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Non-Markovian far-infrared spectra of a diatomic molecule in rare-gas liquids

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The far-infrared spectra of diatomic polar molecules, immersed in a rare-gas liquid, are calculated using two non-Markovian formalisms: the total-time-ordering-cumulant (TTOC) and the partial-time-ordering-cumulant (PTOC) formalisms. Both TTOC and PTOC spectra coincide in the Markovian limit. The interaction between the diatomic molecule and the liquid is described by means of a directing intermolecular field with known statistical properties. In the secular approximation both TTOC and PTOC spectra contain a sum of resonances which become Lorentzian in the Markovian limit. The interference effect among resonances is taken into account using iterative methods in which the secular profile is the first term in the iterative process. We apply the theory to calculate the far-infrared spectra (0—200 cm^{-1}) of a HCl molecule in Ar, Kr, and Xe liquids. There is good agreement between experimental and theoretical absorption spectra.

I. INTRODUCTION

In a recent paper[1] two of us and coauthors studied two different master equations for the relaxation to the equilibrium of a multilevel quantum system S that is weakly coupled to a thermal bath B. Both equations are obtained without invoking the Markovian hypothesis using two different temporal ordering prescriptions for Kubo's cumulant expansion:[2–4] the total-time-ordering-cumulant (TTOC) and the partial-time-ordering-cumulant (PTOC) formalisms. In the Markovian limit, i.e., when the bath correlation time is much smaller than the relaxation time, the TTOC and the PTOC equations coincide.

In another paper[5] we considered that the system S has a certain dipole moment and we related, in both TTOC and PTOC formalisms, the corresponding absorption spectra with the relaxation equations of S in B.

The purpose of the present paper is to use the non-Markovian TTOC and PTOC formalisms to calculate the far-infrared spectrum of a polar diatomic molecule immersed in a rare-gas liquid. There are many experimental[6–9] and theoretical[10–14] works devoted to the study of the far-infrared spectra of diatomic molecules dissolved in a nonpolar liquid solvent. Bonamy and Hoang[13] have noted that these spectra can be built from a superposition of Lorentzian resonances modified by essentially two correcting factors: a finite correlation time of the interaction and a nonadditivity effect of the resonances. Therefore, the study of these kinds of spectra gives us a very striking example of the application of these two non-Markovian formalisms.

In Sec. II we shall present the model for the total system. The bath correlation functions are proposed following a model developed by Galatry *et al.*[15–17] and also used by Bonamy and Hoang.[13,14] In this model the interaction between the impurity and the solvent molecules is described assuming that the diatomic molecule is submitted to a time-independent average directing intermolecular field (DIF). In Sec. III we shall derive the Markovian, TTOC, and PTOC absorption spectra in the secular approximation, i.e., when the off-diagonal matrix elements (coherences) of the reduced density operator of the system S evolve independently among themselves, and the corresponding corrected profiles when this approximation is not reasonable. Section IV contains a numerical discussion of the absorption spectra of a HCl molecule immersed in Ar, Kr, and Xe liquids. These results are also compared with the experimental spectra. Some conclusions are summarized in Sec. V.

II. THE MODEL

We deal with a very diluted solution of diatomic polar molecules immersed in a rare-gas liquid solvent. In order to explain its far-infrared spectrum, this system can be adequately represented by a single diatomic molecule surrounded by a huge number of solvent molecules.

The far-infrared spectrum of such a diatomic molecule does not involve the vibrational motion, since it remains in its vibrational ground state. Therefore, the system S is only constituted by the rotational degrees of freedom of a diatomic molecule. All the translational degrees of freedom form the thermal bath B in which S is relaxed.

The total Hamiltonian can be written as

$$H = H_S + H_B + H' , \tag{2.1}$$

where H_S is the rotational Hamiltonian of the diatomic molecule, H_B is the bath Hamiltonian, and H' is the S-B interaction Hamiltonian.

The system S is described by a quantum rigid rotor model.[18] If the spherical harmonic $Y_{j_i}^{m_i}(\Omega)$, where $\Omega \equiv (\theta,\phi)$ denotes the orientation of the diatomic molecule in an adequate reference system, is represented by the ket $|i\rangle \equiv |j_i m_i\rangle$, we have

$$H_S\,|i\rangle = E_{j_i}\,|i\rangle \ , \tag{2.2a}$$

with

$$E_{j_i} = Bhcj_i(j_i+1) \ , \tag{2.2b}$$

where B is the rotational constant of the diatomic molecule.

The TTOC, PTOC, and Markovian reduced equations of motion for $\sigma(t)$ are given as follows.[1,2,4]
its reduced density operator:

$$\sigma(t) = \mathrm{Tr}_B[\rho(t)] \ , \tag{2.3}$$

where $\rho(t)$ is the density operator of the total system $S\oplus B$ and Tr_B refers to the trace over the degrees of freedom of the bath. Neglecting initial statistical correlations between the system S and the bath, we can write

$$\rho(0) = \sigma(0)\rho_B^0 \ , \tag{2.4}$$

where $\sigma(0)$ is the density operator of S at $t=0$ and ρ_B^0 is the equilibrium density operator of the bath.

The TTOC, PTOC, and Markovian reduced equations of motion for $\sigma(t)$ are given as follows.[1,2,4]

(i) TTOC master equation:

$$\dot\sigma(t) = -i\mathcal{L}_S\sigma(t) - \int_0^t d\tau\, \hat W(t-\tau)\sigma(\tau) \ , \tag{2.5}$$

with

$$\hat W(t) = \langle \mathcal{L}'(t)e^{-i\mathcal{L}_S t}\mathcal{L}'\rangle$$
$$= \mathrm{Tr}_B[\mathcal{L}'(t)e^{-i\mathcal{L}_S t}\mathcal{L}'\rho_B^0] \ , \tag{2.6a}$$

$$\mathcal{L}'(t) = e^{i\mathcal{L}_B t}\mathcal{L}'e^{-i\mathcal{L}_B t} \ , \tag{2.6b}$$

where $\langle\ \rangle$ means the bath average and $\mathcal{L}_S$, $\mathcal{L}_B$, and $\mathcal{L}'$ are the Liouvillians corresponding to the Hamiltonians H_S, H_B, and H', respectively, defined by

$$\mathcal{L}_S X \equiv \hbar^{-1}[H_S,X], \quad \mathcal{L}_B X \equiv \hbar^{-1}[H_B,X], \quad \mathcal{L}' X \equiv \hbar^{-1}[H',X] \ . \tag{2.7}$$

Equation (2.5) has been obtained with the assumption

$$\langle \mathcal{L}'\rangle = \mathrm{Tr}_B(\mathcal{L}'\rho_B^0) = 0 \ , \tag{2.8}$$

which can be always assumed by redefining H_S and H' in a suitable way. [In the present model, due to Eq. (2.25), such redefinition will not be necessary.]

In the free-rotational Hamiltonian eigenvectors basis set $\{\,|i\rangle \equiv |j_i m_i\rangle\}$, Eq. (2.5) takes the form:

$$\dot\sigma_{fi}(t) = -i\omega_{fi}\sigma_{fi}(t) - \sum_{f',i'}\int_0^t d\tau\, \hat W_{fi,f'i'}(t-\tau)\sigma_{f'i'}(\tau) \ , \tag{2.9}$$

where, taking into account Eq. (2.2b),

$$\omega_{fi} = \hbar^{-1}(E_{j_f}-E_{j_i})$$
$$= 2\pi Bc\,[j_f(j_f+1)-j_i(j_i+1)] \tag{2.10}$$

and, from Eq. (2.6),[19]

$$\hat W_{fi,f'i'}(t) = \hbar^{-2}\Big[\delta_{ii'}\sum_{f''}e^{-i\omega_{f''i}t}\langle H'_{ff''}(t)H'_{f''f'}\rangle + \delta_{ff'}\sum_{i''}e^{-i\omega_{fi''}t}\langle H'_{i'i''}H'_{i''i}(t)\rangle - e^{-i\omega_{fi'}t}\langle H'_{i'i}(t)H'_{ff'}\rangle - e^{-i\omega_{f'i}t}\langle H'_{i'i}H'_{ff'}(t)\rangle\Big] \ . \tag{2.11}$$

Henceforth, a sum over an index i denotes a double sum over the quantum numbers j_i and m_i:

$$\sum_i \equiv \sum_{j_i=0}^{\infty}\ \sum_{m_i=-j_i}^{+j_i} \ . \tag{2.12}$$

(ii) PTOC master equation:

$$\dot\sigma(t) = -i\mathcal{L}_S\sigma(t) - \hat K(t)\sigma(t) \ , \tag{2.13}$$

where

$$\hat K(t) = \int_0^t d\tau\, \hat W(\tau)e^{i\mathcal{L}_S\tau} \ . \tag{2.14}$$

In the representation of the basis set $\{\,|i\rangle\}$, Eq. (2.13) leads to:

$$\dot\sigma_{fi}(t) = -i\omega_{fi}\sigma_{fi}(t) - \sum_{f',i'}\hat K_{fi,f'i'}(t)\sigma_{f'i'}(t) \ , \tag{2.15}$$

where, from Eq. (2.14), one gets

$$\hat K_{fi,f'i'}(t) = \int_0^t d\tau\, e^{i\omega_{f'i'}\tau}\hat W_{fi,f'i'}(\tau) \ . \tag{2.16}$$

(iii) Markovian master equation: In the Markovian limit both Eqs. (2.5) and (2.13) have the same form,

$$\dot\sigma(t) = -i\mathcal{L}_S\sigma(t) - \hat R\sigma(t) \ , \tag{2.17}$$

where

$$\hat R = \hat K(\infty) = \int_0^\infty dt\, \hat W(t)e^{i\mathcal{L}_S t} \ . \tag{2.18}$$

In the representation of the basis set $\{\,|i\rangle\}$, Eq. (2.17) yields

$$\dot\sigma_{fi}(t) = -i\omega_{fi}\sigma_{fi}(t) - \sum_{f',i'}\hat R_{fi,f'i'}\sigma_{f'i'}(t) \ , \tag{2.19}$$

where, from Eq. (2.18), one gets

$$\hat{R}_{fi,f'i'} = \int_0^\infty dt\, e^{i\omega_{f'i'}t} \hat{W}_{fi,f'i'}(t) = \hat{W}_{fi,f'i'}(\omega_{f'i'}) \; . \tag{2.20}$$

The superoperators (tetradic) $\hat{W}(t)$, $\hat{K}(t)$, and $\hat{R}$ determine the relaxation properties of the system S in the TTOC scheme, PTOC scheme, and Markovian limit, respectively. From Eqs. (2.11), (2.16), and (2.20), their matrix elements are determined by the natural frequencies ω_{fi} of the system S, given by Eq. (2.10), and by the bath correlation functions

$$\langle H'_{fi}(t) H'_{f'i'} \rangle = \mathrm{Tr}_B [H'_{fi}(t) H'_{f'i'} \rho_B^0] \; . \tag{2.21a}$$

In addition, the following identity holds

$$\langle H'_{fi} H'_{f'i'}(t) \rangle = \langle H'_{i'f'}(t) H'_{if} \rangle^* \; . \tag{2.21b}$$

When H' is known, the bath correlation functions (2.21) may be calculated from an adequate model for the bath. Here we shall follow the model developed in Refs. 13–17, where one assumes that the translational degrees of freedom of the molecules are treated classically. In this model the interaction Hamiltonian H' is given by

$$H' = -\boldsymbol{\mu}\cdot\mathbf{E} = -\mu E P_1(\cos\theta) \; , \tag{2.22}$$

where $\boldsymbol{\mu}$ is the permanent dipole moment of the diatomic molecule, $\mathbf{E}$ is the so-called directing intermolecular field (DIF) which depends on the configurations of the solvent molecules surrounding the diatomic molecule, and P_1 is the first-order Legendre polynomial.

Making use of Eq. (2.22) and writing $\boldsymbol{\mu} = \mu \mathbf{u}$, where $\mathbf{u}$ is a unit vector in the $\boldsymbol{\mu}$ direction, one gets

$$H'_{fi}(t) = \langle f \,|\, H'(t) \,|\, i \rangle = -\mu \sum_\alpha (u_\alpha)_{fi} E_\alpha(t) \; , \tag{2.23a}$$

where

$$(u_\alpha)_{fi} = \langle j_f m_f \,|\, u_\alpha \,|\, j_i m_i \rangle \; . \tag{2.23b}$$

Substitution of Eq. (2.23a) into Eq. (2.21a) allows us to obtain

$$\langle H'_{fi}(t) H'_{f'i'} \rangle = \mu^2 \sum_{\alpha,\beta} (u_\alpha)_{fi} (u_\beta)_{f'i'} \langle E_\alpha(t) E_\beta(0) \rangle \; , \tag{2.24}$$

where the indexes α and β label the vector components in the given reference system. It is interesting to note that Eq. (2.22) has allowed us to separate in Eq. (2.24) the rotational and the translational contributions to the bath correlation functions (2.21), contained in $\boldsymbol{\mu}$ and in $\mathbf{E}$, respectively.

Following the model developed in Ref. 14 we assume that $\mathbf{E}(t)$ is a Gaussian random variable with the statistical properties

$$\langle E_\alpha(t) \rangle = 0 \; , \tag{2.25}$$

$$\langle E_\alpha(t_1) E_\beta(t_2) \rangle = \tfrac{1}{3} \langle E^2 \rangle \Phi(t_1 - t_2) \delta_{\alpha\beta} \; , \tag{2.26}$$

where the function $\Phi(t)$ has an exponential form with a decay constant t_c^{-1}:

$$\Phi(t) = \exp(-\,|\,t\,|\,/t_c) \; . \tag{2.27}$$

Equation (2.25) implies that the condition (2.8) is fulfilled.

Substituting Eq. (2.26) into Eq. (2.24) we can write

$$\langle H'_{fi}(t) H'_{f'i'} \rangle = \tfrac{1}{3} \mu^2 \langle E^2 \rangle \sum_\alpha (u_\alpha)_{fi} (u_\alpha)_{f'i'} \Phi(t) \; . \tag{2.28}$$

The equilibrium average $\langle E^2 \rangle$ of the DIF square modulus and the bath correlation time t_c have been calculated in Ref. 14 using a cell model for the equilibrium liquid structure.

III. SPECTRAL THEORY

Assuming that there is no interaction between two impurity diatomic molecules so that each system S is relaxed in its own bath B, the linear-response theory allows us to write the absorption coefficient as[20]

$$\alpha(\omega) = \frac{4\pi n \omega}{3\hbar c} (1 - e^{-\beta\hbar\omega}) \times \mathrm{Re} \left[\int_0^\infty dt\, e^{i\omega t} \langle\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0) \rangle\rangle \right] , \quad \beta = 1/kT \; , \tag{3.1}$$

where n is the number density of the impurity diatomic molecules, $\boldsymbol{\mu}(t)$ is the dipole moment of a diatomic molecule in the Heisenberg picture, and $\langle\langle \;\; \rangle\rangle$ denotes the equilibrium average over the total system $S \oplus B$.

If the only available information on the total system is its temperature T, we can consider for the equilibrium density operator ρ^0 of $S \oplus B$ that

$$\rho^0 = \sigma^0 \rho_B^0 \; , \tag{3.2}$$

where σ^0 and ρ_B^0 are the canonical distributions referring to the systems S and B, respectively.

Making use of the free-rotational eigenvectors basis set $\{\,|\,i\,\rangle\}$ and following a similar method that in Sec. II of Ref. 5, Eq. (3.1) can be written as

$$\begin{aligned} \alpha(\omega) &= \frac{4\pi n \omega}{3\hbar c} (1 - e^{-\beta\hbar\omega}) \sum_{\substack{i,f \\ (f>i)}} \sigma_i^0 \boldsymbol{\mu}_{fi} \cdot \sum_{\substack{f',i' \\ (f' \neq i')}} \boldsymbol{\mu}_{i'f'} \,\mathrm{Re} \left[\int_0^\infty dt\, e^{i\omega t} \sigma_{f'i'}^{(fi)}(t) \right] \\ &= \frac{4\pi n \omega}{3\hbar c} (1 - e^{-\beta\hbar\omega}) \mu^2 \sum_\alpha \sum_{\substack{i,f \\ (f>i)}} \sigma_i^0 (u_\alpha)_{fi} \sum_{\substack{f',i' \\ (f' \neq i')}} (u_\alpha)_{i'f'} \,\mathrm{Re}[\bar{\sigma}_{f'i'}^{(fi)}(\omega)] \; , \end{aligned} \tag{3.3}$$

where

$$\sigma_i^0 \equiv \sigma_{j_i m_i}^0 = Z_S^{-1} \exp(-\beta E_{j_i}), \quad \beta = 1/kT , \tag{3.4a}$$

with

$$Z_S = \mathrm{Tr}_S(e^{-\beta H_S}) , \tag{3.4b}$$

where Tr_S means a trace over the rotational states $|\,i\,\rangle$ and k is the Boltzmann constant. Moreover, in Eq. (3.3), $\sigma_{f'i'}^{(fi)}(t)$ denotes the matrix element $\sigma_{f'i'}(t)$ derived with the condition

$$\sigma_{f'i'}(0) = \delta_{f'f}\delta_{i'i} \quad \forall\ (f',i') . \tag{3.5}$$

Equation (3.3) relates the absorption coefficient $\alpha(\omega)$ with the problem of the relaxation of S in B. We shall obtain two different expressions for $\alpha(\omega)$ depending on whether the evolution of $\sigma(t)$ to the equilibrium is governed by the TTOC [Eq. (2.9)] or the PTOC [Eq. (2.15)] equations. Both absorption coefficients must coincide in the Markovian limit.

A. Markovian secular spectrum

In the Markovian limit the rotational relaxation of the diatomic molecule is governed by Eq. (2.19). From this equation, the spectral function $\bar{\sigma}_{f'i'}^{(fi)}(\omega)$ associated with $\sigma_{f'i'}^{(fi)}(t)$ is given, in the secular approximation,[1] by[5]

$$\bar{\sigma}_{f'i'}^{(fi)}(\omega) = \frac{i\delta_{f'f}\delta_{i'i}}{\omega - \omega_{f'i'} + i\hat{R}_{f'i',f'i'}} , \tag{3.6}$$

which substituted into Eq. (3.3) allows one to write the secular absorption coefficient as

$$\alpha_0^M(\omega) = \frac{4\pi n\omega}{3\hbar c}(1 - e^{-\beta\hbar\omega})\mu^2 \times \sum_{\substack{f,i \\ (f>i)}} \sigma_i^0 \sum_\alpha (u_\alpha)_{fi}(u_\alpha)_{if}\mathrm{Re}[\Lambda_{fi}^M(\omega)] \tag{3.7a}$$

where

$$\Lambda_{fi}^M(\omega) = i(\omega - \omega'_{fi} + i\Gamma_{fi})^{-1} , \tag{3.7b}$$

with

$$\omega'_{fi} = \omega_{fi} + \Delta_{fi} , \tag{3.7c}$$

$$\Delta_{fi} = \mathrm{Im}(\hat{R}_{fi,fi}) , \tag{3.7d}$$

$$\Gamma_{fi} = \mathrm{Re}(\hat{R}_{fi,fi}) . \tag{3.7e}$$

Making use of Eqs. (2.11) and (2.28), from Eq. (2.20) one gets

$$\hat{R}_{fi,fi} = \tfrac{1}{3}\mu^2\langle E^2\rangle\hbar^{-2}\sum_\alpha \left[\sum_{f''\neq f} (u_\alpha)_{ff''}(u_\alpha)_{f''f}\bar{\Phi}(\omega_{ff''}) + \sum_{i''\neq i} (u_\alpha)_{ii''}(u_\alpha)_{i''i}\bar{\Phi}(\omega_{i''i}) + [\,|(u_\alpha)_{ff}|^2 + |(u_\alpha)_{ii}|^2 - 2(u_\alpha)_{ii}(u_\alpha)_{ff}]\bar{\Phi}(0) \right] , \tag{3.8}$$

where $\bar{\Phi}(\omega)$ denotes the Fourier-Laplace transformation of $\Phi(t)$,

$$\bar{\Phi}(\omega) = \int_0^\infty dt\, e^{i\omega t}\Phi(t) = [-i\omega + t_c^{-1}]^{-1} . \tag{3.9}$$

On the other hand, the following identity can be easily verified:

$$\sum_\alpha \sum_{f''} (u_\alpha)_{ff''}(u_\alpha)_{f''f} = \sum_{j_{f''}} A_{j_f j_{f''}} , \tag{3.10a}$$

with

$$A_{j_f j_{f''}} = \sum_\alpha \sum_{m_{f''}} \langle j_f m_f\,|\,u_\alpha\,|\,j_{f''} m_{f''}\rangle\langle j_{f''} m_{f''}\,|\,u_\alpha\,|\,j_f m_f\rangle = (2j_{f''}+1)\left|\begin{pmatrix} j_f & 1 & j_{f''} \\ 0 & 0 & 0 \end{pmatrix}\right|^2 , \tag{3.10b}$$

where the term in large parentheses is a Wigner 3-j coefficient.[21]

In Eq. (3.10b) the triangle rule requires that

$$|\,j_f - j_{f''}\,| \leq 1 . \tag{3.11}$$

Thus the only nonzero $A_{j_f j_{f''}}$ coefficients are

$$A_{j_f, j_f - 1} = \frac{j_f}{2j_f + 1} , \tag{3.12a}$$

$$A_{j_f, j_f + 1} = \frac{j_f + 1}{2j_f + 1} . \tag{3.12b}$$

Taking into account Eqs. (3.10) and (3.12), Eq. (3.8) can be written as

$$\hat{R}_{fi,fi} \equiv \hat{R}_{j_f j_i, j_f j_i} = \tfrac{1}{3}\mu^2 \langle E^2 \rangle \hbar^{-2} t_c \left[\frac{1}{2j_f+1} \left\{ \frac{j_f}{i\omega_{j_f-1,j_f} t_c + 1} + \frac{j_f+1}{i\omega_{j_f+1,j_f} t_c + 1} \right\} + \frac{1}{2j_i+1} \left\{ \frac{j_i}{i\omega_{j_i,j_i-1} t_c + 1} + \frac{j_i+1}{i\omega_{j_i,j_i+1} t_c + 1} \right\} \right] \tag{3.13}$$

which is independent of the quantum number m. Therefore, $\Lambda_{fi}^{M}(\omega)$, given by Eq. (3.7b), is also m independent. Due to this property it is possible to carry out in Eq. (3.7a) the summations over all the m_i and m_f which appear only in the matrix elements of u_α. A straightforward calculation leads to the following absorption coefficient in the Markovian limit and secular approximation:

$$\alpha_0^M(\omega) = \frac{4\pi n \omega}{3\hbar c} (1 - e^{-\beta\hbar\omega}) Z_S^{-1} \mu^2 \sum_{j_i=0}^{\infty} (j_i+1) e^{-\beta B h c j_i (j_i+1)} \mathrm{Re}[\Lambda_{j_i+1,j_i}^{M}(\omega)] , \tag{3.14}$$

where $\Lambda_{j_i+1,j_i}^{M}(\omega)$ can be obtained from Eqs. (3.7) and (3.13).

B. TTOC spectrum

1. Secular approximation

In the TTOC scheme the rotational relaxation of the diatomic molecule is governed by Eq. (2.9). Taking the Fourier-Laplace transformation in Eq. (2.9) and making use of the secular approximation, the spectral functions $\bar{\sigma}_{f'i'}^{(fi)}(\omega)$ are given by[5]

$$\bar{\sigma}_{f'i'}^{(fi)}(\omega) = \frac{i\delta_{f'f}\delta_{i'i}}{\omega - \omega_{f'i'} + i\overline{\hat{W}}_{f'i',f'i'}(\omega)} . \tag{3.15}$$

Inserting Eq. (3.15) into Eq. (3.3) we obtain

$$\alpha_0^T(\omega) = \frac{4\pi n \omega}{3\hbar c} (1 - e^{-\beta\hbar\omega}) \mu^2 \sum_{\substack{f,i \\ (f>i)}} \sigma_i^0 \sum_{\alpha} (u_\alpha)_{fi} (u_\alpha)_{if} \mathrm{Re}[\Lambda_{fi}^{T}(\omega)] , \tag{3.16a}$$

with

$$\Lambda_{fi}^{T}(\omega) = i[\omega - \omega_{fi} + i\overline{\hat{W}}_{fi,fi}(\omega)]^{-1} , \tag{3.16b}$$

where $\overline{\hat{W}}_{fi,fi}(\omega)$ is the Fourier-Laplace transformation of $\hat{W}_{fi,fi}(t)$.

A similar method used for the derivation of Eq. (3.13) leads to

$$\begin{aligned} \overline{\hat{W}}_{fi,fi}(\omega) &= \overline{\hat{W}}_{j_f j_i, j_f j_i}(\omega) \\ &= \tfrac{1}{3}\mu^2 \langle E^2 \rangle \hbar^{-2} \left[\sum_{j_{f''}} A_{j_f j_{f''}} \bar{\Phi}(\omega - \omega_{j_{f''} j_i}) + \sum_{j_{i''}} A_{j_i j_{i''}} \Phi(\omega - \omega_{j_f j_{i''}}) \right] \\ &= \tfrac{1}{3}\mu^2 \langle E^2 \rangle \hbar^{-2} t_c \left[\frac{1}{2j_f+1} \left\{ \frac{j_f+1}{i(\omega_{j_f+1,j_i} - \omega) t_c + 1} + \frac{j_f}{i(\omega_{j_f-1,j_i} - \omega) t_c + 1} \right\} \right. \\ &\qquad \left. + \frac{1}{2j_i+1} \left\{ \frac{j_i+1}{i(\omega_{j_f,j_i+1} - \omega) t_c + 1} + \frac{j_i}{i(\omega_{j_f,j_i-1} - \omega) t_c + 1} \right\} \right] \end{aligned} \tag{3.17}$$

which is m independent. Therefore, $\Lambda_{fi}^{T}(\omega)$ is also m independent. Substituting Eq. (3.17) into Eq. (3.16) one obtains for the TTOC absorption coefficient in the secular approximation the expression:

$$\alpha_0^T(\omega) = \frac{4\pi n \omega}{3\hbar c} (1 - e^{-\beta\hbar\omega}) \mu^2 Z_S^{-1} \sum_{j_i=0}^{\infty} (j_i+1) e^{-\beta B h c j_i (j_i+1)} \mathrm{Re}[\Lambda_{j_i+1,j_i}^{T}(\omega)] , \tag{3.18}$$

where $\Lambda_{j_i+1,j_i}^{T}(\omega)$ can be obtained from Eqs. (3.16b) and (3.17).

2. Interference effect

If the effect of the nonsecular terms of the kind of $\overline{\hat{W}}_{fi,f'i'}(\omega)\bar{\sigma}_{f'i'}(\omega)$, with $(f,i) \neq (f',i')$, in the Fourier-Laplace transformation of Eq. (2.9) is small but nonnegligible, we can tackle the problem of the derivation of the spectral functions $\bar{\sigma}_{f'i'}^{(fi)}(\omega)$ by an iterative method. Taking the secular solution (3.15) as the zeroth-order solution, one gets for the first order in the iterative process[5]

$$\bar{\sigma}_{f'i'}^{(fi)}(\omega)=\frac{1}{\omega-\omega_{f'i'}+i\overline{\hat{W}}_{f'i',f'i'}(\omega)}\left[i\delta_{f'f}\delta_{i'i}+\frac{\overline{\hat{W}}_{f'i',fi}(\omega)}{\omega-\omega_{fi}+i\overline{\hat{W}}_{fi,fi}(\omega)}(1-\delta_{f'f}\delta_{i'i})\right], \tag{3.19}$$

which, substituted into Eq. (3.3), leads to the TTOC absorption coefficient:

$$\alpha^{T}(\omega)=\alpha_0^{T}(\omega)+\alpha_1^{T}(\omega)\ , \tag{3.20}$$

where $\alpha_0^T(\omega)$ is given by Eq. (3.18) and

$$\alpha_1^T(\omega)=-\frac{4\pi n\omega}{3\hbar c}(1-e^{-\beta\hbar\omega})\mu^2\sum_{\substack{f,i\\(f>i)}}\sum_{\alpha}\sigma_i^0(u_\alpha)_{fi}\sum_{\substack{f',i'\\(f'\neq i')\\(f',i')\neq(f,i)}}(u_\alpha)_{i'f'}\,\mathrm{Re}[\overline{\hat{W}}_{f'i',fi}(\omega)\Lambda_{f'i'}^T(\omega)\Lambda_{fi}^T(\omega)] \tag{3.21}$$

is the correcting term, up to the second order with respect to the interaction, due to the interference effect between the time evolution of the coherences $\sigma_{f'i'}(t)$ and $\sigma_{fi}(t)$. This correction can be significant if the functions $\Lambda_{f'i'}^T(\omega)$ and $\Lambda_{fi}^T(\omega)$ take appreciable values in the same range of the ω values (overlapping effect).

Proceeding in a similar way to the derivation of Eq. (3.17), one has

$$\overline{\hat{W}}_{f'i',fi}(\omega)=-\tfrac{1}{3}\mu^2\langle E^2\rangle\hbar^{-2}\sum_{\alpha'}(u_{\alpha'})_{ii'}(u_{\alpha'})_{f'f}[\bar{\Phi}(\omega-\omega_{f'i})+\bar{\Phi}(\omega-\omega_{fi'})],\quad f'\neq f,\ i'\neq i\ . \tag{3.22}$$

Substitution of Eq. (3.22) into Eq. (3.21) leads to

$$\alpha_1^T(\omega)=\frac{4\pi n\omega}{3\hbar c}(1-e^{-\beta\hbar\omega})\mu^2(\tfrac{1}{3}\mu^2\langle E^2\rangle\hbar^{-2})\sum_{\alpha,\alpha'}\sum_{\substack{f,i\\(f>i)}}\sigma_i^0(u_\alpha)_{fi}\sum_{\substack{f',i'\\(f'\neq i')\\(f',i')\neq(f,i)}}(u_{\alpha'})_{ii'}(u_\alpha)_{i'f'}(u_{\alpha'})_{f'f}$$
$$\times\,\mathrm{Re}\{\Lambda_{f'i'}^T(\omega)\Lambda_{fi}^T(\omega)[\bar{\Phi}(\omega-\omega_{f'i})+\bar{\Phi}(\omega-\omega_{fi'})]\}. \tag{3.23}$$

Since the populations σ_i^0 and the last factor in Eq. (3.23) are m independent, we can carry out the summations over all values of m ($m_i,m_f,m_{i'},m_{f'}$) in this equation. In order to do so, we now introduce the coefficients

$$\begin{aligned}A_{j_fj_i,j_{f'}j_{i'}}&=\sum_{\alpha,\alpha'}\sum_{m_i,m_f}\sum_{m_{i'},m_{f'}}\langle j_fm_f\,|\,u_\alpha\,|\,j_im_{i'}\rangle\langle j_im_i\,|\,u_{\alpha'}\,|\,j_{i'}m_{i'}\rangle\langle j_{i'}m_{i'}\,|\,u_\alpha\,|\,j_{f'}m_{f'}\rangle\langle j_{f''}m_{f'}\,|\,u_{\alpha'}\,|\,j_fm_f\rangle\\&=(2j_f+1)(2j_{f'}+1)(2j_i+1)(2j_{i'}+1)\begin{Bmatrix}j_f & j_i & 1\\ j_{i'} & j_{f'} & 0\end{Bmatrix}\begin{pmatrix}j_f & 1 & j_i\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}j_i & 1 & j_{i'}\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}j_i' & 1 & j_{f'}\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}j_{f'} & 1 & j_f\\ 0 & 0 & 0\end{pmatrix}\end{aligned} \tag{3.24}$$

where the term in large curly braces is a Racah 6-j coefficient.[21]

In Eq. (3.24) the triangle rule requires that

$$\begin{aligned}&|j_f-j_i|\leq 1,\quad |j_{f'}-j_{i'}|\leq 1\ ,\\&|j_i-j_{i'}|\leq 1,\quad |j_f-j_{f'}|\leq 1\ .\end{aligned} \tag{3.25}$$

Thus for $j_f=j_i+1$, the only nonzero $A_{j_fj_i,j_{f'}j_{i'}}$ coefficients are

$$A_{j_i+1,j_i;j_i+2,j_i+1}=\frac{(j_i+1)(j_i+2)}{2j_i+3}\ , \tag{3.26a}$$

$$A_{j_i+1,j_i;j_i,j_i+1}=\frac{j_i+1}{(2j_i+1)(2j_i+3)}\ , \tag{3.26b}$$

$$A_{j_i+1,j_i;j_i,j_i-1}=\frac{j_i(j_i+1)}{2j_i+1}\ . \tag{3.26c}$$

From Eqs. (3.23), (3.24), and (3.26) a straightforward calculation leads to

$$\alpha_1^T(\omega)=\frac{4\pi n\omega}{3\hbar c}(1-e^{-\beta\hbar\omega})\mu^2(\tfrac{1}{3}\mu^2\langle E^2\rangle\hbar^{-2})Z_S^{-1}$$

$$\times\sum_{j_i=0}^{\infty}(j_i+1)e^{-\beta Bhcj_i(j_i+1)}\left[\frac{j_i+2}{2j_i+3}\operatorname{Re}\{\Lambda^T_{j_i+2,j_i+1}(\omega)\Lambda^T_{j_i+1,j_i}(\omega)[\overline{\Phi}(\omega-\omega_{j_i+2,j_i})+\overline{\Phi}(\omega)]\}\right.$$

$$+\frac{j_i}{2j_i+1}\operatorname{Re}\{\Lambda^T_{j_i,j_i-1}(\omega)\Lambda^T_{j_i+1,j_i}(\omega)[\overline{\Phi}(\omega-\omega_{j_i+1,j_i-1})+\overline{\Phi}(\omega)]\}$$

$$\left.+\frac{2}{(2j_i+1)(2j_i+3)}\operatorname{Re}[\Lambda^T_{j_i,j_i+1}(\omega)\Lambda^T_{j_i+1,j_i}\overline{\Phi}(\omega)]\right], \tag{3.27}$$

where the $\Lambda^T_{j_fj_i}(\omega)$ can be obtained from Eq. (3.16b) and $\overline{\Phi}(\omega)$ is given by Eq. (3.9).

As can easily be seen, there are three contributions in the right-hand side of Eq. (3.29). All of them are due to influences on the absorption line $j\rightarrow j+1$. The first one ($R1$) represents the one arising from the absorption line $j+1\rightarrow j+2$. The second term ($R2$) represents the one coming from the absorption line $j-1\rightarrow j$. Finally, the third term antiresonant (AR) comes from the influence of the emission line $j+1\rightarrow j$. Notice that only these three contributions appear. This is due to the fact that we have considered an interaction of the type $P_1(\cos\theta)$ [Eq. (2.22)] which implies the selection rules (3.25).

C. PTOC spectrum

1. Secular approximation

From Eq. (2.15), the $\sigma^{(fi)}_{f'i'}(t)$ is given in the PTOC scheme and in the secular approximation by[5]

$$\sigma^{(fi)}_{f'i'}(t)=e^{i\omega_{f'i'}t}\exp\left[-\int_0^t dt_1\hat{K}_{f'i',f'i'}(t_1)\right]\delta_{f'f}\delta_{i'i}\ . \tag{3.28}$$

Substituting Eq. (3.28) into Eq. (3.3) one obtains for the PTOC secular absorption coefficient

$$\alpha_0^P(\omega)=\frac{4\pi n\omega}{3\hbar c}(1-e^{-\beta\hbar\omega})\mu^2$$

$$\times\sum_{\substack{f,i\\(f>i)}}\sigma_i^0\sum_{\alpha}(u_\alpha)_{fi}(u_\alpha)_{if}\operatorname{Re}[\Lambda^P_{fi}(\omega)]\ , \tag{3.29a}$$

where

$$\Lambda^P_{fi}(\omega)=\int_0^\infty dt\, e^{i(\omega-\omega_{fi})t}e^{-\Omega_{fi}(t)} \tag{3.29b}$$

and, taking into account Eq. (2.16), one has

$$\Omega_{fi}(t)=\int_0^t dt_1\hat{K}_{fi,fi}(t_1)$$

$$=\int_0^t d\tau(t-\tau)e^{i\omega_{fi}\tau}\hat{W}_{fi,fi}(\tau)\ . \tag{3.29c}$$

From Eqs. (2.11), (2.28), and (3.10), Eq. (3.29c) can be written as

$$\Omega_{fi}(t)\equiv\Omega_{j_fj_i}(t)=\tfrac{1}{3}\mu^2\langle E^2\rangle\hbar^{-2}$$

$$\times\int_0^t d\tau(t-\tau)e^{(i\omega_{j_fj_i}-t_c^{-1})\tau}\left[\frac{j_f+1}{2j_f+1}e^{-i\omega_{j_f+1,j_i}\tau}+\frac{j_f}{2j_f+1}e^{-i\omega_{j_f-1,j_i}\tau}\right.$$

$$\left.+\frac{j_i+1}{2j_i+1}e^{-i\omega_{j_f,j_i+1}\tau}+\frac{j_i}{2j_i+1}e^{-i\omega_{j_f,j_i-1}\tau}\right]. \tag{3.30}$$

Since $\Omega_{fi}(t)$ is m independent, from Eq. (3.29b), $\Lambda^P_{fi}(\omega)$ is also m independent. Then, carrying out the summations over m_i and m_f in Eq. (3.29a), one gets

$$\alpha_0^P(\omega)=\frac{4\pi n\omega}{3\hbar c}(1-e^{-\beta\hbar\omega})\mu^2Z_S^{-2}\sum_{j_i=0}^{\infty}(j_i+1)e^{-\beta Bhcj_i(j_i+1)}\operatorname{Re}[\Lambda^P_{j_i+1,j_i}(\omega)]\ , \tag{3.31}$$

where $\Lambda^P_{j_i+1,j_i}(\omega)$ can be calculated from Eqs. (3.29b) and (3.30).

We would like to show now that using an expansion procedure we can obtain a simpler expression than Eq. (3.31) for $\alpha_0^P(\omega)$ which will give results very close to the exact (numerical) solution (3.31), as we shall see later on. To do so, we note that the factor $\exp[-\Omega_{fi}(t)]$ can be written with the help of Eq. (3.29c) as

$$\exp\left[-\lambda^2\int_0^t d\tau(t-\tau)f(\tau)\right],$$

where λ is a parameter that characterizes the intensity of the interaction. Using the expansion

$$\exp\left[-\lambda^2\int_0^t d\tau(t-\tau)f(\tau)\right]=\left[\exp\left[-\lambda^2t\int_0^\infty d\tau f(\tau)\right]\right]\left[1+\lambda^2\left[t\int_0^\infty d\tau f(\tau)-\int_0^t d\tau(t-\tau)f(\tau)\right]+O(\lambda^4)\right] \tag{3.32}$$

$$\int_0^\infty d\tau\, e^{i\omega_{fi}\tau}\hat{W}_{fi,fi}(\tau)=\hat{R}_{fi,fi}=\Gamma_{fi}+i\Delta_{fi}\ ,$$

we can write, up to the second order in the interaction,

$$e^{-\Omega_{fi}(t)}\simeq e^{-t\hat{R}_{fi,fi}}[1+t\hat{R}_{fi,fi}-\Omega_{fi}(t)]\ . \tag{3.33}$$

Substitution of Eq. (3.33) into Eq. (3.31) yields for the PTOC secular absorption coefficient

$$\alpha_0^P(\omega)\simeq\alpha_0^M(\omega)+\alpha_0^D(\omega)\ , \tag{3.34}$$

where $\alpha_0^M(\omega)$ is the Markovian secular absorption coefficient, given by Eq. (3.14). The term $\alpha_0^D(\omega)$, given by

$$\alpha_0^D(\omega)=\frac{4\pi n\omega}{3\hbar c}(1-e^{-\beta\hbar\omega})\mu^2 Z_S^{-1}\sum_{j_i=0}^{\infty}(j_i+1)e^{-\beta Bhcj_i(j_i+1)}\mathrm{Re}[\Lambda_{j_i+1,j_i}^D(\omega)]\ , \tag{3.35a}$$

with

$$\Lambda_{j_fj_i}^D=\frac{\overline{\hat{W}}_{j_fj_i,j_fj_i}(\omega-\Delta_{j_fj_i}+i\Gamma_{j_fj_i})-\overline{\hat{W}}_{j_fj_i,j_fj_i}(\omega_{j_fj_i})}{(\omega-\omega'_{j_fj_i}+i\Gamma_{j_fj_i})^2} \tag{3.35b}$$

gives the PTOC deviation with respect to the Markovian behavior due to the fact of considering a finite bath correlation time.

2. *Interference effect*

If the nonsecular terms of the kind of $\hat{K}_{fi,f'i'}(t)\sigma_{f'i'}(t)$, with $(f,i)\neq(f',i')$, in Eq. (2.14) are not neglected, the effect of such terms can be analyzed by an iterative method similar to the one developed in the TTOC scheme. Taking the PTOC secular solution (3.28) as the zeroth-order solution one gets, for the first order in the iterative process,[5]

$$\sigma_{f'i'}^{(fi)}(t)=e^{-i\omega_{f'i'}t}e^{-\Omega_{f'i'}(t)}\left[\delta_{f'f}\delta_{i'i}-(1-\delta_{f'f}\delta_{i'i})\int_0^t d\tau\,\hat{K}_{f'i',fi}(\tau)e^{-i(\omega_{fi}-\omega_{f'i'})\tau}e^{-[\Omega_{fi}(\tau)-\Omega_{f'i'}(\tau)]}\right]\ . \tag{3.36}$$

Substitution of Eq. (3.32) into Eq. (3.3) leads to the following PTOC absorption coefficient:

$$\alpha^P(\omega)=\alpha_0^P(\omega)+\alpha_1^P(\omega)\ , \tag{3.37}$$

where $\alpha_0^P(\omega)$ is the PTOC secular absorption coefficient, given by Eq. (3.31). The term $\alpha_1^P(\omega)$ which has the form

$$\alpha_1^P(\omega)=-\frac{4\pi n\omega}{3\hbar c}(1-e^{-\beta\hbar\omega})\mu^2\sum_{\alpha}\sum_{\substack{f,i\\(f>i)}}\sigma_{i'}^0(u_\alpha)_{fi}\sum_{\substack{f',i'\\(f'\neq i')\\(f',i')\neq(f,i)}}(u_\alpha)_{i'f'}\,\mathrm{Re}\left[\int_0^\infty dt\, e^{i(\omega-\omega_{f'i'})t}e^{-\Omega_{f'i'}(t)}I_{fi,f'i'}(t)\right]\ , \tag{3.38a}$$

with

$$I_{fi,f'i'}(t)=\int_0^t d\tau\,\hat{K}_{f'i',fi}(\tau)e^{-i(\omega_{fi}-\omega_{f'i'})\tau}e^{-[\Omega_{fi}(\tau)-\Omega_{f'i'}(\tau)]} \tag{3.38b}$$

as is the correcting term in the absorption coefficient, up to the second order in the interaction, due to the interference effect between the time evolution of the coherences $\sigma_{f'i'}(t)$ and $\sigma_{fi}(t)$ in the PTOC scheme.

The matrix elements $\hat{K}_{f'i',fi}(t)$, with $f'\neq f$ and $i'\neq i$, are given by

$$\begin{aligned}\hat{K}_{f'i',fi}(t)&=\int_0^t d\tau\, e^{i\omega_{fi}\tau}\hat{W}_{f'i',fi}(\tau)\\&=\tfrac{1}{3}\mu^2\langle E^2\rangle\hbar^{-2}\sum_{\alpha'}(u_{\alpha'})_{ii'}(u_{\alpha'})_{f'f}[(e^{(i\omega_{i'i}-t_c^{-1})t}-1)\overline{\Phi}(\omega_{i'i})+(e^{(i\omega_{ff'}-t_c^{-1})t}-1)\overline{\Phi}(\omega_{ff'})]\ .\end{aligned} \tag{3.39}$$

Substituting Eq. (3.39) into Eqs. (3.38), carrying out the summations over all m $(m_i,m_f,m_{i'},m_{f'})$ and taking into account the selection rules for the coefficients $A_{j_fj_i,j_{f'}j_{i'}}$, given by Eq. (3.24), one gets for the PTOC absorption coefficient

$$
\begin{aligned}
\alpha_1^P(\omega)=&-\frac{4\pi n\omega}{3\hbar c}(1-e^{-\beta\hbar\omega})\mu^2(\tfrac{1}{3}\mu^2\langle E^2\rangle\hbar^{-2})Z_S^{-1}\\
&\times\sum_{j_i=0}^{\infty}(j_i+1)e^{-\beta Bhcj_i(j_i+1)}\left[\frac{j_i+2}{2j_i+3}\,\mathrm{Re}\left[\int_0^\infty dt\,e^{i(\omega-\omega_{j_i+2,j_i+1})t}e^{-\Omega_{j_i+2,j_i+1}(t)}I'_{j_i+1,j_i;j_i+2,j_i+1}(t)\right]\right.\\
&\qquad+\frac{j_i}{2j_i+1}\,\mathrm{Re}\left[\int_0^\infty dt\,e^{i(\omega-\omega_{j_i,j_i-1})t}e^{-\Omega_{j_i,j_i-1}(t)}I'_{j_i+1,j_i;j_i,j_i-1}(t)\right]\\
&\qquad\left.+\frac{1}{(2j_i+1)(2j_i+3)}\,\mathrm{Re}\left[\int_0^\infty dt\,e^{i(\omega-\omega_{j_i,j_i+1})t}e^{-\Omega_{j_i,j_i+1}(t)}I'_{j_i+1,j_i;j_i,j_i+1}(t)\right]\right]
\end{aligned}
\tag{3.40}
$$

where

$$
\begin{aligned}
I'_{j_fj_i;j_{f'}j_{i'}}(t)=&\int_0^t d\tau\,e^{-i(\omega_{j_fj_i}-\omega_{j_{f'}j_{i'}})\tau}e^{-[\Omega_{j_fj_i}(\tau)-\Omega_{j_{f'}j_{i'}}(\tau)]}\\
&\times[(e^{(i\omega_{j_{i'}j_i}-t_c^{-1})\tau}-1)\overline{\Phi}(\omega_{j_{i'}j_i})+(e^{(i\omega_{j_fj_{f'}}-t_c^{-1})\tau}-1)\overline{\Phi}(\omega_{j_fj_{f'}})]
\end{aligned}
\tag{3.41}
$$

and the corresponding $\Omega_{j_fj_i}(t)$ can be obtained from Eq. (3.30). The three contributions in Eq. (3.40) have a similar physical interpretation as the one given for the expression (3.27).

IV. NUMERICAL ANALYSIS AND DISCUSSIONS

In order to apply the results obtained in Sec. III to the derivation of the far-infrared spectra of HCl in Ar, Kr, and Xe liquids, we introduce reduced units ($2\pi Bc$ for frequencies and Bhc for energies) which will be expressed by tildes ($\sim$). Thus, the reduced mean square of the intensity of the interaction $\tilde{\lambda}^2$ is given by

$$\tilde{\lambda}^2=\frac{\mu^2\langle E^2\rangle}{(Bhc)^2} \tag{4.1}$$

and the reduced bath correlation time $\tilde{t}_c$ by

$$\tilde{t}_c=(2\pi Bc)t_c\ . \tag{4.2}$$

The HCl rotational constant (in the ground vibrational state) is taken as[22] $B=10.4\ \mathrm{cm}^{-1}$.

The absorption coefficient $\alpha(\omega)$ depends on the parameters $\tilde{\lambda}^2$, $\tilde{t}_c$, and the temperature T of the liquid. Values for the parameters $\tilde{\lambda}^2$ and $\tilde{t}_c$ have been calculated by Hoang and Bonamy[14] using a cell variational Kirwood model for the liquid structure. Table I shows the values for $\tilde{\lambda}^2$, $\tilde{t}_c$, and T, used in the present analysis.

We emphasize that the summation over j which appears in the different expressions for the absorption coefficient has been performed up to some maximum value $j_{\max}$ which depends on the temperature in each case. The present set of calculations was carried out in simple precision (Eclipse MV4000) with $j_{\max}$ never greater than 10, which is sufficient to ensure the convergence of all summations which appear in the problem.

TABLE I. Parameters used in the calculations. Values of Hoang and Bonamy (Ref. 14).

	HCl-Ar	HCl-Kr	HCl-Xe
T (K)	105	125	175
$\tilde{\lambda}^2$	40	40	40
$\tilde{t}_c$	0.18	0.20	0.20

Equations (3.14), (3.18), and (3.31) show that in the secular approximation the absorption coefficient can be built as a superposition of basic resonances located close to the natural frequencies $\omega_{j+1,j}$ and given by the real part of $\Lambda^M_{j+1,j}(\omega)$ [Eq. (3.7b)], $\Lambda^T_{j+1,j}(\omega)$ [Eq. (3.16b)], and $\Lambda^P_{j+1,j}(\omega)$ [Eq. (3.29b)] in the Markovian limit and TTOC and PTOC schemes, respectively.

In the Markovian limit these resonances are Lorentzian with linewidth $\Gamma_{j+1,j}$ and shift $\Delta_{j+1,j}$ with respect to the corresponding frequency $\omega_{j+1,j}$. Table II gives the values of $\tilde{\Gamma}_{j+1,j}$ and $\tilde{\Delta}_{j+1,j}$ calculated from the real and the imaginary parts of Eq. (3.13) for different j values. This table shows that the shifts are very much smaller than the corresponding linewidths and that both decrease rapidly with increasing j.

In Fig. 1 the basic resonances in the secular approximation for the specific case of HCl-Kr are drawn. Note that the non-Markovian TTOC and PTOC formalisms lead to different predictions for the higher j values. So, Fig. 1 suggests the range of validity of the Markovian hypothesis. This hypothesis is valid when the bath correlation time $\tilde{t}_c$ is very small compared with the inverse linewidths,[1] i.e.,

$$\tilde{t}_c \ll \tilde{\Gamma}^{-1}_{j+1,j}\quad \forall j\ . \tag{4.3}$$

We check this condition in the third column of Table II and, clearly, condition (4.3) is verified for the higher j states.

Figure 2 illustrates the shape of the secular absorption coefficients $\alpha_0^M(\omega)$, $\alpha_0^T(\omega)$, and $\alpha_0^P(\omega)$, given by Eqs. (3.14), (3.18), and (3.31), respectively. Two essential remarks should be made in regard to this figure. Firstly, there is

TABLE II. Shifts and linewidths obtained from the imaginary and real parts of Eq. (3.13). The Markovian limit is checked in the third column: these values must be compared to unity. The secular approximation is checked in the fourth column: these values must be compared to unity.

	$\tilde{\Delta}_{j+1,j}$		$\tilde{\Gamma}_{j+1,j}$		$\tilde{\Gamma}_{j+1,j}\tilde{t}_c$		$\frac{1}{2}\tilde{\Gamma}_{j+1,j}$	
j	HCl-Ar	HCl-Kr HCl-Xe	HCl-Ar	HCl-Kr HCl-Xe	HCl-Ar	HCl-Kr HCl-Xe	HCl-Ar	HCl-Kr HCl-Xe
0	0.261	0.358	3.886	4.149	0.699	0.829	1.943	2.074
1	0.241	0.294	3.058	3.156	0.550	0.631	1.529	1.578
2	0.132	0.143	2.217	2.202	0.399	0.440	1.108	1.101
3	0.063	0.062	1.582	1.525	0.284	0.305	0.791	0.762
4	0.030	0.028	1.149	1.086	0.206	0.217	0.574	0.543
5	0.015	0.013	0.859	0.802	0.154	0.106	0.429	0.401
6	0.008	0.007	0.661	0.611	0.118	0.122	0.330	0.305
7	0.004	0.003	0.522	0.480	0.093	0.081	0.261	0.240
8	0.002	0.002	0.421	0.385	0.075	0.077	0.210	0.192
9	0.001	0.001	0.346	0.316	0.062	0.063	0.173	0.158
10	0.001	0.000	0.289	0.263	0.052	0.052	0.144	0.131

no big difference among the curves sketched. This is a consequence of the fact that even for low j states the system is not very far from the Markovian limit. Secondly, the rotational structure remains only in the high-frequency range. This effect is a signal that for low j values the linewidths $\tilde{\Gamma}_{j+1,j}$ are very much larger than for higher j values (see Table II).

In Fig. 2 also the PTOC secular absorption coefficient $\alpha_0^P(\omega)$ obtained from exact Eq. (3.31) and from approximated Eq. (3.34) are compared. In the range of ω values analyzed (0–200 cm^{-1}) the difference between both equations is never larger than 2.5%. Thus, Eq. (3.34) is a very good approximation for the PTOC secular absorption coefficient and it has the advantage that, in the present case, it can be calculated analytically. Figure 2 also shows the correction $\alpha_0^D(\omega)$ [Eq. (3.35)] which gives explicit information on the effect of the finite bath correlation time considered in the PTOC scheme.

In a spectroscopic framework the secular approximation corresponds to the additivity of the basic resonances which should be obtained if they were decoupled among them. Therefore, this approximation is equivalent to neglect the interference effect among such resonances. In Ref. 1 we have seen that when the relaxation of the system takes place in conditions not too far from the Markovian limit, the secular approximation will be guaranteed by the sufficient conditions

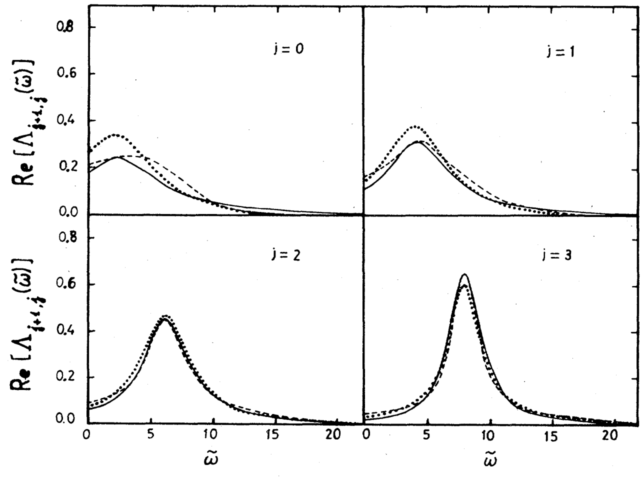

FIG. 1. Basic resonances Re[$\Lambda^M_{j+1,j}(\omega)$] (——), Re[$\Lambda^T_{j+1,j}(\omega)$] (— — —), and Re[$\Lambda^P_{j+1,j}(\omega)$] (· · · ·) for $j=0,1,2,3$, and parameters given by Table I for HCl-Kr.

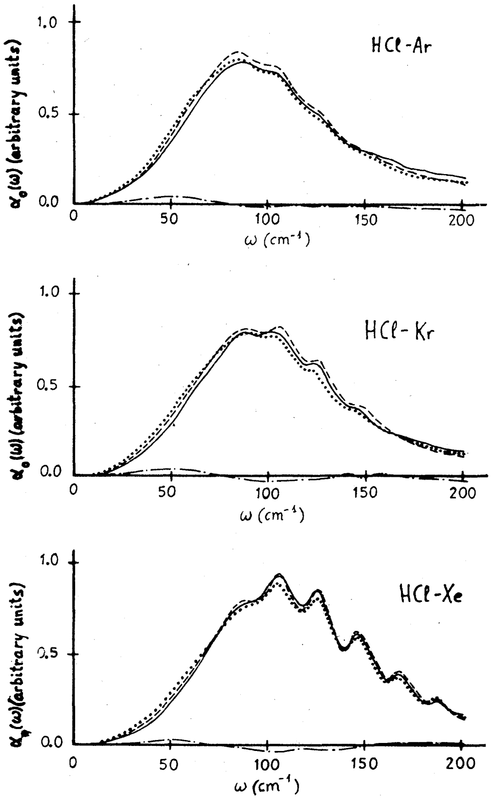

FIG. 2. Secular absorption coefficients $\alpha_0^M(\omega)$ (——), $\alpha_0^T(\omega)$ (— — —), and $\alpha_0^P(\omega)$ (· · · ·), and the non-Markovian correcting term $\alpha_0^D(\omega)$ (—·—·—·) for HCl in Ar, Kr, and Xe liquids and parameters depicted in Table I.

$$| \tilde{\hat{R}}_{fi,fi} | , | \tilde{\hat{R}}_{f'i',f'i'} | \ll | \tilde{\omega}_{fi} - \tilde{\omega}_{f'i'} | \; , \tag{4.4a}$$

$$| \tilde{\hat{R}}_{f'i',fi} | \ll | \tilde{\omega}_{fi} - \tilde{\omega}_{f'i'} | \; , \tag{4.4b}$$

where $(f,i) \neq (f',i')$. In the present case the modulus of the off-diagonal matrix elements of $\hat{R}$ are smaller than the modulus of the diagonal matrix elements and, thus, it is only necessary to analyze the condition (4.4a).

The selection rules (3.11) imply that only the diagonal matrix elements of $\hat{R}$ with $j_f = j_i + 1$ are not zero, and, taking into account Eq. (2.2b), condition (4.4a) can be written as

$$| \tilde{\hat{R}}_{j_i+1,j_i;j_i+1,j_i} | , | \tilde{\hat{R}}_{j_{i'}+1,j_{i'};j_{i'}+1,j_{i'}} | \ll 2 \, | j_i - j_{i'} | \; . \tag{4.5}$$

The smaller value of the right-hand side (rhs) in condition (4.5) occurs for $j_{i'} = j_i \pm 1$, which corresponds to consider the distance between consecutive resonances. Moreover, we have seen that $\tilde{\Delta}_{j+1,j} \ll \tilde{\Gamma}_{j+1,j}$ and so

$$| \tilde{\hat{R}}_{j+1,j;j+1,j} | \simeq \tilde{\Gamma}_{j+1,j} \; .$$

Therefore, the sufficient condition (4.5) for the validity of the secular approximation can be written as

$$\tilde{\Gamma}_{j+1,j} \ll 2 \quad \forall j \; . \tag{4.6}$$

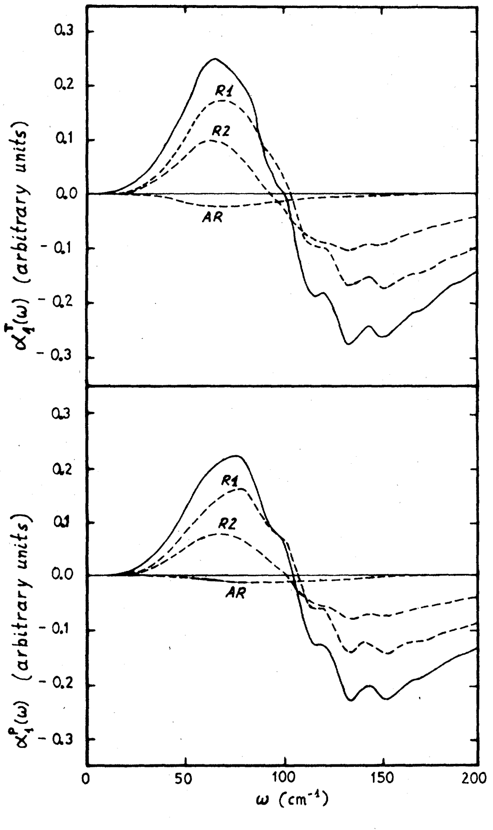

FIG. 3. Correcting term $\alpha_1(\omega)$ due to consider the overlapping effect in the TTOC and PTOC formalisms for HCl-Kr (continuous curves). The dotted curves refer to the resonant ($R1$ and $R2$) and antiresonant (AR) contributions. (Same scale as that in Fig. 2.)

In the fourth column of Table II we can see that the condition (4.6) is verified only for very high j states. Thus, the main j states ($j \leq 6$) which give a significant contribution to the absorption coefficient are excluded of the range of validity of the secular approximation.

Since the values of $\frac{1}{2}\tilde{\Gamma}_{j+1,j}$ in Table II are not very large compared to unity, we can apply the iterative methods developed in Sec. III. These methods incorporate the effect of the nonsecular terms in the evolution equations. Such terms give rise to the interference effect among resonances through a correcting term over the secular results, which constitute the first-order term in the iterative process.

Figure 3 shows the behavior of $\alpha_1^T(\omega)$ [Eq. (3.27)] and $\alpha_1^P(\omega)$ [Eq. (3.40)] and the contribution of the resonant terms $R1$ and $R2$ and of the antiresonant term Ar. This figure presents some interesting features. It shows the importance of the interference effect: $\alpha_1(\omega)$ reaches values up to 30% of the corresponding secular absorption coefficient $\alpha_0(\omega)$. It also gives information on the contribution of $\alpha_1(\omega)$ to the total absorption coefficient: The interference effect implies an increase (decrease) of the absorption in the low (high) frequency range. Lastly, it is shown there that the explicit contribution to $\alpha_1(\omega)$ coming from the resonant and antiresonant terms: the contribution of the antiresonant term AR is practically negligible.

Figure 4 shows the total TTOC [Eq. (3.20)], PTOC [Eq.

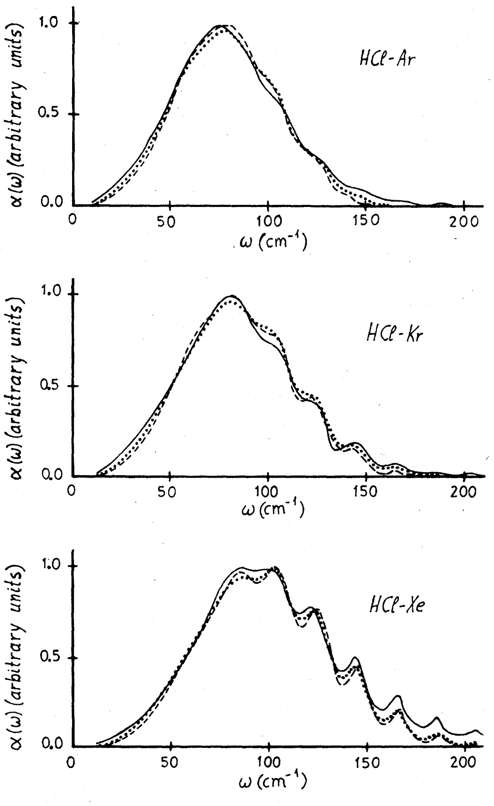

FIG. 4. Far-infrared spectra of HCl in Ar, Kr, and Xe liquids: experimental spectra (——), TTOC spectra (— — —), and PTOC spectra (· · · ·). The theoretical spectra correspond to the values of parameters depicted in Table I. (Same scale as that in Fig. 2.)

(3.37)], and the experimental[6,7] absorption coefficients to the cases of HCl in Ar, Kr, and Xe liquids. The most striking point is that both non-Markovian formalisms lead to very similar results. This is due to the fact that the rotational relaxation under study is not very far from the Markovian limit. In any case, there is very good agreement between the experimental and the TTOC and PTOC spectra.

V. SUMMARY

In this paper we have shown how the non-Markovian TTOC and PTOC formalisms can be applied to the problem of the calculation of the far-infrared spectra of a diatomic polar molecule immersed in a rare-gas liquid. We have shown that in the secular approximation (i.e., when the nonsecular terms in the reduced master equation are neglected and, therefore, the coherences evolve independently among themselves) such spectra can be built as a superposition of resonances located near the rotational frequencies of the diatomic molecules whose shapes should be the same as if they were decoupled among them. These resonances are different in each TTOC and PTOC formalism, but they become Lorentzian in the Markovian limit. Using an iterative method in which the secular result is the first term in the iteration, we have obtained a correcting term which incorporates the interference effect among such resonances.

We have calculated the absorption coefficient in the frequency range from 0 to 200 cm^{-1} for a HCl molecule in Ar, Kr, and Xe liquids. Although the main j states which contribute significantly to the absorption coefficient are not very far from the Markovian limit, they are excluded of the range of validity of the secular approximation. Using the expressions which take into account the interference effect, both non-Markovian TTOC and PTOC spectra are in agreement with the experimental results. However, the PTOC spectra give a slightly better agreement in the wings of the whole band profile. On the other hand, the use of the TTOC formalism is easier from a computational point of view.

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