Franck–Condon approach to collisional dephasing of spectral lines in liquids

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We consider the broadening of spectral lines in liquids at low temperatures. To lowest order in density, the relevant microscopic information is given by the spectral function $J(\omega)$ which is related to the single perturber spectrum. The line shape may then be calculated using $J(\omega)$. We have calculated $J(\omega)$ both classically and quantum mechanically for a collinear model and show quantitatively how different they are for typical experiments in cryogenic liquids. The absorption line shape $I(\Delta)$ is then evaluated using $J(\omega)$ and we discuss how sensitive it is to the details of $J(\omega)$. This gives us an estimate of the microscopic information content of collisionally broadened line shapes.

I. INTRODUCTION

The theory of collisional broadening of spectral lines is well established and has been widely used for the analysis of gas phase spectra. In these cases, the calculation is usually done using classical mechanics for the translational motion of perturbers.[1–7]

In recent years, there has been an increasing amount of information regarding the line broadening in liquids.[8–13] The theoretical studies done in this field are all classical. In addition, one usually invokes the Markovian and perturbative limits where the line is assumed to be a Lorentzian. It is our purpose in this paper to use a binary collinear collision model to treat the line broadening in liquids in a more precise way. We define a line broadening function $J(\omega)$ which is related to the spectrum of the absorber with a single perturber. This function contains all the microscopic information relevant for the line broadening to lowest order in density. $J(\omega)$ is then evaluated both quantum-mechanically (using Franck–Condon factors) and classically, and the calculations show significant differences for cryogenic liquids. We then evaluate the line shape $I(\Delta)$ using $J(\omega)$. We show how, in the Markovian limit, where the line is narrow compared with the inverse duration of a collision and assumes a Lorentzian form, $I(\Delta)$ is insensitive to the details of $J(\omega)$, and the experimental line shape contains very little microscopic information [namely $J(0)$]. On the other hand, when we approach the static limit, the information content of $I(\Delta)$ increases. The present calculations predict very significant quantum effects for line shapes in cryogenic liquids and provide a quantitative algorithm for their evaluation. In Sec. II, we present the line shape function and define the quantum and classical expressions for $J(\omega)$. In Sec. III, we reduce the results of Sec. II to the collinear case. In Sec. IV, we discuss the Markovian and static limits and finally in Sec. V we present the numerical calculations and analyze their significance.

II. THE LINE SHAPE FUNCTION

We consider a two-level absorber in a fluid. We assume pairwise additive interactions and the total Hamiltonian is

$$H = |a\rangle \tilde{H}_a \langle a| + |b\rangle (\omega_{ba} + \tilde{H}_b)\langle b| \ , \tag{1a}$$

where

$$\tilde{H}_a = T_s + \sum_i T_i + \sum_i V_a^{si}(Q_s - Q_i) + \sum_{i>j} V^{ij}(Q_i - Q_j) \tag{1b}$$

and

$$\tilde{H}_b = T_s + \sum_i T_i + \sum_i V_b^{si}(Q_s - Q_i) + \sum_{i>j} V^{ij}(Q_i - Q_j) \ . \tag{1c}$$

Here $|a\rangle$ and $|b\rangle$ are the two internal states of the absorber (s) with frequency ω_{ba}. T_s and T_i are the kinetic energy terms of the absorber and the ith perturber, respectively. V^{si} is the absorber–perturber interaction which depends on the internal state of the former ($V_a^{si} \neq V_b^{si}$) and V^{ij} is the interperturber interactions. $Q_r (r = i, j, s)$ denotes the position of the rth particle. Upon performing a cluster expansion[6,7] for the absorption line shape of this system we get that, to lowest order in perturber density, the normalized absorption line shape of this system $I(\Delta)$ may be expressed in terms of the *single perturber spectrum* $I_1(\Delta)$. If we consider a system consisting of the absorber plus a single perturber in a volume Ω and if we eliminate the center-of-mass motion, we have

$$H_a = -\frac{1}{2\mu}\frac{\partial^2}{\partial Q^2} + V_a(Q) \ , \tag{2a}$$

and

$$H_b = -\frac{1}{2\mu}\frac{\partial^2}{\partial Q^2} + V_b(Q) \ , \tag{2b}$$

where Q is the absorber-perturber relative separation, μ is their reduced mass, and we have taken $\hbar = 1$. The spectrum in this case has the form

$$I_1(\Delta) = \frac{1}{\pi}\,\mathrm{Re}\int_0^\infty d\tau \left[1 - \frac{1}{\Omega} g(\tau)\right]\exp(-i\Delta\tau) \ , \tag{3}$$

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where

$$\Delta = \omega_L - \omega_{ba} , \tag{4}$$

ω_L being the light frequency and

$$g(\tau) = \Omega \,\mathrm{Tr}\{[1 - \exp(iH_b\tau)\exp(-iH_a\tau)]\rho_a\} . \tag{5}$$

ρ_a is the canonical distribution of initial states

$$\rho_a = \frac{\exp(-H_a/k_B T)}{\mathrm{Tr}\exp(-H_a/k_B T)} , \tag{6}$$

and k_B is the Boltzmann constant.

The spectrum of our macroscopic system consisting of N perturbers in the volume Ω is then[2,5,6]

$$I(\Delta) = \frac{1}{\pi}\,\mathrm{Re}\int_0^\infty d\tau \exp[-i\Delta\tau - ng(\tau)] , \tag{7}$$

where $n = N/\Omega$ is the perturber density. Equation (7) together with Eq. (5) is our basic starting equation to be used in this paper. We should note that it is valid to lowest order in n and the general line shape will include terms $o(n^2)$, $o(n^3)$, etc. in the exponent which correspond to two-perturber, three-perturber spectra, etc. If we neglect the interperturber interactions [i.e., assume $V^{ij} = 0$ in Eq. (1a)], then we have the Anderson–Talman model and Eq. (7) becomes the exact solution of the line shape. An important point to note in Eq. (7) is that $g(\tau)$, which is related to the single perturber spectrum, is the only microscopic information relevant for our absorption line shape at low densities.

In order to calculate $g(\tau)$, we shall introduce the complete basis of eigenstates of H_a and H_b $\{|\alpha\rangle\}$ and $\{|\beta\rangle\}$ i.e.,

$$H_a|\alpha\rangle = E_\alpha|\alpha\rangle , \tag{8a}$$

$$H_b|\beta\rangle = E_\beta|\beta\rangle . \tag{8b}$$

Using Eqs. (5) and (8) we have

$$g(\tau) = \Omega\sum_{\alpha,\beta} P(\alpha)|\langle\alpha|\beta\rangle|^2[1 - \exp(i\omega_{\beta\alpha}\tau)] , \tag{9a}$$

where

$$\omega_{\beta\alpha} = E_\beta - E_\alpha , \tag{9b}$$

and

$$P(\alpha) = \langle\alpha|\rho_a|\alpha\rangle . \tag{9c}$$

The function $g(\tau)$ has the undesirable feature that it diverges for long times [$g(\tau)\to\infty$ as $\tau\to\infty$]. Therefore, for computational purposes, we shall slightly transform Eq. (7) using the identity[14]

$$g(\tau) \equiv g'(0)\tau + \int_0^\tau d\tau_1(\tau - \tau_1)g''(\tau_1) . \tag{10}$$

Here g' and g'' denote derivatives with respect to time $g' = dg/d\tau$, etc. and we have used the fact that $g(0) = 0$. We shall see that $g''(\tau)$ [unlike $g(\tau)$] is a well behaved function even at long times. We thus have

$$g''(\tau) = \Omega\sum_{\alpha,\beta} P(\alpha)|\langle\alpha|\beta\rangle|^2\omega_{\beta\alpha}^2\exp(i\omega_{\beta\alpha}\tau) \tag{11}$$

and

$$g'(0) = -i\Omega\sum_{\alpha,\beta} P(\alpha)|\langle\alpha|\beta\rangle|^2\omega_{\beta\alpha}$$

$$= -i\Omega\,\mathrm{Tr}(U\rho_a) = -i\Omega\sum_\alpha P(\alpha)\langle\alpha|U|\alpha\rangle , \tag{12}$$

where

$$U \equiv H_b - H_a = V_b(Q) - V_a(Q) . \tag{13}$$

Equations (11) and (12) allow us to calculate $g''(\tau)$ and $g'(0)$ quantum-mechanically using the eigenstates of H_a and H_b. It is common in the theories of line broadening to evaluate these quantities classically thus avoiding the necessity to solve the eigenvalue problems [Eq. (8)]. To that end we use the definition Eq. (5) and the relations

$$\exp(iH_b\tau)\exp(-iH_a\tau) = 1 + i\int_0^\tau U(\tau_1)\,d\tau_1 + (i)^2$$

$$\times\int_0^\tau d\tau_1\int_0^{\tau_1} d\tau_2 U(\tau_2)U(\tau_1) + \cdots \equiv \exp_-\left[i\int_0^\tau U(\tau_1)\,d\tau_1\right] . \tag{14}$$

where

$$U(\tau) = \exp(iH_a\tau)\,U\exp(-iH_a\tau) , \tag{15}$$

and $\exp_-$ is the negative time-ordered exponential. In the classical limit, the time-ordered exponential [Eq. (14)] reduces to an ordinary exponential [since the various operators in Eq. (14) commute]. We then have

$$g_c(\tau) = \Omega\,\mathrm{Tr}\left\{\left[1 - \exp\left[i\int_0^\tau U(\tau_1)\,d\tau_1\right]\right]\rho_a\right\} = \Omega\int d\mathbf{P}_0$$

$$\times\int d\mathbf{Q}_0\left\{1 - \exp\left[i\int_0^\tau d\tau_1\, U(\tau_1|\mathbf{P}_0,\,\mathbf{Q}_0)\right]\right\}\rho_a(\mathbf{P}_0,\,\mathbf{Q}_0) . \tag{16}$$

In Eq. (16), $\mathbf{P}_0$ and $\mathbf{Q}_0$ are the initial phase-space coordinates of our perturber, and integration over these coordinates is the classical analog of the quantum trace. Also, $U(\tau|\mathbf{P}_0,\,\mathbf{Q}_0)$ is the classical analog of the operator $U(\tau)$ defined in Eq. (15) and is obtained by solving the classical Hamiltonian equations with the initial conditions $\mathbf{P}_0$ and $\mathbf{Q}_0$, using the Hamiltonian H_a. Hereafter, we shall use the subscripts c and Q to denote classical or quantum quantities. Using Eq. (16) we have

$$g_c''(\tau) = \Omega\int d\mathbf{P}_0\int d\mathbf{Q}_0\left[-i\frac{\partial U(\tau|\mathbf{P}_0,\,\mathbf{Q}_0)}{\partial\tau} + U^2(\tau|\mathbf{P}_0,\,\mathbf{Q}_0)\right]$$

$$\times\exp\left[i\int_0^\tau U(\tau_1|\mathbf{P}_0,\,\mathbf{Q}_0)\,d\tau_1\right]\rho_a(\mathbf{P}_0,\,\mathbf{Q}_0) , \tag{17}$$

and

$$g_c'(0) = -i\Omega\iint d\mathbf{P}_0\,d\mathbf{Q}_0\,U(0|\mathbf{P}_0,\,\mathbf{Q}_0)\rho_a(\mathbf{P}_0,\,\mathbf{Q}_0)$$

$$= -i\Omega\int d\mathbf{Q}\,U(\mathbf{Q})\exp[-V_a(\mathbf{Q})]/k_B T\Big/$$

$$\int d\mathbf{Q}\exp(-V_a(\mathbf{Q})/k_B T) . \tag{18}$$

In conclusion, we have shown how the spectrum may be expressed in terms of the single perturber quantities $g''(\tau)$ and $g'(0)$ i.e.,

$$I(\Delta)=\frac{1}{\pi}\,\mathrm{Re}\int_0^\infty d\tau\exp[-i\Delta\tau-ng'(0)\tau]\times\exp\left[-n\int_0^\tau d\tau_1(\tau-\tau_1)g''(\tau_1)\right], \tag{19}$$

where quantum-mechanically $g'(0)$ and $g''(\tau)$ are given by Eqs. (11) and (12), whereas classically they are given by Eqs. (17) and (18). [Note that $g'(0)$ is pure imaginary so that $ng'(0)$ is merely a static level-shift.]

III. COLLINEAR EVALUATION OF THE LINE BROADENING

In our subsequent calculations, we shall use a collinear model for the bindary collision. Collinear models are often used in the theories of line broadening since the information content of experimental line shapes is so much averaged that a detailed three-dimensional model is usually superfluous. The theoretical effort involved in a collinear calculation is, of course, much smaller than in a detailed calculation. The reduction to one dimension of the quantum expression [Eq. (9a)] is done in Appendix A. To that end we need to introduce an effective cross section σ and a frequency of collisions f, where

$$f=\sigma n\bar{v} \tag{20}$$

and $\bar{v}$ is a mean velocity. We then have

$$ng_Q(\tau)=2\pi f\int_0^\infty\frac{d\epsilon}{k_BT}\exp(-\epsilon/k_BT)\int_{-\infty}^\infty d\omega|\langle\chi_\epsilon^a|\chi_{\epsilon+\omega}^b\rangle|^2\times[1-\exp(i\omega\tau)]. \tag{21}$$

Here the subscript Q denotes that $g(\tau)$ is evaluated quantum mechanically. χ_ϵ^a, $\chi_{\epsilon'}^b$ are the radial wave functions corresponding to the states $|\alpha\rangle$ and $|\beta\rangle$ with energies ϵ and ϵ' respectively, i.e.,

$$\left[-\frac{1}{2\mu}\frac{d^2}{dQ^2}+V_a(Q)\right]\chi_\epsilon^a=\epsilon\chi_\epsilon^a, \tag{22a}$$

$$\left[-\frac{1}{2\mu}\frac{d^2}{dQ^2}+V_b(Q)\right]\chi_{\epsilon'}^b=\epsilon'\chi_{\epsilon'}^b. \tag{22b}$$

The functions χ_ϵ^a, $\chi_{\epsilon'}^b$ are taken to be energy normalized

$$\langle\chi_\epsilon^a|\chi_{\epsilon'}^a\rangle=\langle\chi_\epsilon^b|\chi_{\epsilon'}^b\rangle=\delta(\epsilon-\epsilon'). \tag{23}$$

Similarly, the classical collinear model yields (see Appendix B)

$$ng_c(\tau)=f\int_{-\infty}^\infty dt_0\int_0^\infty\frac{d\epsilon}{k_BT}\exp(-\epsilon/k_BT)\times\left\{1-\exp\left[i\int_0^\tau d\tau_1\,U(\tau_1|\epsilon,\,t_0)\right]\right\}, \tag{24}$$

where we are using the energy ϵ, and the time at the classical turning point t_0, to describe the initial conditions (instead of Q_0, P_0) and $dP_0\,dQ_0=d\epsilon\,dt_0$.

We shall now introduce the auxiliary functions

$$\langle U\rangle\equiv i\frac{n}{f}g'(0)=i\frac{g'(0)}{\sigma\bar{v}}, \tag{25a}$$

$$\tilde{J}(\tau)\equiv\frac{ng''(\tau)}{f}=\frac{g''(\tau)}{\sigma\bar{v}}, \tag{25b}$$

and

$$J(\omega)=\frac{1}{2\pi}\int_{-\infty}^\infty d\tau\exp(-i\omega\tau)\tilde{J}(\tau). \tag{26}$$

The line shape function now assumes the final form

$$I(\Delta)=\frac{1}{\pi}\,\mathrm{Re}\int_0^\infty d\tau\exp[-i(\Delta-f\langle U\rangle)\tau]\times\exp\left[-f\int_0^\tau d\tau_1(\tau-\tau_1)\tilde{J}(\tau_1)\right]. \tag{27}$$

We note that $\tilde{J}(\tau)$ [or $J(\omega)$], $\langle U\rangle$, and f are the only quantities necessary for evaluating the line shape. It can be easily shown that

$$\langle U\rangle=PP\int d\omega\frac{J(\omega)}{\omega}, \tag{28}$$

so that $\langle U\rangle$ may be also calculated using $J(\omega)$. To summarize, using Eqs. (21), (24), and (25), we have, quantum mechanically,

$$J_Q(\omega)=2\pi\int_0^\infty\frac{d\epsilon}{k_BT}\exp(-\epsilon/k_BT)\omega^2|\langle\chi_\epsilon^a|\chi_{\epsilon+\omega}^b\rangle|^2, \tag{29a}$$

$$\langle U\rangle_Q=2\pi\int_0^\infty\frac{d\epsilon}{k_BT}\exp(-\epsilon/k_BT)\langle\chi_\epsilon^a|U|\chi_\epsilon^a\rangle, \tag{29b}$$

and classically,

$$\tilde{J}_c(\tau)=\int_{-\infty}^\infty dt_0\int_0^\infty\frac{d\epsilon}{k_BT}\exp(-\epsilon/k_BT)\left[-i\frac{\partial U(\tau|\epsilon,\,t_0)}{\partial\tau}+U^2(\tau|\epsilon,\,t_0)\right]\exp\left[i\int_0^\tau U(\tau_1|\epsilon,\,t_0)\,d\tau_1\right], \tag{30a}$$

$$\langle U\rangle_c=\int_{-\infty}^\infty dt_0\int_0^\infty\frac{d\epsilon}{k_BT}\exp(-\epsilon/k_BT)\,U(0|\epsilon,\,t_0)=\sqrt{\frac{2\pi\mu}{k_BT}}\int dQ\exp[-V_a(Q)/k_BT]\,U(Q). \tag{30b}$$

Equations (27)–(30) were used in the calculations presented in Sec. V.

IV. THE MARKOVIAN AND STATIC LIMITS

We shall now present the limiting forms of our line shape function [Eq. (27)] in the limits of fast and slow collisions (relative to the line broadening). The Markovian (fast collision) limit is obtained by taking the long time behavior of Eq. (27), i.e.,

$$f\int_0^\tau d\tau_1(\tau-\tau_1)\tilde{J}(\tau_1)\to\left[f\int_0^\infty d\tau_1\tilde{J}(\tau_1)\right]\cdot\tau-f\int_0^\infty d\tau_1\tau_1\tilde{J}(\tau_1). \tag{31}$$

We then have upon substituting Eq. (31) into Eq. (27)

$$I(\Delta)\simeq\frac{\exp(\eta')}{\pi}\left[\cos\eta''\cdot\frac{\Gamma}{(\Delta+\tilde{\Delta})^2+\Gamma^2}+\sin\eta''\cdot\frac{\Delta+\tilde{\Delta}}{(\Delta+\tilde{\Delta})^2+\Gamma^2}\right], \tag{32}$$

where

$$\Gamma = f\mathrm{Re}\int_0^\infty d\tau\,\tilde{J}(\tau) = \pi f J(\omega=0)\,, \tag{33a}$$

$$\tilde{\Delta} = -f\langle U\rangle + f\mathrm{Im}\int_0^\infty d\tau\,\tilde{J}(\tau)\,, \tag{33b}$$

and

$$\eta \equiv \eta' + i\eta'' \equiv f\int_0^\infty d\tau\,\tau\,\tilde{J}(\tau)\,. \tag{33c}$$

Usually in the Markovian limit, $|\eta| \ll 1$ so that the second (dispersive) term in Eq. (32) may be neglected and the line assumes a simple Lorentzian form, whose full width at half-maximum is $2\pi f J(0)$.

In the static limit (slow collisions), we neglect the kinetic energy terms in Eq. (5) and get

$$g(\tau) \to \Omega\,\mathrm{Tr}\{[1-\exp(iU\tau)]\rho_a\}\,, \tag{34}$$

so that

$$J_Q(\tau) = 2\pi\int_0^\infty \frac{d\epsilon}{k_B T}\langle\epsilon|\,U^2\exp(iU\tau)|\,\epsilon\rangle\exp(-\epsilon/k_B T) \tag{35}$$

and

$$J_c(\tau) = \int_{-\infty}^{\infty} dt_0\int_0^\infty \frac{d\epsilon}{k_B T}\exp(-\epsilon/k_B T)\,U^2\exp(iU\tau)$$

$$= \sqrt{\frac{2\pi\mu}{k_B T}}\int dQ\exp[-V_a(Q)/k_B T]\,U^2(Q)\exp(iU(Q)\tau]\,. \tag{36}$$

V. NUMERICAL CALCULATIONS

We have used an exponential repulsive potential model for the absorber-perturber interaction:

$$V_a = A_1\exp(-Q/L)\,, \tag{37a}$$

$$V_b = A_2\exp(-Q/L)\,. \tag{37b}$$

Here Q is the absorber-perturber separation and L is the range of the interaction. The potential V_b can be viewed as a shifted V_a potential, by writing

$$V_b = A_1\exp[-(Q-\bar{Q})/L]\,, \tag{38a}$$

where the shift $\bar{Q}$ is

$$\bar{Q} = L\log(A_2/A_1)\,. \tag{38b}$$

For these potentials, $J_Q(\omega)$ [Eq. (29a)] was evaluated using the following analytical expression for the Franck–Condon factors[15]

$$\langle\chi^a_\epsilon|\chi^b_{\epsilon+\omega}\rangle = -\mu L^2\frac{C}{C+1}(1+C)^{-ik_1L}$$

$$\times\frac{[\sinh(2\pi Lk_1)\sinh(2\pi Lk_2)]^{1/2}}{\sinh[\pi L(k_1+k_2)]\sinh[\pi L(k_1-k_2)]}$$

$$\times{}_2F_1\left[1+i\frac{k_1+k_2}{2}\,;\;1+i\frac{k_1-k_2}{2}\,;\;2\,;\;C/(C+1)\right], \tag{39a}$$

where

$$k_1 = \sqrt{2\mu\epsilon}\,, \tag{39b}$$

$$k_2 = \sqrt{2\mu(\epsilon+\omega)}\,, \tag{39c}$$

$$C = (A_2/A_1) - 1\,, \tag{39d}$$

and ${}_2F_1$ is a hypergeometric function. The dimensionless parameter C [Eq. (39d)] is a measure of the difference between the two potentials, i.e., of the interaction responsible for the line broadening (when $C=0$ there is no line broadening).

The classical line broadening function $\tilde{J}_c(\tau)$ [Eq. (30)], for these potentials was obtained using the following expression for $U(\tau)$[16]

$$U(\tau|\,\epsilon,\;t_0) = V_b - V_a = C\epsilon\,\mathrm{sech}^2[\sqrt{(\epsilon/2\mu L^2)}(\tau-t_0)]\,. \tag{40}$$

Our spectra were calculated by substituting Eq. (39a) in Eq. (29) and Eq. (40) in Eq. (30) for the quantum and classical case respectively, and using Eq. (27). The static level shift $\langle U\rangle$ may be also evaluated from Eq. (28). A standard Fast Fourier Transform program was used in these computations.

We have studied a two-level absorber in liquid nitrogen ($T=77\,^\circ$K), in liquid neon ($T=27\,^\circ$K) and in liquid helium ($T=4.2\,^\circ$K). For each case we varied the magnitude of the interaction responsible for the line broadening by varying C [Eq. (39d)]. The various parameters were chosen as follows: The two-level absorber was assumed to have the mass of N_2 ($M_1=28$) and μ was taken to be the reduced mass of the absorber and the solvent (N_2, Ne, and He with masses $M_2=28$, 20, and 4) resulting in $\mu=14$, 11.7, and 3.5 respectively. L was taken to be 0.2 Å and f the frequency of binary collisions was given the typical value of 0.8×10^{13} Hz.[9,11] Figure 1(a) shows the quantum-mechanical and classical $J(\omega)$ for the two-level absorber in N_2, whereas Fig. 1(b) gives the corresponding line shapes. Figures 2 and 3 contain the same quantities for the other solvents Ne and He, respectively. Figure 4 presents the full width at half-maximum of $J(\omega)$ for the various cases studied. More precise characteristics of the calculated line shapes are given in Table I. For each calculation we give the full width at half maximum of the line shape $\hat{\Gamma}$ the position of its maximum $\hat{\Delta}$ (where $\hat{\Delta}=0$ denotes the position of the unperturbed line) and an asymmetry parameter a, defined as follows: let $\Delta_\pm$ denote the values of Δ for which

$$I(\Delta_\pm) = \tfrac{1}{2}I(\hat{\Delta})\,, \tag{41a}$$

where $\Delta_+ > \hat{\Delta}$ and $\Delta_- < \hat{\Delta}$, $\Delta_+(\Delta_-)$ is the half-width at half maximum to the blue (red) of $\hat{\Delta}$. The asymmetry parameter a is then defined by the following expression[8]

$$a = \left|\frac{\hat{\Delta}-\Delta_-}{\hat{\Delta}-\Delta_+}\right| - 1\,, \tag{41b}$$

where for a symmetric line, $a=0$.

The following points should now be made:

(1) The duration of collision τ_c is given by the inverse spectral width of $J(\omega)$ which in all cases is of the order of 0.01 ps. By decreasing the line broadening interaction C, we are decreasing the observed linewidth and, when C is small enough, the resulting line is narrower than the duration of collision τ_c (Markovian limit)

$$\hat{\Gamma}\tau_c \ll 1. \tag{42}$$

Our calculations for $C=0.65\times10^{-2}$ are always in the Markovian limit and, as C increases, we tend towards the static limit, although the condition $\hat{\Gamma}\tau_c \gg 1$ is never

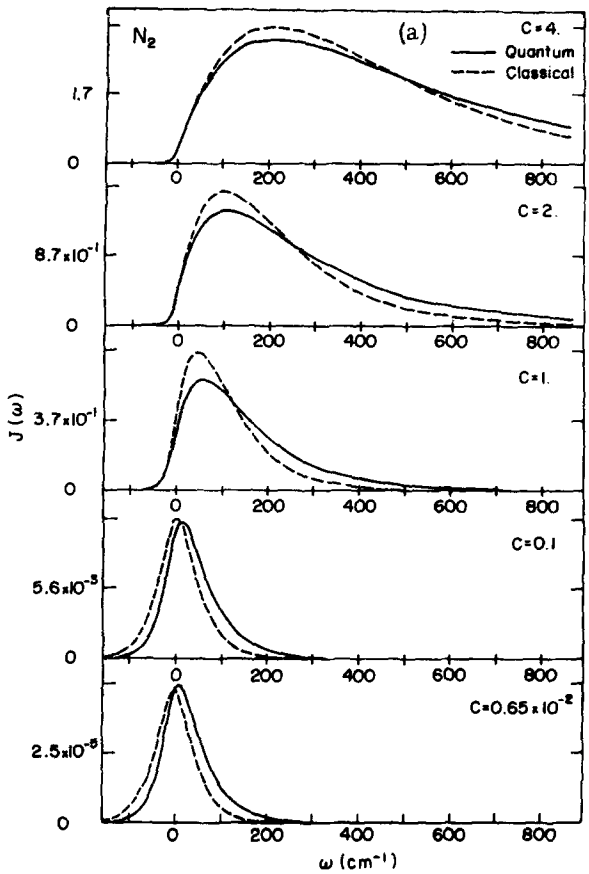

FIG. 1. Quantum and classical calculations for a two-level absorber in N_2, for several values of the interaction strength parameters C [Eq. (39d)]. $T=77°K$, $\mu=28\times28/(28+28)=14$, $f=0.8\times10^{13}$ Hz, $L=0.2$ Å. (a) The single perturber spectral function $J(\omega)$; (b) the absorption line shape $I(\Delta)$.

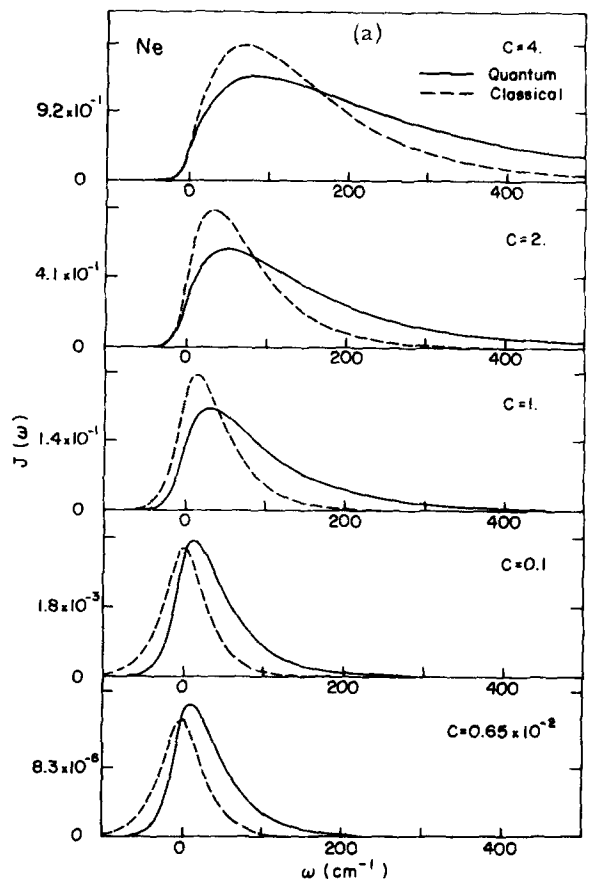

FIG. 2. Quantum and classical calculations for a two-level absorber in Ne, for several values of the interaction strength parameters C [Eq. (39d)]. $T=27°K$, $\mu=20\times28/(20+28)=11.7$, $f=0.8\times10^{13}$ Hz, $L=0.2$ Å. (a) The single perturber spectral function $J(\omega)$; (b) the absorption line shape $I(\Delta)$.

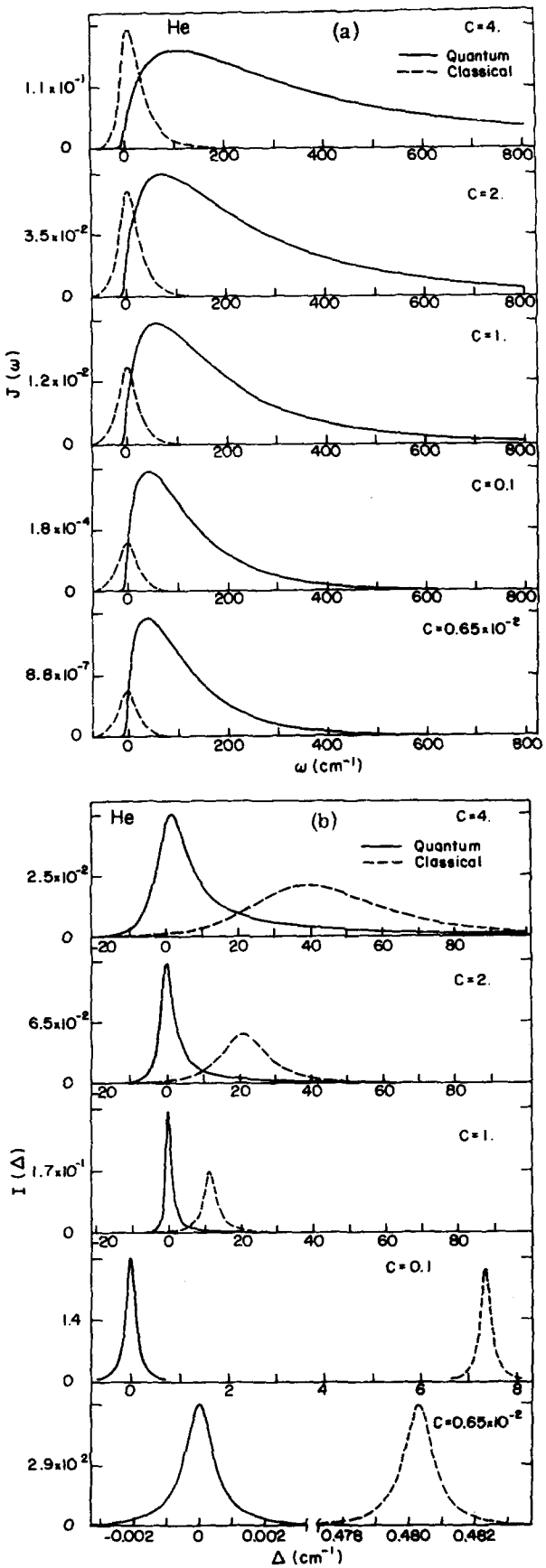

FIG. 3. Quantum and classical calculations for a two-level absorber in He, for several values of the interaction strength parameters C [Eq. (39d)]. $T=4.2°K$, $\mu=4\times28/(4+28)=3.5$, $f=0.8\times10^{13}$ Hz, $L=0.2$ Å. (a) The single perturber spectral function $J(\omega)$; (b) the absorption line shape $I(\Delta)$.

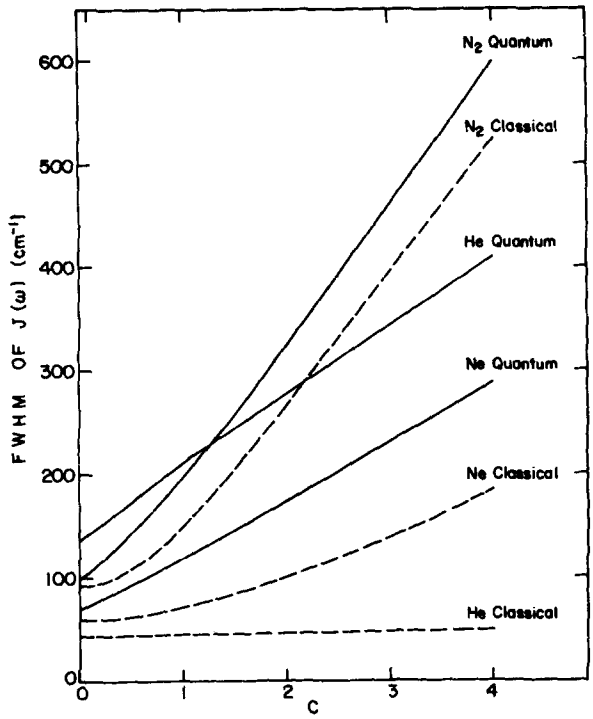

FIG. 4. Quantum and classical full width at half maximum values of $J(\omega)$ for a two-level system in N_2, Ne, He. Other parameters same as in Figs. (1)–(3).

realized for our parameters so that we do not reach the static limit. In the strong coupling case ($C=4$), the line is broad and asymmetric and does not tend towards a Gaussian as implied by simple stochastic models.[14]

(2) The line shapes all exhibit a blue shift ($\hat{\Delta}>0$). This arises since we are using a purely repulsive potential and take $A_2>A_1$ so that U is always positive. By including an attractive part in the potential we may get a red shift, as is usually the case for solvent shifts.

(3) The quantum effects on $J(\omega)$ and $I(\Delta)$ increase dramatically as we go from N_2 to Ne and to He, since in this direction the mass of the perturber becomes smaller and the temperature decreases. N_2 is almost classical and the difference between the quantum and classical results is insignificant. For He, the classical calculations of $J(\omega)$ are very different from the quantum ones. Thus, when studying line broadening in cryogenic liquids[13] it is necessary to perform quantum Franck–Condon type calculations of the line broadening.

(4) The microscopic information content of $I(\Delta)$ is very small in the Markovian limit (small C), since then $I(\Delta)$ depends essentially on $J(0)$ [Eq. (33a)] and is insensitive to the details of $J(\omega)$. Only for the larger values of C, $I(\Delta)$ contains significant microscopic information.

(5). Finally we would like to make a comment regarding the Markovian perturbative limit where we expand $J(0)$ to second order in U. This is the conventional model used in the field of vibrational dephasing.[8–11] From Eqs. (29a) and (33a) we get

$$\Gamma_Q^{(2)}=2\pi^2 f\int_0^\infty \frac{d\epsilon}{k_B T}\exp(-\epsilon/k_B T)\left|\langle\chi_\epsilon^a|U|\chi_\epsilon^a\rangle\right|^2 . \qquad (43)$$

TABLE I. Width, shift, and asymmetry of the line shapes.

Solvent	C	FWHM $\hat{\Gamma}$ (cm^{-1}) quantum	FWHM $\hat{\Gamma}$ (cm^{-1}) classical	Shift $\hat{\Delta}$ (cm^{-1}) quantum	Shift $\hat{\Delta}$ (cm^{-1}) classical	Asymmetry a (%) quantum	Asymmetry a (%) classical
N_2	0.6510^{-2}	0.08	0.08	0	4.1	0	0
	0.1	2.7	3.0	0	10	−3.6	+22.0
	1	97.0	118.0	24	60	−47.6	−43.0
	2	213.0	241.5	80	100	−58.7	−55.0
	4	452.0	488.0	176	192	−58.7	−56.0
Ne	0.6510^{-2}	0.02	0.01	0	2.2	0	0
	0.1	0.8	0.9	0	5.4	0	+19.0
	1	35.5	53.0	8	44.0	−22.5	−20.0
	2	92.0	119.0	32	76.0	−49.2	−38.8
	4	210.5	245.0	96	72.0	−54.0	−43.2
He	0.6510^{-2}	0.001	0.001	0	0.5	0	0
	0.1	0.2	0.3	0	7.4	0	0
	1	1.9	4.0	0	11.5	−27	0
	2	4.7	14.5	0.6	22.0	−24	−3.0
	4	11.5	40.0	1.3	40.0	−47	0

Note that Eq. (43) is given in terms of a single basis set χ_ϵ^a only. Using the matrix element[16,17]:

$$\langle \chi_\epsilon^a | U | \chi_\epsilon^a \rangle = \frac{C}{\pi} \sqrt{2\mu L^2 \epsilon} , \tag{44}$$

we have

$$\Gamma_Q^{(2)} = 4fC^2 \mu L^2 k_B T . \tag{45}$$

In the classical case, substitution of Eq. (14) to second order in U in Eq. (5) leads to the Markovian perturbative width

$$\Gamma^{(2)} = n\Omega \int_0^\infty d\tau \, \mathrm{Tr}\{U(\tau) U(0) \rho_a\} . \tag{46}$$

Reduction to a collinear model (Appendix B) results in

$$\Gamma_c^{(2)} = f \int_0^\infty d\tau \int_0^\infty \frac{d\epsilon}{k_B T} \exp(-\epsilon/k_B T) \int_{-\infty}^{+\infty} dt_0 \, C^2 ; \tag{47}$$

$$\epsilon^2 \, \mathrm{sech}^2\left[\sqrt{\frac{\epsilon}{2\mu L^2}} (\tau + t_0)\right] \mathrm{sech}^2\left(\sqrt{\frac{\epsilon}{2\mu L^2}} t_0\right) .$$

After integration, we find that in this case

$$\Gamma_c^{(2)} = \Gamma_Q^{(2)} . \tag{48}$$

If $|a\rangle$ and $|b\rangle$ are taken to be the $v=0$ and $v=1$ states of a harmonic oscillator with coordinate R and if we assume[9]

$$V = \exp[-(Q - \gamma R)/L] , \tag{49}$$

so that

$$V_a = \langle 0 | \exp(\gamma R/L) | 0 \rangle \exp(-Q/L) , \tag{50a}$$

and

$$V_b = \langle 1 | \exp(\gamma R/L) | 1 \rangle \exp(-Q/L) , \tag{50b}$$

then we have to second order in γ,

$$C \simeq \frac{\gamma^2}{2mL^2\omega_0^2} . \tag{51}$$

Here m is the reduced mass of the oscillator, ω_0 is its frequency, and

$$\gamma = \frac{m_1}{m_1 + m_2} \tag{52}$$

(m_1 and m_2 are the masses of the two atoms and the perturber is assumed to approach the side of atom 2). We then get the result

$$\Gamma_Q^{(2)} = \Gamma_c^{(2)} = \frac{\mu\gamma^4}{m^2\omega_0^2 L^2} k_B T , \tag{53}$$

which is the commonly used expression for vibrational dephasing. Our choice $C = 0.65 \times 10^{-2}$ is the value obtained from Eq. (51) for self-broadening in N_2. Since $\Gamma = \pi f J(0)$, we get an interesting conclusion from Eq. (48). In the perturbative limit $C \to 0$, $J(0)$ will be the same classically and quantum mechanically. We see that even for He where $J_Q(\omega)$ is very different from $J_c(\omega)$, still $J_c(0) = J_Q(0)$. In the Markovian perturbative limit, we may therefore evaluate the line shape using classical mechanics and even if $J(\omega)$ is totally wrong, the Markovian line shape will be the same! This is a specific property of our exponential repulsive interaction Eq. (37) and we do not expect it to hold for arbitrary V_a and V_b.

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APPENDIX A: REDUCTION TO A COLLINEAR MODEL-QUANTUM

Assuming spherically symmetric interaction potentials V_a and V_b, we have

$$|\alpha\rangle = |\epsilon_a\rangle |lm\rangle , \tag{A1a}$$

$$|\beta\rangle = |\epsilon_b\rangle |lm\rangle . \tag{A1b}$$

$$\langle r\theta\phi | \alpha \rangle = \chi_{\epsilon l}^a(r) \, Y_l^m(\theta, \phi) , \tag{A2a}$$

$$\langle r\theta\phi | \beta \rangle = \chi_{\epsilon l}^b(r) \, Y_l^m(\theta, \phi) , \tag{A2b}$$

where r, θ, ϕ are the spherical coordinates in a

spherical container of volume $\Omega = \frac{4}{3}\pi R^3$, $\epsilon_i (i = a, b)$ is the relative translational energy and l, m are angular quantum numbers. Orthonormalization of the spherical harmonics Y_l^m reduces the sum in $g(\tau)$ [Eq. (9a)] to a sum over initial and final states that have identical angular momentum quantum numbers l and m:

$$\sum_{\alpha,\beta} \to \sum_{\epsilon_a,\epsilon_b} \sum_{l,m} . \tag{A3}$$

We shall approximate the three-dimensional sums by taking only the term $l = 0$ and replacing $\sum_{l,m}$ by an effective cross section in the following way. We write $P(\alpha)$ as a product

$$P(\alpha) = P(\epsilon_a) P_l , \tag{A4}$$

where $P(\epsilon_a)$ is the probability that an initial state has energy ϵ_a and P_l the probability that it has angular momentum l. Let us call L the maximum angular quantum number for a perturber in volume Ω with energy ϵ_a (or wave number k_a), i.e., $L \equiv k_a R$. Normalization condition on P_l, $\sum_{l=0}^{L} (2l+1) P_l = 1$ leads to $P_l \simeq 1/L^2$. Now we write

$$ng(\tau) = n\Omega \sum_{\epsilon_a,\epsilon_b} P(\epsilon_a) \sum_{lm} \frac{1}{L^2} |\langle \epsilon_a | \epsilon_b \rangle|^2 [1 - \exp(i\omega\tau)] , \tag{A5}$$

where we have adopted the notation $\omega = \epsilon_b - \epsilon_a$. Since the perturbers contributing to the line broadening have impact parameters $b \ll R$, we define an effective cross section $\sigma_Q = 4\pi b_{\max}^2$ corresponding to a maximum impact parameter $b_{\max}$ beyond which perturbers are ineffective in broadening the line. We can then define a corresponding maximum angular momentum quantum number $l_{\max} = k_a b_{\max}$ so that

$$\sum_{l,m} P_l = \sum_{l=0}^{l_{\max}} (2l+1) P_l \simeq \frac{l_{\max}^2}{L^2} = \frac{b_{\max}^2}{R^2} = \frac{\sigma_Q}{4\pi R^2} . \tag{A6}$$

In this simplified treatment we assume that the overlap $\langle \epsilon_a | \epsilon_b \rangle$ does not depend on l and we choose its value for $l = 0$. We can thus reduce our three-dimensional problem to a collinear problem and express $g(\tau)$ in terms of one dimensional overlap integrals

$$ng(\tau) = n\sigma_Q \frac{R}{3} \sum_{\epsilon_a,\epsilon_b} P(\epsilon_a) |\langle \epsilon_a | \epsilon_b \rangle|^2 [1 - \exp(i\omega\tau)] . \tag{A7a}$$

For large volume Ω, we replace the discrete sums by integrals

$$\sum_{\epsilon} \to \int d\epsilon \, \rho(\epsilon) , \tag{A7b}$$

where $\rho(\epsilon)$ is the density of states at energy ϵ. This density of states corrsponds to that of a "one dimensional" box of radius R and takes the value

$$\rho(\epsilon) = \mu R / \pi k , \tag{A8}$$

where k is the wave number, $k = \sqrt{2\mu\epsilon}$. Now

$$ng(\tau) = n\sigma_Q \frac{R}{3} \int_0^\infty d\epsilon_a \rho(\epsilon_a) P(\epsilon_a) \int_0^\infty d\epsilon_b \rho(\epsilon_b) \times |\langle \epsilon_a | \epsilon_b \rangle|^2 [1 - \exp(i\omega\tau)] \tag{A9}$$

and

$$P(\epsilon_a) = \exp(-\epsilon_a / k_B T) \Big/ \int_0^\infty d\epsilon \, \rho(\epsilon) \exp(-\epsilon / k_B T)$$

$$= \exp(-\epsilon_a / k_B T) \Big/ \frac{\mu R}{\pi} \sqrt{\frac{\pi k_B T}{2\mu}} , \tag{A10}$$

k_B is the Boltzmann constant.

By expressing each quantity as a function of R in Eq. (A9), and assuming a box normalization for the radial wavefunctions (i.e., their dependence in R is like $R^{-1/2}$), we readily verify that $ng(\tau)$ does not depend on the dimensions of the container. For further convenience, we will adopt an energy normalization so that the radial wave functions will have the asymptotic form

$$\chi_\epsilon \sim \sqrt{\frac{2\mu}{\pi k}} \frac{1}{r} \cos(kr + \delta) . \tag{A11}$$

Multiplying and dividing χ_ϵ^a and χ_ϵ^b by the normalization factor $\sqrt{(2\mu/\pi k_i)}$ $(i = a, b)$, we finally get the following collinear form:

$$ng(\tau) = f 2\pi \int_0^\infty \frac{d\epsilon}{k_B T} \times \exp(-\epsilon / k_B T) \int_0^\infty d\epsilon' |\langle \chi_\epsilon^a | \chi_{\epsilon'}^b \rangle|^2 [1 - \exp(i\omega\tau)] , \tag{A12}$$

where f is the frequency of collisions

$$f = (1/12) n\sigma_Q \sqrt{(k_B T / 2\pi\mu)} \tag{A13}$$

and χ_ϵ^a and $\chi_{\epsilon'}^b$ are energy normalized functions. The factor 2π is introduced so that classical and quantum widths be identical in the Markovian limit for an exponential potential. Equation (A12) leads to Eq. (21) with the substitution $\epsilon' = \epsilon + \omega$.

APPENDIX B: REDUCTION TO A COLLINEAR MODEL—CLASSICAL

Let us assume a collinear approach of the perturber within an effective cylindrical cross section σ_c. Integration over $\mathbf{Q}_0$ and $\mathbf{P}_0$ is then reduced

$$d\mathbf{P}_0 \, d\mathbf{Q}_0 \to \sigma_c \, dQ_0 \, dP_0 . \tag{B1}$$

We choose to express the integrals in $g(\tau)$ [Eq. (16)] in terms of the variable ϵ, initial energy, and t_0, time at the classical turning point. Then

$$dP_0 = \sqrt{\frac{\mu}{2\epsilon}} \, d\epsilon , \tag{B2a}$$

$$dQ_0 = \sqrt{\frac{2\epsilon}{\mu}} \, dt_0 . \tag{B2b}$$

For collisions coming from the right, we need to integrate t_0 from $-\infty$ to $+\infty$ and P_0 from 0 to $+\infty$, since negative times for t_0 mean that the corresponding perturber goes away from the absorber and never collids with it. Considering also collisions coming from the left gives a factor 2. We thus have

$$ng(\tau) = n\Omega\sigma_c 2\int_{-\infty}^{+\infty} dt_0 \int_0^{\infty} d\epsilon \exp(-\epsilon/k_B T)\left\{1 - \exp\left[i\int_0^{\tau} U(\tau_1)\,d\tau_1\right]\right\} \Big/ 2\int_{-\infty}^{\infty} dQ_0 \int_0^{\infty} \sqrt{\frac{\mu}{2\epsilon}} \exp(-\epsilon/k_B T)\,d\epsilon$$

$$= f\int_{-\infty}^{\infty} dt_0 \int_0^{\infty} \frac{d\epsilon}{k_B T} \exp(-\epsilon/k_B T)\left\{1 - \exp\left[i\int_0^{\tau} U(\tau_1)\,d\tau_1\right]\right\}, \tag{B3}$$

where f has the dimensions of a frequency of collision and takes the value

$$f = n\sigma_c\sqrt{(2k_B T/\pi\mu)}\ . \tag{B4}$$

Equation (B4) is identical to Eq. (24).

[1](a) P. W. Anderson, Phys. Rev. **86**, 809 (1952); (b) P. W. Anderson and J. D. Talman, Bell Telephone System, Technical Publication No. 3117 (1956).
[2]M. Baranger, Phys. Rev. **111**, 481 (1958).
[3]U. Fano, Phys. Rev. **131**, 259 (1963).
[4]A. Ben-Reuven, Adv. Chem. Phys. **33**, 235 (1975).
[5]J. Szudy and W. E. Baylis, J. Quant. Spectrosc. Radiat. Transfer **15**, 641 (1975).
[6](a) A. Royer, Phys. Rev. A **6**, 1741 (1972); (b) A. Royer, Phys. Rev. A **7**, 1078 (1973); (c) A. Royer, Phys. Rev. A **22**, 1625 (1980); (d) R. G. Breene, Jr., *Theories of Spectral Line Shapes* (Wiley, New York, 1981).
[7]S. Mukamel, Phys. Rev. A (in press).
[8]A. Laubereau and W. Kaiser, Rev. Mod. Phys. **50**, 607 (1978).
[9]S. F. Fischer and A. Laubereau, Chem. Phys. Lett. **35**, 6 (1975); *ibid.* **55**, 189 (1978).
[10](a) C. B. Harris, M. Auwater, and S. M. George, Phys. Rev. Lett. **44**, 737 (1980); (b) S. M. George, H. Auweter, and C. B. Harris, J. Chem. Phys. **73**, 5573 (1980).
[11](a) D. W. Oxtoby, Adv. Chem. Phys. **40**, 1 (1979); (b) D. W. Oxtoby (preprint).
[12]C. K. N. Patel, A. C. Tam, and R. J. Kerl, J. Chem. Phys. **71**, 1470 (1979).
[13](a) I. Messing, B. Raz, and J. Jortner, J. Chem. Phys. **66**, 2239 (1977); (b) For a recent review see N. Schwentner, E. Eckhard Koch, and J. Jortner in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, to be published), Vol. 3.
[14]R. Kubo, in *Fluctuation Relaxation and Resonance in Magnetic Systems*, edited by Ter-Haar (Oliver and Boyd, Edinburgh, 1962).
[15]L. Eno, G. G. Balint-Kurti, and R. Saktreger, Chem. Phys. **29**, 453 (1978).
[16]D. Rapp and T. Kassal, Chem. Rev. **69**, 61 (1969).
[17]J. M. Jackson and N. F. Mott, Proc. R. Soc. London Ser. A **137**, 703 (1932).