MO 6: SYED: Electronic 2D Spectroscopy from Small to Large Systems II

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

Invited Talk MO 6.1 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 MO 6.2 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 MO 6.3 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 MO 6.4 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).