

MO 22: Ultrafast Dynamics III

Time: Thursday 11:00–13:00

Location: HS XVI

MO 22.1 Thu 11:00 HS XVI

Ultrafast Relaxation Dynamics of the Q-Bands in Chlorophyll a in Ethanol — •LENA BAÜML, FERDINAND POINTNER, SEBASTIAN REITER, and REGINA DE VIVIE-RIEDLE — Department of Chemistry, LMU Munich, Germany

The natural pigment chlorophyll adopts different functions during the conversion of sunlight to chemical energy. Depending on its environment, its role in photosynthetic light-harvesting varies significantly.

In this work we investigate the excited states dynamics of chlorophyll *a* in ethanol. In a previously published study^[1], conducted in the gas phase, we focused on the relaxation process after excitation into the Q-band. There, we found the Q_x and Q_y band to be strongly coupled via internal vibrations. It is known, that solvents significantly alter the spectral shape of e.g. absorption or fluorescence spectra and influence the population decay times in the ultrafast relaxation process. Therefore, now the influence of solvent environment, specifically ethanol, on the coupling situation and the relaxation dynamics is under investigation. We present a variation of a QD/MD scheme developed in our group^[2] and discuss the observed changes compared with our results for chlorophyll *a* in the gas phase.

- [1] L. Bäuml *et al.*, *Phys. Chem. Chem. Phys.* **24**, 27212 (2022).
[2] S. Reiter *et al.*, *J. Am. Chem. Soc.* **140**, 8714 (2018).

MO 22.2 Thu 11:15 HS XVI

Linear and Two-Dimensional IR Spectroscopy of an Isotopically Labeled Multifunctional Vibrational Probe — •CLAUDIA GRÄVE, JÖRG LINDNER, STEFAN FLESCHE, LUIS IGNACIO DOMENIANNI, and PETER VÖHRINGER — Clausius-Institute, University of Bonn, Wegelerstr. 12, 53115 Bonn, Germany

Vibrational spectroscopy of biomacromolecules often relies on the introduction of infrared probes, whose vibrations are highly sensitive to the local environment. Here, we report on the prospective IR probe, 3-(4-azidophenyl)propionitrile, which contains several IR-active functional groups.

Its linear FTIR spectrum is highly perturbed in the spectral region of the asymmetric azide stretching fundamental due to the presence of Fermi resonances. We managed to assign the fundamental transition via isotope labeling of the azide group. In combination with DFT calculations, this allowed us to construct a two-tiered Fermi resonance Hamiltonian to identify the involved combination tones.

Additionally, we performed ultrafast vibrational spectroscopy on the isotopically labeled IR probe. 2D-IR spectra exhibit a delayed appearance of cross-peaks between the azide asymmetric and the in-phase propionitrile stretching modes. Along with narrowband IR-pump/IR-probe spectroscopy, these results reveal an irreversible intramolecular vibrational energy redistribution (IVR) that involves couplings of the two oscillators to different subsets of low-frequency modes. Our data shows a time constant of 2.3 ps for the IVR, whereas energy dissipation to the solvent occurs on a time scale of 18 ps.

MO 22.3 Thu 11:30 HS XVI

Isolating (multi-)exciton dynamics via fluorescence-detected pump-probe spectroscopy — •STEFAN MUELLER¹, AJAY JAYACHANDRAN¹, CHRISTOPH LAMBERT², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Action-detected nonlinear spectroscopy has received increasing attention in the past years. While useful, it has recently been identified that action-based nonlinear spectra can be subject to undesired background stemming from incoherent mixing. This effect obscures single-exciton dynamics and is especially dramatic in systems with an increasing number of chromophores [1]. Moreover, inevitable pulse overlap causes artificial multiple-quantum coherences [2]. Both incoherent mixing and artificial multiple-quantum coherence reduce the meaningfulness of action-based spectra and exacerbate their interpretation. Here we introduce a technique that eliminates both undesired contributions. We demonstrate our approach using fluorescence-detected pump-probe spectroscopy (F-PP) on squaraine dimers and polymers. We extract fourth- and sixth-order F-PP spectra to isolate single- and

bi-exciton dynamics, respectively, without spurious background. This works even in polymers which suffer to a particularly large degree from incoherent mixing due to the large number of involved chromophores.

- [1] L. Bolzonello *et al.*, *J. Phys. Chem. Lett.* **14**, 11438 (2023).
[2] U. Bangert *et al.*, *Opt. Lett.* **48**, 538–541 (2023).

MO 22.4 Thu 11:45 HS XVI

Higher-order signal separation in nonlinear spectroscopy: An intensity-based general approach — •LUIA BRENNEIS¹, JACOB J. KRICH^{2,3}, PETER A. ROSE², KATJA MAYERSHOFER¹, SIMON BÜTTNER¹, JULIAN LÜTTIG⁴, PAVEL MALÝ⁵, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Department of Physics, University of Ottawa, Ottawa, ON, Canada — ³Nexus for Quantum Technologies, University of Ottawa, Ottawa, ON, Canada — ⁴Department of Physics, University of Michigan, Ann Arbor, MI, USA — ⁵Faculty of Mathematics and Physics, Charles University, 121 16 Prague, Czech Republic

Nonlinear spectroscopic techniques, like two-dimensional electronic spectroscopy (2DES), are powerful tools for investigating multiparticle correlations and complex dynamics. However, depending on the pulse intensities, the detected signal consists of multiple perturbative orders exhibiting different lineshapes and dynamics. Separating these orders remains a universal challenge, especially while maintaining a high signal-to-noise ratio. Recently, we published an intensity-cycling scheme to extract nonlinear orders in transient absorption spectroscopy^[1]. Now we present a generalized version to separate the perturbative orders in a wide range of spectroscopy techniques. In an experimental demonstration, we perform order separation in 2DES of squaraine polymers. We also derive the optimal intensities to minimize the combined effect of random and systematic errors.

- [1] P. Malý *et al.*, *Nature* **616**, 280 (2023).

MO 22.5 Thu 12:00 HS XVI

Resolving higher-order signals through intensity cycling in two-dimensional electronic spectroscopy on the example of a squaraine dimer — •KATJA MAYERSHOFER¹, JACOB J. KRICH^{2,3}, LUIA BRENNEIS¹, SIMON BÜTTNER¹, PETER A. ROSE², JULIAN LÜTTIG⁴, PAVEL MALÝ⁵, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Department of Physics, University of Ottawa, Ottawa, Ontario, Canada — ³Nexus for Quantum Technologies, University of Ottawa, Ottawa, Ontario, Canada — ⁴Department of Physics, University of Michigan, Ann Arbor, MI, USA — ⁵Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

Recently, we developed a variant of transient absorption spectroscopy that separates different perturbative orders of nonlinear response through “intensity cycling” [1]. We now extend this method, enabling separation of third- and higher-order contributions in two-dimensional (2D) spectra, by multiplication of a Vandermonde matrix with fluence-dependent 2D data. We apply this new method on a squaraine dimer to resolve nonlinear orders, allowing us to analyze uncontaminated signals and compare the lineshapes of different orders of nonlinear response. We perform simulations using the Ultrafast Spectroscopy Suite toolbox [2,3] to gain insight into the differences in lineshapes.

- [1] P. Malý *et al.*, *Nature* **2023**, 616, 280.
[2] P. A. Rose & J. J. Krich, *J. Chem. Phys.* **2021**, 154, 034108.
[3] P. A. Rose & J. J. Krich, *J. Chem. Phys.* **2021**, 154, 034109.

MO 22.6 Thu 12:15 HS XVI

Investigation of Multi-Exciton Interactions in a Chiral Squaraine Homopolymer Employing Higher-Order Pump-Probe Spectroscopy and Fluorescence-Detected Two-Dimensional Spectroscopy — •KARINA HEILMEIER¹, STEFAN MUELLER¹, EMELY FREYTAG², PETER A. ROSE³, JACOB J. KRICH^{3,4}, CHRISTOPH LAMBERT², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ³Department of Physics, University of Ottawa, Ottawa, Ontario, Canada — ⁴Nexus for Quantum Technologies, University of Ottawa, Ottawa, Ontario, Canada

Third-order spectroscopy such as transient absorption (TA) is often used to investigate the dynamics of single-exciton states. The measurement of higher orders provides information on the interactions of an increasing number of excitons and their dynamics. We recently showed how nonlinear orders can be separated using intensity cycling [1]. Here, we study multi-exciton interaction in a related but structurally different chemical system, a chiral squaraine homopolymer. We use intensity-dependent TA to separate odd orders of nonlinear response. In addition, we employ fluorescence-detected two-dimensional spectroscopy. In that case, we extract the even orders by phase cycling and compare the two approaches.

[1] P. Malý, J. Lüttig, P. A. Rose, A. Turkin, C. Lambert, J. J. Krich, T. Brixner, *Nature* 616, 280 (2023).

MO 22.7 Thu 12:30 HS XVI

Femtosecond-spectroscopy of novel Fe(III)-complexes demonstrating a reservoir effect — ●SAMIRA LABELSTEIN¹, LENNART SCHMITZ², FRANZISKA FENNEL¹, MIGUEL ANDRE ARGÜELLO CORDERO¹, JAKOB STEUBE², MATTHIAS BAUER², and STEFAN LOCHBRUNNER¹ — ¹University of Rostock, Germany — ²Paderborn University, Germany

Conventional photosensitizers for photocatalysis are typically derived from rare and valuable precious metals, prompting the search for alternatives based on first-row transition metals. Among these, iron-based photosensitizers emerge as potential candidates but are limited by their short-lived charge transfer states. To overcome this limitation, targeted ligand design is employed as a strategy. This study presents a series of emitting iron(III) complexes modified with chromophores, featuring either phenyl or anthracene groups. The chromophores are attached to the ligand via a methyl spacer. While the phenyl-extended complexes exhibit behavior similar to the original complex, the anthracene-extended complexes reveal a reservoir effect, characterized by a population transfer from the ligand-to-metal charge

transfer state to the triplet state of anthracene. Additionally, a correlation is observed between the number of attached anthracene units and the rate of population transfer. Our findings, obtained through time-resolved methods, specifically femtosecond transient absorption UV-Vis spectroscopy and streak camera measurements, are discussed in detail.

MO 22.8 Thu 12:45 HS XVI

Halide Modulated Excited States of Dinuclear Copper Complexes — ●DANIEL MARHÖFER¹, CLARA ADAM², ANNA MAURI³, MARTIN NIEGER⁴, OLAF FUHR⁵, PATRICK WEIS⁶, GEREON NIEDNER-SCHATTEBURG¹, WOLFGANG WENZEL³, and STEFAN BRÄSE² — ¹Department of Chemistry and State Research Center OPTIMAS, RPTU Kaiserslautern — ²Institute of Organic Chemistry (IOC), Karlsruhe Institute of Technology (KIT) — ³Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT) — ⁴Department of Chemistry, University of Helsinki — ⁵Karlsruhe Nano-Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT) — ⁶Institute of Biological and Chemical Systems, Functional Molecular Systems (IBCS-FMS), Karlsruhe Institute of Technology (KIT)

Organic Light-Emitting-Diodes (OLEDs) are a key technology in state-of-the-art display applications, offering unparalleled efficiency and color purity. Copper as an earth-abundant metal shows promising characteristics regarding luminescence lifetimes and quantum yields. However, energy efficiency necessitates quantum yields close to 100 % as e.g. achievable through Thermally Activated Delayed Fluorescence (TADF). We investigated by luminescence, time-correlated single photon counting and step-scan FTIR spectroscopy a series of five isostructural, dinuclear copper complexes. Variation of the two (pseudo-)halide ligands modulates excited state lifetimes and luminescence patterns. Our interpretation of the TADF behaviour revealed significant variations of the singlet-triplet gap, beyond obvious trends. Quantum chemical modelling partly challenges these findings.