

## MO 4: Femtosecond Spectroscopy I

Time: Monday 14:30–16:00

Location: TOE 317

MO 4.1 Mon 14:30 TOE 317

**Coherent two-dimensional nanoscopy** — MARTIN AESCHLIMANN<sup>1</sup>, TOBIAS BRIXNER<sup>2</sup>, ALEXANDER FISCHER<sup>1</sup>, CHRISTIAN KRAMER<sup>2</sup>, PASCAL MELCHIOR<sup>1</sup>, WALTER PFEIFFER<sup>3</sup>, CHRISTIAN SCHNEIDER<sup>1</sup>, CHRISTIAN STRÜBER<sup>3</sup>, PHILIP TUCHSCHERER<sup>2</sup>, and DMITRI V. VORONINE<sup>3</sup> — <sup>1</sup>Fachbereich Physik and Research Center OPTIMAS, Technische Universität Kaiserslautern, Erwin-Schrödinger-Str. 46, 67663 Kaiserslautern — <sup>2</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>3</sup>Fakultät für Physik, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld

We introduce a new spectroscopic method that determines nonlinear quantum-mechanical response functions beyond the optical diffraction limit. While in established coherent two-dimensional (2D) spectroscopy a four-wave-mixing response is measured using three ingoing and one outgoing wave, in 2D nanoscopy we employ four ingoing and no outgoing waves. The final state is detected via photoemission electron microscopy with sub-50 nm spatial resolution. We record 2D nanospectra from an (18 nm)<sup>2</sup> detection area and observe local lineshape variations for plasmonic excitations on a corrugated silver surface. Electronic phase memory persists for longer than 150 fs. 2D nanoscopy makes possible the nonlinear spectroscopic investigation of coherences with nanometer spatial resolution. This allows studying a broad range of phenomena not accessible otherwise such as space-time-resolved coupling, transport, and nonlocal correlations.

MO 4.2 Mon 14:45 TOE 317

**Theoretical investigations on 2D electronic spectra of a  $\pi$ -aggregated dimer upon intermolecular torsional motion** — JOACHIM SEIBT and ALEXANDER EISFELD — MPI for the Physics of Complex Systems, Nöthnitzer Straße 38, Dresden

The influence of relaxation and dephasing effects on two-dimensional electronic spectra of a  $\pi$ -aggregated dimer is investigated, where an intermolecular torsional degree of freedom is taken into account on the basis of a simple model system. While absorption from the ground state mainly populates the upper 1-exciton state, the system can pass a conical intersection upon nuclear motion during a sufficiently large relaxation time, which results in subsequent dynamics at the lower singly excited state potential. In this context, characteristic changes in the 2D-spectrum are discussed with specific attention to the role of the relevant excitation pathways.

MO 4.3 Mon 15:00 TOE 317

**Fully noncollinear coherent 2D-UV spectroscopy** — ULRIKE SELIG, CARL-FRIEDRICH SCHLEUSSNER, MICHAEL FOERSTER, FLORIAN LANGHOJER, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

In the last decade coherent two-dimensional (2D) spectroscopy in the infrared and visible spectral range has proven its ability to unravel couplings and associated transfer processes. The extension of this powerful technique to the ultraviolet (UV) may ultimately help to clarify the much-debated role of electronic excitons in the efficient energy redistribution within DNA strands, protecting them from severe photodamage.

Here we introduce fully noncollinear coherent 2D spectroscopy in the ultraviolet domain with an all-reflective and miniaturized setup design. Phase stability is achieved via pairwise beam manipulation and the concept can be transferred to all wavelength regimes. We present results from an implementation that has been optimized for wavelengths between 250 nm and 375 nm. Interferometric measurements prove phase stability over several hours. We obtained 2D spectra of the nonpolar UV chromophore p-terphenyl in ethanol, excited with 50 fs pulses at 287 nm.

MO 4.4 Mon 15:15 TOE 317

**Ultrafast time resolved spectroscopy of coumarin derivatives** — JENS MÖHRING<sup>1</sup>, TIAGO BUCKUP<sup>1</sup>, MARCUS MOTZKUS<sup>1</sup>, CAROLINE M. KRAUTER<sup>2</sup>, and MARKUS PERNPOINTNER<sup>2</sup> — <sup>1</sup>Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-

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Coumarins are an important class of molecules which exhibits a broad range of photochemical and photophysical applications. Prominent examples are coumarin dimers applied in photochemical controlled drug release or the wide application of coumarin dyes as laser gain media. The latter application is based on the strong fluorescence observed in coumarin derivatives, whereas the unsubstituted coumarin is completely non fluorescent in solution. To gain insight into these and other differences between the members of the coumarin class, ultrafast time resolved datasets are required. Here, we present ultrafast, spectrally resolved, transient absorption of the prototype coumarin derivatives with femtosecond UV excitation (35 fs pulse duration) and probing by CaF<sub>2</sub> generated UV/VIS supercontinuum. We discuss the ultrafast dynamics of coumarin and its derivatives, especially considering an overlap of the ground state bleach with a much stronger excited state absorption and the complex dynamics of the stimulated emission region. Based on comparison to quantum chemical computations and global or target analysis schemes, a preliminary kinetic model for the system is presented.

MO 4.5 Mon 15:30 TOE 317

**Exciton Diffusion in thin Organic Films influenced by Inhomogeneous Broadening** — FRANZISKA FENNEL and STEFAN LOCHBRUNNER — Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock

We investigate a disordered material system which has the potential for long exciton diffusion lengths in combination with a high versatility. The perylene bisimide dye Perylene Red is incorporated in a polymer matrix with a high concentration. Excitons can be efficiently exchanged between the dye molecules by Förster resonance energy transfer (FRET). The dye molecules represent active sites with a narrow energy distribution for the electronically excited state, which reduces the trapping probability. The mobility of the excitons and their diffusion length is measured by the energy transfer to an acceptor. An exciton diffusion length of 30 nm is found for a Perylene Red concentration of 0.1 M [1]. This demonstrates that long distance energy transfer is possible in the disordered material system. However, the observed diffusion constant is about two times smaller than the theoretical predicted one. The relevant mechanism limiting the exciton diffusion distance might be inhomogeneous broadening of the transition energy of Perylene Red in the system. The amount of inhomogeneous broadening is quantified by femtosecond spectroscopy and its influence on the energy transfer is described by energy dependent migration models. [1] F. Fennel and S. Lochbrunner, PCCP, 2010, DOI: 10.1039/c0cp01211d.

MO 4.6 Mon 15:45 TOE 317

**Electron Injection from Perylene Derivates to ZnO Nanorods Studied by Time Resolved Optical and Terahertz Absorption Spectroscopy** — CHRISTIAN STROTHKAEMPER, ROBERT SCHÜTZ, ANDREAS BARTELT, THOMAS HANNAPPEL, and RAINER EICHBERGER — Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner Platz 1, 14019 Berlin, Germany

We investigated the photo-induced heterogeneous electron transfer from perylene derivatives to ZnO nanorods by transient absorption (TA) and optical pump terahertz probe (OPTP) spectroscopy. The perylene derivatives where systematically varied by changing the length of the molecular bridge group. While TA spectroscopy allows for a selective probing of the different states of the dye OPTP is sensitive only to the injected electrons in the ZnO. The recombination of the injected electron with the cationic dye was found to slow down with increasing bridge length. This can be explained by a reduced electron-cation interaction for longer bridges. On the other hand the injection velocity as measured by OPTP shows no clear trend concerning the bridge length. Furthermore we observed a discrepancy between the buildup of the cationic signal (TA) and that of free electrons (OPTP). Reasons for the observed difference are discussed and compared to existing models.