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

I-K-1 The Fifth- and Seventh-Order Two-Dimensional Raman Spectroscopy for Harmonic System with Nonlinear System-Bath Interactions: Gaussian-White Case

STEFFEN, Thomas[1]; TANIMURA, Yoshitaka
(*[1]Univ. Groningen*)

The quantum Fokker-Planck equation is derived for a system that is nonlinearly coupled to a harmonic heat bath. The interaction between the two subsystems is assumed to be linear in the bath coordinate but quadratic in the system coordinate. The relaxation-induced dynamics of the system are investigated by simulating the third-, fifth-, and seventh-order Raman response of a harmonic mode. The Wigner phase space representation of the wave packet dynamics provides useful insight in the nonlinear character of the system-bath coupling. For weak system-bath coupling the third-order Raman response can be explained by the perturbation theory of Okumura and Tanimura, which predicts a line width linear proportional to temperature. When the two subsystems interact strongly, the first-order perturbation theory breaks down. The impulsive fifth- order Raman response shows that in addition to the frequency fluctuations induced by the bath higher-order energy transfer between system and bath has to be considered. The nonlinearity of the system-bath interaction yields also an interesting feature in the impulsive seventh-order Raman echo response: The calculations predict a finite signal for the case of a harmonic potential and a linear coordinate dependence of the polarizability while for linear system-bath coupling this response vanishes completely due to destructive interference of different Liouville space pathways.

I-K-2 The Fifth and Seventh Order 2D Raman Spectroscopy for Harmonic System with Nonlinear System-Bath Interactions: Gaussian-Markovian Case

TANIMURA, Yoshitaka; STEFFEN, Thomas[1]
(*[1]Univ. Groningen*)

A potential system nonlinnealy coupled to a Gaussian-Markovian heat bath is considered. The interaction between the two subsystems is assumed to be linear in the bath coordinate but quadratic in the system coordinate. This model delivers the frequency modulation of the potential and can be regarded as a half-breed of a Brownian oscillator model and stochastic two-level model. We deduce the quantum Fokker-Planck equation for a Gaussian-Markovian noise bath for this nonlinear system-bath interaction in the hierarchy form. An inhomogeneous broadening of molecules, which was traditionally modeled by the overdamped limit of a stochastic two-level system, is studied for a harmonic potential system by numerically integrating the equation of motion. The third-, fifth- and seventh-order off-resonant Raman signal, which are expressed by the two-, three-, and four-time correlation function of polarizability, respectively, are calculated as the subject of two-dimensional Raman spectroscopy. Theses signals are very different from the result of a Brownian oscillator case. Raman echo peaks, which were predicted from the stochastic two-level theory, are observed in the two-dimensional seventh-order signal. It was shown that the seventh-order two- dimensional Raman spectroscopy is useful to measure the inhomogeneity of liquids, in the case where the fifth-order 2D signals were very weak.

I-K-3 Structural Information from Two-Dimensional Fifth-Order Raman Spectroscopy

OKUMURA, Ko; TANIMURA, Yoshitaka; TOKMAKOFF, Andrei[1]
(*[1]MIT*)

Two-dimensional (2-D) fifth-order Raman spectroscopy is a coherent spectroscopy that can be used as a structural tool, in a manner analogous to 2-D nuclear magnetic resonance (NMR) but with much faster time scale. By including the effect of dipole-induced dipole interactions in the molecular polarizability, it is shown that 2-D Raman experiments can be used to extract distances between coupled dipoles, and thus elucidate structural information on a molecular level. The amplitude of cross peaks in the 2-D Raman spectrum arising from dipole-induced dipole interactions is related to the distance between the two dipoles (r) and the relative orientation of the dipoles. In an isotropic sample with randomly distributed dipole orientations, such as a liquid, the cross peak amplitude scales as r^6 In an anisotropic sample such as a solid, where the orientational averaging effects do not nullify the leading order contribution, the amplitude scales as r^3. These scaling relationships have analogy to the dipole coupling relationships that are observed in solid state and liquid 2-D NMR measurements.

I-K-4 Two-Dimensional Line Shape Analysis of Photon Echo Signal

OKUMURA, Ko; TOKMAKOFF, Andrei[1]; TANIMURA, Yoshitaka
(*[1]MIT*)

We analyze the two-dimensional (2D) line shape obtained by 2D Fourier transforming the time-domain response of a photon echo signal as a function of the two coherence periods, t_1 and t_3. The line shape obtained for a two level system with homogeneous and inhomogeneous broadening is shown to be sensitive to the magnitude of both of these line-broadening mechanisms. It is shown that the ellipticity of the 2D

line shape can be related to the ratio of homogeneous to inhomogeneous broadening.

I-K-5 Cage Dynamics in the Third-Order Off-Resonant Response of Liquid Molecules: A Theoretical Realization

OKUMURA, Ko; BAGCHI, Biman[1]; TANIMURA, Yoshitaka
(*[1]Indian Inst. Sci.*)

It is generally believed that the ultrafast initial spectroscopic response from the molecules in the condensed phase originates from small amplitude inertial motions within the cage formed by the nearest-neighbor solvent molecules surrounding the probe, or the cage effect. However, no quantitative estimate of this dynamics has been available for the currently popular experiments which measure the third-order off-resonant response. In this work, we fill this gap by a microscopic approach and demonstrate that the cage dynamics alone can produce the initial rise in the subpicosecond (≈ 200 fs) range in the third-order response. A simple analytical expression for the initial Gaussian time constant relevant to various kinds of the third-order off-resonant experiments is presented, which is found to be rather strongly dependent on the temperature. Connection with the non-polar solvation dynamics is also discussed.

I-K-6 Dynamical Stokes Shift Observed by Two-Dimensional Raman Spectroscopy

SUZUKI, Yoko; TANIMURA, Yoshitaka

We analyze the effect of relaxation process of wavepackets created in the electronic excited state on off-resonant two-dimensional Raman spectroscopy, employing the Brownian motion model with a non-equilibrium initial condition described by a displaced Gaussian wavepacket. We calculate three-time correlation functions of the excited state polarizability, which correspond to the fifth-order Raman signal in the excited state by using the Feynman's path integral formalism. It is found that the fifth-order signal is sensitive to the initial position of the Gaussian wavepacket not only for the underdamped case but also for the overdamped case.

I-K-7 A Thermal Bath Induced New Resonance in Linear and Nonlinear Spectra of Two-Level Systems

GANGOPADHAYAY, Gautam[1]; GHOSHAL, Sharmistha[1]; TANIMURA, Yoshitaka
(*[1]S. N. Bose Natl. Cent. Basic Sci.*)

Within the scope of generalized master equation we have shown the effect of bath with finite bandwidth on the linear absorption and on the resonance fluorescence and absorption spectra of a driven two-state system. It is found that depending on the bandwidth and temperature of the bath a reversible dynamics may set in even in the case of linear absorption induced by weak field. At higher temperature the bath induces new resonance on the spectral profiles.

I-L Ab Initio Molecular Orbital Studies of Organic Conductors

I-L-1 Structures and Electronic Phases of the Bis(Ethylenedithio)Tetrathiafulvalene (BEDT-TTF) Clusters and κ-(BEDT-TTF) Salts: A Theoretical Study Based on Ab Initio Molecular Orbital Methods

IMAMURA, Yutaka[1]; TEN-NO, Seiichiro; YONEMITSU, Kenji; TANIMURA, Yoshitaka
(*[1]GUAS*)

Electronic and geometrical structures of bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecules are studied using ab initio molecular orbital methods. The optimized structure of a BEDT-TTF monomer is close to the experimental one within errors of 0.02 Å and 0.5 degree in bond length and angle, respectively, except the ethylene group. Ab initio parameters such as transfer integrals and Coulomb interactions are determined from the BEDT-TTF dimer and tetramer calculations. Using model Hamiltonians with the ab initio parameters, we investigate the electronic states based on the exact diagonalization method. The results show that the ground state has antiferromagnetic correlation which is consistent with experimental results. We study the effects of long-range Coulomb interactions employing the 2-D extended Hubbard model with the Hartree-Fock approximation. It is found that the ground state shows various phases; antiferromagnetic, charge ordering, and paramagnetic ones, controlled by the long-range interactions.

I-L-2 Ab Initio MO Studies on Electronic States of DCNQI Molecules

IMAMURA, Yutaka[1]; TEN-NO, Seiichiro; TANIMURA, Yoshitaka
(*[1]GUAS*)

Electronic and geometrical structures of DR-DCNQI molecules (R = H, Cl, Br, I, Me and OMe) were studied by performing ab initio MO calculations at the HF/DZP level. We carried out DCNQI monomer calculations and found that the optimized structures are close to experimental ones within errors of 0.04 Å in a six-

membered ring. We then discussed the basis set dependence of geometrical parameters and concluded that the polarization functions improve the description for double and triple bond states. Ab initio parameters such as transfer integrals were calculated for DCNQI dimers and trimers and compared with formerly calculated parameters. We found that the transfer integrals correlate well with lattice parameters of the c axis.

I-L-3 Theoretical Study on Electron Correlation of 1-D (DCNQI)$_2$M (M = Li, Ag)

IMAMURA, Yutaka[1]; **TEN-NO, Seiichiro**; **YONEMITSU, Kenji**; **TANIMURA, Yoshitaka**
(*[1]GUAS*)

We study electronic states of the (DCNQI)$_2$M (M = Li and Ag) salts based on the full configuration interaction (FCI) method using effective Hamiltonians derived from the ab initio molecular orbital theory. FCI results of the DCNQI tetramer and octamer models indicate that the ground state has the antiferromagnetic and charge ordering correlations. It corresponds to the 2 kF spin density wave and 4 kF charge density wave states (SDW and CDW). In the octamer model, it is also found that some low-lying excited states have similar spin-flipped CDW correlations and the antiferromagnetic correlation is weakened.Electronic and geometrical structures of DR-DCNQI molecules (R = H, Cl, Br, I, Me and OMe) were studied by performing ab initio MO calculations at the HF/DZP level. We carried out DCNQI monomer calculations and found that the optimized structures are close to experimental ones within errors of 0.04 Å in a six-membered ring. We then discussed the basis set dependence of geometrical parameters and concluded that the polarization functions improve the description for double and triple bond states. Ab initio parameters such as transfer integrals were calculated for DCNQI dimers and trimers and compared with formerly calculated parameters. We found that the transfer integrals correlate well with lattice parameters of the *c* axis.