MO 32: Molecular Spectroscopy III

Time: Friday 11:00–13:00 Location: P 204

Invited Talk MO 32.1 Fri 11:00 P 204

Time-resolved photoelectron spectroscopy of polycyclic hydrocarbons in rare-gas clusters — •Leonie Werner, Ulrich Bangert, Sebastian Hartweg, Yilin Li, Arne Morlok, Felix Riedel, Frank Stienkemeier, and Lukas Bruder — Institute of Physics, University of Freiburg, Hermann-Herder-Straße 3, 79104 Freiburg, Germany

Time-resolved photoelectron spectroscopy (TRPES) is a powerful tool for probing ultrafast molecular dynamics, yet its application to molecules embedded in condensed environments remains challenging. We address this by studying polycyclic aromatic hydrocarbons (PAHs) dissolved in liquid-helium and solid-argon clusters, enabling controlled variations of environmental interactions. Despite the surrounding medium, we achieve high energy resolution and resolve environment-dependent differences in the molecular dynamics. In a first demonstration, we investigated the ultraviolet-induced ultrafast internal conversion in tetracene which is building on our previous work on isolated tetracene molecules in the gas phase [1]. In the next step, we intend to extend this to a systematic study of various acene molecules.

[1] A. Scognamiglio et al., J. Chem. Phys. (2024), 161, 024302

MO 32.2 Fri 11:30 P 204

Solvent-dependent relaxation pathways in Liquid-Jet Time-Resolved Photoelectron Spectroscopy — •Filippo Aria[1], Alina Khodko[2], and Oleg Kornilov[1] — [1]Max-Born-Institut, Berlin, Germany — [2]Institute of Physics NAS of Ukraine, Kyiv, Ukraine

Successful engineering of biomimetic carbon-carbon photoswitches with quantum yields comparable to natural systems requires understanding how solvent environments govern their relaxation pathways. Here, we investigate the solvent-dependent excited-state lifetime of 4-dimethylamino-4'-nitrostilbene (DMANS), a benchmark push-pull photoswitch. The measurements were carried out using UV pump-XUV probe liquid-jet time-resolved photoelectron spectroscopy (LJ-TRPES) with harmonic selection via a time-delay compensated monochromator. This approach yields precise energetic shifts and lifetimes of the active excited state across a series of solvents of moderate to high polarity. The results enable assessment of ultrafast photoswitching efficiency, identification of potential long-lived dark states inaccessible to conventional optical techniques, and establish the mechanistic role of solvation in controlling switching performance. This work demonstrates XUV LJ-TRPES as an essential tool for characterizing ultrafast dynamics in both synthetic and biologically inspired molecular photoswitches.

MO 32.3 Fri 11:45 P 204

Photoelectron Photoion Multicoincidence Study of Micro-Solvated Bio-Relevant Molecules — •Brendan Wouterlood[1], Sitanath Mondal[1], Madhusree Roy-Chowdhury[2,3], Gustavo Garcia-Macias[2], Laurent Nahon[2], Frank Stienkemeier[1], and Sebastian Hartweg[1] — [1]Institute of Physics, University of Freiburg — [2]Synchrotron SOLEIL, St. Aubin, France — [3]Institute of Physics, University of Kassel

Studying biomolecular building blocks, such as the nucleobase thymine and its precursor, pyridine, in the gas phase allows detailed insights into energetics and dynamics at the molecular level. As in-vivo biomolecular systems exist in the condensed phase, studying complexes of these molecules with water gives greater insight into decay channels that are available in biological systems, while still allowing the application of typical gas phase experimental approaches. One such technique is electron-ion-ion coincidence spectroscopy, which allows for detailed identification of fragmentation pathways that occur at or above the double-ionisation threshold of molecules and complexes. Here, distinguishing different auto-ionisation processes, such as the non-local intermolecular Coulombic decay (ICD) and electron transfer mediated decay (ETMD), as well as the local Auger-Meitner decay is challenging. Identification of these pathways can be helped by the occurrence of intramolecular proton transfer reactions that stabilise complexes with dicationic moeities. Insight into these processes is important to the field of radiation chemistry since the production of low energy electrons can trigger reactions which damage biological material.

MO 32.4 Fri 12:00 P 204

Helium cluster-isolation spectroscopy of quinacridone — •Aleksandr Demianenko, Kaleb Strahringer, Sebastian Hartweg, and Frank Stienkemeier — Institute of Physics, University of Freiburg, Germany

Organic chromophores are essential components of organic solar cells, field-effect transistors, light-emitting diodes, and supramolecular organic semiconductors. Their electronic and vibrational energy levels play a central role in determining collective molecular behaviors, including charge transport, exciton motion, and self-assembly.

In this talk, I will present helium cluster isolation spectroscopy to study the chromophore quinacridone. Although mostly known as an organic dye, quinacridone also shows highly interesting properties in its aggregation. Since it is a prochiral molecule it can be seen as a chiral object when attached to surfaces, where it can either aggregate in homochiral linear chains or more complex heterochiral structures.

The superfluid helium environment can be seen as isotropic thus allowing the aggregation of quinacridone molecules as non-chiral objects. Additionally, the ultracold temperature of the helium nanodroplets restrict population to vibrational ground states and produces well-resolved spectra for both monomers and oligomers in a minimally perturbing ultracold matrix. By combining a wavelength-tunable nanosecond laser, we obtain high-resolution laser-induced fluorescence spectra. These are presented in comparison with spectra on surfaces and in organic solvents.

MO 32.5 Fri 12:15 P 204

IR spectroscopy of metal complexes tailored by electron transfer reduction in an ion trap — •Philipp Weber[1], Maximilian Emil Huber[1], Jennifer Meyer[1], Katja Heinze[2], and Christoph Riehn[1] — [1]Fachbereich Chemie und Forschungszentrum OPTIMAS, Kaiserslautern, DE — [2]Department of Chemistry, Johannes Gutenberg Universtät Mainz, DE

Understanding intrinsic structural properties of photocatalysts based on renewable 3d metal centers is of central importance when exploring their molecular design and reactivity in various environments [1,2]. Infrared multi-photon photodissociation spectroscopy (IRMPD) was conducted with the FELIX free electron laser on a set of differently charged, isolated Mn, Fe and Co complex species, containing the tridendate ligand dgpy (di-guanidyl-pyridine). This ligand accomodates a wide variety of metal species in different oxidation states, however, gas-phase reduction of tricationic $[\mathrm{Mn}^{III}(\mathrm{dgpy})_2]^{3+}$ produces a monocationic complex, which differs significantly in reactive and spectroscopic characteristics from its isoelectronic Fe^{II} and Co^{III} congeners, yielding fragmentation of the ligand backbone and structural distortion, leading to IR shifts in the characteristic N=C region. Comprehensive electronic structure calculations (DFT) give strong evidence that this behavior is not caused by a reduction of the metal center but alludes to a reduction of the pyridine moiety of the (here non-innocent) ligand. [1] M.Huber, J.Meyer J. Am. Soc. Mass Spectrom. 2024, 35, 11, 2642-2649 [2] N.East, K.Heinze Inorg. Chem. 2022, 61, 37, 14616-14625

MO 32.6 Fri 12:30 P 204

Two-Dimensional Infrared Spectroscopy of the SURMOF Cu(Da-DBDC) — •Claudia Gräve[1], Ana Claudia Fingolo[2], Julian Brückel[3], Luis Ignacio Domenianni[1], Jörg Lindner[1], Stefan Bräse[3], Christof Wöll[2], and Peter Vöhringer[1] — [1]Clausius-Institute, University of Bonn, 53115 Bonn — [2]IFG, Karlsruhe Institute for Technology, 76344 Eggenstein-Leopoldshafen — [3]IOC, Karlsruhe Institute for Technology, 76131 Karlsruhe

In recent years, many significant applications for metal-organic frameworks have emerged. [1] 2D-IR spectroscopy can be used to examine important processes for their catalytic application: intramolecular vibrational redistribution (IVR) and vibrational energy transfer (VET).

We investigate the COO stretching modes and the azide asymmetric stretching fundamental of the surface-mounted metal-organic framework (SURMOF) Cu(Da-DBDC). [2] For reference, we also measured its organic linker, Diazido-tolanedicarboxylic acid, in liquid THF.

In the pump-probe spectra of both samples, the diagonal excited state absorption signal of the azide fundamental blue-shifts with increasing delay because of the involvement of low-frequency modes. The kinetic traces of the linker show a fast and a slow component due to IVR and VET to the solvent, respectively. In the SURMOF, the fast component is nearly identical, while the slow one is accelerated. We attribute this to resonant excitation hopping within the solid lattice, causing canonical heating of the pump-probe focal volume.

[1] H. Furukawa *et al., Science* **2013**, *341*, 1230444. [2] J. Song *et al., Angew. Chem. Int. Ed.* **2023**, *62*, e202306155.

MO 32.7 Fri 12:45 P 204

IR Spectroscopy of Larger Pyrrole Cation Clusters ($\mathrm{Py}_n{}^+$): Evolution of Charge Resonance Interaction — •Dashjargal Arildii and Otto Dopfer — Technische Universität Berlin, Berlin, Germany

Aside from π H-bonding, cation/anion-π, and π-π stacking interactions, the charge resonance (CR) is a fundamental and strong force in charged arene dimers. In aromatic dimer cations, the positive charge is shared between the molecules depending on their ionization energy differences. Previously, we demonstrated a new high-resolution experimental approach (utilizing infrared photodissociation spectroscopy (IRPD)) to precisely probe the charge distribution and the CR interaction in aromatic dimer cations for the prototypical case of the pyrrole dimer cation ($\mathrm{Py}_2{}^+$) in the gas phase. Our further approach focuses on exploring the evolution of charge delocalization in larger $\mathrm{Py}_n{}^+$ (n>2) clusters. Hence, herein, we produce the $\mathrm{Py}_n{}^+$ (n=3-7) and their colder Ar-tagged $\mathrm{Py}_n{}^+\mathrm{Ar}$ (n=3-6) clusters in the supersonic plasma expansion and determine the structures by IRPD and computational approaches by analyzing the structure-sensitive NH stretch frequencies of $\mathrm{Py}_n{}^+$. The analysis of IRPD spectra of mass-selected $\mathrm{Py}_n{}^+(\mathrm{Ar})$ with geometric parameters of intermolecular structures reveals that $\mathrm{Py}_n{}^+$ grows through solvating of CR-stabilized $\mathrm{Py}_2{}^+$ by additional Py ligands through the formation of NH...π H-bonds rather than by sharing the positive charge in the $\mathrm{Py}_n{}^+$ units.