

## MO 3: Novel Spectroscopies

Time: Monday 17:00–19:00

Location: HS 1015

MO 3.1 Mon 17:00 HS 1015

**Two-Dimensional IR Spectroscopy of Bifunctional Vibrational Probes** — ●CLAUDIA GRÄVE, STEFAN FLESCH, LUIS IGNACIO DOMENIANNI, JÖRG LINDNER, and PETER VÖHRINGER — Universität Bonn, Wegelerstr. 12, 53115 Bonn, Germany

The nitrile group is a superb vibrational probe for the dynamics of biomolecular systems.<sup>[1]</sup> Unfortunately, it exhibits a relatively small transition dipole moment, which causes sensitivity issues in IR-spectroscopic studies.

Here, we study the vibrational dynamics of small organic nitriles featuring an azide residue, which can later be utilized for protein incorporation. The two nitriles studied here are 4-azidobenzonitrile ( $N_3-C_6H_4-CN$ ) and 3-(4-azidophenyl)propionitrile ( $N_3-C_6H_4-CC-CN$ ).

We report on the linear Fourier-transform infrared spectra, as well as on the femtosecond pump-probe and 2DIR spectroscopy. The linear spectra in the azide and nitrile stretching region are highly complex due to Fermi resonances involving the  $N_3$ -fundamental. Furthermore, the 2DIR spectra reveal the detailed vibrational energy flows between the azide and the nitrile groups separated by the phenyl ring. Finally, coherent oscillations resulting from impulsive excitation of the Fermi multiplets were observed by means of pump-probe measurements. Our results suggest that propionitrile is a superior vibrational probe as compared to the bare CN.

**Literature:**

[1] H. Kim and M. Cho, *Chem. Rev.* **2013**, *113*, 5817-5847.

MO 3.2 Mon 17:15 HS 1015

**Nonlinear 2D spectroscopy of single molecules** — ●SIMON DURST, SANCHAYEETA JANA, and MARKUS LIPPITZ — Universität Bayreuth

Fluorescence-detected 2D electronic spectroscopy (F-2DES) allows the measurement of ultrafast electron dynamics in complex systems while disentangling this spectral information from energetically similar phenomena, such as molecular vibration. Measuring the 2D spectra of single molecules instead of molecular ensembles should provide an even clearer picture of the underlying physics and give insight into the statistical distribution of optical properties and the environment of the molecules.

To measure these spectra we use four collinear, phase-modulated femtosecond pulses, generated by a four-arm Mach-Zehnder Interferometer to excite single molecules with a confocal microscope. Their emitted fluorescence is modulated at the mixing frequencies of the individual pulses, so we can use phase-sensitive lock-in detection to detect the nonlinear signal and separate it from linear effects. This measurement technique promises high spectral, temporal and spatial resolution.

In this talk, we present our setup and method to measure the 2D spectra of single dibenzoterrylene (DBT) molecules, which are immobilized in a PMMA matrix. We show results from these measurements and compare them with the ensemble data.

MO 3.3 Mon 17:30 HS 1015

**Coherent multidimensional spectroscopy of PTCDA monomers on argon clusters** — ●YILIN LI, ARNE MORLOK, ULRICH BANGERT, FRIEDEMANN LANDMESSER, FRANK STIENKEMEIER, and LUKAS BRUDER — Institute of Physics, University of Freiburg, Germany

The interaction and dynamics between single molecules and the environment is of great interest yet challenging to study. In our approach, we dope rare gas clusters with single molecules in the gas phase [1]. This provides us an ensemble of doped nanoparticles, each particle well isolated from other environmental influences. We study these systems with coherent multidimensional electronic spectroscopy, a versatile technique providing further insights into intra- and intermolecular couplings on ultrashort time scales [2,3]. Recently we started analysing 2D beating maps to obtain information about the electronic and vibrational coherences, which are otherwise covered by line broadening mechanisms, together with pump-probe measurements to study the decoherence and the population decay of the system. First results of PTCDA monomers on argon clusters will be presented.

[1] M. Bohlen et al., *J. Chem. Phys.* **156**, 034305 (2022)

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

[3] U. Bangert, F. Stienkemeier, L. Bruder, *Nat. Commun.* **13**, 3350 (2022)

MO 3.4 Mon 17:45 HS 1015

**Next generation fs transient spectroscopy based on 1030 nm pump** — ●FERDINAND BERGMIEIER and EBERHARD RIEDLE — Lehrstuhl f. BioMolekulare Optik, Fakultät f. Physik, LMU München

The measurement of transient electronic spectra, vital for unraveling complex photophysical, chemical, and biological processes, is achieved through fs excitation and broadband UV to NIR detection. We present an innovative transient absorption spectrometer based on a newly engineered kHz noncollinear optical parametric amplifier (NOPA) pumped by a modern Yb-based 250 fs industrial-grade pump laser. Coupled with a fully redesigned CaF<sub>2</sub>-based ultrabroad probe pulse, this spectrometer retains the positive aspects of the earlier Ti:Sa-based system. This ensures compactness with minimal optics and adjustments, boasting a warm-up time of under ten minutes.

The probe continuum spans 320 to 950 nm with 1030 nm pumping and to below 280 nm with 515 nm pumping. The pump is tunable from 220 to 950 nm with a sub-20 fs pulse length and no spectral gaps. The instrumental response function is below 40 fs. Single-shot spectral referencing achieves a sensitivity of approximately 20 uOD for a half-hour measurement, near the shot noise limit. The continuum splitting onto the signal and reference arm is achromatic and dispersion-free. A perfectly round probe focus is achieved with a Schief-Spiegler.

With the extreme precision of the setup, we address surface-resolved coherent artifacts that are crucial for investigating processes on the 100 fs time scale. Detailed reference and precise chirp measurements of the probe continuum enable sub-10 fs time-zero correction.

MO 3.5 Mon 18:00 HS 1015

**Effects of Strong Coupling on the Chemiluminescent Reaction of Dioxetane** — ●MARKUS KOWALEWSKI and MAHESH GUDEM — Stockholm University, Stockholm, Sweden

Chemiluminescence, seen in phenomena like firefly light emission, involves thermally activated chemical processes. Dioxetane, the smallest cyclic peroxide, exhibits chemiluminescence with a lower quantum yield than firefly dioxetane. Utilizing strong light-matter coupling as an alternative strategy, we investigate its impact on dioxetane's chemiluminescence reaction within an optical cavity. The extended Jaynes-Cummings model is used to incorporate the cavity couplings for electronic and vibrational degrees of freedom. Results reveal that cavity interactions can either accelerate or suppress the formation of excited-state products in the dioxetane decomposition, depending on molecular orientation relative to cavity polarization.

MO 3.6 Mon 18:15 HS 1015

**Exploring the scaling factors for infrared modes of polycyclic aromatic nitrogen heterocycles** — ●DOMENIK SCHLEIER<sup>1,2</sup>, JERRY KAMER<sup>1</sup>, JONATHAN MARTENS<sup>3</sup>, GIEL BERDEN<sup>3</sup>, JOS OOMENS<sup>3,4</sup>, and JORDY BOUWMAN<sup>5,6,7</sup> — <sup>1</sup>Leiden Observatory, Leiden, The Netherlands — <sup>2</sup>Uni Paderborn, Paderborn, Germany — <sup>3</sup>FELIX Laboratory, Nijmegen, The Netherlands — <sup>4</sup>University of Amsterdam, Amsterdam, The Netherlands — <sup>5</sup>Laboratory for Atmospheric and Space Physics, Boulder, USA — <sup>6</sup>Department of Chemistry, Boulder, USA — <sup>7</sup>Institute for Modeling Plasma, Atmospheres and Cosmic Dust, Boulder, USA

Infrared (IR) emission bands by interstellar Polycyclic Aromatic Hydrocarbons (PAHs) offer detailed insights into the chemistry and physics of the interstellar medium. It has been suggested that hetero atom substituted species such as Polycyclic Aromatic Nitrogen Heterocycles (PANHs) also contribute to the aromatic IR emission bands. The analysis of the emission bands, and thus the interpretation of the molecular characteristics of the carriers, heavily relies on the use of density functional theory (DFT) calculated IR spectra. However, there are significant challenges in accurately predicting the experimental IR band positions, particularly for PANH emission vibrational modes around 6  $\mu\text{m}$ . In this work, we present gas-phase mid-infrared (mid-IR) spectra of cationic 3-azafluoranthene and its protonated cation to investigate their experimental IR band positions in relation to DFT calculated bands.

MO 3.7 Mon 18:30 HS 1015

**VUV Photoionization spectroscopy of cyano-substituted PAHs** — ●MADHUSREE ROY CHOWDHURY<sup>1,2</sup>, GUSTAVO GARCIA<sup>2</sup>, HELGI HRODMARSSON<sup>3</sup>, JEAN-CHRISTOPHE LOISON<sup>4</sup>, and LAURENT NAHON<sup>2</sup> — <sup>1</sup>Institute of Physics and CINSaT, University of Kassel, Kassel, 34132, Germany — <sup>2</sup>Synchrotron SOLEIL, L'Orme des Merisiers, Départementale 128, 91190 Saint Aubin, France — <sup>3</sup>LISA Laboratory, Universités Paris Est-Paris Diderot-Paris 7, UMR CNRS 7583, Créteil, France — <sup>4</sup>Université Bordeaux, CNRS, Bordeaux INP, ISM, UMR 5255, Talence F-33400, France

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the interstellar medium (ISM), accounting for about a quarter of the total carbon mass of the ISM. The aromatic infrared emission bands (AIBs) are the signatures of the existence of PAHs in the ISM. Although their presence is well acknowledged, the individual detection of PAHs is notoriously difficult. Substituted PAHs being less symmetric are promising candidates, leading to the detection of the two isomers of cyanonaphthalenes (McGuire et.al. Science 2021) in TMC-1. Upon absorbing the VUV radiation, PAHs relax via photoionization and photodissociation processes in competition with radiative cooling. The VUV photoionization and fragmentation of 1- and 2-cyanonaphthalenes is studied using a double imaging photoelectron photoion coincidence spectrometer (i<sup>2</sup>PEPICO). The KE distribution of the photoelectrons is useful to model the photoelectric heating for radiation fields while the state-selected fragmentation of the cations shed light on the photostability

of the cyano substituted PAHs.

MO 3.8 Mon 18:45 HS 1015

**Photoelectron Photoion Multicoincidence Study of Micro-Solvated Thymine Molecules** — ●BRENDAN WOUTERLOOD<sup>1</sup>, STEPHAN SCHMITZ<sup>1</sup>, MADHUSREE ROY-CHOWDHURY<sup>2</sup>, GUSTAVO GARCIA-MACIAS<sup>2</sup>, LAURENT NAHON<sup>2</sup>, FRANK STIENKEMEIER<sup>1</sup>, and SEBASTIAN HARTWEG<sup>1</sup> — <sup>1</sup>Institute of Physics, University of Freiburg — <sup>2</sup>Synchrotron SOLEIL, St. Aubin, France

Studying biomolecules, such as amino acids and nucleobases, in the gas phase allows unparalleled detail and fundamental insights into energetics and dynamics at the molecular level. However, in-vivo biomolecular systems exist mostly in the condensed phase, which can affect ionisation energies as well as fragmentation and relaxation pathways. Micro-solvation can be exploited to bridge the gap between the gas and the condensed phases and allows for the application of double imaging photoelectron photoion photoion coincidence (i<sup>2</sup>PEPIPICO) spectroscopy. The ion-ion coincidence detection enables identification of signals arising from non-local auto-ionisation processes of clusters, such as from intermolecular Coulombic decay. These processes are important to the field of radiation chemistry since the production of low energy electrons can trigger reactions which damage biological material. Here, preliminary results of a i<sup>2</sup>PEPIPICO study of small water clusters (H<sub>2</sub>O)<sub>n</sub> (n=1-10) and water-thymine complexes, will be presented.