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A FAR-WING LINE SHAPE THEORY WHICH SATISFIES  
THE DETAILED BALANCE PRINCIPLE

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## ABSTRACT

A far-wing theory in which the validity of the detailed balance principle is maintained in each step of the derivation is presented. The role of the total density matrix including the initial correlations is analyzed rigorously. By factoring out the rapidly varying terms in the complex-time development operator in the interaction representation, better approximate expressions can be obtained. As a result, the spectral density can be expressed in terms of the line-coupling functions in which two coupled lines are arranged symmetrically and whose frequency detunings are  $\omega - \frac{1}{2}(\omega_{j_i} + \omega_{j_i'})$ . Using the approximate values  $\omega - \omega_{j_i}$  results in expressions that do not satisfy the detailed balance principle. However, this principle remains satisfied for the symmetrized spectral density in which not only the coupled lines are arranged symmetrically, but also the initial and final states belonging to the same lines are arranged symmetrically as well.

## I. INTRODUCTION

During the last dozen years, a number of line shape theories have been formulated, primarily to calculate the far-wing absorption of molecular systems of interest in atmospheric spectra.<sup>1-9</sup> In many of these theories detailed balance which is important for times comparable to the thermal time  $\tau$ , where  $\tau = \hbar/kT$ , or equivalently for frequency displacements  $\Delta\omega$  of the order  $\tau^{-1}$  from the line center, is not maintained at each step in the development, rather it is enforced by ad hoc symmetrization procedures.<sup>10</sup> By introducing the complex-time development operator to analyze the role of the total density matrix including the initial correlations Davies et al.<sup>1</sup> have derived a theory in which the principle of detailed balance is rigorously satisfied. However, due to the complexity of their formalism, the practical calculation of the far-wing absorption for molecular systems of interest is formidable. In the present study, based on a similar method we introduce a new complex-time development operator instead. This operator is obtained by factoring out the rapidly varying terms in the complex-time development operators used by Davies et al.<sup>1</sup> The advantage of introducing the new operator arises from the fact that its lower-order approximate expression incorporates the old one's higher-order effects. By adopting its lowest-order approximate expression, we obtain a formalism in which the symmetric arrangement of two coupled lines and the correct frequency detunings follow naturally from the derivation. As a result, the formalism satisfies detailed balance, but still remains tractable.

In the present paper, we present the theory for the calculation of the far-wing absorption for molecular system, calculated within the binary collision and quasistatic approximations. In Sec. II A, we first briefly review the relation between the absorption coefficient and the spectral density (frequency regime) or correlation function (time regime) and their requirements so as to satisfy the principle of detailed balance. Next in Sec. II B, we review the correlation function obtained within the framework of the theory of Davies et al.<sup>1</sup> including the introduction of the complex-time development operator. In Sec. II C,

we discuss improvements one can make by factoring out the rapidly varying parts of the complex-time development operators. Then in Sec. II D, we treat the short-time limit of the correlation function within the binary collision approximation. The simplification resulting from the quasistatic approximation and the introduction of the line coupling functions are discussed in Sec. II E. The symmetry relations of the line coupling functions and their relationship to the principle of detailed balance, and intercomparisons between different theories are discussed in Sec. II F and G, respectively. Finally, in Sec. II H we derive the explicit form for the absorption coefficient in terms of the line coupling functions that is the starting point for numerical calculations. These calculations and further simplifications will be presented in a subsequent paper.<sup>13</sup>

## II. THEORY

### A. The correlation function and the spectral density

As is well known, the absorption of radiation at frequency  $\omega$  ( $\text{cm}^{-1}$ ) by a unit volume of a gaseous sample in thermal equilibrium at temperature  $T$  is characterized by the absorption coefficient  $\alpha(\omega)$ :

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

where  $n_a$  is the number density of the absorber molecule. The spectral density,  $F(\omega)$  is the Fourier transform of the correlation function  $C(t)$  of the dipole moment operator in the Heisenberg representation

$$F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} C(t) dt, \quad (2)$$

$$C(t) = \text{Tr}[\rho(\mathbb{H}) \vec{\mu}^{(\mathbb{H})}(0) \cdot \vec{\mu}^{(\mathbb{H})}(t)], \quad (3)$$

where  $\rho(\mathbb{H})$  is the canonical density matrix. We note that the definition of the Fourier transform in Eq. (2) is the same as that used by Davies et al.<sup>1</sup> but differs from that used in our previous papers<sup>6</sup> by a minus sign in the exponential. In general, the total dipole operator of the gas,  $\vec{\mu}(t)$ , is determined by the equation

$$\frac{d}{dt} \vec{\mu}(t) = i[H(t), \vec{\mu}(t)]/\hbar, \quad (4)$$

which can easily be solved by

$$\vec{\mu}(t) = e^{iHt/\hbar} \vec{\mu}(0) e^{-iHt/\hbar} \quad (5)$$

as long as the total Hamiltonian  $H$  is explicitly independent of time. For simplicity, in the above expressions we have dropped the Heisenberg superscript. The spectral density must satisfy the detailed balance requirement

$$F(-\omega) = e^{-\beta\hbar\omega} F(\omega), \quad (6)$$

or expressed more symmetrically

$$e^{\beta\hbar\omega/2} F(-\omega) = e^{-\beta\hbar\omega/2} F(\omega), \quad (7)$$

where  $\beta = 1/kT$ . Equivalently, the correlation function must satisfy the condition

$$C(-t) = C(t + i\beta\hbar), \quad (8)$$

or more symmetrically

$$C(-t + i\beta\hbar/2) = C(t + i\beta\hbar/2). \quad (9)$$

## B. The Davies et al. expression for the correlation function

Davies et al.<sup>1</sup> have derived a general expression for the correlation function which satisfies the detailed balance requirement. They assume that the total Hamiltonian  $H$  is independent of time and separate it into two parts: one commutes with the internal coordinates of the molecules while the second does not. We note that this distinction of Hamiltonian  $H$  usually coincides with the division of the interaction into two parts:  $V_{\text{iso}}$  and  $V_{\text{ani}}$ , the isotropic and the anisotropic interactions, respectively, and we use the same subscripts to label them in the present study. However, in some cases (e.g. when the vibrational dephasing becomes significant) a part of the isotropic interaction does not commute with the internal coordinates since it depends on them (e.g. the vibrational coordinates) and this part must be grouped with  $V_{\text{ani}}$ . Accordingly, the total Hamiltonian  $H$  is decomposed as

$$H = H_a + H_b + V_{\text{iso}} + V_{\text{ani}} \equiv H_0 + V_{\text{ani}}, \quad (10)$$

where  $H_a$  and  $H_b$  are the unperturbed Hamiltonians of the absorber and the bath molecules, respectively. Davies et al. introduce the time development operator  $U(t)$  defined in the interaction representation by

$$e^{-iHt/\hbar} = e^{-iH_0t/\hbar}U(t), \quad (11a)$$

or more generally, for complex time  $z$ ,

$$e^{-iHz/\hbar} = e^{-iH_0z/\hbar}U(z). \quad (11b)$$

The adjoint relations of Eqs. (11a) and (11b) are given by

$$e^{iHt/\hbar} = U^\dagger(t)e^{iH_0t/\hbar}, \quad (12a)$$

and

$$e^{iHz^*/\hbar} = U^\dagger(z)e^{iH_0z^*/\hbar}, \quad (12b)$$

respectively. Then, with Eqs. (3), (5), (11), and (12), the correlation function  $C(t)$  can be expressed as

$$\begin{aligned} C(t) &= \text{Tr}[\vec{\mu} \cdot e^{-iH(t-i\beta\hbar)/\hbar} \vec{\mu} e^{iHt/\hbar}] / \text{Tr}[e^{-\beta H}] \\ &= \nu \text{Tr}[e^{iH_0t/\hbar} \vec{\mu} \rho(H_0) e^{-iH_0t/\hbar} \cdot U(t-i\beta\hbar) \vec{\mu} U^\dagger(t)], \end{aligned} \quad (13)$$

where the zero-time argument of the dipole moment has been dropped,  $\rho(H_0) = e^{-\beta H_0} / \text{Tr}[e^{-\beta H_0}]$  and  $\nu = \text{Tr}[e^{-\beta H_0}] / \text{Tr}[e^{-\beta H}]$ . Since  $H_a$ ,  $H_b$ , and  $V_{iso}$  which are the three components of  $H_0$  commute with each other, one is able to express  $\rho(H_0)$  by the product of three components

$$\rho(H_0) = \rho_a \rho_b \rho_{iso}. \quad (14)$$

In addition, with the fact that both of  $H_b$  and  $V_{iso}$  commute with  $\vec{\mu}$ ,  $C(t)$  can be written as

$$C(t) = \nu \text{Tr}\{e^{iH_a t/\hbar} \vec{\mu} \rho_a e^{-iH_a t/\hbar} \cdot [\rho_b \rho_{iso} U(t-i\beta\hbar) \vec{\mu} U^\dagger(t)]_b\}_a, \quad (15)$$

where the subscript  $a$  indicates the trace over the absorber molecule only and the subscript  $b$  denotes the trace over the remaining variables, i.e., the bath average operation.

As mentioned by Davies et al.<sup>1</sup>, if one ignores the initial correlations by approximating  $\rho(H) \simeq \rho(H_0)$  in Eq. (3), one obtains an expression similar to Eq. (15) except for the replacement of  $\nu$  by 1 and the replacement of  $U(t-i\beta\hbar)$  by  $U(t)$ . In that case, the

correlation function obtained does not satisfy the detailed balance requirement.

### C. The complex-time development operator $U(z)$

The complex-time development operators  $U(z)$  and  $U^\dagger(z)$  are determined by the following integral equations

$$U(z) = 1 - \frac{i}{\hbar} \int_0^z V_i(z') U(z') dz', \quad (16a)$$

$$U^\dagger(z) = 1 + \frac{i}{\hbar} \int_0^z U^\dagger(z') V_i(z') dz', \quad (16b)$$

where

$$V_i(z) = e^{iH_0 z/\hbar} V_{ani} e^{-iH_0 z/\hbar}. \quad (17)$$

The explicit expression of  $U(z)$  is given by

$$\begin{aligned} U(z) &= 1 - \frac{i}{\hbar} \int_0^z V_i(z') dz' + \left(-\frac{i}{\hbar}\right)^2 \int_0^z V_i(z') dz' \int_0^{z'} V_i(z'') dz'' + \dots \\ &= P \exp\left[-\frac{i}{\hbar} \int_0^z V_i(z') dz'\right], \end{aligned} \quad (18)$$

where  $P$  denotes the Dyson chronological ordering operator.

It is worth mentioning that by changing the integration variables one is able to make the upper and lower integral limits more symmetric and to express  $U(z)$  as

$$\begin{aligned} U(z) &= e^{\frac{i}{2}H_0 z/\hbar} \left\{ 1 - \frac{i}{\hbar} \int_{-\frac{z}{2}}^{\frac{z}{2}} V_i(z') dz' \right. \\ &+ \left. \left(-\frac{i}{\hbar}\right)^2 \int_{-\frac{z}{2}}^{\frac{z}{2}} V_i(z') dz' e^{\frac{i}{2}H_0(z'-\frac{z}{2})/\hbar} \int_{-\frac{1}{2}(z'+\frac{z}{2})}^{\frac{1}{2}(z'+\frac{z}{2})} V_i(z'') dz'' e^{-\frac{i}{2}H_0(z'-\frac{z}{2})/\hbar} + \dots \right\} e^{-\frac{i}{2}H_0 z/\hbar} \\ &\equiv e^{\frac{i}{2}H_0 z/\hbar} U'(z) e^{-\frac{i}{2}H_0 z/\hbar}. \end{aligned} \quad (19)$$

At first, it seems unnecessary to introduce a new  $U'(z)$  instead of  $U(z)$  because the expansion in terms of  $U'(z)$  looks less compact than the expansion in  $U(z)$ . However, the advantage of  $U'(z)$  lies in its approximated expression. As is well known, the exact formal expression of  $U(z)$  is used for theoretical analysis only and, in practice, in order to evaluate

it some approximations have to be introduced. For example, in the above expansion of  $U(z)$  one usually truncates and keeps only first few terms. In contrast with  $U(z)$ , for each term of  $U'(z)$  the  $n$ -th integration of the odd integrand over the variable  $z^{(n)}$  is zero. Since the integration over the variable  $z^{(n)}$  gives a function depending on the variable  $z^{(n-1)}$ , the above fact implies that part of the contribution from the  $n$ -th integration has already been taken into account. In the other words,  $U'(z)$  varies with its argument  $z$  more slowly than  $U(z)$  does. It is worth mentioning that the higher the expansion term of  $U(z)$  considered, the less is the fraction of the total resulting from the integrations of the corresponding  $U'(z)$  term. The reason is that for each step of the integration, only the even integrands survive. We note that an alternative way to introduce  $U'(z)$  is directly from a definition of  $e^{-iHz/\hbar} \equiv e^{-\frac{i}{2}H_0z/\hbar} U'(z) e^{-\frac{i}{2}H_0z/\hbar}$ . In comparison with the definition of  $U(z)$ , Eq. (11b),  $U'(z)$  is introduced more symmetrically. Based on the arguments given above, one expects that in comparison between the expressions of  $e^{-iHz/\hbar}$  obtained in terms of the same order approximations of  $U'(z)$  and  $U(z)$ , the former is closer to the exact result than the latter. Therefore, we will pursue further discussion in terms of  $U'(z)$ .

#### D. A short-time limit of $C(t)$ in the binary collision approximation

With Eqs. (15) and (19), the correlation function  $C(t)$  can be expressed as

$$\begin{aligned}
 C(t) &= \nu \text{Tr} \{ e^{iH_a t/\hbar} \vec{\mu} \rho_a e^{-iH_a t/\hbar} \\
 &\cdot [\rho_b \rho_{\text{iso}} e^{\frac{i}{2}H_0(t-i\beta\hbar)/\hbar} U'(t-i\beta\hbar) e^{-\frac{i}{2}H_0(t-i\beta\hbar)/\hbar} \vec{\mu} e^{\frac{i}{2}H_0 t/\hbar} U^\dagger(t) e^{-\frac{i}{2}H_0 t/\hbar}]_b \}_a \\
 &= \nu \text{Tr} \{ e^{\frac{i}{2}H_a t/\hbar} \vec{\mu} \sqrt{\rho_a} e^{-\frac{i}{2}H_a t/\hbar} \cdot [\sqrt{\rho_b} \rho_{\text{iso}} U'(t-i\beta\hbar) e^{-\frac{i}{2}H_a t/\hbar} \sqrt{\rho_a \rho_b} \vec{\mu} e^{\frac{i}{2}H_a t/\hbar} U^\dagger(t)]_b \}_a. \quad (20)
 \end{aligned}$$

The expression of  $C(t)$  given in Eq. (20) is exact and satisfies the detailed balance requirement, Eq. (8), which can be directly verified as pointed out by Davies et al.<sup>1</sup> For later convenience, we can introduce a symmetric correlation function  $\tilde{C}(t)$  defined by

$$\begin{aligned}
 \tilde{C}(t) &\equiv C(t+i\beta\hbar/2) \\
 &= \text{Tr} [\vec{\mu} \cdot e^{-iH(t-i\beta\hbar/2)} \vec{\mu} e^{iH(t+i\beta\hbar/2)}] / \text{Tr} [e^{-\beta H}]
 \end{aligned}$$



$$\begin{aligned}
&= \nu \text{Tr} \left\{ e^{\frac{i}{2} H_a t / \hbar} \rho_a^{\frac{1}{4}} \vec{\mu} \rho_a^{\frac{1}{4}} e^{-\frac{i}{2} H_a t / \hbar} \right. \\
&\quad \cdot \left. [\sqrt{\rho_b} \rho_{\text{iso}} U'(t-i\beta\hbar/2) e^{-\frac{i}{2} H_a t / \hbar} (\rho_a \rho_b)^{\frac{1}{4}} \vec{\mu} (\rho_a \rho_b)^{\frac{1}{4}} e^{\frac{i}{2} H_a t / \hbar} U'^{\dagger}(t-i\beta\hbar/2)]_b \right\}_a. \quad (21)
\end{aligned}$$

It is obvious that the expression  $\bar{C}(t)$  has more symmetry than  $C(t)$ . Its physical advantage will be discussed later. It is easy to verify that  $\bar{C}(t)$  given above is an even function. This is consistent with Eq. (9) which represents the detailed balance principle expressed symmetrically. Similarly, in the frequency domain, in comparison with  $F(\omega)$ , one expects that  $\bar{F}(\omega)$ , the Fourier transform of  $\bar{C}(t)$ , has more symmetry also.

In practice, to evaluate the complex-time development operators and to perform their bath average are formidable tasks for the system consisting of one absorber molecule and all the bath molecules. Fortunately, for atmospheric applications where the gas pressures are low one can introduce the binary collision approximation which enable one to focus on a much simpler system consisting of one absorber and one bath molecules. It is worth mentioning that the formalism obtained so far is based on the assumption that the total Hamiltonian is independent of time. However, when one adopts the binary collision approximation and the classical translational approximation discussed later and focuses on two interacting molecules, the total Hamiltonian of interest, in general, is dependent on time. Therefore, for the two-molecule system the validity of the formulas which are derived for one absorber molecule and the whole bath must be carefully checked but this is not the topic of the present study. For the short-time limit (corresponding to the far-wing region of the resonant lines of interest in the present study) we expect that the expressions of the correlation functions  $C(t)$  and  $\bar{C}(t)$  given by Eqs. (20) and (21), respectively, are directly applicable for the two-molecule system. For simplicity, we don't introduce new symbols for the two-molecule system and keep the same notations used previously. Therefore, in all the following formulas, the quantities belong to one absorber molecule and one bath molecule only.

In order to analyze the short-time behavior of the correlation function  $C(t)$ , we first

derive an expression for  $U'(z)$  as  $z \rightarrow 0$

$$U'(z) = 1 - \frac{i}{\hbar} \int_{-\frac{z}{2}}^{\frac{z}{2}} e^{iH_0 z'/\hbar} V_{\text{ani}} e^{-iH_0 z'/\hbar} dz' + \dots$$

$$\simeq e^{-iV_{\text{ani}} z/\hbar}. \quad (22)$$

Then, with Eq. (22) one can express  $C(t)$  as

$$C(t) = \nu \text{Tr} [e^{\frac{i}{2} H_a t/\hbar} \vec{\mu} \sqrt{\rho_a \rho_b} e^{-\frac{i}{2} H_a t/\hbar}$$

$$\cdot \rho_{\text{iso}} e^{-\beta V_{\text{ani}}} e^{-iV_{\text{ani}} t/\hbar} e^{-\frac{i}{2} H_a t/\hbar} \sqrt{\rho_a \rho_b} \vec{\mu} e^{\frac{i}{2} H_a t/\hbar} e^{iV_{\text{ani}} t/\hbar}]$$

$$= \nu \text{Tr} [(e^{-\frac{i}{2} L_a t} \sqrt{\rho_a \rho_b} \vec{\mu})^\dagger \cdot \rho_{\text{iso}} e^{-\beta V_{\text{ani}}} (e^{-iL_{\text{ani}} t} e^{-\frac{i}{2} L_a t} \sqrt{\rho_a \rho_b} \vec{\mu})], \quad (23)$$

where the Liouville operator  $L_a$  and  $L_{\text{ani}}$  that act on the line space have been introduced.<sup>6</sup>

By introducing a vector  $\vec{A}_0(t)$  defined by

$$\vec{A}_0(t) = e^{-\frac{i}{2} L_a t} \sqrt{\rho_a \rho_b} \vec{\mu}$$

$$= \sum_{ij} e^{\frac{i}{2} \omega_{ji} t} \sqrt{\rho_i} \langle i | \vec{\mu} | j \rangle |ij^\dagger\rangle \times \sum_{i_b} \sqrt{\rho_{i_b}} |i_b i_b^\dagger\rangle, \quad (24)$$

$C(t)$  can be simply expressed as

$$C(t) = \nu \text{Tr} \{ \vec{A}_0(t)^\dagger \cdot \rho_{\text{iso}} e^{-\beta V_{\text{ani}}} [e^{-iL_{\text{ani}} t} \vec{A}_0(t)] \}. \quad (25)$$

The physical meaning of the vector  $\vec{A}_0(t)$  in the line space of the interacting molecular system is clearly shown in Eq. (24). It is a direct product of two vectors. The first vector that is defined in the line space of the absorber molecule represents an unperturbed dipole transition vector of the absorber molecule. The components of this vector undergo harmonic motions with the frequencies equals to  $\omega_{ji}/2$  and their magnitudes are related to the dipole matrix elements  $\sqrt{\rho_i} \langle i | \vec{\mu} | j \rangle$ . The second vector that is defined in the line space of the bath molecule is simply a thermal equilibrium density vector of the bath molecule. If the interaction between the molecules is ignored,  $C(t)$  reduces to a scalar product of the vector  $\vec{A}_0(t)$  with its adjoint vector  $\vec{A}_0(t)^\dagger$  given by

$$\langle \vec{A}_0(t) | \vec{A}_0(t) \rangle = \text{Tr} [\vec{A}_0(t)^\dagger \cdot \vec{A}_0(t)]$$

$$\begin{aligned}
&= \sum_{ij} \rho_i \langle i | \vec{\mu} | j \rangle^\dagger \cdot \langle i | \vec{\mu} | j \rangle \times \sum_{i_b} \rho_{i_b} \\
&= \sum_{ij} \rho_i |\mu_{ij}|^2,
\end{aligned} \tag{26}$$

where  $\mu_{ij}$  is the reduced dipole matrix elements defined by

$$\langle i | \mu_m | j \rangle = (2i + 1) C(j \ 1 \ i; m_j \ m \ m_i) \mu_{ij}. \tag{27}$$

In this case, the correlation function  $C(t)$  is simply a constant.

The effects of the anisotropic interaction  $V_{\text{ani}}$  and the isotropic interaction  $V_{\text{iso}}$  on  $C(t)$  are also clearly shown in Eq. (25). The former plays a more important role than the latter since it rotates the unperturbed vector  $\vec{A}_0(t)$  in the line space to a new perturbed vector  $e^{-iL_{\text{ani}}t} \vec{A}_0(t)$ . Thus, the correlation function  $C(t)$  is simply a scalar product between the perturbed and the unperturbed vectors with  $\rho_{\text{iso}} e^{-\beta V_{\text{ani}}}$  as its metric.

Similarly, the approximate expression for the symmetric correlation function  $\tilde{C}(t)$  in the short-time limit is given by

$$\begin{aligned}
\tilde{C}(t) &= \nu \text{Tr} \{ [e^{-\frac{i}{2}L_{\text{a}}t} (\rho_a \rho_b)^{\frac{1}{4}} \vec{\mu} (\rho_a \rho_b)^{\frac{1}{4}}]^\dagger \\
&\quad \cdot \rho_{\text{iso}} e^{-\frac{1}{2}\beta V_{\text{ani}}} [e^{-iL_{\text{ani}}t} e^{-\frac{i}{2}L_{\text{a}}t} (\rho_a \rho_b)^{\frac{1}{4}} \vec{\mu} (\rho_a \rho_b)^{\frac{1}{4}}] e^{-\frac{1}{2}\beta V_{\text{ani}}} \} \\
&= \nu \text{Tr} \{ \vec{A}_0^\dagger(t) \cdot \rho_{\text{iso}} e^{-\frac{1}{2}\beta V_{\text{ani}}} [e^{-iL_{\text{ani}}t} \vec{A}_0^\dagger(t)] e^{-\frac{1}{2}\beta V_{\text{ani}}} \},
\end{aligned} \tag{28}$$

where

$$\begin{aligned}
\vec{A}_0^\dagger(t) &= e^{-\frac{i}{2}L_{\text{a}}t} (\rho_a \rho_b)^{\frac{1}{4}} \vec{\mu} (\rho_a \rho_b)^{\frac{1}{4}} \\
&= \sum_{ij} e^{-\frac{i}{2}\omega_{ij}t} (\rho_i \rho_j)^{\frac{1}{4}} \langle i | \vec{\mu} | j \rangle |ij\rangle^\dagger \times \sum_{i_b} \sqrt{\rho_{i_b}} |i_b i_b\rangle^\dagger.
\end{aligned} \tag{29}$$

In this case, the scalar product of  $\vec{A}_0^\dagger(t)$  with its adjoint vector  $\vec{A}_0^\dagger(t)^\dagger$  is given by

$$\langle \vec{A}_0^\dagger(t) | \vec{A}_0^\dagger(t) \rangle = \sum_{ij} \sqrt{\rho_i \rho_j} |\mu_{ij}|^2. \tag{30}$$

A similar discussion about the physical meaning of the symmetric correlation function  $\tilde{C}(t)$  will not be repeated here.

Before going to the next topic associated with the translational motion, we note

that both of the lowest order approximate expressions for  $C(t)$  and  $\bar{C}(t)$  still satisfy the detailed balance principle given in Eqs. (8) and (9), respectively. This conclusion is easy to verify directly from Eqs. (23) and (28). Although we will not check this conclusion further in the present study, we expect that it remains true even for higher-order approximate expressions for  $C(t)$  and  $\bar{C}(t)$  as claimed by Davies et al.<sup>1</sup>

We assume that the translational motion of the two interacting molecules can be treated classically. For a specified intermolecular separation  $\vec{r}$  designated by its orientation  $\Omega$  and its distance  $r$  in a space-fixed frame, we express the anisotropic interaction as

$$V_{\text{ani}}(\vec{r}) = G(\Omega)R(r), \quad (31)$$

where  $G(\Omega)$  also depends on the internal coordinates of the absorber and the perturber which span a Hilbert space for the molecules; this has not been explicitly indicated in the above notation. Since  $V_{\text{ani}}(\vec{r})$  does not commute with  $H_a$  and  $H_b$ , neither does  $G(\Omega)$ . Therefore, one has to find its eigenvectors and eigenvalues denoted by  $|\alpha\rangle$  and  $G_\alpha$ , respectively,

$$G(\Omega)|\alpha\rangle = G_\alpha|\alpha\rangle. \quad (32)$$

Then, with Eqs. (23), (31), and (32) one is able to express  $C(t)$  as

$$C(t) = \sum_{ij} \sum_{i'j'} e^{\frac{i}{\hbar}(\omega_{ji} + \omega_{j'i'})t} \sqrt{\rho_i \rho_{i'}} \mu_{ij} \mu_{i'j'} \xi_{ij,i'j'}(t), \quad (33)$$

where the summation indices  $i, j, i'$  and  $j'$  exclude their magnetic quantum numbers and

$\xi_{ij,i'j'}(t)$  are defined by

$$\begin{aligned} \xi_{ij,i'j'}(t) \equiv & \frac{\nu}{\mu_{ij}\mu_{i'j'}} \sum_{\{m\}} \sum_{i_b} \sum_{i'_b} \sqrt{\rho_{i_b} \rho_{i'_b}} \sum_{\alpha\beta} (\langle a | i i_b \rangle \langle i | \mu_m | j \rangle \langle j_b | \beta \rangle)^* \\ & \times \langle a | i' i'_b \rangle \langle i' | \mu_m | j' \rangle \langle j' i'_b | \beta \rangle \text{Tr}[\rho_{\text{iso}}(r) e^{-G_\alpha R(r)/kT - iG_{\alpha\beta} R(r)t} ]_{\vec{r}}. \end{aligned} \quad (34)$$

In the above expression,  $\{m\}$  indicates the summation over all magnetic quantum numbers,  $G_{\alpha\beta} = G_\alpha - G_\beta$ , and the  $r$  dependence of  $\rho_{\text{iso}}$  has been explicitly indicated by  $\rho_{\text{iso}}(r)$ . The remaining trace over the classical translational variables is indicated by  $\text{Tr}[\rho_{\text{iso}}(r)]_{\vec{r}}$ .

Similarly,  $\bar{C}(t)$  is given by

$$\bar{C}(t) = \sum_{ij} \sum_{i'j'} e^{\frac{i}{2}(\omega_{ji} + \omega_{j'i'})t} (\rho_i \rho_j \rho_{i'} \rho_{j'})^{\frac{1}{4}} \mu_{ij} \mu_{i'j'} \tilde{g}_{ij;i'j'}(t), \quad (35)$$

where

$$\begin{aligned} \tilde{g}_{ij;i'j'}(t) \equiv & \frac{\nu}{\mu_{ij} \mu_{i'j'}} \sum_{\{m\}} \sum_{i_b} \sum_{i'_b} \sqrt{\rho_{i_b} \rho_{i'_b}} \sum_{\alpha\beta} (\langle a | i i_b \rangle \langle i | \mu_m | j \rangle \langle j'_b | \beta \rangle)^* \\ & \times \langle a | i' i'_b \rangle \langle i' | \mu_m | j' \rangle \langle j'_b | \beta \rangle \text{Tr}[\rho_{\text{iso}}(r) e^{-\frac{1}{2}(G_\alpha + G_\beta)R(r)/kT - iG_{\alpha\beta}R(r)t}]_{\vec{r}}. \end{aligned} \quad (36)$$

It is worth mentioning that in Eqs. (33) and (35) two pairs of the summation indices  $\{i j\}$  and  $\{i' j'\}$  are not independent of each other. For a specified pair  $\{i j\}$ , the  $\{i' j'\}$  are limited to those pairs whose  $i'$  are coupled to  $i$  and whose  $j'$  are coupled to  $j$  by the anisotropic interaction  $V_{\text{ani}}(\vec{r})$ , respectively. In other words, due to the symmetry of the interaction, the coupling occurs only for those lines for which the indices  $i$  and  $i'$  have the same symmetry, and also the indices  $j$  and  $j'$  have the same symmetry. We note that both  $g_{ij;i'j'}(t)$  and  $\tilde{g}_{ij;i'j'}(t)$  are symmetric for the exchange  $\{i j\} \leftrightarrow \{i' j'\}$ . However, they have the different behaviors for the exchanges  $\{i j\} \rightarrow \{j i\}$  and  $\{i' j'\} \rightarrow \{j' i'\}$ , viz.

$$g_{j i, j' i'}(-t) = g_{ij;i'j'}(t + i\hbar/kT), \quad (37a)$$

and

$$\tilde{g}_{j i, j' i'}(-t) = \tilde{g}_{ij;i'j'}(t), \quad (37b)$$

which arise from the detailed balance requirement as are easily verified from their definitions.

### E. The quasistatic approximation and the line coupling functions

With the quasistatic approximation, the intermolecular separation  $\vec{r}$  is assumed to be fixed in the space during the time period of interest. Without loss of generality, we can take  $\vec{r}$  to lie along the space-fixed  $Z$  axis and ignore its orientation parameter  $\Omega$  introduced previously. The classical partition sum for  $\rho_{\text{iso}}(r)$  is approximately equal to  $1/n_b$  where  $n_b$  is the number density of the perturber molecules.<sup>2,3</sup> Then, based on the quasistatic

approximation one is able to replace the classical ensemble average of an arbitrary function  $f(\mathbf{r})$  over the translational variable  $\mathbf{r}$ ,  $\text{Tr}[\rho_{\text{iso}}(\mathbf{r})f(\mathbf{r})]_{\overline{\mathbf{r}}}$ , by an integration over  $\mathbf{r}$

$$\text{Tr}[\rho_{\text{iso}}(\mathbf{r})f(\mathbf{r})]_{\overline{\mathbf{r}}} \simeq 4\pi n_b \int_0^\infty e^{-V_{\text{iso}}(\mathbf{r})/kT} f(\mathbf{r})r^2 d\mathbf{r}. \quad (38)$$

With the replacement of the ensemble average over  $\mathbf{r}$  given above, we pursue further discussion in the frequency domain. The spectral density  $F(\omega)$  corresponding to  $C(t)$  given by Eqs. (33) and (34) is

$$\begin{aligned} F(\omega) &= \frac{1}{\pi} \text{Re} \sum_{ij} \sum_{i'j'} \sqrt{\rho_i \rho_{i'}} \mu_{ij} \mu_{i'j'} \int_0^\infty e^{-i[\omega - \frac{1}{2}(\omega_{ji} + \omega_{j'i'})]t} g_{ij,i'j'}(t) dt \\ &\equiv \frac{1}{\pi} \sum_{ij} \sum_{i'j'} \sqrt{\rho_i \rho_{i'}} \mu_{ij} \mu_{i'j'} \chi_{ij,i'j'}[\omega - \frac{1}{2}(\omega_{ji} + \omega_{j'i'})]. \end{aligned} \quad (39)$$

In Eq. (39), the coupling functions  $\chi_{ij,i'j'}(\omega)$  are defined by

$$\begin{aligned} \chi_{ij,i'j'}(\omega) &= \frac{\nu}{\mu_{ij} \mu_{i'j'}} \sum_{\{m\}} \sum_{i_b} \sum_{i'_b} \sqrt{\rho_{i_b} \rho_{i'_b}} \sum_{\alpha\beta} (\langle a | i i_b \rangle \langle i | \mu_m | j \rangle \langle j i_b | \beta \rangle)^* \\ &\times \langle a | i' i'_b \rangle \langle i' | \mu_m | j' \rangle \langle j' i'_b | \beta \rangle \text{Im} 4\pi n_b \int_0^\infty e^{-V_{\text{iso}}(\mathbf{r})/kT - G_\alpha R(\mathbf{r})/kT} \frac{1}{\omega - G_{\beta\alpha} R(\mathbf{r})} r^2 d\mathbf{r} \\ &= \frac{\nu}{\mu_{ij} \mu_{i'j'}} \sum_{\{m\}} \sum_{i_b} \sum_{i'_b} \sqrt{\rho_{i_b} \rho_{i'_b}} \sum_{\alpha\beta} (\langle a | i i_b \rangle \langle i | \mu_m | j \rangle \langle j i_b | \beta \rangle)^* \\ &\times \langle a | i' i'_b \rangle \langle i' | \mu_m | j' \rangle \langle j' i'_b | \beta \rangle H_{\beta\alpha}(\omega), \end{aligned} \quad (40)$$

where

$$H_{\beta\alpha}(\omega) \equiv 4\pi^2 n_b r_c^2 \frac{1}{|G_{\beta\alpha} R'(r_c)|} e^{-V_{\text{iso}}(r_c)/kT - G_\alpha R(r_c)/kT}, \quad (41)$$

$R'(r) = dR(r)/dr$ , and  $r_c$  are the positive solutions of the equation

$$\omega - G_{\beta\alpha} R(r_c) = 0. \quad (42)$$

In deriving the above expression, the well-known formal identity

$$\lim_{\epsilon \rightarrow 0} \frac{1}{\omega - G_{\beta\alpha} R(r) - i\epsilon} = P \frac{1}{\omega - G_{\beta\alpha} R(r)} + i\pi \delta[\omega - G_{\beta\alpha} R(r)] \quad (43)$$

has been used to obtain the imaginary parts which are the only ones of interest here. The functions  $\chi_{ij,i'j'}(\omega)$  represent the coupling effects between the  $\{ij\}$  lines and the  $\{i'j'\}$  lines.

Similarly, the symmetric spectral density  $\tilde{F}(\omega)$  corresponding to the symmetric

correlation function  $\bar{C}(t)$  is given by

$$\begin{aligned}\bar{F}(\omega) &= \frac{1}{\pi} \text{Re} \sum_{ij} \sum_{i'j'} (\rho_i \rho_j \rho_{i'} \rho_{j'})^{\frac{1}{4}} \mu_{ij} \mu_{i'j'} \int_0^{\infty} e^{-i[\omega - \frac{1}{2}(\omega_{ji} + \omega_{j'i'})]t} \tilde{g}_{ij,i'j'}(t) dt \\ &\equiv \frac{1}{\pi} \sum_{ij} \sum_{i'j'} (\rho_i \rho_j \rho_{i'} \rho_{j'})^{\frac{1}{4}} \mu_{ij} \mu_{i'j'} \tilde{\chi}_{ij,i'j'}[\omega - \frac{1}{2}(\omega_{ji} + \omega_{j'i'})],\end{aligned}\quad (44)$$

where

$$\begin{aligned}\tilde{\chi}_{ij,i'j'}(\omega) &= \frac{\nu}{\mu_{ij} \mu_{i'j'}} \sum_{\{m\}} \sum_{i_b} \sum_{i'_b} \sqrt{\rho_{i_b} \rho_{i'_b}} \sum_{\alpha\beta} (\langle a | i i_b \rangle \langle i | \mu_m | j \rangle \langle j_b | \beta \rangle)^* \\ &\quad \times \langle a | i' i'_b \rangle \langle i' | \mu_m | j' \rangle \langle j' i'_b | \beta \rangle \bar{H}_{\beta\alpha}(\omega),\end{aligned}\quad (45)$$

and

$$\bar{H}_{\beta\alpha}(\omega) \equiv 4\pi^2 n_b r_c^2 \frac{1}{|G_{\beta\alpha} R'(r_c)|} e^{-V_{\text{iso}}(r_c)/kT - \frac{1}{2}(G_\alpha + G_\beta)R(r_c)/kT}.\quad (46)$$

It is obvious that

$$\bar{H}_{\beta\alpha}(\omega) = e^{-\hbar\omega/2kT} H_{\beta\alpha}(\omega),\quad (47a)$$

and

$$\bar{H}_{\alpha\beta}(-\omega) = \bar{H}_{\beta\alpha}(\omega).\quad (47b)$$

The properties of  $\bar{H}_{\beta\alpha}(\omega)$  given in Eqs. (47a) and (47b) are important for further developments. With Eqs. (47a) and (47b), it is easy to derive similar properties for other functions associated with  $\bar{H}_{\beta\alpha}(\omega)$ . For example, the coupling functions  $\chi_{ij,i'j'}(\omega)$  and  $\tilde{\chi}_{ij,i'j'}(\omega)$  given in Eqs. (40) and (44), respectively, obey the relationship,

$$\tilde{\chi}_{ij,i'j'}(\omega) = e^{-\hbar\omega/2kT} \chi_{ij,i'j'}(\omega).\quad (48)$$

We note that  $\tilde{\chi}_{ij,i'j'}(\omega)$  introduced here is nothing but so called the symmetric line coupling functions  $\hat{\chi}_{ij,i'j'}(\omega)$  with Eq. (48) as their definitions in literatures.<sup>2-6</sup>

## F. The detailed balance principle

The coupling functions  $\chi_{ij,i'j'}(\omega)$  and  $\tilde{\chi}_{ij,i'j'}(\omega)$  discussed above have the following symmetry properties: both of them are symmetric for the exchange of indices  $\{i j\} \leftrightarrow \{i' j'\}$ , but obey

$$\chi_{j_i, j_i', (-\omega)} = e^{-\hbar\omega/2kT} \chi_{i_j, i_j', (\omega)}, \quad (49a)$$

and

$$\tilde{\chi}_{j_i, j_i', (-\omega)} = \tilde{\chi}_{i_j, i_j', (\omega)}, \quad (49b)$$

for the exchanges of indices  $\{i j\} \rightarrow \{j i\}$  and  $\{i' j'\} \rightarrow \{j' i'\}$ . Similar to the symmetry properties of their partners in the time domain shown in Eqs. (37a) and (37b), the above symmetry properties of  $\chi_{i_j, i_j', (\omega)}$  and  $\tilde{\chi}_{i_j, i_j', (\omega)}$  are easily verified from their definitions.

With Eqs. (39) and (49a), it is easy to prove that the detailed balance principle given in Eq. (6) is also satisfied by  $F(\omega)$  expressed in terms of  $\chi_{i_j, i_j', (\omega)}$ . However, we note that in the expression of  $F(\omega)$  the frequency detunings  $\omega - \frac{1}{2}(\omega_{j_i} + \omega_{j_i'})$  of the coupling functions  $\chi_{i_j, i_j', (\omega)}$  are crucial to guarantee that detailed balance is satisfied exactly. In the case where  $|\omega - \omega_{j_i}| \geq \frac{1}{2}|\omega_{j_i} - \omega_{j_i'}|$ , to replace the frequency detunings  $\omega - \frac{1}{2}(\omega_{j_i} + \omega_{j_i'})$  by their approximate values (for example,  $\omega - \omega_{j_i}$ ) results in failure to satisfy this principle. One can easily check this conclusion.

With respect to the symmetric spectral density  $\tilde{F}(\omega)$  which is the Fourier transform of  $\tilde{C}(t) [\equiv C(t+i\hbar/2kT)]$ , it is obvious that

$$\tilde{F}(\omega) = e^{-\hbar\omega/2kT} F(\omega). \quad (50)$$

Therefore, the detailed balance principle given in Eq. (7) requires  $\tilde{F}(\omega)$  simply to be an even function as  $\tilde{C}(t)$  is,

$$\tilde{F}(-\omega) = \tilde{F}(\omega). \quad (51)$$

With Eq. (49b), it is easy to prove that Eq. (51) is valid for the expression of  $\tilde{F}(\omega)$  expressed in terms of  $\tilde{\chi}_{i_j, i_j', (\omega)}$  given in Eq. (44). It is interesting to note that for  $\tilde{F}(\omega)$  the frequency detunings  $\omega - \frac{1}{2}(\omega_{j_i} + \omega_{j_i'})$  of the coupling functions  $\tilde{\chi}_{i_j, i_j', (\omega)}$  are not crucial for the validity of Eq. (51). Instead, to replace the exact frequency detunings  $\omega - \frac{1}{2}(\omega_{j_i} + \omega_{j_i'})$  of  $\tilde{\chi}_{i_j, i_j', (\omega)}$  in the expression of  $\tilde{F}(\omega)$  by their approximate values  $\omega - \omega_{j_i}$  or  $[(\omega - \omega_{j_i})(\omega - \omega_{j_i'})]^{\frac{1}{2}}$  does not affect the validity. This advantage arises from the fact that in the expression of  $\tilde{F}(\omega)$  not only two coupled lines are treated equally, but also the initial



and final states which belong to the same lines are treated equally as well. On the other hand, in the expression of  $F(\omega)$ , the initial and final states are not treated equally. It is well known that detailed balance is associated to an interchange of the initial and the final states in emission and absorption processes. It implies that a functional form with a more symmetrical arrangement between the initial and final states is a better choice to exhibit this principle. Therefore, it is not surprising that after approximations for the frequency detunings have been made the validity of detailed balance remains for  $\bar{F}(\omega)$ , but not for  $F(\omega)$ . For example, for  $|\omega - \omega_{ji}| \geq \frac{1}{2}|\omega_{ji} - \omega_{j'i'}|$  one adopts the frequency detuning approximation  $\omega - \frac{1}{2}(\omega_{ji} + \omega_{j'i'}) \simeq \omega - \omega_{ji}$  and simply expresses  $\bar{F}(\omega)$  as

$$\bar{F}(\omega) \simeq \frac{1}{\pi} \sum_{ij} \sum_{i'j'} (\rho_i \rho_j \rho_{i'} \rho_{j'})^{\frac{1}{4}} \mu_{ij} \mu_{i'j'} \tilde{\chi}_{ij, i'j'}(\omega - \omega_{ji}). \quad (52)$$

Owing to the symmetries of the summation indices  $i$  and  $j$ , and also  $i'$  and  $j'$ ,  $\bar{F}(\omega)$  remains an even function as required by the detailed balance principle. Therefore, we use  $\bar{F}(\omega)$  instead of  $F(\omega)$  in the expression of the absorption coefficient  $\alpha(\omega)$  given in Eq. (1) with a replacement of  $[F(\omega) + F(-\omega)]$  by  $2\cosh(\hbar\omega/2kT)\bar{F}(\omega)$ .

### G. Comparisons between different formalisms

Starting from the Fano's formalism<sup>11</sup> and based on the binary collision and quasistatic approximations, Rosenkranz<sup>2,3</sup> (extended by Ma and Tipping<sup>6</sup>) has derived a far-wing theory and obtained an expression of  $F(\omega)$  which can be expressed in the present notation as

$$F(\omega) = \frac{1}{\pi} \sum_{ij} \sum_{i'j'} \rho_i \mu_{ij} \mu_{i'j'} \chi_{ij, i'j'}(\omega - \omega_{ji}). \quad (53)$$

It is obvious that the above expression does not satisfy detailed balance. In order to remedy this, Rosenkranz used a method to force the detailed balance principle given in Eq. (6) to be valid. The basic idea of this method is that since the detailed balance principle establishes the relation between the values of  $F(\omega)$  associated with its positive argument

and that associated with the negative argument, then for one-half the argument range one assumes that the coupling functions are represented by the theoretical expression and for the other half range, one assumes that they are obtained from the former ones by imposing the detailed balance principle. Thus, the validity is forced to be maintained in the formalism.

Based on the Davies et al.<sup>1</sup> formalism and adopting the lowest order approximation for  $U(z)$  instead of  $U'(z)$  used in the present study, Boulet et al.<sup>4,5</sup> have developed a quasistatic resonant theory and obtained an expression of  $F(\omega)$  similar to Eq. (53). They also noticed that the above expression did not satisfy detailed balance. In order to improve it they replaced their theoretical coupling functions by model functions which are the theoretical ones times the energetically correction factors  $\sqrt{\rho_i}/\sqrt{\rho_i}$  and obtained the so called energetically corrected quasistatic resonant formula<sup>4,5</sup>

$$F(\omega) = \frac{1}{\pi} \sum_{ij} \sum_{i'j'} \sqrt{\rho_i \rho_{i'}} \mu_{ij} \mu_{i'j'} \chi_{ij, i'j'}(\omega - \omega_{ji}), \quad (54)$$

in which two coupled lines are arranged more symmetrically than before. It is interesting to note that their model is similar to our expression of  $F(\omega)$  given in Eq. (39) except that the frequency detunings of the coupling functions are  $\omega - \omega_{ji}$  instead of  $\omega - \frac{1}{2}(\omega_{ji} + \omega_{j,i'})$ . In general, the resonance frequencies of the strongly coupled lines are close to each other. One expects that when the frequencies of interest are far away from band centers, i.e., the criterion of  $|\omega - \omega_{ji}| \geq \frac{1}{2}|\omega_{ji} - \omega_{j,i'}|$  is valid, the frequency detuning approximations, such as the replacement of  $\omega - \frac{1}{2}(\omega_{ji} + \omega_{j,i'})$  by  $\omega - \omega_{ji}$  as Boulet et al.<sup>4,5</sup> did or by other choices, such as  $[(\omega - \omega_{ji})(\omega - \omega_{j,i'})]^{\frac{1}{2}}$ , can be introduced. However, it turns out that due to the sensitivity of the line coupling functions to their arguments, the validity of the frequency detuning approximation is poor for frequencies which are not far enough away from the band centers. In addition, as we have discussed above and as Boulet et al.<sup>4,5</sup> have noticed, their model does not satisfy detailed balance exactly. Therefore, based on the discussions given above one is able to understand the origin and also the weakness of their

empirical energetically corrected formalism.

Recently, by arranging the real parts of the upper and lower integral limits of  $U(z)$  symmetrically, Hartmann and Boulet<sup>12</sup> have demonstrated that the frequency detunings of the line coupling functions should be  $\omega - \frac{1}{2}(\omega_{ji} + \omega_{j,i})$ . But, they have not gone further to simultaneously arrange the imaginary parts of the integral limits symmetrically.

Unfortunately, the lack of this step results in the failure to obtain the energetically correction factors  $\sqrt{\rho_i}/\sqrt{\rho_i}$  introduced artificially in their energetically corrected formalism.

More recently, starting from a more symmetric form of  $F(\omega)$

$$F(\omega) = \frac{1}{\pi} \text{Re Tr} \int_0^{\infty} e^{-i\omega t} [\vec{\mu} \sqrt{\rho} \cdot e^{-iLt} \sqrt{\rho} \vec{\mu}] dt, \quad (55)$$

and with the assumption that

$$e^{-iLt} \simeq e^{-iL_0 t} e^{-iL_1 t}, \quad (56)$$

in which  $L$ ,  $L_0$ , and  $L_1$  are the Liouville operators corresponding to the total Hamiltonian  $H$ , the unperturbed Hamiltonian  $H_a + H_b$ , and the interaction  $V$  between the absorber and the perturber molecules, respectively, Ma et al.<sup>10</sup> have demonstrated that one is able to obtain a theoretical expression for  $F(\omega)$  similar to Boulet's Eq. (54). In addition, by using a better approximation of  $\exp(-iLt)$  to take into account the next order contribution arising from the non-commutation of  $L_0$  and  $L_1$

$$e^{-iLt} \simeq \frac{1}{2} (e^{-iL_0 t} e^{-iL_1 t} + e^{-iL_1 t} e^{-iL_0 t}) \quad (57)$$

combined with the more symmetric form of  $F(\omega)$ , i.e., Eq. (55) used previously, Ma et al.<sup>10</sup> were able to show that the frequency detunings of the line coupling functions given in Eq. (54) should be  $\omega - \frac{1}{2}(\omega_{ji} + \omega_{j,i})$  instead of  $\omega - \omega_{ji}$  and to obtain the result given in Eq. (39). But, these authors stopped at this stage and did not discuss the role played by the frequency detunings for the validity of the detailed balance principle.

In contrast with the theories mentioned above, in the present study the validity of detailed balance is carefully checked in every step of the development. In addition, the role of the total density matrix  $\rho(H)$ , especially the role of the initial correlations are analyzed

more rigorously. More specifically, the main procedures and advantages resulting from the present study are outlined as follows.

First of all, by factoring out the factor  $\rho(H_0) = \rho_a \rho_b \rho_{iso}$  from  $\rho(H)$  where  $\rho_{iso}$  represents the initial correlations related to the isotropic interaction, the remaining part of  $\rho(H)$  associated with the initial correlations related to the anisotropic interaction is implicitly contained in the complex-time development operator  $U(z)$  introduced. At this stage of development, both expressions  $C(t)$  and  $\bar{C}(t)$  derived are exact and satisfy the detailed balance principle.

Then, based on the binary collision and quasistatic approximations, we derive an expression for  $U(z)$  that is valid at small  $z$  limits. In order to improve the accuracy of the approximate expression for  $U(z)$ , a new method is introduced. By factoring out the rapidly oscillating terms  $\exp(iH_0 z/2\hbar)$  and  $\exp(-iH_0 z/2\hbar)$  which are easy to deal with in the complex-time development operator  $U(z)$ , the remaining part of  $U(z)$  denoted by  $U'(z)$  varies with  $z$  more slowly. This implies that the accuracy achieved by the approximate expression for  $U'(z)$  at small  $z$  limits is better than that for  $U(z)$ . Consequently, combining with the oscillation factors, a lower-order approximate expression for  $U'(z)$  incorporates higher-order results for  $U(z)$ . In addition, in terms of approximate expressions for  $U'(z)$ , both  $C(t)$  and  $\bar{C}(t)$  satisfy the detailed balance principle, as do their Fourier transform partners  $F(\omega)$  and  $\bar{F}(\omega)$ . When the lowest order approximation for  $U'(z)$  is used, the initial correlations related to the anisotropic interaction simply contribute to  $C(t)$  and  $\bar{C}(t)$  (and also  $F(\omega)$  and  $\bar{F}(\omega)$ ) a factor  $\exp[-V_{ani}(\vec{r})/kT]$  or two separate factors  $\exp[-V_{ani}(\vec{r})/2kT]$  symmetrically located, respectively. Based on the quasistatic approximation, the classical ensemble average over the translational motion is replaced by an integration over  $r$ , and these factors as well as the initial correlations related to the isotropic interaction,  $\rho_{iso}$ , become the statistical weight of the integration.

Finally, the spectral densities  $F(\omega)$  and  $\bar{F}(\omega)$  obtained are expressed in terms of the line coupling functions  $\chi_{ij,i'j'}(\omega)$  and  $\tilde{\chi}_{ij,i'j'}(\omega)$  which are related to each other and can be

calculated based on a knowledge of the interactions. In these expressions, the frequency detunings of the coupling functions are  $\omega - \frac{1}{2}(\omega_{j_i} + \omega_{j_i'})$  which result from using  $U'(z)$  instead of  $U(z)$ . However, comparing expressions of  $F(\omega)$  and  $\bar{F}(\omega)$  in the line space one sees that for  $\bar{F}(\omega)$  not only are two coupled lines arranged symmetrically, but also the initial and final states belonging to the same lines are arranged symmetrically as well. The latter's advantage becomes clear when the frequency detuning approximation  $\omega - \frac{1}{2}(\omega_{j_i} + \omega_{j_i'}) \simeq \omega - \omega_{j_i}$  is introduced to simplify the calculation. In that case, the validity of the detailed balance remains for  $\bar{F}(\omega)$  but not for  $F(\omega)$ .

H. The absorption coefficient  $\alpha(\omega)$

With Eqs. (1) and (44), we can express the absorption coefficient as

$$\begin{aligned} \alpha(\omega) &= \frac{8\pi^2}{3\hbar c} n_a \omega \sinh(\hbar\omega/2kT) \frac{1}{\pi} \sum_{ij} \sum_{i'j'} (\rho_i \rho_j \rho_{i'} \rho_{j'})^{\frac{1}{4}} \mu_{ij} \mu_{i'j'} \tilde{\chi}_{ij, i'j'}[\omega - \frac{1}{2}(\omega_{j_i} + \omega_{j_i'})] \\ &= \frac{8\pi^2}{3\hbar c} n_a \omega \sinh(\hbar\omega/2kT) \frac{1}{\pi} \nu \sum_{ij} \sum_{i'j'} \sum_{\{m\}} \sum_{i_b} \sum_{i'_b} \sum_{\alpha\beta} (\langle a | i i_b \rangle \sqrt{\rho_b} \langle i | \rho_a^{\frac{1}{4}} \mu_m \rho_a^{\frac{1}{4}} | j \rangle \langle j i_b | \beta \rangle)^* \\ &\quad \times \langle a | i' i'_b \rangle \sqrt{\rho_b} \langle i' | \rho_a^{\frac{1}{4}} \mu_m \rho_a^{\frac{1}{4}} | j' \rangle \langle j' i'_b | \beta \rangle \bar{H}_{\beta\alpha}[\omega - \frac{1}{2}(\omega_{j_i} + \omega_{j_i'})]. \end{aligned} \quad (58)$$

The value of  $\nu$  is usually assumed to be 1.<sup>2,3</sup> If the anisotropic interaction and the isotropic interaction are known, at least for some simple systems (for example,  $\text{CO}_2$  broadened by Ar), the above expression for  $\alpha(\omega)$  can be used to do numerical calculations. However, since in the above expression the arguments of the function  $\bar{H}_{\beta\alpha}$  depend on the summation indices, the direct calculation requires a lot of CPU time for more complicated systems. Therefore, some further approximations, such as the frequency detuning approximation and the band-average approximation are introduced. These will be discussed in detail along with numerical results in a forthcoming paper.<sup>13</sup>

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