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 dynamics 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 Two-Dimensional Line Shape Analysis of Photon Echo Signal

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[*Chem. Phys. Lett.* **314**, 488(1999)]

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-2 Cage Dynamics in the Third-Order Off-Resonant Response of Liquid Molecules: A Theoretical Realization

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[*Bull. Chem. Soc. Jpn.* **73**, 873 (2000)]

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-3 Two-Dimensional Spectroscopy for Harmonic Vibrational Modes with Nonlinear System-Bath Interactions: Gaussian-Markovian Case

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[*J. Phys. Soc. Jpn.* **69**, 4095 (2000)]

The relaxation processes in a quantum system nonlinearly coupled to a harmonic Gaussian-Markovian heat bath are investigated by the quantum Fokker-Planck equation in the hierarchy form. This model describes frequency fluctuations in the quantum system with an arbitrary correlation time and thus bridges the gap between the Brownian oscillator model and the stochastic model by Anderson and Kubo. The effects of the finite correlation time and the system-bath coupling strength are studied for a harmonic model system by numerically integrating the equation of motion. The one-time correlation function of the system coordinate, which is measured in conventional Raman and infrared absorption experiments, already reflects the inhomogeneous character of the relaxation process. The finite correlation time of the frequency fluctuations, however, is directly evident only in the two- and three-time correlation function as probed by multidimensional spectroscopic techniques such as the Raman echo and the fifth-order 2D Raman experiment.

I-K-4 Two-Dimensional Spectroscopy and the Harmonically Coupled Anharmonic Oscillators

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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-K-5 Two-Dimensional Raman and Infrared Signals Measured from Different Phase-Matching Conditions

KATO, Tsuyoshi; TANIMURA, Yoshitaka

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 achived experimentally.

I-L Quantum dynamics in the condensed phases

We investigate quantum dynamics of molecules in the 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-L-1 Path-Integral Approach to Rotational Relaxation Processes of a Molecule in Solvation

SUZUKI, Yoko; TANIMURA, Yoshitaka

A two-dimensional rotator coupled to a Brownian oscillators bath is considered to study rotational relaxation processes in a dissipative environment. Nonequilibrium generating functional of the rotator is evaluated by transforming the Hamiltonian in diagonal form and by carrying out the functional integrals of the bath coordinates and the rotator angel. The difference between the free particle and the rotator arises from the cyclic boundary condition supplied for the rotator angel. Using the generating functional, we obtain the analytical expression of optical response function, which is defined by the two-time correlation function of dipole moment or polarizability of the rotator, is obtained from the generating functional. The qunatal dynamics of rotator under the influence of the heat-bath is investigated by calculating Raman spectrum for various temperatures and the coupling strength between the rotator and the bath.

I-L-2 Proton Tunneling in a Dissipative Environment: Raman Response and Reaction Rate

TANIMURA, Yoshitaka

A double well potential system coupled to a colored Brownian oscillators bath is considered to study tunneling dynamics in a dissipative environment. The quantum Fokker-Planck equation for a colored nose bath in a low temperature is reduced in a multi-dimensional hierarchy form. A chemical reaction rate and Raman response spectrum are calculated for various coupling strength and temperature. Compared with the classical results, which are obtained by solving classical Fokker-Planck equation, we investigate the effects of tunneling processes on the reaction rate and spectrum. In the quantal case, the low frequency peak is observed in the Raman spectrum, which is due to the level splitting of vibrational levels induced by tunneling.

I-M Soft Matter Physics in Biomimetic Systems

Various efforts have been undertaken to make smart things useful in daily life by mimicking biomaterials. Such field has been propelled mainly from technological and practical viewpoint. However, this field has a great potential to give new ideas, concepts, and problems to soft matter physics as pure science. We have been studied two such examples, *i.e.*, nacre, which typically constitutes seashells, and a certain kind of artificial muscle, which can be driven by a small electric field.

I-M-1 On the Toughness of Biocomposites

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[*C. R. Acad. Sci. Paris* **IV**, 257 (2000)]

The fracture energy G of nacre (a stacking of aragonite/organic layers) is much larger than the corresponding energy G_0 for pure aragonite (although the organic cement thickness d_0 is very small: nanometers). We present here a qualitative explanation for this difference. The basic idea is that a weak cement reduces drastically the stress concentration near the fracture tip.

I-M-2 Why is Nacre Strong?: Elastic Theory and Fracture Mechanics for Biocomposites with Stratified Structures

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[*Eur. Phys. J. E.* submitted]

Nacre, stratified ceramic layers surrounded by organic matrix, is a tough material found inside certain seashells. We construct a coarse grained elastic energy

for such an anisotropic system and present an analytic solution for a notch crack normal to the stratified sheets. This analysis proves the reduction in stress concentration which was announced in our earlier work (P. G. de Gennes and K. Okumura, *C. R. Acad. Sci. Paris* t.1, Serie IV, 257 (2000)) and the related increase in toughness.

I-M-3 Mechanoelectric Effects in Ionic Gels

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[*Europhys. Lett.* **50**, 513 (2000)]

Certain fluorinated ion-exchange membranes, when swollen and suitably plated by conducting electrodes, display a spontaneous curvature increasing with the applied electric field E. There is also an inverse effect, where an imposed curvature induces an electric field (in open circuit conditions). We present here a compact description of these effects in the linear regime, and in static conditions: this is based on linear irreversible thermodynamics, with two driving forces (E and a water pressure gradient Δp) and two fluxes (electric current and water current). We also give some qualitative estimates of the three Onsager coefficients, which come into play.