Collisional broadening and spectral line shape of an entire rotational band

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The impact approximation is applied to the classical binary collision operator making it possible to derive an expression for the dipole correlation function for real systems in a form which is computationally tractable and contains no adjustable parameters. Trajectory calculations are performed (in order to evaluate the microscopic expression for the relaxation parameter in the correlation function) for the system CO in dense Ar gas. Comparison is made with experimental data and excellent agreement is found for certain densities when a quantum correction is included. At higher densities (i.e., $\rho^{-1/3} <$ "the range of the potential") one approximation is not valid and comparison with experiment illustrates this point.

I. INTRODUCTION

The connection between spectral lineshapes and time correlation functions is well known.[1,2] The usefulness of this connection as a means of predicting line shapes depends upon the availability of theoretical techniques to predict molecular motion. Even for a very dilute gas where only isolated binary interactions contribute the dynamics often cannot be solved exactly, although there have been many approximation methods developed quantum mechanically,[3] semiclassically,[4(a)] and classically.[5] Alternative and popular approaches to the approximation of molecular motion are the so-called relaxation time models.[6,7] Instead of attempting to calculate directly the result of molecular collisions the relaxation time models make basic assumptions about the motion (often time involving at least one adjustable parameter) and from there calculate the time correlation function and the spectrum. Common models in the current literature include the extended rotational diffusion models called J and M diffusion originally derived for linear molecules by Gordon.[8] Also derived for rotational diffusion is the Fokker–Planck model of Fixman and Rider[6] which appears to work better than Gordon's,[9] but the parameter in the latter has been microscopically calculated.[10] The purpose of this paper will be to introduce an approximation which makes it relatively easy to calculate the relaxation parameter in the rotational correlation function, by numerically following the results of classical binary collisions.

The necessary definitions and theory are summarized in Sec. II, where use is made of techniques used by Chandler[10] to derive J diffusion for hard sphere systems. The impact approximation is made to evaluate the binary collision operator, making it possible to arrive at expressions which are relatively straightforward to evaluate. The sample calculation is discussed in Sec. III and the results in Sec. IV. The comparison of the results is made in the frequency (rather than time) domain since this is the experimental observable and it is therefore desirable to compare well with it, although a time-domain comparison is also made. This theory is classical, so one immediate problem when comparing to experiment is that the predicted spectrum will show little asymmetry while the observed will be quite asymmetric. A quantum mechanical correction motivated by Schofield[11] and correct to order[12] $\hbar$ is applied to the classical calculation. This correction correctly accounts for much of the observed asymmetry. The range of validity of these calculations as well as some applications to other types of relaxation phenomena is discussed in Sec. V. Calculations are planned for vibrational dephasing.

II. THEORY

A. The binary collision expansion

We consider an argument which parallels the one used by Chandler for hard spheres.[10] Consider a system made up of N particles with pairwise additive potentials. The Hamiltonian for this system can be decomposed into two parts

$$H = H_0 + H_1 , \tag{2.1}$$

where H_0 denotes the Hamiltonian for the system when the particles do not interact and

$$H_1 = \sum_{i>j} U_{ij}(\mathbf{r}_i - \mathbf{r}_j) \tag{2.2}$$

with $U_{ij}(\mathbf{r}_i - \mathbf{r}_j)$ being the interaction potential between a particle at position $\mathbf{r}_i$ and a particle at $\mathbf{r}_j$. The propagation of a dynamical variable A is given by[13]

$$A(t) = e^{Lt}A(t=0) , \tag{2.3}$$

where L is related to Liouville's operator by a factor of $\sqrt{-1}$. Taking the Laplace transform of Eq. (2.3) gives

$$A(s) = [s - L]^{-1}A \equiv G(s)A , \tag{2.4}$$

where $G(s)$ is the resolvent operator for the N-particle system. The dependence of $G(s)$ on the coordinates and momentum of the N-particle system has not been explicitly shown. If one decomposes L into two parts (L_0 and L_1) corresponding to the Hamiltonian H_0 and H_1, one can write $G(s)$ as[14]

$$G(s) = G_0(s)[1 - L_1 G_0(s)]^{-1} , \tag{2.5}$$

where $G_0(s) = [s - L_0]^{-1}$ is the resolvent operator for propagation in the system with no interactions, that is, for free-particle streaming. The binary collision operator $T_\alpha(s)$ is defined by[15]

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$$G_\alpha(s) = G_0(s,\alpha) - G_0(s,\alpha)T_\alpha(s)G_0(s,\alpha), \tag{2.6}$$

where α denotes a pair of molecules, and $G_0(s,\alpha)$ the two-particle free-streaming resolvent operator. Expanding the denominator in Eq. (2.5) and using Eq. (2.6) gives the well-known binary collision expansion[15(a)]

$$G(s) = G_0(s) - \sum_\alpha G_0(s)T_\alpha(s)G_0(s) + \sum_\alpha \sum_{\alpha\neq\gamma} \times G_0(s)T_\alpha(s)G_0(s)T_\gamma(s)G_0(s) + \cdots, \tag{2.7}$$

where γ, like α, represents a pair of particles. The impact approximation can now be made which neglects incomplete collisions, and thereby $T_\alpha(s)$ is replaced by its value at zero frequency T_α

$$T_\alpha(s) \xrightarrow{\text{impact approx}} T_\alpha. \tag{2.8}$$

Since the impact approximation considers only complete collisions, once a pair of α particles have collided and then undergone free-particle motion they will not as an isolated pair undergo a second collision with each other. Thereby,

$$T_\alpha G_0(s) T_\alpha = 0. \tag{2.9}$$

The resolvent operator can now be written as

$$G(s) \approx \left(s - L_0 + \sum_\alpha T_\alpha\right)^{-1}. \tag{2.10}$$

In arriving at this expression for $G(s)$, Eqs. (2.9), (2.8), and (2.7) are combined in a straightforward manner. Comparing Eq. (2.10) with Eq. (2.4) shows that in the impact approximation

$$L \approx L_0 - \sum_\alpha T_\alpha. \tag{2.11}$$

This result will be used in Sec. II. B.

B. Approximation for the memory function

The memory function of a time correlation function is defined in terms of its Laplace transform as[16]

$$C(s) \equiv [s + M(s)]^{-1}. \tag{2.12}$$

Following Mori, Zwanzig, and others[16] it can be shown that the memory function for a dynamical variable u can be written as

$$M_u(t) = \langle Bu\, e^{Bt} Bu \rangle, \tag{2.13}$$

where B denotes $(1-P_u)L$ and is a projection operator defined by its operation on arbitrary x as

$$P_u x \equiv \langle u \cdot x \rangle u / \langle u \cdot u \rangle. \tag{2.14}$$

Specializing Eq. (2.13) to the case where u is the dipole moment[17] operator, it can readily be shown[17] in the case of a rigid rotor that u has a constant magnitude, and so $(1-P_u)L$ u equals the value of du/dt at $t=0$, which will be denoted by ω. Introducing a double bracket notation, one has

$$M_u(t) = \langle \omega^2 \rangle \langle\langle e^{Bt} \rangle\rangle, \tag{2.15}$$

where $\langle\langle A \rangle\rangle = \langle \omega \cdot A\omega \rangle / \langle \omega^2 \rangle$. For exponential operators one has (e.g., Ref. 18)

$$\langle\langle e^{Bt} \rangle\rangle = \exp \sum_{n=1}^{\infty} K_u t^n / n!, \tag{2.16}$$

where the K_u are cumulants, for example, $K_1 = \langle\langle B \rangle\rangle$ and $K_2 = \langle\langle B^2 \rangle\rangle - \langle\langle B \rangle\rangle^2$. The memory function Eq. (2.15) can now be rewritten[10] using Eq. (2.16)

$$M_u(t) = M_u^0(t) \exp \sum_{n=1}^{\infty} (K_n - K_n^0) t^n / n!, \tag{2.17}$$

where $M_u^0(t)$ is the zero interaction memory function (i.e., ideal gas) and the K_n^0 is the zero interaction cumulant.[19] Comparing Eqs. (2.11), (2.16), and (2.18) and noting that u and ω are perpendicular vectors (since $|u|$ is constant) one obtains for the $n=1$ term in Eq. (2.17)

$$M_u(t) \approx M_u^0(t) \exp\left(-\left\langle\left\langle \sum_\alpha T_\alpha \right\rangle\right\rangle t\right) \equiv M_u^0(t) \exp\left(\frac{-t}{\tau}\right). \tag{2.18}$$

Cumulants vanish[18] if any one of the quantities then become uncorrelated; this implies that keeping only the $n=1$ term from Eq. (2.18) is equivalent to considering only binary collisions and neglecting correlations between successive collisions.[10] The T_α between absorbing and perturbing molecules gives the same results for each α, and so one can write

$$\frac{1}{\tau} = \left\langle\left\langle \sum_\alpha T_\alpha \right\rangle\right\rangle = (N-1)\frac{\langle \omega_1 \cdot T_{12}\omega_1 \rangle}{\langle \omega_1^2 \rangle}. \tag{2.19}$$

ω_1 is the angular velocity of a given rigid rotor 1, and T_{12} is the binary collision operator for collision between particles 1 and 2, while T_α is T_{1i}, $i = 2, \ldots, N$. The Laplace transform of Eq. (2.18) is

$$M_u(s) \approx M_u^0(s + \tau^{-1}). \tag{2.20}$$

Inserting this into Eq. (2.12) gives after some manipulation

$$C_u(s) \approx \frac{C_u^0(s+\tau^{-1})}{1 - \tau^{-1} C_u^0(s+\tau^{-1})}, \tag{2.21}$$

where $C_u^0(s+\tau^{-1})$ is the Laplace transform of the free rotor dipole correlation function shifted by τ^{-1} along the s axis. The parameter τ^{-1} must now be calculated and Eq. (2.21) will be the approximate dipole correlation function for real systems.

C. The binary collision operator

The binary collision operator for hard spheres, both rough and smooth, is well known.[10,15] A derivation is given in Ref. 15(b) and the extension to molecules within the impact approximation is described here. From Eq. (2.6) it is seen that the binary collision operator $T_\alpha(s)$ obeys the following equation

$$G_\alpha(s) - G_0(s) = -G_0(s)T_\alpha(s)G_0(s). \tag{2.22}$$

In time–space the left-hand side of Eq. (2.22) operating on the angular velocity of the rotor ω is

$$(e^{Lt} - e^{L_0 t})\omega = 0, \text{ (no collision)} \tag{2.23a}$$

for times t such that there has been no collision. For times t long enough for there to have been a completed

collision one would have instead of Eq. (2.23a)

$$(e^{\mathcal{L}t} - e^{\mathcal{L}_0 t})\omega = \omega' - \omega, \text{ (complete collision)}, \quad (2.23b)$$

where ω' is the post-collision value of ω. Equations (2.23a) and (2.23b) can be combined into a single equation, Eq. (2.25) below, as follows. If one supposes that a collision has occurred when the distance of closest approach (r_c) has been reached one can[15] require, as a condition for a collision in time t, that $z_c < z < z_c + v_\alpha t$, when z is the coordinate along the relative velocity direction v_α in the usual collisional impact parameter coordinate system and z_c is the value of z at the "instant of collision." If $\Theta(x)$ is a step function equal to unity for $x > 0$ and zero otherwise (the following function is unity when z lies inside the above interval and zero otherwise)[15(a)]

$$\Theta(z_c + v_\alpha t - z) - \Theta(z_c - z) = \int_0^t d\tau v_\alpha \delta(z_c + v_\alpha \tau - z). \quad (2.24)$$

One can now combine Eqs. (2.23a), (2.23b), and (2.24) into a single expression valid for all time

$$(e^{\mathcal{L}t} - e^{\mathcal{L}_0 t})\omega = \left(\int_0^t d\tau\, v_\alpha \delta(z_c + v_\alpha \tau - z)\right)(\omega' - \omega). \quad (2.25)$$

Simple manipulation and the insertion of the operator S_α which replaces the precollision momentum with the post-collision value gives[15(b),15(c)]

$$(e^{\mathcal{L}t} - e^{\mathcal{L}_0 t})\omega = \int_0^t d\tau\, e^{\mathcal{L}_0 \tau}[\delta(z_c - z)v_\alpha(S_\alpha - 1)]e^{\mathcal{L}_0(t-\tau)}\omega. \quad (2.26)$$

Transforming Eq. (2.26) back to Laplace transform space, using the convolution theorem and comparing with Eq. (2.22), one sees that

$$T_\alpha = -v_\alpha \delta(z_c - z)(S_\alpha - 1). \quad (2.27)$$

This expression enables one to immediately write the relevant integral for this calculation[20]

$$\langle \omega \cdot T_\alpha(s)\omega \rangle \approx \langle \omega \cdot T_\alpha \omega \rangle = -\int d\mathbf{p} \int d\mathbf{r}\, d\Omega v_\alpha \times f(\mathbf{p}) g(\mathbf{r}, \Omega)\delta(z_c - z)\omega \cdot \frac{\omega' - \omega}{V}, \quad (2.28)$$

where p, r, and Ω represent all of the momenta, relative translational coordinates and internal coordinates such as Euler angles, $f(p)$ is the Boltzman momentum distribution function, $g(\mathbf{r}, \Omega)$ is the coordinate probability distribution function, V is the volume, and ω is the precollisional angular momentum, while ω' is the postcollisional one (apart from a constant factor of the moment of inertia). For a rigid rotor atom Ω involves only the angle between the axis of the rotor and the line connecting the atom with the center of mass of the rotor. For a vibrating molecule Ω would also include the vibrational phase. The only difference between Eq. (2.28) and the hard-sphere result is the dependence of the collision distance on initial conditions and the need to use exact numerical dynamics in order to evaluate $\omega' - \omega$.

When evaluated for the rigid rotor-atom system Eq. (2.28) becomes, using cylindrical coordinates for $d\mathbf{r}(= b db d\phi dz$, where ϕ is the angle about the z axis)

$$\langle \omega \cdot T_\alpha \omega \rangle = -\int 2\pi b db d\mathbf{p}\, d\Omega v_\alpha f(\mathbf{p}) g(r_c, \Omega)\omega \cdot \frac{\omega' - \omega}{V}. \quad (2.29)$$

III. CALCULATIONS

The functional form of the intermolecular potential to be used as well as the coordinates necessary to describe the motion have been discussed extensively elsewhere.[4(b)] The potential was of the form

$$U(R, \gamma) = 4\epsilon\{(\sigma/R)^{12} - (\sigma/R)^6[1 + a_p P_2(\cos\gamma)]\}, \quad (3.1)$$

where the R is the distress between the atom and the center of mass of the rotor, and γ denotes the angle the axis of the rotor makes with R. The parameters used were $\epsilon = 110$ °K, $\sigma = 3.59$ Å; a_p calculated from Eq. (3.3) of Ref. 4(a) using the parallel and perpendicular polarizabilities in Ref. 21, was 0.16, for CO–Ar. The molecular parameter for the rotor used was[22] r_e (the distance between the carbon and oxygen atoms) = 1.13 Å; the moment of inertia and rotational constant were evaluated from this r_e.

The radial distribution function used was that calculated from the standard first order density correction

$$g_{12}(\mathbf{r}, \Omega) = e^{-\beta U(\mathbf{r}, \Omega)}\left(1 + \rho \int d\mathbf{r}_3 d\Omega f_{13} f_{23}\right), \quad (3.2)$$

where $f_{mn} = (e^{-\beta U(r_{mn}, \Omega)} - 1)$, and the other terms have their usual definitions, $\beta = 1/kT$ and $U(r_{12})$ is given by Eq. (3.1) for CO–Ar. The Ar–Ar potential parameters in Eq. (3.1) are $a_p = 0$, $\epsilon = 124$ °K, and $\sigma = 3.42$ Å. One should note that although this correction was used, its effect was negligible on the 14 A calculation and was much less than the numerical error in τ^{-1} at 143 A.

IV. RESULTS

In order to calculate the spectra, Eq. (2.29) must be evaluated to obtain τ^{-1}. The integral was evaluated numerically using Monte Carlo techniques. The points needed for the Monte Carlo evaluation were generated by choosing random initial conditions in action-angle variables for the rotor atom then integrating the equations of motion numerically, in Cartesian coordinates, through the collision to find the postcollisional rotational angular frequency vector.[4(b)] The equations of motion were integrated in Cartesian coordinates after choosing the initial conditions in action-angle variables.[4(b)] The numerical error in this evaluation of τ^{-1} was about 10%.

Comparison with experiment at this point would be poor because the classical correlation function is even in time and real. Therefore, it will produce a spectra without a large asymmetry,[23] while the experimental one is asymmetric. The imaginary part of a time correlation function is simply related to the real part[11] for quantum mechanical systems by the following formula

$$\mathrm{Im}C(t) = -\tan[(\hbar/2kt)\partial/\partial t]\mathrm{Re}C(t), \quad (4.1)$$

where Im and Re refer to the imaginary and real parts

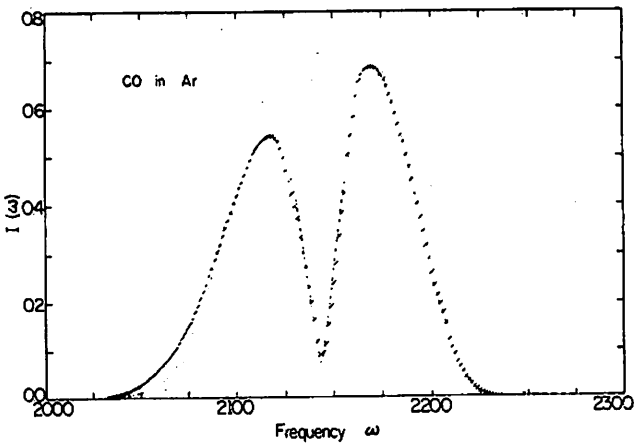

FIG. 1. Experimental and theoretical infrared spectra of CO in Ar at 14 A. τ^{-1} from Eq. (2.19) is 6.4×10^{-12} s for this density. The experimental points are denoted by -x-x-, the theoretical spectrum without quantum correction by small dashes, and the theoretical spectrum with quantum correction by large dashes.

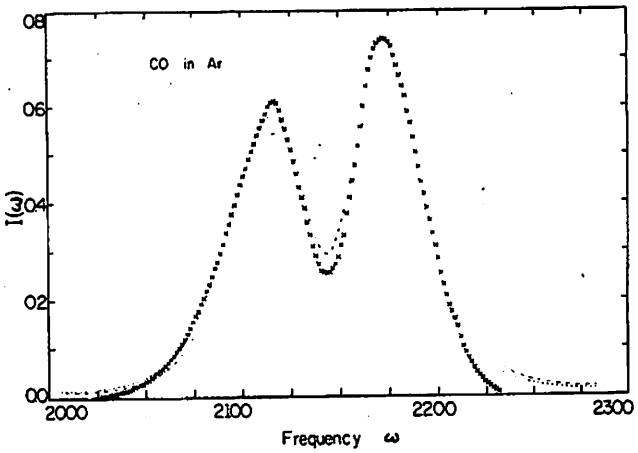

FIG. 3. Experimental and theoretical infrared spectrum of CO in Ar at 143 A. τ^{-1} is 6.3×10^{-13} s. Symbols are the same as in Fig. 1.

of the time-correlation function, respectively. The relationship of Eq. (4.1) leads naturally to an approximation of the imaginary part simply by using the real classical correlation function; this leads to the following expression for the Fourier transform of the quantum correlation functions[24]

$$C_{qm}(\omega)\approx e^{-\hbar\omega/2kT}C_{Cl}(\omega). \tag{4.2}$$

yielding thereby a physically expected Boltzmann factor for the P and R branches. There have been other approximations suggested[12] but Eq. (4.2) is correct to order $\hbar$, with higher order terms contributing little for this system. This approximation has been tested on other infrared spectra with success.[24]

The spectrum predicted at two densities are plotted in Figs. 1 and 3, along with that predicted by the correction given by Eq. (4.2) and the experimental data points[25] taken from dense gas measurements. The real part of the time correlation function predicted is compared with the Fourier transform of the experimental spectrum in Fig. 2.

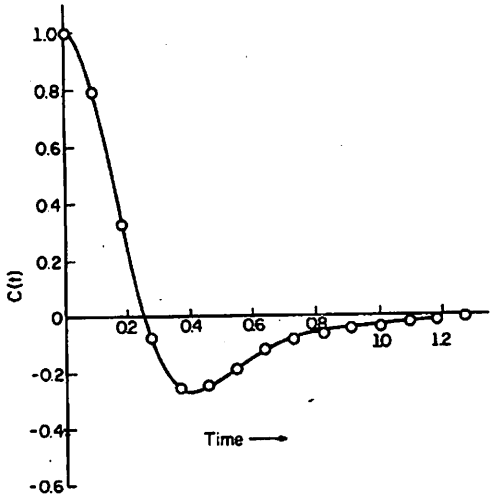

FIG. 2. The real part of the time correlation function obtained from the spectra in Fig. 1, plotted vs the time in picoseconds. The experimental points are indicated by circles and theoretical curve by a solid line.

V. CONCLUSION

The quantum corrected spectrum is shown in Fig. 1. The real part of the time-correlation function obtained from the spectrum and shown in Fig. 2 shows good agreement between the theory and experiment, there being no adjustable parameters. The observed spectrum, which is a low resolution envelope, is essentially the same in the wings of the band at densities of 14, 143, 364 and 510 A.[25] Similar behavior was found in our calculated spectrum at low densities. The main function of the pressure broadening of the entire band is the filling in of the center of the band, where there was no absorption at low pressures. This portion of the center of the spectrum was matched well by the theory, as in Fig. 1 for 14 A Ar. The quantum correction given by Eq. (4.1) accounts for much of the asymmetry: The R-branch envelope matches almost exactly except in the wings, the P branch does not match as well, so the experimental data does not fit Eq. (4.1). Other experiments[24] have shown excellent agreement with Eq. (4.1) so the present rather old experimental data may be somewhat suspect in this respect.

At higher density of 143 A of Ar a discrepancy appears at the band center. Here, one must evaluate some of the approximations made in view of the physical situation. The cross sections for rotational energy transfer are expected to be large enough that the impact parameters which give rise to appreciable probability can be comparable with $\rho^{-1/3}$ at 143 A, since $\rho^{-1/3}=7$ Å there. When this is the case the impact approximation must begin to break down, since the rotor is essentially now never undergoing free rotation. The results at 143 A are shown in Fig. 3, and in fact, the agreement near the band center is not nearly so good as at 14 A.

The independent binary collision (IBC) approximation may also account for some of the discrepancy. At higher densities the probability of finding more than two particles within the range of the potential becomes appreciable (the "range" would be the distance at which the potential is at least several percent of the rotational energy). Under these conditions the concept of isolated and independent binary collisions is no longer valid. A check of the IBC approximation has been made[9] for the hard-sphere fluid by a comparison to molecular dynamic studies in Ref. 10. It was found that the IBC expression has errors in the rotational time-correlation function of about 10% at liquid densities. (For the hard-sphere fluid, the impact approximation itself is automatically fulfilled since hard-sphere collisions are impulsive.)

The approach used in this paper may well work at higher densities for calculations involving only a dynamical variable related to the vibration motion of a molecule. The vibrational coordinate changes much more rapidly than translational or rotational motion and except at very close distances the potential varies much more slowly as a function of the vibrational coordinate. The impact approximation should remain valid to higher densities as should the IBC approximation. In order to test this idea a calculation of vibrational phase relaxation is planned.

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