

Relaxation of Elementary Excitations,

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Unified Theory of Collisional Redistribution in Near-Resonance Light Scattering

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ABSTRACT

The tetradic scattering formalism is used to solve for the spectral distribution of light scattered from collisionally perturbed molecules with binary interactions. Using a systematic density expansion it is shown that the necessary four-time N -particle dipole correlation functions may be rigorously expressed in terms of three two-time single-particle correlation functions, two of which are associated with the absorption and emission line broadening, and the third is a cross correlation function. The present results provide a unified treatment valid all the way from the impact to the statistical limits.

I. Tetradic scattering formulation of resonance light scattering

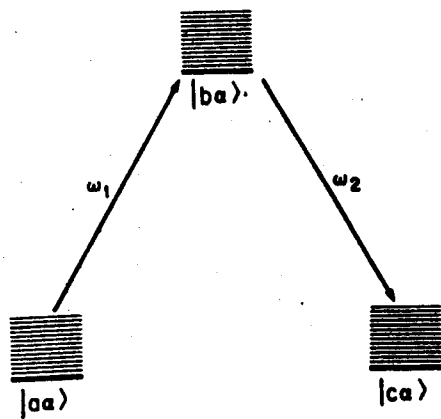
In the preceding lecture (TCMP) we have developed a general formalism suitable for the description of multiphoton processes of relaxing systems. The theoretical analysis is performed in two steps: The first is to express the quantities of interest in terms of an appropriate set of correlation functions. This step is formal and does not depend on the details of the system. The second step is to actually calculate the correlation functions using microscopic models. It is at this stage where the fine details of the specific system need to be considered. The problem considered in TCMP namely multiphoton processes of polyatomic molecules, is very complicated and as a result the second step could be treated only approximately using statistical arguments such as the random phase approximation. In this lecture we shall consider the simplest multiphoton problem (i.e. two-photon) where the solution may be carried out rigorously to the very end including the exact evaluation of the necessary correlation functions. As we shall see, the first (formal) step is strikingly similar to what was done in the preceding lecture although the problem to be considered is very different and the difference appears only in the second step of evaluating the correlation functions.

We consider a molecule having three levels (the "system") which undergoes near-resonance light scattering (RLS) and is collisionally perturbed by a low pressure bath of inert molecules which do not interact with the radiation field and with each other. The total Hamiltonian for the combined system + bath + the radiation field within the rotating-wave approximation, which describes the process $|a\omega_1\rangle \rightarrow |b\text{vac}\rangle \rightarrow |c\omega_2\rangle$ (see Fig. 1) is [1]

$$H = H_S + H_I + V \quad (1)$$

$$H_S = |a\rangle(\epsilon_a + \omega_1 - \frac{i}{2}\gamma_a)\langle a| + |b\rangle(\epsilon_b - \frac{i}{2}\gamma_b)\langle b| + |c\rangle(\epsilon_c + \omega_2 - \frac{i}{2}\gamma_c)\langle c| \quad (1a)$$

Fig.1 The molecular levelscheme for resonance light scattering



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

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

Here H_0 is the zero-order system Hamiltonian, H_1 describes the bath interacting with the system and V is the coupling of the system to the radiation field. ϵ_i , γ_i and $F_i(Q_B)$ denote the energy, inverse lifetime, and the interaction with the bath of our system molecule in the i 'th state $i=a,b,c$; $\omega_1(\omega_2)$ are the frequencies of the incoming (outgoing) photons. $\mu_{ij}(Q_B)$ is the dipole operator which depends on the coordinates (Q_B) of the N perturber bath molecules. For simplifying the notation we denote here the direct product states of the system + the radiation field $|a\omega_1\rangle$, $|bvac\rangle$ and $|c\omega_2\rangle$ simply by $|a\rangle$, $|b\rangle$ and $|c\rangle$ respectively. The system interacting with the bath will be described following the approach of JABLONSKI and BARANGER [2-4]. We place our "system" molecule in the center of a macroscopic sphere with volume Ω and assume that the bath consists of N perturber molecules whose interaction with the system is a sum of binary contributions (the binary interaction approximation, BIA), i.e.

$$F_i(Q_B) = \sum_v F_{iv}(Q_{Bv}) \quad , \quad i=a,b,c \quad (2)$$

where v stands for the v 'th bath particle. Denoting the eigenstates of $F_i(Q_B)$ by $|i\alpha\rangle$ ($i=a,b,c$) where α is the collection of all bath quantum numbers, with eigenvalues ϵ_α we immediately have within the BIA

$$|i\alpha\rangle = |i\rangle \prod_v |\alpha_v\rangle \quad , \quad \epsilon_\alpha = \sum_v \epsilon_{\alpha v} \quad (3)$$

The RLS cross section for this model system was solved in the past [5] assuming separation of time scales between the system and the bath, and its behavior in the two extremes of fast collision (impact) limit and slow collision (static) limit, relative to the line broadening, is well understood. In addition, a stochastic formulation of the problem was recently developed by TAKAGAHARA, HANAMURA and KUBO [6] which interpolates between the two limits. It is our purpose here to present the exact solution to the RLS problem defined by the Hamiltonian (Eq. 1) without invoking any further dynamical approximations.

The photon scattering cross section will be evaluated using the tetradic scattering formalism [7-9]. This approach is based on formulating scattering

theory in terms of density matrices in Liouville space (rather than wavefunctions in Hilbert space) and is particularly convenient for performing averages over irrelevant degrees of freedom. The tetradic T matrix T is defined [7-9] as

$$T(\omega) = V + V G(\omega) V \quad (4)$$

where V is the tetradic operator corresponding to V , i.e. $V=[V,]$, and $G(\omega)$ is the tetradic Green's operator for the entire system and bath

$$G(\omega) \equiv (\omega - L + i\eta)^{-1} = -i \int_0^{\infty} d\tau \tilde{G}(\tau) \exp(i\omega\tau). \quad (5)$$

Here $\tilde{G}(\tau) = \exp(-iL\tau)$ is the propagator in Liouville space and $L(L_1, L_0)$ being the Liouville operators corresponding to $H(H_1, H_0)$ i.e. $L=[H,]$ etc. For the subsequent manipulations we define also $G_0(\omega)$ and $\tilde{G}_0(\tau)$ by replacing L by L_0 in Eq. (5). The RLS cross section is given (up to a proportionality constant) by [1,6]

$$I(\omega_1, \omega_2) = -i \langle T(0)_{cc,aa} \rangle \equiv -i \sum_{\alpha\gamma} \langle \langle YY | T(0) | \alpha\alpha \rangle \rangle P(\alpha). \quad (6)$$

Here $\langle \dots \rangle$ 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.

$$\langle A_{ij,k1} \rangle \equiv \sum_{\alpha\beta} \langle \langle {}^{\alpha\beta} A_{ij,k1} | \alpha\alpha \rangle \rangle P(\alpha). \quad (7)$$

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

$$P(\alpha) = \exp(-\epsilon_{\alpha}/kT) / \text{Tr}(\exp(-F_{\alpha}/kT)). \quad (8)$$

Upon expansion of T to fourth order in V (which is the lowest order contributing to Eq. (6), see Fig. 3 of TCMP) we get

$$T(\omega) = V G_0(\omega) V G_0(\omega) V G_0(\omega) V, \quad (9)$$

which may be recast in the fully time-ordered form

$$T(\omega) = (-i)^3 \int_0^{\infty} d\tau \int_0^{\tau} d\tau_1 \int_0^{\tau_1} d\tau_2 \exp(i\omega\tau) V \tilde{G}_0(\tau - \tau_1) V \tilde{G}_0(\tau_1 - \tau_2) V \tilde{G}_0(\tau_2) V, \quad (10)$$

or alternatively

$$T(\omega) = (-i)^3 \int_0^{\infty} d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \exp[i\omega(\tau_1 + \tau_2 + \tau_3)] \cdot V \tilde{G}_0(\tau_1) V \tilde{G}_0(\tau_2) V \tilde{G}_0(\tau_3) V. \quad (11)$$

Utilizing the form of the radiative coupling V (Eq. (1c)) and making use of Fig. 2 of TCMP, 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 symmetry [8,9]

$$G_{ab,cd}(\omega) = -G_{ba,dc}^*(-\omega), \quad (12)$$

we see that there are only three independent paths. We thus have, using Eq.(11),

$$I(\omega_1, \omega_2) = \int_0^{\infty} d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 [I + II + III] + \text{C.C.} \equiv I_1 + I_2 + I_3 + \text{C.C.} \quad (13)$$

where

$$I = \exp[-i \omega_{cb} \tau_1 - i \omega_{ab} \tau_3 - \frac{\gamma_a}{2} \tau_3 - \frac{\gamma_b}{2} (\tau_1 + 2\tau_2 + \tau_3) - \frac{\gamma_c}{2} \tau_1] K_I(\tau_1, \tau_2, \tau_3), \quad (13a)$$

$$II = \exp[i \omega_{cb} \tau_1 - i \omega_{ab} \tau_3 - \frac{\gamma_a}{2} \tau_3 - \frac{\gamma_b}{2} (\tau_1 + 2\tau_2 + \tau_3) - \frac{\gamma_c}{2} \tau_1] K_{II}(\tau_1, \tau_2, \tau_3), \quad (13b)$$

and

$$III = \exp[i \omega_{cb} \tau_1 - i \omega_{ac} \tau_2 - i \omega_{ab} \tau_3 - \frac{\gamma_a}{2} (\tau_2 + \tau_3) - \frac{\gamma_b}{2} (\tau_1 + \tau_3) - \frac{\gamma_c}{2} (\tau_1 + \tau_2)] K_{III}(\tau_1, \tau_2, \tau_3). \quad (13c)$$

Here

$$K_I(\tau_1, \tau_2, \tau_3) = \sum_{\substack{\alpha\beta \\ \beta^*\gamma}} \langle\langle \overset{\gamma\gamma}{cc} | V(\tau_1 + \tau_2 + \tau_3) | \overset{\beta\beta}{cb} \rangle\rangle \langle\langle \overset{\gamma\beta}{cb} | V(\tau_2 + \tau_3) | \overset{\beta^*\beta}{bb} \rangle\rangle \\ \langle\langle \overset{\beta^*\beta}{bb} | V(\tau_3) | \overset{\alpha\beta}{ab} \rangle\rangle \langle\langle \overset{\alpha\beta}{ab} | V(0) | \overset{\alpha\alpha}{aa} \rangle\rangle P(\alpha) \quad (14a)$$

$$= \langle V_{ab}(0) V_{bc}(\tau_1 + \tau_2 + \tau_3) V_{cb}(\tau_2 + \tau_3) V_{ba}(\tau_3) \rangle,$$

$$K_{II}(\tau_1, \tau_2, \tau_3) = \sum_{\substack{\alpha\beta \\ \beta^*\gamma}} \langle\langle \overset{\gamma\gamma}{cc} | V(\tau_1 + \tau_2 + \tau_3) | \overset{\beta^*\gamma}{bc} \rangle\rangle \langle\langle \overset{\beta^*\gamma}{bc} | V(\tau_2 + \tau_3) | \overset{\beta^*\beta}{bb} \rangle\rangle \\ \langle\langle \overset{\beta^*\beta}{bb} | V(\tau_3) | \overset{\alpha\beta}{ab} \rangle\rangle \langle\langle \overset{\alpha\beta}{ab} | V(0) | \overset{\alpha\alpha}{aa} \rangle\rangle P(\alpha) \quad (14b)$$

$$= \langle V_{ab}(0) V_{bc}(\tau_2 + \tau_3) V_{cb}(\tau_1 + \tau_2 + \tau_3) V_{ba}(\tau_3) \rangle,$$

and

$$K_{III}(\tau_1, \tau_2, \tau_3) = \sum_{\substack{\alpha\beta \\ \beta^*\gamma}} \langle\langle \overset{\gamma\gamma}{cc} | V(\tau_1 + \tau_2 + \tau_3) | \overset{\beta^*\gamma}{bc} \rangle\rangle \langle\langle \overset{\beta^*\gamma}{bc} | V(\tau_2 + \tau_3) | \overset{\alpha\gamma}{ac} \rangle\rangle \\ \langle\langle \overset{\alpha\gamma}{ac} | V(\tau_3) | \overset{\alpha\beta}{ab} \rangle\rangle \langle\langle \overset{\alpha\beta}{ab} | V(0) | \overset{\alpha\alpha}{aa} \rangle\rangle P(\alpha), \quad (14c)$$

$$= \langle V_{ab}(0) V_{bc}(\tau_3) V_{cb}(\tau_1 + \tau_2 + \tau_3) V_{ba}(\tau_2 + \tau_3) \rangle.$$

In Eqs. (14) we have introduced the definitions

$$V(\tau) = \exp(iL_1\tau) V \exp(-iL_1\tau), \quad (15a)$$

$$V(t) = \exp(iH_1t) V \exp(-iH_1t), \quad (15b)$$

and

$$\langle V_{ab}(t_1) V_{bc}(t_2) V_{cb}(t_3) V_{ba}(t_4) \rangle \equiv \sum_{\alpha\beta\beta^*} P(\alpha) V_{ab}^{\alpha\beta}(t_1) V_{bc}^{\beta\gamma}(t_2) V_{cb}^{\gamma\beta^*}(t_3) V_{ba}^{\beta^*\alpha}(t_4). \quad (16)$$

We have also defined $\omega_{ab} \equiv \epsilon_a + \omega_1 - \epsilon_b$, $\omega_{cb} \equiv \epsilon_c + \epsilon_2 - \epsilon_b$ and $\omega_{ac} \equiv \omega_{ab} - \omega_{cb}$.

II. Microscopic evaluation of the correlation functions - the density expansion

In Section I we have expressed the RLS cross section in terms of the four-time N particle correlation functions K_i (Eqs. (14)). We are now in a position to evaluate K_i rigorously in terms of single particle correlation functions. Within the BIA (Eqs. (2) and (3)), $K_i(\tau_1, \tau_2, \tau_3)$ are factorized to a product of N identical factors i.e.

$$K_i(\tau_1, \tau_2, \tau_3) = |\mu_{ab}|^2 |\mu_{bc}|^2 k_i^N(\tau_1, \tau_2, \tau_3) \quad i=I, II, III \quad (17)$$

where k_i are four-time single-particle correlation functions defined in an analogous manner to K_i (Eqs. (14)), 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. We have also defined $\mu_{ab} \equiv \mu_{ab}(\infty)$ and $\mu_{bc} \equiv \mu_{bc}(\infty)$.

The evaluation of k_i will 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. (17)) corresponds to a density expansion of K_i (in powers of N/Ω). To that end we first note that $F_{ij}(Q_{B\gamma})$ $i=a,b,c$ are finite only in a small $Q_{B\gamma}$ region of microscopic dimensions. As a result, the bath states corresponding to $|a\rangle, |b\rangle$ and $|c\rangle$ 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 that [1-4]

$$|\langle a\alpha|V|b\alpha\rangle|^2 = 1 - O\left(\frac{1}{\Omega}\right), \quad (18a)$$

so that

$$\sum_{\beta \neq \alpha} |\langle a\alpha|V|b\beta\rangle|^2 = O\left(\frac{1}{\Omega}\right), \quad (18b)$$

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 $E_\alpha=E_\beta=E_{\beta'}=E_\gamma$ 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 (14)). 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

$$k_i(\tau_1, \tau_2, \tau_3) = 1 - \frac{1}{\Omega} W_i(\tau_1, \tau_2, \tau_3) + O\left(\frac{1}{\Omega^2}\right), \quad (19)$$

where W_i is $O(1)$. As a result then in the thermodynamic limit ($\Omega \rightarrow \infty, N \rightarrow \infty, N/\Omega$ finite) we get

$$K_i(\tau_1, \tau_2, \tau_3) = |\mu_{ab}|^2 |\mu_{bc}|^2 \left[1 - \frac{1}{\Omega} W_i(\tau_1, \tau_2, \tau_3)\right]^N + |\mu_{ab}|^2 |\mu_{bc}|^2 \exp\left(-\frac{N}{\Omega} W_i(\tau_1, \tau_2, \tau_3)\right), \quad i=I, II, III \quad (20)$$

where

$$W_I(\tau_1, \tau_2, \tau_3) = g_{aba}(\tau_3) + g_{cbc}^*(\tau_1) + g_{abc}(\tau_1 + \tau_2 + \tau_3) + g_{abc}^*(\tau_2) - g_{abc}(\tau_2 + \tau_3) - g_{abc}^*(\tau_1 + \tau_2), \quad (21a)$$

$$\begin{aligned}
W_{II}(\tau_1, \tau_2, \tau_3) &= g_{aba}(\tau_3) + g_{cbc}(\tau_1) + g_{abc}(\tau_2 + \tau_3) \\
&+ g_{abc}^*(\tau_1 + \tau_2) - g_{abc}(\tau_1 + \tau_2 + \tau_3) - g_{abc}^*(\tau_2) ,
\end{aligned}
\tag{21b}$$

and

$$\begin{aligned}
W_{III}(\tau_1, \tau_2, \tau_3) &= g_{abc}(\tau_3) + g_{abc}^*(\tau_1) + g_{aba}(\tau_2 + \tau_3) \\
&+ g_{cbc}(\tau_1 + \tau_2) - g_{abc}(\tau_1 + \tau_2 + \tau_3) - g_{abc}^*(-\tau_2) .
\end{aligned}
\tag{21c}$$

In Eqs. (20) and (21) we have expressed the four-time correlation functions (14) in terms of the three two-time correlation functions g_{aba} , g_{cbc} and g_{abc} , defined as follows:

$$\begin{aligned}
g_{aba}(\tau) &= \Omega [1 - \langle V_{ab}(0) V_{ba}(\tau) \rangle / \langle V_{ab}(0) V_{ba}(0) \rangle] \\
&= \frac{\Omega}{|\mu_{ab}|^2} \sum_{\alpha\beta} P(\alpha) |V_{ab}^{\alpha\beta}|^2 (1 - \exp(i\omega_{\beta\alpha}\tau)) ,
\end{aligned}
\tag{22a}$$

$$\begin{aligned}
g_{cbc}(\tau) &= \Omega [1 - \langle V_{cb}(0) V_{bc}(\tau) \rangle / \langle V_{cb}(0) V_{bc}(0) \rangle] \\
&= \frac{\Omega}{|\mu_{bc}|^2} \sum_{\alpha\beta} P(\alpha) |V_{cb}^{\alpha\beta}|^2 (1 - \exp(i\omega_{\beta\alpha}\tau)) .
\end{aligned}
\tag{22b}$$

and

$$\begin{aligned}
g_{abc}(\tau) &= \Omega [1 - \langle V_{ab}(0) V_{bc}(\tau) \rangle / \langle V_{ab}(0) V_{bc}(0) \rangle] \\
&= \frac{\Omega}{\mu_{ab} \mu_{bc}} \sum_{\alpha\beta} P(\alpha) V_{ab}^{\alpha\beta} V_{bc}^{\beta\alpha} (1 - \exp(i\omega_{\beta\alpha}\tau)) .
\end{aligned}
\tag{22c}$$

We should bear in mind that the Ω factor in Eqs. (22) simply cancels the $1/\Omega$ dependence of the sum so that $g(\tau)=0(1)$. Equations (13) together with Eqs. (20)-(22) constitute our final result for the RLS cross section. In conclusion we note the following:

1) Formal analogy with molecular multiphoton processes

In Section I we have expressed the RLS cross section $I(\omega_1, \omega_2)$ in terms of the four-time correlation functions K_i of the dipole operator (Eqs. (14)). It is interesting to note that K_I , K_{II} and K_{III} of the present paper correspond exactly to the same pathways that contributed to the I, II and III terms which appeared in the evaluation of $M^{(4)}$ in TCMP (see Eqs. 23 and Fig. 3 of TCMP). This is not surprising in view of Eqs. (10) and (11) which relate the tetradic T matrix (in fourth order) to $M^{(4)}$ of TCMP. (In this lecture we have used Eq. (11) whereas in TCMP we have used the alternative form 10). We should also note that the same relations hold also for higher order terms where $M^{(2n)}$ is associated with $T^{(2n)}$.

2) The relevant molecular information

The main result of the present formulation of RLS is that the four-time N-particle dipole correlation functions appearing in the general expressions for the RLS cross section (Eqs. (14)) may be rigorously expressed (within the BIA) in terms of the three two-time single particle correlation functions $g_{aba}(\tau)$, $g_{cbc}(\tau)$ and $g_{abc}(\tau)$ (Eqs. (22)). 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 [4,10,11] i.e.

$$S_{ab}(\omega_1) \propto \text{Re} \int_0^{\infty} d\tau \exp(i\omega_{ab}\tau) \exp[-\frac{N}{\Omega} g_{aba}(\tau)] . \quad (23a)$$

$$S_{bc}(\omega_2) \propto \text{Re} \int_0^{\infty} d\tau \exp(i\omega_{bc}\tau) \exp[-\frac{N}{\Omega} g_{cbc}(\tau)] . \quad (23b)$$

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 [4,10,11]. 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. The quantum mechanical evaluation of $g_{abc}(\tau)$ (22c) is a straightforward generalization of these methods.

3) Fast collisions - the impact limit

In the impact (Markovian) limit of fast collisions (relative to the line broadening) [1-6] we take $g(\tau)$ to be linear in τ . In this case the triple integrals [13] are factorized into three single integrals in τ_1 , τ_2 and τ_3 since

$$K_i = K_{i1}(\tau_1) K_{i2}(\tau_2) K_{i3}(\tau_3) \quad i=I,II,III \quad (24)$$

and we get [1]

$$I(\omega_1, \omega_2) = \frac{|\mu_{ab} \mu_{bc}|^2}{(\epsilon_a + \omega_1 - \epsilon_b)^2 + (\hat{\Gamma} + \frac{1}{2} \gamma_b)^2} \quad (25)$$

$$[2\pi\delta(\epsilon_a + \omega_1 - \epsilon_c - \omega_2) + \frac{4\hat{\Gamma}}{\gamma_b} \frac{\hat{\Gamma} + \frac{1}{2} \gamma_b}{(\epsilon_b - \epsilon_c - \omega_2)^2 + (\hat{\Gamma} + \frac{1}{2} \gamma_b)^2}] .$$

This result was previously derived by several authors [5,6,1]. $I(\omega_1, \omega_2)$ consists, in this case, of a narrow coherent Raman component and a broad incoherent redistribution term. Equation (25) holds in the impact limit when levels $|a\rangle$ and $|c\rangle$ are assumed similar, i.e. $F_a = F_c$ so that $g(\tau) = g_{aba}(\tau) = g_{cbc}(\tau) = g_{abc}(\tau) = \hat{\Gamma}\tau$ and we have also assumed $\gamma_a = \gamma_c = 0$ (long lifetime of $|a\rangle$ and $|c\rangle$). The Raman component is not broadened since the bath cannot dephase the a-c transition as we have assumed $F_a = F_c$ and we have ignored the lifetime broadening of these levels.

4) Slow collisions - the quasistatic limit

In the inverse (static) limit of slow collisions relative to the broadening, we need consider only the short-time behavior of $g(\tau)$ which is $g(\tau) = \Delta^2 \tau^2 / 2$

In this case (unlike the Markovian limit) the integrals (13) no longer factorize in τ_1 and τ_3 . Instead the natural variables for the integrations will now be $\tau_1 \pm \tau_3$ and τ_2 . Upon changing variables and performing two of the integrations we get [1]

$$I(\omega_1, \omega_2) = \frac{8\pi}{\gamma_b} \left[\int_0^\infty dy \exp(-\gamma_b y - \frac{1}{2} \Delta^2 y^2) \cos \omega_{ab} y \right] \delta(\epsilon_a + \omega_1 - \epsilon_c - \omega_2). \quad (26)$$

No redistribution terms appears in this case and the RLS spectrum consists of the Raman δ -function component whose absolute intensity is affected by the inhomogeneous line broadening.

5) The stochastic Gaussian model

The results of the stochastic Gaussian model of frequency modulation, developed by TAKAGAHARA, HANAMURA and KUBO [6] may be obtained from our general expressions by taking $F_a = F_c \neq F_b$, $\gamma_a = \gamma_c = 0$ and using the Brownian oscillator correlation function for $g(\tau)$ [10], i.e.

$$g_{aba}(\tau) = g_{cbc}(\tau) = g_{abc}(\tau) = \frac{\Delta^2}{\Gamma^2} (\exp(-\Gamma\tau) - 1 + \Gamma\tau). \quad (27)$$

6) On the validity of the factorization assumption

SZÖKE, CARLSTEN and RAYMER [12] (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 found to be strongly asymmetric with respect to the sign of the detuning (i.e. it depends on the sign of $(\epsilon_a + \omega_1 - \epsilon_b)$). This is in contrast to the Markovian expression (25). SCR then made a phenomenological assumption that Eq. (25) 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 $\hat{f}(\omega)$ to be a frequency dependent. The assumption of SCR is equivalent to solving for the tetradic T matrix [9] by invoking the factorization approximation [13] which amounts to setting

$$\langle T(0) \rangle = \langle V G_0(0) V G_0(0) V G_0(0) V \rangle \approx \langle V G_0(0) \rangle \langle V G_0(0) \rangle \langle V G_0(0) \rangle \quad (28)$$

where each $\langle G_0(0) \rangle$ is an ensemble-averaged reduced molecular propagator defined using an appropriate projection operator. Equation (28) is formally equivalent to the factorization (24). Using our general expressions (20,21) we note that the factorization assumption ((24) or (28)) is exact in the Markovian limit ($g(\tau)$ linear). However, once this is not the case, the integrand in (13) is no longer factorized in terms of τ_1, τ_2 and τ_3 . In fact, we have seen that in the static limit $\tau_1 + \tau_3$, $\tau_1 - \tau_3$ should be used as the natural times within the integrations [13]. It is thus formally inconsistent [13] to invoke the separation approximation far from the Markovian limit.

7) Extension to other problems

The present formulation applies as it stands also to collisional redistribution in two-photon absorption which is formally equivalent to RLS. It is also possible, using the same density expansion to solve rigorously for the n-time correlation functions, $n \geq 4$. This enables us to extend the unified theories to strong field phenomena, e.g. saturation in absorption and RLS. This extension was made recently [14].

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