIO POZZOLI<sup>2</sup>, MARIO SIGALOTTI<sup>2</sup>, UGO BOSCAIN<sup>3</sup>, and CHRISTIANE P. KOCH<sup>4,1</sup> — <sup>1</sup>Theoretische Physik, Universität Kassel, Kassel, Germany — <sup>2</sup>Inria, Sorbonne Université, Université de Paris, CNRS, Laboratoire Jacques-Louis Lions, Paris, France — <sup>3</sup>CNRS, Sorbonne Université, Inria, Université de Paris, Laboratoire Jacques-Louis Lions, Paris, France — <sup>4</sup>Theoretische Physik, Freie Universität Berlin, Berlin, Germany

Three-wave mixing (3WM) spectroscopy of chiral molecules allows for enantio-selective population transfer despite random orientation of the molecules [1]. Three-wave mixing is usually regarded as a three-state process [2]. However, due to the M-degeneracy of the rotational spectrum, the underlying rotational dynamics is far more complex and the usual 3WM schemes do not reach complete selectivity. To investigate the prospects of complete enantio-selective population transfer in systems with degenerate states, we extend a recent controllability analysis of symmetric rotors [3] and introduce the concept of enantio-selective controllability. Our analysis shows that an asymmetric top is enantio-selective controllable despite the M-degeneracy. Moreover, we demonstrate that 3WM schemes [2] have to be extended to at least five different microwave pulses to achieve complete separation of the enantiomers. [1] D. Patterson, M. Schnell, and J. M. Doyle, *Nature* **497**, 475 (2013). [2] M. Leibscher, T. F. Giesen, C. P. Koch, *J. Chem. Phys.* **151**, 014302 (2019). [3] U. Boscaïn, E. Pozzoli, M. Sigalotti, arXiv:1910.01924 (2019).

MO 3.2 Mon 14:30 f102

**Enantiomer-specific state transfer between rotational levels of cold, chiral molecules** — ●JOHANNES BISCHOFF, ALICIA O. HERNANDEZ-CASTILLO, JU HYEON LEE, MARCO DE PAS, GERARD MEIJER, and SANDRA EIBENBERGER-ARIAS — Fritz-Haber-Institut

der Max-Planck-Gesellschaft, Berlin, Germany

Chiral molecules are important in nature and exist in one of two mirror-image versions (enantiomers), that cannot be transformed into each other by mere rotation or translation. The understanding and control of chiral molecules plays a crucial role in many biological processes in the human body and therefore in drug development. However, most physical properties of enantiomers are identical, making chiral analysis challenging. The enantiomer-specific state transfer<sup>1</sup> method was recently developed. It can selectively populate or depopulate a rotational level of an enantiomer. This method builds on microwave three-wave mixing<sup>2</sup>, which allows for detecting chiral molecules enantiomer-specifically using microwave spectroscopy. We have designed, built, and characterized a compact spectrometer capable of performing chirped-pulse Fourier transform microwave spectroscopy and electronic spectroscopy. By combining optical methods with microwave spectroscopy, we seek to maximize the state-specific enantiomeric enrichment. Recent experimental results and details on the new spectrometer will be discussed.

1. Eibenberger et al **2017**. *Phys. Rev. Lett.*, **118**(12), 123002.

2. Patterson et al **2013**. *Nature*, **497**(7450), 475.

MO 3.3 Mon 14:45 f102

**Chiral resonant energy transfer in a medium** — ●FRANZ JANINE<sup>1</sup>, BENNETT ROBERT<sup>1</sup>, BUHMANN STEFAN YOSHI<sup>1</sup>, and SALAM AKBAR<sup>2</sup> — <sup>1</sup>Physikalische Institut, Albert-Ludwigs-Universität Freiburg, Hermann-Herder-Strasse 3, 79104 Freiburg, Germany — <sup>2</sup>Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109, USA

It has been shown that resonance energy transfer (RET) between chiral molecules can be used to discriminate enantiomers<sup>(1)</sup>. The RET rate between two molecules of the same handedness is slightly different than between molecules with opposite chirality. By using macroscopic quan-

tum electrodynamics we can study how to enhance this effect using an intervening medium and hence propose a distinct but related way to discriminate between enantiomers by using a medium with known chirality. However, when embedding a donor or acceptor molecule in a macroscopic medium, the microscopic structure of the medium close to the embedded molecule needs to be taken into account, which can be achieved using the so-called local-field correction. This turns out to be quite challenging for a chiral medium where contributions from light of opposite circular polarisation needs to be distinguished. In this talk I will outline the challenges encountered and propose some possible solutions. We also extend our theory to the related process of interatomic Coulombic decay (ICD), which offers different possibilities for the discrimination compared to resonant energy transfer.

(1) D. P. Craig, T. Thirunamachandran, *J. Chem. Phys.* **109** (1998)

MO 3.4 Mon 15:00 f102

**Spatio-temporally Resolved Probing of Chiral Near-Fields in an Electron Microscope** — ●JAN-WILKE HENKE, TYLER HARVEY, OFER Kfir, and CLAUS ROPERS — IV. Physical Institute: Solids and Nanostructures, University of Göttingen, Germany

Chirality, the lack of symmetry under spatial inversion, is central to many modern research topics, including the broken symmetry in biochemistry or magnetism. Insight into these phenomena can be gained by probing the optical response of the system with circular dichroism spectroscopy, which, however, has a limited spatial resolution. In scanning transmission electron microscopes, probes with a small spot size are routinely achieved, while the inelastic scattering of ultrashort electron pulses with the localised fields at the specimen (IELS) allows for the characterisation of the optical response [1,2].

In this presentation, we demonstrate the employment of IELS for probing chiral near-fields of a prototypical nanostructure. Similar to optical circular dichroism, a dichroic signal is obtained from the difference in coupling strength for incident illumination with left- or right-handed circularly polarised light. As the near-field is probed by femtosecond electron pulses [3], investigation of ultrafast phenomena is readily possible, while exploiting a wavelength-tunable pulsed light source enables recording dichroic spectra.

[1] B. Barwick et al., *Nature* 462 (2009)

[2] A. Feist et al., *Nature* 521 (2015)

[3] A. Feist et al., *Ultramicroscopy* 176 (2017)

MO 3.5 Mon 15:15 f102

**Controlling the axis of rotation in polyatomic molecules with the optical centrifuge** — ●EMIL ZAK<sup>1</sup>, ANDREY YACHMENEV<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, Hamburg — <sup>2</sup>Center for Ultrafast Imaging, Universität Hamburg — <sup>3</sup>Department of Physics, Universität Hamburg

Due to their electronic polarizability, molecules can align with their most polarizable axis along the direction of an electric field. We showed that with the use of an optical centrifuge it is possible to control which two principal polarizability axes of the molecule align in the plane of the electric field. We computationally demonstrated concepts of controlling the pathway of rotational excitation through robust modifications of the centrifuge field, without the need for modulations of the field intensity, which was demonstrated before [1]. On the examples of D<sub>2</sub>S and 2H-imidazole molecules we generated practically arbitrary coherent superpositions of rotational states, in which the molecule rotates simultaneously along the two different stable principal axes *a* and *c*. The proposed new method of tailoring rotational wavepackets provides the possibility of steering the 3D probability density of atoms in the molecule, e.g., to control the stereodynamics in reactive scattering experiments or to customly align even complex molecules in 3D space.

[1] A. Owens, A. Yachmenev, J. Küpper, *J. Chem. Phys. Lett.* **9**, 4206 (2018), \*arXiv:1807.04016 [physics]

MO 3.6 Mon 15:30 f102

**Multiphoton ionization of chiral molecules: what can we control and where's the button to control it?** — ●ANDRES ORDONEZ<sup>1,2</sup> and OLGA SMIRNOVA<sup>1,2</sup> — <sup>1</sup>Max-Born-Institut, Berlin, Germany — <sup>2</sup>Technische Universität Berlin, Berlin, Germany

We have developed a new approach to analyse the photoelectron angular distribution (PAD) resulting from multiphoton ionization of isotropic molecular samples. It reveals how the correlations encoded in the tensor that describes the orientation averaged photoelectron angular distribution can be cleanly written as a sum of products between molecular tensor invariants (MTIs) and electric field tensor invariants

(ETIs). By explicitly determining this connection between MTIs and ETIs we show which polarizations of the electric field must be used to address specific MTIs. Our findings provide not only a solid basis for the characterization of MTIs, but also allow a transparent application of coherent control of the correlations in the PAD. Using our formalism we have successfully identified the MTIs and ETIs responsible for the enantiosensitive asymmetry observed in the photoionization of isotropically oriented chiral molecules via a phase-locked crossed-polarized  $\omega$ - $2\omega$  fields in Ref. [PRL 121, 253201]. Our results clearly reveal the role of the chiral setup [PRA 98, 063428] in the absence of a well defined rotation direction of the electric field, expose the fundamental connection between the chiral setup and the ETIs, and reveal the role of the molecular phase in the formation of the asymmetry. This approach vastly extends our previous ideas [PRA 98, 063428] into the realm of multiphoton ionization and coherent control.

MO 3.7 Mon 15:45 f102

**Photoelectron circular dichroism via multiphoton ionization with varying pulse duration** — ●HAN-GYEOL LEE, SIMON RANECKY, SUDHEENDRAN VASUDEVAN, ALEXANDER KASTNER, NICOLAS LADDA, TOM RING, CONSTANTIN WITTE, HENDRIKE BRAUN, DANIEL REICH, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Photoelectrons from randomly oriented chiral molecules ionized by circularly polarized light can have an asymmetric momentum distribution with respect to the propagation direction of the laser beam. This effect is called photoelectron circular dichroism (PECD). In this contribution, we studied PECD of a few monoterpenes, such as fenchone, thiofenchone and camphor, by using laser pulses with different time durations from 50 fs to 5 ns. The laser pulses were centered at 380 nm to induce 2+1 resonant-enhanced multiphoton ionization via B- and C-band [1] and photoelectrons from each band were distinguished by different photoelectron energies. As the pulse duration increases, the effect of different relaxation dynamics of B- and C-band were clearly observed as a change of the ratio between photoelectron contributions from B- and C-band. We could model the observed behavior by simplified quantum mechanical model using Lindblad formalism including decoherence.

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

MO 3.8 Mon 16:00 f102

**High-resolution resonance-enhanced multiphoton photoelectron circular dichroism** — ALEXANDER KASTNER<sup>1</sup>, GRETA KOUMARIANOU<sup>2</sup>, PAVLE GLODIC<sup>2</sup>, PETER C. SAMARTZIS<sup>2</sup>, NICOLAS LADDA<sup>1</sup>, SIMON T. RANECKY<sup>1</sup>, SUDHEENDRAN VASUDEVAN<sup>1</sup>, CONSTANTIN WITTE<sup>1</sup>, HENDRIKE BRAUN<sup>1</sup>, HAN-GYEOL LEE<sup>1</sup>, ●ARNE SENFTLEBEN<sup>1</sup>, ROBERT BERGER<sup>3</sup>, G. BARRATT PARK<sup>4,5</sup>, TIM SCHÄFER<sup>4,5</sup>, and THOMAS BAUMERT<sup>1</sup> — <sup>1</sup>Universität Kassel, D-34132 Kassel — <sup>2</sup>Institute of Electronic Structure and Lasers, FORTH, 71110 Heraklion, Greece — <sup>3</sup>Philipps-Universität Marburg, D-35032 Marburg — <sup>4</sup>Georg-August-Universität Göttingen, D-37077 Göttingen — <sup>5</sup>MPI for Biophysical Chemistry, D-37077 Göttingen

Photoelectron circular dichroism (PECD) is a highly sensitive enantiospecific spectroscopy for studying chiral molecules in the gas phase using either single-photon ionization or multiphoton ionization. In the short pulse limit investigated with femtosecond lasers, resonance-enhanced multiphoton ionization (REMPI) is rather instantaneous while exciting several intermediate states simultaneously. In contrast, vibrational resolution in the REMPI spectrum can be achieved using nanosecond lasers. In this work, we follow the high-resolution approach using a tunable narrow-band nanosecond laser to measure REMPI-PECD through distinct vibrational levels in the intermediate 3s and 3p Rydberg states of fenchone. We observe the PECD to be largely independent of the vibrational level.

MO 3.9 Mon 16:15 f102

**Controlling and optimising the circular dichroism in the ion yield of chiral molecules using ultrashort laser pulses in the IR, visible and UV** — ●HENDRIKE BRAUN, TOM RING, CONSTANTIN WITTE, NICOLAS LADDA, CRISTIAN SARPE, SIMON RANECKY, SUDHEENDRAN VASUDEVAN, HAN-GYEOL LEE, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Circular dichroism, the difference of a system's response to interaction with left and right circularly polarized light, shows up in the absorption spectra of chiral molecules or in the polarization of transmitted light. CD was recently also observed in the ion yield of chiral molecules af-

ter REMPI (resonance enhanced multiphoton ionisation) experiments employing nano- and femtosecond laser pulses. The effect in the total ion yield is often related to the CD in absorption of the resonant intermediate. Using ultrashort laser pulses of different wavelengths, we can access the intermediate states of chiral molecules with different photonicities, ranging from multiphoton absorption for 800 nm pulses to one-photon absorption for 324 nm or 266 nm pulses. In combina-

tion with spectral phase shaping we are investigating the possibilities to control and optimise the measured CD value in the ion yield. Especially non-perturbative light matter interaction control schemes like Rabi oscillations and RAP are of interest as well as the potential use of composite pulses, that are currently also under review from theoretical side.

## MO 4: Electronic Spectroscopy I

Time: Monday 14:00–16:30

Location: f142

### Invited Talk

MO 4.1 Mon 14:00 f142

**Structure and dynamics of gas phase metal clusters** — ●BERND VON ISSENDORFF — Physikalisches Institut, Universität Freiburg, Germany

One of the clearest examples of a quantum size effect is the electron shell structure of simple (and not so simple) metal clusters, which has been studied in detail since the beginning of cluster physics. Photoelectron spectroscopy on size-selected clusters turned out to be an ideal tool to monitor this special electronic structure. Angle resolved photoelectron spectroscopy is even able to yield information about the wavefunctions of the electrons, as well as on the dynamics of the photoemission process [1]. The recent years have seen a constant improvement of the experimental techniques as well as of the theoretical methods used to simulate the results, which yields a new quality of insight, as was for example demonstrated for complex systems like zinc clusters [2]. Additionally the rapid development of new light sources like high intensity synchrotrons, free electron lasers and high harmonic sources offers a huge potential for experiments on clusters. I will discuss a number of experiments which have been done recently or are under development.

[1] C. Bartels et al., *Science* 323, 1323 (2009)

[2] A. Aguado, *Nanoscale*, 10, 19162 (2018)

MO 4.2 Mon 14:30 f142

**Threshold Photoelectron Spectroscopy of IO and HOI** — ●DOMENIK SCHLEIER<sup>1</sup>, ENGELBERT REUSCH<sup>1</sup>, LISA LUMMEL<sup>1</sup>, PATRICK HEMBERGER<sup>2</sup>, and INGO FISCHER<sup>1</sup> — <sup>1</sup>Institute for physical and theoretical Chemistry, Würzburg, Germany — <sup>2</sup>Paul-Scherrer-Institute (PSI), Villigen, Switzerland

IO and HOI represent key intermediates and precursors in the formation iodine oxide particles (IOPs). During their formation they catalytically destroy ozone and ultimately influence cloud lifetimes, contributing negatively to earths radiative balance. Both molecules have been characterized using multiple spectroscopic techniques like UV/Vis, IR, EPR, microwave spectroscopy and photoelectron detachment. However, information on the cations and thermodynamic data is still scarce. We therefore employ PEPICO (Photoelectron Photoion Coincidence) spectroscopy to record mass-selected threshold photoelectron spectra (ms-TPES). The CRF-PEPICO (Combustion Reactions Followed by PEPICO) setup at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source (SLS) uses a slow-flow reactor in which IO and HOI were produced from photolyzing an I<sub>2</sub>/O<sub>3</sub> mixture at 532 nm. The ionization energies were determined to be 9.71 ± 0.02 eV and 9.79 ± 0.02 eV for IO and HOI, respectively. While HOI+ shows a vibrational frequency of 660 cm<sup>-1</sup>, IO+ exhibits a spin-spin splitting resulting in the separation the 3Σ<sup>-</sup> ground states. This splitting results in two different determined vibrational frequencies for the cation of 810 cm<sup>-1</sup> and 730 cm<sup>-1</sup>.

MO 4.3 Mon 14:45 f142

**From wavelike dynamics to anomalous diffusion: Exciton transport in polymers of varying length, observed by EEI2D spectroscopy** — ●PAVEL MALÝ<sup>1</sup>, JULIAN LÜTTIG<sup>1</sup>, ARTHUR TURKIN<sup>1</sup>, JAKUB DOSTÁL<sup>1,2</sup>, CHRISTOPH LAMBERT<sup>1</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 12116 Prague, Czech Republic

Exciton transport and interaction in molecular aggregates and polymers are key processes in solar light harvesting and organic electronics. While the initial dynamics following photoexcitation proceeds in a delocalized, wavelike fashion, the subsequent exciton transport has

diffusive character. In this work we use our newly-developed exciton-exciton interaction two-dimensional (EEI2D) spectroscopy [1], in combination with microscopic theoretical modelling, to study exciton dynamics and annihilation in squaraine copolymers of varying length [2]. By directly probing interacting exciton pairs, we observe the transition from wavelike to diffusive exciton motion, dependent on the exciton delocalization length relative to the polymer size. Contrary to the common assumption, we find that the exciton diffusion has anomalous, sub-diffusive character, indicating trapped excitons. Our results demonstrate the potential of high-order spectroscopy, such as EEI2D, to provide new insights into exciton transport and interaction.

[1] J. Dostál et al., *Nat. Commun.* 2018, 9, 2466-2473

[2] P. Malý et al., *Chem. Sci.* 2020, DOI:10.1039/C9SC04367E

MO 4.4 Mon 15:00 f142

**Time- and frequency-resolved TOF-MS and photoion imaging on tetracene multimers** — ●MARCO FLOCK and INGO FISCHER — University of Wuerzburg, Institute of Physical Chemistry

Singlet fission (SF) describes the spin-allowed splitting of a photoexcited singlet state into two triplet states localized at two chromophores in a molecular system. To enable SF, the triplet energy of the chromophore must be half or lower than its singlet energy. This condition is fulfilled by tetracene making it a promising model system for the investigation of the SF process. The photophysical properties of the tetracene dimer and trimer were investigated by time- and frequency-resolved time of flight (TOF) photoionization and photoion imaging experiments in a molecular beam. The latter ones allow the exclusion of signals originating from fragmentation of higher order clusters. Frequency-resolved measurements revealed an ongoing red-shift of the dimer and trimer absorption compared to the monomeric species. Time-resolved measurements offered a completely different behavior for all three species: While monomeric tetracene shows no activity on the ps timescale, the dimer signal decays monoexponentially on the order of 100 ps and the trimer species shows a two-step relaxation with time constants of around 50 ps and 1 ns. The observed dynamics can be attributed to photophysical processes after photoexcitation and thus might play a role in the SF process of tetracene multimers.

MO 4.5 Mon 15:15 f142

**Dispersed fluorescence spectroscopy on Cyanoindoles** — ●HENRICH CHRISTIAN and SCHMITT MICHAEL — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The fluorescence of tryptophan and its derivatives is utilized for the spectroscopy of proteins. Through the introduction of substituents with different inductive (and mesomere) effects in different positions of the indole chromophore, the polarity of the environment can be affected. The energetic order of the two first electronically excited singlet states of indole,  $L_a$  and  $L_b$  strongly depends on this polarity. Different positions of the cyano group lead into different stabilization of these two states. We used laser induced fluorescence and dispersed fluorescence spectroscopy along with Franck-Condon theory in order to determine the changes of the geometry in the cyanoindoles upon electronic excitation. We perform fits of the rotational constants from high resolution laser induced spectroscopy and the Franck-Condon factors of different  $L_a/L_b \rightarrow S_0$  transitions of cyanoindoles.

MO 4.6 Mon 15:30 f142

**High resolution laser induced Stark spectroscopy: Position dependent study on 3-, 4- and 5-Cyanoindole** — ●MARIE-LUISE HEBESTREIT, HILDA LARTIAN, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

In this contribution we present investigations of the electronic nature of 3-, 4- and 5-cyanoindole [1-3]. Indole and most of its derivatives have

two close lying electronically excited singlet states labeled  $^1L_a$  and  $^1L_b$  in the nomenclature of Platt, which can be distinguished by the orientation of their transition dipole moment and by the magnitude and orientation of the permanent dipole moment [4,5]. In combination with *ab initio* calculations it is possible to determine the electronic nature for the lowest excited states via rotationally resolved Stark spectroscopy. The studies showed  $^1L_a$  character for the lowest excited state of 4- and 5-cyanoindole, while for 3-cyanoindole the lowest excited state was determined to be an  $^1L_b$  state. Reasons for this behavior are given by the influence of the inductive and mesomeric effect of the cyano group and the resulting electron density flow in the chromophore, depending if the cyano group is attached at the pyrrole ring or at the benzene ring.

- [1] Schneider *et al*, *Phys. Chem. Chem. Phys.*, 2018, **20**, 23441
- [2] Hebestreit *et al*, *Phys. Chem. Chem. Phys.*, 2019, **21**, 14766
- [3] Wilke *et al*, *Chem. Phys. Chem.*, 2016, **17**, 2736.
- [4] Platt, *J. Chem. Phys.*, 1949, **17**, 484.
- [5] Weber, *Biochem. J.*, 1960, **75**, 335.

MO 4.7 Mon 15:45 f142

**Exciton Interaction and Exciton Diffusion in Artificial Light-Harvesting Complexes Probed with High-Order Multidimensional Spectroscopy** — ●JULIAN LÜTTIG<sup>1</sup>, BJÖRN KRIETE<sup>2</sup>, TENZIN KUNSEL<sup>2</sup>, PAVEL MALÝ<sup>1</sup>, THOMAS L. C. JANSEN<sup>2</sup>, JASPER KNOESTER<sup>2</sup>, MAXIM S. PSHENICHNIKOV<sup>2</sup>, and TOBIAS BRIKNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, Netherlands

Two-dimensional electronic spectroscopy (2DES) has become a powerful tool for the investigation of single-exciton dynamics in various molecular systems, e.g., self-assembled artificial light-harvesting complexes. Here we use the recently developed technique of exciton-exciton-interaction two-dimensional (EEI2D) spectroscopy to disentangle the exciton dynamics in single-walled and double-walled tubular aggregates [1]. The technique of EEI2D spectroscopy allows us to follow the transport of excitons through the different systems by measuring exclusively exciton-exciton annihilation. We combine the technique of EEI2D spectroscopy with a microfluidic system to identify the influence of the supramolecular structure on the single- and double-exciton processes. EEI2D spectroscopy uncovers the different processes of exciton diffusion, energy transfer and exciton-exciton annihilation in these artificial-light harvesting complexes.

- [1] B. Kriete *et al.*, *Nat. Commun.* **10**, 4651 (2019)

MO 4.8 Mon 16:00 f142

**Direct measurement of multiexcitonic structure in colloidal CdSeS/ZnS quantum dots by multiple-quantum 2D fluorescence spectroscopy** — ●STEFAN MÜLLER, JULIAN LÜTTIG, LUISA

BRENNEIS, and TOBIAS BRIKNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

The multiexcitonic states of semiconductor quantum dots are of great relevance for their optoelectronic applications such as lasers and photovoltaics. Especially hot multiexcitons are discussed to be involved in the mechanism of carrier multiplication, a process that can significantly enhance solar cell efficiencies [1]. However, it is difficult to observe hot multiexcitons directly spectroscopically due to their short lifetime. To address this, we demonstrate our recently developed method of multiple-quantum two-dimensional (2D) fluorescence spectroscopy on colloidal CdSeS/ZnS alloyed core/shell quantum dots. We report a systematic measurement protocol that simultaneously probes biexcitonic and triexcitonic quantum coherences by fourth- and sixth-order nonlinear processes. This is achieved by appropriate phase cycling of fully collinear femtosecond multipulse trains in combination with fluorescence detection, as previously demonstrated [2]. Our results directly reveal various hot multiexcitonic states, enabling to measure the binding energies of these many-body species.

- [1] R. D. Schaller *et al.*, *Nat. Phys.* **1**, 189-194 (2005).
- [2] S. Mueller *et al.*, *Nat. Commun.* **10**, 4735 (2019).

MO 4.9 Mon 16:15 f142

**Excited state lifetimes of indole, 3-,4-, and 5-cyanoindole and pKa values of cyanoindoles in the ground and first excited state.** — ●HILDA LARTIAN, MARIE-LUISE HEBESTREIT, CAROLIN BORBECK, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

In this contribution the excited state lifetimes of indole, 3-cyanoindole ( $d_1$ ), 4-cyanoindole ( $d_1$ ) and 5-cyanoindole in  $D_2O$  and ethylacetate solution, obtained from time correlated single photon counting (TC-SPC), are presented and compared to excited state lifetimes in the gas phase. The excited state lifetime of 4-cyanoindole ( $d_1$ ) in ethylacetate and  $D_2O$  solution is longer than of bare indole and the other cyanoindoles. 4-cyanoindole ( $d_1$ ) shows a different behavior in the gas phase and has a shorter lifetime than 3-cyanoindole ( $d_1$ ), while 3-cyanoindole has a shorter excited state lifetime than 4-cyanoindole. The different behavior of 3-, 4-, and 5-cyanoindole is discussed on the basis of the different electronic nature of the electronically excited singlet states. Furthermore the pKa values of cyanoindoles in the ground and excited state have been measured using UV/Vis absorption spectroscopy. 2- and 3-cyanoindole have lower ground state pKa values (<13) than the other cyanoindoles (>14). Only for 4- and 7-cyanoindole a significant shift in pKa upon excitation can be detected which might be due to low fluorescence lifetimes of the other cyanoindoles.

- [1] Schneider *et al*, *Phys. Chem. Chem. Phys.*, 2018, **20**, 23441
- [2] Hebestreit *et al*, *Phys. Chem. Chem. Phys.*, 2019, **21**, 14766
- [3] Wilke *et al*, *Chem. Phys. Chem.*, 2016, **17**, 2736.

## MO 5: MO Poster 1

Time: Monday 17:00–19:00

Location: Empore Lichthof

MO 5.1 Mon 17:00 Empore Lichthof

**Data fusion for photoelectron spectroscopy @FLASH: a GPU accelerated approach** — ●FABIANO LEVER<sup>1</sup>, DENNIS MAYER<sup>1</sup>, JAN METJE<sup>1</sup>, MARKUS BRAUNE<sup>2</sup>, STEFAN DÜSTERER<sup>2</sup>, and MARKUS GÜHR<sup>1</sup> — <sup>1</sup>University of Potsdam, Germany — <sup>2</sup>Deutsches Elektronen- Synchrotron, Hamburg, Germany

We present a collection of data analysis techniques that are used to extract information from the large amount of data produced at the newly-built URSA-PQ instrument at the free electron laser FLASH. Data fusion procedures are used to combine together information from diverse sources, providing a more unified picture of the physical process under study. Graphical processing units (GPU) accelerated computing is used to increase the efficiency of the data processing algorithms.

MO 5.2 Mon 17:00 Empore Lichthof

**Small waist multimode cavity design for spatially resolved imaging of cold molecules** — ●JANNIS SCHNARS<sup>1</sup>, KAI VOGES<sup>1</sup>, PHILIPP GERSEMA<sup>1</sup>, TORSTEN HARTMANN<sup>1</sup>, ALESSANDRO ZENESINI<sup>1</sup>, KLEMENS HAMMERER<sup>2</sup>, and SILKE OSPELKAUS<sup>1</sup> — <sup>1</sup>Institut für Quantenoptik, Universität Hannover — <sup>2</sup>Institut für Theoretische Physik, Universität Hannover

Ultracold polar molecules offer exciting research perspectives due to strong dipole-dipole interactions. Pathways for the creation of ultracold ground state molecules are nowadays well known, the most common is to cool two atomic species close to quantum degeneracy, to associate atoms into loosely bound Feshbach molecules and transfer the molecular ensemble to the ground state by a stimulated Raman adiabatic passage. However, imaging techniques for atoms cannot be applied to molecules due to their complex internal structure with rotational and vibrational degrees of freedom, which often forbids optical cycling on a closed transition. For imaging, the creation process is therefore often reversed, dissociating molecules into atoms for convenient fluorescence or absorption imaging. This technique is highly destructive. Here we present a technique that allows to directly observe the molecules inside a 2D-optical lattice. The detection scheme relies on a dispersive matter-light interaction in the low saturation regime. The interaction is enhanced by a small-waist cavity. Furthermore the cavity is pursued in the multimode regime facilitating spatial resolution of several lattice sites. We present possible resonator geometries combining both requirements of a small waist and frequency degeneracy.

MO 5.3 Mon 17:00 Empore Lichthof

**Reconstructing Nanoclusters from Single Wide-Angle Scattering Images with Neural Networks** — ●THOMAS STIELOW, THOMAS FENNEL, and STEFAN SCHEEL — Institut für Physik, Universität Rostock, Albert-Einstein-Straße 23, 18059 Rostock

Single-shot diffraction imaging by soft X-ray laser pulses is a valuable tool for structural analyses of unsupported and short-lived nanosystems, although inversion of the scattering patterns still prove challenging [1]. Deep learning, on the other hand, is widely used in data sciences for the extraction of information from images and sees more and more application in various sciences. Recently, several advances have showcased how the predictive power of neural networks can be harnessed for extracting certain features from wide angle X-ray scattering patterns [2, 3]. We aim to solve the full inversion problem of wide-angle X-ray scattering with neural networks. Our approach is based on reconstructing the scatterer's density based on a training set of arbitrary convex bodies. We demonstrate the predictive capability of the trained networks by using real-world experimental data.

- [1] I. BARKE et al., Nat. Comm. **6**, 6187 (2015).
- [2] J. ZIMMERMANN, et al., Phys. Rev. E, 063309 (2019).
- [3] T. STIELOW et al., arXiv:1906.06883 (2019).

MO 5.4 Mon 17:00 Empore Lichthof

**Attosecond pulse induced ionization dynamics in a molecular charge-transfer system with correlated electrons** — ●KARL MICHAEL ZIEMS<sup>1,2</sup>, FRIEDRICH GEORG FRÖBEL<sup>1</sup>, STEFANIE GRÄFE<sup>1,2</sup>, and ALEXANDER SCHUBERT<sup>1</sup> — <sup>1</sup>Institute of Physical Chemistry, Friedrich-Schiller-University Jena, Germany — <sup>2</sup>Max Planck School of Photonics, Germany

The attosecond ultrafast ionization dynamics of correlated two- or many-electron systems have, so far, been mainly addressed investigating atomic systems. In the case of single ionization, it is well known that electron-electron correlation modifies the ionization dynamics and observables beyond the single active electron picture, resulting in effects such as the Auger effect or shake-up and knock up processes. Here, we extend these works by investigating the attosecond ionization of a molecular system involving the correlated two-electron dynamics, as well as the non-adiabatic nuclear dynamics. We demonstrate, employing a charge-transfer molecular model system, how elastic and inelastic correlation-driven processes can be observed. As the model system investigated here involves two differently bound electrons, a stronger and a weaker bound electron, we can distinguish different pathways leading to ionization, be it direct ionization or ionization involving elastic and inelastic electron scattering processes. We find that different pathways result in a difference in the electronic population of the parent molecular ion, which, in turn, involves different subsequent (non-adiabatic) vibrational dynamics.

MO 5.5 Mon 17:00 Empore Lichthof

**PhotoElectron Circular Dichroism (PECD) of Anionic Metal Complexes** — ●JENNY TRIPTOW, GERARD MELJER, and ANDRÉ FIELICKE — Fritz-Haber-Institut der Max Planck Gesellschaft, Berlin, Deutschland

Experiments on PECD are typically done with neutral chiral molecules and reveal asymmetries in the Photoelectron distribution of up to 10%. To perform these experiments, fs-lasers or synchrotron beamlines have to be used.

In our experiment, the PECD method is performed on anionic chiral molecules where a tabletop ns-laser is sufficient to photo-detach the relatively weakly-bound electron. Since a neutral chiral molecule and an electron are left behind, the missing long range interaction of the Coulomb potential can reveal the influence of short range interactions between the electron and the dipole moments of the molecule on the PECD effect.

Our initial approach to create chiral anions was to bind a neutral chiral molecule to an atomic gold anion. Atomic gold anions are easily produced in a laser ablation source. Our current procedure is deprotonation in a Plasma Entrainment Source followed by a supersonic expansion. Both the production of the chiral molecules bound to gold anions and the deprotonated molecules are verified by a Wiley-McLaren time-of-flight mass spectrometer and a velocity map imaging spectrometer.

MO 5.6 Mon 17:00 Empore Lichthof

**Finding molecules for consecutive photoinduced electron transfer (conPET)** — ●CARINA ALLACHER, PATRICK NUERNBERGER, and BERNHARD DICK — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Germany

In photosynthesis, nature combines the energy of several photons to perform a chemical reaction. In 2014 König et al. [1] proposed the conPET mechanism (consecutive photoinduced electron transfer) in order to combine two photons in a photochemical reaction. The first photon excites a photocatalyst molecule **M** to the excited state **M\*** which extracts an electron from a donor molecule **D**. The resulting radical **M•** is excited by a second photon, and the excited radical **M\*\*** transfers the electron to an acceptor molecule **A** which is reduced and undergoes further chemical reactions. In a search for such photocatalysts we generate the radical **M•** electrochemically. This allows a study of the photophysics of the conPET species **M•** separated from the photochemistry involved in generating the radical. Cyclic voltammetry in combination with fs transient spectroscopy yields the reduction potential of **M•** and the lifetime **M\*\***. First results obtained with the photocatalyst R6G show that the properties and reactivities of the electrochemically generated radical are the the same as those of the photochemically generated radical.

- [1] I. Gosh, T. Gosh, J. I. Bardagi, B. König, *Science* **2014**, 346, 725–728.

MO 5.7 Mon 17:00 Empore Lichthof

**Hydrogen Atom Transfer (HAT) between phenol and phenoxy-radical** — ●UWE FALTERMEIER and BERNHARD DICK — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Germany

Hydrogen Atom Transfer (HAT) reactions involving phenoxy radicals occur in various biological processes, like the breaking of free-radical chain reactions by tocopherol (Vitamin E). The self-exchange of a hydrogen atom between phenol and its corresponding phenoxy radical is the simplest-case scenario for such reactions. As such, it lends itself as calibration point for theoretical models. Despite its seemingly simple nature, almost no experimental data exists for this reaction. We present a method for determining the rate constant of this exchange and its thermal behavior by looking at the pseudo-self-exchange between phenol and phenol-d5. The radicals are produced by photolysis and the transient absorption of the samples in the  $\mu\text{s}$  range is recorded with a streak camera. Measurements at temperatures ranging from  $-5^\circ\text{C}$  to  $35^\circ\text{C}$  yield rate constants for the exchange of  $\approx 4 \times 10^5 \text{s}^{-1} \text{mol}^{-1}$ . Reversing the direction of the exchange, from phenol to phenoxy-d5, we find the same rate constants. This shows that our system is a good approximation to the phenoxy/phenol self-exchange reaction.

MO 5.8 Mon 17:00 Empore Lichthof

**Study of the photophysics and photochemistry of the phenol-ammonia complex** — ●STEFAN FUCHS and BERNHARD DICK — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Germany

Excited-state hydrogen transfer (ESHT) reactions provide photostability of biomolecules and are applied for the photoprotection of compounds (e.g. plastics) exposed to sunlight. Mechanistic proposals include hydrogen transfer and electron coupled proton transfer (ECPT). Clusters of phenol with ammonia have been used as model systems for the study of the mechanism. Previous studies on the dissociation of such clusters into a neutral phenoxy radical and the neutral hydrated ammonia cluster have considered clusters containing 5 ammonia molecules [1,2]. We use time-of-flight mass spectroscopy in combination with quantum chemical calculations which yields data on the phenol-ammonia(1) cluster.

- [1] M. Miyazaki, R. Ohara, K. Daigoku, K. Hashimoto, J. R. Woodward, C. Dedonder, Ch. Jouvét, M. Fujii, *Angew. Chem. Int. Ed.* **2015**, 54, 15089–15093.
- [2] M. Miyazaki, R. Ohara, C. Dedonder, Ch. Jouvét, M. Fujii *Chem. Eur. J.* **2018**, 24, 881 – 890.

MO 5.9 Mon 17:00 Empore Lichthof

**Understanding Geometric and Electronic Properties of Small Silicon Oxides Relevant in Interstellar Dust Formation Processes** — ●KAI POLLW, KARIM SAROUKH, ROBERT RADLOFF, LARS DAHLÖF, MARKO FÖRSTEL, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstraße 36, D-10623 Berlin, Germany

Interstellar dust is an important ingredient in the formation of solar systems like our own. Some properties of interstellar dust are known, many questions, however, are still unanswered. Molecular SiO can form in the atmospheres of oxygen-rich stars and interstellar dust contains particles made of macroscopic silicates of various compositions. Intermediates have been elusive to observations.

We present fragmentation pathways, geometric structure and optical properties of several possible intermediate species obtained via photodissociation spectroscopy and quantum chemical calculations. Knowledge of these parameters may help to model the complex formation processes and enable an observational search for these intermediate species.

MO 5.10 Mon 17:00 Empore Lichthof

**Optical Properties of Diamondoid Cations and Their Astrochemical Relevance** — ●PARKER CRANDALL, DAVID MÜLLER, PETER MEINHOLD, MARKO FÖRSTEL, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

Diamondoids, also known as nanodiamonds, are a class of highly stable, aliphatic cycloalkanes arranged into cage-like structures by the sp<sup>3</sup> hybridization of the carbon atoms. Members of the astrochemical community have demonstrated similarities between the IR spectra of diamondoids and unidentified infrared emission bands seen in the spectra of young stars with circumstellar disks. A ubiquitous presence of diamondoids is hypothesized, which could account for more than 5 % of cosmic and 40 % of tertiary carbon in interstellar environments. Due to their low ionization energy, it is also suggested that the radical cations of these molecules, which are predicted to absorb in the IR-UV/VIS range, are also present in high abundances and might be responsible for features in the well-known diffuse interstellar bands. However, optical spectra of these cations have not previously been reported. In this contribution, we present the first optical spectra via laser spectroscopy of the simplest diamondoid cation, the adamantane radical cation, by ion trapping in a cryogenic 22-pole trap. Fragmentation channels of the parent ion were also investigated by reflectron time-of-flight mass spectrometry. The astrophysical implications and future work are also described.

MO 5.11 Mon 17:00 Empore Lichthof

**IR Photodissociation spectra of Si<sub>x</sub>H<sub>4x-4</sub><sup>+</sup> (x=4-8): Evidence for Si-H-Si proton bridges** — ●MARTIN ANDREAS ROBERT GEORGE and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

Silicon hydride clusters (Si<sub>x</sub>H<sub>y</sub><sup>+</sup>) play a significant role in plasma chemistry and astrochemistry. Despite this importance their structural and energetic properties are largely unexplored. Building upon our previous investigations of Si<sub>2</sub>H<sub>6</sub><sup>+</sup> [1], Si<sub>2</sub>H<sub>7</sub><sup>+</sup> [2], Si<sub>3</sub>H<sub>8</sub><sup>+</sup> [3], we present infrared photodissociation (IRPD) spectra of previously unknown Si<sub>x</sub>H<sub>y</sub><sup>+</sup> ions of the form Si<sub>x</sub>H<sub>4x-4</sub><sup>+</sup> with x=4-8 (Si<sub>4</sub>H<sub>12</sub><sup>+</sup>-Si<sub>8</sub>H<sub>24</sub><sup>+</sup>) [4]. Our spectral analysis, supported by dispersion-corrected density functional calculations, reveals that all Si<sub>x</sub>H<sub>4x-4</sub><sup>+</sup> ions have at least one Si-H-Si bridge. The characteristic fingerprint of these three-center two-electron (3c-2e) bonds is the strongly IR active antisymmetric stretch fundamental of the Si-H-Si bridge. The frequency of this vibration depends strongly on the structural and energetic details of the Si-H-Si bridge. Our investigations reveal the correlations between the properties of the various Si-H-Si bridges (bond distances, bond angles, binding energies, stretch frequencies). The bond strength varies from strong symmetric 3c-2e chemical bonds to weak hydrogen or van der Waals bonds. [1] M. Savoca et al. (2013), Phys. Chem. Chem. Phys., 15, 2774 [2] M. Savoca et al., Angew. Chem. Int. Ed. (2013), 52, 1568 [3] M.A.R. George et al., Chem. Eur. J. (2013), 19, 15315-15328 [4] M.A.R. George, O. Dopfer (2019), Int. J. Mass Spectrom. (2019), 435, 51

MO 5.12 Mon 17:00 Empore Lichthof

**High-resolution infrared study of carbon-rich clusters C<sub>3</sub>X and XC<sub>3</sub>X (X = Se, Te)** — SVEN THORWIRTH<sup>1</sup>, ●THOMAS SALOMON<sup>1</sup>, JOHN B. DUDEK<sup>2</sup>, YURY CHERNYAK<sup>2</sup>, SOPHIA BURGER<sup>3</sup>, JÜRGEN GAUSS<sup>3</sup>, and STEPHAN SCHLEMMER<sup>1</sup> — <sup>1</sup>I. Physikalisches Institut, Universität zu Köln, Köln, Germany — <sup>2</sup>Department of Chemistry, Hartwick College, Oneonta, NY, U.S.A. — <sup>3</sup>Department Chemie, Johannes Gutenberg-Universität Mainz, Mainz, Germany

To date, carbon-rich clusters harboring heavy elements have received little attention from both experiment and quantum chemistry. Recent high-resolution infrared survey scans of laser ablation products from carbon-selenium and carbon-tellurium targets in the 5 μm wavelength regime have revealed several vibration-rotation bands not observed previously. On the basis of comparison with results from density-functional theory (DFT) calculations and high-level quantum-chemical calculations performed at the CCSD(T) level of theory these bands are attributed to new linear chains of the form C<sub>3</sub>X and XC<sub>3</sub>X with X being either Se or Te.

MO 5.13 Mon 17:00 Empore Lichthof

**High-resolution infrared and millimeter-wave spectroscopy of CNH<sub>n</sub><sup>+</sup> (n = 0,4,6) ions** — ●SVEN THORWIRTH<sup>1</sup>, OSKAR ASVANY<sup>1</sup>, CHARLIE MARKUS<sup>2</sup>, JOSE DOMENECH<sup>3</sup>, THOMAS SALOMON<sup>1</sup>, PHILIPP SCHMID<sup>1</sup>, MATTHIAS TÖPFER<sup>1</sup>, PHILIP SCHREIER<sup>1</sup>, and STEPHAN SCHLEMMER<sup>1</sup> — <sup>1</sup>I. Physikalisches Institut, Universität zu Köln — <sup>2</sup>Department of Chemistry, University of Illinois, Urbana, IL, U.S.A. — <sup>3</sup>Instituto de Estructura de la Materia (IEM-CSIC), Madrid, Spain

Molecular ions play crucial roles in the astrochemistry associated with star formation and planetary atmospheres. In this project, we have studied three fundamental cations CNH<sub>n</sub><sup>+</sup> (n = 0,4,6) using action spectroscopic techniques in a 22-pole ion trap at a nominal temperature of 4K [1]. The fundamental diatomic CN<sup>+</sup> [2] as well as protonated methylene imine, H<sub>2</sub>C=NH<sub>2</sub><sup>+</sup>, and protonated methyl amine, H<sub>3</sub>C=NH<sub>3</sub><sup>+</sup>, were all studied by their pure rotational spectra in the millimeter-wave region employing the method of rotational state-selective He-attachment [3]. CN<sup>+</sup> and H<sub>2</sub>C=NH<sub>2</sub><sup>+</sup> were also studied at high spectral resolution in the infrared using LIICG (Laser Induced Inhibition of Complex Growth) [1,4].

[1] O. Asvany, S. Brünken, L. Kluge, and S. Schlemmer 2014, Appl. Phys. B 114, 203 [2] S. Thorwirth, P. Schreier, T. Salomon, S. Schlemmer, and O. Asvany 2019, Astrophys. J. Lett. 882, L6 [3] S. Brünken, L. Kluge, A. Stoffels, J. Peres-Rios, and S. Schlemmer 2017, J. Mol. Spectrosc. 322, 67 [4] S. Chakrabarty, M. Holz, E. K. Campbell, A. Banerjee, D. Gerlich, and J. P. Maier 2013, J. Phys. Chem. Lett. 4, 4051

MO 5.14 Mon 17:00 Empore Lichthof

**phase transitions of nanoconfined water in self-assembled L,L-diphenylalanine peptides studied by vibrational spectroscopy** — ●ABUZER ORKUN AYDIN<sup>1</sup>, FERID SALEHLI<sup>1</sup>, SVITLANA KOPYL<sup>2</sup>, and ANDREI KHOLKIN<sup>2</sup> — <sup>1</sup>Physics Department, Istanbul Technical University, Istanbul, Turkey — <sup>2</sup>Physics Department and CICECO, Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal

Self-assembly of diphenylalanine (FF) molecules results in highly organised tubular nanostructures. Water molecules are confined in FF rings with diameter about 1nm along these nanocavities. This work is a fresh look into phase behavior of nanoconfined water in natural synthetic biomacromolecule.

We obtained MIR spectra in the temperature range between 90K and 330 K. Five OH-stretching modes were identified in absorbance spectra as tetrahedral water in different confinements in FF rings, consequently (k<sub>1</sub>=3105 cm<sup>-1</sup>, k<sub>2</sub>=3150 cm<sup>-1</sup>, k<sub>3</sub>=3200 cm<sup>-1</sup>, k<sub>4</sub>=3275 cm<sup>-1</sup>) and non-completed tetrahedral water molecules between rings (k<sub>5</sub>=3375 cm<sup>-1</sup>). We found that these modes exhibit pronounced integral anomalies in the region of 195 K and 230 K, red shift and blue shift around 20 cm<sup>-1</sup>, consequently. First anomaly indicates the onset of long-range tetrahedral water order, whereas the second anomaly signifies the mentioned order. Three OH-bending modes at 1520 cm<sup>-1</sup>, 1515 cm<sup>-1</sup> and 1620 cm<sup>-1</sup> demonstrate redshift about 5 cm<sup>-1</sup> around 230 K confirming the phase transition.

MO 5.15 Mon 17:00 Empore Lichthof

**URSA-PQ@FLASH: A mobile, highly flexible endstation for pump-probe electron spectroscopy at the FLASH free electron laser** — ●JAN METJE<sup>1</sup>, DENNIS MAYER<sup>1</sup>, FABIANO LEVER<sup>1</sup>, MARIO NIEBUHR<sup>1</sup>, MATTHEW ROBINSON<sup>1</sup>, AXEL HEUER<sup>1</sup>, RICHARD SQUIBB<sup>2</sup>, RAIMUND FEIFEL<sup>2</sup>, STEFAN DÜSTERER<sup>3</sup>, and MARKUS GÜHR<sup>1</sup> — <sup>1</sup>University of Potsdam, Potsdam, Germany — <sup>2</sup>University of Gothenburg, Gothenburg, Sweden — <sup>3</sup>DESY, Hamburg, Germany

We designed and built a mobile, highly flexible endstation designated for users at the free electron laser FLASH called URSA-PQ (Ultraschnelle Röntgenspektroskopie zur Abfrage der Photoenergiekonversion in Quantensystemen). The main instrument consists of a vacuum chamber with molecular capillary oven, a magnetic bottle time-of-flight electron spectrometer, and various tools to perform pump-probe experiments with optical laser pulses and x-ray pulses. The main chamber body adheres to CAMP-standards and thus many different compatible instruments may be incorporated.

We present the design of the vacuum apparatus and its mobile frame together with the control system of the experiment. The performance of the instrument was evaluated from commissioning at the beamline FL24. We present static as well as time resolved data to show various characteristics of the instrument.

MO 5.16 Mon 17:00 Empore Lichthof

**Electron imaging of noble gases clusters under MIR laser-fields** — ●CHRISTIAN MEDINA<sup>1</sup>, DOMINIK SCHOMAS<sup>1</sup>, MARKUS DEBATIN<sup>1</sup>, LTAIF LTAIF<sup>2</sup>, ROBERT MOSHAMMER<sup>3</sup>, THOMAS PFEIFER<sup>3</sup>, FRANK STIENKEMEIER<sup>1</sup>, and MARCEL MUDRICH<sup>2</sup> — <sup>1</sup>Albert-Ludwigs-Universität, Freiburg — <sup>2</sup>Aarhus University, Aarhus — <sup>3</sup>Max-Planck-Institut für Kernphysik, Heidelberg

In this project, we studied the behavior of the nanoplasma explosion of helium (He) and neon (Ne) droplets exposed to a strong and short mid-infrared laser field. The nanoplasma is initiated by strong-field ionization of the cluster or dopant atoms, creating an impact-ionization avalanche in the cluster and ending in a Coulomb explosion of the nanoplasma. Clusters provide a large variety of additional effects compared to strong-field ionization in single atoms, such as enhanced ionization due to electron impact ionization, or collective oscillations of quasi-free electrons. He droplets are particularly interesting, due to their extremely high ionization potential. Additionally, they offer unique doping properties, which allows us to investigate the effect of the dopant species and to design an optimal doping system to ignite the process. The large number of charged particles emitted from a single nanoplasma explosion allows us to collect both full electron energy distributions (VMI) and ion mass-over-charge distributions (TOF) from a single hit. We can measure correlated single shot-single hit spectra and we can assign features in the photoelectron spectra to certain charge states of the cluster. We discuss the impact of doping with various species (Xe and Ca) to trigger the nanoplasma formation.

MO 5.17 Mon 17:00 Empore Lichthof

**Photoelectron circular dichroism using 1+1 resonance-enhanced multi-photon ionization with UV laser pulses** — ●NICOLAS LADDA, CONSTANTIN WITTE, TOM RING, SIMON RANNECKY, SUDHEENDRAN VASUDEVAN, ALEXANDER KASTNER, HANGYEOL LEE, CHRISTIAN SARPE, HENDRIKE BRAUN, ARNE SENFTLEBEN, and THOMAS BAUMERT — Institut für Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

The forward/backward asymmetry of the photoelectron angular dis-

tribution (PAD) with respect to the propagation direction of ionizing circularly polarized light of a randomly orientated chiral molecule is known as photoelectron circular dichroism (PECD). The measurement of the PAD asymmetry can be performed using velocity-map imaging (VMI) technique, where the gas phase provides a nearly collision and interaction free environment. UV fs pulses from fourth harmonic generation (196 nm, 6.3 eV) of our Ti:Sa laser enable a 1+1 resonance-enhanced multi-photon ionization (REMPI) process via energetically higher lying intermediate states of molecules such as fenchone or camphor. In the future, these pulses could also be used to invert the handedness of a chiral molecule by pump-dump-probe experiment, where the UV pulses are required to access an achiral excited state.

MO 5.18 Mon 17:00 Empore Lichthof

**High Repetition Rate Studies of Laser-Driven Electron Rescattering in Spatially Aligned Molecules** — ●FEDERICO BRANCHI, HORST ROTTKE, MARK MERO, MARC J.J. VRACKING, and JOCHEN MIKOSCH — Max-Born-Institut, Berlin, Germany

In Laser-Induced Electron Diffraction (LIED), a valence electron in an atom or molecule tunnels through the Coulomb potential dressed by a strong laser field, is accelerated by the oscillating field of the laser and driven back to its parent, from which it can elastically rescatter. Structural information can be extracted from measured scattering angle distributions. In particular for mid-infrared lasers the energy of the returning electron can be sufficient to determine bond angles and lengths with LIED. Importantly, since LIED is phase locked to the cycle of the driving laser field, it has inherent time resolution and is hence a promising probe for molecular dynamics studies.

We have recently combined a high repetition-rate (100kHz), mid-IR (1550/3100nm), ultrashort (50fs pulse duration) laser system based on optical parametrical chirped pulse amplification (OPCPA) with a reaction microscope to investigate laser-driven electron rescattering in polyatomic molecules. Current results on laser-aligned 1,3-butadiene molecules are presented, for which coincidence measurements of electron and ion momenta allow to obtain ionization-channel resolved molecular frame information.

## MO 6: Electronic Spectroscopy II

Time: Tuesday 14:00–16:30

Location: f102

MO 6.1 Tue 14:00 f102

**Determination of excited state dipole moments in solution via thermochromic methods - an overview** — ●MIRKO LINDIC, MATTHIAS ZAJONZ, and MICHAEL SCHMITT — Heinrich-Heine-University, Düsseldorf

In the last years considerable effort has been invested to develop and optimize excited state dipole determinations in solution with thermochromic methods. The aim was to obtain a complete method, which incorporates the measurement and evaluation of all necessary parameters, which are the cavity volume which is occupied by the solute, the refractive index and permittivity of the solution, and the temperature dependence of the absorption and fluorescence spectra.

Additionally, all results are compared with results from quantum chemical calculations at the SCS-CC2/cc-pVTZ (COSMO) level of theory, and, if obtainable, to the results of Stark measurements from the gas phase.

An overview of all used techniques and evaluation steps will be given, including published results from the past as well as an outlook to future plans with this project.

MO 6.2 Tue 14:15 f102

**Determination of dipole moments in the electronically excited state of different constitutional isomers of cyanoin-dole via thermochromic methods** — ●MATTHIAS ZAJONZ, MIRKO LINDIC, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

In this contribution we present the determination of dipole moments in the electronically excited state of different cyanoin-doles via thermochromic methods. These methods were introduced by Gryczynski and Kowski due to their advantages over solvatochromic methods [1]. Their basic advantage is that the combination of solvent and solute is kept constant and the required variation of the permittivity  $\epsilon$  and index of refraction  $n$  to generate spectroscopic shifts of the absorption and

emission spectra is mediated through temperature changes. Our goal is to improve the methods of dipole moment determination in solution via thermochromic methods, since the superior Stark spectroscopy in the gas phase is not feasible for all molecules. In addition, investigations are carried out to better understand the temperature dependence of the variables  $\epsilon$ ,  $n$  and the cavity volume, which replaces the inaccurate Onsager-Radius in thermochromic equations [2]. Cyanoin-doles were selected because they can be measured in gas phase using Stark spectroscopy within the research group [3], so values can be compared with gas phase values and *ab initio* calculations as well.

[1] Gryczynski *et al*, *Zeit. f. Nat.*, 1975, **30**

[2] Lindic *et al*, *Spec. Acta Part A*, 2019, **in press**

[3] Schneider *et al*, *Phys. Chem. Chem. Phys.*, 2018, **20**

MO 6.3 Tue 14:30 f102

**Photoelectron spectroscopy of Boron containing reactive intermediates using synchrotron radiation and photoelectron/photoion coincidence (i2PEPICO) spectroscopy** — ●DEB PRATIM MUKHOPADHYAY<sup>1</sup>, DOMENIK SCHLEIER<sup>1</sup>, INGO FISCHER<sup>1</sup>, JEAN-CHRISTOPHE LOISON<sup>2</sup>, CHRISTIAN ALCARAZ<sup>3</sup>, and GUSTAVO GARCIA<sup>4</sup> — <sup>1</sup>Institute for Physical and Theoretical Chemistry, University of Würzburg, Würzburg, Germany — <sup>2</sup>Université de Bordeaux, Talence, France. — <sup>3</sup>Univ. Paris-Sud and Paris Saclay, Orsay, France. — <sup>4</sup>Synchrotron SOLEIL, Gif sur Yvette, France

Determination of accurate ionization and appearance energies, as well as recording photoelectron spectra (PES), are always crucial for any reactive intermediate as it permits to derive accurate binding energies, standard heats of formation and nature of bonding. BH2, a simple hydride and a free radical with only seven electrons but the IE, as well as PES, was not measured yet. As the photoionization leads to a linear cation from a bent neutral molecule, recording of vibrationally resolved PES, as well as spectral simulation, are both challenging. In this study, we report the first recorded slow photoelectron spectrum (SPES) of BH2 and precisely determined its IE as about 8.12

eV. Recorded SPES portrayed a long progression of bending vibration indicating a large change of bond angle upon ionization. Spectral simulation is also done by calculating Franck-Condon (FC) factors between neutral and cationic states. Apart from that we also record SPES of BH from both ground singlet and triplet states which allow us to first experimentally determined the singlet/triplet gap of BH.

MO 6.4 Tue 14:45 f102

**Ultrafast non-local decay of core vacancies: from noble gas clusters to the suppression of radiation damage** — ●ANDREAS HANS<sup>1</sup>, CATMARN KÜSTNER-WETEKAM<sup>1</sup>, PHILIPP SCHMIDT<sup>1</sup>, SASCHA DEINERT<sup>2</sup>, FLORIAN TRINTER<sup>2</sup>, GREGOR HARTMANN<sup>1</sup>, ARNO EHRESMANN<sup>1</sup>, LORENZ CEDERBAUM<sup>3</sup>, NIKOLAI KRZYŻEVOI<sup>3</sup>, and ANDRÉ KNIE<sup>1</sup> — <sup>1</sup>Institut für Physik und CINsAT, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany — <sup>2</sup>Deutsches Elektronen-Synchrotron (DESY), Notkestrasse 85, 22607 Hamburg, Germany — <sup>3</sup>Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

We discuss the influence of an environment on the decay of core vacancies. In isolated atoms or molecules, core ionization is typically followed by Auger decay into doubly ionized states. In molecules, the severe consequence is the irreparable fragmentation. In an environment, charge and energy dissipation to the surrounding may protect the dicationic molecule from fragmentation. Here, we present experimental evidence that the protective effect of the environment sets in even earlier, namely by direct intermolecular decay of the initial core vacancy.

MO 6.5 Tue 15:00 f102

**Investigation of the fragmentation of Isocyanic acid HNCO after inner-shell excitation by soft x-ray radiation** — ●MARIUS GERLACH<sup>1</sup>, FABIAN HOLZMEIER<sup>2</sup>, MARKUS GÜHR<sup>3</sup>, JOHN BOZEK<sup>4</sup>, CHRISTOPHE NICOLAS<sup>4</sup>, ENGELBERT REUSCH<sup>1</sup>, LILITH WOHLFART<sup>1</sup>, DENNIS MAYER<sup>3</sup>, KARINA KOPP<sup>1</sup>, and INGO FISCHER<sup>1</sup> — <sup>1</sup>Würzburg/De — <sup>2</sup>Milan/It — <sup>3</sup>Potsdam/De — <sup>4</sup>St. Aubin/Fr

Hydrogen, oxygen, nitrogen, and carbon are the basic building blocks of all organic life. Isocyanic acid, HNCO, is the smallest molecule that consists of those elements. Isocyanic acid is also ubiquitous in interstellar systems[1] and has been linked to the formation of formamide, a potentially prebiotic molecule.[2]

Our group previously investigated the normal and resonant Auger electron spectra of isocyanic acid.[3] In order to further elucidate the interaction of HNCO with cosmic x-ray radiation we investigated the fragmentation after these Auger processes. These experiments were carried out at the PLÉIADES Beamline at the SOLEIL Synchrotron in St. Aubin, France. The fragmentation was examined with the EPICEA detector. With this setup we simultaneously recorded the Auger electrons and the time of flight of the created ions. This information reveals detailed insights into the various fragmentation pathways.

Literature: [1] Nguyen-Q-Rieu et al., *Astron. Astrophys.* 1991, 241, L33.

[2] M. Ferus et al., *Astron. Astrophys.* 2018, 616, A150.

[3] F. Holzmeier et al., *J. Chem. Phys.* 2018, 149, 034308.

MO 6.6 Tue 15:15 f102

**Studying the dynamics and decay channels of C<sub>4</sub>O<sup>-</sup> in the electrostatic Cryogenic Storage Ring** — ●V.C. SCHMIDT<sup>1</sup>, K. BLAUM<sup>1</sup>, P. FISCHER<sup>2</sup>, S. GEORGE<sup>2</sup>, M. GRIESER<sup>1</sup>, F. GRUSSIE<sup>1</sup>, J. GÖCK<sup>1</sup>, R. VON HAHN<sup>1</sup>, Á. KÁLÓSI<sup>1</sup>, H. KRECKEL<sup>1</sup>, P.M. MISHRA<sup>1</sup>, D. MÜLL<sup>1</sup>, O. NOVOTNÝ<sup>1</sup>, F. NUSSLER<sup>1</sup>, D. PAUL<sup>1</sup>, S. SAURABH<sup>1</sup>, C. SCHUMACHER<sup>1</sup>, L. SCHWEIKHARD<sup>2</sup>, P. WILHELM<sup>1</sup>, and A. WOLF<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — <sup>2</sup>Institut für Physik, Universität Greifswald, 17489 Greifswald, Germany

The electrostatic Cryogenic Storage Ring (CSR) at the Max Planck Institute for Nuclear Physics in Heidelberg offers a variety of experimental methods for the study of charged molecules. By cooling the experimental vacuum chambers down to 6K, a unique environment with nearly negligible blackbody radiation is created, allowing even infrared-active systems to lower their internal energies down to a few Kelvin through radiative cooling [1].

Photo-induced electron detachment and fragmentation of the astrophysically relevant C<sub>4</sub>O<sup>-</sup> anion were studied as a benchmark system. To this end, a tunable, pulsed OPO laser was used to induce resonant fragmentation into the neutral CO and the charged C<sub>3</sub><sup>-</sup> fragments. The fragmentation process in dependence of photon energy as well as

its evolution with storage time in the CSR were studied. Preliminary results will be presented and discussed.

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

MO 6.7 Tue 15:30 f102

**Structural Properties of Small Silicon Oxide Cations** — ●KAI POLLOW, KARIM SAROUKH, ROBERT RADLOFF, LARS DAHLÖF, MARKO FÖRSTEL, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstraße 36, D-10623 Berlin, Germany

Interstellar dust is an important ingredient in the formation of solar systems like our own. Some properties of interstellar dust are known, many questions, however, are still unanswered. Molecular SiO can form in the atmospheres of oxygen-rich stars and interstellar dust contains particles made of macroscopic silicates of various compositions. Intermediates have been elusive to observations.

We present fragmentation pathways, geometric structure and optical properties of several possible intermediate species obtained via photodissociation spectroscopy and quantum chemical calculations. Knowledge of these parameters may help to model the complex formation processes and enable an observational search for these intermediate species.

MO 6.8 Tue 15:45 f102

**Probing the Valence Electronic Structure of Aqueous Diazines Using Resonant X-ray Photoelectron Spectroscopy** — ●MD SABBIR AHSAN<sup>1,2</sup> and IAIN WILKINSON<sup>1</sup> — <sup>1</sup>Methods for Material Development, Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — <sup>2</sup>Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Aqueous diazines play important roles in the photophysicochemical properties of bio-molecules such as DNA and RNA. We present liquid microjet based soft x-ray resonant photoelectron spectroscopy (RPES) measurements that probed the valence electronic structure of aqueous diazines. A number of core-valence resonances were identified by RPES scans over the diazine N K-edges and photoelectron spectra were subsequently recorded at different resonances. The solute signal was selectively enhanced in the RPES spectra with respect to solvent contributions. Moreover, by comparing the resonant Auger contributions with the non-resonant Auger signals, participator and spectator features were identified in the photoelectron spectra. Identification of participator peaks allowed us to determine aqueous-phase binding energies (BEs) associated with valence orbitals which are more generally hidden in non-resonant experiments. The associated BE information allowed us to map the valence electronic structure of the aqueous diazines and yielded valuable information for the interpretation of ongoing valence excited state time-resolved liquid-jet photoelectron spectroscopy experiment.

MO 6.9 Tue 16:00 f102

**Time-resolved soft x-ray photoelectron spectroscopy on 2-thiouracil at FLASH2** — ●DENNIS MAYER<sup>1</sup>, JAN METJE<sup>1</sup>, FABIANO LEVER<sup>1</sup>, AXEL HEUER<sup>1</sup>, MARIO NIEBUHR<sup>1</sup>, MATTHEW S. ROBINSON<sup>1</sup>, SKIRMANTAS ALISAUSKAS<sup>2</sup>, FRANCESCA CALEGARI<sup>2</sup>, STEFAN DUESTERER<sup>2</sup>, BASTIAN MANSCHWETUS<sup>2</sup>, ANDREA TRABATTONI<sup>2</sup>, TOMMASO MAZZA<sup>3</sup>, RAIMUND FEIFEL<sup>4</sup>, RICHARD SQUIBB<sup>4</sup>, MÄNS WALLNER<sup>4</sup>, THOMAS J. A. WOLF<sup>5</sup>, and MARKUS GÜHR<sup>1</sup> — <sup>1</sup>University of Potsdam, Germany — <sup>2</sup>Deutsches Elektronen-Synchrotron, Hamburg, Germany — <sup>3</sup>European XFEL GmbH, Hamburg, Germany — <sup>4</sup>University of Gothenburg, Sweden — <sup>5</sup>Stanford PULSE Institute, Menlo Park, USA

Sulfur-substituted nucleobases show an interesting photophysical and photochemical behavior attributed to their efficient relaxation to long living triplet states [1,2].

We performed ultrafast UV pump - x-ray probe spectroscopy at the FLASH 2 free electron laser in Hamburg to monitor the ultrafast relaxation processes of 2-thiouracil into the triplet states. In this talk, we present delay-dependent core level photoelectron and Auger electron spectra taken at and close to the sulfur L-edges. We use the spectra to elucidate the dynamics from an element specific point of view.

We used the newly built URSA-PQ instrument, which is now open for users and compatible with beamlines at FLASH1 and FLASH2 in Hamburg.

[1] Arslançan et al. *Molecules* 22, 998 (2017)

[2] Ashwood et al. *Photochem. Photobiol.* 95, 33-58 (2019)

MO 6.10 Tue 16:15 f102

**Development of a software-based lock-in amplifier for non-linear spectroscopy** — •DANIEL UHL, ULRICH BANGERT, MARCEL BINZ, LUKAS BRUDER, FRIEDEMANN LANDMESSER, ANDREAS WITUSCHEK, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

Lock-in amplification of modulated signals is widely used to improve detection sensitivity. We use this technique in phase-modulated wave packet interferometry and two-dimensional spectroscopy, which drastically improves the sensitivity [1,2].

To further improve our detection scheme, we've developed a software-based lock-in amplifier that provides additional flexibility in the data analysis and readily enables up-scaling of demodulation channels. With this approach, multiple signals can be demodulated simultaneously and custom demodulators and filters can be implemented. As an application example, we have used this technique to improve the phase noise characteristics in wave packet interferometry experiments performed in the XUV spectral range.

- [1] L. Bruder et al., *Phys. Chem. Chem. Phys.* 17, 23877 (2015).  
[2] L. Bruder et al., *Nat Commun* 9, 4823 (2018).

## MO 7: Clusters II (joint session MO/A)

Time: Tuesday 14:00–15:45

Location: f142

MO 7.1 Tue 14:00 f142

**Molecular Rotation in floppy Molecules: He-H<sub>3</sub><sup>+</sup>** — THOMAS SALOMON<sup>1</sup>, IGOR SAVIC<sup>2</sup>, OSKAR ASVANY<sup>1</sup>, DIETER GERLICH<sup>3</sup>, AD VAN DER AVOIRD<sup>4</sup>, MICHAEL E. HARDING<sup>5</sup>, JÜRGEN GAUSS<sup>6</sup>, FILIPPO LIPPARINI<sup>7</sup>, and •STEPHAN SCHLEMMER<sup>1</sup> — <sup>1</sup>I. Physikalisches Institut, Universität zu Köln — <sup>2</sup>Department of Physics, University of Novi Sad, Serbia — <sup>3</sup>Institut für Physik, Technische Universität Chemnitz — <sup>4</sup>Theoretical Chemistry, Radboud University Nijmegen, The Netherlands — <sup>5</sup>Fakultät für Chemie und Biowissenschaften Karlsruhe Institut für Technologie (KIT) — <sup>6</sup>Department Chemie, Johannes Gutenberg-Universität Mainz — <sup>7</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Italy

The ro-vibrational predissociation spectrum of He-H<sub>3</sub><sup>+</sup> has been recorded via the  $\nu_2$  vibrational mode in a cold 22-pole ion trap. The spectrum for the bare H<sub>3</sub><sup>+</sup> consists of only a few ro-vibrational lines. Instead, the spectrum of the complex is very rich ( $\sim 465$  lines) even at the low temperature (4 K) of the experiment. Part of this complexity is associated with the (almost) free internal rotation of H<sub>3</sub><sup>+</sup>. The experimental results are compared to theoretical predictions of ro-vibrational spectra on the basis of ab initio calculations of the He-H<sub>3</sub><sup>+</sup> potential energy surface. The energy levels result in transitions which agree in many cases with experimental results within a few wavenumbers. In addition, an experimental energy term diagram is reconstructed from the observed transitions. The influence of the Coriolis interaction resulting from the H<sub>3</sub><sup>+</sup> internal rotation in a rotating He-H<sub>3</sub><sup>+</sup> frame will be discussed.

MO 7.2 Tue 14:15 f142

**Competition between inter- and intra-atomic ionization phenomena: Observation of Electron-Transfer-Mediated decay and Auger decay in Xenon-doped water clusters** — •AARON NGAI<sup>1</sup>, RUPERT MICHELS<sup>1</sup>, NORA BERRAH<sup>2</sup>, CARLO CALLEGARI<sup>3</sup>, EDWIN CHAPMAN<sup>1</sup>, RAIMUND FEIFEL<sup>4</sup>, MICHELE DI FRAIA<sup>3</sup>, JAKOB KRULL<sup>1</sup>, AARON C. LAForge<sup>2</sup>, PAOLO PISERI<sup>5</sup>, OKSANA PLEKAN<sup>3</sup>, KEVIN PRINCE<sup>3</sup>, RICHARD J. SQUIBB<sup>4</sup>, VIT SVOBODA<sup>6</sup>, DANIEL UHL<sup>1</sup>, HANS-JAKOB WÖRNER<sup>6</sup>, ANDREAS WITUSCHEK<sup>1</sup>, and FRANK STIENKEMEIER<sup>1</sup> — <sup>1</sup>Institute of Physics, University of Freiburg — <sup>2</sup>Department of Physics, University of Connecticut — <sup>3</sup>Elettra-Sincrotrone Trieste — <sup>4</sup>Department of Physics, University of Gothenburg — <sup>5</sup>Dipartimento di Fisica and CIMaINa — <sup>6</sup>Laboratorium für Physikalische Chemie, ETH Zürich

Electron-transfer-mediated decay (ETMD) is a subset of the more general inter-coulombic decay (ICD). In condensed-matter or cluster systems, ETMD competes with other ionization processes such as autoionization (e.g. Auger decay). Using XUV-XUV pump-probe spectroscopy, we observe the competition between ETMD and Auger decay of Xe<sup>+</sup> (4d<sub>3/2</sub> and 4d<sub>5/2</sub>) embedded in water clusters. In particular, we can distinguish between these two similar processes by observing the resulting Xe<sup>N+</sup> ions in addition to time-resolving their femtosecond dynamics. In our experiment using the FERMI FEL at Elettra, two main features differentiating these decays are expected: the charges of the final Xe<sup>N+</sup> ions, and kinetic energy broadening of Auger electrons through post-collision interactions (PCI).

MO 7.3 Tue 14:30 f142

**Cryogenically Cooled Beams of Bio-Nanoparticles** — •LENA WORBS<sup>1,2</sup>, JANNIK LÜBKE<sup>1,2,3</sup>, ARMANDO ESTILLORE<sup>1</sup>, AMIT K. SAMANTA<sup>1</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, Deutsches-Elektronen Synchrotron DESY, Hamburg —

<sup>2</sup>Fachbereich Physik, Universität Hamburg — <sup>3</sup>Center for Ultrafast Imaging, Hamburg

Coherent diffractive imaging at free-electron lasers promises to allow the reconstruction of the three-dimensional molecular structures of isolated particles at atomic resolution [1]. However, because of the typically low signal to noise ratio, this requires the collection of a large amount of diffraction patterns. Since every intercepted particle is destroyed by the intense x-ray pulse, a new and preferably identical sample particle has to be delivered into every pulse.

We present novel approaches for the production of high density particle beams of shock-frozen bio-nanoparticles using a cryogenic buffer-gas cooling technique [2]. We have also developed a numerical simulation infrastructure that allows quantitative simulation of isolated particle trajectories inside the buffer-gas cell. The cryogenically-cooled nanoparticle beams are characterized using laboratory-based light-scattering [3]. To further improve the resulting particle beam, an aerodynamic lens is implemented to increase its density.

- [1] M. M. Seibert, et al., *Nature* 470, 78 (2011).  
[2] A. K. Samanta, et al., arXiv:1910.12606 [physics.bio-ph]  
[3] L. Worbs, et al., *Opt. Expr.*, arXiv:1909.08922 [physics.optics]

MO 7.4 Tue 14:45 f142

**Ultrafast Spectroscopy of Perylene Derivative Nanoparticles** — •CHRIS REHHAGEN<sup>1,2</sup>, SHAHNAWAZ RAFIQ<sup>2</sup>, STEFAN LOCHBRUNNER<sup>1</sup>, and GREGORY SCHOLE<sup>2</sup> — <sup>1</sup>Institute for Physics and Department of Life, Light and Matter, University of Rostock, 18051 Rostock, Germany — <sup>2</sup>Frick Laboratory, Princeton University, 08540 Princeton, USA

Organic dye nanoparticles and nanostructures are of increasing interest in opto-electronic applications due to their potentially large exciton mobilities. While as inorganic nanoparticles are already applied in many scenarios, the properties of organic nanostructures are yet to be explored. Among a breadth of organic systems available, Perylene derivatives especially attract much interest as they provide a high oscillator strength, photostability, and a tuneability of the transition energy and supramolecular structure by changing the bay-substitutes.

We use flash precipitation to prepare nanoparticles of the Perylene Red (PR) and Perylene Orange (PO) dyes and correlate their optical spectra, quantum yields, emission lifetimes and their size. Ultrafast pump-probe spectroscopy is then performed on samples of different size classes to characterize their excited state dynamics. In PR nanoparticles, a new electronic state, formed after photoexcitation, was observed. Remarkably, no such intermediate state was observed in the PR monomer. In PO nanoparticles, we observe an ultrafast excimer formation. In both systems and for different size classes, we characterize the exciton diffusion in the nanoparticles by analyzing signatures in the transient dynamics resulting from exciton-exciton annihilation.

MO 7.5 Tue 15:00 f142

**Spectroscopic investigation of gas-phase silvercluster-porphyrin hybrids** — •CARL FREDERIC USSLING<sup>1</sup>, TOBIAS BISCHOFF<sup>1</sup>, ANDRE KNECHT<sup>1</sup>, ANDREA MERLI<sup>1</sup>, MERLE I. S. RÖHR<sup>2</sup>, POLINA G. LISINETSAYA<sup>2</sup>, ROLAND MITRIĆ<sup>2</sup>, and THOMAS MÖLLER<sup>1</sup> — <sup>1</sup>Institut für Optik und Atomare Physik, Technische Universität Berlin — <sup>2</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg

In the last decades the size and structure-dependent optical properties of noble metal clusters have been widely investigated [1][2]. In the smallest size regime, both the cluster geometry and optical

properties turned out to be particularly effected by the number of constituents [3]. Due to their strong UV and Vis absorption it has been predicted, that small silver clusters could be useful to develop new biomolecular sensors [4]. Hybrid systems consisting of small metal clusters and small molecular units have been developed and their optical behavior experimentally explored [5]. We investigated the possibility to combine small cationic silver clusters with single porphyrins in a collision cell and studied first the optical properties of  $\text{Ag}_3[\text{Ag}(\text{OEP})]^+$  in the UV range.

[1] E. M. Fernández et al., *Phys. Rev. B* **70**, 165403 (2004)

[2] C. Sönnichsen et al., *New J. Phys.* **4**, 93 (2002)

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

[4] T. Tabarin et al., *J. Chem. Phys.* **127**, 134301 (2007)

[5] V. Bonačić-Koutecký et al., *Phys. Chem. Chem.* **14**, 9282 (2012)

MO 7.6 Tue 15:15 f142

**Investigation of isolated aggregates of coumarin derivatives in the gas phase by applying combined IR/UV spectroscopy** —

•POL BODEN, ANKE STAMM, MICHAEL BORCHERS, DOMINIC BERNHARD, DOMINIQUE MAUÉ, and MARKUS GERHARDS — TU Kaiserslautern and State Research Center OPTIMAS, Germany

Coumarin and its derivatives are well known for their photo-induced reactivity leading to their importance as photobiological and photochemical substances. Here we report on 7-Hydroxy-4-methylcoumarin (7-H4MC) and its amino analogue 7-amino-4-methylcoumarin (7-A4MC). The examination of 7-A4MC is of great interest because aminocoumarins show an intramolecular charge-transfer (ICT) between the amino group and the benzopyrone unit in solvents of moder-

ate to high polarity. In order to investigate intrinsic effects with respect to ICT and structure of the 7-A4MC dimer in the neutral and cationic ground states as well as in the  $S_1$  state, combined IR/UV spectroscopy is applied in molecular beam experiments. A comparison of the measured IR transitions with calculated frequencies and optimized structures allows clear structural assignments. Furthermore the 7H4MC dimer and its mono- and dihydrate are investigated both in their neutral and cationic ground state with regard to structural changes occurring upon UV photoionization. The tendencies of coumarins for self-aggregation observed in aqueous solution are investigated in detail on isolated species giving (in combination with hydration) a closer look on structure and function of coumarins.

MO 7.7 Tue 15:30 f142

**Rayleigh scattering of a pulsed supersonic jet of Ar and CO<sub>2</sub> at high particle densities** — •SARA FAZLI and WOLFGANG CHRISTEN — Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Straße 2, 12489 Berlin

We present an experimental setup for the investigation of Rayleigh scattering of a pulsed supersonic jet and present first results for the scattered light intensity as a function of cluster source conditions. A jet of pure Ar or CO<sub>2</sub>, respectively, is expanded through a parabolic nozzle at source temperatures between 230 K and 410 K and source pressures between 2 MPa and 10 MPa. The change of the Rayleigh scattering signal with source pressure and temperature is compared with the prediction of Hagen's scaling law (*J. Chem. Phys.* **56**, 1793, 1972). Results show a pronounced dependence of the scaling parameters on the aggregation state (gas versus liquid) of the expanding fluid.

## MO 8: MO Poster 2

Time: Tuesday 17:00–19:00

Location: Empore Lichthof

MO 8.1 Tue 17:00 Empore Lichthof

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

We report on the progress with a new technique, molecular-beam coherent two-dimensional (2D) electronic spectroscopy, enabling multidimensional electronic spectroscopy of gas-phase samples with mass-resolved ion detection. Using time-of-flight mass spectrometry, we have introduced cations as a new observable in coherent 2D spectroscopy [1]. Using a pulse shaper based on an acousto-optic programmable dispersive filter and rapid scanning [2] we focus a train of four collinear pulses in the visible regime into an interaction region with a molecular beam. Via phase cycling [3] the signals of the time-of-flight mass spectrometer can be disentangled to extract the different contributions, like the photon-echo response. We have recently installed a preparation chamber for a supersonic molecular beam with argon as a seed gas. This allows us to investigate not only gaseous samples but also liquid and solid ones that are evaporated by an oven.

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

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

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

MO 8.2 Tue 17:00 Empore Lichthof

**Ultrafast photo-ion probing of the ring-opening process in trans-stilbene oxide** — •MATTHEW SCOTT ROBINSON, MARIO NIEBUHR, FABIANO LEVAR, DENNIS MAYER, JAN METJE, and MARKUS GÜHR — Universität Potsdam, Institut für Physik und Astronomie, Karl-Liebknecht-Straße 24/25, 14476 Potsdam-Golm, Germany

We study the ultrafast photo-induced ring-opening processes of trans-stilbene oxide through UV/UV pump-probe time-of-flight experiments with photoion probing and synchrotron-based vacuum ultraviolet ionisation studies, before comparing these results to predictions derived from Woodward-Hoffmann rules.[1]

We fit two major time-dependent features to the parent ion; one sub-90 fs and another of  $\sim 260$  fs, which match well to theory.[2] We attribute these constants to the primary ring-opening process, likely

proceeding via a non-concerted pathway, starting with a sub-90 fs dissociation of the C-C bond in the oxirane ring, followed by the rotation of the phenyl groups to produce the ring-open carbonyl ylide 260 fs after excitation.

We also investigate the appearance of fragment ions, with one in particular (deprotonated diphenylmethane) suggesting an alternative ring-opening pathway not predicted by Woodward-Hoffmann rules, in which dissociation of one of the C-O bonds of the oxirane ring initiates a 1,2-migration of a phenyl group to produce diphenylmethane.

1. Woodward & Hoffmann, *Angew. Chemie* **81**, 797-870 (1969).

2. Friedrichs & Frank, *Chem. - A Eur. J.* **15**, 10825-10829 (2009).

MO 8.3 Tue 17:00 Empore Lichthof

**Accessing chiral dynamics via broadband time-resolved circular dichroism spectroscopy** — •LEA RESS<sup>1</sup>, HEIKO HILDENBRAND<sup>1</sup>, HOPE BRETSCHER<sup>2</sup>, AKSHAY RAO<sup>2</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Department of Physics, Cavendish Laboratory, University of Cambridge, 19 JJ Thompson Avenue, Cambridge, United Kingdom

Time-resolved circular dichroism (TRCD) spectroscopy enables the investigation of the ultrafast dynamics of photoinduced chirality changes on a sub-picosecond timescale. We use a pump-probe approach by exciting the sample with a linearly or circularly polarized pump pulse and detecting the difference in absorption of left- and right-circularly polarized probe pulses on a shot-to-shot basis. For this, we developed a setup that is capable of mirroring the polarization state of an ultrashort broadband laser pulse [1].

Here we demonstrate TRCD spectroscopy of monolayer MoS<sub>2</sub> as a proof-of-principle experiment, validating the setup with respect to literature results [2]. In addition to spectroscopy of surfaces, we also investigate the change in chirality of a perylene bisimide folda-dimer in solution [3]. Furthermore, we analyze the arrangement of chiral surfactants around the achiral dye Congo red and the ultrafast change in chirality after excitation.

[1] A. Steinbacher, et al., *Opt. Express* **25**, 21735 (2017)

[2] S. Dal Conte, et al., *Phys. Rev. B* **92**, 235425 (2015)

[3] C. Kaufmann, et al., *J. Am. Chem. Soc.* **140**, 31, 9986 (2018)

MO 8.4 Tue 17:00 Empore Lichthof

**Ultrafast processes in Ru(II)-Au(I)-complexes bridged via**

**paracyclophane with varying metal-metal-distances** — •LARS SCHÜSSLER<sup>1</sup>, ROUMANY ISRAÏL<sup>2</sup>, MARCEL SCHMITT<sup>2</sup>, CHRISTOPH ZIPPEL<sup>3</sup>, DANIEL M. KNOLL<sup>3</sup>, STEFAN BRÄSE<sup>3</sup>, CHRISTOPH RIEHN<sup>2</sup>, and ROLF DILLER<sup>1</sup> — <sup>1</sup>Dept. of Physics, TU Kaiserslautern, 67663 Kaiserslautern — <sup>2</sup>Dept. of Chem., TU Kaiserslautern, 67663 Kaiserslautern — <sup>3</sup>Dept. of Org. Chem., KIT, 76131 Karlsruhe

The novel complex [Ru(bpy)<sub>2</sub>(ppy)-PCP-(PPh<sub>2</sub>)AuCl]<sup>+</sup> (**1**) (bpy = 2,2'-bipyridine, ppy = 2-phenylpyridine, PCP = paracyclophane, PPh<sub>2</sub> = diphenylphosphine) [1] - where a Ru(II)-antenna-unit is bridged via PCP to a catalytically active Au(I)-unit - is perfectly suited to systematically investigate the electronic communication between the two metal centers by tuning their distance and the electronic coupling via structurally diverse PCP-bridges (binding sites at the PCP unit, e.g. pseudo-para-position with longer metal-metal-distance as compared to pseudo-ortho-position). We employ fs transient absorption spectroscopy in the UV/Vis in solution combined with gas phase studies by fs pump-probe fragmentation action spectroscopy [2] to elucidate the underlying ultrafast photophysics and -chemistry as well as the metal-metal-interaction. First results on (**1**) in dichloromethane with lifetimes  $\tau_{1,2,3} = 1.3, 14.1, 590$  ps suggest strongly altered kinetics compared to results on [Ru(bpy)<sub>3</sub>]<sup>2+</sup> [3].

[1] D. M. Knoll et al. Dalton Trans., 2019, DOI: 10.1039/C9DT04366G

[2] D. Imanbaev et al. Angew. Chem. Int. Ed., 2017, 56, 5471-5474

[3] Q. Sun et al. Coord. Chem. Rev., 2015, 282-283, 87-99

MO 8.5 Tue 17:00 Empore Lichthof

**Ultrafast study of a systematically tuned Ru(II)-polypyridine-series in gas phase and solution** — •LARS SCHÜSSLER<sup>1</sup>, ROUMANY ISRAÏL<sup>2</sup>, PATRICK HÜTCHEN<sup>2</sup>, WERNER R. THIEL<sup>2</sup>, CHRISTOPH RIEHN<sup>2</sup>, and ROLF DILLER<sup>1</sup> — <sup>1</sup>Dept. of Physics, TU Kaiserslautern, 67663 Kaiserslautern — <sup>2</sup>Dept. of Chem., TU Kaiserslautern, 67663 Kaiserslautern

Ru(II)-polypyridine complexes are widely used in technology and medicine in applications ranging from photovoltaics or catalysis to photoactivatable prodrugs [1]. The respective photoinduced dynamics strongly depend on the relative energies of the <sup>3</sup>MLCT- and the <sup>3</sup>MC-excited states. Long living phosphorescence competes with photodissociation and -substitution. According to the specific application, a highest possible yield of one of the pathways is desirable and could be controlled by rational ligand design.

Thus, we study a series of the type [Ru(X-bpy)<sub>2</sub>(pyr-na)<sub>2</sub>]<sup>2+</sup> (bpy = 2,2'-bipyridine, pyr-na = N-nicotinoyl-pyrrolidine) where X is a varying substituent of different electron withdrawing / donating character to systematically tune the energetics of the <sup>3</sup>MLCT- and <sup>3</sup>MC-excited states. The photoinduced primary processes are investigated in solution and gas phase by femtosecond transient UV/Vis absorption spectroscopy and pump-probe fragmentation action spectroscopy [2], respectively.

[1] S. E. Greenough et al. PCCP, 2014, 16, 19141-19155

[2] D. Imanbaev et al. Angew. Chem. Int. Ed., 2017, 56, 5471-5474

MO 8.6 Tue 17:00 Empore Lichthof

**Investigation of the Nitrogen Release Mechanism of a Carbenonitrene Precursor** — •NIKLAS GESSNER<sup>1</sup>, JULIEN ROWEN<sup>2</sup>, WOLFRAM SANDER<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — <sup>2</sup>Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Carbenes and the closely related nitrenes are classes of highly reactive molecules. They are commonly generated by photolysis of a diazo or an azido functional group, respectively, releasing molecular nitrogen (N<sub>2</sub>). This process is well understood e.g. for the carbene 9-fluorenylidene [1] or the nitrene 2-fluorenylnitrene [2] that are both long-lived. However, the release mechanism of the carbenonitrene 2-nitreno-9-fluorenylidene (NFI) is still unknown due to the fact that its precursor needs to release in total two molecules of N<sub>2</sub>. This leads to the question whether photochemically, the diazo-nitrene or the azido-carbene is generated first and what happens in subsequent processes.

To address this issue, the generation of NFI in the aprotic solvent acetonitrile has been studied with ultrafast transient absorption spectroscopy. Indications for both a carbene and a nitrene intermediate are found on a picosecond time scale. These transient species can eventually lead to the formation of a carbenonitrene with a quintet ground state, as we identified in separate studies where the compounds are embedded in cryogenic rare-gas matrices.

[1] J. Wang et al., *J. Am. Chem. Soc.* **129**, 13683-13690 (2007).

[2] J. Wang et al., *Org. Lett.* **25**, 5211-5214 (2007).

MO 8.7 Tue 17:00 Empore Lichthof

**Reaction pathways of a chiral salicylimine studied by ultrafast spectroscopy and vibrational circular dichroism** — •KEVIN ARTMANN<sup>1</sup>, CORINA POLLOK<sup>2</sup>, CHRISTIAN MERTEN<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — <sup>2</sup>Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Due to its prominent reaction mechanism and its simple molecular structure, salicylimines were intensively investigated in the past. Upon excitation, an excited-state intramolecular proton transfer (ESIPT) leads to the formation of a keto conformer. In addition, the ESIPT competes with a torsional angle rotation that produces a twisted enol conformer. It has been therefore suggested that the excitation wavelength can influence the population of the different conformers, but there is still no experimental evidence available. In this study, we combine the results from ultrafast transient absorption spectroscopy and matrix-isolation vibrational circular dichroism spectroscopy (M-VCD) to elucidate the influence of the excitation energy and of the solvent on the reaction mechanism. Besides unraveling the characteristic time scales of the different reaction pathways, it is demonstrated that a higher excitation energy correlates with a lower population of the keto conformer. A higher excitation energy is needed to excite molecules that are already twisted before excitation, therefore the rotational pathway is preferred. Furthermore, we show that the concentration of the keto conformer increases if a solvent with a larger dielectric constant is used.

MO 8.8 Tue 17:00 Empore Lichthof

**Towards fs UV Measurements of Mass Selective Circular Dichroism in the Gas Phase** — •CONSTANTIN WITTE, TOM RING, NICOLAS LADDA, ALEXANDER KASTNER, SIMON RANECKY, SUDHEENDRAN VASUDEVAN, HAN-GYEOL LEE, CHRISTIAN SARPE, HENDRIKE BRAUN, ARNE SENFTLEBEN, and THOMAS BAUMERT — Institut für Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

The difference in absorption of left and right circularly polarized light is defined as Circular Dichroism (CD). Due to the ubiquity of chirality, its analysis is of great importance. Here, we attempt to measure the CD in the gas phase in the ion yield of chiral showcase molecules camphor and fenchone that have been ionized using a femtosecond laser system. Mass selectivity is achieved via a Time of Flight Mass Spectrometer in Wiley-McLaren Configuration. Generating the third harmonic of our Ti:Sa laser system at 266 nm allows us to reach the  $n \rightarrow \pi^*$  transition in ketones which promises a high CD according to ns measurements [1]. Generally, a lot of chiral molecules have their absorption bands in the UV. Accessing these with a single photon is beneficial for reaching higher, energetically closer lying states. In the future, this set-up is to be used to investigate and enhance CD effects, determine enantiomeric excess and potentially for enantiomeric purification using coherent control techniques.

[1] Logé, C., Boesl, U.; Multiphoton Ionization and Circular Dichroism: New Experimental Approach and Application to Natural Products, *Chem. Phys. Chem.* **12**, 2011, 1940-1947

MO 8.9 Tue 17:00 Empore Lichthof

**Photoelectron Circular Dichroism of different monoterpenes and lifetime of their resonances** — •SIMON RANECKY, HAN-GYEOL LEE, SUDHEENDRAN VASUDEVAN, ALEXANDER KASTNER, NICOLAS LADDA, TOM RING, CONSTANTIN WITTE, HENDRIKE BRAUN, DANIEL REICH, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Short lightpulses of 380 nm are able to ionize monoterpenes like fenchone in a resonant 2+1 multi-photon scheme. The ionisation takes place via resonances in the B- and C-Band [1], which can be distinguished by different photoelectron energies. Depending on the pulse length of the laser, the time for relaxation dynamics changes, leading to a different ratio between the photoelectrons from the B- and C-band. By comparison of this pulse length dependence with a quantum-mechanical model system, we estimate the lifetime of the resonances.

The photoelectrons of randomly oriented chiral molecules ionized with circularly polarized light can have an asymmetric momentum distribution in the direction of the laser beam. This effect is called photoelectron circular dichroism (PECD). It can be found in single photon [2], as well as multi-photon ionisation processes with pulse lengths from femtoseconds [1] to nanoseconds [3].

In this study, we examine fenchone, thiofenchone and camphor with pulselengths from femtoseconds to nanoseconds.

- [1] A. Kastner et al., *J. Chem. Phys.* 147, 013926, (2017)
- [2] L. Nahon et al., *J. El. Spectr.* 204, 322-334, (2018)
- [3] A. Kastner et al., *Chem. Phys. Chem.* 20, 1416-1419 (2019)

MO 8.10 Tue 17:00 Empore Lichthof

**Unraveling the ultrafast dynamics in indole-water** — ●JOLIUN ONVLEE<sup>1,2</sup>, JOSS WIESE<sup>1,3</sup>, JOVANA PETROVIC<sup>1</sup>, TERRY MULLINS<sup>1</sup>, SEBASTIAN TRIPPEL<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,3,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — <sup>2</sup>Center for Ultrafast Imaging, Universität Hamburg — <sup>3</sup>Department of Chemistry, Universität Hamburg — <sup>4</sup>Department of Physics, Universität Hamburg

For a protein in water, hydrogen bonds between the protein and surrounding water molecules strongly affect its folding and thereby also its function. When hydrogen bonds between a protein and surrounding water molecules break, for instance via absorption of UV radiation, the protein structure changes and inactivation of the protein can occur.

We investigated the ultrafast dynamics of the hydrogen-bond breaking between proteins and water in a bottom-up approach by studying the indole molecule – the chromophore of tryptophan, which is the most strongly near-UV absorbing common amino acid – and the indole-water complex, which serves as a model system for the interaction between proteins and water. We produce pure samples of indole and the indole-water complex in the gas phase using a molecular beam and the electrostatic deflector, with which we spatially separate molecular species. The ultrafast dynamics following UV absorption of these molecular species were studied in a pump-probe ion-imaging approach. We also performed laser-induced electron diffraction experiments, with which we aim to record a molecular movie of the hydrogen-bond breaking in indole-water with high spatiotemporal resolution.

MO 8.11 Tue 17:00 Empore Lichthof

**Photoelectron circular dichroism of chalcogen-substituted fenchone molecules using near UV femtosecond laser pulses** — ●SUDHEENDRAN VASUDEVAN, HAN-GYEOL LEE, TOM RING, SIMON RANECKY, CONSTANTIN WITTE, NICOLAS LADDA, HENDRIKE BRAUN, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Photoelectron circular dichroism (PECD) is a technique used for sensing molecular chirality with high sensitivity, which arises due to an electric dipole effect [1]. PECD is an asymmetry of the photoelectron emission from a chiral molecule in the forward/backward direction relative to the propagation direction of circularly polarized light field. In this experimental work, we investigate PECD on fenchone molecules where different chalcogen atoms have been substituted in the keto group, e.g. fenchone (oxygen), thiofenchone (sulfur), selenofenchone (selenium). Near ultraviolet laser pulses centred around wavelength of 380 nm, with a pulse duration of around 250 fs and pulse energy of approximately 5  $\mu$ J are used to probe these molecules in the gas phase. In the future, a comparative study of the PECD will be done on these molecules by using a wavelength-tunable femtosecond laser source, since PECD is highly dependent on photon energies and energy levels of the molecules [3] which are expected to change by the chemical substitution.

- [1] C.Lux et al., *Angewandte Chemie* 51 (2012): 5001-5005.
- [2] C.Lux et al., *ChemPhysChem* 16 (2015): 115-137.
- [3] A.Kastner et al., *J. Chem. Phys.* 147, 013926 (2017).

MO 8.12 Tue 17:00 Empore Lichthof

**Frequency-resolved optical gating of low energetic optical pulses** — ●LARS-STEPHAN KLEIN, LUKAS BRUDER, ULRICH BANGERT, DANIEL UHL, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

We are exploring methods to characterize sub-20 fs pulses with pulse energies < 5nJ. To this end, we investigate the use of second harmonic (SH) frequency-resolved optical gating (FROG), cross-correlation SH FROG and an approach using phase-modulated optical pulses combined with lock-in amplification. The latter is a specialized technique used in two-dimensional electronic spectroscopy (2DES) to improve sensitivity and would allow us to perform pulse characterization directly at the sample position of our 2DES setup. In this context, we also explore the possibility to combine FROG measurements with photoionization.

MO 8.13 Tue 17:00 Empore Lichthof

**Effect of Chemical Modification and Oxygen Interaction on the Singlet Fission in Azaacene Dimers** — ●NICOLÒ ALAGNA<sup>1,2</sup>, JOSE L.P. LUSTRES<sup>1,2</sup>, SEBASTIAN HAHN<sup>3</sup>, MARCUS MOTZKUS<sup>1,2</sup>, UWE H.F. BUNZ<sup>3</sup>, and TIAGO BUCKUP<sup>1,2</sup> — <sup>1</sup>Physikalisch Chemisches Institut, Ruprecht-Karls University Heidelberg, Germany — <sup>2</sup>Centre for Advanced Materials, University of Heidelberg, Germany — <sup>3</sup>Organisch Chemisches Institut, Ruprecht-Karls University, Germany

The solar energy conversion in photovoltaics can be enhanced by singlet fission (SF), a carrier multiplication process where two triplet states  $T_1$  are generated from one absorbed photon. Studies of phenothiazine derivatives have shown that morphology, packing and chemical structure play a central role in the SF dynamics. Covalently linked dimers can be employed as a model system to selectively study the intramolecular SF. In this work, time-resolved spectroscopy is used to investigate the effect of chemical modification on the intramolecular singlet fission in three directly linked Azaacene-dimers. The analysis of transient absorption and fluorescence dynamics reveals a complex branching mechanism for the singlet ( $S_1S_0$ ) and the correlated triplet pair  $^1(TT)$  states. We show that the decay rate and the evolution of the  $S_1S_0$  and  $^1(TT)$  states are strongly dependent on the chemical structure. Moreover, the analysis of deaerated solutions reveals the role of oxygen in altering the  $^1(TT)$  dynamics by introducing new decay pathways.

MO 8.14 Tue 17:00 Empore Lichthof

**Correlated Electronic Dynamics of Helium in a Chiral Environment** — ●MANEL MONDELO-MARTELL<sup>1,2</sup>, CHRISTIANE P. KOCH<sup>1,2</sup>, and DANIEL M. REICH<sup>1,2</sup> — <sup>1</sup>Theoretische Physik, Freie Universität Berlin — <sup>2</sup>Institut für Physik, Universität Kassel

Chirality is the fundamental symmetry property defining an object that cannot be superimposed on its mirror image by any translation or rotation. Its relevance in different fields, from AMO physics to drug design, originates in the importance of *chiral interactions*: while both mirror images of a chiral object (enantiomers) will give the same response in front of a non-chiral probe, this is not true when interacting with another chiral system, such as circularly polarized light or aminoacids. This difference allows for chiral discrimination of samples using light, and determines the effects of drugs in our bodies.

In molecular systems, chirality is usually understood in terms of the spacial arrangement of the nuclei. Nevertheless its imprint on the electronic motion, made evident by the Photoelectron Circular Dichroism (PECD) —the asymmetry in forward-backward scattering of the photoelectrons emitted via irradiation with left and right circularly polarized light—, is still not fully understood. Hereby we present time-resolved simulations of the electronic dynamics of the photoionization process of the helium atom in a chiral environment. Through the use of the MCTDHF method[2] we are able to include correlation effects, and give more insight on the role of chirality in the electronic motion.

[1] I. Powis, in *Adv. Chem. Phys.* (2008), pp. 267-329. [2] J. Zanghellini, et al., *Laser Phys.* 13, 1064 (2003)

MO 8.15 Tue 17:00 Empore Lichthof

**TDCIS Simulations on Chiral Helium** — ●MAREC W. HEGER<sup>1</sup>, CHRISTIANE P. KOCH<sup>2</sup>, and DANIEL M. REICH<sup>1,2</sup> — <sup>1</sup>Theoretische Physik, Universität Kassel — <sup>2</sup>Institut für Physik, Freie Universität Berlin

Chirality is the property that defines systems that cannot be superimposed on their own mirror image. Current research explores methods for chiral recognition, chiral separation and chiral conversion.

A prominent example for chiral recognition is the photoelectron circular dichroism (PECD). In PECD experiments a chiral molecule is ionized by left and right circular polarized light and the photoelectron angular distribution then yields a difference for the two polarization directions. Changing the handedness of the chiral molecule inverts the PECD signal which allows for recognition.

Whereas experimental setups for PECD measurements are fairly widespread, theoretical predictions are still sparse. In particular, the simultaneous representation of bound and continuum states for molecular systems, which is necessary for the simulations of time dependent ionization experiments, is still challenging.

Here we present results of the time dependent configuration interaction singles (TDCIS) method performed on a PECD simulation setup. Our approach features a discrete variable representation (DVR) as a numerical basis to represent bound and continuum states and the

physical system of interest is helium with an artificial chiral potential. For helium, full configuration interaction can be performed and consequently we identify the role of electron correlations for PECD.

MO 8.16 Tue 17:00 Empore Lichthof

**Exciton Dynamics in Squaraine-based Thin Films** — ●STEFFEN WOLTER<sup>1</sup>, MANUELA SCHIEK<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institute of Physics, University of Rostock, 18051 Rostock, Germany — <sup>2</sup>Institute of Physics, Carl von Ossietzky University of Oldenburg, 26111 Oldenburg, Germany

Squaraine dyes are promising candidates for light harvesting electron donor materials in small molecule solar cells, since they combine strong absorption in the visible spectral region with a high stability compared to other organic compounds like low bandgap polymers. Bulk-

heterojunction solar cells based on squaraine:fullerene blends have been shown to suffer from low mobility and recombination losses [1]. In depth understanding of the loss mechanism requires investigation of fundamental processes upon light absorption on ultra-fast time scales.

In this contribution, the light induced processes in different squaraine based thin films are investigated by femtosecond pump-probe spectroscopy. The dynamics in pure films of 2,4-bis[4-(N,N-diisobutylamino)-2,6-dihydroxyphenyl] squaraine (SQIB) is studied to obtain a picture of the possible electronic relaxation pathways in the donor material. In a next step, the results are compared to films of SQIB blended with a fullerene acceptor (PCBM). Strong differences in the kinetics and the spectral signatures are observed and attributed to the population of charge separated states.

[1] Scheunemann, Kollege, Wilken, Mack, Parisi, Schulz, Lützen, Schiek. Appl. Phys. Lett. 111 (2017) 183502.

## MO 9: Femtosecond Spectroscopy I

Time: Wednesday 11:00–13:00

Location: f102

MO 9.1 Wed 11:00 f102

**Ultrafast 2D-Vis spectroelectrochemistry** — ●JULIA HEITMÜLLER<sup>1</sup>, KLAUS ECKSTEIN<sup>1</sup>, PASCAL KUNKEL<sup>1</sup>, KARL THORLEY<sup>2</sup>, REBECCA RENNER<sup>2</sup>, TOBIAS HERTEL<sup>1</sup>, FRANK WÜRTHNER<sup>2</sup> und TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Coherent 2D spectroscopy is a well established method to investigate dynamic processes with femtosecond time resolution and to observe couplings between different energetic states. Electrochemistry, on the other hand, can be used to generate different oxidized and reduced molecular species in solution. The combination of these two techniques leads to coherent 2D spectroelectrochemistry. For the infrared regime different spectroelectrochemical cells were described and used for 2D measurements in the literature [1,2], but not so far for the visible. We developed a setup using a commercial electrochemical cell (HX-301, Hokuto Denko), which we modified for the experimental requirements. As a model system we investigate a tetraphenoxyperylene bisimide and obtain 2D as well as other spectroscopic measurements of the different redox states *in situ* without requiring oxidizing or reducing agents.

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

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

MO 9.2 Wed 11:15 f102

**Ultrafast excitation energy localization dynamics following delocalized excitation** — ●YANG LI, PAVEL MALÝ, JULIAN LÜTTIG, STEFAN MÜLLER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The efficiency of organic photovoltaic materials, such as conjugated polymers, aggregates and dendrimers, depends on the interplay between molecular architecture and light-induced electronic energy redistribution. The spatial localization of the excitation energy is relevant for conversion efficiency and has been a point of intense research for artificial systems that are designed and synthesized to produce solar fuels. While the delocalized excitation followed by localized emission universally appears in a variety of dendrimers [1], the localization process itself has not yet been probed in real time. In this work, polarization-controlled two-dimensional electronic spectroscopy is applied to track the excitation-wavelength-dependent anisotropy evolution of a molecular heterodimer upon broadband excitation with 11 fs pulses. 2D anisotropy reveals a transient delocalization of the excited-state wave function with Frenkel-exciton character at the moment of excitation. The spatial localization of electronic excitation gives rise to 2D anisotropy depolarization within 200 fs.

[1] D. Aulimer et al., J. Am. Chem. Soc. **16**, 5742-5743 (2009).

MO 9.3 Wed 11:30 f102

**Ultrafast photo-ion probing of the relaxation processes of 2-Thiouracil**. — ●MATTHEW SCOTT ROBINSON, MARIO NIEBUHR, and MARKUS GÜHR — Universität Potsdam, Institut für Physik und Astronomie, Karl-Liebknecht-Straße 24/25, 14476 Potsdam-Golm, Germany

We study the ultrafast relaxation process of 2-thiouracil after UV photo-excitation with the use of multi-photon pump-probe time-of-flight mass spectroscopy, supported by synchrotron-based single-photon vacuum ultraviolet (VUV) photo-ionization studies performed at the Swiss Light Source.

Here we show that most of the observable dynamics are completed 1 ps after excitation, and identify that the parent is primarily produced through 2-photon processes (when using 266 nm photons), whilst all fragments are 3-photon dependent. In addition, through the use of pump and probe beams with different powers we are able to determine if fragments are produced through [1+2] processes or [2+1] processes.

The VUV studies also suggest that the substitution of one of the oxygen atoms of uracil with sulfur to produce 2-thiouracil, introduces a new fragmentation route for the pyrimidine ring, with either CO or HCNH being ejected to produce a 100 amu fragment; the equivalent fragment in uracil (84 amu) is not observed in similar studies. [1]

1. H.W. Jochims, M. Schwell, H. Baumgärtel, and S. Leach, Chem. Phys. **314**, 263 (2005).

MO 9.4 Wed 11:45 f102

**Effect of External Electric Field on Vibronic and Excitonic Properties of P3HT Studied by Femtosecond Time-Resolved Spectroscopy and Density Functional Theory** — ●DEBKUMAR RANA, PATRICE DONFACK, VLADISLAV JOVANOVIĆ, VEIT WAGNER, and ARNULF MATERNY — Jacobs University Bremen, Department of Physics and Earth Sciences, Campus Ring 1, 28759 Bremen

Poly(3-hexylthiophene-2,5-diyl) (P3HT) is of interest for solar cell applications. However, important elementary processes under operational conditions, *i.e.*, in the presence of applied electric fields, are not yet completely understood. In our work, we have used density functional theory (DFT) to evaluate the field-effect on the vibronic properties of P3HT within and beyond the range of typical external electric field strengths. We demonstrate that charge-phonon coupling and hence charge localization increase with field strength. In parallel, we have used femtosecond time-resolved spectroscopy to study the excitonic properties of P3HT thin films in a model P3HT device under operational conditions. We show that polaron-pair (PP) dissociation into charge carriers occurs in the P3HT device more significantly with increasing reverse bias, consistent with the electric field-induced dissociation of oppositely charged species. Moreover, besides PPs directly originating from hot excitons, we experimentally observe PP formation during exciton dissociation via a field-mediated generation process resulting in a slower contribution to the overall decay dynamics. Transient-absorption anisotropy measurements elucidate the excitation polarization memory loss due to external electric fields.

MO 9.5 Wed 12:00 f102

**Population of long-lived excited states in 7- and 9-methylpurine probed by femtosecond transient vibrational absorption spectroscopy** — ●REBECCA HOLTSMANN, AMKE NIMM-RICH, HENDRIK BOEHNKE, and FRIEDRICH TEMPS — Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Germany

We investigated the photo-induced dynamics of 7- and 9-methylpurine (7-MePur, 9-MePur) as model systems for purine-based DNA building blocks. The ensuing processes upon photoexcitation at  $\lambda = 267$  nm

were probed by structure-sensitive time-resolved vibrational absorption spectroscopy. After excitation to the  $S_2(\pi\pi^*)$  state, the excited-state population is transferred to the  $S_1(n\pi^*)$  state by ultrafast internal conversion within  $\tau_1 \approx 300$  fs. Aided by ab initio calculations, our results reveal two parallel deactivation pathways from the  $^1n\pi^*$  state for both isomers: Recovery of the ground state associated with vibrational cooling within  $\tau_2 \approx 10$  ps and intersystem crossing to a  $^3\pi\pi^*$  state with  $\tau_3 = 250$  ps for 7-MePur and  $\tau_3 = 480$  ps for 9-MePur, respectively. Exclusively for 9-MePur, an additional deactivation pathway on the nanosecond time scale from the initially populated  $S_2(\pi\pi^*)$  state has been identified. In summary, canonical nucleobases like adenine and guanine typically feature excited-state lifetimes of  $< 1$  ps. Consequently, the reported long-lived excited states involved in the electronic deactivation after photoexcitation in 7-MePur and 9-MePur highlight the crucial effects of structural modifications on the dynamics of the purine related nucleobases.

MO 9.6 Wed 12:15 f102

**Structural Changes in Metal-To-Ligand Charge Transfer States Investigated by Time-Resolved Vibrational Spectroscopy** — ●F. HAINER<sup>1</sup>, N. ALAGNA<sup>1</sup>, E. DOMENICHINI<sup>2</sup>, M. DARARI<sup>3</sup>, P. GROS<sup>3</sup>, S. HAACKE<sup>2</sup>, and T. BUCKUP<sup>1</sup> — <sup>1</sup>Institute of Physical Chemistry, Ruprecht-Karls University Heidelberg, Germany — <sup>2</sup>University of Strasbourg, CNRS, IPCMS, Strasbourg, France — <sup>3</sup>University of Lorraine, CNRS, L2CM, Nancy, France

Iron(II) complexes with nitrogen-heterocyclic carbene (NHC) ligands are about to become promising chromophores for solar energy applications. In spite of the great interest in these compounds, the assignment of the electronic states involved in the excited state relaxation dynamics is still an open question. In this work, we employed femtosecond transient absorption as well as (pump-)impulsive vibrational spectroscopy to investigate the electronic and vibrational dynamics in the relaxation pathway of such an iron(II)NHC complex. Three contributions are identified and the vibrational dynamics in the low-frequency region is discussed. The photoexcitation of an  $^1$ MLCT state is followed by ultrafast intersystem crossing (ISC), which is accompanied by an intermolecular vibrational redistribution of  $100\text{cm}^{-1}$  mode. The vibrational modes appearing below  $100\text{cm}^{-1}$  and at  $150\text{cm}^{-1}$  correspond to metal-ligand stretch vibrations and are assigned to the electronic excited state manifold. A deformation vibration of the ligand backbone at  $350\text{cm}^{-1}$  is found to survive the ISC, indicating that the charge remains on the ligand. The results point to a ground state recovery from a  $^3$ MLCT without a  $^3$ MC state taking part in the dynamics.

MO 9.7 Wed 12:30 f102

**High-intensity effects in two-dimensional electronic spec-**

**troscopy** — ●MARCEL BINZ<sup>1</sup>, LUKAS BRUDER<sup>1</sup>, LIPENG CHEN<sup>2</sup>, MAXIM F. GELIN<sup>3</sup>, WOLFGANG DOMCKE<sup>4</sup>, and FRANK STIENKEMEIER<sup>1</sup> — <sup>1</sup>Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany — <sup>2</sup>Institute of Chemical Sciences and Engineering, EPFL Lausanne, 1015 Lausanne, Switzerland — <sup>3</sup>School of Science, Hangzhou Dianzi University, 310018 Hangzhou, China — <sup>4</sup>Department of Chemistry, Technical University of Munich, 85747 Garching, Germany

Usually, two-dimensional electronic spectroscopy (2DES) experiments are performed in the regime where perturbation theory holds and the signal can be described by the third-order polarization. However, to measure nonlinear signals, higher laser intensities are generally of advantage as the signal scales with higher order of the incident light fields. Non-perturbative theoretical description of 2DES experiments indicate that compromising effects, such as peak shape distortions and phase shifts, should occur at laser intensities beyond the perturbative limit [1]. Here, we explore these high-intensity effects by studying a simple, clean model system comprising of a rubidium atom vapor in collinear 2DES experiments, supported by non-perturbative numerical simulations.

[1] L. Chen et al., *J. Chem. Phys.* **147**, 234104 (2017)

MO 9.8 Wed 12:45 f102

**Revealing delocalized states using multiple-quantum two-dimensional spectroscopy** — ●FRIEDEMANN LANDMESSER, LUKAS BRUDER, ULRICH BANGERT, MARCEL BINZ, ELENA LEISSLER, DANIEL UHL, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

Many-body quantum states are considered to play a crucial role in atomic and molecular systems with respect to dissipation, excitation, and energy transfer (cf. [1]). We aim at investigating collective effects by multiple-quantum coherence experiments, where multiphoton processes can be separated from one-photon transitions [2] and delocalized excitons can be probed with extraordinary sensitivity [3]. We now extend our detection scheme to phase-modulated multiple-quantum two-dimensional coherent spectroscopy [4]. Our focus will lie on the investigation of dilute alkali atom vapors, where we observe dipolar couplings at extremely low densities [3], as well as molecular networks formed on cold rare gas clusters. In the latter system, we previously observed intriguing cooperative processes such as superradiance and singlet fission [5].

[1] F. Fassioli et al., *J. Royal Soc. Interface* **11**, 20130901 (2014).[2] L. Bruder et al., *Phys. Rev. A* **92**, 053412 (2015).[3] L. Bruder et al., *Phys. Chem. Chem. Phys.* **21**, 2276 (2019).[4] S. Yu et al., *Opt. Lett.* **44**, 2795 (2019).[5] S. Izadnia et al., *J. Phys. Chem. Lett.* **8**, 2068 (2017).

## MO 10: Collisions and Reactions

Time: Wednesday 11:00–13:30

Location: f142

MO 10.1 Wed 11:00 f142

**Electron emission asymmetry in multiphoton dissociation of  $\text{H}_2$**  — ●PATRICK FROSS, DENHI MARTINEZ, NICOLAS CAMUS, THOMAS PFEIFER, and ROBERT MOSHAMMER — Max-Planck-Institut für Kernphysik, Heidelberg, Germany

When a diatomic molecule dissociates the released electron can either propagate along the neutral or the ionized atom. Depending on the dissociation pathways the electron is preferentially emitted in the direction of one or the other. This so-called electron localization asymmetry can be measured and gives information on the underlying dissociation pathways. We present results from multiphoton-dissociation of molecular hydrogen using single 35fs pulses with a central wavelength of 400nm ( $I=1 \cdot 10^{14}$  W/cm<sup>2</sup>) and a reaction microscope to image ions and electrons in coincidence. We report and explain the characteristic electron localization asymmetry behavior observed for the dissociation of  $\text{H}_2$  depending on the nuclear electron correlation. To our knowledge these results are the first of their kind in the regime of multiphoton-ionization.

MO 10.2 Wed 11:15 f142

**XUV-photoinduced addition reactions from ethene measured with a radio frequency ion trap** — ●SIMON REINWARDT<sup>1</sup>, IVAN BAEV<sup>1</sup>, JULIUS SCHWARZ<sup>1</sup>, FRIDTJOF KIELGAST<sup>1</sup>, KAROLIN

MERTENS<sup>1</sup>, FLORIAN TRINTER<sup>2,3</sup>, and MICHAEL MARTINS<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Universität Hamburg, Hamburg, Germany — <sup>2</sup>FS-PETRA-S, DESY, Hamburg, Germany — <sup>3</sup>Molecular Physics, Fritz-Haber-Institut, Berlin, Germany

The interstellar formation of larger hydrocarbons is not fully clarified yet. There are different models in which the larger hydrocarbons are formed by dehydrogenation and fragmentation as well as isomerization of hydrocarbons [1]. In conventional experiments the formation of larger hydrocarbon systems is investigated by their fragmentation via X-rays. In contrast to that, the reverse path of generating larger hydrocarbons by XUV-induced addition reactions is realized here. An ideally suited setup for such experiments is the ion trap of the photon ion spectrometer (PIPE) [2] at the soft X-ray beamline P04 of the synchrotron PETRA III in Hamburg. For these experiments ethene ( $\text{C}_2\text{H}_4$ ) was used as starting molecule. Consequently, photoactivation was achieved by the absorption of XUV-photons in the carbon K-edge region ( $\sim 290$  eV). In this way it was possible to find reaction products such as  $\text{C}_6\text{H}_x^+$  and  $\text{C}_5\text{H}_x^+$ , which were generated from a double collision.

[1] O. Berné and A. G. G. M. Tielens, *PNAS* **109**, 401 (2012).[2] S. Schippers et al., *J. Phys. B: At. Mol. Opt. Phys.* **47**, 115602 (2014).

MO 10.3 Wed 11:30 f142

**Excited state proton transfer in solvated molecules studied by XUV time-resolved photoelectron spectroscopy** — ●EVGENII IKONNIKOV, JOHAN HUMMERT, and OLEG KORNILOV — Max-Born-Institute, Berlin

Photoelectron pump-probe time resolved spectroscopy is a powerful tool for studies of relaxation dynamics of electronically excited states. There are many pump-probe techniques developed for the gas phase but very few implementations for liquids. However, biological molecules in natural conditions, which often interact with their environment and, due to protic and polar nature of water solvent, besides intramolecular relaxation process there are additional processes possible such as proton transfer and solvent rearrangement upon photoexcitation. In this project we study ultrafast relaxation of molecules dissolved in water. We combine visible pump/XUV probe time-resolved photoelectron spectroscopy and the microliquid jet technique with high efficiency time-of-flight electron detector based on the "magnetic bottle" design. This experimental setup allows us to measure ground state energy of dissolved molecules with concentrations down to 500  $\mu\text{M}$  and follow relaxation dynamics of excited states for samples with molecular concentrations down to 2 mM. We investigate relaxation of molecules exhibiting excited state proton transfer in solvents with different pH values.

MO 10.4 Wed 11:45 f142

**X-ray-induced ignition of a helium nanoplasma** — ●CRISTIAN MEDINA<sup>1</sup>, DOMINIK SCHOMAS<sup>1</sup>, MARKUS DEBATIN<sup>1</sup>, LTAIF LTAIF<sup>2</sup>, ROBERT MOSHAMMER<sup>3</sup>, THOMAS PFEIFER<sup>3</sup>, FRANK STIENKEMEIER<sup>1</sup>, and MARCEL MUDRICH<sup>2</sup> — <sup>1</sup>Albert-Ludwigs-Universität, Freiburg — <sup>2</sup>Aarhus University, Aarhus — <sup>3</sup>Max-Planck-Institut für Kernphysik, Heidelberg

Helium Nanoplasmas are usually created by intense near-infrared laser pulses. After tunnel-ionization of the cluster or some dopant atoms, the cluster fully avalanche-ionizes as the electrons are driven back and forth through the cluster by the laser field. Here, we demonstrate a different scheme for igniting the nanoplasma on helium nanodroplets doped with heavy rare gas atoms. An ultrashort x-ray pulse (FLASH-1 at DESY, Hamburg) first inner-shell ionizes the dopant cluster, followed by Auger decay and charge-transfer ionization of the helium shell. A second near-infrared pulse then drives the nanoplasma at variable delay with respect to the x-ray pulse. The yields of electrons and helium ions are recorded for different dopant species (Ar, Kr, Xe), helium droplet sizes, and laser pulse intensities.

MO 10.5 Wed 12:00 f142

**Z  $\rightarrow$  E and E  $\rightarrow$  Z Photoisomerization Dynamics of an Oxygen-Heterodiazocine upon S<sub>1</sub>(n $\pi^*$ ) Photoexcitation** — ●DENNIS BANK<sup>1</sup>, BIRTHE BEHR<sup>1</sup>, FALK RENTH<sup>1</sup>, MELANIE HAMMERICH<sup>2</sup>, RAINER HERGES<sup>2</sup>, and FRIEDRICH TEMPS<sup>1</sup> — <sup>1</sup>Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Germany — <sup>2</sup>Institute of Organic Chemistry, Christian-Albrechts-University Kiel, Germany

Heterodiazocines are a novel class of azobenzene-related photochromic molecules with an intramolecular bridge consisting a CH<sub>2</sub>-heteroatom linker group between their phenyl rings. This bridge initiates a steric tension that results in superior photophysical properties. We investigated the very efficient photo-induced isomerization ( $\Phi_{Z \rightarrow E} = 0.7$  and  $\Phi_{E \rightarrow Z} = 0.55$ ) dynamics of 12*H*-dibenzo[b,f][1,4,5]oxadiazocine (ODz) by a combination of femtosecond time-resolved electronic absorption spectroscopy and ab initio quantum chemical calculations. After photoexcitation of the thermodynamically stable *Z*<sub>boat</sub> isomer at  $\lambda_{\text{pump}} = 387$  nm the populated S<sub>1</sub>(n $\pi^*$ ) state deactivates within  $\tau \leq 150$  fs. The subsequent complex ground-state dynamics of the *Z*<sub>boat</sub>  $\rightarrow$  *E*<sub>twist</sub> isomerization proceeds via formation of the vibrationally hot intermediate *E*<sub>chair</sub> species with  $\tau = 3$  ps and crossing of an energy barrier of  $E = 0.55$  eV within  $\tau = 15$  ps. In contrast, the *E*<sub>twist</sub>  $\rightarrow$  *Z*<sub>boat</sub> photoisomerization upon excitation at  $\lambda_{\text{pump}} = 530$  nm is completed after only  $\tau = 230$  fs followed by vibrational cooling in the ground state with  $\tau = 20$  ps.

MO 10.6 Wed 12:15 f142

**Consecutive photoinduced electron transfer: The mechanism of the photocatalyst rhodamine-6G.** — ●FABIAN BRANDL, SEBASTIAN BERGWINKL, CARINA ALLACHER, and BERNHARD DICK — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Universitätsstrasse 31, 93053 Regensburg, Germany.

The dye Rhodamine-6G (R6G) acts as photocatalyst via photoinduced electron transfer by forming the R6G radical (reduction potential ca. -0.90 V) after excitation with green light. König et al. proposed a strategy, termed consecutive photoinduced electron transfer (conPET), that adds the energy of two photons for a photoreduction, using a photogenerated radical as an intermediate [1]. Subsequently it has been reported that photoexcitation of the R6G radical at 420 nm splits aryl bromides, suggesting a conPET process [2]. Here we present a study of the mechanism of the formation and photoreactions of the R6G radical by using transient spectroscopy (femtoseconds to minutes) and quantum chemical calculations. We conclude that one photon of 540 nm light produces two R6G radicals. The photoexcited radical decays in ca. 350 fs, either relaxing to the ground state or releasing an electron to the solvent, which returns on a timescale of nanoseconds. Unless the substrate is already attached to the radical, it is reduced by solvated electrons. Vibrational cooling of hot R6G and hot R6G radical occurs within 10ps.

[1] B. König et al. Science. 2014, 346, 725-728.

[2] B. König et al. Chem Commun. 2016, 52, 8695-8698.

MO 10.7 Wed 12:30 f142

**Velocity map imaging of chlorine from photodissociation with a [1+1]-REMPI scheme** — ●CHRISTIAN MATTHAEI, DEB PRATIM MUKHOPADHYAY, and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Velocity map imaging (VMI) is a well-established method for studying the photodissociation dynamics of molecules [1]. When studying chlorine fragments, a [2+1] resonance-enhanced multiphoton ionization (REMPI) scheme is usually employed, requiring a laser with a wavelength of around 235 nm. Since many molecules and radicals also absorb light of this wavelength, the dissociation is generally performed with the same laser. The major disadvantages of these one-colour experiments are that a clean study of the molecules of interest is not always feasible and the dissociation wavelength cannot be changed.

Here, we present a technique for first dissociating molecules with one dye laser and then ionizing chlorine with a second dye laser via a novel [1+1]-REMPI scheme. For the ionization the output of a dye-laser is tripled in a noble gas-filled cell, generating 118 nm light in order to directly promote the electron into the excited state. Following ionization, the chlorine atoms are then detected via time-of-flight mass spectrometry and VMI. First measurements on test systems are shown.

Literature:

[1] M. N. R. Ashfold et al., Phys. Chem. Chem. Phys. 2006, 8, 26-53

MO 10.8 Wed 12:45 f142

**Photochemical and spectroscopic investigation of highly soluble fluorinated TADF copper complexes** — ●SOPHIE STEIGER<sup>1</sup>, PIT BODEN<sup>1</sup>, PATRICK DI MARTINO-FUMO<sup>1</sup>, JASMIN BUSCH<sup>2</sup>, DANIEL ZINK<sup>2</sup>, FLORIAN REHAK<sup>3</sup>, STEFAN BRÄSE<sup>2</sup>, WIM KLOPPER<sup>3</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>Physical Chemistry, TU Kaiserslautern, Germany — <sup>2</sup>Organic Chemistry, KIT, Germany — <sup>3</sup>Physical and Theoretical Chemistry, KIT, Germany

This contribution presents the investigation of fluorinated copper complexes capable for TADF (Thermally Activated Delayed Fluorescence) analyzed by time-resolved FTIR and emission (luminescence) spectroscopy. The highly soluble fluorinated complexes show good (photo)chemical stability in common solvents. With the help of emission spectroscopy, the stability was investigated and the energetic position of the excited states and their lifetime were determined. Furthermore, the TADF capability of the complexes in solids was investigated using temperature-dependent, time-resolved FTIR and emission spectroscopy. The measured spectra are compared and interpreted with (TD)DFT calculations, observing a clear TADF process at room temperature for all structures. A strong lifetime extension and a distinct redshift of the emission band around 20K confirm phosphorescence at low temperatures in contrast to the TADF process observed at room temperature.

MO 10.9 Wed 13:00 f142

**Switching between proton vacancy and excess proton transfer using a bifunctional photoacid with the help of a third reaction partner** — ●MARIUS-ANDREI CODESCU, OLEG KORNILOV, and ERIK T.J. NIBBERING — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, 12489 Berlin, DE

Proton exchange between an acid and a base in protic solvents may in general occur along two different pathways. Recent results obtained on the bifunctional photoacid 7-hydroxyquinoline (7HQ) in water-methanol mixtures has been concluded to take place via a methoxide/hydroxide transport mechanism between the proton-donating OH group and the proton-accepting quinoline group on a timescale of tens to hundreds of picoseconds [Ekimova et al., J. Am. Chem. Soc. 141, 14581 (2019)]. Here, we show that by using cesium formate (Cs+HCOO-) as a third reaction partner, it is possible to steer the reaction dynamics in such a fashion that the excess proton transfer pathway takes over as a dominant reaction mechanism. We follow the reaction kinetics by probing IR-active marker modes of different charged states of 7HQ, and of formic acid, in methanol solution using femtosecond UV-pump IR-probe spectroscopy. A dedicated analysis of the transient IR spectra results in a consistent and quantitative picture of the reaction mechanism for the 7HQ-formate reaction pairs, where the formate acts as an essential component in facilitating a full excess proton transport pathway from the proton-donating OH group to the proton-accepting quinoline group of 7HQ, before the regular proton vacancy (methoxide) transfer pathway can come in full effect.

MO 10.10 Wed 13:15 f142

**Femtosecond-resolved study of x-ray induced fragmentation of buckyballs** — ●ZOLTAN JUREK<sup>1</sup>, NORA BERRAH<sup>2</sup>, ALVARO SANCHEZ-GONZALEZ<sup>3</sup>, SANG-KIL SON<sup>1</sup>, and ROBIN SANTRA<sup>1,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg, Germany — <sup>2</sup>Physics Department, University of Connecticut, Storrs, CT, USA — <sup>3</sup>Department of Physics, Imperial College London, London, UK — <sup>4</sup>Department of Physics, Universität Hamburg, Hamburg, Germany

In this talk we report on a joint experimental-theoretical time resolved study of the dynamics of gas phase C<sub>60</sub> molecules exposed to ultrashort intense X-ray Free Electron Laser (XFEL) pulses [1]. In the experiment two consecutive x-ray pulses were applied: the first (pump) pulse initiated the time evolution by multiply ionizing the molecule, while the second one (probe pulse) altered the system by further ionization, creating pump-probe delay dependent spectroscopy signals. Our theoretical simulations reveal exciting details of the complex fragmentation, such as the release of neutral atomic fragments. Moreover, the simulations also connect delay times appearing in the observed pump-probe data directly to real timescales of the dynamics initiated by a single pulse. Our study is an important step in the understanding of XFEL-matter interaction, crucial for high intensity XFEL applications.

[1] N. Berrah et al, Nat. Phys. (2019) doi:10.1038/s41567-019-0665-7

## MO 11: Annual General Meeting

Time: Wednesday 13:30–14:00

Location: f142

Duration: 30 min.

## MO 12: Lunch talk: German Research Foundation (DFG) (joint session A/K/P/MO/MS/Q)

Time: Wednesday 13:10–13:55

Location: f303

### Lunch Talk

MO 12.1 Wed 13:10 f303

**Funding by the German Research Foundation (DFG) – a brief overview** — ●ANDREAS DESCHNER — Deutsche Forschungsgemeinschaft (DFG), Kennedyallee 40, 53175 Bonn, Germany

During the last 100 years, the German Research Foundation (DFG) and its predecessors have been funding research in Germany. Today, the DFG is the central third party funding organization for basic re-

search in Germany. It offers a broad spectrum of funding opportunities from individual grants to larger coordinated programs.

This talk will give a brief outline of the financial framework, the decision-making processes and the funding portfolio of the DFG. I will mostly focus on the different programs that offer support to early career scientists, e.g. the new Walter Benjamin for postdoctoral positions and the Emmy Noether program for junior research groups.

## MO 13: Cold Molecules (joint session MO/Q)

Time: Wednesday 14:00–15:15

Location: f102

MO 13.1 Wed 14:00 f102

**Optical pumping of metastable helium: state purification and spin-state selection** — ●J. GUAN, T. SIXT, A. TSOUKALA, F. STIENKEMEIER, and K. DULITZ — Institute of Physics, University of Freiburg, Herman-Herder-Str.3, 79104 Freiburg, Germany

Discharge and electron-impact excitation lead to the production of metastable helium atoms in two metastable states,  $2^3S_1$  and  $2^1S_0$ . However, many applications require purified beams containing only one of these species. For atom magnetometers and spin-controlled collisions, even magnetic quantum state selection is required.

Recently, we have successfully applied optical quenching via the  $4^1P_1 \leftarrow 2^1S_0$  transition at 397 nm to fully deplete the  $2^1S_0$  population in a  $^4\text{He}$  gas beam.<sup>1</sup> Equipped with a tunable laser at 1083 nm for excitation of  $2^3S_1 \rightarrow 2^3P$  transitions, we continue to make progresses on preparing the spin-labelled  $2^3S_1$  state after optical quenching. In this talk, I will show our results on the optical quenching of He ( $2^1S_0$ ) and on the optical pumping of He ( $2^3S_1$ ). The spin-controlled metastable He atoms ( $2^3S_1, m_J = 1, 0$  or  $-1$ ) are an ideal source for studying cold and controlled reactive collisions and I will outline possible experiments using this setup.

Reference: 1. Guan et al., Phys. Rev. Appl. 11, 054073 (2019).

MO 13.2 Wed 14:15 f102

**The diatomic molecular spectroscopy database for laser cooling and trapping** — ●XIANGYUE LIU, STEFAN TRUPPE, GERARD MEIJER, and JESUS PEREZ-RIOS — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Convenient access to the spectroscopic constants of molecules is essential for the screening of potential candidates for laser cooling and trapping techniques. To this end, we present a user-friendly database-driven website that provides the ground and excited states spectroscopy constants of polar diatomic molecules, implemented with Linux, Apache, MySQL, and PHP (LAMP) on the back end. The Franck-Condon factors, which directly determine the transition probabilities between two vibrational states, are directly calculated from the spectroscopic constants. In this website, the user can either search for the spectroscopic constants from the web page user interface or access freely to the data from the application programming interface (API). In the API, the data is given in in lightweight data-interchange formats, including JSON and CSV. The user, after registration, is also allowed to contribute to the database. We believe that this database may advance the research in molecular spectroscopy and, ultimately, in ultracold molecules.

MO 13.3 Wed 14:30 f102

**Suppression of Penning ionization by orbital angular momentum conservation** — ●TOBIAS SIXT, JIWEN GUAN, JONAS GRZESIAK, MARKUS DEBATIN, FRANK STIENKEMEIER, and KATRIN DULITZ — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg im Breisgau, Germany

The efficient suppression of Penning-ionizing collisions is a stringent requirement to achieve quantum degeneracy in metastable rare gases. In our experiment, we study quantum-state-controlled Penning collisions between laser-cooled lithium atoms (Li) and metastable helium

atoms ( $\text{He}^*$ ) to investigate new ways of controlling the outcome of Penning-ionizing collisions.

In this contribution, we report on the efficient suppression of  $\text{He}^*$ -Li Penning ionization by laser excitation of the Li atoms. The results illustrate that not only the electron spin, but also  $\Lambda$  - the projection of the total molecular orbital angular momentum along the internuclear axis - is conserved during the ionization process. Our findings suggest that  $\Lambda$  conservation can be used as a more general means of reaction control, for example, to improve schemes for the simultaneous laser cooling and trapping of  $\text{He}^*$  and alkali atoms.

MO 13.4 Wed 14:45 f102

**Line shape investigation of the electronic origin of phthalocyanines, porphyrins and their clusters with  $\text{H}_2\text{O}$  I: Helium nanodroplet studies** — ●JOHANNES FISCHER, FLORIAN SCHLAGHAUFER, and ALKWIN SLENCZKA — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany

Despite vanishing viscosity the spectral shape of the zero phonon line at the electronic origin of molecules embedded into superfluid helium nanodroplets does not reveal the band system of a free rotor. According to previous investigations, helium induced inhomogeneous line broadening dominates the experimentally observed optical line shape. To decipher pure molecular and helium induced contributions the line shapes of various organic compounds and their clusters with  $\text{H}_2\text{O}$  were recorded by means of electronic spectroscopy as well as electronic Stark spectroscopy. In order to learn about the dopant species its spectroscopic response must be separated from the helium induced spectral features. We present electronic spectra and Stark-spectra of phthalocyanine- $\text{H}_2\text{O}$  clusters, dipolar chloroaluminiumphthalocyanine, and of chloroaluminiumphthalocyanine- $\text{H}_2\text{O}$  clusters. Thereby we observe field induced optical anisotropy and spectral changes of the

line shape. A final analysis requires in addition high-level *ab initio* calculations for the corresponding isolated species [1]. Moreover, the helium droplet work is accompanied by corresponding investigations in the gas phase, which are subject of a follow up talk (F. Schlaghauser).

[1] J. Fischer et al., *J. Phys. Chem.*, **123**, 10057, (2019).

MO 13.5 Wed 15:00 f102

**Line shape investigation of the electronic origin of phthalocyanines, porphyrins and their clusters with  $\text{H}_2\text{O}$  II: gas phase studies** — ●FLORIAN SCHLAGHAUFER, JOHANNES FISCHER, and ALKWIN SLENCZKA — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany

The spectral shape of the zero-phonon-line in the electronic and Stark spectra of organic molecules such as phthalocyanines [1] and porphine [2] and their clusters with small molecules (e.g.  $\text{H}_2\text{O}$ ) recorded in superfluid helium nanodroplets is determined by pure molecular contributions and the influence of the helium environment. As discussed in an accompanying talk (J. Fischer), the analysis of such line shapes is not straightforward. Therefore, corresponding gas phase studies are essential for dissecting helium induced spectral features from molecular rotor fingerprints. The observed rotational band shapes of jet cooled molecules and associated simulations give insight into the structure and polarity of the molecular systems for both the ground and the electronically excited state. By means of a rule of thumb for transition from gas phase to helium droplet conditions we compare these simulations with experimental spectra measured in helium droplets. Mismatches reveal the influence of helium induced contributions to the line shapes. Ultimately, this project heads for a better understanding of microsolvation and the dynamics of electronic excitation of molecules inside superfluid helium nanodroplets.

[1] *J. Chem. Phys.* 2018, 148, 144301.

[2] *J. Chem. Phys.* 2018, 149, 244306.

## MO 14: Vibrational and Rotational Spectroscopy

Time: Wednesday 14:00–16:30

Location: f142

**Invited Talk** MO 14.1 Wed 14:00 f142  
**Elucidating transition metal clusters and complexes in cryo isolation** — ●GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie and State Research Center OPTIMAS, TU Kaiserslautern, Germany

We utilize cryogenic ion trapping to record adsorption and activation kinetics, normal vibrations and magnetic moments of isolated transition metal (TM) clusters and their coordination complexes when held isolated void of environmental interferences. The characterization of such intrinsic properties in combination allows for far fetching conclusions on e.g. the morphologies and adsorbate induced reorganization of TM clusters, and the magnetostructural correlations within oligomeric TM complexes. We refer to published [1-7] as well as to most recent yet unpublished results [8-9].

[1] S. Dillinger, J. Mohrbach, J. Hewer, M. Gaffga, GNS, PCCP 17, 10358 (2015). [2] J. Mohrbach, S. Dillinger, GNS, *J. Phys. Chem. C* 121, 10907 (2017). [3] J. Mohrbach, S. Dillinger, GNS, *J. Chem. Phys.* 147, 184304 (2017). [4] S. Dillinger, J. Mohrbach, GNS, *J. Chem. Phys.* 147, 184305 (2017). [5] S. Dillinger, M. P. Klein, A. Steiner, D. C. McDonald, M. A. Duncan, M. M. Kappes, GNS, *J. Phys. Chem. Lett.* 9, 914 (2018). [6] M. P. Klein, A. Ehrhard, S. Dillinger, J. Mohrbach, GNS, *Topics in Catalysis* 61, 106 (2018). [7] J. Lang, J. M. Hewer, M. Klein, C. van Wüllen GNS, PCCP 20, 16673-16685 (2018). [8] D. V. Fries, M. P. Klein, A. Steiner, H. Schwarz, GNS, work in progress [9] A. Steiner, M. P. Klein, C. Wiehn, M. Prosenic, P. Armentrout, GNS, work in progress

**Invited Talk** MO 14.2 Wed 14:30 f142  
**Rotational Studies of (chiral) Molecules/Complexes in Jets (& Flames)** — ●JENS-UWE GRABOW — Leibniz Universität, Hannover, Germany

Rotational spectroscopy is the most precise and unambiguous method to detect and characterize molecular species important in environmental and astro-chemistry.

The dual excitation-emission propagation in-phase/quadrature-phase modulation passage-acquired coherence technique (DEEP-IMPACT) Fourier-transform microwave (FTMW) spectrometer deliv-

ers broadband spectra at a resolution similar to the resolving power of the narrowband but more sensitive excitation pulse-induced coherence coaxial orientation beamresonator arrangement (EPIC-COBRA) FTMW spectroscopy.

Nevertheless, the single-horn feed used in the dual off-axis parabolic reflector arrangement limits the applicable excitation power and therefore is severely reducing the polarization efficiency. Rotating of the field vector direction of the linearly polarized microwave radiation allows for a dual-feed horn. This novel setup prevails the high spectral resolution but increases the sensitivity dramatically while allowing the very high-power needed for less polar species. In this contribution we present the apparatus in detail as well as experimental results obtained with the EPIC-COBRA FT-MW spectrometer that also adopts instrumental aspects of the DEEP-IMPACT FTMW technique. Furthermore, we will try to elucidate the nature of double-quantum coherence and some of its recent applications towards chiral molecules as well as jet-sources to observe more reactive intermediates produced in combustion reactions.

MO 14.3 Wed 15:00 f142

**IR Photodissociation spectra of  $\text{Si}_x\text{H}_{4x-4}^+$  ( $x=4-8$ ): Evidence for Si-H-Si proton bridges** — ●MARTIN ANDREAS ROBERT GEORGE and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

Silicon hydride clusters ( $\text{Si}_x\text{H}_y^+$ ) play a significant role in plasma chemistry and astrochemistry. Despite this importance their structural and energetic properties are largely unexplored. Building upon our previous investigations of  $\text{Si}_2\text{H}_6^+$  [1],  $\text{Si}_2\text{H}_7^+$  [2],  $\text{Si}_3\text{H}_8^+$  [3], we present infrared photodissociation (IRPD) spectra of previously unknown  $\text{Si}_x\text{H}_y^+$  ions of the form  $\text{Si}_x\text{H}_{4x-4}^+$  with  $x=4-8$  ( $\text{Si}_4\text{H}_{12}^+$ ,  $\text{Si}_8\text{H}_{24}^+$ ) [4]. Our spectral analysis, supported by dispersion-corrected density functional calculations, reveals that all  $\text{Si}_x\text{H}_{4x-4}^+$  ions have at least one Si-H-Si bridge. The characteristic fingerprint of these three-center two-electron (3c-2e) bonds is the strongly IR active anti-symmetric stretch fundamental of the Si-H-Si bridge. The frequency of this vibration depends strongly on the structural and energetic details of the Si-H-Si bridge. Our investigations reveal the correlations between the properties of the various Si-H-Si bridges (bond distances,

bond angles, binding energies, stretch frequencies). The bond strength varies from strong symmetric 3c-2e chemical bonds to weak hydrogen or van der Waals bonds. [1] M. Savoca et al. (2013), *Phys. Chem. Chem. Phys.*, 15, 2774 [2] M. Savoca et al., *Angew. Chem. Int. Ed.* (2013), 52, 1568 [3] M.A.R. George et al., *Chem. Eur. J.* (2013), 19, 15315-15328 [4] M.A.R. George, O. Dopfer (2019), *Int. J. Mass Spectrom.* (2019), 435, 51

MO 14.4 Wed 15:15 f142

**Contact Ion Pairs of Phosphate Groups in Water** — ●JAKOB SCHAUSS, ACHINTYA KUNDU, BENJAMIN P. FINGERHUT, and THOMAS ELSAESSER — Max-Born-Institut, Berlin, Deutschland

Negatively charged phosphate groups in the RNA backbone are key to the formation of an ordered solvation shell around the molecule. Interactions of these phosphate groups with alkali and alkaline earth ions in the surrounding solvent strongly impact RNA structure and folding dynamics. Dynamics of ionic arrangements as well as molecular coupling mechanisms of these interactions still escape our current understanding.

In our investigations we employ 2D infrared spectroscopy and microscopic density functional theory simulations on phosphate vibrations. Using the model system dimethyl phosphate in water with an added excess of  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $Na^+$  ions we were able to observe and analyze the formation of contact ion pairs. [1]

[1] Schauss et al., *J. Phys. Chem. Lett.*, 10, 6281-6286 (2019)

MO 14.5 Wed 15:30 f142

**Dynamics of polar polarizable rotors acted upon by unipolar electromagnetic pulses** — ●MALLIKARJUN KARRA<sup>1</sup>, MARJAN MIRAHMADI<sup>2</sup>, BURKHARD SCHMIDT<sup>2</sup>, and BRETISLAV FRIEDRICH<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>Institut für Mathematik, Freie Universität Berlin, Berlin, Germany

We study, analytically as well as numerically, the dynamics that arises from the interaction of a polar polarizable rigid rotor with single unipolar electromagnetic pulses of varying length with respect to the rotational period of the rotor. In the sudden, non-adiabatic limit, we derive analytic expressions for the rotor's wavefunctions, kinetic energies, and field-free evolution of orientation and alignment. The corresponding time-dependent Schrödinger equation is solved numerically in the finite pulse-width regime, extending all the way to the adiabatic limit where general analytic solutions beyond the field-free case are no longer available. The effects of the orienting and aligning interactions as well as of their combination on the post-pulse populations of the rotational states are visualized as functions of the orienting and aligning kick strengths in terms of population quilts, while the evolution of the wavepacket itself is visualized in terms of space-time probability densities. In the intermediate temporal regime, we find that the wavepackets as functions of the orienting and aligning kick strengths show resonances that correspond to diminished kinetic energies at particular values of the pulse duration. Based on this surprising finding, we propose a scheme for the rotational cooling of molecules via iterative 'braking'.

MO 14.6 Wed 15:45 f142

**Wide range, high resolution M-IR spectroscopy of C<sub>2</sub>H<sub>2</sub>** — ●ULRICH EISMANN<sup>1</sup>, DAVID B. FOOTE<sup>2</sup>, MATT CICH<sup>2</sup>, WALTER HURLBUT<sup>2</sup>, DANIEL J. CHRISTENSEN<sup>3</sup>, FELIX ROHDE<sup>1</sup>, and CHRIS HAIMBERGER<sup>2</sup> — <sup>1</sup>TOPTICA Photonics AG, Lochhamer Schlag 19, D-82166 Graefelfing, Germany — <sup>2</sup>TOPTICA Photonics, Inc., 5847 County Rd. 41, Farmington, NY 14425, USA — <sup>3</sup>now with Lumencor Inc., 14940 NW Greenbrier Parkway, Beaverton, OR 97006 USA

Continuous-wave optical parametric oscillators are a flexible tool for

high-resolution spectroscopy, potentially covering from the D-UV to the M-IR range, with tunable narrow-linewidth output powers exceeding 10 W and versatile frequency referencing.

Here, we demonstrate more than 50 nm of automatic, effectively-mode-hop-free idler tuning of our commercial source DLC TOPO by using stand-off digital control. We achieve an absolute accuracy in the low  $10^{-3} \text{ cm}^{-1}$  range ( $\approx 100 \text{ MHz}$ ) at a scan speed of  $2 \text{ cm}^{-1}/\text{min}$ . We present continuous spectroscopy on  $C_2H_2$  and  $CH_4$  near  $3 \mu\text{m}$ . The M-IR frequency referencing is established by monitoring the pump and signal wavelengths in the N-IR using a wavelength meter, and our data suggests an improvement of the HITRAN database.

Our scheme can be extended to fully automatic operation within the entire  $2.2 - 4.0 \mu\text{m}$  idler emission range. For demonstration, we obtain similar performance at the minimum and maximum idler wavelengths. Using a frequency frequency comb as a reference, ultimate accuracies can be achieved, and we demonstrate measurements of the DLC TOPO locked to a commercial comb system DFC CORE.

MO 14.7 Wed 16:00 f142

**IR/UV Ion Dip Spectroscopy of the 2-Methyl-Allyl-Radical and its High Temperature Bimolecular Reaction Products** — ●TOBIAS PREITSCHOPF<sup>1</sup>, FLORIAN HIRSCH<sup>1</sup>, ALEXANDER LEMMENS<sup>2</sup>, ANOUK M. RIJS<sup>2</sup>, and INGO FISCHER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>FELIX Laboratory, Faculty of Science, Radboud University, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands

As recent studies suggest, small hydrocarbon radicals such as the 2-methyl-allyl radical (2-MAR) are considered as highly reactive intermediates in combustion processes [1]. Studies of these isolated radicals are scarce but bear important information on their reactions for kinetic modelling of combustion processes.

In this work we investigate the gas phase IR-spectra of the 2-MAR and its high temperature bimolecular reaction products in a free jet using IR/UV Ion-Dip-Spectroscopy. This double resonance spectroscopic method combines the structural sensitivity of mid-infrared spectroscopy with mass information from UV photoionization. The 2-MAR is generated by flash pyrolysis from the corresponding bromide precursor. Additionally, the pyrolysis-tube serves as a flow reactor to foster bimolecular reactions. While a dye-laser ionizes the various products in a one-color two-photon process, the mid-IR-radiation is provided by the free electron laser FELIX, Nijmegen/NL. This intense IR light source can be scanned over the fingerprint region for unambiguous identification of the dilute reaction products.

[1] V. D. Knyazev et al., *J. Phys. Chem. A*. 1998, 102, 8932-8940

MO 14.8 Wed 16:15 f142

**Millimeter Wave Spectrum of Styrene Oxide C<sub>8</sub>H<sub>8</sub>O** — ●PASCAL STAHL<sup>1</sup>, ARENAS BENJAMIN<sup>2</sup>, SERGIO DOMINGOS<sup>2</sup>, GUIDO W. FUCHS<sup>1</sup>, MELANIE SCHNELLE<sup>2</sup>, and THOMAS GIESEN<sup>1</sup> — <sup>1</sup>Institute of Physics, University Kassel, Heinrich-Plett Str. 40, 34132 Kassel, Germany — <sup>2</sup>Spectroscopy of Molecular Processes, DESY, Notkestraße 85, 22607 Hamburg, Germany

We investigated the astrochemically-relevant, chiral molecule styrene oxide  $C_8H_8O$  and analysed the rotational spectrum of its ground state. Chirped-pulse Fourier-transform microwave and millimeter-wave spectroscopy and frequency modulation absorption spectroscopy was applied to record spectra in the region of 2 GHz to 330 GHz. Spectral analysis produced a set of precise rotational constants and centrifugal distortion constants up to the sextic order. Our accurate predictions of styrene oxide into the (sub-)millimetre range are necessary for radio astronomy searches. In addition, we assigned the spectra of all singly-substituted  $^{13}C$  and the  $^{18}O$  isotopologues, which allowed us to investigate the gas-phase structure of the molecule.

## MO 15: MO Poster 3

Time: Wednesday 17:00–19:00

Location: Empore Lichthof

MO 15.1 Wed 17:00 Empore Lichthof

**Photochemical formation and photophysical properties of photocatalyst radicals** — ●SEBASTIAN BERGWINKL and BERNHARD DICK — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Germany

Recently, organic radicals have been proposed as photocatalysts. Al-

though such radicals are sensitive to oxygen, their electronic excitation leads to potentially strong reducing species that may be used in photoredox catalysis. When these radicals are themselves produced by a photochemical reaction, the catalytic process uses the energy of two photons [1]. Results of time-resolved spectroscopic measurements will be presented that follow the kinetics of the photochemical formation of the rhodamine radical.

Transient absorption spectra obtained with a streak camera show that a single photon absorbed by a rhodamine molecule produces two radicals of this species. One is formed by direct photoinduced electron transfer, the second by a dark reaction on a microsecond time scale, allowing for a theoretical upper limit of the quantum yield of 2. The rhodamine radical is stable for many minutes, but decomposes quickly upon excitation with a second photon.

[1] I. Gosh, T. Gosh, J. I. Bardagi, B. König, *Science* **2014**, 346, 725–728.

MO 15.2 Wed 17:00 Empore Lichthof

**Monitoring the photochemistry of a formazan over 12 orders of magnitude in time** — ●SVENJA WORTMANN, ROGER JAN KUTTA, and PATRICK NUERNBERGER — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg, Germany

Photoreaction of 2,3,5-triphenyltetrazolium chloride (TTC) in water yields 1,3,5-triphenyltetrazolium formazan (TPF) [1,2], used in TTC assays to indicate cellular respiration or cell growth [3]. From previous studies of formazan analogues only stationary spectra were reported. Exciting at 530 nm, the stable TPF conformer [4] performs an E-Z isomerization to a TPF-stereoisomer, observable by a hypsochromic shift [5]. At least 10 more isomers exist. So far, two conflicting mechanisms are suggested for the light-induced processes in TPF [6].

We studied the photochemistry of TPF in dependence on temperature, excitation wavelength, and solvent environment by time-resolved spectroscopy over 12 orders of magnitude in time. Additionally, vertical excitation energies for each potential TPF conformer were determined by time-dependent density functional theory for assignment of all observed intermediates. Thus, it is shown that the phototriggered dynamics have both ultrafast and very slow contributions with several isomers being accessed along the reaction path.

[1] T. Bolze et al., *ChemPhysChem*, 2018, 19, 138. [2] J. Hausser et al., *Chem. Ber.*, 1949, 82, 195. [3] J. N. Eloff, *Planta Medica*, 1998, 64, 711. [4] F. Kanal et al., *ChemPhysChem*, 2015, 16, 3143. [5] L. S. Atabekyan et al., *High Energy Chem*, 2011, 45, 52. [6] C. Veas-Arancibia, *Diss.*, Louisiana State University, 1986

MO 15.3 Wed 17:00 Empore Lichthof

**Temperature and time dependent spectroscopy of tetranuclear  $d^{10}$ -complexes with thermochromic emission** — ●PATRICK DI MARTINO-FUMO<sup>1</sup>, PIT BODEN<sup>1</sup>, JASMIN BUSCH<sup>2</sup>, STEFAN BRÄSE<sup>2</sup>, WIM KLOPPER<sup>3</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>Physical Chemistry, TU Kaiserslautern and State Research Center OPTIMAS, Germany — <sup>2</sup>Organic Chemistry, KIT, Germany — <sup>3</sup>Physical and Theoretical Chemistry, KIT, Germany

In this contribution a multispectroscopic approach is presented. The combination of spectroscopy with temperature controlled conditions allow the investigation of electronically excited states with respect to structure, energy and lifetimes. The influence of temperature is investigated by a stepwise cooling of the solid samples down to 20 K. The presented molecular systems consist of a series of OLED relevant tetranuclear Cu(I)-complexes in which four Cu(I) centers are bridged by four halides ( $X^- = F, Br, Cl^-$ ) and two *N,P*-units. The main focus is put here on a system with a  $Cu_4I_4$  core and two 6-MePyrPhos ligands, showing an unusual dual emission from two structurally different excited states. The structural changes in the electronically excited states are discussed on the basis of quantum chemical calculations. The emission color is switchable from orange-red to blue by cooling down the sample to 20 K.

MO 15.4 Wed 17:00 Empore Lichthof

**Universal Pure Aromatic Hydrocarbon Hosts for High-Efficiency Phosphorescent Organic Light-Emitting Diodes** —

●QIANG WANG<sup>2,3</sup>, FABIEN LUCAS<sup>1</sup>, CASSANDRE QUINTON<sup>1</sup>, LIANGSHENG LIAO<sup>2</sup>, ZUO-QUAN JIANG<sup>2</sup>, and CYRIL PORIEL<sup>1</sup> — <sup>1</sup>Univ Rennes, CNRS, ISCR- UMR 6226 35000 Rennes, France — <sup>2</sup>Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu 215123, China. — <sup>3</sup>Institut für Physik & IRIS Adlershof Humboldt-Universität zu Berlin 12489 Berlin, Germany

In the field of phosphorescent organic light-emitting diodes (PhOLEDs), heteroatoms are prescriptively used to design host materials with controlled optoelectronic properties. To date, all the very high efficiency universal hosts reported incorporate heteroatoms. However, one of the inherent issues of heteroatom-based hosts is the fragile heteroatom bonds, which causes instability in device performance.

Here, we show that pure aromatic hydrocarbons hosts designed with the spirobifluorene scaffold are highly efficient and versatile hosts for PhOLEDs. With external quantum efficiencies of 27.1%, 26.0% and 27.3% for red, green and blue PhOLEDs respectively, this work not only reports the first example of high efficiency pure hydrocarbon host in RGB PhOLEDs but also among the highest performance reported universal host. The overall performance demonstrates that pure aromatic hydrocarbons can provide new perspectives in the design of functional materials for PhOLEDs.

MO 15.5 Wed 17:00 Empore Lichthof

**pH-Dependence of Retinal Isomerization in Anabaena Sensory Rhodopsin** — ●OSKAR KEFER<sup>1</sup>, REI ABE-YOSHIZUMI<sup>2</sup>, HIDEKI KANDORI<sup>2</sup>, and TIAGO BUCKUP<sup>1</sup> — <sup>1</sup>Physikalisch-Chemisches Institut, Ruprecht-Karls Universität Heidelberg, Germany — <sup>2</sup>OptoBioTechnology Research Center, Nagoya Institute of Technology, Japan

Anabaena sensory rhodopsin (ASR) is an unique microbial retinal protein. In dark adaption the protein contains mostly AT- (all-trans,15-anti) retinal and in photo-equilibrium (light adaptation) a combination of 13C- (13-cis,15-syn) or AT-isomers are present. This enables the investigation of the ultrafast isomerization of these two isomeric chromophores in the same protein environment. pH-Titration experiments in acidic solution have shown two major pKa values (with 4.0 and 6.5) for protonation of residual amino acids, which are involved in the retinal to protein hydrogen-bonding network and influence the steady-state absorption. We use ultrafast transient absorption spectroscopy to investigate the photo-reaction of ASR until the formation of photoproduct "K" under dark and light adaptation. The investigated pH values are chosen to give insight into the effect of the protonation of these amino acids on the isomerization. Our findings indicate a (i) significant acceleration of initial dynamics for AT only for pH 3 and deceleration of "K"-Formation at more acidic solutions and (ii) a monotonic acceleration of the isomerization dynamics of 13C-isomer with increasing pH.

MO 15.6 Wed 17:00 Empore Lichthof

**Optical and excitonic properties of molecular aggregates on dielectric surfaces** — ●FULU ZHENG, SIDHARTHA NAYAK, and ALEXANDER EISFELD — Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Strasse 38, D-01187 Dresden, Germany

Aggregates of fluorescent dye molecules on dielectric surfaces are of great interest for various technological applications. Due to strong interactions between the molecular transition dipoles, the excitonic eigenstates are coherently delocalized over many molecules [1]. These eigenstates and the corresponding optical transitions are determined by the molecular arrangement. We discuss the dependence of dark and bright states on the molecular arrangement and the spatial shape of the electromagnetic radiation used to probe the aggregate [2]. Strongly inhomogeneous fields can be generated via radiation from the apex of a metallic tip, which allows also scanning across the aggregate. Resulting spatially resolved spectra provide extensive information on the eigenenergies and wave functions [2, 3]. We also found that these delocalized eigenfunctions can be directly reconstructed from spatially resolved near field spectra using convolutional neural networks [3].

[1] A. Eisfeld, C. Marquardt, A. Paulheim, and M. Sokolowski, *Phys. Rev. Lett.* 119, 097402 (2017). [2] X. Gao and A. Eisfeld, *J. Phys. Chem. Lett.* 9, 6003 (2018). [3] F. Zheng, X. Gao and A. Eisfeld, *Phys. Rev. Lett.* 123, 163202 (2019).

MO 15.7 Wed 17:00 Empore Lichthof

**Ion-molecule reaction dynamics of atomic oxygen anions with methane** — ●ATILAY AYASLI, BJÖRN BASTIAN, TIM MICHAELSEN, JENNIFER MEYER, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Technikerstraße 25/3, 6020 Innsbruck, Austria

We study ion-molecule reactions using a crossed-beam setup with kinematically complete velocity map imaging (VMI) [1]. Currently, we aim to investigate reactive scattering of methane with atomic oxygen anions. The major product channel of the  $O^- + CH_4$  reaction forms  $OH^-$  via hydrogen abstraction in an exothermic reaction [4]. Energy dependent experiments ranging from 0.34 eV to 0.63 eV collision energy by Carpenter and Farrar [2] revealed two atomistic mechanisms. The major pathway leads to forward scattering at higher collision energies and a significant backward contribution at the lowest collision energy. Recent theoretical studies suggest a minor reaction pathway forming  $OCH_3^-$  through an endothermic nucleophilic substitution ( $S_N2$ ) pro-

cess at high collision energies [3]. The second pathway has not been previously observed in experiments, as a high entry barrier of 2.54 eV requires higher collision energies. Here, we report on our progress towards  $O^- + CH_4$  scattering at higher collision energies to investigate the proposed new reaction pathway.

[1] Wester, Phys. Chem. Chem. Phys. 16, 396 (2014) [2] Carpenter and Farrar, J. Chem. Phys. 106, 5951 (1997) [3] Wang et al., Molecules, 23(10), 2495 (2018) [4] Viggiano et al., J. Chem. Phys. 106, 8455 (1997)

MO 15.8 Wed 17:00 Empore Lichthof

**Microsolvation and rotation of \*large\* molecular impurities inside helium nanodroplets upon electronic excitation** — ●MALLIKARJUN KARRA<sup>1</sup>, ALEXANDER A. AUER<sup>2</sup>, MIKHAIL LEMESHKO<sup>3</sup>, GIACOMO BIGHIN<sup>3</sup>, IGOR CHEREPANOV<sup>3</sup>, GIOVANNI BISTONI<sup>2</sup>, JOHANNES FISCHER<sup>4</sup>, STEFAN FUCHS<sup>4</sup>, EVA-MARIA LOTTNER<sup>4</sup>, ALKWIN SLENCZKA<sup>4</sup>, and BRETISLAV FRIEDRICH<sup>4</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>Max-Planck-Institut für Kohlenforschung, Mülheim, Germany — <sup>3</sup>Institute of Science and Technology Austria, Klosterneuburg, Germany — <sup>4</sup>Universität Regensburg, Regensburg, Germany

High-resolution electronic spectroscopy (Stark or field-free) of large organic molecules and molecular complexes doped into superfluid helium nanodroplets poses many intriguing questions at the interface of physics and chemistry – especially with regard to solvation and rotation. In our recent work, we have noted the apparent absence of the predicted free rotation of phthalocyanine and porphine in He droplets upon electronic excitation. Extending the study to clusters formed and probed in helium droplets, we also present our surprising finding of a lack of additional helium-stabilized phthalocyanine-water cluster configurations as compared to the gas-phase. We further investigate the absence of a rotational sub-structure in the electronic spectra of dopants larger than glyoxal via a multi-pronged approach that involves the study of the dopant-He PESs before and after electronic excitation, and the invoking of the theory of the angulon quasiparticle in the strong coupling regime.

MO 15.9 Wed 17:00 Empore Lichthof

**Quantum chemical studies on chromone/alcohol aggregates - a carbonyl balance for dispersion interactions** — ●PATRICK H. STREBERT and MARKUS GERHARDS — Physical Chemistry, TU Kaiserslautern and State Research Center OPTIMAS, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

Dispersion forces have often been underestimated in the description of intra- and intermolecular interactions. It is one goal to probe dispersion interactions in dimers with two or more possible binding motifs systematically. In this work, chromone was investigated by quantum chemical methods to examine the binding preference of different aggregating alcohols to the two free electron pairs of the carbonyl group. The balance between dispersion and electrostatic forces can be the deciding factor for the preference of a certain pocket and is difficult to model with current methods. Furthermore, this system is designed to probe weak C-H interactions which further influence the energetic order. Results from different dispersion corrected density functional theory approaches were compared to higher level theory leading to interesting trends.

MO 15.10 Wed 17:00 Empore Lichthof

**Investigating the vibronic structure of photosynthetic pigments using screened range-separated hybrid functionals** — ●ALEXANDER SCHUBERT<sup>1,2,3</sup>, YIN SONG<sup>2</sup>, AKSU HUSEYIN<sup>3</sup>, JENNIFER P. OGILVIE<sup>2</sup>, EITAN GEVA<sup>2</sup>, and BARRY D. DUNIETZ<sup>3</sup> — <sup>1</sup>Friedrich-Schiller Universität Jena, Germany — <sup>2</sup>University of Michigan, Ann Arbor, USA — <sup>3</sup>Kent State University, USA

Bacteriochlorophyll a (Bchl a) and chlorophyll a (Chl a) play an important role in the initial charge-separation steps in photosynthetic reaction centers. We investigate the interplay of electronic and vibrational states within the Q-band by means of time-dependent density functional theory (TDDFT) employing a recently developed framework based on a screened range-separated hybrid functional within a polarizable continuum model (SRSH-PCM). Our simulations support the interpretation of polarized two-dimensional electronic spectroscopic measurements. We find that in Bchl a, the Q<sub>x</sub> and Q<sub>y</sub> transitions lead to two independent bands with a relative transition dipole angle of 76°, whereas in Chl a, three distinct peaks of different polarizations are obtained which are traced back to a spectral overlap between two electronic transitions and their vibrational replicas[1]. Furthermore,

employing the SRSH-PCM scheme to the pseudo-symmetric pigments pairs in bacterial reaction centers reveals that spectral asymmetries may result from locally different effective dielectric environments[2].

[1] Chem.Sci., 10, p.8143 (2019); [2] J.Phys.Chem.B., 123(42), p.8970 (2019).

MO 15.11 Wed 17:00 Empore Lichthof

**Linearized survival probability for revivals in a Morse oscillator** — ●SREEJA LOHO CHOUDHURY and FRANK GROSSMANN — Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden, Germany

We extend the Husimi (coherent state) based version of linearized semiclassical theories [1] for the calculation of correlation functions to the case of survival probabilities. This is a case that could be dealt with before only by use of the Wigner version of linearized semiclassical theory [2, 3]. Numerical comparisons of the Husimi and the Wigner case with full quantum results as well as with full semiclassical ones will be given for the revival dynamics in a Morse oscillator with and without coupling to an additional harmonic degree of freedom.

[1] S. V. Antipov, Z. Ye, and N. Ananth, J. Chem. Phys. 142, 184102 (2015)

[2] J. Cao and G. A. Voth, J. Chem. Phys. 104, 273 (1996)

[3] E. J. Heller, J. Chem. Phys. 65, 1289 (1976)

MO 15.12 Wed 17:00 Empore Lichthof

**A modified approach for simulating nonadiabatic dynamics via the generalized quantum master equation** — ELLEN MULVIHILL<sup>1</sup>, ●ALEXANDER SCHUBERT<sup>1,2,3</sup>, XIANG SUN<sup>4</sup>, XING GAO<sup>1</sup>, YUDAN LIU<sup>1</sup>, BARRY D. DUNIETZ<sup>3</sup>, and EITAN GEVA<sup>1</sup> — <sup>1</sup>University of Michigan, Ann Arbor, USA — <sup>2</sup>Friedrich-Schiller Universität Jena, Germany — <sup>3</sup>Kent State University, USA — <sup>4</sup>New York University Shanghai, China

An approach for simulating nonadiabatic dynamics based on the Nakajima-Zwanzig generalized quantum master equation (GQME) is presented. Unlike the most common GQME-based approaches, the modified approach (M-GQME) does not require casting the overall Hamiltonian in a system-bath form, which is neither natural nor convenient in the case of the molecular Hamiltonian that governs the nonadiabatic dynamics. Within the M-GQME framework, the effect of the degrees of freedom of the environment on the time evolution of the reduced density operator is fully captured by a memory kernel superoperator. Two numerical implementations are presented, where the memory kernel is calculated either employing the Ehrenfest mean-field method [1] or via a combination of the mapping Hamiltonian (MH) approach and the linearized semi-classical (LSC) approximation [2]. Both approaches are demonstrated on a benchmark spin-boson model and shown to lead to significantly more accurate results than a direct application of the Ehrenfest method while being computationally more robust than other GQME-based approaches. [1] J.Chem.Phys.150, p.034101 (2019). [2] J.Chem.Phys.151, p.074103 (2019).

MO 15.13 Wed 17:00 Empore Lichthof

**A compact UV/VUV spectrometer with fixed VLS gratings for overview luminescence measurements** — ●NILS KIEFER, ANDREAS HANS, ARNO EHRESMANN, and ANDRÉ KNIE — Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSA-T), Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

We present a design study for the energy resolved photon detection in the UV and XUV energy regime. A grating with Variable Line Spacing (VLS) allows for dispersion of a wide spectral range onto flat detector surfaces. With two VLS gratings on one substrate, spectra from 30nm to 120nm and 120nm to 300nm can be imaged simultaneously, but spatially separated. In order to achieve single photon detection, two position and time resolving MCP-based detectors will be used. Exemplary showcase-applications at FAIR (Facility of Antiproton and Ion Research) and synchrotron radiation facilities will be outlined. With this compact spectrometer with high efficiency and high resolution from 30nm to 300nm, it will be possible to collect time efficiently wide range luminescence spectra in experiments for the characterization of the highly charged ion beams or synchrotron radiation served AMO experiments.

MO 15.14 Wed 17:00 Empore Lichthof

**Chirped-Pulse Microwave Spectroscopy of Complex Molecules** — ●BETTINA HEYNE<sup>1</sup>, MARIUS HERMANN<sup>1</sup>, NADINE WEHRES<sup>1</sup>, CHRISTIAN ENDRES<sup>2</sup>, and STEPHAN SCHLEMMER<sup>1</sup> — <sup>1</sup>First

Physics Institute, University of Cologne, Germany — <sup>2</sup>Max Planck Institute for Extraterrestrial Physics, Garching, Germany

The Cologne chirped-pulse microwave spectrometer for molecules relevant for astrophysics is operational between 12 and 26.5 GHz and has been described before [1]. Here, the basic principle and the experimental setup will be presented [2]. First, noise measurements taken with the hot-cold method will be discussed. Furthermore, the sensitivity was determined by using a spectrum of OCS and its different isotopologs. Moreover, a closer examination of OCS at different temperatures will be shown and an intensity calibration will be performed. In addition, a spectrum of 2-cyanobutane recorded with a heatable nozzle will be presented.

References: [1] M. Hermanns, N. Wehres, F. Lewen, H.S.P. Müller, S. Schlemmer, *Journal of Molecular Spectroscopy*, 358, 25-36 (2019)

[2] B. Heyne, Master Thesis 'Chirped-Pulse Fourier Transform Spectroscopy of Complex Molecules' (2019)

MO 15.15 Wed 17:00 Empore Lichthof

**Emission spectroscopy using heterodyne receivers** — ●NADINE WEHRES, BETTINA HEYNE, MARIUS HERMANN, JAKOB MASSEN, KIRILL BORISOV, KATHARINA VON SCHOELER, PATRICK PÜTZ, CORNELIA NONINGH, URS GRAF, FRANK LEWEN, and STEPHAN SCHLEMMER — I. Physics Institute, University of Cologne, Cologne, Germany  
Two laboratory emission spectrometers between 70-110 GHz (coincident with ALMA Band 3) and 300-400 GHz (coincident with ALMA Band 7) have been described before [1,2] and will be discussed here with special focus on its stability and sensitivity, as well as its prospects on absolute intensity calibration [3]. Following-up on these recent advances towards heterodyne detection, we present preliminary results using the SOFIA (Stratospheric Observatory for IR Astronomy) up-GREAT laboratory setup, operational around 2 THz, for the spectroscopy of complex molecules. First spectra focus on pure rotational transitions of vinyl cyanide (C<sub>2</sub>H<sub>3</sub>CN). These spectra are used to estimate intensities of ro-vibrational transitions coming from low-lying vibrational bands of polycyclic aromatic hydrocarbons (PAHs). The results are used as feasibility study to exploit future research directions for the spectroscopy of the fingerprint-like ro-vibrational transitions of PAHs at around 2 THz.

References:

[1] N. Wehres, et al. *IAUS* 332 (2018)

[2] N. Wehres, et al. *PCCP* 20, 5530 (2018)

[3] N. Wehres, et al. *IAUS* 350 (2019, accepted)

MO 15.16 Wed 17:00 Empore Lichthof

**Novel sample delivery system for small nanoparticles and biomolecules** — ●LENA WORBS<sup>1,2</sup>, JANNIK LÜBKE<sup>1,2,3</sup>, ARMANDO ESTILLORE<sup>1</sup>, AMIT K. SAMANTA<sup>1</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> —

<sup>1</sup>Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — <sup>2</sup>Fachbereich Physik, Universität Hamburg — <sup>3</sup>Center for Ultrafast Imaging, Hamburg

Coherent diffractive imaging with free-electron lasers promises to allow the reconstruction of the three-dimensional molecular structures of isolated particles at atomic resolution [1]. However, because of the typically low signal-to-noise ratio, this requires the collection of a large amount of diffraction patterns. Since every intercepted particle is destroyed by the intense x-ray pulse, a new and preferably identical sample particle has to be delivered into every pulse.

We present a novel injection scheme, combining electrospray ionization for aerosolization of the sample, followed by shock-freezing and focusing techniques to produce a collimated or focused nanoparticle beams of a broad variety of biological nanoparticles, ranging from large nanoparticles to small single-domain proteins. These nanoparticle beams can be further manipulated to separate, for instance, charge states or conformational states, to allow pure samples to be delivered into the x-ray focus.

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

MO 15.17 Wed 17:00 Empore Lichthof

**Efficient Ytterbium Near-Infrared Luminophore Based on a Nondeuterated Ligand** — ●PARIYA NAZARI<sup>1</sup>, CHRISTIAN KRUCK<sup>2</sup>, CAROLIN DEE<sup>2</sup>, MICHAEL SEITZ<sup>2</sup>, IAN HOWARD<sup>1,3</sup>, BRYCE S. RICHARDS<sup>1,3</sup>, and ANDREY TURSHATOV<sup>1</sup> — <sup>1</sup>Institute of Microstructure Technology (IMT), Karlsruhe Institute of Technology (KIT) — <sup>2</sup>Institute of Inorganic Chemistry, University of Tübingen — <sup>3</sup>Light Technology Institute (LTI), Karlsruhe Institute of Technology (KIT)

Near-infrared lanthanoid(III) luminophores are highly interesting for technological applications such as biomedical imaging, and spectral conversion materials. The main challenge for the development of efficient, molecular, near-IR emitter complexes is the vibrational deactivation of metal-centered states by multiphonon relaxation where the energy is transferred from the lanthanoid to high-energy oscillators such as O-H and C-H in its vicinity. The two main strategies to alleviate the problem in the ligands are removing these oscillators by either deuteration or halogenation. While the development of deuterated/halogenated near-IR ytterbium luminophores has made great progress, there is still a need for molecular emitters that are relatively simple to prepare, yet still able to exhibit acceptable luminescence efficiency. In this study, we comprehensively characterize the photophysics of a novel molecular ytterbium complex with a new tetradentate ligand based on the 2,2-bipyridine-6,6-dicarboxylic acid scaffold. The ytterbium complex shows a rather high absolute luminescence quantum yield of 3.0% and a luminescence lifetime of 72 μs at room temperature in deuterated-methanol solution.

## MO 16: Femtosecond Spectroscopy II

Time: Thursday 14:00–16:15

Location: f102

MO 16.1 Thu 14:00 f102

**Sensitized photoswitching by ultrafast electronic energy transfer in a benzimidazole-naphthopyran donor-acceptor dyad** — SHUANGQING WANG, SEBASTIAN MEGOW, MATS BOHNSACK, ●FALK RENTH, and FRIEDRICH TEMPS — Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, 24098 Kiel, Deutschland

The excited-state dynamics of a molecular dyad with a benzimidazole (PPBI) donor and a naphthopyrane (DPNP) photochromic switch as acceptor was studied by static and femtosecond time-resolved spectroscopies and quantum chemical calculations. The static absorption spectrum of the dyad and calculations indicate that the electronic coupling between the donor and acceptor in the electronic ground state is weak. Selective photoexcitation of the PPBI subunit at 310 nm shows a strong quenching of the PPBI fluorescence in the dyad compared to free PPBI. The corresponding transient absorption maps for the dyad and its constituents and measurements of the transient absorption anisotropy decay reveal a quantitative electronic energy transfer (EET) from the PPBI\*-DPNP donor-excited state to the PPBI-DPNP\* acceptor-excited state with a time constant of 2.90 ± 0.60 ps. This reduces the excited-state lifetime of PPBI from 1.4 ns to a few ps and enables ultrafast ring-opening of the DPNP to the merocya-

nine form. Quantitative modeling assuming Förster resonance energy transfer (FRET) provided an EET time estimate of 1.2–4.2 ps and confirmed FRET as EET mechanism. Our results highlight the feasibility of functional devices utilizing FRET for sensitized photoswitching.

MO 16.2 Thu 14:15 f102

**Ultrafast Triplet Formation and Molecular Vibrations in Halogenated Tetraazaperopyrenes** — ●NIKOLAUS WOLLSCHIED<sup>1</sup>, BENJAMIN BENJAMIN<sup>2</sup>, VAISHNAVI RAO<sup>1</sup>, FELIX BERGER<sup>1</sup>, JOSE L.P. LUSTRES<sup>1</sup>, MARCUS MOTZKUS<sup>1</sup>, SEBASTIAN HÖFENER<sup>3</sup>, JANA ZAUMSEIL<sup>1</sup>, LUTZ H. GADE<sup>2</sup>, and TIAGO BUCKUP<sup>1</sup> — <sup>1</sup>Institute of Physical Chemistry, Ruprecht-Karls University Heidelberg, Germany — <sup>2</sup>Institute of Organic Chemistry, Ruprecht-Karls University Heidelberg, Germany — <sup>3</sup>Institut für Physikalische Chemie, Karlsruher Institut für Technologie, Germany

Tetraazaperopyrenes are air-stable n-type semiconductors which can be used in organic field effect transistors. By introducing halogen substituents to the aromatic backbone, structure property relationships such as energy levels can be tuned systematically. [1] This allows for a methodical investigation of photodynamics via femtosecond transient absorption in solution and zonecast thin films. In both cases, triplet formation is observed, occurring on vastly different timescales and via two different pathways: In solution, intersystem crossing is observed

on the nanosecond timescale, correlating with substituent mass and energy detuning. In thin films, the triplet states are formed by singlet fission in a much faster time scale. Moreover, Raman activity of low frequency vibrational modes during singlet fission is observed and correlated with the formation of the biexcitonic state. Quantum chemical calculations of electronic states energy and spectra are presented. [1] Hahn et al., Chem. Eur. J., 21, 17691, (2015).

MO 16.3 Thu 14:30 f102

**Intramolecular Singlet Fission in Tetraaza-TIPS-Pentacene Oligomers: Triplet formation via the Biexcitonic State** — ●NICOLÒ ALAGNA<sup>1,2</sup>, JOSE L.P. LUSTRES<sup>1,2</sup>, NIKOLAUS WOLLSCHIED<sup>1,2</sup>, QINGQING LUO<sup>1</sup>, JIE HAN<sup>3</sup>, ANDREAS DREUW<sup>2,3</sup>, FLORIAN GEYER<sup>4</sup>, VICTOR BROSIUS<sup>4</sup>, UWE H.F. BUNZ<sup>4</sup>, TIAGO BUCKUP<sup>1,2</sup>, and MARCUS MOTZKUS<sup>1,2</sup> — <sup>1</sup>Physikalisch Chemisches Institut, Ruprecht-Karls University, Germany — <sup>2</sup>Centre for Advanced Materials, University of Heidelberg, Germany — <sup>3</sup>Interdisziplinäres Zentrum für Wissenschaftliches Rechnen, Ruprecht-Karls University, Germany — <sup>4</sup>Organisch Chemisches Institut, Ruprecht-Karls University, Germany

Singlet fission (SF) is a photo-induced process where an excited singlet exciton is converted into two triplet states of nearly half energy. It has been shown for several systems in the liquid phase and in thin films. In this work, we investigate SF in diethynylbenzene-linked tetraaza-TIPS-pentacene dimers with different geometry configurations. Analysis of transient absorption and fluorescence measurements shows an efficient SF ( $\Phi_T > 160\%$ ) in the ortho and meta dimer as well as in the (1,3,5) trimer. Our results show that the formation of the long-lived triplet state  $T_1$  takes place via an intermediate component, called the correlated triplet pair or biexcitonic state. The long-lived triplet state  $T_1$  formed by SF is, however, only a fraction compared to the total amount of the triplet-pair generated. We show that the  $^1(TT)$  state decays via annihilation and triplet fusion mechanisms.

MO 16.4 Thu 14:45 f102

**Signatures of halogen-bond interactions in time-resolved fluorescence spectroscopy** — ●BASTIAN GEISSLER<sup>1</sup>, SARAH KHANI<sup>2</sup>, ELRIC ENGELAGE<sup>3</sup>, CHRISTOF HAETTIG<sup>3</sup>, STEFAN HUBER<sup>3</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — <sup>2</sup>Center for Theoretical Chemistry, Ruhr-Universität Bochum, 44780 Bochum — <sup>3</sup>Organische Chemie I, Ruhr-Universität Bochum, 44780 Bochum

The formation of non-covalent halogen bonds between a halogenated organic compound and a Lewis base in solution is an active field of research with relevance to various chemical reactions and biological processes. However, the complex spectroscopic behavior of such mixtures and the assignment of (transient) spectroscopic signatures to halogen-bond formation in solution are still rather unexplored.

In this contribution, we focus on benzoimidazolium derivatives serving as halogen bond donors and pyridine derivatives as Lewis base acceptors dissolved in acetonitrile. We identify the impact of additional counterions [OTf]<sup>-</sup> and [BAR<sup>F</sup><sub>4</sub>]<sup>-</sup> on the fluorescence properties of these donor-acceptor pairs. In addition to ultrafast transient absorption measurements, we perform time-resolved fluorescence streak imaging studies to scrutinize halogen bonding and competing complex formations. Whereas transient absorption indicates an ultrafast reversible halogen-bond cleavage upon illumination, the fluorescence studies additionally reveal new insights concerning the role of complexation with [OTf]<sup>-</sup> and [BAR<sup>F</sup><sub>4</sub>]<sup>-</sup>.

MO 16.5 Thu 15:00 f102

**Understanding ring-closing and ring-opening reaction of photochromic molecule fulgide in bulk crystal** — ●SOUMYAJIT MITRA<sup>1</sup>, SIMON.F BITTMANN<sup>1</sup>, SCOTT MURPHY<sup>2</sup>, AJAY JHA<sup>1</sup>, and R.J.DWAYNE MILLER<sup>1,3</sup> — <sup>1</sup>Atomically Resolved Dynamics Group, Max Planck Institute for the Structure and Dynamics of Matter, CFEL, Luruper Chaussee 149, 22761, Hamburg, Germany — <sup>2</sup>Department of Chemistry and Biochemistry, Research and Innovation Centre, University of Regina, 3737, Wascana Parkway, Regina, SK S4S 0A2, Canada — <sup>3</sup>Departments of Chemistry and Physics, University of Toronto, 80 St. George Street, Toronto, ON M5S3H6, Canada

Coupling of resonant light field with photochromic molecules (also known as molecular photoswitches) changes the orientation within the molecular structure, which gets manifested in differential optical or mechanical properties. The structural understanding of this photo-switching process holds the key to the rational design of next generation molecules. In this work, we are employing ultrafast transient

absorption measurements in fulgide crystals to study complex interplay of different electronic states due to the presence of two possible reaction pathways: isomerization and electrocyclization. The role of lattice phonons in directing localized chemical reactions will be discussed. Our work pave the way towards understanding and thereby controlling of reaction pathways in complex molecules with multi-photoswitching centers.

MO 16.6 Thu 15:15 f102

**Simulating the XUV spectra of ultrafast dissociating vinyl bromide** — ●FLORIAN ROTT<sup>1</sup>, MAURIZIO REDUZZI<sup>2,3</sup>, THOMAS SCHNAPPINGER<sup>1</sup>, STEPHEN R. LEONE<sup>2,4,5</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Department of Chemistry, LMU Munich, Germany — <sup>2</sup>Department of Chemistry, University of California, Berkeley, USA — <sup>3</sup>ICFO - The Institute of Photonics Sciences, The Barcelona Institute of Science and Technology, Spain — <sup>4</sup>Chemical Sciences Division, Lawrence Berkeley National Laboratory, USA — <sup>5</sup>Department of Physics, University of California, Berkeley, USA

The ultrafast dissociation of vinyl bromide after strong-field excitation is characterized experimentally and theoretically. After a multiphoton excitation of the  $\pi\pi^*$  transition, the relaxation process is illuminated via Attosecond Transient Absorption Spectroscopy (ATAS) using the bromine M-edge. Using non-adiabatic molecular dynamics at the complete active space self-consistent field (CASSCF) level of theory including singlet and triplet states we simulated the dissociation after excitation to the bright  $\pi\pi^*$  state. For the calculation of the XUV absorption spectra the bromine  $3d$  core-excited states as well as the valence excited states of vinyl bromide were computed using the restricted active space perturbation theory (RASPT2). Combining the structural information from the dynamics simulation with the calculated XUV spectra we are able to simulate the corresponding time-dependent transient absorption spectrum of vinyl bromide.

The simulated spectrum shows a good agreement with the experimental ATAS trace in the relevant energy range.

MO 16.7 Thu 15:30 f102

**Ultrafast Dynamics of Fe(II)-based Photosensitizers** — ●AYLA PÄPCKE<sup>1</sup>, JAKOB STEUBE<sup>2</sup>, PHILIPP DIERKS<sup>2</sup>, YANNIK VUKADINOVIC<sup>2</sup>, MATTHIAS BAUER<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institute of Physics and Department of Life, Light and Matter, University of Rostock, 18051 Rostock (Germany) — <sup>2</sup>Institute of Inorganic Chemistry and Center for Sustainable Systems Design (CSSD), University of Paderborn, Warburger Straße 100, 33098 Paderborn (Germany)

Water splitting systems are currently intensively investigated as a potential source for renewable energy. In these systems metal complexes are often used as photosensitizers for absorbing the sunlight. Most of these complexes contain noble metals like iridium and ruthenium. To replace these rare and expensive metals, iron is a promising candidate since it is earth-abundant, inexpensive, environmentally benign, and results in broad absorption bands in the visible spectral region. After absorption of light a metal-to-ligand charge transfer state is populated which should have a long lifetime in the ns-regime to allow for efficient intermolecular interaction. However, in iron(II)-complexes this lifetime is in the fs to ps-range and thereby relatively short. To extend the lifetime several approaches in the design of the complexes are pursued, e.g. the use of strong  $\sigma$ -donating N-heterocyclic carbene or cyclometalating ligands. Here we present ultrafast pump-probe experiments on such complexes. The electronic relaxation path is characterized by means of the transient absorption spectra and the success of the chemical design strategy is assessed on the basis of the observed lifetimes.

MO 16.8 Thu 15:45 f102

**Point-Mutation (W76F) in Anabaena Sensory Rhodopsin Investigated by Femtosecond Time-Resolved Spectroscopy** — ●OSKAR KEFER<sup>1</sup>, REI ABE-YOSHIZUMI<sup>2</sup>, NICOLÒ ALAGNA<sup>1</sup>, HIDEKI KANDORI<sup>2</sup>, and TIAGO BUCKUP<sup>1</sup> — <sup>1</sup>Physikalisch-Chemisches Institut, Ruprecht-Karls Universität Heidelberg, Germany — <sup>2</sup>OptoBioTechnology Research Center, Nagoya Institute of Technology, Japan

ASR is a microbial retinal protein (MRP) that contains two isomeric chromophores, which can undergo ultrafast photo-isomerization. Point mutation inside the retinal pocket of anabaena sensory rhodopsin (ASR) is an efficient way to investigate the structural changes during the isomerization of the retinal protonated Schiff-base (RPSB). Pre-distortion of the conjugated  $\pi$ -framework of retinal is believed to be a major factor in the acceleration of the isomerization rate. This pre-distortion is observable in the ground-state vibrational Raman ac-

tivity of the C<sub>14</sub>-H-out-of-plane (HOOP) mode (around 800cm<sup>-1</sup>) and present in some ASR mutants with accelerated dynamics. Coherent time-resolved vibrational and femtosecond pump-probe experiments were used to investigate the structural changes of RPSB in a W76F point-mutated ASR derivative. By comparing resonant DFWM-measurements with non-resonant DFWM-measurements the vibrational modes of the excited-state manifold can be obtained. This mutant shows no significant HOOP-mode activity in the ground state vibrational Raman spectrum compared to wild-type ASR, further corroborating the role of pre-distortion in the Retinal isomerization.

MO 16.9 Thu 16:00 f102

**Generation of broad bandwidth sub-30 fs deep ultraviolet pulses at high repetition rates** — ●LUKAS BRUDER<sup>1</sup>, LUKAS WITTENBECHER<sup>2</sup>, PAVEL KOLESNICHENKO<sup>2</sup>, and DONATAS ZIGMANTAS<sup>2</sup> — <sup>1</sup>Institute of Physics, University of Freiburg,

Hermann-Herder-Str. 3, 79104 Freiburg, Germany — <sup>2</sup>Department of Chemical Physics, Lund University, P.O. Box 124, 22100 Lund, Sweden

The generation of deep ultraviolet optical pulses featuring broad spectral bandwidth and short pulse durations is a challenging task, especially when using high repetition rate (> 100 kHz) laser systems that provide only low pulse energies (< 10 μJ) to drive the nonlinear conversion processes. Yet, high repetition rates are highly desirable in spectroscopic applications to improve statistics. Based on achromatic phase matching [1], we have recently accomplished the generation of 265 nm-pulses with 10-20 nm bandwidth using input pulse energies of 0.5 μJ at a repetition rate of 200 kHz. Despite the low pulse energies, we reach comparable conversion efficiencies (25 %) than in [1]. We currently compress the pulses to 25 fs, but compression to the sub-10 fs regime should be feasible.

[1] P. Baum, S. Lochbrunner, and E. Riedle, *Opt. Lett.* **29**, 1686 (2004).

## MO 17: Theory

Time: Thursday 14:00–16:00

Location: f142

MO 17.1 Thu 14:00 f142

**Towards Machine-Learned Coordinate Grids for Wave Packet Dynamics** — ●SEBASTIAN REITER, THOMAS SCHNAPPINGER, and REGINA DE VIVIE-RIEDLE — Department of Chemistry, LMU Munich

The dynamics of ultrafast (photo)chemical processes are frequently studied quantum mechanically by propagating wave packets on a spatial grid of nuclear coordinates, thus solving the time-dependent Schrödinger equation. Here, dimensionality reduction is imperative for all but the smallest systems, as the number of grid points scales exponentially with the number of dimensions. This issue is commonly addressed by manually constructing a reduced-dimensional subspace that describes the process in question, for example by employing a few selected normal modes or a linear combination thereof as basis vectors. However, finding such a subspace can prove challenging as it requires a large amount of prior knowledge about the system.

We therefore present a semi-automatic technique to generate non-linear coordinate grids for use in quantum dynamics. It relies on a special type of artificial neural network, called autoencoder, which is capable of learning a low-dimensional representation of trajectory data. Starting from standard quantum chemical reaction path calculations, our software package is designed to assist the user in generating a suitable data set of molecular geometries, setting up and training the neural network and finally constructing the grid. We discuss the advantages of using non-linear over linear coordinate subspaces and present applications for our technique to quantum dynamics in both the ground state and excited states.

MO 17.2 Thu 14:15 f142

**The [H,C,N] dynamics project** — ●GEORG CH. MELLAU<sup>1</sup>, VLADIMIR YU. MAKHNEV<sup>2</sup>, NIKOLAY F. ZOBOV<sup>2</sup>, ALEKSANDRA A. KYUBERIS<sup>2</sup>, and OLEG L. POLYANSKY<sup>2,3</sup> — <sup>1</sup>University of Giessen, Institute of Physical Chemistry, Giessen, Germany — <sup>2</sup>Institute of Applied Physics, Russian Academy of Science, Nizhny Novgorod, Russia — <sup>3</sup>Department of Physics and Astronomy, University College London, London, UK

A chemical reaction is a reorganization of particles in a complex many-body quantum system. Within the frequency domain description, the eigenstates relevant for chemical dynamics are the highly excited eigenstates. I started 20 years ago the [H,C,N] Chemical Dynamics project to get a model-free description of a chemical reaction in the frequency domain. The [H,C,N] molecular system has two HCN and HNC minima and the transition between the localized states corresponds to a prototypical chemical reaction. With numerical methods is not possible to calculate the exact eigenstates of a molecular system, but we can use spectroscopic experiments to measure the complete set of model-free exact eigenstates and thus solve the many-body Schrödinger equation exactly. I will give an overview of this project and the current results of the MAP Data Science project, where the experimental and a vibrational assigned ab initio eigenenergy list are correlated with new ab initio lists. Since the quality of a global PES is determined by its ability to reproduce experimental rovibrational energies this project gives an immediate automatic quality map of a PES or any theoretical model of the molecule.

MO 17.3 Thu 14:30 f142

**Charge Transfer Through Redox Molecular Junctions in Non-Equilibrated Solvents** — ●HENNING KIRCHBERG<sup>1</sup>, MICHAEL THORWART<sup>1</sup>, and ABRAHAM NITZAN<sup>2</sup> — <sup>1</sup>I. Institut für Theoretische Physik, Universität Hamburg, Jungiusstraße 9, 20355 Hamburg, Deutschland — <sup>2</sup>Department of Chemistry, University of Pennsylvania, 231 s 34th St. Philadelphia, PA 19104, USA

Charge transport in solvated molecular junctions is commonly described by sequential electron hopping between molecular sites as well as between the molecule and the metal leads. Each such hopping event is accompanied by complete solvent relaxation and the process is thus described by Marcus electron transfer theory, which accounts for thermally activated processes under equilibrium conditions. When the time scale of the solvent relaxation is finite, the thermal distribution determining the charge transfer rates needs to be replaced by a time-dependent probability distribution. We determine this distribution by suitable diffusion equations in the high- and low-friction limits and calculate the nonequilibrium charge current and the Fano factor as a function of the solvent damping strength. The charge hopping becomes correlated by a finite solvent relaxation. Moreover, we find a Kramers-like turnover of the nonequilibrium current as a function of the solvent induced damping.

MO 17.4 Thu 14:45 f142

**Synthetic spin-orbit coupling mediated by a bosonic environment** — ●MIKHAIL MASLOV, MIKHAIL LEMESHKO, and ENDER-ALP YAKABOYLU — Institute of Science and Technology Austria, 3400 Klosterneuburg, Austria

We study a mobile quantum impurity, possessing internal rotational degrees of freedom, confined on a circular ring in the presence of a many-particle bath. By considering the recently introduced rotating polaron problem [1], we define the Hamiltonian and examine the energy spectrum. The weak-coupling regime is studied by means of a variational ansatz in the truncated Fock space. The corresponding spectrum, presented for selected angular quantum numbers of the impurity, indicates the emergence of a coupling between the angular momenta of circular motion and internal impurity rotation due to the phonon exchange mediated by the bosonic environment. We interpret the arising coupling as a phonon-induced spin-orbit coupling, which is quantified by the correlation function between the external and internal angular momentum operators. The same observation in the regime of strong impurity-bath coupling is elaborated within the Pekar approach. The correlation function shows a kink at a critical coupling, which is explained by a sharp transition between the ground state of the system and the states maximizing the interaction with surroundings. This result is of particular interest for the related fields involving the phenomena induced by spin-orbit interaction, such as spintronics and topological insulators.

[1] E. Yakaboylu, et al., *Physical Review B* **98**, 224506 (2018)

MO 17.5 Thu 15:00 f142

**Efficient Charge Generation Via Hole Transfer in Dilute Organic Donor-Fullerene Blends: A High-Dimensional Multi-**

**Step Kinetics Approach Based On Fermi's Golden Rule Rate Theory** — ●ALEXANDER SCHUBERT<sup>1,2,3</sup>, YIN SONG<sup>2</sup>, SRIJANA BHANDARI<sup>3</sup>, JENNIFER P. OGLIVIE<sup>2</sup>, BARRY D. DUNIETZ<sup>3</sup>, and EITAN GEVA<sup>2</sup> — <sup>1</sup>Friedrich-Schiller Universität Jena, Germany — <sup>2</sup>University of Michigan, Ann Arbor, USA — <sup>3</sup>Kent State University, USA

For efficient organic photovoltaics a broadband photoabsorption that exploits all charge generating pathways would be highly desirable. Electron transfer from organic donors to acceptors has been well-studied and is considered the primary path to charge photogeneration in OPVs, whereas much less is known about the hole transfer pathway. Here we study charge photogeneration in an archetypical system comprising tetraphenylidibenzoperiflanthene(DBP):C70 blends via time-dependent density functional theory (TDDFT) employing a recently developed framework based on a screened range-separated hybrid functional within a polarizable continuum model (SRSH-PCM). Based on such first principles calculations Fermi's golden rule (FGR) rate theory is applied to reveal the multi-state transition kinetics at the donor-acceptor interface. Our simulations support the interpretation of recent multispectral two-dimensional electronic spectroscopy (M-2DES) measurements revealing charge transfer pathways originating in donor and acceptor excitons. We find that both electron and hole transfer occur with comparable rates and efficiencies.

MO 17.6 Thu 15:15 f142

**From spectral Lines to Energy Terms without a Model** — ●STEFAN BRACKERTZ, SVEN KRISTKEITZ, OSKAR ASVANY, and STEPHAN SCHLEMMER — I. Physikalisches Institut, University of Cologne, Cologne, Germany

The fundamental Ritz combination principle originally found in 1908 for atoms has also been applied to molecules as a method to reconstruct the energy states from measured transitions without relying on any model Hamiltonian. In 2006 Nesbitt and coworkers proposed to apply it to protonated methane,  $\text{CH}_5^+$ , which was first done in 2015 and extended in 2017 by our group. Currently, we are elaborating this method to a universal, easy to use tool which can be used for arbitrary spectra as there is a broad field of potential applications:

- Preprocessing for the assignment of rich experimental spectra to analytical models or numerical data
- First step of understanding of molecular spectra for which not even a zeroth order Hamiltonian exists, as for  $\text{CH}_5^+$  in 2015
- Separation of mixed spectra consisting either of spectra of different molecules, e.g., from an experiment in a discharge tube or spectra consisting of subspectra originating from different nuclear spin species, e.g., para- and ortho- $\text{He-H}_3^+$

The challenges in generalizing the method and first results will be discussed.

MO 17.7 Thu 15:30 f142

## MO 18: Cold Molecules II (joint session Q/MO)

Time: Thursday 14:00–15:45

Location: f442

**Invited Talk** MO 18.1 Thu 14:00 f442  
**Long-range interactions between polar molecules and Rydberg atoms** — ●MARTIN ZEPPENFELD — MPI für Quantenoptik, Hans-Kopfermann Str. 1, 85748 Garching

Due to large dipole moments in polar molecules and huge dipole moments in Rydberg atoms, strong interactions between polar molecules and Rydberg atoms persist for separations beyond  $1 \mu\text{m}$ . This provides exciting opportunities in quantum science, with applications such as cooling of internal or motional molecular degrees of freedom, nondestructive molecule detection, and quantum information processing.

In my talk, I will provide an overview of these opportunities and present my work on realizing such ideas experimentally. In particular, we have investigated Förster resonant energy transfer between molecules and Rydberg atoms at room temperature in the past, observing huge interaction cross sections and electric-field-controlled collisions. Currently we are setting up a new experiment to investigate interactions between cold molecules and Rydberg atoms, providing many new opportunities.

**Is nuclear motion classical? The success of the Maxwell-Boltzmann distribution** — ●IRMGARD FRANK — Theoretical Chemistry, Leibniz University of Hannover, Callinstr. 3A, 30167 Hannover

The Born-Oppenheimer approximation can be replaced by a better approximation in a very simple way. The consideration starts from the notion that it is problematic to describe the nuclear motion and the electronic cloud in a similar way, hoping that the Schrödinger equation will generate meaningful results for both of these two completely different types of objects. As the result of the simulation of a chemical reaction one wants to obtain well localized nuclei which clearly define the product state, not a nuclear cloud. The only consistent way to achieve this is by treating the motion of the nuclei classically right from the beginning. The immediate result is *ab-initio* molecular dynamics (AIMD). Movies of chemical reactions generated with AIMD show clearly that this approach is working well at normal energies. Tunneling is electronic tunneling in every case. Chemical reactions are explained by outliers of the classical Maxwell-Boltzmann velocity distribution. The development of this distribution is guaranteed in a molecular dynamics run as it is the most likely distribution and defines the temperature of the system. In the present study we investigate some critical cases, namely the ammonia inversion and the heat capacities of hydrogen and water.

MO 17.8 Thu 15:45 f142

**On the Molecular Symmetry of Protonated Methane** — ●STEFAN BRACKERTZ<sup>1</sup>, BENJAMIN NUKIC<sup>1</sup>, THOMAS SALOMON<sup>1</sup>, PER JENSEN<sup>2</sup>, and STEPHAN SCHLEMMER<sup>1</sup> — <sup>1</sup>I. Physikalisches Institut, University of Cologne — <sup>2</sup>Physikalische und theoretische Chemie, Universität Wuppertal

The energy term diagram of the lowest energy ro-vibrational states of  $\text{CH}_5^+$  has eluded any analytical description until Schmiedt et al. proposed a 5d superrotor model in 2015. In 2018 Fábri and Császár used quantum graphs to describe the internal motions. Numerical results have been published in 2016 by Wang et al. All of these approaches describe the experimental energies reasonably well but seem to be incompatible regarding molecular symmetry.

We present results on the relations between these approaches:

- Schmiedt et al. showed the non-existence of equivalent rotations for the permutations of  $\text{CH}_5^+$  because  $S_5$  is not isomorphic to any subgroup of  $\text{SO}(n) \times \{E, E^*\}$  for  $n < 5$ . This can also be understood geometrically using the results of Fábri and Császár.
- Fábri and Császár do a splitting of  $S_5 = S_4 \times S_2$  associated with an internal equivalent rotation for the  $S_4$  part. This approach gives some clues to the interpretation of the 5d superrotor model.

These considerations are also used for the modeling of a simpler case of a fluxional molecule,  $\text{He-H}_3^+$ , which is subject to internal as well as end-over-end rotation.

MO 18.2 Thu 14:30 f442

**Heteronuclear long-range Rydberg molecules** — ●MICHAEL PEPPER<sup>1</sup> and JOHANNES DEIGLMAYR<sup>2</sup> — <sup>1</sup>Laboratory of Physical Chemistry, ETH Zürich — <sup>2</sup>Felix-Bloch Institut, University of Leipzig

The binding of long-range Rydberg molecules is based on the low-energy scattering of an Rydberg atom's electron off a neutral ground-state atom within its orbit. Improving the quantitative understanding of this binding mechanism thus carries the potential to extract electron-atom-scattering potentials, important quantities to benchmark *ab-initio* atomic structure calculations [1], from photoassociation spectra of long-range Rydberg molecules. Current theoretical models are, however, challenged by the necessity to accurately model the scattering interaction while including all relevant spin couplings, such as the hyperfine interaction [2].

We propose to rigorously test the modelling of long-range Rydberg molecules by isoelectronic substitution, *i.e.*, by systematically varying isotopic variant and chemical species of both Rydberg and ground-state atom. To this end we have completed the construction of a dual-species ultracold atom experiment, which allows for simultaneous trapping of

ultracold cesium and potassium atoms. We will present our current progress towards performing photoassociation spectroscopy of homo- and heteronuclear long-range Rydberg molecules in this setup.

[1] H. Safmannshausen, F. Merkt, and J. Deiglmayr, PRL 114, 133201 (2015); F. Engel *et al.*, PRL 123, 073003 (2019); J.L. MacLennan, Y.-J. Chen, and G. Raithel, PRA 99, 033407 (2019) [2] C. Fey *et al.*, New J. Phys. 17, 055010 (2015)

MO 18.3 Thu 14:45 f442

**Stability of quantum degenerate Fermi gases of tilted polar molecules** — ●VLADIMIR VELJIĆ<sup>1</sup>, AXEL PELSTER<sup>2</sup>, and ANTUN BALAZ<sup>1</sup> — <sup>1</sup>Center for the Study of Complex Systems, Institute of Physics Belgrade, University of Belgrade, Serbia — <sup>2</sup>Physics Department and Research Center OPTIMAS, Technische Universität Kaiserslautern, Germany

A recent experimental realization of quantum degenerate gas of <sup>40</sup>K<sup>87</sup>Rb molecules opens up prospects of exploring strongly dipolar Fermi gases and many-body phenomena arising in that regime [1]. Here we derive a mean-field variational approach based on the Wigner function for the description of ground-state properties of such systems [2,3]. We show that the stability of dipolar fermions in a general harmonic trap is universal as it only depends on the trap aspect ratios and the dipoles orientation. We calculate the species-independent stability diagram and the deformation of the Fermi surface (FS) for polarized molecules, whose electric dipoles are oriented along a preferential direction. Compared to atomic magnetic species [2], the stability of a molecular electric system turns out to strongly depend on its geometry and the FS deformation significantly increases [3]. We also show that tuning the trap frequencies appropriately reduces the 3D system to a quasi-2D system of either a pancake- or a cigar-shaped gas cloud, which turn out to have smaller stability regions.

- [1] L. De Marco *et al.*, Science **363**, 853 (2019)  
 [2] V. Veljić *et al.*, New J. Phys. **20**, 093016 (2018)  
 [3] V. Veljić *et al.*, Phys. Rev. Res. **1**, 012009 (2019)

MO 18.4 Thu 15:00 f442

**Progress on Zeeman slowing of CaF** — ●MARIA STEPANOVA, PAUL KAEBERT, TIMO POLL, MAURICE PETZOLD, SUPENG XU, MIRCO SIERCKE, and SILKE OSPELKAUS — Institut für Quantenoptik, Leibniz Universität Hannover, Germany

Experiments with ultracold molecules promise to have a large impact on many fields of physics such as quantum simulations and computation, metrology and ultracold chemistry. Due to the complex energy level structure of molecules, direct laser cooling yields a relatively low number of particles that can be trapped. In this talk I will present a novel method of direct slowing of molecules, reminiscent of Zeeman slowing of atoms, which promises a significant increase in flux of slow molecules. I will show data from a proof-of-principle experiment using the D1-line of 39K, demonstrating the efficiency of the method. Comparing our proof-of-principle results shows a flux and slowing efficiency comparable to traditional D2-line Zeeman slowing, and a factor of ~20 increase in flux below 35m/s compared to white-light slowing. I will also highlight the newest developments in our experiment such

as our efforts on implementing a chemical cell for molecule production in reaction of ablated Ca and SF<sub>6</sub> gas. This will be followed up by our latest results in measurement of the CaF hyperfine structure as well as the Zeeman splitting in CaF energy levels at high magnetic fields.

MO 18.5 Thu 15:15 f442

**Towards Direct Laser Cooling of Barium Monofluoride** — ●RALF ALBRECHT, MARIAN ROCKENHÄUSER, and TIM LANGEN — 5. Physikalisches Institut and Center for Integrated Quantum Science and Technology IQST, Universität Stuttgart

We report on the progress of our experiment for the direct laser cooling and trapping of barium monofluoride molecules. Laser cooling of molecules had long been considered impossible due to their complex vibrational and rotational level structure. However, beneficial Franck-Condon factors and selection rules allow for optical cycling in many molecular species, including barium monofluoride. Hot molecules are generated through laser ablation of a pressed pellet inside a cold cell and precooled by collisions with a cold buffer gas of helium atoms. The thermalized gas mixture exits the cell through a few-millimeter-sized aperture and enters a high vacuum region as a cold and intense beam. A careful characterization of this beam and demonstration of optical cycling is presented in [1], which paves the way for the implementation of transversal laser cooling of the beam. The current status of this effort will be presented.

[1]R.Albrecht *et al.*, arXiv: 1906.08798 (2019)

MO 18.6 Thu 15:30 f442

**Manipulation of molecular hydrogen in a Rydberg-Stark state on a chip to study cold collisions** — ●KATHARINA HÖVELER<sup>1</sup>, JOHANNES DEIGLMAYR<sup>2</sup>, JOSEF AGNER<sup>1</sup>, HANSJÜRGEN SCHMUTZ<sup>1</sup>, and FRÉDÉRIC MERKT<sup>1</sup> — <sup>1</sup>Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zurich, Switzerland — <sup>2</sup>Felix-Bloch Institut, Universität Leipzig, Linnéstraße 5, 04103 Leipzig, Germany

The exothermic, barrierless H<sub>2</sub><sup>+</sup>+H<sub>2</sub> → H<sub>3</sub><sup>+</sup>+H reaction has been studied in the collision-energy range  $E_{\text{coll}}/k_{\text{B}} = 0.3 - 50$  K. To reach such low collision energies, we use a merged-beam approach and substitute the H<sub>2</sub><sup>+</sup> reactants by the ionic cores of H<sub>2</sub> molecules in high-*n* Rydberg-Stark states. The Rydberg electron does not influence the reaction but shields the ion from heating by space-charge effects and stray electric fields. A curved surface-electrode device is used to deflect a supersonic beam of H<sub>2</sub> molecules excited to high-*n* Rydberg-Stark states and to merge it with a supersonic beam containing ground-state H<sub>2</sub> molecules. The collision energy is tuned by varying the temperature of the valve generating the H<sub>2</sub> ground-state beam for selected velocities of the deflected H<sub>2</sub> beam. The reaction cross section is found to follow the classical Langevin capture model down to  $E_{\text{coll}}/k_{\text{B}} = 5$  K. At lower temperatures, a deviation is observed and attributed to ion-quadrupole long-range interactions. An expected different cross section for a pure para H<sub>2</sub>(*J*=0) neutral reactant will be tested. Investigation of the reactions H<sub>2</sub><sup>+</sup>+D<sub>2</sub> and H<sub>2</sub><sup>+</sup>+HD enables us to distinguish between charge transfer, D or H atom transfer and H<sup>+</sup> ion transfer and to determine the ratio of the two competing reaction channels.

## MO 19: MO Poster 4

Time: Thursday 17:00–19:00

Location: Empore Lichthof

MO 19.1 Thu 17:00 Empore Lichthof

**Coherent control of Lanthanides as molecular quantum bits using shaped femtosecond laser pulses** — ●MIRALI GHEIBI, JAYANTA GHOSH, CRISTIAN SARPE, BASTIAN ZIELINSKI, TILLMAN KALAS, RAMELA CIOBOTEA, ARNE SENFTLEBEN, HENDRIKE BRAUN, and THOMAS BAUMERT — Universität Kassel, Institute of Physics, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

SMolBits - Scalable Molecular Quantum Bits - is a project in the framework of LOEWE (Hessian Initiative for the Development of Scientific-Economic Excellence). Its aim is the realization of ideal quantum systems with long-lived levels, isolated from the environment to form quantum bits as key building blocks for advanced quantum technologies. Lanthanides are particularly promising with respect to possible applications in quantum-based information storage at the atomic and molecular level. Their energy levels and electronic states are barely influenced by the environment and their bonds to the ligands attached

to the lanthanides. Some of them show a prominent absorption feature around 800 nm, the central wavelength of typical Ti:Sapphire laser systems. We have begun investigations of the electronic coherences excited in lanthanide salts by interaction with IR femtosecond laser pulses and their lifetimes using phase-locked double pulses and fluorescence detection under a confocal microscope. As a next step we will study the influence of spectrally phase shaped femtosecond laser pulses in the non-perturbative regime onto the excitation and the created electronic coherence.

MO 19.2 Thu 17:00 Empore Lichthof

**Impact of ab initio data in simulations of coherent control of bond making** — ●ARCHANA SHUKLA<sup>1,3</sup>, DANIEL M. REICH<sup>1,3</sup>, WOJCIECH SKOMOROWSKI<sup>1</sup>, ZOHAR AMITAY<sup>2</sup>, ROBERT MOSZYŃSKI<sup>4</sup>, TATIANA KORONA<sup>4</sup>, and CHRISTIANE P. KOCH<sup>1,3</sup> — <sup>1</sup>Theoretische Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany — <sup>2</sup>Schulich Faculty of Chemistry, Technion-Israel Institute

of Technology, Haifa 32000, Israel — <sup>3</sup>Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — <sup>4</sup>Faculty of Chemistry, University of Warsaw, L. Pasteura 1, 02093 Warszawa, Poland

Coherent control of photoassociation has been successfully achieved in hot magnesium atoms [L. Levin et al., Phys. Rev. Lett. 114, 233003 (2015)] using strong femtosecond laser pulses. The yield of photoassociated magnesium dimers is detected by measuring the UV emission. We study the emission signature of magnesium dimers by combining ab initio electronic structure and molecular quantum dynamics calculations [S. Amaran et al., J. Chem. Phys. 139, 164124 (2013)]. It is found numerically that the UV emission is highly sensitive to the ab initio. In particular we find that enhancement/suppression of the UV emission when using positively/negatively chirped pulses is heavily influenced by the polarisabilities of the excited electronic states which are insufficiently converged in our current ab initio data sets. We present new results for these polarisabilities obtained with the multireference configuration interaction method (MRCI), with which we hope to obtain a more accurate description of the photoassociation dynamics.

MO 19.3 Thu 17:00 Empore Lichthof

**Role of coherence for photoelectron circular dichroism after multi-photon excitation in randomly oriented chiral molecules** — ●ALEXANDER BLECH<sup>1</sup>, R. ESTEBAN GOETZ<sup>1</sup>, TIMUR A. ISAEV<sup>2</sup>, BEHNAM NIKOBAKH<sup>2</sup>, ROBERT BERGER<sup>2</sup>, LOREN GREENMAN<sup>3</sup>, and CHRISTIANE P. KOCH<sup>1</sup> — <sup>1</sup>Universität Kassel, Deutschland — <sup>2</sup>Philipps-Universität Marburg, Deutschland — <sup>3</sup>Kansas State University, Manhattan KS, USA

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

Here we present an extended model that explicitly takes into account the coherence between non-resonant multi-photon excitation and one-photon ionisation as well as the chirality of the photoelectron continuum by solving the scattering problem for the photoelectron. Our new theoretical description allows us to distinguish the contributions of intermediate and final states to PECD. This will be a first step towards refining our quantum optimal control approach in order to determine the ultimate strength of the chiral response.

MO 19.4 Thu 17:00 Empore Lichthof

**Towards molecular quantum bits** — ●MARKUS DEBATIN, JOSEFIN BERNARDOFF, DAQING WANG, SAMUEL T. DAWKINS, and KILIAN T. T. SINGER — Universität Kassel, Germany

Lanthanoides embedded into molecules are expected to show long coherence since transitions within the f-shell are expected to be reasonably unperturbed by the surrounding chemical bonds. Our experimental setup, which allows for implantation of ions [1,2,3], will be used to study optical transitions in molecular ions as well as deposition of the molecular ions onto surfaces. On the poster we present our experimental design and discuss possible roadmaps.

[1] W. Schnitzler et al. Phys. Rev. Lett. 102, 070501 (2009). [2] G. Jacob, et al. Phys. Rev. Lett. 117, 043001 (2016). [3] K. Groot-Berning et al. Phys. Rev. Lett. 123, 106802 (2019)

MO 19.5 Thu 17:00 Empore Lichthof

**Far Infrared Spectroscopy of neutral boron clusters using tunable VUV generated by 4-wave mixing** — ●SASCHA SCHALLER, ALAN GÜNTHER, GERARD MEIJER, and ANDRÉ FIELICKE — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Previous experiments in combination with calculations [1,2] have shown that Boron cluster are able to form versatile structures like planar, ring-like and cages. To record far-infrared spectra for the neutral clusters, a FIR-VUV two-color ionization scheme can be used [3]. In our first experiments, an F2 excimer laser (157 nm) has been used for the ionization step [4]. As the ionization energy depends on cluster size, there is access to only a limited number of cluster sizes for a given VUV photon energy. To overcome the limitation in photon energy given by the fixed frequency F2 laser (7.9 eV), VUV photons are generated by four-wave mixing in Xenon. In the present configuration, which covers an energy range of 6.5 eV to 8.2 eV, two dye lasers ( $\omega_1$ ,

$\omega_2$ ) interact in a static gas cell and the resulting ( $2\omega_1 - \omega_2$ ) difference frequency is used for ionization. We verified that after creating 7.9 eV photons in this way, the spectra obtained via FIR-VUV ionization reproduce the results obtained via F2 laser ionization.

[1] L. S. Wang, International Reviews in Physical Chemistry 35, 69 (2016). [2] H. J. Zhai et al., Nature Chemistry 6, 727 (2014). [3] M. Putter, G. von Helden, and G. Meijer, Chem Phys Lett 258, 118 (1996). [4] C. Romanescu, D. J. Harding, A. Fielicke, and L. S. Wang, Journal of Chemical Physics 137 (2012).

MO 19.6 Thu 17:00 Empore Lichthof

**Photoelectron spectroscopy of size-selected metal clusters at FLASH 2** — ●FABIAN BÄR<sup>1</sup>, NORMAN IWE<sup>2</sup>, KARIMAN ELSHIMI<sup>1</sup>, KLARA RASPE<sup>2</sup>, SIMON DOLD<sup>1</sup>, FRANKLIN MARTINEZ<sup>2</sup>, JOSEF TIGGESBÄUMKER<sup>2</sup>, KARL-HEINZ MEIWES-BROER<sup>2</sup>, and BERND VON ISSEENDORFF<sup>1</sup> — <sup>1</sup>Fakultät für Physik, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany — <sup>2</sup>Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany

A newly designed XUV magnetic bottle photoelectron spectrometer (MBPES) has been tested at the free electron laser FLASH2 in Hamburg in combination with a cluster source and two time-of-flight spectrometers in order to address the core levels of metal clusters. The high photon energy of 47 eV with decent bandwidth allowed us to investigate the *5d* levels of lead and the *4d* band of silver clusters with a unique resolution and short measurement time. In this high intensity regime, multiphoton absorption and therefore up to five different charge states have been observed. The results provide a rather comprehensive characterization of the size dependence of the valence and shallow core states density of lead cluster anions in the size range from  $n = 3$  to  $n = 50$  and silver cluster anions in the size range from  $n = 8$  to  $n = 70$ .

MO 19.7 Thu 17:00 Empore Lichthof

**Software adaptation of a quadrupole mass spectrometer for the investigation of cluster fragmentation** — ●REBECCA SCHAF, DANA BLOSS, ANDREAS HANS, ARNO EHRESMANN, and ANDRÉ KNIE — Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

The exploration of the properties of weakly bound cluster is often hampered by fragmentation as a consequence of ionization or other interactions with light or matter. Therefore, many investigations benefit from a detailed understanding of the cluster fragmentation processes. Here, we present the application of a quadrupole mass spectrometer to analyze the fragmentation in dependency of different ionization parameters. Especially for heterogeneous cluster such investigations are crucial for a reliable distinction of effects occurring in cluster formation or fragmentation.

MO 19.8 Thu 17:00 Empore Lichthof

**Experimental evidence for core-level intermolecular Coulombic decay in hydrated pyrimidine** — ●DANA BLOSS<sup>1</sup>, CATMARN KÜSTNER-WETEKAM<sup>1</sup>, PHILIPP SCHMIDT<sup>1</sup>, SASCHA DEINERT<sup>2</sup>, FLORIAN TRINTER<sup>2</sup>, GREGOR HARTMANN<sup>1</sup>, ARNO EHRESMANN<sup>1</sup>, LORENZ S. CEDERBAUM<sup>3</sup>, NIKOLAI V. KRZYŻEWOI<sup>3</sup>, ANDRÉ KNIE<sup>1</sup>, and ANDREAS HANS<sup>1</sup> — <sup>1</sup>Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany — <sup>2</sup>Deutsches Elektronen-Synchrotron (DESY), Notkestrasse 85, 22607 Hamburg — <sup>3</sup>Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

We investigated the effect of the presence or absence of an aqueous environment for bio-relevant molecules after their exposure to X-ray irradiation in a photoelectron-ion-ion coincidence experiment performed at the P04 at Petra III. In the decay of carbon inner-shell vacancies of hydrated pyrimidine we found evidence for direct intermolecular Coulombic decay. This process protects the molecule from reaching dicationic states via Auger decay and the inevitable fragmentation. The observations are compared with the results of theoretical calculations for a deeper understanding of the occurring effects.

MO 19.9 Thu 17:00 Empore Lichthof

**Multi-electron coincidence study on inner-shell ionized water clusters** — ●CHRISTINA ZINDEL<sup>1</sup>, ANDREAS HANS<sup>1</sup>, ARNO EHRESMANN<sup>1</sup>, UWE HERGENHAHN<sup>2</sup>, and ANDRÉ KNIE<sup>1</sup> — <sup>1</sup>Institut für Physik und CINSaT, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany — <sup>2</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

Since the environment of a single atom or molecule plays an important role regarding its decay behavior, new possible relaxation processes emerge by changing from an isolated system to clusters of weakly bound particles. An example is the Intermolecular or -atomic Coulombic Decay (ICD), a non-local charge distribution process that recently gained attention due to its possible role in radiation damage in biological systems. In water clusters, ICD following inner valence ionization has already been observed experimentally. However, that is not the case for ICD following inner-shell ionization and subsequent Auger decay as theoretically predicted about 20 years ago.

We used a magnetic bottle type time-of-flight spectrometer to reveal different de-excitation pathways and to extract the characteristic electron signal. Three emitted electrons (expected to occur due to 1s-photoionization followed by Auger emission and subsequent Intermolecular Coulombic Decay) were detected in coincidence.

MO 19.10 Thu 17:00 Empore Lichthof

**Optical properties of cationic gold clusters** — ●MARKO FÖRSTEL<sup>1</sup>, KAI POLLW<sup>1</sup>, KARIM SAROUKH<sup>1</sup>, ESTE A. NAJIB<sup>1</sup>, ALICE GREEN<sup>2</sup>, STUART MACKENZIE<sup>2</sup>, and OTTO DOPFER<sup>1</sup> — <sup>1</sup>Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany — <sup>2</sup>Department of Chemistry, University of Oxford, Oxford, UK

Gold is one of the most important model systems in catalysis research. The catalytic properties are strongly dependent on local structure and electronic properties and may change drastically by changing the number of atoms by only one [1]. Unfortunately, due to intrinsic properties of Au, theoretical calculations are not straight forward and methods still need to be improved.

Our newly enhanced setup allows measuring the optical absorption spectra of small gold clusters in hitherto unprecedented quality [2, 3]. Here we present our latest results on small bare and substituted gold clusters cations. We compare the experimentally obtained optical spectra to TD-DFT calculations to draw conclusions about the structure of the excited states, or, correspondingly, use the known structures to benchmark theoretical methods.

- [1] S. Lang et al., *Angew. Chem. Int. Ed.* 10, 2017
- [2] M. Förstel et al., *Rev. Sci. Instr.* 88, 2017
- [3] M. Förstel et al., *Angew. Chem. Int. Ed.* 131, 2019

MO 19.11 Thu 17:00 Empore Lichthof

**Understanding the Geometric and Optical Properties of Cationic Silicon Carbide Clusters** — ●ROBERT RADLOFF, LARS DAHLÖF, KAI POLLW, KARIM AHMED SAROUKH, MARKO FÖRSTEL, and OTTO DOPFER — Technische Universität Berlin, Institut für Optik und Atomare Physik, Germany

Silicon carbide (SiC) possesses a unique set of properties that make it a suitable material for high-temperature electronics applications: a wide bandgap, high thermal stability, chemical inertness and high thermal conductivity [1]. Additionally, small SiC molecules like SiC [2], Si<sub>2</sub>C [3], etc. as well as SiC dust grains [4] have been observed in the circumstellar environment of carbon-rich stars.

We present the energetic, geometric, and optical properties of small cationic SiC clusters obtained via photodissociation spectroscopy, mass spectrometry, and quantum chemical calculations. We show the first optical spectrum of a SiC cation and present hitherto unreported fragmentation channels and ground state geometries of some cationic SiC clusters.

- [1] J. B. Casady and R. W. Johnson, *Solid State Electron*, **39** (10), 1409-1422 (1996)
- [2] J. Cernicharo et al., *Astrophys. J. Lett.* **341**, L25 (1989)
- [3] J. Cernicharo et al., *Astrophys. J. Lett.* **806**, L3 (2015)
- [4] R. Treffers and M. Cohen, *Astrophys. J.* **188**, 545-552 (1974)

MO 19.12 Thu 17:00 Empore Lichthof

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

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

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

Here the results for small copper cluster are presented. Although

copper clusters have been studied intensively, there are still undiscovered features of their photoelectron spectra. For example Cu<sub>5</sub> shows a strong vibrational structure, which is in good agreement with DFT calculations.

MO 19.13 Thu 17:00 Empore Lichthof

**Quantum-state-controlled Penning collisions between lithium and metastable helium atoms** — ●ALEXANDRA TSOUKALA, TOBIAS SIXT, JIWEI GUAN, FRANK STIENKEMEIER, and KATRIN DULITZ — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg im Breisgau, Germany

Our research focuses on understanding the mechanistic details of reactive collisions in order to enable control of their outcome. In our experiment, we study quantum-state-controlled Penning collisions between lithium (Li) and metastable helium (He\*) atoms. For this purpose, a supersonic beam source of He\* atoms is combined with a target of ultracold lithium (Li) atoms confined in a magneto-optical trap (MOT). The full quantum-state control of the reaction partners is achieved by producing a pure beam of He(2<sup>3</sup>S<sub>1</sub>) via the optical depletion of the He(2<sup>1</sup>S<sub>0</sub>) state using a novel excitation scheme. Additionally, both Li and He\* atoms are optically pumped into selected electronically excited or magnetic substates. By alternating the combination of quantum-states for both He\* and Li, we observe strong dependencies of the reactivity on the mutual electron spin and angular momentum orientation.

In this contribution, I will give an overview over the different techniques used to achieve quantum-state control of the reaction partners and I will discuss recent experimental results.

MO 19.14 Thu 17:00 Empore Lichthof

**Analysis of the coupled states (2)<sup>2</sup>Σ<sup>+</sup> and (1)<sup>2</sup>Π of LiCa** — ●JULIA GERSCHMANN<sup>1,2</sup>, ERIK SCHWANKE<sup>1,2</sup>, HORST KNÖCKEL<sup>1,2</sup>, SILKE OSPELKAUS<sup>1,2</sup>, and EBERHARD TIEMANN<sup>1,2</sup> — <sup>1</sup>Inst. f. Quantenoptik, Leibniz Universität Hannover — <sup>2</sup>Laboratory for Nano- and Quantum Engineering, Leibniz Universität Hannover

Molecules consisting of an alkaline and an alkaline earth atom have permanent electric and magnetic dipole moments. This allows manipulations of their states by external fields. Several ab initio calculations have been published on various combinations of a group IA and a group IIA atom. Experimentally, not so much is known about the molecular electronic states.

In 2011, we reported on spectroscopic work on <sup>7</sup>Li<sup>40</sup>Ca in a heat pipe. Via high resolution Fourier transform spectroscopy some states were investigated. Potential energy curve for the ground state (1)<sup>2</sup>Σ<sup>+</sup> was described up to  $v = 19$ . However, the transitions between the states (1)<sup>2</sup>Σ<sup>+</sup> and (2)<sup>2</sup>Σ<sup>+</sup> provided at that time only the description of  $v' \leq 1$  and  $N'$  up to 92 of the state (2)<sup>2</sup>Σ<sup>+</sup>. Now we extend the experiment and analysis to include transitions from  $v' \leq 4$  up to  $N' = 120$  of this state.

In addition, we see perturbations of (2)<sup>2</sup>Σ<sup>+</sup> rotational levels indicating a coupling to the (1)<sup>2</sup>Π state, which will give molecular parameters of the (1)<sup>2</sup>Π state.

We will report on the status of the investigations.

MO 19.15 Thu 17:00 Empore Lichthof

**A Buffer Gas Beam Source for Barium Monofluoride and Progress Towards Laser Cooling of the Molecular Beam** — ●MARIAN ROCKENHÄUSER, RALF ALBRECHT, MICHAEL SCHARWÄCHTER, and TIM LANGEN — 5. Physikalisches Institut and Center for Integrated Quantum Science and Technology IQST, Universität Stuttgart, Germany

Cold molecular gases are the starting point for a large number of novel and interdisciplinary applications ranging from few- and many-body physics to cold chemistry and precision measurements. Especially heavy polar molecules, such as barium monofluoride, are perfect candidates for tests of fundamental symmetries and studies of complex quantum systems with strong, long-range interactions. However, in comparison to atoms, the preparation of molecular gases in the sub-Kelvin regime is complicated by their complex vibrational and rotational level structure and the lack of closed transitions for optical cycling. Nevertheless, thanks to favorable Franck-Condon factors and selection rules, quasi-cycling transitions can be identified for many molecular species, including barium monofluoride. In this contribution, we will report on our buffer-gas beam source for slow and internally cold barium monofluoride molecules. Moreover, we will present our progress towards one-dimensional Doppler cooling of the molecular beam.

MO 19.16 Thu 17:00 Empore Lichthof  
**Towards photodissociation of cold OH<sup>+</sup> in a 16-pole wire trap** — ●CHRISTINE MARIA LOCHMANN, MARKUS NÖTZOLD, ROBERT WILD, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Technikerstraße 25/3, 6020 Innsbruck, Austria

The hydroxyl cation OH<sup>+</sup> plays an important role in astrochemistry. Its formation represents one of the first steps in the rich oxygen chemistry in the interstellar media, while its column density in these regions could provide a successful tracer of cosmic ray and X-ray ionization rates. The recently published photodissociation spectrum of OH<sup>+</sup> provides the transition frequencies to probe the system in the UV regime [1]. Here we present our progress to probe the distribution of the rotational states of cold OH<sup>+</sup> with a UV-photodissociation scheme. Analogously state-selective photodetachment spectroscopy on cold OH<sup>-</sup> has been done previously in our group [2].

The experiments will be carried out in our new multipole wire trap, which can be cooled down to 6K. The trap consists of 16 wires, which can be individually addressed. Accessibility perpendicular to the trap axis allows for laser spectroscopy measurements.

- [1] Hechtfisher U. *et al.*, *J. Chem. Phys.* **151**, 044303 (2019)  
 [2] Otto R. *et al.*, *Phys. Chem. Chem. Phys.*, 2013, **15**, 612

MO 19.17 Thu 17:00 Empore Lichthof  
**Reaction studies of astrophysically relevant anions** — ●MARKUS NÖTZOLD, ROBERT WILD, CHRISTINE LOCHMANN, and ROLAND WESTER — Universität Innsbruck, Inst. für Ionenphysik und Angewandte Physik, A-6020 Innsbruck

After the radioastronomical discovery of the first interstellar anions, interest has grown in understanding the formation and destruction pathways of negative ions in the interstellar medium (ISM). The simplest anion, H<sup>-</sup>, is expected to be present in the ISM, but its detection is difficult as it possess only a single bound state. The most fundamental reaction of H<sup>-</sup> is the proton transfer reaction with H<sub>2</sub>, and occurs via tunneling through the reaction barrier at low temperatures. Starting with D<sup>-</sup>, we have studied the reaction D<sup>-</sup> + H<sub>2</sub> → H<sup>-</sup> + HD in a cryogenic 22-pole trap. Furthermore, we present results on the reaction Cl<sup>-</sup> + H<sub>2</sub> + H<sub>2</sub> → H<sub>2</sub>Cl<sup>-</sup> + H<sub>2</sub> and H<sup>-</sup> + C<sub>2</sub>H<sub>2</sub> → C<sub>2</sub>H<sup>-</sup> + H<sub>2</sub>. The former reaction also serves as a temperature diagnostics for our 22-pole trap and our newly developed multipole wire trap.

MO 19.18 Thu 17:00 Empore Lichthof  
**High-resolution infrared and millimeter-wave spectroscopy of CNH<sub>n</sub><sup>+</sup> (n = 0,4,6) ions** — ●PHILIPP C. SCHMID<sup>1</sup>, SVEN THORWIRTH<sup>1</sup>, OSKAR ASVANY<sup>1</sup>, CHARLIE R. MARKUS<sup>1,2</sup>, JOSÉ L. DOMÉNECH<sup>3</sup>, THOMAS SALOMON<sup>1</sup>, MATTHIAS TÖPFER<sup>1</sup>, PHILIPP SCHREIER<sup>1</sup>, and STEPHAN SCHLEMMER<sup>1</sup> — <sup>1</sup>I. Physikalisches Institut, Universität zu Köln, Köln, Germany — <sup>2</sup>Department of Chemistry, University of Illinois, Urbana, IL, U.S.A. — <sup>3</sup>Instituto de Estructura de la Materia (IEM-CSIC), Madrid, Spain

Molecular ions play crucial roles in the astrochemistry associated with star formation and planetary atmospheres. In this project we have studied three fundamental cations CNH<sub>n</sub><sup>+</sup> (n = 9,4,6) using action spectroscopic techniques in a 22-pole ion trap at a nominal temperature of 4 K [1]. The fundamental diatomic CN<sup>+</sup> [2] as well as the protonated methylene imine, H<sub>2</sub>C=NH<sub>2</sub><sup>+</sup>, and protonated methyl amine, H<sub>3</sub>C-NH<sub>3</sub><sup>+</sup>, were all studied by their pure rotational spectra in the millimeter-wave region employing the method of rotational state-selective He-attachment [3]. CN<sup>+</sup> and H<sub>2</sub>C=NH<sub>2</sub><sup>+</sup> were also studied at high spectral resolution in the infrared using Laser Induced Inhibition of Complex Growth (LIICG) [1,4].

- [1] O.Asvany *et al.*, *Appl. Phys. B* 114 (2014) 203.  
 [2] S. Thorwirth *et al.*, *Astrophys. J. Lett.* 882 (2019) L6.  
 [3] S. Brünken *et al.*, *J. Mol. Spectrosc.* 332 (2017) 67.  
 [4] S. Chakrabarty *et al.*, *J. Phys. Chem. Lett* 4 (2013) 4051.

MO 19.19 Thu 17:00 Empore Lichthof  
**Improving and understanding a cryogenic buffer-gas cell based on comparing Monte-Carlo simulations and experiments** — ●FLORIAN JUNG, THOMAS GANTNER, MANUEL KOLLER, JINDARATSAMEE PHROMPAO, ISABEL RABEY, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Straße 1, 85748 Garching bei München

Unlike atoms, molecules can exhibit a permanent electric dipole moment, which makes them amenable to guiding and trapping via electric fields and allows the study of anisotropic dipolar interactions. In addition, they exhibit a rich internal structure that allows to envi-

sion applications of molecules in such diverse fields as cold chemistry, quantum information science and quantum simulation. For all of these applications the prerequisite is that molecules are cold. To produce cold molecules at a temperature of a few Kelvin, buffer-gas cells are now established workhorses, cooling molecules via thermalisation with cold atomic gases independent of the molecule type. However, many aspects of the physics of buffer-gas cells are still to be understood.

We here present a comprehensive study of buffer-gas cells in the low-density regime, employing Monte-Carlo simulations and comparing these to experimental data, finding a good agreement between the simulated and measured data. We formulate design guidelines that we employ in our set-up, reaching a signal increase of at least a factor of 2. Combining the cryogenic buffer-gas source with a centrifuge decelerator and an electrostatic trap, collision studies on cold molecular ensembles are now within reach.

MO 19.20 Thu 17:00 Empore Lichthof  
**Towards trapping ultracold polar molecules in a dark repulsive dipole trap** — ●REN-HAO TAO — Max-PlanckInstitut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Ultra-cold molecules, by virtue of their rich ro-vibrational states and significant dipolar moments, offer us an exciting platform to study new quantum many-body physics. Ample experiments on molecules reactive and nonreactive alike, however, all point to their short in-trap lifetime (a few seconds) as one of the most immediate challenges before we fully take advantage of them. A recent proposal suggests that the trapping light in these experiments, despite being far-detuned from molecule transitions, is still energetic enough to excite two-molecules complexes in a so-called sticky state to higher energy states, the decays from which might lead to losses. To test this theory, we trap molecules using a far blue-detuned light away from the transition between ground and the first rotational excited state of 23Na40K. Such a transition, owing to its small linewidth ( $2\pi \times 297\text{Hz}$ ), allows us to effectively reduce trapping intensity without sacrificing trap depth. This leads to trap depth of 4kB · μK and an intensity as low as 4W/cm<sup>2</sup> seen by most molecules. The molecule lifetime in such a trap is projected to increase by a factor of 20. If observed, such a reduced trap loss might pave the way for a deeper understanding of molecular collisional dynamics in particular and the feasibility of using molecules as a potentially more interesting alternative in simulating quantum many-body interaction in the long run.

MO 19.21 Thu 17:00 Empore Lichthof  
**Towards enantiomer-specific spectroscopy and control of cold, chiral molecules** — ●JU HYEON LEE, JOHANNES BISCHOFF, A. O. HERNANDEZ-CASTILLO, MARCO DE PAS, GERARD MEIJER, and SANDRA EIBENBERGER-ARIAS — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Chiral molecules are of paramount importance in the activity of biological molecules. Even though chemical and biological functionalities of different enantiomers are significantly different, their energy levels are equal, making detecting and quantifying them challenging. Therefore, there is a need for fast and reliable methods that can differentiate and/or separate enantiomers. Recently, the enantiomer-specific state transfer (ESST) method was developed where three mutually orthogonally polarized, resonant, phase-controlled microwave pulses are used to drive connected rotational transitions, resulting in controlled, enantiomer-specific population transfer [1]. We recently designed, built, and characterized a compact spectroscopy setup. It is capable of performing experiments in the 2-25 GHz regime, making studies of a large variety of molecules possible. Furthermore, our setup is equipped with a time-of-flight (TOF) mass spectrometer, and we implemented a combination of optical methods and microwave spectroscopy. Here we present preliminary results towards ESST of chiral molecules that are relatively rigid and simple, and have an aromatic ring, for example: 1-indanol.

1. S. Eibenberger, J. Doyle, & D. Patterson, *Phys. Rev. Lett.* 118, 123002 (2017).

MO 19.22 Thu 17:00 Empore Lichthof  
**Isomer Selected Ion-Molecule Reactions of C<sub>2</sub>H<sub>2</sub><sup>+</sup> + C<sub>3</sub>H<sub>4</sub>** — ●PHILIPP C. SCHMID<sup>1,2</sup>, JAMES GREENBERG<sup>1</sup>, MIKHAIL I. MILLER<sup>1</sup>, THANH L. NGUYEN<sup>3</sup>, JAMES H. THORPE<sup>3</sup>, JOHN F. STANTON<sup>3</sup>, and HEATHER J. LEWANDOWSKI<sup>1</sup> — <sup>1</sup>JILA and the Department of Physics, University of Colorado, Boulder, Colorado, USA — <sup>2</sup>I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, 50937 Köln, Germany — <sup>3</sup>Quantum Theory Project, Departments of Chemistry and Physics,

University of Florida, Gainesville, Florida, USA

One of the fundamental questions in molecular reactions is to determine how the structure of molecules governs the reaction and thus leads to different reaction products. Studies of isomer resolved chemical reactions can shed light directly on the foundation of how form leads to function. We present the results of gas-phase reactions between acetylene cations  $C_2H_2^+$  with two different isomers of  $C_3H_4$ : propyne ( $HC_3H_3$ ) and allene ( $H_2C_3H_2$ ). The highly controlled environment of an ion trap allows us to precisely measure the reaction products and branching ratios. The difference in observed reaction products from the two different isomers points directly to the role molecular structure plays in these reactions. Through the synergy of experimental results and quantum chemical potential energy surface calculations, we are able to explicate the different reaction mechanisms for the two isomers.

MO 19.23 Thu 17:00 Empore Lichthof  
Progress on Zeeman slowing of CaF — ●MARIIA STEPANOVA,

PAUL KAEBERT, TIMO POLL, MAURICE PETZOLD, SUPENG XU, MIRCO SIERCKE, and SILKE OSPELKAUS — Institut für Quantenoptik, Leibniz Universität Hannover

Ultracold molecules provide distinct advantages in research on precision measurements, ultracold chemistry and simulations of solid state physics. Current experiments are, however, severely restricted by the initial flux of slow and cold molecules, which limits the size of the trappable ensembles. Our group has developed a novel slowing scheme capable of improving this flux by orders of magnitude. We have already demonstrated the feasibility of our method in a proof of principle experiment and are now in the process of combining our scheme with an optimized buffer gas source to greatly enhance the flux of slow, cold molecules. We present our results of the proof of principle experiment on 39K D1-line and our buffer gas cell as a source of rotationally cold molecules. We further show our recent results of mapping out the CaF hyperfine structure in magnetic fields up to 500 Gauss, a necessary step towards implementing Zeeman slowing, and give insights into the future of our experiment.

## MO 20: Control (joint session MO/Q)

Time: Friday 14:00–16:00

Location: f102

MO 20.1 Fri 14:00 f102  
**Control of molecular alignment using tailored picosecond laser pulses** — ●STEFANIE KERBSTADT<sup>1</sup>, EMIL ZAK<sup>1</sup>, ANDREY YACHMENEV<sup>1</sup>, SEBASTIAN TRIPPEL<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — <sup>2</sup>Center for Ultrafast Imaging, Universität Hamburg — <sup>3</sup>Department of Physics, Universität Hamburg

The control of molecular axes is essential for fundamental studies of molecular structure and of chemical reactions. Strong non-resonant laser fields have been established as powerful tool to control and to fix molecular axes in space, providing access to molecular-frame spectroscopy and imaging experiments. Here, we present experimental as well as theoretical results on the refined control of field-free molecular alignment and angular-momentum alignment by employing shaped picosecond pulses to a ground state-selected cold molecular beam of carbonylsulfid (OCS).

MO 20.2 Fri 14:15 f102  
**A comparative study on ionization-induced dissociation of hydrogen, irradiated by 800 nm and 400 nm laser fields** — ●RENÉ WAGNER<sup>1</sup>, SABA ARIFE BOZPOLAT<sup>2</sup>, PATRIK GRYSCHTOL<sup>1</sup>, ILHAN YAVUZ<sup>2</sup>, and MICHAEL MEYER<sup>1</sup> — <sup>1</sup>Small Quantum Systems Group, European XFEL GmbH, 22869 Schenefeld, Germany — <sup>2</sup>Physics Department, Marmara University, 34722 Ziverbey, Istanbul, Turkey

We present a two color investigation of the hydrogen molecule to benchmark our tabletop experiment dedicated to ultrafast investigations of electronic correlations in atoms and molecules from the near infrared (NIR) to the extreme ultraviolet (EUV) range. Our setup focuses on the study of dissociating molecules by different pump-probe techniques aiming to obtain invaluable and novel insights into atomic and molecular dynamics. For this purpose, we have built a femtosecond laser driven EUV source based on high harmonic generation (HHG) combining it with a pulsed molecular jet, a delay-line based velocity map imaging (VMI) detector and a time-of-flight (TOF) spectrometer. We are going to show first experimental as well as theoretical results quantifying the performance of our apparatus having captured and analysed the angular ion momentum distribution of the photo-induced dissociation process of hydrogen, irradiated by ultrafast 800 nm and 400 nm laser fields.

[1] Ibrahim *et al.*, J. Phys B: At. Mol. Opt. Phys. **51** (2018) 042002.

MO 20.3 Fri 14:30 f102  
**Electron-vibrational coupling dynamics in SF<sub>6</sub>** — ●PATRICK RUPPRECHT<sup>1</sup>, LENNART AUFLEGER<sup>1</sup>, ALEXANDER MAGUNIA<sup>1</sup>, SIMON HEINZE<sup>2</sup>, THOMAS DING<sup>1</sup>, MARC REBHOLZ<sup>1</sup>, STEFANO AMBERG<sup>1</sup>, NIKOLA MOLLOV<sup>1</sup>, FELIX HENRICH<sup>1</sup>, MAURITS HAVERKORT<sup>2</sup>, CHRISTIAN OTT<sup>1</sup>, and THOMAS PFEIFER<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, Heidelberg — <sup>2</sup>Universität Heidelberg, Institut für Theoretische Physik

Visible and infrared vibrational spectroscopy, probing non-localized

electronic molecular states, is commonly used in chemistry and biology. In combination with core-level spectroscopy, studies of coherently coupled electronic and vibrational dynamics with site and element specificity are possible. We report on the investigation of sulfur hexafluoride (SF<sub>6</sub>) using attosecond transient absorption spectroscopy driven by mJ-level, few-cycle 15 fs FWHM pulses centered at 1550 nm in the short-wave infrared (SWIR) spectral region. The excited  $6a_{1g}$ ,  $2t_{2g}$  and  $4e_g$  molecular states related to the sulfur L<sub>2,3</sub> absorption edge were probed. First, altering the absorption spectrum in the 160 eV to 200 eV soft X-ray (SXR) region under the presence of a strong SWIR field was demonstrated. Furthermore, varying the delay between the SXR and SWIR pulses resulted in an oscillatory behavior of the resonance lines' intensities, with a leading SWIR pulse. The extracted oscillation period of  $(773 \pm 16)$  cm<sup>-1</sup> matches the Raman-active symmetric breathing mode  $\nu_1 = 775$  cm<sup>-1</sup>. This result implies sensitivity to nonresonant impulsive stimulated Raman scattering via probing electronic transitions to states localized near the sulfur atom.

MO 20.4 Fri 14:45 f102  
**Laser-induced alignment of nanoparticles** — ●HAKAN AKARSU<sup>1,2</sup>, MUHAMED AMIN<sup>1</sup>, LENA WORBS<sup>1,2</sup>, JANNIK LÜBKE<sup>1,2,3</sup>, ARMANDO ESTILLORE<sup>1</sup>, AMIT K. SAMANTA<sup>1</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, Deutsches Elektronen Synchrotron DESY, Hamburg — <sup>2</sup>Fachbereich Physik, Universität Hamburg — <sup>3</sup>Center for Ultrafast Imaging, Universität Hamburg

Single-particle imaging (SPI) experiments at free-electron lasers (FELs) promise high-resolution-imaging of the structure and dynamics of nanoparticles. By guiding sample molecules in the gas phase into the x-ray focus of an FEL, diffraction patterns of individual particles can be collected. Sufficient amounts of patterns of identical nanoparticles are needed to overcome the inherently small signal-to-noise ratio and reconstruct the underlying 3D structure [1]. Laser-induced alignment of nanoparticles has potential to improve the achievable resolution and to push it toward the atomic scale [2,3].

Here, we present simulation results on laser-induced alignment of gold nanorods by integrating the Euler equation of rotational motion. We have also tested different laser pulse profiles for improvement of the alignment. In addition, we will present first experimental investigations of the laser-induced alignment of gold nanorods.

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

[2] J. C. H. Spence, *et al.*, Phys. Rev. Lett. 92, 198102 (2004)

[3] J. Küpper, *et al.*, Phys. Rev. Lett. 112, 083002 (2014)

MO 20.5 Fri 15:00 f102  
**Rotational spectroscopy of molecular superrotors: probing high rotational states of O<sub>2</sub> via REMPI technique combined with an optical centrifuge.** — ●AUDREY SCOGNAMIGLIO<sup>1</sup>, JORDAN FORDYCE<sup>2</sup>, IAN MACPHAIL-BARTLEY<sup>2</sup>, KATRIN DULITZ<sup>1</sup>, FRANK STIENKEMEIER<sup>1</sup>, and VALERY MILNER<sup>2</sup> — <sup>1</sup>Institut of Physics, University of Freiburg, Germany — <sup>2</sup>Department of Physics and Astronomy, University of British Columbia, Canada

To access highly excited rotational states (e.g.  $N=100$  in  $O_2$ ), the use of an optical centrifuge has been demonstrated to be a powerful and unique experimental tool.

To start from a well-defined initial ro-vibrational state, oxygen molecules are cooled to 10K by means of supersonic expansion. Due to the relatively low density, spectroscopic techniques combining high frequency resolution and high sensitivity are required. For this purpose, resonance enhanced multiphoton ionization of oxygen is employed in a "2+1" scheme with a two-photon transition from the ground state  $X^3\Sigma_g^-$  ( $\nu = 0$ ) to the excited state  $C^3\Pi_g$  ( $\nu = 2$ ) from which another photon ionizes the molecule.

In this contribution, experimental results of REMPI spectroscopy of oxygen superrotors, as well as their numerical analysis, will be presented.

MO 20.6 Fri 15:15 f102

**Setting the basis for a good Carrier Envelope Phase control** — ●FRANZISKA SCHÜPPEL, THOMAS SCHNAPPINGER, and REGINA DE VIVIE-RIEDEL — Department Chemie, Ludwig-Maximilians-Universität München

Controlling the process of photo reactions is a major goal in chemistry. For synthetic application, for example, it is significant to have the desired product in the best possible yield. To achieve this, one approach is to apply a few-cycle IR laser pulse to a system in the vicinity of a conical intersection (CoIn).[1] This influences the system in a way to build a superposition between the states of interest. By changing the CEP (Carrier Envelope Phase) of the laser pulse, the superposition can be controlled to lead to the preferred transfer through the CoIn and by that to the preferred product.

In this theoretical work, we want to investigate the effectiveness of a CEP control on the basis of a dissociative model system. For that, we use quantum dynamic simulations with two coupled states in the adiabatic representation. We want to describe the interaction of the laser pulse, the transition dipole moment and the non-adiabatic coupling on the CEP control and find the basis needed for an effective control of a system. By changing the shape of the CoIn of the model system, we want to test the influence of a different topography on the CEP control.

[1] P. von den Hoff *et al.*, *IEEE J SEL TOP QUANT*, **18** (2012), 119-129.

MO 20.7 Fri 15:30 f102

**Controlling the nuclear- and electron-dynamics at a conical intersection** — ●THOMAS SCHNAPPINGER, FRANZISKA SCHÜPPEL, and REGINA DE VIVIE-RIEDEL — Department of Chemistry, LMU Munich, Germany

The combination of ultra-fast optical techniques with quantum dynamics simulations give extensive insights into the nuclear and electronic dynamics of molecules and give rise to the possibility of modifying or even controlling the dynamics.

In this theoretical work we aim to control the coupled nuclear- and electron-dynamics in the vicinity of a conical intersection (CoIn). The control scheme relies on the carrier envelope phase (CEP) of a few-cycle IR pulse. The laser interaction creates an electronic superposition of the involved states before the wavepacket reaches the CoIn and influences the population transfer through the CoIn. To simulate the coupled nuclear- and electron-motion of this process we are using the NEMol (coupled nuclear- and electron-dynamics in molecules) ansatz developed in our group. In this purely quantum mechanical ansatz the quantum-dynamical description of the nuclear motion is combined with the calculation of the electron-dynamics in the eigenfunction basis.

We want to show two examples the molecule NO<sub>2</sub> and the nucleobase uracil. Both systems show relaxation dynamics back in the ground state via a CoIn after photoexcitation. But the circumstances, e.g. the transitional dipole moment and the localization of the wavepacket, differ significantly in both systems. These facts should be reflected in the controllability of the relaxation.

MO 20.8 Fri 15:45 f102

**Laser induced electron diffraction in the molecular frame** — ●JOSS WIESE<sup>1,2</sup>, JOLIUN ONVLEE<sup>1,3</sup>, ANDREA TRABATTONI<sup>1,3</sup>, EVANGELOS KARAMATSKOS<sup>1,4</sup>, SEBASTIAN TRIPPEL<sup>1,3</sup>, and JOCHEN KÜPPER<sup>1,2,3,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — <sup>2</sup>Department of Chemistry, Universität Hamburg — <sup>3</sup>The Hamburg Center for Ultrafast Imaging, Universität Hamburg — <sup>4</sup>Department of Physics, Universität Hamburg

Laser-induced electron diffraction (LIED) has the potential to provide time-dependent images of molecules at sub-femtosecond and few-picometer resolution and is therefore ideally suited to record quantum molecular movies. Here we present our work on LIED and strong field ionization off strongly aligned molecular samples. Our samples include simple linear molecules like OCS as well as prototypical biomolecules such as indole and its microsolvated clusters. Effects of the overall strong-field recollision dynamics on the orientation of the molecules will be presented and compared with time dependent density-functional theory (TDDFT) simulations as well as with novel highly efficient semiclassical simulations based on the adiabatic tunneling theory. Our findings have strong impact on the interpretation of self-diffraction experiments, where the photoelectron momentum distribution is used to retrieve molecular structures.

## MO 21: Astrophysics and Ions

Time: Friday 14:00–16:00

Location: f142

### Invited Talk

MO 21.1 Fri 14:00 f142

**Laboratory experiments as tool to understand the infrared sky at high spectral resolution** — ●GUIDO W. FUCHS — Laborastrophysik, Physik Institut, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel

In the universe, chemistry starts when atoms are expelled from the hot inner regions of evolved stars and form molecules in the cooler outer atmospheres and stellar envelopes. Thus, at the end of their lifetime low and intermediate mass asymptotic giant branch (AGB) stars and the more massive red super giants, are building up strong stellar winds which are major sources of small to intermediate sized molecules and dust in the universe. Especially molecules composed of refractory materials like metal atoms, carbon or silicon are crucial for dust formation. To understand these formation processes these precursor molecules need to be observed and identified which can be done at infrared wavelengths using high resolution spectrographs. But in addition, high resolution gas-phase spectra of possible precursor molecules are needed to compare with those from astronomical observations. In our laboratories we study the gas-phase spectra of these kinds of molecules via high resolution infrared spectroscopy. Our experimental setups will be presented and examples of investigated molecules, like TiO, Al<sub>2</sub>O and C<sub>3</sub>, will be given. In addition, recent observations using the TEXES spectrograph on the infrared telescope IRTF observations will be shown. Examples are the late-type stars, Canis Majoris, o-ceti

(Mira) and others. The observational and experimental results will be related and discussed.

MO 21.2 Fri 14:30 f142

**Rotational state selective electron recombination of CH<sup>+</sup> molecules** — ●DANIEL PAUL<sup>1</sup>, KLAUS BLAUM<sup>1</sup>, SEBASTIAN GEORGE<sup>1,2</sup>, JÜRGEN GÖCK<sup>1</sup>, MANFRED GRIESER<sup>1</sup>, FLORIAN GRUSSIE<sup>1</sup>, ROBERT VON HAHN<sup>1</sup>, NAMAN JAIN<sup>1</sup>, ÁBEL KÁLOSI<sup>1</sup>, CLAUDE KRANTZ<sup>1</sup>, HOLGER KRECKEL<sup>1</sup>, CHRISTIAN MEYER<sup>1</sup>, DAMIAN MÜLL<sup>1</sup>, OLDŘICH NOVOTNÝ<sup>1</sup>, FELIX NUESLEIN<sup>1</sup>, SUNNY SAURABH<sup>1</sup>, DANIEL W. SAVIN<sup>3</sup>, VIVIANE C. SCHMIDT<sup>1</sup>, XAVIER URBAIN<sup>4</sup>, PATRICK WILHELM<sup>1</sup>, and ANDREAS WOLF<sup>1</sup> — <sup>1</sup>Max Planck Institute for Nuclear Physics, Heidelberg, Germany — <sup>2</sup>University of Greifswald, Germany — <sup>3</sup>Columbia University, New York, NY, USA — <sup>4</sup>Institute of Condensed Matter and Nanosciences, UCLouvain, Belgium

Molecular cations in the interstellar medium (ISM) are used to trace the properties of diffuse interstellar clouds, out of which stars and planets are formed. These cations can be destroyed by dissociative recombination (DR) with electrons. Laboratory studies of DR are needed to understand molecular evolution in space. Here we have studied DR of CH<sup>+</sup>, which is of particular interest for diffuse cloud observations. In the electrostatic cryogenic storage ring CSR, CH<sup>+</sup> ions in lowest rovibrational states can be stored for DR studies at ISM-relevant con-

ditions. Using merged ion and electron beams with a recently implemented electron cooler, low energy (meV) collisions can be studied. Here, we report on rotational state selective DR rate coefficient measurements of the  $\text{CH}^+$  ion. In addition, final state branching ratios and angular fragmentation characteristics were observed.

MO 21.3 Fri 14:45 f142

**Electron Recombination Studies of  $\text{TiO}^+$  molecules** — ●NAMAN JAIN<sup>1</sup>, KLAUS BLAUM<sup>1</sup>, SEBASTIAN GEORGE<sup>1,2</sup>, JÜRGEN GÖCK<sup>1</sup>, MANFRED GRIESER<sup>1</sup>, FLORIAN GRUSSIE<sup>1</sup>, ROBERT VON HAHN<sup>1</sup>, ÁBEL KÁLOSI<sup>1</sup>, HOLGER KRECKEL<sup>1</sup>, DAMIAN MÜLL<sup>1</sup>, OLDŘICH NOVOTNÝ<sup>1</sup>, FELIX NUSSLIN<sup>1</sup>, DANIEL PAUL<sup>1</sup>, SUNNY SAURABH<sup>1</sup>, VIVIANE C. SCHMIDT<sup>1</sup>, ALBERT A. VIGGIANO<sup>3</sup>, PATRICK WILHELM<sup>1</sup>, and ANDREAS WOLF<sup>1</sup> — <sup>1</sup>Max Planck Institute for Nuclear Physics, Heidelberg, Germany — <sup>2</sup>University of Greifswald, Greifswald, Germany — <sup>3</sup>AFR Laboratory, New Mexico, USA

The complex chemical processes observed in the gas-phase of interstellar medium (ISM) are majorly based on ion reactions. Dissociative recombination (DR) of molecular ions is a dominant process in such environments that neutralizes the plasma and leads to the fragmentation of molecules. In the ISM, the titanium oxide ( $\text{TiO}^+$ ) cation can be formed by the associative ionization process between atomic titanium and oxygen. The process has been proposed to be responsible for the production of free electrons and severe atomic depletion of Ti in gas phase ISM. The inverse process, DR, is expected to be endothermic, contrary to most other cases. Precise laboratory studies on the DR of  $\text{TiO}^+$  are needed for a concrete proof of the reaction energetics, thus elucidating the molecular reaction dynamics. Such experiments are being conducted at the electrostatic Cryogenic Storage Ring (CSR) in similar conditions as in the cold ISM. Here, we report on our initial results of a  $\text{TiO}^+$  DR experiment with the electron cooler at CSR.

MO 21.4 Fri 15:00 f142

**Direct detection of nuclear scattering of sub-GeV dark matter using molecular excitations** — ●JESÚS PÉREZ-RÍOS<sup>1</sup>, HARIKRISHNAN RAMANI<sup>2</sup>, OREN SLONE<sup>3</sup>, and ROUVEN ESSIG<sup>4</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — <sup>2</sup>Berkeley Center for Theoretical Physics, Department of Physics, University of California, Berkeley, California 94720, USA — <sup>3</sup>Princeton Center for Theoretical Science, Princeton University, Princeton, New Jersey 08544, USA — <sup>4</sup>C. N. Yang Institute for Theoretical Physics, Stony Brook University, New York 11794-384, USA

The evidence for the existence of dark matter, which makes up about 85% of the matter density in the Universe, is overwhelming. Efforts to detect galactic dark matter particles in the laboratory are crucial for developing a detailed understanding of the particle nature of dark matter. The past decades have seen tremendous progress in direct-detection searches for Weakly Interacting Massive Particles, which have masses above the proton. However, dark matter with masses below the proton is woefully underexplored, despite being theoretically well-motivated. We propose a novel direct detection concept to search for dark matter with masses in the 100 keV to 100 MeV range. Here, dark matter particles scatter off molecules in a gas and exciting a vibrational and rotational state of the molecule. The excited rovibrational mode relaxes rapidly and produces a spectacular signal consisting of multiple infrared photons, which can be observed with ultrasensitive photodetectors

MO 21.5 Fri 15:15 f142

**Towards *para-ortho* conversion in ammonia** — ●GUANG YANG<sup>1,4</sup>, DOMINIC LAUMER<sup>2,4</sup>, CHRISTOPH HEYL<sup>2</sup>, ANDREY YACHMENEV<sup>1,3</sup>, INGMAR HARTL<sup>2</sup>, and JOCHEN KÜPPER<sup>1,3,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg — <sup>2</sup>DESY, Hamburg — <sup>3</sup>The Hamburg Center for Ultrafast Imaging, Hamburg — <sup>4</sup>Department of Physics, Universität of Hamburg, Hamburg

The spectrum of ammonia can be considered as the combination of the spectra of two distinct molecules, *para* and *ortho*, which have different total-nuclear-spin number  $I=1/2$  and  $I=3/2$ , respectively, of the

three hydrogen atoms. It is considered a good approximation that interconversions of nuclear spin isomers are forbidden. However, weak hyperfine couplings weakly allow the conversion happen.

We present a combined theoretical and experimental study of the hyperfine-resolved spectrum of ammonia. The calculations have been performed using the variational approach TROVE, a new spectroscopically determined potential energy surface, and *ab initio* quadrupole, spin-spin, and spin-rotation coupling surfaces. For the spectroscopic observation of the *para-ortho* conversion, we utilized a mid-infrared frequency-comb Fourier-transform spectrometer [2] to perform first survey scans of the absorption spectrum in the 4  $\mu\text{m}$  region. We investigated the self-broadening and self-shift. Currently, we are optimizing the experimental setup to improve the resolution and sensitivity and search the weak *para-ortho* conversion lines.

[1] S. N. Yurchenko, et al., *J. Mol. Spectrosc.*, **245**, 126 (2007)

[2] V. Silva de Oliveira, et al., *arXiv:1904.02611*, (2019)

MO 21.6 Fri 15:30 f142

**Delayed electron detachment and fragmentation of laser-excited  $\text{Al}_4^-$  clusters** — ●FELIX NUSSLIN<sup>1</sup>, KLAUS BLAUM<sup>1</sup>, PAUL FISCHER<sup>2</sup>, SEBASTIAN GEORGE<sup>2</sup>, JÜRGEN GÖCK<sup>1</sup>, MANFRED GRIESER<sup>1</sup>, ROBERT VON HAHN<sup>1</sup>, ODED HEBER<sup>3</sup>, ÁBEL KÁLOSI<sup>1</sup>, STAV KNAFFO<sup>4</sup>, MICHAEL LEMBACH<sup>5</sup>, YANNICK MEES<sup>5</sup>, DAMIAN MÜLL<sup>1</sup>, GEREON NIEDNER-SCHATTEBURG<sup>5</sup>, OLDŘICH NOVOTNÝ<sup>1</sup>, DANIEL PAUL<sup>1</sup>, HILEL RUBINSTEIN<sup>3</sup>, SUNNY SAURABH<sup>1</sup>, VIVIANE C. SCHMIDT<sup>1</sup>, LUTZ SCHWEIKHARD<sup>2</sup>, RAJ SINGH<sup>3</sup>, YONI TOKER<sup>4</sup>, PATRICK WILHELM<sup>1</sup>, ANDREAS WOLF<sup>1</sup>, and YITZHAK YONAS<sup>4</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — <sup>2</sup>Universität Greifswald, Institut für Physik, 17487 Greifswald, Germany — <sup>3</sup>Weizmann Institute of Science, 76100 Rehovot, Israel — <sup>4</sup>Bar-Ilan University, 5290002 Ramat-Gan, Israel — <sup>5</sup>Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany

The Delayed Electron Detachment (DED) and fragmentation of  $\text{Al}_4^-$  ions were studied in the Heidelberg electrostatic Cryogenic Storage Ring (CSR) [1] by merging nanosecond OPO laser pulses with the stored  $\text{Al}_4^-$  ion beam in one of the four  $\sim 2.6$  m linear, field-free experimental sections. Up to 600  $\mu\text{s}$  after a laser pulse, neutrals due to electron detachment were detected downstream with a MicroChannel Plate (MCP) detector. With a second, movable MCP detector, we observed prompt and delayed fragment events on a 300  $\mu\text{s}$  timescale. To examine DED near the Adiabatic Electron Affinity (AEA  $\sim 2.2$  eV) of  $\text{Al}_4^-$ , we varied the photon energy in 5 meV steps from 1.8–2.3 eV. For up to 65 s, cooling of the ions in the extremely low blackbody radiation field of CSR ( $T_{\text{eff}} \sim 15$  K [2]) was observed. The studies yield insight into the cooling and AEA of the  $\text{Al}_4^-$  clusters.

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

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

MO 21.7 Fri 15:45 f142

**The electronic spectrum of  $\text{Au}_3^+$  and  $\text{Au}_3\text{N}_2\text{O}^+$**  — ●MARKO FÖRSTEL<sup>1</sup>, KARIM SAROUKH<sup>1</sup>, KAI POLLOW<sup>1</sup>, ESTE A. NAJIB<sup>1</sup>, ALICE GREEN<sup>2</sup>, STUART MACKENZIE<sup>2</sup>, and OTTO DOPFER<sup>1</sup> — <sup>1</sup>Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany — <sup>2</sup>Department of Chemistry, University of Oxford, Oxford, UK

In this talk we present our latest findings on the optical spectra of  $\text{Au}_3^+$  and  $\text{Au}_3\text{N}_2\text{O}^+$  clusters. By using our recently enhanced setup we are able to record the optical spectra of very dilute targets in a quality that is sufficient to resolve vibrational progressions [1,2]. This allows comparisons to TD-DFT calculations on a hitherto unavailable precision. This is especially interesting in the case of gold, where theoretical models tend to have difficulties due to relativistic effects, spin-orbit coupling, and the participation of d electrons in bonding and charge\*transfer effects. Thus our results will lead to a better understanding of electronic structure and the resulting catalytic properties of Au at a molecular level.

[1] M. Förstel et al., *Rev. Sci. Instr.* **88**, 2017

[2] M. Förstel et al., *Angew. Chem. Int. Ed.* **131**, 2019