Molecular fluorescence and near resonance Raman yield as a probe for solvation dynamics

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A microscopic theory for spontaneous emission line shapes of polyatomic molecules in condensed phases is developed. The distinction between the Raman and the fluorescence component is discussed and a rigorous transform relation between the total Raman excitation profile and the absorption line shape is obtained. The effects of solvation are introduced via generalized solvent line shape functions corresponding to the solvent dynamics before and after the reorganization process which follows the electronic excitation. The Raman yield and its frequency dependence are shown to provide a sensitive probe for the solvent dynamics. Detailed calculations for model systems and for the retinal chromophore in bacteriorhodopsin are presented.

I. INTRODUCTION

Spontaneous Raman and fluorescence (SRF) line shapes provide a sensitive spectroscopic probe for polyatomic molecules in condensed phases. The SRF experiment is illustrated in Fig. 1. It involves exciting the molecule with a laser field of frequency \( \omega_L \) and detecting the generated spontaneous emission with frequency \( \omega_S \). A distinction should be made between frequency-domain SRF, whereby the incoming field and the signal field are stationary, and time-domain SRF, whereby both fields are pulsed. There is currently considerable interest in extracting useful structural and dynamical information on complex molecular systems from SRF line shapes. In this article, we develop efficient methods for the calculation of SRF line shapes of large polyatomic molecules in condensed phases (e.g., solutions, solid matrices, and glasses), and relating them to the microscopic dynamics. In Sec. II, we present general expressions, within the rotating wave approximation, for time- and frequency-resolved SRF line shapes in terms of four-time correlation functions of the dipole operator. In Sec. III, we divide the material degrees of freedom into an optically active part (the system) and the optically inactive part (the bath), and propose a unified microscopic model for the absorption and the SRF line shapes. The nature of the bath depends on the physical system of interest. It could be the solvent, a host crystal, or an amorphous medium. Hereafter the bath will be denoted as the “solvent.” We further divide the solvent modes into two groups depending on their time scales. The fast solvent modes are treated in Sec. IV using the factorization approximation, resulting in two solvent broadening functions, \( J_S(t) \) and \( J_L(t) \), corresponding to solvent motions before and after the solvent reorganization which follows the electronic excitation. The slow solvent modes contribute to inhomogeneous broadening and are treated in Sec. V. In Sec. VI, we show that the total SRF line shape can be partitioned into a fluorescence component and a Raman component and that the Raman excitation profile can be expressed as a square of a Raman amplitude. In Sec. VII, we present the expressions for the fluorescence cross section and the Raman cross section and relate them to the absorption cross section. The Raman yield, which is defined as the ratio of the Raman and the absorption cross sections, may provide a sensitive probe for the solvent dynamics. For demonstrating the results of Secs. IV to VII, a stochastic model for the solvent is developed in Sec. VIII. In Sec. IX, we propose a microscopic model for the solvent broadening functions. Detailed calculations for simple model systems and for the retinal chromophore in bacteriorhodopsin are presented in Sec. X. Finally our results are summarized in Sec. XI.

II. CORRELATION FUNCTION EXPRESSION FOR SRF SPECTROSCOPY

We consider a medium consisting of noninteracting optically active polyatomic molecules (absorbers) and a set of

![FIG. 1. The molecular level scheme for the spontaneous Raman and fluorescence processes.](image)
bath (solvent) degrees of freedom, which do not interact with the electromagnetic field, but do interact with the absorbers. We apply a classical external electromagnetic field on this optical medium. The total Hamiltonian of the system is

\[ H_T = H + H_{\text{int}}(t) \]  

(1)

Here \( H \) is the Hamiltonian for the material system in the absence of the radiation field and \( H_{\text{int}} \) represents the dipolar radiation–matter interaction, i.e., \(^{19}\)

\[ H_{\text{int}}(t) = E(r,t)V, \]  

(2)

where we focus on one absorber located at \( r \) with the dipole operator \( V \). \( E(r,t) \) in Eq. (2) is the electric field, which for a SRF process (Fig. 1) can be decomposed into the incoming and the emitted modes:

\[ E(r,t) = E_L(r,t) + E_S(r,t) \]  

(3a)

The incoming field \( E_L(r,t) \) will be treated classically,

\[ E_L(r,t) = E(t)\exp(ik_Lr - io_Lt) + E^*(t)\exp(-ik_Lr + io_Lt), \]  

(3b)

where \( E(t) \) is the temporal envelope of the incoming field. The scattered field \( E_S(r,t) \) will be treated quantum mechanically, since it is generated by spontaneous emission. For that field we have \(^ {19}\)

\[ E_S(r,t) = i(2\pi\hbar\omega_S/\Omega)^{1/2}\{a_S^\dagger\exp(ik_Sr - io_St) - a_S^2\exp(ik_Sr + io_St)\} \]  

(3c)

where \( a_S^\dagger \) (\( a_S \)) is the creation (annihilation) operator for the scattered photon with wave vector \( k_S \), and \( \Omega \) is the volume of the optical medium. In order to calculate the SRF spectrum, we start at \( t = -\infty \) and assume that the system is in thermal equilibrium with respect to the material Hamiltonian \( H \) (without the radiation field). Its initial density matrix \( \rho(-\infty) \) is

\[ \rho(-\infty) = \exp(-H/kT)/\text{Tr}\exp(-H/kT). \]  

(4)

The system then evolves in time according to the Liouville equation

\[ \frac{d\rho}{dt} = -i[H,\rho] - i[H_{\text{int}}(t),\rho]. \]  

(5)

Equation (5) can be recast in Liouville space notation, \(^ {16}\)

\[ \frac{d\rho}{dt} = -iL\rho - iL_{\text{int}}(t)\rho, \]  

(6)

where the Liouville operator is defined by its action on an arbitrary operator \( A \):

\[ L_{\text{int}}(t)A \equiv [H_{\text{int}}(t),A]. \]  

(7b)

In Eqs. (4)–(7) and in the rest of this work, we set \( \hbar = 1 \). In an SRF experiment, we monitor the scattered field with both time and frequency resolution. The operator representing the rate of emission of \( \omega_S \) photons is

\[ B = \frac{d}{dt}a_S^\dagger a_S = [H_{\text{int}}(t), a_S^\dagger a_S] = iL_{\text{int}}(t)a_S^\dagger a_S. \]  

(8)

The rate of photon emission with frequencies between \( \omega_S + d\omega \) and \( \omega_S + d\omega \) is given by \( \langle B \rho(t) \rangle \) and is obtained by integrating the expectation value of \( B \) over spatial angles and summing over the possible polarizations of the emitted light, resulting in

\[ \langle B \rho(t) \rangle = \frac{\Omega\omega_S^5}{c^3\pi^2} \langle \langle B \rangle \hat{S}(t) \rangle. \]  

(9)

Here \( c \) is the speed of light. In Eq. (9) we have used the double bracket notation \(^ {16}\) to denote an inner product of operators. For any two operators,

\[ \langle A | B \rangle = \text{Tr}(A^\dagger B). \]  

(10)

We shall also define a Liouville space “matrix element” by

\[ \langle A | L | B \rangle = \text{Tr}(A^\dagger LB). \]  

(11)

For an SRF process \(^ {18}\) in a weak external field, we need to calculate \( \rho(t) \) perturbatively to third order in \( L_{\text{int}} \). We then get

\[ \langle B \rangle = \frac{\Omega\omega_S^5}{c^3\pi^2} \langle \langle B \rangle \hat{S}(t) \rangle \times L_{\text{int}}(t - t_2)G(t_2)L_{\text{int}}(t - t_2 - t_3)G(t_1) \times L_{\text{int}}(t - t_1 - t_2 - t_3)\rho(-\infty)), \]  

(12)

Here the Green function \( G(t) \) is the formal solution of Eq. (6) in the absence of the electromagnetic field:

\[ G(t) = \exp(-it\tau). \]  

(13)

The interpretation of Eq. (12) is as follows: the system starts at \( t = -\infty \) with a density matrix \( \rho(-\infty) \). It then interacts three times with the electromagnetic field at times \( t = t_1 - t_2 - t_3 \), \( t = t_2 - t_3 \), and \( t = t_3 \). During the intervals between interactions \( (t_1, t_2, t_3) \) it evolves in time according to \( G(t) \). At time \( t \) we finally calculate the SRF spectrum \( \hat{S} \). Each \( L_{\text{int}} \) term in Eq. (12) is a commutator and it can act either from the left or from the right. When Eq. (12) is explicitly evaluated, we find that it has three terms plus their complex conjugates. We then have\(^ {16,17}\)

\[ \hat{S}(\omega_L, \omega_S, t) = \frac{2\omega_S^3}{9\pi c^3} \int_0^\infty dt_1 \int_0^\infty dt_2 \int_0^\infty dt_3 \left( F(0, t_1 + t_2 + t_3, t_1 + t_2, t_3) \exp(-i\omega_L t_1 - i\omega_S t_3) E(t - t_2 - t_3) E^*(t - t_1 - t_2 - t_3) \right. \]

\[ + F(0, t_1 + t_2, t_1 + t_2, t_3) \exp(-i\omega_L t_1 + i\omega_S t_3) E(t - t_2 - t_3) E^*(t - t_1 - t_2 - t_3) \]

\[ + F(0, t_1 + t_2 + t_3, t_1 + t_2) \exp[-i\omega_L t_1 - i(\omega_L - \omega_S) t_2 + i\omega_S t_3] E(t - t_3) E^*(t - t_1 - t_2 - t_3) + \text{c.c.}, \]  

(14)
where the four-time correlation function of the dipole operator is defined as

\[
F(t_1,t_2,t_3,t_4) = \text{Tr} \left[ V(t_1) V(t_2) V(t_3) V(t_4) \rho(-\infty) \right] \\
= \text{Tr}_S \cdot \text{Tr}_B \left[ V(t_1) V(t_2) V(t_3) V(t_4) \rho(-\infty) \right] \\
= \langle \text{Tr}_B \left[ V(t_1) V(t_2) V(t_3) V(t_4) \rho(-\infty) \right] \rangle 
\]

(15)

with

\[
V(\tau) = \exp(iH\tau) V \exp(-iH\tau)
\]

(16)

and the trace (Tr) is taken over all the bath and the system degrees of freedom. We have used the angular brackets \(\langle \cdot \rangle\) to represent Tr, the partial trace over the bath degree of freedom. Tr\(_S\) denotes a partial trace over the system degrees of freedom. The three terms in the right-hand side of Eq. (14) correspond to the contributions of the pathways I, II, and III of Fig. 2, respectively. At this point we shall consider the two limiting cases of ideal time-domain and frequency-domain SRF. In an ideal time-domain SRF, the incoming field is an infinitely short pulse, i.e.,

\[
E(t) = E\delta(t).
\]

(17)

In this case the emission spectrum does not depend on \(\omega_L\) and Eq. (14) reduces to

\[
\tilde{S}(\omega_L,\omega_S,t) = \frac{4\omega_L^3}{3\pi c^3} |E|^2 \text{Re} \int_0^\infty dt \, F(0,\tau,t) \exp[i\omega_S(t-\tau)].
\]

(18)

In a steady state experiment, the envelope of the incoming field \(E(t)\) is independent on time. We now introduce the differential photon scattering cross section \(\sigma'(\omega_L,\omega_S)\), where \(\sigma'(\omega_L,\omega_S)\,d\omega_S\) is the number of photons emitted between \(\omega_S\) and \(\omega_S+d\omega_S\) per unit time divided by the incident photon flux. Substituting \(E(t) = E\) in Eq. (14) and dividing by the incident photon flux \(|c|E|^2/(2\pi\omega_L)|\) results in

\[
\sigma'(\omega_L,\omega_S) = \frac{4\omega_L^3 \omega_S^3}{9c^3} S(\omega_L,\omega_S),
\]

(19)

where the SRF line shape is given by

\[
S(\omega_L,\omega_S) = \int_0^\infty dt_1 \int_0^\infty dt_2 \int_0^\infty dt_3 \, F(0,t_1+t_2+t_3,t_1+t_2+t_3) \exp(-i\omega_L t_1 - i\omega_S t_3)
+i F(0,t_1+t_2+t_3,t_1+t_2) \exp(-i\omega_L t_1 + i\omega_S t_2)
+i F(0,t_1+t_2+t_3,t_1+t_2) \exp[-i\omega_L t_1 - i(\omega_L - \omega_S) t_2 + i\omega_S t_3] + \text{c.c.}
\]

(20)

In concluding this section, we introduce the photon absorption cross section. Using first order perturbation theory for the density matrix, we have

\[
\sigma_A(\omega_L) = (2\pi\omega_L/3c) S_A(\omega_L)
\]

(21)

with the absorption line shape

\[
S_A(\omega_L) = 2 \text{Re} \int_0^\infty dt \exp(i\omega_L t) \text{Tr} [V(t) V(0) \rho(-\infty)].
\]

(22)

In the absence of nonradiative decay channels of the excited state, the system emits one photon per every absorbed photon and using the optical theorem we get

\[
\sigma_A(\omega_L) = \int_0^\infty d\omega_S \, \sigma'(\omega_L,\omega_S).
\]

(23)

In the coming sections we shall develop a microscopic theory for the SRF line shape \(S\) [Eq. (20)] and for the absorption line shape \(S_A\) [Eq. (22)] of polyatomic molecules in condensed phases.

III. A MOLECULAR MICROSCOPIC MODEL FOR THE FOUR-POINT CORRELATION FUNCTION

We shall now apply the results of Sec. II to a specific model system, commonly used in molecular SRF.16–18 We consider a molecular level scheme for the absorber, consisting of a manifold of vibronic levels belonging to the ground electronic state, denoted \(|\alpha\rangle, |\beta\rangle \ldots\) and a manifold of vi-

FIG. 2. The Liouville space coupling scheme and the three pathways contributing to the SRF process (Ref. 16). The three terms in Eq. (14) or Eqs. (43) correspond, respectively, to the pathways I, II, and III.
bronic levels belonging to an excited electronic state, denoted \(|b\rangle\), \(|a\rangle\), etc. (Fig. 1). The ground and the excited electronic states will be denoted \(|g\rangle\) and \(|e\rangle\), respectively. The absorber is further coupled to a thermal bath, and the combined Hamiltonian for the molecule and the bath is

\[
H = |g\rangle \langle H_e | Q_S \rangle + h_e | Q_B \rangle \langle g | + |e\rangle \langle H_e | Q_S \rangle + h_e | Q_B \rangle \langle e |. \quad (24)
\]

Here the ground state Hamiltonian is partitioned into a system part \(H_e\), which depends on the system coordinates \(Q_S\) and a bath part \(h_e\), which depends on the bath coordinates \(Q_B\). Similar partitioning of the excited state Hamiltonian into \(H_e\) and \(h_e\) is made. The interaction between the system and the bath is reflected in the difference between \(h_e\) and \(h_e\). This implies that the bath eigenstates are different, depending on the state of the system. The Hamiltonian Eq. (24) does not allow a direct coupling between the bath and the nuclear motions of the system. Such coupling is responsible for vibrational relaxation processes which will not be considered in this article. These processes may be introduced phenomenologically into the final expressions derived here.\(^{21,22}\)

The eigenstates of the ground-state and of the excited-state Hamiltonian are

\[
(H_e + h_e) \vert \nu \rangle = (\epsilon_{\nu} - i \gamma_{\nu}/2 + \epsilon_{g}) \vert \nu \rangle , \quad \nu = a, c, \ldots , \quad (25a)
\]

and

\[
(H_e + h_e) \vert \nu \beta \rangle = (\epsilon_{\nu} - i \gamma_{\nu}/2 + \epsilon_{g}) \vert \nu \beta \rangle , \quad \nu = b, d, \ldots . \quad (25b)
\]

Here \(\gamma_{\nu}\) is the inverse lifetime of the system state \(|\nu\rangle\) and \(a, b, c, d, \ldots\) stand for the collection of all system quantum numbers, whereas \(\alpha\) and \(\beta\) represent the solvent quantum numbers, when the system is in the \(|g\rangle\) or the \(|e\rangle\) state, respectively. The electronic dipole operator in Eq. (2) is taken to be of the form

\[
V = \mu \langle Q_S \rangle \mu_B \langle Q_B \rangle \left[ |g\rangle \langle e | + |e\rangle \langle g | \right] , \quad (26)
\]

where \(\mu_B\) is the electronic transition dipole operator for the absorber (bath) and couples vibronic levels belonging to different electronic states, i.e.,

\[
\mu = \sum_{a, b} (\mu_{ab} \langle a | + \mu_{ba} \langle b | a \rangle . \quad (27)
\]

Here the summation runs over the entire manifolds of ground and excited electronic states of the system. A similar expression holds for the bath dipole by changing \(\mu\), \(a\), and \(b\) to \(\mu_B\), \(\alpha\), and \(\beta\). The molecule is taken to be initially at thermal equilibrium in the ground-state manifold, and its density matrix is the direct product of a system part \((\sigma_g)\) and a bath part \((\rho_e)\), i.e.,

\[
\rho(\infty) = \sigma_g \langle Q_S \rangle \rho_e \langle Q_B \rangle \quad (28)
\]

with

\[
\sigma_g = \exp(-H_e/kT)/\text{Tr} \exp(-H_e/kT) = \sum_{a} \langle a | P(a) \langle a | . \quad (29a)
\]

\[
\rho_e = \exp(-h_e/kT)/\text{Tr} \exp(-h_e/kT) = \sum_{a} \langle a | \rho_e (a) \langle a | . \quad (29b)
\]

Here

\[
P(a) = \exp(-\epsilon_a/kT)/\sum_{a} \exp(-\epsilon_a/kT) , \quad (30a)
\]

\[
\rho_e (a) = \exp(-\epsilon_a/kT)/\sum_{a} \exp(-\epsilon_a/kT) . \quad (30b)
\]

For subsequent manipulations we introduce also the bath density matrix corresponding to thermal equilibrium within the electronically excited state,

\[
\rho_e = \exp(-h_e/kT)/\text{Tr} \exp(-h_e/kT) = \sum_{\beta} \langle \beta | \rho_e (\beta) \langle \beta | . \quad (31)
\]

where the summation runs over the excited state manifold of the bath, and \(\rho_e (\beta)\) is defined by Eq. (30b) with changing the indexes \(g\) and \(\alpha\) to \(e\) and \(\beta\), respectively. We further define the following solvent operators:

\[
(f(t) = \exp(ih_e t) \mu_B \exp(-ih_e t) \mu_B , \quad (32a)
\]

\[
(f(t) = \exp(ih_e t) \mu_B \exp(-ih_e t) \mu_B , \quad (32b)
\]

\[
(f(t) = \mu_B \rho_e \exp(-ih_e t) \mu_B \exp(ih_e t) , \quad (32c)
\]

and their thermal averages

\[
J_g (t) = \langle \rho_e f(t) \rangle = \langle \langle \langle f(t) \rangle \rangle \rangle = \langle \rho_g \exp(ih_e t) \mu_B \exp(-ih_e t) \mu_B \rangle , \quad (33a)
\]

\[
J_e (t) = \langle \rho_e f(t) \rangle = \langle \rho_e \exp(ih_e t) \mu_B \exp(-ih_e t) \mu_B \rangle . \quad (33b)
\]

Note that

\[
J_g (-t) = J_g^* (t) , \quad (34a)
\]

\[
J_e (-t) = J_e^* (t) , \quad (34b)
\]

\(J_g(t)\) is the solvent line broadening function when the solvent is equilibrated with the system in the ground state so that the solvent density matrix is \(\rho_e\). This corresponds to line broadening in absorption. \(J_e(t)\), on the other hand, represents the line broadening when the solvent is equilibrated with the system that is electronically excited and the solvent density matrix is \(\rho_e\). This corresponds to line broadening after the solvent reorganization process in which the solvent adjusts its state to the electronically excited system.\(^{23,24}\) This is therefore a line broadening function corresponding to emission. We are now in a position to develop the expressions for the absorption line shape [Eq. (22)] and the SRF line shape [Eq. (20)] for our molecular system [Eq. (24)]. Without loss of generality, we set

\[
\langle \rho_e a^2 \rangle = \langle \rho_e a^2 \rangle = 1 , \quad (35a)
\]

\[i.e., \quad J_g (0) = J_e (0) = 1 . \quad (35b)\]

The ordinary absorption line shape of Eq. (22) can be rewritten as\(^{22}\):

\[
S_f (\omega_L) = 2 \text{Re} \int_{0}^{\infty} dt \exp(i \omega_L t) \sigma(t) \langle J_e (t) \rangle , \quad (36)
\]

where

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\[ S_{\alpha} (\omega_L) = 2 \text{Re} \sum_{a,b} \mathcal{P} (a) \mu_{ab} \mu_{ba} \int_0^\infty dt \exp (i \omega_L t) I_{ab} (t) J_g (t) \]
\[ = -2 \text{Im} \sum_{a,b} \mathcal{P} (a) \mu_{ab} \mu_{ba} I_{ab} (\omega_L) \] (39)

where

\[ I_{\mu \nu} (t) = \exp (- i \omega_{\mu \nu} t - \Gamma_{\mu \nu} t) \]
\[ \omega_{\mu \nu} = \epsilon_\mu - \epsilon_\nu \]
\[ \Gamma_{\mu \nu} = (\gamma_\mu + \gamma_\nu)/2 \]

with

\[ I_{\nu \mu} (t) = I_{\mu \nu} (t) = I_{\mu \nu} (-t) \] (41)

and

\[ I_{\mu \nu} (\omega) = -i \int_0^\infty dt \exp (i \omega t) I_{\mu \nu} (t) J_g (t) \] (42a)

For subsequent manipulations we shall also define

\[ \overline{I}_{\mu \nu} (\omega) \equiv -i \int_0^\infty dt \exp (i \omega t) I_{\mu \nu} (t) J^* (t) \] (42b)

\[ I_{\mu \nu} (\omega) \] is an absorption line shape function and \( \overline{I}_{\mu \nu} (\omega) \) is the emission line shape function of levels \( \mu \) and \( \nu \) broadened by the bath. Similarly the four-time correlation function \( F(t_1, t_2, t_3, t_4) \) of Eq. (15) can also be factorized into a system part \( \{ W \} \) and a solvent part \( \{ M \} \), and the SRF line shape [Eq. (20)] assumes the form

\[ S_{\alpha} (\omega_L) = \sum_{t_1, t_2, t_3} \{ W_1 (t_1, t_2, t_3) M_1 (t_1, t_2, t_3) \} \exp (- i \omega_L t_1 - i \omega_S t_3) \]
\[ + W_{11} (t_1, t_2, t_3) M_{11} (t_1, t_2, t_3) \exp (- i \omega_L t_1 + i \omega_S t_3) \]
\[ + W_{111} (t_1, t_2, t_3) M_{111} (t_1, t_2, t_3) \exp [- i \omega_L t_1 - i (\omega_L - \omega_S) t_2 + i \omega_S t_3] + c.c., \] (43)

where the indexes I, II, and III correspond to the pathways I, II, and III, of Fig. 2, respectively. We shall now expand the system correlation functions in terms of the system eigenstates and keep the formal expressions for the bath correlation functions. This is analogous to our expression for the absorption [Eq. (39)]. We then have

\[ W_1 (t_1, t_2, t_3) = \sum_{a,b,d} \mathcal{P} (a) \mu_{ab} \mu_{bc} \mu_{cd} I_{ab} (t_1) I_{bc} (t_2) I_{cd} (t_3) \] (44a)

\[ W_{11} (t_1, t_2, t_3) = \sum_{a,b,d} \mathcal{P} (a) \mu_{ab} \mu_{bc} \mu_{cd} \mu_{de} I_{ab} (t_1) I_{cd} (t_2) I_{de} (t_3) \] (44b)

\[ W_{111} (t_1, t_2, t_3) = \sum_{a,b,d} \mathcal{P} (a) \mu_{ab} \mu_{bc} \mu_{cd} \mu_{de} I_{ab} (t_1) I_{cd} (t_2) I_{de} (t_3) \] (44c)

and

where \( \sigma(t) \equiv \text{Tr}_{S} [\mu(t) \mu(0) \sigma_S] \) (37a)

with

\[ \mu(t) = \exp (i H_g t) \mu \exp (- i H_g t) \] (37b)

and

\[ J_g (t) \equiv \text{Tr}_{S} [\mu_S (t) \mu_S (0) \rho_S] \] (38a)

with

\[ \mu_S (t) = \exp (i H_S t) \mu \exp (- i H_S t) \] (38b)

Equation (36) together with Eq. (22) show that the electronic dipole correlation functions can in this case be factorized into contributions from the system [\( \sigma(t) \)] and from the bath [\( J_g (t) \)]. \( \sigma(t) \) and \( J_g (t) \) have similar formal expressions [Eqs. (37a) and (38a)]. However, in practice their evaluation should be done very differently. Normally there are only a few optically active system modes which are strongly coupled to the electronic transition. The spectra will depend in a significant way on the nature of these modes. It is therefore natural to express \( \sigma(t) \) in terms of the eigenstates of the system. On the other hand, the solvent has a very large number of modes and is practically infinite. Each of the individual solvent mode does not affect the spectra significantly and \( J_g (t) \) is built out of a very large number of small contributions from the solvent modes. It is therefore impossible and unnecessary to calculate \( J_g (t) \) in terms of the solvent eigenstates. We shall therefore keep \( J_g (t) \) at this stage in a formal form and in the coming sections we shall develop microscopic and stochastic models towards the direct evaluation of \( J_g (t) \) without performing summations over solvent eigenstates. If any of the solvent modes plays a special role in the spectrum we can always partition the Hamiltonian differently and include that mode in the system. We thus recast Eq. (36) in the form

\[ S_{\alpha} (\omega_L) \]

IV. HOMOGENEOUS BROADENING: THE FACTORIZATION APPROXIMATION

Equation (43) expresses the SRF line shape in terms of the four-point correlation functions of the bath, \( M_1, M_{11}, \) and \( M_{111} \) [Eqs. (45)]. In general, their evaluation requires
calculating the correlated dynamics of the system and the bath degrees of freedom. In this section, we shall develop an approximate expression for these four-time correlation functions, which is based on the assumption of separation of time scales between the system and the bath. Under very general conditions, which will be precisely specified, it is possible to factorize the average of the product of operators in Eqs. (45) into a product of averages. This result is in a considerable simplification of the final expressions and provides a useful method of modeling realistic molecules in solutions. Let us consider Eqs. (44) and (45) in more detail. During the time intervals \( t_1 \) and \( t_2 \), the system is in the optical coherence \((a, b, c, d, \ldots)\) and the bath undergoes a time evolution. During the time interval \( t_3 \), the system is either in the excited electronic state \( |e\rangle \) (cf. \( W_1 \) and \( W_{11} \) representing pathways I and II of Fig. 2) or in the ground electronic state \( |g\rangle \) (cf. \( W_{111} \) representing pathway III of Fig. 2). The solvent dynamics will then be governed by the Hamiltonians \( h_s \) or \( h_g \), respectively. The relevant duration of the \( t_2 \) period is of the order of the lifetime \( \Gamma_\mu^{-1} (\mu, \nu = a, b, c, d, \ldots) \). This time (typically \( 10^{-9} \) s) is expected to be much longer than the characteristic solvent relaxation time \( \Lambda^{-1} (10^{-13} \text{ s}) \), which restores the solvent to equilibrium with the system in the excited state \( |e\rangle \) (for pathways I and II) or in the ground state \( |g\rangle \) (for pathway III), i.e.,

\[
\Lambda \gg \Gamma_\mu, \quad \mu, \nu = a, b, c, d, \ldots
\]

(46)

This is the rapid fluctuation limit \(^{18b}(b)\) in which we can safely assume that at the beginning and at the end of the period the solvent is in thermal equilibrium and its density matrix is either \( \rho_s \) (for pathways I and II) or \( \rho_s \) (for pathway III). This assumption results in the factorization of Eqs. (45) as

\[
M_1(t_1, t_2, t_3) = \langle J(t_1) \rangle \langle \rho_e \exp(ih_e t_2) J(t_3) \exp(-ih_e t_2) \rangle
\]

\[
= J^*_e(t_1)J_e(t_3),
\]

(47a)

\[
M_{11}(t_1, t_2, t_3) = \langle J(t_1) \rangle \langle \rho_e \exp(ih_e t_2) J^*(t_3) \exp(-ih_e t_3) \rangle
\]

\[
= J^*_e(t_1)J_e(t_3),
\]

(47b)

\[
M_{111}(t_1, t_2, t_3) = \langle \rho_e \delta(t - t_1) \rangle \langle \rho_e \exp(ih_e t_2) f(t_3) \exp(-ih_e t_3) \rangle
\]

\[
= J^*_e(t_1)J_e(t_3),
\]

(47c)

where we have made use of Eqs. (33) and (34). Substituting Eqs. (44) and (47) into Eq. (43) and making use of Eqs. (41) and (42), we get

\[
S(\omega_L, \omega_S) = -2 \text{Im} \sum_{a,b,c,d} P(a) \mu_{ab} \mu_{bc} \mu_{cd} \mu_{da} \times
\]

\[
I_{ab}(\omega_S) \left\{-\frac{I_{bc}(\omega_S) + I_{dc}(\omega_S)}{\omega_{bd} + i\Gamma_{bd}} + \frac{I_{dc}(\omega_S)}{\omega_S - \omega_L + \omega_{ca} + i\Gamma_{ca}}\right\}.
\]

(48)

Equation (48) represents the factorization approximation in which the SRF line shape is expressed in terms of the generalized absorption and emission line shapes functions [Eqs. (42)]. When Eqs. (46)–(48) hold, the line broadening is denoted as homogeneous. This is in contrast to the inhomogeneous (static) broadening mechanism which will be introduced in the next section. For homogeneous broadening, Eqs. (45) simplifies considerably since the four-time correlation functions are expressed in terms of products of two-time correlation functions which can be easily evaluated. It should be noted that this factorization approximation appears more naturaly when Eqs. (45) are written in Liouville space using the notation of Eq. (12). For the sake of simplicity of the presentation we have avoided using that notation here. A detailed analysis of the factorization approximation was given elsewhere.\(^{16,22,26}\)

V. THE ROLE OF INHOMOGENEOUS BROADENING

The thermal bath is in general characterized by a multitude of time scales corresponding to the various possible types of solvent motions. In Sec. IV, we treated the fast motions of the solvent using the factorization approximation, which is valid when Eq. (46) holds. In addition to these fast modes the solvent may also have slow degrees of freedom with \( \Lambda = 0 \). For these degrees of freedom the factorization approximation is no longer valid. In this section we shall discuss the role of these modes using the microscopic model presented in Sec. III. We assume that the total solvent Hamiltonian \( h_s \) can be represented as a sum of contributions of the slow modes and the fast modes. We further assume that the solvent dipole operator \( \mu_B \) is independent of the solvent coordinates (the Condon approximation). In this case, the total solvent correlation functions \( M_1, M_{11}, \) and \( M_{111} \) may be written as products of a contribution from the fast modes and from the slow modes. We shall now consider the effect of the slow solvent modes on the SRF line shape. To that end we write the solvent Hamiltonians \( h_s \) and \( h_e \) corresponding to the slow modes \( \{Q_n\} \)

\[
h_s = T_B + V_s (Q_B)
\]

(49a)

and

\[
h_e = T_B + V_e (Q_B).
\]

(49b)

Here \( T_B \) is the kinetic energy and \( V_e (V_s) \) is the potential energy for the slow solvent modes, when the system is in the ground (excited) electronic state. For the slow modes we neglect the kinetic energy in Eqs. (49) so that \( h_s \) and \( h_e \) commute:

\[
[h_s, h_e] = 0
\]

(50)

We further introduce the static broadening function

\[
\chi(t) \equiv \langle \rho_e \exp(-iUt) \rangle,
\]

(51)

where

\[
U \equiv V_e - V_s.
\]

(52)

Note that \( \chi(t) \) of Eq. (51) is the special case of \( J_e(t) \) [Eq. (38a)] when \( \mu_B = 1 \) and the static limit [Eq. (50)] holds. Substituting Eqs. (50) and (51) into Eqs. (45), and making use of Eqs. (47) for the fast bath modes, we get

\[
M_1(t_1, t_2, t_3) = J^*_e(t_1)J_e(t_3) \chi(-t_1 - t_3),
\]

(53a)

\[
M_{11}(t_1, t_2, t_3) = J^*_e(t_1)J^*_e(t_3) \chi(-t_1 + t_3),
\]

(53b)

\[
M_{111}(t_1, t_2, t_3) = J^*_e(t_1)J_e(t_3) \chi(-t_1 + t_3).
\]

(53c)

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Equation (43) together with Eqs. (44) and (53) constitutes our final expressions for the SRF line shape within the factorization approximation. The four-point bath correlation functions necessary for the SRF line shapes are expressed here in terms of the two time correlation functions $J_\sigma(t)$, $J_\tau(t)$, and $\chi(t)$, whose calculation is considerably simpler. Equations (53) allow for homogeneous and inhomogeneous broadening with arbitrary line shapes. In many phenomenological theories the homogeneous broadening is taken to be Lorentzian [identical for absorption and emission; see Eqs. (92a) and (105a)], and the inhomogeneous broadening is Gaussian [see Eq. (130)]. The present analysis shows that these are just special cases of Eqs. (53). In concluding this section we introduce the Fourier transform of $\chi(t)$, i.e.,

$$
\chi(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \chi(t) \exp(i\omega t) = \langle \rho_\omega \delta(\omega - U) \rangle.
$$

(54)

Equation (54) is well known as the static limit in the theory of line broadening.\textsuperscript{16,27,40} Making use of Eqs. (53) and (54), the SRF line shape [Eq. (43)] can be recast in the form

$$
\overline{S}(\omega_L,\omega_S) = \int_{-\infty}^{\infty} d\omega S(\omega_L - \omega, \omega_S - \omega) \chi(\omega),
$$

(55a)

where $S(\omega_L,\omega_S)$ in the integrand is given by Eq. (48), and $\overline{S}$ denotes the SRF line shape in the presence of inhomogeneous as well as homogeneous broadening. The absorption line shape $S_\sigma(\omega_L)$, in this case, is

$$
\overline{S}_\sigma(\omega_L) = 2 \text{Re} \int_{0}^{\infty} dt \exp(i\omega_L t) \sigma(t) J_\sigma(t) \chi(t)
$$

$$
= \int_{0}^{\infty} d\omega S_\sigma(\omega_L - \omega) \chi(\omega),
$$

(55b)

where $S_\sigma(\omega_L)$ is given by Eq. (39). Page et al.\textsuperscript{14} had modeled the bath by a large number of linearly displaced harmonic oscillators (see Sec. IX). Using a short time expansion they derived equations identical to Eqs. (55) with $\chi(t)$ given by a Gaussian [Eq. (130a)]. In that work the starting point was the Kramers–Heisenberg formula where the bath degrees of freedom were treated explicitly. Of course, when all the degrees of freedom are explicitly included in the description it is possible to work with amplitudes and wave functions and it is not necessary to use the density matrix. The density matrix and Liouville space are essential, however, in the development of reduced description in which the bath is introduced via its correlation functions. The present analysis shows that the effects of inhomogeneous broadening can always be incorporated via the convolution [Eqs. (55)]. This is intuitively clear since when the solvent does not change its state during the SRF process we can simply determine the SRF line shape for a given solvent realization and then average it over the ensemble of solvent realizations. This is not the case for homogeneous broadening where the solvent is changing during the radiative process and it needs to be incorporated explicitly via the correlated dynamics of the system and the solvent.

VI. THE DISTINCTION BETWEEN RAMAN AND FLUORESCENCE LINE SHAPES

It is often possible to distinguish between two types of contributions to the SRF spectra of polyatomic molecules in condensed phases.\textsuperscript{13,16-18,27-35} These are denoted as Raman and fluorescence, respectively. The Raman components are relatively narrow emission lines centered at $\omega_L - \omega_S = \omega_{ee}$, where $|a\rangle$ and $|c\rangle$ are any pair of ground state vibronic levels, and their widths are typically less than a few cm$^{-1}$. The fluorescence lines are much broader (typical width of a few hundreds cm$^{-1}$), and their maxima occur at $\omega_{FL} = \omega_{ee}$, where levels $|b\rangle$ and $|c\rangle$ belong to the excited and the ground electronic states, respectively (Fig. 1). The fluorescence component is sometimes referred to as hot luminescence or redistribution. A clear distinction between these two components may be made by tuning $\omega_L$ across the absorption spectrum. The Raman lines, which are centered at a fixed $\omega_L - \omega_S$, will follow the tuning of $\omega_{FL}$, whereas the fluorescence components will remain roughly in the same positions. It should be emphasized that the general expression derived in this article for the spontaneous emission line shapes [Eq. (43)] represents the total emission spectrum. Its separation into a Raman and a fluorescence component is made merely for the sake of convenience. In particular, the calculation of the Raman component in a large molecule is much easier and its interpretation is simpler than the fluorescence component. Identifying the Raman component is therefore helpful in the theoretical interpretation of SRF line shapes. In this section we shall identify the Raman term and the fluorescence term in Eq. (48) and recast them in a form which is suitable for numerical calculations in large polyatomic molecules. To simplify the derivation we shall assume that the lifetimes of the vibronic levels belonging to the excited electronic state are equal:

$$
\gamma_v = \gamma; \quad v = b, d, \ldots,
$$

(56a)

where

$$
\gamma = \gamma_r + \gamma_{nr}.
$$

(56b)

Here $\gamma^{-1}_r$ and $\gamma^{-1}_{nr}$ denote the radiative and the nonradiative lifetime, respectively, of the excited electronic state. We further assume that the lifetimes of vibronic levels belonging to the ground electronic state are very long, i.e.,

$$
\gamma_v = \gamma < \gamma; \quad v = a, c, \ldots.
$$

(56c)

In the following derivation, we take $\gamma' = 0$. Since the effects of inhomogeneous broadening can be introduced as a simple convolution [Eqs. (55)], we shall not include them in this section and assume $\chi(t) = 1$. We shall now substitute Eqs. (56) into Eq. (48), and make use of the identity

$$
(\omega_S - \omega_L + \omega_{ee})^{-1} = \text{pp}(\omega_S - \omega_L + \omega_{ee})^{-1} - i\pi\delta(\omega_S - \omega_L + \omega_{ee}),
$$

(57)

where pp denotes the principal part. We then partition Eq. (48) into Raman ($S_R$) and fluorescence ($S_F$) components as follows:

$$
S(\omega_L,\omega_S) = S_R(\omega_L,\omega_S) + S_F(\omega_L,\omega_S),
$$

(58a)
with the Raman excitation profile for the |a⟩ to |c⟩ transition
\[ Q_{ca}(\omega_L) = \left| \sum_b \mu_{cb} \mu_{bc} I_{ba}(\omega_L) \right|^2 \] (58c)
and
\[ S_F(\omega_L,\omega_S) = 2 \Im \sum_{a,b,c,d} P(a) \mu_{ab} \mu_{bc} \mu_{cd} \mu_{da} \left( -\frac{\tilde{T}_{ab}(\omega_S) + \tilde{T}_{dc}(\omega_S)}{\omega_{bd} + i\gamma} - \frac{I_{dc}(\omega_S)}{\omega_S - \omega_L + \omega_{ca}} \right) \] (58d)

Equations (58) show that the SRF line shape can be partitioned into a Raman component \( S_R(\omega_L,\omega_S) \) and a fluorescence component, \( S_F \), and that the Raman excitation profile \( Q_{ca} \) (unlike the fluorescence \( S_F \)) can be represented as a square of an amplitude. It should be noted that the Raman component [Eq. (58b)] includes also the Rayleigh line (\( a = c \)) representing elastic scattering. The effect of the bath on the Raman profiles [Eq. (58c)] and on the absorption line shapes [Eq. (59)] enters through the same line broadening function \( J_g(t) \). However in the Raman profiles, unlike the absorption, \( J_g(t) \) enters at the amplitude level. The fluorescence line shape \( S_F \) [Eq. (58d)] depends, on the other hand, on two line broadening functions, \( J_s(t) \) and \( J_g(t) \) [Eqs. (33)]. Equations (58) contain a summation over four indexes, \( a,b,c,d \). It is possible to formally eliminate two of these summations by introducing a Fourier transform. Let us define the \( T \) matrices for the system modes:
\[ T(t) = \mu \exp(-iH_s t - \gamma t/2) \mu \] (59a)
\[ \tilde{T}(t) = \mu \exp(-iH_g t - \gamma t/2) \mu \] (59b)
\[ \tilde{T}_g(t) = \mu_\gamma \exp(-iH_g t - \gamma t/2) \mu \] (59c)
where \( \gamma \) [Eqs. (56)] denotes the inverse lifetime of the excited electronic state, while \( \gamma' \) [Eq. (56c)] denotes the inverse lifetimes of the vibronic levels of the ground electronic state. Note that we are relaxing here the assumption \( \gamma' = 0 \) made in Eqs. (58). We further define the one-sided Fourier transforms of the \( T \) matrices:
\[ K(\omega) = -i \int_0^\infty dt \exp(i\omega t) T(t) J_g(t) \] (60a)
\[ \tilde{K}(\omega) = -i \int_0^\infty dt \exp(i\omega t) \tilde{T}(t) J_g(t) \] (60b)
\[ \tilde{K}_g(\omega) = -i \int_0^\infty dt \exp(i\omega t) \tilde{T}(t) J_g(t) \] (60c)
Making use of Eqs. (59) and (60), we can recast Eqs. (39) and (58) in the form
\[ S_A(\omega_L) = -2 \Im \sum_a P(a) K_{aa}(\epsilon_a + \omega_L) \] (61)
and
\[ S_F(\omega_L,\omega_S) = 2 \Im \sum_{a,c} P(a) Q_{ca}(\omega_L) \delta(\omega_S - \omega_L + \omega_{ca}) \] (62a)
with the Raman excitation profile for the |a⟩ to |c⟩ transition
\[ Q_{ca}(\omega_L) = |K_{ca}(\epsilon_a + \omega_L)|^2 \] (62b)
\[ S_F(\omega_L,\omega_S) = 2 \Im \sum_{a,c} P(a) Q_{ca}(\omega_L) \delta(\omega_S - \omega_L + \omega_{ca}) \] (62c)

When the system vibrational degrees of freedom are harmonic, we can derive closed analytic expressions for the matrix elements of \( T(t) \), \( \tilde{T}(t) \), and \( \tilde{T}_g(t) \) of Eqs. (59) (see Sec. IX). The matrix elements of \( K_{ca}(\omega) \), \( \tilde{K}_{bd}(\omega) \), and \( \tilde{K}_g(\omega) \) necessary for the calculation of the SRF line shapes [Eqs. (62)] are then obtained by performing a single Fourier transform [Eqs. (60)]. In the absence of a thermal bath, \( J_g(t) = J_s(t) = 1 \). An interesting destructive interference takes places in this case which makes the fluorescence component to vanish.

The entire SRF line shape is then of the Raman type, and Eqs. (62) reduce to the Kramers–Heisenberg formula:
\[ S(\omega_L,\omega_S) = S_F(\omega_L,\omega_S) \]
\[ = 2 \Im \sum_{a,c} P(a) \left| \sum_b \frac{\mu_{ab} \mu_{cb}}{\omega_L + \epsilon_a - \epsilon_b + i\gamma/2} \right|^2 \times \delta(\omega_S - \omega_L + \omega_{ca}) \] (64)

It should be pointed out that our ability to express the Raman excitation profiles \( Q_{ca}(\omega_L) \) as a square of an amplitude [Eqs. (58c) or (62c)] does not depend on the factorization approximation. This is, instead, the result of the rapid fluctuation condition:
\[ \Lambda > \gamma_a + \gamma_c \] (65)
where \( \Lambda^{-1} \) is the solvent correlation time, and \( \gamma_a^{-1} (\gamma_c^{-1}) \) is the lifetime of the vibronic level \(|a⟩ (|c⟩)\). This point will be clarified further in Sec. VIII, where we present an exact expression for the Raman and fluorescence line shapes for a stochastic model without invoking the factorization approximation. That result [Eqs. (99)] is in the form of an infinite series whose first term corresponds to the factorization approximation. This will enable us to explore quantitatively the range of validity of Eqs. (62).

VII. THE RAMAN QUANTUM YIELD

Making use of Eqs. (62), we can partition the differential photon scattering cross section [Eq. (19)] into the Raman (\( \sigma_R^* \)) and the fluorescence (\( \sigma_F^* \)) components, i.e.,
\[ \sigma^*(\omega_L,\omega_L) = \sigma_R^*(\omega_L,\omega_L) + \sigma_F^*(\omega_L,\omega_L) \] (66a)
with
\[ \sigma_R^*(\omega_L,\omega_S) = \frac{4\omega_L \omega_S}{9c^4} S_R(\omega_L,\omega_S) \] (66b)
\[ \sigma_F(\omega_L, \omega_S) = \frac{4\omega_L \omega_S^3}{9c^2} S_F(\omega_L, \omega_S). \] (66c)

We shall now introduce the integrated Raman and fluorescence cross sections, defined as

\[ \sigma_R(\omega_L) = \int_{-\infty}^{\infty} d\omega_S \sigma'_R(\omega_L, \omega_S), \]

(67a)

\[ \sigma_F(\omega_L) = \int_{-\infty}^{\infty} d\omega_S \sigma'_F(\omega_L, \omega_S). \]

(67b)

We reiterate that the Raman cross section [Eq. (67a)] includes also the Rayleigh line representing elastic scattering. We further define the Raman quantum yield, \( Y_R \), and the fluorescence quantum yield, \( Y_F \), as

\[ Y_R(\omega_L) = \sigma_R(\omega_L)/\sigma_a(\omega_L), \]

(68a)

\[ Y_F(\omega_L) = \sigma_F(\omega_L)/\sigma_a(\omega_L), \]

(68b)

where the absorption cross section \( \sigma_a(\omega_L) \) is given by Eq. (21). Making use of the optical theorem, we have

\[ Y_R(\omega_L) + Y_F(\omega_L) = \gamma_r/\gamma \]

(69a)

and the quantum yield for nonradiative decay is

\[ Y_{nr}(\omega_L) = \gamma_{nr}/\gamma. \]

(69b)

So that

\[ Y_R(\omega_L) + Y_F(\omega_L) + Y_{nr}(\omega_L) = 1. \]

(70)

\( Y_R \) and \( Y_F \) represent the number of emitted Raman and fluorescence photons respectively, per photon absorbed, whereas \( Y_{nr} \) represents the number of molecules undergoing nonradiative decay per photon absorbed. The total radiative yield is \( Y_R + Y_F \). In the following discussion we shall focus on the absorption and the Raman cross sections, and on the Raman yield. The fluorescence cross section or the fluorescence yield may be obtained from Eq. (69a). Using Eqs. (62), we can rewrite the absorption cross section [Eq. (21)] as

\[ \sigma_a(\omega_L) = \sum_a P(a) \sigma'_a(\omega_L), \]

(71a)

where

\[ \sigma'_a(\omega_L) = -\frac{4\pi}{3} (\omega_L/c) \text{Im} K_{ao}(\epsilon_a + \omega_L) \]

\[ = \frac{4\pi}{3} (\omega_L/c) \text{Re} \int_0^\infty dt \]

\[ \times \exp[i(\epsilon_a + \omega_L)t] \left| T_{ao}(t)J_g(t) \right|^2 \]

(71b)

is the absorption cross section when the system is initially in the state \( |a\rangle \). Upon the substitution of Eqs. (66b), (62b), and (62c) into Eq. (67a), we obtain the Raman cross section

\[ \sigma_R(\omega_L) = \sum_{\alpha, \epsilon} \sum_a P(a) \sigma'_R(\omega_L). \]

(72a)

Here

\[ \sigma'_R(\omega_L) = \frac{8\pi \omega_L \omega_S^3}{9c^2} |K_{ao}(\epsilon_a + \omega_L)|^2 \]

\[ = \frac{8\pi \omega_L \omega_S^3}{9c^2} \int_0^\infty dt \exp[i(\epsilon_a + \omega_L)t] \left| T_{ao}(t)J_g(t) \right|^2 \]

(72b)

is the cross section for the \(|a\rangle \rightarrow |c\rangle \) Raman transition. For simplicity, we hereafter adopt the Condon approximation for the molecular system and assume that \( \mu = \mu_a \) is independent of the nuclear coordinates. In this case the \( T \) matrix of Eq. (59a) reduces to

\[ T(t) = \mu_a^2 G(t) \]

(73)

with the Green function defined by

\[ G(t) = \exp(-iH_f t). \]

(74)

Furthermore, assuming that the electronic (0-0) transition energy \( \epsilon_a \) is much larger than any vibronic transition frequency \( \omega_v \ll \omega_a \), the radiative width (in \( cm^{-1} \)) is given by

\[ \gamma_r = \frac{\mu_a^2}{\omega_a/c^2}. \]

(75)

Making use of Eqs. (73) and (75), we can rewrite Eqs. (71b) and (72b) as

\[ \sigma'_R(\omega_L) = C \text{Re} \int_0^\infty dt \exp[i(\epsilon_a + \omega_L)t] G_{ao}(t)J_g(t) \]

(76a)

and

\[ \sigma'_R(\omega_L) = \frac{1}{2} \gamma_r C \left| \int_0^\infty dt \exp[i(\epsilon_a + \omega_L)t] G_{ao}(t)J_g(t) \right|^2 \]

(76b)

with

\[ C = \frac{4\pi}{3} \mu_a^2 (\omega_a/c). \]

(76c)

Equations (76) constitute our final results for \( \sigma'_R(\omega_L) \), the absorption line shape of the system in the \(|a\rangle \) state, and for \( \sigma'_R(\omega_L) \), the Raman profile of the \(|a\rangle \rightarrow |c\rangle \) transition. Both expressions contain the solvent broadening via the function \( J_g(t) \). The system enters however differently. The absorption profile contains only the diagonal matrix elements of the Green function [Eq. (74)], \( G_{ao}(t) \), while the individual Raman excitation profile depends on the off-diagonal matrix elements, \( G_{ao}(t) \). In other words, one cannot calculate the individual Raman excitation profile exactly from a knowledge of the absorption line shape alone. A considerable effort was made by several authors to develop a transform method which would uniquely relate the individual Raman and the absorption cross sections.\(^{11,14}\) Equations (76) show that it is impossible to achieve that goal in general since \( G_{ao}(t) \) is not related to \( G_{ao}(t) \) in a simple way. A transform method may however be useful for a limited class of models (e.g., linearly displaced harmonic oscillators) for which a relation between \( G_{ao}(t) \) and \( G_{ao}(t) \) does exist. In order to analyze this problem more carefully we considered the total Raman cross section, \( \sigma_R(\omega_L) \) [Eq. (72a)], instead of the individual Raman profile \( \sigma'_R(\omega_L) \). In the following analysis [Eqs. (78)–(81)], we shall include also the contribution of inhomogeneous line broadening [Eqs. (55)]. Making use of the relation

\[ \sum \sigma_{ao}(\epsilon_a) G_{ao}(\epsilon_a(t)) = G_{ao}(t_1 - t_2), \]

(77)

we obtain after some simple formal manipulations,
\[ \sigma_A(\omega_L) = C \Re \int_0^\infty dt \exp(i\omega_L t) \sigma_\gamma(t) \chi(t) J_g(t), \quad (78a) \]

\[ \sigma_R(\omega_L) = \gamma C \Re \int_0^\infty dt \exp(i\omega_L t) \sigma_\gamma(t) \chi(t) J_R(t) \]

with

\[ \sigma_\gamma(t) = \sum_{\lambda} P(\lambda) \exp(i\varepsilon_\lambda t) G_{\omega t}(t) = \mu_\omega^{-1} \sigma(t), \quad (79) \]

where \( \sigma(t) \) is defined by Eq. (37a). Note that in Eqs. (78) and (76) we have incorporated also the inhomogeneous line broadening function \( \chi(t) \) [Eq. (51)]. \( J_R(t) \) is the Raman broadening function given by

\[ J_R(t) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \exp(-i\omega t + \gamma t|/2)|J(\omega)|^2, \quad (80a) \]

with

\[ J(\omega) \equiv -i \int_0^\infty dt \exp(i\omega t - \gamma t/2) J_g(t). \]

From Eq. (80a), we have

\[ |J(\omega)|^2 = 2 \Re \int_0^\infty dt \exp(i\omega t - \gamma t/2) J_R(t). \quad (80c) \]

The Raman yield [Eq. (68a)] may be calculated by dividing Eq. (78b) by Eq. (78a). Equations (78) show that both the absorption and the total Raman line shape depend on the system through \( \sigma_\gamma(t) \) and depend on the inhomogeneous broadening through \( \chi(t) \). The homogeneous broadening enters \( \sigma_A(\omega_L) \) and \( \sigma_R(\omega_L) \) via \( J_g(t) \) and \( J_R(t) \), respectively. These functions however are not independent. Using \( J_g(t) \) we may calculate \( J_R(t) \) via Eqs. (80). We have thus established that the total Raman cross section (which includes also the Rayleigh line) is a quantity that is much more naturally related to the absorption than the individual Raman cross sections. It should be emphasized that the present transform relation [Eqs. (78)–(80)] holds for any level scheme for the system and does not depend on the introduction of a special model of linearly displaced harmonic oscillators as is the case for other transform relations.11.14 We shall now discuss briefly how it may be possible to obtain the three line broadening functions \( J_g(t), J_R(t), \) and \( \chi(t) \) from experimental data. Making use of Eqs. (78) and (80), the ratio of the Fourier transform of the Raman cross section to that of the absorption cross section is given by

\[ \int_{-\infty}^{\infty} d\omega_L \exp(-i\omega_L t) \sigma_R(\omega_L) / \int_{-\infty}^{\infty} d\omega_L \exp(-i\omega_L t) \sigma_A(\omega_L) \]

\[ = [2\pi J_g(t)]^{-1} \gamma \int_{-\infty}^{\infty} d\omega \exp(-i\omega t + \gamma t/2) \]

\[ \times \left| \int_0^\infty dt \exp(i\omega t - \gamma t/2) J_g(t) \right|^2. \]

Here we have made use of Eqs. (78). The left-hand side of Eq. (81) is known experimentally while the right-hand side of Eq. (81) depends only on the homogeneous broadening function \( J_g(t) \). This provides a direct method for obtaining the solvent broadening function \( J_g(t) \) by fitting Eq. (81). The Fourier transform of \( \sigma_A(\omega_L) \) results in the product of \( \sigma_\gamma(t) \chi(t) J_g(t) \). Since \( J_g(t) \) may be independently obtained from Eq. (81), we then have \( \sigma_A(\omega_L) \chi(t) \chi(t) \) may be determined by fitting the individual Raman profiles and absorption cross section (see Sec. X). We can therefore obtain all three quantities \( \sigma_A(\omega_L) \), \( \chi(t) \), and \( J_g(t) \) by a careful analysis of the absorption and the Raman cross sections. Detailed calculations demonstrating these points will be carried out in Sec. X.

We shall consider now the two electronic level system \( |e \rangle \) and \( |g \rangle \) (no vibronic structure) in the absence of the inhomogeneous bath broadening. We thus set

\[ \chi(t) = 1 \quad (82a) \]

and

\[ \sigma_\gamma(t) = G_{\omega t}(t) = \exp(-i\omega_{eg} t - \gamma t/2), \quad (82b) \]

It will be useful to split \( J(\omega) \) [Eq. (80b)] into its real and imaginary parts:

\[ J(\omega) \equiv J^r(\omega) + ij^*J^s(\omega), \]

where \( J^r \) and \( J^s \) satisfy the Kramers–Kronig relation:

\[ J^r(\omega) = \frac{1}{\pi} \text{pp} \int_{-\infty}^{\infty} d\omega \frac{J^s(\omega)}{\omega - \omega}, \quad (84a) \]

\[ J^s(\omega) = \frac{1}{\pi} \text{pp} \int_{-\infty}^{\infty} d\omega \frac{J^r(\omega)}{\omega - \omega}. \]

We then have

\[ \sigma_A(\omega_L) = -\gamma J^s(\omega_L - \omega_{eg}), \quad (85a) \]

\[ \sigma_R(\omega_L) = 1/2\gamma C |J(\omega_L - \omega_{eg})|^2, \quad (85b) \]

\[ \gamma R(\omega_L) = -1/2\gamma J^s(\omega_L - \omega_{eg})^2 / J^r(\omega_L - \omega_{eg}). \]

We further define

\[ J(\omega) \equiv [\omega + iy/2 - R(\omega)]^{-1} \quad (86a) \]

with

\[ R(\omega) \equiv \Delta(\omega) - \frac{i}{2} \hat{\Delta}(\omega). \]

Here \( \Delta(\omega) \) is the level shift and \( \hat{\Delta}(\omega) \) is a frequency-dependent linewidth. They are also related by the Kramers–Kronig relation18:

\[ \Delta(\omega) = \frac{1}{2\pi} \text{pp} \int_{-\infty}^{\infty} d\omega' \frac{\hat{\Delta}(\omega')}{\omega' - \omega}, \quad (87a) \]

\[ \hat{\Delta}(\omega) = -\frac{2}{\pi} \text{pp} \int_{-\infty}^{\infty} d\omega' \frac{\Delta(\omega')}{\omega' - \omega}. \]

Equations (85a) and (85b) result in

\[ \sigma_A(\omega_L) = \frac{C}{2} \left[ \omega_L - \omega_{eg} - \Delta(\omega_L - \omega_{eg}) \right]^2 + \frac{1}{4}[\hat{\Delta}(\omega_L - \omega_{eg}) + \gamma]^2 \quad (88a) \]

and the Rayleigh cross section:
\[
\sigma_R(\omega_L) = \frac{1}{2} \gamma_r C \frac{1}{[\omega_L - \omega_R - \Delta(\omega_L - \omega_R)]^2 + \frac{\gamma}{4}[\Delta(\omega_L - \omega_R) + \gamma]^2}.
\]

Making use of Eqs. (68a) and (69a), we get

\[
Y_R(\omega_L) = \frac{\gamma_r}{\Gamma(\omega_L - \omega_R) + \gamma_r + \gamma_m},
\]

\[
Y_F(\omega_L) = \frac{\gamma_r}{\gamma_r + \gamma_m} Y_R(\omega_L).
\]

Equations (89) may be interpreted as follows. After the photon absorption, the molecular dynamics are governed by a competition between three channels: a Raman emission with a rate \( \gamma_r \), a fluorescence which is induced by the effective frequency dependent dephasing rate \( \Gamma(\omega_L - \omega_R) \), and a nonradiative decay with rate \( \gamma_m \). Usually the dephasing rate \( \Gamma(\omega) \) vanishes for large detunings when \( \omega \) is large compared to the linewidth and \( \Lambda \). When the magnitude of \( \Gamma(\omega) \) becomes comparable or smaller than \( \gamma_r \), \( Y_F \) will rapidly drop to zero and for large detunings the fluorescence component will vanish.\(^{16,26}\) The Raman quantum yield \( Y_R \) will then assume a limiting value independent on the detuning of \( \omega_L \). The detailed calculations in Sec. X will demonstrate these points. It should be noted that for realistic systems \( \gamma_m \) should also be frequency dependent and it usually vanishes at large detunings\(^{39}\) resulting in \( Y_F = 1 \). We shall not consider this situation in the present article.

** VIII. A STOCHASTIC MODEL OF LINE BROADENING **

In this section, we present a simple stochastic model for line broadening in SRF processes. This is a simplified, exactly solvable model for the solvet dynamics.\(^{16,18,34,46}\) The final expression for the SRF line shape can be written in terms of a power series expansion\(^{18(b)}\) in the solvent correlation time \( \Lambda^{-1} \). The first term of this series corresponds to the factorization approximation of Sec. IV. The stochastic model thus enables us to explore systematically the precise range of validity of the factorization approximation and to correct for deviations if necessary. The stochastic model further interpolates continuously between homogeneous and inhomogeneous broadening. We shall derive analytic expressions for \( J_g(t), J_s(t) \) of Eq. (79a) and \( J(\omega) \) of Eq. (79b) for this model. The Hamiltonian for the stochastic model is given by

\[
H = |g\rangle H_g |g\rangle \pm |e\rangle [H_e + \omega_R + \delta \omega_{eg}(t)] |e\rangle,
\]

(90)

where only the system degrees of freedom with Hamiltonians \( H_g \) and \( H_e \) are considered explicitly. The effects of the random motions of the solvent modes on the system are taken into account by introducing a stochastic fluctuation \( \delta \omega_{eg}(t) \) of the electronic energy gap \( \omega_{eg} \). \( \delta \omega_{eg}(t) \) is taken to be a Gaussian–Markovian process\(^{39}\) with zero mean

\[
\langle \delta \omega_{eg}(t) \rangle = 0,
\]

(91a)

and correlation function

\[
\langle \delta \omega_{eg}(t) \delta \omega_{eg}(0) \rangle = \Delta^2 \exp(-\Lambda |t|).
\]

(91b)

Here \( \langle \cdots \rangle \) denotes averaging over the stochastic variables. \( \Delta \) is the amplitude of the modulation, and \( \Lambda^{-1} \) is its time scale (i.e., the solvent correlation time as discussed in Sec. IV). In this section we use the stochastic model to account for the fast bath modes. We thus assume that Eq. (46) holds and we neglect the inhomogeneous broadening. The exact expressions for SRF line shapes for the present model were derived earlier\(^{18}\). In the present notation, we have

\[
J_g(t) = J_s(t) = \exp[-g(t)],
\]

(92a)

where

\[
g(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \langle \delta \omega_{eg}(t_2) \delta \omega_{eg}(0) \rangle = \kappa^{-2} \exp[-\Lambda t] - 1 + \Lambda t,
\]

(92b)

and

\[
\kappa \equiv \Lambda/\Delta.
\]

(93)

\( \kappa \) is an important parameter which determines the nature of the line broadening mechanism. Its significance will be discussed below. Within the stochastic model ( unlike the microscopic models developed in the previous sections) the solvent is affecting the system but the system does not affect the solvent. This is why \( J_g(t) = J_s(t) \), which is a fundamental limitation of the stochastic model. The four-point correlation functions [Eqs. (45)] for the bath are

\[
M_{11}(t_1, t_2, t_3) = M_{\pm 1}(t_1, t_2, t_3),
\]

(94a)

\[
M_{12}(t_1, t_2, t_3) = M_{\pm 1}(t_1, t_2, t_3),
\]

(94b)

\[
M_{13}(t_1, t_2, t_3) = M_{\pm 1}(t_1, t_2, t_3),
\]

(94c)

where

\[
M_{\pm 1}(t_1, t_2, t_3) = \exp[-g(t_1) - g(t_3)] \exp(\pm \kappa^2 \exp(-\Lambda t_2) \times[1 - \exp(-\Lambda t_1)][1 - \exp(-\Lambda t_2)]) = \exp[-g(t_1) - g(t_3)] \sum_{n=0}^{\infty} \frac{(\pm 1)^n}{n!} \kappa^{-2n} \times \exp(-n \Lambda t_2)[1 - \exp(-\Lambda t_1)]^n \times [1 - \exp(-\Lambda t_2)]^n.
\]

(95)

We further define

\[
I^{(n)}(\omega) = -i \kappa^{-n} \int_0^\infty \frac{dt \exp(\pm it \omega) I_{1n}(t)}{\sqrt{n!}} = -i \kappa^{-n} \int_0^\infty \frac{dt \exp(\pm it \omega) I_{1n}(t)}{\sqrt{n!}} \times [1 - \exp(-\Lambda t)]^n; \quad n = 0, 1, 2, ...
\]

(96)

with \( I_{1n}(t) \) being given by Eq. (40a). Upon the substitution of Eqs. (92a) and (96) into Eq. (40), we obtain for the absorption line shape

\[
S_A(\omega_L) = -2 \text{Im} \sum_{n=0}^{\infty} \langle a | \mu_{ab} \mu_{ab} J_{1n}(\omega_L) | a \rangle,
\]

(97)

where we denote

J. Chem. Phys., Vol. 86, No. 11, 1 June 1987

\[
S_A(\omega_L) = -2 \text{Im} \sum_{n=0}^{\infty} \langle a | \mu_{ab} \mu_{ab} J_{1n}(\omega_L) | a \rangle,
\]

(97)

where we denote
\[ I_{\text{es}}(\omega) = I^{(0)}_{\text{es}}(\omega). \]  
(98)

Substituting Eqs. (94)–(96) and (44) into Eq. (43), and separating the Raman and the fluorescence components, we get

\[ S(\omega, \omega_S) = S_R(\omega, \omega_S) + S_F(\omega, \omega_S), \]  
(99a)

\[ S_R(\omega, \omega_S) = 2\pi \sum_{\alpha} P(\alpha) Q_{\text{es}}(\omega, \omega_S) \delta(\omega - \omega_L + \omega_o), \]  
(99b)

with the Raman excitation profile for \(|a\) to \(|c\) transition

\[ Q_{\text{es}}(\omega, \omega_S) = \left| \sum_b \mu_{ab} \mu_{bc} \mathcal{J}_{ba}(\omega) \right|^2, \]  
(99c)

and

\[ S_F(\omega, \omega_S) = -2 \text{Im} \sum_{\alpha \beta \gamma} p(p) \mu_{\alpha \beta} \mu_{\beta \gamma} \mu_{\gamma \delta} \sum_n I^{(n)}_{\text{es}}(\omega, \omega_S) \times \left[ \frac{(-1)^n I^{(n)}_{\text{es}}(\omega_S) + I^{(n)}_{\text{es}}(\omega_S)}{\omega_{\beta d} + i(\gamma + n\Lambda)} \right] \times pp \frac{I^{(n)}_{\text{es}}(\omega_S)}{\omega_{\beta d} + i(\gamma + n\Lambda)} \times \sum_n K^{(n)}_{\text{es}}(\omega, \omega_S) \]  
(99d)

The \( n = 0 \) terms in Eqs. (99) correspond to the results of the stochastic model in the factorization approximation [cf. Eqs. (58)]. Equations (99) constitute our final expressions for the SRF line shapes. They contain four summations over molecular states \((a, b, c, d)\). It is possible to formally eliminate two of these summations, resulting in an expression which is more suitable for calculations for large molecules, where these summations are intractable. In analogy to the deviation in the Sec. VI, we define

\[ K^{(n)}(\omega) = -i \frac{\Delta \Gamma}{\sqrt{n!}} \int_0^\infty dt \exp(i\omega t) T(t) \times \exp[-g(t)][1 - \exp(-\Lambda t)]^n, \]  
(100a)

\[ \mathcal{K}^{(n)}(\omega) = -i \frac{\Delta \Gamma}{\sqrt{n!}} \int_0^\infty dt \exp(i\omega t) \mathcal{T}(t) \times \exp[-g(t)][1 - \exp(-\Lambda t)]^n, \]  
(100b)

\[ \mathcal{K}^{(n)}(\omega) = -i \frac{\Delta \Gamma}{\sqrt{n!}} \int_0^\infty dt \exp(i\omega t) \mathcal{T}(t) \times \exp[-g(t)][1 - \exp(-\Lambda t)]^n, \]  
(100c)

\[ R(\omega) \equiv \Delta(\omega) - \frac{i}{2} \Gamma(\omega) = \frac{\Delta^2}{\omega + i(\Lambda + \gamma/2) - \frac{2\Delta^2}{\omega + i(3\Lambda + \gamma/2) - \cdots}. \]  
(103b)

In the Appendix we derive alternative expressions for \( J(\omega) \) and \( J_{\text{es}}(t) \) in terms of the incomplete gamma function, or the confluent hypergeometric function. When these expressions are expanded we obtain

\[ J(\omega) = \frac{1}{\omega + i(\Delta^2 + \Lambda + \gamma/2)} \sum_m \frac{\Gamma(1 + \kappa^2 + \gamma/2\Lambda - i\omega/\Lambda) \mathcal{K}^{-2m}, \]  
(104a)
\[ J_R(t) = \frac{1}{2\Delta^2/\Lambda + \gamma} \sum_{m=0}^{\infty} \frac{\Gamma(1 + 2\kappa^{-2} + \gamma/\Lambda)}{\Gamma(\frac{m+1}{2})} \kappa^{-2m}(1 + \exp(-\Delta t))^m. \]  

(104b)

Here \( J_g(t) \) is given by Eq. (92a) and \( \Gamma(z) \) represents the gamma function of \( z \). In the fast modulation limit, i.e., \( \kappa \to \infty, J_g(t) = \exp(-\Delta^2 t/\Lambda) \), only the \( m = 0 \) terms in Eq. (104) contribute. We then have

\[ J(\omega) = (\omega + i(2\Delta^2/\Lambda + \gamma)/2)^{-1} \]  

(105a)

with

\[ \hat{\Gamma}(\omega) = 2\Delta^2/\Lambda \equiv \hat{\Gamma} \]  

(105b)

and

\[ J_R(t) = \frac{1}{\hat{\Gamma} + \gamma} J_G(t). \]  

(105c)

Substitution of Eqs. (105) into Eq. (78c) shows that the Raman yield in the fast modulation limit does not depend on the detuning of \( \omega_L \), i.e.,

\[ Y_R(\omega) = \frac{\gamma_r}{\gamma_r + \gamma_{nr} + \hat{\Gamma}} \]  

(106)

which is a special case of Eq. (89). In this case the absorption line shape is Lorentzian. In the opposite limit \( \kappa \ll 1 \), we have \( J_g(t) = \exp(-1/2\Delta^2 t^2) \) and the absorption line shape is Gaussian. In the absence of the bath, \( \hat{\Gamma} = 0 \), Eq. (106) reduces to Eq. (69a) with \( Y_g = 0 \). In concluding this section, we note that when \( \Lambda = 0 \), the stochastic model represents a static bath with Gaussian inhomogeneous broadening \( \chi(t) \) [Eq. (130a)] with \( a = \Delta \). Equation (53) can then be obtained by postulating the existence of two independent stochastic mechanisms. One is homogeneous with \( J_g(t) = J_g(t) \) [Eq. (93a)] and the other is inhomogeneous [Eq. (130a)].

**IX. FLUORESCENCE LINE SHAPES OF A HARMONIC MOLECULE IN A HARMONIC BATH**

In this section, we present an exact microscopically solvable model for the SRF line shapes [Eqs. (61)]. We consider a harmonic molecule with \( N \) vibrational degrees of freedom. Its Hamiltonian is

\[ H_S = |g\rangle H_g |g\rangle + |e\rangle (H_e + \omega_{es} - i\gamma/2) |e\rangle \]  

(107a)

with

\[ H_g = \frac{1}{2} \sum_{j=1}^{N} \omega_j^r (p_j^r)^2 + q_j^r - 1, \]  

(107b)

\[ H_e = \frac{1}{2} \sum_{j=1}^{N} \omega_j^e (p_j^e)^2 + q_j^e - 1, \]  

(107c)

and where

\[ q^e = \mathcal{S} q^r + D. \]  

(108)

\( \omega_{es} \) is the fundamental (0-0) transition frequency and we have adopted the common spectroscopic notation, whereby we label ground-state quantities by a double prime and excited-state quantities by a single prime. \( p^r \) and \( q^r \) are the dimensionless momentum and coordinate vectors, whose elements correspond to the normal modes:

\[ p_j^r = \left( \frac{1}{m_j \omega_j^r \hbar} \right)^{1/2} P_j, \]  

(109a)

\[ q_j^r = \left( \frac{m_j \omega_j^r \hbar}{\hbar} \right)^{1/2} Q_j. \]  

(109b)

\( P_j \) and \( Q_j \) being the conjugate momentum and the normal coordinate, respectively, of the \( j \)th mode of the excited state.

A similar transformation between \( p_j^e, q_j^e \) and \( P_j, Q_j \) is defined by changing all 'indices in Eqs. (109) to 'r'. \( \mathcal{S} \) is the Dushinsky rotation matrix which allows the ground-state and the excited-state normal modes to be different. \( D \) is the dimensionless displacement between the equilibrium configurations of the two electronic states. In this section, we shall denote the vibronic levels of \( H_g \) and \( H_e \) by

\[ \{|a\} \equiv \{|m\} \equiv |m_1 \cdots m_N\rangle, \]  

(110a)

\[ \{|c\} \equiv \{|n\} \equiv |n_1 \cdots n_N\rangle, \]  

(110b)

\[ \{|b\} \equiv \{|j\} \equiv |j_1 \cdots j_N\rangle, \]  

(110c)

\[ \{|d\} \equiv \{|k\} \equiv |k_1 \cdots k_N\rangle. \]  

(110d)

We further adopt the Condon approximation and assume that \( \mu = \mu_{es} \) is independent of the nuclear coordinates. In this case, Eqs. (60) can be rewritten as

\[ K(\omega) = -i\mu_{es}^2 \int_0^\infty dt \exp(-i\omega t/2) G(t) J_g(t), \]  

(111a)

\[ \bar{K}(\omega) = -i\mu_{es}^2 \int_0^\infty dt \exp(-i\omega t/2) \bar{G}(t) J_g(t), \]  

(111b)

\[ \bar{K}(\omega) = -i\mu_{es}^2 \int_0^\infty dt \exp(-i\omega t/2) \bar{G}(t) J_g(t), \]  

(111c)

with the Green functions given by

\[ G(t) \equiv \exp(-iH_g t), \]  

(112a)

\[ \bar{G}(t) \equiv \exp(-iH_g t), \]  

(112b)

\[ \bar{G}(t) \equiv \exp(-iH_g (t-i\Delta T)) / \exp(-H_g/kT) \]  

(112c)

The SRF line shapes [Eqs. (61) and (62)] are given in terms of the matrix elements of \( G \) matrices [Eqs. (111)], which in turn may be expressed in terms of the matrix elements of \( G \) matrices defined in Eqs. (112), and the bath broadening functions \( J_g(t) \) and \( J_e(t) \). The explicit expressions for \( J_g(t) \) and \( J_e(t) \) using a microscopic model will be given later in this section. At this point, we shall be interested in calculating the matrix elements of \( G, \bar{G}, \) and \( \bar{G} \) [Eqs. (112)]. Their calculation is formally very similar and the expressions for \( G_{\alpha\alpha}(t) \) may be applied to calculation the matrix element \( G_{\alpha\beta}(t) \) and \( \bar{G}_{\alpha\beta}(t) \) as well. By simply changing \( D \) to \( \mathcal{S}^{-1} \), \( \mathcal{S} \) to \( \mathcal{S}^{-1} \), and changing \( \omega_{es} \) and \( \omega_{es}^r \), one can change the expressions for \( G_{\alpha\alpha}(t) \) to \( \bar{G}_{\alpha\beta}(t) \) and further using Eq. (112c) to get \( \bar{G}_{\alpha\beta}(t) \). We shall, therefore, give only the expression of \( G_{\alpha\alpha}(t) \). The general expression for \( G_{\alpha\alpha}(t) \) was given in Appendix B of Ref. 36(a). In this paper, we shall only present the expression for the matrix element
$G_{m0}(t)$. Since the main focus of this article is on solvation dynamics, we shall hereafter consider the simplest model for the system, i.e., a harmonic molecule with linearly displaced normal modes, $\omega_i = \omega'_i = \omega''_i$ and $S_i = \delta_i$. We can now factorize the $G_{m0}(t)$ as

$$ G_{m0}(t) = \sum_{j=1}^{N} G_{mj0}(t). \quad (113a) $$

We shall further consider the expression for the absorption correlation function $\sigma_4(t)$ [Eq. (79)], for the model system of Eqs. (107). The general expression was given in Appendix D of Ref. 36(a). For a linearly displaced harmonic molecule, $\sigma_4(t)$ can also be factorized as

$$ \sigma_4(t) = \sum_{j=1}^{N} \sigma_{4j}(t). \quad (113b) $$

For simplifying the notation, we shall consider a single mode and omit all the $j$ subscripts from $\omega_{ij}, \omega'_{ij}, \omega''_{ij}, D_i, n_j, m_j$. The final expression for the single mode Green function $G_{m0}(t)$ of linearly displaced harmonic molecules is given by

$$ G_{m0}(t) = (m!2^m)^{-1/2} D^m [\exp(-i\omega t) - 1] \times \exp(1/2D^2[\exp(-i\omega t) - 1]) \quad (114a) $$

and for the absorption we get

$$ \sigma_4(t) = \exp(1/2D^2(\bar{n} + 1)[\exp(-i\omega t) - 1]$$

$$ + 1/2D^2\bar{n}[\exp(i\omega t) - 1]) \quad (114b) $$

and

$$ \bar{n} = [\exp(\hbar\omega/kT) - 1]^{-1}. \quad (114c) $$

The limit of linearly displaced oscillators [Eqs. (114)] has been extensively studied in the literature.16,17,36,42 Extension to quadratic changes in potentials has also been made.43,44 This concludes our discussion of the system. We shall now turn to the solvent correlation functions [Eqs. (33)]. The present formulation provides rigorous microscopic relations of SRF line shapes to standard correlation functions of the medium $J_\alpha(t)$ and $J_\nu(t)$, which can be evaluated by a variety of methods. Such methods include density expansions for pressure broadening in the gas phase and in liquids,46,47 cumulant expansions for phonon broadening,31 and semiclassical and molecular dynamics simulations.48 For polar solvents, it may be possible to use a continuum dielectric model for the solvent and relate the necessary correlation functions to the frequency-dependent dielectric constant.49-53 Dielectric continuum models were used in the past mainly to account for spectral shifts, and they need to be extended towards the calculation of the solvent broadening functions $J_\alpha(t)$ and $J_\nu(t)$ which will account for spectral shift as well as broadening. Recently, using picosecond excitation and detection, Fleming and co-workers were able to observe a time-dependent shift of the spontaneous emission line shape.52 This shift arises from the reorganization process of the solvent and also from vibrational relaxation which occurs during the $t_0$ time interval [Eq. (20)]. A similar behavior was observed by Shank and co-workers in femtosecond hole burning (pump probe) experiments.52 A proper treatment of these effects requires going beyond the factorization approximation which assumes an instantaneous reorganization. The present formalism is ideally suited for developing microscopic models for the solvent reorganization. We have recently shown how line broadening in time resolved fluorescence in polar solvents may be interpreted in terms of the stochastic model $\kappa$ and $\Lambda$ [Eqs. (92)] may be related to the dielectric properties of the solvent. The vibrational relaxation processes, may be another factor contributing to the spectral shift and broadening.21,22 We shall now present a harmonic model for the solvent. Unlike the stochastic model of Sec. VII, the harmonic model proposed here gives the explicit dependence of the line shape on the microscopic parameters of the solvent. Using this model, it should be possible to explain solvation effects such as the red shift, line broadening, and their temperature dependence. In the harmonic solvent model, we assume that solvent consists of $N (\rightarrow \infty)$ harmonic modes with the Hamiltonian

$$ H_B = \sum_{j=1}^{N} \hat{h}_j \hat{g}_j \hat{g}_j + \epsilon \hat{h}_j \hat{e}_j, \quad (115) $$

where $\hat{h}_j$ and $\hat{h}_j$ are given by Eqs. (107b) and (107c), respectively, by changing $H_2$ to $h_2, H_3$ to $h_3, \ldots$, and $N, \omega'_j, \omega''_j, p'_j, q'_j, p''_j, q''_j$ to $\bar{n}, \bar{\omega}_j, \bar{\alpha}_j, \bar{\beta}_j, \bar{\gamma}_j, \bar{\delta}_j$, respectively, with

$$ \bar{\omega}_j = (\bar{\omega}_j/\bar{\alpha}_j)^{1/2} \bar{\delta}_j + \bar{\beta}_j \quad (116) $$

Here $\bar{\omega}_i(\bar{\delta}_i)$ represents the frequency while $\bar{\beta}_i(\bar{\gamma}_i)$ are the dimensionless momentum and coordinate, respectively, of the $j$th solvent mode of the excited (ground) state. $\bar{D}_j$ represents the dimensionless linear displacement between the equilibrium positions of the two electronic states for the $j$th bath mode. Mathematically, the expressions for $J_\alpha(t)$ and $J_\nu(t)$ are similar. In the following, we shall consider only the absorption kernel $J_\alpha(t)$. By exchanging the ground state parameters and the excited state parameters, one can get $J_\nu(t)$ from $J_\alpha(t)$. For simplicity, we adopt the Condon approximation for the solvent as well and set

$$ \mu_B = 1. \quad (117) $$

As indicated earlier, $J_\alpha(t)$ consists of an infinitely large number of small contributions from the various modes of the bath. It is therefore convenient to recast it in the form

$$ J_\alpha(t) = \prod_{j=1}^{N} J^{(j)}_\alpha(t) = \exp \left[ \sum_{j=1}^{N} \log J^{(j)}_\alpha(t) \right], \quad (118) $$

where $J^{(j)}_\alpha(t)$ is the absorption kernel for the $j$th solvent mode. We can now replace the summation in the bracket of the right-hand side of Eq. (118) by an integration. We denote by $P(\bar{\omega}, \alpha, \bar{D})d\bar{\omega}d\alpha d\bar{D}$ the number of solvent modes with the ground state frequencies between $\bar{\omega}$ and $\bar{\omega} + d\bar{\omega}$, the excited state frequencies between $\bar{\alpha}$ and $\bar{\alpha} + d\bar{\alpha}$, and the displacement between $\bar{D}$ and $\bar{D} + d\bar{D}$. Equation (118) now assumes the form

$$ J_\alpha(t) = \exp [\eta(t)] \quad (119a) $$

with

$$ \eta(t) = \int \int d\bar{\omega} d\alpha \int d\bar{D} P(\bar{\omega}, \alpha, \bar{D}) \log J(\bar{\omega}, \alpha, \bar{D}; t), \quad (119b) $$

where $J(\bar{\omega}, \alpha, \bar{D}; t)$ is the absorption kernel for the solvent mode with the ground state frequency $\bar{\omega}$, the excited state

J. Chem. Phys., Vol. 86, No. 11, 1 June 1987
frequencies $\bar{\omega}' = (1 + \alpha)\bar{\omega}$, and the linear displacement $\bar{D}$.
Using the results of Ref. 36, we get
\[
\log J(\bar{\omega}, \alpha, \bar{D}) = \bar{D}^2 \Phi(t) - \frac{1}{2} \log \psi(t) \tag{120a}
\]
with
\[
\Phi(t) = -\frac{\bar{\omega}C_{A-}}{\bar{\omega}C_{A+} + \bar{\omega}C_{A+}}
\]
\[
= -\left[ C_{A-} + (1 + \alpha)C_{A+} \right]^{-1}C_{A-} \tag{120b}
\]
and
\[
\psi(t) = \frac{1}{4\bar{\omega}^2}(\bar{\omega}C_{A+} - \bar{\omega}C_{A+})
\]
\[
\times (\bar{\omega}C_{A+} - \bar{\omega}C_{A+})
\]
\[
= \frac{1}{4}[C_{A-} + (1 + \alpha)C_{A+}]
\]
\[
\times [C_{A-} + (1 + \alpha)^{-1}C_{A+}] \tag{120c}
\]
where
\[
C_{\pm} = 1 \pm \exp (-\bar{\omega}t), \tag{121a}
\]
\[
A_{\pm} = (n_B + 1) \pm n_B \exp(\bar{\omega}t), \tag{121b}
\]
\[
n_B = [\exp(\bar{\omega}/kT) - 1]^{-1}, \tag{121c}
\]
and
\[
\bar{\omega}' = (1 + \alpha)\bar{\omega}. \tag{121d}
\]
We shall now present some simple models for the distribution function $P(\bar{\omega}, \alpha, \bar{D})$ which appears in the right-hand side of Eq. (119b) and derive simplified expressions for the solvent absorption kernel $J_\chi(t)$.

**A. Harmonic bath with linear displacements**

We first assume that the solvent is a collection of low frequency modes with $\bar{\omega} = \bar{\omega}$, i.e., $\alpha = 0$. We have
\[
P(\bar{\omega}, \alpha, \bar{D}) = P_1(\bar{\omega}, \bar{D})\delta(\alpha), \tag{122}
\]
where $P_1(\bar{\omega}, \bar{D})$ is the joint probability distribution function for the frequency $\bar{\omega}$ and the displacement $\bar{D}$. In this case, Eq. (119b) reduces to
\[
\eta(t) = \int d \bar{\omega} \int d\bar{D} P_1(\bar{\omega}, \bar{D}) \eta_1(\bar{\omega}, \bar{D}; t), \tag{123a}
\]
where\[\text{[cf. Eq. (114b)]}\]
\[
\eta_1(\bar{\omega}, \bar{D}; t) = 1/2\bar{D}^2 \{ (n_B + 1) \left[ \exp(-\bar{\omega}t) - 1 \right] + n_B \left[ \exp(i\bar{\omega}t) - 1 \right] \}. \tag{123b}
\]
In the high temperature limit, $kT >> \bar{\omega}$, we can replace $n_B + 1$ and $n_B$ by $n_B + 1/2$, and approximate Eq. (123b) by
\[
\eta_1(\bar{\omega}, \bar{D}; t) \approx -\bar{D}^2(2n_B + 1)\sin^2(\bar{\omega}/2). \tag{124}
\]
Performing a Taylor expansion of the right-hand side of Eq. (124), we have
\[
J_\chi(t) \approx \exp(-\xi^2 t^2/2). \tag{125a}
\]
This results in a Gaussian line shape with a width $\xi$:
\[
\xi^2 = \int d\bar{\omega} d\bar{D} P(\bar{\omega}, \bar{D}) \bar{D}^2(n_B + 1/2)\bar{\omega}^2. \tag{125b}
\]

**B. Harmonic bath with frequency shifts**

Another simplified model for the solvent is obtained by assuming that the linear displacements vanish, i.e., $\bar{D} = 0$, but that $h_\beta$ and $h_\alpha$ have slightly different frequencies. We then have
\[
P(\bar{\omega}, \alpha, \bar{D}) = P_2(\bar{\omega}, \alpha)\delta(\bar{D}), \tag{126}
\]
where $P_2(\bar{\omega}, \alpha)$ is the joint probability distribution function for the ground state frequency $\bar{\omega}$ and the excited state frequency $\bar{\omega}' = (1 + \alpha)\bar{\omega}$. Equation (119b) then reduces to
\[
\eta(t) = \int d\bar{\omega} \int d\bar{\omega}' P_2(\bar{\omega}, \alpha) \eta_2(\bar{\omega}, \bar{\omega}'; t), \tag{127a}
\]
By using Eqs. (119), (120), and Taylor's expansion up to the second order in $\alpha$, we have
\[
\eta_2(\bar{\omega}, \alpha; t) = -in_B\bar{\omega}t\alpha - 1/2\alpha^2(n_B^2 + n_B)\bar{\omega}'^2t^2
\]
\[
-1/8\alpha^2[(n_B + 1)^2 - n_B^2 \exp(i2\bar{\omega}t)]
\]
\[
\times [1 - \exp(-i2\bar{\omega}t)]. \tag{127b}
\]
Equations (119a) and (127) give the solvent broadening function $J_\chi(t)$. The first term in the right-hand side of Eq. (127b) results in a spectral shift given by
\[
\int d\bar{\omega} d\bar{\omega}' P_2(\bar{\omega}, \alpha)\alpha^2(n_B^2 + n_B)\bar{\omega}'^2 \tag{128a}
\]
while the second term gives the extra asymmetric broadening width. Equations (123) or (127) allow us to predict the dependence of the line shape on the bath temperature, since they contain the bath occupation number $n_B$ [Eq. (121c)], which depends on the bath temperature $T$.

**FIG. 3.** The frequency dependent dephasing rate $\Gamma(\omega)$ [Eq. (103b)] for the stochastic model with $\gamma = 0$ cm$^{-1}$. Equation (104a) was used in the calculation. The various curves correspond to different values of $\Lambda$ and $\Lambda$ keeping $\Gamma_{\gamma} = 250$ cm$^{-1}$ constant [Eq. (131)]. The values of $\Lambda$ (in cm$^{-1}$) are indicated in the figure. This figure demonstrate that $\Gamma(\omega)$ always vanishes at large detunings. This vanishing becomes slower as $\Lambda$ is increased.
X. NUMERICAL CALCULATIONS

In the previous sections, we showed that the solvation effects on the SRF line shapes may be incorporated in the three solvent broadening functions: $J_e(t)$ [Eq. (33a)], $J_e(t)$ [Eq. (33b)], and $\chi(t)$ [or $\chi(\omega)$] [Eqs. (51) and (54)]. All the relevant microscopic information regarding the solvent dynamics is contained in these broadening functions, and one of the major goals of SRF spectroscopy is to extract these quantities from the experimental line shapes.

FIG. 4. (A) The SRF line shape [Eqs. (99)] for a single oscillator with \( \omega = \omega' = \omega'' = 1000 \text{ cm}^{-1} \), \( D = 1.4 \), and \( \gamma = \gamma' = \gamma'' = 2 \text{ cm}^{-1} \) and the broadening parameters are \( \kappa = 10 \), \( \Gamma_H = 250 \text{ cm}^{-1} \), and \( \Gamma_L = 0 \), which corresponds to \( \Delta = 1250 \text{ cm}^{-1} \), and \( \Lambda = 12500 \text{ cm}^{-1} \) [Eqs. (132a) and (93)]. The dispersed emission vs \( \omega_e \) is shown for several values of the detunings of \( \omega_s - \omega_{eg} \), as indicated in each panel. (B) Same as (A) but for different broadening parameters with \( \kappa = 1 \) and the same \( \Gamma_H, \Delta = 166 \text{ cm}^{-1} \). (C) Same as (A) but for different broadening parameters with \( \kappa = 0.1 \) and the same \( \Gamma_H, \Delta = 130 \text{ cm}^{-1} \) and \( \Lambda = 13 \text{ cm}^{-1} \).
FIG. 5. The absorption cross section $\sigma_a$, the Raman cross section $\sigma_R$, and the Raman yield $Y_R$ for a two level system with $\Gamma_H = 250$ cm$^{-1}$, $\Gamma_L = 0$, and $\gamma = \gamma_L = 2$ cm$^{-1}$. The stochastic model for the homogeneous broadening function is used [Eq. (129)]. The upper left panel of this figure shows the absorption cross section. From top to bottom (at the centers of the curves), the values of $\kappa$ are 0.1, 1, 2, and 5, respectively. A common scaling constant is chosen such that $\sigma_a(0) = 1$, for $\kappa = 0.1$. The upper right panel shows the same line shapes on a logarithmic scale (base 10). The middle left panel shows the Raman cross sections for the same system. The middle right panel shows these spectra on a logarithmic scale. In this panel, the curves with different values of $\kappa$ are indistinguishable. The two lower panels show the Raman yield [Eq. (68a)]. The value of $\kappa$ is indicated in the plots.

$J_\chi (t)$ may be obtained directly from the absorption and the total Raman cross section via Eq. (81). The inhomogeneous broadening function $\chi(\omega)$ may be obtained from the Raman excitation profiles and absolute cross sections, as demonstrated by Myers et al. Finally $J_\chi (t)$ may be obtained from the fluorescence line shape [Eqs. (58b) or (62d)]. In this section, we present numerical calculations demonstrating the effects of $J_\chi (t)$, $J_\chi (t)$, and $\chi(t)$ on the absorption and the Raman cross sections. For simplicity, we have adopted the stochastic model for the homogeneous broadening function:

$$J_\chi (t) = J_\chi (t) = \exp\{-\kappa^{-3}[\exp(-\Lambda t) - 1 + \Lambda t]\}.$$  

(129)

We further use a Gaussian line shape for the inhomogeneous broadening function:

$$\chi(t) = \exp(-1/2\alpha^2 t^2)$$  

(130a)

or

$$\chi(\omega) = \frac{1}{\sqrt{2\pi} a} \exp\left(-\frac{1}{2} \frac{\omega^2}{\alpha^2}\right).$$  

(130b)

A useful parameter in our subsequent analysis is $\Gamma_H$, which denotes the FWHM of the homogeneous broadening function $J^*(\omega)$ [Eq. (83)]. For the stochastic model [Eq. (129)] we may use the Padé approximant\textsuperscript{18(b)}:

$$\Gamma_H = \frac{2.355 + 1.76\kappa}{\kappa + 0.85\kappa^2 + 0.88\kappa^3} \Lambda.$$

(131)

FIG. 6. The absorption cross section $\sigma_a$ [Eq. (78a)], the Raman cross section $\sigma_R$ [Eq. (78b)], and the Raman yield $Y_R$ [Eq. (68a)] for the displaced oscillator of Fig. 4(C) ($\Delta = 130$ cm$^{-1}$ and $\Lambda = 13$ cm$^{-1}$). A common scaling constant is chosen such that $\sigma_a(0) = 1$.

FIG. 7. The same as Fig. 6 but with different broadening parameters corresponding to $\kappa = 1$ and the same value of $\Gamma_H$ ($\Delta = \Lambda = 166$ cm$^{-1}$).

FIG. 8. The same as Fig. 6 but with different broadening parameters corresponding to $\kappa = 2$ and the same value of $\Gamma_H$ ($\Delta = 260$ cm$^{-1}$ and $\Lambda = 520$ cm$^{-1}$).
In addition, we introduce $\Gamma_r$ to denote the FWHM of the inhomogeneous broadening function $\chi(\omega)$. For the Gaussian line shape [Eq. (130b)] we have $\Gamma_r = (8 \ln 2)^{1/2}a$. In the following calculations, the molecule was assumed to be harmonic with the Hamiltonian of Eq. (107). We have taken the ground state and the excited state frequencies to be equal ($\omega' = \omega''$) and assumed no Dushinsky rotation $S_{ij} = \delta_{ij}$. We further used the Condon approximation [Eq. (117)] and did not include nonradiative decay channels so that $\gamma = \gamma_r$. In Fig. 3, we show the frequency-dependent dephasing rate $\Gamma(\omega)$ calculated using Eqs. (103a) and (104a) with $\gamma = 0$ for various levels of $\kappa$. The figure shows that $\Gamma(\omega)$ always vanishes for large detunings $\omega \gg \Lambda, \Gamma_H$. The precise way in which $\Gamma(\omega)$ vanishes depends on the solvent broadening parameters $\Delta$ and $\Lambda$. The vanishing of $\Gamma(\omega)$ at large detunings results in the disappearance of the fluorescence component, so that the Raman yield goes to unity [Eqs. (89)]. The behavior of the Raman yield with detuning provides therefore a direct measure of the solvent time scale $\Lambda^{-1}$ and coupling strength $\Delta$. Figure 4 illustrates this point. In Fig. 4(A) we display the dispersed emission for a single linearly displaced oscillator vs $\omega_S$ for various detunings of $\omega_L$ when the broadening is in the fast modulation limit $\kappa = 10$. Figures 4(B) and 4(C) repeat this series for line broadening with the same FWHM ($\Gamma_H$) but with different values of $\kappa$ and $\gamma'$. We clearly see a progression of narrow Raman lines (width $\gamma'$) and a broad fluorescence (with $\Gamma_H$). When exciting the fundamental $\omega_L - \omega_S = 0$, all three figures have a significant intensity of the Raman as well as the fluorescence components. However, as $\omega_L$ is detuned, they behave very differently. For detuning of $\omega_L - \omega_S = 500$ cm$^{-1}$ the relative intensity of the Raman and the fluorescence components did not change appreciably for $\kappa = 10$ [Fig. 4(A)]. However, for $\kappa = 0.1$ [Fig. 4(C)] the fluorescence disappeared almost completely. As we tune further to $\omega_L - \omega_S = 1000$ cm$^{-1}$, we are again exciting on resonance and the fluorescence ap-
Rayleigh yield goes to one. The variation of the Raman yield with detuning depends strongly on $\kappa$ and may therefore be used to extract $\kappa$ from the experimental data. Figures 6–9 display the absorption cross section, $\sigma_A(\omega)$, the Raman cross section, $\sigma_R(\omega)$, and the Raman yield, $Y_R(\omega)$, for a single linearly displaced harmonic oscillator [Eqs. (107) for $N = 1$]. In these four figures we chose different values of $\Delta$ and $\Lambda$ such that $\Gamma_H$ was fixed and $\kappa$ was varied ($\kappa = 0.1, 1, 2, 5$) changing from the slow modulation to the fast modulation limits. A normalization is chosen for Figs. 6–9 such that $\sigma_A(\omega = 0) = 1$ for $\kappa = 0.1$. These figures again illustrate the sensitivity of the Raman yield to $\kappa$. For large $\kappa$ it changes very slowly with detuning (Fig. 9), whereas for small $\kappa$ (Fig. 6) it goes very rapidly to one. In Fig. 10, we display the Raman yield for the model system of Figs. 6–9 for various values of $\kappa$ (and keeping $\Gamma_H$ fixed) for negative detunings ($\omega_L - \omega_{eg} < 0$). The sensitivity of the Raman yield to $\kappa$ is clearly demonstrated. The role of the inhomogeneous broadening is demonstrated in Figs. 11–13. We have used the same displaced oscillator model of Fig. 6 with a homogeneous broadening (with $\kappa = 1$ and FWHM $\Gamma_H$) and an inhomogeneous broadening with FWHM $\Gamma_I$. In these figures we have taken $\Gamma_H + \Gamma_I = 250 \text{ cm}^{-1}$ and varied the relative magnitudes of $\Gamma_H$ and $\Gamma_I$. As $\Gamma_H$ is reduced, the Raman yield approaches unity for all detunings. Figures 6–9 and 11–13 demonstrate the effect of two factors on the Raman yield. One factor is $\kappa$. The other is the relative magnitude of the homogeneous and the inhomogeneous broadening $\Gamma_H/\Gamma_I$. A close examination of these calculations shows that it may be possible to fit the experimental absorption cross section and the Raman yield equally well either by using a larger $\kappa$ with smaller $\Gamma_H/\Gamma_I$ or by smaller $\kappa$ with larger $\Gamma_H/\Gamma_I$. This ambiguity may be resolved by the individual Raman cross sections (or the Raman profiles). Figure 14 displays the 0 to 1 Raman profile, $Q_{10}$ [Eq. (102c)],
for different values of $\Gamma_H/\Gamma_I$. The calculations show that the individual Raman cross section (or the absolute Raman profiles) are sensitive to the ratio $\Gamma_H/\Gamma_I$, but are insensitive to the values of $\kappa$. When the homogeneous width is increased, the intensities of the absolute Raman profiles will decrease.\(^8\) Finally, we have applied the present stochastic model to the calculation of the Raman line shapes of the retinal chromophore in bacteriorhodopsin at 278 K. In Ref. 8 it was found that this system has 29 Raman active modes. Our calculations were made using Eqs. (78) and (114) and the frequencies and displacements reported in Ref. 8. The resulting absorption, Raman cross sections and Raman yields for various values of $\kappa$ (keeping $\Gamma_H$ and $\Gamma_I$ fixed) are shown in Figs. 15–17. In Fig. 18 we display the Raman yields of this system for negative detunings using several values of $\kappa$ and keeping $\Gamma_H$ and $\Gamma_I$ fixed. The sensitivity of the yield to $\kappa$ is clearly demonstrated. We predict that a careful study of the detuning behavior of Raman yield should result in the precise determination of the solvent dynamical parameters $\Delta$ and $\Lambda$.

\section{XI. CONCLUDING REMARKS}

In this paper, we developed a unified microscopic model for the homogeneous and the inhomogeneous broadening mechanisms for polyatomic molecules in solution. The microscopic solvent information is contained in the two homogeneous broadening functions corresponding to absorption $J_g(t)$ and emission $J_e(t)$, and in the inhomogeneous function $\chi(t)$. The homogeneous broadening is the result of rapid solvent fluctuations [Eq. (48)], whereby the bath correlation time $\Lambda^{-1}$ is much shorter than the lifetimes of the vibronic levels and the factorization approximation is valid (Sec. IV). The inhomogeneous broadening results from the slow bath modes (Sec. VI) with $\Lambda = 0$. We further considered the partitioning the SRF signal into a Raman ($S_R$) and a fluorescence ($S_F$) component [Eqs. (58) or (62)]. The absorption [Eqs. (39) or (61)] and the Raman [Eqs. (58b) or (62b)] depend only on $J_g(t)$ and $\chi(t)$, while the fluorescence [Eqs. (58d) or (62d)] depends on all three broadening functions, $J_g(t)$, $J_e(t)$, and $\chi(t)$. The homogeneous broadening function $J_g(t)$ enters in the Raman excitation profiles at the amplitude level [Eqs. (58c) or (62c)] while the inhomogeneous broadening function $\chi(\omega)$, which is the Fourier transform of $\chi(t)$, enters in the amplitude square level as a convolution [Eq. (55a)]. This difference may be used to determine the relative weight of the homogeneous and the inhomogeneous contributions (Fig. 14). The absorption cross section alone cannot distinguish between homogeneous and inhomogeneous broadening since it depends only on the product $J_g(t)\chi(t)$. However, the absorption and the total Raman cross section [Eq. (78b)] may allow us to extract the homogeneous broadening function $J_g(t)$ [cf. Eq. (81)]. With the knowledge of $J_g(t)$ and $\chi(t)$, it is possible to obtain $J_e(t)$ from the fluorescence line shape. Equations (119), (123), and (127) provide two possible models for

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig16.png}
\caption{The same as Fig. 15, but with $\kappa = 1$ keeping $\Gamma_H$ and $\Gamma_I$ fixed ($\Delta = \Lambda = 325 \text{ cm}^{-1}$).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig18.png}
\caption{The Raman yield for the retinal chromophore in bacteriorhodopsin for large negative detunings with various values of $\kappa$ as indicated, keeping $\Gamma_H (= 500 \text{ cm}^{-1})$ and $\Gamma_I (= 1760 \text{ cm}^{-1})$ fixed. Other parameters are same as Fig. 15. The figure demonstrates the sensitivity of the Raman yield to $\kappa$. The plot is made on logarithmic scale (base 10).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig17.png}
\caption{The same as Fig. 15, but with $\kappa = 5$ keeping $\Gamma_H$ and $\Gamma_I$ fixed ($\Delta = 1250 \text{ cm}^{-1}$ and $\Lambda = 6250 \text{ cm}^{-1}$).}
\end{figure}
\[ J_s(t) \text{ in terms of microscopic parameters, which may be very useful to construct the line shapes and account for the temperature dependent solvent shift and spectral broadening. Equations (89) and Fig. 3 for } \hat{\Gamma}(\omega) \text{ show that, in the absence of inhomogeneous broadening, the absorption [Eq. (88a)] for large detunings } (\omega_L - \omega \gg \Lambda, \Gamma_H) \text{ is} \]
\[ \sigma_s(\omega) \sim \hat{\Gamma}(\omega)/\omega^2 \quad (132a) \]
which is sensitive to the broadening function \( J_s(t) \), while the Raman profile [Eq. (88b)] is given by
\[ \sigma_R(\omega) \sim \gamma/\omega^2 \quad (132b) \]
which is independent of \( J_s(t) \). A close examination of the absorption or the Raman yield at large detunings may allow us to obtain \( J_s(t) \). We have shown that the Raman yield and its variation with detuning provide a very sensitive probe for the solvent dynamics and its time scales. Although Eqs. (88) were derived for a two level system, they should hold for large detunings for any molecular level scheme. The calculations of Sec. X clearly demonstrate these points. It should be noted that the present formalism may be applied to intramolecular line broadening in the SRF process of ultracold polyatomic molecules in supersonic beams.55-57 In this case the bath consists of the molecular vibrational modes which are not directly coupled to the optical transition. We have recently demonstrated how the present model may be used to interpret the dispersed fluorescence in ultracold anthracene.57

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APPENDIX: EVALUATION OF \( J(\omega) \) AND \( J_n(t) \) FOR THE STOCHASTIC MODEL

In this Appendix we use the stochastic model (Sec. VIII) to develop explicit expressions [Eqs. (103) and (104)] for the solvent line broadening functions. We start with the following definition of auxiliary functions:

\[ J_n(\omega) \equiv -i \int_0^\infty dt \exp(iot - \gamma t/2) \times \exp[-g(t)][1 - \exp(-\Lambda t)]^n \quad (A1) \]

with

\[ g(t) \equiv \kappa^{-2}[\exp(-\Lambda t) - 1 + \Lambda t], \quad (A2) \]

where \( \kappa \) and \( \Lambda \) are defined by Eqs. (93) and (91b). Note that

\[ J(\omega) = J_0(\omega) \quad (A3) \]

is the line shape function, defined by Eq. (80b), for the stochastic model. Using Eq. (A1), we may derive the following recurrence relations:

\[ \frac{i}{2} \hat{\Gamma}J_1(\omega) = 1 - (\omega + i\gamma/2)J_0(\omega) \quad (A4a) \]

and

\[ \frac{i}{2} \hat{\Gamma}J_{n+1}(\omega) = n\Lambda J_{n-1}(\omega) + i[\omega + i(n\Lambda + \gamma/2)]J_n(\omega) \quad (A4b) \]

with

\[ \hat{\Gamma} = 2\Delta^2/\Lambda. \quad (A5) \]

Solving Eqs. (A4), we obtain the continued fraction form, Eq. (103), for \( J(\omega) = J_0(\omega) \).

An alternative useful expression for \( J_\nu(\omega) \) may be derived in terms of the confluent hypergeometric function. Upon changing the integration variable of Eq. (A1) to

\[ y = 1 - \exp(-\Lambda t), \]

we get

\[ J_n(\omega) = \frac{1}{i\Lambda} \int_0^\infty dy \exp(\kappa^{-2}y)y^n(1-y)^{b-1} \]

\[ = \frac{n\Gamma(b)}{i\Lambda\Gamma(b+n+1)} M(n+1,b+n+1,\kappa^{-2}) \quad (A6) \]

with

\[ b \equiv \kappa^{-2} + \gamma/2\Lambda - i\omega/\Lambda. \quad (A7) \]

\( M(a,b,x) \) in the right-hand side of Eq. (A6) is the confluent hypergeometric function,41 defined by

\[ M(a,b,x) \equiv \frac{\Gamma(b)}{\Gamma(b-a)\Gamma(a)} \int_0^1 dt \exp(-t) = -1 \]

\[ = \sum_{m=0}^\infty \frac{(a)_m\kappa^m}{m!b_m} \quad (A8) \]

with

\[ (a)_m \equiv \Gamma(a+m)/\Gamma(a) = a(a+1)\cdots(a+m-1); \quad (a)_0 = 1 \quad (A9) \]

and \( \Gamma(z) \) represents the gamma function. In particular we have

\[ J(\omega) = J_0(\omega) = [\omega + i(\hat{\Gamma} + \gamma)/2]^{-1} M(1,b+1,\kappa^{-2}) \]

\[ = [\omega + i(\hat{\Gamma} + \gamma)/2]^{-1} \sum_{m=0}^\infty \kappa^{-2m}/(b+1)_m \quad (A10) \]

which is identical to Eq. (104a).

We shall now show how \( J_s(t) \) can also be represented by the confluent hypergeometric function, i.e., Eq. (104b). From Eqs. (A1) and (A3), we have

\[ J(\omega)^2 = \int_0^\infty dt_1 \int_0^\infty dt_2 \exp[i\omega(t_1 - t_2) - \gamma(t_1 + t_2)/2] \times \exp[-g(t_1) - g(t_2)]. \]

\[ = 2 \exp(2\kappa^{-2}) \Im \int_0^\infty dt_1 \int_0^\infty dt_2 \exp[i\omega(t_1 - t_2) - (\hat{\Gamma} + \gamma)/2(t_1 + t_2)] \times \exp[-\kappa^{-2}[\exp(-\Lambda t_1) + \exp(-\Lambda t_2)]. \quad (A11) \]

Changing the integration variables to \( \tau = t_1 + t_2, \quad t = t_1 - t_2 \) and changing the order of integration
\[ J(\omega) = \exp(2\omega^2) \text{Re} \int_0^\infty dt \exp(i\omega t) \]
\[ \times \int_0^\infty d\tau \exp\left[-(\hat{\Gamma} + \gamma)/(\tau + t)/2\right] \]
\[ \times \exp[-\kappa^2 \left(1 + \exp(-\Lambda t)\right)] \times \exp[-\Lambda(\tau - t)/2]. \]
\[ \text{(A12)} \]

Upon the substitution of Eq. (A12) into Eq. (80a) or (80c), we have
\[ J_R(t) = \frac{1}{\Lambda} \exp(2\omega^2 - \hat{\Gamma} t/2) \]
\[ \times \int_0^\infty d\tau \exp\left[-(\hat{\Gamma} + \gamma)/(\tau + t)/2\right] \]
\[ \times \exp[-z(t)\exp(-\Lambda(\tau - t)/2)]. \]
\[ \text{(A13)} \]

Changing the integration variable:
\[ y = 1 - \exp(-\Lambda(\tau - t)/2) \]

we can recast Eq. (A13) as
\[ J_R(t) = \frac{1}{\Lambda} \exp(-g(t)) \int_0^\infty dy \exp[(1 - y)2\omega^2 + \gamma/\Lambda - 1] \]
\[ \times \exp[-g(t)M(12\omega^2 + \gamma/\Lambda + 1)z(x)] \times \frac{1}{\hat{\Gamma} + \gamma} \exp[-g(t)M(12\omega^2 + \gamma/\Lambda + 1)z(x)]. \]
\[ \text{(A15)} \]

Equation (A15) is identical to Eq. (104b).