

Unified Theory of Solvation Dynamics in Nonlinear Optical Processes and Electron Transfer

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A novel semiclassical theory which provides a unified description of nonlinear optical lineshapes and molecular rate processes was developed recently.^[1-4] Consider a molecular system with two electronic levels ($|a\rangle$ and $|b\rangle$) in a solvent, whose Hamiltonian is

$$H = |a\rangle H_a \langle a| + |b\rangle H_b \langle b| + H_{\text{int}} \quad (1)$$

where

$$H_{\text{int}} = V (|a\rangle\langle b| + |b\rangle\langle a|). \quad (2)$$

Here H_a and H_b represent nuclear degrees of freedom (both intramolecular and solvent). In nonlinear optical measurements $|a\rangle$ is the ground state and $|b\rangle$ is an electronically excited state and $V = -\mu E(r,t)$ is the dipole coupling with an external electromagnetic field. The same Hamiltonian may represent a rate process (such as electron transfer, or isomerization).^[5,6] In that case V is the nonadiabatic coupling between the two reacting species. In order to express our results in a compact form we introduce two auxiliary quantities. The first is

$$\sigma_j(x) \equiv \langle \delta(x-U) \rho_j \rangle \quad (3)$$

where

$$\rho_j \equiv \exp(-H_j/kT) / \text{Tr} \exp(-H_j/kT), \quad j = a, b \quad (4)$$

$$U + E^0 \equiv H_b - H_a \quad (5)$$

Here U is the solvation coordinate and $E^0 = \hbar\omega_{ba}$ is the energy difference of the minima of H_a and H_b . $\sigma_j(x)$ is the probability distribution of the solvation coordinate U when the system is in the state j . The second quantity is the conditional probability for the solvation coordinate to have the value x at time t , given that it had the value y at $t=0$ and that the system is in the state j , i.e.,

$$W_j(x,t;y) \equiv [\sigma_a(y)]^{-1} \langle \delta[x-U_j(t)] \delta(y-U) \rho_a \rangle, \quad j=a,b \quad (6)$$

$$U_j(t) = \exp(iH_j t) U \exp(-iH_j t), \quad j=a,b. \quad (7)$$

Note that by definition, $W_j(x,0;y) = \delta(x-y)$, and $W_j(x,\infty;y) = \sigma_j(x)$.

The absorption spectrum is simply given by $\sigma_a(\omega - \omega_{ba})$. Similarly, $\sigma_b(\omega - \omega_{ba})$ is the emission (fluorescence) spectrum in a steady state experiment. We next consider two time-resolved spectroscopic techniques which are commonly used in the studies of solvation: fluorescence and hole-burning (pump-probe) spectroscopies.^[3,7] Both measurements are related to the nonlinear polarization $P^{(3)}$, and start with the application of a short pump pulse centered at $t=0$ with frequency ω_1 . In a time-resolved fluorescence measurement, the solvation dynamics when the solute is in the excited electronic state $|b\rangle$ is probed by collecting a spontaneously emitted photon with frequency ω_2 at time t . The fluorescence signal is given by

$$S_{FL}(\omega_1, \omega_2, t) = \omega_1 \omega_2^3 W_b(\omega_2 - \omega_{ba}, t; \omega_1 - \omega_{ba}) \sigma_a(\omega_1 - \omega_{ba}) \quad (8)$$

In a time-resolved hole-burning measurement the absorption spectrum is measured with a probe pulse that is delayed relative to the pump pulse by time t . The hole-burning lineshape $S_{HB}(\omega_1, \omega_2, t)$ is defined as the difference between the absorption coefficient at ω_2 in the absence of a pump pulse and the absorption coefficient at ω_2 measured with a probe pulse that follows a pump pulse, and is given by

$$S_{HB}(\omega_1, \omega_2, t) = \omega_1 \omega_2 [W_b(\omega_2 - \omega_{ba}, t; \omega_1 - \omega_{ba}) + W_a(\omega_2 - \omega_{ba}, t; \omega_1 - \omega_{ba})] \sigma_a(\omega_1 - \omega_{ba}). \quad (9)$$

The rate of a chemical process (e.g., electron transfer) from $|a\rangle$ to $|b\rangle$ is given by^[4]

$$K = \frac{2\pi (V^2/\hbar) \sigma_a(-E^0)}{1 + 2\pi (V^2/\hbar) \sigma_a(-E^0) (\tau_a + \tau_b)} \quad (10)$$

$$\tau_j = [\sigma_a(-E^0)]^{-1} \int_0^\infty dt [W_j(-E^0, t; -E^0) - W_j(-E^0, \infty; -E^0)], \quad j=a,b. \quad (11)$$

Here τ_j is the relaxation time for a fluctuation of the solvation coordinate U at the transition state $U = -E^0$, when the system is in the state j . In the adiabatic limit (small V) the rate is proportional to V^2 and is given by the Fermi Golden Rule. In the opposite (adiabatic) limit the rate is given by the solvent relaxation time $(\tau_a + \tau_b)^{-1}$.

Eqs.(8-11) show that within the semiclassical approximation, the hole-burning and fluorescence measurements probe the same solvent quantities σ_j and W_j which enter into the calculation of rate processes. These equations provide a unique insight on the dynamics of optical and rate processes. The present derivation is very general and does not require the introduction of a specific model for solvation. Apart from considering a two state model and making a semiclassical approximation, we did not have to specify the model any further. We have derived explicit expressions for σ_j and W_j for polar solvents, which relate them to the dielectric function of the solvent $\epsilon(\omega)$.^[3,4]

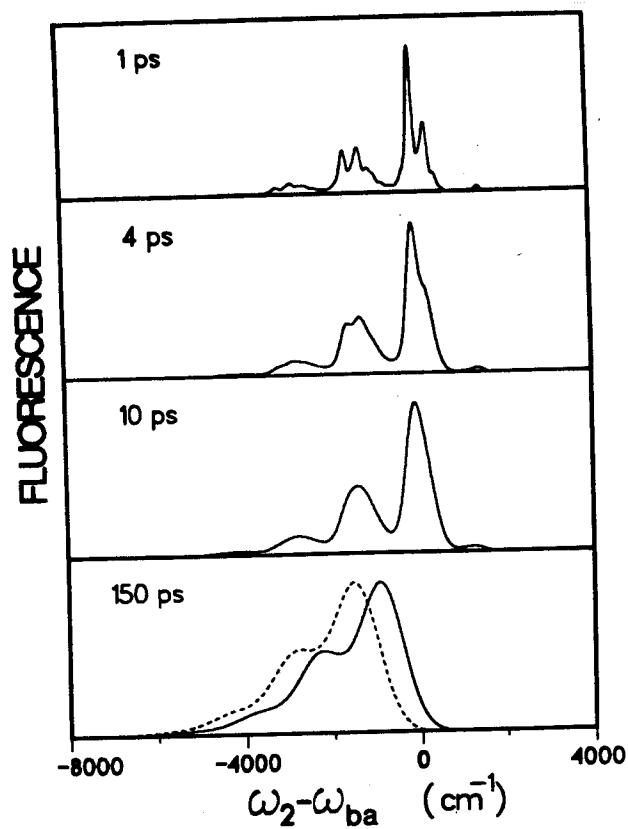
We have calculated fluorescence and hole-burning lineshapes of a polar solute in ethanol at 247 K. For the dielectric function we assumed a Debye model^[3] with a longitudinal relaxation timescale $\tau_L = 150$ ps. In Figure 1 we display the calculated time-resolved fluorescence spectrum of the retinal chromophore in bacteriorhodopsin, which has 29 optically active vibrational modes. The frames show fluorescence spectra measured at successively longer times. Each spectrum is labeled with the observation times in ps, measured from the time at which the sample interacts with the peak of the excitation pulse. The fluorescence spectrum at 1 ps resembles a Raman spectrum, with distinct resonances when $\omega_1 - \omega_2$ equals the frequency difference of two vibronic states of the electronic ground state. The fluorescence spectrum for times short compared to τ_L shows substantial line narrowing relative to the steady-state spectrum, because the excitation pulse is not sufficiently short to excite the entire inhomogeneous distribution of solute molecules. The excitation pulse selects a subset of solute molecules and surrounding solvent environments whose transition frequencies are close to the excitation frequency. For observation times much less than

τ_L , the solvent is effectively static, and the emission is narrow. For observation times comparable to τ_L , the solvent around each excited solute has begun to relax, and the emission broadens, in addition to displaying a red shift. In the final frame the steady-state fluorescence spectrum is reproduced (dashed line) for comparison with the spectrum at $t = \tau_L$. In Figure 2 we show the hole-burning lineshapes for the same system.^[3,7b] The time evolution of the hole-burning lineshape in Figure 2 is qualitatively similar to the behavior of the fluorescence lineshape in Figure 1. The principal difference between the fluorescence and hole-burning measurements is that the former probes only electronically excited molecules, while the latter probes ground-state molecules as well. The hole-burning system contains, therefore, more features corresponding to W_a and W_b .

The general theoretical framework described here provides a unified approach for calculating reaction rates and nonlinear optical lineshapes of polyatomic molecules in solution. Our theory of rate processes, such as electron transfer and isomerization in condensed phases, generalizes the Kramers and the Marcus theories and interpolates between the nonadiabatic and the adiabatic limits. We have demonstrated how solvation dynamics extracted from linear and nonlinear optical measurements (absorption, fluorescence, hole-burning, and $\chi^{(3)}$) may be used to predict electron transfer rates.

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Time-resolved fluorescence spectra of a polyatomic solute in ethanol at 247 K following a 1 ps excitation pulse.^[3] The pump frequency ω_1 is 1528 cm^{-1} above the 0-0 transition.

Hole-burning lineshapes for the same molecular model as Figure 1.

