I-J Theoretical Studies of Ultrafast Nonlinear Optical Spectroscopy of Molecules in Condensed Phases

Nonlinear optical interactions of laser fields with matter provide powerful spectroscopic tools for the understanding of microscopic interactions and dynamic processes. We attempt to provide theoretical basis for a wide class of nonlinear spectroscopic techniques, focusing on the underlying physical processes in the condensed phases.

I-J-1 Energy-Level Diagrams and Their Contribution to Two-Dimensional Spectroscopic Signal: Distinction between Relaxation Mechanisms by Two-Dimensional Spectroscopy

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We develop a Feynman rule for energy-level diagrams emphasizing their connections to the double-sided Feynman diagrams and physical processes in the Liouville space. Thereby, we completely identify such diagrams and processes contributing to the 2D response function in the Brownian oscillator model. We classify such diagrams or processes in quartets and numerically present signals separately from each quartet of diagrams or Liouville-space processes. We find that the signal from each quartet is distinctly different from the others; we can identify each peak in the frequency domain with a certain quartet. This provides the basis for analyzing and assigning actual 2D peaks and suggests the possibility of Liouville-space path-selective spectroscopy. As an application, we demonstrate an example in which two familiar homogeneous models of relaxation are distinguished by the existence or nonexistence of certain peaks on the 2D map; the appearance or disappearance of certain peaks is sensitive to the choice of coupling models. We also point out some confusion in the literature with regard to the inclusion of relaxation effects.

I-J-2 Two-Dimensional Spectroscopy for a Two-Dimensional Rotator Coupled to a Gaussian-Markoffian Noise Bath

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The dynamics of a system in the condensed phase are more clearly characterized by the multi-time correlation functions of physical observables than two-time ones. We investigate a two-dimensional motion of a rigid rotator coupled to a Gaussian-Markovian harmonic oscillator bath. The analytical expression of a four-time correlation function of a dipole that is the observable of the two-dimensional microwave or infrared spectroscopy is obtained from a generating functional approach. The spectra in the absence of damping are discrete and reveal transitions between eigenstates of the angular momentum quantized due to the cyclic boundary condition. For the weakly damped case, the result predicts an echo-like signal that can be explained by the Liouville space path ways. The two-dimensional spectra are more sensitive to the noise effects than the one-dimensional (linear-absorption) spectra, which mean two-time correlation functions of dipole. It is because the effects of the initial thermal distribution are cancelled through the higher-order optical transition process in the two-dimensional spectroscopy, while such thermal effects determine the profile of the line shape in the one-dimensional spectroscopy. The two-dimensional spectrum reveals three peaks corresponding to transition processes between the rotational energy levels even in the damped case, which cannot be observed in the one-dimensional spectroscopy. For the strongly damped case, the two-dimensional spectra reveal peaks that arise from the strongly damped motion and librational motion caused by the strong coupling between the system and the heat bath oscillators with narrow band spectral distribution. Whereas the effects of these motions are shown in the bimodal line of the one-dimensional spectroscopy, the profile of the two-dimensional spectrum clearly implies the origin of these two peaks.

I-J-3 Two-Dimensional Vibrational Spectroscopy of a Double Minimum System in a Dissipative Environment

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A dissipative bistable system presents the simplest model to describe condensed phase reaction dynamics. Using a quantum master equation approach to calculate multitime dipole correlation functions we demonstrate how the dissipative dynamics can be characterized by time-resolved third-order infrared spectroscopy. Thereby we incorporate bilinear and linear–quadratic system–bath interaction into the Redfield relaxation tensor. Investigating equilibrium and nonequilibrium initial conditions for a symmetric system it is shown that bath-induced coherence transfer can have a dramatic influence on the two-dimensional signals. This occurs when the inverse of the ground state tunneling splitting is of the order of the coherence transfer time.