

Stochastic theory of resonance Raman line shapes of polyatomic molecules in condensed phases

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A stochastic model is proposed for the calculation of resonance Raman line shapes of polyatomic molecules in condensed phases. The model assumes that the random force exerted on the molecule by the solvent causes a stochastic modulation of the electronic energy gap. Explicit expressions are derived for the absorption, the excitation spectra, and the dispersed Raman line shapes. The model interpolates all the way from homogeneous broadening (fast modulation) to inhomogeneous broadening (slow modulation). The effects of line broadening cannot be incorporated into the Kramers–Heisenberg formula, commonly used to interpret these spectra, since dephasing-induced terms appear which dominate the line shapes for large dephasing rates. A simple explanation is provided for the nature of the homogenous linewidth and for the broadening of the dispersed Raman line shapes, without having to assume an unrealistically short lifetime.

I. INTRODUCTION

Considerable progress has been made in recent years in extracting microscopic structural and dynamical information on complex molecular systems in condensed phases from Raman line shapes (excitation spectra and dispersed fluorescence).^{1–12} Some of the systems extensively studied are conjugated polyenes, aromatic molecules, and molecules of biological interest, such as porphyrins and β carotenes in solution. The Raman process is shown in Fig. 1. A molecule initially in the state $|a\rangle$ and energy ϵ_a absorbs a photon ω_L and emits a photon ω_s , and ends up in the state $|c\rangle$ with energy ϵ_c . $|b\rangle$ and $|b'\rangle$ denote a manifold of vibronic states belonging to an electronically excited state, whereas $|a\rangle$ and $|c\rangle$ usually belong to the ground electronic state. The conventional theoretical treatments of this process start with the Kramers–Heisenberg (KH) expression for the Raman line shape¹³

$$\hat{I}_0(\omega_L, \omega_s) = \sum_{a,c} P(a) |\chi_{ca}(\omega_L)|^2 \delta(\omega_{ca} + \omega_s - \omega_L), \quad (1)$$

where

$$\chi_{ca}(\omega_L) = \sum_b \frac{\mu_{cb} \mu_{ba}}{\omega_{ab} + \omega_L + i\gamma_b/2} \quad (1a)$$

and

$$\omega_{ij} \equiv \epsilon_i - \epsilon_j. \quad (2)$$

Here ϵ_i is the energy of state $|i\rangle$ and γ_i is its inverse lifetime, $P(a)$ is the equilibrium population of $|a\rangle$, χ_{ca} is the Raman amplitude, and μ_{ij} is the dipole matrix element. Usually we can assume the dipole to be weakly dependent on the nuclear coordinates, so that μ_{ij} are simply the Franck–Condon factors,¹⁴ i.e.,

$$\mu_{ij} = \langle i|j\rangle. \quad (3)$$

The absorption line shape is given by the Fermi Golden rule

$$\sigma(\omega_L) = \sum_{a,b} P(a) |\mu_{ba}|^2 \delta(\omega_{ba} - \omega_L). \quad (4)$$

Equation (1) applies to isolated molecules which do not interact with the environment. Molecular Raman spectra taken at low pressure gas phase or in supersonic beams^{15–19} may, therefore, be adequately interpreted using the KH expression [Eq. (1)]. The situation is drastically different, however, for typical Raman spectra in condensed phases (solutions, matrices, molecular crystals, glasses, chromophores on proteins). In these cases, the molecule is subject to a random force, resulting from its interaction with a macroscopic number of external degrees of freedom, which constitute a thermal bath. The random force results in a significant line broadening and a loss of much of the structure in these spectra. A common model used in the calculation of Raman profiles is of a harmonic molecule with two linearly displaced harmonic surfaces.^{1–12,19} The experimental spectra are then used to get the ground state and excited state frequencies as well as the coordinate equilibrium displacements. Line broadening was incorporated phenomenologically into these calculations in order to obtain a better fit with experiment. A few definitions need now be introduced in order to clarify the nature of these treatments. Theories of spectral line broadening traditionally make a distinction between homogeneous and inhomogeneous contributions to spectral line shapes. When different molecules absorb at different frequencies because of different local environments or different initial states, the line is said to be *inhomogeneously broadened*. This broadening is *static* in nature, reflecting the spread in molecular transition frequencies and carries no dynamical information. It can be shown, using the central limit theorem, that when the interaction with the environment is the sum of many small contributions, the resulting line shape is a Gaussian. However, in general, the inhomogeneously broadened line can assume any form and is not necessarily a Gaussian. *Homogeneous broadening* arises from an interaction with a

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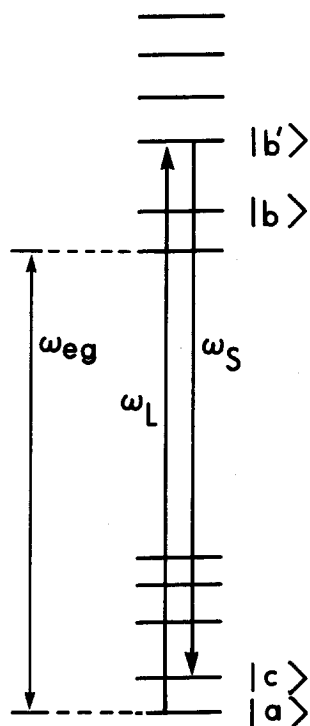


FIG. 1. The level scheme for a Raman process.

bath with a very fast time scale, such as rapid fluctuations in the local environment. As far as the radiation field is concerned, all molecules on the average appear identical, and the resulting line shape is a Lorentzian. The inclusion of line broadening in the calculation of molecular Raman line shapes is usually made in two ways^{1,5-8}: (i) by introducing the lifetime γ_b^{-1} in Eq. (1). This results in a Lorentzian profile and was referred to as “homogeneous broadening”; (ii) by postulating an *inhomogeneous broadening* mechanism. This results from the fact that different molecules have a slightly different environment, which changes the electronic energy gap (0-0 transition). The incorporation of a static inhomogeneous broadening is straightforward and can be accomplished by convoluting the line shape [Eq. (1)] with the distribution $S(\omega)$ of the electronic energy gap, i.e.,

$$\langle \hat{I}(\omega_L, \omega_s) \rangle = \int d\omega \hat{I}(\omega_L + \omega, \omega_s + \omega) S(\omega), \quad (5)$$

where $\langle \dots \rangle$ denotes averaging over the inhomogeneous distribution. The calculations of Raman line shapes made using the KH formula [Eq. (1)], together with these two broadening mechanisms are not always in satisfactory agreement with experiment.⁵⁻⁸ The fit of the calculated absorption and excitation profiles with experiment is not perfect. Some extremely large γ_b ($\sim 100 \text{ cm}^{-1}$) need to be assumed which correspond to an unrealistically short lifetime $\tau = \hbar/\gamma_b$, which contradicts the direct measurements of the lifetime. Moreover, the dispersed fluorescence [$\hat{I}(\omega_L, \omega_s)$ as a function of ω_s for a fixed ω_L] is not broadened at all by these mechanisms, resulting in an infinitely sharp dispersed spectra, in contrast to experiment. Other attempts were made to add phenomenologically a number of low-frequency modes in order to fit the experimental data.^{6,12}

It should be noted that one of the most important broadening mechanisms of spectral lines is that of *homogen-*

*eous dephasing*²⁰⁻²⁸ caused by rapid fluctuations in the local environment of the molecule. For a two-level system, this results in a Lorentzian absorption line whose width may be much larger than the inverse lifetime. The inclusion of this broadening in Raman line shapes is less trivial than the mechanisms (i) and (ii) mentioned earlier. We can no longer use Eq. (1a) and calculate an *amplitude* for the Raman process; instead the Raman cross section (*amplitude square*) need to be calculated directly, using the density matrix. Moreover, although the limits of homogeneous and inhomogeneous broadening are well defined, the classification of the broadening mechanisms into homogeneous or inhomogeneous is not always feasible. Consider a molecule coupled to a bath with a characteristic time scale τ_c . If τ_c^{-1} is much smaller than the observed linewidth, the line is inhomogeneously broadened. As τ_c^{-1} is increased, the line shape will change, and only when τ_c^{-1} is much larger than the observed linewidth, will a Lorentzian, homogeneously broadened line emerge. For intermediate τ_c^{-1} , the line cannot be classified as either homogeneously or inhomogeneously broadened. Stochastic models that interpolate between these limits were first introduced by Kubo for the ordinary line shape²⁹ and later generalized to fluorescence spectra by Takagahara, Hanamura, and Kubo.^{25,30} In this article we develop a stochastic theory for line broadening in Raman spectra of polyatomic molecules in condensed phases. We assume that the random force exerted by the solvent on the absorber modulates the electronic energy gap by a stochastic Gaussian-Markovian process. The magnitude of the modulation is Δ and its time typical scale is Λ^{-1} . The nature of the broadening mechanism is determined by the dimensionless parameter $\kappa \equiv \Lambda/\Delta$. For fast modulation ($\kappa \gg 1$) the model corresponds to homogeneous dephasing, whereas in the slow modulation limit ($\kappa \ll 1$) it represents inhomogeneous broadening [Eq. (5) with $S(\omega)$ a Gaussian]. In general, however, the model holds for any value of κ and interpolates continuously between these limits.^{19,25,30,31} In Sec. II we present the stochastic model and its solution in the homogeneous limit. We show that the general expression in the presence of dephasing cannot, in general, be written as an amplitude square. The Raman line shape contains a Kramers-Heisenberg (amplitude square) term and additional *dephasing-induced* contributions. For large homogeneous dephasing width, the latter terms are dominant. The theories of Raman line shapes in solution should, therefore, focus on developing efficient algorithms towards calculating the dephasing-induced terms, in addition to the KH part.^{1,5,7,12,32} In Sec. III we present the general solution of the stochastic model which interpolates between the limits of homogeneous and inhomogeneous broadening. Finally, Sec. IV contains a discussion of these results.

II. RESONANCE RAMAN WITH HOMOGENEOUS DEPHASING

We shall now present our general stochastic model for the Raman line shapes of polyatomic molecules in condensed phases. This is a unified model which interpolates between homogeneous and inhomogeneous broadening. In this section, however, we shall present the solution in the

limit of fast modulation (homogeneous broadening). This is done for the sake of clarity, since the final result [Eq. (17)] is much simpler in this case and still contains the essential features of the general stochastic model. The two most prominent features of our analysis are that the simple KH formula [Eq. (1)], which focuses on the amplitude for the process, is no longer applicable since in the presence of dephasing the Raman process cannot be described in terms of an amplitude. Also, the conservation of energy $\delta(\omega_{ca} + \omega_s - \omega_L)$ no longer holds, since the system is not isolated. In the next section we shall relax the assumption of fast modulation and present the general solution of the stochastic model.

We consider a molecule with two electronic states, the ground state $|g\rangle$ and an excited state $|e\rangle$. The molecular Hamiltonian is

$$H = |g\rangle H_g \langle g| + |e\rangle (H_e + \omega_{eg}) \langle e|. \quad (6)$$

ω_{eg} is the electronic energy gap (0-0 transition) between the two states. For an isolated molecule ω_{eg} is simply a constant. We shall assume, however, that due to the interaction with an external bath (conformational changes, solvent motions) ω_{eg} is a stochastic function of time, i.e.,

$$\omega_{eg} = \bar{\omega}_{eg} + \delta\omega_{eg}(t), \quad (7)$$

where $\bar{\omega}_{eg}$ is the mean energy gap. $\delta\omega_{eg}(t)$ is taken to be a Gaussian Markovian process with zero mean^{25,28,29}

$$\langle \delta\omega_{eg}(t) \rangle = 0 \quad (8a)$$

and a correlation function

$$\langle \delta\omega_{eg}(t) \delta\omega_{eg}(0) \rangle = \Delta^2 \exp(-\Lambda t). \quad (8b)$$

Here $\langle \dots \rangle$ denotes averaging over the stochastic variables. Δ denotes the amplitude of the modulation and Λ^{-1} is its time scale (correlation time). In this section we shall assume that the fluctuations are rapid compared to their magnitude, i.e., $\Lambda/\Delta \gg 1$. In this case, the absorption line shape is homogeneously broadened with a dephasing rate $\hat{\Gamma}$, i.e., $\hat{\Gamma} = \Delta^2/\Lambda$. Equation (4) then becomes

$$\sigma(\omega_L) = \sum_{a,b} P(a) |\mu_{ba}|^2 \sigma_{ba}(\omega_L), \quad (9)$$

where $\sigma_{ba}(\omega_L)$ is the contribution of the ab transition to the line shape

$$\sigma_{ba}(\omega_L) = \frac{\Gamma/\pi}{(\omega_L - \omega_{ba})^2 + \Gamma^2}, \quad (10)$$

and where

$$\Gamma = 1/2(\gamma_a + \gamma_b) + \hat{\Gamma} \quad (11a)$$

and

$$\hat{\Gamma} = \Delta^2/\Lambda. \quad (11b)$$

Here γ_i is the inverse lifetime of level i . The states $|a\rangle, |c\rangle$, etc. (Fig. 1) are the vibronic eigenstates of H_g :

$$H_g |i\rangle = \epsilon_i |i\rangle, \quad i = a, c, \dots, \quad (12)$$

whereas the states $|b\rangle, |b'\rangle$ are the vibronic eigenstates of H_e , i.e.,

$$(\bar{\omega}_{eg} + H_e) |i\rangle = \epsilon_i |i\rangle, \quad i = b, b', \dots \quad (13)$$

Note that the total width Γ is the sum of a contribution from the lifetimes $1/2(\gamma_a + \gamma_b)$ and the proper dephasing width $\hat{\Gamma}$

resulting from the fluctuations. The absorption line shape is a sum of Lorentzians. If the only available information is the absorption line shape, it is impossible to tell which fraction of Γ is due to lifetime and which is due to homogeneous dephasing ($\hat{\Gamma}$). The Raman spectra, however, as we shall see, are vastly different in both cases.

The calculation of the Raman line shape requires solving the Liouville equation for the density matrix. A detailed derivation is given in the next section for the general stochastic model. Three terms need to be considered (Figs. 2 and 3), resulting in^{19,28,30,31}

$$\hat{I}(\omega_L, \omega_s) = \sum_{a,c} P(a) \hat{I}_{ca}(\omega_L, \omega_s), \quad (14)$$

where

$$\hat{I}_{ca}(\omega_L, \omega_s) = K_I + K_{II} + K_{III}, \quad (14a)$$

and where

$$K_I = -i \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \times \frac{1}{\omega_{ba} - \omega_L + i\Gamma} \frac{1}{\omega_{bb'} + i\gamma} \times \frac{1}{\omega_{bc} - \omega_s + i\Gamma} + \text{c.c.}, \quad (14b)$$

$$K_{II} = -i \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \times \frac{1}{\omega_{ba} - \omega_L + i\Gamma} \frac{1}{\omega_{bb'} + i\gamma} \times \frac{1}{\omega_{cb'} + \omega_s + i\Gamma} + \text{c.c.}, \quad (14c)$$

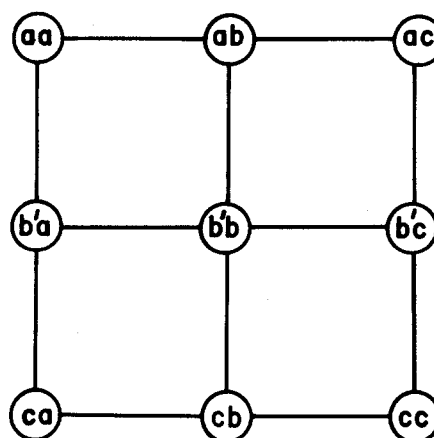


FIG. 2. Pictorial representation of the possible pathways in Liouville space, which contribute to Raman spectra. Solid lines denote radiative coupling \mathcal{V} . Horizontal (vertical) lines represent action of \mathcal{V} from the right (left). The Raman process is obtained by all pathways, which start at $|aa\rangle$ and end at $|cc\rangle$ in fourth order (four bonds). There are six pathways, which contribute. However, due to symmetry we need consider only three. The other three are obtained by a complex conjugation and permutation of b and b' .

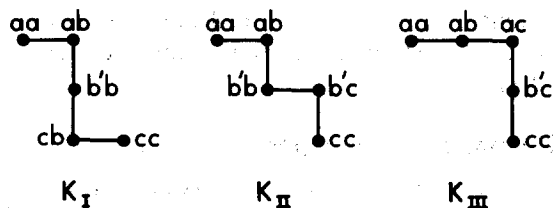


FIG. 3. The three pathways in Liouville space corresponding to K_I , K_{II} , and K_{III} [Eqs. (14) and (27)].

$$K_{III} = -i \sum_{b, b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \times \frac{1}{\omega_{ba} - \omega_L + i\Gamma} \frac{1}{\omega_{ca} + \omega_s - \omega_L + i\eta} \times \frac{1}{\omega_{cb'} + \omega_s + i\Gamma} + \text{c.c.} \quad (14d)$$

In Eqs. (14) we have assumed

$$\gamma_a = \gamma_c = 0, \quad (15a)$$

$$\gamma_b = \gamma_{b'} = \gamma, \quad (15b)$$

we also denote

$$\Gamma = 1/2\gamma + \hat{\Gamma}, \quad (16a)$$

$$\hat{\Gamma} = \Delta^2/\Lambda, \quad (16b)$$

and

$$\omega_{ij} = (\epsilon_i - \epsilon_j)/\hbar. \quad (16c)$$

η is a small positive number, and at the end of the calculation we should set $\eta \rightarrow 0$. A better insight regarding the role of dephasing is obtained if we rearrange Eqs. (14). This rearrangement is similar to previous works on collisional redistribution in three-level systems, and nonlinear susceptibilities (dephasing induced resonances in four-wave mixing).^{28,33-36} The details are given in Appendix A. The final result, which is identical to Eq. (14), is

$$\hat{I}(\omega_L, \omega_s) = \sum_{\substack{a, c \\ b, b'}} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} P(a) \times \frac{1}{\omega_{ba} - \omega_L + i\Gamma} \frac{1}{\omega_{b'a} - \omega_L - i\Gamma} \times \left\{ 2\pi\delta(\omega_{ac} + \omega_L - \omega_s) - \frac{2\hat{\Gamma}}{\omega_{bb'} + i\gamma} \right. \\ \left. \times \left[\frac{1}{\omega_{bc} - \omega_s + i\Gamma} + \frac{1}{\omega_{cb'} + \omega_s + i\Gamma} \right] \right\}. \quad (17)$$

Equation (17) is our final expression for the homogeneously broadened Raman line shape. When the molecule has only one $|b\rangle$ state (i.e., $b = b'$), it reduces to

$$\hat{I}(\omega_L, \omega_s) = 2\pi \sum_{a, c} |\mu_{ab}|^2 |\mu_{bc}|^2 P(a) \times \frac{1}{(\omega_{ba} - \omega_L)^2 + \Gamma^2} \left[\delta(\omega_{ca} + \omega_s - \omega_L) + \frac{2\hat{\Gamma}}{\gamma} \frac{\Gamma/\pi}{(\omega_{bc} - \omega_s)^2 + \Gamma^2} \right]. \quad (18)$$

The curly brackets in Eq. (17) contain two terms. In the absence of dephasing ($\hat{\Gamma} = 0$) the second term vanishes, and the first term becomes identical with the KH formula [Eq. (1)]

$$\hat{I}(\omega_L, \omega_s) = \hat{I}_0(\omega_L, \omega_s). \quad (19)$$

The proper dephasing rate $\hat{\Gamma}$ has a double role in Eq. (17). First it broadens the KH terms by adding to the width Γ . In addition, however, there are *dephasing induced* (redistribution) terms given by the second term in the curly brackets, and which are proportional to $\hat{\Gamma}$. Here are the main features of the homogeneously broadened Raman line shapes:

(1) In the presence of dephasing, we can no longer define a Raman amplitude χ_{ca} [Eq. (1a)] and express the cross section $\hat{I}(\omega_L, \omega_s)$ in terms of $|\chi_{ca}|^2$. This is a fundamental difference between isolated molecules and molecules in condensed phases, since due to the random force the latter are not in a pure state and cannot be represented by a wave function, but rather by a density matrix.

(2) If we integrate the first and the second terms in Eq. (17) over ω_s , we get the total excitation spectrum

$$\hat{I}_{\text{exc}}(\omega_L) \equiv \int \hat{I}(\omega_L, \omega_s) d\omega_s = 2\pi \sum_{\substack{a, c \\ b, b'}} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} P(a) \left[1 + \frac{2i\hat{\Gamma}}{\omega_{bb'} + i\gamma} \right] \times \frac{1}{\omega_{ba} - \omega_L + i\Gamma} \frac{1}{\omega_{b'a} - \omega_L - i\Gamma}. \quad (20)$$

Using Eq. (20), we note that for a single excited state ($b = b'$ and $\omega_{bb'} = 0$) the area ratio of the second (redistribution) term of the KH (first) term is $2\hat{\Gamma}/\gamma$. This is also the order of magnitude for the ratio in the multistate case [Eq. (20)]. Since typically in condensed phases $\hat{\Gamma}/\gamma \gg 1$ we need consider also the redistribution term, which is expected to dominate the spectrum.

(3) The dispersed emission spectrum (\hat{I} vs ω_s) is broadened since conservation of energy $\delta(\omega_{ca} + \omega_s - \omega_L)$ no longer holds. This is natural, since our molecule can exchange energy with the bath.

(4) The redistribution terms allow us to broaden the excitation and emission spectra by a Lorentzian without affecting the lifetime. This is precisely what is needed in order to eliminate the unphysical lifetimes $\gamma_b \sim 100 \text{ cm}^{-1}$ introduced when calculations did not take the homogeneous dephasing into account.⁵⁻⁸

III. THE GENERAL STOCHASTIC MODEL INTERPOLATION BETWEEN HOMOGENEOUS AND INHOMOGENEOUS BROADENING

In the previous section we analyzed the solution of the stochastic model [Eqs. (6)–(8)] in the homogeneous limit. We shall now consider the general solution of the model. We start with the absorption spectrum. This was solved by Kubo²⁹ for a two-level system, and the extension to our multilevel system is straightforward (see Appendix C). It is given by Eq. (9) with

$$\sigma_{ba}(\omega_L) = 1/\pi \text{Re} J_0 [\gamma/2 + i(\omega_L - \omega_{ba})]. \quad (21)$$

The line shape function $J_0(s)$ is given by

$$J_0(s) = \int_0^\infty d\tau \exp(-s\tau) J_0(\tau), \quad (22a)$$

where

$$J_0(\tau) = \exp[-g(\tau)], \quad (22b)$$

and where

$$g(\tau) = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \delta\omega_{eg}(\tau_2) \delta\omega_{eg}(0) \rangle. \quad (23)$$

Upon the substitution of Eq. (8) in Eq. (23) we get

$$g(\tau) = \frac{\Delta^2}{\Lambda^2} [\exp(-\Lambda\tau) - 1 + \Lambda\tau]. \quad (24)$$

It is possible to derive a continued fraction expansion for $J_0(s)$, i.e.,^{25,29}

$$J_0(s) = \frac{1}{s + \frac{\Delta^2}{s + \Lambda + \frac{2\Delta^2}{s + 2\Lambda + \frac{3\Delta^2}{s + 3\Lambda \dots}}}}. \quad (25)$$

We shall turn now to the Raman line shape. The detailed calculation is given in Appendix B. It is based on the same three pathways (Figs. 2 and 3) which contributed in the homogeneous limit in Sec. II. However, the calculation is now more complicated. The final result is given in terms of the auxiliary functions:

$$\begin{aligned} \Phi^\pm(\tau_1, \tau_2, \tau_3) \equiv & \exp\{-g(\tau_1) - g(\tau_3) \\ & \pm [g(\tau_1 + \tau_2 + \tau_3) + g(\tau_2) - g(\tau_2 + \tau_3) - g(\tau_1 + \tau_2)]\} \end{aligned} \quad (26)$$

i.e.,

$$\hat{I}(\omega_L, \omega_s) = \sum_{a,c} P(a) \hat{I}_{ca}(\omega_L, \omega_s), \quad (27)$$

$$\hat{I}_{ca}(\omega_L, \omega_s) = K_I + K_{II} + K_{III}, \quad (27a)$$

$$\begin{aligned} K_I = & \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ & \times \exp[-i(\omega_s - \omega_{bc})\tau_1 - i\omega_{b'b}\tau_2 - i(\omega_L - \omega_{ba})\tau_3 \\ & - 1/2\gamma(\tau_1 + 2\tau_2 + \tau_3)] \Phi^+(\tau_1, \tau_2, \tau_3) + \text{c.c.}, \end{aligned} \quad (27b)$$

$$\begin{aligned} K_{II} = & \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ & \times \exp[-i(\omega_{b'c} - \omega_s)\tau_1 - i\omega_{b'b}\tau_2 - i(\omega_L - \omega_{ba})\tau_3 \\ & - 1/2\gamma(\tau_1 + 2\tau_2 + \tau_3)] \Phi^-(\tau_1, \tau_2, \tau_3) + \text{c.c.}, \end{aligned} \quad (27c)$$

$$\begin{aligned} K_{III} = & \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ & \times \exp[-i(\omega_{b'c} - \omega_s)\tau_1 - i(\omega_{ac} + \omega_L - \omega_s)\tau_2 \\ & - i(\omega_L - \omega_{ba})\tau_3 - 1/2\gamma(\tau_1 + \tau_3)] \Phi^-(\tau_1, \tau_2, \tau_3) \\ & + \text{c.c.} \end{aligned} \quad (27d)$$

We are now in a position to analyze the absorption and the Raman line profiles [Eqs. (25) and (27)]. To that end, we introduce the dimensionless parameter

$$\kappa \equiv \Lambda / \Delta, \quad (28)$$

which determines the nature of the broadening mechanism. We first consider the homogeneous and the inhomogeneous limits and then the general case.

A. The fast modulation (homogeneous) limit

This limit is obtained when the correlation time of the bath fluctuations is much faster than their magnitude, i.e., $\kappa \gg 1$. In this case, the $\exp(-\Lambda\tau)$ on the right-hand side of Eq. (24) vanishes very rapidly and may be ignored. We then get

$$g(\tau) = \hat{\Gamma}\tau, \quad (29)$$

where

$$\hat{\Gamma} = \Delta^2 / \Lambda. \quad (30)$$

Upon the substitution of Eq. (29) in Eq. (22) we get

$$J_0(s) = \frac{1}{s + \hat{\Gamma}}, \quad (31)$$

so that the absorption line shape assumes a Lorentzian form corresponding to homogeneous dephasing. Upon the substitution of Eq. (31) in Eq. (21) we get Eq. (10). In Fig. 4, we display the line shape function $\sigma_{ba}(\omega_L)$ [Eq. (21)] together with Eq. (25) for several values of κ . The $\kappa = 5$ line is close to a Lorentzian. Turning now to the Raman spectra, Eqs. (29) and (26) result in

$$\Phi^\pm(\tau_1, \tau_2, \tau_3) = \exp[-\hat{\Gamma}\tau_1 - \hat{\Gamma}\tau_3]. \quad (32)$$

The three integrations in Eqs. (27) can be trivially performed upon the substitution of Eq. (32), resulting in Eqs. (14).

We have thus confirmed the statements made in Sec. II that the homogeneous dephasing is the fast modulation limit of the present model. The absorption line shape is then given

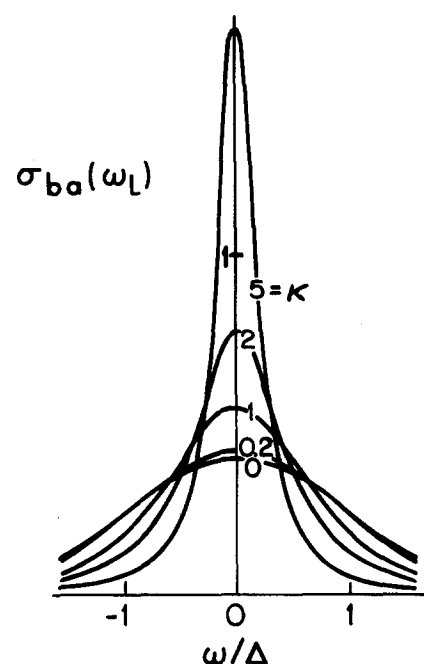


FIG. 4. The absorption line shape function [Eq. (21)] for a two-level system with a stochastic modulation (Ref. 29). The parameter $\kappa \equiv \Lambda / \Delta$ determines the nature of the modulation. $\kappa \gg 1$ corresponds to a homogeneous broadening (a Lorentzian line shape), whereas $\kappa \ll 1$ corresponds to static inhomogeneous broadening (a Gaussian line shape). $\gamma = 0$.

by Eq. (10), and the Raman line shape is given by Eq. (17). These results were analyzed in detail in Sec. II.

B. The slow modulation (static, inhomogeneous) limit

When $\Lambda \ll \Delta$, i.e., $\kappa \ll 1$, we can make a Taylor expansion of Eq. (24) (short-time approximation) resulting in

$$g(\tau) = 1/2\Delta^2 \tau^2. \quad (33)$$

The absorption line shape [Eq. (21)] assumes in this case the Voigt profile (a convolution of a Gaussian and a Lorentzian)

$$\sigma_{ba}(\omega_L) = \frac{1}{\sqrt{2\pi}\Delta} \int d\omega' \frac{\gamma/2\pi}{(\omega_L - \omega_{ba} - \omega')^2 + \gamma^2/4} \times \exp[-\omega'^2/2\Delta^2] \quad (34)$$

and when $\gamma \ll \Delta$, it becomes a Gaussian (Fig. 4):

$$\sigma_{ba}(\omega_L) = \frac{1}{\sqrt{2\pi}\Delta} \exp[-(\omega_L - \omega_{ba})^2/2\Delta^2]. \quad (35)$$

We shall turn now to the Raman line shape. Upon the substitution of Eq. (33) in Eq. (26), we get

$$\Phi^\pm(\tau_1, \tau_2, \tau_3) = \exp[-\Delta^2/2(\tau_1 \pm \tau_3)^2]. \quad (36)$$

It will prove convenient to perform a Fourier transform of Eq. (36), i.e.,

$$\Phi^\pm(\tau_1, \tau_2, \tau_3) = \int d\omega \exp[i\omega(\tau_1 \pm \tau_3)] S(\omega), \quad (37)$$

where $S(\omega)$ is the Gaussian distribution

$$S(\omega) = \frac{1}{\sqrt{2\pi}\Delta} \exp(-\omega^2/2\Delta^2) \quad (38)$$

when Eq. (37) is substituted in Eq. (27), we get

$$K_\nu(\omega_L, \omega_s) = \int d\omega K_\nu^0(\omega_L + \omega, \omega_s + \omega) S(\omega), \quad \nu = \text{I, II, III}. \quad (39)$$

Here K_ν^0 are K_ν for the isolated molecule (no dephasing). Making use of Eq. (17) with $\hat{T} = 0$, we have

$$K_{\text{I}}^0 + K_{\text{II}}^0 + K_{\text{III}}^0 = |\chi_{ca}(\omega_L)|^2 \delta(\omega_{ca} + \omega_s - \omega_L), \quad (40)$$

where χ_{ca} is the Raman amplitude for the isolated molecule [Eq. (1a)]. Equations (27) and (27a) together with Eqs. (39) and (40) result in

$$\hat{I}(\omega_L, \omega_s) = \sum_{a,c} P(a) \langle |\chi_{ca}(\omega_L)|^2 \rangle \delta(\omega_{ca} + \omega_s - \omega_L), \quad (41)$$

where the $\langle \dots \rangle$ denotes averaging over the distribution of the energy gap, i.e.,

$$\langle |\chi_{ca}(\omega_L)|^2 \rangle \equiv \int d\omega |\chi_{ca}(\omega_L + \omega)|^2 S(\omega) \quad (42)$$

and $S(\omega)$ is given in Eq. (38). Equations (41) and (42) are identical to Eq. (5). They simply imply that in the slow modulation (inhomogeneous) limit we calculate the Raman cross section for a particular realization of the energy gap, using the KH formula [Eq. (1)] and then average over the distribution of energy gaps. Since the bath is static, we could have written Eqs. (41) and (42) immediately without going

through the general formalism. Equations (41) and (42) demonstrate that Eq. (27) reduces to the static result in the limit of slow modulation.

C. The general solution of the stochastic model

The general expression for the absorption line shape was given in Eq. (25) in terms of a continued fraction. The Raman line shape [Eq. (27)] may be similarly expanded in a series. We first define the triple Laplace transform of Φ^\pm , i.e.,

$$\Psi^\pm(s_1, s_2, s_3) \equiv \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \times \exp(-s_1\tau_1 - s_2\tau_2 - s_3\tau_3) \Phi^\pm(\tau_1, \tau_2, \tau_3), \quad (43)$$

we can then express Eqs. (27) in terms of Ψ^\pm , i.e.,

$$\hat{I}(\omega_L, \omega_s) = \sum_{a,c} P(a) \hat{I}_{ca}(\omega_L, \omega_s), \quad (44)$$

$$\hat{I}_{ca}(\omega_L, \omega_s) = K_{\text{I}} + K_{\text{II}} + K_{\text{III}}, \quad (44a)$$

$$K_{\text{I}} = \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \times \Psi^+[\gamma/2 + i(\omega_s - \omega_{bc}), \gamma + i\omega_{b'b}, \gamma/2 + i(\omega_L - \omega_{ba})] + \text{c.c.}, \quad (44b)$$

$$K_{\text{II}} = \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \times \Psi^-[\gamma/2 + i(\omega_{b'c} - \omega_s), \gamma + i\omega_{b'b}, \gamma/2 + i(\omega_L - \omega_{ba})] + \text{c.c.}, \quad (44c)$$

$$K_{\text{III}} = \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \times \Psi^-[\gamma/2 + i(\omega_{b'c} - \omega_s), i(\omega_{ac} + \omega_L - \omega_s), \gamma/2 + i(\omega_L - \omega_{ba})] + \text{c.c.} \quad (44d)$$

A continued-fraction expansion for Ψ^\pm is developed in Appendix C. This may be used to conveniently calculate the Raman spectrum in the intermediate case, when the line broadening is neither homogeneous nor inhomogeneous.

IV. DEPHASING IN HARMONIC MOLECULES WITH LINEAR EQUILIBRIUM DISPLACEMENTS

A commonly used microscopic model in the interpretation of Raman line shapes of polyatomic molecules in solution is the linearly displaced harmonic model. The potential functions of H_g and H_e are taken to be harmonic (i.e., quadratic in nuclear displacements), and the equilibrium position is displaced between these states, i.e.,

$$H_g = 1/2 \sum_{\nu=1}^N \hbar\omega_\nu (p_\nu^2 + q_\nu^2), \quad (45a)$$

$$H_e = H_g + \sum_{\nu=1}^N s_\nu q_\nu. \quad (45b)$$

Here p_ν and q_ν are the dimensionless momenta and coordinates of the ν th oscillator and s_ν is the dimensionless dis-

placement. This model is a realistic zero order approximation for polyatomic molecules with N vibrational degrees of freedom. The simplicity of this model allows performing all the summations over intermediate states [Eqs. (27)] analytically, resulting in compact time-domain expressions. The reason is, that harmonic coordinates are Gaussian variables, and a standard second order cumulant expression is exact in this case. If we add our stochastic modulation to this model, it will still be solvable. A detailed derivation of the harmonic problem was given elsewhere.^{19,37} Using the same method, we can derive the complete expression for the stochastic model,

$$H = |g\rangle H_g \langle g| + |e\rangle [\bar{\omega}_{eg} + \delta\omega_{eg}(t) + H_e] \langle e|, \quad (46)$$

where H_e and H_g are given by Eq. (45).

The Raman line shape is given by

$$\hat{I}(\omega_L, \omega_s) = K_I + K_{II} + K_{III}, \quad (47)$$

where

$$\begin{aligned} K_I &= |\mu_{eg}|^4 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ &\times \exp[-i(\omega_s - \bar{\omega}_{eg})\tau_1 - i(\omega_L - \bar{\omega}_{eg})\tau_2 \\ &- 1/2\gamma(\tau_1 + 2\tau_2 + \tau_3)] \Phi^+(\tau_1, \tau_2, \tau_3) + \text{c.c.}, \end{aligned} \quad (47a)$$

$$\begin{aligned} K_{II} &= |\mu_{eg}|^4 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ &\times \exp[-i(\bar{\omega}_{eg} - \omega_s)\tau_1 - i(\omega_L - \bar{\omega}_{eg})\tau_2 \\ &- 1/2\gamma(\tau_1 + 2\tau_2 + \tau_3)] \Phi^-(\tau_1, \tau_2, \tau_3) + \text{c.c.}, \end{aligned} \quad (47b)$$

$$\begin{aligned} K_{III} &= |\mu_{eg}|^4 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ &\times \exp[-i(\bar{\omega}_{eg} - \omega_s)\tau_1 - i(\omega_L - \omega_s)\tau_2 \\ &- i(\omega_L - \bar{\omega}_{eg})\tau_3] - 1/2\gamma(\tau_1 + \tau_3)] \\ &\times \Phi^-(\tau_1, \tau_2, \tau_3) + \text{c.c.}, \end{aligned} \quad (47c)$$

where Φ^\pm are given by Eq. (26) and where

$$g(\tau) = g_1(\tau) + g_2(\tau). \quad (48)$$

$g_1(\tau)$ is the harmonic part

$$\begin{aligned} g_1(\tau) &= \sum_{\nu=1}^N \frac{s_\nu^2}{\omega_\nu^2} \{(\bar{n}_\nu + 1) [\exp(i\omega_\nu\tau) - i\omega_\nu\tau - 1] \\ &+ \bar{n}_\nu [\exp(-i\omega_\nu\tau) + i\omega_\nu\tau - 1]\}, \end{aligned} \quad (49a)$$

and $g_2(\tau)$ is the stochastic part, responsible for the line broadening

$$g_2(\tau) = \frac{\Delta^2}{\Lambda^2} [\exp(-\Lambda\tau) - 1 + \Lambda\tau]. \quad (49b)$$

\bar{n}_ν is the mean occupation number of the ν th oscillator at temperature T , i.e.,

$$\bar{n} = [\exp(\hbar\omega_\nu/kT) - 1]^{-1}. \quad (50)$$

Equations (47) could be obtained starting with Eqs. (27), by using the expressions for the Franck-Condon factors³⁸ and performing the summations over a , b , b' , and c . However, the cumulant expansion^{12,19,24,37} allows us to derive Eq. (47)

directly. In the absence of dephasing, ($g_2 = 0$) it is possible to combine K_I , K_{II} , and K_{III} as

$$\begin{aligned} K_I + K_{II} + K_{III} &= \int_{-\infty}^{\infty} dt \int_0^\infty dt_1 \int_0^\infty dt_2 \\ &\times \exp[i(\omega_{ba} - \omega_L)t_1 - i(\omega_{ba} - \omega_L)t_2 \\ &+ i(\omega_{ca} + \omega_s - \omega_L)t] \\ &\times \Phi^+[-t, t_2, t + t_1 - t_2]. \end{aligned} \quad (51)$$

Equation (51) forms the basis for the transform methods developed recently for performing the triple integrations and obtaining the Raman excitation spectrum from the absorption line shapes.^{12,24,37} Note, however, that Eq. (51) is equivalent to the KH expression [Eq. (11)] and is valid only in the absence of dephasing. When dephasing processes exist, we have to calculate K_I , K_{II} , and K_{III} separately, and only then combine them to get the spectrum. The present theory allows us to evaluate critically the inversion procedure, which is based on the transform methods used to calculate Raman spectra, using the absorption line shapes. First it should be noted that in general absorption line shapes contain less information than Raman spectra. In terms of correlation functions, absorption line shapes are related to a two-time correlation function of the dipole operator, whereas Raman spectra are related to a four-time correlation function of the dipole operator.^{19,28,31} It is a special feature of the displaced harmonic model [Eq. (45)] that both spectra are given in terms of the same quantity $g_1(\tau)$ [Eq. (49a)] and thus carry the same information. When line broadening exists, there is no unique relation, however, between absorption and Raman line shapes, even for the displaced harmonic oscillator model. As an illustration, suppose the absorption line is a sum of Lorentzians [Eqs. (9) and (10)]. Let us consider the following three mechanisms which may lead to this absorption spectrum:

- (i) Broadening due to the lifetime, i.e., $\Gamma = 1/2 \gamma_b$.
- (ii) Pure dephasing (the stochastic model in the homogeneous limit), i.e., $\Gamma = \hat{\Gamma}$.
- (iii) Inhomogeneous broadening with a Lorentzian distribution of energy gaps, i.e., taking $S(\omega)$ [Eq. (38)] to be a Lorentzian

$$S(\omega) = \frac{\Gamma/\pi}{\omega^2 + \Gamma^2}. \quad (52)$$

If our only available information is the absorption line shape [Eqs. (9) and (10)], we cannot distinguish between these three models. The Raman spectra corresponding to each model will be, however, very different. For model (i) it is given by Eq. (1). For model (ii) the Raman line shape is given by Eq. (17), whereas for model (iii) we need Eqs. (41) and (42), together with Eq. (52). Unless more information is available regarding the nature of the broadening, it is impossible to invert broadened absorption line shapes and obtain the Raman spectra. The inversion method^{12,24,37} holds only when the broadening is due to lifetime [model (i)]. Using our stochastic model and Eqs. (47), we can develop an alternative inversion procedure which will include the effects of dephasing processes.

V. DISCUSSION

In this article, we developed a stochastic model which allows the incorporation of line broadening (dephasing) mechanisms in the calculations of molecular Raman line shapes. The model is particularly useful for extracting structural and dynamical information from complex absorption and Raman spectra of polyatomic molecules in condensed phases. The main assumption of the present model is that the molecule is subjected to a random force which modulates stochastically the electronic energy gap. This modulation is assumed to be a Gaussian–Markov process, characterized by two parameters: a magnitude Δ and a time scale (correlation time) Λ^{-1} . The dimensionless parameter $\kappa \equiv \Lambda / \Delta$ determines the nature of this process. $\kappa \gg 1$ corresponds to a fast modulation, whereby all molecules appear identical to the radiation field (homogeneous broadening). When $\kappa \ll 1$, the modulation is static, and the model corresponds to a Gaussian (inhomogeneous) distribution of the energy gap. Explicit expressions were derived for the absorption and the Raman line shapes in the homogeneous limit [Eqs. (9) and (17)] in the inhomogeneous limit [Eqs. (34), (41), and (42)], and for the general (intermediate) case [Eqs. (21), (22), and (44)]. In the presence of dephasing, it is impossible to express the Raman cross section as a square of an amplitude, instead, we have to calculate directly the ensemble averaged cross section. The Kramers–Heisenberg formula [Eq. (1)] is, therefore, no longer valid for molecules in condensed phases. In the homogeneous limit, the absorption line shape is a Lorentzian. The Raman cross section [Eq. (17)] contains two terms. The first is a KH-type term, which reduces to the KH formula in the absence of dephasing, whereas the second consists of dephasing-induced (redistribution) contributions, which vanish in the absence of dephasing. The relative intensity of the second to the first term is $\sim 2\hat{\Gamma} / \gamma$, where γ is the lifetime of the excited state and $\hat{\Gamma}$ is the proper dephasing rate [Eq. (20)]. We expect that usually for molecules in a solution $\hat{\Gamma} \gg \gamma$, so that typically the KH-type terms are weak, and the spectrum will be dominated by the redistribution terms. This poses some restrictions on the applicability of many theoretical treatments which are based on calculating Raman amplitudes.^{5–8,12,32} The dephasing-induced terms calculated in this work are analogous to the redistribution terms observed in resonance Raman in the gas phase (collisional broadening)^{21,22,28,33} and in solids.^{26,39} Dephasing-induced resonances were also predicted and observed in nonlinear optical susceptibilities ($\chi^{(3)}$) in the gas phase and in condensed phases.^{34–36} In the static (inhomogeneous) limit, the Raman cross section may be obtained by averaging the cross section for the isolated molecule with respect to the distribution of energy gaps [Eq. (42)]. We have derived a closed form expression for the Raman line shape in the general case (i.e., arbitrary time scale of the bath) [Eq. (44)].

Some additional comments need now be made:

(1) Suppose we have independent broadening mechanisms due to two types of motions or interactions which are uncorrelated. If these mechanisms are Gaussian–Markovian processes, then Eqs. (22), (26), and (27) still hold, but with

$$g(\tau) = g_1(\tau) + g_2(\tau), \quad (53)$$

so that [Eq. (22b)]

$$J_0(\tau) = J_0^{(1)}(\tau) J_0^{(2)}(\tau) \quad (54)$$

and

$$\sigma_{ba}(\omega_L) = \int d\omega \sigma_{ba}^{(1)}(\omega_L - \omega) \sigma_{ba}^{(2)}(\omega). \quad (55)$$

Here $J_0^{(v)}$ and $\sigma_{ba}^{(v)}$ are given by Eqs. (21) and (22) with $g(\tau)$ replaced by $g_v(\tau)$. The absorption line shape is then simply the convolution of the line shapes corresponding to each broadening mechanism. Similarly, for the Raman line shape, Eqs. (26) and (27) still hold with $g(\tau)$ given by Eq. (45), i.e.,

$$\Phi^\pm(\tau_1, \tau_2, \tau_3) = \Phi_1^\pm(\tau_1, \tau_2, \tau_3) \Phi_2^\pm(\tau_1, \tau_2, \tau_3), \quad (56)$$

where Φ_1^\pm and Φ_2^\pm are given by Eq. (26) with $g(\tau)$ replaced by $g_1(\tau)$ and $g_2(\tau)$, respectively. The extension of Eqs. (54) or (56) to n broadening mechanisms ($n > 2$) is straightforward. The calculation of $\Psi^\pm(s_1, s_2, s_3)$ [Eq. (43)] corresponding to Eq. (56) involves a triple convolution. However, if one of the broadening mechanisms is inhomogeneous, the calculation is much simpler. Suppose, e.g., that we have a homogeneous and an inhomogeneous mechanism which coexist, i.e.,

$$g_1(\tau) = \hat{\Gamma}_1 \tau, \quad (57a)$$

$$g_2(\tau) = 1/2 \Delta_2^2 \tau^2. \quad (57b)$$

In this case, we can calculate the homogeneously broadened line (ignoring g_2) via Eq. (17). We then write for the Raman line shape

$$\langle \hat{I}(\omega_L, \omega_s) \rangle = \int \hat{I}(\omega_L + \omega, \omega_s + \omega) S(\omega). \quad (58)$$

Here \hat{I} is calculated from Eq. (17) with $\hat{\Gamma} = \hat{\Gamma}_1$. $S(\omega)$ is given by Eq. (38) with $\Delta = \Delta_2$. Equation (58) together with Eq. (17), provides a simple method for the interpretation of experimental data in the presence of homogeneous and inhomogeneous broadening. The existing theories use the KH expression for \hat{I}_0 [Eq. (1)] instead of \hat{I} on the right-hand side of Eq. (58) and correspond to lifetime broadening with no homogeneous dephasing.^{5–8,12,32}

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APPENDIX A

Figures 2 and 3 show the pathways in Liouville space which contribute to the Raman cross section. Each bond represents a radiative coupling (see Appendix B for more detail). We shall use here the Liouville space notation.²⁸ The initial state is $|aa\rangle\rangle$ and the final state is $|cc\rangle\rangle$. There are six pathways which lead from $|aa\rangle\rangle$ to $|cc\rangle\rangle$ in *fourth order* (i.e., with four bonds). Symmetry allows us, however, to consider only three (Fig. 3). For the sake of brevity, let us introduce the following notation:

$$E_a = \epsilon_a + \omega_L,$$

$$\begin{aligned}
E_c &= \epsilon_c + \omega_s, \\
E_b &= \epsilon_b, \\
E'_b &= \epsilon'_b, \\
\Omega_{ij} &= E_i - E_j, \\
\omega_{ij} &= \epsilon_i - \epsilon_j.
\end{aligned} \tag{A1}$$

We further define the following functions: for any pair of levels ν and μ , belonging to different electronic states, we define

$$\begin{aligned}
I_{\nu\mu} &= \frac{1}{E_\mu - E_\nu + i/2(\gamma_\nu + \gamma_\mu) + \hat{\Gamma}}, \\
\nu\mu &= ab, ab', cb, cb'.
\end{aligned} \tag{A2}$$

If ν and μ belong to the same electronic state, we set $\hat{\Gamma} = 0$, i.e.,

$$I_{\nu\mu} = \frac{1}{E_\mu - E_\nu + i/2(\gamma_\nu + \gamma_\mu)}, \quad \nu\mu = ac, bb'. \tag{A3}$$

Note also that

$$I_{\mu\nu} = -I_{\nu\mu}^*. \tag{A4}$$

The contribution of each of the pathways (Fig. 3) to \hat{I} is simply the product of the $I_{\nu\mu}$ functions corresponding to the three intermediate points in the path (i.e., excluding $|aa\rangle$ and $|cc\rangle$) and the appropriate four matrix elements of the dipole operator. As noted in Eq. (14), to each path we need add the complex conjugate. This can be done using Eq. (A4). It will prove more convenient to interchange the indices b and b' in the complex conjugate path. Since Eqs. (14) include a summation over all $|b\rangle$ and $|b'\rangle$, this does not affect the sum. We then get

$$\begin{aligned}
K_I &= -i \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \\
&\quad \times [I_{ab} I_{b'b} I_{cb} + I_{b'a} I_{b'b} I_{b'c}], \\
K_{II} &= -i \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \\
&\quad \times [I_{ab} I_{b'b} I_{b'c} + I_{b'a} I_{b'b} I_{cb}], \\
K_{III} &= -i \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \\
&\quad \times [I_{ab} I_{ac} I_{b'c} + I_{b'a} I_{ca} I_{cb}].
\end{aligned} \tag{A5}$$

From now on, for brevity, we shall eliminate the summation and the μ factors. We shall write them explicitly in the final

expressions. We further assume that the ground state levels have a zero width, and the excited states have the same width, i.e.,

$$\begin{aligned}
\gamma_a &= \gamma_c = 0, \\
\gamma_b &= \gamma_{b'} = \gamma.
\end{aligned} \tag{A6}$$

Combining K_I and K_{II} [Eq. (A5)], we get

$$K_I + K_{II} = (I_{ab} + I_{b'a}) I_{b'b} (I_{cb} + I_{b'c}). \tag{A7}$$

We now make use of the trivial identities

$$\begin{aligned}
I_{ab} + I_{b'a} &= I_{ab} I_{b'a} [I_{ab}^{-1} + I_{b'a}^{-1}], \\
I_{cb} + I_{b'c} &= I_{cb} I_{b'c} [I_{bc}^{-1} + I_{b'c}^{-1}].
\end{aligned} \tag{A8}$$

Upon the substitution of Eq. (A8) in Eq. (A7) and using Eq. (A3), we finally get

$$\begin{aligned}
K_I + K_{II} &= I_{ab} I_{b'a} I_{cb} I_{b'c} \\
&\quad \times [I_{ab}^{-1} + I_{b'a}^{-1}] [I_{bc}^{-1} + I_{b'c}^{-1}] I_{b'b} \\
&= I_{ab} I_{b'a} I_{cb} I_{b'c} \\
&\quad \times [\omega_{bb'} + i(\gamma + 2\hat{\Gamma})]^2 \frac{1}{\omega_{bb'} + i\gamma}.
\end{aligned} \tag{A9}$$

We now turn to K_{III} . We first split I_{ac} into its real and imaginary parts:

$$\begin{aligned}
I_{ac} &= I'_{ac} - i I''_{ac}, \\
I_{ca} &= -I_{ac}^* = -I'_{ac} - i I''_{ac},
\end{aligned} \tag{A10}$$

where

$$I'_{ac} = pp \frac{1}{\Omega_{ca}}$$

and

$$I''_{ac} = \pi\delta(\Omega_{ca}). \tag{A11}$$

Using Eqs. (A5), (A10), and (A11), we get

$$\begin{aligned}
K_{III} &= I'_{ac} (I_{ab} I_{b'c} - I_{b'a} I_{cb}) - i I''_{ac} (I_{ab} I_{b'c} + I_{b'a} I_{cb}) \\
&\equiv K_{III}^{(1)} + K_{III}^{(2)}.
\end{aligned} \tag{A12}$$

$K_{III}^{(1)}$ can be trivially rearranged in the form

$$K_{III}^{(1)} = I'_{ac} I_{ab} I_{b'a} I_{cb} I_{b'c} [I_{b'a}^{-1} I_{cb}^{-1} - I_{ab}^{-1} I_{b'c}^{-1}]. \tag{A13}$$

Upon the substitutions of Eqs. (A3) in Eq. (A13), we get

$$\begin{aligned}
K_{III}^{(1)} &= I_{ab} I_{b'a} I_{cb} I_{b'c} 1/\Omega_{ca} \{ [\Omega_{ac} + \Omega_{cb'} + i/2(\gamma + 2\hat{\Gamma})] \\
&\quad \times [\Omega_{bc} + i/2(\gamma + 2\hat{\Gamma})] - [\Omega_{ba} + i/2(\gamma + 2\hat{\Gamma})] [\Omega_{cb'} + i/2(\gamma + 2\hat{\Gamma})] \} \\
&= I_{ab} I_{b'a} I_{cb} I_{b'c} 1/\omega_{ca} \{ \Omega_{ac} [\Omega_{bc} + i/2(\gamma + 2\hat{\Gamma})] + \Omega_{ac} [\Omega_{cb'} + i/2(\gamma + 2\hat{\Gamma})] \},
\end{aligned} \tag{A14}$$

which finally yields

$$K_{III}^{(1)} = -I_{ab} I_{b'a} I_{cb} I_{b'c} [\omega_{bb'} + i(\gamma + 2\hat{\Gamma})]. \tag{A15}$$

From Eqs. (A9) and (A15) we note that there is a cancellation (interference) between $K_I + K_{II}$ and $K_{III}^{(1)}$. When these are combined, we get

$$\begin{aligned}
K_I + K_{II} + K_{III}^{(1)} \\
= I_{ab} I_{b'a} I_{cb} I_{b'c} [\omega_{bb'} + i(\gamma + 2\hat{\Gamma})] \frac{2i\hat{\Gamma}}{\omega_{bb'} + i\gamma}.
\end{aligned} \tag{A16}$$

Using Eq. (A3) we have

$$I_{cb} I_{b'c} = (I_{cb} + I_{b'c}) [\omega_{bb'} + i(\gamma + 2\hat{\Gamma})]^{-1}. \quad (\text{A17})$$

Equations (A16) and (A17) finally result in

$$K_I + K_{II} + K_{III}^{(1)} = I_{ab} I_{b'a} (I_{cb} + I_{b'c}) \frac{2i\hat{\Gamma}}{\omega_{bb'} + i\gamma}. \quad (\text{A18})$$

We now turn to $K_{III}^{(2)}$. Using Eqs. (A11) and (A12), we have

$$K_{III}^{(2)} = -i\pi\delta(\Omega_{ac}) I_{ab} I_{b'a} [I_{b'c} I_{b'a}^{-1} + I_{cb} I_{ab}^{-1}] \quad (\text{A19})$$

due to the δ function, we can change indexes c and a in the bracket, resulting in

$$\begin{aligned} K_{III}^{(2)} &= -2\pi i\delta(\Omega_{ac}) I_{ab} I_{b'a} \\ &= -2\pi i\delta(\omega_{ca} + \omega_s - \omega_L) I_{ab} I_{b'a}. \end{aligned} \quad (\text{A20})$$

Combining Eqs. (A18) and (A20) with Eq. (14), we finally get

$$\begin{aligned} \hat{I}(\omega_L, \omega_s) &= \sum_{\substack{a,c \\ b,b'}} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} P(a) \\ &\quad \times I_{ab} I_{b'a} \left\{ 2\pi\delta(\omega_{ac} + \omega_L - \omega_s) \right. \\ &\quad \left. + \frac{2\hat{\Gamma}}{\omega_{bb'} + i\gamma} [I_{cb} + I_{b'c}] \right\}. \end{aligned} \quad (\text{A21})$$

Equation (A21) is identical to Eq. (17).

APPENDIX B

We consider a four-level system $|a\rangle$, $|b\rangle$, $|b'\rangle$, and $|c\rangle$ (Fig. 1). In the rotating wave approximation, we can include the photon energies (ω_L and ω_s) in the energies of these states, resulting in the following molecular Hamiltonian^{28,30}:

$$\begin{aligned} H_0 &= |a\rangle(\epsilon_a + \omega_L)\langle a| + |c\rangle(\epsilon_c + \omega_s)\langle c| \\ &\quad + |b\rangle[\epsilon_b + \delta\omega_{eg}(t)]\langle b| + |b'\rangle[\epsilon_{b'} + \delta\omega_{eg}(t)]\langle b'| \end{aligned} \quad (\text{B1})$$

and the coupling with the radiation field is

$$\begin{aligned} V &= \mu_{ab}|a\rangle\langle b| + \mu_{ba}|b\rangle\langle a| + \mu_{ab'}|a\rangle\langle b'| \\ &\quad + \mu_{b'a}|b'\rangle\langle a| + \mu_{cb}|c\rangle\langle b| + \mu_{bc}|b\rangle\langle c| \\ &\quad + \mu_{cb'}|c\rangle\langle b'| + \mu_{b'c}|b'\rangle\langle c|. \end{aligned} \quad (\text{B2})$$

$\delta\omega_{eg}(t)$ is a stochastic Gaussian random modulation [Eqs. (7) and (8)]. The molecular density matrix ρ obeys the Liouville equation

$$\frac{d\rho}{dt} = -iL\rho = -iL_0\rho - i\mathcal{V}\rho - \Gamma\rho. \quad (\text{B3})$$

Here

$$\begin{aligned} L_0\rho &\equiv [H_0, \rho], \\ \mathcal{V}\rho &\equiv [V, \rho]. \end{aligned} \quad (\text{B4})$$

Γ is a relaxation matrix representing the lifetimes of the various levels with the only nonvanishing elements

$$\langle\langle\nu\mu|\Gamma|\nu\mu\rangle\rangle = 1/2(\gamma_\nu + \gamma_\mu), \quad (\text{B5})$$

γ_ν^{-1} being the phenomenological lifetime of level ν . We further define the molecular propagator or from the time t_1 to time t_2 , i.e.,

$$\mathcal{G}(t_2, t_1) \equiv \exp_+ \left[-i \int_{t_1}^{t_2} d\tau L_0(\tau) - \Gamma(t_2 - t_1) \right], \quad (\text{B6})$$

where \exp_+ is the usual time ordered exponential. \mathcal{G} is a diagonal matrix in Liouville space, and its only nonvanishing elements are

$$\begin{aligned} \langle\langle\nu\mu|\mathcal{G}(t_2, t_1)|\nu\mu\rangle\rangle &= \exp \left[-i(E_\nu - E_\mu)(t_2 - t_1) \right. \\ &\quad \left. - 1/2(\gamma_\nu + \gamma_\mu)(t_2 - t_1) - i \int_{t_1}^{t_2} d\tau \delta\omega_{eg}(\tau) \right], \end{aligned} \quad (\text{B7})$$

where we had defined

$$\begin{aligned} E_a &= \epsilon_a + \omega_L, \\ E_c &= \epsilon_c + \omega_s, \\ E_b &= \epsilon_b, \\ E_{b'} &= \epsilon_{b'}. \end{aligned} \quad (\text{B8})$$

Equation (B7) holds for pairs of levels which belong to different electronic states, i.e., $\nu\mu = ab, ab', cb, cb'$. When ν and μ belong to the same electronic state, i.e., $\nu\mu = aa, ac, bb, b'b', bb'$, then the $\delta\omega_{eg}(\tau)$ term should be eliminated. Using the tetradic notation,²⁸ our Raman process (Fig. 1) is described in Fig. 2, where we start in $|aa\rangle$ and end up in $|cc\rangle$. This requires four radiative interactions \mathcal{V} . We then have

$$\begin{aligned} \hat{I}_{ca}(\omega_L, \omega_s) &= (-i)^4 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ &\quad \langle\langle cc|\mathcal{V}\mathcal{G}(\tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3) \\ &\quad \times \mathcal{V}\mathcal{G}(\tau_2 + \tau_3, \tau_3)\mathcal{V}\mathcal{G}(\tau_3, 0)\mathcal{V}|aa\rangle\rangle. \end{aligned} \quad (\text{B9})$$

We shall now write the contribution of the three pathways displayed in Fig. 3 to \hat{I} .

$$\begin{aligned} K_I &= \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ &\quad \langle\langle cb|\mathcal{G}(\tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3)|cb\rangle\rangle \\ &\quad \times \langle\langle b'b|\mathcal{G}(\tau_2 + \tau_3, \tau_3)|b'b\rangle\rangle \\ &\quad \times \langle\langle ab|\mathcal{G}(\tau_3, 0)|ab\rangle\rangle + \text{c.c.}, \end{aligned} \quad (\text{B10a})$$

$$\begin{aligned} K_{II} &= \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ &\quad \langle\langle b'c|\mathcal{G}(\tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3)|b'c\rangle\rangle \\ &\quad \times \langle\langle b'b|\mathcal{G}(\tau_2 + \tau_3, \tau_3)|b'b\rangle\rangle \\ &\quad \times \langle\langle ab|\mathcal{G}(\tau_3, 0)|ab\rangle\rangle + \text{c.c.}, \end{aligned} \quad (\text{B10b})$$

and

$$\begin{aligned} K_{III} &= \sum_{b,b'} \mu_{ab} \mu_{bc} \mu_{cb'} \mu_{b'a} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ &\quad \langle\langle b'c|\mathcal{G}(\tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3)|b'c\rangle\rangle \\ &\quad \times \langle\langle ac|\mathcal{G}(\tau_2 + \tau_3, \tau_3)|ac\rangle\rangle \\ &\quad \times \langle\langle ab|\mathcal{G}(\tau_3, 0)|ab\rangle\rangle + \text{c.c.} \end{aligned} \quad (\text{B10c})$$

Equations (B10) need to be then averaged over the stochastic variable $\delta\omega_{eg}(t)$. This averaging was described in detail recently,³¹ resulting in Eqs. (27).

APPENDIX C

We wish to evaluate Ψ^\pm [Eq. (43)], which is the triple Laplace transform of Ψ^\pm [Eq. (26)]. The present derivation is based on the work of Takagahara, Hanamura, and Kubo.²⁵ To that end, we shall first write Eq. (26) explicitly by substituting Eq. (24) in it, i.e.,

$$\Phi^\pm(\tau_1, \tau_2, \tau_3) = \exp\{-g(\tau_1) - g(\tau_3) \pm \eta \exp(-\Lambda\tau_2)\} \\ \times [1 - \exp(-\Lambda\tau_1)] [1 - \exp(-\Lambda\tau_3)], \quad (C1)$$

where

$$\eta \equiv \Delta^2 / \Lambda^2. \quad (C2)$$

If we expand Eq. (C1) in a Taylor series in $\exp(-\Lambda\tau_2)$ and substitute back in Eq. (43), we can carry out the τ_2 integration, resulting in

$$\Psi^-(s_1, s_2, s_3) = \sum_{n=0}^{\infty} (-1)^n \frac{\eta^n}{n!} \frac{1}{s_2 + n\Lambda} J_n(s_1) J_n(s_3), \quad (C3)$$

$$J_n(s) = \int_0^{\infty} d\tau [1 - \exp(-\Lambda\tau)]^n \exp[-s\tau - g(\tau)]. \quad (C4)$$

Ψ^+ is also given by Eq. (C3) without the $(-1)^n$ factor. Upon integrating Eq. (C4) by parts, we get a recursion relation

$$\eta\Lambda J_{n+1}(s) = n\Lambda J_n(s) - (s + n\Lambda) J_n(s), \quad n = 1, \dots, \quad (C5)$$

and

$$\xi\Lambda J_1(s) = 1 - s J_0(s). \quad (C6)$$

Equation (C5) can now be used to generate a continued fraction representing of J_0 :

$$J_0(s) = \frac{1}{s + \frac{\Delta^2}{s + \Lambda + \frac{2\Delta^2}{s + 2\Lambda + \frac{3\Delta^2}{s + 3\Lambda + \dots}}}}, \quad (C7)$$

which was used in Eq. (25). Equations (C5)–(C7) allow us to calculate J_n recursively.

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