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Ultrafast time-resolved fluorescence spectroscopy

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We present a theory of time-resolved emission spectroscopy in the femtosecond region. It is shown that a femtosecond time-resolved emission spectrum consists of the contributions from the population and coherence of the system. Theoretical expressions for describing femtosecond time-resolved emission molecular spectra based on the use of the adiabatic approximation are derived. Detailed numerical calculations have been carried out to show the effect of the time evolution of the population and coherence on the time-resolved emission spectra.

I. INTRODUCTION

Ultrafast emission spectroscopy of fluorescent molecules in solution has recently been used to probe the mechanism and dynamics of solvation and investigate how dynamic solvation affects chemical processes such as electron transfer, proton transfer, etc.[1-7] The basic experiment was first carried out by Ware *et al.*[8] Typically, a fluorescent probe molecule is electronically excited, and the fluorescence spectrum is monitored as a function of time. Relaxation of the solvent polarization about the newly created excited-state dipole leads to a red shift of the fluorescence spectrum. The microscopic solvation relaxation is conventionally probed by monitoring the spectral shift as a function of time. In this paper we shall report the theoretical treatment of ultrafast time-resolved fluorescence spectroscopy. In this regard, it is important to note that when an ultrashort laser pulse is used to pump a molecule system, in general more than one state is coherently pumped, and the resulting time-resolved emission spectra will in general consist of the contribution from the evolution of both population and coherence. In other words, the band-shape functions associated with both population and coherence are required in order to deconvolute an observed ultrafast time-resolved spectrum.

Time-domain measurement using optical techniques has been promoted to the femtosecond regime.[9] Certain nonlinear-optical processes have to be employed in order to take full advantage of ultrafast optical response, even though often what we study is essentially a linear decay process. In the pump-probe technique to obtain temporal emission profile, an up-conversion process is used in detection.[10] Many molecular properties and chemical reactions are opened for study by ultrafast time-scale measurements. Examples are transition-state spectroscopy, orientational relaxation,[11] thermalization,[12] charge separation,[13] isomerization,[14] hydration and aqueous dissociation,[15] and exciton-excimer relaxation.[16] At such a short time scale, nonclassical evolution begins to surface; the excited state does not act like a classical oscillator any more, and the effect of coherence is significant. We consider a molecular system in which an upper state is strongly coupled to local modes as well as heat bath modes, and find how the emission spectrum and its temporal behavior are affected.

The present paper is organized as follows. In Sec. II the general theoretical treatment of ultrafast time-resolved emission spectroscopy based on the quantum theory of radiation is presented. In Sec. III we apply the theoretical results of Sec. II to molecular systems. In Sec. IV we show how to calculate the molecular-spectroscopic band-shape functions associated with the population and coherence of a dynamical system. Numerical calculations are presented in Sec. V to demonstrate the contributions from the dynamics of the population and coherence to time-resolved emission spectra.

II. GENERAL THEORY

We consider the evolution of the density matrix $\hat{\rho}$ of the total system which consists of the molecular system and radiation field,[17]

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{H},\hat{\rho}] - \hat{R}\,\hat{\rho} = -i\hat{L}\,\hat{\rho} - \hat{R}\,\hat{\rho}\ , \tag{2.1}$$

where $\hat{R}$ denotes the damping operator due to the coupling between the system and heat bath, and $\hat{L}$ represents the Liouville operator corresponding to the Hamiltonian $\hat{H}$ of the total system. $\hat{H}$ can be written as a summation of $\hat{H}_s$, the Hamiltonian of the molecular system, $\hat{H}_r$, the Hamiltonian of the radiation field, and $\hat{V}$, the interaction between the molecular system and radiation field,

$$\hat{H} = \hat{H}_r + \hat{H}_s + \hat{V} = \hat{H}_0 + \hat{V}\ . \tag{2.2}$$

It follows that

$$\frac{d\hat{\rho}}{dt} = -i\hat{L}_0\hat{\rho} - i\hat{L}\,'\hat{\rho} - \hat{R}\,\hat{\rho}\ , \tag{2.3}$$

where $\hat{L}\,'$ corresponds to $\hat{V}$.

If we let

$$\hat{\rho} = \exp(-i\hat{L}\,'_0 t)\hat{\sigma}\ , \tag{2.4}$$

where $\hat{L}\,'_0 = \hat{L}_0 - i\hat{R}$, we obtain

$$\frac{d\hat{\sigma}}{dt} = -ie^{it\hat{L}'_0}\hat{L}'e^{-it\hat{L}'_0}\hat{\sigma} , \tag{2.5}$$

which can be integrated as

$$\begin{aligned}\hat{\sigma}(t) &= \hat{\sigma}_i - i\int_{t_i}^{t} d\tau\, e^{i\tau\hat{L}'_0}\hat{L}'e^{-i\tau\hat{L}'_0}\hat{\sigma}(\tau) \\ &= \hat{\sigma}_i + \Delta\hat{\sigma}(t) ,\end{aligned} \tag{2.6}$$

where $\hat{\sigma}_i$ denotes $\hat{\sigma}$ at $t=t_i$. For time-resolved emission, we calculate

$$\begin{aligned}\langle \dot{H}_r \rangle &= \left\langle \frac{d\hat{H}_r}{dt} \right\rangle = \mathrm{Tr}\left[\hat{\rho}\frac{d\hat{H}_r}{dt}\right] \\ &= \frac{i}{\hbar}\mathrm{Tr}(\hat{\rho}[\hat{H},\hat{H}_r]) \\ &= \frac{i}{\hbar}\mathrm{Tr}\{e^{-it\hat{L}'_0}\Delta\hat{\sigma}(t)[\hat{V},\hat{H}_r]\} .\end{aligned} \tag{2.7}$$

Notice that for a molecular system, $\hat{V}$ can be expressed as[17,18]

$$\hat{V} = -\mathbf{X}\cdot\mathbf{Y} , \tag{2.8}$$

where $\mathbf{X}=\mathbf{A}/c$, $\mathbf{A}$ being the vector potential and c, the light velocity, and $\mathbf{Y}=e\mathbf{P}/m$, e and m representing the charge and mass of the electron. Here $\mathbf{P}=\sum_k \mathbf{P}_k$ and $\mathbf{P}_k$ denotes the momentum of the kth electron. Using Eq. (2.8) Eq. (2.7) can be written as

$$\langle \dot{H}_r \rangle = \mathrm{Tr}[\hat{G}(t)\Delta\hat{\sigma}(t)(\dot{\mathbf{X}}\cdot\mathbf{Y})] , \tag{2.9}$$

where $\dot{\mathbf{X}}=d\mathbf{X}/dt$, and $\hat{G}(t)=\exp(-it\hat{L}'_0)$.

It follows that

$$\langle \dot{H}_r \rangle = \sum_{nm} G(t)^{nm}_{nm}\Delta\sigma(t)_{nm}(\dot{\mathbf{X}}\cdot\mathbf{Y})_{mn} \tag{2.10}$$

and

$$\begin{aligned}\Delta\sigma(t)_{nm} &= -\frac{i}{\hbar}\sum_{n'}\int_0^{t-t_i} d\tau[V(t-\tau)_{nn'}\sigma(t-\tau)_{n'm} - \sigma(t-\tau)_{nn'}V(t-\tau)_{n'm}] \\ &= \frac{i}{\hbar}\int_0^{t-t_i} d\tau[\mathbf{X}(t-\tau)\mathbf{Y}(t-\tau),\hat{\sigma}(t-\tau)]_{nm} ,\end{aligned} \tag{2.11}$$

where, for example, $V(t-\tau)_{nn'}=\exp[i(t-\tau)(\omega_{nn'}-iR_{nn'})]V_{nn'}$ and $R_{nn'}$ represents the dephasing constant. Substituting Eq. (2.11) into Eq. (2.9) yields

$$\langle \dot{H}_r \rangle = \frac{i}{\hbar}\int_0^{t-t_i} d\tau\,\mathrm{Tr}\{\hat{\sigma}(t-\tau)[\dot{\mathbf{X}}(t)\cdot\mathbf{Y}(t),\mathbf{X}(t-\tau)\cdot\mathbf{Y}(t-\tau)]\} , \tag{2.12}$$

which can be rewritten as

$$\begin{aligned}\langle \dot{H}_r \rangle = \frac{i}{\hbar}\int_0^{t-t_i} d\tau\{&\langle \dot{\mathbf{X}}(t)\mathbf{X}(t-\tau)\rangle_0 : \mathrm{Tr}[\hat{\sigma}^{(s)}(t-\tau)\mathbf{Y}(t)\mathbf{Y}(t-\tau)] \\ &- \langle \mathbf{X}(t-\tau)\dot{\mathbf{X}}(t)\rangle_0 : \mathrm{Tr}[\hat{\sigma}^{(s)}(t-\tau)\mathbf{Y}(t-\tau)\mathbf{Y}(t)]\} ,\end{aligned} \tag{2.13}$$

where, for example, $\langle \dot{\mathbf{X}}(t)\mathbf{X}(t-\tau)\rangle_0$ denotes the vacuum average of $\dot{\mathbf{X}}(t)\mathbf{X}(t-\tau)$ for the radiation field. $\hat{\sigma}^{(s)}(t)$ represents the density matrix of the molecular system.

Notice that

$$\mathbf{X} = \sum_r \left[\frac{2\pi\hbar}{V\omega_r}\right]^{1/2}(\hat{a}_r + \hat{a}_r^*)\mathbf{e}_r , \tag{2.14}$$

where $(\hat{a}_r,\hat{a}_r^*)$ denote the boson operators, $\mathbf{e}_r$ represents the unit polarization vector, ω_r is the optical frequency, and V is the volume of the system. Substituting Eq. (2.14) into Eq. (2.13) we obtain

$$\langle \dot{H}_r \rangle = \frac{2\pi}{V}\sum_r\int_0^{t-t_i} d\tau\,\mathrm{Tr}(\hat{\sigma}^{(s)}(t-\tau)\{[\mathbf{e}_r\cdot\mathbf{Y}(t)][\mathbf{e}_r\cdot\mathbf{Y}(t-\tau)]e^{-i\tau\omega_r} + [\mathbf{e}_r\cdot\mathbf{Y}(t-\tau)][\mathbf{e}_r\cdot\mathbf{Y}(t)]e^{i\tau\omega_r}\}) . \tag{2.15}$$

Notice that

$$\sum_r \rightarrow \frac{V}{4\pi^3c^3}\int_0^\infty d\omega\,\omega^2\int_\Omega d\Omega . \tag{2.16}$$

Here a factor of 2 has been introduced for polarizations. Using Eq. (2.16), the time-resolved emission spectrum measured in terms of the number of emitted quanta per unit time $P(\omega,t)$ is given by

$$P(\omega,t) = \frac{2\omega}{\pi\hbar c^3}\int_0^{t-t_i} d\tau\,\mathrm{Tr}(\hat{\sigma}^{(s)}(t-\tau)\{[\mathbf{e}\cdot\mathbf{Y}(t)][\mathbf{e}\cdot\mathbf{Y}(t-\tau)]e^{-i\tau\omega} + [\mathbf{e}\cdot\mathbf{Y}(t-\tau)][\mathbf{e}\cdot\mathbf{Y}(t)]e^{i\tau\omega}\}) , \tag{2.17}$$

which can be written as

$$P(\omega,t)=\frac{2\omega}{\hbar c^3}\sum_{nmm'}[\hat{G}^{(s)}(\Delta t)\hat{\rho}_0^{(s)}]_{nm}(\mathbf{e}\cdot\mathbf{Y}_{mm'})(\mathbf{e}\cdot\mathbf{Y}_{m'n})\left[\delta(\omega-\omega_{mm'})+\delta(\omega+\omega_{m'n})+\frac{i}{\pi}\mathrm{P}\frac{\omega_{mn}}{(\omega+\omega_{m'n})(\omega-\omega_{mm'})}\right]. \tag{2.18}$$

In obtaining Eq. (2.18), the Markov approximation has been used. In Eq. (2.18), $\delta(\Delta\omega)$ denotes the δ function and P means that the principal value should be taken. A better approximation will be to replace the δ function by the Lorentzian due to the damping $\hat{R}$. For a randomly oriented molecular system, Eq. (2.18) becomes

$$P(\omega,t)=\frac{2\omega}{3\hbar c^3}\sum_{nmm'}[\hat{G}^{(s)}(\Delta t)\hat{\rho}_0^{(s)}]_{nm}(\mathbf{Y}_{mm'}\cdot\mathbf{Y}_{m'n})\left[\delta(\omega-\omega_{mm'})+\delta(\omega+\omega_{m'n})+\frac{i}{\pi}\mathrm{P}\frac{\omega_{mn}}{(\omega+\omega_{m'n})(\omega-\omega_{mm'})}\right]. \tag{2.19}$$

Equations (2.17)–(2.19) are central results of this paper. In the remaining portion of this paper, we shall show the application of these results. It should be noted that $P(\omega,t)$ consists of two parts; while $[\hat{G}^{(s)}(\Delta t)\hat{\rho}_0^{(s)}]_{nm}$ describes the dynamical behavior of the molecular system, the remaining part of $P(\omega,t)$ describes the emission spectroscopic behavior of the molecular system. The Einstein A coefficient (i.e., the spontaneous-emission rate constant) can be obtained from Eq. (2.19) by setting $[\hat{G}^{(s)}(\Delta t)\hat{\rho}_0^{(s)}]_{nm}=\delta_{nm}(\hat{\rho}_0^{(s)})_{nn}$ where $(\hat{\rho}_0^{(s)})_{nn}$ denotes the equilibrium distribution; in this case we have

$$\begin{aligned}A&=\frac{4}{3\hbar c^3}\sum_{nm'}(\hat{\rho}_0^{(s)})_{nn}|\mathbf{Y}_{nm'}|^2\omega_{nm'}\\&=\frac{4}{3\hbar c^3}\sum_{nm'}(\hat{\rho}_0^{(s)})_{nn}|\boldsymbol{\mu}_{nm'}|^2\omega_{nm'}^3\ ,\end{aligned} \tag{2.20}$$

where $\boldsymbol{\mu}_{nm'}$ denotes the transition moment. Here the relation $\mathbf{Y}_{nm'}=i\omega_{nm'}\boldsymbol{\mu}_{nm'}$ has been used. In Appendix A we show how to calculate $[\hat{G}^{(s)}(\Delta t)\hat{\rho}_0^{(s)}]_{nm}$.

III. TIME-RESOLVED EMISSION SPECTROSCOPY OF ELECTRONIC TRANSITIONS

We shall now analyze the expression for $P(\omega,t)$ given in the preceding section in the Born-Oppenheimer adiabatic approximation. The adiabatic approximation is applicable to low electronic states of molecules. For this purpose, we let (βv) denote the vibronic states in the excited electronic state manifold, while (αw) denote the vibronic states in the ground-electronic-state manifold. In this case, Eq. (2.19) can be written as

$$P(\omega,t)=\frac{2\omega}{3\hbar c^3}\sum_{vv'w}\rho^{(s)}(\Delta t)_{\beta v,\beta v'}(\mathbf{Y}_{\beta v'\alpha w}\cdot\mathbf{Y}_{\alpha w,\beta v})\left[\delta(\omega-\omega_{\beta v',\alpha w})+\delta(\omega+\omega_{\alpha w,\beta v})+i\mathrm{P}\frac{\omega_{\beta v',\beta v}}{(\omega+\omega_{\alpha w,\beta v})(\omega-\omega_{\beta v',\alpha w})}\right], \tag{3.1}$$

where $\hat{\rho}^{(s)}(\Delta t)=\hat{G}^{(s)}(\Delta t)\hat{\rho}_0^{(s)}$. From Eq. (3.1) we can see that $P(\omega,t)$ consists of the incoherent contribution $P(\omega,t)_n$ and the coherent contribution $P(\omega,t)_c$, i.e.,

$$P(\omega,t)=P(\omega,t)_n+P(\omega,t)_c\ , \tag{3.2}$$

where

$$P(\omega,t)_n=\frac{4\omega}{3\hbar c^3}\sum_{vw}\rho^{(s)}(\Delta t)_{\beta v,\beta v}|\mathbf{Y}_{\alpha w,\beta v}|^2\delta(\omega-\omega_{\beta v,\alpha w}) \tag{3.3}$$

or

$$P(\omega,t)_n=\frac{4\omega^3}{3\hbar c^3}\sum_{vw}\rho^{(s)}(\Delta t)_{\beta v,\beta v}|\boldsymbol{\mu}_{\alpha w,\beta v}|^2\delta(\omega-\omega_{\beta v,\alpha w})=\sum_{v}\rho^{(s)}(\Delta t)_{\beta v,\beta v}F_{\beta v,\beta v}(\omega) \tag{3.4}$$

and

$$\begin{aligned}P(\omega,t)_c&=\frac{2\omega}{3\hbar c^3}\sum_{v}^{v\neq v'}\sum_{v'}{}'\sum_{w}\rho^{(s)}(\Delta t)_{\beta v,\beta v'}(\mathbf{Y}_{\beta v',\alpha w}\cdot\mathbf{Y}_{\alpha w,\beta v})\left[\delta(\omega-\omega_{\beta v',\alpha w})+\delta(\omega+\omega_{\alpha w,\beta v})+\frac{i}{\pi}\mathrm{P}\frac{\omega_{\beta v',\beta v}}{(\omega+\omega_{\alpha w,\beta v})(\omega-\omega_{\beta v',\alpha w})}\right]\\&=\sum_{v}^{v\neq v'}\sum_{v'}\rho^{(s)}(\Delta t)_{\beta v,\beta v'}F_{\beta v,\beta v'}(\omega)\ ,\end{aligned} \tag{3.5}$$

where $F_{\beta v,\beta v}(\omega)$ and $F_{\beta v,\beta v'}(\omega)$ represent the band-shape functions

$$F_{\beta v,\beta v}(\omega)=\frac{4\omega^3}{3\hbar c^3}\sum_w |\boldsymbol{\mu}_{aw,\beta v}|^2\delta(\omega-\omega_{\beta v,aw}) \tag{3.6}$$

and

$$F_{\beta v,\beta v'}(\omega)=\frac{2\omega}{3\hbar c^3}\sum_w (\mathbf{Y}_{\beta v',aw}\cdot\mathbf{Y}_{aw,\beta v})\left[\delta(\omega-\omega_{\beta v',aw})+\delta(\omega+\omega_{aw,\beta v})+\frac{i}{\pi}\mathrm{P}\frac{\omega_{\beta v',\beta v}}{(\omega+\omega_{aw,\beta v})(\omega-\omega_{\beta v',aw})}\right] . \tag{3.7}$$

From the expression of $P(\omega,t)_n$ we can see that it consists of the dynamics of the population $\rho^{(s)}(\Delta t)_{\beta v,\beta v}$ and the associated band-shape function $F_{\beta v,\beta v}(\omega)$. Similarly, $P(\omega,t)_c$ can be separated into the coherence $\rho^{(s)}(\Delta t)_{\beta v,\beta v'}$ and the associated band-shape function $F_{\beta v,\beta v'}(\omega)$. For the case in which the Condon approximation applies (i.e., the electronic transition is an allowed transition), the band-shape functions $F_{\beta v,\beta v}(\omega)$ and $F_{\beta v,\beta v'}(\omega)$ become

$$F_{\beta v,\beta v}(\omega)=\frac{4\omega^3}{3\hbar c^3}|\boldsymbol{\mu}_{\alpha\beta}|^2\sum_w |\langle\Theta_{aw}|\Theta_{\beta v}\rangle|^2\delta(\omega-\omega_{\beta v,aw}) \tag{3.8}$$

and

$$F_{\beta v,\beta v'}(\omega)=\frac{2\omega}{3\hbar c^3}|\boldsymbol{\mu}_{\alpha\beta}|^2\sum_w \omega_{\beta v',aw}\omega_{\beta v,aw}\langle\Theta_{\beta v'}|\Theta_{aw}\rangle\langle\Theta_{aw}|\Theta_{\beta v}\rangle$$
$$\times\left[\delta(\omega-\omega_{\beta v',aw})+\delta(\omega+\omega_{aw,\beta v})+\frac{i}{\pi}\mathrm{P}\frac{\omega_{\beta v',\beta v}}{(\omega+\omega_{aw,\beta v})(\omega-\omega_{\beta v',aw})}\right] , \tag{3.9}$$

where Θ_{aw}, $\Theta_{\beta v}$, and $\Theta_{\beta v'}$ represent the nuclear wave functions.

It should be noted that when the dephasing is much faster than the relaxation, in the time scale of molecular relaxation $\rho^{(s)}(\Delta t)_{\beta v,\beta v'}$ vanishes and we have $P(\omega,t)=P(\omega,t)_n$.

IV. BAND-SHAPE FUNCTIONS

In Sec. III we have shown that the time-resolved emission spectra $P(\omega,t)$ can be separated into the product of the population or coherence and the associated band-shape functions. In this section we shall show how to obtain the band-shape functions $F_{\beta v,\beta v}(\omega)$ and $F_{\beta v,\beta v'}(\omega)$. For this purpose, we shall consider only the case where one degree of freedom is nonstationary and other degrees of freedom are in thermal equilibrium. In other words, only one optical mode is coherently pumped and the other modes maintain or reach equilibrium in the time scale under consideration. In this case,

$$F_{\beta v,\beta v}(\omega)=\frac{4\omega^3}{3\hbar c^3}|\boldsymbol{\mu}_{\alpha\beta}|^2\sum_v{}'\sum_w |\langle X_{\beta v_0}|X_{aw_0}\rangle|^2\prod_i{}' P_{\beta v_\iota}|\langle X_{\beta v_\iota}|X_{aw_\iota}\rangle|^2\delta(\omega_{\beta v,aw}-\omega) , \tag{4.1}$$

where $(X_{\beta v_0},X_{aw_0})$ and $(X_{\beta v_\iota},X_{aw_\iota})$ represent the wave functions of the optically pumped mode and the remaining other modes and $P_{\beta v_\iota}$ denotes the Boltzmann factor. For the case of harmonic oscillators, $F_{\beta v,\beta v}(\omega)$ can be written as[19]

$$F_{\beta v,\beta v}(\omega)=\frac{2\omega^3}{3\pi\hbar c^3}|\boldsymbol{\mu}_{\alpha\beta}|^2\int_{-\infty}^{\infty}dt\,\exp[it(\omega-\omega_{\beta\alpha})]K_{v_0}(t)\prod_i{}' G_i(t) , \tag{4.2}$$

where

$$K_{v_0}(t)=\sum_{w_0}|\langle X_{\beta v_0}|X_{aw_0}\rangle|^2\exp\{it[(w_0+\tfrac{1}{2})\omega_0'-(v_0+\tfrac{1}{2})\omega_0]\} \tag{4.3}$$

and

$$G_\iota(t)=\sum_{v_\iota}\sum_{w_\iota}P_{\beta v_\iota}|\langle X_{\beta v_\iota}|X_{aw_\iota}\rangle|^2\exp\{it[(w_i+\tfrac{1}{2})\omega_i'-(v_\iota+\tfrac{1}{2})\omega_i]\} . \tag{4.4}$$

For the case of a harmonic oscillator, $G_i(t)$ has been evaluated[19]

$$G_i(t)=2\beta_i\beta_i'\sinh\frac{\hbar\omega_i}{2kT}\exp\left[-\frac{k_i(t)}{[h_i(t)]^{1/2}}\right] , \tag{4.5}$$

where

$$k_i(t)=\frac{\beta_i^2\beta_i'^2d_i^2}{\beta_i'^2\coth(\lambda_i/2)+\beta_i^2\coth(\mu_i'/2)} , \tag{4.6}$$

$$h_i(t)=\sinh\lambda_1\sinh\mu_\iota'\left[\beta_i'^2\coth\frac{\mu_i'}{2}+\beta_i^2\coth\frac{\lambda_i}{2}\right]\left[\beta_i'^2\tanh\frac{\mu_\iota'}{2}+\beta_i^2\tanh\frac{\lambda_i}{2}\right], \tag{4.7}$$

$\mu_i'=-it\omega_i'$ and $\lambda_i=it\omega_i+\hbar\omega_i/kT$. Similarly $K_{v_0}(t)$ is given by

$$K_{v_0}(t)=K_{0_0}(t)\Delta K_{v_0}(t), \tag{4.8}$$

where

$$K_{0_0}(t)=\exp\left[-\frac{\beta_0^2d_0^2}{2}(1-e^{-\mu_0})\right] \tag{4.9}$$

and

$$\Delta K_{v_0}(t)=\sum_{n_0=0}^{v_0}\frac{v_0!}{(n_0!)^2(v_0-n_0)!}\left[\frac{\beta_0^2d_0^2}{2}(e^{\mu_0/2}-e^{-\mu_0/2})^2\right]^{n_0}. \tag{4.10}$$

Here it is assumed that the oscillator is displaced but not distorted. The case of displaced and distorted oscillator is shown in Appendix B. It should be noted $K_{0_0}(t)$ given by Eq. (4.8) is equal to $G_{0_0}(t)$ at $T=0$.

Substituting Eqs. (4.5) and (4.8) into Eq. (4.2) and using the short-time approximation (i.e., the strong-coupling case), $F_{\beta v,\beta v}(\omega)$ becomes

$$F_{\beta v,\beta v}(\omega)=\frac{2\omega^3}{3\pi\hbar c^3}|\boldsymbol{\mu}_{\alpha\beta}|^2\Delta K_{v_0}(t^*)\left[\frac{\pi}{D}\right]^{1/2}\exp\left[-\frac{(\omega_{\beta\alpha}-\omega_s-\omega)^2}{4D}\right], \tag{4.11}$$

where

$$D=\sum_\iota{}'\frac{\omega_\iota^2}{4}\left[\rho_i^2\left[1-\frac{\rho_i}{2}\right]^2\coth^2\frac{\hbar\omega_\iota}{2kT}+\beta_i^2d_i^2(1-\rho_i)^4\coth\frac{\hbar\omega_\iota}{2kT}\right]+\frac{\omega_0^2}{4}\beta_0^2d_0^2, \tag{4.12}$$

$$\omega_s=\sum_\iota{}'\frac{\omega_i}{2}\left[\beta_i^2d_i^2(1-\rho_i)^2-\rho_i\left[1-\frac{\rho_i}{2}\right]\coth\frac{\hbar\omega_\iota}{2kT}\right]+\frac{\omega_0}{2}\beta_0^2d_0^2, \tag{4.13}$$

and

$$t^*=\frac{i(\omega-\omega_{\beta\alpha}+\omega_s)}{2D},\quad \omega_\iota'=\omega_i(1-\rho_i). \tag{4.14}$$

Due to the term $\Delta K_{v_0}(t^*)$, $F_{\beta v,\beta v}(\omega)$ takes the modified Gaussian form. Notice at $v_0=0$, $\Delta K_{v_0}(t^*)=1$; in other words, only for this case would $F_{\beta v,\beta v}(\omega)$ take the Gaussian form.

Next we consider $F_{\beta v,\beta v'}(\omega)$, which can be rewritten as

$$\begin{aligned}F_{\beta v,\beta v'}(\omega)=\frac{2\omega}{3\pi\hbar c^3}|\boldsymbol{\mu}_{\alpha\beta}|^2\sum_w\sum_v{}'P_{\beta v}\omega_{\beta v',\alpha w}\omega_{\beta v,\alpha w}\langle\Theta_{\beta v}|\Theta_{\alpha w}\rangle\langle\Theta_{\alpha w}|\Theta_{\beta v'}\rangle\\ \times\int_0^\infty dt\,\{\exp[it(\omega-\omega_{\beta v',\alpha w})]+\exp[-it(\omega+\omega_{\alpha w,\beta v})]\}.\end{aligned} \tag{4.15}$$

$F_{\beta v,\beta v'}(\omega)$ consists of two terms, i.e.,

$$F_{\beta v,\beta v'}(\omega)=F_{\beta v,\beta v'}(\omega)_1+F_{\beta v,\beta v'}(\omega)_2, \tag{4.16}$$

where

$$F_{\beta v,\beta v'}(\omega)_1=\frac{2\omega}{3\pi\hbar c^3}|\boldsymbol{\mu}_{\alpha\beta}|^2\int_0^\infty dt\,e^{it(\omega-\Delta v_0\omega_0)}\left[\frac{\partial^2}{\partial\theta^2}-\Delta v_0\omega_0\frac{\partial}{\partial\theta}\right]I_{vv'}(-\theta), \tag{4.17}$$

$$F_{\beta v,\beta v'}(\omega)_2=\frac{2\omega}{3\pi\hbar c^3}|\boldsymbol{\mu}_{\alpha\beta}|^2\int_0^\infty dt\,e^{-it\omega}\left[\frac{\partial^2}{\partial\theta^2}+\Delta v_0\omega_0\frac{\partial}{\partial\theta}\right]I_{vv'}(\theta), \tag{4.18}$$

and

$$I_{vv'}(\theta)=\sum_w\sum_v{}'P_{\beta v}\langle\Theta_{\beta v'}|\Theta_{\alpha w}\rangle\langle\Theta_{\alpha w}|\Theta_{\beta v}\rangle e^{\theta\omega_{\beta v,\alpha w}}. \tag{4.19}$$

Here $\theta = it$ and $v_0' = v_0 + \Delta v_0$. Equations (4.15)–(4.19) indicate that, to evaluate $F_{\beta v,\beta v'}(\omega)$, it is necessary to evaluate $I_{vv'}(\theta)$. Notice that $I_{vv'}(\theta)$ can be expressed as

$$I_{vv'}(\theta) = e^{\theta\omega_{\beta\alpha}} K_{v_0 v_0'}(\theta) \prod_i{}' G_i(\theta) , \tag{4.20}$$

where

$$K_{v_0 v_0'}(\theta) = \sum_{w_0} \langle X_{\beta v_0'} | X_{\alpha w_0} \rangle \langle X_{\alpha w_0} | X_{\beta v_0} \rangle \exp\{\theta[(v_0 + \tfrac{1}{2})\omega_0 - (w_0 + \tfrac{1}{2})\omega_0')]\} \tag{4.21}$$

and

$$G_i(\theta) = \sum_{v_i} \sum_{w_i} P_{\beta v_i} |\langle X_{\beta v_i} | X_{\alpha w_i} \rangle|^2 \exp\{\theta[(v_i + \tfrac{1}{2})\omega_i - (w_i + \tfrac{1}{2})\omega_i']\} . \tag{4.22}$$

$G_i(\theta)$ is exactly the same as $G_i(t)$ given by Eq. (4.3) by replacing $t = i\theta$. We now calculate $K_{v_0 v_0'}(\theta)$ which can be accomplished in the same way as that for $K_{v_0}(t)$. We obtain, for the displaced oscillator case,

$$K_{v_0, v_0'}(\theta) = K_{0_0, 0_0}(\theta) \Delta K_{v_0 v_0'}(\theta) , \tag{4.23}$$

where

$$K_{0_0, 0_0}(\theta) = \exp\left[-\frac{\beta_0^2 d_0^2}{2}(1 - e^{-\omega_0 \theta}) \right] \tag{4.24}$$

and

$$\Delta K_{v_0 v_0'}(\theta) = \sum_{n_0 = 0}^{v_0} \frac{(v_0! v_0'!)^{1/2}}{n_0!(v_0 - n_0)!(v_0' - n_0)!} e^{(v_0 - n_0)\omega_0 \theta} \left[\frac{\beta_0 d_0}{\sqrt{2}}(1 - e^{-\omega_0 \theta}) \right]^{v_0' + v_0 - 2n_0} \tag{4.25}$$

for $v_0' > v_0$. Similarly for the displaced oscillator case, $G_i(\theta)$ is given by

$$G_i(\theta) = \exp\left\{ -\frac{\beta_i^2 d_i^2}{2} \left[\coth\frac{\hbar\omega_i}{2kT} - \operatorname{csch}\frac{\hbar\omega_i}{2kT} \cosh\left[\omega_i \theta - \frac{\hbar\omega_i}{2kT} \right] \right] \right\} . \tag{4.26}$$

In this case, we have

$$\begin{aligned} I_{vv'}(\theta) = \exp\left\{ -\frac{\beta_0^2 d_0^2}{2}(1 - e^{-\omega_0 \theta}) + \omega_{\beta\alpha}\theta - \sum_i{}' \frac{\beta_i^2 d_i^2}{2} \left[\coth\frac{\hbar\omega_i}{2kT} - \operatorname{csch}\frac{\hbar\omega_i}{2kT} \cosh\left[\omega_i \theta - \frac{\hbar\omega_i}{2kT} \right] \right] \right\} \\ \times \sum_{n_0 = 0}^{v_0} \frac{(v_0! v_0'!)^{1/2}}{n_0!(v_0 - n_0)!(v_0' - n_0)!} e^{(v_0 - n_0)\omega_0 \theta} \left[\frac{\beta_0 d_0}{\sqrt{2}}(1 - e^{-\theta\omega_0}) \right]^{v_0 + v_0' - 2n_0} . \end{aligned} \tag{4.27}$$

In particular, at low temperatures, Eq. (4.27) reduces to

$$\begin{aligned} I_{vv'}(\theta) = \exp\left[-\sum_i \frac{\beta_i^2 d_i^2}{2}(1 - e^{-\omega_i \theta}) + \omega_{\beta\alpha}\theta \right] \\ \times \sum_{n_0 = 0}^{v_0} \frac{(v_0! v_0'!)^{1/2}}{n_0!(v_0 - n_0)!(v_0' - n_0)!} e^{(v_0 - n_0)\omega_0 \theta} \left[\frac{\beta_0 d_0}{\sqrt{2}}(1 - e^{-\omega_0 \theta}) \right]^{v_0 + v_0' + 2n_0} . \end{aligned} \tag{4.28}$$

V. DISCUSSION

In this section we shall show some numerical results of time-resolved emission spectra. For this purpose, we consider the case in which only the two lowest vibrational levels of a particular mode are coherently pumped and the temperature effect is neglected. In this case, we have

$$P(\omega, t)_n = \rho^{(s)}(\Delta t)_{\beta 0,\beta 0} F_{\beta 0,\beta 0}(\omega) + \rho^{(s)}(\Delta t)_{\beta 1,\beta 1} F_{\beta 1,\beta 1}(\omega) \tag{5.1}$$

and

$$P(\omega, t)_c = \rho^{(s)}(\Delta t)_{\beta 0,\beta 1} F_{\beta 0,\beta 1}(\omega) + \rho^{(s)}(\Delta t)_{\beta 1,\beta 0} F_{\beta 1,\beta 0}(\omega) , \tag{5.2}$$

where, for the displaced oscillator case,

$$F_{\beta0,\beta0}(\omega)=\frac{2\omega^3}{3\pi\hbar c^3}|\mu_{\alpha\beta}|^2\int_{-\infty}^{\infty}dt\,\exp\left[it(\omega-\omega_{\beta\alpha})-\sum_i S_i(1-e^{it\omega_i})\right]$$

$$=\frac{2\omega^3}{3\pi\hbar c^3}|\mu_{\alpha\beta}|^2\left[2\pi\Big/\left[\sum_i S_i\omega_i^2\right]\right]^{1/2}\exp\left[-\left[\omega_{\beta\alpha}-\sum_i S_i\omega_i-\omega\right]^2\Big/\left[2\sum_i S_i\omega_i^2\right]\right] \tag{5.3}$$

and

$$F_{\beta1,\beta1}(\omega)=\frac{2\omega^3}{3\hbar\pi c^3}|\mu_{\alpha\beta}|^2\int_{-\infty}^{\infty}dt[(1-2S_0)+S_0(e^{it\omega_0}+e^{-it\omega_0})]\exp\left[it(\omega-\omega_{\beta\alpha})-\sum_i S_i(1-e^{it\omega_i})\right], \tag{5.4}$$

where $S_i=\frac{1}{2}\beta_i^2d_i^2$, the Huang-Rhys constant (or the coupling constant). $F_{\beta1,\beta1}(\omega)$ can be expressed as

$$F_{\beta1,\beta1}(\omega)=(1-2S_0)F_{\beta0,\beta0}(\omega)+S_0\left[\frac{\omega}{\omega+\omega_0}\right]^3F_{\beta0,\beta0}(\omega+\omega_0)+S_0\left[\frac{\omega}{\omega-\omega_0}\right]^3F_{\beta0,\beta0}(\omega-\omega_0)\ . \tag{5.5}$$

Notice that, from Appendix A, we obtain

$$\rho^{(s)}(\Delta t)_{\beta0,\beta0}=(\hat{\rho}_0^{(s)})_{\beta0,\beta0}+(\hat{\rho}_0^{(s)})_{\beta1,\beta1}(1-e^{-R_{\beta1}\Delta t}) \tag{5.6}$$

and

$$\rho^{(s)}(\Delta t)_{\beta1,\beta1}=(\hat{\rho}_0^{(s)})_{\beta1,\beta1}e^{-R_{\beta1}\Delta t}\ , \tag{5.7}$$

where $R_{\beta1}$ denotes the relaxation rate constant of the $\beta1$ level. Here for simplicity we have assumed that $R_{\beta0}$ is negligible in the time scale under consideration.

Next we consider the coherence contribution. Notice that in this case we obtain the real parts of $F_{\beta0,\beta1}(\omega)$ and $F_{\beta1,\beta0}(\omega)$,

$$F_{\beta0,\beta1}(\omega)=F_{\beta1,\beta0}(\omega)=\left[\frac{\beta_0d_0}{\sqrt{2}}\right]|\mu_{\alpha\beta}|^2\frac{\omega^2(\omega-\omega_0)}{3\pi\hbar c^3}\left[2\pi\Big/\left[\sum_i S_i\omega_i^2\right]\right]^{1/2}$$

$$\times\left\{\exp\left[-\left[\omega_{\beta\alpha}+\omega_0-\sum_i S_i\omega_i-\omega\right]^2\Big/\left[2\sum_i S_i\omega_i^2\right]\right]\right.$$

$$\left.-\exp\left[-\left[\omega_{\beta\alpha}-\sum_i S_i\omega_i-\omega\right]^2\Big/\left[2\sum_i S_i\omega_i^2\right]\right]\right\}$$

$$+\frac{\beta_0d_0}{\sqrt{2}}|\mu_{\alpha\beta}|^2\frac{\omega^2(\omega+\omega_0)}{3\pi\hbar c^3}\left[2\pi\Big/\left[\sum_i S_i\omega_i^2\right]\right]^{1/2}$$

$$\times\left\{\exp\left[-\left[\omega_{\beta\alpha}-\omega-\sum_i S_i\omega_i\right]^2\Big/\left[2\sum_i S_i\omega_i^2\right]\right]\right.$$

$$\left.-\exp\left[-\left[\omega_{\beta\alpha}-\omega_0-\omega-\sum_i S_i\omega_i\right]^2\Big/\left[2\sum_i S_i\omega_i^2\right]\right]\right\} \tag{5.8}$$

and

$$\rho^{(s)}(\Delta t)_{\beta0,\beta1}=(\hat{\rho}_0^{(s)})_{\beta0,\beta1}\exp[-\Delta t(i\omega_{\beta0,\beta1}+R_{\beta0,\beta1})]\ , \tag{5.9}$$

where $R_{\beta0,\beta1}$ denotes the dephasing constant and $\omega_{\beta0,\beta1}=-\omega_0$. We use the form $R_{\beta\upsilon,\beta1}=R_{\beta1}/2+R_{\mathrm{ph}}$ in numerical calculation where R_{ph} is the rate for pure dephasing. It follows that

$$
\begin{aligned}
P(\omega,t)_c ={}& \rho^{(s)}(0)_{\beta 0,\beta 1}\exp(-\Delta t R_{\beta 0,\beta 1})\left[\frac{\beta_0 d_0}{\sqrt{2}}\right]\left[\frac{2\omega^2(\omega-\omega_0)}{3\pi\hbar c^3}\right]|\mu_{\alpha\beta}|^2\left[2\pi\Big/\left[\sum_i S_i\omega_i^2\right]\right]^{1/2} \\
&\times\left\{\exp\left[-\left[\omega_{\beta\alpha}+\omega_0-\sum_i S_i\omega_i-\omega\right]^2\Big/\left[2\sum_i S_i\omega_i^2\right]\right]\right. \\
&\left.\quad-\exp\left[-\left[\omega_{\beta\alpha}-\omega-\sum_i S_i\omega_i\right]^2\Big/\left[2\sum_i S_i\omega_i^2\right]\right]\right\}\cos\omega_0\Delta t \\
&+\rho^{(s)}(0)_{\beta 0,\beta 1}\exp(-\Delta t R_{\beta 0,\beta 1})\left[\frac{\beta_0 d_0}{\sqrt{2}}\right]\left[\frac{2\omega^2(\omega+\omega_0)}{3\pi\hbar c^3}\right]|\mu_{\alpha\beta}|^2\left[2\pi\Big/\left[\sum_i S_i\omega_i^2\right]\right]^{1/2} \\
&\times\left\{\exp\left[-\left[\omega_{\beta\alpha}-\omega-\sum_i S_i\omega_i\right]^2\Big/\left[2\sum_i S_i\omega_i^2\right]\right]\right. \\
&\left.\quad-\exp\left[-\left[\omega_{\beta\alpha}-\omega_0-\sum_i S_i\omega_i-\omega\right]^2\Big/\left[2\sum_i S_i\omega_i^2\right]\right]\right\}\cos\omega_0\Delta t\ . \qquad (5.10)
\end{aligned}
$$

Here the contributions from the principal values of $F_{\beta 0,\beta 1}(\omega)$ and $F_{\beta 1,\beta 0}(\omega)$ have been neglected.

In the previous papers,[20-22] we have shown that if the pumping laser pulse has a constant amplitude with duration T, then

$$(\hat{\rho}_0^{(s)})_{\beta v,\beta v'}=\frac{T^2}{\hbar^2}V'_{\beta v,\alpha 0}V'_{\alpha 0,\beta v'}\ , \qquad (5.11)$$

where $V'_{\beta v,\alpha 0}$ and $V'_{\alpha 0,\beta v'}$ denotes the interaction matrix element involved in the pumping laser. Using the Condon approximation and Eq. (5.11) we obtain

$$\frac{(\hat{\rho}_0^{(s)})_{\beta 1,\beta 1}}{(\hat{\rho}_0^{(s)})_{\beta 0,\beta 0}}=\frac{|\langle X_{\beta 1_0}|X_{\alpha 0_0}\rangle|^2}{|\langle X_{\beta 0_0}|X_{\alpha 0_0}\rangle|^2} \qquad (5.12)$$

and

$$\frac{(\hat{\rho}_0^{(s)})_{\beta 0,\beta 1}}{(\hat{\rho}^{(s)})_{\beta 0,\beta 0}}=\frac{\langle X_{\beta 1_0}|X_{\alpha 0_0}\rangle}{\langle X_{\beta 0_0}|X_{\alpha 0_0}\rangle}\ . \qquad (5.13)$$

For the displaced oscillator we obtain

$$\frac{(\hat{\rho}_0^{(s)})_{\beta 1,\beta 1}}{(\hat{\rho}_0^{(s)})_{\beta 0,\beta 0}}=\frac{\beta_0^2 d_0^2}{2}=S_0 \qquad (5.14)$$

and

$$\frac{(\hat{\rho}_0^{(s)})_{\beta_0,\beta 1}}{(\hat{\rho}_0^{(s)})_{\beta 0,\beta 0}}=-\frac{\beta_0 d_0}{\sqrt{2}}\ . \qquad (5.15)$$

Equations (5.1)–(5.15) have been employed for numerical calculations. For this purpose, we introduce an average frequency in $\sum_i S_i\omega_i$ and $\sum_i S_i\omega_i^2$ so that $\sum_i S_i\omega_i=S\bar{\omega}$ and $\sum_i S_i\omega_i^2=S\bar{\omega}^2$ where $S=\sum_i S_i$. Equations (5.3), (5.5), and (5.8) provide a convenient approximation for band-shape functions that include solvent effects in transient emission spectra. However, for testing purposes, we carry out the single-mode case, using Eq. (3.9), and neglect all both modes. Results are shown in Figs. 1 and 2. The coherence effect is obvious in the early stage by comparing the two figures. Coherence is also shown in the oscillatory behavior of emission in Fig. 3. Note that 1 KK^{-1} in time scale corresponds to 33 fs. Figures 4 and 5 show a similar pattern of evolution for the upper state initially populated at $v=1$ and 2. A large dephasing constant (Figs. 2 and 5) quickly damps the coherent part of the emission intensity and, therefore, allows us to see the evolution of the incoherent contribution. Analytical expressions in Eqs. (5.3), (5.5), and (5.8) give similar results with slightly different Stokes's shift determined by the total Huang-Rhys factor S instead of S_0.

The net dephasing effect, as caused by both relaxation and pure dephasing, can come from strong anharmonicity and intermode coupling, as well as strong vibronic coupling in the excited state.[23,24] Nonlinear coupling among different vibrational modes is especially strong when the molecule is vertically pumped from the lower

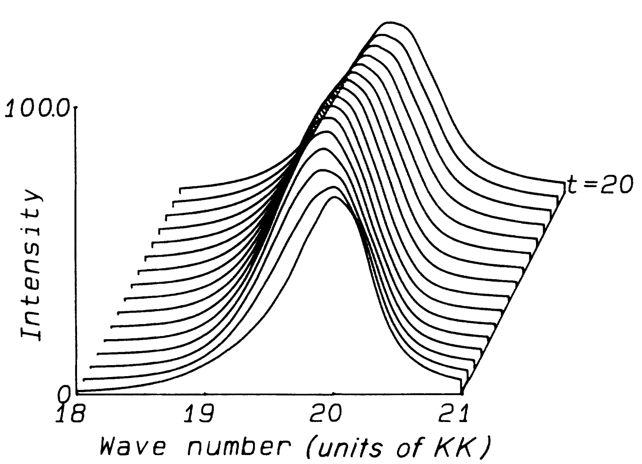

FIG. 1. Time-resolved fluorescence spectra from upper state initially populated at $v=0$ and 1. $\omega_{\beta\alpha}=20$ KK, $\omega_0=R_{\beta 1}=0.2$ KK, $R_{\text{ph}}=0$, $S_0=2$. Time in units of KK^{-1}. Intensity in arbitrary units.

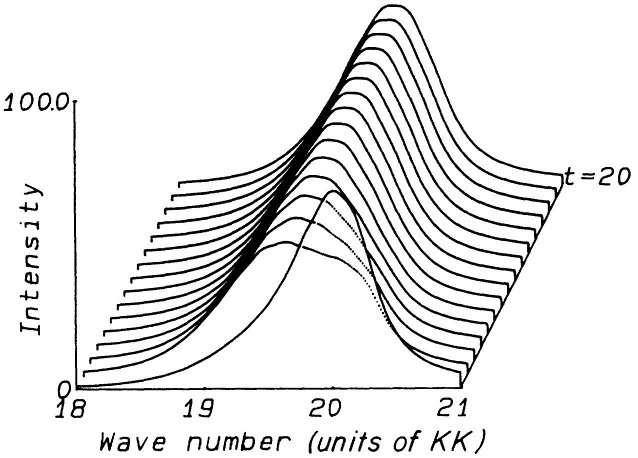

FIG. 2. Same as Fig. 1, except $R_{\text{ph}}=5$ KK.

state and is located in a highly anharmonic range of vibrational coordinates of the excited state. By this reasoning, a planar chromophore having a nonplanar excited state would have a strong coupling and hence fast relaxation dephasing takes place before or along with emission.

The present work can be applied to probe the solvation dynamics using the time-resolved emission. In this case it is more convenient to separate $\hat{\rho}^{(s)}$ into two subsystems, one due to the solute molecule $\hat{\rho}_s^{(s)}$ and the other due to the solvent cage molecules $\hat{\rho}_b^{(s)}$ which affect the electronic energy levels of the solute molecule (i.e., the solvent effect). In this way we can see that the observed spectral shift as a function of time will describe the dynamics of the local solvent molecules. Notice that, in this case, the coherence of $\hat{\rho}_s^{(s)}$ can be expressed as

$$\frac{d}{dt}\rho_s^{(s)}(t)_{mn}=-[i\omega_{mn}+i\Delta\omega_{mn}(t)]\rho_s^{(s)}(t)_{mn}$$
$$-R_s(t)_{mn}\rho_s^{(s)}(t)_{mn}\ , \tag{5.16}$$

where ω_{mn} denotes the energy gap of the solute molecule, while $\Delta\omega_{mn}(t)$ denotes the changes of the energy gap induced by the interaction $\hat{H}'$ between the solute molecule and the solvent cage molecules. It is given by

$$\Delta\omega_{mn}(t)=\frac{1}{\hbar}\sum_{\gamma}\rho^{(s)}(t)_{m\gamma,m\gamma}\left[H'_{m\gamma,m\gamma}+\sum_{\delta}\sum_{m'}{}'\frac{|H'_{m\gamma,m'\delta}|^2}{\omega_{m\gamma,m'\delta}}\right]-\frac{1}{\hbar}\sum_{\gamma'}\rho_b^{(s)}(t)_{n\gamma',n\gamma'}\left[H'_{n\gamma',n\gamma'}+\sum_{\delta'}\sum_{n'}{}'\frac{(H'_{n\gamma',n'\delta'}|^2}{\omega_{n\gamma',n'\delta'}}\right]\ , \tag{5.17}$$

where $\rho_b^{(s)}(t)$ is determined by

$$\frac{d\hat{\rho}_b^{(s)}}{dt}=-i\hat{L}_b^{(s)}\hat{\rho}_b^{(s)}-\hat{R}_b\hat{\rho}_b^{(s)}\ . \tag{5.18}$$

Here $\hat{R}_b$ denotes the damping operator describing the dynamics of the solvent cage molecules due to their coupling with the heat bath.

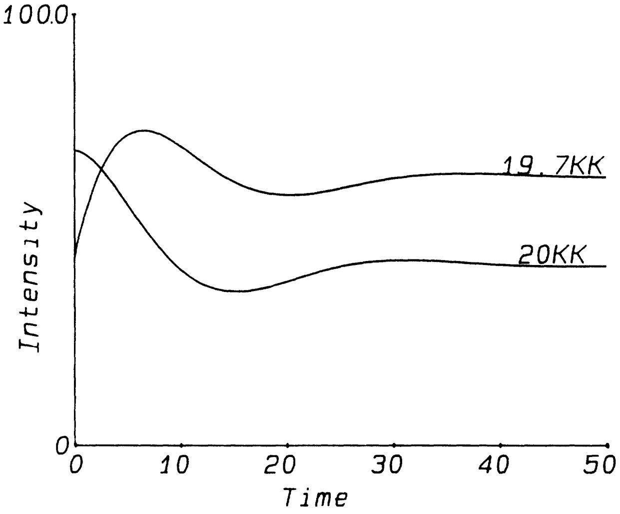

FIG. 3. Time dependence of fluorescence from upper state initially populated at $v=0$ and 1 for two frequencies: 19.7 and 20 KK. For parameters, see caption of Fig. 1.

From Eq. (5.17), we can see that the energy-level shift of the solute molecule changes with time due to the dynamics of the solvent cage molecules. Some preliminary results on the solvent effect on time-resolved emission spectra have been reported.[25]

In concluding the paper, we have shown that coherence is significant at short time scale, especially when coupling between electronic motion and nuclear motion is large, as is shown in our model calculation. With our calculation scheme, not only the dynamics of polarization of fluorescence but also the steady-state emission spectra can be treated.

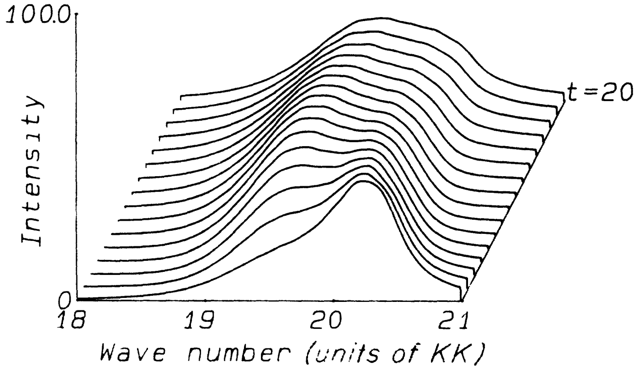

FIG. 4. Time-resolved fluorescence spectra from upper state initially populated at $v=1$ and 2. $\omega_{\beta\alpha}=20$ KK, $\omega_0=R_{\beta 1}=0.2$ KK, $R_{\text{ph}}=0$, $S_0=2$.

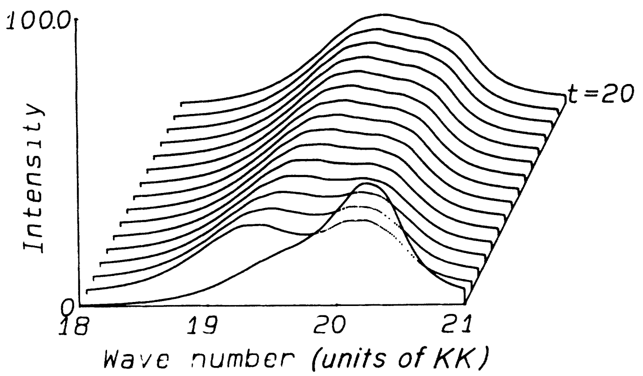

FIG. 5. Same as Fig. 4, except $R_{\mathrm{ph}}=5$ KK.

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APPENDIX A

In this appendix we are concerned with the calculation of $[\hat{G}^{(s)}(t)\hat{\rho}_0^{(s)}]_{nm}$. To demonstrate the theoretical approach, we consider a two-level (say, m and n) system. We first consider the diagonal case, i.e.,

$$[\hat{G}^{(s)}(t)\hat{\rho}_0^{(s)}]_{mm}=G^{(s)}(t)^{mm}_{mm}(\hat{\rho}_0^{(s)})_{mm}+G^{(s)}(t)^{nn}_{mm}(\hat{\rho}_0^{(s)})_{nn} . \tag{A1}$$

Here $[\hat{G}^{(s)}(t)\hat{\rho}_0^{(s)}]_{mm}$ denotes the population of the m level at time t, while $(\hat{\rho}_0^{(s)})_{mm}$ and $(\hat{\rho}_0^{(s)})_{nn}$ represent the initial populations. We shall assume that the m level is higher than the n level. Notice that

$$\hat{G}^{(s)}(t)=\exp[-it(\hat{L}_s-i\hat{R})] \tag{A2}$$

and

$$\frac{d\hat{\rho}^{(s)}}{dt}=-i\hat{L}_s\hat{\rho}^{(s)}-\hat{R}\,\hat{\rho}^{(s)} . \tag{A3}$$

Carrying out the Laplace transformation of Eq. (A2) yields

$$\hat{G}^{(s)}(p)=\int_0^\infty dt\, e^{-pt}\hat{G}^{(s)}(t)=\frac{1}{p+i(\hat{L}_s-i\hat{R})} . \tag{A4}$$

We now calculate $G^{(s)}(p)^{mm}_{mm}$ and $G^{(s)}(p)^{nn}_{mm}$. From Eq. (A4) we find

$$(p+R^{mm}_{mm})G^{(s)}(p)^{mm}_{mm}+R^{nn}_{mm}G^{(s)}(p)^{mm}_{nn}=1 \tag{A5}$$

and

$$(p+R^{nn}_{nn})G^{(s)}(p)^{mm}_{nn}+R^{mm}_{nn}G^{(s)}(p)^{mm}_{mm}=0 , \tag{A6}$$

where R^{mm}_{mm} and R^{nn}_{nn} denote the relaxation rate constants for $m \rightarrow n$ and $n \rightarrow m$, respectively, and $-R^{nn}_{mm}=R^{nn}_{nn}$ and $-R^{mm}_{nn}=R^{mm}_{mm}$.

Solving Eqs. (A5) and (A6) for $G^{(s)}(p)^{mm}_{mm}$ and $G^{(s)}(p)^{mm}_{nn}$, we obtain

$$G^{(s)}(p)^{mm}_{mm}=\frac{p+R^{nn}_{nn}}{p(p+R^{nn}_{nn}+R^{mm}_{mm})} \tag{A7}$$

and

$$G^{(s)}(p)^{mm}_{nn}=\frac{R^{mm}_{mm}}{p(p+R^{nn}_{nn}+R^{mm}_{mm})} . \tag{A8}$$

Carrying out the inverse Laplace transformation of Eqs. (A7) and (A8) yields

$$G^{(s)}(t)^{mm}_{mm}=\frac{R^{nn}_{nn}}{R^{nn}_{nn}+R^{mm}_{mm}}+\frac{R^{mm}_{mm}}{R^{nn}_{nn}+R^{mm}_{mm}}\exp[-t(R^{nn}_{nn}+R^{mm}_{mm})] \tag{A9}$$

and

$$G^{(s)}(t)^{mm}_{nn}=\frac{R^{mm}_{mm}}{R^{nn}_{nn}+R^{mm}_{mm}}\{1-\exp[-t(R^{nn}_{nn}+R^{mm}_{mm})]\} . \tag{A10}$$

Similarly, we obtain

$$G^{(s)}(t)^{nn}_{nn}=\frac{R^{mm}_{mm}}{R^{nn}_{nn}+R^{mm}_{mm}}+\frac{R^{nn}_{nn}}{R^{mm}_{nn}+R^{mm}_{mm}}\exp[-t(R^{nn}_{nn}+R^{mm}_{mm})] , \tag{A11}$$

$$G^{(s)}(t)^{nn}_{mm}=\frac{R^{nn}_{nn}}{R^{nn}_{nn}+R^{mm}_{mm}}\{1-\exp[-t(R^{nn}_{nn}+R^{mm}_{mm})]\} , \tag{A12}$$

and

$$[\hat{G}^{(s)}(t)\hat{\rho}_0^{(s)}]_{nm}=G^{(s)}(t)^{nm}_{nm}(\hat{\rho}_0^{(s)})_{nm} , \tag{A13}$$

where

$$G^{(s)}(t)^{nm}_{nm}=\exp[-t(i\omega_{nm}+R^{nm}_{nm})] , \tag{A14}$$

where R^{nm}_{nn} denotes the dephasing constant.

It should be noted that to obtain $[\hat{G}^{(s)}(t)\hat{\rho}_0^{(s)}]_{nm}$ and $[\hat{G}^{(s)}(t)\hat{\rho}_0^{(s)}]_{nn}$, one can also solve the generalized master equations given by Eq. (A3).

APPENDIX B

Here we consider the calculation of $K_{v_0}(t)$ defined by

$$K_{v_0}(t)=\sum_{w_0}|\langle X_{\beta v_0}|X_{\alpha w_0}\rangle|^2 \times\exp[-\mu_0'(w_0+\tfrac{1}{2})-\lambda_0(v_0+\tfrac{1}{2})] , \tag{B1}$$

where $\mu_0'=-it\omega_0'$ and $\lambda_0=it\omega_0$. Using the Mehler formula,[19] we can rewrite Eq. (B1) as

$$K_{v_0}(t)=\frac{\beta'_0\exp[-\lambda_0(v_0+\frac{1}{2})]}{(2\pi\sinh\mu'_0)^{1/2}}\int_{-\infty}^{\infty}\int dQ\,d\bar{Q}\,X_{\beta v_0}(Q)X_{\beta v_0}(\bar{Q})\exp\left[-\frac{\beta_0'^2}{4}\left[(Q'+\bar{Q}')^2\tanh\frac{\mu'_0}{2}+(Q'-\bar{Q}')^2\coth\frac{\mu'_0}{2}\right]\right], \tag{B2}$$

where $\beta'_0=(\omega'_0/\hbar)^{1/2}$. Using the contour integral representation for the Hermite polynomial and performing the integrations with respect to Q and $\bar{Q}$, we obtain

$$K_{v_0}=\frac{\beta_0\beta'_0\exp[-\lambda_0(v_0+\frac{1}{2})]}{\{[\beta_0^2\sinh(\mu'_0/2)+\beta_0'^2\cosh(\mu'_0/2)][\beta_0^2\cosh(\mu'_0/2)+\beta_0'^2\sinh(\mu'_0/2)]\}^{1/2}}\left[\frac{v_0!}{2^{v_0}}\right]\left[\frac{1}{2\pi i}\right]^2$$
$$\times\int_c\frac{dz_1}{z_1^{v_0+1}}\int_c\frac{dz_2}{z_2^{v_0+1}}\exp\left[-(z_1^2+z_2^2)-\frac{\beta_0^2\beta_0'^2d_0^2}{[\beta_0'^2+\beta_0^2\coth(\mu'_0/2)]}+\frac{\beta_0^2(z_2-z_1)^2}{\beta_0^2+\beta_0'^2\coth(\mu'_0/2)}\right.$$
$$\left.+\frac{\beta_0^2(z_2+z_1)^2}{\beta_0^2+\beta_0'^2\tanh(\mu'_0/2)}+\frac{2\beta_0'^2\beta_0d_0(z_1+z_2)}{\beta_0'^2+\beta_0^2\coth(\mu'_0/2)}\right], \tag{B3}$$

where $Q'_0=Q_0+d_0$, i.e., d_0 denotes the normal coordinate displacement. Carrying out the contour integrals in Eq. (B3) yields

$$K_{v_0}(t)=K_{0_0}(t)\Delta K_{v_0}(t), \tag{B4}$$

where

$$K_{0_0}(t)=\frac{\beta_0\beta'_0\exp\left[-\frac{\lambda_0}{2}-\frac{\beta_0^2\beta_0'^2d_0^2}{[\beta_0'^2+\beta_0^2\coth(\mu'_0/2)]}\right]}{\{[\beta_0^2\sinh(\mu'_0/2)+\beta_0'^2\cosh(\mu'_0/2)][\beta_0^2\cosh(\mu'_0/2)+\beta_0'^2\sinh(\mu'_0/2)]\}^{1/2}} \tag{B5}$$

and

$$\Delta K_{v_0}(t)=\exp(-\lambda_0v_0)\sum_{n_0=0}^{v_0}\frac{v_0!}{(n_0!)^2(v_0-n_0)!}\left[\frac{a_2}{2}\right]^{v_0-n_0}\left[\frac{a_1}{2}\right]^{n_0}H_{n_0}\left[\frac{-a_3}{\sqrt{4a_1}}\right]. \tag{B6}$$

Here $H_{n_0}(x)$ denotes the Hermite polynomial,

$$a_1=\frac{-\beta_0^4+\beta_0'^4}{[\beta_0^2+\beta_0'^2\tanh(\mu'_0/2)][\beta_0^2+\beta_0'^2\coth(\mu'_0/2)]}, \tag{B7}$$

$$a_2=\frac{2\beta_0^2\beta_0'^2}{[\beta_0^2\cosh(\mu'_0/2)+\beta_0'^2\sinh(\mu'_0/2)[\beta_0^2\sinh(\mu'_0/2)+\beta_0'^2\cosh(\mu'_0/2)]}, \tag{B8}$$

and

$$a_3=\frac{2\beta_0\beta_0'^2d_0}{[\beta_0'^2+\beta_0^2\coth(\mu'_0/2)]}. \tag{B9}$$

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