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Extension of the quasistatic far-wing line shape theory to multicomponent anisotropic potentials

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The formalism developed previously for the calculation of the far-wing line shape function and the corresponding absorption coefficient using a single-component anisotropic interaction term and the binary collision and quasistatic approximations is generalized to multicomponent anisotropic potential functions. Explicit expressions are presented for several common cases, including the long-range dipole-dipole plus dipole-quadrupole interaction and a linear molecule interacting with a perturber atom. After determining the multicomponent functional representation for the interaction between CO₂ and Ar from previous published data, we calculate the theoretical line shape function and the corresponding absorption due to the ν_3 band of CO₂ in the frequency region 2400–2580 cm⁻¹ and compare our results with previous calculations carried out using a single-component anisotropic interaction, and with the results obtained assuming Lorentzian line shapes. The principal uncertainties in the present results, possible refinements of the theoretical formalism, and the applicability to other systems are discussed briefly.

I. INTRODUCTION

During the past decade, substantial progress has been made on the longstanding problem of the accurate calculation of the absorption of radiation by the far wings of allowed spectral lines. Since the publication of a quasistatic theory for the line shape calculated within the binary collisions approximation by Rosenkranz,^{1,2} several authors have extended and generalized this formalism. Boulet *et al.*³ published a line-by-line generalization of the quasistatic theory, and Ma and Tipping, in a series papers,^{4–12} have improved or eliminated many of the restrictions and assumptions that limited the accuracy and applicability of the original Rosenkranz theory. Although the theoretical results for the specific cases considered (H₂O–H₂O, H₂O–N₂, H₂O–CO₂, and CO₂–Ar) are in substantial agreement with both laboratory data and atmospheric measurements, some discrepancies remain.

All the calculations discussed above have been carried out using only a single-component anisotropic interaction that is responsible for the broadening. Because of the sensitivity of the results to changes in the anisotropic interaction, both the magnitude and the temperature dependence of the line shapes and the absorption, and also because of the inapplicability to represent well the anisotropic potential by a single-component anisotropic model, we present in the present paper a generalization of the quasistatic formalism to the multicomponent anisotropic potential. The new formalism is presented in Sec. II. In Sec. III, we discuss several cases, including the long-range dipole-dipole plus dipole-quadrupole interaction and a linear molecule interacting with a perturber atom. After obtaining a representation for the interaction between a CO₂ molecule and an Ar atom, we apply the theory in Sec. IV to the high-frequency wing of the ν_3 band of CO₂; we compare the present results for the ab-

sorption coefficient in the 2400–2580 cm⁻¹ spectral regions to those obtained from a similar theory using only a single-component anisotropic model and to those obtained by assuming Lorentzian line shapes. The conclusions concerning the present work, the principal theoretical uncertainties and possible refinements of the formalism, and the applicability to other systems are discussed briefly in Sec. V.

II. GENERAL FORMALISM

A. The absorption coefficient and spectral density

For a low-density gas sample, we divide it into absorber molecules and the remaining bath molecules and we focus on one absorber molecule only. Then, with n_a absorber molecules per unit volume, the absorption coefficient per unit volume can be expressed as

$$\alpha(\omega) = \frac{4\pi^2}{3\hbar c} n_a \omega \tanh(\hbar\omega/2kT) [F(\omega) + F(-\omega)]. \quad (1)$$

In this expression, $F(\omega)$ the spectral density is given by

$$F(\omega) = \frac{1}{\pi} \text{Re} \text{Tr} \int_0^\infty e^{i\omega t} \langle \mu_a^{(H)}(0) \cdot \mu_a^{(H)}(t) \rangle dt, \quad (2)$$

where the angular brackets denote the ensemble average over all (one absorber molecule plus bath) variables. The dipole operator of an absorber molecule in the Heisenberg representation $\mu_a^{(H)}(t)$ is determined by

$$\mu_a^{(H)}(t) = e^{iHt/\hbar} \mu_a^{(H)}(0) e^{-iHt/\hbar} = e^{iLt} \mu_a^{(H)}(0). \quad (3)$$

In the above expression, H is the total Hamiltonian which consists of the unperturbed Hamiltonian of the absorber molecule and the bath, $H_0 = H_a + H_b$, and the interaction V between them. In the last step of Eq. (3), the Liouville repre-

sensation in which the total Liouville operator L corresponds to the absorber molecule, the bath, and the interaction

$$L = L_a + L_b + L_1 = L_0 + L_1 \quad (4)$$

has been introduced. In terms of the Liouville representation, the spectral density can be written as

$$F(\omega) = \frac{1}{\pi} \text{Re Tr} \int_0^\infty e^{i\omega t} (\mu_a \cdot e^{-iL_1 t} \rho \mu_a) dt. \quad (5)$$

In the above expression, the superscript (H) of the Heisenberg representation and the zero-time argument of $\mu_a^{(H)}(0)$ have been dropped. It is well known 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 L_1 .

We assume that

$$e^{-iL_1 t} \approx e^{-iL_0 t} e^{-iL_1 t}. \quad (6)$$

The limitation of this approximation has been discussed in previous papers.^{7,11} Then $F(\omega)$ can be expressed as

$$\begin{aligned} F(\omega) &= \frac{1}{\pi} \text{Re Tr} \int_0^\infty \{ \mu_a \cdot \exp[i(\omega - L_0)t] e^{-iL_1 t} \rho \mu_a \} dt \\ &= \frac{1}{\pi} \text{Im} \frac{1}{2\pi i} \int_{-\infty}^\infty d\omega' \\ &\quad \times \text{Tr} \left(\mu_a \cdot \frac{1}{\omega - \omega' - L_a} \left\langle \frac{1}{\omega' - L_1} \right\rangle_b \rho^{(a)} \mu_a \right), \end{aligned} \quad (7)$$

where

$$\left\langle \frac{1}{\omega' - L_1} \right\rangle_b = \text{Tr} \left[\frac{1}{\omega' - L_1} \rho^{(b)} \right], \quad (8)$$

and the summation indices of the trace a and b indicate the absorber and bath molecular variables, respectively. In the above expression for $F(\omega)$, at least formally, the bath variables have been isolated. 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. In general, the anisotropic interaction consists of several components and each of them has a specific spherical symmetry and r dependence. This implies that the diagonalization would have to be carried out for every r , but this is not feasible in practice. Therefore, in previous work¹⁻¹³ an assumption has been made that only one component of anisotropic interaction is dominant and all others can be ignored in the calculations.

In order to overcome this fundamental drawback, a new method is introduced in the present work in which several components of the anisotropic interaction can be taken into account. We assume that the Liouville operator L_1 corresponding to the anisotropic interaction can be expressed as the sum of several terms with different spherical symmetries and r dependencies

$$L_1 = L_1^{(0)} + L_1^{(1)} + \dots = GR_1(r) + FR_2(r) + \dots \quad (9)$$

For clarity, only two terms are included explicitly in L_1 in the following expressions, although the inclusion of more terms is straightforward. In general, $L_1^{(0)}$ and $L_1^{(1)}$ represent the leading and the next leading terms of the anisotropic interaction, respectively. Consequently, we have

$$GR_1(r) > FR_2(r). \quad (10)$$

We denote by $|\alpha\beta\rangle (\equiv |\alpha\rangle\langle\beta|)$ and $G_{\alpha\beta} (\equiv G_\alpha - G_\beta)$ the eigenvectors and eigenvalues, respectively, of the Liouville operator G in line space notation constructed from $|\alpha\rangle$ and G_α , the eigenvectors and eigenvalues of the related matrix operator G , i.e.,

$$G|\alpha\beta\rangle = G_{\alpha\beta}|\alpha\beta\rangle. \quad (11)$$

Similarly, for the Liouville operator F , we have

$$F|\gamma\delta\rangle = F_{\gamma\delta}|\gamma\delta\rangle, \quad (12)$$

where $|\gamma\delta\rangle (\equiv |\gamma\rangle\langle\delta|)$ and $F_{\gamma\delta} (\equiv F_\gamma - F_\delta)$ are the eigenvectors and eigenvalues, respectively, of the Liouville operator F constructed from $|\gamma\rangle$ and F_γ , the eigenvectors and eigenvalues of the related matrix operator F .

We make the approximation

$$e^{-iL_1 t} \approx e^{-iL_1^{(0)} t} e^{-iL_1^{(1)} t} \quad (13)$$

which is valid if the contributions from the commutator $[L_1^{(0)}, L_1^{(1)}]$ are small. It is worth mentioning that the cutoff on the overlap factor introduced later is consistent with this approximation. Introducing both Laplace transformations of $e^{-iL_1^{(0)} t}$ and $e^{-iL_1^{(1)} t}$, we have

$$\begin{aligned} e^{-iL_1 t} &= \left(\frac{1}{2\pi i} \right)^2 \int_{-\infty}^\infty d\omega' \int_{-\infty}^\infty d\omega'' \exp[-i(\omega' + \omega'')t] \\ &\quad \times \frac{1}{\omega' - L_1^{(0)}} \times \frac{1}{\omega'' - L_1^{(1)}}. \end{aligned} \quad (14)$$

Then, the spectral density $F(\omega)$ can be expressed as

$$\begin{aligned}
F(\omega) &= \frac{1}{\pi} \operatorname{Re} \left(\frac{1}{2\pi i} \right)^2 \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \\
&\quad \times \int_0^{\infty} \operatorname{Tr} \left\{ \mu_a \cdot \exp[i(\omega - \omega' - \omega'' - L_0)t] \right. \\
&\quad \times \left. \frac{1}{\omega' - L_1^{(0)}} \frac{1}{\omega'' - L_1^{(1)}} \rho \mu_a \right\} dt \\
&= -\frac{1}{\pi} \operatorname{Im} \left(\frac{1}{2\pi i} \right)^2 \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \\
&\quad \times \operatorname{Tr} \left(\mu_a \cdot \frac{1}{\omega - \omega' - \omega'' - L_0} \right. \\
&\quad \times \left. \frac{1}{\omega' - L_1^{(0)}} \times \frac{1}{\omega'' - L_1^{(1)}} \rho \mu_a \right) \\
&= -\frac{1}{\pi} \operatorname{Im} \left(\frac{1}{2\pi i} \right)^2 \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \\
&\quad \times \operatorname{Tr} \left(\mu_a \cdot \frac{1}{\omega - \omega' - \omega'' - L_a} \right. \\
&\quad \times \left. \left(\frac{1}{\omega' - L_1^{(0)}} \times \frac{1}{\omega'' - L_1^{(1)}} \right)_b \rho^{(a)} \mu_a \right) . \quad (15)
\end{aligned}$$

Thus, we obtain an expression of $F(\omega)$ in which the bath variables have also been isolated analogous to Eq. (7).

B. The matrix elements of the resolvent Liouville operator $\langle 1/(\omega' - L_1^{(0)}) \times 1/(\omega'' - L_1^{(1)}) \rangle_b$

The resolvent operator $\langle 1/(\omega' - L_1^{(0)}) \times 1/(\omega'' - L_1^{(1)}) \rangle_b$ in Eq. (15) is an operator acting on the line space of the absorber molecule a . Therefore, in general, it can be expressed as

$$\begin{aligned}
&\left\langle \frac{1}{\omega' - L_1^{(0)}} \times \frac{1}{\omega'' - L_1^{(1)}} \right\rangle_b \\
&= \sum_{i_1 j_1} \sum_{i'_1 j'_1} \langle i_1 j_1 | \left\langle \frac{1}{\omega' - L_1^{(0)}} \times \frac{1}{\omega'' - L_1^{(1)}} \right\rangle_b | i'_1 j'_1 \rangle \\
&\quad \times | i_1 j_1 \rangle \langle i'_1 j'_1 | . \quad (16)
\end{aligned}$$

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

$$\begin{aligned}
&\langle i_1 j_1 | \left\langle \frac{1}{\omega' - L_1^{(0)}} \times \frac{1}{\omega'' - L_1^{(1)}} \right\rangle_b | i'_1 j'_1 \rangle \\
&= \sum_{i_2 j_2} \langle (i_1 j_1) | (i_2 j_2) | \frac{1}{\omega' - L_1^{(0)}} \times \frac{1}{\omega'' - L_1^{(1)}} \rho^{(b)} \\
&\quad \times | (i'_1 j'_1) \rangle \langle j_2 j_2 \rangle . \quad (17)
\end{aligned}$$

We note that the summation over the bath variables in line space in Eq. (17) includes only the states $|i_2 j_2\rangle$ because of the assumption that the bath molecule is not involved in the transition.

In the present work, the translational motion is not treated quantum mechanically; rather one uses the quasistatic approximation. The classical ensemble average over the translational motion indicated by a subscript r is represented by an integration over r , the separation between two interacting molecules, with the statistical weight $n_b \exp[-V_{\text{aniso}}(\mathbf{r})/kT] \exp[-V_{\text{iso}}(\mathbf{r})/kT]$ for a pair of molecules, where n_b is the number density of the bath molecules. Since the anisotropic potential consists of two terms, each contributes to the total statistical weight which can be approximately expressed as a product form

$$\begin{aligned}
&\exp[-V_{\text{aniso}}(\mathbf{r})/kT] \\
&\approx \exp[-V_{\text{aniso}}^{(0)}(\mathbf{r})/kT] \exp[-V_{\text{aniso}}^{(1)}(\mathbf{r})/kT] . \quad (18)
\end{aligned}$$

In line space, the weight factors corresponding to each component of the anisotropic interaction can be expressed as operators constructed from their eigenvalues and eigenvectors

$$\exp[-V_{\text{aniso}}^{(0)}(\mathbf{r})/kT] = \sum_{\alpha\beta} |\alpha\beta\rangle \exp[-G_{\alpha} R_1(\mathbf{r})/kT] \langle \alpha\beta| \quad (19)$$

and

$$\exp[-V_{\text{aniso}}^{(1)}(\mathbf{r})/kT] = \sum_{\gamma\delta} |\gamma\delta\rangle \exp[-F_{\gamma} R_2(\mathbf{r})/kT] \langle \gamma\delta| . \quad (20)$$

Therefore, the ensemble-averaged component of the resolvent operator $\langle 1/(\omega' - L_1^{(0)}) \times 1/(\omega'' - L_1^{(1)}) \rangle_{b,r}$ can be approximately written as

$$\begin{aligned}
&\langle i_1 j_1 | \left\langle \frac{1}{\omega' - L_1^{(0)}} \times \frac{1}{\omega'' - L_1^{(1)}} \right\rangle_{b,r} | i'_1 j'_1 \rangle \\
&= 4\pi n_b \sum_{i_2 j_2} \langle (i_1 j_1) | (i_2 j_2) \rangle \int_0^{\infty} dr r^2 \exp[-V_{\text{iso}}(\mathbf{r})/kT] \\
&\quad \times \left\{ \frac{1}{\omega' - L_1^{(0)}} \exp[-V_{\text{aniso}}^{(0)}(\mathbf{r})/kT] \right. \\
&\quad \times \left. \frac{1}{\omega'' - L_1^{(1)}} \exp[-V_{\text{aniso}}^{(1)}(\mathbf{r})/kT] \right\} \rho^{(b)} | (i'_1 j'_1) \rangle \langle j_2 j_2 \rangle \\
&= 4\pi n_b \sum_{i_2 j_2} \sum_{\alpha\beta} \sum_{\gamma\delta} \langle (i_1 j_1) | (i_2 j_2) | \alpha\beta \rangle \int_0^{\infty} dr r^2 \\
&\quad \times \exp\{-[V_{\text{iso}}(\mathbf{r}) + V_{\text{aniso}}(\alpha\gamma; \mathbf{r})]/kT\} \\
&\quad \times \frac{1}{\omega' - G_{\alpha\beta} R_1(\mathbf{r})} \times \frac{1}{\omega'' - F_{\gamma\delta} R_2(\mathbf{r})} \langle \alpha\beta | \gamma\delta \rangle \\
&\quad \times \langle \gamma\delta | \rho^{(b)} | (i'_1 j'_1) \rangle \langle j_2 j_2 \rangle , \quad (21)
\end{aligned}$$

where

$$V_{\text{aniso}}(\alpha\gamma; \mathbf{r}) = G_{\alpha} R_1(\mathbf{r}) + F_{\gamma} R_2(\mathbf{r}) . \quad (22)$$

In the above expression, the factors $\langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle \equiv \langle \alpha | \gamma \rangle \langle \beta | \delta \rangle$ describe the overlap between the eigenvectors of the Liouville operator G and the eigenvectors of the Liouville operator F . If G and F commute, they have common eigenvectors and $\langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle = \delta_{\alpha\gamma} \delta_{\beta\delta}$.

To obtain an expression for $\text{Im} \langle i_1 j_1^\dagger | \langle 1/(\omega' - L_1^{(0)}) \times 1/(\omega'' - L_1^{(1)}) \rangle_{b,r} | i_1' j_1'^\dagger \rangle$, we use the well-known formal identity

$$\lim_{\epsilon \rightarrow 0} \frac{1}{\omega - L + i\epsilon} = P \frac{1}{\omega - L} - i\pi \delta(\omega - L), \quad (23)$$

where P indicates the Cauchy principal value of the integral and δ is a Dirac function with a Liouville operator as its argument, and find

$$\begin{aligned} & \text{Im} \langle i_1 j_1^\dagger | \left\langle \frac{1}{\omega' - L_1^{(0)}} \times \frac{1}{\omega'' - L_1^{(1)}} \right\rangle_{b,r} | i_1' j_1'^\dagger \rangle \\ &= -4\pi^2 n_b \sum_{i_2 j_2} \sum_{\alpha\beta} \sum_{\gamma\delta} \langle (i_1 j_1^\dagger) (i_2 j_2^\dagger) | \alpha \beta^\dagger \rangle \int_0^\infty dr r^2 \exp\{-[V_{\text{iso}}(r) + V_{\text{aniso}}(\alpha\gamma; r)]/kT\} \\ & \quad \times \left\{ P \frac{1}{\omega' - G_{\alpha\beta} R_1(r)} \delta[\omega'' - F_{\gamma\delta} R_2(r)] + \delta[\omega' - G_{\alpha\beta} R_1(r)] P \frac{1}{\omega'' - F_{\gamma\delta} R_2(r)} \right\} \langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle \langle \gamma \delta^\dagger | \rho^{(b)} | (i_1' j_1'^\dagger) (j_2 j_2^\dagger) \rangle \\ &= - \sum_{i_2 j_2} \sum_{\alpha\beta} \sum_{\gamma\delta} \langle (i_1 j_1^\dagger) (i_2 j_2^\dagger) | \alpha \beta^\dagger \rangle \left\{ P \frac{1}{\omega' - G_{\alpha\beta} R_1[R_2^{-1}(\omega''/F_{\gamma\delta})]} \times \frac{1}{|F_{\gamma\delta}|} u \left[R_2^{-1} \left(\frac{\omega''}{F_{\gamma\delta}} \right) \right] \right. \\ & \quad \times \exp \left\{ -V_{\text{aniso}} \left[\alpha\gamma; R_2^{-1} \left(\frac{\omega''}{F_{\gamma\delta}} \right) \right] / kT \right\} + \frac{1}{|G_{\alpha\beta}|} v \left[R_1^{-1} \left(\frac{\omega'}{G_{\alpha\beta}} \right) \right] \exp \left\{ -V_{\text{aniso}} \left[\alpha\gamma; R_1^{-1} \left(\frac{\omega'}{G_{\alpha\beta}} \right) \right] / kT \right\} \\ & \quad \times P \frac{1}{\omega'' - F_{\gamma\delta} R_2[R_1^{-1}(\omega'/G_{\alpha\beta})]} \left. \right\} \langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle \langle \gamma \delta^\dagger | \rho^{(b)} | (i_1' j_1'^\dagger) (j_2 j_2^\dagger) \rangle, \end{aligned} \quad (24)$$

where $R_2^{-1}(\omega''/F_{\gamma\delta})$ is the positive solution of the equation $\omega'' - F_{\gamma\delta} R_2(r) = 0$ and $R_1^{-1}(\omega'/G_{\alpha\beta})$ is the positive solution of the equation $\omega' - G_{\alpha\beta} R_1(r) = 0$, respectively. In the above expression, $u(r)$ and $v(r)$ are defined by

$$u(r) = 4\pi^2 n_b \Theta(r) \frac{r^2}{|R_2'(r)|} \exp[-V_{\text{iso}}(r)/kT] \quad (25)$$

and

$$v(r) = 4\pi^2 n_b \Theta(r) \frac{r^2}{|R_1'(r)|} \exp[-V_{\text{iso}}(r)/kT], \quad (26)$$

where $R'(r) = dR(r)/dr$ and $\Theta(r)$ is the unit step function defined as follows:

$$\Theta(r) = 1, \quad \text{if } r > 0,$$

$$\Theta(r) = 0, \quad \text{if } r < 0.$$

C. The individual line shape functions

To simplify the notation, we omit the subscript 1 of i_1 and j_1 indicating the absorber molecule. With Eqs. (15) and (24), the spectral density can be rewritten as

$$\begin{aligned} F(\omega) &= -\frac{1}{\pi} \sum_{ij} \sum_{i'j'} \langle j | \mu_a | i \rangle \cdot \left(\frac{1}{2\pi i} \right)^2 \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \frac{1}{\omega - \omega' - \omega'' - \omega_{ij}} \\ & \quad \times \text{Im} \langle ij^\dagger | \left\langle \frac{1}{\omega' - L_1^{(0)}} \times \frac{1}{\omega'' - L_1^{(1)}} \right\rangle_{b,r} | i' j'^\dagger \rangle \langle i' | \rho^{(a)} \mu_a | j' \rangle \\ &= \frac{1}{\pi} \sum_{ij} \sum_{i'j'} \langle j | \mu_a | i \rangle \cdot \sum_{i_2 j_2} \sum_{\alpha\beta} \sum_{\gamma\delta} \langle (ij^\dagger) (i_2 j_2^\dagger) | \alpha \beta^\dagger \rangle \left(\frac{1}{2\pi i} \right)^2 \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \frac{1}{\omega - \omega' - \omega'' - \omega_{ij}} \end{aligned}$$

$$\begin{aligned}
& \times \left\{ P \frac{1}{\omega' - G_{\alpha\beta} R_1 [R_2^{-1}(\omega'/F_{\gamma\delta})]} \times \frac{1}{F_{\gamma\delta}} \mu \left[R_2^{-1} \left(\frac{\omega''}{F_{\gamma\delta}} \right) \right] \exp \left\{ -V_{\text{aniso}} \left[\alpha \gamma; R_2^{-1} \left(\frac{\omega''}{F_{\gamma\delta}} \right) \right] / kT \right\} \right. \\
& + \frac{1}{G_{\alpha\beta}} \nu \left[R_1^{-1} \left(\frac{\omega'}{G_{\alpha\beta}} \right) \right] \exp \left\{ -V_{\text{aniso}} \left[\alpha \gamma; R_1^{-1} \left(\frac{\omega'}{G_{\alpha\beta}} \right) \right] / kT \right\} \times P \frac{1}{\omega'' - F_{\gamma\delta} R_2 [R_1^{-1}(\omega'/G_{\alpha\beta})]} \left. \right\} \\
& \times \langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle \langle \gamma \delta^\dagger | \rho^{(b)} | (i' j'^\dagger) (j_2 j_2^\dagger) \rangle \langle i' | \rho^{(a)} \mu_a | j' \rangle. \quad (27)
\end{aligned}$$

By carrying out the integrations in Eq. (27) (see the Appendix), we obtain

$$\begin{aligned}
F(\omega) &= \frac{1}{\pi} \sum_{ij} \sum_{i'j'} \langle j | \mu_a | i \rangle \cdot \sum_{i_2 j_2} \sum_{\alpha\beta} \sum_{\gamma\delta} \langle (ij^\dagger) (i_2 j_2^\dagger) | \alpha \beta^\dagger \rangle \\
&\quad \times I_{\alpha\beta\gamma\delta}(\omega - \omega_{ij}) \langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle \\
&\quad \times \langle \gamma \delta^\dagger | \rho^{(b)} | (i' j'^\dagger) (j_2 j_2^\dagger) \rangle \langle i' | \rho^{(a)} \mu_a | j' \rangle \\
&= \frac{1}{\pi} \sum_{ij} \langle j | \mu_a | i \rangle \cdot \sum_{i_2} \sum_{\alpha\beta} \sum_{\gamma\delta} \langle (ij^\dagger) (i_2 j_2^\dagger) | \alpha \beta^\dagger \rangle \\
&\quad \times I_{\alpha\beta\gamma\delta}(\omega - \omega_{ij}) \langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle \langle \gamma | \rho^{(b)} \rho^{(a)} \mu_a | \delta \rangle \\
&= \frac{1}{\pi} \sum_{ij} \sum_{\{m\}} \sum_{i_2} \sum_{\alpha\beta} \sum_{\gamma\delta} \langle \langle \alpha | i i_2 \rangle \langle i | \mu_m | j \rangle \langle j i_2 | \beta \rangle \rangle^* \\
&\quad \times I_{\alpha\beta\gamma\delta}(\omega - \omega_{ij}) \langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle \langle \gamma | \rho^{(b)} \rho^{(a)} \mu_m | \delta \rangle. \quad (28)
\end{aligned}$$

In the last expression for $F(\omega)$, the summation indices i and j exclude their magnetic quantum numbers since the latter are included in the summation over the magnetic quantum numbers indicated by $\{m\}$. If we introduce the individual line shape function $\chi_{ij}(\omega - \omega_{ij})$ defined by

$$\begin{aligned}
\chi_{ij}(\omega - \omega_{ij}) &= (\omega - \omega_{ij})^2 \sum_{\{m\}} \sum_{i_2} \sum_{\alpha\beta} \sum_{\gamma\delta} \langle \langle \alpha | i i_2 \rangle \langle i | \mu_m | j \rangle \\
&\quad \times \langle j i_2 | \beta \rangle \rangle^* I_{\alpha\beta\gamma\delta}(\omega - \omega_{ij}) \langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle \\
&\quad \times \langle \gamma | \rho^{(b)} \rho^{(a)} \mu_m | \delta \rangle / \rho_i |\mu_{ij}|^2, \quad (29)
\end{aligned}$$

where the reduced matrix elements μ_{ij} is defined by

$$\langle i | \mu_m | j \rangle = C(j1i; m_j m m_i) \mu_{ij} / (2i+1)^{1/2}, \quad (30)$$

then the spectral density takes a more familiar form

$$F(\omega) = \frac{1}{\pi} \sum_{ij} \rho_i |\mu_{ij}|^2 \frac{1}{(\omega - \omega_{ij})^2} \chi_{ij}(\omega - \omega_{ij}). \quad (31)$$

We can also introduce the symmetric individual line shape functions which correspond to the replacement of $I_{\alpha\beta\gamma\delta}(\omega - \omega_{ij})$ by their symmetric partners $\hat{I}_{\alpha\beta\gamma\delta}(\omega - \omega_{ij})$ (see the Appendix) in the expression for $\chi_{ij}(\omega - \omega_{ij})$,

$$\begin{aligned}
\hat{\chi}_{ij}(\omega - \omega_{ij}) &\equiv \exp[\hbar(\omega - \omega_{ij})/2kT] \chi_{ij}(\omega - \omega_{ij}) \\
&= (\omega - \omega_{ij})^2 \sum_{\{m\}} \sum_{i_2} \sum_{\alpha\beta} \sum_{\gamma\delta} \langle \langle \alpha | i i_2 \rangle \langle i | \mu_m | j \rangle \\
&\quad \times \langle j i_2 | \beta \rangle \rangle^* \hat{I}_{\alpha\beta\gamma\delta}(\omega - \omega_{ij}) \langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle \\
&\quad \times \langle \gamma | \rho^{(b)} \rho^{(a)} \mu_m | \delta \rangle / \rho_i |\mu_{ij}|^2. \quad (32)
\end{aligned}$$

To satisfy the detailed balance requirement,¹⁴ the spectral density must take the following form:

$$\begin{aligned}
F(\omega) &= \frac{1}{\pi} \sum_{\omega_{ij} > 0} \exp[-\hbar(\omega - \omega_{ij})/2kT] \\
&\quad \times \left[\frac{1}{(\omega - \omega_{ij})^2} \hat{\chi}_{ij}(\omega - \omega_{ij}) \right. \\
&\quad \left. + \frac{1}{(\omega + \omega_{ij})^2} \hat{\chi}_{ji}(\omega + \omega_{ij}) \right] \rho_i |\mu_{ij}|^2, \quad (33)
\end{aligned}$$

with

$$\hat{\chi}_{ij}(\omega) = \hat{\chi}_{ji}(-\omega). \quad (34)$$

Consequently, in terms of $\hat{\chi}_{ij}(\omega)$, the total absorption coefficient $\alpha(\omega)$ is given by

$$\begin{aligned}
\alpha(\omega) &= n_a \sum_{\omega_{ij} > 0} S_{ij} \frac{\omega \sinh(\hbar\omega/2kT)}{\omega_{ij} \sinh(\hbar\omega_{ij}/2kT)} \frac{1}{\pi} \left[\frac{1}{(\omega - \omega_{ij})^2} \right. \\
&\quad \left. \times \hat{\chi}_{ij}(\omega - \omega_{ij}) + \frac{1}{(\omega + \omega_{ij})^2} \hat{\chi}_{ji}(\omega + \omega_{ij}) \right], \quad (35)
\end{aligned}$$

where S_{ij} is the usual line strength.¹⁵

D. The band-averaged line shape function

For practical calculation, we introduce the intensity weighted band-averaged line shape function defined by

$$\begin{aligned}
\hat{\chi}(\omega) &\equiv \sum_{ij} \rho_i |\mu_{ij}|^2 \hat{\chi}_{ij}(\omega) / \sum_{ij} \rho_i |\mu_{ij}|^2 \\
&= \omega^2 \sum_{\alpha\beta} \sum_{\gamma\delta} \langle \alpha | \mu_m | \beta \rangle^* \hat{I}_{\alpha\beta\gamma\delta}(\omega) \langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle \langle \gamma | \rho^{(b)} \rho^{(a)} \mu_m | \delta \rangle / \sum_{ij} \rho_i |\mu_{ij}|^2
\end{aligned}$$

$$= 4\pi^2 n_b \omega^2 \sum_{\alpha\beta} \sum_{\gamma\delta} \langle \alpha | \mu_m | \beta \rangle^* \Theta(r_c) \left| \frac{1}{G_{\alpha\beta} R_1'(r_c) + F_{\gamma\delta} R_2'(r_c)} \right| r_c^2 \\ \times \exp\{-V_{\text{iso}}(r_c)/kT - [(G_\alpha + G_\beta)R_1(r_c) + (F_\gamma + F_\delta)R_2(r_c)]/2kT\} \langle \alpha\beta^\dagger | \gamma\delta^\dagger \rangle \langle \gamma | \rho^{(b)} \rho^{(a)} \mu_m | \delta \rangle / \sum_{ij} \rho_i |\mu_{ij}|^2, \quad (36)$$

where r_c is determined by

$$\omega = G_{\alpha\beta} R_1(r_c) + F_{\gamma\delta} R_2(r_c), \quad (37)$$

or approximately by

$$r_c = R_1^{-1} \left\{ \frac{\omega}{G_{\alpha\beta}} - \frac{1}{G_{\alpha\beta}} F_{\gamma\delta} R_2 \left[R_1^{-1} \left(\frac{\omega}{G_{\alpha\beta}} \right) \right] \right\}. \quad (38)$$

In general, for a specified pair of α and β , the value of r_c and the weighting factor $\exp\{-V_{\text{iso}}(r_c)/kT - [(G_\alpha + G_\beta)R_1(r_c) + (F_\gamma + F_\delta)R_2(r_c)]/2kT\}$ depends on γ and δ . However, in practice, due to the overlap factor $\langle \alpha\beta^\dagger | \gamma\delta^\dagger \rangle$, the summations over γ and δ can be limited to those pairs which significantly overlap with α and β only. It turns out that the most overlapping pair of γ and δ is that whose eigenvalues F_γ and F_δ are the closest to $F_\alpha \equiv \langle \alpha | F | \alpha \rangle$ and $F_\beta \equiv \langle \beta | F | \beta \rangle$, respectively. In fact, we can express F_α and F_β as

$$F_\alpha = \sum_\gamma \langle \alpha | \gamma \rangle F_\gamma \langle \gamma | \alpha \rangle \quad (39a)$$

and

$$F_\beta = \sum_\delta \langle \beta | \delta \rangle F_\delta \langle \delta | \beta \rangle, \quad (39b)$$

respectively. Since they are the average values of F_γ and F_δ over γ and δ with the overlapping weights $|\langle \alpha | \gamma \rangle|^2$ and $|\langle \beta | \delta \rangle|^2$, they are more likely close to the most heavily weighted values. The more overlapping of $\langle \alpha\beta^\dagger | \gamma\delta^\dagger \rangle$, the closer is the average values and the most heavily weighted values. Then as an approximation we can replace F_γ and F_δ by F_α and F_β , and replace $\langle \alpha\beta^\dagger | \gamma\delta^\dagger \rangle$ by $\delta_{\alpha\gamma} \delta_{\beta\delta}$. These replacements can also be made for the case of $GR_1(r) \gg FR_2(r)$ since the usual perturbation method is applicable. In these cases, the corresponding value of r_c denoted by \bar{r}_c ,

$$\bar{r}_c = R_1^{-1} \left\{ \frac{\omega}{G_{\alpha\beta}} - \frac{1}{G_{\alpha\beta}} F_{\alpha\beta} R_2 \left[R_1^{-1} \left(\frac{\omega}{G_{\alpha\beta}} \right) \right] \right\}, \quad (40)$$

and the weighting factors are independent of γ and δ . Then the expression for $\hat{\chi}(\omega)$ can be simplified by omitting the summations over γ and δ , i.e.,

$$\hat{\chi}(\omega) = 4\pi^2 n_b \omega^2 \sum_{\alpha\beta} \langle \alpha | \mu_m | \beta \rangle^* \Theta(\bar{r}_c) \\ \times \left| \frac{1}{G_{\alpha\beta} R_1'(\bar{r}_c) + F_{\alpha\beta} R_2'(\bar{r}_c)} \right| \bar{r}_c^2 \exp\{-V_{\text{iso}}(\bar{r}_c)/kT \\ - [(G_\alpha + G_\beta)R_1(\bar{r}_c) + (F_\alpha + F_\beta)R_2(\bar{r}_c)]/2kT\} \\ \times \langle \alpha | \rho^{(b)} \rho^{(a)} \mu_m | \beta \rangle / \sum_{ij} \rho_i |\mu_{ij}|^2. \quad (41)$$

More suitably, we can also introduce the positive and negative frequency resonance-average line shape functions $\hat{\chi}_+(\omega)$ and $\hat{\chi}_-(\omega)$ as we did previously.⁷ We define the intensity weighted positive frequency resonance-average line shape function by

$$\hat{\chi}_+(\omega) \equiv \sum_{\omega_{ij}>0} \hat{\chi}_{ij}(\omega) \rho_i |\mu_{ij}|^2 / \sum_{\substack{ij \\ E_i > E_j}} \rho_i |\langle i | \mu_m | j \rangle|^2, \quad (42)$$

and the intensity weighted negative frequency resonance-average line shape function by

$$\hat{\chi}_-(\omega) \equiv \sum_{\omega_{ij}>0} \hat{\chi}_{ji}(\omega) \rho_j |\mu_{ji}|^2 / \sum_{\substack{ij \\ E_i > E_j}} \rho_j |\langle j | \mu_m | i \rangle|^2. \quad (43)$$

Their explicit expressions are easily obtained by comparing with the expression for $\hat{\chi}(\omega)$, but are not presented here. With the two average line shape functions, the absorption coefficient can be written as

$$\alpha(\omega) = n_a \sum_{\omega_{ij}>0} S_{ij} \frac{\omega \hbar \omega / 2kT}{\omega_{ij} \hbar \omega_{ij} / 2kT} \frac{1}{\pi} \left[\frac{1}{(\omega - \omega_{ij})^2} \right. \\ \left. \times \hat{\chi}_+(\omega - \omega_{ij}) + \frac{1}{(\omega + \omega_{ij})^2} \hat{\chi}_-(\omega + \omega_{ij}) \right]. \quad (44)$$

If one does not distinguish between these two different functions, then in terms of the band-average line shape function $\hat{\chi}(\omega)$, the absorption coefficient $\alpha(\omega)$ is given by

$$\alpha(\omega) = n_a \sum_{\omega_{ij}>0} S_{ij} \frac{\omega \hbar \omega / 2kT}{\omega_{ij} \hbar \omega_{ij} / 2kT} \frac{1}{\pi} \left[\frac{1}{(\omega - \omega_{ij})^2} \right. \\ \left. \times \hat{\chi}(\omega - \omega_{ij}) + \frac{1}{(\omega + \omega_{ij})^2} \hat{\chi}(\omega + \omega_{ij}) \right]. \quad (45)$$

III. SOME EXAMPLES

As a first example, we consider a system in which the leading anisotropic interaction is the dipole-dipole interaction and the next leading term is the dipole-quadrupole interaction. This implies that

$$R_1(r) = \frac{1}{r^3} \quad \text{and} \quad R_2(r) = \frac{1}{r^4}. \quad (46)$$

With the assumption $G(1/r^3) \gg F(1/r^4)$, it is easy to find the approximate values for r_c in Eq. (38)

$$r_c \approx r_0 \left[1 + \frac{1}{3} \left(\frac{1}{G_{\alpha\beta}} \right)^{4/3} F_{\gamma\delta} \omega^{1/3} \right], \quad (47)$$

where

$$r_0 = \left(\frac{G_{\alpha\beta}}{\omega} \right)^{1/3}. \quad (48)$$

It is obvious that r_0 is the lowest-order approximation for r_c . Then Eq. (A12) can be expressed as

$$\begin{aligned} \hat{I}_{\alpha\beta\gamma\delta}(\omega) = & \frac{4\pi^2}{3} n_b \frac{1}{\omega^2} \left[1 + \frac{2}{3} \left(\frac{1}{G_{\alpha\beta}} \right)^{4/3} F_{\gamma\delta} \omega^{1/3} \right] \\ & \times \Theta(r_c) |G_{\alpha\beta}| \exp\{-V_{\text{iso}}(r_c)/kT \\ & - [(G_{\alpha} + G_{\beta})/r_c^3 + (F_{\gamma} + F_{\delta})/r_c^4]/2kT\}. \end{aligned} \quad (49)$$

Accordingly, we find the symmetric band-averaged line shape function

$$\begin{aligned} \hat{\chi}(\omega) = & \frac{4\pi^2}{3} n_b \sum_{\alpha\beta} \langle \alpha | \mu_m | \beta \rangle^* \Theta(r_c) |G_{\alpha\beta}| \sum_{\gamma\delta} \exp\{-V_{\text{iso}}(r_c)/kT - [(G_{\alpha} + G_{\beta})/r_c^3 + (F_{\gamma} + F_{\delta})/r_c^4]/2kT\} \langle \alpha\beta^{\dagger} | \gamma\delta^{\dagger} \rangle \\ & \times \left[\langle \gamma | \rho^{(b)} \rho^{(a)} \mu_m | \delta \rangle + \frac{2}{3} \left(\frac{1}{G_{\alpha\beta}} \right)^{4/3} \omega^{1/3} \langle \gamma | F_{\gamma\delta} \rho^{(b)} \rho^{(a)} \mu_m | \delta \rangle \right] / \sum_{ij} \rho_i |\mu_{ij}|^2 \\ = & \frac{4\pi^2}{3} n_b \sum_{\alpha\beta} \langle \alpha | \mu_m | \beta \rangle^* \Theta(\bar{r}_c) |G_{\alpha\beta}| \exp\{-V_{\text{iso}}(\bar{r}_c)/kT - [(G_{\alpha} + G_{\beta})/\bar{r}_c^3 + (F_{\alpha} + F_{\beta})/\bar{r}_c^4]/2kT\} \\ & \times \left[\langle \alpha | \rho^{(b)} \rho^{(a)} \mu_m | \beta \rangle + \frac{2}{3} \left(\frac{1}{G_{\alpha\beta}} \right)^{4/3} \omega^{1/3} \langle \alpha | [F, \rho^{(b)} \rho^{(a)} \mu_m] | \beta \rangle \right] / \sum_{ij} \rho_i |\mu_{ij}|^2, \end{aligned} \quad (50)$$

where F is the matrix operator and

$$[F, \rho^{(b)} \rho^{(a)} \mu_m] = F \rho^{(b)} \rho^{(a)} \mu_m - \rho^{(b)} \rho^{(a)} \mu_m F.$$

In the last expression of Eq. (50), a simplified form is given by using average values. The lowest-order approximation to $\hat{\chi}(\omega)$ takes a form corresponding to the one component case of the anisotropic interaction (the leading dipole-dipole term) considered previously⁷

$$\begin{aligned} \hat{\chi}^{(0)}(\omega) = & \frac{4\pi^2}{3} n_b \sum_{\alpha\beta} \langle \alpha | \mu_m | \beta \rangle^* \Theta(r_0) |G_{\alpha\beta}| \exp\{-V_{\text{iso}}(r_0)/kT - [(G_{\alpha} + G_{\beta})/r_0^3]/2kT\} \\ & \times \langle \alpha | \rho^{(b)} \rho^{(a)} \mu_m | \beta \rangle / \sum_{ij} \rho_i |\mu_{ij}|^2. \end{aligned} \quad (51)$$

As a second example, we consider a case in which the two components of the anisotropic interaction have the same r dependence, i.e., $R_1(r) = R_2(r) \equiv R(r)$. Then Eq. (A12) can be expressed as

$$\begin{aligned} \hat{I}_{\alpha\beta\gamma\delta}(\omega) = & 4\pi^2 n_b \Theta(r_c) \left| \frac{1}{(G_{\alpha\beta} + F_{\gamma\delta}) R'(r_c)} \right| r_c^2 \exp[-V_{\text{iso}}(r_c)/kT - (G_{\alpha} + G_{\beta} + F_{\gamma} + F_{\delta}) R(r_c)/2kT] \\ = & 4\pi^2 n_b \frac{1}{|\omega|} \Theta(r_c) \left| \frac{R(r_c)}{R'(r_c)} \right| r_c^2 \exp[-V_{\text{iso}}(r_c)/kT - (G_{\alpha} + G_{\beta} + F_{\gamma} + F_{\delta}) R(r_c)/2kT] \end{aligned} \quad (52)$$

where

$$r_c = R^{-1} \left(\frac{\omega}{G_{\alpha\beta} + F_{\gamma\delta}} \right). \quad (53)$$

Then,

$$\begin{aligned}
\hat{\chi}(\omega) &= 4\pi^2 n_b |\omega| \sum_{\alpha\beta} \langle \alpha | \mu_m | \beta \rangle^* \sum_{\gamma\delta} \Theta(r_c) \left| \frac{R(r_c)}{R'(r_c)} \right| r_c^2 \exp\{-V_{\text{iso}}(r_c)/kT - (G_\alpha + G_\beta + F_\gamma + F_\delta)R(r_c)/2kT\} \\
&\quad \times \langle \alpha\beta^\dagger | \gamma\delta^\dagger \rangle \langle \gamma | \rho^{(b)} \rho^{(a)} \mu_m | \delta \rangle \bigg/ \sum_{ij} \rho_i |\mu_{ij}|^2 \\
&= 4\pi^2 n_b |\omega| \sum_{\alpha\beta} \langle \alpha | \mu_m | \beta \rangle^* \Theta(\bar{r}_c) \left| \frac{R(\bar{r}_c)}{R'(\bar{r}_c)} \right| \bar{r}_c^2 \exp\{-V_{\text{iso}}(\bar{r}_c)/kT - (G_\alpha + G_\beta + F_\alpha + F_\beta)R(\bar{r}_c)/2kT\} \\
&\quad \times \langle \alpha | \rho^{(b)} \rho^{(a)} \mu_m | \beta \rangle \bigg/ \sum_{ij} \rho_i |\mu_{ij}|^2,
\end{aligned} \tag{54}$$

where

$$\bar{r}_c = R^{-1} \left(\frac{\omega}{G_{\alpha\beta} + F_{\alpha\beta}} \right). \tag{55}$$

These expressions are consistent with those obtained directly from one component formalism.

Finally, we consider a system consisting of a linear absorber molecule and a perturber atom. The isotropic potential is assumed to be a Lennard-Jones model

$$V_{\text{iso}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \tag{56}$$

where ϵ and σ are the usual parameters. In general, the anisotropic potential can be expressed as

$$V_{\text{aniso}}(r, \theta) = \sum_l P_l(\cos \theta) V_l(r), \tag{57}$$

where θ is the angle between the absorber-perturber axis and the linear molecular axis, and $P_l(\cos \theta)$ is the associated Legendre polynomial. For a highly anisotropic system, several components $P_l(\cos \theta)$ have to be included in the expansion of Eq. (57). As an example, we consider the CO₂-Ar system where only even l occur because of the symmetry of CO₂. Therefore, the anisotropic interaction takes the form

$$\begin{aligned}
V_{\text{aniso}}(r, \theta) &= P_2(\cos \theta) V_2(r) + P_4(\cos \theta) V_4(r) \\
&\quad + P_6(\cos \theta) V_6(r) + \dots
\end{aligned} \tag{58}$$

For convenience, we model $V_l(r)$ by

$$\begin{aligned}
\hat{I}_{\alpha\beta\gamma\delta\zeta\eta}(\omega) &= 4\pi^2 n_b \Theta(r_c) \left| \frac{1}{G_{\alpha\beta} V_2'(r_c) + F_{\gamma\delta} V_4'(r_c) + H_{\zeta\eta} V_6'(r_c)} \right| r_c^2 \\
&\quad \times \exp\{-V_{\text{iso}}(r_c)/kT - [(G_\alpha + G_\beta) V_2(r_c) + (F_\gamma + F_\delta) V_4(r_c) + (H_\zeta + H_\eta) V_6(r_c)]/2kT\},
\end{aligned} \tag{61}$$

where r_c is determined by

$$\omega = G_{\alpha\beta} V_2(r_c) + F_{\gamma\delta} V_4(r_c) + H_{\zeta\eta} V_6(r_c). \tag{62}$$

Then, one can write the symmetric band-averaged line shape function as

$$V_l(r) = 4\epsilon \left[B_l \left(\frac{\sigma}{r} \right)^{12} - A_l \left(\frac{\sigma}{r} \right)^6 \right], \tag{59}$$

where B_l and A_l are the parameters. Then the potential energy surface of the system is simply determined by ϵ , σ , B_l , and A_l .

Taking the absorber-perturber axis along the z direction of a space-fixed frame, the orientation of CO₂ with respect to the space-fixed frame is represented by θ and φ , and the anisotropic potential is independent of φ . Writing $P_l(\cos \theta) = [(4\pi)/(2l+1)] Y_{l0}(\theta, \varphi)$, it is easy to diagonalize the components $P_l(\cos \theta)$ in the rotational basis $|lm\rangle$ since all the matrices of the components $P_l(\cos \theta)$ take exactly the same block form, and each of these subblocks is labeled by the magnetic quantum number m . Then, in the subspace labeled by m , one can use the notation $|\alpha m\rangle$, $|\gamma m\rangle$, $|\zeta m\rangle$, ... and G_α , F_γ , H_ζ , ... to represent the eigenvectors and the eigenvalues of the components $P_2(\cos \theta)$, $P_4(\cos \theta)$, $P_6(\cos \theta)$, etc.,

$$\begin{aligned}
P_2(\cos \theta) |\alpha m\rangle &= G_\alpha |\alpha m\rangle, \\
P_4(\cos \theta) |\gamma m\rangle &= F_\gamma |\gamma m\rangle, \\
P_6(\cos \theta) |\zeta m\rangle &= H_\zeta |\zeta m\rangle.
\end{aligned} \tag{60}$$

For simplifying the notation, the label m will not be written explicitly in further expressions. Including the three components given above, one is able to derive an expression for $\hat{I}_{\alpha\beta\gamma\delta\zeta\eta}(\omega - \omega_{ij})$ similar to Eq. (A12), viz.

$$\hat{\chi}(\omega) = 4\pi^2 n_b \omega^2 \sum_{\alpha\beta} \langle \alpha | \mu_m | \beta \rangle^* \langle \alpha | \rho^{(b)} \rho^{(a)} \mu_m | \beta \rangle \sum_{\gamma\delta} \langle \alpha \beta^\dagger | \gamma \delta^\dagger \rangle \langle \gamma \delta^\dagger | \alpha \beta^\dagger \rangle \Theta(\bar{r}_c) \\ \times \left| \frac{1}{G_{\alpha\beta} V_2'(\bar{r}_c) + F_{\gamma\delta} V_4'(\bar{r}_c) + H_{\alpha\beta} V_6'(\bar{r}_c)} \right| \bar{r}_c^2 \\ \times \exp\{-V_{\text{iso}}(\bar{r}_c)/kT - [(G_\alpha + G_\beta)V_2(\bar{r}_c) + (F_\gamma + F_\delta)V_4(\bar{r}_c) + (H_\alpha + H_\beta)V_6(\bar{r}_c)]/2kT\} / \sum_{ij} \rho_{ij} |\mu_{ij}|^2. \quad (66)$$

Furthermore, if $V_2(r) \gg V_4(r) \gg V_6(r)$, one can set $\gamma = \alpha$ and $\delta = \beta$ further and replace r_c by the approximate values \bar{r}_c determined by the following equation:

$$\omega = G_{\alpha\beta} V_2(\bar{r}_c) + F_{\alpha\beta} V_4(\bar{r}_c) + H_{\alpha\beta} V_6(\bar{r}_c), \quad (67)$$

where

$$F_{\alpha\beta} = \langle \alpha | P_4(\cos \theta) | \alpha \rangle - \langle \beta | P_4(\cos \theta) | \beta \rangle. \quad (68)$$

Then, \bar{r}_c is independent of γ , δ , ζ , and η . Consequently, the symmetric band-averaged line shape function can be simplified to

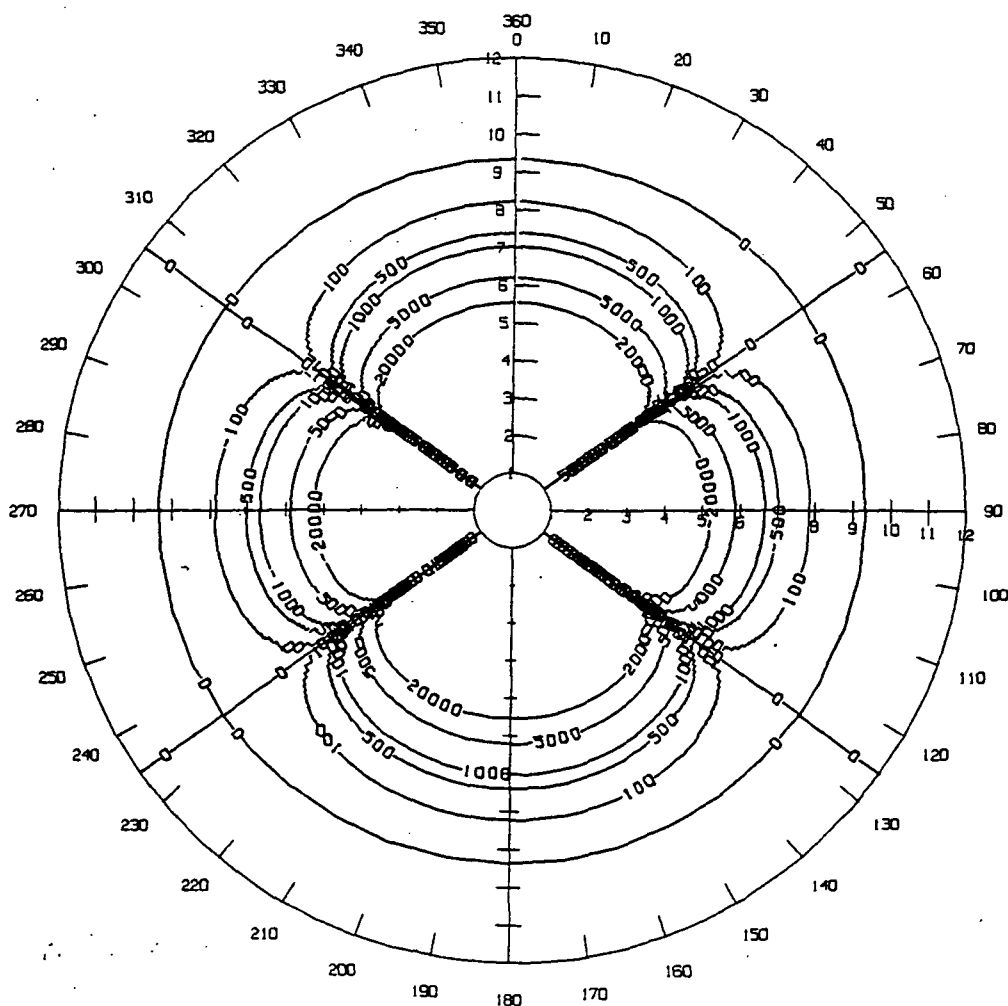


FIG. 2. The anisotropic part of the potential energy surface (in units of Kelvin) for $\text{CO}_2\text{-Ar}$ [Eq. (70)] given by Boissioles *et al.* (Ref. 13). The distances are in atomic units and the angles are in degrees.

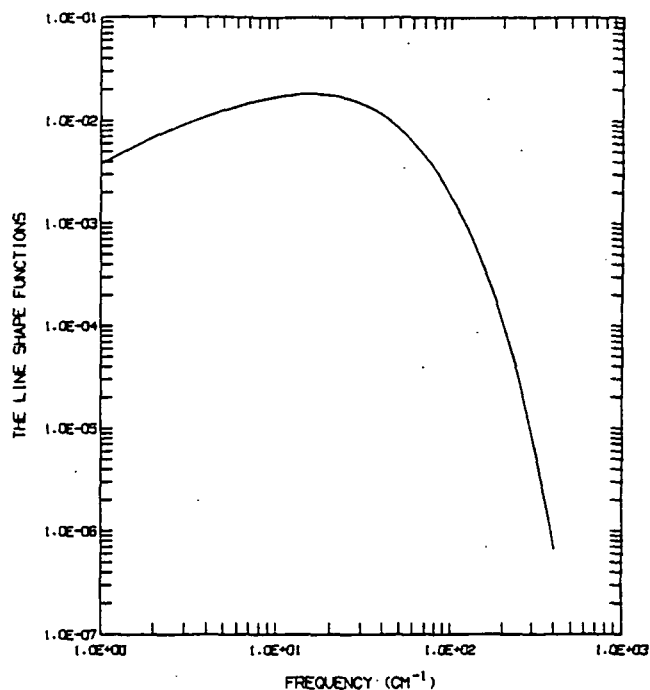


FIG. 3. The band-averaged line shape function (in units of $\text{cm}^{-1} \text{atm}^{-1}$) as a function of frequency ω (in units of cm^{-1}) for lines in the Ar-broadened ν_3 band of CO_2 calculated for $T=296 \text{ K}$ using the potential surface shown in Fig. 1.

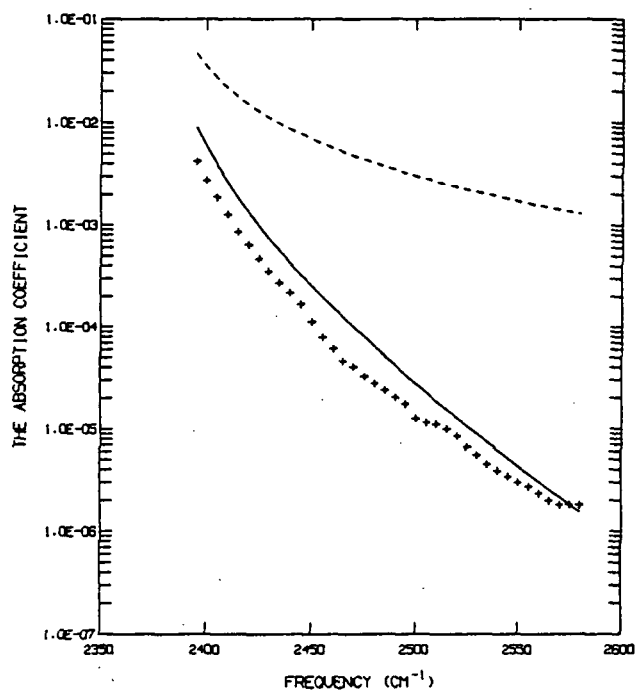


FIG. 4. A comparison between the calculated absorption coefficient (in units of $\text{cm}^2 \text{molecule}^{-1} \text{atm}^{-1}$) for $T=296 \text{ K}$ in the $2400\text{--}2580 \text{ cm}^{-1}$ spectral region of $\text{CO}_2\text{--Ar}$ with experimental data. The solid line is the theoretical values calculated by Boissoules *et al.* (Ref. 13) using the potential energy surface given by Eq. (70); the dashed curve is the results obtained assuming Lorentzian line shapes; and the experimental results (Ref. 13) are denoted by +.

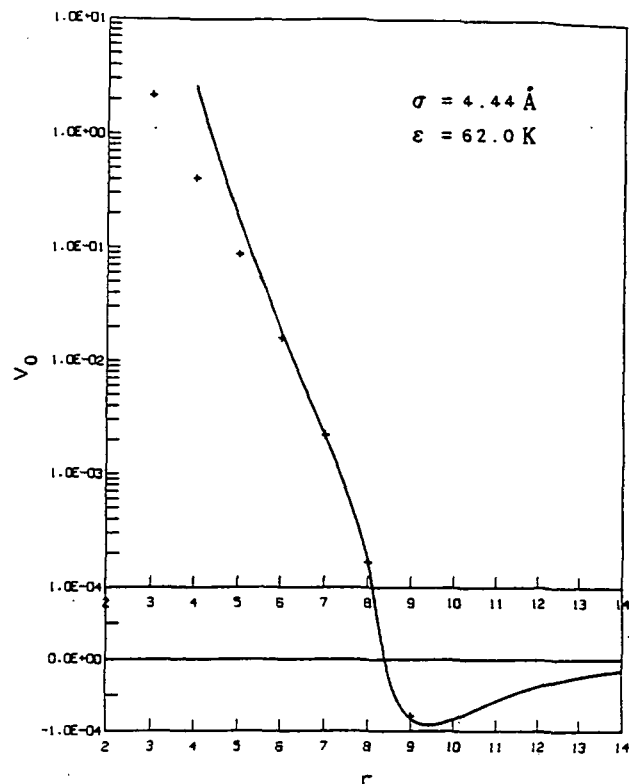


FIG. 5. The function $V_0(r)$ (solid line) vs r obtained by fitting a Lennard-Jones model to the data of Parker and co-workers (Ref. 17) (denoted by +). All quantities are in atomic units.

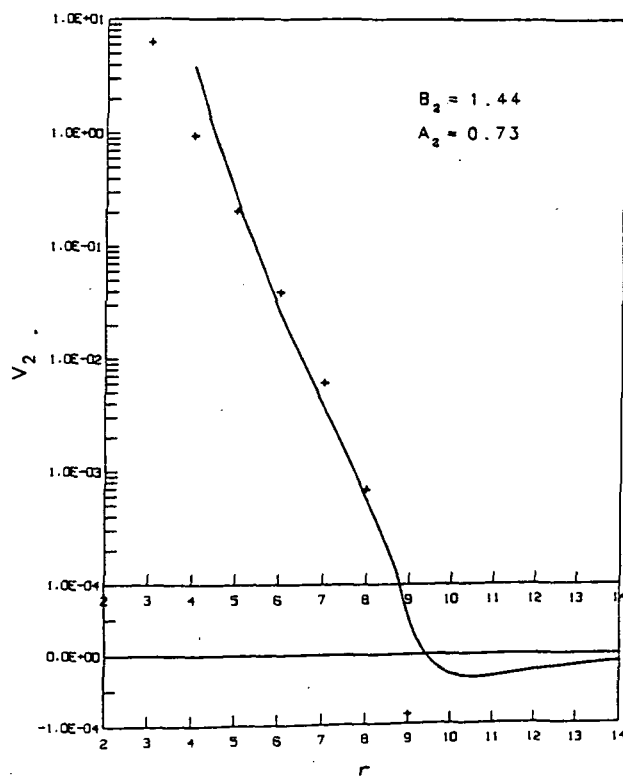


FIG. 6. The same as Fig. 5 for the function $V_2(r)$.

$$\hat{\chi}(\omega) = 4\pi^2 n_b \omega^2 \sum_{\alpha\beta} \langle \alpha | \mu_m | \beta \rangle^* \langle \alpha | \rho^{(b)} \rho^{(a)} \mu_m | \beta \rangle \Theta(\bar{r}_c) \left| \frac{1}{G_{\alpha\beta} V_2'(\bar{r}_c) + F_{\alpha\beta} V_4'(\bar{r}_c) + H_{\alpha\beta} V_6'(\bar{r}_c)} \right| \bar{r}_c^2 \\ \times \exp\{-V_{\text{iso}}(\bar{r}_c)/kT - [(G_\alpha + G_\beta)V_2(\bar{r}_c) + (F_\alpha + F_\beta)V_4(\bar{r}_c) + (H_\alpha + H_\beta)V_6(\bar{r}_c)]/2kT\} / \sum_{ij} \rho_i |\mu_{ij}|^2. \quad (69)$$

IV. APPLICATION TO THE ν_3 BAND OF CO₂ BROADENED BY Ar

We consider the ν_3 band of CO₂ broadened by Ar in which both the experimental measurement of the absorption coefficient and some knowledge of the interaction potential between CO₂ and Ar are available at the present time. The wing of the Ar-broadened ν_3 band of CO₂ for $T=296$ K has been studied by Boisssoles *et al.*¹³ recently using an effective "one-component" potential determined empirically from the spectral moments of the infrared vibration-rotation bands. The form of the potential used in their calculations is

$$V(r, \theta) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + 4\epsilon \left[B_2 \left(\frac{\sigma}{r} \right)^{12} - A_2 \left(\frac{\sigma}{r} \right)^6 \right] P_2(\cos \theta), \quad (70)$$

where the parameters are $\epsilon/k=153$ K, $\sigma=3.91$ Å, $B_2=1.09$, and $A_2=0.266$.

We note that the formula used by Boisssoles *et al.*¹³ to calculate the band-averaged line shape function is similar to our formula obtained previously corresponding to the one-component anisotropic potential case. However, they have

introduced an energetically corrected function in their formalism. As we discuss elsewhere,¹⁶ this correction corresponds to rewriting the spectral density in a more symmetric form

$$F(\omega) = \frac{1}{\pi} \text{Re Tr} \int_0^\infty e^{i\omega t} [\mu_a \sqrt{\rho} \cdot e^{-iLt} \sqrt{\rho} \mu_a] dt. \quad (71)$$

Similarly, we follow the same energetically corrected procedure in the present calculations, but we do not reproduce the expressions here since they are easily obtained from the expressions given above. For the frequency of interest here 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,¹⁵ there are 109 line listed in this band and all of them are included in the calculations. In Figs. 1 and 2, we present the total potential energy surface and the anisotropic potential energy surface of the CO₂-Ar system, respectively, given by Eq. (70). In Fig. 3, the theoretically calculated band-averaged line shape function for $T=296$ K based on the potential used by Boisssoles *et al.* is shown. In Fig. 4, the comparison between the calculated absorption coefficient and the experimental data for $T=296$ K

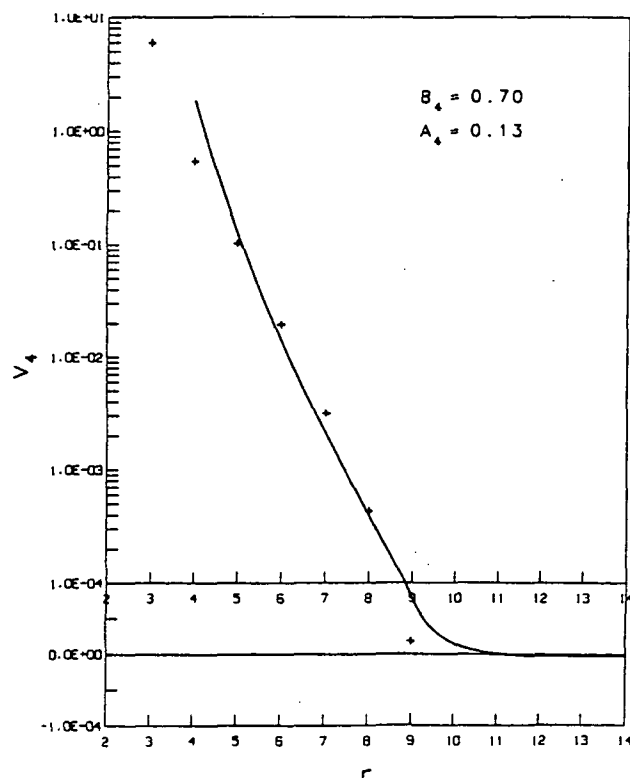


FIG. 7. The same as Fig. 5 for the function $V_4(r)$.

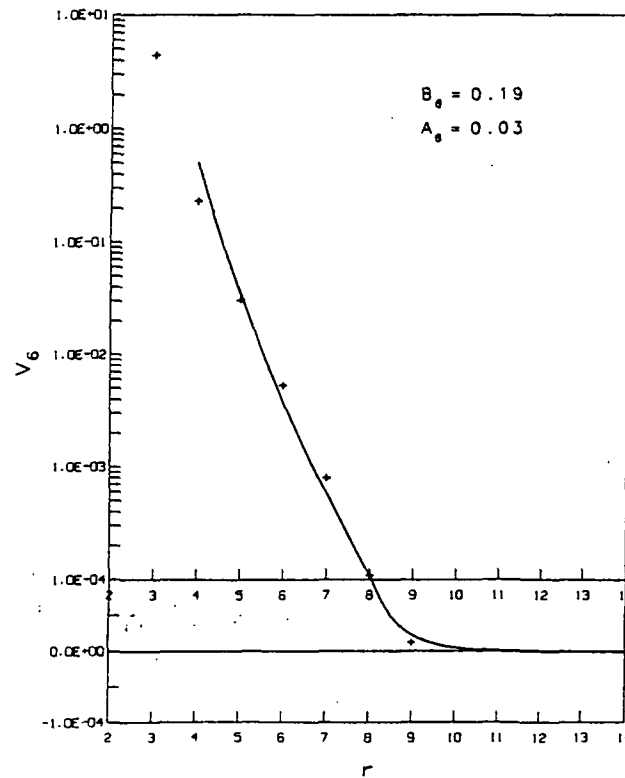


FIG. 8. The same as Fig. 5 for the function $V_6(r)$.

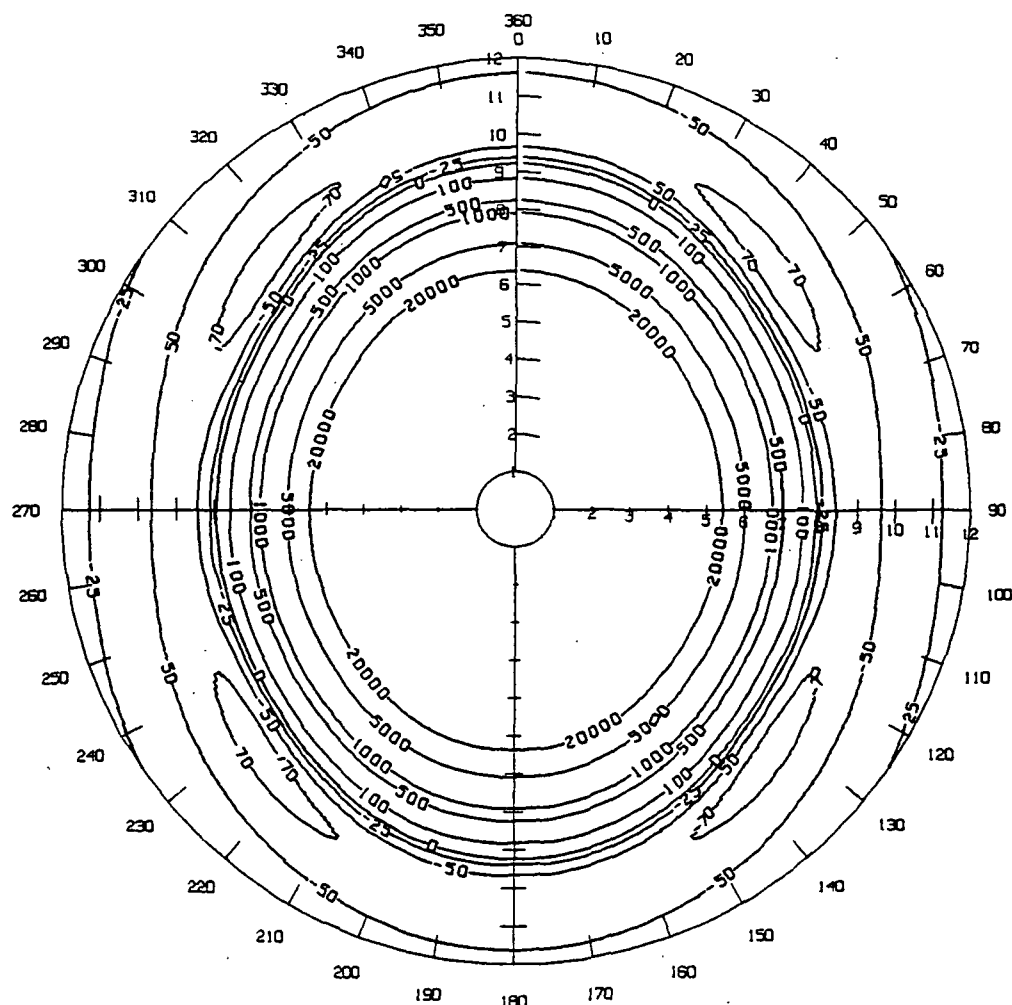


FIG. 9. The total potential energy surface (in units of Kelvin) for $\text{CO}_2\text{-Ar}$ obtained by fitting a Lennard-Jones model to the data of Parker and co-workers (Ref. 17). The distances are in atomic units and the angles are in degrees.

is presented. The results obtained from a Lorentzian line shape are also given in the figure.

For the potential energy surface of the $\text{CO}_2\text{-Ar}$ system, there are some theoretical calculations done by Parker *et al.*¹⁷ In their calculations, the short range potential consists of two terms— $V_{\text{HF}}(r, \theta)$ to take into account the Coulomb, kinetic, and exchange contributions to the interaction energy and $V_{\text{COR}}(r, \theta)$ to take into account the correlation contribution. The values of $V_{\text{HF}}(r, \theta)$ and $V_{\text{COR}}(r, \theta)$ obtained are tabled as the functions of distance and angle (see Tables III and IV of Ref. 17). By fitting these results with an expansion of the Legendre polynomials at each r ,

$$V_{\text{HF}}(r, \theta) = \sum_{l=0,2,4,\dots} V_l^{\text{HF}}(r) P_l(\cos \theta),$$

$$V_{\text{COR}}(r, \theta) = \sum_{l=0,2,4,\dots} V_l^{\text{COR}}(r) P_l(\cos \theta), \quad (72)$$

the values of $V_l^{\text{HF}}(r)$ and $V_l^{\text{COR}}(r)$ at this r are obtained and listed in Tables VII and VIII respectively, of Ref. 17. They have further modified the values of $V_l^{\text{COR}}(r)$ obtained to take into account the proper van der Waals behavior at large distances. However, since the far-wing line shapes are mainly determined by the short range behavior of the interaction

potential, we will not follow their next step and only use the values given in these tables in our calculation.

For simplifying our calculation, analytical expressions for $V_l^{\text{HF}}(r)$ and $V_l^{\text{COR}}(r)$ instead of the tabulated values are necessary. In addition, for later convenience, we prefer to have them take the form of the generalized Lennard-Jones model mentioned previously. It turns out that one is able to fit some coefficients pretty well and to fit others only reasonably well by adjusting the parameters of the Lennard-Jones model. We note that there are some uncertainties in the parameters obtained due to the difficulty of the fitting. In the present calculation, we consider the terms up to $l=6$ only since the magnitudes of the higher terms are much smaller than the lower terms. In Figs. 5–8, we plot the results of fitting for $V_0(r)$, $V_2(r)$, $V_4(r)$, and $V_6(r)$. The potential parameters obtained are $\epsilon/k=62.0$ K, $\sigma=4.44$ Å, $B_2=1.44$, $A_2=0.73$, $B_4=0.70$, $A_4=0.13$, $B_6=0.19$, and $A_6=0.03$. In Figs. 9 and 10, the total potential energy surface and the anisotropic potential energy surface corresponding to the potential parameters given above are presented. Based on this potential, we first calculate the energetically corrected band-averaged line shape function for $T=296$ K from Eq. (69) in which the summations over the pair of γ and δ and the pair

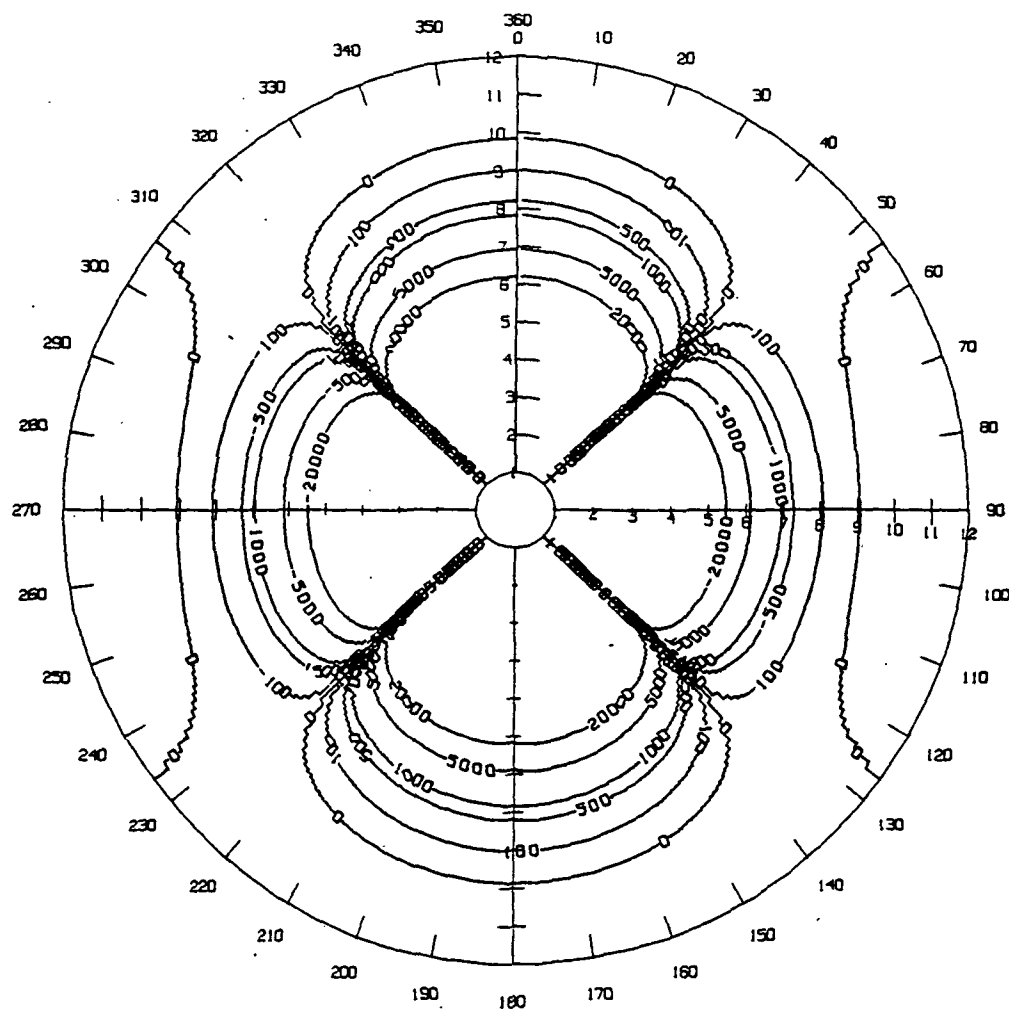


FIG. 10. The anisotropic part of the energy surface (in units of Kelvin) for $\text{CO}_2\text{-Ar}$ obtained by fitting a Lennard-Jones model to the data of Parker and co-workers (Ref. 17). The distances are in atomic units and the angles are in degrees.

of ζ and η have been averaged out and only the summation over the pair of α and β is performed. Then we repeat the same calculation with Eq. (66), in which only the summation over the pair of ζ and η has been averaged out and the summation over the pair of γ and δ is performed corresponding to those pairs with an overlapping restriction, i.e., a cutoff. This cutoff is necessary to be introduced in calculations. It represents a measure of how wide the averaged angular distribution of the CO_2 wave functions with the same magnetic quantum number m spreads. However, in the present study, we do not discuss it further and simply choose $|\langle\alpha|\gamma\rangle|^2 \geq 0.01$ and $|\langle\delta|\beta\rangle|^2 \geq 0.01$. Since the eigenvectors of $P_2(\cos \theta)$ more or less likely overlap with the eigenvectors of $P_4(\cos \theta)$, for a specified $|\alpha\rangle$, the summation over γ with the restriction $|\langle\alpha|\gamma\rangle|^2 \geq 0.01$ includes at least 94% of the states $|\gamma\rangle$. We present the line shape functions obtained in Fig. 11 and the corresponding absorption coefficients in Fig. 12. For comparison, the results obtained with the "one-component" model of Boisssoles *et al.*¹³ are also presented in Fig. 12.

It is well known that the profile of the line shape function is determined by the interaction potential surface. How-

ever, the behavior of the far wing of the line shape function is mainly governed by the short range interaction. More specifically, first of all, the anisotropic potential energy surface determines beyond what kind of positions labeled by r and θ for the $\text{CO}_2\text{-Ar}$ system are able to contribute to the values of shape function at a specified ω . Second, the total potential energy surface determines how much will contribute to it from these locations. For example, in order to estimate the relative magnitude of the shape function around $\omega=200\text{ cm}^{-1}$ in comparison with that around 50 cm^{-1} , one first has to locate the areas in the anisotropic energy surface in which the absolute values of anisotropic energy are at least equal to or larger than the corresponding ω values. Then, in a graph of the total energy surface, one has to find out whether there are significant probabilities to locate a pair of CO_2 and Ar at these areas. Therefore, it is not the total potential energy surface alone, but the relationship between the total and the anisotropic interaction energy surface to determine the profile of the far-wing line shape. These conclusions are easily understood since the first one comes from a basic requirement of the energy conservation and the second one is re-

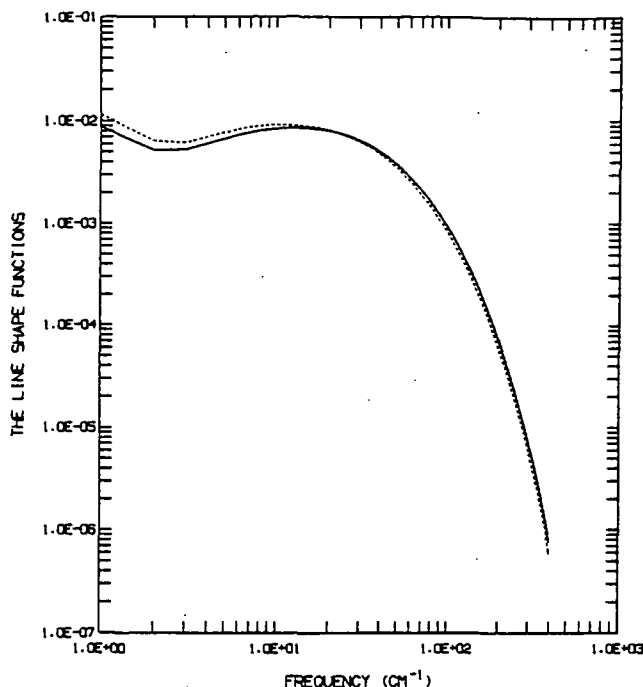


FIG. 11. A comparison between the line shape functions (in units of $\text{cm}^{-1} \text{atm}^{-1}$) for $T=296 \text{ K}$ obtained with the multicomponent anisotropic model given by Eqs. (66) (solid line) and (69) (dotted line), respectively.

lated to a statistically probability to find a pair of CO_2 and Ar at a specified location.

V. DISCUSSION AND CONCLUSIONS

As can be seen clearly from Figs. 3, 11, and 12 that there are substantial differences between the single-component and the multicomponent results for both the line shape and the absorption coefficient. The differences between the results obtained from the two different multicomponent formulations are small. The present theory can reproduce accurately the experimental data for the absorption of the high-frequency wing of the ν_3 band of CO_2 broadened by Ar. Because this spectral region lies beyond the bandhead, most of the absorption arises from the far wings of lines. Therefore, in the present calculations, we have not included either the near-wing corrections¹¹ resulting from the non-commutation of the Liouville operator describing the unperturbed system and that describing the interaction [cf. Eq. (6)], or corrections arising from molecular motion.¹² Of course, for the accurate calculation of the near wing of the lines or absorption resulting from this region (e.g., near the bandhead or closer to the band center), these refinements should be included.

In the present work, we have introduced a cutoff for the overlap factors and arbitrarily chose the values 0.01 for all the subblocks labeled by m . In fact, the cutoff depends on m since the cutoff is related to the averaged angular distribution functions of the CO_2 wave functions with the same magnetic quantum numbers. On the other hand, we have fit the tabular data for the CO_2 -Ar interaction to a Lennard-Jones model to facilitate the calculations. However, this model lacks the

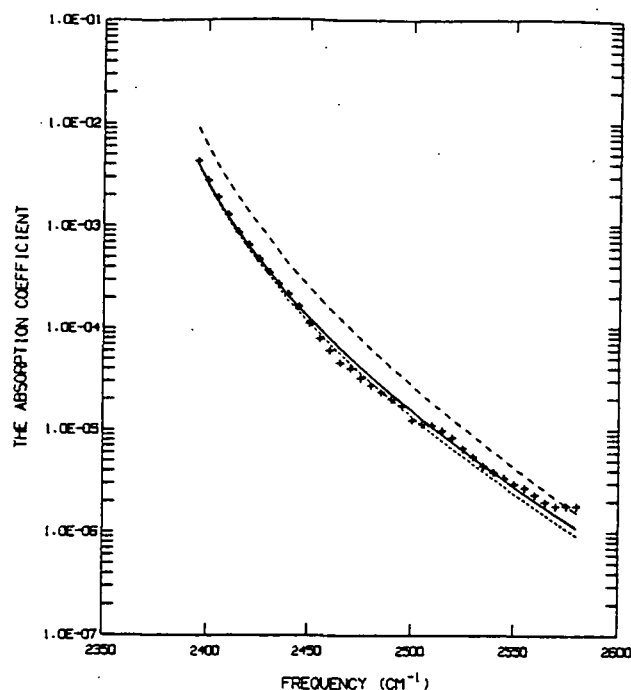


FIG. 12. A comparison between the calculated absorption coefficient (in units of $\text{cm}^2 \text{molecule}^{-1} \text{atm}^{-1}$) for $T=296 \text{ K}$ in the $2400\text{--}2580 \text{ cm}^{-1}$ spectral region of CO_2 -Ar with experimental data. The solid line is the results obtained using Eq. (66), the dotted line is the results obtained using Eq. (69), and the dashed line is the results of Boissoles *et al.* (Ref. 13).

flexibility to present the r dependence well especially for the low-order (e.g., $l=0$ and 2) components. Thus, there is some uncertainty introduced by this procedure as well as in the original data, and these uncertainties affect the magnitude of the absorption. In fact, the absorption is very sensitive to the details of the interaction potential.

With the improvement in the theory detailed in the present paper, one is now able to relate the absorption in the far-wing region of pure rotational or vibration-rotational bands directly to the interaction potential. Although for simplicity in the present paper we considered a linear molecule perturbed by an atom, the basic theory is also applicable to more complicated problems, e.g., molecule-molecule systems. We are in the process of making such calculations, and after the results are compared with experimental data, we will be in a better position to assess the overall accuracy of the theory. Nevertheless, we feel that the present theory provides a consistent framework for the calculation of the far wings of spectral lines within the binary collision approximation. Together with improved impact models valid near the centers of lines, we can now calculate accurately the line shape for both small and large frequency displacements from the line centers. However, there is still considerable uncertainty for intermediate displacements that must be resolved before one can attain the goal of computing accurate line shapes over their complete extent.

ACKNOWLEDGMENTS

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APPENDIX

In order to carry out the integrations denoted by $I_{\alpha\beta\gamma\delta}(\omega - \omega_{ij})$ in Eq. (27),

$$I_{\alpha\beta\gamma\delta}(\omega - \omega_{ij}) = \left(\frac{1}{2\pi i} \right)^2 \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \frac{1}{\omega - \omega' - \omega'' - \omega_{ij}} \left\{ P \frac{1}{\omega' - G_{\alpha\beta}R_1[R_2^{-1}(\omega''/F_{\gamma\delta})]} \times \frac{1}{|F_{\gamma\delta}|} u \left[R_2^{-1} \left(\frac{\omega''}{F_{\gamma\delta}} \right) \right] \right. \\ \times \exp \left\{ -V_{\text{aniso}} \left[\alpha\gamma; R_2^{-1} \left(\frac{\omega''}{F_{\gamma\delta}} \right) \right] / kT \right\} + \frac{1}{|G_{\alpha\beta}|} v \left[R_1^{-1} \left(\frac{\omega'}{G_{\alpha\beta}} \right) \right] \\ \times \exp \left\{ -V_{\text{aniso}} \left[\alpha\gamma; R_1^{-1} \left(\frac{\omega'}{G_{\alpha\beta}} \right) \right] / kT \right\} \times P \frac{1}{\omega'' - F_{\gamma\delta}R_2[R_1^{-1}(\omega'/G_{\alpha\beta})]} \right\}. \quad (\text{A1})$$

we have to keep in mind that both the integral variables ω' and ω'' have small imaginary parts $i\sigma'$ ($\sigma' > 0$) and $i\sigma''$ ($\sigma'' > 0$) which have not been expressed explicitly in the formalism and that σ' and σ'' will go to 0^+ after the integrations are completed. Also we have to keep in mind that the frequency ω has a small imaginary part $i\epsilon$ ($\epsilon > 0$) too and that finally ϵ will go to 0^+ after all of the calculations are completed. Now we begin to calculate the first term in Eq. (27), i.e.,

$$\left(\frac{1}{2\pi i} \right)^2 \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \frac{1}{\omega - \omega' - \omega'' - \omega_{ij}} \times P \frac{1}{\omega' - G_{\alpha\beta}R_1[R_2^{-1}(\omega''/F_{\gamma\delta})]} \\ \times \frac{1}{|F_{\gamma\delta}|} u \left[R_2^{-1} \left(\frac{\omega''}{F_{\gamma\delta}} \right) \right] \exp \left\{ -V_{\text{aniso}} \left[\alpha\gamma; R_2^{-1} \left(\frac{\omega''}{F_{\gamma\delta}} \right) \right] / kT \right\}. \quad (\text{A2})$$

We carry out the integration over ω' first and construct a closed curve C which consists of three parts: (1) a straight line along axis $i\sigma'$ from $-\infty + i\sigma'$ to $G_{\alpha\beta}R_1[R_2^{-1}(\omega''/F_{\gamma\delta})] - \delta + i\sigma'$ and from $G_{\alpha\beta}R_1[R_2^{-1}(\omega''/F_{\gamma\delta})] + \delta + i\sigma'$ to $\infty + i\sigma'$; (2) C_δ , a half-circle with the point $G_{\alpha\beta}R_1[R_2^{-1}(\omega''/F_{\gamma\delta})] + i\sigma'$ as its center and with a radius δ on the upper plane; (3) C_R , a half-circle with the point $i\sigma'$ as its center and with an infinity radius on the upper plane. Then we have

$$\frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \frac{1}{\omega - \omega' - \omega'' - \omega_{ij}} \times P \frac{1}{\omega' - G_{\alpha\beta}R_1[R_2^{-1}(\omega''/F_{\gamma\delta})]} \\ = \frac{1}{2\pi i} \left(\oint_C - \int_{C_R} - \int_{C_\delta} \right) d\omega' \frac{1}{\omega - \omega' - \omega'' - \omega_{ij}} \times \frac{1}{\omega' - G_{\alpha\beta}R_1[R_2^{-1}(\omega''/F_{\gamma\delta})]} = \frac{1}{2\pi i} \oint_C d\omega' \frac{1}{\omega - \omega' - \omega'' - \omega_{ij}} \\ \times \frac{1}{\omega' - G_{\alpha\beta}R_1[R_2^{-1}(\omega''/F_{\gamma\delta})]} - \frac{1}{2\pi i} \int_{C_\delta} d\omega' \frac{1}{\omega - \omega' - \omega'' - \omega_{ij}} \times \frac{1}{\omega' - G_{\alpha\beta}R_1[R_2^{-1}(\omega''/F_{\gamma\delta})]} \\ = \frac{1}{2} \frac{1}{G_{\alpha\beta}R_1[R_2^{-1}(\omega''/F_{\gamma\delta})] + \omega'' - \omega + \omega_{ij}}. \quad (\text{A3})$$

With Eq. (A3), Eq. (A2) can be written as

$$\frac{1}{4\pi i} \int_{-\infty}^{\infty} d\omega'' \frac{1}{G_{\alpha\beta}R_1[R_2^{-1}(\omega''/F_{\gamma\delta})] + \omega'' - \omega + \omega_{ij}} \frac{1}{|F_{\gamma\delta}|} u \left[R_2^{-1} \left(\frac{\omega''}{F_{\gamma\delta}} \right) \right] \exp \left\{ -V_{\text{aniso}} \left[\alpha\gamma; R_2^{-1} \left(\frac{\omega''}{F_{\gamma\delta}} \right) \right] / kT \right\}. \quad (\text{A4})$$

In order to carry out the second integration over ω'' , we introduce a new integration variable $y = y(\omega'')$ defined by

$$y \equiv G_{\alpha\beta}R_1 \left[R_2^{-1} \left(\frac{\omega''}{F_{\gamma\delta}} \right) \right] + \omega'', \quad (\text{A5})$$

or alternatively given by the pair of equations

$$\omega'' = F_{\gamma\delta}R_2(r_c), \\ y = G_{\alpha\beta}R_1(r_c) + F_{\gamma\delta}R_2(r_c). \quad (\text{A6})$$

We have

$$\frac{dy}{d\omega''} = \frac{1}{F_{\gamma\delta}} G_{\alpha\beta} \frac{R_1'(r_c)}{R_2'(r_c)} \bigg|_{r_c=R_2^{-1}(\omega''/F_{\gamma\delta})} + 1. \quad (\text{A7})$$

With Eqs. (A5) and (A7), Eq. (A4) can be rewritten as

$$\begin{aligned}
& \frac{1}{4\pi i} \int_{-\infty}^{\infty} dy \frac{1}{y - \omega + \omega_{ij}} \frac{1}{|F_{\gamma\delta}|} u \left\{ R_2^{-1} \left[\frac{\omega''(y)}{F_{\gamma\delta}} \right] \right\} \exp \left\{ -V_{\text{aniso}} \left[\alpha\gamma; R_2^{-1} \left(\frac{\omega''(y)}{F_{\gamma\delta}} \right) \right] / kT \right\} \frac{1}{|dy(\omega'')/d\omega''|} \\
&= \frac{1}{2} \left(u \left\{ R_2^{-1} \left[\frac{\omega''(y)}{F_{\gamma\delta}} \right] \right\} \exp \left\{ -V_{\text{aniso}} \left[\alpha\gamma; R_2^{-1} \left(\frac{\omega''(y)}{F_{\gamma\delta}} \right) \right] / kT \right\} \left| \frac{R_2'(r_c)}{G_{\alpha\beta}R_1'(r_c) + F_{\gamma\delta}R_2'(r_c)} \right| \right)_{y=(\omega - \omega_{ij})} \\
&= \frac{1}{2} u(r_c) \left| \frac{R_2'(r_c)}{G_{\alpha\beta}R_1'(r_c) + F_{\gamma\delta}R_2'(r_c)} \right| \exp \{ -V_{\text{aniso}}(\alpha\gamma; r_c)/kT \} \\
&= 2\pi^2 n_b \Theta(r_c) \left| \frac{1}{G_{\alpha\beta}R_1'(r_c) + F_{\gamma\delta}R_2'(r_c)} \right| r_c^2 \exp \{ -[V_{\text{iso}}(r_c) + G_{\alpha}R_1(r_c) + F_{\gamma}R_2(r_c)]/kT \}, \quad (\text{A8})
\end{aligned}$$

where r_c is determined by

$$\omega - \omega_{ij} = G_{\alpha\beta}R_1(r_c) + F_{\gamma\delta}R_2(r_c). \quad (\text{A9})$$

We note that r_c will be the same if the value of $(\omega - \omega_{ij})$ is changed by a sign and both of the indices α and β and the indices γ and δ are interchanged simultaneously.

Similarly, we can calculate the second term in Eq. (27), i.e.,

$$\begin{aligned}
& \left(\frac{1}{2\pi i} \right)^2 \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \frac{1}{\omega - \omega' - \omega'' - \omega_{ij}} \frac{1}{|G_{\alpha\beta}|} v \left[R_1^{-1} \left(\frac{\omega'}{G_{\alpha\beta}} \right) \right] \exp \left\{ -V_{\text{aniso}} \left[\alpha\gamma; R_1^{-1} \left(\frac{\omega'}{G_{\alpha\beta}} \right) \right] / kT \right\} \\
& \times P \frac{1}{\omega'' - F_{\gamma\delta}R_2[R_1^{-1}(\omega'/G_{\alpha\beta})]} \quad (\text{A10})
\end{aligned}$$

However, by comparing Eqs. (A2) and (A10), one is able to find out that one integrand becomes another integrand simply by interchanging between one set of symbols $\omega' \omega'' \alpha \beta \gamma \delta F G R_1 R_2$ and another set of symbols $\omega'' \omega' \gamma \delta \alpha \beta G F R_2 R_1$, simultaneously. In addition, we note that the final result of the first part integration given in Eqs. (A8) and (A9) is independent of interchanging between one set of symbols $\alpha \beta \gamma \delta F G R_1 R_2$ and another set of symbols $\gamma \delta \alpha \beta G F R_2 R_1$. Therefore, one concludes that the contributions from these two parts of integration are the same and is able to find

$$I_{\alpha\beta\gamma\delta}(\omega - \omega_{ij}) = 4\pi^2 n_b \Theta(r_c) \left| \frac{1}{G_{\alpha\beta}R_1'(r_c) + F_{\gamma\delta}R_2'(r_c)} \right| r_c^2 \exp \{ -[V_{\text{iso}}(r_c) + G_{\alpha}R_1(r_c) + F_{\gamma}R_2(r_c)]/kT \}. \quad (\text{A11})$$

For later convenience, we can introduce symmetric functions $\hat{I}_{\alpha\beta\gamma\delta}(\omega - \omega_{ij})$ defined by

$$\begin{aligned}
\hat{I}_{\alpha\beta\gamma\delta}(\omega - \omega_{ij}) &\equiv \exp[\hbar(\omega - \omega_{ij})/2kT] I_{\alpha\beta\gamma\delta}(\omega - \omega_{ij}) \\
&= 4\pi^2 n_b \Theta(r_c) \left| \frac{1}{G_{\alpha\beta}R_1'(r_c) + F_{\gamma\delta}R_2'(r_c)} \right| r_c^2 \\
&\quad \times \exp \{ -V_{\text{iso}}(r_c)/kT - [(G_{\alpha} + G_{\beta})R_1(r_c) + (F_{\gamma} + F_{\delta})R_2(r_c)]/2kT \}. \quad (\text{A12})
\end{aligned}$$

It is worth mentioning that these functions have a symmetric property

$$\hat{I}_{\alpha\beta\gamma\delta}(\omega - \omega_{ij}) = \hat{I}_{\beta\alpha\delta\gamma}(-\omega + \omega_{ij}). \quad (\text{A13})$$

Based on the knowledge about r_c given previously, one is able to derive this property easily.

¹P. W. Rosenkranz, J. Chem. Phys. **83**, 6139 (1985).

²P. W. Rosenkranz, J. Chem. Phys. **87**, 163 (1987).

³C. Boulet, J. Boisssoles, and D. Robert, J. Chem. Phys. **89**, 625 (1988).

⁴Q. Ma and R. H. Tipping, J. Chem. Phys. **93**, 6127 (1990).

⁵Q. Ma and R. H. Tipping, J. Chem. Phys. **93**, 7066 (1990).

⁶Q. Ma and R. H. Tipping, J. Chem. Phys. **95**, 1428 (1991).

⁷Q. Ma and R. H. Tipping, J. Chem. Phys. **95**, 6290 (1991).

⁸Q. Ma and R. H. Tipping, J. Chem. Phys. **96**, 8655 (1992).

⁹Q. Ma and R. H. Tipping, J. Chem. Phys. **97**, 818 (1992).

¹⁰R. H. Tipping and Q. Ma, Atmos. Res. (to be published).

¹¹Q. Ma and R. H. Tipping, J. Chem. Phys. **100**, 2537 (1994).

¹²Q. Ma and R. H. Tipping, J. Chem. Phys. **100**, 5567 (1994).

¹³J. Boisssoles, V. Menoux, R. Le Doucen, C. Boulet, and D. Robert, J. Chem. Phys. **91**, 2163 (1989).

¹⁴Q. Ma and R. H. Tipping, J. Quant. Spectrosc. Radiat. Transfer (to be published).

¹⁵L. S. Rothman, R. R. Gamache, R. H. Tipping, C. P. Rinsland, M. A. H. Smith, D. Chris Benner, V. Malathy Devi, J.-M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S. T. Massie, L. R. Brown, and R. A. Toth, J. Quant. Spectrosc. Radiat. Transfer **48**, 469 (1992).

¹⁶Q. Ma, R. H. Tipping, and C. Boulet (unpublished).

¹⁷G. A. Parker, R. L. Snow, and R. T. Pack, J. Chem. Phys. **64**, 1668 (1976); R. K. Preston and R. T. Pack, *ibid.* **66**, 2480 (1977).