**Theory of Higher Order Nonlinear Optical Spectra:**
**Application to Dissolved Chromophores and Biological Chromophore Complexes**

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Starting from the simulation of an third order pump-probe spectrum we want to pave the way for higher order spectroscopy. In general, calculating nonlinear spectra is a three step process. First the model Hamiltonian has to be created, identifying a few important degrees of freedom e. g. by quantum-chemical calculations. In a second step the coupling to the other degrees of freedom has to be considered, defining if a density matrix description including dissipation is necessary. As a last step particular spectra - as measured in the experiment - are calculated either by a perturbation expansion with respect to the electric field, or by multiple propagations using a field dependent Hamiltonian.

We begin with the simulation of the third order transient absorption spectra of a chromophore [1]. Then we focus on higher order spectra and address what specific information about dynamics in the excited states can be gained. A few examples from recent work will be given:
Exciton-exciton annihilation probes the mobility of excitons and their relaxation pathways in chromophore complexes [2]. Transient stimulated Raman tests the wavepacket motion in the excited state and the excited state Raman profile. Finally, using the optimal control algorithm in a pump - shaped dump - probe scheme one directly receives a picture of the multidimensional wavepacket motion in the excited state.

[1] B. Brüggemann, P. Persson, H.-D. Meyer, and V. May: Frequency dispersed transient absorption spectra of dissolved Perylene: A case study using the density matrix version of the MCTDH Method, Chem. Phys. 347, 152 (2008).

[2] B. Brüggemann, N. Christensson, T. Pullerits: Temperature dependent exciton-exciton annihilation in the LH2 antenna complex, Chem. Phys. 357, 140 (2009).