

SYED 1: Electronic 2D Spectroscopy from Small to Large Systems I

Time: Monday 11:00–13:00

Location: E 415

Invited Talk

SYED 1.1 Mon 11:00 E 415

Signatures of vibronic and vibrational coherences in electronic 2D-spectra of monomers and aggregates — FRANZ MILOTA¹, TOMAS MANCAL², HARALD F. KAUFFMANN^{3,4}, and JÜRGEN HAUER¹ — ¹Photonics Institute, Vienna University of Technology, Gusshausstrasse 27, 1040 Vienna, Austria — ²Institute of Physics, Faculty of Mathematics and Physics, Charles University, KeKarlovu 5, Prague 121 16, Czech Republic — ³Faculty of Physics, University of Vienna, Strudlhofgasse 4, 1090 Vienna, Austria — ⁴Faculty of Physics, Vienna University of Technology, WiednerHauptstrasse 8-10, 1040 Vienna, Austria

From a quantum mechanical perspective, most molecular systems can be reduced to certain simple discrete level structures. Many properties of such multilevel systems do not depend on their exact nature, e.g. vibrational or electronic. While reflecting distinctly different physics, one common feature is the possibility to excite a coherent superposition of energy eigenstates, referred to as a wavepacket. As shown in numerous recent studies on natural light harvesting complexes, two-dimensional electronic spectroscopy (2D-ES) has a unique disposition for the study of such coherences due to its ability to resolve cross peaks. We identify and describe vibrational and vibronic modulations in electronic 2D-spectra in experimental studies on monomers and molecular J-aggregates. We discuss coherences in coupled molecular aggregates involving both electronic and nuclear degrees of freedom. We conclude that a general distinguishing criterion based on the experimental data alone cannot be devised.

Invited Talk

SYED 1.2 Mon 11:30 E 415

Beatings in Electronic 2D Spectroscopy — TÖNU PULLERITS — Chemical Physics, Lund University, Sweden

Ever since the first report of oscillating electronic 2D signals in photosynthetic light harvesting complexes, such observations have received considerable attention by the community leading to various exciting interpretations.

Taking a Fourier transform over the waiting time t_2 visualizes the oscillatory signal amplitude, phase and damping in a 3D representation. Such a third order electronic 3D spectroscopy contains detailed information about evolution of coherences created by the excitation sequence of the laser pulses. The physical nature of the coherences will be discussed and possible explanation of the observed long lifetimes will be given.

Invited Talk

SYED 1.3 Mon 12:00 E 415

Resonant 2D Raman Spectroscopy — TIAGO BUCKUP, JAN PHILIP KRAACK, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

The coupling between structural degrees-of-freedom plays a major role in the evolution of photo-activated chemical reactions. In general, Franck-Condon active modes are not necessarily reactive modes, but can excite reactive modes via intramolecular vibrational coupling. Such a coupling originates from strong anharmonicity terms, which are normally hidden from lower order spectroscopic techniques. Nevertheless, this issue can be addressed by using higher order time domain experiments, like fifth- and seventh-order spectroscopic methods. In this work, we present a resonant fifth-order time-resolved approach to probe the coupling between Raman active modes in electronic excited states. It is based on two consecutive pairs of resonant excitations (k_1/k_2 , k_3/k_4) followed by a resonant probe interaction (k_5). The first two pairs of excitations (k_1/k_2) and (k_3/k_4) are resonant with different electronic transitions, inducing vibrational coherences from Raman transitions in, e.g., the excited electronic state. Since the resonant signal is orders of magnitude stronger than non-resonant contributions, cascaded $\chi^{(3)}$ -contributions are strongly suppressed. Our method is applied to a series of structurally different samples (dyes, carotenoids, etc.) in condensed phase. The results show that vibrational coupling can survive e.g. relaxation dynamics that involve conical intersections.

Invited Talk

SYED 1.4 Mon 12:30 E 415

Coherent Two-Dimensional Electronic Spectroscopy With Triggered Exchange — PATRICK NUERNBERGER, STEFAN RUETZEL, MARTIN KULLMANN, JOHANNES BUBACK, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We demonstrate how diverse femtosecond spectroscopy approaches coalesce to a comprehensive understanding of the photochemical reaction pathways of a molecule. Two ring-open forms of 6,8-dinitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] coexist in solution, differing by a cis/trans configuration of a double bond. Pump-probe transient absorption spectroscopy shows that both isomers may undergo a photo-induced ring closure, whereas coherent two-dimensional (2D) electronic spectra directly visualize that cis/trans isomerization among the isomers is a negligible reaction channel.

Via pump-repump-probe spectroscopy, the photodynamics accessible by further excitation are explored and the formation of a radical cation species is identified. By combining the benefits of pump-repump-probe with coherent 2D spectroscopy, we then introduce coherent triggered-exchange 2D (TE2D) electronic spectroscopy, so that reactants can be connected with products formed by the repump pulse after the pump sequence but before the probe event. This approach unveils that only one of the isomers is the reactant from which the radical cation is formed. TE2D electronic spectroscopy thus is a versatile tool for analyzing excited states and associated reaction pathways, with the information from where the reaction started intrinsically preserved.