

Non-Markovian theory of collisional dephasing in near resonance light scattering

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We present a general microscopic theory for near resonance light scattering (RLS) from collisionally perturbed atoms and molecules. The theory is based on the tetradic scattering formalism of Fano and Ben-Reuven. We perform a systematic density expansion and show that the four-time, many-body, dipole correlation functions necessary for the evaluation of the RLS cross section may be rigorously expressed (to lowest order in pressure) in terms of three single-particle, two-time, correlation functions, two of which are associated with the absorption and emission line broadening and the third is a cross correlation function. Our most general expressions are valid for an arbitrary value of the bath correlation time (relative to the broadening), and interpolate smoothly all the way from the static limit of inhomogeneous broadening up to the reverse, the Markovian (homogeneous) limit. The stochastic Gaussian model of Takagahara, Hanamura, and Kubo is obtained also as a special case of the present formulation.

I. INTRODUCTION

In recent years there has been a considerable experimental¹⁻¹² and theoretical¹³⁻²³ activity in the studies of resonance and near resonance light scattering (RLS) from collisionally perturbed atoms and molecules, impurities, and from large "isolated" molecules. In these experiments, done either under time-resolved or frequency-resolved conditions, it is sometimes possible to observe both a direct (coherent) and an indirect (incoherent) component of the scattered light. The former (often referred to as resonance Raman) may be viewed as a direct photon scattering from the initial to the final molecular level and is insensitive to the exact nature of the intermediate molecular levels and their relaxation properties. The latter (often referred to as resonance fluorescence) results from a two-step process of absorption and subsequent emission and is intimately connected to the characteristics of the intermediate molecular levels. The relative intensity of the two components, as well as their temporal or spectral features, may be studied under a variety of experimental conditions (detuning of the exciting wavelength, pressure, temperature, etc.), thus providing a very convenient probe for intramolecular as well as collisional dynamical properties of molecules. RLS techniques often have many advantages (e.g., better sensitivity) over absorption spectroscopy. Saturation behavior of resonant light scattering using intense laser beams²⁴ may also provide useful dynamical information regarding atoms and molecules.

The simplest level scheme for a molecular system undergoing RLS consists of a three-level system coupled to the radiation field and to a bath of other degrees of freedom. The nature of the bath and its interaction with the three-level system depend on the particular experimental situation. Some typical examples are collisional broadening in the gas and liquid phases, impurities and electron-phonon systems, and intramolecular line broadening in large polyatomic molecules. Apart from the broad direct interest in RLS experiments on various systems, these experiments are a prototype for molec-

ular multiphoton processes.²⁵ RLS is a two-photon process and as such provides the simplest nontrivial test case for checking various assumptions and methods used in the theoretical treatment of the latter.

The problem of RLS in the low pressure gas phase was treated in the past by several authors.^{13-15,19,20,23} The existing formulations of, for example, Fiutak and Van Kranendonk,¹³ Omont, Smith, and Cooper,¹⁵ and Huber¹⁴ are all confined either to the impact (Markovian) limit or to the reverse, statistical (static) limit. Takagahara, Hanamura, and Kubo have recently extended the stochastic line shape formalism²⁶ and applied it to RLS. These authors have used several different stochastic models (two-state jump, Gaussian modulation, off diagonal random coupling). These models contribute to our understanding of RLS phenomena, as they are capable of interpolating smoothly from the Markovian to the static limits. Their limitation, however, is that they depend on some stochastic parameters whose exact microscopic nature is not at all clear.

In this paper we present the exact general solution of the RLS problem by collisionally perturbed molecules at low pressures. In Sec. II we define the general model Hamiltonian for RLS including a three-level molecular system and intralevel (dephasing) interactions with a bath of a general nature. We then make use of the tetradic scattering formulation of Fano and Ben-Reuven²⁷⁻²⁹ to derive the formal expressions for the RLS cross section [Eqs. (19)], which are expressed in terms of four-time dipole correlation functions [Eqs. (24)] (similar correlation functions were discussed recently in the context of molecular multiphoton processes).²⁵ In Sec. III we turn to the collisional broadening problem. We carry out a systematic density expansion of the many-body four-time correlation functions (24) and show that they may be expressed exactly (to lowest order in pressure) in terms of three different single-particle two-time dipole correlation functions $g_{aba}(\tau)$, $g_{cbc}(\tau)$, and $g_{abc}(\tau)$ [Eqs. (37)]. These latter quantities thus provide the complete dynamical information required for the evaluation of RLS cross sections to lowest order in the pressure. This is the most important result of the present work since, apart from the density expansion to lowest order, no further dynamical

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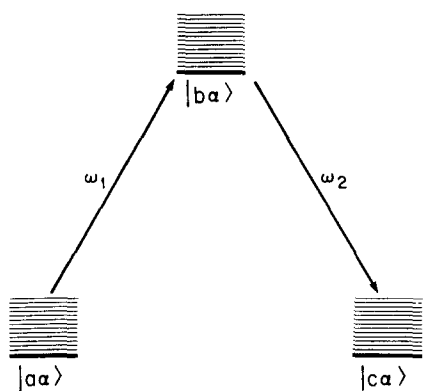


FIG. 1 The molecular level-scheme for resonance light scattering.

approximations are made; our general expressions provide a unified theory for RLS valid all the way from the Markovian to the static limits. We should note further that $g_{a\alpha b\alpha}(\tau)$ and $g_{c\alpha b\alpha}(\tau)$ are the dipole correlation functions associated with the absorption ($a-b$) and emission ($b-c$) line shapes of the three-level system. $g_{a\alpha c\alpha}(\tau)$, however, is a cross correlation function which does not appear in ordinary line shapes and is characteristic of two-photon processes. Finally, in Sec. IV we analyze our general expressions and discuss their behavior in various limits of physical interest. We show how simple assumptions regarding the single-particle correlation functions may lead to the well-known Markovian and static results. The stochastic Gaussian model of Takagahara, Hanamura, and Kubo¹⁷ is also obtained as a special case of our general expressions by a particular choice of $g_{a\alpha b\alpha}(\tau)$, $g_{c\alpha b\alpha}(\tau)$, and $g_{a\alpha c\alpha}(\tau)$.

II. THE RESONANCE LIGHT SCATTERING CROSS SECTION: TETRADIC FORMULATION

We consider a three-level molecular system $|a\rangle$, $|b\rangle$, and $|c\rangle$ (Fig. 1) coupled to other degrees of freedom (the bath). We further assume that the bath is interacting with each level separately but does not cause interlevel couplings (i. e., the bath cannot cause relaxation of population, " T_1 "). Apart from that, we leave the definition of the bath completely open; the model may apply, for example, to any of the physical situations discussed in the introduction.

In addition to the bath, the system is coupled to the radiation field. Since we are interested in weak field phenomena, then only the vacuum state $|\text{vac}\rangle$ and single photon $|\omega\rangle$ states need to be considered. For the sake of RLS experiments involving weak radiation fields, we may further invoke the rotating wave approximation (RWA)³⁰ and consider only the following direct-product states of the system and bath and the radiation field: $|a, \omega_1, \alpha\rangle$, $|b, \text{vac}, \alpha\rangle$, and $|c, \omega_2, \alpha\rangle$. $|a, \omega_1, \alpha\rangle$ denotes the initial molecular state and the incident photon with frequency ω_1 , and the bath in the state $|\alpha\rangle$. $|b, \text{vac}, \alpha\rangle$ denotes the intermediate molecular state $|b\rangle$ with no photon and is near resonant with $|a, \omega_1, \alpha\rangle$; $|c, \omega_2, \alpha\rangle$ is the final molecular state $|c\rangle$ with the scattered photon ω_2 . For simplifying the notation we shall hereafter omit the explicit specification of the radiation field state and denote these states by $|a\alpha\rangle$, $|b\alpha\rangle$, and $|c\alpha\rangle$ with

energies $E_a = \epsilon_a + \omega_1$, $E_b = \epsilon_b$, and $E_c = \epsilon_c + \omega_2$, respectively, where $|a\rangle$ stands for $|a, \omega_1\rangle$, etc., and ϵ_a , ϵ_b , and ϵ_c are the energies of the bare molecular states (without the radiation field).

The total Hamiltonian for the combined system and bath and the radiation field is

$$H = H_s + H_1 + V \equiv H_0 + V, \quad (1)$$

where

$$H_s = |a\rangle \left(E_a - \frac{i}{2} \gamma_a \right) \langle a| + |b\rangle \left(E_b - \frac{i}{2} \gamma_b \right) \langle b| + |c\rangle \left(E_c - \frac{i}{2} \gamma_c \right) \langle c|, \quad (1')$$

$$H_1 = |a\rangle F_a(Q_B) \langle a| + |b\rangle F_b(Q_B) \langle b| + |c\rangle F_c(Q_B) \langle c|, \quad (1'')$$

and

$$V = |a\rangle \mu_{ab}(Q_B) \langle b| + |b\rangle \mu_{ba}(Q_B) \langle a| + |b\rangle \mu_{bc}(Q_B) \langle c| + |c\rangle \mu_{cb}(Q_B) \langle b|. \quad (1''')$$

Here H_s is the zero-order system and field Hamiltonian where E_a , E_b , and E_c are the energies of the system states (dressed to zero order by the field) whereas γ_a^{-1} , γ_b^{-1} , and γ_c^{-1} are their lifetimes (radiative or nonradiative). H_1 describes the bath interacting with the system, and F_a , F_b , and F_c are operators in the bath coordinates Q_B . Finally, μ is the radiation-matter dipole coupling which may also depend on the bath coordinates Q_B . The eigenstates of H_0 are assumed to be known and will be denoted $|a\alpha\rangle$, $|b\beta\rangle$, and $|c\gamma\rangle$, i. e.,

$$F_a(Q_B) |a\alpha\rangle = E_\alpha |a\alpha\rangle, \quad (2a)$$

$$F_b(Q_B) |b\beta\rangle = E_\beta |b\beta\rangle, \quad (2b)$$

$$F_c(Q_B) |c\gamma\rangle = E_\gamma |c\gamma\rangle, \quad (2c)$$

where α , β , and γ are collections of all bath quantum numbers. From (1) and (2) we note that $|a\alpha\rangle$, $|b\beta\rangle$, and $|c\gamma\rangle$ are also eigenstates of H_0 with eigenvalues

$$E_{a\alpha} = E_a + E_\alpha = \epsilon_a + \omega_1 + E_\alpha, \quad (3a)$$

$$E_{b\beta} = E_b + E_\beta = \epsilon_b + E_\beta, \quad (3b)$$

and

$$E_{c\gamma} = E_c + E_\gamma = \epsilon_c + \omega_2 + E_\gamma, \quad (3c)$$

respectively.

The photon scattering cross section will now be evaluated using the tetradic scattering formalism of Fano and Ben-Reuven.²⁷⁻²⁹ This approach is based on formulating scattering theory in terms of density matrices in Liouville space (rather than wave functions in Hilbert space) and is particularly convenient for performing averages over irrelevant degrees of freedom. The tetradic T matrix \mathcal{T} is defined²⁷⁻²⁹ as

$$\mathcal{T}(\omega) = \mathcal{U} + \mathcal{U} \mathcal{G}(\omega) \mathcal{U}, \quad (4)$$

where \mathcal{U} is the tetradic operator corresponding to V , i. e.,

$$\mathcal{U} = [V,] \quad (5)$$

and $\mathcal{G}(\omega)$ is the tetradic Green's operator for the entire system and bath,

$$\mathcal{G}(\omega) \equiv (\omega - L + i\eta)^{-1} = -i \int_0^\infty d\tau \tilde{\mathcal{G}}(\tau) \exp(i\omega\tau - \eta\tau), \quad (6)$$

$$\tilde{\mathcal{G}}(\tau) = \theta(\tau) \exp(-iL\tau), \quad (7)$$

$L(L_1, L_0)$ being the Liouville operators corresponding to $H(H_1, H_0)$, i. e.,

$$L = [H, \] , \quad (8)$$

etc. $\theta(\tau)$ is the Heavyside step function ($\theta = 1$ for $\tau > 0$ and $\theta = 0$ for $\tau < 0$). For the subsequent manipulations we shall define also

$$\mathcal{G}_1(\omega) = (\omega - L_1 + i\eta)^{-1}, \quad (9)$$

and

$$\mathcal{G}_0(\omega) = (\omega - L_0 + i\eta)^{-1}, \quad (10)$$

and their Fourier transforms $\tilde{\mathcal{G}}_1(\tau)$, $\tilde{\mathcal{G}}_0(\tau)$, in analogy with $\tilde{\mathcal{G}}(\tau)$ [Eq. (7)].

The RLS cross section is given by^{28,29,19}

$$\sigma(\omega_1, \omega_2) = \frac{1}{\Phi_a} I(\omega_1, \omega_2), \quad (11)$$

where

$$I(\omega_1, \omega_2) = -i \langle \mathcal{T}(0)_{cc,aa} \rangle \equiv -i \sum_{\alpha\gamma} \langle \langle \mathcal{T}(0)_{cc}^{\gamma\gamma} | \mathcal{A}^{\alpha\alpha} \rangle \rangle P(\alpha). \quad (12)$$

Here Φ_a is the incident photon flux and $\langle \dots \rangle$ denotes a thermal average of a tetradic operator over the bath degrees of freedom (averaging over all possible initial bath states and summing over all final bath states), i. e.,

$$\langle A_{ij,kl} \rangle \equiv \sum_{\alpha\beta} \langle \langle A_{ij}^{\beta\beta} | \mathcal{A}^{\alpha\alpha} \rangle \rangle P(\alpha). \quad (13)$$

$|i\alpha\rangle\langle j\beta|$ is the tetradic state corresponding to $|i\alpha\rangle\langle j\beta|$ and $P(\alpha)$ is the equilibrium distribution of bath states,

$$P(\alpha) = \exp(-E_\alpha/kT) / \text{Tr}[\exp(-F_\alpha/kT)]. \quad (14)$$

We now expand \mathcal{T} to fourth order in \mathcal{V} (which is the lowest order necessary for RLS), resulting in

$$\mathcal{T}(\omega) = \mathcal{V} \mathcal{G}_0(\omega) \mathcal{V} \mathcal{G}_0(\omega) \mathcal{V} \mathcal{G}_0(\omega) \mathcal{V}, \quad (15)$$

which may be recast in the fully time-ordered form

$$\mathcal{T}(\omega) = (-i)^3 \int_0^\infty dt \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \exp(i\omega t) \mathcal{V} \times \tilde{\mathcal{G}}_0(t - \tau_1) \mathcal{V} \tilde{\mathcal{G}}_0(\tau_1 - \tau_2) \mathcal{V} \cdot \tilde{\mathcal{G}}_0(\tau_2) \mathcal{V}, \quad (16)$$

or alternatively,

$$\mathcal{T}(\omega) = (-i)^3 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3$$

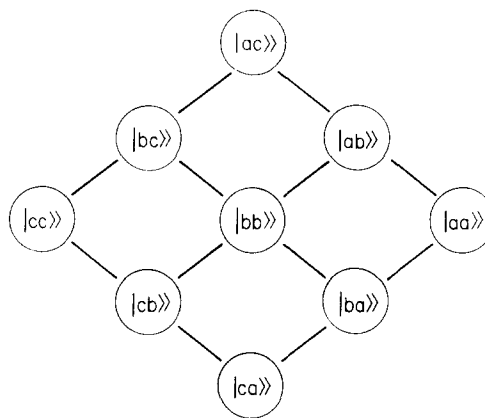


FIG. 2. Liouville-space coupling scheme for resonance light scattering. Note that there are six different pathways to go from $|aa\rangle$ to $|cc\rangle$ in fourth order.

$$\times \exp[i\omega(\tau_1 + \tau_2 + \tau_3)] \cdot \mathcal{V} \tilde{\mathcal{G}}_0(\tau_1) \mathcal{V} \tilde{\mathcal{G}}_0(\tau_2) \mathcal{V} \tilde{\mathcal{G}}_0(\tau_3) \mathcal{V}. \quad (17)$$

Utilizing the form of the radiative coupling \mathcal{V} [Eq. (1'')] and making use of Fig. 2, we notice that there are six pathways in Liouville space to go from $|aa\rangle$ to $|cc\rangle$ in fourth order. However, utilizing the general Liouville conjugation symmetry²⁸

$$\mathcal{G}_{ab,cd}(\omega) = -\mathcal{G}_{ba,dc}^*(-\omega), \quad (18)$$

we see that there are only three independent paths; the contribution of the latter three is simply the complex conjugate of the former. We may thus write, using Eq. (17),

$$I(\omega_1, \omega_2) = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \times [I + II + III] + c. c. \equiv I_1 + I_2 + I_3 + c. c., \quad (19)$$

where

$$I = \exp[-i\omega_{cb}\tau_1 - i\omega_{ab}\tau_3 - \frac{1}{2}\gamma_a\tau_3 - \frac{1}{2}\gamma_b(\tau_1 + 2\tau_2 + \tau_3) - \frac{1}{2}\gamma_c\tau_1] K_I(\tau_1, \tau_2, \tau_3), \quad (19')$$

$$II = \exp[i\omega_{cb}\tau_1 - i\omega_{ab}\tau_3 - \frac{1}{2}\gamma_a\tau_3 - \frac{1}{2}\gamma_b(\tau_1 + 2\tau_2 + \tau_3) - \frac{1}{2}\gamma_c\tau_1] K_{II}(\tau_1, \tau_2, \tau_3), \quad (19'')$$

and

$$III = \exp[i\omega_{cb}\tau_1 - i\omega_{ac}\tau_2 - i\omega_{ab}\tau_3 - \frac{1}{2}\gamma_a(\tau_2 + \tau_3) - \frac{1}{2}\gamma_b(\tau_1 + \tau_3) - \frac{1}{2}\gamma_c(\tau_1 + \tau_2)] K_{III}(\tau_1, \tau_2, \tau_3). \quad (19''')$$

Here

$$K_I(\tau_1, \tau_2, \tau_3) = \sum_{\alpha\beta\gamma} \langle \langle \mathcal{T}_{cc}^{\gamma\gamma} | \mathcal{V}(\tau_1 + \tau_2 + \tau_3) |_{cb}^{\gamma\beta} \rangle \rangle \langle \langle \mathcal{T}_{cb}^{\beta\gamma} | \mathcal{V}(\tau_2 + \tau_3) |_{bb}^{\beta\beta} \rangle \rangle \langle \langle \mathcal{T}_{bb}^{\beta\beta} | \mathcal{V}(\tau_3) |_{ab}^{\alpha\beta} \rangle \rangle \langle \langle \mathcal{V}(0) |_{aa}^{\alpha\alpha} \rangle \rangle P(\alpha), \quad (20a)$$

$$K_{II}(\tau_1, \tau_2, \tau_3) = \sum_{\alpha\beta\gamma} \langle \langle \mathcal{T}_{cc}^{\gamma\gamma} | \mathcal{V}(\tau_1 + \tau_2 + \tau_3) |_{bc}^{\beta\gamma} \rangle \rangle \langle \langle \mathcal{T}_{bc}^{\beta\gamma} | \mathcal{V}(\tau_2 + \tau_3) |_{bb}^{\beta\beta} \rangle \rangle \langle \langle \mathcal{T}_{bb}^{\beta\beta} | \mathcal{V}(\tau_3) |_{ab}^{\alpha\beta} \rangle \rangle \langle \langle \mathcal{V}(0) |_{aa}^{\alpha\alpha} \rangle \rangle P(\alpha), \quad (20b)$$

$$K_{III}(\tau_1, \tau_2, \tau_3) = \sum_{\alpha\beta\gamma} \langle \langle \mathcal{T}_{cc}^{\gamma\gamma} | \mathcal{V}(\tau_1 + \tau_2 + \tau_3) |_{bc}^{\beta\gamma} \rangle \rangle \langle \langle \mathcal{T}_{bc}^{\beta\gamma} | \mathcal{V}(\tau_2 + \tau_3) |_{ac}^{\alpha\gamma} \rangle \rangle \langle \langle \mathcal{T}_{ac}^{\alpha\gamma} | \mathcal{V}(\tau_3) |_{ab}^{\alpha\beta} \rangle \rangle \langle \langle \mathcal{V}(0) |_{aa}^{\alpha\alpha} \rangle \rangle P(\alpha), \quad (20c)$$

and

$$\omega_{ab} = E_a - E_b = \epsilon_a + \omega_1 - \epsilon_b, \quad (21a)$$

$$\omega_{cb} = E_c - E_b = \epsilon_c + \omega_2 - \epsilon_b, \quad (21b)$$

$$\omega_{ac} = \omega_{ab} - \omega_{cb}, \quad (21c)$$

and

$$v(\tau) = \exp(iL_1\tau) v \exp(-iL_1\tau). \quad (22)$$

In the derivation of (20) we have multiplied the integrand in (17) by $\exp[iL_1(\tau_1 + \tau_2 + \tau_3)]$ from the left bearing in mind that $\langle \langle L_1 \rangle \rangle = 0$. Since L_1 is Hermitian (unlike L_0), we could then rearrange (17) to the form (20).

Equations (20) will now be recast in the dyadic (Hilbert space) form using the relation^{28,29}

$$v_{ij,kl} = V_{ik} \delta_{j,l} - V_{jl}^* \delta_{i,k}, \quad (23)$$

i. e.,

$$\begin{aligned} K_{\text{I}}(\tau_1, \tau_2, \tau_3) &= \sum_{\substack{\alpha\beta \\ \beta'\gamma}} \langle c\gamma | V^*(\tau_1 + \tau_2 + \tau_3) | b\beta' \rangle \langle c\gamma | V(\tau_2 + \tau_3) | b\beta' \rangle \langle b\beta' | V(\tau_3) | a\alpha \rangle \langle b\beta | V^*(0) | a\alpha \rangle P(\alpha) \\ &\equiv \langle V_{ab}(0) V_{bc}(\tau_1 + \tau_2 + \tau_3) V_{cb}(\tau_2 + \tau_3) V_{ba}(\tau_3) \rangle, \end{aligned} \quad (24a)$$

$$\begin{aligned} K_{\text{II}}(\tau_1, \tau_2, \tau_3) &= \sum_{\substack{\alpha\beta \\ \beta'\gamma}} \langle c\gamma | V(\tau_1 + \tau_2 + \tau_3) | b\beta' \rangle \langle c\gamma | V^*(\tau_2 + \tau_3) | b\beta' \rangle \langle b\beta' | V(\tau_3) | a\alpha \rangle \langle b\beta | V^*(0) | a\alpha \rangle P(\alpha) \\ &\equiv \langle V_{ab}(0) V_{bc}(\tau_2 + \tau_3) V_{cb}(\tau_1 + \tau_2 + \tau_3) V_{ba}(\tau_3) \rangle, \end{aligned} \quad (24b)$$

and

$$\begin{aligned} K_{\text{III}}(\tau_1, \tau_2, \tau_3) &= \sum_{\substack{\alpha\beta \\ \beta'\gamma}} \langle c\gamma | V(\tau_1 + \tau_2 + \tau_3) | b\beta' \rangle \langle b\beta' | V(\tau_2 + \tau_3) | a\alpha \rangle \langle c\gamma | V^*(\tau_3) | b\beta \rangle \langle b\beta | V^*(0) | a\alpha \rangle P(\alpha) \\ &\equiv \langle V_{ab}(0) V_{bc}(\tau_3) V_{cb}(\tau_1 + \tau_2 + \tau_3) V_{ba}(\tau_2 + \tau_3) \rangle. \end{aligned} \quad (24c)$$

Here,

$$V(t) = \exp(iH_1 t) V \exp(-iH_1 t), \quad (25a)$$

i. e.,

$$V_{ab}(t) = \sum_{\alpha\beta} |a\alpha\rangle \langle a\alpha | V | b\beta \rangle \exp(i\omega_{\alpha\beta} t) \langle b\beta |, \quad (25b)$$

and $V_{bc}(t)$ is defined in an analogous manner.

Equations (19) together with (24) and (25) are the most general expressions for the RLS cross section given in terms of the four-time correlation functions (K_i) of the dipole operator V . Expressions similar to (24) appear also in the theory of multiphoton processes where level $|c\rangle$ corresponds to the absorption of another photon (rather than emission).²⁵ These results hold irrespective of the detailed nature of the bath [i. e., the exact form of the F_a , F_b , and F_c operators in Eq. (1)]. In the next section we shall make a specific application to the low pressure collisional broadening problem where we shall be able to evaluate exactly the correlation functions (24).

III. APPLICATION TO PRESSURE BROADENING—THE DENSITY EXPANSION

We shall now consider the problem of collisional line broadening in RLS by a foreign perturber in the gas phase at low pressure. Following the approach of Jablonski and Baranger,³¹⁻³³ we place our "system" molecule in the center of a macroscopic sphere with volume Ω and assume that the bath consists of N perturber mol-

ecules which do not interact with the radiation field. We further ignore the translational motion (and the Doppler inhomogeneous broadening) of our molecule and the interactions among the bath molecules (which do not contribute to lowest order in pressure). For the sake of convenience we also assume that the dipole operator V [Eq. (1'')] is independent of the bath coordinates (Q_B), i. e., we neglect collision-induced contributions to the light scattering. This assumption, however, is not essential and will be relaxed later. Making use of these assumptions, we have

$$F_i(Q_B) = \sum_{\nu} F_{i\nu}(Q_{B\nu}), \quad i = a, b, c, \quad (26)$$

$$|\xi\rangle = \prod_{\nu} |\xi_{\nu}\rangle, \quad \xi = \alpha, \beta, \gamma, \quad (27)$$

and

$$P(\alpha) = \prod_{\nu} P_{\nu}(\alpha_{\nu}), \quad (28)$$

where ν denotes the ν th bath particle. Utilizing Eqs. (26)–(28), we note that the N -particle four-time correlation functions $K_i(\tau_1, \tau_2, \tau_3)$ [Eq. (24)] are now factorized to a product of N identical factors, i. e.,

$$K_i(\tau_1, \tau_2, \tau_3) = |\mu_{ab}|^2 |\mu_{bc}|^2 k_i^N(\tau_1, \tau_2, \tau_3), \quad i = \text{I, II, III}, \quad (29)$$

where k_i are four-time single-particle correlation functions defined in an analogous manner to K_i [Eqs. (24)], where α , β , β' , and γ denote a single particle state (rather than a macroscopic N particle state) and V_{ab} ,

V_{bc} are replaced by $V_{ab}/\mu_{ab} = |a\rangle\langle b|$ and $V_{bc}/\mu_{bc} = |b\rangle\langle c|$, respectively.

The evaluation of k_i will now be made making use of the fact that Ω is a large parameter so that k_i may be expanded in powers of $1/\Omega$. This expansion [as may be seen from Eq. (29)] corresponds to a density expansion of K_i (in powers of N/Ω). To that end we first note that $F_{i\alpha}$ ($Q_{B\nu}$, $i = a, b, c$ are finite only in a small $Q_{B\nu}$ region of microscopic dimensions. As a result, the bath states corresponding to $|a\alpha\rangle$, $|b\beta\rangle$ and $|c\gamma\rangle$ will be almost identical. Consequently the diagonal matrix elements $\langle a\alpha|V|b\alpha\rangle$ will be close to unity. In fact, it is clear that³¹⁻³³

$$|\langle a\alpha|V|b\alpha\rangle|^2 = 1 - O\left(\frac{1}{\Omega}\right), \quad (30a)$$

so that

$$\sum_{\beta \neq \alpha} |\langle a\alpha|V|b\beta\rangle|^2 = O\left(\frac{1}{\Omega}\right), \quad (30b)$$

and for large Ω the dominant contribution to the four-time correlation functions $k_i(\tau_1, \tau_2, \tau_3)$ will come from the completely diagonal sequence $\alpha = \beta = \beta' = \gamma$, which will be $O(1)$. This contribution, however, has almost no time dependence since $E_\alpha \approx E_\beta \approx E_{\beta'} \approx E_\gamma$ and thus it appears only in $k_i(0, 0, 0)$. The next largest terms will correspond to all possible sequences $\alpha\beta\beta'\gamma$ where the bath state changes twice [single changes do not contribute to (24)]. Since each k_i is a product of four operators, there will be six such terms (corresponding to all possibilities of choosing two terms out of four). All these terms will be $O(1/\Omega)$. We can thus write

$$k_i(\tau_1, \tau_2, \tau_3) = 1 - \frac{1}{\Omega} W_i(\tau_1, \tau_2, \tau_3) + O\left(\frac{1}{\Omega^2}\right), \quad (31)$$

where W_i is $O(1)$. As a result then, in the thermodynamic limit we get

$$K_i(\tau_1, \tau_2, \tau_3) = |\mu_{ab}|^2 |\mu_{bc}|^2 \left(1 - \frac{1}{\Omega} W_i(\tau_1, \tau_2, \tau_3)\right)^N$$

$$\xrightarrow[N/\Omega \text{ finite}]{N \rightarrow \infty, \Omega \rightarrow \infty} |\mu_{ab}|^2 |\mu_{bc}|^2 \exp\left(-\frac{N}{\Omega} W_i(\tau_1, \tau_2, \tau_3)\right), \quad (32)$$

$i = \text{I, II, III}$,

where

$$W_{\text{I}}(\tau_1, \tau_2, \tau_3) = g_{aba}(\tau_3) + g_{abc}^*(\tau_1) + g_{abc}(\tau_1 + \tau_2 + \tau_3) + g_{abc}^*(\tau_2) - g_{abc}(\tau_2 + \tau_3) - g_{abc}^*(\tau_1 + \tau_2), \quad (33a)$$

$$W_{\text{II}}(\tau_1, \tau_2, \tau_3) = g_{aba}(\tau_3) + g_{cbc}(\tau_1) + g_{abc}(\tau_2 + \tau_3) + g_{abc}^*(\tau_1 + \tau_2) - g_{abc}(\tau_1 + \tau_2 + \tau_3) - g_{abc}^*(\tau_2), \quad (33b)$$

and

$$W_{\text{III}}(\tau_1, \tau_2, \tau_3) = g_{abc}(\tau_3) + g_{abc}^*(\tau_1) + g_{aba}(\tau_2 + \tau_3) + g_{cbc}(\tau_1 + \tau_2) - g_{abc}(\tau_1 + \tau_2 + \tau_3) - g_{abc}^*(-\tau_2). \quad (33c)$$

In Eqs. (32) and (33) we have expressed the four-time correlation functions (24) in terms of the three two-time correlation functions g_{aba} , g_{cbc} , and g_{abc} . The former two are associated with the line broadening of

the ab and bc transitions [see discussion of Eqs. (38)], whereas g_{abc} is a cross correlation function associated with the two-photon Raman process, i. e.,

$$g_{abc}(\tau) = \frac{\Omega}{\mu_{ab}\mu_{bc}} \sum_{\alpha\beta} P(\alpha) V_{ab}^{\alpha\beta} V_{bc}^{\beta\alpha} [1 - \exp(i\omega_{\beta\alpha}\tau)], \quad (34a)$$

$$g_{aba}(\tau) = \frac{\Omega}{|\mu_{ab}|^2} \sum_{\alpha\beta} P(\alpha) |V_{ab}^{\alpha\beta}|^2 [1 - \exp(i\omega_{\beta\alpha}\tau)], \quad (34b)$$

$$g_{cbc}(\tau) = \frac{\Omega}{|\mu_{bc}|^2} \sum_{\alpha\beta} P(\alpha) |V_{cb}^{\alpha\beta}|^2 [1 - \exp(i\omega_{\beta\alpha}\tau)]. \quad (34c)$$

We should bear in mind that the Ω factor in Eqs. (34) simply cancels the $1/\Omega$ dependence of the sum so that $g(\tau) = O(1)$.

In the derivation of Eqs. (33) and (34) we have made use of the relations

$$\langle a\alpha|V(\tau)|b\beta\rangle = -\langle a\beta|V(\tau)|b\alpha\rangle^* + O\left(\frac{1}{\sqrt{\Omega}}\right), \quad (35a)$$

$$\langle b\beta|V(\tau)|c\gamma\rangle = -\langle b\gamma|V(\tau)|c\beta\rangle^* + O\left(\frac{1}{\sqrt{\Omega}}\right), \quad (35b)$$

and

$$g_{abc}(\tau) = g_{cba}^*(-\tau). \quad (36)$$

Equation (35) is obtained by expanding $|b\alpha\rangle$ and $|b\beta\rangle$ around $|a\alpha\rangle$ and $|a\beta\rangle$, respectively, using $F_a - F_b$ as a perturbation.

The correlation functions (34) are expressed simply in terms of the Franck-Condon factors V_{ab} , V_{bc} within our assumption that the dipole operator ($1'''$) is independent of the position of the perturber. If we relax this assumption and allow the dipole to vary with Q_B , then (up to higher order terms in N/Ω) we should simply replace (34) by

$$g_{abc}(\tau) = \Omega [1 - \langle V_{ab}(0)V_{bc}(\tau) \rangle / \langle V_{ab}(0)V_{bc}(0) \rangle], \quad (37a)$$

$$g_{aba}(\tau) = \Omega [1 - \langle V_{ab}(0)V_{ba}(\tau) \rangle / \langle V_{ab}(0)V_{ba}(0) \rangle], \quad (37b)$$

and

$$g_{cbc}(\tau) = \Omega [1 - \langle V_{cb}(0)V_{bc}(\tau) \rangle / \langle V_{cb}(0)V_{bc}(0) \rangle], \quad (37c)$$

where $V(\tau)$ are given by Eq. (25b).

IV. DISCUSSION

The main result of the present paper is that the four-time N -particle dipole correlation functions appearing in the general expressions for the RLS cross section [Eqs. (24)] may be *rigorously* expressed (to lowest order in N/Ω) in terms of the three two-time single-particle correlation functions $g_{aba}(\tau)$, $g_{cbc}(\tau)$, and $g_{abc}(\tau)$ [Eqs. (37)]. The former two are associated with the spectral broadening of the line shapes corresponding to the ab and bc transitions [$S_{ab}(\omega_1)$ and $S_{bc}(\omega_2)$, respectively],²⁶ i. e.,

$$S_{ab}(\omega_1) \propto \text{Re} \int_0^\infty d\tau \exp(i\omega_{ab}\tau) \exp\left(-\frac{N}{\Omega} g_{aba}(\tau)\right), \quad (38a)$$

$$S_{bc}(\omega_2) \propto \text{Re} \int_0^\infty d\tau \exp(i\omega_{bc}\tau) \exp\left(-\frac{N}{\Omega} g_{cbc}(\tau)\right). \quad (38b)$$

However, $g_{abc}(\tau)$ is a *cross-correlation* function characteristic of the two-photon RLS process and does not

appear in ordinary line shape formulations.²⁶ We have thus reduced the complete molecular information relevant for RLS and expressed it in terms of these three simple correlation functions. The evaluation of $g_{aba}(\tau)$ and $g_{cbc}(\tau)$ may be achieved by one of the many standard methods developed for ordinary line shapes.^{28, 31-34} The quantum-mechanical evaluation of $g_{abc}(\tau)$ (34a) is straightforward. However, the application of classical or semiclassical techniques toward its evaluation is not so obvious as in the case of $g_{aba}(\tau)$ and $g_{cbc}(\tau)$. We should also note that if states $|a\rangle$ and $|c\rangle$ have similar interactions with the bath ($F_a = F_c$), then all three correlation functions become identical. Only when $F_a \neq F_c$ may we single out the contribution of the cross-correlation function $g_{abc}(\tau)$.

In order to gain further insight regarding the behavior of the RLS cross section and make the connection with previous works, we shall consider now several limiting cases.

A. The stochastic Gaussian model of Takagahara, Hanamura, and Kubo

Equations (24), (32), and (33) reduce to the expressions of Takagahara, Hanamura, and Kubo¹⁷ for the stochastic Gaussian model of frequency modulation if we invoke the following assumptions:

(a) Levels $|a\rangle$ and $|c\rangle$ are similar and have practically the same interaction with the bath, i. e.,

$$F_a = F_c \neq F_b. \quad (39)$$

(This is often the case when the two molecular levels $|a\rangle$ and $|c\rangle$ belong to the same electronic state whereas $|b\rangle$ is electronically excited.) As a result of (39) we may express the RLS cross section in terms of a single correlation function

$$g(\tau) \equiv g_{abc}(\tau) = g_{aba}(\tau) = g_{cbc}(\tau); \quad (40)$$

$$(b) \gamma_a = \gamma_c = 0; \quad (41)$$

(c) $g(\tau)$ is replaced by the dipole correlation function of an oscillator whose frequency undergoes a stochastic Gaussian process. This correlation function is well known from the theory of Brownian motion³⁵ and ordinary line shapes,²⁶ i. e.,

$$g(\tau) = \Omega \left[1 - \exp\left(-\frac{\Omega_0}{\Omega} \frac{\Delta_0^2}{\Gamma^2} [\exp(-\Gamma\tau) - 1 + \Gamma\tau]\right) \right], \quad (42)$$

where Δ_0 is the frequency modulation amplitude, Γ^{-1} is its correlation time, and Ω_0 is a microscopic volume (say the volume of a single molecule).

In the thermodynamic limit ($\Omega \rightarrow \infty$) we may expand the exponential (42) to lowest order in $1/\Omega$, resulting in

$$g(\tau) \approx \Omega_0 \frac{\Delta_0^2}{\Gamma^2} [\exp(-\Gamma\tau) - 1 + \Gamma\tau]. \quad (43)$$

The expansion (43) is justified since in the thermodynamic limit the contribution of each perturber to the broadening is very small [$O(1/\Omega)$]. Utilizing the definition

$$\Delta^2 = \Delta_0^2 N \Omega_0 / \Omega, \quad (44)$$

we get

$$\begin{aligned} \frac{N}{\Omega} W_I(\tau_1, \tau_2, \tau_3) &= \frac{\Delta^2}{\Gamma^2} \{ \exp(-\Gamma\tau_1) + \Gamma\tau_1 - 1 + \exp(-\Gamma\tau_3) \\ &+ \Gamma\tau_3 - 1 + \exp(-\Gamma\tau_2) [1 - \exp(-\Gamma\tau_1)] \\ &\times [1 - \exp(-\Gamma\tau_3)] \}. \end{aligned} \quad (45a)$$

$$\begin{aligned} \frac{N}{\Omega} W_{II}(\tau_1, \tau_2, \tau_3) &= \frac{N}{\Omega} W_{III}(\tau_1, \tau_2, \tau_3) \\ &= \frac{\Delta^2}{\Gamma^2} \{ \exp(-\Gamma\tau_1) - 1 + \Gamma\tau_1 + \exp(-\Gamma\tau_3) - 1 + \Gamma\tau_3 \\ &- \exp(-\Gamma\tau_2) [1 - \exp(-\Gamma\tau_1)] [1 - \exp(-\Gamma\tau_3)] \}, \end{aligned} \quad (45b)$$

which is equivalent to the results of Takagahara, Hanamura, and Kubo.¹⁷

B. The impact (Markovian, motional narrowing) limit

Let us assume that the correlation functions $g(\tau)$ are linear in τ ³¹⁻³³ (this implies that the RLS process is insensitive to their short time behavior which goes as $\sim \tau^2$).²⁶ We thus write

$$g_{aba}(\tau) = (\hat{\Gamma}_{ab} - i\Delta_{ab})\tau, \quad (46a)$$

$$g_{cbc}(\tau) = (\hat{\Gamma}_{cb} - i\Delta_{cb})\tau, \quad (46b)$$

$$g_{abc}(\tau) = (\hat{\Gamma}_{abc} - i\Delta_{abc})\tau. \quad (46c)$$

Substitution of Eqs. (46) in (33) results in

$$W_I(\tau_1, \tau_2, \tau_3) = (\hat{\Gamma}_{ab} - i\Delta_{ab})\tau_3 + [\hat{\Gamma}_{bc} + i(\Delta_{cb} - 2\Delta_{abc})]\tau_1, \quad (47a)$$

$$W_{II}(\tau_1, \tau_2, \tau_3) = (\hat{\Gamma}_{ab} - i\Delta_{ab})\tau_3 + [\hat{\Gamma}_{cb} - i(\Delta_{cb} - 2\Delta_{abc})]\tau_1, \quad (47b)$$

and

$$\begin{aligned} W_{III}(\tau_1, \tau_2, \tau_3) &= (\hat{\Gamma}_{ab} - i\Delta_{ab})\tau_3 + [\hat{\Gamma}_{cb} - i(\Delta_{cb} - 2\Delta_{abc})]\tau_1 \\ &+ [\hat{\Gamma}_{ab} + \hat{\Gamma}_{cb} - 2\hat{\Gamma}_{abc} - i(\Delta_{ab} + \Delta_{cb} - 2\Delta_{abc})]\tau_2. \end{aligned} \quad (47c)$$

Using Eqs. (47) we note that each K_i term [Eq. (32)] may now be factorized in the form

$$K_i(\tau_1, \tau_2, \tau_3) = K_{i_1}(\tau_1)K_{i_2}(\tau_2)K_{i_3}(\tau_3), \quad i = I, II, III, \quad (48)$$

so that each triple integral appearing in the RLS cross section (19) is factorized into a product of three single integrals in τ_1 , τ_2 , and τ_3 . For the sake of simplicity and comparison with previous results we shall now assume again that levels $|a\rangle$ and $|c\rangle$ have similar interactions with the bath, i. e., that Eq. (39) holds and we have

$$\hat{\Gamma}_{ab} = \hat{\Gamma}_{cb} = \hat{\Gamma}_{abc} = \hat{\Gamma}, \quad (49a)$$

and

$$\Delta_{ab} = \Delta_{cb} = \Delta_{abc} = \Delta'. \quad (49b)$$

Furthermore, we assume that γ_a and γ_c are much smaller than γ_b and $\hat{\Gamma}$ and we set

$$\gamma_a = \gamma_c = 0. \quad (49c)$$

Substitution of (47) and (49) into (33) and (19) results in

$$\begin{aligned} I_1(\omega_1, \omega_2) &\equiv \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 I \\ &= - \frac{|\mu_{ab}\mu_{bc}|^2}{\gamma_b(\omega'_{cb} - i\Gamma')(\omega'_{ab} - i\Gamma')}, \end{aligned} \quad (50a)$$

$$I_2(\omega_1, \omega_2) \equiv \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \text{ II} \\ = \frac{|\mu_{ab}\mu_{bc}|^2}{\gamma_b(\omega'_{cb} + i\Gamma')(\omega'_{ab} - i\Gamma')}, \quad (50b)$$

and

$$I_3(\omega_1, \omega_2) \equiv \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \text{ III} \\ = \frac{i|\mu_{ab}\mu_{bc}|^2}{\omega'_{ac}(-\omega'_{cb} - i\Gamma')(\omega'_{ab} - i\Gamma')}, \quad (50c)$$

where

$$\Gamma' = \frac{1}{2}\gamma_b + \hat{\Gamma}, \quad (51a)$$

$$\omega'_{ab} = \omega_{ab} - \Delta', \quad (51b)$$

$$\omega'_{cb} = \omega_{cb} - \Delta', \quad (51c)$$

$$\omega'_{ac} = \omega_{ac}. \quad (51d)$$

Substitution of (50) in (19) finally results in

$$I(\omega_1, \omega_2) = \frac{|\mu_{ab}\mu_{bc}|^2}{(\epsilon_a + \omega_1 - \epsilon_b - \Delta')^2 + \Gamma'^2} \left\{ 2\pi\delta(\epsilon_a + \omega_1 - \epsilon_c - \omega_2) \right. \\ \left. + \frac{4\hat{\Gamma}}{\gamma_b} \frac{\Gamma'}{(\epsilon_b - \epsilon_c - \omega_2 + \Delta')^2 + \Gamma'^2} \right\}. \quad (52)$$

This is the well-known result derived in the past by several authors.^{14,15,5,9,20} It may also be obtained as a limiting case of the stochastic Gaussian model.¹⁷ If we assume

$$\Gamma \gg \Delta \quad (53)$$

in Eqs. (45), we recover Eq. (52) with

$$\hat{\Gamma} = \Delta^2/\Gamma \quad (54a)$$

and

$$\Delta' = 0. \quad (54b)$$

The emission spectrum in the impact limit thus contains two components, a direct (Raman) scattering and a fluorescence (redistribution) term [the first and the second terms in Eq. (52), respectively]. The Raman component is not broadened in this case due to our assumptions (49) that the lifetimes of $|a\rangle$ and $|c\rangle$ are long and that they interact similarly with the bath so that the bath cannot dephase the $a-c$ transition. There will be a broadening, however, of the Raman component if we relax assumption (49) and use the more general relations (47). We further note that the relative area of the incoherent component [the second term in (52)] is proportional to $\hat{\Gamma}/\gamma_b$ so that it is proportional to the pure dephasing rate of the ab and bc transitions ($\hat{\Gamma}$) and to the lifetime γ_b^{-1} of the intermediate level.

Szöke, Carlsten, and Raymer¹¹ (SCR) have recently studied the RLS from strontium vapor in argon. They were able to detune the excitation wavelength up to 1000 cm^{-1} off resonance both above and below the atomic transition. The relative magnitude of the coherent and incoherent components was found¹¹ to be strongly asymmetric with respect to the sign of the detuning [i. e., it depends on the sign of $(\epsilon_a + \omega_1 - \epsilon_b - \Delta')$]. This is in contrast to the Markovian expression (52). SCR then

made a phenomenological assumption that Eq. (52) should be modified in the non-Markovian limit by replacing the Lorentzian corresponding to incoherent scattering by the emission line shape $S_{bc}(\omega_2)$ and taking $\hat{\Gamma}(\omega)$ to be a frequency dependent. The assumption of SCR is equivalent to solving for the tetradic T matrix (12) by invoking the separation approximation^{19,20,23} which amounts to setting

$$\langle \mathcal{T}(0) \rangle = \langle \psi \mathcal{G}_0(0) \psi \mathcal{G}_0(0) \psi \mathcal{G}_0(0) \psi \rangle \\ \equiv \psi \langle \mathcal{G}_0(0) \rangle \psi \langle \mathcal{G}_0(0) \rangle \psi \langle \mathcal{G}_0(0) \rangle \psi, \quad (55)$$

where each $\langle \mathcal{G}_0(0) \rangle$ is an ensemble-averaged reduced molecular propagator defined using an appropriate projection operator. Equation (55) is formally equivalent to the factorization (48). Using our general expressions [(32), (33)], we note that the separation assumption [(48) or (55)] is exact in the Markovian limit [$g(\tau)$ linear, Eq. (46)]. However, once this is not the case, the integrand in (19) is no longer factorized in terms of τ_1 , τ_2 , and τ_3 . In fact, we shall see in the next section that in the static limit $\tau_1 + \tau_3$, $\tau_1 - \tau_3$ should be used as the natural times within the integrations (19). It is thus formally inconsistent to invoke the separation approximation far from the Markovian limit as was done in Ref. 23.

C. The statistical (static) limit

If the collisions are slow (duration of a collision is large compared with the inverse line broadening) it may be sufficient to consider the short time behavior of $g(\tau)$.^{14,26,28} We thus set

$$g(\tau) \equiv g_{aba}(\tau) = g_{cbc}(\tau) = g_{abc}(\tau) = \frac{\Delta^2}{2} \tau^2. \quad (56)$$

Upon substitution of (56) into (33) we get

$$W_{\text{I}}(\tau_1, \tau_2, \tau_3) = \frac{\Delta^2}{2} (\tau_1 + \tau_3)^2, \quad (57a)$$

and

$$W_{\text{II}}(\tau_1, \tau_2, \tau_3) = W_{\text{III}}(\tau_1, \tau_2, \tau_3) = \frac{\Delta^2}{2} (\tau_1 - \tau_3)^2. \quad (57b)$$

In this case (unlike the Markovian limit) the integrals (19) no longer factorize in τ_1 and τ_3 . Instead the natural variables for the integrations will now be $x = \tau_1 + \tau_3$; $y = \tau_1 - \tau_3$ and τ_2 . Upon changing variables and performing two of the integrations we get

$$I_1(\omega_1, \omega_2) = \frac{2}{i\gamma_b(\omega_{cb} - \omega_{ab})} \int_0^\infty dx \exp(-\gamma_b x - \frac{1}{2}\Delta^2 x^2) \\ \times [\exp(i\omega_{cb} x) - \exp(i\omega_{ab} x)], \quad (58)$$

and

$$I_2(\omega_1, \omega_2) + I_3(\omega_1, \omega_2) = \frac{2}{i\gamma_b(\omega_{ab} - \omega_{cb})} \\ \times \int_0^\infty dy \exp(-\gamma_b y - \frac{1}{2}\Delta^2 y^2) \\ \times [\exp(-i\omega_{ab} y) + \exp(i\omega_{cb} y)], \quad (59)$$

which finally yields

$$\begin{aligned}
 I(\omega_1, \omega_2) &= I_1 + I_2 + I_3 + c.c. \\
 &= \frac{8\pi}{\gamma_b} \left(\int_0^\infty dy \exp(-\gamma_b y - \frac{1}{2}\Delta^2 y^2) \right. \\
 &\quad \left. \times \cos \omega_{ab} y \right) \delta(\omega_{cb} - \omega_{ab}). \quad (60)
 \end{aligned}$$

In this limit the bath does not change its state during the photon scattering process and the emission spectrum (60) contains only the Raman (direct) term whose absolute intensity is influenced by the static (inhomogeneous) broadening of the bath. This result may also be obtained from the stochastic Gaussian model [Eqs. (45)] in the limit where

$$\Delta \gg \Gamma, \quad (61)$$

i. e., the frequency-modulation amplitude is large compared with the inverse correlation time (i. e., duration of a collision).

D. Additional inhomogeneous broadening

The effect of the Doppler inhomogeneous broadening (or any other inhomogeneous broadening mechanism) may be easily incorporated by convoluting the general expression (19) with the distribution of molecular frequencies ω_{ab} and ω_{bc} . This will affect the line shapes of the two components but will not affect their relative intensity. The absolute integrated ratio of the two components provides us thus with a tool for measuring dynamical information which may be very hard to get directly from the line shapes. This may be particularly useful in large molecules¹² and in condensed phases.^{9c} In the case where levels $|a\rangle$ and $|c\rangle$ interact similarly with the bath then the Raman component will remain narrow (ω_{ac} unaffected by inhomogeneous broadening) and only the fluorescence term will be broadened further by the inhomogeneities.

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