I-K 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-K-1 Probing a Colored-Noise Induced Peak of a Strongly Damped Brownian System by One- and Two-Dimensional Spectroscopy

SUZUKI, Yoko; TANIMURA, Yoshitaka

[*Chem. Phys. Lett.* **358**, 51 (2002)]

When dynamics of a system strongly coupled to a white-noise environment is overdamped, in linear spectroscopy, the spectrum is observed as one peak near zero vibrational frequency. We found, however, that if the noise induced by the environment is colored and its correlation time is long, there is an additional peak at a frequency different from the system. We study the multi-dimensional spectrum, to observe the interplay between the overdamped motion and the weakly damped motion induced by the colored noise. Finally, we discuss the connection between the peak due to the colored noise and the Boson peak found in glass materials and supercooled liquids.

I-K-2 Vibrational Spectroscopy of a Harmonic Oscillator System Nonlinearly Coupled to a Heat Bath

KATO, Tsuyoshi; TANIMURA, Yoshitaka

[*J. Chem. Phys.* **117**, 6221 (2002)]

Vibrational relaxation of a harmonic oscillator nonlinearly coupled to a heat bath is investigated by the Gaussian-Markovian quantum Fokker-Planck equation approach. The system-bath interaction is assumed to be linear in the bath coordinate but linear plus square in the system coordinate modeling the elastic and inelastic relaxation mechanisms. Interplay of the two relaxation processes induced by the linear-linear and square-linear interactions in Raman or infrared spectra is discussed for various system-bath couplings, temperatures and correlation times for the bath fluctuations. The one-quantum coherence state created through the interaction with the pump laser pulse relaxes through different pathways in accordance with the mechanisms of the system-bath interactions. Relations between the present theory, Redfield theory and stochastic theory are also discussed.

I-K-3 Two-Dimensional Raman and Infrared Vibrational Spectroscopy for a Harmonic Oscillator System Nonlinearly Coupled with a Colored Noise Bath

KATO, Tsuyoshi; TANIMURA, Yoshitaka

[*J. Chem. Phys.* submitted]

Higher-order vibrational response functions of a harmonic oscillator are reconsidered by assuming a nonlinear coupling with a heat-bath from a quantum Fokker-Planck equation approach. In addition to a conventional linear-linear (LL) system-bath interaction, we consider a square-linear (SL) interaction in a Brownian oscillator model. The LL interaction yields vibrational energy relaxation, while the SL interaction mainly yields phase relaxation. The dynamics of a harmonic system are investigated by numerically integrating the Gaussian-Markovian Fokker-Planck equation under the condition of a colored and strong system-bath fluctuation, where the conventional perturbative approach cannot be applied. The response functions for the fifth-order nonresonant Raman and the third-order infrared (or equivalently the second-order infrared and the seventh-order nonresonant Raman) processes are calculated under the various combination of the LL and SL coupling strength. Results of two-dimensional response demonstrate that this spectroscopic technique is very sensitive to the mechanism of system-bath coupling and the correlation time of bath fluctuation; the signals exhibit echolike peak both in the fifth-order Raman and the third-order IR case, if the SL coupling is strong and the bath fluctuation is slow. We discuss the primary optical transition pathways involved in two-dimensional spectroscopy to study the echolike behavior. The optical pathways of the fifth-order Raman response from an "anisotropic" medium are newly found which were predicted by neither the weak system-bath coupling theory nor the conventional Brownian harmonic oscillator model.

I-K-4 Two-Time Correlation Function of a Two-Dimensional Quantal Rotator in a Colored Noise

SUZUKI, Yoko; TANIMURA, Yoshitaka

[*J. Phys. Soc. Jpn.* **71**, 2414 (2002)]

We study an absorption spectrum of a two-dimensional rotator coupled to a colored harmonic-oscillator bath. The absorption spectrum is analytically calculated from the generating functional of a reduced density matrix element for the rotator degrees of freedom. In the previous letter,[1)] the analysis of spectrum is limited to a white noise case. In this paper, we extend our theory to a colored noise case. We present the spectra for different temperatures, damping strength, and the correlation time of the noise. For a weakly damped rotator, at low temperatures, the spectra are sensitive to the system

dynamics that is determined by the quantization of the rotational motion. Such a quantized rotational motion depends on the noise effects. Hence we observe the peak shifts by the noise correlation time. For a strongly damped rotator, we find the bimodal spectrum in the slow modulation case. One of the peaks is caused by the effect of the colored noise, which dose not appear in the case of the white noise. This peak is related to a librational motion induced by the coupling between the system and the bath oscillators with the near zero frequencies.

Reference

1) Y. Suzuki and Y. Tanimura, *J. Phys. Soc. Jpn.* **70**, 1167 (2001).

I-K-5 Energy-Level Diagrams and Their Contribution to Two-Dimensional Spectroscopic Signal: Distinction between Relaxation Mechanisms by Two-Dimensional Spectroscopy

OKUMURA, Ko[1]; TANIMURA, Yoshitaka
([1]Ochanomizu Univ.)

We develop explicit Feynman rule for energy-level diagram or the corresponding physical processes in the Liouville space. Thereby we completely identify such diagrams and processes contributing to the two-dimensional response function in the Brownian oscillator model. We classify such diagrams or processes in quartet and numerically present signal separately from each quartet of diagrams or Liouville-space processes. We find that signal from each quartet is distinctly different from the others; we can identify each peaks in frequency domain with a certain quartet. This offers the basis for analyzing and assigning actual two-dimensional peaks and suggests the possibility of Liouville-space-path selective spectroscopy. As an application and also as a demonstration we present an example in which two familiar homogeneous mechanisms of relaxation are distinguished by existence or non-existence of certain peaks on the two-dimensional map; appearance or disappearance of certain peak is sensitive to the coupling mechanism. We also comment on some controversy on the result of a response function in the bilinear Brownian oscillator model.

I-K-6 Two-Dimensional Spectroscopy for a Two-Dimensional Rotator Coupled to a Gaussian-Markoffian Noise Bath

SUZUKI, Yoko; TANIMURA, Yoshitaka

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-K-7 Absorption Spectra for Two-Dimensional Rotator with Nonlinear System-Bath Coupling

SUZUKI, Yoko; TANIMURA, Yoshitaka

We investigate the relaxation process in a two-dimensional rotator system nonlinearly coupled to a harmonic heat bath with the use of the perturbation theory. In the previous works, we restricted our study to the linear-linear coupling between the system and the bath and obtained the continuous spectra. However, in the many realistic problems, the absorption spectra show discrete lines. To take into account experiments, we assume the system-bath interaction to be linear in the bath coordinate but the periodic function in the system coordinate. Using this coupling, we derive the absorption spectra of the rotator system which relates to a two-time correlation function of the dipole moment.

I-L 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 Monte Carlo method for a reduced density matrix. Effects of dissipation on a spin system, proton tunneling and electron transfer processes are investigated and compared with the classical dynamics.

I-L-1 The Energy Landscape for Solvent Dynamics in Electron Transfer Reactions: A Minimalist Model

TANIMURA, Yoshitaka; LEITE, Vitor B. P.[1]; ONUCHIC, Jose' Nelson[2]
([1]Univ. Estadual Paulista; [2]Univ. California, San Diego)

[*J. Chem. Phys.* **117**, 2172 (2002)]

Energy fluctuations of a solute molecule embedded in a polar solvent are investigated to depict the energy landscape for solvation dynamics. The system is modeled by a charged molecule surrounded by two layers of solvent dipolar molecules with simple rotational dynamics. Individual solvent molecules are treated as simple dipoles that can point toward or away from the central charge Ising spins. Single-spin-flip Monte Carlo kinetics simulations are carried out in a two-dimensional lattice for different central charges, radii of outer shell, and temperatures. By analyzing the density of states as a function of energy and temperatures, we have determined the existence of multiple freezing transitions. Each of them can be associated with the freezing of a different layer of the solvent.

I-L-2 A Quantum Master Equation with a Langevin Force; a Realization of a Real-Time Quantum Monte-Carlo Simulation in a Dissipative Environment

TANIMURA, Yoshitaka

A reduced description of a two-level system for a spin-Boson system in a functional integral form is considered. The thermal activation term in the Feynman-Vernon influence functional is expressed as a contribution from a Langevin force with use of an auxiliary function with Gaussian probability distribution. A quantum master equation with the Langevin force, which is valid at any bath temperature without using a rotating wave approximation, is deduced by constructing the finite difference expression of the density matrix elements. The equation amenable to carry out a real-time Monte Carlo simulation, since in addition to a damping term, it contains an external random force. The temperature effects are taken into account through the correlation function of the random force, which is related with the damping term through the fluctuation-dissipation theorem. Trajectories of a quantum random walk numerically generated by solving the equation are presented and discussed.

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

HINO, Osamu[1]; TANIMURA, Yoshitaka; TEN-NO, Seiichiro[2]
([1]Univ. Florida; [2]Nagoya Univ.)

[*J. Chem. Phys.* **115**, 7865 (2001)]

A biorthogonal formulation is applied to the non-Hermite transcorrelated Hamiltonian, which treats a large amount of the dynamic correlation effects implicitly. We introduce biorthogonal canonical orbitals diagonalizing the non-Hermitian Fock operator. We also formulate many-body perturbation theory for the transcorrelated Hamiltonian. The biorthogonal self-consistent field followed by the second order perturbation theory are applied to some pilot calculations including small atoms and molecules.

I-M-2 Application of the Transcorrelated Hamiltonian to the Linearized Coupled Cluster Singles and Doubles Model

HINO, Osamu[1]; TANIMURA, Yoshitaka; TEN-NO, Seiichiro[2]
([1]Univ. Florida; [2]Nagoya Univ.)

[*Chem. Phys. Lett.* **353**, 317 (2002)]

Explicitly correlated calculations using the trans-

correlated Hamiltonian are performed at the level of linearized coupled cluster (LCC) theory. Two deferent reference functions are employed in the calculations and the results are compared with those of the conventional LCC. The application to the water molecule shows a markedly better convergence of the correlation energies when the transcorrelated Hamiltonian is used than in the conventional approach. We also present results for some other ten-electron systems, Ne, HF, NH_3, and CH_4.