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**INTERMOLECULAR AND INTRAMOLECULAR
VIBRATIONAL RELAXATION AND ENERGY TRANSFER****FINAL REPORT**

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(i) Molecular Semiclassical Dynamics in Liouville Space: A Unified Description of Vibrational Relaxation, Nonlinear Spectroscopy and Rate Processes

Much of the current effort in semiclassical molecular dynamics is focused on the development of efficient methods for the numerical solution of the Schrödinger equation for interacting many-body systems. The calculation of molecular dynamical processes such as energy transfer, vibrational relaxation, scattering processes, and spectral lineshapes depends crucially on the development of suitable approximate methods for propagating the molecular wave function. Performing dynamical calculations in Liouville space,^[1-6] using the density matrix (instead of the wavefunction) offers a major theoretical challenge. The connection between classical and quantum mechanics is much more transparent in Liouville space, particularly if we make use of the Wigner representation, which allows for a systematic expansion of the dynamics in powers of $\hbar$. The development of a reduced description of molecular processes in which we follow explicitly only a few chosen degrees of freedom, can only be achieved using the density matrix, since an ensemble-averaged wavefunction (unlike the density matrix) has no physical significance. The future of molecular dynamics in large polyatomic molecules and in condensed phases depends, therefore, on the extension of the semiclassical methods to the evolution of the density matrix in Liouville space. We have developed a new type of self-consistent semiclassical reduced equations of motion in Liouville space,^[1-6] which are based on projection operator techniques of nonequilibrium statistical mechanics. To lowest order, the equations provide a time-dependent mean field approximation, which can be systematically improved. The method is based on constructing a Gaussian propagator, whose equations of motion are obtained by requiring that the first two moments of the coordinates and the momenta have the exact time evolution. It is particularly suitable for the calculation of intramolecular and intermolecular dynamics, correlation functions, and electronic lineshapes. The key quantity in our formulation is the Liouville space generating function (LGF).

When applied to the quantum propagation of interacting many body systems, the LGF is simply a maximum entropy approximation for the density matrix. In problems involving electronic transitions (optical lineshapes, nonadiabatic transitions) the LGF is not equal to the density matrix since its propagation from the left and from the right may be with different Hamiltonians corresponding to the various relevant electronic states. In that case the LGF is not hermitian and acquires a complex phase, which plays an important role in the system dynamics and spectral properties. The definition of the LGF and the systematic computational scheme for its evaluation constitute one of the major accomplishments of this research program. The LGF allowed us to develop a unified description of molecular dynamics and vibrational relaxation, as reflected in nonlinear optical spectroscopy and rate processes such as electron transfer or isomerization.^[7-13] In the case of electron transfer we start with a nonadiabatic (two-state) model and expand the rate perturbatively in the nonadiabatic coupling V . Optical lineshapes are usually calculated by expanding the molecular response in powers of the electrical field E . Both expansions are expressed in terms of correlation functions. To lowest order (V^2), the nonadiabatic rate is given by the Fermi golden rule; the optical response to first order in E (e.g., the absorption lineshape) is given by the linear susceptibility $\chi^{(1)}$. Both quantities are related to a two time correlation function of the solvent. In the next order (V^4), the rate is related to a four point correlation function. The same correlation function enters in the calculations of the third order nonlinear susceptibility (to order E^3), $\chi^{(3)}$ and 4WM. This connection provides a novel way of interpreting both types of experiments in a unified way. Optical measurements constitute the most sensitive and accurate probes for solvation dynamics. The relations established in this work allow the direct use of information obtained in optical measurements in the calculation of rate processes. A new insight is provided for the transition from nonadiabatic to adiabatic rates, and the relevant solvent timescale which controls the adiabaticity is precisely defined. The recent feature article in J. Phys. Chem.^[12] summarizes these developments.

(ii) Intramolecular Vibrational Redistribution

The effort in the field of intramolecular dynamics was devoted towards developing efficient correlation function, "eigenstate-free" methods for the calculation of intramolecular line broadening in absorption and dispersed fluorescence spectra of large anharmonic polyatomic molecules.^[14-16] A comprehensive calculation was performed on the dispersed supersonic beam fluorescence spectra of Anthracene.^[16] Our calculations provided a quantitative interpretation for the experimental lineshapes and allowed us to extract intramolecular vibrational relaxation rates as well as electronic dephasing timescales from these frequency domain spectra. We have also calculated

the absorption lineshapes and the Raman excitation profiles of model anharmonic molecules at finite temperatures using the Liouville-space generating function (LGF). Excellent agreement with the exact spectra was obtained.^[5] In addition we have explored the possibility of achieving a selective vibrational excitation. We found that it is possible to eliminate intramolecular vibrational redistribution when a sufficiently strong laser field is used. This is analogous to the selective averaging technique in NMR.^[17,18]

iii) Vibrational and Radiative Dynamics in Molecular Clusters

Supersonic beam studies of molecular clusters provide detailed information regarding intermolecular interactions and dynamical processes. Molecular clusters provide a unique link between microscopic properties of isolated molecules and molecular dynamics in condensed phases. In addition there is a considerable interest in the studies of molecular aggregates in condensed phases.

The calculation of energy transfer and radiative relaxation in molecular aggregates is a fundamental problem which we addressed.^[19] Consider an aggregate consisting of N identical two level molecules. Simple back of the envelope calculation shows that when the aggregate size is much smaller than the optical wavelength, its radiative decay rate will scale linearly with N and will be given by $N\gamma$, γ being the radiative decay rate of a single molecule. This simple relation is sometimes used to evaluate the aggregate size by measuring its radiative decay rate. It is clear that this scaling will not hold as N is sufficiently large so that the aggregate size becomes comparable to the optical wavelength, and the dipole approximation no longer holds. This is the reason why the radiative lifetime in a solid ($N \rightarrow \infty$) is not infinitely short. An important effect which was not incorporated in the above argument is the role of the other degrees of freedom (e.g. intramolecular vibrations, and the solvent). The $N\gamma$ radiative rate is a result of a coherent interaction of all the molecules in the aggregate with the radiation field. The interaction with a thermal bath introduces fluctuations which may affect the different molecules in a different way. One possible outcome of such fluctuations is the introduction of intermolecular dephasing which will destroy the coherence among different molecules. We expect that due to the dephasing processes, the $N\gamma$ rate will change into $N_{\text{eff}}\gamma$, where $N_{\text{eff}} < N$ is the effective number of coherently coupled molecules. N_{eff} is expected to attain the limiting value $N_{\text{eff}} = 1$ as the dephasing rate becomes sufficiently large to decouple the radiative dynamics of each molecule.

We have developed a general theory for the radiative and the nonradiative dynamics of molecular aggregates^[19] using an effective Hamiltonian which properly takes the radiative interactions into account. An averaging over the continuum of photons provides a compact way

for calculating the radiative rates and energy transfer in isolated aggregates (in the absence of a thermal bath). In order to treat the dephasing processes we considered the density matrix in Liouville space and developed an effective Liouville operator.^[20] An averaged radiative decay rate S was defined and a closed form expression for N_{eff} was derived.

We have developed a systematic method for calculating nonlinear optical susceptibilities in condensed phases, which incorporates intermolecular forces and spontaneous emission in a consistent way, using the multipolar ($\underline{\mu} \cdot \underline{D}$) Hamiltonian.^[21-23] Reduced equations of motion which couple the electromagnetic field and material variables, were derived for a crystal of point dipoles. The Bloch equations in the local field approximation, which were derived previously using macroscopic considerations, were obtained as a limiting case of the present microscopic theory. We showed that correlations among the molecules and the radiation field are not treated rigorously in the local field approximation, whereas they can be incorporated in a systematic way using the present formalism. An expression for the frequency and wavevector dependent dielectric function $\epsilon(k, \omega)$ was obtained, which generalizes Hopfield's exciton-polariton model. This theory is ideally suited for the calculation of solvation effects on clusters and for studying very large clusters which are expected to have bulk dynamical properties.

(iv) Coherent and Spontaneous Raman, Fluorescence and Four Wave Mixing Spectroscopy

Optical lineshapes of polyatomic molecules provide a direct probe for intramolecular and intermolecular dynamics. The spectral shifts and line broadening and their temporal evolution reflect the intermolecular forces, resulting in vibrational relaxation and electronic and vibrational dephasing processes. Recent developments in laser spectroscopy provide a broad range of frequency-domain and time-domain (femtosecond) linear and nonlinear optical techniques. The absorption lineshapes of polyatomic molecules in condensed phases are usually broad and relatively featureless due to spectral congestion and inhomogeneous broadening, and therefore yield little microscopic information. Nonlinear optical techniques on the other hand usually provide useful dynamical information. The spontaneous emission lineshapes, often consist of progressions of sharp lines (Raman) accompanied by relatively diffuse lineshapes (fluorescence). The Raman lines and their excitation profiles may be used to extract structural constants (vibrational frequencies and nuclear displacements) as well as line broadening parameters. The fluorescence component may yield additional information not present in the Raman profiles. For example, the fluorescence lineshape depends directly on the population distribution of the vibrational levels following the excitation; consequently it provides an excellent probe for

intramolecular and intermolecular vibrational dynamics. Four wave mixing (4WM) spectroscopy constitutes another class of experiments which probe molecular dynamics and relaxation processes. A 4WM process involves the interaction of three laser fields with wavevectors k_1 , k_2 , and k_3 and frequencies ω_1 , ω_2 , and ω_3 , respectively, with the system. A coherently generated signal with a wavevector k_s and frequency ω_s is then detected, where $k_s = \pm k_1 \pm k_2 \pm k_3$ and $\omega_s = \pm \omega_1 \pm \omega_2 \pm \omega_3$. k_s and ω_s are given by any linear combination of the incoming wavevectors and frequencies. The various types of 4WM processes differ by the particular choices of k_s and ω_s , and by the temporal characteristics of the incoming fields. The transient grating, coherent anti-Stokes Raman (CARS), hole-burning, photon-echoes, degenerate four-wave mixing, the Kerr effect are a few examples of common 4WM techniques. 4WM is a phase-matched process in which a macroscopic polarization is created, and the molecules in the sample emit in phase. This results in the directionality of the signal. The Spontaneous Raman and Fluorescence Process, on the other hand, is not phase matched, and the light is emitted in all directions.

We have developed efficient methods for the calculation of 4WM and fluorescence processes of large polyatomic molecules in condensed phases (e.g., solutions, solid matrices, and glasses).^[24-41] The key quantity in this formulation is the nonlinear response function $R(t_3, t_2, t_1)$, which contains all the microscopic information relevant for any type of 4WM and fluorescence spectroscopy. This approach provides an insight into the interrelations among the various 4WM techniques, and it was used to develop several useful models for 4WM in solution and in molecular crystals. A microscopic theory was developed for the transient grating.^[24] The nonlinear susceptibility $\chi^{(3)}$ was calculated for a molecular crystal with interacting absorbers, and a frequency-domain analog of the transient grating was predicted.^[25] The latter is a transport-induced extra resonance, whose lineshape and intensity provide a sensitive probe for the transport processes. This prediction provides an alternative to the current picosecond grating experiments. In addition, we have shown that it is possible to use 4WM spectroscopy to probe long-range spatial correlations near critical points.^[26,27] This is done making use of the two-particle cooperative origin of these processes. A unified stochastic model was developed for $\chi^{(3)}$ and for the nonlinear response function.^[20,30-32] This model is particularly useful for polyatomic molecules in solution and has two distinctively clear advantages over existing theories. First, it allows us to treat a general broadening mechanism with an arbitrary timescale of the bath. Previous treatments were limited to either very slow timescale (inhomogeneous broadening) or very fast time scale (homogeneous broadening). Second, Green function techniques allow us to eliminate most of the summations over intermediate states, which usually make these calculations impossible for large polyatomic molecules.^[29] A theory for picosecond CARS spectroscopy of vibrational dephasing in liquids was developed^[33,34] and resolved an ongoing controversy

regarding the selectivity of the technique (i.e., its capacity to distinguish between homogeneous and inhomogeneous line broadening). We have extended the Liouville space generating function described earlier to incorporate reduced dynamics via Langevin forces. We then derived a closed form expression for the nonlinear response function $R(t_3, t_2, t_1)$, for a general model representing a polyatomic molecule in a thermal bath.^[6] The model consists of a molecule with two electronic levels, each having its vibronic manifold. Coupling to the bath is described by a collective coordinate which is modeled using a stochastic Langevin formulation. In the high friction (Smoluchowski) limit, the model reduces to the Kubo-Anderson stochastic model of spectral lineshapes. Using this model we have calculated a variety of spontaneous Raman, fluorescence and four wave mixing processes. The fluorescence lineshapes and Raman excitation profiles of tetrademethyl- β -carotene in isopentane at 190 and 230 K were analyzed and related to the solvation dynamics and vibrational relaxation.^[36,37] Measurements of the fluorescence were made by the group of Tasumi at the University of Tokyo following our predictions. Our theoretical analysis of these lineshapes resulted in structural information (molecular frequencies and displacements) as well as a detailed understanding of the excited state and solvent dynamics of this system. We found a solvation timescale of 125 fs at 190K, 111 fs at 230K, and a vibrational relaxation timescale of 250 fs at both temperatures. The magnitude of the fluctuations of the electronic energy gap due to interactions with the solvent and with molecular low frequency modes is 423 cm^{-1} at 190K and 480 cm^{-1} at 230K. We further applied our Liouville space generating function to calculate the spontaneous Raman and the coherent anti-Stokes Raman (CARS) lineshapes of β -carotene in various solvents (Alkanes and CS_2). CARS is a coherent four wave mixing technique which provides similar but complementary information to spontaneous Raman. Excellent agreement was obtained with the available experimental spontaneous Raman excitation profiles. The magnitude of the solvent-solute interaction and the solvation timescale for the various solvents were obtained from our theoretical analysis.

We have further extended our Liouville space methodology to develop a general theory for solvation in polar solvents.^[38] The dielectric response of a polar fluid has traditionally been investigated with dielectric relaxation experiments, in which one measures the absorption and dispersion of an applied electromagnetic field, typically in the radio frequency or the microwave regimes. In such an experiment, the fluid responds to an electric field whose wavelength is large (macroscopic) compared to molecular dimensions. The dielectric response of a fluid may also be studied by dissolving a chromophore in the fluid and performing an optical experiment on the chromophore. If the electronic charge distribution of the chromophore changes substantially upon optical excitation, then the solvent response to this electronic rearrangement can have a significant effect on the spectroscopy of the chromophore. In such an experiment, one probes the response of

the fluid to a microscopic electric field that varies spatially on molecular length scales, in contrast to a conventional dielectric relaxation measurement. A primary motivation for understanding the dielectric response of fluids is the role played by the solvent in determining chemical reaction dynamics in solution. The electric fields to which the solvent responds during a chemical transformation vary spatially on molecular length scales.

The development of sources of light pulses of picosecond or femtosecond duration has made possible fluorescence measurements that are both time and frequency resolved. In such an experiment, a short pulse is applied to the sample, and the fluorescence spectrum is measured. The spectrum reflects the dynamics of the solvation process and manifests a time-dependent Stokes shift and line broadening. Femtosecond hole-burning measurements allow the extraction of similar information with a better temporal resolution. Shank and co-workers have recently demonstrated the capabilities of hole-burning spectroscopy in polar dyes in alcohol solvents. We have developed a microscopic theory of time- and frequency-resolved fluorescence and hole-burning measurements of polar, polyatomic molecules in a polar solvent.^[39-41] The lineshapes were expressed in terms of gas phase spectroscopic parameters of the solute, vibrational relaxation rates, laser pulse shapes, and the dynamics of a solvation coordinate. The dynamics are then related to the frequency and wave vector dependent dielectric function of the solvent. Both fluorescence and hole-burning lineshapes were predicted to show significant line narrowing at short times, and to undergo broadening and a red shift as the solvent relaxes. Calculations of fluorescence and hole-burning lineshapes of a polar solute in ethanol were performed.

(v) Excitation Transport and Localization in Disordered Molecular Systems

We have developed the effective dephasing approximation (EDA) which yields a self-consistent mode-coupling equation in Liouville space that provides a simple and systematic method to calculate the localization and transport properties of a quantum particle in a disordered medium.^[42-53] The EDA is based on the physical intuition that the time evolution of the ensemble-averaged density matrix of the particle may be represented by an effective Liouville operator, which, in turn, can be expressed in terms of a generalized frequency-dependent dephasing rate $\Gamma(\epsilon)$, where ϵ is the Laplace transform variable conjugate to the time. The signature of the Anderson localization transition is the crossover from a dephasing rate that is finite at small frequencies to one that displays an infrared divergence. This approach provides a straightforward way to calculate energy or electron transport in a condensed phase medium. The EDA was first applied to the motion of excitons in disordered molecular crystals.^[42-46] The transient grating signal for a crystal, characterized by the Anderson Hamiltonian, was calculated, and it was

demonstrated that four wave mixing spectroscopy provides a sensitive probe of the optical analog of the Anderson transition. We further calculated the ac conductivity for this model.^[45] We have shown that the predictions of the EDA are in full agreement with the results of scaling theories of localization. The EDA was also applied successfully to calculate quantum percolation,^[47] topological and dynamical (time-dependent) disorder with a finite timescale,^[48] and incoherent transport.^[49-53] By transforming to the Wigner representation, it was shown that $\Gamma(\epsilon)$ can be viewed as a generalized scattering rate in a Boltzmann equation with a strong collision kernel. The mapping of the ensemble-averaged equation of motion onto an effective Liouville(Boltzmann) equation is ideally suited for treating a broad range of models with general types of disorder, whether static (the Anderson model, topological disorder, quantum percolation) or dynamical (e.g., electron-phonon and electron-electron coupling). Because it focuses on the ensemble-averaged density matrix rather than on the wave function, the EDA may be used to treat classical as well as quantum systems, and to develop a semiclassical theory of energy and electron localization. This is one of the major advantages of the EDA. Dephasing processes play an important role in controlling the optical properties of matter and form the basis for the theory of coherent and incoherent motion of excitons. The EDA provides a natural connection between the transport and the optical properties of the disordered medium. The EDA represents the first treatment of quantum transport in disordered systems with which coherent motion, incoherent motion, and localization can be treated in a unified fashion.

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