A far wing line shape theory and its application to the water continuum absorption in the infrared region. I

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A theory is presented for the calculation of the continuous absorption due to the far wing contributions of allowed lines. The theory is based on the quasistatic approximation for the far wing limit and the binary collision approximation of one absorber molecule and one bath molecule. In line space, the motion of the dipole moment of the absorber molecule, determined by the time displacement Liouville operator related to the total Hamiltonian of the absorber molecule and the bath molecule, is approximately expressed as the ordered product of two time displacement Liouville operators, one related to the intermolecular potential and the other to the unperturbed Hamiltonian. Using a Laplace transformation, the spectral density is expressed in terms of a Cauchy integral whose integrand is a product of two resolvent operators corresponding to the interaction and to the unperturbed Hamiltonian, respectively. After isolating the effects of the bath variables, the spectral density and subsequently the absorption coefficient are expressed in terms of the individual line coupling functions, or the individual line shape functions. By using two average line shape functions instead of the individual ones, the expression of the absorption coefficient closely matches empirical models. The validity of the present theory is discussed, and some numerical results of the water continuum absorption in the infrared region are presented for comparison with experimental data. A good agreement in both the magnitude and the temperature dependence of the absorption coefficients is obtained. Some further extensions and applications of the present theory are also discussed briefly.

I. INTRODUCTION

The continuum absorption of radiation in the infrared windows of the Earth's atmosphere has been known for a long time. The history of this topic, together with many references to earlier work, has been reviewed recently by a number of authors. There is nearly unanimous agreement concerning the density dependence of this absorption (quadratic), and general agreement on the temperature dependence (strong, negative), but there is considerable disagreement as to its magnitude and the physical mechanism responsible for the absorption. Water dimers, collision-induced absorption, and the superposition of the far wings of collisionally broadened lines have all been proposed as possible candidates. While the first two mechanisms are undoubtedly present and contribute to the absorption (in varying amounts in the different spectral regions), it is now generally accepted that the major contribution to the absorption coefficient in the spectral region between 300-1100 cm\(^{-1}\) is due to the wings of the strong self-broadened pure rotational transitions of water.

This conclusion has been bolstered recently by the theoretical results published by Rosenkranz, who was able to reproduce not only the magnitude of the absorption coefficient, but also its negative temperature dependence. In a previous paper, we have reviewed and extended Rosenkranz's framework and confirmed his conclusions. In the present work, we present a new formalism and obtain improved theoretical results. In particular, we obtain better agreement with the temperature dependence of the absorption coefficient. Based on the quasistatic approximation that is valid for the far wing limit and the binary collision approximation of one absorber molecule and one bath molecule, and by formally isolating the bath variables, we express in Sec. II the spectral density and subsequently the absorption coefficients in terms of the individual line coupling functions or the individual line shape functions. Furthermore, in terms of two averaged line shape functions, the absorption coefficient takes a simple form that closely matches empirical models. We also discuss the validity of the formalism. In Sec. III we present numerical results of the water continuum absorption in the infrared region for different temperatures and compare them with the experimental data with an emphasis on the temperature dependence of the absorption. A better agreement is obtained in comparison with Rosenkranz's results, especially for the temperature dependence. Some further extensions and applications are indicated briefly.

II. THE GENERAL FORMALISM

A. The absorption coefficient and spectral density

As is well known, the absorption of radiation at frequency \(\omega\) (cm\(^{-1}\)) by a gaseous sample in thermal equilibrium at
temperature $T$ is characterized by the absorption coefficient 
\[ \alpha(\omega) = (4\pi^2/3\hbar c)\omega(e^{\hbar\omega/kT} - 1)F(\omega), \]  
where $c$ is the speed of light, and $F(\omega)$, the spectral density, is given by
\[ F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \langle \mu^{(H)}(t) \cdot \mu^{(H)}(0) \rangle dt \]
\[ = \frac{1}{\pi} \text{Re} \text{Tr} \int_{0}^{\infty} e^{i\omega t} \langle \mu^{(H)}(0) \cdot \mu^{(H)}(t) \rangle dt. \]  

In this expression, $\mu^{(H)}(t)$ is the total dipole operator of the gas in the Heisenberg representation
\[ \mu^{(H)}(t) = e^{iHt/\hbar}\mu^{(H)}(0)e^{-iHt/\hbar}, \]  
and the angular brackets denote the ensemble average (i.e., the correlation function),
\[ \langle \mu^{(H)}(0) \cdot \mu^{(H)}(t) \rangle = \sum_i \rho_i \langle i | \mu^{(H)}(0) \cdot \mu^{(H)}(t) | i \rangle, \]
where $\rho_i$ is the normalized Boltzmann factor of the initial state $i$. The spectral density $F(\omega)$ satisfies the condition
\[ F(\omega) = e^{-\hbar\omega/kT} F(-\omega), \]
so that Eq. (1) is often written in the symmetric form
\[ \alpha(\omega) = (4\pi^2/3\hbar c)\omega \text{tanh}(\hbar\omega/2kT) [F(\omega) + F(-\omega)], \]
\[ \times [F(\omega) + F(-\omega)], \]  
\[ \]  

The Fourier transform of the dipole moment correlation function, Eq. (2), can be conveniently expressed in terms of the Liouville representation. The density operator $\rho$ for the gas
\[ \rho = e^{-H/\hbar}\text{Tr}(e^{-H/\hbar}), \]  
where $H$ is the total Hamiltonian excluding the applied field but including all the interactions between molecules, satisfies the Schrödinger equation
\[ \frac{d\rho}{dt} = -\frac{i}{\hbar}(H\rho - \rho H), \]
\[ \]  
This can be compactly written in the form
\[ \frac{dL}{dt} = -iL\rho, \]  
where $L$ is the Hermitian Liouville operator defined by
\[ L = (H^* - IH^*)/\hbar. \]  

The Liouville operator $L$ is an operator that acts on the space of ordinary quantum mechanical operators; this space was called "line space" by Baranger. If an ordinary operator is represented by a matrix, then the corresponding Liouville operator is represented by a tensor having four indices. If an ordinary operator is represented by a vector, then the Liouville operator is represented by a matrix.

It is usually assumed that $\rho$ commutes with $H$. Then, using the Liouville operator $L$ and the cyclic property of the trace, Eq. (2) can be written as
\[ F(\omega) = \frac{1}{\pi} \text{Re} \text{Tr} \int_{0}^{\infty} \left[ \mu(0) \cdot e^{i(\omega - L)\rho(0)} \right] dt \]
\[ = \lim_{\epsilon \to 0} -\frac{1}{\pi} \text{Im} \text{Tr} \left[ \mu(0) \cdot \frac{1}{\omega - L + i\epsilon} \rho(0) \right], \]
or simply
\[ F(\omega) = -\langle 1/(\pi) \rangle \text{Im} \text{Tr} \left[ \mu \cdot [1/(\omega - L + i\epsilon)] \rho \right], \]  
where the zero-time argument of $\mu(0)$ has been dropped, and it is understood that the limit $\epsilon \to 0$ will eventually be taken.

**B. Fano’s theory**

Fano used the approach of Zwanzig to simplify the calculation of $F(\omega)$ starting from Eq. (12). He imagined the gas to be divided into a large number of small identical elements, called "systems," and focused on a single system, upon which the remaining gas acted as a thermal bath. Accordingly, he wrote the total Hamiltonian of the gas as
\[ H = H_{(a)} + H_{(b)} + V, \]
where $H_{(a)}$ and $H_{(b)}$ are the Hamiltonian of the system and the bath, respectively, and $V$ is the interaction between them. Assuming that the correlation between the system and the bath is negligible (low-density limit), the absorption coefficient per unit volume can be approximated by
\[ \alpha(\omega) = (4\pi^2/3\hbar c)n_s\omega \text{tanh}(\hbar\omega/2kT) \]
\[ \times [F(\omega) + F(-\omega)], \]  
\[ \]  

In these expressions, $n_s$ is the number of systems per unit volume, and $\mu_s$ is the dipole moment operator of a single system. The trace, however, is over all (system plus bath) variables.

Assuming that the total density operator can be approximated by the product
\[ \rho = \rho^{(a)} \cdot \rho^{(b)}, \]
and introducing the Liouville operator corresponding to the system, the bath, and the interaction [cf. Eq. (13)],
\[ L = L_0 + L_1 = L_{(a)} + L_{(b)} + L, \]
\[ \]  
one can write
\[ F(\omega) = -\frac{1}{\pi} \text{Im} \text{Tr} \left[ \mu_s \cdot \frac{1}{\omega - L_{(a)}} \right] \]
\[ \times \left( 1 + \langle M(\omega) \rangle_b \frac{1}{\omega - L_{(a)}} \rho^{(a)} \mu_s \right) \]
\[ = -\frac{1}{\pi} \text{Im} \text{Tr} \left[ \mu_s \cdot \frac{1}{\omega - L_{(a)} - \langle M(\omega) \rangle_b} \rho^{(a)} \mu_s \right]. \]  

The subscript $s$ on the trace indicates that it is taken only over the variables of the system. The Liouville operator $\langle M(\omega) \rangle_b$ contains all the information about the bath molecules and the interaction dynamics between the system and the bath, and is given by
\[ F(\omega) = -\frac{1}{\pi} \text{Im} \text{Tr} \left[ \mu_s \cdot \frac{1}{\omega - L_{(a)} - \langle M(\omega) \rangle_b} \rho^{(a)} \mu_s \right]. \]
\[ \langle M_\omega (\omega) \rangle_b = \frac{1}{1 + \langle M(\omega) \rangle_b (\omega - L^{(a)})^{-1} \langle M(\omega) \rangle_b} \]  

(here the operator \( M(\omega) \) is defined by  
\[ M(\omega) = L_1 + L_1 [1/(\omega - L_0 - L_1)] L_1, \]  
where \( \langle M(\omega) \rangle_b \) denotes the ensemble average over the bath variables  
\[ \langle M(\omega) \rangle_b = \text{Tr}[M(\omega)\rho^{(b)}]_b. \]  

In the present paper, we are interested in a low-density gas with \( n_a \) absorber molecules and \( n_b \) bath molecules per unit volume, and we choose for the system a single molecule \((n_s = n_a)\).

### C. The isolation of the bath variables

We follow Fano's approach and divide the gaseous sample into the absorber molecule \( a \) and the remaining bath molecules. Based on the binary collision approximation, we focus on the absorber molecule and one bath molecule. We express the dipole operator of the absorber molecule using the interaction representation instead of the Heisenberg representation by a transformation  
\[ \mu_\omega^{(H)}(t) = e^{iHt} \mu_\omega^{(I)}(0) e^{-iHt} \]  
\[ = e^{iHt} \mu_\omega^{(I)}(0) e^{-iHt} \]  
\[ = e^{iHt} e^{-iHt} \mu_\omega^{(I)}(0) e^{iHt} e^{-iHt}. \]  

Then, the spectral density \( F(\omega) \) can be written as  
\[ F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \text{Tr}[\mu_\omega^{(I)}(t) e^{-iHt} \mu_\omega^{(I)}(0) e^{iHt}] \]  
\[ = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \text{Tr}[\mu_\omega^{(I)}(t) e^{-iHt} \mu_\omega^{(I)}(0) e^{iHt}] dt, \]  

where we have assumed that \( e^{-iHt} \) is diagonal. As it  
\[ = e^{-iHt} \mu_\omega^{(I)}(0) e^{-iHt} \]  
and consequently \( F(\omega) \) will be discussed later. The limitation of this approximation will be discussed later. This can be rewritten in terms of Liouville operators  
\[ F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \text{Tr}[\mu_\omega^{(I)}(t) e^{-iHt} \mu_\omega^{(I)}(0)] dt \]  
\[ = \frac{1}{\pi} \text{Re} \text{Tr} \int_{0}^{\infty} [\mu_\omega^{(I)}(t) e^{i\omega t - L_0} e^{-i\omega t} \mu_\omega^{(I)}(0)] dt \]  
\[ = \frac{1}{\pi} \text{Re} \text{Tr} \int_{0}^{\infty} [\mu_\omega^{(I)}(t) e^{i\omega t - L_0} e^{-i\omega t} \mu_\omega^{(I)}(0)] dt. \]  

In the last step of Eq. \( (24) \), we have dropped the superscript \( (I) \) of the interaction representation, which does not need to be indicated at \( t = 0 \) and the zero-time argument of the dipole moment operator.

By making a Laplace transformation of \( e^{-i\omega t} \mu_\omega \),  
\[ e^{-i\omega t} \mu_\omega = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} e^{-i\omega t} \mu_\omega \, d\omega', \]  
and carrying out the integration over time, Eq. \( (24) \) can be rewritten as  
\[ F(\omega) = \frac{1}{\pi} \text{Im} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \times \text{Tr} \left[ \mu_\omega^{(a)} \mu_\omega^{(b)} \rho^{(b)} \rho^{(a)} \rho_\omega \right]. \]  

In order to separate the summations over the absorber molecule variables and the bath variables, we first explicitly write the summation indices of the trace in the Eq. \( (26) \),  
\[ \text{Tr} \left[ \mu_\omega^{(a)} \mu_\omega^{(b)} \times \left( \frac{1}{\omega_\omega - L_0} \times \frac{1}{\omega_\omega - L_1} \rho^{(b)} \rho^{(a)} \rho_\omega \right) \right]. \]  

Then we 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 directly acts on \( \mu_\omega \). Therefore, the trace in Eq. \( (26) \) can be written as  
\[ \text{Tr} \left[ \mu_\omega^{(a)} \times \left( \frac{1}{\omega_\omega - L_0} \times \frac{1}{\omega_\omega - L_1} \rho^{(b)} \rho^{(a)} \rho_\omega \right) \right]. \]  

Thus, we obtain an important expression for the spectral density in which, at least formally, the bath variables have been isolated,  
\[ F(\omega) = \frac{1}{\pi} \text{Im} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \times \left( \frac{1}{\omega - \omega' - L_0} \times \frac{1}{\omega - \omega' - L_1} \rho^{(b)} \rho^{(a)} \rho_\omega \right). \]  

Let us compare our formula for the spectral density \( F(\omega) \), Eq. \( (29) \), with Fano's formula Eq. \( (18) \). Similar to Fano's Liouville operator \( \langle M_\omega (\omega) \rangle_b \), the Liouville operator \( \langle 1/(\omega - L_1) \rangle_b \) contains all the information about the bath molecules and the interaction dynamics between the absorber molecule and the bath. By comparing the expression of this operator with the expressions in Eq. \( (19) \), \( (20) \), and \( (21) \), which are used to calculate Fano's operator \( \langle M_\omega (\omega) \rangle_b \), it turns out that this new operator is more easily evaluated. Formally, the expression of the spectral density still contains an integral. However, this integral does not introduce any opacity in the calculations since it is easily carried out by the Cauchy integral formula. Furthermore, it is worth mentioning that the calculation of the operator \( \langle 1/(\omega - L_1) \rangle_b \) avoids the difficulties of diagnosing two ordinary operators with different \( r \) dependencies (where \( r \) is the separation between the centers of mass of the absorber and the bath molecules) which occurs in the calculations of the spectral density with Fano's expression Eq. \( (18) \) and limits its applicability.\(^{10,16}\)

### D. The matrix elements of the resolvent Liouville operator \( \langle 1/(\omega - L_1) \rangle_b \)

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. As it will be noted later, the isotropic interaction between the two molecules does not contribute to \( L_1 \), and consequently we
need only to consider the eigenvectors of the anisotropic inter­
teractions, which are dominated by the dipole–dipole inter­
action for water vapor.

The Liouville operator corresponding to the dipole–dipole interaction is

\[ L_1 = \left[ V_{d-d}(r) I^* - I V_{d-d}^*(r) \right] / \hbar \]

\[ = (G_{d-d} I^* - I G_{d-d}^*) / r^3 \]

\[ = G / r^3. \]  

(30)

We denote by \( \alpha \) and \( G_\alpha \), the eigenvectors and eigenvalues, respectively, of the matrix operator \( G_{d-d} \); that is,

\[ G_{d-d} | \alpha \rangle = G_\alpha | \alpha \rangle, \]  

(31)

or, equivalently, for the Liouville operator \( G \) in line space

\[ G | \alpha \rangle \langle \beta | = (G_\alpha - G_\beta) | \alpha \rangle \langle \beta | \]

\[ \equiv G_{\alpha \beta} | \alpha \rangle \langle \beta |. \]  

(32)

Then, the matrix elements of the Liouville resolvent operator 
\( 1/(\omega - L_1) \) in the representation constructed from its eigenvectors can be written as

\[ \langle \alpha \beta | 1/(\omega - L_1) | \alpha \beta' \rangle = \frac{1}{\omega - G_{\alpha \beta}} \delta_{\alpha \beta}. \]  

(33)

In order to find the eigenvectors and eigenvalues of \( L_1 \), we have to diagonalize the matrix operator \( G_{d-d} \). First, one must choose a convenient basis set for the calculation of the matrix elements of \( G_{d-d} \), such as the symmetric-top functions \([J,K,M]\), \(17\) or the asymmetric-top functions \([J,T,M]\). \(18\) Second, one has to diagonalize this matrix. Simplifying the notation, we use one symbol \( i \) to indicate three quantum numbers, \( j,a \), and \( \alpha \), depending on the choice of basis. In this notation, the coefficients of the unitary transformation related the diagonalization of \( G_{d-d} \) are simply expressed as \( \langle \alpha | i_j \rangle \).

The resolvent operator \( \langle 1/(\omega - L_1) \rangle_b \) in Eq. (29) is an operator acting on the line space of the absorber molecule \( a \). Therefore, in general, it can be expressed as

\[ \left\{ \frac{1}{\omega - L_1} \right\}_b = \sum_{\omega \neq 0} \sum_{\omega \neq 0} \langle i_j^+ \rangle \left( \frac{1}{\omega - L_1} \right)_b | i_j^+ \rangle \times | i_j^+ \rangle \left( \frac{1}{\omega - L_1} \right)_b | i_j^+ \rangle. \]  

(34)

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

\[ \langle i_j^+ \rangle \left( \frac{1}{\omega - L_1} \right)_b | i_j^+ \rangle \]

\[ = \sum_{\omega \neq 0} \sum_{\omega \neq 0} \langle i_j^+ \rangle \left( \frac{1}{\omega - L_1} \right)_b | i_j^+ \rangle \times \left\{ \frac{1}{\omega - L_1} \right\}_b | i_j^+ \rangle. \]  

(35)

where \( \rho(b) \) are the degeneracy factors due to nuclear spin (having the values 1 or 3, depending on the state), \( E_j \) are the energies associated with the state \( |j \rangle \), and \( Q_b \) is the partition function for the bath molecule. We note that the summation over the bath variables in the line space in Eq. (35) includes only the states \( |i_j^+ \rangle \) because of the assumption that the bath molecule is not involved in the transition.

### E. Quasistatic approximation and the intermolecular potential

In general, two complementary theories, the impact and the quasistatic, have been proposed to treat the effects of collisions on the shape of spectral lines. In the impact theory, the duration of a collision is assumed to be infinitesimal, and the resulting shape for isolated lines is Lorentzian; however, it is well known that the Lorentzian line shape is not valid in the far wings. On the other hand, in the quasistatic theory, the collisions are assumed to be of infinite duration; the corresponding line shape is simple only for interaction potentials having simple functional forms. Despite the amount of work that has been done on the theory of line shapes, the accurate calculation of the absorption coefficient, especially for complex molecules like water whose rotational band contains a larger number of overlapping lines, is still a complex problem.

In the statistical theory, the translational motion is not treated quantum mechanically, rather one uses the quasistatic approximation. In this approximation, for each value of \( r \), the separation between two interacting molecules, one assigns a statistical weight \( \rho(r) \). The statistical weight for a pair of molecules is given by

\[ \rho(r) = e^{-V(r)/kT}/U, \]  

(36)

where \( V(r) \) is the interaction between the absorber molecule and the bath molecule, and the normalization factor \( U \) is given by

\[ U = 4\pi \int_0^{r_{\text{max}}} e^{-V(r)/kT} r^2 \, dr. \]  

(37)

This expression can be rewritten in the form

\[ U = -4\pi \int_0^{r_{\text{max}}} (1 - e^{-V(r)/kT}) r^2 \, dr + 4\pi \int_0^{r_{\text{max}}} r^2 \, dr + V, \]  

(38)

where \( V \) is the volume that can be replaced by \( 1/n_b \), i.e., by the inverse of the number density of the bath molecules. Because of the asymptotic dependence of the integrand in Eq. (38), we can let \( r_{\text{max}} \) go to infinity. Then, from the definition of the second virial coefficient \( B(T) \), we can rewrite Eq. (38) in the form

\[ U = -2B(T)/N_A + 1/n_b, \]  

(39)

where \( N_A \) is the Avagadro constant. For moderate densities and temperatures, \( U \approx 1/n_b \) and therefore, from Eq. (36) we obtain

\[ \rho(r) = n_b e^{-V(r)/kT}. \]  

(40)

Now, we discuss the intermolecular potential, which plays an important role in our calculation. Because of the large permanent dipole moment of a water molecule, the anisotropic interaction between two water molecules can be represented by the leading term in the long-range multipolar expansion; i.e., the dipole–dipole potential
\[ V_{d-d}(r) = \left[ (\mu_1, \mu_2) - 3(\mu_1, r)(\mu_2, r)/r^2 \right]/r^2, \]  
(41)

in which the two molecules are labeled 1 and 2. For calculation convenience, this can be expressed in terms of spherical tensors.\(^{21,22}\)

\[ V_{d-d}(r) = \sum_{m_1 m_2} (-1)^{m_1 + m_2} C(112; m_1, m_2, m_1 + m_2) \times \mu_{m_1}(1) \mu_{m_2}(2) / r^2, \]  
(42)

where \( C \) is a Clebsch–Gordan coefficient, \( T \) is the dipole propagator, and \( \Omega \) describes the orientation of the intermolecular separation \( r \) in the space-fixed frame. Because in the quasistatic approximation we treat the translational motion of the molecules classically, we can with no loss of generality take the intermolecular axis \( r \) to lie along the space-fixed \( Z \) axis. In this case, we can write the interaction potential as

\[ V_{d-d}(r) = -\sqrt{6} \sum_{m_1} (1) C(112; m_1, -m_1, 0) \mu_{m_1}(1) \mu_{m_1}(2) / r^2. \]  
(43)

For the isotropic interaction \( V_\alpha(r) \), we adopt a simple Lennard–Jones type model,

\[ V_\alpha(r) = C \sigma^{-6} \left[ (\sigma/r)^6 + (\sigma/r)^{12} \right], \]  
(44)

where \( C, \sigma, \) and \( s \) are constants that can be determined from other experimental data\(^9\) (e.g., second virial coefficient, compressibility, etc.). Thus, in the present case, the total interaction between the absorber molecule and the bath molecule, \( V(r) \) in Eq. (40), is given by

\[ V(r) = V_{d-d}(r) + V_\alpha(r). \]  
(45)

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, \( V_\alpha(r) \) need not be included in the interaction Liouville operator \( L_1 \). However, in the quasistatic approximation, it still plays a significant role.

### F. The individual line coupling functions

Within the quasistatic approximation, the statistical averages of the matrix elements of the Liouville resolvent operator (denoted by the subscript \( st \) in order to avoid confusion with other ensemble averages) are given by

\[
\text{Re} \langle \alpha \beta^+ | \left[ 1/((\omega - L_1)) \right] | \alpha' \beta' + \rangle \big|_{st} \\
\quad + \text{Im} \langle \alpha \beta^+ | \left[ 1/((\omega - L_1)) \right] | \alpha' \beta' + \rangle \big|_{st} \\
= 4\pi^2 n_b \int_0^{\infty} r^2 \, dr \text{Re} \langle \alpha \beta^+ | \\
\quad \times \left[ 1/((\omega - L_1)) \right] e^{-\nu(r)/kT} | \alpha' \beta' + \rangle. \\
(46)
\]

The real parts \( \text{Re} \langle \alpha \beta^+ | \left[ 1/((\omega - L_1)) \right] | \alpha' \beta' + \rangle \big|_{st} \) are not of interest in the present calculation, and we only consider the imaginary part \( \text{Im} \langle \alpha \beta^+ | \left[ 1/((\omega - L_1)) \right] | \alpha' \beta' + \rangle \big|_{st} \). To obtain an expression for \( \text{Im} \langle \alpha \beta^+ | \left[ 1/((\omega - L_1)) \right] | \alpha' \beta' + \rangle \big|_{st} \) from Eq. (46), we use the well-known formal identity

\[
\lim_{\varepsilon \to 0} \frac{1}{\omega - L_1 - i\varepsilon} = P \frac{1}{\omega - L_1} - i\pi \delta(\omega - L_1), \\
(47)
\]

where \( P \) indicates the Cauchy principal value of the integral and \( \delta \) is a Dirac delta function with the Liouville operator \( \omega - L_1 \) as its argument, and find

\[
\text{Im} \langle \alpha \beta^+ | \left[ \frac{1}{\omega - L_1} \right] | \alpha' \beta' + \rangle \big|_{st} \\
= -4\pi^2 n_b \int_0^{\infty} r^2 \, dr \text{Re} (\omega - G_{\alpha \beta})/r^3 \\
\quad \times e^{-\nu(r)/kT} \delta_{\alpha \beta} \\
= -4\pi^2 n_b \frac{1}{3} |G_{\alpha \beta}| e^{-\nu(\sigma^2 \omega_0^2)/kT} \\
\quad \times \delta_{\alpha \beta} |G_{\alpha \beta}|. \\
(48)
\]

where, \( \Theta(x) \) is the unit step function defined as follows:

\[
\Theta(x) = 1, \quad \text{if} \; x > 0, \\
\Theta(x) = 0, \quad \text{if} \; x < 0. \\
\]

Within the quasistatic approximation, the resolvent operator \( \left[ 1/((\omega' - L_1)) \right] \) in Eq. (29) is replaced by its statistically averaged operator \( \left[ 1/((\omega' - L_1)) \right]_{st} \), and similar to Eq. (34), the latter can be expressed as

\[
\left[ 1/((\omega - L_1)) \right]_{st} = \sum_{i \neq j} \sum_{\omega} \langle i | j^+_1 \left[ \frac{1}{\omega - L_1} \right]_{st} | i^+_1 \rangle \\
\times \langle i^+_1 \rangle \langle j^+_1 \rangle. \\
(49)
\]

Again, we focus on the imaginary parts of its components and with Eqs. (35) and (48), we express them as

\[
\text{Im} \langle i | j^+_1 \left[ \frac{1}{\omega - L_1} \right]_{st} | i^+_1 \rangle \\
= \text{Im} \sum_{\omega} \langle (i \rightarrow j^+_1) (i \rightarrow i^+_1) \rangle | \left[ \frac{1}{(\omega - L_1)} \right]_{st} \rangle \\
\quad \times \rho_{ij}^{(b)} | \langle j^+_1 \rangle \langle j^+_1 \rangle \rangle \\
= \text{Im} \sum_{\omega} \sum_{\omega'} \langle (i \rightarrow j^+_1) (i \rightarrow i^+_1) \rangle | \langle \alpha \beta^+ \rangle \rangle \\
\quad \times | \langle \alpha \beta^+ \rangle \rangle | \rho_{ij}^{(b)} \rangle | \langle \alpha \beta^+ \rangle \rangle \\
\quad \times e^{-\nu(\sigma^2 \omega_0^2)/kT} \\
\quad \times \langle \alpha \beta^+ \rangle \langle \alpha \beta^+ \rangle \\
\quad \times e^{-\nu(\sigma^2 \omega_0^2)/kT} Q_{ij}, \\
(50)
\]

where we have defined the individual line coupling functions \( X_{ij, i'j'}(\omega) \) as

\[
X_{ij, i'j'}(\omega) = \\
\equiv \frac{4\pi^2}{3} n_b \sum_{\omega} \sum_{\omega'} \Theta \left( \frac{G_{ij, i'j'}}{\omega} \right) \langle G_{ij, i'j'} \rangle | \langle (i \rightarrow j^+_1) (i \rightarrow i^+_1) \rangle | \langle \alpha \beta^+ \rangle \rangle \\
\quad \times e^{-\nu(\sigma^2 \omega_0^2)/kT} \langle \alpha \beta^+ \rangle \langle \alpha \beta^+ \rangle \\
\quad \times e^{-\nu(\sigma^2 \omega_0^2)/kT} Q_{ij}, \\
(51)
\]

Therefore, within the quasistatic approximation, the
imaginary part of the resolvent Liouville operator in Eq. (29), \(\text{Im}(1/(\omega - L_{1}))\) can be expressed in terms of the individual line coupling functions as

\[
\text{Im}\left(\frac{1}{\omega - L_{1}}\right)_{st,b} = -\frac{1}{\omega} \sum_{i,j} \sum_{a} \chi_{i,j,a}(\omega) |i_j^+ \rangle \langle j_i^+|.
\]

(52)

It is worth mentioning that in order to calculate all of the individual line coupling functions, we need only to diagonalize the dipole–dipole interaction once, and the remaining calculations are straightforward.

We also can define symmetric individual line coupling functions as

\[
\hat{\chi}_{i,j,a}(\omega) = e^{\mu a/(2kT)} \chi_{i,j,a}(\omega) = \frac{4\pi^2}{3} n_b \sum_{ij} \Theta\left(\frac{G_{ab}}{\omega}\right) G_{ab} |(i_j^+)(i_j,+)| e^{-\mu a/(2kT) - \nu_{in}(\mu a/(2kT))/kT} \\
\times \left(\alpha|\beta|^2 + (i^+_j|j^+_i)\right) g_{i^+_j} e^{-E_{i^+_j}/kT}/Q_a.
\]

(53)

We note that the arguments of each individual line coupling functions in Eq. (57) take the desirable values after the Cauchy integration over \(\omega\) in Eq. (55) was carried out. Equation (57) is another basic formula in the present formalism. Now, the remaining problem is to calculate the individual line coupling functions \(\chi_{i,j,a}(\omega)\). Although these individual line coupling functions include all the information about how the lines are coupled and broadened, it is more convenient to condense this information into the individual line shape functions defined as follows.

**G. The individual line shape functions**

In order to express the spectral density in a more convenient form, we rewrite it as

\[
F(\omega) = \frac{1}{\pi} \sum_{i,j} \langle j_i|\mu_a|i_j\rangle \frac{1}{(\omega - \omega_{i,j})^2} \chi_{i,j,a}(\omega - \omega_{i,j}) g_{i^+_j} e^{-E_{i^+_j}/kT} Q_a.
\]

(55)

With the Cauchy integral formula

\[
F(\omega) = \frac{1}{\pi} \sum_{i,j} \langle j_i|\mu_a|i_j\rangle \frac{1}{(\omega - \omega_{i,j})^2} \chi_{i,j,a}(\omega - \omega_{i,j}) g_{i^+_j} e^{-E_{i^+_j}/kT} Q_a.
\]

(56)

\[
\frac{f(a)}{z-a} \frac{1}{2\pi i} dz,
\]

it is easy to carry out the integration in Eq. (55) to obtain

\[
F(\omega) = \frac{1}{\pi} \sum_{i,j} \langle j_i|\mu_a|i_j\rangle \frac{1}{(\omega - \omega_{i,j})^2} \chi_{i,j,a}(\omega - \omega_{i,j}) g_{i^+_j} e^{-E_{i^+_j}/kT} Q_a.
\]

(57)
With the reduced matrix elements,

\[ \langle i | \mu_m | j \rangle = C(j_1; m_j, m_m, i_1; m_{i_1}) \langle i | \mu | j \rangle = C(j_1; m_j, m_m) \frac{\mu_y}{(2i + 1)^{1/2}}, \]  

we complete the summation over the magnetic quantum numbers and obtain

\[ F(\omega) = \frac{4\pi n_b}{3} \sum_{\mu_{ij}} \frac{1}{(2i + 1)^{1/2}} \sum_{m_{i_1} m_{i_1}} \sum_{\mu_{ij}} \sum_{i_1} \langle \beta | j_1, i_2 \rangle C(j_1; m_j, m_m) \langle i_1 | \mu | i_1 \rangle \Theta \left( \frac{G_{ab}}{\omega - \omega_{i_1}} \right) | G_{ab} | \]

\[ \times e^{-\frac{\mu_y}{(2i + 1)^{1/2}}} \langle \alpha | \rho^{(b)} | \mu_m | \beta \rangle \left( \frac{(G_{ab}^{(b)})^{(b)}}{(\omega - \omega_{i_1})} \right) \chi_{ij} \left( \omega - \omega_{i_1}, \rho_i | \mu_{ij} \right), \]  

(59)

where we have defined the individual line shape functions as

\[ \chi_{ij}(\omega) = \frac{4\pi n_b}{3} \frac{1}{(2i + 1)^{1/2}} \sum_{m_{i_1} m_{i_1}} \sum_{\mu_{ij}} \sum_{i_1} \langle \beta | j_1, i_2 \rangle \]

\[ \times C(j_1; m_j, m_m) \langle i_1 | \mu | i_1 \rangle \Theta \left( \frac{G_{ab}}{\omega - \omega_{i_1}} \right) | G_{ab} | \]

\[ \times e^{-\frac{\mu_y}{(2i + 1)^{1/2}}} \langle \alpha | \rho^{(b)} | \mu_m | \beta \rangle \left( \frac{(G_{ab}^{(b)})^{(b)}}{(\omega - \omega_{i_1})} \right) \chi_{ij} \left( \omega - \omega_{i_1}, \rho_i | \mu_{ij} \right), \]  

(60)

Therefore, in terms of the individual line shape functions, the spectral density can be written in a more familiar form,

\[ F(\omega) = \frac{1}{\pi} \sum_{\omega_{ij} > 0} \frac{1}{(\omega - \omega_{ij})^2} \chi_{ij}(\omega - \omega_{ij}) \rho_i | \mu_{ij} |^2 \]

\[ = \frac{1}{\pi} \sum_{\omega_{ij} > 0} \frac{1}{(\omega - \omega_{ij})^2} \chi_{ij}(\omega - \omega_{ij}) + e^{-\mu_y/kT} \]

\[ \times \frac{1}{\omega + \omega_y} \chi_{ij}(\omega + \omega_y) \rho_i | \mu_{ij} |^2. \]  

(61)

Comparing the positive frequency resonant terms in Eq. (62) with the same terms in Eq. (63), the following identity must hold:

\[ \chi_{ij}(\omega - \omega_{ij}) = e^{-\mu_y/kT} \chi_{ij}(\omega + \omega_y). \]  

(64)

Also, comparing the negative frequency resonant terms in Eq. (62) with the same terms in Eq. (63), the following identity must also hold:

\[ \chi_{ij}(\omega - \omega_{ij}) = e^{-\mu_y/kT} \chi_{ij}(\omega + \omega_y). \]  

(65)

Accordingly, we can define the symmetric individual line shape functions

\[ \hat{\chi}_{ij}(\omega) \equiv e^{\mu_y/kT} \chi_{ij}(\omega). \]  

(66)

In terms of the symmetric individual line shape functions, the identities (64) and (65) are simply written as

\[ \hat{\chi}_{ij}(\omega - \omega_{ij}) = \hat{\chi}_{ij}(\omega + \omega_y), \]

(67)

\[ \hat{\chi}_{ij}(\omega - \omega_{ij}) = \hat{\chi}_{ij}(\omega + \omega_y). \]  

(68)

For simplicity, since we will use these symmetrized forms instead of the original ones in the following, we will omit the adjective "symmetric."
\[ \hat{\chi}\left(\omega\right) \neq \hat{\chi}\left(-\omega\right); \]  
(70)

these imply that the line shapes are asymmetric with respect to their centers and cannot be completely represented only by their part with \( \omega > 0 \), neither can they only by their part with \( \omega < 0 \).

Finally, the absorption coefficients \( \alpha(\omega) \) can be written in the familiar form

\[
\alpha(\omega) = \frac{4\pi^2}{\hbar c} \omega n_a \tanh\left(\frac{\hbar \omega}{2kT}\right) \left[ F(\omega) + F(-\omega) \right]
\]

\[
= \frac{n_a}{\omega} \sum_{\omega_i > 0} S_{ij} \left( \frac{\omega}{2kT} \right)^2 \left( \frac{1}{\omega - \omega_i} \right) \hat{\chi}(\omega - \omega_i)
+ \frac{1}{\omega + \omega_i} \hat{\chi}(\omega + \omega_i) \right),
\]
(71)

where the line strengths are

\[
S_{ij} = \frac{4\pi^2 \omega n_a}{3\hbar c Q_a} \left| \mu_{ij} \right|^2 \left( e^{-E_i/\kappa T} - e^{-E_j/\kappa T} \right).
\]
(72)

We have now obtained an expression for the absorption coefficient in a convenient form. Prior to presenting the results of our calculations using Eq. (71), we discuss its validity in greater detail. In summary, it is based on the following approximations.

1. The quasistatic approximation in which the durations of collisions, \( \tau \), are treated as infinite. Therefore, the resulting line shape functions are valid for frequencies of interest separated from the resonant centers by at least \( 1/\tau \) wave numbers. The duration of the mean collision can be estimated from the cross section of pressure broadening and the mean molecular speed. For many molecules at atmospheric temperatures, the duration is about \( 10^{-12} \) s. Therefore, the results are valid for frequency greater than a decade of wave numbers (cm\(^{-1}\)) from the resonant frequencies.

2. The binary collision approximation. The experimental measurements of continuum absorption for the pressures of interest in atmospheric applications, indicate that the absorption is proportional to the square of the density. This fact implies that the binary collision approximation is valid for the pressure region of interest. With the binary collision approximation, we only need to consider two-body interactions. Based on this approximation, we are able to reduce the calculation of the whole gaseous sample dramatically to only one absorber molecule and one bath molecule. Consequently, the final expression of absorption coefficient, Eq. (71), has a factor of \( n_a \) explicitly and a factor \( n_b \) included in the \( \hat{\chi} \) functions, as expected.

3. The approximation of \( e^{-i(H_0 + V) t} \) or \( e^{-iH_0 t} e^{-iV t} \) expressed in line space, made in Sec. II C. The physical idea is that in line space, we consider the motion of the dipole moment of the absorber molecule, determined by the time displacement Liouville operator \( e^{-iL t} \), which is related to the total Hamiltonian of the absorber molecule and the bath molecule, as an ordered product of two time displacement Liouville operators \( e^{-iL_0 t} \) and \( e^{-iL t} \). One is related to the intermolecular potential and the other is related to the unperturbed Hamiltonian. Therefore, the validity of this approximation is limited by the requirement of \( [L_0, L_1] \tau^2 \ll 1 \), where \( [L_0, L_1] \) is the commutator of \( L_0 \) and \( L_1 \). Let us consider the matrix elements of the commutator \([L_0, L_1]\). It is well known that all of the diagonal matrix elements of a commutator operator are zero, i.e., \( \langle \bar{j}^+ | [L_0, L_1] | \bar{i} \bar{j}' \rangle = 0 \), where, for simplicity, the index \( i \) stands for \( i_1 \) and \( i_2 \). For the off-diagonal matrix elements of \([L_0, L_1]\), we have

\[
\langle \bar{j}^+ | [L_0, L_1] | \bar{i} \bar{j}' \rangle = \begin{align*}
\left( \omega_{ij} - \omega_{ij'} \right) \left( \langle i | V | i' \rangle \delta_{ij} - \langle j | V | j' \rangle \delta_{ii'} \right),
\end{align*}
\]
(73)

It is obvious that if \( \bar{i} \neq \bar{i}' \) and \( \bar{j} \neq \bar{j}' \), the matrix elements are also zero. The only nonzero matrix elements are related to those two lines that have the same initial states, but with different final states or have the same final states, but with different initial states, respectively. For example, let us consider the case of \( \bar{i} \neq \bar{i}' \) and \( \bar{j} = \bar{j}' \). With Eq. (73), the criterion of this approximation can be written as

\[
\langle \bar{i} | V | \bar{i}' \rangle = 1.
\]
(74)

Since the matrix elements \( \langle \bar{i} | V | \bar{i}' \rangle \) are of order \( 1/\tau \), this condition can be rewritten as

\[
| \omega_{ii'} \tau | \ll 1,
\]
(75)

or

\[
| \omega_{ii'} | \ll | \omega_{ij} |.
\]
(76)

This implies that the frequencies of validity will differ from resonance frequencies by an amount large compared to the differences between this line and other lines coupled by dipole–dipole interaction. We note that Boulet et al.\(^{23} \) have mentioned the similar criterion in their theory. However, based on the argument above, the presence of a few nearby weak lines that do not satisfy this requirement at the frequencies of interest will not significantly affect the final results. Therefore, we expect that this approximation is valid in the atmospheric window regions for which most strong lines are far away.

In conclusion, we expect that the expression for the absorption coefficients, Eq. (71), is valid for the window regions and can be used to calculate the far wing contributions arising from either the pure rotational or vibration–rotational bands. It is also worth mentioning that there is no
H. The positive and negative frequency resonance—average line shape functions

In Eq. (71), the individual lines have different line shapes and their shapes are asymmetric with respect to their centers. However, in present calculations, for simplicity and for comparison with empirical models, we use averaged line shape functions instead of the individual ones. We note that the first terms of Eq. (71) are related to the positive frequency resonance and the second terms are related to the negative frequency resonance. The summation is carried out with the restriction \( \omega_q = E_i - E_j > 0 \). Keeping mind in these restrictions, we can get two averaged functions that are different from each other.

We define the intensity weighted positive frequency resonance-average line shape function by

We need only to evaluate \( \tilde{\Phi}(\omega) \) and \( \tilde{\Psi}(\omega) \) for \( \omega > 0 \). From Eq. (70), it is obvious that the values of these functions for \( \omega < 0 \) are approximately equal or equal to their partner's values for \( \omega > 0 \), i.e., \( \tilde{\Phi}(\omega) \equiv \tilde{\Psi}(\omega) \).

If we do not distinguish between these two different averages, i.e., if we carry out the average without the restrictions \( \omega_q = E_i - E_j > 0 \), we obtain Rosenkranz's band average results.\(^7,8,10\)

We note that Rosenkranz's function \( \tilde{\chi}(\omega) \) is an even function, but the functions \( \tilde{\Phi}(\omega) \) and \( \tilde{\Psi}(\omega) \), like the individual line shape functions \( \tilde{\chi}_q(\omega) \), are not.

With these two line shape functions, the absorption coefficients can be written as

\[
\alpha(\omega) = \sum_{\omega_q > 0} S_{\omega_q} \frac{\omega \cdot \delta(\omega - \omega_q)}{\omega_q \cdot \delta(\omega_q) / 2kT} \times \left( \frac{1}{\omega - \omega_q} \tilde{\Phi}(\omega - \omega_q) + \frac{1}{(\omega + \omega_q)^2} \tilde{\Psi}(\omega + \omega_q) \right).
\]  

Equation (80) is the final formula with which we perform our numerical calculations of the absorption coefficients.

It is worth mentioning that this expression for the absorption coefficients closely matches the semiempirical formula of Clough et al.\(^2\) Furthermore, the shapes of the line shape functions, as shown in Figs. 1–3, are similar to Clough's model. However, instead of using only one function \( \tilde{\chi}(\omega) \) as Clough et al., we use two line shape functions \( \tilde{\Phi}(\omega) \) and \( \tilde{\Psi}(\omega) \). Since the line shape function is not an even function as we mentioned before, we have to use two functions, \( \tilde{\Phi}(\omega) \) with \( \omega > 0 \) and \( \tilde{\Psi}(\omega) \) with \( \omega > 0 \), to represent its part with \( \omega > 0 \) and its part with \( \omega < 0 \), respectively. Clough et al. assume that the line shape function is an even function. Therefore, they only use one function, \( \tilde{\chi}(\omega) \) with \( \omega > 0 \), to represent it. In light of the previous discussion, the function

\[
\tilde{\chi}(\omega) = \frac{4\pi^2}{3} \sum_{\omega_q > 0} \frac{\omega \cdot \delta(\omega - \omega_q)}{\omega_q \cdot \delta(\omega_q) / 2kT} \times \left( \frac{1}{\omega - \omega_q} \tilde{\Phi}(\omega - \omega_q) + \frac{1}{(\omega + \omega_q)^2} \tilde{\Psi}(\omega + \omega_q) \right).
\]
FIG. 1. The positive and negative frequency resonance-average line shape functions (in units of cm\(^{-1}\)/atm), \(\hat{\Phi}(\omega)\) (dashed curve), and \(\hat{\Psi}(\omega)\) (dotted curve), as functions of frequency \(\omega\) (in units of cm\(^{-1}\)), calculated for \(T = 296\) K. The solid curve is the Rosenkranz's band-averaged relaxation parameter with modified normalization factor.

FIG. 2. The same as in Fig. 1 for \(T = 338\) K.

FIG. 3. The same as in Fig. 1 for \(T = 430\) K.

\[\hat{\chi}(\omega)\] used by Clough et al. is an averaged result obtained by ignoring the difference between \(\hat{\Phi}(\omega)\) and \(\hat{\Psi}(\omega)\).

III. THE APPLICATION OF THE WATER CONTINUUM ABSORPTION

A. The boxcar approximation

As mentioned previously, the most costly calculation is the diagonalization of the dipole–dipole interaction and we must first choose a proper basis set to calculate the matrix elements. In general, the basis set is infinite, but in practice it must be truncated. Rosenkranz introduced a cutoff, \(J_{\text{max}}\), as a limitation for the rotational states to be included. To compensate for problems associated with this finite basis set, he made another approximation called the "boxcar approximation." In this approximation, the density operators \(\rho^{(a)}\) and \(\rho^{(b)}\) are independent of the rotational quantum numbers for \(J < J_{\text{max}}\). This implies that states with the angular quantum numbers \(J \leq J_{\text{max}}\) are equally occupied, whereas states with \(J > J_{\text{max}}\) are completely unoccupied. In this case, due to symmetries, use of the symmetric-top wave functions is a better choice for the basis set. By choosing the set of the products of the two symmetric-top wave functions \(|J_aK_aM_aJ_bK_bM_b\rangle\) as the basis to calculate the matrix elements, the matrix of \(G_{\text{dd}}\) takes a block-diagonal form with respect to the proper arrangement of the quantum numbers \(K_a, K_b, M_a,\) and \(M_b\). In the present calculations, in order to simplify the calculation and to compare with Rosenkranz's results, we use the boxcar approximation with the modified normalization factor\(^{10}\) and we choose \(J_{\text{max}} = 4\). However, since the water molecule is an asymmetric top, its density operator is diagonal in the basis of the asymmetric-top wave functions.
Therefore, without the boxcar approximation, the latter provides a convenient choice. The effects of the choice of the basis set and the limitation that the boxcar approximation imposes on the calculation of the absorption coefficients will be discussed elsewhere. 24

B. The computational results and comparison with experiment measurements

For comparison with Rosenkranz's theoretical results, the same parameters of the intermolecular potential have been used. They are the following:

\[ C/k = 8.0 \times 10^8 \, \text{Å}^6 \text{K}, \ \alpha = 48, \ \text{and} \ \sigma = 3.13 \, \text{Å}, \quad (81) \]

and the magnitude of the dipole moment of the water molecule used in the calculation is \( \mu = 1.8546 \, \text{D} \).

We calculate the positive and negative frequency resonance-average line shape functions, \( \Phi(\omega) \) and \( \Psi(\omega) \), for the temperature \( T = 296, 338, \) and \( 430 \) K. The former is obtained from Eq. (77), except we have replaced the restriction \( E_{i_1} > E_{i_2} \) by \( J_{i_1} > J_{i_2} \), consistent with the boxcar approximation. Similarly, the latter is obtained from Eq. (78), except that we have replaced the restriction \( E_{i_1} < E_{i_2} \) by \( J_{i_1} < J_{i_2} \).

The results are shown in Figs. 1–3. Rosenkranz's band-averaged resonance parameters with modified normalization factor \( \chi(\omega) \), are also shown in these figures. First, as shown in the figures, these two line shape functions have different shapes. Roughly speaking, the positive frequency resonance-average line shape functions are flat when the frequency is less than about 50 cm\(^{-1}\) and then their magnitude increases. In the frequency region 100–300 cm\(^{-1}\), they have a significant enhancement that decreases as the temperature increases. At higher frequencies, the positive line shape functions have a very rapid rolloff. On the other hand, the negative frequency resonance-average line shape functions have a flat form over a larger frequency range with some structures that decrease as the temperature increases. After reaching maxima in the frequency range near 300 cm\(^{-1}\), the negative line shape functions also fall off rapidly. The locations of inflection points depend on temperature. For example, the inflection point is located at 600 cm\(^{-1}\) for \( T = 296 \) K, while it decreases to about 400 cm\(^{-1}\) for \( T = 430 \) K. Second, as also shown in these figures, the magnitudes of both the positive and negative line shape functions decrease as the temperature increases. All of these temperature-dependent features of the line shape functions are responsible for the strong negative temperature dependence of the absorption coefficients. It is also obvious from these figures that Rosenkranz's shape functions correspond to the average of two shape functions. It is worth mentioning that the empirical \( \chi \) function used by Clough et al.\(^{25} \) to fit the measurements has a similar profile, more or less, to those mentioned above.

With the HITRAN compilation\(^{25} \) to provide the line strengths and the resonant frequencies of the pure rotational band of the water molecule, we have also calculated the absorption coefficients of the water molecule in the spectral region between 300–1100 cm\(^{-1}\) for the temperatures \( T = 296, 338, \) and \( 430 \) K, and present the results in Figs. 4–6. Rosenkranz's results and the experimental results of Burch et al.\(^{9} \) are also shown in these figures.

As shown in Figs. 4–6, within the band, i.e., in the 300–

---

FIG. 4. The absorption coefficient \( \alpha(\omega) \) (in units of cm\(^2\) molecule\(^{-1}\) atm\(^{-1}\)) as a function of frequency \( \omega \) (in units of cm\(^{-1}\)) calculated for \( T = 296 \) K. The experimental values of Burch et al.\(^{9} \) are denoted by \( \circ \), while \( \Delta \) corresponds to the theoretical values and \( \circ \) corresponds to Rosenkranz's results.

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FIG. 5. The same as in Fig. 4 for \( T = 338 \) K.
600 cm\(^{-1}\) region, our calculated absorption coefficients are similar to Rosenkranz's results. However, in the window of 600–1100 cm\(^{-1}\), the results are quite different. Our results are lower than Rosenkranz's results, especially for \(T = 430\) K, as is clearly seen in Fig. 6. However, in comparison with the measurements of Burch et al., our new results are in much better agreement than Rosenkranz's, especially, in the term of the temperature dependence of the absorption coefficients, as is clearly shown in Figs. 4 and 6. We note that there is an apparent discontinuity in the magnitude of the experimental results for \(T = 296\) K near 700 cm\(^{-1}\); this is an experimental artifact insomuch as the experimental data for frequencies above 700 cm\(^{-1}\) were obtained from a new set of the experiments than those below 700 cm\(^{-1}\). This comparison and the improved agreement with the measurements imply that two line shape functions are required to calculate the absorption coefficients instead of a single line shape function, as in Rosenkranz's approach.

Finally, we would like to make a few remarks about extensions and other applications of the present formalism. First, one can straightforwardly calculate the foreign-broadening absorption, such as \(\text{H}_2\text{O}–\text{N}_2\) in which the only difference results from using the dipole–quadrupole interaction between \(\text{H}_2\text{O}\) and \(\text{N}_2\) instead of the dipole–dipole interaction between \(\text{H}_2\text{O}\) and \(\text{H}_2\text{O}\). Second, we have extended the formalism to other window regions by considering the contributions from the far wings of vibration–rotational transitions of the water molecule instead of the pure rotational band. We will report these elsewhere.

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FIG. 6. The same as in Fig. 4 for \(T = 430\) K.

24 Q. Ma and R. H. Tipping (to be published).