

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 BRIKNER¹ — 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 BRIKNER¹ — 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 BRIKNER¹ — 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 BRIKNER — 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 excitonic 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).