NON-IMPACT COLLISIONAL BROADENING OF RESONANCE RAMAN SPECTRA IN STRONG RADIATION FIELDS

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We present a theory for the Raman lineshape of a three level system (a, b and c) being driven by a strong radiation field and perturbed by dephasing collisions. The present theory is not limited to the impact limit of fast collisions and incorporates properly the dynamics of the collisions. The final expression is given in terms of the three ordinary weak field lineshapes corresponding to the ab, bc and ac transitions. Numerical calculations are presented and the qualitative and quantitative differences between the impact and non-impact regions are discussed.

Consider a three level system $|a\rangle$, $|b\rangle$ and $|c\rangle$ interacting with a bath of perturbers via collisions, with a strong, single mode, radiation field (frequency ω_L), and with a scattered radiation field mode (frequency ω_S). We shall be interested in calculating the lineshape function for the resonance Raman process in which a photon ω_L is being absorbed and a photon ω_S is scattered, i.e.

$$|a, n_L, 0\rangle \to |b, n_L - 1, 0\rangle \to |c, n_L - 1, 1\rangle. \qquad (1)$$

Here the first quantum number in each ket denotes the state of the three level system, and the second and third quantum numbers denote the number of photons in the ω_L and ω_S modes, respectively. We further define the detunings of the ω_L and ω_S photons relative to the frequencies of the ab and bc transitions, i.e.

$$\Delta_L \equiv \omega_L - E_b + E_a, \qquad \Delta_S \equiv \omega_S - E_b + E_c. \qquad (2)$$

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We wish to calculate the cross section for the Raman process (1), $\hat{I}(\Delta_L, \Delta_S)$, in the presence of a laser field ω_L with arbitrary strength, characterized by a Rabi frequency μ_L. This problem was solved for weak μ_L in the presence of dephasing collisions of arbitrary duration [1]. The strong field case was treated previously only in the impact limit (fast collisions) where the Bloch equations may be used with phenomenological relaxation parameters T_1 and T_2 [2]. This is similar to the fluorescence in a strong field (the Mollow lineshape) [3,4]. We have recently developed an expansion for the Raman spectrum $\hat{I}(\Delta_L, \Delta_S)$ for an arbitrary strength of the Rabi frequency, μ_L [5]. This is an extension of methods developed recently for multiphoton processes in general [6]. The expansion parameter is roughly $\mu_L \tau_C$ where τ_C is a duration of a collision. To lowest order in $\mu_L \tau_C$ we get an approximate expression for $\hat{I}(\Delta_L, \Delta_S)$ in terms of the ordinary absorption and emission lineshapes corresponding to the ab, bc and ac transitions. It should be stressed that in general $\hat{I}(\Delta_L, \Delta_S)$ contains more microscopic information (i.e. higher order correlation functions) than contained in the ordinary lineshapes, and only the lowest order expression is given in terms of these simple lineshapes [5].

Before writing our expression for $\hat{I}(\Delta_L, \Delta_S)$ we shall introduce a few definitions. Let us consider the ab transition. The ordinary absorption lineshape from a to b $f''_{ab}(\Delta)$ $(\Delta = \Delta_L)$ is given by [7–9]

$$f''_{ab}(\Delta) = -\mathrm{Im}\, f_{ab}(\Delta), \tag{3}$$

where

$$f_{ab}(\Delta) = -\mathrm{i} \int_0^\infty \mathrm{d}\tau \exp[\mathrm{i}\Delta\tau - \tfrac{1}{2}(\gamma_a + \gamma_b)\tau - g_{ab}(\tau)]$$
$$\equiv f'_{ab}(\Delta) + \mathrm{i} f''_{ab}(\Delta), \tag{4}$$

f' and f may be calculated from the absorption spectrum f'' using the Kramers-Kronig relations:

$$f'_{ab}(\Delta) = \frac{1}{\pi} \mathrm{PP} \int_{-\infty}^{\infty} \mathrm{d}\Delta' \frac{f''_{ab}(\Delta')}{\Delta' - \Delta}, \tag{5}$$

and we have adopted the normalization

$$\int \mathrm{d}\Delta\, f''_{ab}(\Delta) = \pi. \tag{6}$$

A systematic expansion was developed recently [5] for the resonance Raman spectrum of this system, making use of the tetradic scattering formalism. To lowest order in the expansion parameters $\mu_L \tau_C$ the resonance Raman cross section (up to a proportionality constant) assumes the form:

$$\hat{I}(\Delta_L, \Delta_S) = [1 - (4\mu_L^2/\gamma'_b) f''_{ab}(\Delta_L)]^{-1}$$
$$\times \Bigg\{ \frac{2}{\gamma_b} f''_{ab}(\Delta_L) f''_{bc}(\Delta_S)$$
$$+ \mathrm{Im}\Bigg\{ \frac{-1}{[f^*_{ac}(\Delta_L - \Delta_S) f_{bc}(\Delta_S)]^{-1} + \mu_L^2}$$
$$\times [-f^*_{ab}(\Delta_L) + (2\mu_L^2/\gamma_b) f''_{ab}(\Delta_L) f_{bc}(\Delta_S)] \Bigg\}\Bigg\}. \tag{7}$$

Here

$$\gamma'_b = \gamma_b (1 + \gamma_{cb}/2\gamma_c)^{-1} \tag{8}$$

where γ_{cb} is the T_1 relaxation rate from level c to b and γ_a, γ_b and γ_c are the inverse lifetimes of levels a, b and c. $g_{ab}(\tau)$ is the line-broadening function which may be easily calculated from the microscopic hamiltonian [7–9] f^* is the complex conjugate of f. In a similar manner we may define $f_{ac}(\Delta)$ as the absorption lineshape from a to c and $f_{bc}(\Delta)$ as the emission lineshape from b to c, by simply changing indexes in eqs. (3)–(6). In the impact of fast collisions we have [7–9]

$$g_{ab}(\tau) = \hat{\Gamma}_{ab}\tau, \tag{9}$$

so that

$$f_{ab}(\Delta) = 1/(\Delta + \mathrm{i}\Gamma_{ab}), \tag{10}$$

where

$$\Gamma_{ab} = \hat{\Gamma}_{ab} + \tfrac{1}{2}(\gamma_a + \gamma_b), \tag{11}$$

(similar expressions hold for $g_{bc}(\tau)$ and $g_{ac}(\tau)$). $\hat{\Gamma}_{ab}$ is the dephasing rate $(1/T_2)$ of the ab transition. Upon substitution of eq. (10) (and the corresponding equations for f_{bc} and f_{ac}) in eq. (7) we get:

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

Equation (12) may be derived directly from the Bloch equations [2].

We have performed some numerical calculations of eq. (7) using the stochastic lineshape function of Kubo [10]. For the sake of simplicity we have assumed that levels a and c are identical as far as their interaction with the bath is concerned. We then have [10]

$$g_{ab}(\tau) = g_{bc}(\tau) = (\delta^2/\Lambda^2)[\exp(-\Lambda\tau) - 1 + \Lambda\tau], \tag{13a}$$

$$g_{ac}(\tau) = 0. \tag{13b}$$

Here δ is a measure of the interaction strength responsible for the linebroadening whereas $\tau_c = \Lambda^{-1}$ is roughly the duration of a collision. The nature of the ordinary lineshape function (eqs. (3) and (4)) is governed by the dimensionless parameter $\kappa \equiv \Lambda/\delta$. When $\kappa \gg 1$ we get the impact limit, eqs. (9) and (10),

$$\exp[-g_{ab}(\tau)] \approx \exp(-\hat{\Gamma}_{ab}\tau), \tag{14a}$$

where

$$\hat{\Gamma}_{ab} = \hat{\Gamma}_{bc} = \delta^2/\Lambda, \tag{14b}$$

$$\hat{\Gamma}_{ac} = 0. \tag{14c}$$

$f''_{ab}(\Delta)$ assumes in this case a simple lorentzian form and the Raman spectrum reduces to eq. (12). When $\kappa \ll 1$ we get the static limit

$$\exp[-g_{ab}(\tau)] \approx \exp(-\delta^2\tau^2/2), \tag{15}$$

and $f''_{ab}(\Delta)$ (eq. (3)) 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. 1 we show the weak field ($\mu_L = 0$) profiles for both cases. At $\Delta_L = 0$ 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. 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 $2\hat{\Gamma}_{ab}/\gamma_b$. In the other extreme $\kappa = 0.1$ (left column) we see how the redistribution term gradually disappears. This may be interpreted by saying that $\hat{\Gamma}_{ab}$ is actually frequency dependent $\hat{\Gamma}_{ab}(\Delta_L)$, and it vanishes at large detunings, where the impact limit fails [11]. In the present formulation we do not need to invoke this argument and the vanishing of the redistribution

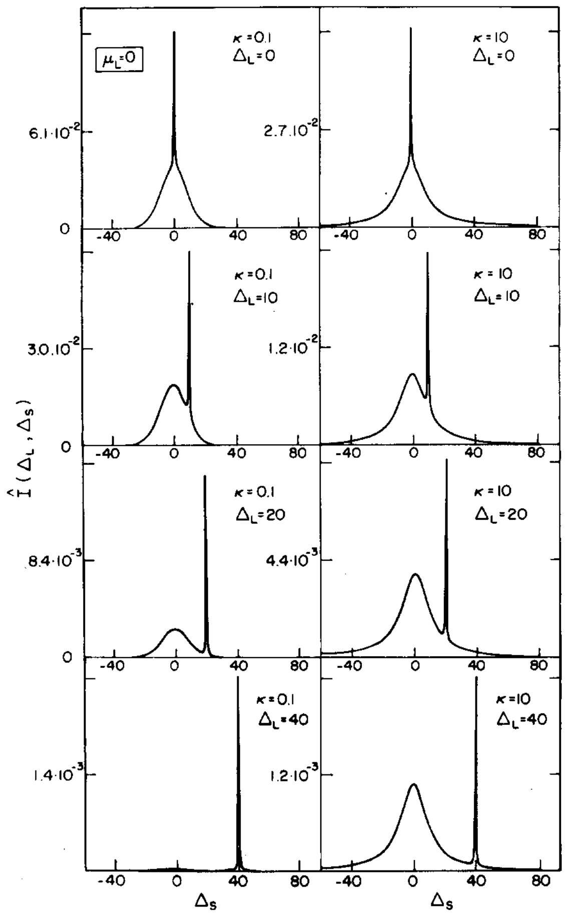

Fig. 1. The resonance Raman spectra (eq. (7)) at zero field $\mu_L = 0$. $\gamma_a = 0$, $\gamma_b = 1$, $\gamma_c = 0.5$, $\gamma_{cb} = 0$. The $\kappa = 10$ lines were calculated using $\delta = 100$ and $\Lambda = 1000$ whereas the $\kappa = 0.1$ lines were calculated using $\delta = 8.49$ and $\Lambda = 0.849$, 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.

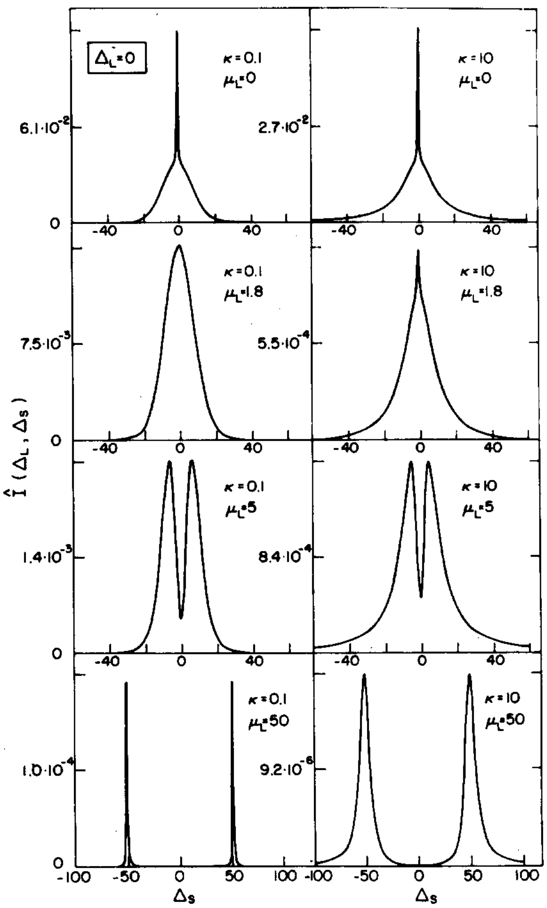

Fig. 2a.

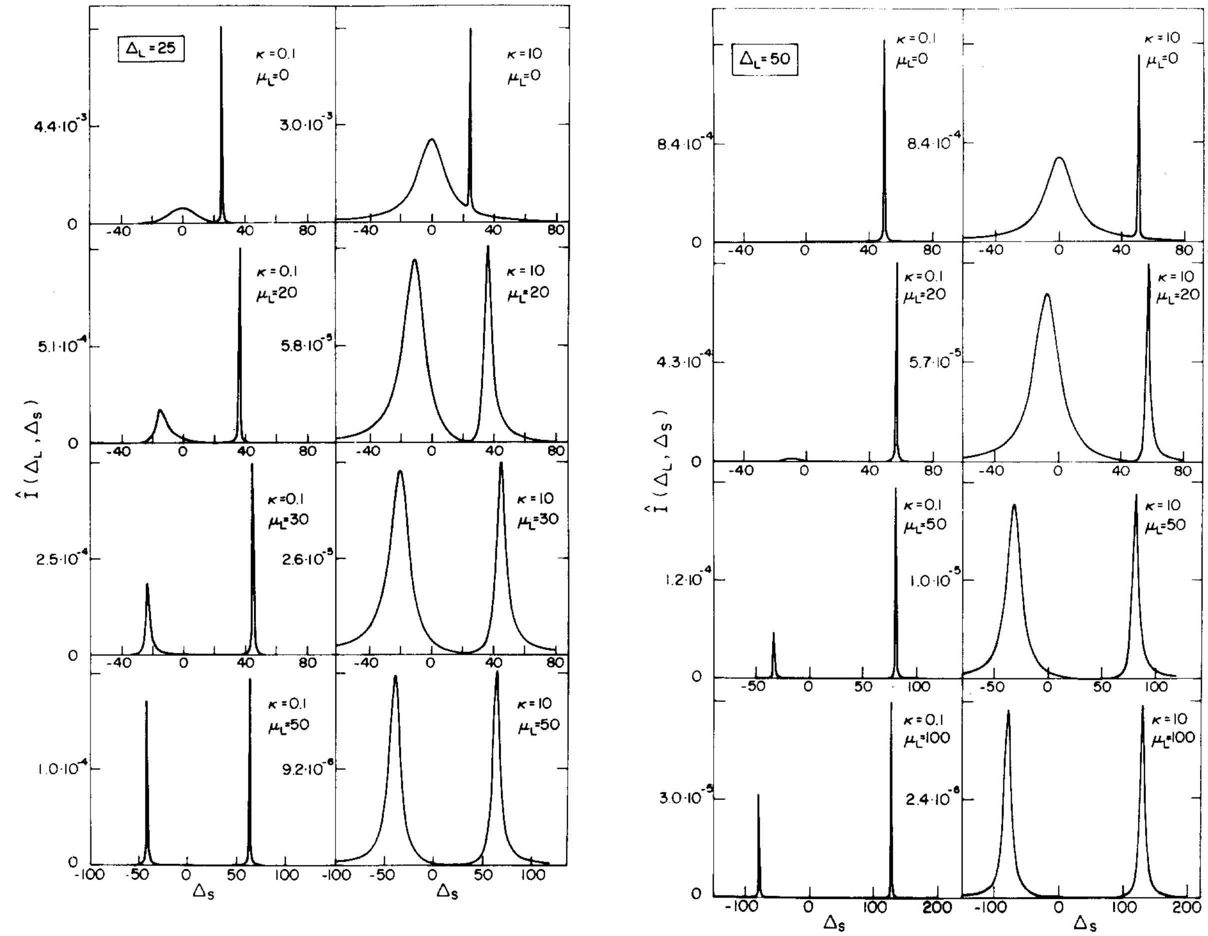

Fig. 2. The saturation behaviour of the resonance Raman spectrum for three values of the detuning of the exciting laser. Fig. 2A $\Delta_L = 0$, fig. 2B $\Delta_L = 25$, fig. 2C $\Delta_L = 50$. Other parameters same as in fig. 1.

component arises naturally from the frequency dependence of the actual lineshape $f''_{ab}(\Delta)$. Fig. 2 shows the saturation behaviour of these lineshapes as a function of the Rabi frequency μ_L for $\Delta_L = 0.25$ and 50 (where $\gamma_b = 1$). When μ_L is the largest parameter in the problem, we get two equal lines at $\Delta_S = \pm\mu_L$ which are much broader in the impact limit. Fig. 2 shows how the spectra are gradually changing from the weak to the strong field limits. We note that as Δ_L increases we need a stronger μ_L in order to achieve the asymptotic behaviour mentioned above. A Rabi frequency of $\mu_L = 50$ is sufficient to split the line into two equal components at $\Delta_L = 0$ (fig. 2A) but is not large enough for the $\Delta_L = 50$ case (fig. 2C). 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.

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