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Nonimpact theory of resonance Raman line shapes in strong radiation fields

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We develop an expansion for the resonance Raman line shape of a three-level system $|a\rangle$, $|b\rangle$, and $|c\rangle$ in an arbitrary strong radiation field, being perturbed by dephasing collisions with foreign gas particles. The microscopic information relevant to the line broadening is expresssed in terms of a hierarchy of n-time correlation functions of the transition dipole operator ($n=2,4,6,\ldots$). To lowest order ($n=2$) the spectrum is expressed in terms of the three ordinary line-shape functions corresponding to the *ab*, *bc*, and *ac* transitions. The present theory is not restricted to the impact limit and, depending on the collision time scale, may yield very different results from the well-known impact spectra. Explicit calculations of the predicted spectra are presented for a model system.

I. INTRODUCTION

In this work we extend the methods used in Ref. 1 to treat resonance Raman scattering (RRS) of arbitrarily strong coherent radiation from an atomic (molecular) system undergoing collisions with structureless perturbers (foreign gas broadening). The term RRS is used for the case in which the final state of the atom (after the scattering of radiation) is different from the initial one. If the initial and final atomic states are the same, the process is commonly referred to as resonance fluorescence (RF). In the presence of dephasing collisions the two processes exhibit similar features in the weak-field case,[1-10] i.e., both spectra have a two-peak structure due to a coherent component (Raman in RRS, Rayleigh in RF) and an incoherent one (redistribution, hot luminescence). In the strong-field case, the collisionally broadened RF spectrum develops a third peak reflecting the fact that a coherent description of RF involves transitions between the states of a four-level system[11-20] (in the dressed-atom picture) while RRS is always confined to a three-level system.[16,17] In addition to the fundamental interest in the study of radiation-matter interactions, RRS spectra have also some practical implications in view of the recent work on optically pumped electronic transition lasers (OPEL).[21,22] In the OPEL, a pump laser is tuned close to resonance with an electronic transition in a diatomic molecule (I_2, Na_2, S_2, etc.) and lasing occurs on RRS-type transitions to excited vibrational levels of the electronic ground state. Foreign gas broadening plays a particularly important role in the case of alkali dimer OPEL (since the presence of foreign perturbers is necessary for the operation of the heat pipe). For this reason and since the RRS problem is simpler (strong field RRS is a three-level problem whereas strong field RF is a four-level problem), we shall concentrate here on the derivation of the RRS spectrum. The extension to the RF case can be carried out using the methods of this work.[1,10,17]

The purpose of this work is to establish a unified framework for the treatment of RRS spectra, valid for arbitrary detunings from resonance (both of the incident and the scattered radiation field modes) and for arbitrary intensities of the incident radiation. The microscopic information content of RRS spectra is shown to increase with the incident

laser intensity (the contribution of higher-order dipole correlation functions becomes more prominent at higher intensities). In Sec. II we present the Hamiltonian for the atom plus bath plus field system and introduce the level (T_1) relaxation matrix for a closed three-level system. In Sec. III we give the expression for the non-Markovian RRS line shape, valid for arbitrary field strengths. The derivation is given in Appendix A. The line shape is then expanded in powers of the coupling coefficient associated with the incident radiation. A quasi-Markovian spectrum is obtained (see Appendix B for details of the derivation) by retaining the contributions due to two-time correlation functions only, thus generalizing the impact limit expressions.[17] The results are then discussed in Sec. IV where we also present some numerical calculations for a model system.

II. MODEL HAMILTONIAN

Consider a three-level system ($|a\rangle, |b\rangle, |c\rangle$) interacting with a bath of foreign perturbers, with a strong, single-mode radiation field (laser frequency ω_L) and with a scattered radiation field mode (frequency ω_S) (Fig. 1). We assume that the interlevel spacings are large compared to all the other parameters in the problem. Therefore, both collision-induced initial (and final) correlations and deviations from the rotating-wave approximation are neglected in the following. In addition, we assume that the perturbers have only diagonal (dephasing) interactions with the system; no relaxation of population (T_1) is induced by the collisions. The total Hamiltonian for the system plus bath plus both radiation field modes is

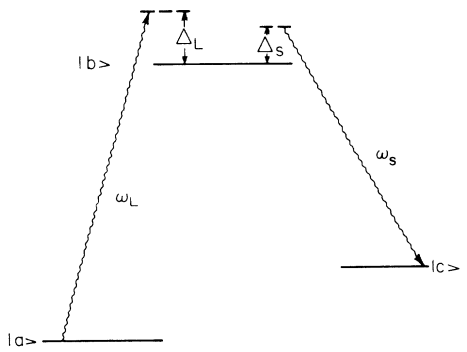

FIG. 1. RRS in the three-level ($|a\rangle, |b\rangle, |c\rangle$) system. The laser and the scattered frequencies are ω_L and ω_S, respectively. The corresponding frequency detunings are denoted by Δ_L and Δ_S.

$$H = H_0 + V , \tag{1}$$

where

$$H_0 = |a\rangle[\Delta_L + H_a(Q_B)]\langle a| + |b\rangle H_b(Q_B)\langle b| + |c\rangle[\Delta_S + H_c(Q_B)]\langle c| . \tag{2}$$

The Hamiltonians $H_a(Q_B)$, $H_b(Q_B)$, and $H_c(Q_B)$ contain the bath degrees of freedom (including the bath-system couplings). The detunings from the corresponding transitions (see Fig. 1) are

$$\Delta_L = \omega_L - (E_b - E_a) \tag{3}$$

and

$$\Delta_S = \omega_S - (E_b - E_c) . \tag{4}$$

The system-radiation coupling can be separated into two parts:

$$V = V_L + V_S , \tag{5}$$

Here, the dipole interaction with the laser field is given by

$$V_L = \mu_L(|a\rangle\langle b| + |b\rangle\langle a|) , \tag{6}$$

and the interaction with the scattered (detected) photons is

$$V_S = \mu_S(|b\rangle\langle c| + |c\rangle\langle b|) , \tag{7}$$

μ_L being the Rabi frequency associated with the laser transition ($a \leftrightarrow b$ transition dipole moment times the laser field amplitude), and μ_S is the coupling coefficient for the scattered mode [the $b \leftrightarrow c$ transition dipole moment times the scattered field amplitude $(\omega_S/2\Omega)^{1/2}$, where Ω is the normalization volume].

In order to specify the system-bath interaction, we take the system particle to be stationary in a macroscopic spherical box of volume Ω, together with N perturbers. Furthermore, we make the assumption that the perturbers do not interact with the radiation field or with each other, so that the Hamiltonians H_a, H_b, and H_c are additive in single perturber contributions, i.e.,

$$H_i(Q_B) = \sum_\nu \bar{H}_{i\nu}(Q_{B_\nu}) \quad (i = a,b,c) \tag{8}$$

with

$$\bar{H}_{i\nu}(Q_{B_\nu}) = -\frac{1}{2M_\nu}\frac{\partial^2}{\partial^2 Q_{B_\nu}} + V_i(Q_{B_\nu}) . \tag{9}$$

Here, $V_i(Q_{B_\nu})$ are the adiabatic potentials for interaction of the νth perturber coordinate Q_{B_ν} with

the system in state $|i\rangle$ (nonadiabatic contributions that can cause transitions between the levels of the system, have been neglected).

The eigenstates of H_a, H_b, and H_c are denoted $|a\alpha\rangle$, $|b\beta\rangle$, and $|c\gamma\rangle$ with eigenvalues E_α, E_β, and E_γ, respectively. Since the above Hamiltonians are separable in the perturber coordinates, their eigenstates are products of single-particle states,

$$|a\alpha\rangle = |a\rangle \prod_\nu |\alpha_\nu\rangle \ , \tag{10a}$$

$$|b\beta\rangle = |b\rangle \prod_\nu |\beta_\nu\rangle \ , \tag{10b}$$

$$|c\gamma\rangle = |c\rangle \prod_\nu |\gamma_\nu\rangle \ , \tag{10c}$$

and the eigenvalues satisfy (Fig. 2)

$$E_\alpha = \sum_\nu E_{\alpha_\nu} \ , \tag{11a}$$

$$E_\beta = \sum_\nu E_{\beta_\nu} \ , \tag{11b}$$

and

$$E_\gamma = \sum_\nu E_{\gamma_\nu} \ . \tag{11c}$$

A box normalization is adopted for the eigenstates, so that

$$\langle \alpha_\nu | \alpha'_\nu \rangle = \delta_{\alpha\alpha'} \ , \tag{12a}$$

$$\langle \beta_\nu | \beta'_\nu \rangle = \delta_{\beta\beta'} \ , \tag{12b}$$

and

$$\langle \gamma_\nu | \gamma'_\nu \rangle = \delta_{\gamma\gamma'} \ . \tag{12c}$$

In addition to the Hamiltonian in Eq. (1) we postulate the existence of an independent T_1 relaxation mechanism (due to spontaneous emission or due to a coupling with another bath with a short correlation time) so that the system can reach a steady state in the presence of radiation. This is necessary for the definition of a spectral line shape in a strong field.

The time evolution of the entire (system plus bath plus laser and scattered field modes) density matrix ρ is given by the Liouville equation

$$\frac{d\rho}{dt} = -iL\rho \ , \tag{13}$$

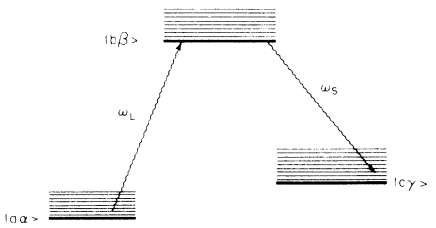

FIG. 2. Energy diagram for the system plus bath states. To each state of the system ($|a\rangle$, $|b\rangle$, $|c\rangle$) corresponds an appropriate manifold of bath eigenstates ($|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$, respectively).

where

$$L = [H, \ ] + \tilde{L} \tag{14}$$

is the Liouville operator. Here $\tilde{L}$ is the T_1 relaxation matrix. We assume that the three-level system is closed under relaxation which proceeds only downwards on the energy scale,[23] i.e., $\tilde{L}$ is a 3×3 matrix in the space of level populations,

$$\tilde{L} = -i \begin{bmatrix} \gamma_b & 0 & 0 \\ -\gamma_{cb} & \gamma_c & 0 \\ -\gamma_{ab} & -\gamma_c & 0 \end{bmatrix} , \tag{15}$$

where the rows and columns are labeled in decreasing order on the energy scale (b,c,a).

The level (T_1) relaxation rates for the levels $|b\rangle$ and $|c\rangle$ are given by γ_b and γ_c, respectively, and we assumed $\gamma_a = 0$ ($|a\rangle$ being the ground state of the system). The $b\rightarrow c$ and $b\rightarrow a$ cross-relaxation rates γ_{cb} and γ_{ab} satisfy

$$\gamma_{cb} + \gamma_{ab} = \gamma_b \ . \tag{16}$$

We assume that initially (at $t\rightarrow -\infty$) the bath and the system are uncorrelated,[24] i.e.,

$$\rho(-\infty) = \rho_B^0 \rho_S^0 \ , \tag{17}$$

where

$$\rho_S^0 = |a\rangle\langle a| \ , \tag{18}$$

and the bath is a canonical equilibrium

$$\rho_B^0 = \exp(-H_a/kT)/\mathrm{Tr}_B \exp(-H_a/kT) \ , \tag{19}$$

Tr_B being the trace over the bath degrees of freedom.

III. STRONG-FIELD RRS LINE SHAPE

We have derived an expansion for the RRS line shape in a strong radiation field using the tetradic scattering formalism.[25–29] The present expansion is an extension and application of the methods developed recent-

ly for the studies of relaxation in multiphoton processes.[10,29–32] The derivation is quite lengthy and requires the introduction of the tetradic notation as well as some auxiliary quantities which do not show up in the final expressions. For the sake of clarity in the presentation we have therefore carried all these manipulations in detail in Appendix A. We shall discuss here the nature of the expansion and present the final results. Our *exact* expansion for the RRS line shape $I(\Delta_L,\Delta_S)$ for the three-level model system of Sec. II, in an arbitrarily strong pump field has the following form:

$$I(\Delta_L,\Delta_S)=\mu_S^2\mu_L^2\hat{I}(\Delta_L,\Delta_S)\ , \tag{20a}$$

where

$$\hat{I}(\Delta_L,\Delta_S)=\frac{1}{1-\frac{2}{\gamma_b'}\chi_1(\Delta_L)}\left\{\chi_6(\Delta_L,\Delta_S)-\frac{1}{\gamma_b}\chi_1(\Delta_L)[\chi_6(\Delta_L,\Delta_S)+\chi_7(\Delta_L,\Delta_S)]\right.$$
$$+\mathrm{Im}\left[\frac{\chi_3(\Delta_L,\Delta_S)}{[f_{ac}(\Delta_L-\Delta_S)]^{-1}-\chi_2(\Delta_L,\Delta_S)}\left[\chi_4(\Delta_L,\Delta_S)-\frac{1}{\gamma_b}\chi_1(\Delta_L)\right.\right.$$
$$\left.\left.\left.\times[\chi_4(\Delta_L,\Delta_S)+\chi_5(\Delta_L,\Delta_S)]\right]\right]\right\} \tag{20b}$$

with

$$\gamma_b'=\gamma_b\left[1+\frac{\gamma_{cb}}{2\gamma_c}\right]^{-1}\ , \tag{21}$$

and $f_{ac}(\Delta_L-\Delta_S)$ is defined in Eq. (24) (with a change of indices).

The functions χ_i $(i=1,\ldots,7)$ contain the interaction with the external field to an arbitrary order (all orders in μ_L). The functions χ_1 and χ_2 are of zeroth order in μ_S, the functions χ_3, χ_4, and χ_5 are of first order in μ_S, and χ_6 and χ_7 are of second order in μ_S (the line shape is proportional to the scattered intensity, i.e., to μ_S^2). Hence, they can be expanded in powers of μ_L^2:

$$\chi_i=\mu_L^2\chi_i^{(2)}+\mu_L^4\chi_i^{(4)}+\cdots\quad(i=1,2) \tag{22a}$$

$$\chi_j=\mu_S\mu_L\chi_j^{(2)}+\mu_S\mu_L^3\chi_j^{(4)}+\cdots\quad(j=3,4,5) \tag{22b}$$

and

$$\chi_k=\mu_S^2\chi_k^{(2)}+\mu_S^2\mu_L^2\chi_k^{(4)}+\cdots\quad(k=6,7)\ . \tag{22c}$$

The expansion (22) is exact and, in general, the $\chi_i^{(n)}$ $(i=1,2,\ldots,7;\ n=2,4,\ldots)$ terms involve n-time correlation functions of the dipole operator and therefore knowledge of successively higher-order correlation functions is needed for the calculation of the line shape when the field strength is increased (already in the weak-field limit, four-time correlation functions should be introduced)[10]. Thus, in principle, the information content of the RRS experiments increases with the applied field strength. However, although exact formal expressions for the χ_i's are given in Appendix A, their evaluation in terms of n-time correlation functions $(n>2)$ is quite tedious and will not be attempted here.

In the following we consider only the contribution of the two-time correlation functions $\chi_i^{(2)}$ to the RRS line shape. This is done by truncating the expansions (22) and retaining only the leading term. Consequently, we shall be able to express the RRS spectrum in terms of the three ordinary line-shape functions $f_{ab}(\Delta)$, $f_{bc}(\Delta)$, and $f_{ac}(\Delta)$ of the present model. Let us introduce the line-shape function corresponding to the ab transition $f_{ab}(\Delta)$. The unified theory of spectral broadening gives us the following exact expression for the absorption line shape $I(\Delta)$ from a to b (Refs. 31 and 33):

$$I_{ab}(\Delta)=\frac{-1}{\pi}f_{ab}''(\Delta)\ , \tag{23}$$

where

$$f_{ab}(\Delta)=-i\int_0^\infty d\tau\exp\left[-i\Delta\tau-\frac{\gamma_a+\gamma_b}{2}\tau-g_{ab}(\tau)\right]$$
$$\equiv f_{ab}'(\Delta)-if_{ab}''(\Delta)\ , \tag{24}$$

and where f' and f'' are the real and the imaginary parts of the line-shape function f which satisfy the Kramers-Kronig relations:

$$f'_{ab}(\Delta)=\frac{1}{\pi}\int d\Delta'\frac{f''_{ab}(\Delta)}{\Delta'-\Delta}\ . \tag{25}$$

The line-shape function f is normalized such that

$$\int f''_{ab}(\Delta)d\Delta=\pi\ . \tag{26}$$

The line-broadening function $g_{ab}(\Delta)$ is given by

$$g_{ab}(\tau)=-\frac{N}{\Omega}\Omega\sum_{\alpha,\beta}P(\alpha)\,|\,\langle a\alpha\,|\,b\beta\rangle\,|^2\times[\exp(i\omega_{\beta\alpha}\tau)-1]\ . \tag{27a}$$

Here the summation is over the single-particle states $|\,\alpha_\nu\rangle$, $|\,\beta_\nu\rangle$ defined in Sec. II, $\omega_{\beta\alpha}=E_{\beta_\nu}-E_{\alpha_\nu}$ is the energy difference of these states, and N/Ω is the number density of perturbers, Ω being the volume of the system.

Similarly we may define the line-shape functions $f_{bc}(\Delta)$ and $f_{ac}(\Delta)$ by simply interchanging indices. We then have the additional line-broadening functions $g_{bc}(\tau)$ and $g_{ac}(\tau)$, i.e.,

$$g_{bc}(\tau)=-\frac{N}{\Omega}\Omega\sum_{\alpha,\beta}P(\alpha)\,|\,\langle c\alpha\,|\,b\beta\rangle\,|^2\times[\exp(i\omega_{\beta\alpha})-1]\ , \tag{27b}$$

and

$$g_{ac}(\tau)=-\frac{N}{\Omega}\Omega\sum_{\alpha,\beta}P(\alpha)\,|\,a\alpha\,|\,c\gamma\rangle\,|^2\times[\exp(i\omega_{\gamma\alpha}\tau)-1]\ . \tag{27c}$$

To lowest order in the expansion (22) we then have (see Appendix B)

$$\chi_1^{(2)}=2f''_{ab}(\Delta_L)\ , \tag{28a}$$

$$\chi_2^{(2)}=\chi_3^{(2)}=f_{bc}(\Delta_S)\ , \tag{28b}$$

$$\chi_4^{(2)}=f_{ab}(\Delta_L)\ , \tag{28c}$$

$$\chi_5^{(2)}=-f_{ab}(\Delta_L)-f_{bc}(\Delta_S)\ , \tag{28d}$$

$$\chi_6^{(2)}=0\ , \tag{28e}$$

$$\chi_7^{(2)}=-2f''_{bc}(\Delta_S)\ . \tag{28f}$$

Upon substitution of Eqs. (28) in (20) we finally get[32]

$$I(\Delta_L,\Delta_S)=\mu_S^2\mu_L^2\hat{I}(\Delta_L,\Delta_S)\ , \tag{29a}$$

where

$$\hat{I}(\Delta_L,\Delta_S)=\frac{1}{1-\frac{4\mu_L^2}{\gamma'_b}f''_{ab}(\Delta_L)}\times\left\{\frac{2}{\gamma_b}f''_{ab}(\Delta_L)f''_{bc}(\Delta_S)+\mathrm{Im}\left[\frac{-1}{[f^*_{ac}(\Delta_L-\Delta_S)f_{bc}(\Delta_S)]^{-1}+\mu_L^2}\times\left[-f^*_{ab}(\Delta_L)+\frac{2\mu_L^2}{\gamma_b}f''_{ab}(\Delta_L)f_{bc}(\Delta_S)\right]\right]\right\}\ . \tag{29b}$$

and

$$\gamma'_b=\gamma_b\left[1+\frac{\gamma_{cb}}{2\gamma_c}\right]^{-1}\ . \tag{29c}$$

Equation (29) is our final result and expresses the RRS spectrum in terms of f_{ab}, f_{bc}, and f_{ac}. In the impact (Markovian) limit we set

$$\exp[-g_{ab}(\tau)]\cong\exp(-\hat{\Gamma}_{ab}\tau)\ , \tag{30}$$

where $\hat{\Gamma}_{ab}$ is the *proper dephasing* rate for the ab transition. The ab line-shape function $f_{ab}(\Delta)$ then assumes the form

$$f_{ab}(\Delta)=\frac{1}{\Delta+i\Gamma_{ab}}\ , \tag{31}$$

where

$$\Gamma_{ab}=\tfrac{1}{2}(\gamma_a+\gamma_b)+\hat{\Gamma}_{ab} \tag{32}$$

is the *total dephasing* rate of the ab transition. Using Eq. (24) and (31) we have

$$f'_{ab}(\Delta)=\frac{\Delta}{\Delta^2+\Gamma_{ab}^2} \tag{33a}$$

and

$$f''_{ab}(\Delta)=\frac{-\Gamma_{ab}}{\Delta^2+\Delta_{ab}^2}\ . \tag{33b}$$

Similar expressions hold for f_{bc} and f_{ac} with the proper dephasing rates $\hat{\Gamma}_{bc}$ and $\hat{\Gamma}_{ac}$, respectively, i.e.,

$$f_{bc}(\Delta)=\frac{1}{\Delta+i\Gamma_{bc}} \tag{34}$$

and

$$f_{ac}(\Delta)=\frac{1}{\Delta+i\Gamma_{ac}}\ . \tag{35}$$

Upon substitution of Eqs. (31), (34), and (35) into Eq. (29) we obtain the strong-field Markov result[17]:

$$\hat{I}(\Delta_L,\Delta_S)=\frac{1}{\Delta_L^2+\Gamma_{ab}^2+4\mu_L^2\Gamma_{ab}/\gamma'_b}\,\mathrm{Im}\left[\frac{(\Delta_S-\Delta_L+i\Gamma_{ac})(2\Gamma_{ab}/\gamma_b-1)+\Delta_S+i(\Gamma_{ac}+\Gamma_{ab})}{(\Delta_S+i\Gamma_{bc})(\Delta_S-\Delta_L+i\Gamma_{ac})-\mu_L^2}\right]. \tag{36}$$

IV. DISCUSSION

We have derived a formal expression [Eq. (20)] for the collision-broadened RRS line shape, that is valid for arbitrary field strengths (μ_L) and detunings (Δ_L,Δ_S). The line shape was then expanded in terms of the $\chi_i^{(n)}$ ($i=1,2,\ldots,7$; $n=2,4,6,\ldots$) functions [Eq. (22)]. In Appendix B we show that the $\chi_i^{(2)}$ functions can be expressed in terms of Laplace transforms of two-time correlation functions of the transition-dipole operators (in the interaction picture with respect to $H_a+H_b+H_c$). Similarly, the $\chi_i^{(n)}$ ($n>2$) functions are related to n-time correlation functions.[1] We would like to point out that since higher-order correlation functions appear with higher powers of the field strength (μ_L) and the time integrations contribute powers of the correlation time τ_c (usually associated with the duration of a single collision), the expansion (22) is actually an expansion in the dimensionless parameter $\mu_L\tau_c$.

We have considered the medium-field strength case, defined by the condition

$$\mu_L << \tau_c^{-1} \tag{37}$$

i.e., although the field can be strong enough to saturate the ab transition (if $\mu_L \geq \frac{1}{2}\sqrt{\gamma_b\Gamma_{ab}}$), the period ($\mu_L^{-1}$) of the associated (on-resonance) Rabi oscillation is much longer than the collision time (τ_c) and hence, only single-photon absorption can occur during the collision with the perturber. In this approximation only the lowest-order terms ($\chi_i^{(2)}$) in the expansion of the χ_i's contribute to the RRS spectrum which is thus completely determined by the two-time correlation functions ($g_{aba}, g_{cbc}, g_{aca}$). A similar result (valid only in the medium-field limit) was recently obtained for the resonance fluorescence spectrum in a two-level system.[18] The advantage of the present approach is that the evaluation of the corrections (due to higher-order correlation functions) to the line shape is straightforward though somewhat tedious [using Eqs. (20), (A20), and (22) and expanding the denominator in Eq. (A7) in the radiative interaction]. A further advantage of the present method is that since the interactions with the laser and the scattered modes are treated on the same footing, it does not incorporate the fluctuation regression approximation[34] which is perfectly valid in the Markovian limit[11,34] but is not expected to hold when non-Markovian effects are significant. A recent application of this theory had led to the erroneous conclusion that the information content of fluorescence spectra is the same in the weak- and strong-field cases.[18]

We have performed some numerical calculations of Eq. (29). For the sake of simplicity we have assumed that levels $|a\rangle$ and $|c\rangle$ have identical interactions with the bath (for instance, when they are different vibrational levels of the ground electronic state and $|b\rangle$ belongs to an excited electronic state). As a result $V_a=V_c$ in Eq. (9) and we get

$$g(\tau)\equiv g_{ab}(\tau)=g_{bc}(\tau) \tag{38a}$$

and

$$g_{ac}(\tau)=0\ . \tag{38b}$$

$g(\tau)$ was taken from the stochastic line-shape theory of Kubo,[35] i.e.,

$$g(\tau)=\frac{\delta^2}{\Lambda^2}[\exp(-\Lambda\tau)-1+\Lambda\tau]\ . \tag{39}$$

Here δ is a measure of the interaction strength responsible for the line broadening, whereas $\tau_c=\Lambda^{-1}$ is roughly the duration of a collision. The nature of the ordinary line-shape function [Eqs. (23) and (24)] is governed by the dimensionless parameter $\kappa\equiv\Lambda/\delta$. When $\kappa>>1$ we get the impact limit, [Eq. (30)],

$$\exp[-g_{ab}(\tau)]\cong\exp(-\hat{\Gamma}_{ab}\tau)\ , \tag{40a}$$

where

$$\hat{\Gamma}_{ab}=\hat{\Gamma}_{bc}=\delta^2/\Lambda\ , \tag{40b}$$

$$\hat{\Gamma}_{ac}=0\ . \tag{40c}$$

$f''_{ab}(\Delta)$ assumes in this case a simple Lorentzian form and the Raman spectrum reduces to Eq. (36). When $\kappa<<1$ we get the static limit

$$\exp[-g_{ab}(\tau)]\cong\exp(-\delta^2\tau^2/2)\ , \tag{41}$$

and $f''_{ab}(\Delta)$ [Eq. (24)] reduces to the Voigt profile (a convolution of a Gaussian with width δ and a Lorentzian with width $(\gamma_a+\gamma_b)/2$). We have calculated $\hat{I}(\Delta_L,\Delta_S)$ using $\kappa=10$ (impact) and $\kappa=0.1$ (static) line profiles for $f_{ab}(\Delta)$.

In Fig. 3 we show the weak-field ($\mu_L=0$) profiles for both cases. At $\mu_L=0$ we see two components: a narrow (Raman) component at $\Delta_S=\Delta_L$ and a broad (redistribution) component at $\Delta_S=0$. The δ and Λ parameters for the $\kappa=10$ and $\kappa=0.1$ lines are chosen so that $f''_{ab}(\Delta)$ has the same full width at half maximum (FWHM). As Δ_L is detuned, the ratio of integrated intensities of the redistribution and Raman components does not change in the impact limit $\kappa=10$ (right column) and is equal to $2\hat{\Gamma}_{ab}/\gamma_b$. This may be easily seen by setting $\mu_L=0$ in the impact equation (36) resulting in the well-known expression[2–10]:

$$I(\Delta_L,\Delta_S)=\frac{\mu_L^2\mu_S^2}{\Delta_L^2+\Gamma_{ab}^2}\times\left[\pi\delta(\Delta_S-\Delta_L)+\frac{2\hat{\Gamma}_{ab}}{\gamma_b}\frac{\Gamma_{bc}}{\Delta_S^2+\Gamma_{bc}^2}\right]\ , \tag{42}$$

where we have further set $\gamma_a=\gamma_c=0$. In the other extreme $\kappa=0.1$ (left column) we see how the redistribution term gradually disappears. This may be interpreted by saying the $\hat{\Gamma}_{ab}$ is actually frequency dependent $\hat{\Gamma}_{ab}(\Delta_L)$, and it vanishes at large detunings, where the impact limit fails.[14] In the present formulation we do not need to invoke this argument and the vanishing of the redistribution component arises naturally from the frequency dependence of the actual line shape $f''_{ab}(\Delta)$.

Figure 4 shows the variation of the RRS spectra for resonance pumping ($\Delta_L=0$) with the pumping intensity. As in Fig. 3 the right ($\kappa=10$) column is in the impact limit and the left ($\kappa=0.1$) column is in the static limit. The strong-field limit is obtained whenever the generalized Rabi frequency

$$\theta=(\Delta_L^2+4\mu_L^2)^{1/2} \tag{43}$$

is the largest parameter in the problem (except for the inverse duration of a collision). The spectrum separates in this case into two (non-Lorentzian) peaks centered at

$$\Delta_S^{(\pm)}=\tfrac{1}{2}(\Delta_L\pm\theta)\ . \tag{44}$$

In the weak-field limit, the $\Delta_S^{(+)}$ peak reduces to the coherent Raman component (around $\Delta_S=\Delta_L$) and the $\Delta_S^{(-)}$ gives the incoherent redistribution component (around $\Delta_S=0$). This gradual change is shown in Fig. 4 as we move from bottom (strong field) to the top and is common to the impact and nonimpact lines (right and left panels). The difference between the impact and nonimpact lines is in the shape of the two peaks. We note further that the two equal components when μ_L is large are much narrower in the static ($\kappa=0.1$) case. This may be again interpreted by invoking the frequency dependence of $\hat{\Gamma}_{bc}(\Delta)$ which exists at large detunings in this case but is absent, by assumption, in the impact ($\kappa=10$) case.

Figures 5 and 6 show the variation of the RRS spectra with the detuning of the pump field for finite intensities $\mu_L=20$ and $\mu_L=40$, respectively. We note that as Δ_L increases we need a stronger μ_L in order to achieve the asymptotic behavior mentioned above. Thus a $\mu_L=20$ field is "strong" for $\Delta_L=0$ (upper panels in Fig. 5) and the spectra are split into two equal components. The same field for $\Delta_L=40$ (lower panel) is weak and the two components are not equal neither in their intensity nor in their width. We also note that the lines are narrower in the nonimpact ($\kappa=0.1$) case. Finally we note that the two components are roughly equal in magnitude in the impact case but a dramatic change occurs for the nonimpact lines where the redistribution component disappears with the detuning.

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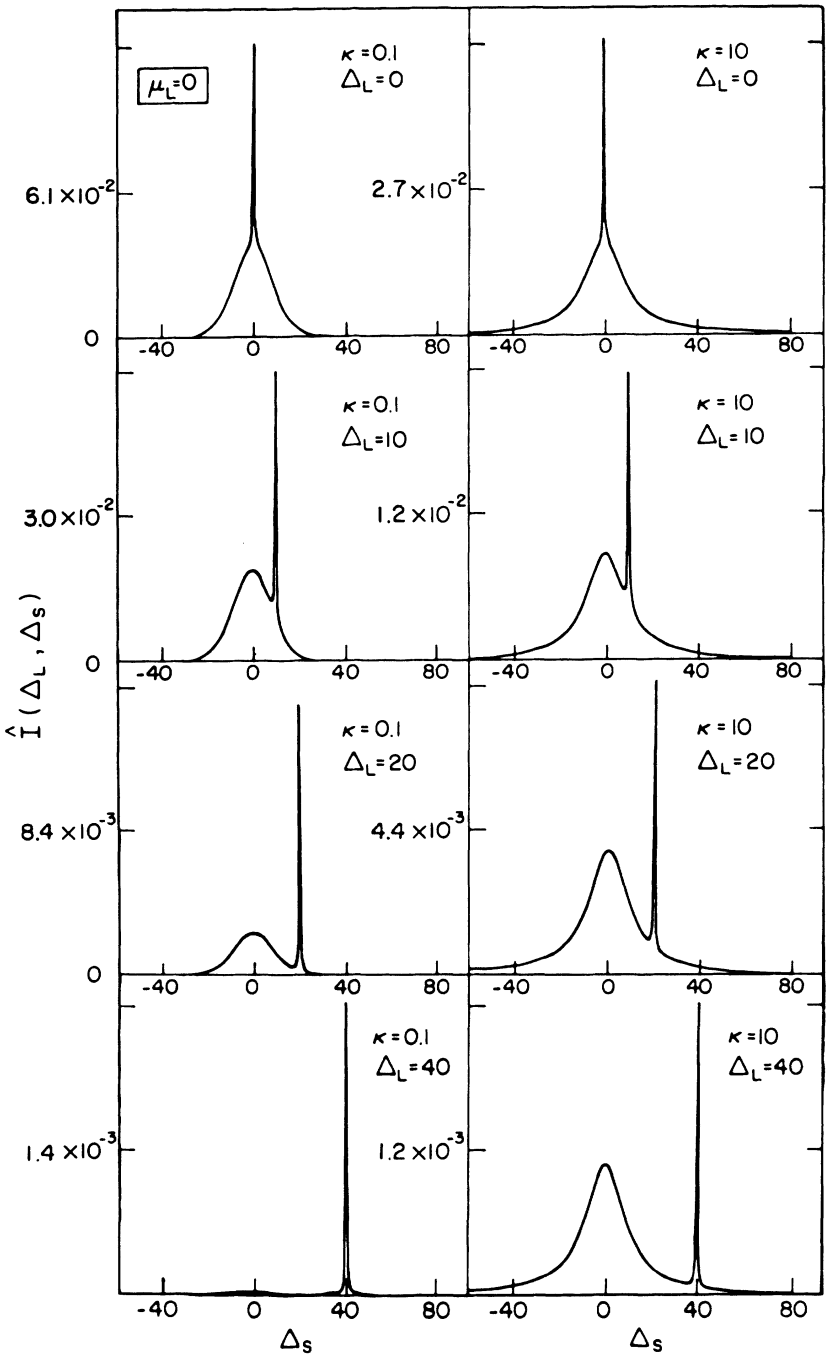

FIG. 3. Resonance Raman spectra [Eq. (29)] at zero field $\mu_L=0$. $\gamma_a=0,\gamma_b=1,\gamma_c=0.5.\gamma_{cb}=0$. The $\kappa=10$ lines were calculated using $\delta=100$ and $\Lambda=1000$, whereas the $\kappa=0.1$ lines were calculated using $\delta=8.49$ and $\Lambda=0.849$, so that the $f''_{ab}(\Delta)$ has the same width in both cases. Note that the ratio of intensities of the Raman and the redistribution terms does not change with the detuning in the impact ($\kappa=10$) limit, whereas in the $\kappa=0.1$ case the redistribution component vanishes at large detunings.

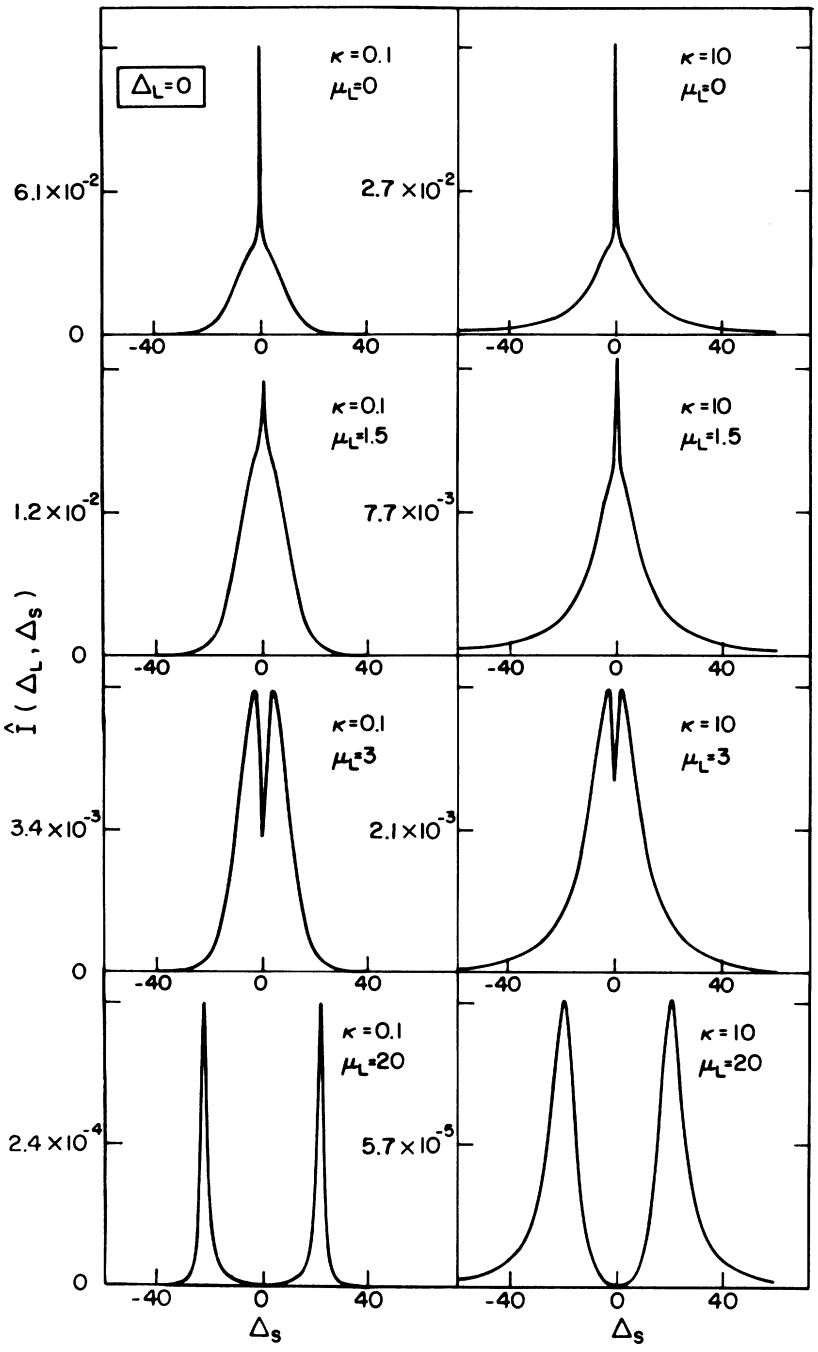

FIG. 4. Saturation behavior of the RRS spectrum for $\mu_L=0$, 1.5, 3, and 20. The pump field is tuned on resonance $\Delta_L=0$. Other parameters are the same as in Fig. 3. Note that the two components in the strong field are much broader in the impact ($\kappa=10$) limit than is the static ($\kappa=0.1$) case.

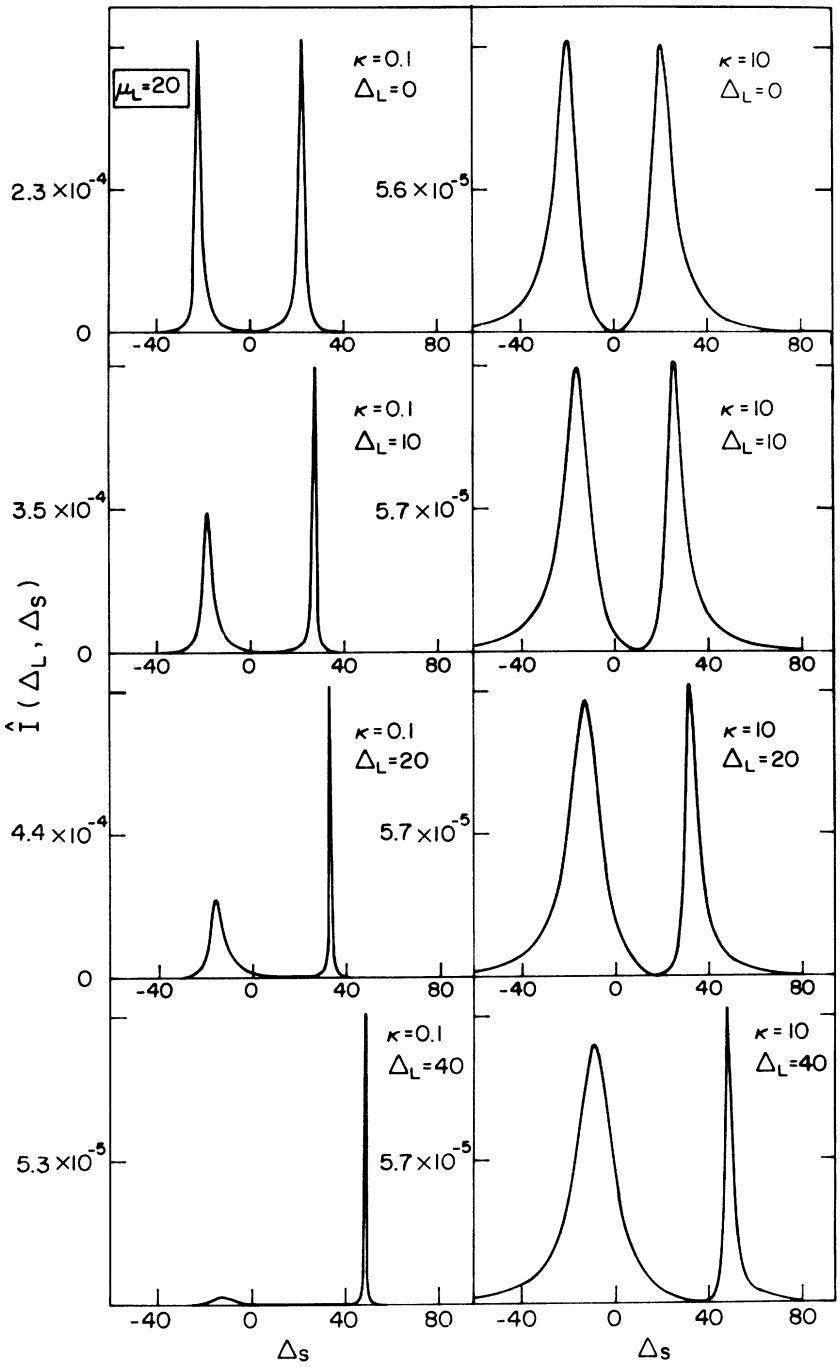

FIG. 5. Same as Fig. 3 but for $\mu_L = 20$.

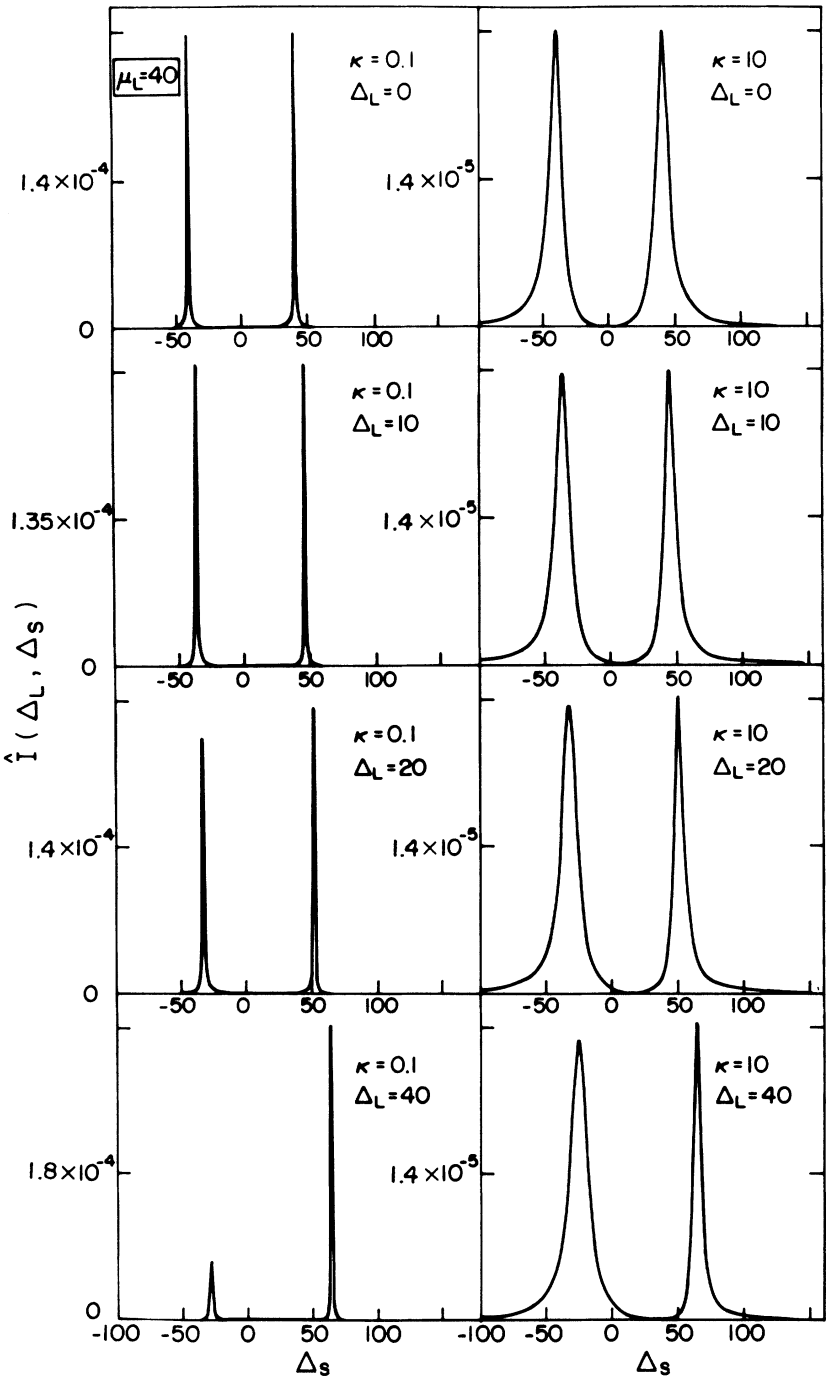

FIG. 6. Same as Fig. 3 but for $\mu_L = 40$.

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APPENDIX A

Using the tetradic scattering formalism,[10,26–29] the RRS spectrum for arbitrary field strength is given by

$$I(\Delta_S,\Delta_L)=-i\mathrm{Tr}_B\langle\langle cc\,|\,\mathscr{T}(0)\,|\,\rho(-\infty)\rangle\rangle\ , \tag{A1}$$

where $|\,cc\rangle\rangle$ is a shorthand notation for the state $|\,cc;1_s1_s\rangle\rangle$ containing a scattered mode photon, and $\mathscr{T}(\omega)$ is the tetradic scattering matrix,

$$\mathscr{T}(\omega)=v+v\frac{1}{\omega-L}v\ . \tag{A2}$$

Here, L is the total Liouvillian defined in Eq. (14) and v is the tetradic interaction operator corresponding to V [see Eq. (5)], i.e.,

$$v=[V,\ ]\ . \tag{A3}$$

We define the following tetradic projection operator[25]:

$$P=[\ |aa\rangle\rangle\langle\langle aa\,|+|bb\rangle\rangle\langle\langle bb\,|+|cc\rangle\rangle\langle\langle cc\,|+|ca\rangle\rangle\langle\langle ca\,|+|ac\rangle\rangle\langle\langle ac\,|\ ]\rho_B^0\mathrm{Tr}_B\ , \tag{A4}$$

and its complementary projection operator

$$Q=1-P\ . \tag{A5}$$

The spectrum in Eq. (A1) is given by matrix elements of $P\mathscr{T}(0)P$. Now, for any projection operator P we have

$$P\mathscr{T}(\omega)P=R(\omega)+P\mathscr{T}(\omega)P\mathscr{G}^0(\omega)PR(\omega)\ , \tag{A6}$$

with

$$R(\omega)=PvP+PvQ\frac{1}{\omega-QLQ}QvP\ , \tag{A7}$$

and

$$\mathscr{G}^0(\omega)=\frac{1}{\omega-L_0-\tilde{L}}\ , \tag{A8}$$

where $L_0=[H_0,\ ]$.

Solving Eq. (A6) for $P\mathscr{T}P$ we get

$$P\mathscr{T}(\omega)P=R(\omega)\frac{1}{1-P\mathscr{G}^0(\omega)PR(\omega)}\ . \tag{A9}$$

The operator $\mathscr{T}(\omega)$ and hence also $R(\omega)$, may contain the interaction v_L to all orders. However, $\mathscr{T}(\omega)$ must be of second order in v_s, i.e.,

$$\langle\langle cc\,|\,P\mathscr{T}(\omega)P\,|\,aa\rangle\rangle=\langle\langle cc\,|\,R^{(2)}(\omega)\frac{1}{\omega-P\mathscr{G}^0(\omega)PR^{(0)}(\omega)}\,|\,aa\rangle\rangle+\langle\langle cc\,|\,R^{(1)}(\omega)\frac{1}{\omega-P\mathscr{G}^0(\omega)PR^{(1)}(\omega)}\,|\,aa\rangle\rangle\ , \tag{A10}$$

where $R^{(2)}$ is of order v_s^2, $R^{(1)}$ is of order v_s, and $R^{(0)}$ does not contain any v_s operators.

Denoting

$$\mathscr{A}_{ab;cd}=\langle\langle ab\,|\,\mathscr{A}(0)\,|\,cd\rangle\rangle \tag{A11}$$

for any tetradic operator $\mathscr{A}(\omega)$, we collect the nonvanishing contributions to the line shape, i.e.,

$$(P\mathscr{T}P)_{cc;aa}=R^{(2)}_{cc;bb}\left[\frac{1}{1-P\mathscr{G}^0PR^{(0)}}\right]_{bb;aa}+R^{(2)}_{cc;aa}\left[\frac{1}{1-P\mathscr{G}^0PR^{(0)}}\right]_{aa;aa}+2i\,\mathrm{Im}\left[R^{(1)}_{cc;aa}\left[\frac{1}{1-P\mathscr{G}^0PR^{(1)}}\right]_{ac;aa}\right]\ . \tag{A12}$$

The last matrix element in the above equation can be further simplified since it can be expanded to first order in $R^{(1)}$ (the higher-order terms will be of order v_s^2 and will not contribute to the line shape), giving

$$\left[\frac{1}{1-P\mathscr{G}^0PR^{(1)}}\right]_{ac;aa}=\frac{1}{[(P\mathscr{G}^0P)_{ac;ac}]^{-1}-R^{(0)}_{ac;ac}}\left[R^{(1)}_{ac;aa}\left[\frac{1}{1-P\mathscr{G}^0PR^{(0)}}\right]_{aa;aa}+R^{(1)}_{ac;bb}\left[\frac{1}{1-P\mathscr{G}^0PR^{(0)}}\right]_{bb;aa}\right]\ . \tag{A13}$$

In deriving Eq. (A13) we have used the assumption that relaxation does not couple "populations" ($|\,ii\rangle\rangle$, with $i=a,b,c$) to "coherences" ($|\,ij\rangle\rangle$, $i\neq j$, with $i,j=a,b,c$), i.e., that all relaxation rates can be identified as

belonging to the T_1 or the T_2 type. In this case,

$$(P\mathcal{G}^0PR^{(0)})_{ac;ac}=(P\mathcal{G}^0P)_{ac;ac}R^{(0)}_{ac;ac} \tag{A14}$$

and Eq. (A13) follows.

We still have to invert the (3×3) matrix $1-P\mathcal{G}^0PR^{(0)}$ in the population space. Using Eqs. (A8) and (15), we have

$$P\mathcal{G}^0(\omega)P=\begin{bmatrix} \omega+i\gamma_b & 0 & 0 \\ -i\gamma_{cb} & \omega+i\gamma_c & 0 \\ -i(\gamma_b-\gamma_{cb}) & -i\gamma_c & \omega \end{bmatrix}, \tag{A15}$$

where the rows and columns are labeled by *bb*, *cc*, and *aa* (in decreasing order on the energy scale).

Note that the radiative coupling posesses the following symmetry:

$$v_L\,|\,aa\rangle\rangle=-v_L\,|\,bb\rangle\rangle=\mu_L(\,|\,ab\rangle\rangle-|\,ba\rangle\rangle)\,. \tag{A16}$$

Applying this relation to the definition of $R(\omega)$ in Eq. (A7), we obtain

$$R^{(0)}_{aa;aa}(\omega)=R^{(0)}_{bb;bb}(\omega)=-R^{(0)}_{aa;bb}(\omega)=-R^{(0)}_{bb;aa}(\omega)\,, \tag{A17}$$

and since v_L does not couple $|\,aa\rangle\rangle$ to $|\,cc\rangle\rangle$, the $R^{(0)}$ matrix is given by

$$R^{(0)}(\omega)=R^{(0)}_{aa;aa}(\omega)\begin{bmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{bmatrix}. \tag{A18}$$

Inversion of the 3×3 matrix $1-P\mathcal{G}^0PR^{(0)}$ is straightforward (the limit $\omega\to0$ should be taken *after* forming the product $P\mathcal{G}^0PR^{(0)}$) and gives

$$[1-P\mathcal{G}^0(0)PR^{(0)}(0)]^{-1}=\frac{1}{1-\frac{2}{\gamma'_b}(-iR^{(0)}_{aa;aa})}\begin{bmatrix} 1-\frac{-iR^{(0)}_{aa;aa}}{\gamma_b}\left[1+\frac{\gamma_{cb}}{\gamma_c}\right] & 0 & -\frac{-iR^{(0)}_{aa;aa}}{\gamma_b} \\ \frac{\gamma_{cb}}{\gamma_c}\frac{-iR^{(0)}_{aa;aa}}{\gamma_b} & 1-\frac{-2iR^{(0)}_{aa;aa}}{\gamma'_b} & -\frac{\gamma_{cb}}{\gamma_c}\frac{-iR^{(0)}_{aa;aa}}{\gamma_b} \\ -\frac{-iR^{(0)}_{aa;aa}}{\gamma_b}\left[1+\frac{\gamma_{cb}}{\gamma_c}\right] & 0 & 1-\frac{-iR^{(0)}_{aa;aa}}{\gamma_b} \end{bmatrix}, \tag{A19}$$

with γ'_b given by Eq. (21).

Substituting the appropriate matrix elements into Eqs. (A12) and (A13), and introducing the notation

$$\chi_1(\Delta_L)=-iR^{(0)}_{aa;aa}\,, \tag{A20a}$$

$$\chi_2(\Delta_L,\Delta_S)=R^{(0)}_{ac;ac}\,, \tag{A20b}$$

$$\chi_3(\Delta_L,\Delta_S)=R^{(1)}_{cc;ac}\,, \tag{A20c}$$

$$\chi_4(\Delta_L,\Delta_S)=R^{(1)}_{ac;aa}\,, \tag{A20d}$$

$$\chi_5(\Delta_L,\Delta_S)=R^{(1)}_{ac;bb}\,, \tag{A20e}$$

$$\chi_6(\Delta_L,\Delta_S)=-iR^{(2)}_{cc;aa}\,, \tag{A20f}$$

$$\chi_7(\Delta_L,\Delta_S)=-iR^{(2)}_{cc;bb}\,, \tag{A20g}$$

and

$$f_{ac}(\Delta_L-\Delta_S)=(P\mathcal{G}^0(0)P)_{ac;ac}\,, \tag{A21}$$

we obtain the RRS line shape for arbitrary field strengths [Eq. (30)]. However, the actual calculation of the χ_i's involves inverting the matrix $\omega-QLQ$, i.e., taking into account the contributions from all the possible ways in which the bath can be excited. Owing to the complicated structure of the Q space we did not proceed to evaluate the $\chi_i^{(n)}$s $(n\geq4)$.

APPENDIX B

Terms involving $\chi_i^{(4)}$ and higher orders in the expansion (22) contain integrals over n-time correlation functions (with $n\geq4$) resulting in increasing

powers of $\mu_L \tau_c$, where τ_c is the correlation time usually associated with the duration of a single collision. Hence, if the external field is not too strong, i.e., if the condition $\mu_L \tau_c << 1$ is satisfied, we can consider only the $\chi_i^{(2)}$ $(i=1,\ldots,7)$ terms in the expansion (22). In this case, the operator R [Eq. (A7)] can be written as

$$R(\omega)=PvP+PvQ\frac{1}{\omega-QL_0Q-Q\tilde{L}Q}QvP\ . \tag{B1a}$$

Since the interaction v satisfies

$$PvP=0\ , \tag{B1b}$$

and within the space spanned by the states $|bc\rangle\rangle$, $|cb\rangle\rangle$, $|ab\rangle\rangle$, and $|ba\rangle\rangle$, Q can be replaced by the unit operator, we can write

$$R(\omega)=Pv\mathcal{G}^0(\omega)vP\ , \tag{B1c}$$

with $\mathcal{G}^0(\omega)$ defined in Eq. (A8).

Using Eqs. (22) and (A20) we obtain

$$\begin{aligned}\mu_L^2\chi_1^{(2)}&=-i(Pv_L\mathcal{G}^0(0)v_LP)_{aa;aa}\\&=-i(v_{aa;ab}\mathcal{G}^0_{ab;ab}v_{ab;aa}+v_{aa;ba}\mathcal{G}^0_{ba;ba}v_{ba;aa})\\&=2\mu_L^2\,\mathrm{Im}\mathcal{G}^0_{ab;ab}\ ,\end{aligned} \tag{B2a}$$

where the Liouvillian conjugation symmetry[28] implying

$$\mathcal{G}^0_{ab;cd}(\omega)=-\mathcal{G}^{0*}_{ba;dc}(-\omega) \tag{B3}$$

has been used. In a similar way we obtain

$$\chi_2^{(2)}=\mathcal{G}^0_{bc;bc}\ , \tag{B2b}$$

$$\chi_3^{(2)}=\mathcal{G}^0_{bc;bc}\ , \tag{B2c}$$

$$\chi_4^{(2)}=\mathcal{G}^0_{ab;ab}\ , \tag{B2d}$$

$$\chi_5^{(2)}=-(\mathcal{G}^0_{ab;ab}+\mathcal{G}^0_{bc;bc})\ , \tag{B2e}$$

$$\chi_6^{(2)}=0\ , \tag{B2f}$$

and

$$\chi_7^{(2)}=2\,\mathrm{Im}\mathcal{G}^0_{bc;bc}\ . \tag{B2g}$$

The functions $\mathcal{G}^0_{bc;bc}$ and $\mathcal{G}^0_{ab;ab}$ can be represented in terms of their Laplace transforms

$$\mathcal{G}^0_{bc;bc}=\lim_{\omega,\epsilon\to 0}\left[-i\int_0^\infty d\tau\,\tilde{\mathcal{G}}^0_{bc;bc}(\tau)\exp(i\omega\tau-\epsilon\tau)\right] \tag{B4a}$$

and

$$\mathcal{G}^0_{ab;ab}=\lim_{\omega,\epsilon\to 0}\left[-i\int_0^\infty d\tau\,\tilde{\mathcal{G}}^0_{ab;ab}(\tau)\exp(i\omega\tau-\epsilon\tau)\right]\ . \tag{B4b}$$

The $\tilde{\mathcal{G}}^0(\tau)$ functions can be obtained by inspection of Eqs. (19), (32), and (33) in Ref. 10 giving

$$\mathcal{G}^0_{bc;bc}=f_{bc}(\Delta_S) \tag{B5a}$$

and

$$\mathcal{G}^0_{ab;ab}=f_{ab}(\Delta_L)\ , \tag{B5b}$$

with f_{ab} and f_{bc} defined in Eqs. (24) (with a change of indices). The function $(P\mathcal{G}^0P)_{ac;ac}$ appearing in Eq. (A13) can be obtained in a similar manner, resulting in

$$(P\mathcal{G}^0P)_{ac;ac}=f_{ac}(\Delta_L-\Delta_S)\ , \tag{B5c}$$

with f_{ac} defined in (24). Substitution of Eqs. (B2) and (B5) into Eq. (20) gives the generalized, quasi-Markovian line shape [Eq. (29)].

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