

New 2D Methods For Studying Molecular Interactions

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We developed several methods concerning the study of molecular interactions: 1) A theorem states conditions for the unique inversion of electronic 2D spectra toward the complete population-transfer matrix; 2) we present 2D spectroscopy of exciton–exciton interactions; 3) we introduce 2D spectroscopy on interaction-free molecular beams using mass-resolved ion detection.

Coherent electronic 2D spectroscopy is particularly useful for studying energy transfer in multichromophore systems. But how is the multi-state population transfer connected quantitatively to experimental 2D spectra? Analysis of peak intensities and peak shapes is often complicated and carried out in an indirect fashion, i.e., based on model calculations whose parameters are successively varied, with the goal of reaching close similarity between theoretical and measured 2D spectra. But it is frequently unclear whether the solution thus obtained is unique. We have derived a mathematical theorem proving that a unique “inversion” of experimental data is indeed possible yielding the complete state-to-state population transfer matrix. Conditions are discussed under which such inversion is possible, and a numerical example is shown.

Another problem frequently encountered in the nonlinear spectroscopy of multichromophore systems is the presence of higher-order effects such as exciton–exciton annihilation complicating the acquired signals. Thus, if one desires to know the “pure” single-exciton dynamics of the system, one is often forced to employ very low excitation light levels that in turn may lead to low signal-to-noise ratios. With increasing light intensity, the population dynamics are mixed up with exciton–exciton interaction kinetics, making a clear separation difficult. We have developed a phase-cycling scheme that allows us to retrieve the exclusive fifth-order exciton–exciton-interaction signal, without interference from the third-order population dynamics. The signal is only present if exciton–exciton interactions exist and zero otherwise. Furthermore, the measurement scheme acquires the conventional third-order and the fifth-order signals simultaneously. Many applications for studying various processes in natural and artificial materials can be envisioned, such as excitonic interactions in light harvesting, exciton diffusion in optoelectronic organic materials, or singlet fission in photovoltaics.

In the third part of the talk, the impact of intermolecular interactions is investigated by taking the “opposite approach” and simply “turning off” all interactions. This is achieved in a molecular beam. Generally, particle densities in a molecular beam are too low to generate a measurable coherent four-wave-mixing response. However, we developed an action-based variant of 2D spectroscopy using mass-resolved ion detection. We successfully disentangle different Liouville pathways contributing to the ion signal by employing a 1x3x3x3 phase-cycling scheme in a rotating frame. The pulse-train parameters (delays and phases) are varied on a shot-to-shot basis, enabling rapid scanning and the acquisition of a 2D spectrum within one minute. Thus it is possible to record, at the same time, not only the 2D spectra of the isolated parent molecule but also of all its photoproducts upon a chemical reaction. The method is exemplified on highly excited NO₂.