TIME- AND FREQUENCY-RESOLVED FLUORESCENCE LINE SHAPES AS A PROBE OF SOLVATION DYNAMICS

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Received 21 November 1986; in final form 23 December 1986

The time- and frequency-resolved fluorescence spectrum of a polar molecule in a polar solvent is expressed in terms of gas phase spectroscopic parameters of the solute, vibrational relaxation rates, the dielectric properties of the solvent, and the temporal profile of the excitation pulse. The fluorescence spectrum is narrow at short times, and displays line broadening and a red-shift as the solvent relaxes about the excited solute.

The capacity of a solvent to accommodate a change in the electronic charge distribution of a solute plays an important role in determining the rates of chemical reactions which involve substantial rearrangements of this distribution, such as electron transfer reactions. Fluorescence measurements on polar solutes which undergo a change in dipole moment upon electronic excitation provide an important probe of the solvation process [1–3]. Let us consider a solute molecule and its solvent environment during such an experiment. Prior to the absorption of a photon, the solvent molecules are in equilibrium with the ground-state solute. Upon excitation, the solute–solvent system undergoes a Franck–Condon transition to a state in which the solute dipole has its excited-state value, but the solvent molecules still occupy their previous configuration. The solvent molecules then relax to a configuration of lower energy, which is in equilibrium with the electronically excited solute. If the excited-state lifetime of the solute is long compared to the reorientation time of the solvent dipoles, then a steady-state fluorescence measurement yields the fluorescence spectrum of the solute–solvent system when the solvent is in equilibrium with the excited solute. The peak of this spectrum occurs at lower energy than the peak of the absorption spectrum. The magnitude of this solvent-dependent Stokes' shift is related to the change in dipole moment of the solute and to the dielectric constant and refractive index of the solvent in an equation derived by Ooshika [4], Lippert [1], Mataga [2], McRae [5] and Bakshiev [3]. This equation allows the estimation of the magnitudes of excited-state dipole moments from Stokes' shift measurements. The result is obtained from the Onsager cavity model [6,7], in which the solute is represented by a point dipole in a spherical cavity surrounded by a dielectric continuum.

The development of sources of light pulses of picosecond or femtosecond duration has made possible fluorescence measurements that are both time and frequency resolved [8–11]. In such an experiment, a short pulse is applied to the sample, and the fluorescence spectrum is measured after a given time delay. If the delay time is comparable to the solvent reorientation time, then the spectrum reflects the dynamics of the solvation process, and manifests a time-dependent Stokes' shift. The Ooshika equation for the steady-state Stokes' shift has been generalized to treat the time-dependent Stokes' shift by Mazurenko and Bakshiev [12], Bagchi, Oxtoby and Fleming [13], and van der Zwan and Hynes [14]. Their work is based on a generalized Onsager cavity model, in which the dielectric continuum is characterized by a frequency-dependent dielectric function. It must be noted, however, that a time- and frequency-resolved fluorescence measurement provides more information than the time-dependent Stokes' shift. Fluorescence spectra of polar molecules in polar solvents are typically

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0 009-2614/87/$ 03.50

quite broad (hundreds of wavenumbers), and it is clearly desirable to have a theory that explains the time dependence of the entire fluorescence line shape, as well as the time dependence of the position of the peak of the spectrum. In this work we present a microscopic treatment of the fluorescence experiment, which yields an expression for the complete time- and frequency-resolved fluorescence spectrum in terms of gas phase spectroscopic parameters of the solute, vibrational relaxation rates, dielectric properties of the solvent, and the duration of the excitation pulse.

We consider a solution composed of solute and solvent molecules. The solute molecules are assumed to be present in sufficiently low concentration that interactions between solute molecules are negligible, and we may treat a single solute in its solvent environment. The Hamiltonian $H(t)$ is given by

$$H(t)=H_0-E(t)\sum_{a,b}V_{ab}(|a\rangle\langle b|+|b\rangle\langle a|)+\hbar\omega_2 a_2^+ a_2\,, \tag{1a}$$

$$E(t)=2E_1\cos(\omega_1 t)\exp(-W^2t^2)+\hat{E}_2+\hat{E}_2^+\,, \tag{1b}$$

$$\hat{E}_2=-\mathrm{i}E_2 a_2\exp(-\mathrm{i}\omega_2 t)\,, \tag{1c}$$

$$H_0=|\mathrm{g}\rangle(H_\mathrm{g}+h_\mathrm{g})\langle\mathrm{g}|+|\mathrm{e}\rangle(H_\mathrm{e}+h_\mathrm{e}+\Omega)\langle\mathrm{e}|\,. \tag{1d}$$

H_0 is the Hamiltonian of the material system, the second term in eq. (1a) is the interaction between the material and the radiation field, and the third term in eq. (1a) is the Hamiltonian of the mode of the radiation field into which the molecule emits. The creation and annihilation operators for this mode are a_2^+ and a_2, respectively, and the frequency of the mode is ω_2. The electronic ground and excited states of the solute molecule are denoted $|\mathrm{g}\rangle$ and $|\mathrm{e}\rangle$, respectively. The Hamiltonian of the ground state solute and its solvent environment is partitioned into H_g, which depends on the nuclear coordinates of the solute, and h_g, which depends on the nuclear and electronic coordinates of the solvent. An analogous partitioning is carried out for the electronic excited state. The time dependence of the fluorescence spectrum reflects the sensitivity of the solvent to the electronic state of the solute, which implies that $h_\mathrm{g}\neq h_\mathrm{e}$. Ω denotes the frequency of the 0–0 transition from the lowest vibronic state in the ground electronic state to the lowest vibronic state in the excited electronic state in a gas phase solute molecule. In this work, the labels a and c will be used to refer to vibronic states in the ground state manifold (eigenstates of H_g), and the labels b and d will denote vibronic states in the excited state manifold (eigenstates of H_e). The molecular energy levels that are involved in fluorescence are represented schematically in fig. 1. The frequency of the 0–0 absorption transition in the solvated molecule is denoted ω_{eg}, and is the sum of Ω and a solvent shift. V_{ab} is the transition dipole moment of states a and b. The electric field $E(t)$ is expressed as the sum of two terms. The first term in eq. (1b) is the applied field, which is treated classically, and the second and third terms are operators representing the emitted field, which is treated quantum mechanically. ω_1 is the central frequency of the applied field. In eq. (1c), $E_2=(2\pi\hbar\omega_2/\Omega_0)^{1/2}$, where Ω_0 is the volume of the system. The applied pulse is assumed to have a Gaussian temporal profile, but the treatment that follows can be carried out for a pulse of arbitrary shape. The time-dependent fluorescence spectrum, $S(\omega_1,\omega_2,t)$, is given by the expectation value of the operator $\hat{S}$, which represents the time derivative of the number of photons in the emitted mode:

$$S(\omega_1,\omega_2,t)=\mathrm{Tr}\left[\hat{S}\exp_+\left(-\mathrm{i}\int_0^t \mathrm{d}\tau\, H(\tau)\right)\rho(0)\exp_+\left(\mathrm{i}\int_0^t \mathrm{d}\tau\, H(\tau)\right)\right], \tag{2a}$$

$$\hat{S}=(\mathrm{i}/\hbar)[H(t),a_2^+ a_2]\,. \tag{2b}$$

In eq. (2a), $\rho(0)$ is the density of the material and the radiation at $t=0$, and $\exp_+$ denotes the time-ordered exponential. Substitution of eqs. (1) into eqs. (2) yields a formally exact expression for the time- and frequency-resolved fluorescence spectrum.

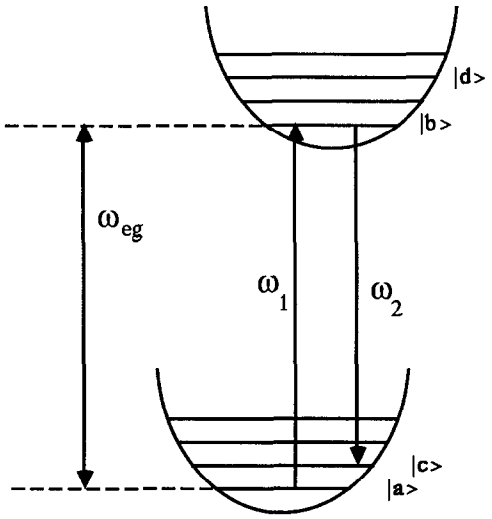

Fig. 1. Molecular energy levels involved in fluorescence. $|a\rangle$ and $|c\rangle$ denote vibronic states of the ground state manifold, and $|b\rangle$ and $|d\rangle$ denote vibronic states of the excited state manifold. A photon of frequency ω_1 is absorbed and a photon of frequency ω_2 is emitted. ω_{eg} is the frequency corresponding to the 0–0 absorption transition in the solvated molecule.

Evaluation of eq. (2a) to fourth order in perturbation theory in the interaction between the material and the radiation [15] yields the following expression for the fluorescence spectrum:

$$S(\omega_1,\omega_2,t)=\frac{2^{1/2}\pi^{3/2}E_1^2E_2^2\exp(-\gamma t)}{\hbar^4\Delta W\{\Delta^2[1-K^2(t)]+W^2\}^{1/2}}$$

$$\times\sum_{a,b,c,d}P(a)|V_{ab}|^2|V_{cd}|^2G_{dd,bb}(t)\exp\left(-\frac{[\Omega+\langle U(0)\rangle+\omega_{ba}-\omega_1]^2}{2(\Delta^2+W^2)}\right)$$

$$\times\exp\left[-\left(\frac{\Delta^2+W^2}{2\Delta^2\{\Delta^2[1-K^2(t)]+W^2\}}\right)\right.$$

$$\left.\times\left(\Omega+\langle U(t)\rangle+\omega_{dc}-\omega_2-\frac{\Delta^2}{\Delta^2+W^2}K(t)[\Omega+\langle U(0)\rangle+\omega_{ba}-\omega_1]\right)^2\right], \tag{3a}$$

$$\hbar U(t)=\exp(ih_et/\hbar)(h_e-h_g)\exp(-ih_et/\hbar), \tag{3b}$$

$$\langle\delta U(t)\,\delta U(0)\rangle\equiv\Delta^2K(t),\quad K(0)=1, \tag{3c}$$

$$\delta U\equiv U-\langle U\rangle, \tag{3d}$$

$\omega_{ba}\equiv\omega_b-\omega_a$, where $H_g|a\rangle=\hbar\omega_a|a\rangle$ and $H_e|b\rangle=\hbar\omega_b|b\rangle$. $P(a)$ is the population of $|a\rangle$ at thermal equilibrium. The inverse lifetime of the electronic excited state is denoted γ. The solvent Hamiltonian (h_e or h_g) includes a contribution from the interactions of each of the solvent molecules with the solute. If this solute–solvent interaction depends on the electronic state of the solute, then $h_e\neq h_g$. $U(t)$ represents the difference between the interactions of the solvent with the ground-state solute and with the excited-state solute. In deriving eq. (3a), we have treated the solute quantum mechanically, but have treated the solvent classically by taking $U(t)$ to be a stochastic variable. Since $U(t)$ is composed of contributions from each of the solvent molecules, we invoke the central limit theorem, and assume that $U(t)$ obeys Gaussian statistics [16]. The angular brackets

in eqs. (3c) and (3d) indicate an average over the stochastic process. Inspection of eq. (3a) shows that the line shift is determined by $\langle U(t)\rangle$, while the line broadening is related to W, the inverse temporal width of the excitation pulse, and to the correlation function of the fluctuations in $U(t)$, $\langle \delta U(t)\, \delta U(0)\rangle$. According to the form of the Hamiltonian of the material system in eq. (1d), the solvent is sensitive to the electronic state of the solute, but not to its vibrational state. In actuality, the solute molecule may be highly vibrationally excited following the optical excitation, and interactions with the solvent will result in vibrational relaxation leading to the equilibration of the solute vibrations with the solvent temperature. Vibrational relaxation can be incorporated phenomenologically in the present model by postulating a Pauli master equation that describes transitions between vibronic states of the excited electronic state [17]. Eq. (3a) includes the effects of vibrational relaxation through $G_{dd,bb}(t)$, the Green function of the master equation, which is the conditional probability that the vibronic state $|d\rangle$ is occupied at time t, if the vibronic state $|b\rangle$ is occupied at $t=0$. If there is no vibrational relaxation, then $G_{dd,bb}(t)=\delta_{bd}$, and if vibrational relaxation is complete at time t, then $G_{dd,bb}(t)$ is the probability that $|d\rangle$ is occupied at thermal equilibrium. The derivation of eq. (3a) is based on three further assumptions. First, it is assumed that the time delay between excitation and measurement is greater than the duration of the excitation pulse ($t> W^{-1}$). Second, the frequency difference of each pair of vibronic levels of the excited electronic state is taken to be large compared to the inverse of the duration of the excitation pulse ($\omega_{bd}/W \gg 1$). Third, Δ, the root-mean-squared magnitude of the fluctuations in U, is assumed to be large compared to the inverse of the time scale of $\langle U(t)\rangle$. According to this assumption, solvent relaxation is negligible on the time scale corresponding to the inverse line width of a single vibronic transition. In this case, the line broadening arising from the interactions of the solute with the solvent dipoles is inhomogeneous, and the linewidth represents a static distribution of different solvent environments. This assumption will be valid in most situations of experimental interest. For example, the longitudinal relaxation time of methanol at 293 K is 8 ps [14]. The absorption profile of a single vibronic transition of a polar solute in methanol will therefore be inhomogeneously broadened if the linewidth is significantly greater than 1.5 cm^{-1}. Since line broadening of polar molecules in polar solvents is typically several hundred cm^{-1} (depending on the magnitude of the change in dipole moment), this condition is easily satisfied.

According to eq. (3a), we require two pieces of information concerning the solvent to calculate the fluorescence spectrum: $\langle U(t)\rangle$ and $\langle \delta U(t)\, \delta U(0)\rangle$. These quantities can be obtained either from an analytical theory or from a molecular dynamics simulation of the solvent, and in this work, we shall adopt the former approach. $\langle U(t)\rangle$ has been calculated for a time-dependent generalization of the Onsager cavity model, by Mazurenko and Bakshiev [12], Bagchi, Oxtoby and Fleming [13], and van der Zwan and Hynes [14]. In this approach, the solute is represented by a point dipole located at the center of a spherical cavity of radius a that is surrounded by a dielectric continuum characterized by a dielectric function $\epsilon(\omega)$. The point dipole has a moment $\boldsymbol{\mu}_g$, when the solute is in the ground state, and a moment $\boldsymbol{\mu}_e$, when the solute is in the excited state. The energy of the system at any time can be related to $\epsilon(\omega)$ with classical electromagnetic theory. Within the Debye model [7] for the dielectric response, in which $\epsilon(\omega)=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)/(1-i\omega\tau_D)$, $\langle U(t)\rangle$ is given by

$$\langle U(t)\rangle-\langle U(\infty)\rangle=6(\boldsymbol{\mu}_e-\boldsymbol{\mu}_g)^2 a^{-3}[(\epsilon_0-\epsilon_\infty)/(2\epsilon_0+1)(2\epsilon_\infty+1)]\exp(-t/\tau_S), \tag{4a}$$

$$\langle U(\infty)\rangle=-\boldsymbol{\mu}_e\cdot(\boldsymbol{\mu}_e-\boldsymbol{\mu}_g)\, 2(\epsilon_0-1)/a^3(2\epsilon_0+1)\,, \tag{4b}$$

$$\tau_S\equiv\tau_D(2\epsilon_\infty+1)/(2\epsilon_0+1)\,. \tag{4c}$$

The characteristic time scale of $\langle U(t)\rangle$ is the solvation time τ_S, which is related to the macroscopic relaxation time, τ_D, in eq. (4c). τ_S is very close in magnitude to the longitudinal relaxation time of a dielectric continuum [18,19], which is usually defined to be $\tau_L=\tau_D\epsilon_\infty/\epsilon_0$. Since $U(t)$ is a Gaussian stochastic variable, $\langle \delta U(t)\, \delta U(0)\rangle$ can be calculated from $\langle U(t)\rangle$. In the high-temperature limit, these quantities are related by the fluctuation–dissipation relation:

$$\langle \delta U(t)\, \delta U(0)\rangle=kT(\langle U(t)\rangle-\langle U(\infty)\rangle)\,. \tag{5}$$

Eq. (5) has been employed by Mazurenko [20], and the $t \to 0$ limit of eq. (5) was derived by Marcus [21] in his treatment of steady-state fluorescence spectra. The fluorescence spectrum can now be calculated upon substitution of eqs. (4) and (5) into eq. (3a).

The time-dependent fluorescence spectrum of a model solute with one harmonic vibrational mode, calculated from eqs. (3)–(5), is shown in fig. 2. The vibrational frequencies in the ground and excited electronic states are 400 and 380 cm^{-1}, respectively, and the equilibrium position of the excited state vibrational coordinate is displaced from that of the ground state vibrational coordinate by 1.4 $(\hbar/m\omega)^{1/2}$, where m is the reduced mass and ω is the excited-state frequency. The dipole moments of the solute in the ground and excited electronic states are parallel and have magnitudes of 2 and 8 D, respectively. The effective radius of the solute is $a = 3$ Å. The solvent is characterized by the dielectric parameters of ethanol [22] at 247 K: $\epsilon_0 = 33.5$, $\epsilon_\infty = 4.8$, and $\tau_S = 164$ ps. The fluorescence frequency, ω_2, is expressed relative to $\omega_{eg} \equiv \Omega + \langle U(0) \rangle$, which is the frequency of the 0–0 absorption transition of the fully solvated solute. The excitation frequency, ω_1, equals ω_{eg}. The temporal profile of the excitation pulse has a full width at half maximum of 1 ps. Vibrational relaxation in the excited electronic state is not included. The top frame of fig. 2 shows the steady-state absorption and fluorescence spectra for this model system. The steady-state fluorescence spectrum is calculated under the assumption that $\tau_S \ll \gamma^{-1}$ (the excited-state lifetime). The absorption spectrum is shown as a function of $\omega_{eg} - \omega_1$. The following frames show fluorescence spectra measured at successively longer times. Each spectrum is labelled with the observation time 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 ground electronic state. The fluorescence

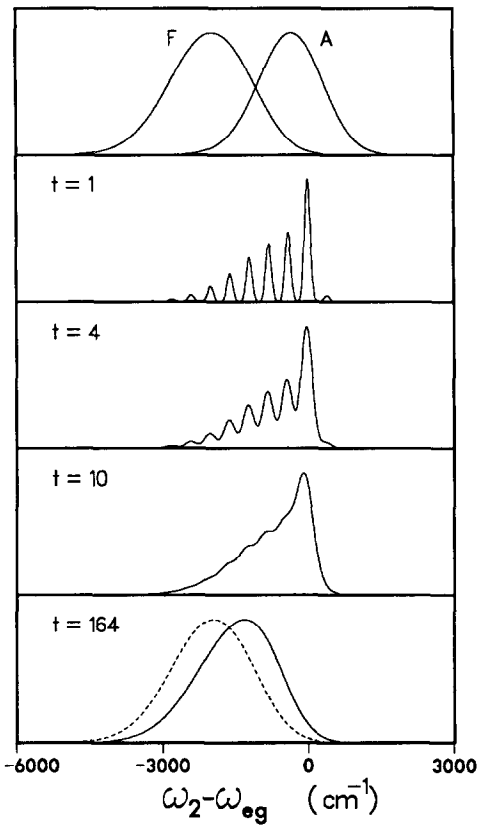

Fig. 2. The top frame shows the steady-state absorption (A) and fluorescence (F) spectra of a model solute with one harmonic vibration in ethanol at 247 K. The absorption spectrum is plotted versus $\omega_{eg} - \omega_1$, and the fluorescence spectra are plotted versus $\omega_2 - \omega_{eg}$. For the fluorescence spectra, the excitation frequency ω_1 equals ω_{eg}, the frequency of the 0–0 absorption transition of the solvated solute. In the electronic ground state, the vibrational frequency is 400 cm^{-1} and the dipole moment is 2 D, and in the electronic excited state, the vibrational frequency is 380 cm^{-1} and the dipole moment is 8 D. The effective radius of the solute is $a = 3$ Å. The following frames show the fluorescence spectrum measured at successively later times after the application of a 1 ps excitation pulse. The solvation time, τ_S, is 164 ps. Each spectrum is labelled with the time of observation in ps. The steady state fluorescence spectrum, which corresponds to $t \gg \tau_S$, is shown by the dashed curve in the last frame. Vibrational relaxation is not included.

spectrum at short times 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 small compared to τ_S, the solvent is effectively static, and the emission is narrow. For observation times comparable to τ_S, the solvent around each excited solute has begun to relax, and the emission broadens, in addition to displaying a red-shift. Fig. 2 illustrates that the red-shift occurs on a time scale of τ_S, but that the broadening takes place on a shorter time scale, as can be deduced from eqs. (3)–(5). In the final frame, the steady-state fluorescence spectrum, which corresponds to $\gamma^{-1} \gg t \gg \tau_S$, is reproduced (dashed line), for comparison with the spectrum at $t = \tau_S$. In figs. 2–4, the excited-state lifetime γ^{-1} is assumed to be long compared to τ_S. In fig. 3, the calculation of fig. 2 is repeated for a different value of the excitation frequency, $\omega_1 = \omega_{eg} + 2000\ \mathrm{cm}^{-1}$. In the absence of vibrational relaxation, this larger value of ω_1 produces a very different Franck–Condon profile from that of fig. 2.

The expression for the fluorescence spectrum in eq. (3a) contains four summations over vibronic eigenstates, and evaluation of these sums rapidly becomes a formidable numerical task as the number of vibrational modes increases. This calculational difficulty can be circumvented with the use of an "eigenstate-free" Green function method [23]. An "eigenstate-free" version of eq. (3a) will be presented elsewhere [24]. Fig. 4 shows the time-dependent fluorescence spectrum for a model polyatomic solute with vibrational relaxation that is rapid on the time scale of the measurement. In this case, fluorescence occurs from thermally populated vibronic states of the excited electronic state. We have used the 29 Raman active vibrational modes of the retinal chromophore in

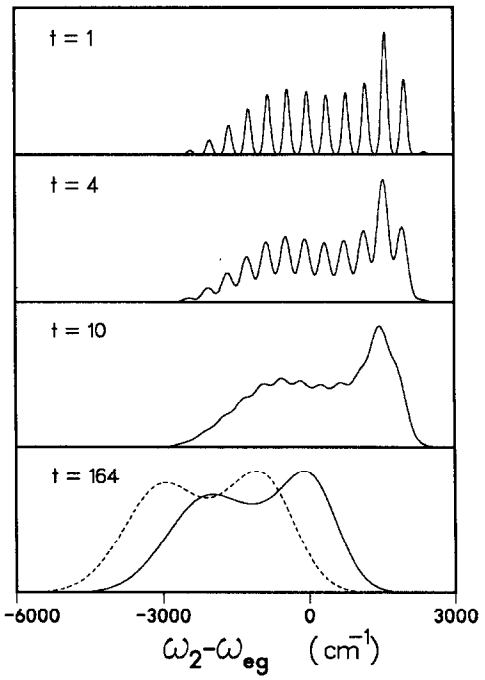

Fig. 3. The calculation of fig. 2 is repeated for $\omega_1 = \omega_{eg} + 2000\ \mathrm{cm}^{-1}$. In the absence of vibrational relaxation, this change in the excitation frequency results in a different Franck–Condon profile from that of fig. 2.

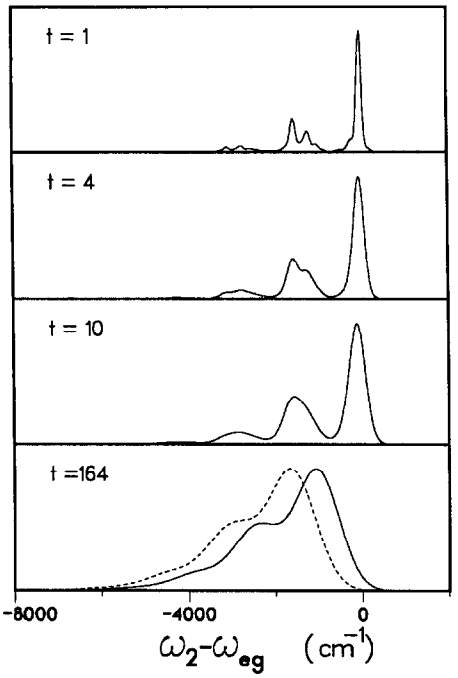

Fig. 4. The fluorescence spectrum measured at successively later times after the application of a 1 ps excitation pulse is shown for a polyatomic solute in ethanol at 247 K. The model solute has the 29 Raman active vibrational modes of the retinal chromophore in bacteriorhodopsin, and undergoes rapid vibrational relaxation. All other parameters are identical to those of figs. 2 and 3.

bacteriorhodopsin, whose frequencies and displacements were obtained from Raman measurements by Myers, Harris and Mathies [25]. All other parameters are identical to those used in figs. 2 and 3. As in figs. 2 and 3, the spectrum at short times shows dramatic narrowing, and undergoes line broadening and a red-shift as the excited solute becomes solvated. Figs. 2–4 demonstrate that the time dependence of the entire fluorescence line shape provides a direct probe of solvation dynamics.

The support of the National Science Foundation, the Office of Naval Research, the US Army Research Office, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

References

[1] E. Lippert, in: Organic molecular photophysics, ed. J.B. Birks (Wiley, New York, 1975).
[2] N. Mataga, Bull. Chem. Soc. Japan 36 (1963) 654.
[3] N.G. Bakshiev, Opt. Spectry. 16 (1964) 446.
[4] Y. Ooshika, J. Phys. Soc. Japan 9 (1954) 594.
[5] E.G. McRae, J. Phys. Chem. 58 (1954) 1002.
[6] L. Onsager, J. Am. Chem. Soc. 58 (1936) 1486.
[7] C.J.F. Bottcher and P. Bordewijk, Theory of electric polarization (Elsevier, Amsterdam, 1978).
[8] L.A. Hallidy and M.R. Topp, J. Phys. Chem. 82 (1978) 2415.
[9] Yu.T. Mazurenko and V.S. Udaltsov, Opt. Spectry. 44 (1977) 417.
[10] T. Okamura, M. Sumitami and K. Yoshihara, Chem. Phys. Letters 94 (1983) 339.
[11] M. Maroncelli, E.W. Castner, S.P. Webb and G.R. Fleming, in: Ultrafast phenomena, Vol. 5, eds. G.R. Fleming and A. Siegman (Springer, Berlin, 1986);
E.W. Castner, M. Maroncelli and G.R. Fleming, J. Chem. Phys., to be published.
[12] Yu.T. Mazurenko and N.G. Bakshiev, Opt. Spectry. 28 (1970) 490.
[13] B. Bagchi, D.W. Oxtoby and G.R. Fleming, Chem. Phys. 86 (1984) 257.
[14] G. van der Zwan and J.T. Hynes, J. Phys. Chem. 89 (1985) 4181.
[15] S. Mukamel, Phys. Rept. 93 (1982) 1; J. Phys. Chem. 89 (1985) 1077.
[16] N.G. van Kampen, Stochastic processes in physics and chemistry (North-Holland, Amsterdam, 1981).
[17] S. Mukamel and R.E. Smalley, J. Chem. Phys. 73 (1980) 4156;
J. Sue, S. Mukamel, H. Okamoto, H. Hamaguchi and M. Tasumi, Chem. Phys. Letters 134 (1987) 87.
[18] D.F. Calef and P.G. Wolynes, J. Chem. Phys. 78 (1983) 4145.
[19] R.L. Fulton, Mol. Phys. 29 (1975) 405.
[20] Yu.T. Mazurenko, Opt. Spectry. 48 (1980) 388.
[21] R.A. Marcus, J. Chem. Phys. 43 (1965) 1261.
[22] D. Bertolini, M. Cassettari and G. Salvetti, J. Chem. Phys. 78 (1983) 365.
[23] Y.J. Yan and S. Mukamel, J. Chem. Phys. 85 (1986) 5908;
S. Mukamel, Advan. Chem. Phys., to be published.
[24] R.F. Loring, Y. Yan and S. Mukamel, to be published.
[25] A.B. Myers, R.A. Harris and R.A. Mathies, J. Chem. Phys. 79 (1983) 603.