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An improved quasistatic line-shape theory: The effects of molecular motion on the line wings

Q. Ma

Department of Applied Physics, Columbia University and Institute for Space Studies, Goddard Space Flight Center, New York, New York 10025

R. H. Tipping

Department of Physics and Astronomy, University of Alabama, Tuscaloosa, Alabama 35487

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A theory is presented for the modification of the line-shape functions and absorption coefficient due to the breakdown of the quasistatic approximation. This breakdown arises from the effects of molecular motion and increases the absorption in the near wings. Numerical calculations for the high-frequency wing of the ν_3 band of CO_2 broadened by Ar are reported and it is shown that these effects are significant near the bandhead. The importance of such corrections in other spectral regions and for other systems is discussed briefly.

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I. INTRODUCTION

The calculation of accurate frequency profiles for molecular vibration-rotational transitions valid over a range of different physical parameters (e.g., number density, temperature, etc.) remains an unsolved problem. Various theories valid for small frequency displacements from the resonant line center have been proposed over the years.¹ For instance, the impact theory in which the duration of collisions is assumed to be zero leads to Lorentzian-shaped profiles that apply quite generally to non-overlapping lines arising in low density gases.^{2,3} On the other hand, only relatively recently have tractable theories been proposed that are valid for large frequency displacements. Rosenkranz,^{4,5} starting the basic formalism given by Fano,⁶ has developed a far-wing theory based on the quasistatic and binary collision approximations and was able to obtain theoretical results for self- and N_2 -broadened H_2O spectra (the so-called continuum absorption) which are in substantial agreement with the experimental data.⁷ But because of the assumptions made, this theory is applicable only to the high-frequency wing of the pure rotational band. Rosenkranz's theory has been subsequently extended and improved by other authors.⁸⁻¹³ Boulet *et al.*⁸ proposed a line-by-line generalization of Rosenkranz's theory, but because of the extensive computations involved this approach has been implemented only for atom-molecule systems.¹⁴ Ma and Tipping⁹⁻¹³ in a series of papers have considered a number of improvements, removed the restriction for the applicability only to high-frequency wings, and applied their results to the calculation of self- and foreign-broadened H_2O for frequencies up to $10\,000\text{ cm}^{-1}$. Their results are generally in good agreement with both laboratory and atmospheric data.^{9-13,15} However, in all the formalisms mentioned above, the time dependence of the interaction between an absorber and a perturber is ignored.

In the present paper we consider corrections to the quasistatic theory implicit in all the theoretical treatments discussed above.^{4,5,8-15} In Sec. II, we present the general formalism and give results for the effects of molecular motion (neglected in the quasistatic approximation) on the spectral density and on the line shapes. This formalism is applied in

Sec. III to the case of the ν_3 band of CO_2 broadened by Ar. A discussion of the numerical results and conclusions of the present work are presented on Sec. IV.

II. THEORY

A. The basic approximations

In order to take into account the molecular motion for the wing region, we make some basic approximations besides the binary collision approximation.

(1) The quasistatic approximation. In the quasistatic approximation, the duration of a collision is assumed to be infinite and the positions of interacting molecules are fixed in space during the period of time of interest. One usually treats the relative motion of the two molecules classically; i.e., the ensemble average over the relative motion is carried out by integrating over r , the separation between two interacting molecules, with a statistical weight for a pair of molecules $\rho^{(in)}(r)$ related to the interaction between them. We note that since the interaction is independent of time, the molecular motion is totally ignored. This approximation limits the applicability of the theory to the far-wing regions. In the near-wing region, although we can still assume the duration of the collision is very large, we cannot take it as infinite as we did previously. Therefore, the molecular motion should be taken into account during the time of interest.

We assume the duration of collision, τ , is very large. Therefore, during the time of interest ($t \sim 1/\Delta\omega$, which is small), the displacements of molecules are small and the interaction between them changes only slightly. We are thus able to write the interaction as two components: a main component V independent of time and a small correction term $V_1(t)$ that is dependent on time. Consequently, the total Hamiltonian of two interacting molecules similarly consists of two parts, a main part independent of time and a small time-dependent correction term

$$H(t) = H_a + H_b + V + V_1(t) \equiv H + V_1(t); \quad (1)$$

here the subscripts a and b refer to the absorber and perturber, respectively.

(2) The closest region approximation. The interaction between two molecules depends on their separation. In general, during the whole collision process, the closer the distance between two interacting molecules becomes, the stronger the anisotropic interaction. As is well known, the anisotropic interaction is mainly responsible for collision broadening which is related to the coupling between the interaction and the transition of the absorber molecule during the collision process. Therefore, the strongest coupling effect takes place when two interacting molecules are near the separation of closest approach (we choose that time as $t=0$). In comparison with other parts of the collision trajectory, the contribution of this coupling comes mainly from the closest region, and we can assume that it can be ignored elsewhere.

(3) The classical ensemble average approximation. We do not treat the relative translational motion of two interacting molecules quantum mechanically, rather we consider their motion as a classical trajectory. In this case, the ensemble average over the relative motion is an ensemble average over all classical trajectories. However, based on the closest region approximation, the coupling effects from the whole trajectory arise mainly from separations around the closest point r_0 . We introduce a parameter η to estimate the fraction of the trajectory consistent with the closest region approximation that contributes significantly. With a straight line trajectory approximation, one is able to carry out this ensemble average. Based on the approximations discussed above, we can develop a formalism to take into account the effects of the molecular motion on the line wing shapes.

B. General formalism

The correlation function of the dipole moment is defined by

$$\langle \mu_a^{(H)}(0) \cdot \mu_a^{(H)}(t) \rangle = \sum_i \rho_i \langle i | \mu_a^{(H)}(0) \cdot \mu_a^{(H)}(t) | i \rangle, \quad (2)$$

where ρ_i is the normalized Boltzmann factor of the initial state i . In the above expression, $\mu_a^{(H)}(t)$ is the dipole operator of the absorber molecule in the Heisenberg representation which satisfies the equation

$$\frac{d}{dt} \mu_a^{(H)}(t) = i[H(t), \mu_a^{(H)}(t)]/\hbar, \quad (3)$$

where the square brackets indicate commutating operator. In the present case, the Hamiltonian $H(t)$ explicitly depends on time and we are unable to simply express $\mu_a^{(H)}(t)$ as $e^{iH(t)t/\hbar} \mu_a^{(H)}(0) e^{-iH(t)t/\hbar}$ as we did previously. However, we are able to solve Eq. (3) using a perturbational method as follows. For simplicity, we will omit the subscript a of $\mu_a^{(H)}(t)$ indicating the absorber molecule and the superscript (H) indicating the Heisenberg representation. We introduce a time displacement operator $U(t)$ and assume that

$$\mu(t) = U(t) \mu(0) U(t)^\dagger. \quad (4)$$

With Eqs. (3) and (4), we obtain

$$\frac{d}{dt} U(t) = iH(t)U(t)/\hbar. \quad (5)$$

From Eq. (1) and the perturbational method, we obtain

$$U(t) = e^{iHt/\hbar} \left\{ 1 + i \int_0^t V_1'(t') dt' + (i)^2 \int_0^t V_1'(t') dt' \int_0^{t'} V_1'(t'') dt'' + \dots \right\}, \quad (6)$$

where

$$V_1'(t) \equiv e^{-iHt/\hbar} V_1(t) e^{iHt/\hbar} = e^{-iLt} V_1(t). \quad (7)$$

In the above expression, we have introduced the Liouville operator L defined by

$$L = (HI^* - IH^*)/\hbar. \quad (8)$$

Then, we have

$$\begin{aligned} \mu(t) &= e^{iHt} \left\{ 1 + i \int_0^t V_1'(t') dt' + \dots \right\} \mu(0) \\ &\times \left\{ 1 - i \int_0^t V_1'(t') dt' + \dots \right\} e^{-iHt} \\ &= e^{iLt} \mu(0) + i e^{iHt} \left[\int_0^t V_1'(t') dt', \mu(0) \right] e^{-iHt} + \dots \\ &= \mu_0(t) + i e^{iLt} \left[\int_0^t V_1'(t') dt', \mu(0) \right] + \dots, \end{aligned} \quad (9)$$

where

$$\mu_0(t) \equiv e^{iHt} \mu(0) e^{-iHt} = e^{iLt} \mu(0). \quad (10)$$

It is obvious that

$$\mu_0(0) = \mu(0). \quad (11)$$

The correlation function can be written as

$$\begin{aligned} \text{Tr}\{\rho \mu(0) \cdot \mu(t)\} &= \text{Tr}\{\rho \mu_0(0) \cdot e^{iLt} \mu_0(0)\} + \text{Tr}\left\{ \rho \mu_0(0) \right. \\ &\quad \left. \cdot i e^{iLt} \left[\int_0^t V_1'(t') dt', \mu_0(0) \right] \right\} \\ &\quad + \dots, \end{aligned} \quad (12)$$

and its Fourier transform, the spectral density $F(\omega)$, as

$$\begin{aligned} F(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \text{Tr}\{\rho \mu(0) \cdot \mu(t)\} dt = F_0(\omega) \\ &\quad + F_1(\omega) + \dots \end{aligned} \quad (13)$$

The zero-order term of the spectral density, $F_0(\omega)$, is defined by

$$\begin{aligned} F_0(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \text{Tr}\{\rho \mu_0(0) \cdot e^{iLt} \mu_0(0)\} dt \\ &= \frac{1}{\pi} \text{Re} \int_0^{\infty} e^{i\omega t} \text{Tr}\{\mu \cdot e^{-iLt} \rho \mu\} dt, \end{aligned} \quad (14)$$

where for simplifying the notation, we have omitted the subscript and the zero-time argument of the dipole moment operator $\mu_0(0)$. The first-order term of the spectral density can be expressed as (see Appendix A)

$$F_1(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \text{Tr} \left\{ \rho \mu \cdot i e^{iL t} \left[\int_0^t V_1'(t') dt', \mu \right] \right\} dt, \\ = \frac{1}{\pi} \text{Re} \int_0^{\infty} e^{i\omega t} \text{Tr} \left\{ \mu \cdot e^{-iL t} \tilde{V}_1(t) \frac{1}{\omega - L} \rho \mu \right\} dt, \quad (15)$$

where $\tilde{V}_1(t)$ is a Liouville operator corresponding to $V_1(t)$.

It is well known⁹⁻¹³ that since the isotropic interaction does not depend on the rotational quantum numbers, the Liouville operator associated with it will cancel out when it acts on the line space. Therefore, the isotropic interaction need not be included in the Liouville operator L nor in its time-dependent correction part $\tilde{V}_1(t)$.

$$V_{\text{aniso}}(r, \theta) = V_{\text{aniso}}(r_0, 0) + t \left(\frac{dr}{dt} \frac{\partial}{\partial r} + \frac{d\theta}{dt} \frac{\partial}{\partial \theta} \right) V_{\text{aniso}}(r, \theta) \Big|_{t=0} + \frac{1}{2} t^2 \left[\left(\frac{dr}{dt} \right)^2 \frac{\partial^2}{\partial r^2} + 2 \left(\frac{dr}{dt} \right) \left(\frac{d\theta}{dt} \right) \frac{\partial^2}{\partial r \partial \theta} + \frac{d^2 r}{dt^2} \frac{\partial}{\partial r} \right. \\ \left. + \left(\frac{d\theta}{dt} \right)^2 \frac{\partial^2}{\partial \theta^2} + \frac{d^2 \theta}{dt^2} \frac{\partial}{\partial \theta} \right] V_{\text{aniso}}(r, \theta) \Big|_{t=0} + \dots \\ = V_{\text{aniso}}(r_0, 0) + t \frac{d\theta}{dt} \frac{\partial}{\partial \theta} V_{\text{aniso}}(r_0, 0) \\ + \frac{1}{2} t^2 \left[\frac{d^2 r}{dt^2} \frac{\partial}{\partial r} + \left(\frac{d\theta}{dt} \right)^2 \frac{\partial^2}{\partial \theta^2} + \frac{d^2 \theta}{dt^2} \frac{\partial}{\partial \theta} \right] V_{\text{aniso}}(r_0, 0) + \dots, \quad (17)$$

where in the last step of deriving Eq. (17) we have used the fact that $(dr/dt)=0$ at the closest point. Since the set of trajectories has rotational symmetry with respect to the axis k , we expect that the contribution from the second term will be zero and we will simply omit this term in Eq. (17). Consequently, we are able to express $V_{\text{aniso}}(r, \theta)$ as two parts: a dominant part $V_{\text{aniso}}(r_0, 0)$ which is independent of the time and a small correction part which is proportional to t^2 . It is worth mentioning that the correction term is an even function of time. Thus, we rewrite $V_1(t)$ as

$$V_1(t) = t^2 V_1', \quad (18)$$

where

$$V_1' = \frac{1}{2} \left[\frac{d^2 r}{dt^2} \frac{\partial}{\partial r} V_{\text{aniso}}(r_0, 0) + \left(\frac{d\theta}{dt} \right)^2 \frac{\partial^2}{\partial \theta^2} V_{\text{aniso}}(r_0, 0) \right. \\ \left. + \frac{d^2 \theta}{dt^2} \frac{\partial}{\partial \theta} V_{\text{aniso}}(r_0, 0) \right]. \quad (19)$$

Based on classical dynamics, we have

$$m \frac{d^2 r}{dt^2} = m r \left(\frac{d\theta}{dt} \right)^2 - \frac{d}{dr} V_{\text{iso}}(r) - \frac{\partial}{\partial r} V_{\text{aniso}}(r, \theta), \quad (20)$$

C. The interaction at the closest region

In the present paper, we assume that the anisotropic interaction takes a product form

$$V_{\text{aniso}}[\mathbf{r}(t)] \equiv R[r(t)] G_{\text{aniso}}[\theta(t), \varphi(t)], \quad (16)$$

where $r(t)$, $\theta(t)$, and $\varphi(t)$ are the spherical coordinate components of $\mathbf{r}(t)$. We note that for simplifying the notation, the orientations of the two interacting molecules have not been explicitly indicated in the above expression. Since the vector $\mathbf{r}(t)$ is time dependent, the anisotropic interaction explicitly depends on time. However, based on the closest region and the quasistatic approximations, we are only interest in the behavior of this interaction around the closest point r_0 and for time $t \ll \tau$. We choose r_0 as the k axis of a space-fixed frame (i, j , and k) and $\mathbf{r}(t)$ is on the plane with $\varphi=0$. We can expand $V_{\text{aniso}}(r, \theta)$ around $t=0$ as

$$m \left(2 \frac{dr}{dt} \frac{d\theta}{dt} + r \frac{d^2 \theta}{dt^2} \right) = -\frac{1}{r} \frac{\partial}{\partial \theta} V_{\text{aniso}}(r, \theta), \quad (21)$$

where m is the reduced mass of the two interacting molecules. Then, we obtain

$$\frac{d^2 r}{dt^2} \Big|_{r=r_0, \theta=0} = r_0 \left(\frac{d\theta}{dt} \right)^2 - \frac{1}{m} \frac{d}{dr} V_{\text{iso}}(r_0) - \frac{1}{m} \frac{\partial}{\partial r} V_{\text{aniso}}(r_0, 0) \\ = \frac{1}{r_0} v_{\infty}^2 - \frac{2}{m r_0} V_{\text{iso}}(r_0) - \frac{2}{m r_0} V_{\text{aniso}}(r_0, 0) \\ - \frac{1}{m} \frac{d}{dr} V_{\text{iso}}(r_0) - \frac{1}{m} \frac{\partial}{\partial r} V_{\text{aniso}}(r_0, 0). \quad (22)$$

In the last step of deriving Eq. (22), conservation of the energy

$$\frac{1}{2} m r_0^2 \left(\frac{d\theta}{dt} \right)^2 = \frac{1}{2} m v_{\infty}^2 - V_{\text{iso}}(r_0) - V_{\text{aniso}}(r_0, 0), \quad (23)$$

has been taken into account. In the above expression, v_{∞} is an initial relative velocity when the separation between two interacting molecules is infinity. Since $\frac{1}{2} m r_0^2 (d\theta/dt)^2 \geq 0$, the range of r_0 which can be approached is limited. This fact will be used later. From Eq. (21) we obtain

$$\left. \frac{d^2 \theta}{dt^2} \right|_{r=r_0, \theta=0} = -\frac{1}{mr_0^2} \frac{\partial}{\partial \theta} V_{\text{aniso}}(r_0, 0). \quad (24)$$

Using Eqs. (22) and (24), V'_1 can be expressed as

$$\begin{aligned} V'_1 = & \frac{1}{2mr_0} \left\{ mv_\infty^2 - \left(2 + r_0 \frac{d}{dr} \right) [V_{\text{iso}}(r_0) \right. \\ & \left. + V_{\text{aniso}}(r_0, 0)] \right\} \frac{\partial}{\partial r} V_{\text{aniso}}(r_0, 0) \\ & + \frac{1}{2} \left(\frac{d\theta}{dt} \right)^2 O^2 V_{\text{aniso}} - \frac{1}{2mr_0^2} (OV_{\text{aniso}})^2, \end{aligned} \quad (25)$$

where $O^2 V \equiv \partial^2 V / \partial \theta^2$ and $(OV)^2 \equiv (\partial V / \partial \theta)^2$. We note that the first term of Eq. (25) depends on the velocity v_∞ while the last term is related to a torque.¹⁶ For simplifying the notation, we will omit the subscript of r_0 in the following discussion.

D. The effect of the molecular motion on the expression of $F_1(\omega)$

In a previous paper,¹⁰ we have derived an expression for $F_0(\omega)$ in which, at least formally, the bath variables have been isolated

$$\begin{aligned} F_0(\omega) = & \frac{1}{\pi} \text{Im} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \text{Tr} \left[\mu \cdot \frac{1}{\omega - \omega' - L_a} \right. \\ & \left. \times \left\langle \frac{1}{\omega' - L_1} \right\rangle_b \rho^{(a)} \mu \right]_a, \end{aligned} \quad (26)$$

where

$$\left\langle \frac{1}{\omega' - L_1} \right\rangle_b = \text{Tr} \left[\frac{1}{\omega' - L_1} \rho^{(b)} \right]_b. \quad (27)$$

In the above expressions we explicitly denote the summation indices of the trace, a or b , for the absorber or bath molecular variables, respectively.

Now we focus on the correction term $F_1(\omega)$. With Eqs. (A4), (A5) and (18), we have

$$\begin{aligned} F_1(\omega) = & \frac{1}{\pi} \text{Re} \text{Tr} \int_0^{\infty} \left[\mu \cdot t^2 e^{i(\omega-L)t} \tilde{V}'_1 \frac{1}{\omega-L} \rho \mu \right] dt, \\ = & \frac{1}{\pi} \text{Re} \text{Tr} \int_0^{\infty} \left[\mu \cdot t^2 e^{i(\omega-L_0)t} \tilde{V}'_1 \frac{1}{\omega-L} \rho \mu \right] dt, \end{aligned} \quad (28)$$

where the time-independent Liouville operator L consists of two components,

$$L = L_0 + L_1. \quad (29)$$

corresponding to the unperturbed Hamiltonian of the absorber and bath molecule and the time-independent interaction, $V_{\text{aniso}}(r_0, 0)$, respectively. We assume that

$$e^{-iLt} \approx e^{-iL_0 t} e^{-iL_1 t}, \quad (30)$$

where the limitation of this approximation has been discussed in a previous paper.¹⁰ Based on it, we can rewrite the resolvent operator $[1/(\omega-L)]$ in Eq. (28) as

$$\begin{aligned} \frac{1}{\omega-L} & \approx -i \int_0^{\infty} e^{-iL_1 t} e^{i(\omega-L_0)t} dt \\ & = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \frac{1}{\omega' - L_1} \times \frac{1}{\omega - \omega' - L_0}. \end{aligned} \quad (31)$$

Then $F_1(\omega)$ can be expressed as

$$\begin{aligned} F_1(\omega) = & -\frac{1}{\pi} \text{Re} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \text{Tr} \left[\mu \cdot \int_0^{\infty} t^2 e^{i(\omega-L_0)t} dt \tilde{V}'_1 \frac{1}{\omega' - L_1} \times \frac{1}{\omega - \omega' - L_0} \rho \mu \right] \\ = & \frac{1}{\pi} \text{Re} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \text{Tr} \left[\mu \cdot \frac{d^2}{d\omega'^2} \int_0^{\infty} e^{i(\omega-L_0)t} dt \tilde{V}'_1 \frac{1}{\omega' - L_1} \times \frac{1}{\omega - \omega' - L_0} \rho \mu \right] \\ = & -\frac{1}{\pi} \text{Im} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \text{Tr} \left[\mu \cdot \frac{d^2}{d\omega'^2} \left(\frac{1}{\omega - L_0} \right) \tilde{V}'_1 \frac{1}{\omega' - L_1} \times \frac{1}{\omega - \omega' - L_0} \rho \mu \right] \\ = & -\frac{2}{\pi} \text{Im} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \text{Tr} \left[\mu \cdot \frac{1}{(\omega - L_0)^3} \tilde{V}'_1 \frac{1}{\omega' - L_1} \times \frac{1}{\omega - \omega' - L_0} \rho \mu \right]. \end{aligned} \quad (32)$$

In order to separate the summations over the absorber variables and the bath variables, we first explicitly write the summation indices of the trace in Eq. (32)

$$\text{Tr} \left[\mu \cdot \frac{1}{(\omega - L_0)^3} \tilde{V}'_1 \frac{1}{\omega' - L_1} \times \frac{1}{\omega - \omega' - L_0} \rho \mu \right]$$

$$= \text{Tr} \left[\mu \cdot \frac{1}{(\omega - L_0)^3} \tilde{V}'_1 \frac{1}{\omega' - L_1} \times \frac{1}{\omega - \omega' - L_0} \rho^{(b)} \rho^{(a)} \mu \right]_{a,b}$$

Then we can carry out the summation over the bath variables of the trace using the fact that there is no contribution from

the Liouville operator $L^{(b)}$ whenever it acts directly on μ . Therefore, the trace in Eq. (32) can be written as

$$\text{Tr} \left[\mu \cdot \frac{1}{(\omega - L_a)^3} \left\langle \tilde{V}'_1 \frac{1}{\omega' - L_1} \right\rangle_b \frac{1}{\omega - \omega' - L_a} \rho^{(a)} \mu \right]_a, \quad (33)$$

where

$$\left\langle \tilde{V}'_1 \frac{1}{\omega' - L_1} \right\rangle_b = \text{Tr} \left[\tilde{V}'_1 \frac{1}{\omega' - L_1} \rho^{(b)} \right]. \quad (34)$$

Thus we obtain an expression of $F_1(\omega)$ in which the bath variables have also been isolated just as in the expression of $F_0(\omega)$

$$F_1(\omega) = -\frac{2}{\pi} \text{Im} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \text{Tr} \left[\mu \cdot \frac{1}{(\omega - L_a)^3} \times \left\langle \tilde{V}'_1 \frac{1}{\omega' - L_1} \right\rangle_b \frac{1}{\omega - \omega' - L_a} \rho^{(a)} \mu \right]_a. \quad (35)$$

In comparing Eq. (35) with Eq. (26), we find that the molecular motion introduces complexities in the trace over perturber variables in the calculation of the spectral density.

E. The resolvent operator $\langle \tilde{V}'_1 [1/(\omega' - L_1)] \rangle_b$ and its trajectory average

The resolvent operator $[1/(\omega - L_1)]$ is defined only in the representation constructed from its eigenvectors. Therefore, we have to find the basis in which L_1 is diagonal. The Liouville operator L_1 corresponding to the time-independent part is¹⁰

$$L_1 = (V_{\text{aniso}} I^* - I V_{\text{aniso}}^*) / \hbar \\ = R(r)(G_{\text{aniso}} I^* - I G_{\text{aniso}}^*) = R(r)G. \quad (36)$$

We denote by $|\alpha\rangle$ and G_α , the eigenvectors and eigenvalues, respectively, of the matrix operator G_{aniso} ; that is

$$G_{\text{aniso}} |\alpha\rangle = G_\alpha |\alpha\rangle, \quad (37)$$

or, equivalently, for the Liouville operator G in line space notation

$$G|\alpha\rangle\langle\beta| = (G_\alpha - G_\beta)|\alpha\rangle\langle\beta| \equiv G_{\alpha\beta}|\alpha\rangle\langle\beta|. \quad (38)$$

Then, the matrix elements of the Liouville resolvent operator in the representation constructed from its eigenvectors can be written as

$$\langle \alpha\beta^\dagger | \frac{1}{\omega - L_1} | \alpha'\beta'^\dagger \rangle = \frac{1}{\omega - R(r)G_{\alpha\beta}} \delta_{\alpha\alpha'} \delta_{\beta\beta'}. \quad (39)$$

Based on the knowledge about the resolvent operator $[1/(\omega - L_1)]$ obtained above, we now discuss the resolvent operator

$$\left\langle \tilde{V}'_1 \frac{1}{\omega' - L_1} \right\rangle_b$$

in Eq. (35). It is an operator acting on the line space of the absorber molecule a . Therefore, in general, it can be expressed as

$$\left\langle \tilde{V}'_1 \frac{1}{\omega' - L_1} \right\rangle_b = \sum_{i_1 j_1} \sum_{i'_1 j'_1} \langle i_1 j_1^\dagger | \left\langle \tilde{V}'_1 \frac{1}{\omega' - L_1} \right\rangle_b | i'_1 j'_1 \rangle \rangle \times | i_1 j_1^\dagger \rangle \langle i'_1 j'_1 |. \quad (40)$$

By explicitly writing the summation over the bath molecular variables, its components can be written as

$$\langle i_1 j_1^\dagger | \left\langle \tilde{V}'_1 \frac{1}{\omega' - L_1} \right\rangle_b | i'_1 j'_1 \rangle \rangle \\ = \sum_{i_2 j_2} \langle (i_1 j_1^\dagger)(i_2 j_2^\dagger) | \tilde{V}'_1 \frac{1}{\omega' - L_1} \rho^{(b)} | (i'_1 j'_1)(j_2 j_2^\dagger) \rangle. \quad (41)$$

We note that the summation over the bath variables in line space in Eq. (41) includes only the states $|i_2 j_2^\dagger\rangle$ because of the assumption that the bath molecule is not involved in the transition.

Based on our classical ensemble average approximation, the ensemble average over the classical trajectories (indicated by a subscript *traj.*) is replaced by a weighted integral over r times the parameter η . Therefore, the trajectory-averaged component of the resolvent operator $\langle \tilde{V}'_1 [1/(\omega' - L_1)] \rangle_{b, \text{traj.}}$ can be written as

$$\langle i_1 j_1^\dagger | \left\langle \tilde{V}'_1 \frac{1}{\omega' - L_1} \right\rangle_{b, \text{traj.}} | i'_1 j'_1 \rangle \rangle \\ = \sum_{i_2 j_2} \sum_{\alpha\beta} \sum_{\alpha'\beta'} \langle (i_1 j_1^\dagger)(i_2 j_2^\dagger) | \alpha\beta^\dagger \rangle \langle \alpha\beta^\dagger | \tilde{V}'_1 \frac{1}{\omega' - L_1} | \alpha'\beta'^\dagger \rangle_{\text{traj.}} \langle \alpha'\beta'^\dagger | \rho^{(b)} | (i'_1 j'_1)(j_2 j_2^\dagger) \rangle \\ = 4\pi n_b \eta \sum_{i_2 j_2} \sum_{\alpha\beta} \sum_{\alpha'\beta'} \langle (i_1 j_1^\dagger)(i_2 j_2^\dagger) | \alpha\beta^\dagger \rangle \int_{r_{\min}}^{\infty} r^2 dr \left[1 - \frac{V_{\text{iso}}(r)}{\frac{1}{2} m v_\infty^2} \right]^{1/2} \langle \alpha\beta^\dagger | \tilde{V}'_1 \frac{1}{\omega' - R(r)G} | \alpha'\beta'^\dagger \rangle \\ \times \langle \alpha'\beta'^\dagger | \rho^{(b)} | (i'_1 j'_1)(j_2 j_2^\dagger) \rangle \quad (42)$$

where the factor

$$n_b \left[1 - \frac{V_{\text{iso}}(r)}{\frac{1}{2} m v_{\infty}^2} \right]^{1/2}$$

is a statistical weight¹⁷ and n_b is the number density of the bath molecules. We note that in Eq. (42) the lower limit of the integration is not zero but rather the turning point r_{min} which comes from conservation of energy and consequently depends on v_{∞} , the relative velocity of two interacting

molecules at infinity. Since both the operator \tilde{V}'_1 and r_{min} depend on the velocity v_{∞} , when we carry out the trajectory average, we have also to take into account velocity averaging, assuming a Maxwellian distribution function. However, for simplifying the calculations, the average over v_{∞} will not be treated exactly, but approximately. We simply replace v_{∞} by a properly chosen value \bar{v}_{∞} in the corresponding expressions. Using Eqs. (25) and (39), the matrix elements $\langle \alpha \beta^\dagger | \tilde{V}'_1 [1/(\omega' - L_1)] | \alpha' \beta'^\dagger \rangle$ in Eq. (42) can be expressed as follows:

$$\begin{aligned} \langle \alpha \beta^\dagger | \tilde{V}'_1 \frac{1}{\omega' - L_1} | \alpha' \beta'^\dagger \rangle &= \langle \alpha \beta^\dagger | \tilde{V}'_1 | \alpha' \beta'^\dagger \rangle \frac{1}{\omega' - R(r)G_{\alpha'\beta'}} \\ &= \left\{ \frac{1}{2mr^2} \left[m\bar{v}_{\infty}^2 - \left(2 + r \frac{d}{dr} \right) (V_{\text{iso}}(r) + R(r)G_{\alpha\beta}^+) \right] r \frac{d}{dr} R(r)G_{\alpha\beta} \delta_{\alpha\alpha'} \delta_{\beta\beta'} \right. \\ &\quad \left. + \frac{1}{2} \langle \alpha \beta^\dagger | \left(\frac{d\theta}{dt} \right)^2 O^2 V_{\text{aniso}} | \alpha' \beta'^\dagger \rangle - \frac{1}{2mr^2} \langle \alpha \beta^\dagger | (OV_{\text{aniso}})^2 | \alpha' \beta'^\dagger \rangle \right\} \frac{1}{\omega' - R(r)G_{\alpha'\beta'}}, \quad (43) \end{aligned}$$

where $G_{\alpha\beta}^+ = (G_{\alpha} + G_{\beta})$. It turns out that the contributions to $F_1(\omega)$ from the last two terms of Eq. (43) approximately cancel. In fact, if we replace $\frac{1}{2} (d\theta/dt)^2$ by (kT/mr^2) and then perform a trace operation, they can be approximated by

$$\begin{aligned} &\left[\frac{kT}{2mr^2} \langle O^2 V \rangle - \frac{1}{2mr^2} \langle (OV)^2 \rangle \right] \\ &\times \frac{1}{\omega' - R(r)G_{\alpha'\beta'}} \delta_{\alpha\alpha'} \delta_{\beta\beta'}, \end{aligned}$$

where

$$\langle O^2 V \rangle = \int d\mathbf{r} \langle O^2 V_{\text{aniso}} e^{-V(r)/kT} \rangle_{\Omega}, \quad (44)$$

and $\langle (OV)^2 \rangle$ is the mean squared torque defined by

$$\langle (OV)^2 \rangle = \int d\mathbf{r} \langle (OV_{\text{aniso}})^2 e^{-V(r)/kT} \rangle_{\Omega}, \quad (45)$$

where $\langle \rangle_{\Omega}$ indicates the average over all orientation of two interacting molecules. As is well known classically

$$kT \langle O^2 V \rangle = \langle (OV)^2 \rangle, \quad (46)$$

and, therefore, the contributions from these two terms cancel out. Based on the argument given above, we need only to focus on the first term of Eq. (43) and we obtain

$$\begin{aligned} &\langle \alpha \beta^\dagger | \tilde{V}'_1 \frac{1}{\omega' - L_1} | \alpha' \beta'^\dagger \rangle \\ &= \frac{1}{2mr^2} \left\{ m\bar{v}_{\infty}^2 - \left(2 + r \frac{d}{dr} \right) (V_{\text{iso}}(r) + R(r)G_{\alpha\beta}^+) \right\} \\ &\times r \frac{d}{dr} R(r)G_{\alpha\beta} \frac{1}{\omega' - R(r)G_{\alpha'\beta'}} \delta_{\alpha\alpha'} \delta_{\beta\beta'}. \quad (47) \end{aligned}$$

However, in the present calculation we are interested in the imaginary part $\text{Im} \langle \alpha \beta^\dagger | \tilde{V}'_1 [1/(\omega'' - L_1)] | \alpha' \beta'^\dagger \rangle$ only. With the well-known formal identity

$$\begin{aligned} &\lim_{\epsilon \rightarrow 0} \frac{1}{\omega - R(r)G_{\alpha\beta} + i\epsilon} \\ &= P \frac{1}{\omega - R(r)G_{\alpha\beta}} - i\pi \delta[\omega - R(r)G_{\alpha\beta}], \quad (48) \end{aligned}$$

where P indicates the Cauchy principal value of the integral and δ is a Dirac delta function, it can be expressed as

$$\begin{aligned} &\text{Im} \langle \alpha \beta^\dagger | \tilde{V}'_1 \frac{1}{\omega' - L_1} | \alpha' \beta'^\dagger \rangle \\ &= -\frac{\pi}{2mr^2} \left\{ m\bar{v}_{\infty}^2 - \left(2 + r \frac{d}{dr} \right) (V_{\text{iso}}(r) + R(r)G_{\alpha\beta}^+) \right\} \\ &\times r \frac{d}{dr} R(r)G_{\alpha\beta} \delta[\omega' - R(r)G_{\alpha'\beta'}] \delta_{\alpha\alpha'} \delta_{\beta\beta'}. \quad (49) \end{aligned}$$

Finally, using Eqs. (42) and (49) we can write (see Appendix B for the details)

$$\text{Im} \langle i_{1j_1}^\dagger | \tilde{V}'_1 \frac{1}{\omega' - L_1} | i'_{1j'_1} \rangle_{b, \text{traj.}} = \frac{1}{2} \mathcal{R}_{i_1 j_1, i'_1 j'_1}(\omega'), \quad (50)$$

where

where $r_{\alpha\beta}(\omega)$ are the positive solutions of the equation $\omega - R(r)G_{\alpha\beta} = 0$. In Eq. (58), the line strength S_{ij} is defined by the usual expression¹⁰⁻¹²

$$S_{ij} = \frac{4\pi^2\omega_{ij}}{3\hbar c Q_a} g_j |\mu_{ij}|^2 (e^{-E_j/kT} - e^{-E_i/kT}). \quad (60)$$

On the other hand, using the results derived above the correction term can be written in the form

$$\begin{aligned} \alpha_1(\omega) &= \frac{4\pi^2}{3\hbar c} \omega n_a \tanh(\hbar\omega/2kT) [F_1(\omega) + F_1(-\omega)] \\ &= n_a \sum_{\omega_{ij} > 0} S_{ij} \frac{\omega \sinh(\hbar\omega/2kT)}{\omega_{ij} \sinh(\hbar\omega_{ij}/2kT)} \frac{1}{\pi} \\ &\quad \times \left\{ \frac{1}{(\omega - \omega_{ij})^3} \hat{\mathcal{C}}(\omega - \omega_{ij}) \right. \\ &\quad \left. + \frac{1}{(\omega + \omega_{ij})^3} \hat{\mathcal{C}}(\omega + \omega_{ij}) \right\}. \end{aligned} \quad (61)$$

In comparing the expressions for $\alpha_1(\omega)$ and $\alpha_0(\omega)$, we find that they are similar except for the additional power of $(\omega - \omega_{ij})$ and $(\omega + \omega_{ij})$ in Eq. (61). This is consistent with the expectation that the correction contribution should decrease faster than the leading term as the frequency displacements increases.

III. NUMERICAL RESULTS FOR THE Ar-BROADENED ν_3 BAND OF CO₂

As an example, we consider the effect of molecular motion on the wing of the Ar-broadened ν_3 band of CO₂ for the temperature $T=296$ K. In this case, the bath molecule is simply an Ar atom and its internal quantum states need not be considered. In order to simplify the calculations, we model the isotropic potential between CO₂ and Ar by the Lennard-Jones model

$$V_{iso}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (62)$$

The expression of the anisotropic potential, Eq. (16) is the product of the functions

$$R(r) = 4\epsilon \left[R_2 \left(\frac{\sigma}{r} \right)^{12} - A_2 \left(\frac{\sigma}{r} \right)^6 \right], \quad (63)$$

and

$$G_{\text{aniso}} = P_2(\cos \Theta), \quad (64)$$

where Θ is the angle between \mathbf{r} and the CO₂ molecular axis, and R_2 and A_2 are adjustable parameters. We first adopt the same values used by Boisssoles *et al.*¹⁴ with $\sigma=3.91$ Å, $\epsilon/k=153$ K, $R_2=1.09$ and $A_2=0.266$. For the frequency range of interest in the present calculations, 2400–2580 cm⁻¹, we consider the contributions from the ν_3 band of CO₂ only and exclude any contributions from other bands. From the HITRAN data base,¹⁸ there are 109 lines listed for this band and the maximum value of the rotational quantum numbers among them is 108. Although all of them are included in the

calculations, the diagonalization of the anisotropic interaction matrix whose size depends on how many states are included in the complete set remains tractable.

The formula used by Boisssoles *et al.*¹⁴ to calculate the band-averaged line shape function of ν_3 band of CO₂ is similar to Eq. (59). However, they introduced an energetically corrected function in their formalism. This correction corresponds to rewriting the spectral density in a more symmetric form¹⁹

$$F_0(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty e^{i\omega t} \text{Tr} \{ \mu \sqrt{\rho} \cdot e^{-iLt} \sqrt{\rho} \mu \} dt. \quad (65)$$

Consequently, the expression of the band-averaged line shape function $\hat{\chi}(\omega)$ is given by

$$\begin{aligned} \hat{\chi}(\omega) &= 4\pi^2 n_b \omega \sum_{\alpha\beta} \sum_m |\langle \alpha | \sqrt{\rho} \mu_m | \beta \rangle|^2 \\ &\quad \times e^{-\hbar\omega[(G_\alpha + G_\beta)/(G_\alpha - G_\beta)]/2kT} \\ &\quad \times \left\{ r^2 \left| \frac{R(r)}{dR(r)/dr} \right| e^{-V_{iso}(r)/kT} \right\} \Bigg|_{r=r_{\alpha\beta}(\omega)} \\ &\quad / \sum_{ij} \rho_i |\mu_{ij}|^2. \end{aligned} \quad (66)$$

Similarly, we follow the same energetically corrected procedure to calculate $\hat{\mathcal{C}}(\omega)$. As we mentioned previously, in the present calculations we do not treat the velocity average exactly. Since the Maxwellian distribution function has a sharp maximum at $v_{\text{max}} = \sqrt{2kT/m}$, we choose $\hat{v}_\infty = v_{\text{max}}$ in the trajectory average calculations. With respect to the turning points r_{min} , we assume that they are determined by the isotropic potential only and that the effect from the anisotropic potential is averaged out. In the present calculation, we simply use the equation, $\frac{1}{2}m\hat{v}_\infty^2 - V_{iso}(r_{\text{min}}) = 0$ to determine the turning point r_{min} . Of course, more sophisticated methods could be used to deal with the velocity averaging and the determination of the turning points, however, we do not discuss them in the present paper. Thus the formula used for the numerical calculations for $\hat{\mathcal{C}}(\omega)$ is

$$\begin{aligned} \hat{\mathcal{C}}(\omega) &= -8\pi^2 n_b \eta \frac{kT}{m} \sum_{\alpha\beta} \sum_m |\langle \alpha | \sqrt{\rho} \mu_m | \beta \rangle|^2 e^{\hbar\omega/2kT} \\ &\quad \times \left\{ \left[1 - \frac{V_{iso}(r)}{kT} \right]^{1/2} \text{Sign} \left[\frac{dR(r)}{dr} G_{\alpha\beta} \right] \right. \\ &\quad \times r \left[1 - \frac{1}{2kT} \left(2 + r \frac{d}{dr} \right) (V_{iso}(r) \right. \\ &\quad \left. \left. + R(r)G_{\alpha\beta}^+ \right) \right] \Bigg|_{r=r_{\alpha\beta}(\omega)} / \sum_{ij} \rho_i |\mu_{ij}|^2. \end{aligned} \quad (67)$$

As mentioned previously, the value of the parameter η introduced to make the classical trajectory average approximation consistent with the closest region approximation is unknown. Using a classical model (see Appendix C), we estimate $\eta \approx 0.3$ which we use in the present calculations.

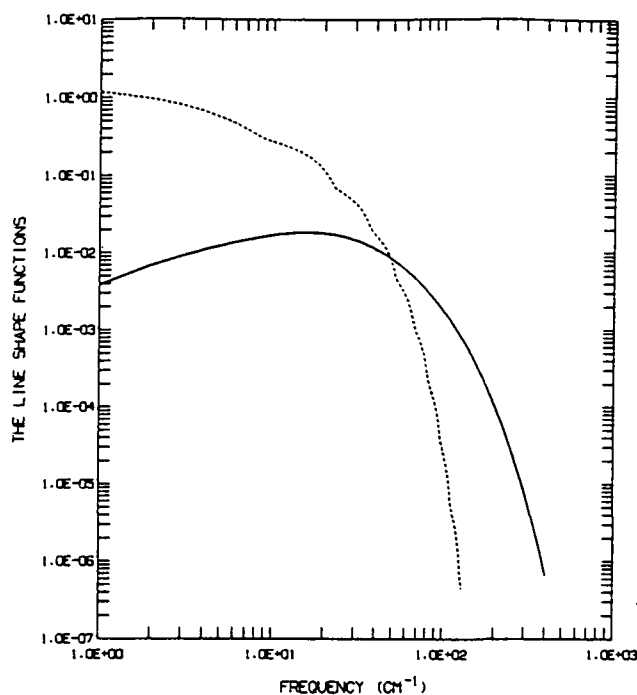


FIG. 1. The band-averaged line shape function $\hat{\chi}(\omega)$ in units of $\text{cm}^{-1} \text{atm}^{-1}$ (solid curve) and the correction to the band-averaged line shape function, $\hat{\mathcal{H}}(\omega)/\omega$ with $\eta=0.3$ (dotted curve), as functions of frequency ω (in units of cm^{-1}) calculated for $T=296 \text{ K}$.

The calculated band averaged line shape function $\hat{\chi}(\omega)$ and the calculated correction of the band averaged line shape function $\hat{\mathcal{H}}(\omega)$ are shown in Fig. 1. In this figure we present $\hat{\mathcal{H}}(\omega)/\omega$ instead of $\hat{\mathcal{H}}(\omega)$ since not only $\hat{\mathcal{H}}(\omega)/\omega$ has the same dimension as $\hat{\chi}(\omega)$, but also the comparison between them makes more sense. The frequency at which $\hat{\mathcal{H}}(\omega)/\omega$ becomes comparable to $\hat{\chi}(\omega)$ depends on the short-range anisotropic potential and on the value of the parameter η , in the present case, this occurs around 45 cm^{-1} . For smaller frequencies, $\hat{\mathcal{H}}(\omega)/\omega$ exceeds $\hat{\chi}(\omega)$ implying that the quasistatic approximation breaks down and the effects of molecular motion must be taken into account. As shown in the Fig. 1, $\hat{\mathcal{H}}(\omega)/\omega$ falls off faster than $\hat{\chi}(\omega)$ as the frequency increases and becomes negligible beyond 80 cm^{-1} which validates the quasistatic approximation for this frequency region.

The calculated contributions of absorption coefficients from the main part $F_0(\omega)$ which corresponds to Boissolles *et al.*'s results¹⁴ are shown in Fig. 2. The total absorption coefficients are also shown in Fig. 2 together with the results obtained using a Lorentzian line shape and the experimental results.¹⁴ In order to investigate how sensitive these results are to the choice of the potential parameters, we have repeated the calculations varying the parameters σ , ϵ/k , R_2 , and A_2 in Eqs. (62) and (63). As expected the results depend sensitively on σ but less so on ϵ/k : small changes in the relative weighting of the long- and short-range parts A_2 and R_2 can affect the magnitude. We obtained the agreement with the experimental data shown in Fig. 3 using the values: $\sigma=3.2 \text{ \AA}$, $\epsilon/k=100 \text{ K}$, $R_2=1.22$, and $A_2=0.35$. Finally, we note that the comparisons discussed above are based on calculations made with a simplified one-component anisotropic

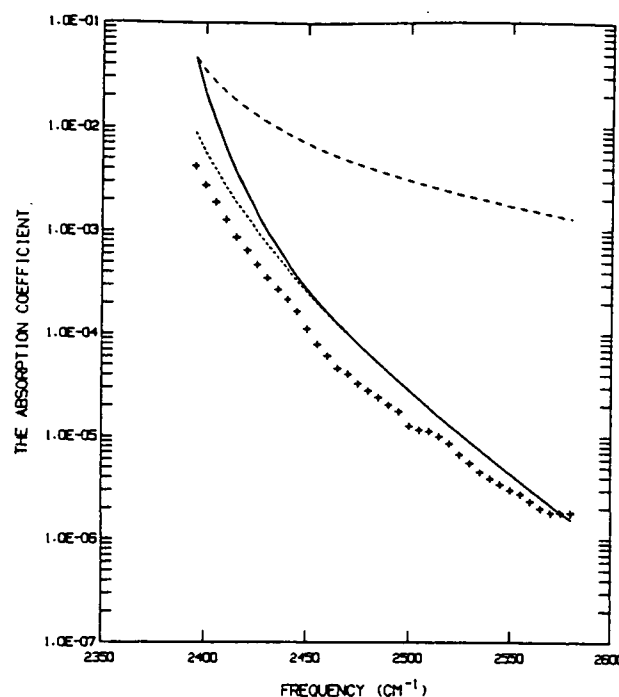


FIG. 2. The absorption coefficient $\alpha(\omega)$ (in units of $\text{cm}^2 \text{molecule}^{-1} \text{atm}^{-1}$) vs the frequency ω (in units of cm^{-1}) calculated for $T=296 \text{ K}$. The curve ... is the contribution from the band-averaged line shape function and — is the total. Also shown are the results calculated using a Lorentzian line shape denoted by --- and the experimental data denoted by +, respectively.

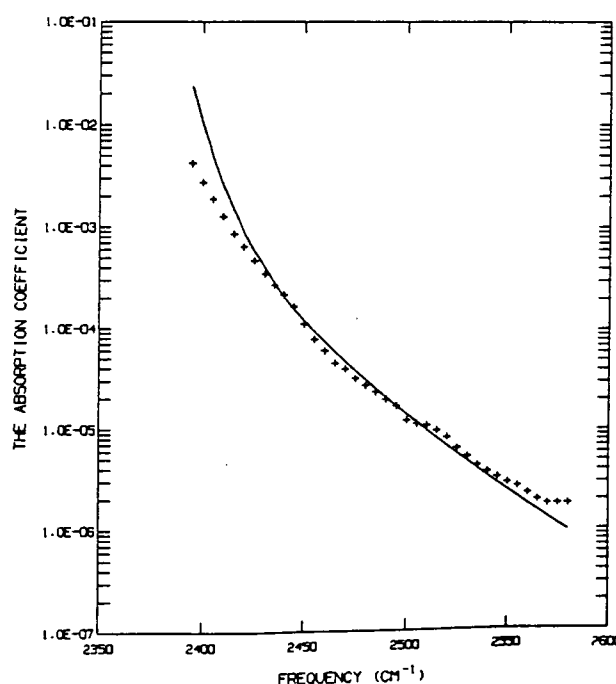


FIG. 3. Comparison between the present theoretical results calculated using the modified potential parameters and the experimental data.

potential. Before accurate quantitative comparisons can be made, a more realistic multicomponent potential must be used.

IV. DISCUSSION AND CONCLUSIONS

As a result of the present work, several conclusions can be drawn. First, the effects of molecular motion significantly affect the quasistatic line shape for displacements $\Delta\omega$ less than 50 cm^{-1} from the line centers. As noted above for smaller displacements, the correction term can exceed the quasistatic contributions; however, in this region $1/\tau_c < \Delta\omega \approx 1/\tau$ where τ_c and τ are time between collision and the duration, respectively, both the quasistatic and the impact theories break down. As a result, the corrections for molecular motion will be more important nearer the band origin or in the microwindows between the lines²⁰ than in the windows between vibration-rotational bands. Second, the correction depend on the interaction potential, and because the motion is greater for higher temperatures or for lighter molecules, one would expect larger corrections in these cases. Conversely, by varying the parameters in the potential in order to obtain agreement between theory and experiment, one can infer these parameters. However, we note that one of the drawbacks of the present quasistatic formalism is that only a simplified form of the anisotropic potential having one spherical harmonic can be incorporated. Further work to include more general potentials is needed before realistic potential-energy parameters can be accurately determined.

Finally, although the present work is a first attempt to consider the molecular motion a number of simplifying assumptions have been introduced in the calculations; nevertheless to take into account of the correction of the quasistatic formalism due to molecular motion is necessary in the near-wing region and this becomes a tractable problem especially for some simple interacting systems.

Some refinements of the approximations can be incorporated in the formalism. For example, one can improve the trajectory average and avoid the introduction of the parameter η . Because a main uncertainty in the present calculation is related to the interaction potential, there are two challenges facing us. One is to find a more reliable but still tractable potential models to represent the interaction. The other is to find a theoretical method to calculate the resolvent operator corresponding to more realistic anisotropic potentials which consists of more than one spherical harmonic component. Further work is needed in this direction.

ACKNOWLEDGMENTS

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APPENDIX A

The first-order term of the spectral density is

$$F_1(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \text{Tr} \left\{ \rho \mu \cdot i e^{iL t} \left[\int_0^t V_1'(t') dt', \mu \right] \right\} dt = \frac{1}{\pi} \text{Re} \int_0^{\infty} e^{i\omega t} \text{Tr} \left\{ \rho \mu \cdot i e^{iL t} \left[\int_0^t V_1'(t') dt', \mu \right] \right\} dt. \quad (\text{A1})$$

In the step of deriving Eq. (A1), we have used the fact that

$$\left\{ i e^{-iL t} \left[\int_0^{-t} V_1'(t') dt', \mu \right] \right\}^* = -i e^{iL t} \left[\int_0^{-t} V_1'(t')^* dt', \mu \right] = i e^{iL t} \left[\int_0^t V_1'(-t')^* dt', \mu \right] = i e^{iL t} \left[\int_0^t V_1'(t') dt', \mu \right],$$

since $V_1(t)$ is an even function as mentioned in the text. Then,

$$F_1(\omega) = -\frac{1}{\pi} \text{Re} \int_0^{\infty} e^{i\omega t} \text{Tr} \left\{ \mu \cdot \left[i \int_0^t V_1'(t') dt', e^{-iL t} \rho \mu \right] \right\} dt = \frac{1}{\pi} \text{Im} \int_0^{\infty} e^{i\omega t} \text{Tr} \left\{ \mu \cdot \left[\int_0^t V_1'(t') dt', e^{-iL t} \rho \mu \right] \right\} dt. \quad (\text{A2})$$

The integration of Eq. (A2) can expressed as follows:

$$\begin{aligned} \int_0^{\infty} dt e^{i\omega t} \left[\int_0^t V_1'(t') dt', e^{-iL t} \rho \mu \right] &= \int_0^{\infty} dt \left[\int_0^t V_1'(t') dt', e^{i(\omega-L)t} \rho \mu \right] = \int_0^{\infty} \left[\int_0^t V_1'(t') dt', \int_0^t e^{i(\omega-L)t'} dt' \rho \mu \right] \\ &= \left[\int_0^t V_1'(t') dt', \int_0^t e^{i(\omega-L)t'} dt' \rho \mu \right] \Big|_0^{\infty} - \int_0^{\infty} dt \left[V_1'(t), \int_0^t e^{i(\omega-L)t'} dt' \rho \mu \right] \\ &= \left[\int_0^{\infty} V_1'(t') dt', \int_0^{\infty} e^{i(\omega-L)t'} dt' \rho \mu \right] \end{aligned}$$

$$\begin{aligned}
& + i \int_0^\infty dt \left[V_1'(t), e^{i(\omega-L)t'} \right] \frac{1}{\omega-L} \rho \mu, \\
& = i \int_0^\infty dt e^{i\omega t} \left[e^{-iLt} V_1(t), e^{-iLt} \frac{1}{\omega-L} \rho \mu \right] \\
& = i \int_0^\infty dt e^{i(\omega-L)t} \left[V_1(t), \frac{1}{\omega-L} \rho \mu \right] = i \int_0^\infty dt e^{i(\omega-L)t} \tilde{V}_1(t) \frac{1}{\omega-L} \rho \mu,
\end{aligned} \tag{A3}$$

where $\tilde{V}_1(t)$ is a Liouville operator corresponding to $V_1(t)$. With Eq. (A3), we rewrite the first-order term as

$$F_1(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty e^{i\omega t} \text{Tr} \left\{ \mu \cdot e^{-iLt} \tilde{V}_1(t) \frac{1}{\omega-L} \rho \mu \right\} dt. \tag{A4}$$

To further simplify the calculations, we introduce another approximation in Eq. (A4). As discussed in the text, the part of $V_1(t)$, i.e., the term of $\frac{1}{2}t^2(d^2r/dt^2)[dR(r)/dr]G_{\text{aniso}}$, which contributes to $F_1(\omega)$ only, commutes with the time-independent interaction V ; therefore, $e^{-iLt}V_1(t) \approx e^{-iL_0t}V_1(t)$. With this fact and keeping in mind that we expect the effects due to the molecular motion to be significant only in near wings, we will approximate the Liouville operator e^{-iLt} by its main part e^{-iL_0t} in Eq. (A4). Then we obtain the simple formula

$$F_1(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty e^{i\omega t} \text{Tr} \left\{ \mu \cdot e^{-iL_0t} \tilde{V}_1(t) \frac{1}{\omega-L} \rho \mu \right\} dt. \tag{A5}$$

APPENDIX B

With Eqs. (42) and (49), the trajectory averaged component of the resolvent operator $\langle \tilde{V}_1' [1/(\omega' - L_1)] \rangle_b$ can be expressed

$$\begin{aligned}
\text{Im} \langle i_1 j_1^\dagger | \left[\tilde{V}_1' \frac{1}{\omega' - L_1} \right]_{b, \text{traj.}} | i_1' j_1'^\dagger \rangle &= -2\pi^2 n_b \eta \tilde{v}_\infty^2 \sum_{i_2 j_2} \sum_{\alpha \beta} \int_{r_{\min}}^\infty r dr \langle (i_1 j_1^\dagger) (i_2 j_2^\dagger) | \alpha \beta^\dagger \rangle \left[1 - \frac{V_{\text{iso}}(r)}{\frac{1}{2}m\tilde{v}_\infty^2} \right]^{1/2} \\
&\times \left\{ 1 - \frac{1}{m\tilde{v}_\infty^2} \left(2 + r \frac{d}{dr} \right) (V_{\text{iso}}(r) + R(r)G_{\alpha\beta}^+) \right\} \frac{d}{dr} R(r) G_{\alpha\beta} \delta[\omega' - R(r)G_{\alpha\beta}] \\
&\times \langle \alpha \beta^\dagger | (i_1' j_1'^\dagger) (j_2 j_2^\dagger) \rangle g_{j_2} e^{-E_{j_2}/kT} / Q_b,
\end{aligned} \tag{B1}$$

where g_j are the degeneracy factors due to nuclear spin, E_j are the energies associated with the state $|j\rangle$, and Q_b is the partition function for the bath molecules. By carrying out the integration with the help of the δ function, we obtain

$$\begin{aligned}
\text{Im} \langle i_1 j_1^\dagger | \left[\tilde{V}_1' \frac{1}{\omega' - L_1} \right]_{b, \text{traj.}} | i_1' j_1'^\dagger \rangle &= -2\pi^2 n_b \eta \tilde{v}_\infty^2 \sum_{i_2 j_2} \sum_{\alpha \beta} \langle (i_1 j_1^\dagger) (i_2 j_2^\dagger) | \alpha \beta^\dagger \rangle \\
&\times \left\{ \left[1 - \frac{V_{\text{iso}}(r)}{\frac{1}{2}m\tilde{v}_\infty^2} \right]^{1/2} \text{Sign} \left[\frac{dR(r)}{dr} G_{\alpha\beta} \right] \right. \\
&\times \left. r \left[1 - \frac{1}{m\tilde{v}_\infty^2} \left(2 + r \frac{d}{dr} \right) (V_{\text{iso}}(r) + R(r)G_{\alpha\beta}^+) \right] \right\} \bigg|_{r=r_{\alpha\beta}(\omega')} \\
&\times \langle \alpha \beta^\dagger | (i_1' j_1'^\dagger) (j_2 j_2^\dagger) \rangle g_{j_2} e^{-E_{j_2}/kT} / Q_b, \\
&\equiv \frac{1}{2} \mathcal{U}_{i_1 j_1, i_1' j_1'}(\omega'),
\end{aligned} \tag{B2}$$

where $r_{\alpha\beta}(\omega')$ are the positive solutions of the equation $\omega' - R(r)G_{\alpha\beta} = 0$ which are larger than r_{\min} . In the above expression,

$$\begin{aligned}
\mathcal{U}_{i_1 j_1, i_1' j_1'}(\omega') &= -4\pi^2 n_b \eta \tilde{v}_\infty^2 \sum_{i_2 j_2} \sum_{\alpha \beta} \langle (i_1 j_1^\dagger) (i_2 j_2^\dagger) | \alpha \beta^\dagger \rangle \left\{ \left[1 - \frac{V_{\text{iso}}(r)}{\frac{1}{2}m\tilde{v}_\infty^2} \right]^{1/2} \text{Sign} \left[\frac{dR(r)}{dr} G_{\alpha\beta} \right] r \left[1 - \frac{1}{m\tilde{v}_\infty^2} \left(2 + r \frac{d}{dr} \right) \right. \right. \\
&\times \left. \left. (V_{\text{iso}}(r) + R(r)G_{\alpha\beta}^+) \right] \right\} \bigg|_{r=r_{\alpha\beta}(\omega')} \langle \alpha \beta^\dagger | (i_1' j_1'^\dagger) (j_2 j_2^\dagger) \rangle g_{j_2} e^{-E_{j_2}/kT} / Q_b.
\end{aligned} \tag{B3}$$

With Eqs. (35) and (B2), the correction term of the spectral density, $F_1(\omega)$, can be rewritten as

$$\begin{aligned} F_1(\omega) &= -\frac{2}{\pi} \text{Im} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \text{Tr} \left[\mu \cdot \frac{1}{(\omega - L_a)^3} \left\langle \tilde{V}_1 \frac{1}{\omega' - L_1} \right\rangle_{b, \text{traj.}} \frac{1}{\omega - \omega' - L_a} \rho^{(a)} \mu \right]_a \\ &= -\frac{1}{\pi} \sum_{ij} \sum_{i'j'} \langle j | \mu | i \rangle \cdot \frac{1}{(\omega - \omega_{ij})^3} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \mathcal{Z}_{ij,i'j'}(\omega') \frac{1}{\omega - \omega' - \omega_{i'j'}} \rho_{i'j'} \langle i' | \mu | j' \rangle \\ &= \frac{1}{\pi} \sum_{ij} \sum_{i'j'} \langle j | \mu | i \rangle \frac{1}{(\omega - \omega_{ij})^3} \mathcal{Z}_{ij,i'j'}(\omega - \omega_{i'j'}) \rho_{i'j'} \langle i' | \mu | j' \rangle. \end{aligned} \quad (\text{B4})$$

Using the reduced matrix elements,

$$\langle i | \mu_m | j \rangle = \left[\frac{1}{(2i+1)} \right]^{1/2} C(j1i; m_j m m_i) \mu_{ij}, \quad (\text{B5})$$

and reduced functions, $\mathcal{Z}_{ij,i'j'}^{\text{redu}}(\omega)$, defined by

$$\mathcal{Z}_{ij,i'j'}^{\text{redu}}(\omega) = \left[\frac{1}{(2i+1)(2i'+1)} \right]^{1/2} \sum_m \sum_{m_i} \sum_{m_j} \sum_{m'_i} \sum_{m'_j} C(j1i; m_j m m_i) C(j'1i'; m'_j m'_i m'_i) \mathcal{Z}_{ij,i'j'}(\omega), \quad (\text{B6})$$

we complete the summation over the magnetic quantum numbers and obtain

$$\begin{aligned} F_1(\omega) &= \frac{1}{\pi} \sum_{ij} \sum_{i'j'} \mu_{ij}^* \frac{1}{(\omega - \omega_{ij})^3} \\ &\quad \times \mathcal{Z}_{ij,i'j'}^{\text{redu}}(\omega - \omega_{i'j'}) \rho_{i'j'} \mu_{i'j'}, \end{aligned} \quad (\text{B7})$$

where the summation indices exclude their magnetic quantum numbers. For simplicity, since we will use these reduced forms instead of the original ones in the results that follow, we will omit the superscript *redu*.

APPENDIX C

In general for a specified relative velocity at infinity, v_∞ , the trajectory is determined by the impact parameter b and the interaction potential $V(r)$, and the relative position of molecules along the trajectory $s(t)$ is a function of time whose zero has been chosen in the present work as the time of closest approach. In order to calculate averages of the functions of interest over all trajectories, one has to average over b and $s(t)$. However, the functions of interest are usually expressed in terms of the intermolecular separation r and, therefore, the dynamic variables b and $s(t)$ are not appropriate and have to be transformed to spherical coordinates. Assuming that the trajectory is mainly determined by the isotropic potential, we have

$$\frac{dr}{dt} = v_\infty \left[1 - \frac{2V_{\text{iso}}(r)}{m v_\infty^2} - \frac{b^2}{r^2} \right]^{1/2}. \quad (\text{C1})$$

For a specified r the maximum impact parameter is given by

$$b_{\text{max}}(r) = r \left[1 - \frac{2V_{\text{iso}}(r)}{m v_\infty^2} \right]^{1/2}. \quad (\text{C2})$$

With the straight line trajectory approximation, the integral

of a function $F(r)$ over all trajectories can be expressed as

$$\begin{aligned} I &= 2\pi \int_0^\infty b db \int_{-\infty}^\infty F(r) v_\infty dt, \\ &= 4\pi \int_{r_{\text{min}}}^\infty F(r) dr \int_0^{b_{\text{max}}(r)} \left[1 - \frac{2V_{\text{iso}}(r)}{m v_\infty^2} - \frac{b^2}{r^2} \right]^{-1/2} b db, \\ &= 4\pi \int_{r_{\text{min}}}^\infty \left[1 - \frac{2V_{\text{iso}}(r)}{m v_\infty^2} \right]^{1/2} F(r) r^2 dr, \end{aligned} \quad (\text{C3})$$

where r_{min} is given by

$$\frac{1}{2} m v_\infty^2 - V_{\text{iso}}(r_{\text{min}}) = 0. \quad (\text{C4})$$

However, based on the closest region approximation the contribution to the integral I comes mainly from the region near the turning point of trajectories and, in fact, the function $F(r)$ has been expressed in terms of an expansion around this point. For consistency, this implies that a cutoff has to be enforced on the integration along trajectories. One method to introduce the cutoff is to replace 0, the lower limit of the integration over b in Eq. (C3), by $b_{\text{min}}(r)$ and to assume that

$$b_{\text{min}}(r) = b_{\text{max}}(r) \cos \theta_0, \quad (\text{C5})$$

where θ_0 is a parameter. Then, one is able to recast Eq. (C3) as

$$\begin{aligned} I &= 4\pi \int_{r_{\text{min}}}^\infty F(r) dr \int_{b_{\text{min}}(r)}^{b_{\text{max}}(r)} \left[1 - \frac{2V_{\text{iso}}(r)}{m v_\infty^2} - \frac{b^2}{r^2} \right]^{-1/2} b db, \\ &= 4\pi \eta \int_{r_{\text{min}}}^\infty \left[1 - \frac{2V_{\text{iso}}(r)}{m v_\infty^2} \right]^{1/2} F(r) r^2 dr, \end{aligned} \quad (\text{C6})$$

where the parameter η finally used in the text is defined by

$$\eta = \sin \theta_0 = \left[1 - \frac{b_{\text{min}}^2}{b_{\text{max}}^2} \right]^{1/2}. \quad (\text{C7})$$

In order to estimate the parameter η , we consider a straight line trajectory with the closest distance denoted by $r_0 (=b)$. In the present case, the function $F(r)$ of interest is $V'_1 = \frac{1}{2}(d^2r/dt^2)(\partial/\partial r)V_{\text{aniso}}(r)$. If we assume that around the distance of closest approach the repulsive part of the anisotropic potential dominates, then $F(r) \propto r^{-16}$ and its magnitude drops to 1/2 the maximum value for $s \approx 0.3r_0$. With this assumption, the interaction takes place along the trajectory between $-0.3r_0 < s < +0.3r_0$. It corresponds to $b_{\text{min}} = r_0$ and $b_{\text{max}} = [1 + (s^2/r_0^2)]^{1/2}r_0$. Therefore, one is able to estimate the parameter $\eta = (s/b_{\text{max}}) \approx 0.3$ which we use in the calculations. In Eq. (C6) and consequently in Eq. (67) the parameter η is simply a scale parameter and it is easy to calculate results which correspond to different values of η . For example, the correction contribution is comparable to the leading contribution at about 27 cm^{-1} for $\eta=0.1$ while this occurs at 45 cm^{-1} for $\eta=0.3$. Although there is considerable uncertainty in the potential for small separations and arbitrariness in the cutoff discussed above and thus in the value of η , we note that the general conclusion that molecular motion is important for the near wings of the lines but can be ignored in the far-wing region does not depend on the value of η assumed.

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