Symposium Electronic 2D Spectroscopy from Small to Large Systems (SYED)

jointly organized by
the Molecular Physics Division (MO), and
the Quantum Optics and Photonics Division (Q)

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Coherent two-dimensional (2D) spectroscopy is one of the hottest topics in modern optical investigations. The methods originally developed for NMR measurements have been adapted first to the IR region but now more and more groups have pushed the reachable spectral range via the 800 nm region to the visible and lately even to the UV and XUV. The symposium is aimed to introduce a general audience to the topic and technologies. We want to promote full harvesting of the scientific possibilities for new insight into physical, chemical and biological processes and ultrafast dynamics. The talks span the full range from electrons in atoms to biological systems.

Overview of Invited Talks and Sessions

(lecture room E 415)

Invited Talks

SYED 1.1	Mon	11:00–11:30	E 415	**Signatures of vibronic and vibrational coherences in electronic 2D-spectra of monomers and aggregates** — Franz Milota, Tomas Mancal, Harald F. Kauffmann, •Jürgen Hauer
SYED 1.2	Mon	11:30–12:00	E 415	**Beatings in Electronic 2D Spectroscopy** — •Tönu Pullerits
SYED 1.3	Mon	12:00–12:30	E 415	**Resonant 2D Raman Spectroscopy** — •Tiago Buckup, Jan Philip Kraack, Marcus Motzkus
SYED 1.4	Mon	12:30–13:00	E 415	**Coherent Two-Dimensional Electronic Spectroscopy With Triggered Exchange** — •Patrick Nuernberger, Stefan Ruetzel, Martin Kullmann, Johannes Buback, Tobias Brixner
SYED 2.1	Mon	14:00–14:30	E 415	**Two-dimensional UV and visible spectroscopy of biological system** — •Majed Chergui, Gerald Auböck, Cristina Consani, Roberto Monni, André El Haddad, Frank van Mourik
SYED 2.2	Mon	14:30–15:00	E 415	**Ultrabroad 2D-UV spectroscopy: from coherent internal conversion in pyrene towards exciton dynamics in DNA** — •Igor Pugliesi, Nils Krebs, Eberhard Riedle
SYED 2.3	Mon	15:00–15:30	E 415	**Multidimensional XUV-NIR spectroscopy of electronic dynamics in small quantum systems** — •Christian Ott, Andreas Kaldun, Kristina Meyer, Philipp Raith, Martin Laux, Alexander Blättermann, Thomas Ding, Thomas Pfeifer
SYED 2.4	Mon	15:30–16:00	E 415	**Correlated Two-electron Wave-Packets in Helium** — •Javier Madronero

Sessions

SYED 1.1–1.4	Mon	11:00–13:00	E 415	**Electronic 2D Spectroscopy from Small to Large Systems I**
SYED 2.1–2.4	Mon	14:00–16:00	E 415	**Electronic 2D Spectroscopy from Small to Large Systems II**

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 Milota[1], Tomas Mancal[2], Harald F. Kauffmann[3,4], and •Jürgen Hauer[1] — [1]Photonics Institute, Vienna University of Technology, Gusshausstrasse 27, 1040 Vienna, Austria — [2]Institute of Physics, Faculty of Mathematics and Physics, Charles University, KeKarlovu 5, Prague 121 16, Czech Republic — [3]Faculty of Physics, University of Vienna, Strudlhofgasse 4, 1090 Vienna, Austria — [4]Faculty 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 t2 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.

SYED 2: Electronic 2D Spectroscopy from Small to Large Systems II

Time: Monday 14:00–16:00 Location: E 415

Invited Talk SYED 2.1 Mon 14:00 E 415

Two-dimensional UV and visible spectroscopy of biological system — •Majed Chergui, Gerald Auböck, Cristina Consani, Roberto Monni, André El Haddad, and Frank van Mourik — Laboratoire de spectroscopie ultrarapide, ISIC-EPFL, CH-1015 Lausanne, Switzerland

We report on 2D UV transient absorption (TA) studies of ferric myoglobins using our recently implemented setup, which operates at 20 kHz with a spectral bandwidth of >80 nm in both pump and probe beams, allowing to cover the broad spectra of aromatic amino acids below 300 nm. Our results reveal a hitherto unknown electron transfer (ET) mechanism from one of the Trp residues to the porphyrin, whilst such deexcitation channels were always attributed to Förster resonant energy transfer (FRET). The implications of this work go beyond the peculiar systems studied here, in that the lifetimes of Trp residues are invariant in all haem proteins (ferrous or ferric), suggesting that Trp-porphyrin ET also occurs in ferrous proteins. They also question the widespread assumption of FRET-mediated decay of Trp in studies of protein dynamics. We will also present our newly developed 2D coherent set-up in the visible and its application to the study of porphyrin dynamics.

Invited Talk SYED 2.2 Mon 14:30 E 415

Ultrabroad 2D-UV spectroscopy: from coherent internal conversion in pyrene towards exciton dynamics in DNA — •Igor Pugliesi, Nils Krebs, and Eberhard Riedle — BioMolekulare Optik, LMU München

The congested absorption spectra of proteins and DNA strands pose a major limitation in the investigation of their photochemistry through pump-probe experiments. This limitation is hoped to be overcome with 2D-UV spectroscopy, which resolves both the excitation and detection frequency. In contrast to 2D-Vis, where a bandwidth up to 150 nm can be reached, experimental realizations in the UV are so far limited to about 5 nm. Here we present 2D-UV results on pyrene, a model system for photophysical relaxation, obtained with our new setup comprising 25 nm broad UV pump pulses and a super-continuum

probe covering 250 - 720 nm. The pulses are wide enough to cover two vibronic bands of the S_2 $^1B_{2u} \leftarrow S_0$ electronic transition at 312 nm and clearly resolve the off-diagonal peaks between the vibronic bands. The ultrabroad supercontinuum probe visualizes the excitation dependent ultrafast 100 fs S_2-S_1 internal conversion and the S_1 vibrational relaxation. The coherent excitation of vibrational states survives the internal conversion to the S_1 state and results in wavepackets in the S_1 state - as seen directly in the excited state absorption. 2D-UV is now ready for the investigation of UV absorbing chromophores ubiquitous in organic chemistry and biochemistry. In conjunction with achromatic second harmonic generation producing up to 100 nm broad UV pulses the full potential of 2D-UV spectroscopy can be reached.

Invited Talk SYED 2.3 Mon 15:00 E 415

Multidimensional XUV-NIR spectroscopy of electronic dynamics in small quantum systems — •Christian Ott, Andreas Kaldun, Kristina Meyer, Philipp Raith, Martin Laux, Alexander Blättermann, Thomas Ding, and Thomas Pfeifer — Max-Planck-Institut für Kernphysik, Heidelberg, Germany

In a recent experimental study [1], we investigated the two-electron system helium using nonlinear absorption spectroscopy in the XUV. Combining short-pulsed excitation, laser manipulation, a multidimensional parameter space (laser-pulse intensity, temporal delay, photon energy), and high spectral resolution in the XUV (20 meV @ 60 eV) enables us to observe the coupling among several doubly-excited states where both electrons are active. We show how the spectroscopic analysis of these couplings can be understood and how the electronic wavefunction can be manipulated using ultrashort laser pulses. Towards the study of fundamental multi-electron processes with increasing complexity, possible routes to measuring atoms with more than two electrons will also be discussed.

[1] C. Ott et al., arXiv:1205.0519 (2012)

Invited Talk SYED 2.4 Mon 15:30 E 415

Correlated Two-electron Wave-Packets in Helium — •Javier Madronero — Universität Duisburg-Essen

A natural and probably the most simple candidate to investigate the possibility of manipulating the correlated electronic dynamics with the help of external fields is the helium atom. In this theoretical contribution we address two different scenarios: on the one hand, under near-resonant driving certain highly doubly excited helium states might transform in two-electron nondispersive wave packets, i.e. robust quantum objects that evolve along classical trajectories without dispersion. On the other hand, we explore to what extend the time delay in attosencond transient absorption experiments of helium dressed by a few-cycle visible pulse [1] can be used to control the shape of two-electron correlated wave functions.

[1] C. Ott et al., arXiv:1205.0519 (2012).