

## MO 7: Femtosecond Spectroscopy I: Electronic 2D Spectroscopy (contributed for SYED in MO)

Time: Monday 16:30–17:45

Location: F 102

MO 7.1 Mon 16:30 F 102

**Coherent two-dimensional electronic spectroscopy of a directly linked porphyrin dimer in the Soret band** — ●FEDERICO KOCH<sup>1</sup>, MARTIN KULLMANN<sup>1</sup>, ULRIKE SELIG<sup>1</sup>, PATRICK NUERNBERGER<sup>1</sup>, DANIEL C. G. GÖTZ<sup>2</sup>, GERHARD BRINGMANN<sup>2</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We examined the excitonic coupling of two states resulting from Davydov splitting in the Soret band of a directly  $\beta, \beta'$ -linked porphyrin dimer. In a transient absorption study the absorption change of the energetically higher lying state decreased on a timescale of  $\approx 100$  fs; in contrast, the absorption change linked to the energetically lower lying state decreased on a microsecond timescale ( $\approx 50 \mu\text{s}$ ) [1]. Adapting previous models for covalently-linked porphyrin dimers, these dynamics were explained with an excitonic approach, but the states connected by coupling could only be inferred indirectly in the analysis. With coherent 2D electronic spectroscopy, we directly visualize the predicted population transfer between the corresponding excitonic states as a result of electronic coupling [2].

[1] M. Kullmann, A. Hipke, P. Nuernberger, T. Bruhn, D. C. G. Götz, M. Sekita, D. M. Guldi, G. Bringmann, and T. Brixner, *Phys. Chem. Chem. Phys.* 2012, 14, 8038-8050

[2] F. Koch, M. Kullmann, U. Selig, P. Nuernberger, D. C. G. Götz, G. Bringmann, and T. Brixner, *New J. Phys.*, accepted 28 Nov 2012

MO 7.2 Mon 16:45 F 102

**The role of non-equilibrium vibrational structures in electronic coherence and recoherence in pigment protein complexes** — ●FELIPE CAYCEDO-SOLER<sup>1</sup>, ALEX W. CHIN<sup>1,2</sup>, JAVIER PRIOR<sup>3</sup>, ROBERT ROSENBAUGH<sup>1</sup>, SUSANA F. HUELGA<sup>1</sup>, and MARTIN B. PLENIO<sup>1</sup> — <sup>1</sup>Institute of Theoretical Physics, Universität Ulm, Albert-Einstein-Allee 11, 89069 Ulm, Germany — <sup>2</sup>Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge, J J Thomson Avenue, Cambridge, CB3 0HE, UK — <sup>3</sup>Departamento de Física Aplicada, Universidad Politécnica de Cartagena, Cartagena 30202, Spain

Recent observations of oscillations in the non-linear optical response of photosynthetic complexes, have revealed evidence for surprisingly long-lasting electronic coherences which can coexist with energy transport. Here we show that the non-trivial spectral structures of protein fluctuations can generate non-equilibrium processes that lead to the spontaneous creation and sustenance of electronic coherence, even at physiological temperatures. Developing new advanced simulation tools to treat these effects, we provide a firm microscopic basis to successfully reproduce the time-scale for survival of the experimentally observed coherence in the Fenna\*Matthews\*Olson complex, and illustrate how detailed quantum modelling and simulation can shed further light on a wide range of other non-equilibrium processes which may be important in different photosynthetic systems.

MO 7.3 Mon 17:00 F 102

**Pulse-Shaping-Based Two Dimensional Electronic Spectroscopy in a Modified Pump-Probe geometry: Applications to the Photosystem II Reaction Center** — ●FRANKLIN FULLER, DANIEL WILCOX, and JENNIFER OGILVIE — University of Michigan, Ann Arbor, MI, USA

Two dimensional spectroscopy has been performed with pulse shapers in the pump probe geometry at both visible and infrared frequencies. The pulse shaped pump probe geometry affords many benefits, such as ease of alignment, lack of moving parts, and automatic global phasing. Also, the geometry lends itself to broad-band probing, which is key for

deciphering the congested spectra of the photosystem II reaction center (PSII RC). However, since the method is not background free, the signal-to-noise ratio in the pump-probe geometry is limited compared to background-free approaches. We demonstrate a simple and low-cost modification to the pulse-shaped 2D setup which enables one to collect the signal in a background free manner. In the case of Q<sub>x</sub> band of PSII, where the transient extinction coefficient is 100 times weaker than the Q<sub>y</sub> band, we show that this modification in conjunction with a NOPA affords over an order of magnitude improvement in signal to noise compared to traditional white-light probing. Furthermore, we show that the technique may also be applied to standard pump-probe measurements to similar effect.

MO 7.4 Mon 17:15 F 102

**How to probe (photo)chemistry in the infrared beyond the vibrational lifetime - Electronically-enhanced 2D-IR exchange spectroscopy used as structural probe** — ●LUUK VAN WILDEREN, ANDREAS MESSMER, and JENS BREDENBECK — Institute of Biophysics, Goethe-University, Frankfurt am Main, Germany

Conventional 2D-infrared spectroscopy (2D-IR) is limited to probing dynamics on the time scale of the vibrational lifetime, which typically is on the order of a few picoseconds. Processes extending beyond that time so far remained inaccessible. However, many important structural phenomena (e.g. conformational transitions, intermolecular interactions, reactions) can occur in this regime. Here we present a new mixed IR/VIS pulse sequence that allows for the measurement of such processes by means of storing information on vibrational excitation in an electronically excited state. This novel method employs double excitation by a resonant, narrow, tunable infrared pulse and an off-resonant visible pulse, followed by infrared detection. The visible pulse only becomes resonant after vibrational excitation, making the vibrational excitation a prerequisite for entering the electronically excited state. Therefore, the information that vibrational excitation occurred is stored in the electronic excitation and the 2D-IR signal of the vibrational ground state (providing structural molecular information) persists with the electronic lifetime, which can dramatically increase the observation time for exchange phenomena. We illustrate the method by measurements on a mixture of free and hydrogen bonded molecules.

MO 7.5 Mon 17:30 F 102

**New multi-channel detection for Femtosecond Stimulated Raman Microscopy** — ●LARS CZERWINSKI, BENJAMIN MARX, and PETER GILCH — Institut für Physikalische Chemie, HHU Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf

A couple of years ago we have introduced femtosecond stimulated Raman spectroscopy into microscopy[1,2]. As conventional Raman microscopy femtosecond stimulated Raman microscopy (FSRM) yields spectra for each pixel of the micrograph. Our system for the FSRM consist of a fiber laser amplifier for a picosecond pulse (Raman pump) and Ti:Sa oscillator for a femtosecond pulse (Raman probe). At the focus of the microscope stimulated Raman scattering occurs. Chemical entities in the sample are identified via the spectral signature of the process. The transmitted probe light is fed into a spectrograph and recorded by a multi-channel detector. The requirements for the detector are high. It ought to feature about 500 pixels to allow for a reasonable spectral resolution as well as complete spectral coverage. The aim is to record a complete Raman spectrum simultaneously for each focal point in a millisecond or below. The new 20 kHz detector will be presented and compared with the previous detection system.

[1] E. Ploetz, S. Laimgruber, S. Berner, W. Zinth, P. Gilch, *Appl. Phys. B* 87, 389-393 (2007), [2] E. Ploetz, B. Marx, T. Klein, R. Huber, P. Gilch, *Opt. Express* 17 18612-20 (2009)