

## 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 JUDT<sup>1</sup>, JULIUS SCHWARZ<sup>1</sup>, FABIANO LEVER<sup>2</sup>, ALJOSCHA ROERIG<sup>3</sup>, KAROLIN BAEV<sup>4</sup>, DENNIS MAYER<sup>2</sup>, IVAN BAEV<sup>1</sup>, MATZ NISSEN<sup>1</sup>, STEFFEN PALUTKE<sup>4</sup>, MARKUS GUEHR<sup>2</sup>, MARKUS DRESCHER<sup>1</sup>, MARION KUHLMANN<sup>4</sup>, MICHAEL MEYER<sup>3</sup>, MATTHIAS DREIMANN<sup>5</sup>, HELMUT ZACHARIAS<sup>5</sup>, and MICHAEL MARTINS<sup>1</sup> — <sup>1</sup>Universität Hamburg, Hamburg, Germany — <sup>2</sup>Universität Potsdam, Potsdam, Germany — <sup>3</sup>European XFEL, Schenefeld, Germany — <sup>4</sup>Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany — <sup>5</sup>Center 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<sub>2</sub>, ClBrC<sub>2</sub>H<sub>4</sub> and ClBrC<sub>3</sub>H<sub>6</sub> 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<sub>2</sub> 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<sub>2</sub> 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  $\sigma$  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<sup>+</sup> 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<sup>1,2</sup>, JANNIK LÜBKE<sup>1,2,3</sup>, ARMANDO ESTILLORE<sup>1</sup>, AMIT SAMANTA<sup>1</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> —

<sup>1</sup>Center for Free-ElectronLaser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — <sup>2</sup>Department of Physics, Universität Hamburg, Hamburg, Germany — <sup>3</sup>Center 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<sup>1,2</sup>, NIDIN VADASSERY<sup>1</sup>, LUDMILA SCHNEIDER<sup>2</sup>, HUBERTUS BROMBERGER<sup>1</sup>, SEBASTIAN TRIPPEL<sup>1,3</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — <sup>2</sup>Department of Physics, Universität Hamburg — <sup>3</sup>Center 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-water<sub>1</sub> 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 THEIL<sup>1</sup>, MARIUS GERLACH<sup>1</sup>, EMIL KARAEV<sup>1</sup>, JEAN-CHRISTOPHE LOISON<sup>2</sup>, CHRISTIAN ALCARAZ<sup>3</sup>, LAURENT NOHAN<sup>4</sup>, and INGO FISCHER<sup>1</sup> — <sup>1</sup>Universität Würzburg, 97074 Würzburg, Germany — <sup>2</sup>Université de Bordeaux, 33405 Talence, France — <sup>3</sup>Université Paris-Saclay, 91190 Gif-sur-Yvette, France — <sup>4</sup>Synchrotron SOLEIL, 91190 Gyf-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 discharge 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<sup>-1</sup>) 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 NEUFELD<sup>1</sup>, PATRICK KASPAR<sup>1</sup>, FABIAN MUNKES<sup>1</sup>, LEA EBEL<sup>1</sup>, YANNICK SCHELLANDER<sup>2</sup>, ROBERT LÖW<sup>1</sup>, TILMAN PFAU<sup>1</sup>, and HARALD KÜBLER<sup>1</sup> — <sup>1</sup>Physikalisches Institut und Center for Integrated Quantum Science and Technology IQST, Universität Stuttgart — <sup>2</sup>Institut 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, optogalvanic 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 optogalvanic 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 BONA<sup>1</sup>, OLIVER ZINGSHEIM<sup>1</sup>, SVEN THORWIRTH<sup>1</sup>, HOLGER S. P. MÜLLER<sup>1</sup>, FRANK LEWEN<sup>1</sup>, JEAN-CLAUDE GUILLEMIN<sup>2</sup>, and STEPHAN SCHLEMMER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität zu Köln, Köln, Germany — <sup>2</sup>ENSC, 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, Pgofer 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 isotopi-

cally 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](https://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 — 1. 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 (CH<sub>3</sub>CN) 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. Nepliyakh, 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<sup>a</sup> 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.<sup>b</sup> 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,<sup>c</sup> which is linked to a plethora of other spectroscopic, collisional, and kinetic databases via the VAMDC portal.

<sup>a</sup> Shortcut: [cdms.de](https://cdms.de); web address: <https://cdms.astro.uni-koeln.de/>

<sup>b</sup> H. S. P. Müller et al., *Astron. Astrophys.* 370 (2001) L49

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

MO 8.16 Tue 16:30 P

**Merged-beams experiments on molecular ion-neutral reactions for astrochemistry** — ●PIERRE-MICHEL HILLENBRAND<sup>1</sup>, XAVIER URBAIN<sup>2</sup>, and DANIEL WOLF SAVIN<sup>3</sup> — <sup>1</sup>Justus-Liebig Universität, Giessen, Germany — <sup>2</sup>Université catholique de Louvain, Louvain-la-Neuve, Belgium — <sup>3</sup>Columbia 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<sub>2</sub><sup>-</sup>** — ●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<sup>-</sup> 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<sub>2</sub><sup>-</sup>, 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<sup>-</sup>. *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 BU<sup>1</sup>, BENJAMIN C. BOSTICK<sup>2</sup>, STEVE N. CHILLRUD<sup>2</sup>, DEBORAH L. DOMINGUE<sup>3</sup>, DENTON S. EBEL<sup>4</sup>, GEORGE E. HARLOW<sup>4</sup>, ROSEMARY M. KILLEN<sup>5</sup>, ●DANIEL SCHURY<sup>1</sup>, KYLE P. BOWEN<sup>1</sup>, PIERRE-MICHEL HILLENBRAND<sup>1</sup>, XAVIER URBAIN<sup>6</sup>, RUITIAN ZHANG<sup>1</sup>, DMITRY IVANOV<sup>1</sup>, and DANIEL W. SAVIN<sup>1</sup> — <sup>1</sup>Columbia Astrophysics Laboratory, Columbia University, New York — <sup>2</sup>Lamont-Doherty Earth Observatory, Columbia University, Palisades — <sup>3</sup>Planetary Science Institute, Tucson — <sup>4</sup>American Museum of Natural History, New York — <sup>5</sup>NASA-Goddard Space Flight Center, Greenbelt — <sup>6</sup>Université 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 BÄUML<sup>1</sup>, SEBASTIAN REITER<sup>1</sup>, EVA SEXTL<sup>2</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Department of Chemistry, LMU Munich, Germany — <sup>2</sup>Department 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  $\text{Mo}(\text{CO})_6$ . By transient absorption spectroscopy, we observed energy transfer from BP to the complex resulting in the formation of the dissociation products  $\text{Mo}(\text{CO})_5$  and  $\text{Mo}(\text{CO})_4$ . 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 MUTH<sup>1</sup>, FRANZ SCHMIDT<sup>2</sup>, NIKOLAUS KORBER<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — <sup>2</sup>Institut 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  $\text{Ph}_2\text{Se}_2$  and diphenylselenide  $\text{Ph}_2\text{Se}$  and the subsequent recombination dynamics of the transient radicals** — ●DANIEL GREYDA<sup>1</sup>, CARINA ALLACHER<sup>1</sup>, ELIAS HARRER<sup>1</sup>, ROGER JAN KUTTA<sup>1</sup>, ALEXANDER BREDER<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — <sup>2</sup>Institut 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  $\text{Ph}_2\text{Se}$  and  $\text{Ph}_2\text{Se}_2$  after photodissociation of the carbon-selenium or the selenium-selenium bond, respectively, forming the radicals  $\text{PhSe}^\bullet$  and  $\text{Ph}^\bullet$ . 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  $\text{Ph}_2\text{Se}_2$  and  $\text{Ph}_2\text{Se}$  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  $\text{Ph}_3\text{N}$  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  $\text{Ph}_3\text{N}$  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  $\text{Ph}_3\text{N}$ , 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 photoinstability due to intra- and intermolecular photoconversion of  $\text{Ph}_3\text{N}$ , 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 MARHÖFER<sup>1</sup>, PIT BODEN<sup>1</sup>, SOPHIE STEIGER<sup>1</sup>, CHRISTOPH KAUB<sup>2</sup>, PETER ROESKY<sup>2</sup>, GEREON NIEDNER-SCHATTEBURG<sup>1</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>Department of Chemistry, TU Kaiserslautern, Erwin-Schrödinger-Str. 52-54, 67663 Kaiserslautern — <sup>2</sup>Institute 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.