I-I 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-I-1 Two-Dimensional Spectroscopy and the Harmonically Coupled Anharmonic Oscillators

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[*Chem. Phys.* **266**, 237 (2001)]

Experimentally it is established that the 4th-order anharmonicity plays significant roles in many molecules; based on the local (anharmonic) modes picture with couplings between them, the Darling-Dennison coupling manifests itself, which has been confirmed experimentally. It has been shown that this order of anharmonicity can be selectively studied via the 7th order off-resonant optical processes (Okumura and Tanimura, *J. Chem. Phys*. **106**, 1687 (1997)). We obtained fairly compact analytical result for the 7th-order signal and numerically present the signal from CH stretch vibrations in methylene chloride as two-dimensional contour maps. By virtue of the two-dimensionality the results demonstrate the possibility of giving further insight into such mechanism that is not available in the one-dimensional high-resolution spectroscopy.

I-I-2 Two-Dimensional Raman and Infrared Signals Measured from Different Phase-Matching Conditions

KATO, Tsuyoshi; TANIMURA, Yoshitaka

[*Chem. Phys. Lett.* **341**, 329 (2001)]

We developed a theoretical method that can explicitly treat the phase-matching condition of two-dimensional optical measurements. This method might be a rational tool for the analysis of observed signals under non-impulsive excitation. We use this method to separate the contribution of the signal from different Liouville pathways associated with the different phase-matched condition. It is expected that the effects of mode coupling, anharmonicity of the system potential and nonlinearity of the polarizability will be pronounced by the spatial discrimination of the signal, which can be achieved experimentally.

I-I-3 Nonequilibrium Initial Conditions of a Brownian Oscillator System Observed by Two-Dimensional Spectroscopy

SUZUKI, Yoko; TANIMURA, Yoshitaka

[*J. Chem. Phys.* **115**, 2267 (2001)]

We study effects of a nonequilibrium initial condition of a Brownian oscillator system upon two-, three-, and four-time correlation functions of an oscillator coordinate as a subject of multi-dimensional spectroscopy. A nonequilibrium initial condition is set by a displacement of a Gaussian wave packet in an oscillator potential. Such situation may be found in a vibrational motion of molecules after a sudden bond breaking between a fragmental molecule and a targeting vibrational system or a movement of wave packet in an electronic excited state potential surface created by a laser pump pulse. Multi-time correlation functions of oscillator coordinate for a nonequilibrium initial condition are calculated analytically with the use of generating functional from a path integral approach. Two-, three- and four-time correlation functions of oscillator coordinates correspond to the third-, fifth-, and seventh-order Raman signals or the first-, second-, and third order infrared signals. We plotted these correlation functions as a signal in multi-dimensional spectroscopy. The profile of the signal depends on the initial position and momentum of the wave packet in the fifth- and seventh-order Raman or the second and third order infrared measurement, which makes it possible to measure the dynamics of the wave packet directly in the phase space by optical means.

I-I-4 Higher-Order Vibrational Correlation Functions of a Single Harmonic Oscillator Nonlinearly Coupled with a Thermal Bath I: Gauss-White Noise Case

KATO, Tsuyoshi; TANIMURA, Yoshitaka

Higher-order vibrational correlation functions of a single harmonic oscillator system nonlinearly coupled with harmonic oscillators bath are studied in relation to the 2D Raman or IR spectroscopy. The nonlinear system-bath coupling models the vibrational relaxation dynamics under the presence of the elastic and inelastic relaxation mechanisms. A quantum Fokker-Planck equation is derived to describe the relaxation processes for the Gaussian-white noise. Effects of the simultaneous existence of two relaxation mechanisms, the system-bath coupling strength and the temperature are investigated and compared with the Brownian oscillator model by numerically integrating the Fokker-Planck equation. We observe new optical responses induced by the coexistence of the two relaxation mechanisms, which can possibly be very pronounced in the fifth-order Raman (or second-order IR) spectroscopy rather than the seventh-order Raman (or third-order IR)

spectroscopy.

I-I-5 Higher-Order Vibrational Correlation Functions of a Single Harmonic Oscillator Nonlinearly Coupled with a Thermal Bath II: Gauss-Markov Noise Case

KATO, Tsuyoshi; TANIMURA, Yoshitaka

A single harmonic oscillator system nonlinearly coupled to harmonic oscillators bath is considered to study the effects of the finiteness of the Gaussian-Markovian bath correlation time. The previously derived quantum Fokker-Planck equation is extended in a hierarchy form to treat arbitrary bath correlation time. The equation describes the vibrational frequency fluctuations as well as the vibrational energy relaxation processes, and can treat strong system-bath couplings. The fifth- and seventh-order Raman response functions are calculated by numerically integrating the Fokker-Planck equation for various system-bath coupling strengths and bath correlation times. Echo behaviors can be observed in the seventh-order Raman response under the slow frequency fluctuation and energy relaxation, however, such the behavior is absent in the leading fifth-order response function. This finding cannot be predicted by the available stochastic Gaussian frequency fluctuation model.

I-I-6 Two-Dimensional Spectroscopy for a Two-Dimensional Rotator in a Dissipative Environment

SUZUKI, Yoko; TANIMURA, Yoshitaka

Effects of an environment on the dynamics are more clearly characterized by the multidimensional spectroscopy than one-dimensional spectroscopy measured in the microwave absorption. We investigate the two-dimensional spectroscopy of a two-dimensional quantal rotator coupled to a Gaussian-Markovian harmonic oscillator bath by calculating a four-time correlation function of a dipole whose analytical form is derived from the generating functional. Such spectra are experimentally proved by the third order absorption. 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. The calculations for a damped rotator predict an echo signal that can be understood by the Liouville space path ways. The profile of the two-dimensional spectroscopy depends on a finite correlation time of the bath fluctuation and of a coupling strength.

I-I-7 Two-Dimensional Spectroscopy for Molecular Vibration: An Analysis of Potential Surfaces in a Dissipative Environment

MARUYAMA, Yutaka; TANIMURA, Yoshitaka

A molecular vibrational mode in condensed phases is studied using a quantum Fokker-Planck equation, which can treat a molecular system with any shape of potential coupled to a white noise heat-bath. The two-, three-, and four-time correlation functions of Raman polarizability and the dipole moment are calculated as the subject of two-dimensional (2D) spectroscopy for various potential surfaces with different heat-bath coupling strength. The temporally 2D profiles of signal are very sensitive to the potential surfaces and a coordinate dependence of the polarizability or dipole even in the strong damping case. This indicates that 2D spectroscopy allows us to access information of the potential and the polarizability or dipole in the dissipative environment, where the line shape of conventional 1D Raman or infrared spectroscopy is broadened and does not provide such information.

I-J The Condensed Phase Quantum Dynamics of Molecules and Atoms

We investigate quantum dynamics of molecules or atom in condensed phases by means of various statistical physics approaches involving the path integral and Fokker-Planck equation approaches for a reduced density matrix. Effects of dissipation on a quantum rotator, proton tunneling and electron transfer processes are investigated and compared with the classical dynamics.

I-J-1 Quantum Theory of Two-Dimensional Rotator in a Dissipative Environment: Application to Infrared Spectroscopy

SUZUKI, Yoko; TANIMURA, Yoshitaka

[*J. Phys. Soc. Jpn.* **70**, 1167 (2001)]

Quantum coherence and its destruction by coupling to a dissipative environment play important roles in time-resolved optical response. We study a two-time correlation function of a two-dimensional rotator coupled to a harmonic-oscillator bath. Generating functionals of reduced density matrix elements for the rotator degrees of freedom are calculated by diagonalizing the total Hamiltonian with the use of unitary transformations and then performing path integrals. A closed-form expression of linear absorption spectrum for a dipole rotator, *i.e.*, a Fourier transformation of the dipole two-time correlation function, is derived from the

generating functionals characterized by the bath spectral density. Based on the theory, the spectra for a methyl rotation in a toluene are depicted for various damping constants and temperatures. Because of the cyclic boundary condition that is constrained to fit the rotator degree of freedom, the energy states of the rotator in the absence of damping are discrete: the spectra consist of rotational branches, which correspond to change of the angular momentum. Owing to damping, the spectra exhibit a continuous band which is broadened as temperatures increase.

I-J-2 Two Time Correlation Function of a Two-Dimensional Quantal Rotator in a Colored Noise

SUZUKI, Yoko; TANIMURA, Yoshitaka

We study an absorption spectrum of a two-dimensional rotator coupled to a harmonic Gaussian-Markoffian heat bath. Generating functional of reduced density matrix elements for the rotator degrees of freedom in the Gaussian-White case have been developed and are presented compactly in the recent letter. We extend it to the Gaussian-Markoffian case and show the detailed calculation in this paper. A linear absorption spectrum for a dipole rotator is analytically derived from the generating functional. Representative calculations for a methyl rotator in a toluene of the spectra are presented with the use of the analytical result. Plots for various damping strength, cutoff frequency, and temperatures take into account the environmental effect to the dynamical properties of the dipole moment.

I-J-3 Coherent Control of Nonclassical Effects in Quantum Optical Three-Level Atomic System

DU, Si-de; TANIMURA, Yoshitaka

Nonclassical effects are theoretically investigated in the interaction of a single three-level atom with a single one-mode quantized cavity field. The atom under consideration has two closely spaced excited levels and one ground-state level. When the atom is coherently excited into a superposition of the two excited states, there exists quantum interference between two transition channels which are stimulated by the cavity field initially in coherent states. We have discussed influence of quantum interference on collapses and revivals, squeezing and antibunching. It is discovered that the revival patterns strongly depend on quantum interference, and quantum interference can produce strong squeezing and antibunching. Our results are useful for understanding and controlling nonclassical effects.

I-K Theoretical Studies of Correlated Electron Systems

We study biorthogonal formulation of correlated electron system represented in the second quantized form. We illustrate the transcorrelated Hamiltonian approach and discuss the self-consistent field theory using biorthogonal orbitals.

I-K-1 Biorthogonal Approach for Explicitly Correlated Calculations Using the Transcorrelated Hamiltonian

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A biorthogonal formulation is applied to the nonhermite transcorrelated Hamiltonian, which treats a large amount of the dynamic correlation effects implicitly. We introduce biorthognal canonical orbitals diagonalizing the nonhermite Fock operator. We also formulate many-body perturbation theory for the transcorrelated Hamiltonian. The biorthogonal self-consistent fields followed by the second order perturbation theory are applied to some pilot calculations including small atoms and molecules. We illustrate the transcorrelated Hamiltonian approach and discuss the self-consistent field theory using biorthogonal orbitals. We develop MBPT for the transcorrelated Hamiltonian based on the biorthogonal formalism. We also explain the approximate calculations of three-electron integrals, which appear in the transcorrelated method.