MO 13: Poster – Ultrafast Electronic Dynamics

Time: Tuesday 17:00–19:00 Location: Philo 1. OG

MO 13.1 Tue 17:00 Philo 1. OG

Time-resolved photoelectron spectroscopy of acetone using few-femtosecond pulses — Kate Robertson[1,2,3], Ammar B. Wahid[1], •Aurelien Sanchez[1,2,3], Sergey Riabchuk[1,2,3], Lorenzo Colaizzi[1], Erik Månsson[1], Terence Mullins[1,2,3], Vincent Wanie[1], and Francesca Calegari[1,2,3] — [1]Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron, Germany — [2]The Hamburg Centre for Ultrafast Imaging, Universität Hamburg, Germany — [3]Physics Department, Universität Hamburg

Few-femtosecond ultraviolet (UV) pulses are essential for tracking electron motion in electronically excited neutral molecules. Because UV light drives many key photochemical and biological reactions, the ability to generate pulses of such brevity opens a path to probing these processes with unprecedented temporal sensitivity. In this work, we report a time-resolved photoelectron spectroscopy study of acetone using 2.1-fs transform-limited UV pump pulses together with near-infrared probe pulses, yielding an overall temporal resolution of 5.6 fs. Acetone exhibits intricate Rydberg couplings that strongly shape its excited-state behavior. While earlier time-resolved measurements have examined these dynamics, their temporal resolution was insufficient to resolve processes evolving on a few- to tens-of-femtoseconds timescale. Our measurements uncover strong electronic and vibrational coherences and provide clear evidence for rapid relaxation into the $\pi\pi^*$ state. We observe a slow oscillation of 24 fs persisting for roughly 100 fs in the photoelectron signal, alongside a faster 3.2 fs modulation, which may reflect the presence of an electronic coherence.

MO 13.2 Tue 17:00 Philo 1. OG

ultrafast coherent dynamics in light-harvesting complexes from purple bacteria — •xinpeng xu[1], paul recknagel[1], alastair t. gardiner[2], richard j. cogdell[3], richard hildner[4], and jürgen köhler[1,5,6] — [1]Spectroscopy of Soft Matter, University of Bayreuth, Bayreuth 95440, Germany — [2]Institute of Microbiology of the Czech Academy of Sciences, Třeboň 379 01, Czech Republic — [3]School of Molecular Biosciences, Glasgow University, Glasgow G12 8QQ, U.K. — [4]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 3, Groningen 9747 AG, The Netherlands — [5]Bavarian Polymer Institute, University of Bayreuth, Bayreuth 95440, Germany — [6]Bayreuther Institut für Makromolekülforschung (BIMF), Bayreuth 95440, Germany

Photosynthetic purple bacteria accomodate peripheral light-harvesting complexes, typically termed LH2, for capturing solar energy. The species Rps. acidophila features two different antenna complexes, i.e. the B800-B850 LH2 when grown under high-light conditions (HL LH2) and the B800-B820 LH2 when grown under low-light conditions (LL LH2). The different spectral positions of the absorbing states of these complexes are tuned by the presence (HL LH2) or lack (LL LH2) of specific hydrogen bonds between the chromophores and the protein backbone. Here we investigate how the protein structure controls the excitonic energy levels and their ultrafast coherent dynamics.

MO 13.3 Tue 17:00 Philo 1. OG

Electronic relaxation dynamics of iron(III) complexes functionalized with chromophores — •Samira Dabelstein[1], Ansgar Döring[1], Miguel Andre Argüello Cordero[1], Lennart Schmitz[2], Jakob Steube[2], Matthias Bauer[2], Franziska Fennel[1], and Stefan Lochbrunner[1] — [1]University of Rostock, Rostock, Germany — [2]Paderborn University, Paderborn, Germany

Conventional photosensitizers for photocatalysis are usually made from rare and valuable precious metals. This has prompted the search for alternatives based on first-row transition metals. Iron-based photosensitizers are among these alternatives and emerge as potential candidates, but they are limited by their short-lived charge transfer states. One strategy to overcome this limitation is targeted ligand design. This study presents a series of emitting iron(III) complexes modified with chromophores, featuring either phenyl or anthracene groups, directly attached to the ligand backbone. The anthracene complex shows unexpectedly fast relaxation dynamics in solution, attributed to a charge transfer state extended over the entire ligand, which becomes accessible only after chromophore coplanarization [1]. To investigate this hypothesis further, the complexes were embedded in a polymer matrix to restrict conformational changes. Femtosecond transient absorption UV-Vis spectroscopy, revealed for both complexes decay dynamics differing from the solution case. The results support in the case of anthracene the hypothesis of an additional relaxation pathway driven by chromophore coplanarization.

[1] L. Schmitz et al., Inorg. Chem. 64 (2025), 14101.

MO 13.4 Tue 17:00 Philo 1. OG

Influence of Polymer Structure on Multi-Exciton Interactions in Different Squaraine Polymers — •Karina Heilmeier[1], Emely Freytag[2], Kateřina Charvátová[3], Federico Gallina[4], Stefan Mueller[1], Jacob J. Krich[4,5], Christoph Lambert[2], Pavel Malý[3], and Tobias Brixner[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — [2]Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — [3]Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic — [4]Department of Physics, University of Ottawa, Ottawa, Ontario, Canada — [5]Nexus for Quantum Technologies, University of Ottawa, Ottawa, Ontario, Canada

Higher-order nonlinear signals in ultrafast spectroscopy provide unique information on the interactions of multiple excitons and their dynamics. Recently, we demonstrated how such signals can be extracted using intensity cycling in higher-order transient absorption (TA) measurements [1]. Here, we employ higher-order TA and fluorescence-detected two-dimensional spectroscopy to investigate multi-exciton interactions in two structurally different squaraine polymers built up of the same monomer but with different connectivity. This direct comparison allows us to reveal how the different polymer structures influence the exciton relaxation, transport and exciton–exciton annihilation dynamics.

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

MO 13.5 Tue 17:00 Philo 1. OG

Unraveling Strong Coupling and Excitonic Dipole Reorganization in Macrocyclic Squaraine Dimers via 2DES Anisotropy — •Yi Xu[1], Jonathan Herpich[2], Christoph Lambert[2], and Tobias Brixner[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — [2]Institut für Organische Chemie, Universität Würzburg, Am Hubland 97074 Würzburg

A macrocyclic squaraine (MSQ) consists of two covalently linked squaraine chromophores forming a torus-shaped π-conjugated ring that exhibits H-aggregate-like interactions. When two such macro-cycles associate to form an MSQ dimer, additional inter-macrocycle coupling arises, giving rise to new excitonic states with mixed H- and J-aggregate character, as revealed by UV-vis-NIR and CD spectra.

To probe how local squaraine transition dipole moments reorganize in the MSQ dimer, we employ polarization-resolved 2DES anisotropy. The anisotropy dynamics reveal a clear reorganization of transition dipole moments (TDMs), suggesting the emergence of delocalized excitonic dipoles spanning both macrocycles. Ongoing analysis aims to quantify the relative dipole orientation and the extent of electronic delocalization across the dimer.

These findings offer a microscopic view of dipole reorganization in hierarchical chromophore assemblies and demonstrate that 2DES anisotropy is a powerful tool for disentangling inter-macrocycle coupling and aggregate character in complex π-conjugated systems.

MO 13.6 Tue 17:00 Philo 1. OG

Circular dichroism yield measurements using a magnetic bottle electron spectrometer with twin-focus detection scheme — •Alexander Gerlach, Steffen Leinberger, Horst Rottke, Sagnik Das, Hendrike Braun, and Jochen Mikosch — Institut für Physik, Universität Kassel, Kassel, Germany

We employ time-of-flight (TOF) spectroscopy with a magnetic bottle to explore the circular dichroism (CD) of chiral molecules in the gas phase. Measuring the energy resolved electron yield for right- and left-circularly polarized light with femtosecond UV pulses allows to distinguish the excitation channels for enantiomeric molecular species.

For this purpose we use a modified twin-focus detection scheme [1], which separates the interaction regions of the two polarization states perpendicular to the TOF axis. An MCP delay-line detector is used to obtain the time and spatial distribution of the emitted photoelectrons from the investigated chiral molecule. First test measurements with this newly assembled electron spectrometer are presented, complementing the established CD ion yield measurements [1] for these systems.

[1] T. Ring et al., Rev. Sci. Instrum. 92, 033001 (2021)

MO 13.7 Tue 17:00 Philo 1. OG

Ultrafast Isomerization Dynamics of Amino-Azobenzene Molecules Probed by TRPES — •Alina Khodko[1,4], Artem Norenko[4], Matthew Mgbukwu[3], Evgenii Titov[2], Nataliia Kachalova[4], Valerii Voitsekhovych[4], Igor Dmytruk[4,5], Stefan Haacke[3], Oleg Kornilov[1], and Jérémie Léonard[3] — [1]Max Born Institute, Max-Born-Straße 2A, 12489 Berlin, Germany — [2]Institute of Chemistry, University of Potsdam, Germany — [3]Institut de Physique et Chimie des Matériaux de Strasbourg, Université de Strasbourg, CNRS UMR 7504, Strasbourg, France — [4]Institute of Physics NAS of Ukraine, Nauky Ave, 46, 03028, Kyiv, Ukraine — [5]Taras Shevchenko National University of Kyiv, 64/13 Volodymyrska St., Ukraine, 01601, Kyiv, Ukraine

To access the isomerization dynamics of azobenzenes, Metanil Yellow molecules, time-resolved photoelectron spectroscopy (TRPES) were performed using 400 nm pump and 15th harmonic (23.5 eV) probe pulses. The experimental setup has been described [1]. The excited-state signal, integrated within the range from 2.4 eV to 5.2 eV, is modeled with a bi-exponential decay function. The fit yields the constants of around 0.5 ps and 5.2 ps. In general, the timescales from the TRPES experiments are in good agreement with the results derived from the transient-absorption spectroscopy (TAS). Based on DFT calculations, the dynamics are tentatively assigned to the S2 -> S1 conversion followed by relaxation to a long-lived state, the nature of which (possibly a TICT state) remains to be confirmed. This project was supported by Laserlab (PID: 26494). 1. E. Titov, et. Faraday Discuss., 2021.