

Molecular Physics Division Fachverband Molekülphysik (MO)

Stephan Schlemmer
I. Physikalisches Institut
Zülpicher Straße 77
50937 Köln
schlemmer@ph1.uni-koeln.de

Overview of Invited Talks and Sessions (Lecture halls MO-H5, MO-H6, MO-H7, and MO-H8; Poster P)

Invited Talks

MO 3.1	Mon	16:30–17:00	MO-H5	Electronic Properties of Small Gold Cluster Cations — ●MARKO FÖRSTEL, KAI POLLOW, TAARNA STUEMUND, NIMA-NOAH NAHVI, NIKITA KAVKA, ROLAND MITRIC, OTTO DOPFER
MO 5.1	Tue	10:30–11:00	MO-H6	Extending coherent multidimensional spectroscopy to new target systems and new light sources — ●LUKAS BRUDER
MO 16.1	Thu	10:30–11:00	MO-H5	Infrared Spectroscopy of Ionic Hydrogen-Helium Complexes — ●OSKAR ASVANY, STEPHAN SCHLEMMER
MO 18.1	Thu	14:30–15:00	MO-H5	High-resolution spectroscopic studies of transient carbon-rich species — ●SVEN THORWIRTH, OSKAR ASVANY, STEPHAN SCHLEMMER

Invited talks of the joint symposium Laboratory Astrophysics (SYLA)

See SYLA for the full program of the symposium.

SYLA 1.1	Mon	14:00–14:30	Audimax	Probing chemistry inside giant planets with laboratory experiments — ●DOMINIK KRAUS
SYLA 1.2	Mon	14:30–15:00	Audimax	Inner-shell photoabsorption of atomic and molecular ions — ●STEFAN SCHIPPERS
SYLA 1.3	Mon	15:00–15:30	Audimax	Molecular Astrophysics at the Cryogenic Storage Ring — ●HOLGER KRECKEL
SYLA 1.4	Mon	15:30–16:00	Audimax	Observing small molecules in stellar giants - High spectral resolution infrared studies in the laboratory, on a mountain, and high up in the air — ●GUIDO W. FUCHS
SYLA 2.1	Mon	16:30–17:00	Audimax	State-to-State Rate Coefficients for NH₃-NH₃ Collisions obtained from Pump-Probe Chirped-Pulse Experiments — ●CHRISTIAN P. ENDRES, PAOLA CASELLI, STEPHAN SCHLEMMER
SYLA 2.4	Mon	17:30–18:00	Audimax	A multifaceted approach to investigate the reactivity of PAHs under electrical discharge conditions — ●DONATELLA LORU, AMANDA L. STEBER, JOHANNES M. M. THUNNISSEN, DANIEL B. RAP, ALEXANDER K. LEMMENS, ANOUK M. RIJS, MELANIE SCHNELL
SYLA 2.5	Mon	18:00–18:30	Audimax	Exploring the Femtosecond Dynamics of Polycyclic Aromatic Hydrocarbons Using XUV FEL Pulses — ●JASON LEE, DENIS TIKHONOV, BASTIAN MANSCHWETUS, MELANIE SCHNELL

Invited talks of the joint PhD symposium Solid-state Quantum Emitters Coupled to Optical Microcavities (SYPD)

See SYPD for the full program of the symposium.

SYPD 1.1	Mon	16:30–17:00	AKjDPG-H17	Fiber-based microcavities for efficient spin-photon interfaces — ●DAVID HUNGER
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SYPD 1.2	Mon	17:00–17:30	AKjDPG-H17	A fast and bright source of coherent single-photons using a quantum dot in an open microcavity — ●RICHARD J. WARBURTON
SYPD 1.3	Mon	17:30–18:00	AKjDPG-H17	New host materials for individually addressed rare-earth ions — ●SEBASTIAN HORVATH, SALIM OURARI, LUKASZ DUSANOWSKI, CHRISTOPHER PHENICIE, ISAIAH GRAY, PAUL STEVENSON, NATHALIE DE LEON, JEFF THOMPSON
SYPD 1.4	Mon	18:00–18:30	AKjDPG-H17	A multi-node quantum network of remote solid-state qubits — ●RONALD HANSON

Invited talks of the joint symposium SAMOP Dissertation Prize 2022 (SYAD)

See SYAD for the full program of the symposium.

SYAD 1.1	Tue	14:00–14:30	Audimax	New insights into the Fermi-Hubbard model in and out-of equilibrium — ●ANNABELLE BOHRDT
SYAD 1.2	Tue	14:30–15:00	Audimax	Searches for New Physics with Yb⁺ Optical Clocks — ●RICHARD LANGE
SYAD 1.3	Tue	15:00–15:30	Audimax	Machine Learning Methodologies for Quantum Information — ●HENDRIK POULSEN NAUTRUP
SYAD 1.4	Tue	15:30–16:00	Audimax	Precision Mass Measurement of the Deuteron’s Atomic Mass — ●SASCHA RAU

Invited talks of the joint symposium Rydberg Physics in Single-Atom Trap Arrays (SYRY)

See SYRY for the full program of the symposium.

SYRY 2.1	Wed	10:30–11:00	Audimax	Many-body physics with arrays of Rydberg atoms in resonant interaction — ●ANTOINE BROWAEYS
SYRY 2.2	Wed	11:00–11:30	Audimax	Optimization and sampling algorithms with Rydberg atom arrays — ●HANNES PICHLER
SYRY 2.3	Wed	11:30–12:00	Audimax	Slow dynamics due to constraints, classical and quantum — ●JUAN P. GARRAHAN
SYRY 3.3	Wed	14:30–15:00	Audimax	New frontiers in quantum simulation and computation with neutral atom arrays — ●GIULIA SEMEGHINI
SYRY 3.4	Wed	15:00–15:30	Audimax	New frontiers in atom arrays using alkaline-earth atoms — ●ADAM KAUFMAN
SYRY 3.5	Wed	15:30–16:00	Audimax	Spin squeezing with finite range spin-exchange interactions — ●ANA MARIA REY

Invited talks of the joint symposium Quantum Cooperativity of Light and Matter (SYQC)

See SYQC for the full program of the symposium.

SYQC 1.1	Thu	10:30–11:00	Audimax	Super- and subradiant states of an ensemble of cold atoms coupled to a nanophotonic waveguide — ●ARNO RAUSCHENBEUTEL
SYQC 1.6	Thu	12:00–12:30	Audimax	Cooperative Effects in Pigment-Protein Complexes: Vibronic Renormalisation of System Parameters in Complex Vibrational Environments — ●SUSANA F. HUELGA
SYQC 2.1	Thu	14:00–14:30	Audimax	Quantum simulation with coherent engineering of synthetic dimensions — ●PAOLA CAPPELLARO
SYQC 2.6	Thu	15:30–16:00	Audimax	Quantum Fractals — ●CRISTIANE MORAIS-SMITH

Sessions

MO 1.1–1.4	Mon	10:30–11:30	MO-H5	Quantum-Control
MO 2.1–2.9	Mon	14:00–16:15	MO-H5	X-ray FELs (joint session MO/A)
MO 3.1–3.6	Mon	16:30–18:15	MO-H5	Electronic I
MO 4.1–4.4	Tue	10:30–11:30	MO-H5	Electronic II
MO 5.1–5.6	Tue	10:30–12:15	MO-H6	Femtosecond Spectroscopy I

MO 6.1–6.6	Tue	10:30–12:00	MO-H7	Theory
MO 7.1–7.8	Tue	10:30–12:30	MO-H8	Cold Molecules
MO 8.1–8.24	Tue	16:30–18:30	P	Poster 1
MO 9.1–9.6	Wed	10:30–12:00	MO-H5	Femtosecond Spectroscopy II
MO 10.1–10.7	Wed	10:30–12:15	MO-H6	XUV-spectroscopy
MO 11.1–11.5	Wed	10:30–11:45	MO-H7	Photochemistry I
MO 12	Wed	12:45–13:15	MO-MV	Annual General meeting
MO 13.1–13.5	Wed	14:30–15:45	MO-H5	Femtosecond Spectroscopy III
MO 14.1–14.6	Wed	14:30–16:00	MO-H6	Photochemistry II
MO 15.1–15.23	Wed	16:30–18:30	P	Poster 2
MO 16.1–16.6	Thu	10:30–12:15	MO-H5	Ions
MO 17.1–17.3	Thu	10:30–11:15	MO-H6	Precision
MO 18.1–18.7	Thu	14:30–16:30	MO-H5	High-Resolution Spectroscopy
MO 19.1–19.18	Thu	16:30–18:30	P	Poster 3

Annual General Meeting of the Molecular Physics Division

Wednesday 12:45–13:15 MO-MV

- report
- Miscellaneous

MO 1: Quantum-Control

Time: Monday 10:30–11:30

Location: MO-H5

MO 1.1 Mon 10:30 MO-H5

Coherent control of molecular nitrogen ionization — ●AARON NGAI¹, MATTEO BONANOMI^{2,3}, LUKAS BRUDER¹, DAVID BUSTO^{1,4}, CARLO CALLEGARI⁵, PAOLO CARPEGGIANI⁶, GIOVANNI DE NINNO^{5,7}, MICHELE DEVETTA², MICHELE DI FRAIA⁵, KATRIN DULITZ¹, DAVID FACCIALÀ², LUCA GIANNESI^{5,8}, ALEXEI GRUM-GRZHIMAILO⁹, ELENA GRYZLOVA⁹, KENICHI L. ISHIKAWA^{10,11}, IOANNIS MAKOS¹, PRAVEEN K. MAROJU¹, TOMMASO MAZZA¹², MICHAEL MEYER¹², PAOLO PISERI³, OKSANA PLEKAN⁵, KEVIN C. PRINCE^{5,13}, GIUSEPPE SANSONE¹, SIMONE SPAMPINATI⁵, FRANK STIENKEMEIER¹, KIYOSHI UEDA¹⁴, and CATERINA VOZZI² — ¹Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, Germany — ²Istituto di Fotonica e Nanotecnologie, CNR, Milano, Italy, — ³Dipartimento di Fisica and CIMaNa, Università degli Studi di Milano, Italy — ⁴Department of Physics, Lund University, Sweden — ⁵Elettra - Sincrotrone Trieste S.C.p.A., Basovizza, Trieste, Italy — ⁶Institut für Photonik, Technische Universität Wien, Austria — ⁷Laboratory of Quantum Optics, University of Nova Gorica, Slovenia — ⁸Istituto Nazionale di Fisica Nucleare, Laboratori Nazionali di Frascati, Italy — ⁹Skobel'syn Institute of Nuclear Physics, Lomonosov Moscow State University, Russia — ¹⁰Graduate School of Engineering, The University of Tokyo, Japan — ¹¹Research Institute for Photon Science and Laser Technology, The University of Tokyo, Japan — ¹²European XFEL, Schenefeld, Germany — ¹³Department of Chemistry and Biotechnology, School of Science, Swinburne University of Technology, Australia — ¹⁴Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan

We investigated the coherent control of molecular photoionization by using phase-locked first and second harmonic radiation from the Free-Electron Laser FERMI. As in the case of atomic coherent control [1, 2], interference between single-photon and two-photon ionization of the valence electrons was observed, and was manifested as asymmetry in the photoelectron angular distributions. Oscillations of this asymmetry were observed as a function of the relative phase difference between the two wavelengths. In our recent experimental campaign, we used a gas mixture of molecular nitrogen and atomic neon, with the neon serving as a reference target. We impulsively aligned the nitrogen molecules in the cold molecular beam using infrared pulses, and measured the photoelectron angular distributions using a Velocity Map Imaging spectrometer. Here we present preliminary experimental results as well as preliminary results from theoretical calculations.

[1] K. C. Prince *et al.* *Nat. Photonics* **10**, 176 (2016).

[2] D. You *et al.* *Phys. Rev. X* **10**, 031070 (2020).

MO 1.2 Mon 10:45 MO-H5

Channel- and Full Angle-Resolved Strong-Field Ionization and Electron Rescattering Probabilities in the Molecular Frame — ●FEDERICO BRANCHI¹, FELIX SCHELL¹, TILMANN EHRLICH¹, MARK MERO¹, HORST ROTTKE¹, VARUN MAKHIJA², SERGUEI PATCHKOVSKII¹, MARC J. J. VRAKING¹, and JOCHEN MIKOSCH¹ — ¹Max-Born-Institut, Berlin, Germany — ²Univ. of Mary Washington, Fredericksburg, USA

By analyzing lab frame coherent rotational wavepacket evolution in a reaction microscope experiment [1] we measure the angle- and channel-resolved ionization and electron rescattering probabilities in the asymmetric-top molecule 1,3-butadiene. With this approach we achieve both polar and azimuthal angle-resolved molecular frame information, in contrast to previous works [2,3].

Our results indicate that the nodal structure of the ionizing orbitals is more strongly reflected in the electron rescattering probability rather than in the ionization probability. The molecular frame electron rescattering probability is significantly influenced by structured, channel-specific continuum electron wavepackets. Experimental results are compared with results from a TD-RIS [4] ab-initio simulation.

[1] Wang *et al.*, *Phys. Rev. A* **96**, 023424 (2017)

[2] Mikosch *et al.*, *Phys. Rev. Lett.* **110**, 023004 (2013)

[3] Schell *et al.*, *Sc. Adv.* **4**, 5 aap8148 (2018)

[4] Spanner and Patchkovskii, *Phys. Rev. A* **80**, 063411 (2009)

MO 1.3 Mon 11:00 MO-H5

quantum state control of chiral molecules — ●JUHYEON LEE¹, JOHANNES BISCHOFF¹, ALICIA O. HERNANDEZ-CASTILLO¹, BORIS SARTAKOV^{1,2}, GERARD MEIJER¹, and SANDRA EIBENBERGER-ARIAS¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Molecular Physics, Faradayweg 4-6, D-14195 Berlin — ²Prokhorov General Physics Institute, Russian Academy of Science, Vavilovstreet 38, 119991, Moscow, Russia

Recently, the enantiomer-specific state transfer (ESST) method [1] was demonstrated using tailored microwave fields. This method allows to populate or depopulate a rotational state of a chosen enantiomer, providing a way of quantum-controlled chiral separation. Thus far, the transfer efficiency of ESST has been limited by thermal population of the energy levels participating in ESST [1,2] and by spatial degeneracy [3]. To address these prior limitations, we developed a new experimental scheme which increases the efficiency of ESST by over a factor of ten compared to previously reported values [4]. This scheme enables a quantitative comparison between experiment and theory for the transfer efficiency in the simplest ESST triangle which includes the absolute ground state level. Details of this scheme and experimental results will be discussed in the presentation.

[1] S. Eibenberger, *et al.*, *Phys. Rev. Lett.* **118**, 123002 (2017)

[2] P. Cristóbal, *et al.*, *Angew. Chem. Int. Ed.* **56**, 12512 (2017)

[3] M. Leibscher, *et al.*, arXiv:2010.09296 (2020)

[4] J. H. Lee, *et al.*, arXiv:2112.09058 (2021)

MO 1.4 Mon 11:15 MO-H5

Atom-molecule and molecule-molecule collisions in ultracold quantum gas mixtures of 39K atoms and rovibronic ²³Na³⁹K ground-state molecules — ●PHILIPP GERSEMA¹, MARA MEYER ZUM ALTEN BORGLOH¹, KAI KONRAD VOGES¹, TORSTEN HARTMANN¹, LEON KARPA¹, ALESSANDRO ZENESINI², and SILKE OSPELKAUS¹ — ¹Leibniz Universität Hannover, Institut für Quantenoptik — ²Universita di Trento, Dipartimento di Fisica

Ultracold heteronuclear molecules enable the study of fascinating new physical phenomena in the quantum realm. These arise from the degrees of freedom of vibration and rotation and the large permanent dipole moment of heteronuclear molecules. However, especially for the investigation of novel phenomena in quantum many-body physics, a precise understanding of the collision properties of heteronuclear polar molecules is mandatory. Here we report on our experiments on collisions in pure quantum gases of bosonic NaK molecules and atom-molecule mixtures. We discuss photoinduced collisional processes and hyperfine dependent atom-molecule scattering and report on our progress towards photoassociation of weakly bound triatomic NaK₂ molecules.

MO 2: X-ray FELs (joint session MO/A)

Time: Monday 14:00–16:15

Location: MO-H5

MO 2.1 Mon 14:00 MO-H5

Following excited-state chemical shifts in molecular ultrafast x-ray photoelectron spectroscopy — ●DENNIS MAYER¹, FABIANO LEVER¹, DAVID PICCONI¹, JAN METJE¹, SKIRMAN-TAS ALISAUSKAS², FRANCESCA CALEGARI³, STEFAN DÜSTERER², CHRISTOPHER EHLERT⁴, RAIMUND FEIFFEL⁵, MARIO NIEBUHR¹, BASTIAN MANSCHWETUS², MARION KUHLMANN², TOMASO MAZZA⁶,

MATTHEW S. ROBINSON^{1,3}, RICHARD J. SQUIBB⁵, ANDREA TRABATTONI³, MANS WALLNER⁵, PETER SAALFRANK¹, THOMAS J.A. WOLF⁷, and MARKUS GÜHR¹ — ¹University of Potsdam, Germany — ²DESY, Hamburg, Germany — ³CFEL, Hamburg, Germany — ⁴HITS gGmbH, Heidelberg, Germany — ⁵University of Gothenburg, Sweden — ⁶European XFEL GmbH, Hamburg, Germany — ⁷Stanford PULSE Institute, Menlo Park, USA

We demonstrate the capabilities of time-resolved x-ray photoelectron spectroscopy with a study of the UV-excited dynamics of 2-thiouracil conducted at the FLASH free electron laser in Hamburg, Germany. By probing sulfur 2p core electrons, we discover that a significant part of the excited-state population relaxes to the ground state within 220-250fs. Observed spectral shifts can be directly attributed to a charge redistribution over the molecule during the relaxation process. Additionally, we observe a 250fs oscillation in the kinetic energy of the excited-state population which reveals a coherent population exchange among electronic states.

MO 2.2 Mon 14:15 MO-H5

How to produce nuclear-polarized hydrogen molecules and for what they can be used — ●RALF ENGELS — Institut für Kernphysik, FZ Jülich/GSI Darmstadt

In accelerator experiments polarized proton/deuteron beams and hydrogen/deuterium targets are an important tool to investigate the spin dependence of the nuclear forces. Both can be made with a polarized atomic beam source, a modern version of a Rabi apparatus. By recombination of these atoms hyper-polarized H_2 , D_2 and HD molecules in many hyperfine substates are produced and can be used for further applications. For example, the recombination process itself and his dependence on the electron spin, surface materials or external radiation can be investigated as well as the coupling of the nuclear spins with the rotational magnetic moment. In nuclear physics the polarized molecules allow to increase the target density and with polarized molecular ions a better stripping injection into storage rings is possible. Further applications may be the use as polarized fuel for fusion reactors or the search for an electric dipole moment of the nucleons.

MO 2.3 Mon 14:30 MO-H5

Correlation fingerprints in the x-ray induced Coulomb explosion of iodopyridine — ●BENOÎT RICHARD^{1,2,3}, JULIA SCHÄFER^{1,4}, ZOLTAN JUREK¹, ROBIN SANTRA^{1,2,3,4}, and LUDGER INHESTER^{1,2} — ¹Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany — ²The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany — ³Department of Physics, Universität Hamburg, Notkestr. 9-11, 22607 Hamburg, Germany — ⁴Department of Chemistry, Universität Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

Coulomb explosion induced by XFEL radiation is a promising experimental tool to image individual molecules. However, the amount of information about the original molecule geometry that can be inferred from the measured final momenta of the produced ions is presently unknown. In particular, the data acquired by state of the art multi-coincidence measurement techniques contains information about correlations between the different measured ions, but how to exploit this extra information for geometry reconstruction is currently unclear. In this work we propose a first step in this direction. To this end we analyze simulation data for the x-ray induced Coulomb explosion of 2-iodopyridine and describe its fragmentation dynamics. Crucially, we show that a collision between two ions during the Coulomb explosion causes strong and possibly measurable correlations between their final momenta.

MO 2.4 Mon 14:45 MO-H5

Universal Reconstruction of Nanoclusters from Wide-Angle X-Ray Diffraction Patterns with Physics-Informed Neural Networks — ●THOMAS STIELOW 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 analysis of unsupported and short-lived nanosystems, while the exact inversion of the scattering patterns still proves challenging [1]. Deep learning, on the other hand, is widely used in data sciences for the extraction of information from images and has recently been used to accelerate parameter reconstructions from wide-angle scattering patterns [2]. Here, we show how a deep neural network can be used to reconstruct complete three-dimensional object models of uniform, convex particles from single two-dimensional wide-angle scattering patterns. Through physics-informed training the reconstructions achieve unprecedented levels of detail on real-world experimental data [3].

[1] I. BARKE *et al.* Nat. Commun. **6**, 6187 (2015).

[2] T. STIELOW *et al.* Mach. Learn.: Sci. Technol. **1**, 045007 (2020).

[3] T. STIELOW and S. SCHEEL, Phys. Rev. E **103**, 053312 (2021).

MO 2.5 Mon 15:00 MO-H5

Ultrafast Auger spectroscopy of 2-thiouracil — ●F. LEVER¹, D. MAYER¹, D. PICCONI¹, J. METJE¹, S. ALISAUSKAS², F. CALEGARI², S. DÜSTERER², C. EHLERT³, R. FEIFEL⁴, M. NIEBUHR¹, B. MANSCHWETUS², M. KUHLMANN², T. MAZZA⁶, M. S. ROBINSON⁵, R. J. SQUIBB⁴, A. TRABATTONI⁵, M. WALLNER⁴, P. SAALFRANK¹, T. J. A. WOLF⁷, and M. GÜHR¹ — ¹Universität Potsdam — ²Deutsches Elektronen Synchrotron (DESY) — ³Heidelberg Institute for Theoretical Studies — ⁴Department of Physics, Gothenburg University — ⁵Center for Free-Electron Laser Science (CFEL) — ⁶European XFEL — ⁷SLAC, Stanford

Investigating the effects of UV exposure in thionucleobases can shed light on the mechanisms that cause the formation of DNA lesions. In this talk, we show how ultrafast x-ray spectroscopy can be used to gain information on such processes. We study the sulfur 2p Auger spectrum of 2-thiouracil in a uv-pump, x-ray probe experiment at the free electron laser FLASH. We observe ultrafast dynamics in the electron kinetic energy spectrum, happening on time scales of 100fs to 1ps. Using a simple coulomb model for the electron binding energies, aided by quantum chemical calculations of the electronic states energy, we deduce an elongation of the C-S bond on a 100fs time scale. The geometric changes trigger internal conversion from the initially excited S2 state to the S1 state. For longer pump-probe delays, the observed timescales provide evidence for inter system crossing from the S1 state to the triplet manifold [1].

[1] F Lever et al 2020 J. Phys. B: At. Mol. Opt. Phys. **54** 014002

MO 2.6 Mon 15:15 MO-H5

Control of bionanoparticles with electrical fields — ●JANNIK LÜBKE^{1,2,3}, LENA WORBS^{1,2}, ARMANDO ESTILLORE¹, AMIT SAMANTA¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ²Department of Physics, Universität Hamburg, Hamburg, Germany — ³Center for Ultrafast Imaging, Universität Hamburg, Hamburg, Germany

Single-particle imaging (SPI) experiments at free-electron lasers (FELs) promise high-resolution imaging of the structure and dynamics of nanoparticles and macromolecules. Guiding sample particles into the 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. Optimized delivery of identical nanoparticles is key to efficient and successful SPI experiments. Here, we present an approach for the production of purified high-density beams of a broad variety of biological nanoparticles, demonstrated on a large protein. We establish control through electric fields, aiming at charge state or conformational state selectivity. This is especially relevant for soft biological samples, such as proteins or protein complexes, which in uncontrolled environment are prone to structural instability.

MO 2.7 Mon 15:30 MO-H5

Tracing Inner-Shell-Ionization-Induced Dynamics of Water Molecules Using an X-ray Free-Electron Laser and Ab-Initio Simulations — ●LUDGER INHESTER¹, TILL JAHNKE², RENAUD GUILLEMIN³, and MARIA NOVELLA PIANCASTELLI^{3,4} — ¹Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²European XFEL, Schenefeld — ³Sorbonne Université, CNRS, LCPMR, Paris — ⁴Uppsala University, Uppsala

The response of molecules to ionizing radiation is of utmost relevance to many research areas. Multi-coincidence signals from experiments at x-ray free-electrons lasers provide us new opportunities to study the dynamics of molecules upon inner-shell ionization. In a recent experiment at the European XFEL, water vapor has been exposed to intense x-ray pulses and all the resulting ion fragments have been recorded in coincidence. In this talk, I will discuss how through ab-initio simulations of the multiphoton multiple ionization and fragmentation dynamics we could identify distinct signatures in the ion momentum data with different break-up patterns. By combining experimental results and theoretical modeling, we were able to image the dissociation dynamics of water after core-shell ionization and subsequent Auger decay in unprecedented detail and uncover fundamental dynamical patterns relevant for the radiation damage in aqueous environments. [1]

[1] T. Jahnke et al., Phys. Rev. X **11**, 041044 (2021)

MO 2.8 Mon 15:45 MO-H5

Competition of interatomic Coulombic decay and autoionization in doubly excited helium nanodroplets — ●BJÖRN BAS-

TIAN, JAKOB D. ASMUSSEN, LTAIEF B. LTAIEF, AKGASH SUNDARALINGAM, CATHARINA I. VANDEKERCKHOVE, and MARCEL MUDRICH — Department of Physics and Astronomy, Aarhus University, DK

Double-excitation states in helium atoms are an important model system to study electron-electron correlation. Doubly excited atoms can autoionize and the interference with the direct ionization pathway gives rise to characteristic Fano peaks in the photoexcitation spectrum [1] which has also been observed in helium nanodroplets [2]. In dimers or clusters, the de-excitation energy can instead be transferred and cause ionization of the environment. Theory has shown, that this interatomic Coulombic decay (ICD) pathway becomes fast at small interatomic distances and competes with autoionization especially in large environments [3].

We present photoion-photoelectron coincidence spectra around the Fano resonance below the $N=2$ ionization threshold in helium nanodroplets that have been recorded at our new endstation at the AMO-Line of the ASTRID2 synchrotron at Aarhus. Slow electrons reveal ICD or secondary inelastic scattering. Highly resolved electron spectra recorded at various photon energies across the Fano resonance reveal the details of the decay process.

[1] Domke et al. *Phys. Rev. Lett.* **66**, 1306 (1991). [2] LaForge et al.

Phys. Rev. A **93**, 050502 (2016). [3] Jabbari et al. *Chem. Phys. Lett.* **754**, 137571 (2020).

MO 2.9 Mon 16:00 MO-H5

Simulating Molecular Diffraction Patterns using CMIdiff — •NIDIN VADASSERY^{1,3}, SEBASTIAN TRIPPEL^{1,2}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Department of Physics, Universität Hamburg — ³Department of Chemistry, Universität Hamburg

The structure and time-dependent dynamics of molecules in the gas phase reveal a plethora of information about fundamental processes in nature. X-rays and electrons are typically used to image the molecular structure using diffraction techniques. In that respect, x-ray pulses provided by XFELs have the potential to study the chemical dynamics of gaseous molecules on the ultrafast time scale with sub-picometer spatial resolution. Here, we present our computational results using CMIdiff, an in-house software package developed to compare experimental diffraction images with theory. The package incorporates various aspects of x-ray diffraction experiments, e.g., angular distributions of molecular samples.

MO 3: Electronic I

Time: Monday 16:30–18:15

Location: MO-H5

Invited Talk

MO 3.1 Mon 16:30 MO-H5

Electronic Properties of Small Gold Cluster Cations — •MARKO FÖRSTEL¹, KAI POLLOW¹, TAARNA STUEMUND¹, NIMANOAH NAHVI¹, NIKITA KAVKA², ROLAND MITRICO², and OTTO DOPFER¹ — ¹TU Berlin, Berlin, Germany — ²Uni Würzburg, Würzburg, Germany

Recent instrumental improvements allow us to take a close look at the properties of excited states of metal cluster ions.^[1] The electronic properties of these clusters are of particular interest, as they vary greatly depending on geometry and composition. Thus they hold great potential towards tailored optical or catalytic properties. Unfortunately, theoretical predictions of their properties can be tricky due to relativistic effects and a strong multi-reference character. Detailed experimental information are thus of particular importance.

In this talk we discuss optical spectra of small gold cluster cations and compare them with those obtained by various quantum chemical calculations. We show that TD-DFT calculations make robust predictions only in special cases and even mislead in others.^[2] Furthermore, we discuss the interaction of the clusters with atomic and molecular ligands in the ground and excited states using the example of Au_2^+-X with $X = Ar, N_2$ and N_2O . It can be seen that the Au_2^+ - ligand interaction is weak in the ground state and decreases even further in the excited state.^[3,4]

[1] Förstel et al. *Rev. Sci. Instr.* **88**, 2017 [2] Förstel et al. *Angew. Chem. Int. Ed.* **58**, 2019 [3] Förstel et al. *Angew. Chem. Int. Ed.* **123**, 2020 [4] Förstel et al. *Chem. Eur. J.* **27**, 2021

MO 3.2 Mon 17:00 MO-H5

Simulation of Two-Dimensional Electronic Spectra of molecular aggregates: a Hierarchy of Stochastic Pure State approach — •LIPENG CHEN¹, DORAN I.G. BENNETT², and ALEXANDER EISFELD¹ — ¹Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Str 38, Dresden, Germany — ²Department of Chemistry, Southern Methodist University, PO Box 750314, Dallas, TX, USA

Modern techniques of time-resolved nonlinear optical spectroscopy have expanded our understanding of the photophysics of molecular aggregates, which is of particular importance for unravelling excitonic relaxation and dephasing processes in both artificial materials and photosynthetic complexes. In particular, two dimensional electronic spectroscopy has become a powerful technique to probe molecular excitons in the visible region and reveal couplings and relaxation pathways. We develop a new methodology for simulating two dimensional electronic spectra of molecular aggregates with strong coupling of electronic excitation to a structured environment by combining the stochastic hierarchy of pure states (HOPS) method with the nonlinear response function formalism. In our approach, the third-order response functions are evaluated by employing a novel propagation scheme where

the combined ket and bra states are propagated in an augmented electronic Hilbert space. The new approach shows fast convergence properties with respect to the number of stochastic trajectories, providing a promising technique for numerical calculation of two dimensional spectra of large molecular aggregates.

MO 3.3 Mon 17:15 MO-H5

Chlorophyll Excitation in Photosystem 1 Tuned by the Protein Environment: Insights from Fully Atomistic QM/MM — •SEBASTIAN REITER, FERDINAND KISS, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München, München

Photosystem 1 (PS1) is one of the most efficient natural light-harvesting systems. Energy is absorbed by an antenna complex of chlorophylls and transferred to a reaction core, where it drives one of the fundamental redox processes of photosynthesis. Understanding the high efficiency of PS1 requires an accurate evaluation of the chlorophyll absorption energies, affected by their natural environment (site energies). However, this is challenging because not only the full electrostatic environment but also dynamic effects must be taken into account. In this work, we present accurate site energies of all 96 chlorophylls in the asymmetric unit of PS1 in *S. elongatus*. Therefore, we constructed a fully atomistic model of the trimeric PS1 complex in a solvated lipid membrane to describe the environment as thoroughly as possible. With this extensive structural model, we sampled geometries from classical trajectories and calculated site energies for each chlorophyll with the high-level DFT/MRCI method in a QM/MM scheme. Our results identify dynamic energy sinks in the antenna complex and reveal a fundamental asymmetry in the reaction center. Moreover, we are able to separate the environmental influence into the electrostatic interaction of the chlorophyll with its surroundings and the structural constraints imposed by neighboring residues.

MO 3.4 Mon 17:30 MO-H5

Threshold Photoelectronspectra of pyrolyzed Trimethylantimony and Trimethylarsenic compounds. — EMIL KARAEV¹, •MARIUS GERLACH¹, PATRICK HEMBERGER², and INGO FISCHER¹ — ¹Institut für physikalische und theoretische Chemie, Würzburg, Germany — ²Swiss Light Source, Villigen, Switzerland

Our group already investigated the pyrolysis of methylated group V compounds $X = N[1], P[2], Bi[3]$. While the stable isomers of nitrogen were H-N-CH₂, N-CH₂ and H-N-CH, bismuth showed only Bi-CH₃. For phosphorus the isomers H-P-CH₂, P-CH₃ and P-CH₂ were observed. In order to fill the gap in the periodic table trimethylarsenic and trimethylantimony were pyrolyzed. The emerging reactive species were characterized with the PEPICO setup of the VUV beamline at the Swiss Light Source in Villigen, CH. The observed mass-selected threshold photoelectron spectra were interpreted using quantum chem-

ical calculations and Franck-Condon simulations.

Our results show that Antimony behaves similarly to bismuth, only forming Sb-CH₃. Arsenic on the other hand showed H-As-CH₂, As-CH₃ and As-CH₂, which is analogous to phosphorus.

[1] F. Holzmeier, M. Lang, K. Hader, P. Hemberger, I. Fischer, J. Chem. Phys. 2013, 138, 214310.

[2] D. P. Mukhopadhyay, Unpublished work.

[3] D. P. Mukhopadhyay, D. Schleier, S. Wirsing, J. Ramler, D. Kaiser, E. Reusch, P. Hemberger, T. Preitschopf, I. Krummenacher, B. Engels, I. Fischer, C. Lichtenberg, Chem. Sci. 2020, 11, 7562*7568.

MO 3.5 Mon 17:45 MO-H5

Spectroscopy of Potassium Clusters Isolated in Helium Nanodroplets — ROMAN MESSNER, ROBERT DI VORA, WOLFGANG E. ERNST, and FLORIAN LACKNER — Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

We explore the evolution of the electronic spectrum of potassium clusters isolated in helium droplets from single atoms and molecules up to nanometer sized clusters. A supercontinuum laser equipped with a tunable filter is used to excite the potassium clusters. In combination with a time-of-flight mass spectrometer atomically precise spectra up to K₁₁₀ are recorded. Spectra for larger clusters within a selected size range are also recorded, revealing insight into the properties and

growth of potassium nanoparticles in helium droplets. While small molecules exhibit multiple distinct spectral features, a collective resonance emerges at about 600 nm in the spectra of larger clusters. With increasing cluster size, this resonance continuously shifts towards the blue.

MO 3.6 Mon 18:00 MO-H5

Laser Spectroscopy of Shell-Isolated Au Nanoparticles Functionalized with Rhodamine B Molecules in Helium Nanodroplets — ROMAN MESSNER, WOLFGANG E. ERNST, and FLORIAN LACKNER — Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

Nanoparticles comprising three different materials in a core@shell@shell configuration are synthesized in cold helium droplets by sequential doping. Rhodamine B molecules form complexes in helium droplets that give rise to a strong fluorescence upon laser excitation, which enables an in-situ investigation of the synthesized structures. In the presence of a Au core, the rhodamine B fluorescence is quenched due to excitation transfer from excited shell molecules to the Au particle. The addition of an intermediate hexane layer inhibits the contact between Au core and RB shell, which results in the recovery of the fluorescence.

MO 4: Electronic II

Time: Tuesday 10:30–11:30

Location: MO-H5

MO 4.1 Tue 10:30 MO-H5

Near-Field scanning optical microscopy of molecular aggregates: the role of light polarization — SIDHARTHA NAYAK¹, FULU ZHENG², and ALEXANDER EISEL¹ — ¹MPIPKS, Dresden, Germany — ²BCCMS, University of Bremen, Bremen, Germany

Strong Interaction between transition dipoles of molecules leads to formation of delocalized excitonic eigenstates of molecular aggregates. Using a scattering scanning near-field optical microscope setup one can record position dependent absorption spectra[1] from which we can reconstruct the wavefunctions[2]. In this contribution we focus on the dependence of the spectra on the direction and polarization of the incoming electromagnetic radiation, which induces a Hertz dipole with a specific orientation at the tip-apex. Within a simple description based on the eigenstates of the aggregate, We find that the spatial patterns of the spectra have a strong dependence on the orientation of this tip-dipole, which can be understood by considering three basic functions that only depend on the arrangement of the aggregate and the molecule-tip distance, but not on the orientation of the tip-dipole[3]. This approach is validated by a more detailed description where the incoming radiation and the interaction between tip and molecules is explicitly taken into account.

[1] X. Gao and A. Eisfeld, *J. Phys. Chem. Lett.* 9, 6003 (2018)

[2] F. Zheng, X. Gao and A. Eisfeld, *Phys. Rev. Lett.* 123, 163202 (2019)

[3] S. Nayak, F. Zheng and A. Eisfeld, *J. Chem. Phys.* 155, 134701 (2021)

MO 4.2 Tue 10:45 MO-H5

Detecting Chirality in Mixtures Using Nanosecond Photoelectron Circular Dichroism — SIMON RANECKY¹, BARATT PARK^{2,3}, PETER SAMARTZIS⁴, IOANNIS GIANNAKIDIS⁴, DIRK SCHWARZER², ARNE SENFTLEBEN¹, THOMAS BAUMERT¹, and TIM SCHÄFER² — ¹Uni Kassel — ²Uni Göttingen — ³Texas Tech Lubbock (USA) — ⁴IESL-FORTH Iraklio (Greek)

The ionization of randomly oriented chiral molecules with circularly polarized light leads to an asymmetric angular photoelectron distribution. Depending on the handedness of the molecules and the sense of rotation of the incident light, more electrons are scattered forward or backward with respect to the direction of the incident light. This effect is called photoelectron circular dichroism (PECD). Its size can reach more than 10% for pure enantiomers and decreases for lower enantiomeric excesses (e.e.). It can be applied to determine the e.e. of chiral substances with a precision below 1% [1].

Tunable narrowband nanosecond lasers in combination with a cold molecular beam achieve vibrational resolution in resonance-enhanced multiphoton ionization [2]. As a proof of principle, we made four mix-

tures of pure enantiomers of fenchone and camphor and selectively ionized either fenchone or camphor by tuning the wavelength to the band origin of their B-band and measured their background suppressed PECD. We were able to discriminate the enantiomers of both substances. This opens the perspective to determine the e.e. in mixtures.

[1] A. Kastner et al., *ChemPhysChem*, 17, 1119 - 1122, (2016)

[2] A. Kastner et al., *Phys. Chem. Chem. Phys.*, 22, 7404, (2020)

MO 4.3 Tue 11:00 MO-H5

The gas-phase infrared spectra of the 2-methylallyl radical and its high-temperature reaction products — TOBIAS PREITSCHOPF¹, FLORIAN HIRSCH¹, ALEXANDER LEMMENS², ANOUK RIJS², and INGO FISCHER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Deutschland — ²Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands

The resonance-stabilized 2-methylallyl radical, 2-MA, is considered as a possible intermediate in the formation of polycyclic aromatic hydrocarbons (PAH) in combustion processes. In this work we report on its contribution to molecular growth in a high-temperature microreactor and provide species- and isomer-selective IR/UV ion dip spectra of the various jet-cooled reaction products, employing free electron laser radiation in the mid-infrared region. Small (aromatic) hydrocarbons such as fulvene, benzene, styrene, or para-xylene, as well as polycyclic molecules, like (methylated) naphthalene, were identified with the aid of ab initio DFT computations. Several reaction products differ by one or more methyl groups, suggesting that molecular growth is dominated by (de)methylation in the reactor.

MO 4.4 Tue 11:15 MO-H5

Formation and spectroscopic investigation of molecular clusters of phthalocyanine and water in superfluid helium nanodroplets — JOHANNES FISCHER and ALKWIN SLENCZKA — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany

Superfluid helium nanodroplets serve as a gentle and ultracold (T = 0.37 K) host system for molecular and atomic species as well as weakly bound (van der Waals) clusters [1]. The latter can be synthesized *in situ* by successive pick-up of different species by the droplets. We will present an extended investigation of a cluster consisting of a single phthalocyanine and one water molecule, that possesses a multitude of isomeric structures in helium droplets [2]. The attachment of water to phthalocyanine becomes influential on spectroscopic observables like electronic and vibrational transition frequencies, line shapes, and intramolecular dynamics upon electronic excitation. This study discusses all these features by means of fluorescence excitation spectra

and dispersed emission spectra. The number of configurational variants identified thereby provides evidence that for some of these cluster isomers the contribution of the surrounding helium goes beyond the

stabilization of local minima in the phthalocyanine to water potential hypersurface. [1] A. F. Vilesov et al., *Angew. Chem. Int. Ed.*, **43**, 2622, (2004). [2] J. Fischer et al., *J. Phys. Chem.*, **123**, 10057, (2019).

MO 5: Femtosecond Spectroscopy I

Time: Tuesday 10:30–12:15

Location: MO-H6

Invited Talk

MO 5.1 Tue 10:30 MO-H6

Extending coherent multidimensional spectroscopy to new target systems and new light sources — ●LUKAS BRUDER — Institute of Physics, University of Freiburg, Germany

Coherent multidimensional spectroscopy (CMDS) is a powerful ultrafast spectroscopy technique which reveals couplings and system-bath interactions with unprecedented detail. While CMDS is mainly applied to liquid phase samples, we have recently extended the method to cluster beams prepared in the gas phase [1,2]. In contrast to experiments in the condensed phase, cluster beams provide isolated nanosystems in which fundamental molecular processes can be studied with high resolution. Furthermore, we have implemented wave packet interferometry, the basic principle of CMDS, with new extreme ultraviolet light sources [3,4]. This opens up the perspective of CMDS experiments with attosecond time resolution and element specific probing.

- [1] L. Bruder et al., *Nat Commun* **9**, 4823 (2018).
- [2] U. Bangert et al., arXiv:2112.05418 (2021).
- [3] A. Wituschek et al., *Nat Commun* **11**, 1 (2020).
- [4] A. Wituschek et al., *New J. Phys.* **22**, 092001 (2020).

MO 5.2 Tue 11:00 MO-H6

Time-Resolved Circular Dichroism Spectroscopy of Exciton Relaxations in a Squaraine Polymer — ●LEA RESS¹, JOSHUA SELBY², PAVEL MALÝ^{1,3}, JANN B. LANDGRAF¹, DOMINIK LINDORFER⁴, CHRISTOPH LAMBERT², THOMAS RENGER⁴, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ³Faculty of Mathematics and Physics, Charles University, Prague, Ke Karlovu 5, 121 16 Praha 2, Czech Republic — ⁴Institute for Theoretical Physics, Johannes Kepler University, Linz, Altenbergstrasse 69, 4040 Linz, Austria

We present a new design of a setup for simultaneous time-resolved circular dichroism (TRCD) and transient absorption (TA) spectroscopy with fs temporal resolution. We use a pump-probe approach by exciting the sample with a linearly polarized pump pulse and detecting the difference in absorption of left- and right-circularly polarized probe pulses. The key optical element is a polarization grating, out of which the positive (negative) first order of the diffracted light is left- (right-) circularly polarized. We demonstrate the power of this method on a chiral squaraine polymer, which shows ultrafast relaxations of chiral excitons. According to our calculations that are based on a Frenkel exciton Hamiltonian with quantum chemically parameterized excitonic couplings, using the helix model described in [1], exciton relaxation can be much better resolved with TRCD than with TA.

- [1] A. Turkin, et al., *Chem. Eur. J.* **27**, 8380-8389 (2021)

MO 5.3 Tue 11:15 MO-H6

Ultrafast Spectroelectrochemistry in the Visible Spectral Range on a Perylene Bisimide Cyclophane — ●REBECCA FRÖHLICH¹, JESSICA RÜHE², FRANK WÜRTHNER², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

With spectroelectrochemistry the oxidation states of molecules can be investigated under potential control without the need of a chemical oxidant/reductant. In our setup we combine spectroelectrochemistry with ultrafast spectroscopy and use broadband excitation in the visible spectral range for TA and 2D spectroelectrochemistry [1]. Here we describe new experiments on a perylene bisimide cyclophane. For electrolysis we employ a custom-built flow cell with the organic solvent dichloromethane and the supporting electrolyte TBAHFP. The *meta*-xylene linked cyclophane under investigation creates a rigid system with a small distance of 5 Å between the aromatic units which leads to a coupling of the first excited electronic state with the first

vibrational state [2]. Our time-resolved data show symmetry-breaking charge transfer leading to the generation of radical anionic and cationic species. Upon reduction of the cyclophane the dynamics change depending on the applied potential.

- [1] J. Heitmüller et al., *Spectrochim. Acta Part A*, **253**, 119567 (2021)
- [2] J. Rühle et al., *Organic Materials*, **2**, 149-158 (2020)

MO 5.4 Tue 11:30 MO-H6

Tracking Multi-Exciton Processes in Squaraine Polymers with High-Order Pump-Probe Spectroscopy — ●JULIAN LÜTTIG¹, PAVEL MALÝ¹, PETER A. ROSE², ARTHUR TURKIN³, CHRISTOPH LAMBERT³, JACOB J. KRICH², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Department of Physics, University of Ottawa, Ontario K1N 6N5, Canada — ³Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

The interpretation of time-resolved spectroscopy generally relies on the isolation of a specific nonlinear order of the sample response. Usually the excitation power is chosen to select the wanted signal and to suppress unwanted higher-order contributions such as annihilation. However, measurements at lower power often exhibit low signal-to-noise ratio. In the opposite case of too high powers, the high-order signals are present and have to be considered in the analysis. We solve this dilemma by separating all high-order signals with a novel, simple, data acquisition sequence. Inspired by multidimensional spectroscopy [1], we isolate the different high-order signals by measuring a pump-probe signal at several specific excitation pulse energies. We demonstrate that with our technique annihilation-free measurements of squaraine polymers at high pulse energies are possible. The technique also allows us to measure pure higher-order signals which contain the information on multi-exciton interaction.

- [1] J. Dostál et al., *Nat. Commun.* **9**, 2519 (2018).

MO 5.5 Tue 11:45 MO-H6

Two-dimensional electronic spectroscopy of phthalocyanine on rare gas clusters — ●ULRICH BANGERT, LUKAS BRUDER, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

Two-dimensional electronic spectroscopy (2DES) is an ideal tool to study dynamics with a high spectral-temporal resolution. With recent advances of 2DES towards the gas phase, versatile samples like rare gas cluster beams have become accessible [1]. Rare gas clusters doped with multiple molecules act as miniature cryostats hosting well defined many body systems. Previous experiments on the spectroscopy and life-time measurements of such systems have provided valuable details about singlet fission and superradiance in acene molecules [2,3].

We apply 2DES to this approach and study free-base phthalocyanine in two different environments: embedded in superfluid helium nanodroplets and deposited on the surface of solid neon clusters. First results show 2D spectra of organic molecules with unprecedented spectral resolution and reveal details of the cluster environment, including the homogenous linewidth of 0.42cm⁻¹ on neon clusters.

- [1] L. Bruder et al., *J. Phys. B: At. Mol. Opt. Phys.* **52** 183501 (2019).
- [2] S. Izadnia et al., *J. Phys. Chem. Lett.* **8**, 2068 (2017).
- [3] M. Müller et al., *Phys. Rev. B* **92** (12), 121408 (2015).

MO 5.6 Tue 12:00 MO-H6

Measuring Interexcitonic Coherences in Semiconductor Nanocrystals using Coherent Two-Dimensional Fluorescence Spectroscopy — ●LUIA BRENNEIS, STEFAN MÜLLER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Quantum technologies require the availability of materials with controllable quantum coherences [1]. For this task, quantum dots are

promising materials because their optoelectronic properties depend on their size and composition. However, characterizing coherent superpositions between excitonic states, i.e., interexcitonic coherences, is challenging in semiconductor nanocrystals because of overlapping spectral features and solvent contributions. Moreover, size and shape polydispersity leads to inhomogeneous broadening and ultrafast dephasing (15–25 fs) of interexcitonic coherences at room temperature [1,2].

To detect the ultrafast dynamics of interexcitonic coherences in Cd-SeS/ZnS quantum dots, we prepare coherences between several ex-

citonic states using fluorescence-detected coherent two-dimensional electronic spectroscopy (F-2DES). Due to fluorescence detection, we achieve the absence of solvent contributions [3], which enables us to measure interexcitonic coherences at room temperature. We also investigate the possibility of F-2DES at low temperatures to decrease homogeneous broadening which would further simplify the analysis.

- [1] E. Collini et. al., *J. Phys. Chem. C* **123**, 31286–31293 (2019).
- [2] D. B. Turner et. al., *Nano Lett.* **12**, 880–886 (2012).
- [3] S. Mueller et. al., *ACS Nano* **15**, 4647–4657 (2021).

MO 6: Theory

Time: Tuesday 10:30–12:00

Location: MO-H7

MO 6.1 Tue 10:30 MO-H7

Unsupervised learning as a key tool to explore elements of the efficiency of PS1 in an QM/MM approach — ●FERDINAND KISS, SEBASTIAN REITER, and REGINA DE VIVIE-RIEDLE — Department of Chemistry, LMU Munich, Germany

Modern photovoltaic materials can be seen as biomimetics of photosynthesis in photoautotrophic organisms. Photosystem I (PS1) has one of the highest conversion efficiencies of 88%, from absorbed quanta to the reduction of NADP⁺. A deeper understanding of the effects of structural relations and electrostatic influences on the site energies, low-lying charge transfer states and absorption profiles of photoactive components of the PS1 promises to yield the answer to its outstanding efficiency. We developed an automated protocol for data extraction and processing from MD simulations by unsupervised machine learning. On this basis we set up electronic structure investigations in a QM/MM approach. Our maxim of a bias-free, dimensionality reduced and thus computational affordable approach to QM/MM studies aim towards a post-classical description of processes in large complex systems. With the developed tools at hand, we were able to rationalize relevant structural parameters in the 288 chlorophylls of the PS1 trimer. Furthermore, we were able to approximate electrostatic embedding in different pockets within the PS1 with minimal computational cost. The protocol as mentioned above and its results will guide the understanding of photosynthesis. The insights will help in the development of novel artificial photosynthesis designs.

MO 6.2 Tue 10:45 MO-H7

A Shortcut to Self-Consistent Light-Matter Interaction and Realistic Spectra from First-Principles — ●CHRISTIAN SCHÄFER and GÖRAN JOHANSSON — Department of Microtechnology and Nanoscience, MC2, Chalmers University of Technology, 412 96 Göteborg, Sweden

Nanoplasmonic and optical cavity environments provide a novel handle to non-intrusively control materials and chemistry. We introduce here a simple approach how an electromagnetic environment can be efficiently embedded into state-of-the-art electronic structure methods, taking the form of radiation-reaction forces [1]. We demonstrate that this self-consistently provides access to radiative emission, natural linewidth, Lamb shifts, strong-coupling, electromagnetically induced transparency, Purcell-enhanced and superradiant emission. As an example, we illustrate its seamless integration into time-dependent density-functional theory with virtually no additional cost, presenting a convenient shortcut to light-matter interactions.

- [1] C. Schäfer and G. Johansson, arXiv:2106.07507 (2021).

MO 6.3 Tue 11:00 MO-H7

Novel trimer states in long-range atom-ion Rydberg molecules — ●DANIEL BOSWORTH^{1,2}, FREDERIC HUMMEL¹, and PETER SCHMELCHER^{1,2} — ¹Zentrum für Optische Quantentechnologien, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — ²Hamburg Centre for Ultrafast Imaging, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

Recent theoretical works [1,2] predict p-state Rydberg atoms can form stable dimers with ions, defining a new class of long-range atom-ion Rydberg molecules. In these molecules, the binding arises from avoided crossings between attractive and repulsive polarisation potentials. Observation of these molecules was subsequently confirmed in [3].

We build upon these latest discoveries by studying the interaction between an ion and a *classic* ultra-long-range Rydberg molecule (ULRM). We introduce a third, ground-state atom and calculate Born-

Oppenheimer electronic potential energy surfaces (PES) for the three nuclear species. The PES support three-body vibrational bound states, including both linear and non-linear nuclear arrangements. Estimates for the lifetimes of these trimer states are derived from decay rates to neighbouring PES, obtained using Landau-Zener transition probabilities. This work opens up a fresh avenue of investigation on the interaction of ions with ULRMs.

- [1]: A. Duspayev et al., *Physical Review Research*, 3, 023114 (2021)
- [2]: M. Deiß et al., *Atoms*, 2021, 9(2), 34
- [3]: N. Zuber et al., arXiv preprint arXiv:2111.02680 (2021)

MO 6.4 Tue 11:15 MO-H7

Explicitly correlated wave functions for electron-positron interactions in atoms and molecules — ●JORGE CHARRY, MATTEO BARBORINI, and ALEXANDRE TKATCHENKO — University of Luxembourg, Luxembourg, Luxembourg

Positrons are capable of forming metastable states with atoms and molecules before the electron-positron annihilation process[1]. Such metastable matter-positron complexes are stabilized by a variety of mechanisms, which can have both covalent and non-covalent character. The study of these systems represents a challenge for quantum-chemical methods due to the need to describe the strong attractive correlation effects, which are limited by the employment of atom-centered basis sets to describe the positronic orbitals. In this work, we present a robust variational ansatz based on a combination of an electronic determinant, electron-positron pairing orbitals, and a Jastrow factor to explicitly accounts for the electron-positron correlations in the nuclear field, which are optimized at the level of variational Monte Carlo (VMC). We apply this approach in combination with diffusion Monte Carlo (DMC) to calculate binding energies for a positron e^+ bound to a set of neutral and anionic first-row atoms. To assess our approach for molecules, we study the interaction potential of the previously reported [2] system of two hydrogen anions H^- mediated by a positron ($H^- \cdot e^+ \cdot H^-$). We demonstrate the reliability and transferability of our correlated wavefunctions with respect to state-of-the-art calculations reported in the literature. [1] G. F. Gribakin, et al., *Rev. Mod. Phys* 82, 2557 (2010). [2] J. Charry, et al., *Angew. Chemie* 57, 8859 (2018)

MO 6.5 Tue 11:30 MO-H7

Non-adiabatic dynamics within the cavity-Born-Oppenheimer approximation — ●THOMAS SCHNAPPINGER and MARKUS KOWALEWSKI — Department of Physics, Stockholm University, Sweden

As shown by experiments, strong coupling between light and matter can be used to modify chemical and physical properties. In the case of a molecular system interacting with the vacuum field of a cavity, strong coupling reshapes the potential energy surfaces forming hybrid light-matter states, termed as polaritons or dressed states. In this way, it is possible to manipulate the non-adiabatic dynamics of the molecule and open new photophysical and photochemical reaction pathways.

A theoretical approach to describe such coupled molecular-photon systems is the so-called cavity-Born-Oppenheimer (CBO) ansatz. Analogous to the standard BO approximation, the system is partitioned and only the electronic part of the system is treated quantum mechanically. This separation leads to CBO surfaces depending on both nuclear and photonic coordinates. The interaction between different CBO surfaces can be formulated in terms of non-adiabatic coupling elements. In this work we combine the CBO ansatz with the complete active space self-consistent field (CASSCF) method, to describe the cavity-induced effects on ground and excited states as well as the non-adiabatic couplings. Based on the CBO-CASSCF re-

sults we perform nuclear wave packet dynamics to describe the non-adiabatic processes within the framework of the CBO approximation for a molecular-photon system.

MO 6.6 Tue 11:45 MO-H7

Inelastic H_2+H_2 , H_2+HD and $HD+HD$ collisions in the framework of a quantum-mechanical close-coupling approach — ●RENAT A. SULTANOV — Odessa College, Department of Mathematics, 201 W. University Blvd., Odessa, Texas 79764, USA

Molecular energy transfer collisions such as H_2+H_2 , H_2+HD , $H+H_2/HD$ and $HD+HD$ will be discussed and the results for the cross sections and thermal rate coefficients will be presented. Different H_4 potential energy surfaces (PESs) have been applied in the framework of a pure quantum-mechanical close-coupling approach [1]. The

hydrogen-hydrogen atomic and molecular collisions play an important role in the astrochemistry of the early universe. In the case of the HD collisions it would be necessary to modify existing pure hydrogen H_4 PESs by shifting the center of mass of H_2 to HD. It was done in the framework of two different methods [2, 3]. However, these alternative procedures can provide quite different results for the rotational energy transfer cross sections. Physical and geometrical reasons of these differences will be discussed in our presentation. One of our methods for H_2-H_2 potential modifications [2] have been applied in [4,5].

1. R. A. Sultanov et al., *Chem. Phys. Lett.* **436**, 19 (2007).
2. R. A. Sultanov et al., *AIP Advances* **2**, 012181 (2012).
3. R. A. Sultanov et al., *J. Phys. B* **49**, 015203 (2016).
4. N. Balakrishnan et al., *Astrophys. J.* 866:95 (2018).
5. Y. Wan et al., *MNRAS* **488**, 381 (2019).

MO 7: Cold Molecules

Time: Tuesday 10:30–12:30

Location: MO-H8

MO 7.1 Tue 10:30 MO-H8

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

In our experiment, we study quantum-state-controlled Penning collisions between metastable helium atoms (He^*) and ultracold lithium atoms (Li) in order to investigate efficient ways of controlling the outcome of such ionizing collisions. For this, we have combined a supersonic-beam source for He^* with a magneto-optical trap (MOT) for Li. In order to distinguish in between the contributions of $He(2^3S_1)$ and $He(2^1S_0)$ to the reaction rate, we deplete the population of He^* atoms in the 2^1S_0 level using a novel optical-excitation scheme. Furthermore, we use laser-optical pumping to prepare both $He(2^3S_1)$ and $Li(2^2S_{1/2})$ in selected magnetic sub-levels prior to the collision.

In this contribution, we demonstrate the efficient control of $He(2^3S_1)$ - $Li(2^2S_{1/2})$ Penning ionization by spin-state preparation. Our results imply a strong suppression (enhancement) of Penning-ionizing collisions for non-spin-conserving (spin-conserving) reaction channels. Our results are in good agreement with a model based on spin angular momentum coupling of the prepared atomic states to the molecular reaction channels. Small deviations from the model indicate the contribution of quartet states to the reaction rate, which is in violation of spin-conservation rules.

MO 7.2 Tue 10:45 MO-H8

Bayesian optimization of molecular magneto-optical trapping — ●SUPENG XU, PAUL KAEBERT, MARIIA STEPANOVA, TIMO POLL, MIRCO STIERCKE, and SILKE OSPELKAUS — Institut für Quantenoptik, Leibniz Universität Hannover

Magneto-optical trapping (MOT) is a key technique on the route towards ultracold molecular ensembles. However, the realization and optimization of magneto-optical traps with their wide parameter space is particularly difficult. Here, we present a very general method for the optimization of molecular magneto-optical trap operation by means of Bayesian optimization. We take CaF as an example and optimize the capture velocity, which can lead to significant gains in the number of molecules loaded into a trap. In the simulation, the nonlinear Zeeman sublevels and the magnetic field dependent transition rates are considered to get more accurate results. We obtain a group of parameters for both $A^2\Pi_{1/2} - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Sigma^+$ transitions that are superior to the conventional MOT scheme in both trapping and cooling force, as well as the capture velocity. Three laser frequency components schemes are also given to simplify the experiment. Finally, we use the optical Bloch equations (OBEs) to investigate sub-Doppler heating effects with the optimized schemes and find that, while the program is designed to find the maximum capture velocity, it can also reduce the velocity range over which the sub-Doppler heating effects occur.

MO 7.3 Tue 11:00 MO-H8

Evaporation of microwave-shielded polar molecules to quantum degeneracy — ANDREAS SCHINDEWOLF^{1,2}, ●ROMAN BAUSE^{1,2}, XING-YAN CHEN^{1,2}, MARCEL DUDA^{1,2}, TIJS KARMAN³, IMMANUEL BLOCH^{1,2,4}, and XIN-YU LUO^{1,2} — ¹Max-Planck-Institut für Quan-

tenoptik, 85748 Garching, Germany — ²Munich Center for Quantum Science and Technology, 80799 München, Germany — ³Institute for Molecules and Materials, Radboud University, 6525 AJ Nijmegen, Netherlands — ⁴Fakultät für Physik, Ludwig-Maximilians-Universität, 80799 München, Germany

Ultracold polar molecules offer strong dipole moments and rich internal structure, which makes them ideal building blocks for exotic quantum matter. However, even chemically nonreactive molecules have been shown to undergo inelastic two-body collisions by a mechanism that is not yet fully understood. As these collisions have so far prevented cooling to quantum degeneracy in three dimensions, overcoming them represents an important step towards full quantum control of molecules. In this work, we demonstrate evaporative cooling of a bulk gas of fermionic $^{23}Na^{40}K$ molecules to well below the Fermi temperature. The molecules are prevented from reaching short range with a repulsive barrier engineered by coupling rotational states with a strong microwave field, which suppresses lossy collisions. The microwave field also induces large dipole moments, leading to strong elastic collisions which enable efficient evaporation. This allows us to cool the molecular gas down to 21 nK, which is 36% of the Fermi temperature.

MO 7.4 Tue 11:15 MO-H8

Towards direct laser cooling of barium monofluoride — ●MARIAN ROCKENHÄUSER, FELIX KOGEL, EINIUS PULTINEVICIUS, and TIM LANGEN — Universität Stuttgart, 5. Physikalisches Institut, IQST

Cold molecular gases are the starting point for many novel and interdisciplinary applications ranging from few- and many-body physics to cold chemistry and precision measurements. However, while there has recently been significant progress in the direct cooling of molecules, the preparation of a new molecular species in the cold temperature regime still requires a careful optimization of the available cooling techniques. We have performed vibrational spectroscopy of monofluoride (BaF), to determine the cooling and repumping transitions of this molecule with an accuracy of better than 100 MHz. Together with a detailed modelling of the cooling processes, this brings laser cooling of this species within reach.

MO 7.5 Tue 11:30 MO-H8

Hyperfine resolved optical spectroscopy of the $A^2\Pi \leftarrow X^2\Sigma^+$ transition in MgF — ●MAXIMILIAN DOPPELBAUER¹, SIDNEY C. WRIGHT¹, SIMON HOFÄSS¹, BORIS SARTAKOV², GERARD MEIJER¹, and STEFAN TRUPPE¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²General Physics Institute, Russian Academy of Sciences, Vavilovstreet 38, 119991 Moscow, Russia

The group II monofluoride MgF is a promising candidate for magneto-optical trapping at high densities. However, published information on the $A^2\Pi \leftarrow X^2\Sigma^+$ transition is incomplete, with many important properties not experimentally measured.

Here, we present an extensive set of hyperfine-resolved spectroscopic measurements on MgF. We recorded 25 rotational transitions with an absolute accuracy of <20 MHz. From the fitted line positions, we determined precise spectroscopic parameters for the $A^2\Pi$ state. We also measured the transition isotope shift between 24 rotational lines of

the isotopologues ^{24}MgF and ^{26}MgF , and compared to the predictions within the Born-Oppenheimer approximation. We report the first experimental measurement of the radiative lifetime of the $A^2\Pi$, $v' = 0$ level and the measured electric dipole moments of the $X^2\Sigma^+$ and $A^2\Pi$ states. Electric field induced parity mixing can lead to significant optical cycling losses, unless the fields are controlled to below 1 V/cm. This new set of measurements illustrates the importance of detailed spectroscopic understanding of laser cooling candidates, and forms a stringent set of benchmarks for quantum chemical calculations.

MO 7.6 Tue 11:45 MO-H8

A new perspective on cryogenic buffer gas beams: comparing AlF, CaF, MgF and YbF — ●SIDNEY C. WRIGHT, MAXIMILIAN DOPPELBAUER, XIANGYUE LIU, H. CHRISTIAN SCHEWE, SIMON HOF-SÄSS, SEBASTIAN KRAY, JESÚS PÉREZ-RÍOS, GERARD MEIJER, and STEFAN TRUPPE — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin

Cryogenic buffer gas beams of atoms and molecules are an essential precursor for many experiments with ultracold matter. Whilst the production efficiency and phase-space distribution of the target species determine the scientific applications of a buffer gas source, these properties are not well understood and difficult to compare between experiments.

In the same setup, we produce and compare buffer gas beams of Al, Ca and Yb, with the laser coolable molecules AlF, CaF, MgF and YbF. We deduce that production of AlF from Al is nearly 100% efficient in our source, whereas for the other monofluorides it is about 10%. This is supported by calculations using a combination of molecular dynamics and density functional theory, suggesting it may be possible to predict the production efficiency for other molecular species.

We use a Stark Decelerator to accurately map the longitudinal phase-space distribution of the AlF beam, and measure its rotational state distribution using the convenient optical transitions. Together, this provides new insight into the thermalisation dynamics in the buffer gas cell. Our findings have important implications for the design of future cold molecule sources.

MO 7.7 Tue 12:00 MO-H8

Buffer gas cooling and optical cycling of AlF molecules — ●SIMON HOF-SÄSS¹, MAXIMILIAN DOPPELBAUER¹, SIDNEY WRIGHT¹,

SEBASTIAN KRAY¹, JESUS PEREZ-RIOS¹, BORIS SARTAKOV², GERARD MEIJER¹, and STEFAN TRUPPE¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia

Ultracold, polar molecules promise many new applications in fundamental physics and chemistry. In particular, aluminium monofluoride (AlF) is a promising candidate to produce a dense, ultracold gas through laser cooling. We show that AlF can be produced very efficiently in a bright, pulsed cryogenic buffer gas molecular beam, and demonstrate rapid optical cycling on the Q rotational lines of the $A^1\Pi \leftrightarrow X^1\Sigma^+$ transition near 228 nm. This is the first step towards cooling the molecules to the ultracold regime. Losses from the cooling cycle are sufficiently low to allow loading the molecules into a MOT. We also present our recent progress in creating a dense and cold cloud of cadmium (Cd) atoms using the $^1P_1 \leftarrow ^1S_0$ transition near 229 nm. Cd is an excellent test species for our MOT apparatus as it shares many properties with the more complex case of AlF.

MO 7.8 Tue 12:15 MO-H8

Singlet Pathway to the Ground State of Ultracold Polar Molecules — ANBANG YANG¹, SOFIA BOTSIS¹, SUNIL KUMAR¹, SAMBIT B. PAL¹, MARK M. LAM¹, IEVA CEPAITE¹, ANDREW LAUGHARN¹, VICTOR A. AVALOS PINILLOS¹, CANMING HE¹, XIAOYU NIE¹, and ●KAI DIECKMANN^{1,2} — ¹Centre for Quantum Technologies, 3 Science Drive 2, 117543 Singapore — ²Department of Physics, National University of Singapore, 2 Science Drive 3, 117542 Singapore

Starting from weakly bound Feshbach molecules, we demonstrate a two-photon pathway to the dipolar ground state of bi-alkali molecules that involves only singlet-to-singlet optical transitions. This pathway eliminates the search for a suitable intermediate state with sufficient singlet-triplet mixing and the exploration of its hyperfine structure, as is typical for pathways starting from triplet dominated Feshbach molecules. By selecting a Feshbach state with a stretched singlet hyperfine component and controlling the laser polarizations, we assure coupling to only single hyperfine components of the $A^1\Sigma^+$ excited potential and the $X^1\Sigma^+$ rovibrational ground state. In this way an ideal three level system is established, even if the hyperfine structure is not resolved. We demonstrate this pathway with $^6\text{Li}^{40}\text{K}$ molecules, and discuss our progress on its application to coherent transfer to the dipolar ground state.

MO 8: Poster 1

Time: Tuesday 16:30–18:30

Location: P

MO 8.1 Tue 16:30 P

Two-color X-ray pump-probe experiments with halogenized hydrocarbons — ●ALICE JUDT¹, JULIUS SCHWARZ¹, FABIANO LEVER², ALJOSCHA ROERIG³, KAROLIN BAEV⁴, DENNIS MAYER², IVAN BAEV¹, MATZ NISSEN¹, STEFFEN PALUTKE⁴, MARKUS GUEHR², MARKUS DRESCHER¹, MARION KUHLMANN⁴, MICHAEL MEYER³, MATTHIAS DREIMANN⁵, HELMUT ZACHARIAS⁵, and MICHAEL MARTINS¹ — ¹Universität Hamburg, Hamburg, Germany — ²Universität Potsdam, Potsdam, Germany — ³European XFEL, Schenefeld, Germany — ⁴Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany — ⁵Center for Soft Nanoscience, Westfälische Wilhelms-Universität Münster, Münster, Germany

Charge transfer on the fs time scale is the basis to understand chemical reactions in molecules. A time resolved two-color XUV-pump/XUV-probe method was used to analyze this process in ClBrCH_2 , ClBrC_2H_4 and ClBrC_3H_6 molecules. A short 100 fs 70 eV XUV pump pulse excites a Br 3d electron, inducing a relaxation process within the molecule including charge transfer from Br to Cl. By exciting a chlorine 2p electron with a second (probe) pulse of 210 eV, information about the electronic rearrangement can be obtained.

The experiment was carried out at the FL24 beamline of the free-electron laser FLASH2 at DESY using the new split-and-delay unit. A magnetic bottle electron spectrometer was used to measure the kinetic energy of the electrons. First results and a preliminary analysis of resonant molecular excitations using small pump-photon energy variations will be discussed.

MO 8.2 Tue 16:30 P

Strong field ionization of NO_2 probed by femtosecond soft

X-ray absorption spectroscopy at N K-edge — ●ZHUANG-YAN ZHANG, MAR-OLIVER WINGHART, PENG HAN, CARLO KLEINE, ARNAUD ROUZÉE, and ERIK NIBBERING — Max-Born-Institute, Berlin, Germany

The photoexcitation dynamics of NO_2 at 400 nm is investigated by time-resolved soft X-ray absorption spectroscopy using a table-top, femtosecond soft X-ray source based on high harmonic generation, which delivers femtosecond pulses in a photon energy range between 250 eV and 450 eV. The ionization dynamics of the molecule from its ground state (\tilde{X}^2A_1) by intense 400 nm laser pulses is directly mapped into the transient change of the soft X-ray absorption spectrum near the N K-edge. Before ionization, the molecule is characterized by strong absorption features at 401 eV and 403.5 eV corresponding to transitions from the N 1s σ core-shell state to the singly occupied \tilde{X}^2A_1 ground state and the \tilde{A}^2B_2 first excited state of the molecule, respectively. The ionization of the molecule by the 400 nm laser pulse is accompanied for a strong depletion of the absorption observed near 401 and 403 eV, and is responsible for the appearance of new absorption lines at around 394 eV and 397 eV that we assign to fast dissociation of the molecular cation to form both NO and NO^+ fragments. At lower intensity, these two absorption peaks are shifted by 1 eV towards lower/higher energy, indicating a strong dependence of the ionization dynamics to the laser intensity.

MO 8.3 Tue 16:30 P

Construction of a laser transfer line for the Cryogenic Storage Ring — ●ANNIKA OETJENS, DAMIAN MÜLL, AIGARS ZNOTINS, FLORIAN GRUSSIE, and HOLGER KRECKEL — Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany

The Cryogenic Storage Ring (CSR) at the Max-Planck-Institut für Kernphysik in Heidelberg is a fully electrostatic storage ring with inner vacuum chambers that can be cooled to liquid helium temperatures. Part of the experimental program at the CSR relies on the interaction of laser light with stored molecular ions for photodetachment, photodissociation, and spectroscopy studies. To this end we are currently planning the construction of a new dedicated laser area next to the CSR, which will enable more stable and controlled laser applications. The laser light will be guided through evacuated chambers into which optical components can be placed. Simulations and tests on how to minimize the loss of power for lasers with different beam quality are part of current work. Furthermore, tests of an active beam stabilization system to improve pointing instabilities for both continuous and pulsed lasers during frequency scans are ongoing. Moving all lasers into a temperature-controlled and air-filtered environment will improve experimental stability and increase safety during operation. The beam line is expected to be built in early 2022 and its design allows for adaptations to varying experimental requirements.

MO 8.4 Tue 16:30 P

Laser-heated molecular deposition source — FABIANO LEVER, ALANAS STRAECK, and •LISA MEHNER — University of Potsdam, Potsdam, Germany

We present a setup for the laser-induced desorption of molecular samples, to be used as a sample delivery system in ultrafast experiments in gas-phase.

For the commissioning, we used a phenylalanine sample, which has been used with such a source before [1]. We explore different sample preparation methods, which are then tested for their reliability.

The samples are applied on Al-foil and inserted into a vacuum chamber. An infrared diode-laser heats the foil, causing molecular desorption. We use a quartz-balance to measure the rate of desorption. We systematically vary the experimental parameters, such as the laser intensity, to characterize their relation to the sample desorption rate.

Multiple solvents have been tested, with the most promising being the use of a water-based solution. This produces a thin layer of phenylalanine on the foil after drying off.

[1] F. Calegari et al, *Science* 246, 336 (2014)

MO 8.5 Tue 16:30 P

Signatures of non-adiabatic physics in the vibrational spectrum of Rydberg molecules — •AILEEN ANTJE THERESIA DURST and MATTHEW TRAVIS EILES — Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Str. 38, D-01187 Dresden, Germany

A highly excited valence electron of a Rydberg atom scattering off of a ground state atom forms an ultra-long range molecule. A distinctive feature of these molecules is the so-called butterfly potential curve, which plunges through the potentials associated with low electronic angular momentum and induces a rapid, almost step-like, variation in them. Despite this drop in the potential, which destroys the inner potential barrier, stable vibrational states still exist. The occurrence of such bound states has been explained by quantum reflection from the steep drop in the potential. However, non-adiabatic couplings which arise and may become quite strong near this cliff have been neglected. We have developed approximate potentials which give strong indications that this non-adiabatic coupling can provide an alternative explanation for these unusual bound states. In this poster, we present our study of the vibrational spectrum including non-adiabatic coupling. By numerically calculating the full non-adiabatic problem and extracting the vibrational spectra, we can compare this method to the purely adiabatic approach relying on quantum reflection. Our study shows that long-range Rydberg dimers can provide an extreme environment to test the usual assumptions of Born-Oppenheimer physics and obtain further insights into non-adiabatic phenomena.

MO 8.6 Tue 16:30 P

Improved XUV magnetic bottle photoelectron spectrometer — •KARIMAN ELSHIMI, FABIAN BÄR, PHILIPP ELSÄSSER, and BERND V. ISSENDORFF — Physikalisches Institut der Albert-Ludwigs-Universität Freiburg

A new XUV magnetic bottle photoelectron spectrometer (MBPES) has been constructed for studying the electronic structure and the dynamics of free mass-selected and temperature-controlled clusters at free-electron lasers (FEL). This unique spectrometer system includes cryogenic (< 4K) interaction region and special ion optics designed specifically to suppress the background contribution in the XUV range.

The resolution of the spectrometer can be improved by both static

deceleration and a time-dependent deceleration focusing the electron package. Here, we discuss test measurements on atoms and molecules demonstrating that with the new deceleration scheme resolutions of $\Delta E/E = 0.5\%$ can be reached.

MO 8.7 Tue 16:30 P

Novel sample delivery system for small nanoparticles and biomolecules — •LENA WORBS^{1,2}, JANNIK LÜBKE^{1,2,3}, ARMANDO ESTILLORE¹, AMIT SAMANTA¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ²Department of Physics, Universität Hamburg, Hamburg, Germany — ³Center for Ultrafast Imaging, Universität Hamburg, Hamburg, Germany

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 8.8 Tue 16:30 P

Probing structural dynamics of molecules and clusters using XFEL pulses and synchrotron radiation — •DIMITRIS KOULENTIANOS^{1,2}, NIDIN VADASSERY¹, LUDMILA SCHNEIDER², HUBERTUS BROMBERGER¹, SEBASTIAN TRIPPEL^{1,3}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Department of Physics, Universität Hamburg — ³Center for Ultrafast Imaging, Universität Hamburg

The development of x-ray free-electron laser (XFEL) and third generation synchrotron-radiation (SR) facilities, allowed for the study of molecular dynamics within the (sub)picosecond timescale [1]. In the present work, preliminary results using such light sources will be presented. Here, we will discuss both, delay-dependent hydrogen bond changes upon irradiation of the indole-water₁ cluster, using a UV-pump x-ray-probe scheme offered by the Linac Coherent Light Source (LCLS), as well as the recording of molecular frame photoelectron angular distributions (MFPADs), using SR at PETRA III. Finally, our Timepix 3D camera [2] is expected to play a significant role in such experiments, as it allows us to obtain three dimensional ion velocities and to measure simultaneously all the ejected electrons and ions. First results demonstrating its capabilities, using nitrogen as target species [2], will be presented.

[1] Kierspel et al., *Phys. Chem. Chem. Phys.* **20**, 20205 (2018)

[2] Bromberger et al., arXiv:2111.14407

MO 8.9 Tue 16:30 P

Fluorine reactor study of Pyridine: Formation of Pyridinyl radicals and C5H3N isomers — •KATHARINA THEIL¹, MARIUS GERLACH¹, EMIL KARAEV¹, JEAN-CHRISTOPHE LOISON², CHRISTIAN ALCARAZ³, LAURENT NOHAN⁴, and INGO FISCHER¹ — ¹Universität Würzburg, 97074 Würzburg, Germany — ²Université de Bordeaux, 33405 Talence, France — ³Université Paris-Saclay, 91190 Gif-sur-Yvette, France — ⁴Synchrotron SOLEIL, 91190 Gif-Sur-Yvette, France

Pyridyl radicals are the prototypical heterocyclic radicals containing nitrogen as a heteroatom. Since pyridine is one of the main components of heterocycles in fossil fuels, the formation of pyridyl radicals has been suggested as a possible intermediate in combustion processes. The decomposition of pyridine has been the subject of numerous detailed experimental and theoretical studies, which have shown that the thermal decomposition of pyridine produces, among others, cyanide, acetylene, and hydrogen, starting with the cleavage of the C-H bond that initiates a decomposition cascade with diverse pyrolysis products.

We present measurements on pyridine conducted at the DESIRS beamline at Synchrotron Soleil in France employing the fluorine dis-

charge reactor. One and two Hydrogen loss products are observed and are characterized by evaluating their slow photoelectron spectra and corresponding Franck-Condon simulations.

MO 8.10 Tue 16:30 P

IR-Spectroscopy of Dysprosium-Chromium — ●SASCHA SCHALLER, JOHANNES SEIFERT, NICOLE WALTER, ANDRÉ FIELICKE, GIACOMO VALTOLINA, and GERARD MEIJER — Fritz-Haber-Institute of the Max-Planck-Society Berlin, Deutschland

Spectroscopic characterization of the gas-phase DyCr dimer by a two-color ionization method that combines UV light with infrared photons coming from an infrared free electron laser (IR-FEL).

MO 8.11 Tue 16:30 P

Infrared Action Spectroscopy of Single Nanoparticles in the Gas Phase — ●SOPHIA LEIPPE, BENJAMIN HOFFMANN, and KNUT R. ASMIS — Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, 04103 Leipzig, Germany

The surface of a nanoparticle (NP) can be characterized by infrared spectroscopy in the gas phase in order to avoid perturbing interactions with its environment. Since direct absorption spectroscopy is typically not sensitive enough for this purpose, alternative methods are required, in which the absorption of photons is detected indirectly by way of action spectroscopy. A novel single NP mass spectrometer is used that allows to non-destructively monitor the absolute mass of the NP. Adsorption of messenger compounds onto the NP is enabled by a temperature-controllable (10 - 350 K) ion trap. Absorption of electromagnetic radiation leads to heating of the NP and evaporation of the messenger, which is indirectly detected as a loss of mass. Proof-of-principle experiments showed that UV/VIS action spectra are in reasonable agreement with direct absorption spectra obtained from measurements in solution.[1] We are currently extending this technique to the infrared regime (4200 - 2500 cm⁻¹) and first results are reported here. Single NP infrared action spectroscopy can ultimately provide new insights which are of interest for various fields, such as catalysis, material separation or medicine.

[1] B. Hoffmann, T. K. Esser, B. Abel, K. R. Asmis, *J. Phys. Chem. Lett.* 11, 6051*6056 (2020)

MO 8.12 Tue 16:30 P

Doppler-free spectroscopy of the $H^2\Sigma^+ \leftarrow A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$ transition in nitric oxide — ●PHILIPP NEUFELD¹, PATRICK KASPAR¹, FABIAN MUNKES¹, LEA EBEL¹, YANNICK SCHELLANDER², ROBERT LÖW¹, TILMAN PFAU¹, and HARALD KÜBLER¹ — ¹5. Physikalisches Institut and Center for Integrated Quantum Science and Technology IQST, Universität Stuttgart — ²Institut für Großflächige Mikroelektronik, Universität Stuttgart

On the $A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$ transition in nitric oxide (NO) we employ Doppler-free spectroscopy for different total angular momenta J on the P_{12} branch. Via phase sensitive detection by a lock-in amplifier the hyperfine structure of the $X^2\Pi_{3/2}$ state of NO is partially resolved. The data is compared to previous measurements [1]. On the $H^2\Sigma^+ \leftarrow A^2\Sigma^+$ transition, optical-lattice spectroscopy is performed [2]. Both transitions are driven in continuous wave operation at 226 nm and 540 nm, respectively. Investigation of the dependence of the spectroscopic feature on power and pressure, should yield hyperfine constants, natural transition linewidth and the collisional cross-section between NO molecules. The novel approach of optical-lattice spectroscopy has the potential to facilitate the investigation of the structural details of $H^2\Sigma^+$.

[1] W.L. Meerts and A. Dymanus, *J. of Mol. Spec.* 44, 320-346 (1972)

[2] P. Kaspar et. al., *OSA Optical Sensors and Sensing*, 19-23 July, 2021

MO 8.13 Tue 16:30 P

LLWP - A new Loomis-Wood Software applied to the Example of Propanone-13C1 — ●LUIS BONAH¹, OLIVER ZINGSHEIM¹, SVEN THORWIRTH¹, HOLGER S. P. MÜLLER¹, FRANK LEWEN¹, JEAN-CLAUDE GUILLEMIN², and STEPHAN SCHLEMMER¹ — ¹I. Physikalisches Institut, Universität zu Köln, Köln, Germany — ²ENSC, Univ. Rennes, France

Spectra of complex molecules are dense and complicated, especially if isotopologues, low-lying vibrationally excited states, hyperfine structure and other interactions are present. In addition, the analysis of

these spectra can be difficult due to line confusion. One approach to accommodate this challenge are Loomis-Wood plots (LWPs), which are a visual aid for displaying series of transitions in a spectrum in order to ease assignments. Programs utilizing LWPs exist already in the literature, e.g. AABS, Pgoopher and LWW. Here, we present a newly developed software which focuses on being intuitive and user friendly while simultaneously allowing for fast and confident assignments of molecular spectra. The software is called LLWP and is written in Python. The core functionality and selected features are presented on the example of first results of the analysis of spectra of isotopically enriched propanone-13C1 (13CH₃COCH₃). This molecule was synthesized as its signal at natural abundance only allowed for a very limited analysis. The software and its full documentation are available at ltotheo.github.io/LLWP.

MO 8.14 Tue 16:30 P

Chirped-pulse millimeter wave spectroscopy on complex molecules of astrophysical interest — ●BETTINA HEYNE, MARIUS HERMANN, NADINE WEHRES, FRANK LEWEN, and STEPHAN SCHLEMMER — I. Physikalisches Institut, Universität zu Köln, Deutschland

We present our chirped-pulse Fourier transform millimeter wave spectrometer [1], which is operational between 75 and 110 GHz. This range overlaps with the Atacama Large Millimeter/Submillimeter Array (ALMA) Band 3. The instrument is designed to achieve high stability and sensitivity, which makes it possible to measure spectra of isotopic species of molecules in natural abundance. The principle setup coincides in many aspects with our emission spectrometer [2], thus a comparison of chirped pulse measurements and emission spectroscopy is discussed briefly. Furthermore, a high voltage DC discharge in combination with a supersonic jet is incorporated to observe fragments of molecules. For this application, first tests were performed with methyl cyanide (CH₃CN) as a precursor molecule. We observed HCN as well as HNC discharge products.

References

[1] M. Hermanns, N. Wehres, B. Heyne, K. von Schoeler, G. Neplyakh, M. Töpfer, C. E. Honingh, U. U. Graf and S. Schlemmer, in preparation

[2] N. Wehres, B. Heyne, F. Lewen, M. Hermanns, B. Schmidt, C. Endres, U. U. Graf, D. R. Higgins and S. Schlemmer, *IAU Symposium*, 2018, pp. 332-345

MO 8.15 Tue 16:30 P

A status report on the Cologne Database for Molecular Spectroscopy, CDMS — ●HOLGER MÜLLER, PETER SCHILKE, and STEPHAN SCHLEMMER — I. Physikalisches Institut, Universität zu Köln, Germany

The CDMS^a has been founded more than 20 years ago as a link between laboratory spectroscopy and astrophysics. It provides in its catalog section line lists of mostly molecular species which were or may be detected in space by radio astronomical means.^b The line lists are generated by fitting critically evaluated experimental data, mostly from laboratory spectroscopy, to established Hamiltonian models. Separate entries are generated for different isotopic species and usually also for excited vibrational states. 1110 entries are in the CDMS catalog as of Dec. 2021. Species representing 468 entries have been detected in space, representing a substantial fraction of the more than 260 different molecules detected in space. The catalog is an important resource for secondary data source.

Other sections of the classical incarnation of the CDMS include a page on Molecules in Space and a help page for users of Pickett's SP-FIT/SPCAT programs. A mysql-based incarnation participates in the Virtual Atomic and Molecular Data Centre, VAMDC,^c which is linked to a plethora of other spectroscopic, collisional, and kinetic databases via the VAMDC portal.

^a Shortcut: cdms.de; web address: <https://cdms.astro.uni-koeln.de/>

^b H. S. P. Müller et al., *Astron. Astrophys.* 370 (2001) L49

^c <http://www.vamdc.org/>

MO 8.16 Tue 16:30 P

Merged-beams experiments on molecular ion-neutral reactions for astrochemistry — ●PIERRE-MICHEL HILLENBRAND¹, XAVIER URBAIN², and DANIEL WOLF SAVIN³ — ¹Justus-Liebig Universität, Giessen, Germany — ²Université catholique de Louvain, Louvain-la-Neuve, Belgium — ³Columbia University, New York, USA

The gas-phase formation of complex molecules in the interstellar medium proceeds dominantly through barrierless ion-neutral reactions at typical temperatures of 10 – 100 K. Our merged-beams apparatus

operated at Columbia University in New York City enables us to measure energy-dependent absolute cross sections of molecular formation processes in reactions of singly-charged molecules with neutral atoms and derive temperature-dependent thermal rate coefficients for individual product channels. Focusing on key reactions implemented in astrochemical models as well as on systems of fundamental interest, we have recently studied the reactions $D + H_3^+ \rightarrow H_2D^+ + H$ [1], $D + H_2D^+ \rightarrow D_2H^+ + H$ and $D + D_2H^+ \rightarrow D_3^+ + H$ [2], $C + H_2^+ \rightarrow CH^+ + H$ and $C + D_2^+ \rightarrow CD^+ + D$ [3], as well as $O + H_3^+ \rightarrow OH^+ + H_2$ and $O + H_3^+ \rightarrow H_2O^+ + H$ [4]. For example, the branching ratio of the $O + H_3^+$ reaction is relevant for accurately modeling the gas-phase formation of water in the diffuse and dense molecular clouds.

[1] *Astrophys. J.* **877**, 38 (2019)

[2] *J. Chem. Phys.* **154**, 084307 (2021)

[3] *Phys. Chem. Chem. Phys.* **22**, 27364 (2020)

[4] *Astrophys. J.*, accepted for publication

MO 8.17 Tue 16:30 P

Towards the Threshold Photodetachment Spectroscopic studies of C_2^- — ●SRUTHI PURUSHU MELATH, CHRISTINE LOCHMANN, MARKUS NÖTZOLD, ROBERT WILD, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria

Different neutral and charged interstellar molecules constitute the building blocks for a rich reaction network in the interstellar medium (ISM). Many complex molecules have been detected but many observed spectra still have unidentified features. Photodetachment cross-section studies are crucial for predicting the abundance of anions in the ISM.

The threshold photodetachment spectroscopy of CN^- was performed by our group at both 16 K and 295 K in a 22-pole ion trap and 295 K from a pulsed ion beam using crossed-beam velocity map imaging (VMI) setup [1]. In next experiments we aim to study the threshold photodetachment spectroscopy of C_2^- , which is speculated to exist in the interstellar medium, in a 16-pole radiofrequency ion trap, which can be cooled down to 6 K to mimic conditions in the ISM. For the photodetachment, we will use the frequency-doubled tunable dye laser system (output produces a scanning range of 365 nm - 385 nm) in our lab. The status of the experiment will be presented.

[1] M. Simpson, et al., Threshold photodetachment spectroscopy of the astrochemical anion CN^- . *J. Chem. Phys.* **153**, 184309 (2020).

MO 8.18 Tue 16:30 P

Laboratory simulations of solar wind ion irradiation on the surface of Mercury — CAIXIA BU¹, BENJAMIN C. BOSTICK², STEVE N. CHILLRUD², DEBORAH L. DOMINGUE³, DENTON S. EBEL⁴, GEORGE E. HARLOW⁴, ROSEMARY M. KILLEN⁵, ●DANIEL SCHURY¹, KYLE P. BOWEN¹, PIERRE-MICHEL HILLENBRAND¹, XAVIER URBAIN⁶, RUITIAN ZHANG¹, DMITRY IVANOV¹, and DANIEL W. SAVIN¹ — ¹Columbia Astrophysics Laboratory, Columbia University, New York — ²Lamont-Doherty Earth Observatory, Columbia University, Palisades — ³Planetary Science Institute, Tucson — ⁴American Museum of Natural History, New York — ⁵NASA-Goddard Space Flight Center, Greenbelt — ⁶Université Catholique de Louvain, Louvain-la-Neuve

Mercury possesses a Na exosphere that is thought to be in part formed by solar wind ion sputtering of the planet's regolith surface. However, reliable sputtering data are lacking to confirm this hypothesis. Observations of the planet from satellites such as MESSENGER provide spectral and photometric data of the surface, which is affected by solar wind ion irradiation.

We have developed a novel apparatus to perform solar wind-like ion irradiation of loose regolith-like powders and to measure angular sputter yields and spectral changes. Spectra spanning 350-2500 nm will be collected in-vacuo and in-situ as a function of ion fluence. We will present the experimental setup and provide first results.

MO 8.19 Tue 16:30 P

Excited State Dynamics of the Q-Bands in Chlorophyll a — ●LENA BÄUML¹, SEBASTIAN REITER¹, EVA SEXTL², and REGINA DE VIVIE-RIEDLE¹ — ¹Department of Chemistry, LMU Munich, Germany — ²Department of Physics, LMU Munich, Germany

During the conversion of sunlight to chemical energy via photosynthesis the pigment chlorophyll adopts different functions depending on the environment: absorption of light in the visible range, excitation energy transfer in the antenna complex, primary charge separation

in the reaction centre of the photosystems and subsequent electron transfer to other redox-active cofactors. Thus, nonradiative relaxation of high-energy excited states to the lowest excited state in chlorophylls is central for the understanding of photosynthesis.

In this work, we simulate the ultrafast relaxation process in the Q-bands of chlorophyll a with grid-based wave packet quantum dynamics in several reduced-dimensional coordinate spaces. In particular we discuss the relaxation process in 2D coordinate spaces spanned by the normal modes with the highest overlap with the non-adiabatic coupling vector. The excited state energies and non-adiabatic couplings are computed at the CASPT2 level of theory to model the energy difference between the Q_x and the Q_y state correctly. Our results show from a purely quantum mechanical point of view how the Q_x and the Q_y band are strongly coupled by internal vibrations and should not be considered as isolated transitions.

MO 8.20 Tue 16:30 P

Ligand release from a molybdenum carbonyl complex via an organic photosensitizer — ●MARCEL FISCHER, KEVIN ARTMANN, ROGER JAN KUTTA, and PATRICK NUERNBERGER — Institute of Physical and Theoretical Chemistry, Universität Regensburg, 93040 Regensburg

Carbon monoxide (CO) can be released from metal carbonyl complexes upon excitation by light. To circumvent the population of excited singlet states, also triplet-triplet energy transfer can be employed [1,2]. We investigate the influence of the triplet photosensitizer benzophenone (BP) on the photochemical behavior of molybdenum hexacarbonyl $Mo(CO)_6$. By transient absorption spectroscopy, we observed energy transfer from BP to the complex resulting in the formation of the dissociation products $Mo(CO)_5$ and $Mo(CO)_4$. An intermediate with a lifetime larger than a millisecond is also observed, putatively related to the interaction of two product molecules in solution.

The approach may prove beneficial for mixed carbonyl-nitrosyl complexes, in which the photorelease of a ligand may proceed differently in excited singlet and triplet states, respectively, as implied by calculations and ongoing experiments [3].

[1] A Vogler, *Z. Naturforsch. B* **25**, 1069 (1970).

[2] S. H. C. Askes et al., *J. Am. Chem. Soc.* **139**, 15292 (2017).

[3] N. Gessner et al., *Phys. Chem. Chem. Phys.* **23**, 24187 (2021).

MO 8.21 Tue 16:30 P

Spectroscopic Studies of Carbonyl and Carbonylate Compounds in Liquid Ammonia — ●STEPHAN MUTH¹, FRANZ SCHMIDT², NIKOLAUS KORBER², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — ²Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg

Metal carbonyls have a multitude of applications in chemistry, biology, and beyond. Representing a crucial ingredient in catalysis for a long time, in recent years these complexes even gained attention in applications treating cancer [1]. Reduction of metal carbonyls by alkali metals in liquid ammonia affords ammoniates, showing a vast range of different structures, characterized by single crystal X-ray analysis [2]. Identification by interaction with visible light is cumbersome and hence, less commonly employed.

To unveil the structural arrangement in solution, unknown for many compounds, we monitor carbonyls and its reduction products in liquid ammonia at different temperatures by utilizing a custom-built cryostat. Ion pairs are generated by direct reduction of neutral homoleptic or heteroleptic carbonyls with solutions of alkali metals. The extent of separation of the anionic carbonylates and the cationic ammine complexes in solution is investigated, in dependence on the transition and alkali metals. Our studies aim at identifying characteristics of ion pairing, especially under the impact of this rather exceptional solvent.

[1] H. Pfeiffer et al., *Dalton Trans.*, 4292-4298 (2009).

[2] C. Lorenz et al., *Z. Anorg. Allg. Chem.* **644**, 1678-1680 (2018).

MO 8.22 Tue 16:30 P

Juxtaposition of the photolysis of diphenyldiselenide Ph_2Se_2 and diphenylselenide Ph_2Se and the subsequent recombination dynamics of the transient radicals — ●DANIEL GRENDA¹, CARINA ALLACHER¹, ELIAS HARRER¹, ROGER JAN KUTTA¹, ALEXANDER BREDER², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — ²Institut für Organische Chemie, Universität Regensburg, 93040 Regensburg

Organoselenium compounds can be used as effective catalysts in or-

ganic synthesis [1], they are building up polymers with dynamic covalent bonds [2] and they are working as antioxidants in vivo [3]. This rich chemistry is possible by virtue of the low bond energy of selenium bonds [2] and recombination of selenium-centered radicals.

By transient absorption spectroscopy on a nano- to microsecond timescale, we follow the dynamics of Ph_2Se and Ph_2Se_2 after photodissociation of the carbon-selenium or the selenium-selenium bond, respectively, forming the radicals PhSe^\bullet and Ph^\bullet . Both species photodegrade over prolonged illumination and partially interconvert into each other due to bimolecular radical pair recombination. Comparison of the differences and analogies of the photochemistry of Ph_2Se_2 and Ph_2Se allows a specific identification of the entire reaction pathways, intermediates and products.

[1] J. Trenner *et al.*, *Angew. Chem. Int. Ed.* **52**, 8952 (2013).

[2] S. Ji *et al.*, *Angew. Chem. Int. Ed.* **53**, 6781 (2014).

[3] L. P. Borges *et al.*, *Chem.-Biol. Interact.*, **160**, 99 (2006).

MO 8.23 Tue 16:30 P

Exploring the photophysics and chemistry of triarylamin with regard to the applicability in photocatalysis — ●JOSEPHINE BABEL, PATRICK NUERNBERGER, and ROGER JAN KUTTA — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Germany

Triarylamines Ph_3N generally possess a reversible one-electron oxidation behaviour, allowing the formation of its stable radical cation ($\text{Ph}_3\text{N}^{\bullet+}$). This makes them particularly attractive for photocatalytic oxidations of substrates with extreme high oxidation potentials *via* oxidative consecutive photoinduced electron transfer (con-PET) accumulating two photons of light.

Here, we characterize the photophysics and chemistry of Ph_3N and $\text{Ph}_3\text{N}^{\bullet+}$ in the presence and absence of molecular oxygen *via* transient absorption from fs to ms in the UV-visible spectral range. Starting from Ph_3N , we find $\text{Ph}_3\text{N}^{\bullet+}$ formation upon illumination *via* a bimolecular reaction of two molecules either each in a triplet state or

one in a triplet and the other in the groundstate. The excited state of $\text{Ph}_3\text{N}^{\bullet+}$ is, with a decay in the sub-100 ps, shorter than typical diffusion times for bimolecular reactions, which imposes limitations in terms of photocatalytic applicability. Considering also the determined photostability due to intra- and intermolecular photoconversion of Ph_3N , photocatalytic reactions must outcompete the intrinsic deactivation pathways for applications of photocatalytic con-PET type. Approaches to overcome these limitations such as pre-assembly or enhanced intersystem crossing within the photocatalyst will be discussed.

MO 8.24 Tue 16:30 P

Luminescent and excited state properties of bimetallic coinage metal NHC-complexes — ●DANIEL MARHÖFER¹, PIT BODEN¹, SOPHIE STEIGER¹, CHRISTOPH KAUB², PETER ROESKY², GEREON NIEDNER-SCHATTEBURG¹, and MARKUS GERHARDS¹ — ¹Department of Chemistry, TU Kaiserslautern, Erwin-Schrödinger-Str. 52-54, 67663 Kaiserslautern — ²Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstr. 15, 76131 Karlsruhe

A series of bimetallic coinage metal complexes containing a specific, bipyridyl substituted, N-heterocyclic carbene ligand was investigated via luminescence spectroscopy as well as step-scan FTIR spectroscopy. The emission lifetimes of the different bimetallic compounds as well as the underlying monometallic gold complex and the free ligand itself embedded in a potassium bromide matrix were determined by time-correlated single photon counting in the temperature range of 5 K - 290 K. The excited state structures were studied by electronic excitation by a pulsed UV laser followed by step-scan FTIR probing, allowing the determination of the IR absorption of the electronically excited molecules. The obtained excited state spectra were then compared to both the ground state vibrational spectrum as well as the excited state IR spectra of the other complexes of the series. A pronounced dependence of the excited state IR absorption, the emission colour and the excited state lifetimes on the metal centers could be observed.

MO 9: Femtosecond Spectroscopy II

Time: Wednesday 10:30–12:00

Location: MO-H5

MO 9.1 Wed 10:30 MO-H5

Direct Comparison of Molecular-Beam versus Liquid-Phase Pump-Probe and Two-Dimensional Spectroscopy on the Example of Azulene — ●HANS-PETER SOLOWAN¹, PAVEL MALÝ^{1,2}, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Faculty of Mathematics and Physics, Charles University, Prague, Ke Karlovu 5, 121 16 Praha 2, Czech Republic

With mass-resolved ion detection, we have introduced cations as a new observable in coherent two-dimensional (2D) spectroscopy [1]. Here we present new results of molecular-beam coherent 2D electronic spectroscopy on the example of azulene. We directly compare these gas-phase with liquid-phase measurements of azulene dissolved in cyclohexane. Both schemes probe the same Liouville-space pathway from S_0 to S_2 . Furthermore we show the S_1 excitation dynamics of azulene obtained by pump-probe measurements in both phases and discuss results with respect to a passage through a conical intersection between azulene's S_1 and S_0 state. The comparison allows us to isolate the influence of the environment of the molecule on its excited-state dynamics.

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

MO 9.2 Wed 10:45 MO-H5

Generation and compression of 10-fs deep ultraviolet pulses at high repetition rate using standard optics — ●LUKAS BRUDER¹, LUKAS WITTENBECHER^{2,3,5}, PAVEL KOLESNICHENKO^{3,4,5}, and DONATAS ZIGMANTAS^{3,5} — ¹Institute of Physics, University of Freiburg, Germany — ²Department of Physics, Lund University, 221 00 Lund, Sweden — ³NanoLund, Lund University, 221 00 Lund, Sweden — ⁴Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg — ⁵Chemical Physics, Lund University, 221 00 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 ($< 10 \mu\text{J}$). Based on achromatic phase matching [1], we have accomplished the efficient generation of sub-10-fs pulses at a repetition rate of 200 kHz, tunable in the wavelength range 250-320 nm [2]. We also simplified the pulse compression scheme, avoiding adaptive optics.

[1] P. Baum *et al.*, *Opt. Lett.* **29**, 1686 (2004)

[2] L. Bruder *et al.*, *Opt. Express* **29**, 25593 (2021)

MO 9.3 Wed 11:00 MO-H5

Tracking Ultrafast Exciton-Exciton Annihilation in a Squaraine Dimer by Sixth-Order Fluorescence-Detected Two-Dimensional Spectroscopy — ●STEFAN MÜLLER¹, PAVEL MALÝ¹, JULIAN LÜTTIG¹, CHRISTOPH LAMBERT², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Exciton-exciton annihilation (EEA), that is, the loss of one exciton through the interaction with another exciton, is an integral part of the excitation dynamics in molecular aggregates under high light irradiation. Through recent developments, the dynamics of EEA can be measured directly by coherently detected fifth-order two-dimensional (2D) spectroscopy, whereby the properties of exciton diffusion can also be determined [1]. Nonetheless, it is challenging to isolate ultrafast annihilation events as they may be obscured by coherent artifacts and nonresonant response. Here we introduce a novel 2D spectroscopic method to temporally resolve ultrafast EEA by detecting fluorescence and using only a single excitation beam. This is achieved by isolating specific sixth-order signals via 125-fold phase cycling of a collinear four-pulse excitation sequence [2]. We verify our approach on a squaraine heterodimer with aid of fifth-order 2D spectroscopy [3].

[1] J. Dostál *et al.*, *Nat. Commun.* **9**, 2466 (2018).

[2] S. Mueller *et al.*, *Nat. Commun.* **10**, 4735 (2019).

[3] P. Malý *et al.*, *J. Chem. Phys.* **153**, 144204 (2020).

MO 9.4 Wed 11:15 MO-H5

Tracking Ultrafast Exciton Diffusion in Squaraine Polymers at Various Temperatures — ●SIMON BÜTTNER¹, JULIAN LÜTTIG¹, PAVEL MALÝ^{1,2}, ARTHUR TURKIN³, CHRISTOPH LAMBERT³, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague, Czech Republic — ³Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Exciton diffusion is an important process in solar light harvesting and organic electronics. We use exciton–exciton-interaction two-dimensional (EEI2D) spectroscopy [1], which observes the process of exciton–exciton annihilation (EEA) to track the exciton diffusion in organic materials. Using EEI2D spectroscopy, we recently found in squaraine polymers a change from wavelike transport to a sub-diffusive character of exciton diffusion on an ultrafast timescale [2]. For further investigations we now analyzed the influence of the environment on exciton diffusion. We embedded the squaraine polymers in a polystyrene matrix and used EEI2D spectroscopy in a cryostat to determine the effect of temperature on exciton diffusion. We also compare the results with temperature-dependent measurements on squaraine polymers in solution to demonstrate the differences between a solid and a liquid environment.

[1] J. Dostál et al., Nat. Commun. **9**, 2519, (2018)

[2] P. Malý et al., Chem. Sci. **11**, 456 (2020)

MO 9.5 Wed 11:30 MO-H5

Dynamics of photoexcited Cs atoms attached to helium nanodroplets — ●NICOLAS RENDLER¹, AUDREY SCOGNAMIGLIO¹, MANUEL BARRANCO^{2,3,4}, MARTI PÍ^{2,4}, NADINE HALBERSTADT³, KATRIN DULITZ¹, and FRANK STIENKEMEIER¹ — ¹Institute of Physics, University of Freiburg, Germany — ²Departament FQA, Universitat de Barcelona, Spain — ³IRSAMC, Université de Toulouse, France — ⁴IN2UB, Universitat de Barcelona, Spain

We present an experimental study of the dynamics of photoexcited Cs atoms located in a dimple on the surface of He nanodroplets. The repulsive interaction between the electronically excited alkali atom and the He environment usually leads to the ejection of the excited alkali atom from the surface of the He nanodroplet [1]. This process can

be accompanied by fast electronic relaxation induced by the He environment and by the formation of He-Cs exciplex molecules [2]. After ionization, alkali atoms tend to be attracted by the He nanodroplet which eventually leads to their solvation inside of the droplet interior. Using femtosecond pump-probe spectroscopy combined with velocity-map-imaging and ion-time-of-flight detection, we have determined the time scales for Cs atom ejection and solvation after excitation to the 6p state as well as for CsHe exciplex formation [3]. Our results are compared to results of density-functional-theory simulations [4]. [1] M. Mudrich, F. Stienkemeier, Int. Rev. Phys. Chem. **33**, 301-339 (2014). [2] Reho et al., Faraday Discuss. **108**, 161, (1997). [3] N. Rendler et al., J Phys Chem A. **125** (41), 9048-9059 (2021). [4] Coppens et al., Eur. Phys. J. D **73**, 94, (2019).

MO 9.6 Wed 11:45 MO-H5

Ultrafast Dynamics of Xanthine Derivatives and their Use in a Nickel-Catalysed Cross-Coupling Reaction — ●THOMAS RITTNER¹, RAFAEL E. RODRÍGUEZ-LUGO², KARINA HEILMEIER¹, SVENJA WORTMANN¹, SIMON DIETZMANN², ROBERT WOLF², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — ²Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg

Carbon-carbon and carbon-heteroatom cross-coupling is of high relevance in organic synthesis. In recent years, photo-induced nickel dual-catalysis has been successfully implemented for such bond-forming reactions under exceptionally mild conditions, albeit usually expensive precious metal containing photosensitizers are required [1]. We circumvent this issue with newly developed Xanthine-based ligands.

We employ both stationary and time-resolved absorption and emission spectroscopy to unveil the mechanism of this newly developed catalytic system. Spectral properties and dynamics of the ligands, of the reaction mixture, and of a model complex are juxtaposed. The coordination of the Xanthine ligands to Ni(II) is found to be rather weak. The lack of spectral overlap of ligand absorption and light source, as well as the ligand's short excited-state lifetime queries the direct involvement of the ligand in the primary photostep. We thus aim at identifying alternative mechanisms for the photocatalytic process. Additionally, a competitive photoisomerization in the Xanthine ligand may occur.

[1] C. Zhu et al., Angew. Chem. Int. Ed. **2021**, 60, 17810.

MO 10: XUV-spectroscopy

Time: Wednesday 10:30–12:15

Location: MO-H6

MO 10.1 Wed 10:30 MO-H6

Attosecond pump-probe coincidence spectroscopy of small molecules at 100 kHz — ●MIKHAIL OSOLODKOV, TOBIAS WITTING, FEDERICO J. FURCH, FELIX SCHELL, CLAUS PETER SCHULZ, and MARC J. J. VRAKING — Max Born Institute, Berlin, Germany

It is advantageous to perform attosecond photoionization experiments in molecules with coincidence detection, since it allows resolving particular photoionization channels, such as dissociative channels. Here we report on experiments done at a beamline combining a table top high order harmonic generation (HHG) based extreme ultraviolet (XUV) laser pulse source operating at 100 kHz [1] with a reaction microscope [2], being recently commissioned. A noncollinear optical parametric chirped pulse amplification system (NOPCPA) operating at 800 nm central wavelength [3] serves as a driver. Both XUV attosecond pulse trains (APTs) [1], as well as isolated attosecond pulses (IAPs) are available for attosecond pump-probe experiments with a near infrared (NIR) probe. Employing the coincidence capabilities, the photoionization dynamics corresponding to the predissociative C state of the molecular nitrogen ion was studied state selectively using the RABBIT (reconstruction of attosecond beating by interference of two-photon transitions) technique with short XUV APTs and approximately 7 fs FWHM NIR pulses.

[1] M. Osolodkov et al., J. Phys. B: At. Mol. Opt. Phys. (2020)

[2] Sascha Birkner, PhD thesis, Freien Universität Berlin (2015)

[3] Federico J. Furch et al., Optics Letters (2017)

MO 10.2 Wed 10:45 MO-H6

Experimental control of quantum-mechanical entanglement in an attosecond pump-probe experiment — ●LISAMARIE KOLL¹, LAURA MAIKOWSKI¹, LORENZ DRESCHER^{1,2}, TOBIAS

WITTING¹, and MARC J.J. VRAKING¹ — ¹Max Born Institute, Berlin, Germany — ²Department of Chemistry, University of California, Berkeley, California 94720, USA

The photoionization of atoms or molecules creates a bipartite quantum system consisting of a photoelectron and an ion. In many experiments the observability of a physical quantity of interest relies on the coherence between the ionic or electronic parts of the wave function. However, this coherence can be limited by entanglement [1]. We show the control of entanglement by tuning the delay of two phase-locked XUV pulses in the dissociative ionization of hydrogen molecules [2]. Our experiments show the changing degree of vibrational coherence due to entanglement between the ionic and photoelectronic part of the quantum system.

[1] M. J.J. Vrakking, "Control of Attosecond Entanglement and Coherence", Physical Review Letters **126**, 113203 (2021)

[2] L.-M. Koll et. al., "Experimental control of quantum-mechanical entanglement in an attosecond pump-probe experiment", Physical Review Letters (in press) (or: arXiv:2108.11772 (2021))

MO 10.3 Wed 11:00 MO-H6

Observing the electronic coherence in uracil via simulated XUV spectra — ●LENA BAUML¹, FLORIAN ROTT¹, THOMAS SCHNAPPINGER², and REGINA DE VIVIE-RIEDLE¹ — ¹Department of Chemistry, LMU Munich, Germany — ²Department of Physics, Stockholm University, Sweden

The nucleobase uracil exhibits a high photostability due to its ultrafast relaxation process mediated by a S_1/S_2 conical intersection (CoIn) seam. Here especially the interplay between nuclear and electron dynamics becomes prominent. Applying our NEMol Ansatz^[1,2] for coupled electron and nuclear dynamics on the quantum level, we were

able to observe a seemingly long-lived electronic coherence for the CoIn-mediated relaxation process in uracil. We will discuss the origin of this longevity and will propose a possible experiment to observe this coherence. Our method of choice is the time-dependent transient XUV/X-ray absorption spectroscopy, since this method is sensitive to the fast changes in electronic structure. Therefore we calculated the transient XUV spectra for the O, N, and C edges based on the complete wavepacket relaxation dynamics after laser excitation. The calculations were performed at the restricted active space perturbation theory (RASPT2) level of theory as outlined by Rott *et al.*^[3].

[1] T. Schnappinger *et al.*, *J. Chem. Phys.*, **154**, 134306 (2021).

[2] L. Bäuml *et al.*, *Front. Phys.*, **9**, 246 (2021).

[3] F. Rott *et al.*, *Structural Dynamics*, **8**, 034104 (2021).

MO 10.4 Wed 11:15 MO-H6

X-ray absorption spectroscopy of the hydronium cation

— ●JULIUS SCHWARZ¹, FRIDTJOF KIELGAST¹, IVAN BAEV¹, SIMON REINWARDT¹, FLORIAN TRINTER², STEPHAN KLUMPP³, SADIYA BARI^{3,4}, ALEXANDER PERRY-SASSMANSHAUSEN⁵, TICIA BUHR⁵, STEFAN SCHIPPERS⁵, ALFRED MÜLLER⁵, and MICHAEL MARTINS¹ — ¹Universität Hamburg, Hamburg, Germany — ²Goethe-Universität Frankfurt am Main, Frankfurt am Main, Germany — ³Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ⁴Rijksuniversiteit Groningen, Groningen, The Netherlands — ⁵Justus-Liebig-Universität Gießen, Gießen, Germany

Facilitated by the hydrogen-bond network of water, protons in liquid water are diffused at a rapid rate, with several possible explanations invoking the hydronium cation H_3O^+ . Among the many ways of gaining knowledge about H_3O^+ , the method of soft X-ray absorption spectroscopy has been established as a valuable analysis tool for ionic molecules and clusters [1].

We report the use of a flowing afterglow ion source to record the soft X-ray absorption spectrum of the hydronium H_3O^+ cation at the O 1s edge using the photon ion spectrometer (PIPE) at the synchrotron lightsource PETRA III in Hamburg [2]. H_2O^+ cations have been analyzed for comparison. The spectra show significant shifts in resonance energies and widths compared to neutral H_2O and relative to each other.

[1] Martins *et al.*, *J. Phys. Chem. Lett.*, **12** 5 (2021), 1390–1395

[2] S. Schippers *et al.*, *X-Ray Spectrometry*, **49** 11 (2020)

MO 10.5 Wed 11:30 MO-H6

Revealing ultrafast proton transfer dynamics in ionized aqueous urea solution through time-resolved x-ray absorption spectra and *ab initio* simulations

— ●YASHOJ SHAKYA^{1,2}, LUDGER INHETER¹, ZHONG YIN³, YI-PING CHANG⁴, TADAS BALČIUNAS⁴, JEAN-PIERRE WOLF⁴, HANS JAKOB WÖRNER³, and ROBIN SANTRA^{1,2,5} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²Department of Physics, Universität Hamburg, Hamburg, Germany — ³Laboratory for Physical Chemistry, ETH Zürich, Zürich, Switzerland — ⁴GAP-Biophotonics, Université de Genève, Geneva, Switzerland — ⁵Hamburg Centre for Ultrafast Imaging, Hamburg, Germany

Probing the early dynamics of chemical systems following ionization is essential for our understanding of radiation damage. Time-resolved x-ray absorption spectroscopy (TRXAS) on a femtosecond timescale can provide crucial insights into the ultrafast processes occurring upon ionization due to its element-specificity. However, to get a clear interpretation of the dynamical features in the spectra, one often has to rely on theoretical simulations.

In this theoretical study, we investigate the response of urea in 10M aqueous solution to ionizing radiation and how it can be probed via TRXAS. We are able to interpret the temporal variation in the carbon K-edge resonance signal as an effect of proton transfer between two hydrogen bonded ureas through our *ab initio* simulations. Our results are in good agreement with recent pump-probe experiments on 10 M aqueous urea solution.

MO 10.6 Wed 11:45 MO-H6

Ultrafast photoisomerization studied by time-resolved photoelectron spectroscopy

— CAMILO GRANADOS¹, EVGENII TITOV², JOHAN HUMMERT¹, EVGENII IKONNIKOV¹, STEFAN HAACKE³, ROLAND MITRIC⁴, and ●OLEG KORNILOV¹ — ¹Max Born Institute, Berlin — ²Department of Chemistry, University of Potsdam — ³Institut de physique et de chimie des Matériaux, Strasbourg — ⁴Institute of Physical and Theoretical Chemistry, University of Würzburg

Ultrafast photoinduced isomerization is a fundamental process governing molecular dynamics both in biologically relevant chromophores and in functional materials. It is widely accepted that the isomerization efficiency is governed by the dynamics through conical intersections. However, the influence of the complex environments hosting the chromophores on the dynamics through the conical intersection is not fully understood. XUV time-resolved photoelectron spectroscopy (TRPES), are promising in delivering detectable signals from the regions of conical intersection. TRPES of molecular chromophores requires application of photoemission methods to the liquid phase samples (molecular solutions). By combining an ultrafast tunable XUV source with a micro-liquid jet sample we demonstrated liquid phase TRPES of organic molecules. In this contribution we will report on the recent results applying this method to the prototypical molecules, Methyl Orange and Metanil Yellow[2]. The experimental results are complemented by high-level TDDFT surface hopping calculations to reveal electronic state involved in ultrafast isomerization of the molecules. We will further show preliminary results for several bio-mimetic chromophores.

MO 10.7 Wed 12:00 MO-H6

Molecular environments in the time-domain

— ●CHRISTIAN SCHRÖDER, MAXIMILIAN POLLANKA, PASCAL SCIGALLA, MICHAEL MITTERMAIR, ANDREAS DUENSING, MARTIN WANCKEL, and REINHARD KIENBERGER — Chair for laser and X-ray physics E11, Technische Universität München, Germany

We report on photoemission timing measurements performed on small iodine-substituted organic molecules in the gas phase. The iodine atom's 4d photoemission serves as an intra-molecular timing reference which is clocked against the accurately known He1s photoemission.

Using the iodine atom as an intra-molecular reference is motivated by the presence of a giant resonance in the I4d \rightarrow ϵf photoemission channel which is expected to be largely unaffected by its chemical environment. Therefore, in proximity to the resonance, any difference in the observable photoemission delay between different molecules is expected to a consequence of the differences in molecular environment experienced by the leaving photoelectron wavepacket during its propagation through the molecular potential landscape.

We complement our findings with scattering calculations in order to gain deeper insight into the relationship between the observable photoemission time and molecular geometry, the photoelectron angular distribution and the role of the molecule's orientation during the experiment, thereby paving the road towards establishing photoemission timing experiments as an efficient and accurate means to study molecular environments.

MO 11: Photochemistry I

Time: Wednesday 10:30–11:45

Location: MO-H7

MO 11.1 Wed 10:30 MO-H7

UV and Mid-IR Photo-induced Dissociation of Solvated (Bio)Molecular Complexes

— ●MUKHTAR SINGH^{1,2,3}, MATTHEW SCOTT ROBINSON^{1,2,3}, HUBERTUS BROMBERGER^{1,2}, JOLIJN ONVLEE^{1,3}, SEBASTIAN TRIPPEL^{1,2}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Center for Ultrafast Imaging, Universität Hamburg — ³Department of Physics, Universität Hamburg

We present the ultrafast imaging of UV and thermal energy chemical dynamics of micro-solvated (bio)molecular complexes probed with strong field techniques [1]. We produced a pure sample of the molecule of interest in the gas phase by using a combination of a molecular beam and the electrostatic deflector [2]. To study the induced dynamics, we set up the both, an UV and a mid-IR pump-probe experiment, in which a 266 nm and 2.9 μm beam was used to excite the system. A 1.3 μm beam was used for ionising the system. First experiments focused on the ion imaging of the UV and mid-IR triggered system. Future exper-

iments will use laser-induced electron diffraction (LIED) [3,4] to probe the induced dynamics in order to obtain structural information about the system with atomic resolution.

- [1] J. Onvlee, et al., *arXiv:2103.07171v1* 12 Mar 2021.
- [2] S. Trippel, et al., *Rev. Sci. Instrum.* **89**, 096110 (2018).
- [3] J. Wiese, et al., *Phys. Rev. Research* **3**, 013089 (2021).
- [4] E. T. Karamatskos, et al., *J. Chem. Phys.* **150**, 244301(2019).

MO 11.2 Wed 10:45 MO-H7

Multiphoton light-induced potentials — ●MATTHIAS KÜBEL — Institut für Optik und Quantenelektronik, FSU Jena

We study the strong-field photodissociation of H_2^+ using Cold Target Recoil Ion Momentum Spectroscopy. Our two-color streaking method allows us to produce a coherent wave packet in the molecular cation and expose it to a phase-controlled mid-infrared laser field. The resulting fragmentation pattern exhibits a strikingly structured angular distribution, which depends on various laser parameters. Using two-color Floquet theory as well as numerical solutions of the time-dependent Schrödinger equation, we show that the pattern arises from an interplay of competing multiphoton fragmentation pathways, as well as forced rotational dynamics. On a qualitative level, the dynamics can be intuitively understood by picturing the light-induced potential energy landscape on which the nuclear motion takes place. Interestingly, our experimental approach allows us to shape these potentials and follow the ensuing molecular dynamics. Our results highlight the complexity of intense matter interaction even in the simplest of molecules.

MO 11.3 Wed 11:00 MO-H7

A Velocity Map Imaging Study of the Photodissociation Dynamics of the Trichloromethyl Radical — ●CHRISTIAN MATTHAEI¹, DEB PRATIM MUKHOPADHYAY^{1,2}, and INGO FISCHER¹ — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg — ²Present address: Department of Dynamics of Molecules and Clusters, J. Heyrovský Institute of Physical Chemistry, Dolejškova 2155/3, 182 23 Praha 8, Czech Republic

CCl_3 is one of the numerous halogen-containing molecules that contribute to the catalytic destruction of the ozone layer. Here we investigate the photodissociation dynamics of this molecule following the excitation with light between 250 and 230 nm. We mainly observe the loss of a Cl atom, that is associated with the CCl_2 fragment. However, the generation of CCl could also be observed. Control experiments using CCl_2 as a precursor suggest that the CCl results from the reaction CCl_3 to $CCl + Cl_2$.

MO 11.4 Wed 11:15 MO-H7

Mechanistic Studies on a Deracemization Reaction via a Triplet 1,3-Diradical Induced by Energy Transfer from a

Chiral Sensitizer — ●ROGER JAN KUTTA¹, XINYAO LI², CHRISTIAN JANDL², ANDREAS BAUER², THORSTEN BACH², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Germany — ²Lehrstuhl für Organische Chemie I, Technische Universität München, Germany

The photochemical deracemization[1] of spiro[cyclopropane-1,3'-indolin]-2'-ones (spirocyclopropyl oxindoles) was investigated by time-resolved spectroscopies and computational approaches. The corresponding 2,2-dichloro compound is configurationally labile upon direct irradiation and when sensitized by excited achiral thioxanthone-9-one. In the latter reaction the triplet 1,3-diradical intermediate is generated via triplet energy transfer from the photosensitizer.

Deracemization is achieved by using a chiral thioxanthone photosensitizer with a lactam hydrogen bonding site. Here, three factors co-act favorably for high enantioselectivity: i) a factor 3 differing binding constants to the chiral thioxanthone for the two enantiomers. ii) unequal molecular distances in the complexes, presumably lead to differing energy transfer efficiencies. iii) the 1,3-diradical lifetime exceeds the complex lifetime, facilitating a racemic deactivation back to the ground state.[2]

- [1] *Nature* **2018**, 564, 240-243.
- [2] *Angew. Chem. Int. Ed.* **2020**, 59, 21640-21647.

MO 11.5 Wed 11:30 MO-H7

Selenyl Radicals in Solution: Photogeneration and Reactions — ●CARINA ALLACHER¹, ROGER JAN KUTTA¹, ELIAS HARRER¹, DANIEL GREINDA¹, AMIT KUMAR-DUTTA², SOOYOUNG PARK², ALEXANDER BREDER², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — ²Institut für Organische Chemie, Universität Regensburg, 93040 Regensburg

Due to the low bond energy of selenium bonds, selenium-centered radicals can be formed photochemically with visible or near-UV light [1], thereby opening up new synthetic strategies based on the versatile reactivity of these radical species. A prominent precursor of the phenylselenyl radical ($PhSe^\bullet$) is diphenyl diselenide (Ph_2Se_2) which upon irradiation with UV light may dissociate homolytically [2]. In this work, we identify an additional reaction pathway that is pursued after excitation of Ph_2Se_2 with 355 nm light. To quantify the dynamics of these competing photochemical processes, transient absorption studies on a timescale from nano- to milliseconds are performed in various solvent environments. Solely in the solvent hexafluoro-2-propanol, a further intermediate, namely the radical $PhSeH^{+\bullet}$, can be photogenerated. Beyond Ph_2Se_2 , we present time-resolved studies on further organoselenium compounds as light-triggered sources of $PhSe^\bullet$ and $PhSeH^{+\bullet}$ radicals.

- [1] S. Ji *et al.*, *Angew. Chem. Int. Ed.* **53**, 6781 (2014).
- [2] I. P. Beletskaya *et al.*, *J. Chem. Soc., Perkin Trans. 2*, 107 (2007).

MO 12: Annual General meeting

Time: Wednesday 12:45–13:15

Location: MO-MV

30 min. break

MO 13: Femtosecond Spectroscopy III

Time: Wednesday 14:30–15:45

Location: MO-H5

MO 13.1 Wed 14:30 MO-H5

Ultrafast excited-state dynamics of new Fe(II) photosensitizers with linked organic chromophores — ●MIGUEL ANDRE ARGÜELLO CORDERO¹, AYL A KRUSE¹, PHILIPP DIERKS², MATTHIAS BAUER², and STEFAN LOCHBRUNNER¹ — ¹University of Rostock, Germany — ²University of Paderborn, Germany

Photocatalytic approaches for the generation of solar fuels are of rising interest, due to their potential as source for renewable energy. As one key component they contain typically metal-based photosensitizers (PS) to absorb sunlight. Because of the low costs and availability of iron, PS based on it are currently intensively investigated to replace their rare and noble metal-based analogues. When the PS absorb light a metal-to-ligand charge-transfer state is populated. Its lifetime should be in the ns region to perform chemical reactions. In this work

we present newly synthesized Fe(II)-based PS with an organic chromophore linked to its ligand backbone. With this additional unit the complexes not only show a wider absorption range in the visible. After optical excitation emissive excited states with lifetimes of some ns seem to become populated. Comparison with the emission behaviour of the pure ligands lead to the assumption that the chromophore moiety undergoes electronic decoupling from the rest of the ligand, if the ligand is linked to the Fe(II) centre. This may lay a basis for the exploration of the reservoir effect, facilitating a populated state located on the linked chromophore. Here we present our results on ultrafast pump-probe absorption and time-resolved emission spectroscopy of these new PS and discuss them with respect to the electronic relaxation pathways.

MO 13.2 Wed 14:45 MO-H5
Femtosecond-NeNePo Spectroscopy of Small Silver Clus-

ters — ●MAX GRELLMANN, JIAYE JIN, JÜRGEN JÄSCHKE, MARCEL JOREWITZ, and KNUT R. ASMIS — Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstrasse 2, D-04103 Leipzig, Germany

Vibrational spectroscopy on mass-selected neutral silver clusters is still difficult to be performed due to a lack of efficient methods to directly select a single mass for neutral species in the gas-phase and rare intense and tunable far infrared sources in the vibrational frequency range of metal-metal bonds.

Here, we present experimental results probing the wave packet dynamics on the electronic ground state potential energy surface of the neutral silver tetramer by using femtosecond pump-probe spectroscopy via three charge states, so-called NeNePo (negative-neutral-positive) spectroscopy. Silver clusters are produced in a liquid nitrogen cooled magnetron sputter source. Mass-selected silver tetramer anions are accumulated in a gas-filled ion trap, thermalized to 20 K and subsequently photodetached using an 800 nm ultrafast pump pulse. The wave packet dynamics are then probed using a second, photoionizing ultrafast 400 nm probe pulse. The so produced signal of silver tetramer cations (and its fragments) is monitored mass-selectively as a function of the laser pulses delay time, yielding a NeNePo spectrum. Frequency analysis by Fourier transform reveals evidence for the time-dependent excitation of all six vibrational modes and the time scale of intramolecular vibrational energy redistribution processes.

MO 13.3 Wed 15:00 MO-H5

Time-resolved ultrafast spectroscopy of acene monomers and acene complexes in helium nanodroplets — ●AUDREY SCOGNAMIGLIO, NICOLAS RENDLER, KATRIN DULITZ, LUKAS BRUDER, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder Straße 3, 79104 Freiburg-im-Breisgau

The motivation to study acene molecules such as tetracene and pentacene originates from the recent interest in organic photovoltaics research (OPVs)[1]. Indeed, those molecules are known to produce multiple charge carriers through singlet fission, thus enhancing the efficiency of such devices[2], [3]. On the one hand, we experimentally study acene monomers in the gas phase to get insights into their energy-level structure, and into the possible intramolecular relaxation dynamics and associated time scales. On the other hand, we use the helium nanodroplet matrix isolation technique to synthesize complexes of two or more molecules. So far, experimental studies are available only for crystalline or solution-based systems. We present here time-resolved two-colour pump-probe studies on acene monomers and acene complexes, investigated using photoelectron imaging and high-resolution ion-time-of-flight mass spectrometry over a large mass/charge range.

[1] T. M. Clarke and J. R. Durrant, *Chem. Rev.*, vol. 110(11), 2010

[2] P. M. Zimmerman *et al.*, *J. Am. Chem. Soc.*, vol. 133(49), 2011

[3] P. M. Zimmerman *et al.*, *Nat. Chem.*, vol. 2(8), 2010

MO 13.4 Wed 15:15 MO-H5

MO 14: Photochemistry II

Time: Wednesday 14:30–16:00

Location: MO-H6

MO 14.1 Wed 14:30 MO-H6

Studying the photodynamics of a formazan in binary solvent mixtures — ●SVENJA WORTMANN, SYLVIA SCHLOEGLMANN, and PATRICK NUERNBERGER — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg

1,3,5-Triphenylformazan (TPF) contains an azo group and a hydrazone group, of which both can isomerize upon excitation with visible light. Therefore, TPF can exist in different isomeric forms, which can be converted into each other accompanied by a color change of the solution [1,2]. The ratio of the present formazan isomers and their thermal stability are dependent on the solvent environment and the illumination conditions. Thus, we studied the photodynamic behavior of TPF in toluene solution and with additional admixtures of protic and aprotic cosolvents with transient absorption spectroscopy on different time scales. Especially, the thermal back-isomerization around the C=N double bond shows a high sensitivity regarding the binary solvent mixtures. Finally, it was possible to elucidate the role of solvent polarity as well as the impact of hydrogen bonding. Whereas an increased solvent polarity of the binary mixture results in a decreased

Coherent two-dimensional photoelectron spectroscopy — ●DANIEL UHL, ULRICH BANGERT, LUKAS BRUDER, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Germany.

Coherent multidimensional spectroscopy (CMDS) is a powerful ultrafast spectroscopic technique which provides spectro-temporal information otherwise only accessible in disjunct experiments. Photoelectron spectroscopy, on the other hand, provides detailed information about the chemical composition and electronic states of the sample.

Here we present a combination of both methods in a single experiment [1]. This becomes feasible with the development of an efficient single-counting detection and multichannel software-based lock-in amplification [2]. The approach offers high temporal, spectral and kinetic energy resolution. It enables differential CMDS experiments with unprecedented selectivity and enhances the dynamic range of CMDS by up to two orders of magnitude. The presented concept opens up a new perspective for atomically-resolved CMDS experiments using X-ray photoelectron spectroscopy.

[1] D. Uhl, U. Bangert, L. Bruder, and F. Stienkemeier, *Optica* 8, 1316-1324 (2021)

[2] D. Uhl, L. Bruder, and F. Stienkemeier, *Review of Scientific Instruments* 92, 083101 (2021).

MO 13.5 Wed 15:30 MO-H5

Simulating time-resolved X-ray absorption spectroscopy of pyrazine at the nitrogen K-edge with a full time-domain approach — ●ANTONIA FREIBERT^{1,2}, DAVID MENDIVE-TAPIA², NILS HUSE¹, and ORIOL VENDRELL² — ¹University of Hamburg, Hamburg, Germany — ²Heidelberg University, Heidelberg, Germany

Ultrafast X-ray absorption spectroscopy offers elemental specificity and in principle access to the natural time evolution of valence excitations and materials. Due to the complex nature of probing structural dynamics on the femtosecond timescale, detailed theoretical studies are required to link the spectroscopic observables to the underlying dynamics and thereby access the high information content contained in this experimental method. A large influence of nuclear dynamics can be expected in nonlinear spectroscopy which requires a time-dependent framework that is able to describe non-adiabatic phenomena.

I will present time-resolved X-ray absorption spectroscopy simulations of pyrazine at the nitrogen K-edge including wavepacket dynamics in both the valence- and core-excited state manifolds. We discuss the validity of the widely used short-time (or Lorentzian) approximation which neglects the nuclear dynamics following the X-ray probe transition. We further demonstrate the impact of an explicit description of the external electric field and explicitly calculate the effect of an increasingly longer excitation pulse on the observed photo-triggered wavepacket dynamics.

activation barrier, hydrogen bonding may have the contrary effect on the thermal back-relaxation. Hence, both hydrogen-bond donors and acceptors as cosolvents can slow the isomerization reaction of TPF [3].

[1] R. Kuhn, H.M. Weitz, *Chem. Ber.* 86, 1199-1212 (1953)

[2] U.-W. Grummt, H. Langbein, *J. Photochem.* 15, 329-334 (1981)

[3] S. Wortmann, S. Schloeglmann, P. Nuernberger, *J. Org. Chem.* (2021), DOI:10.1021/acs.joc.1c01928.

MO 14.2 Wed 14:45 MO-H6

Transient FTIR spectroscopy after one- and two-colour excitation on a highly luminescent chromium(III) complex — ●PIT BODEN¹, PATRICK DI MARTINO-FUMO¹, GEREON NIEDNER-SCHATTEBURG¹, WOLFRAM SEIDEL², and KATJA HEINZE³ — ¹TU Kaiserslautern, Fachbereich Chemie and Research Center Optimas, Germany — ²University of Rostock, Institute of Chemistry, Germany — ³JGU Mainz, Department of Chemistry, Germany

In this contribution^[1] the electronic and structural properties of a highly luminescent mononuclear chromium(III) complex with polypyridyl ligands are investigated via luminescence and in particular transient step-scan FTIR spectroscopy at different temperatures.

The relative population of two NIR-emissive energetically close-lying electronically excited doublet states strongly depends on the available thermal energy. In a new kind of two-colour step-scan FTIR experiments the population of the long-lived excited states is further modulated via pump/pump/probe (FTIR) and pump/dump/probe (FTIR) schemes. Hereby, the second pump or dump excitation, following the initial UV pump excitation, is stimulated by a NIR laser pulse with the wavelength being set according to the phosphorescence spectrum. The successful establishment of this new technique is an important step towards investigations on further transition metal complexes.

[1] P. Boden, P. Di Martino-Fumo, G. Niedner-Schatteburg, W. Seidel, K. Heinze, M. Gerhards, *Phys. Chem. Chem. Phys.* 2021, **23**, 13808.

MO 14.3 Wed 15:00 MO-H6

Reversible (photo)chemistry of Cr(0), Mo(0) and W(0) carbonyl complexes — ●SOPHIE STEIGER¹, PIT BODEN¹, PATRICK DI MARTINO-FUMO¹, TOBIAS BENS², DANIEL MARHÖFER¹, BIPRAJIT SARKAR², GERON NIEDNER-SCHATTEBURG¹, and MARKUS GERHARDS¹ — ¹TUK, FB Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern — ²University of Stuttgart, Institute of Inorganic Coordination Chemistry, Pfaffenwaldring 55, 70569 Stuttgart

This contribution presents the investigations of the photochemical reactivity of chromium, molybdenum and tungsten carbonyl complexes containing a bidentate pyridyl-mesoionic carbene ligand. The photochemical reactivity of these complexes in pyridine, acetonitrile or in a KBr pellet was analysed by rapid-scan FTIR spectroscopy or by recording static FTIR spectroscopy at defined time intervals. Hereby, the carbonyl stretching vibrations represented suitable IR probes. In the dark after excitation, a reverse reaction to the initial species occurs. The influence of the metal centre and the solvent on the kinetics of the reverse reaction in solution and the quantum yield of the initial photochemical reaction were determined.

Quantum chemical calculations were performed for conceivable photoproducts to characterise the underlying reaction. The loss of an axial CO ligand was assigned to the photoproduct in the solid state at low temperature, with subsequent occupation of the vacant coordination site by a solvent molecule in fluid solution. This interpretation simultaneously explains the appearance of a signal of free CO in the FTIR spectra.

MO 14.4 Wed 15:15 MO-H6

Photochemistry of the Benzaldehyde-BCl₃ Complex — ●MARTIN PESCHEL¹, PIOTR KABACINSKI², DANIEL SCHWINGER³, ERLING THYRHAUG⁴, THOMAS KNOLL¹, GIULIO CERULLO², THORSTEN BACH³, JÜRGEN HAUER⁴, and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, Ludwig-Maximilians-Universität München — ²IFN-CNR and Dipartimento di Fisica, Politecnico di Milano — ³Department of Chemistry and Catalysis Research Center (CRC), Technische Universität München — ⁴Professur für Dynamische Spektroskopie, Fakultät für Chemie, Technische Universität München

The excited state properties of α , β -enones can be altered by complexation with a Lewis acid to enable otherwise inaccessible photochemical transformations.[1] After excitation, α , β -enones relax to a triplet state from which subsequent reactions can occur. This $\pi\pi^*$ triplet is stabilized by interaction with a Lewis acid and studies using UV/Vis transient absorption spectroscopy and quantum chemical calculations show that its formation only takes a few picoseconds.[2] We expected this behavior to also occur in the aromatic α , β -enone benzaldehyde when

interacting with the Lewis acid BCl₃. Instead, non-adiabatic dynamics calculations showed ultrafast dissociation of a chlorine atom. The resulting benzyl radical could be identified in a theory-guided UV/Vis ultrafast transient absorption experiment and was found to be surprisingly long lived. This led to the discovery of a novel chemical reaction of benzaldehyde which uses the radical chemistry of chlorine.

[1] *Angew. Chem. Int. Ed.* **2018**, *57*, 14338-14349.

[2] *Angew. Chem. Int. Ed.* **2021**, *60*, 10155-10163.

MO 14.5 Wed 15:30 MO-H6

Accurate determination of the Adenine-Thymine binding energy — ●SEBASTIAN HARTWEG¹, MAJDI HOCHLAF², GUSTAVO GARCIA³, and LAURENT NAHON³ — ¹Albert-Ludwigs-Universität Freiburg, Deutschland — ²Université Gustave Eiffel, Champs-sur-Marne, Frankreich — ³Synchrotron SOLEIL, St-Aubin, Frankreich

Among the many intermolecular interactions known between biomolecules, the hydrogen bonding between the nucleobases Adenine (A) and Thymine (T) as well as between Guanine and Cytosine take a special place since they shape the DNA double strand structure. The strength of these hydrogen-bond interactions, at the center of the genetic code, is thus of significant interest for radiobiology.

We will present a study of the single photon ionization of gas phase A and T molecules and their dimers AA, AT and TT using double imaging photoelectron photoion coincidence (i2PEPICO) spectroscopy performed at the VUV beamline DESIRS of the French SOLEIL synchrotron. By evaluating the threshold photoelectron spectra (TPES) and photon energy-dependent ion kinetic energy release data we determined the threshold for photoionization and dissociative photoionization of the different clusters. By comparison with high-level ab initio calculations dealing with neutral and ionic species, we can relate the determined quantities to the binding energy of the neutral AT pair. The favorable comparison between theory and experimental results gives further credibility in theoretical predictions for similar systems.

MO 14.6 Wed 15:45 MO-H6

Exciton Diffusion in Perylene Derivative Microcrystals — ●CHRIS REHHAGEN¹, ALEXANDER VILLINGER², and STEFAN LOCHBRUNNER¹ — ¹Institute for Physics and Department of Life, Light and Matter, University of Rostock, 18051 Rostock, Germany — ²Institute for Chemistry, University of Rostock, 18051 Rostock, Germany

Improving light harvesting and opto-electronic organic devices relies on our knowledge about the transport mechanism of electronic excitations. The transport efficiency of excitons in molecular systems is strongly influenced by the order of the molecules. Amorphous and crystalline structure represent two extreme cases. In this work, we investigate the exciton dynamics in single organic microcrystals consisting of Perylene Red, a member of the perylene bisimide dye class and exploited already in many applications. We characterize the absorption, emission and geometric properties of single crystals in order to get a detailed view of the intermolecular coupling and the exciton distribution inside an irradiated crystalline sample. X-ray structure analysis reveals an orthorhombic unit cell with a volume of 12 nm³ consisting of eight dye molecules. Spatially resolved time-correlated single photon counting at high excitation powers is used to extract the diffusion properties of the excitons from two-exciton interaction. We find, that the excitons are indeed mobile within the sample and their motion can be described by an incoherent 'hopping' process. The diffusion length is about 12 nm.

MO 15: Poster 2

Time: Wednesday 16:30–18:30

Location: P

MO 15.1 Wed 16:30 P

Multiple-Quantum Two-Dimensional Fluorescence Spectroscopy of a Squaraine Polymer — ●AJAY JAYACHANDRAN, STEFAN MÜLLER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Molecular aggregates such as squaraine heteropolymers feature a manifold of multiexcitonic states [1]. These multiexcitonic states are a result of numerous electronically coupled heterochromophoric units. However, it is challenging to investigate the correlations and spectral

properties of the states of a particular multiexciton manifold using conventional spectroscopic tools due to convolution with spectral signatures of singly excited states. Here we make use of advances in fluorescence-based multidimensional spectroscopy to selectively measure multi-quantum correlations by using phase-cycled pulse sequences in a collinear excitation geometry [2]. Spectrally resolved two-quantum and three-quantum coherence signatures are captured through fourth-order and sixth-order signals which are acquired using a 36-fold phase-cycling scheme of a three-pulse excitation sequence. We also examine the eighth-order signals which can be resolved by using 64-fold phase cycling to observe correlations with four- quantum coherences without

signal aliasing.

- [1] S. F. Völker *et al.*, *J. Phys. Chem. C* **118**, 17467 (2014).
 [2] S. Draeger *et al.*, *Opt. Express* **25**, 3259 (2017).

MO 15.2 Wed 16:30 P

Improved mass spectrometer for two-dimensional electronic spectroscopy in the gas phase — ●ARNE MORLOK, ULRICH BANGERT, LUKAS BRUDER, YILIN LI, DANIEL UHL, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Germany

Two-dimensional electronic spectroscopy (2DES) is a very powerful method to study the ultrafast dynamics of matter. In our group, we apply the technique to molecules and cluster beams in the gas phase and combine it with photoion mass-detection [1,2]. To increase the flexibility of the mass spectrometer, we implement a pulsed electron gun for electron impact ionization. This enables beam depletion measurements and cluster beam characterization while avoiding the issue of overcoming the high ionization potentials of most molecules. We will present first characterization results.

- [1] L. Bruder *et al.*, *Nat Commun* **9**, 4823 (2018).
 [2] L. Bruder, U. Bangert, M. Binz, D. Uhl, and F. Stienkemeier, *J. Phys. B: At. Mol. Opt. Phys.* **52**, 183501 (2019)

MO 15.3 Wed 16:30 P

Femtosecond time-resolved pump-probe spectroscopy of benzene isomers — ●LUKAS FASCHINGBAUER¹, TOBIAS PREITSCHOPF¹, LIONEL POISSON², and INGO FISCHER¹ — ¹University of Wuerzburg, Institute for Physical and Theoretical Chemistry, Am Hubland, 97074 Wuerzburg, Germany — ²Universite Paris-Saclay, Institut des Sciences Moléculaires d'Orsay, Rue André Rivière, Bâtiment 520, 91405 Orsay Cedex, France

The excited state dynamics of the benzene isomers 3,4-dimethylenecyclobutene and fulvene were investigated by femtosecond time-resolved pump-probe spectroscopy at ISMO, Paris-Saclay, France. Lifetimes of the excited states were obtained by time-of-flight mass spectrometry, while photoelectron spectroscopy enabled the identification of the states involved in the relaxation processes. Preliminary results are presented.

MO 15.4 Wed 16:30 P

Coherent multidimensional spectroscopy of molecular and cluster beam samples — ●YILIN LI, ARNE MORLOK, ULRICH BANGERT, DANIEL UHL, FRANK STIENKEMEIER, and LUKAS BRUDER — Institute of Physics, University of Freiburg, Germany

Coherent multidimensional spectroscopy is a versatile technique enabling further insight into intra- and inter-molecular couplings on femtosecond time scales. We have recently extended the method to molecular and cluster beam samples in the gas phase [1] and combined it with photoionization probes [2,3]. In preparation for further experiments, we are currently characterizing the optical absorption, fluorescence, and photoelectron/-ion yields of various molecular and cluster samples in the gas phase. We will give an overview of the optical setup and first characterization results.

- [1] L. Bruder *et al.*, *Nat Commun* **9**, 4823 (2018)
 [2] L. Bruder *et al.*, *J. Phys. B: At. Mol. Opt. Phys.* **52**, 183501 (2019)
 [3] D. Uhl *et al.*, *Optica* **8**, 1316 (2021).

MO 15.5 Wed 16:30 P

Studies on the Photocleavage Mechanism of the Manganese Complex $\text{MnBr}(\text{CO})_3(\text{pytz-CH}_2\text{C}_6\text{H}_5)$ — ●NIKLAS GESSNER¹, ULRICH SCHATZSCHNEIDER², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — ²Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg

Photoactivatable carbon monoxide (CO) releasing molecules (PhotoCORMs) have promising applications in medicine and biology, e.g. as cancer treatment agents [1]. In a common approach, one or more CO molecules are bound to an inert transition metal complex that comprises a multidentate organic ligand to control its physical and (bio-)chemical properties [2] like photoexcitation energies or the enrichment efficiency in cancerous tissue.

By using UV pump/mid-IR probe ultrafast transient absorption spectroscopy, the PhotoCORM $[\text{MnBr}(\text{CO})_3(\text{pytz-CH}_2\text{C}_6\text{H}_5)]$, pytz being 2-(1,2,3-triazol-4-yl)pyridine, has been investigated in order to identify the ligand that is cleaved off and to elucidate the reaction

mechanism and the dynamics after photoexcitation. Results are compared to density functional theory calculations of possible transient intermediates and products, as well as to steady-state absorption measurements. It is found that a ligand is cleaved off after photoexcitation and that the dynamics are finished within 100 ps, so that either the reactant complex is retrieved or a persistent photoproduct is formed.

- [1] J. Niesel *et al.*, *Chem. Commun.* **15**, 1798–1800 (2008).
 [2] M. A. Gonzalez *et al.*, *Inorg. Chem.* **21**, 11930–11940 (2012).

MO 15.6 Wed 16:30 P

Ultrafast dynamics of $[\text{Ru}(\text{bipyridine})_2(\text{nicotinamide})_2]^{2+}$ and photoinduced formation of its water splitting adducts in gas and liquid phase — ●ROUMANY ISRAÏL¹, LARS SCHÜSSLER², PATRICK HÜTCHEN¹, WERNER THIEL¹, ROLF DILLER², and CHRISTOPH RIEHN¹ — ¹TU Kaiserslautern, FB Chemie, 52, 54 — ²TU Kaiserslautern, FB Physik, 46

A fundamental understanding of the kinetics of Ru^{II} polypyridyl complexes is essential to exploit their photochemical applicability in areas such as medicine (photoactivatable prodrugs) and material science (photovoltaics/catalysis). In particular, the monodentate ligand nicotinamide in $[\text{Ru}(\text{bpy})_2(\text{na})_2]^{2+}$ (bpy = bipyridine) enables the efficient population of the dissociative triplet metal-centered (³MC) state on a sub-ps time scale, allowing for fast photosolvolytic and subsequent reactions of the complex. Here, the photoactive $[\text{Ru}(\text{bpy})_2(\text{na})_2]^{2+}$, including its related photoproducts such as the penta-coordinate intermediate (PCI, $[\text{Ru}(\text{bpy})_2(\text{na})]^{2+}$) and the mono-aqua species $[\text{Ru}(\text{bpy})_2(\text{na})(\text{H}_2\text{O})]^{2+}$ were object to transient ion action spectroscopy in gas phase and transient absorption spectroscopy in solution. In gas phase, dynamics ($\tau_1 \sim 0.6$ ps, $\tau_2 \sim 3$ ps) of $[\text{Ru}(\text{bpy})_2(\text{na})_2]^{2+}$ is in line with the liquid phase. However, prominent larger time components (~ 10 ps, 100–400 ps) found in solution, do not appear in gas phase, allowing their unequivocal assignment to intermolecular processes. This study is an important step towards controlling the efficiency and photoactivity of Ru^{II} polypyridyl complexes by tailored ligands design.

MO 15.7 Wed 16:30 P

Chirp dependence of the Circular Dichroism in ion yield of 3-methylcyclopentanone — ●SAGNIK DAS, JAYANTA GHOSH, SUDHEENDRAN VASUDEVAN, HANGYEOL LEE, NICOLAS LADDA, SIMON RANECKY, TONIO ROSEN, ARNE SENFTLEBEN, THOMAS BAUMERT, and HENDRIKE BRAUN — Institut für Physik, Universität Kassel, Heinrich-Plett-Strasse 40, 34132 Kassel, Germany

One of the methods to differentiate between the two enantiomers of a chiral molecule is Circular Dichroism (CD). It arises due to the difference in absorption of left and right circularly polarised light. The difference in absorption can also be mapped to the difference in ionisation of the enantiomers and is known as CD in ion yield [1,2]. We use our home-built Time of Flight (ToF) mass spectrometer with our recently established twin peak [3] measurement setup to study the effect of linear chirp (GDD) on the anisotropy. The candidate molecule for this experiment is 3-methylcyclopentanone (3-MCP). The experiments are done at 309 nm and 322 nm, where 3-MCP is known to have anisotropies of up to 4% and 1%, respectively, for bandwidth limited pulse. At these wavelengths, a 1+1+1 resonance-enhanced multiphoton ionisation (REMPI) takes place in 3-MCP through the $\pi^* \leftarrow n$ transition. We observe an asymmetric enhancement of anisotropy for chirped pulses, which we compare to bandwidth limited pulses of equal peak intensity.

- [1] U. Boesl and A. Bornschlegl, *ChemPhysChem*, **7**, 2085, 2006
 [2] H. G. Breunig *et al.*, *ChemPhysChem*, **10**, 1199, 2009
 [3] T. Ring *et al.*, *Rev. Sci. Instrum.*, **92**, 033001, 2021

MO 15.8 Wed 16:30 P

Probing vibrational wave packets in the electronic ground state of methyl p-tolyl sulfoxide via time-resolved PECD — ●NICOLAS LADDA¹, MAX WATERS², VÍT SVOBODA², MIKHAIL BELOZERTSOV², SUDHEENDRAN VASUDEVAN¹, SIMON RANECKY¹, TONIO ROSEN¹, SAGNIK DAS¹, JAYANTA GHOSH¹, HANGYEOL LEE¹, HENDRIKE BRAUN¹, THOMAS BAUMERT¹, HANS JAKOB WÖRNER², and ARNE SENFTLEBEN¹ — ¹Institut für Physik, Universität Kassel, 34132 Kassel, Germany — ²Laboratorium für Physikalische Chemie, ETH Zürich, 8093Zürich, Switzerland

The dynamic change of the chiral character upon the laser-induced vibrational motion in the electronic ground state of methyl p-tolyl sulfoxide (MTSO) is investigated. For this purpose, the forward/backward asymmetry of the photoelectron angular distribution (PAD) with re-

spect to the propagation direction of ionising circularly polarised light of the randomly oriented chiral molecule, known as photoelectron circular dichroism (PECD), was measured. Geometry dependent ionisation rates of a molecule when interacting with an ultrashort laser pulse causes the formation of a coherent oscillating wave packet in the electronic ground state. The vibrational motion - umbrella motion of the sulfoxide molecule - changes the chiral character of the molecule, which can be studied by probing the time-resolved PECD with a VUV femtosecond laser pulse.

MO 15.9 Wed 16:30 P

Spectroscopic investigation of the light-induced rearrangement of a Xanthine derivative — ●KARINA HEILMEIER¹, THOMAS RITTNER¹, RAFAEL E. RODRÍGUEZ-LUGO², ROBERT WOLF², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — ²Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg

The Xanthine derivative 7-(4-methoxyphenyl)-1,3-dimethyl-8-(pyridin-2-yl)-3,7,8,9-tetrahydro-1*H*-purine-2,6-dione possesses a characteristic purine skeleton additionally modified with pyridine and anisole moieties bound to the five-membered ring. Our studies reveal that ultraviolet light induces the migration of the anisole group from the 7-nitrogen of the purine skeleton to the nitrogen of the pyridine moiety. The isomer emerging as rearrangement product could even be isolated, and the structure was determined by single-crystal X-ray diffraction.

For obtaining a comprehensive picture of the light-induced mechanism leading to the rearrangement, results from stationary measurements are compared to those from ultrafast transient absorption and fluorescence upconversion spectroscopy. In addition, we contrast the photodynamics of the in-situ generated isomer with that of the synthetically isolated one. In further systematic studies, we explore whether photoinduced back-isomerization is achievable as well, and address the role of the solvent's polarity on the rearrangement.

MO 15.10 Wed 16:30 P

Low dispersive phase modulation scheme for interferometric XUV experiments — ●FABIAN RICHTER, SARANG DEV GANESHAMANDIRAM, IANINA KOSSE, RONAK SHAH, GIUSEPPE SANSONE, FRANK STIENKEMEIER, and LUKAS BRUDER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

Quantum interference spectroscopy schemes are well established in the visible range to control and resolve the static properties and dynamics of quantum systems. Recently these principles got extended into the XUV regime [1,2]. Here acousto-optical modulators are used to achieve interferometric measurements supported by a phase cycling scheme. However, in this setup a significant amount of material is introduced in the optical beam path at the fundamental frequency which prohibits using ultrashort pulses and high laser intensities. We present a new approach to achieve phase cycling while minimizing the amount of material dispersion by an order of magnitude. We will present the basic concept of this approach and first characterization results.

[1] Wituschek, A., Bruder, L., Allaria, E. et al. Tracking attosecond electronic coherences using phase-manipulated extreme ultraviolet pulses. *Nature Communications* 11, 883 (2020).

[2] Wituschek, A., Kornilov, O., Witting, T., et al. Phase Cycling of Extreme Ultraviolet Pulse Sequences Generated in Rare Gases. *New Journal of Physics* 22, Nr. 9 (September 2020): 092001.

MO 15.11 Wed 16:30 P

A setup for extreme ultraviolet wave packet interferometry using tabletop high harmonic generation — ●SARANG DEV GANESHAMANDIRAM, FABIAN RICHTER, IANINA KOSSE, RONAK SHAH, LUKAS BRUDER, GIUSEPPE SANSONE, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

Quantum interference techniques such as wave packet interferometry (WPI) in the extreme ultraviolet (XUV) regime set the basis for advanced nonlinear spectroscopy methods, such as multidimensional spectroscopy. These methods are however very difficult to implement at short wavelengths due to the required high phase stability and sensitivity. Recently, we have overcome these difficulties and have introduced a concept to implement such experiments with XUV free-electron lasers [1]. We are now developing a new setup optimized for seeding tabletop high-harmonic generation sources which is based on acousto-optic modulation of intense near infrared pulses. In the initial

experiments, photons around 30 eV (19th harmonic) are generated and the effect of temporal and spatial dispersion were studied. Here, we will present the concept of the setup along with first characterization results. 1. A. Wituschek et al., Tracking attosecond electronic coherences using phase-manipulated extreme ultraviolet pulses, *Nature Communications*, 11:883 (2020).

MO 15.12 Wed 16:30 P

EUV absorption and recombination dynamics in atmospheric gas species — ●STEFFEN WOLTER¹, ERIK SCHMÖLTER², JENS BERDERMANN², and STEFAN LOCHBRUNNER¹ — ¹Institute of Physics, University of Rostock, 18051 Rostock, Germany — ²Department for Space Weather Impact, Institute for Solar-Terrestrial Physics, Kalkhorstweg 53, 17235 Neustrelitz, Germany

Ground- and space-based measurements show that the extreme ultraviolet (EUV) part of the solar spectrum changes continuously and can be very dynamic, especially during solar flares. The ionospheric plasma in the upper atmosphere is created by the absorption of this radiation and affected by the related variations. Therefore, exact knowledge of the ionization and recombination rates of the atmospheric gas species, mainly oxygen, nitrogen and their ions, is needed to model the ionospheric response to the EUV variations.

To this end, a high harmonic generation (HHG) setup driven by a femtosecond laser combined with an EUV spectrometer is applied to investigate the ionization cross-sections. The setup and first results for different gas species as well as the approach to measure recombination rates are presented in this contribution.

MO 15.13 Wed 16:30 P

Isosteric molecules in the time-domain — ●MAXIMILIAN POLLANKA, CHRISTIAN SCHRÖDER, PASCAL SCIGALLA, ANDREAS DUENSING, MICHAEL MITTERMAIR, and REINHARD KIENBERGER — Chair for laser and x-ray physics E11, Technische Universität München, Germany

In this work, we report on photoemission timing measurements performed on small isosteric molecules in the gas phase. By comparing the photoemission time delay between the respective σ and π orbitals in the valence band of CO₂ and N₂O we expect to find deeper insight in the characteristics of isosterism in the time-domain. Furthermore, the isoelectronicity of CO and N₂ is investigated in detail as a complementary study. Due to the similarities in molecular structure (isostericity) and electronic configurations (isoelectronicity), the pure effect of the specific element's characteristics is expected to be probed. The results regarding similarities and differences in photoemission dynamics in these molecules can serve as a stepping stone for gaining deeper insight into isosteric characteristics in these molecules and may bear the potential to draw conclusions from these simple systems to unknown or unexplored isosteric molecular bonds in general.

Scattering calculations help us to gain a greater understanding of the correlations between molecular geometry and photoemission time and therefore the isosteric influence, with the focus on assessing the differences between modeling and experimental findings.

MO 15.14 Wed 16:30 P

Probing well aligned molecular environments on surfaces in the time-domain — ●PASCAL SCIGALLA, CHRISTIAN SCHRÖDER, PETER FEULNER, and REINHARD KIENBERGER — Chair for laser and x-ray physics, E11, Technische Universität München, Germany

We report on the photoemission timing measurements of well-aligned ethyl iodine molecules on a platinum crystal surface. The 4*d* photoemission of iodine is clocked against the Pt5*p* photoemission, allowing the extraction of an relative photoemission delay. As the iodines photoemission in the chosen energy region stems from a giant resonance in the 14*d* → ϵf transition its photoemission time is mostly unaffected by its chemical environment. Thus any observed change in the photoemission delay can be attributed to changes in the traversed potential landscape of the molecule.

By carefully selecting the detection angle and coverage of the crystal we can reliably change which parts of the molecular potential landscape were traversed by the detected photoelectron wavepackets.

Complementary scattering simulations are then used in order to gain deeper insight into the observations in order to establish photoemission timing experiments as an efficient and accurate means to study molecular environments on surfaces.

MO 15.15 Wed 16:30 P

Strong-field effects on singly excited vibronic resonances in

the hydrogen molecule — ●PAULA BARBER BELDA¹, GERGANA D. BORISOVA¹, DANIEL FAN¹, SHUYUAN HU¹, MAXIMILIAN HARTMANN¹, PAUL BIRK¹, ALEJANDRO SAENZ², CHRISTIAN OTT¹, and THOMAS PFEIFER¹ — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — ²Institut für Physik, Humboldt-Universität zu Berlin, 12489 Berlin, Germany

Studies of the hydrogen molecule and its interaction with ultrashort light pulses allow for the understanding of many quantum molecular phenomena in the simplest possible case of a molecule with only two nuclei and two electrons. In a transient absorption experiment with H₂ in the spectral range 13-17eV we drive transitions from the molecular ground state to the electronically excited B, C and D states. The included energy levels of the eigenstates of H₂ are calculated numerically, as well as the dipole matrix elements for the considered transitions. We observe intensity-dependent changes in the XUV absorption spectrum in the presence of moderately strong NIR field, coupling different excited states. In a few-level simulation, where we can consciously include and exclude states in the model system, we use numerically calculated energy levels of the eigenstates of H₂, as well as dipole matrix elements for the considered transitions. We aim to understand with it the importance of different couplings to the changing absorption lines and the corresponding time-dependent dipole we reconstruct from the measurement.

MO 15.16 Wed 16:30 P

Channel-Resolved Laser-Driven Electron Rescattering in the Molecular-Frame — ●FEDERICO BRANCHI¹, FELIX SCHELL¹, TILMANN EHRLICH¹, MARK MERO¹, HORST ROTTKE¹, SERGUEI PATCHKOVSKII¹, VARUN MAKHIJA², MARC J.J. VRAKING¹, and JOCHEN MIKOSCH¹ — ¹Max-Born-Institut, Berlin, Germany — ²University of Mary Washington, Fredericksburg, USA

A series of reaction microscope experiments on strong-field ionization and laser-driven electron rescattering of the asymmetric top molecule 1,3-butadiene is presented. Importantly, by virtue of the ion-electron coincidence detection, these experiments separate the ground-state (D₀) and first excited state (D₁) ionization channel. By analyzing coherent rotational wavepacket evolution we extract the polar and azimuthal angle-resolved molecular frame ionization and rescattering probability. By extracting the differential scattering cross section (DCS) for near- to mid-infrared wavelengths we explore the role of different continuum wavepackets for molecular structure determination. By measuring the ellipticity dependence of the return-energy dependent rescattering probability we explore the role of short versus long trajectories. A multi-faceted picture of molecular effects in strong-field ionization and laser-induced electron diffraction ensues.

MO 15.17 Wed 16:30 P

Experimental study of the laser-induced ionization of heavy metal and metalloid ions: Au⁺ and Si²⁺ — ●BO YING^{1,2,3}, FRANK MACHALETT^{1,2,3}, VANESSA HUTH¹, MATTHIAS KÜBEL^{1,2}, A MAX SAYLER^{1,2,4}, THOMAS STÖHLKER^{1,2,3}, GERHARD G PAULUS^{1,2,3}, and PHILIPP WUSTELT^{1,2} — ¹Institute of Optics and Quantum Electronics, Friedrich Schiller University Jena, Max-Wien-Platz 1, 07743 Jena, Germany — ²Helmholtz Institute Jena, Fröbelstieg 3, 07743 Jena, Germany — ³GSI Helmholtzzentrum für Schwerionenforschung, Planckstraße 1, 64291 Darmstadt, Germany — ⁴Benedictine College, Atchison, KS 66002, USA

We implement a liquid metal ion source in a 3D coincidence momentum spectroscopy setup for studying the interaction of ionic targets with intense laser pulses. Laser intensities of up to 4×10^{16} W cm⁻² allow for the observation of up to ten-fold ionization of Au⁺-ions and double ionization of Si²⁺-ions. Further, by utilizing two-color sculpted laser fields to control the ionization process on the attosecond time scale, we demonstrate the capability to resolve the recoil ion momenta of heavy metal atoms. Simulations based on a semiclassical model assuming purely sequential ionization reproduce the experimental data well. This work opens up the use of a range of metallic and metalloid ions, which have hardly been investigated in strong-field laser physics so far.

MO 15.18 Wed 16:30 P

Design and implementation of XUV setup for time resolved photoelectron spectrometry — ●MARTA LUISA MURILLO-SÁNCHEZ, CONSTANTIN WALZ, DENNIS MAYER, and MARKUS GÜHR — Institut für Physik und Astronomie, Universität Potsdam, Karl-Liebknecht-Straße 24/25, 14476 Potsdam-Golm Germany

To investigate photoinduced ultrafast relaxation processes in gas phase isolated molecules, a tabletop setup for time-resolved photoelectron spectroscopy employing ultrashort extreme ultraviolet pulses (XUV) is currently under construction in the laboratory of the Experimental Quantum Physics group at Potsdam University. High-energy XUV pulses obtained by high order generation are achieved by focusing a fraction of the output pulses from an amplified laser system into a cell filled with a rare gas, under proper phase matching conditions. The odd frequency comb constituted by several harmonics is two-step filtered by a silicon wafer and an aluminium bandpass metallic filter to remove the residual infrared radiation. Afterwards, the beam is sent to a toroidal mirror to focus the beam. The different harmonics are spatially separated by a diffraction grating allowing to individually select them by means of a slit. This system for obtaining monochromatic XUV pulses is perhaps the simplest possible nevertheless compromising the optimum temporal duration of the pulses. Focused XUV laser pulses interact with an evaporated sample by an oven in the interaction region of a magnetic bottle spectrometer through which photoelectrons are detected with increased efficiency. XUV pulses can also be recombined with UV pulses in order to perform pump-probe experiments.

MO 15.19 Wed 16:30 P

Development of a glass based supersonic molecular beam source for organic molecules — ●BRENDAN WOUTERLOOD, SEBASTIAN HARTWEG, LUKAS BRUDER, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Germany

Two-dimensional electronic spectroscopy (2DES) is a powerful spectroscopic tool which allows for the probing of atomic and molecular dynamics on ultra-fast timescales [1]. Application of this spectroscopic technique to polycyclic aromatic hydrocarbons (PAHs), such as acenes and porphyrins, promises a detailed understanding of their electronic structure and excited state dynamics. These electronic properties make some of these molecules interesting candidates for application in organic photovoltaics and motivate much past and present research [2]. One challenge of these studies has been the generation of high gas-phase target densities of these molecules due to their low vapour pressure and thermal decomposition by excessive heating.

In order to provide large target densities, since these molecules have relatively low vapour pressures, the supersonic nozzle will need to be heated to around 500°C. A quartz glass nozzle system will thus be developed in order to allow us to heat the molecules to these high temperatures while minimising the risk of thermal decomposition of the sample that can be catalysed by hot metal surfaces. We will present the nozzle design and initial characterisation results.

[1] L. Bruder et al., Nat Commun 9, 4823 (2018).

[2] O. Ostroverkhova, Chemical Reviews 116 (22), 13279-13412 (2016).

MO 15.20 Wed 16:30 P

Setup Of A Spectrometer To Detect Raman Optical Activity — ●KLAUS HOFMANN — Universität Würzburg, Institut für Physikalische und Theoretische Chemie

A custom-built Raman spectrometer was modified to detect Raman optical activity (ROA), a type of vibrational circular dichroism. A modulation scheme was implemented to repeatedly convert linear to right and left circular polarized light for excitation. Python was used to automate the experiment, data acquisition and post-processing. Experimental challenges and their influences on the resulting ROA signal as well as the margins of error are presented. The recorded ROA spectrum of (-)- α -pinene was acquired by subtracting the spectra of both enantiomers and shows good agreement with literature.

MO 15.21 Wed 16:30 P

Towards laser ionisation of H-atoms for kinematically complete coincidence imaging of ion-molecule reactions — ●FLORIAN TRUMMER, DASARATH SWARAJ, TIM MICHAELSEN, ARNAB KHAN, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria

Crossed-beam velocity map imaging (VMI) has proven to be a powerful tool to gain insight into atomistic reaction mechanisms [1-3]. Here we will present concepts and simulations for a new experimental setup that uses coincidence detection of reaction products for a kinematically complete VMI study of certain reaction types, involving neutral hydrogen products. Instead of solely detecting the charged initial product of the reactive encounter, a high power and high repetition rate Lyman-alpha source in combination with a UV laser will be used to ionise the neutral H-atoms, which are a product of the chemical reactions under

study (e.g., $O^- + H_2 \rightarrow OH^- + H$). We will present the planned laser setup for our upcoming project which is currently under construction. The search for quantum resonances in vibrational state-resolved spectroscopic studies of ion-neutral reactions is among the goals that shall be explored in the future.

- [1] R. Wester, *Phys. Chem. Chem. Phys.* **16**, 396 (2014)
 [2] M. Stei *et al.*, *Nature Chemistry* **8**, 2, 151-156 (2016)
 [3] T. Michaelsen *et al.*, *J. Phys. Chem. Lett.* **11**, 11, 4331-4336 (2020)

MO 15.22 Wed 16:30 P

eCOMO - A new endstation for controlled molecule experiments — •WUWEI JIN¹, SEBASTIAN TRIPPEL^{1,3}, HUBERTUS BROMBERGER^{1,3}, TOBIAS RÖHLING¹, KAROL DLUGOLECKI¹, SERGEY RYABCHUK¹, ERIK MÄNSSON¹, ANDREA TRABATTONI¹, VINCENT WANIE¹, IVO VINKLÁREK⁴, FRANCESCA CALEGARI¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Department of Physics, Universität Hamburg — ³Center for Ultrafast Imaging, Universität Hamburg — ⁴Department of Chemical Physics and Optics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

We present details on our newly established transportable endstation eCOMO (Endstation for Controlled Molecules) for investigating the dynamics of small molecules in the gas phase [1]. The endstation consists of three main parts: 1) An Even-Lavie-valve-based gas source. 2) An electrostatic deflector for the generation of pure molecular samples [2-3]. 3) A double-sided VMI spectrometer coupled with two time- and position-sensitive Timepix3 cameras and the PymePix software [4-5].

Time: Thursday 10:30–12:15

Invited Talk

MO 16.1 Thu 10:30 MO-H5

Infrared Spectroscopy of Ionic Hydrogen-Helium Complexes — •OSKAR ASVANY and STEPHAN SCHLEMMER — I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, Köln

Ionic species consisting of only hydrogen and helium, $H_mHe_n^+$, are of interest in astrophysics (those with small n and m) and in molecular physics (because some of them exhibit a floppy behaviour). Using a combination of cryogenic ion-trap machines, operated at 4 K, and different laser sources, the ionic species HHe_n^+ ($n = 2 - 6$), DHe_n^+ ($n = 3 - 6$), H_2He^+ , D_2He^+ and H_3He^+ have been investigated by low- and high-resolution infrared spectroscopy. This contribution gives an overview about the investigations done in the last couple of years, with an emphasis on HHe_n^+ ($n = 2 - 6$). These species are known to consist of a linear $He-H^+-He$ ($n = 2$) chromophore, with additional helium atoms attached to the central proton ($n = 3, 4, \dots$). The IR results confirm this motif, with $n = 3$ and $n = 6$ being of T-shaped C_{2v} and of D_{4h} symmetry, respectively, while the species with $n = 4, 5$ are suggested to exhibit interesting dynamical phenomena related to large-amplitude motion.

MO 16.2 Thu 11:00 MO-H5

Deuteration effects in the reactive scattering of a nucleophilic substitution reaction. — •ATILAY AYASLI¹, THOMAS GSTIR¹, ARNAB KHAN¹, TIM MICHAELSEN¹, DÓRA PAPP², GÁBOR CZAKÓ², and ROLAND WESTER¹ — ¹Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, 6020 Innsbruck, Austria — ²University of Szeged, Szeged, Hungary

Our group studies ion-molecule reactions using a crossed-beam setup with kinematically complete velocity map imaging (VMI). We have investigated reactive scattering of fully deuterated methyl iodide CD_3I with atomic fluorine anions in the energy range from 0.7 to 2.3 eV relative collision energy. The results are compared with the hydrogenated system $F^- + CH_3I$ [1] as well as quasi-classical trajectory (QCT) simulations [2]. The two main reaction channels are nucleophilic substitution (S_N2) and deuteron/proton transfer for both systems. The $F^- + CH_3I$ reaction shows a significant large-impact parameter contribution in the S_N2 channel, a feature that is absent for its deuterated counterpart. While the simulations can fully capture the S_N2 dynamics in the reaction with CD_3I , large-impact parameter events from $F^- + CH_3I$ cannot be reproduced. Such a discrepancy between experimental and theoretical work might hint towards a quantum effect that cannot be

We found a novel damped oscillation dynamics in the UV-IR (pulse duration are both 6 fs) ionization dynamics of carbonyl sulfide (OCS).

- [1] M. Johny, J. Onvlee, et al., *Chem. Phys. Lett.*, **721**, 149 (2019)
 [2] S. Trippel, M. Johny, et al., *Rev. Sci. Instrum.*, **89**, 096110 (2018)
 [3] Y. P. Chang, D. A. Horke, et al., *Int. Rev. Phys. Chem.*, **557**, 34 (2015)
 [4] A. F. Al-Rafaie, M. Johny, et al., *J. Instrum.*, **14**, P10003 (2019)
 [5] A. Zhao, M. van Beuzekom, et al., *Rev. Sci. Instrum.*, **88**, 113104 (2017)

MO 15.23 Wed 16:30 P

Optical Imaging and Tracking of Single Molecules in Ultrahigh Vacuum — •TIANYU FANG, FLORIAN ELSSEN, NICK VOGEL, and DAQING WANG — Institute of Physics, University of Kassel, Heinrich-Plett-StraÙe 40, 34132 Kassel, Germany

Molecule-surface interaction is key to many physical and chemical processes at interfaces. Here, we show that the dynamics of single molecules on a surface under ultrahigh vacuum can be resolved using fluorescence imaging. By adapting oil-immersion microscopy to a thin vacuum window, we measure the surface adsorption and translational and rotational diffusion of single perylene molecules on a fused silica surface with high spatial and temporal resolutions. Time-dependent measurements of the fluorescence signal allow us to deduce two characteristic decay time scales, which can be explained through a simplified model involving two adsorption states and five energy levels. The system presented in this work combines fluorescence imaging with essential ingredients for surface science and promises a platform for probing single-molecule-surface interactions in highly defined conditions.

MO 16: Ions

Location: MO-H5

captured by QCT simulations.

- [1] Michaelsen et al., *J. Phys. Chem. Lett.* **2020**, **11**, 11, 4331-4336
 [2] Olasz et al., *Chem. Sci.*, **2017**, **8**, 3164-3170

MO 16.3 Thu 11:15 MO-H5

Disentangling elimination and nucleophilic substitution dynamics — •TIM MICHAELSEN¹, JENNIFER MEYER¹, VIKTOR TAJTI², EDUARDO CARRASCOSA¹, TIBOR GYÖRI², MARTIN STEI¹, BJÖRN BASTIAN¹, GÁBOR CZAKÓ², and ROLAND WESTER¹ — ¹Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria — ²Interdisciplinary Excellence Centre and Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary

In the presented study we combine angle- and energy-differential cross sections, obtained in a crossed-beam velocity map imaging experiment, with quasi-classical trajectory (QCT) calculations on an accurate 21-dimensional hypersurface to disentangle the competition of base induced elimination (E2) and nucleophilic substitution (S_N2) in the reaction of F^- with CH_3CH_2Cl [1]. As the detected product ion Cl^- is identical for S_N2 , anti and syn-E2, separating the pathways from experiment alone is very challenging. The QCT calculations quantitatively reproduce the measured total experimental cross section due to their novel accuracy for such polyatomic reactions and allow us to differentiate the competing channels and extract detailed information on the underlying reaction mechanisms. We find that the anti-E2 pathway is dominant, but that S_N2 contributions become more important towards larger collision energies.

- [1] J. Meyer, V. Tajti, E. Carrascosa et al., *Nat. Chem.* **13**, 977-981 (2021)

MO 16.4 Thu 11:30 MO-H5

Aromaticity and structure variation from cationic cyclopropenyl by varying the number of hydrogen atoms — •SIMON REINWARDT¹, PATRICK CIESLIK¹, ALEXANDER PERRY-SASSMANNSHAUSEN², TICIA BUHR², ALFRED MÜLLER², STEFAN SCHIPPERS², FLORIAN TRINTER^{3,4}, and MICHAEL MARTINS¹ — ¹Universität Hamburg, Hamburg, Germany — ²Justus-Liebig-Universität Gießen, Gießen, Germany — ³Goethe-Universität Frankfurt am Main, Frankfurt am Main, Germany — ⁴Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Small carbon systems play an important role in the ion chemistry in the interstellar medium [1] and planetary atmospheres [2]. Soft X-ray

spectroscopy enables the analysis of these small structures as well as their aromaticity [3]. This allows a comprehensive understanding of the chemical bonding of these hydrocarbon cations and the transition from rings to chains. The smallest aromatic ion, the cyclopropenyl cation ($C_3H_3^+$), is an ideal system for studying the aromaticity in chemical bonds on a fundamental level. Through the production in an ion source and a subsequent mass analysis, the structure and the aromaticity can be selected by controlling the number of attached hydrogen atoms. We present new results on these systems that we have measured on the photon ion spectrometer (PIPE) [4] at PETRA III in Hamburg.

- [1] D. Smith *et al.*, *Chem. Rev.*, **92** (1992).
- [2] C. A. Nixon *et al.*, *A. J.*, **160** 205 (2020).
- [3] C. Kolczewski *et al.*, *J.Chem.Phys.*, **124** 034302 (2006).
- [4] S. Schippers *et al.*, *X-Ray Spectrometry*, **49** 11 (2020).

MO 16.5 Thu 11:45 MO-H5

Time-resolved photon interactions of size- and charge-state selected polyanionic tin clusters — ●ALEXANDER JANKOWSKI, PAUL FISCHER, MORITZ GRUNWALD-DELITZ, and LUTZ SCHWEIKHARD — Institute of Physics, University of Greifswald, Germany

Small tin clusters (Sn_n^- of sizes $n \lesssim 50$) are formed by so-called building blocks of Sn_7 , Sn_{10} [1-3] and, in the case of anionic clusters, Sn_{15} [3]. These cluster sizes $n = 7, 10$ and 15 lead to corresponding fragmentation patterns [4,5] which have been confirmed and further investigated [6,7] at the ClusterTrap setup [8]. These previous findings suggested for dianionic tin clusters fission processes into two monoanionic fragments in analogy to the case of lead clusters [9]. Recently, photodissociation experiments have been performed on size- and charge-state-selected polyanionic tin clusters. By delaying the ejection/analysis of the trapped clusters with respect to the pulsed photoexcitation, time-resolved measurements allow the reconstruction of the decay pathways.

- [1] C. Majumder *et al.*, *Phys. Rev. B* **64**, 233405 (2001)
- [2] H. Li *et al.*, *J. Phys. Chem. C* **116**, 231-236 (2011)

- [3] A. Lechtken *et al.*, *J. Chem. Phys.* **132**, 211102 (2010)
- [4] E. Oger *et al.*, *J. Chem. Phys.* **130**, 124305 (2009)
- [5] A. Wiesel *et al.*, *Phys. Chem. Chem. Phys.* **14**, 234-245 (2012)
- [6] S. König *et al.*, *Eur. Phys. J. D* **72**, 153 (2018)
- [7] M. Wolfram *et al.*, *Eur. Phys. J. D* **74**, 135 (2020)
- [8] F. Martinez *et al.*, *Int. J. Mass Spectrom.* **266**, 365-366 (2014)
- [9] S. König *et al.*, *Phys. Rev. Lett.* **120**, 163001 (2018)

MO 16.6 Thu 12:00 MO-H5

Cryo Kinetics and IR Spectroscopy of Nitrogen on Tantalum Cluster — ●DANIELA V. FRIES, ANNIKA STRASSNER, MATTHIAS P. KLEIN, MAXIMILIAN HUBER, MARC H. PROSENC, and GEREON NIEDNER-SCHATTEBURG — TU Kaiserslautern, Kaiserslautern, Deutschland

As motivated by prior room temperature studies on Ta_2^+ [1] we investigate larger Ta_n^+ clusters ($3 < n < 8$) and their N_2 adsorption and activation abilities by adsorption kinetics and infrared spectroscopy under cryo conditions compared with DFT calculations. The model system Ta_4^+ appears to be of particular interest with regard to cryo N_2 activation. Experimental results reveal peculiar details for the first and second adsorption kinetics. The absence of any NN stretching signature in $[Ta_4(N_2)_1]^+$ and $[Ta_4(N_2)_2]^+$ indicates cleavage of the first two adsorbed dinitrogen molecules. We unravel a multistep above edge across surface (AEAS) activation mechanism.[2]

In addition to the investigations of these tantalum cations we are interested in the N_2 adsorption on tantalum anions (Ta_n^- , $4 < n < 10$). Initial experiments observe strong size dependencies which are subject of ongoing interpretation.

- [1] Proc. Natl. Acad. of Sci. USA, 2018, 115, 11680-11687.
- [2] Phys. Chem. Chem. Phys., 2021,23, 11345-11354.

MO 17: Precision

Time: Thursday 10:30–11:15

Location: MO-H6

MO 17.1 Thu 10:30 MO-H6

Spin precession with BaF for EDM searches — ●VIRGINIA MARSHALL^{1,2}, PARUL AGGARWAL^{1,2}, HENDRICK L. BETHLEM^{1,3}, ALEXANDER BOESCHOTEN^{1,2}, ANASTASIA BORSCHESKY^{1,2}, MALIKA DENIS^{1,2}, PI HAASE^{1,2}, STEVEN HOEKSTRA^{1,2}, JOOST VAN HOFSLLOT^{1,2}, KLAUS JUNGSMANN^{1,2}, THOMAS B. MEIJKNECHT^{1,2}, MAARTEN C. MOOIJ^{2,3}, ROB G.E. TIMMERMANS^{1,2}, ANNO TOUWEN^{1,2}, WIM UBACHS³, LORENZ WILLMANN^{1,2}, and YANNING YIN^{1,2} — ¹Netherlands, Groningen, RUG — ²Netherlands, Amsterdam, Nikhef — ³Netherlands, Amsterdam, VU

eEDM sensitive searches form a probe into the Standard Model of particle physics and its extensions. A BaF supersonic beam with a velocity of around 600 m/s, moving in a controlled 10 kV/cm electric field and nT magnetic field, forms an experimental setup for eEDM sensitive searches. The eEDM search employs the $X^2\Sigma^+\nu = 0, N = 0$ ground state of BaF, which is controlled solely by interactions with laser fields in order to execute a spin precession measurement in well known E- and B-fields. Our particular interest is on the dependence of the signal on the laser parameters such as intensity, polarization and frequency detuning. With this we aim to complete a first measurement step in the coming year at a sensitivity level 10^{-28} ecm.

MO 17.2 Thu 10:45 MO-H6

eEDM sensitive searches with BaF molecules — ●THOMAS B. MEIJKNECHT^{1,2}, PARUL AGGARWAL^{1,2}, HENDRICK L. BETHLEM^{1,3}, ALEXANDER BOESCHOTEN^{1,2}, ANASTASIA BORSCHESKY^{1,2}, MALIKA DENIS^{1,2}, PI HAASE^{1,2}, STEVEN HOEKSTRA^{1,2}, JOOST VAN HOFSLLOT^{1,2}, KLAUS JUNGSMANN^{1,2}, VIRGINIA MARSHALL^{1,2}, MAARTEN C. MOOIJ^{2,3}, ROB G.E. TIMMERMANS^{1,2}, ANNO TOUWEN^{1,2}, WIM UBACHS³, LORENZ WILLMANN^{1,2}, and YANNING YIN^{1,2} — ¹Netherlands, Groningen, RUG — ²Netherlands, Amsterdam, Nikhef — ³Netherlands, Amsterdam, VU

eEDM sensitive searches form a probe into the Standard Model of particle physics and its extensions. A BaF supersonic beam with a

velocity of around 600 m/s, moving in a controlled 10 kV/cm electric field and nT magnetic field, forms an experimental setup for eEDM sensitive searches. The emphasis lies on characterizing and controlling the electric and magnetic fields. Not only of interest are these fields themselves, but in particular (the use of) the sensitivity of the BaF quantum system in such fields. This provides multiple handles on statistical and systematic effects, critical in EDM searches. With this we aim to complete a first measurement step with the supersonic BaF beam in the coming year at a sensitivity level 10^{-28} ecm.

MO 17.3 Thu 11:00 MO-H6

Electrostatic lens for ThO molecules in the ACME III electron EDM search — ●XING WU^{1,2}, DANIEL ANG², DAVID DEMILLE¹, JOHN DOYLE¹, GERALD GABRIELSE³, ZHEN HAN¹, BINGJIE HAO³, AYAMI HIRAMOTO⁴, PEIRAN HU¹, DANIEL LASCAR³, ZACK LASNER², SIYUAN LIU³, TAKAHIKO MASUDA⁴, and COLE MEISENHEDER² — ¹The University of Chicago — ²Harvard University — ³Northwestern University — ⁴Okayama University

Measurements of the electron electric dipole moment (eEDM) using atoms and molecules shed light on T-symmetry violating new physics beyond the Standard Model. The best upper limit on the eEDM was recently set by the ACME collaboration: $|d_e| < 1.1 \times 10^{-29}$ e-cm, using a cold beam of thorium monoxide (ThO) molecules. This result significantly constrains \mathcal{T} -violating new physics in the $1 \sim 10$ TeV range and above. The next generation of ACME aims to improve the sensitivity to d_e by another order of magnitude. A molecular lens is used to focus, into the EDM measurement region, beams of ThO molecules that have been prepared in the highly polarizable Q state. Our lens system requires several new features: 1) a new, spatially compact rotational cooling scheme which we demonstrated to work with efficiency near its theoretical limit; 2) a STIRAP process to transfer molecules into and out of the Q state, demonstrated with 80% total efficiency; and 3) an electrostatic hexapole lens operated at ± 23 kV, demonstrated to enhance molecular signal by 16 times relative to an unfocused molecular beam.

MO 18: High-Resolution Spectroscopy

Time: Thursday 14:30–16:30

Location: MO-H5

Invited Talk

MO 18.1 Thu 14:30 MO-H5

High-resolution spectroscopic studies of transient carbon-rich species — ●SVEN THORWIRTH, OSKAR ASVANY, and STEPHAN SCHLEMMER — I. Physikalisches Institut, Universität zu Köln

Carbon-rich material is of importance in diverse scientific areas such as material science, structural chemistry, theoretical- and astrochemistry. In space, carbon-rich molecular chains both in their neutral and charged forms are abundant ingredients of molecular clouds and circumstellar shells. In this talk, recent efforts towards spectroscopic characterization of neutral and positively charged carbon-rich species harboring selected heteroelements will be presented. Neutral chains were studied at high spectral resolution using a combination of laser ablation production and infrared laser spectroscopy. Positively charged species were observed as products of electron impact ionization of precursor gases using infrared/millimeter-wave techniques and action spectroscopy in 22-pole ion trap instruments. Spectroscopic analyses were guided and facilitated by high-level quantum-chemical calculations.

MO 18.2 Thu 15:00 MO-H5

High-resolution electronic spectroscopy of phthalocyanines in the gas phase — ●FLORIAN SCHLAGHAUFER 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 atoms and molecules (e.g. H₂O, Ar) recorded in superfluid helium nanodroplets is determined by pure molecular contributions and the influence of the helium environment. Since the analysis of such line shapes is not straightforward, corresponding gas phase studies are essential for dissecting helium induced spectral features from molecular rotor fingerprints.

This talk will give an overview of our recent experimental proceedings on spectroscopy of jet cooled phthalocyanines as well as data analysis used to obtain information on structure and polarity of the molecular systems for both the ground and the electronically excited state. To our best knowledge phthalocyanine is the largest molecule ever studied with respect to its rotational degrees of freedom so far.

Ultimately, this project heads for a better understanding of micro-solvation and the dynamics of electronic excitation of molecules inside superfluid helium nanodroplets via combined gas phase and helium droplet investigations.

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

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

MO 18.3 Thu 15:15 MO-H5

Vibronic couplings in Serotonin — ●CHRISTIAN BRAND^{1,2} and MICHAEL SCHMITT¹ — ¹Heinrich-Heine University, Institute of Physical Chemistry I — ²German Aerospace Center, Institute of Quantum Technologies

We discuss vibronic couplings between the lowest two excited singlet states (L_a and L_b) of the neurotransmitter serotonin. In this derivative of indole, we expect a large energy gap between the two states of ≈ 3300 cm⁻¹ and thus only weak couplings. Nevertheless, using rotationally resolved electronic spectroscopy, we observe a mode-dependent rotation of the L_b transition dipole moment vector in the direction of the L_a . This study bridges the gap between strong and completely suppressed couplings, as previously observed for other indole derivatives.

[1] C. Brand and M. Schmitt, J. Mol. Struct. **1250**, 131819 (2022)

MO 18.4 Thu 15:30 MO-H5

High resolution continuous wave spectroscopy of the $A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$ transition in nitric oxide — ●PATRICK KASPAR¹, FABIAN MUNKES¹, PHILIPP NEUFELD¹, LEA EBEL¹, YANNICK SCHELLANDER², ROBERT LÖW¹, TILMAN PFAU¹, and HARALD KÜBLER¹ — ¹5. Physikalisches Institut and Center for Integrated Quantum Science and Technology IQST, Universität Stuttgart — ²Institut für Großflächige Mikroelektronik, Universität Stuttgart

Within the scope of the development of a new kind of gas sensor[1,2], we employ Doppler-free saturated absorption spectroscopy on the $A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$ transition in nitric oxide (NO) for different total

angular momenta J on the P_{12} branch. Spectroscopy is performed in continuous wave operation at 226 nm in a 50 cm long through-flow cell. Via phase sensitive detection by a lock-in amplifier the hyperfine structure of the $X^2\Pi_{3/2}$ state of NO is partially resolved. The data is compared to previous measurements [3], showing good agreement. Investigation of the dependence of the spectroscopic feature on power and pressure, should yield hyperfine constants, natural transition linewidth and the collisional cross-section between NO molecules.

[1] P. Kaspar et. al., OSA Optical Sensors and Sensing, 19-23 July, 2021

[2] J. Schmidt et. al., Appl. Phys. Lett. **113**, 01113 (2018)[3] W.L. Meerts and A. Dymanus, J. of Mol. Spec. **44**, 320-346 (1972)

MO 18.5 Thu 15:45 MO-H5

Spectral learning for (ro-)vibrational calculations of weakly-bound molecules — ●YAHYA SALEH^{1,2}, JANNIK EGGERS^{1,2}, VISHNU SANJAY⁶, ANDREY YACHMENEV^{1,3}, ARMIN ISKE², and JOCHEN KÜPPER^{1,3,4,5} — ¹Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ²Department of Mathematics, Universität Hamburg, Hamburg, Germany — ³Center for Ultrafast Imaging, Universität Hamburg, Hamburg, Germany — ⁴Department of Physics, Universität Hamburg, Hamburg, Germany — ⁵Department of Chemistry, Universität Hamburg, Hamburg, Germany — ⁶Gran Sasso Science Institute

Weakly-bound complexes of organic molecules with water play diverse roles in various fields ranging from biology to astrochemistry. Planning experiments requires accurate quantum mechanical calculations of (ro-)vibrational energies up to dissociation, which is a challenging task for these systems. Standard predictions for these problems represent the wavefunctions as a linear combination of some fixed basis set. The quality of the predictions deteriorate for highly-excited states. Moreover, the computational costs scale poorly with the dimension of the problem.

We present a nonlinear variational framework to simultaneously compute multiple eigenstates of quantum systems using neural networks. The proposed framework is shown to model excited states more accurately and is believed to scale better with the size of the system. We also present numerical analysis' results and convergence guarantees of the proposed approach.

MO 18.6 Thu 16:00 MO-H5

SFQEDtoolkit: a high-performance library for modeling strong-field QED effects in relativistic laboratory astrophysics — ●SAMUELE MONTEFIORI and MATTEO TAMBURINI — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, D-69117 Heidelberg, Germany

Given the need of modeling strong-field QED (SFQED) processes such as high-energy photon emission and electron-positron pair creation in forthcoming relativistic laboratory experiments at ultrahigh fields, we have developed an open source library that allows the implementation of SFQED effects in existing Monte Carlo and Particle-In-Cell (PIC) codes. The SFQEDtoolkit library is primarily designed to simultaneously achieve high performance and high accuracy in modeling the functions that describe SFQED processes within and beyond the locally constant field approximation (LCFA).

MO 18.7 Thu 16:15 MO-H5

Auger electron spectroscopy of Fulminic acid, HCNO — ●MARIUS GERLACH¹, TOBIAS PREITSCHOPF¹, EMIL KARAEV¹, HEIDY LARA¹, DENNIS MAYER², JOHN BOZEK³, REINHOLD FINK⁴, and INGO FISCHER¹ — ¹Universität Würzburg, 97074 Würzburg, Germany — ²Universität Potsdam, 14476 Potsdam-Golm — ³Synchrotron SOLEIL, 91192 Gif Sur Yvette, France — ⁴Universität Tübingen, 72076 Tübingen

In 2009 fulminic acid, HCNO, was first detected in space in the three starless cores B1, L1544 and L183.[1] The isomer isocyanic acid, HNCO, is also ubiquitous in interstellar systems.[2] Due to their composition of Hydrogen, Carbon, Nitrogen and Oxygen these molecules have been proposed to have a prebiotic role as intermediates for organic life. Investigating the interaction of these molecules with X-ray radiation is critical in understanding their fate in space.

As such, we present the gas phase auger electron spectra of fulminic acid which were recorded at the PLEIADES beamline at the Synchrotron SOLEIL in France. Fulminic acid was synthesized by preparative pyrolysis.[3] The spectra are compared to theoretical simulations and previously recorded spectra of isocyanic acid.

[1] N. Marcelino, J. Cernicharo, B. Tercero, E. Roueff, *Astrophys.*

J., 2009, 690, L27-L30.

[2] Nguyen-Q-Rieu, C. Henkel, J. M. Jackson, R. Mauersberger, *Astron. Astrophys.*, 1991, 241, L33.

[3] C. Wentrup, B. Gerecht, H. Briehl, *Angew. Chem. Int. Ed.*, 1979, 18, 467-468.

MO 19: Poster 3

Time: Thursday 16:30–18:30

Location: P

MO 19.1 Thu 16:30 P

High resolution spectroscopy of biomolecules in a cryogenic 16-pole wire ion trap — ●ENDRES ERIC¹, GEISTLINGER KATHARINA¹, DAHLMANN FRANZISKA¹, MICHAELSEN TIM¹, ONCAK MILAN¹, MOHANDAS SALVI², and WESTER ROLAND¹ — ¹Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria — ²Institute of Science Education and Research, Tirupati, India

Spectroscopy plays an increasingly important role in the study of structural details of complex biological systems and the investigation of UV photodamage of genetic material. In combination with electrospray ionization, ion trap spectroscopy has been successfully used to investigate electronic and vibrational transitions in biomolecules in order to determine geometrical structures or the decay channels following electronic excitation.

In this contribution a recently developed linear cryogenic 16-pole wire ion trap for ion spectroscopy at temperatures below 4K will be presented. The trap offers a large field-free region in the radial direction, reducing radio-frequency heating and provides large optical access perpendicular to the ion beam direction.[1] The low temperatures enabled multiple tagging of glycine ions, allowing high resolution IR action spectroscopy of the OH stretching vibration. Simulated rotational contours of the absorption band yield a rotational temperature of about 6K.[2] Furthermore, preliminary results of photodissociation measurement of [dAMP-H]⁻, a monomer of DNA, will be presented.

[1]Geistlinger et. al., *Rev. Sci. Instrum.* 92, 023204 (2021)

[2]Geistlinger et. al., *J. Mol. Spectrosc.* 379, 111479 (2021)

MO 19.2 Thu 16:30 P

Numerical Justification for Increased Conductance of Ferrocene Molecule at Room Temperature — ●STEPAN MAREK — Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

The conductance of molecular junctions is numerically challenging problem combining physics of macroscopic electrodes/reservoirs and microscopic molecules. Recent experimental advances help guide the theoretical calculations and provide a good testing case for the numerical methods. Perhaps the most widely used approach to numerical electronic structure calculations is the density functional theory (DFT). This method is used to calculate ground state electronic structure of several electrode-plus-ferrocene molecule geometries. The results are then refined in conductance calculations, and by thermal averaging of the conductance in different geometries, predictions on the thermal dependence of the conductance of the junction are made, which qualitatively agree with the experiment.

MO 19.3 Thu 16:30 P

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

The properties of deeply cold niobium clusters Nb₉⁻ to Nb₃₀⁻ and tantalum clusters Ta₅⁻ to Ta₂₂⁻ at 3.9K have been investigated.

In combination with a time-dependent potential applied to the flight tube, our magnetic bottle time-of-flight photoelectron spectrometer has a current resolution of $\Delta E/E = 0.37\%$ [1]. This is at least a factor five better than a standard magnetic bottle spectrometer and still competitive with a hemispherical energy analyzer whose drawback is a significantly worse collection efficiency. Combining the improved spectrometer with a low-jitter, short-pulse excimer laser operating at 157nm, we gain access to bound states down to 7.9eV at a so far unreached precision in such a setup [2].

In this configuration we recorded more detailed photoelectron spectra for small niobium and tantalum clusters cooled down to their

vibrational ground state.

[1] M.Weigt, PhD thesis, Albert-Ludwigs-Universität Freiburg (2021).

[2] O.Kostko, PhD thesis, Albert-Ludwigs-Universität Freiburg (2007).

MO 19.4 Thu 16:30 P

New apparatus for synchrotron-based photoelectron spectroscopy of cold, mass-selected and cold ions in the gas phase — ●PHILLIP STÖCKS, FABIAN BÄR, LUKAS WEISE, and BERND V. ISSENDORFF — Physikalisches Institut der Albert-Ludwigs-Universität Freiburg

A novel instrumentation is under development for photoelectron spectroscopy of gas phase ions, aiming for wide exploitation of the potential of synchrotron radiation sources like BESSY II for the study of mass-selected nanoparticles, complexes and molecules.

The setup will make use of the strongly increased ion density in an ion trap for photoelectron spectroscopy of size-selected cluster or molecular ions with synchrotron radiation. Photoelectrons emitted by the ions inside the ion trap will be guided by a tailored magnetic field out of the ion trap, extracted from the magnetic guiding field by custom designed electron optics, and transferred into a hemispherical energy analyser with a position sensitive detector. By employing this method, photoelectron intensities can be obtained that are orders of magnitude higher than by direct irradiation of an ion beam. This worldwide unique setup will make core-levels and the full valence band of free ions routinely accessible for the first time and can be used for a broad range of studies, from the characterisation of the electronic structure of transition metal clusters and organometallic complexes via core-level shifts, to the examination of reactions on the surface of catalytically active nanoparticles; tackling problems of both, fundamental importance and direct technological relevance.

MO 19.5 Thu 16:30 P

Detailed investigation of unexpected photoelectron spectra via angle resolved spectroscopy of Copper clusters — ●LUKAS WEISE and BERND V. ISSENDORFF — Physikalisches Institut der Albert-Ludwigs-Universität Freiburg

Angle resolved spectroscopy provides an important test of the theoretical description of clusters since these spectra 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, cooled to 7 K and enter a time-of-flight spectrometer for mass measurement and selection. Afterwards electrons are detached by linear polarised laser light and projected onto a MCP detector in a velocity map imaging setup.

The presented analysis utilises the additional information from angle resolved spectroscopy to gain a better understanding of photoelectron spectra, that have not been predicted by theory so far. For Cu₉₁⁻ an electronic shell closing is expected. Previous experiments [1,2], however, have shown an additional peak associated to the occupation of the next orbital, that would be predicted for Cu₉₂⁻. Based on the angle resolved measurements an f-type character can be assigned to the additional state.

[1] O. Kostko, PhD thesis, Albert-Ludwigs-Universität Freiburg (2007).

[2] M. Knickelbein, *Chemical Physics Letters* 192, 1 (1992), 129-134.

MO 19.6 Thu 16:30 P

Disentangling the relationship between S_N2 and E2 reactions in ethyl halides — ●THOMAS GSTIR, ATILAY AYASLI, TIM

MICHAELSEN, ARNAB KHAN, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria

The bimolecular nucleophilic substitution (S_N2) and bimolecular elimination reaction (E2) are two essential reaction types in organic chemistry. As both reactions lead to the same ionic product, it is inherently difficult to distinguish between them solely with experimental approaches. In an attempt to overcome this, we measured the reaction of fluoride with iodoethane (CH_3CH_2I) and its fully β -carbon-fluorinated counterpart (CF_3CH_2I). These lead to the complete suppression of the E2 pathway. Here, we report the results of the reactions in the gas phase at four collision energies between 0.4 and 2 eV. For these measurements, we employed a crossed molecular beam setup combined with a velocity map imaging spectrometer. The obtained energy and angle differential cross sections can reveal a mechanistic understanding of reaction dynamics on an atomic level, especially in cooperation with state-of-the-art theory. In the present experiment we observe an increased signal in the proton transfer channel and at higher collision energies the formation of CF_2CI^- . Both reaction pathways originate from an attack on a α -carbon hydrogen. In CH_3CH_2I this would most likely lead to a hydrogen migration along the C-C bond and a subsequent E2 breakup.

MO 19.7 Thu 16:30 P

Experimental setup towards High-Resolution Ion-Molecule Crossed Beam Imaging — •DASARATH SWARAJ, FLORIAN TRUMMER, TIM MICHAELSEN, ARNAB KHAN, ROBERT WILD, FABIO ZAPPA, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, 6020 Innsbruck, Austria

Detailed insight into the dynamics of elementary reactions in the gas phase can be obtained from crossed-beam reactive scattering experiments. Crossed beam combined with velocity map imaging (VMI), angle and energy differential crosssections can be obtained.[1][2] In this contribution, we present the design plan and relevant simulations for an experimental setup to investigate ion molecule reactions with higher precision than previously attainable. The ions will be created by laser ionization so that they are mostly in the vibrational ground state. In addition, according to our simulation, a proper shaping of the ionization volume and a very weak acceleration of the ions play a crucial role in deciding the ion beam energy resolution. The ion beam is overlapped with the beam of neutral molecules and the collision products are collected by the VMI spectrometer. We also plan a coincidence detection of both the ionic and neutral products after the reaction, which will be further implemented by a laser ionization scheme. With our new setup, we plan to study fundamental astrophysically significant reactions such as $H_2^+ + H_2 \rightarrow H_3^+ + H$.

[1] R. Wester, *Mass Spectrometry Reviews*, 2021.

[2] R. Wester, *Phys. Chem. Chem. Phys.*, vol. 16, pp.396-405,2014.

MO 19.8 Thu 16:30 P

Observation and manipulation of long-lived electronic coherences in lanthanide complexes at room temperature — •MIRALI GHEIBI, JAYANTA GHOSH, CRISTIAN SARPE, BASTIAN ZIELINSKI, TILLMANN KALAS, RAMELA CIOBOTEA, ARNE SENTLEBEN, THOMAS BAUMERT, and HENDRIKE BRAUN — Institute of Physics and CINSA-T, University of Kassel, Heinrich-Plett-Strasse 40, 34132 Kassel, Germany

The aim of SMolBits - Scalable Molecular Quantum Bits - 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 and gate operations at the atomic and molecular levels. 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. In this research, the electronic coherences excited in lanthanide complexes by interaction with IR femtosecond laser pulses and their lifetimes using phase-locked double pulses and fluorescence detection under a confocal-microscope are investigated. An electronic coherence time of more than 600 fs for two different complexes containing Neodymium is observed. Currently, we study Rabi oscillations in these complexes. As a next step, the influence of spectrally phase-shaped femtosecond laser pulses in the non-perturbative regime onto the electronic excitation and the created coherence for quantum gate implementation is researched.

MO 19.9 Thu 16:30 P

Towards quantum control of Calcium ions for the use in molecular spectroscopy — •MANIKA BHARDWAJ, JOSSELINE BERNARDOFF, JAN THIEME, DAQING WANG, MARKUS DEBATIN, and KILIAN SINGER — University of Kassel, Kassel, Germany

We present our advances towards establishing a new two-dimensional spectroscopy method that selectively maps the suitable quantum states. For this purpose, the molecular ions to be investigated are sympathetically cooled and trapped in an ion trap with laser-cooled calcium ions [1]. We will use the photon-recoil spectroscopy method to study the molecular ions through studying the photon-recoil imparted on co-trapped calcium ion [2].

[1] Groot-Berning, Kornher, Jacob, Stopp, Dawkins, Kolesov, Wrachtrup, Singer, Schmidt-Kaler, *Phys. Rev. Lett.* 123, 106802 (2019) [2] Wan, Gebert, Wübbena, Scharnhorst, Amairi, Leroux, Hemmerling, Lörch, Hammerer, Schmidt, *Nat Commun* 5, 3096 (2014)

MO 19.10 Thu 16:30 P

Towards the production of groundstate RbYb molecules — •CHRISTIAN SILLUS, BASTIAN POLLKLESENER, CÉLINE CASTOR, and AXEL GÖRLITZ — Heinrich-Heine Universität Düsseldorf

Ultracold dipolar molecules constitute a promising system for the investigation of topics like ultracold chemistry, novel interactions in quantum gases, precision measurements and quantum information. Here we report on first experiments in our apparatus for the production of ultracold RbYb molecules. This setup constitutes an improvement of our old apparatus, where the interactions in RbYb and possible routes to molecule production have already been studied extensively. In the new setup a major goal is the efficient production of ground state RbYb molecules. We employ optical tweezers to transport individually cooled samples of Rb and Yb from their separate production chambers to a dedicated science chamber. Here we start to study interspecies interactions of different isotopes by overlapping crossed optical dipole traps. We report of first results of implementing an optical lattice and using photoassociation spectroscopy on the way towards groundstate molecules.

MO 19.11 Thu 16:30 P

Self-bound dipolar droplets and supersolids in molecular Bose-Einstein condensates — •MATTHIAS SCHMIDT¹, PHILLIP GROSS¹, LUCAS LASSABLIÈRE², GOULVEN QUÉMÈNER², and TIM LANGEN¹ — ¹Physikalisches Institut und Center for Integrated Quantum Science and Technology, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany — ²Université Paris-Saclay, CNRS, Laboratoire Aimé Cotton, 91405 Orsay, France

We numerically study the many-body physics of molecular Bose-Einstein condensates with strong dipole-dipole interactions. We observe the formation of self-bound droplets, and explore phase diagrams that feature a variety of exotic supersolid states. In all of these cases, the large and tunable molecular dipole moments enable the study of unexplored regimes and phenomena, including liquid-like density saturation and universal stability scaling laws for droplets, as well as pattern formation and the limits of droplet supersolidity. We discuss a realistic experimental approach to realize both the required collisional stability of the molecular gases and the independent tunability of their contact and dipolar interaction strengths. Our work provides both a blueprint and a benchmark for near-future experiments with bulk molecular Bose-Einstein condensates.

MO 19.12 Thu 16:30 P

Preparing and characterizing ultracold bosonic $^{23}Na^{39}K$ spin polarized ground state molecules — •MARA MEYER ZUM ALTEN BORGLÖH¹, PHILIPP GERSEMA¹, KAI KONRAD VOGES¹, TORSTEN HARTMANN¹, LEON KARPA¹, ALESSANDRO ZENESINI², and SILKE OSPELKAUS¹ — ¹Leibniz Universität Hannover, Institut für Quantenoptik — ²INO-CNR BEC Center and Dipartimento di Fisica, Università di Trento

Recently, ultracold polar molecules have become the focus of interest for research in quantum chemistry and metrology. Heteronuclear molecules have a large electric dipole moment, which allows the study of long-range and anisotropic dipole-dipole interactions. Moreover, their large number of degrees of freedom, such as rotation and vibration, opens up new possibilities for quantum simulations. We report the preparation of ground-state bosonic spin-polarized NaK molecules with a large electric dipole moment of 2.7D. Starting from an ultracold quantum gas mixture of K and Na atoms, we first generate weakly bound molecules near a Feshbach resonance. The Feshbach

molecules are then transformed into strongly bound molecules in the absolute molecular ground state by stimulated Raman adiabatic passage (STIRAP). The STIRAP pulse is performed within $12\ \mu\text{s}$ and has an efficiency of about 70%, preparing up to 4200 molecules at a temperature of about 300 nK. Finally, we report the dependence of the energy structure of the vibrational ground state manifold on the electric field and the manipulation of the molecular hyperfine and rotational state.

MO 19.13 Thu 16:30 P

Complex Formation in Three-Body Reactions of Cl^- with H_2 — ●CHRISTINE LOCHMANN, ROBERT WILD, MARKUS NÖTZOLD, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Österreich

Dihydrogen halide clusters are the subject of various theoretical and experimental studies [1]. In their anionic state they are weakly bound complexes and can provide insight into dynamical processes in chemical reactions. Here we report the three-body reaction rate of Cl^- with H_2 forming the $\text{Cl}^-(\text{H}_2)$ complex, as well as the temperature dependence of this reaction in the range of 10 - 26 K [2]. Furthermore, we observe the back-reaction with an unexpected dependence to the third power of the density. Comparisons of the experiment in a 22-pole rod and a newly installed 16-pole wire trap [3] are presented and show that the ions reach lower temperature in the 16-pole trap. We have recently also observed a three-body process in the reaction of C_2^- with two H_2 which leads to the product C_2H^- . In the future we plan on expanding the research of three-body reactions at low temperatures. One focus will be the influence of the nuclear spin state of hydrogen on three-body reaction rates.

- [1] F. Dahlmann, et al., J. Chem. Phys. (in press) (2021);
- [2] R. Wild, et al., J. Phys. Chem. A, 125, 8581 (2021)
- [3] K. Geistlinger, et al., Rev. Sci. Instrum. 92, 023204 (2021)

MO 19.14 Thu 16:30 P

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

Recently, great progress has been made in direct laser cooling of molecules to temperatures close to absolute zero. However, experiments are limited by the number of molecules that can be captured from molecular beams using typical laser-based trapping methods. In Petzold et al. 2018, we proposed to transfer Zeeman deceleration to laser-coolable molecules and thus substantially increase the number of molecules that can be captured by e.g. magneto-optical traps. Here, we now present our characterisation of the Zeeman force for CaF molecules, Kaebert et al. 2021. We find excellent agreement of the force with an optical Bloch equation model. This shows that the generated force profile can compress the initial molecular velocity distribution from a standard buffer gas cell to the velocity required for trapping in a magneto-optical trap (MOT). We present the current status of our experiment as well as theoretical work on a novel Bayesian-optimised molecular MOT scheme for CaF molecules.

MO 19.15 Thu 16:30 P

Characterization of an experimental setup to investigate cold molecule-Rydberg-atom interactions — ●MARTIN ZEPPENFELD — MPI für Quantenoptik

Strong interactions between molecules and Rydberg atom extend to distances larger than $1\ \mu\text{m}$, promising exciting applications in quantum science. This includes possibilities for cooling internal and external molecular degrees of freedom, nondestructive molecule detection and state readout, and performing quantum gates.

Towards these goals, I will present an experimental setup for the investigation of cold molecule-Rydberg-atom interactions. Cold molecules are produced via velocity filtering with an electrostatic quadrupole guide. Rydberg atoms are produced via two-photon excitation of ultracold atoms in a rubidium MOT. A key feature of the setup is a set of 24 electrodes, allowing the electric fields experienced by the Rydberg atoms to be precisely controlled. Combined with mm-waves at roughly 400 – 500 GHz to drive Rydberg transitions and state

selective field ionization for detection, this allows precise control and read-out of the atomic Rydberg states.

MO 19.16 Thu 16:30 P

Modelling laser cooling and molecular structure in BaF — ●FELIX KOGEL, MARIAN ROCKENHÄUSER, EINIUS PULTINEVICIUS, and TIM LANGEN — Universität Stuttgart, 5. Physikalisches Institut, IQST

Cold molecular gases are promising candidates for studies of cold chemistry, precision tests of fundamental symmetries and quantum simulation. Motivated by our experiments on barium monofluoride (BaF), we report here on the simulation of laser cooling for this species, using multi-level rate equations and optical Bloch equations. We present efficient Doppler, sub-Doppler and coherent cooling schemes for both bosonic and fermionic isotopologues of this species. In addition, we discuss the analysis of experimental spectra of the lowest vibrational transitions relevant for laser cooling of BaF .

MO 19.17 Thu 16:30 P

Towards nanoplasma formation from size selected helium droplets using an electrostatic deflector — CRISTIAN MEDINA¹, ●SEBASTIAN TRIPPEL², ROBERT MOSHAMMER³, THOMAS PFEIFER³, JOCHEN KUPPER², FRANK STIENKEMEIER¹, and MARCEL MUDRICH⁴ — ¹University of Freiburg, Freiburg im Breisgau, Germany — ²Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ³Max Planck Institute for Nuclear Physics, Heidelberg, Germany — ⁴Aarhus University, Aarhus, Denmark

It has recently been demonstrated that passing a molecule with a large dipole moment embedded inside a helium nanodroplet across an inhomogeneous electric field allows deflecting the entire droplet depending on its mass [1]. We present the calculations and design for a helium droplet size selector apparatus using CsI molecules as dopants. The doped clusters are deflected transversally by a type-B deflector with an inhomogeneous electric field [2]. In the proposed experiment, a nanoplasma is ignited in the helium droplet by a NIR femtosecond laser, tightly focused by a motorized back-focusing mirror, moving the focus across the diverted beam. The resulting electrons and ions emitted by the nanoplasma are collected by an electron velocity-map imaging and an ion time-of-flight spectrometer. The theoretical calculations of the spatial deflections were done using the CMIfly software developed by the Molecule Imaging group (CMI) at the Centre for Free-Electron Laser Science (CFEL)[2].

- [1]D.J. Merthe et al., j. phys. chem. lett. 7 (2016).
- [2]J-P. Chang et al., comput. phys. commun. 185 (2014).

MO 19.18 Thu 16:30 P

Preparations for experiments with triatomic hydrogen ions at the Cryogenic Storage Ring — ●AIGARS ZNOTINS¹, ANNIKA OETJENS¹, FLORIAN GRUSSIE¹, DAMIAN MULL¹, OLDRICH NOVOTNY¹, FELIX NUSSLIN¹, ANDREAS WOLF¹, ARNAUD DOCHAIN², XAVIER URBAIN², and HOLGER KRECKEL¹ — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — ²Institute of Condensed Matter and Nanoscience, Louvain-la-Neuve B-1348, Belgium

The triatomic hydrogen ion H_3^+ is considered a key species in astrochemistry. It serves as a benchmark system for theoretical calculations of small polyatomic molecules and has been identified as one of the main drivers of an active interstellar ion-neutral chemistry network, contributing to the formation of complex molecules in space. Additionally, electron recombination of H_3^+ has received a lot of attention, owing to the influence of its rate coefficient on the ionization balance of interstellar chemistry networks. Here, we report current efforts to understand the cooling behavior of H_3^+ and H_2D^+ inside the Cryogenic Storage Ring, and the preparation of laser diagnostic schemes and dedicated ion sources for future studies. We explore the feasibility of using multi-color action spectroscopy of cold H_3^+ ions to probe excited states in the energy region above $20000\ \text{cm}^{-1}$.

As the use of a rotationally cold ion source is a crucial component of the foreseen studies, we present the design and characteristics of a pulsed supersonic expansion source to produce molecular ion beams with low rotational temperatures.