MO 7: Poster: Spectroscopy

Time: Tuesday 17:00–19:00 Location: Tent C

MO 7.1 Tue 17:00 Tent C

In Situ Hyperpolarized Benchtop NMR for Biomolecular Analysis at Natural Isotopic Abundance — •Jingyan Xu[1,2,3], Raphael Kircher[1,2,3], and Danila Barskiy[1,2,3] — [1]Johannes Gutenberg University, Mainz, Germany — [2]Helmholtz-Institut, Mainz, Germany — [3]Helmholtzzentrum für Schwerionenforschung, Darmstadt, Germany

Nuclear Magnetic Resonance (NMR) is a key noninvasive tool in fields ranging from research and industry to medicine. Benchtop NMR spectrometers have recently emerged as practical alternatives to traditional high-field NMR systems, especially for on-the-spot analysis and process monitoring. A notable challenge with these systems is the detection of low-abundance heteronuclei like ^{13}C or ^{15}N, hindered by low spin polarization resulting from weak interactions with the magnetic field. Our study introduces a novel hyperpolarization technique to overcome this limitation by integrating Signal Amplification by Reversible Exchange (SABRE) with a Spin-Lock Induced Crossing (SLIC) pulse sequence. Applied to various molecules, this method achieves up to 12% polarization for ^{15}N and 0.4% for ^{13}C, without needing sample transfer. Furthermore, our method allows for continuous hyperpolarization, paving the way for advanced applications in rapid 2D spectroscopy and relaxometry. This development offers a cost-effective, efficient means of detecting diluted chemicals using benchtop NMR, signaling a significant leap forward in diverse industrial and research applications.

MO 7.2 Tue 17:00 Tent C

An experimental setup to study the influence of hydration on small charged molecular systems by rotationally resolved vibrational spectroscopy — •Eric Endres[1], Christian Sprenger[1], Franziska Dahlmann[2], and Roland Wester[1] — [1]Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstraße 25/3, A-6020 Innsbruck, Austria — [2]KTH Royal Institute of Technology, Stockholm, Sweden

Hydration with individual water molecules significantly influences the structure and, consequently, the function of biomolecules. This contribution introduces an experimental setup designed to examine the influence of hydration on the structure of small biomolecules using rotationally resolved pre-dissociation spectroscopy.

Ions are generated using a custom-built Nano-ESI system housed within a controlled environment, regulating e.g. humidity and temperature, enabling the control of the hydration level. A double skimmer setup gently transfer the ions into vacuum, avoiding breaking apart the loosely bound water molecules. Through an octupole guide and a quadrupole guide the water clusters are let into a cryogenic 16-pole wire ion trap. Trap temperatures below 3 K can be achieved, enabled binding of up to four helium atoms on protonated glycine ions. The confined ions are irradiated by a narrow-band laser system with an output linewidth in the IR below 0.1 cm^{-1}

The low temperatures in combination with the small linewidth of the laser system potentially lead to rotationally resolved vibrational spectroscopy. Here the current status will be reported.

MO 7.3 Tue 17:00 Tent C

Towards photodetachment spectroscopic studies of deprotonated naphthalene. — •Michael Hauck, Sruthi Purushu Melath, Christine Lochmann, Robert Wild, Katrin Erath-Dulitz, and Roland Wester — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstraße 25/3, 6020 Innsbruck, Austria

Polycyclic aromatic hydrocarbon (PAH) molecules are important in the study of interstellar chemistry. The discovery of benzonitrile in the molecular cloud TMC-1 hints at the existence of larger aromatic molecules which might explain still unassigned infrared bands [1,2]. We are interested in the spectroscopic study of deprotonated naphthalene ($C_{10}H_7^-$). Photoelectron spectroscopic studies of this molecule were performed, which found the electron affinities of two possible isomers [3].

Here we present a 2D tomography photodetachment scan of deprotonated naphthalene in our cryogenic 16 pole trap, which we measure in order to extract the value of the absolute photodetachment cross section. We further plan to examine the behaviour of the cross section near threshold and measure the electron affinity of the molecule.

[1] J. Gao, G. Berden and J. Oomens, Ap. J. 787, 170 (2014)
[2] B. A. McGuire et al., Science 359, 202 (2018)
[3] M. L. Weichman, J. B. Kim and D. M. Neumark, J. Phys. Chem. A 119, 6140 (2015)

MO 7.4 Tue 17:00 Tent C

Combination of action-based interferometric measurements with depletion spectroscopy — •Leonie Werner, Ulrich Bangert, Yilin Li, Arne Morlok, Lukas Bruder, and Frank Stienkemeier — University of Freiburg, Institute of Physics, Hermann-Herder-Straße 3, 79104 Freiburg im Breisgau, Germany

Isolation spectroscopy in ultracold helium nanodroplets enables the investigation of single and multiple embedded organic molecules in a cold, weakly perturbing environment [1]. In our lab, we combine this method with interferometric techniques, such as wave packet interferometry (WPI) and two-dimensional electronic spectroscopy (2DES) [2, 3]. This allows us to achieve high temporal and energy resolution at the same time. Standard detection techniques are laser-induced fluorescence or photoionization. Yet, these methods have problems to capture non-radiative photochemical processes or pose a challenge in overcoming the high ionization potentials of organic molecules. To solve these issues, we are exploring beam depletion detection methods [1]. First tests will be presented.

[1] J. P. Toennies and A. F. Vilesov, Angew. Chem. Int. Ed. 43, 2622 (2004).
[2] L. Bruder et al., Nat. Commun. 9, 4823 (2018).
[3] L. Bruder et al., J. Phys. B 52, 183501 (2019).

MO 7.5 Tue 17:00 Tent C

Investigating the Photodissociation Dynamics of CH_2Br with VMI — •Lilith Wohlfart, Christian Matthaei, and Ingo Fischer — Julius-Maximilians-Universität, 97074 Würzburg, Germany

Bromomethyl belongs to the class of organic halogen radicals. Therefore, it can potentially influence the atmosphere by reacting with the ozone layer and causing its depletion similar to HCFCs. The photoionization of bromomethyl was already investigated by several groups, including Steinbauer and coworkers. They determined the ionization energy and structure with VUV synchrotron radiation and investigated the dissociative photoionization. To obtain further insights into the dissociation of bromomethyl, we analyzed the fragments of the radical using velocity map imaging (VMI).

CH_2Br-NO_2 was used as a precursor for the halogenated methyl radical, because the weaker C-NO_2 bond can be cleaved through pyrolysis. Subsequently, laser light in the UV region was deployed to dissociate the formed CH_2Br radical. The major dissociation pathway gave the methylene and bromine fragments which were detected with SPI and REMPI respectively. With velocity map ion imaging, the translational kinetic energy distribution of the photofragments was determined. The recorded images of the bromine and methylene photofragments showed an anisotropic distribution, implying a direct dissociation.

MO 7.6 Tue 17:00 Tent C

Photodissociation dynamics of the $CHCl_2$ radical — •Jonas Fackelmayer and Ingo Fischer — Julius-Maximilians-Universität Würzburg, 97074 Würzburg, Germany

Monitoring the atmospheric abundances of the ozone-depleting CFCs has revealed a global increase in emission of these banned substances.[1] Meanwhile the dimensions of the ozone-hole have been reported to be at a all time high in 2023.[2] This makes the photodissociation of these compounds of great importance since it often results in the release of highly reactive halogen radicals. While the dissociation dynamics of molecular halocarbons have been studied in detail in the past, less is known about their open shell counterparts.

The photofragmentation of the open shell $CHCl_2$, generated by pyrolysis from the bromide and iodide precursors $CHCl_2Br$/$CHCl_2I$, was investigated in a free jet utilising time-of-flight mass-spectrometry and velocity map imaging. Photodissociation was achieved by a pulsed dye laser in the range of 230 - 250 nm mainly producing CHCl and Cl fragments, while ionisation was provided by either a second dye laser (REMPI) or a frequency multiplied solid state laser at 118 nm (SPI). Insights into the involved dissociation mechanisms are discussed.

[1] L. M. Western al., Nat. Geosci. **2023**, *16*, 309*313.

[2] European Space Agency, *Ozone hole goes large again*, **2023**.

MO 7.7 Tue 17:00 Tent C

Time-resolved photoelectron and photoion spectroscopy of phenanthridine - an experimental and computational study — •Katharina Theil[1], Jonas Fackelmayer[1], Lionel Poisson[2], Lou Barreau[2], and Ingo Fischer[1] — [1]Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg — [2]Institut des Sciences Moléculaires dOrsay (ISMO) UMR 8214, Rue André Rivière, Bâtiment 520, Université Paris-Saclay, F-91405 Orsay Cedex, France

Understanding the fundamental photophysical processes in molecules is essential for deciphering their photochemistry, given that molecules rarely undergo reactions directly from their initially excited electronic states. Recently, the focus has shifted towards investigating polycyclic aromatic nitrogen heterocycles (PANHs) within the extensive studies of polycyclic aromatic hydrocarbons (PAHs) as potential carriers of 'unidentified infrared bands' and diffuse interstellar bands.[1] Here we investigate the ultrafast excited-state dynamics of phenanthridine, a prototypical PANH, employing femtosecond time-resolved pump-probe spectroscopy conducted in the gas phase. The real-time monitoring of these dynamics is facilitated through time-resolved photoionization and photoelectron imaging. The experimental results are accompanied by theoretical calculations.

[1] D. McNaughton et al., Phys. Chem. Chem. Phys., **2007**, *9*, 591-595.

MO 7.8 Tue 17:00 Tent C

Ultrafast UV-Vis spectroscopy on a series of novel Fe(III) photosensitizers with linked organic chromophores — •Miguel Andre Argüello Cordero[1], Lennart Schmitz[2], Matthias Bauer[2], and Stefan Lochbrunner[1] — [1]University of Rostock, Germany — [2]University of Paderborn, Germany

In recent years, the exploration of photocatalytic methodologies for solar fuel production has garnered attention due to their promise as a sustainable energy source. Central to these approaches are molecular photosensitizers (PS) with a metal component for efficient light absorption. However, the reliance on precious metals in conventional PS has prompted a fervent exploration into alternatives employing cost-efficient metals, like iron. Fe(III)-based PS exhibit a distinctive bichromophoric nature, stemming from the existence of ligand-to-metal charge transfer transitions (LMCT). This unique attribute facilitates the capture of the entire visible spectrum, resulting in the population of enduring LMCT states. The strategic modification of the ligand structure further allows for the modulation of energy levels and excited state lifetimes. In this study, we introduce a series of novel Fe(III) PS featuring organic chromophores attached to their ligand backbones. By extending the chromophores, we uncover intriguing ultrafast electronic dynamics following optical excitation. Their investigation is carried out through fs-UV-Vis transient absorption spectroscopy. This work presents our findings on pump-probe spectroscopy applied to the Fe(III) PS, providing a comprehensive discussion on the observed results in the context of electronic relaxation pathways.

MO 7.9 Tue 17:00 Tent C

Time-Resolved Spectroscopic Studies on the Net Heterolysis of Homopolar Selenium-Carbon Bonds — •Daniel Jan Grenda, Anna Franziska Tiefel, Carina Allacher, Elias Harrer, Roger Jan Kutta, Julia Rehbein, Alexander Breder, and Patrick Nuernberger — Universität Regensburg, 93040 Regensburg

When thinking about chemical bonds, one considers polarity as the major factor determining if a bond cleavage occurs homolytically or heterolytically, as bonds with a negligible dipole moment exclusively undergo homolysis, whereas heterolysis requires a sufficiently high dipole moment or some kind of external bond activation [1]. We demonstrate that by combining photochemistry [2] with the radical chemistry of organoselenium compounds [3] and the properties of the solvent hexafluoroisopropanol [3, 4], net heterolysis of the homopolar selenium-carbon bond can be achieved and utilized in a subsequent S_N1-type substitution. The mechanism of this reaction is disclosed using transient absorption spectroscopy with streak-camera detection [5] and other advanced spectroscopic techniques, as well as theoretical and synthetic investigations.

[1] H. Brueckner, *Reaktionsmechanismen* Springer Spektrum (2008).

[2] B. Koenig *et al.*, *Eur. J. Org. Chem.*, **15**, 1979-1981 (2017).

[3] I. Colomer *et al.*, *Nat. Rev. Chem.*, **1**, 0088 (2017).

[4] S. Park *et al.*, *Angew. Chem. Int. Ed.*, **61**, e202208611 (2022).

[5] R. J. Kutta *et al.*, *Appl. Phys. B*, **111**, 203-216 (2013).

MO 7.10 Tue 17:00 Tent C

Ultrafast Time-Resolved NIR-Spectroscopy of Metal Complexes — •Nina Brauer[1], Miguel Andre Argüello Cordero[1], Samira Dabelstein[1], Jakob Steube[2], Lennart Schmitz[2], Matthias Bauer[2], and Stefan Lochbrunner[1] — [1]University of Rostock, Germany — [2]University of Paderborn, Germany

Light induced charge transfer in metal complexes is a crucial part in many photocatalytic processes and holds great potential for future applications in solar energy harvesting. However, today most of the utilized organo-metallic complexes contain a rare metal center ion, such as ruthenium or iridium. A promising, cost-efficient replacement are iron based complexes, which are the subject of current research to optimize their photoactive properties.

One of the most prominent measurement techniques is transient absorption spectroscopy, during which the sample is photoexcited and probed with a broadband femtosecond laser pulse. Up until now, time-resolved measurements of iron complexes have been limited to the spectral region of visible light. In this work, the supercontinuum from an Yttrium Aluminum Garnet (YAG) crystal is used to probe the transient absorption of Fe(III)-complexes in the near-infrared (NIR). With a probing spectrum ranging from 820 nm up to 1250 nm, the dynamics of the excited state absorption of these complexes are investigated.

MO 7.11 Tue 17:00 Tent C

Simplified photoelectron photoion covariance spectrometer for challenging UV pump-probe experiments — •Nicolas Ladda, Fabian Westmeier, Tonio Rosen, Sudheendran Vasudevan, Hangyeol Lee, Simon Ranecky, Sagnik Das, Jayanta Ghosh, Till Stehling, Hendrike Braun, Jochen Mikosch, Thomas Baumert, and Arne Senftleben — Institut für Physik, Universität Kassel, Heinrich-Plett-Strasse 40, 34132 Kassel, Germany

Velocity Map Imaging spectroscopy is a powerful method for investigating photoionization processes. The technique can be combined with time-of-flight spectrometry to gain further insight into the underlying processes. The resulting device can be used for photoelectron photoion covariance (PEPICO) measurements. Here we want to present our simple, but geometrically optimized PEPICO spectrometer, which can measure photoelectron momenta and photoion masses with high resolution while minimizing the background signal originating from scattered UV photons. The spectrometer will be used to investigate the dynamics of chiral molecules by studying time-resolved photoelectron circular dichroism [1]. In addition to special viewports made of single-crystal calcium fluoride (CaF2) with a broadband AR coating (190 - 900 nm) to minimize reflections and scattering, baffles made of dendritic copper oxide (δ-CuO) with high UV absorption are used to capture the residual scattered photons [2].

[1] Lux, C. et al. Angew. Chem. Int. Ed. 51, 5001*5005 (2012)

[2] Clarkin, O. J., Dissertation, Queen's University, (2012)

MO 7.12 Tue 17:00 Tent C

Resonant double core hole spectroscopy of ultrafast decay dynamics in Fe complexes — •Julius Schwarz[1], Matz Nissen[1], Alberto De Fanis[2], Aljoscha Rörig[2], Karolin Baev[5], Florian Trinter[4], Tim Laarmann[1,6], Nils Huse[1], Philippe Wernet[3], Michael Meyer[2], Thomas Baumann[2], Simon Dold[2], Tommaso Mazza[2], Yevheniy Ovcharenko[2], Sergey Usenko[2], Markus Ilchen[1,2], Andreas Przystawik[1,6], Hampus Wikmark[3], and Michael Martins[1] — [1]Universität Hamburg, Germany — [2]European XFEL, Hamburg, Germany — [3]Uppsala University, Sweden — [4]Fritz-Haber-Institut, Berlin, Germany — [5]DESY, Hamburg, Germany — [6]The Hamburg Centre for Ultrafast Imaging, Hamburg, Germany

Resonant double core hole (DCH) spectroscopy allows for the observation of ultrafast dynamic processes in small 3d-metal compounds in the gas phase with enhanced sensitivity. Using the intense X-Ray pulses of the European XFEL, electron and ion spectroscopy was used to reveal the signature of iron $2p^2$ resonant DCH excitation in iron pentacarbonyl and ferrocene. Comparing the experimental results to theoretical calculations reconstructs single core hole (SCH) and DCH photon-matter interactions in the two targets. The DCH Auger-Meitner electron signals offer insight to the electron dynamics during the core hole lifetime and their dependence on the chemical environment. The product ions show evidence for DCH processes in multiply charged iron cations.

MO 7.13 Tue 17:00 Tent C

Accurate molecular ab initio calculations in support of photodissociation experiments — •Giorgio Visentin[1,2], Bo Ying[2,3], Stephan Fritzsche[1,2,3], and Gerhard Paulus[2,3] — [1]Helmholtz-Institut Jena, Fröbelstieg 3, 07743 Jena, Germany — [2]GSI Helmoltzzentrum für Schwerionenforschung, 64291 Darmstadt, Germany — [3]Friedrich Schiller University, Max-Wien-Platz 1, 07743, Jena, Germany

Novel experimental techniques based on pump-probe femtosecend laser pulses have paved the way to the investigation of ultrafast molecular processes, such as photodissociation. In this process, the molecule is first ionized; then, the collision with the ejected electron induces two competing mechanisms, i.e., dissociation by excitation to a dissociative electronic excited state or dissociation by ionization to a dissociative charge state. Evaluation of these mechanisms is a crucial step in the experimental understanding of the molecular photodissociation dynamics. In this framework, accurate ab initio calculations of the potential energy curves (PECs) of the molecular ions provide a valuable tool in support of the experiment. In this abstract, an accurate relativistic ab initio molecular approach is proposed to model the PECs or $Ar_2{}^+$ in the electronic ground and lowest-lying excited states. This approach yields results in reasonable agreement with the available literature data and supports the ion-beam experiments investigating the dissociation pathways of $Ar_2{}^+$ molecular ion. Furthermore, the success of the aforementioned theoretical approach prospects the investigation on the photodissociation of heavier diatomics.

MO 7.14 Tue 17:00 Tent C

Decoherence in molecular systems with structured spectral densities studied with Gaussian wavepacket propagation — •Sreeja Loho Choudhury[1], Rainer Hegger[1], Rocco Martinazzo[2,3], and Irene Burghardt[1] — [1]Institute of Physical and Theoretical Chemistry, Goethe University Frankfurt, Germany — [2]Department of Chemistry, Università degli Studi di Milano, Italy — [3]Instituto di Scienze e Tecnologie Molecolari, CNR, Milano, Italy

We investigate the time scale of decoherence in complex molecular systems following laser excitation [1]. Vibronic coupling Hamiltonians in conjunction with realistic, structured spectral densities are employed in order to track decoherence on a typical time scale of femtoseconds. Tensor network methods, notably the Gaussian-based Multi-Configuration Time-Dependent Hartree approach [2], are used to obtain accurate decoherence estimates obtained from the time-evolving purity. We focus on a donor-acceptor system that has recently been studied [1], comprising tens of vibrational degrees of freedom. This system is subject to a coherent excitation energy transfer (EET) process and exhibits irreversible decay features despite the finite dimensionality. Numerical decoherence decay is compared with analytical estimates for pure dephasing in spin-boson systems [3-4]. [1] M. Asido et al., Phys. Chem. Chem. Phys. **24**, 1795 (2022). [2] P. Eisenbrandt, M. Ruckenbauer and I. Burghardt, J. Chem. Phys. **149**, 174102 (2018). [3] O. Prezhdo and P. Rossky, Phys. Rev. Lett. **81**, 5294 (1998). [4] M. A. Schlosshauer, Decoherence and the Quantum-To-Classical Transition, Springer (2007).

MO 7.15 Tue 17:00 Tent C

Photoelectron spectroscopy study of anthracene anions in gas phase — •Kevin Schwarz, Aghigh Jalehdoost, and Bernd v. Issendorff — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

Organic semiconductors like anthracene ($C_{14}H_{10}$) show interesting properties and keep being of interest across science and technology. They are used, for instance, in organic solar cells. To get a better understanding of those molecules they are investigated in the gas phase by anion photoelectron spectroscopy (PES) to gain knowledge on the different involved electronic and vibrational modes of the molecules, especially on electronic relaxation processes giving information about the dynamics within the molecules. Furthermore, temperature-resolved studies are of high interest due to changes in the vibrational modes accessible to the clusters, so to address those measurements and also to increase the resolution of the spectra in general a radio frequency ion trap will be added into the setup.

MO 7.16 Tue 17:00 Tent C

Phase-sensitive detection of photons — Lucas Ludwig, •Sanchayeeta Jana, Simon Durst, and Markus Lippitz — Chair for experimental physics III, Universität Bayreuth, Bayreuth, Germany

In quantum optics, the measured signal is often photon detection events. Modulation and phase-sensitive detection of photons is essential for many applications. Even though phase-sensitive or lock-in detection is a compelling technique invented over 90 years ago, all commercial lock-in detectors use an analog voltage measured by a detector (e.g., a photodiode) as the input signal. Thus, one cannot use a commercial lock-in detector with photon counters for phase-sensitive detection of photons. For this reason, we have developed a method for lock-in detection of photons, which we use for measuring 2D spectra of single molecules.

We employ AOMs to phase-modulate four optical pulses for the fluorescence-detected two-dimensional electronic spectroscopy (F-2DES) experiment. A reference diode detects the interference signal, and the output goes to an FPGA, where three phase lock loops (PLL) lock the phase difference between the pulses and send the trigger pulse to a time tagger. A single photon counting detector detects the fluorescence signal from the molecules after excitation with the four phase-modulated pulses. These photons are also registered by the time tagger, thus enabling phase-sensitive detection of photons.

This work will discuss the construction of PLLs in FPGA and their characteristics.

MO 7.17 Tue 17:00 Tent C

Cogwheel phase cycling in action-based two-dimensional spectroscopy — •Stefan Müller, Ajay Jayachandran, and Tobias Brixner — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Coherent two-dimensional (2D) spectroscopies, which detect an action-based signal instead of a coherent signal, have become increasingly popular in recent years. These signals include photoions, internal or external photocurrents, and fluorescence. To extract the coherent information from the incoherent signal, a procedure such as phase cycling can be employed, which is usually carried out in a “nested” fashion, i.e., each pulse phase is incremented sequentially. Here we adapt a procedure from nuclear magnetic resonance spectroscopy, “cogwheel phase cycling,” in which all pulse phases are varied simultaneously in increments given by so-called winding numbers [1]. We show how to perform a numerical search for these winding numbers. Using a pulse-shaper-assisted setup for fluorescence-detected 2D spectroscopy, we demonstrate that fourth-order and higher-order signals can be acquired with fewer cogwheel phase-cycling steps compared to nested phase cycling while maintaining the same signal selectivity [2]. We predict considerable time savings for various pulse-shaper-based multidimensional spectroscopies.

[1] M. H. Levitt et al., J. Magn. Reson. **155**, 300–306 (2002).
[2] A. Jayachandran et al., J. Phys. Chem. Lett. **13**, 11710 (2022).

MO 7.18 Tue 17:00 Tent C

Cross-peak analysis of multiquantum signals with polarization-controlled higher-order transient absorption spectroscopy — •Katja Mayershofer[1], Simon Büttner[1], Julian Lüttig[2], Peter A. Rose[3], Jacob J. Krich[3,4], and Tobias Brixner[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Department of Physics, University of Michigan, Ann Arbor, MI, USA — [3]Department of Physics, University of Ottawa, Ottawa, Ontario, Canada — [4]Nexus for Quantum Technologies, University of Ottawa, Ottawa, Ontario, Canada

A well-established application of two-dimensional (2D) spectroscopy is the characterization of energy transfer processes via analyzing of 2D cross-peaks. In transient absorption (TA) measurements, by contrast, signals from 2D off-diagonal and on-diagonal contributions overlap on the detection axis. In a recent paper, Zanni's group [1] presented a new polarization scheme that suppresses diagonal peaks and makes it possible to investigate cross-peak features with TA spectroscopy. We adapted and applied this polarization scheme to the new method of higher-order TA spectroscopy [2] that separates signals of different orders and thus isolates signals stemming from exciton–exciton interactions (EEI). Through the combination of higher-order TA spectroscopy and polarization control we aim to analyze cross-peak features in fifth-order signals originating from EEI in a squaraine heterodimer.

[1] K. M. Farrell et al., PNAS **2022**, *119*, e2117398118.
[2] P. Malý et al., Nature **2023**, *616*, 280.