# Two-dimensional spectroscopy of electronic couplings

*Tobias Brixner*[*,#] *and Graham R. Fleming*[#]

* Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany, phone: +49-931-888-5705, fax: +49-931-888-4906, email: brixner@physik.uni-wuerzburg.de

# Department of Chemistry, University of California, Berkeley and Physical Biosciences Division, Lawrence Berkeley National Laboratory, CA 94720, USA

Time-resolved optical spectroscopy in general determines transient populations within quantum-mechanical systems. In a prototypical pump–probe experiment, the temporal developments of level occupations are observed on a femtosecond timescale. However, the fundamental cause of such evolution, namely the couplings that lead to transitions between levels, can only be inferred indirectly. We overcome this barrier and for the first time measure electronic couplings in molecules directly, here specifically in the natural Fenna–Matthews–Olson (FMO) photosynthetic light-harvesting complex.[1]

As a tool we employ two-dimensional (2D) spectroscopy for electronic excitations, based on heterodyne detection of three-pulse photon echoes in a recently developed frequency-tunable and intrinsically phase-stabilized setup.[2,3] In contrast to 2D infrared spectroscopy where vibrational properties and structural information can be obtained, we investigate electronic couplings in the visible range and how these couplings lead to energy transfer. These transport processes after photoexcitation are also resolved in time and frequency.

Together with self-consistent simulations, this allows us to follow the pathway of energy transport (i.e., the location of electronic excitation) through space with tens of nanometer spatial resolution and femtosecond temporal resolution.[1] In the FMO example we find that the energy does not simply cascade stepwise down the energy ladder as was thought previously.[4] Rather the detailed spatial properties of excited-state wavefunctions are relevant, as opposed to what purely energetic considerations would suggest.

Thus we get detailed insight into the driving force of biological light harvesting, and applications to larger photosynthetic systems are possible. The spectroscopic technique demonstrated here provides the means to determine electronic couplings and spatiotemporal energy transport of any photoactive system, macromolecular assembly, or nanostructure.

---

[1] T. Brixner, J. Stenger, H.M. Vaswani, M. Cho, R.E. Blankenship, and G.R. Fleming, "Two-dimensional spectroscopy of electronic couplings", to be published, **2005**

[2] T. Brixner, I.V. Stiopkin, and G.R. Fleming, "Tunable two-dimensional femtosecond spectroscopy", Opt. Lett., **2004**, 29, 884-886

[3] T. Brixner, T. Mančal, I.V. Stiopkin, and G.R. Fleming, "Phase-stabilized two-dimensional electronic spectroscopy", J. Chem. Phys., **2004**, 121, 4221-4236

[4] H. van Amerongen, L. Valkunas, R. van Grondelle, "Photosynthetic Excitons" (World Scientific, Singapore, **2000**)