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Quantitative study of memory and nonadditivity effects of the far-infrared spectrum of HCl in dense Ar

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The far-infrared spectra of HCl in Ar at $T = 162.5$ K and at densities of 100, 200, 300, 400, and 480 amagat have been studied by applying a non-Markovian theory in which the theoretical dipolar absorption coefficient is obtained by a superposition of basic resonances (Lorentzian lines in the Markovian limit) modified by nonadditivity effects due to the existence of cross correlations between different rotational transitions. In terms of only two phenomenological parameters (the square interaction strength and its correlation time) obtained by fit to the experimental spectra, we have analyzed, qualitatively and quantitatively, the influence of the memory as well as of the nonadditivity effects on the system under study: while the former are not very significant, it is shown that the latter have great importance in calculating the theoretical dipolar absorption coefficient, even for the Ar-lowest density of 100 amagat. As a consequence, strong deviations from the additive superposition of Lorentzian lines are observed, especially in the minima between lines, which mainly consist in an enhancement of the absorption (constructive interference) in the low-frequency side and in a reduction of the absorption (destructive interference) in the high-frequency side.

I. INTRODUCTION

From a theoretical point of view, the simplest way to study the infrared absorption spectra of small polar molecules dissolved in dense nonpolar media is to consider that the associated absorption coefficient is built from an additive superposition of Lorentzian lines located close to the free rotational transition frequencies of the absorbing molecules. This basic spectrum is based on two fundamental hypotheses: (1) the Markovian (impact) limit, and (2) an assumption of additivity. The first one assumes that the time scale characterizing the correlation of the absorber-perturbers interaction is practically zero compared with any other time scale appearing in the problem. The second one consists of neglecting the cross correlations between the transition lines forming the spectrum. These two simplifications seem to be adequate for the case of low-density gas mixtures, for which the infrared spectra exhibit a clear rotational structure, but they no longer remain valid for dense gas mixtures and liquid solutions, for which the transition lines are not completely resolved. Therefore an accurate description of the infrared spectra of this class of systems must include the influence of a finite correlation time for the absorber-perturbers interaction (non-Markovian effects) as well as the influence of the line coupling (nonadditivity effects). To get this, most of the theoretical works on near-infrared spectra [1–3] assume that each transition line making up the spectrum consists in a Lorentzian line, with a nonzero correlation time, modified by a line coupling coefficient that takes into account all the effects induced by line overlapping. An improved theory of the infrared absorption that takes into account both the initial orientational correlations between colliding molecules and line coupling for each pair of lines, has been recently developed and applied to the CO_2-Ar system at several temperatures [4].

Concerning the pure rotational far-infrared spectra of diatomic polar molecules in dense nonpolar media, Bonamy and Hoang [5] studied the influence of a finite correlation time of the interaction and a nonadditivity effect of the Lorentzian resonances in HCl dissolved in rare-gas liquids. Also, the influence of the first effect in HCl-Ar mixtures was carefully analyzed by Boulet, Robert, and Galatry [6] in terms of the anisotropic part of the intermolecular potential.

The present paper is devoted to a quantitative and qualitative study of the influence of the non-Markovian and nonadditivity effects on the calculated rotational far-infrared spectra of HCl in dense Ar, at $T = 162.5$ K and Ar densities between 100 and 480 amagat. To this end, we shall use a non-Markovian spectral theory developed by Bretón and co-workers [7,8] [called totally time-ordered cumulant (TTOC) spectral theory] and based on a master equation for the relaxation to equilibrium of a multilevel quantum system weakly coupled to a thermal bath. This theory, which has been successfully applied in obtaining the dipolar absorption coefficient of HCl in Ar, Kr, and Xe rare-gas liquids [9] and HCl, DCl [10], and HF [11] in liquid SF_6, enables us to compute explicitly the influence of non-Markovian and nonadditivity effects in terms of only two statistical parameters which are calculated for the system under study by fit to the experimental spectra of Frenkel, Gravesteyn, and van der Elsken [12].

This paper is organized as follows. In Sec. II we present the necessary theoretical background. In Sec. III, the Markovian limit including interference effects is calculated. Then, a detailed study on the influence of the memory effects is presented. Next, in Sec. IV, the nonadditivity effects are evaluated and discussed. Finally, some conclusions are summarized in Sec. V.

II. THEORETICAL BACKGROUND

We are interested in the study of the far-infrared spectrum of a very diluted solution of diatomic polar molecules dissolved in a nonpolar fluid. Our analysis is based on the following assumptions: (i) the solution concentration is low enough to assume that the system under study can be adequately represented by a single diatomic molecule surrounded by a large number of solvent molecules; (ii) the diatomic molecule remains in its ground vibrational state; (iii) the unperturbed rotational states of the diatomic are taken as the eigenstates of a free quantum rigid rotor (system *S*); and (iv) the remaining degrees of freedom (i.e., the translational degrees of freedom of the diatomic and of the solvent molecules) behave as a classical thermal bath (system *B*). The small corrections introduced by a fully quantum study of the thermal bath [13] are not considered in this work.

Using the rotational eigenstates of the Hamiltonian H_S, $\{|i\rangle\}=\{|j_i m_i\rangle\}$, and the corresponding eigenvalues, $E_{ji}=Bhcj_i(j_i+1)$, B being the rotational constant of the active molecule, the dipolar absorption coefficient (DAC) can be written as a function of the reduced density operator $\sigma(t)\equiv\mathrm{Tr}_B[\rho(t)]$ [where $\rho(t)$ is the total density matrix] [7]:

$$\alpha(\omega)=(4\pi n\omega/3\hbar c)(1-e^{-\beta\hbar\omega})\mu^2 \times\sum_{i,f}\sum_{\alpha}\sigma_i^0(u_\alpha)_{fi}\sum_{f',i'}(u_\alpha)_{f'i'}\mathrm{Re}\left[\int_0^\infty dt\, e^{i\omega t}\sigma_{f'i'}^{fi}(t)\right] \tag{2.1}$$

with

$$\sigma_i^0=Z_S^{-1}\exp(-\beta E_{ji})\ , \tag{2.2}$$

$$Z_S^{-1}=\mathrm{Tr}_S(e^{-\beta H_S})=\sum_{ji}(2j_i+1)e^{-\beta E j_i} \tag{2.3}$$

where **u** is a unit vector in the direction of the permanent dipole moment μ of the diatomic (the index α labels the vector components in a given reference system), and $\sigma_{f'i'}^{(fi)}(t)$ denotes the matrix element $\sigma_{f'i'}(t)$ derived from the initial condition $\sigma_{f'i'}(0)=\delta_{f'f}\delta_{i'i}$.

Equation (2.1) relates the theoretical DAC to the problem of the rotational relaxation of the diatomic molecule in the fluid medium, and it constitutes the basic expression in our spectral theory. The interest is thus focused on obtaining closed differential equations for the off-diagonal matrix elements of the reduced density operator $\sigma(t)$. For this, several elegant procedures have been used in the literature. In particular, assuming the absence of correlation at the initial time between the systems *S* and *B* and that the bath equilibrium average of the interaction Hamiltonian is zero, $\langle H'\rangle=0$, the Zwanzig projector operator technique or the totally time-ordered cumulant expansion method lead to the following equation [7,8]:

$$\dot\sigma_{fi}(t)=-i\omega_{fi}\sigma_{fi}(t)-\sum_{f',i'}\int_0^t d\tau\, W_{fi,f'i'}(t-\tau)\sigma_{f'i'}(\tau) \tag{2.4}$$

where $\omega_{fi}=h^{-1}(E_{jf}-E_{ji})$ and $W(t)$ is a relaxation superoperator (tetradic) driving the system *S* to thermal equilibrium. $W(t)$ contains information about memory effects and it is usually known as the memory kernel. From the Fourier-Laplace transform of Eq. (2.4), Bretón *et al.* [7] have obtained for $\sigma_{f'i'}^{(fi)}(\omega)$, at the second order in the *S*-*B* Hamiltonian interaction H', the expression

$$\sigma_{f'i'}^{(fi)}(\omega)=[\omega-\omega_{f'i'}+iW_{f'i',f'i'}(\omega)]^{-1}\{i\delta_{f'f}\delta_{i'i}+W_{f'i',fi}(\omega)[\omega-\omega_{fi}+iW_{fi,fi}(\omega)]^{-1}(1-\delta_{f'f}\delta_{i'i}\} \tag{2.5}$$

where

$$W_{fi,f'i'}(\omega)=\hbar^{-2}\int_0^\infty dt\, e^{i\omega t}\left[\delta_{i'i}\sum_{f''}e^{-i\omega_{f''i}t}\langle H'_{ff''}(t)H'_{f''f'}(0)\rangle+\delta_{f'f}\sum_{i''}e^{-i\omega_{fi''}t}\langle H'_{ii''}(t)H'_{i''i'}(0)\rangle^* -e^{-i\omega_{fi'}t}\langle H'_{i'i}(t)H'_{ff'}(0)\rangle-e^{-i\omega_{f'i}t}\langle H'_{f'f}(t)H'_{ii'}(0)\rangle^*\right] \tag{2.6}$$

with the angular brackets $\langle\ \rangle$ denoting an equilibrium average over the bath variables. Equations (2.5)–(2.6) show that evaluation of the theoretical DAC, Eq. (2.1), requires the knowledge of the bath correlation functions $\langle H'_{fi}(t)H'_{f'i'}(0)\rangle$ for which dynamical models [5,14] or molecular-dynamics calculations [15] can be used. An alternative approach is to use a stochastic bath description instead of a microscopic one, by assuming a set of statistical properties for the interaction where the characteristic parameters are then considered as phenomenological [16]. This method is very useful for the analysis of line shapes, since it allows a considerable reduction in the number of fitting parameters in comparing theory with experiment. We shall follow this procedure here. Thus the rotor-bath interaction Hamiltonian $H'(t)$ is taken to be a Gaussian process with zero mean and a time decay exponential correlation, i.e., as an Ornstein-Uhlenbeck stochastic process, whose H' autocorrelation functions are [13,17]

$$\langle H'_{fi}(t)H'_{f'i'}(0)\rangle=\tfrac{1}{3}\lambda^2 e^{-t/tc}\sum_{\alpha}(u_\alpha)_{fi}(u_\alpha)_{f'i'} \tag{2.7}$$

when substituted in Eqs. (2.4)–(2.6), thus allowing us to write the theoretical DAC, Eq. (2.1), in terms of only two statistical parameters: the mean-square value of the interaction λ^2 and its correlation time t_c.

Using Eqs. (2.5)–(2.7) and the selection rules of the Wigner 3j and Racah 6j coefficients, the theoretical DAC, from Eq. (2.1), becomes [9]

$$\alpha(\omega)=\alpha_0(\omega)+\alpha_1(\omega) \tag{2.8}$$

with

$$\alpha_0(\omega)=(4\pi n\omega/3\hbar c)(1-e^{-\beta\hbar\omega})\mu^2 Z_S^{-1}\sum_j (j+1)e^{-\beta Bhcj(j+1)}\mathrm{Re}[\Lambda_{j+1,j}(\omega)]\ , \tag{2.9}$$

$$\begin{aligned}\alpha_1(\omega)=&(4\pi n\omega/3\hbar c)(1-e^{-\beta\hbar\omega})\mu^2(\tfrac{1}{3}\hbar^{-2}\lambda^2)Z_S^{-1}\\ &\times\sum_j (j+1)e^{-\beta Bhcj(j+1)}([(j+2)/(2j+3)]\mathrm{Re}\{\Lambda_{j+2,j+1}(\omega)\Lambda_{j+1,j}(\omega)[C(\omega-\omega_{j+2,j})+C(\omega)]\}\ .\\ &\qquad+[j/(2j+1)]\mathrm{Re}\{\Lambda_{j,j-1}(\omega)\Lambda_{j+1,j}(\omega)[C(\omega-\omega_{j+1,j-1})+C(\omega)]\}\\ &\qquad+[2/(2j+1)(2j+3)]\mathrm{Re}[\Lambda_{j,j+1}(\omega)\Lambda_{j+1,j}(\omega)C(\omega)])\end{aligned} \tag{2.10}$$

where

$$\Lambda_{j'j}=i[\omega-\omega_{j'j}+iW_{j'j}(\omega)]^{-1}\ , \tag{2.11}$$

$$\begin{aligned}W_{j'j}(\omega)\equiv W_{j'j,j'j}(\omega)=&\tfrac{1}{3}\hbar^{-2}\lambda^2\{[1/(2j+1)][(j+1)C(\omega-\omega_{j',j+1})+jC(\omega-\omega_{j',j-1}]\\ &+[1/(2j'+1)][(j'+1)C(\omega-\omega_{j'+1,j})+j'C(\omega-\omega_{j'-1,j})]\}\ ,\end{aligned} \tag{2.12}$$

$$C(\omega)=(-i\omega+t_c^{-1})^{-1}\ . \tag{2.13}$$

Equations (2.8)–(2.10) show that the theoretical DAC is written as a sum of two contributions: the first one, called the secular contribution, $\alpha_0(\omega)$, is given by an additive superposition of basic resonances $\Lambda_{j+1,j}(\omega)$ weighted by the Boltzmann factor corresponding to the rotational transition line $j\rightarrow j+1$; the second one, called the interference contribution, $\alpha_1(\omega)$, is given as a sum of three terms arising from the cross correlation between the main rotational transition line $j\rightarrow j+1$ and the two adjacent lines $j+1\rightarrow j+2$ $[\Lambda_{j+2,j+1}(\omega)\Lambda_{j+1,j}(\omega)]$, $j\rightarrow j-1$ $[\Lambda_{j,j-1}(\omega)\Lambda_{j+1,j}(\omega)]$, and the antiresonant line $j\rightarrow j+1$ $[\Lambda_{j,j+1}(\omega)\Lambda_{j+1,j}(\omega)]$, respectively. These three terms appear as a consequence of Eq. (2.7), where an anisotropic potential of the type $P_1(\cos\theta)$ for the absorber-perturbers interaction is implicitly assumed.

III. MEMORY EFFECTS

When relaxation of $W_{fi,f'i'}(t)$ and $\sigma_{fi}(t)$ take place on separable time scales, so that the decay time of $W(t)$ is the shortest resolvable time, Eq. (2.4) can be notably simplified by raising the upper limit in the integral to infinite. Then

$$\dot\sigma_{fi}(t)=-i\omega_{fi}\sigma_{fi}(t)-\sum_{f',i'}R_{fi,f'i'}\sigma_{f'i'}(t) \tag{3.1}$$

where

$$R_{f'i',fi}=\int_0^\infty dt\, e^{i\omega_{fi}t}W_{f'i',fi}(t)=W_{f'i',fi}(\omega_{fi}) \tag{3.2}$$

is the time-dependent superoperator governing the relaxation of the system S, which shows a relaxation of $\sigma(t)$ independent of its past history, and it is usually referred to as a Markovian master equation [18].

Roughly speaking, t_c can be considered as a measurement of the decay time of the memory kernel $W(t)$, while the inverse of the factor $\frac{2}{3}\hbar^{-2}\lambda^2 t_c$, appearing in the real part of the coefficients (2.12), can be considered as a time characterizing the relaxation of $\sigma(t)$ [see Eq. (2.4)]. Then, when the condition

$$\tfrac{2}{3}\hbar^{-2}\lambda^2 t_c^2 \ll 1 \tag{3.3}$$

is met, one can use the Markovian equation (3.1) instead of the non-Markovian one (2.4) to develop the spectral theory. Condition (3.3) leads to the usual way of stating the Markovian limit: the bath correlation time is much smaller than the inverse of the interaction strength ($\hbar^{-1}\lambda t_c \ll 1$). Taking into account Eqs. (3.1) and (3.2), the theoretical DAC in the Markovian limit becomes

$$\alpha^M(\omega)=\alpha_0^M(\omega)+\alpha_1^M(\omega) \tag{3.4}$$

with

TABLE I. Values of the parameters λ^2 and t_c used in calculating the theoretical far-infrared spectra of HCl in dense Ar at $T=162.5$ K at densities between 100 and 480 amagat. Numerical values of non-Markovian (D_M), Eq. (3.12), and nonadditivity (D_I), Eq. (4.3), effects. The parameters λ^2 and t_c have been obtained by fitting the experimental results of Frenkel, Gravesteyn, and van der Elsken [12]. The tilde ($\sim$) denotes reduced units ($2\pi Bc$ for frequencies and Bhc for energies with $B=10.4$ cm^{-1} being the rotational constant of HCl in its ground vibrational state).

ρ (amagat)	$\tilde\lambda^2$	$\tilde t_c$	$\frac{2}{3}\tilde\lambda^2\tilde t_c^2$	D_M (%)	D_I (%)
100	10	0.10	0.06	0.83	11.86
200	15	0.11	0.12	1.57	15.87
300	20	0.13	0.22	2.68	20.37
400	25	0.14	0.32	3.77	23.98
480	30	0.15	0.45	4.91	27.08

$$\alpha_0^M(\omega)=(4\pi n\omega/3\hbar c)(1-e^{-\beta\hbar\omega})\mu^2 Z_S^{-1}\sum_j (j+1)e^{-\beta Bhcj(j+1)}\mathrm{Re}[\Lambda_{j+1,j}{}^M(\omega)]\ , \tag{3.5}$$

$$\begin{aligned}\alpha_1^M(\omega)=&(4\pi n\omega/3\hbar c)(1-e^{-\beta\hbar\omega})\mu^2(\tfrac{1}{3}\hbar^{-2}\lambda^2)Z_S^{-1}\\ &\times\sum_j (j+1)e^{-\beta Bhcj(j+1)}([(j+2)/(2j+3)]\mathrm{Re}\{\Lambda_{j+2,j+1}^M(\omega)\Lambda_{j+1,j}^M(\omega)[C(\omega_{j+1,j+2})+C(\omega_{j+1,j})]\}\\ &\qquad +[j/(2j+1)]\mathrm{Re}\{\Lambda_{j,j-1}^M(\omega)\Lambda_{j+1,j}^M(\omega)[C(\omega_{j-1,j})+C(\omega_{j+1,j})]\}\\ &\qquad +[2/(2j+1)(2j+3)]\mathrm{Re}[\Lambda_{j,j+1}^M(\omega)\Lambda_{j+1,j}^M(\omega)C(\omega_{j+1,j})])\end{aligned} \tag{3.6}$$

where

$$\Lambda_{j'j}^M(\omega)=i(\omega-\omega_{j'j}+i\Gamma_{j'j}^M)^{-1} \tag{3.7}$$

with

$$\omega_{j'j}=\omega_{j'j}+\Delta_{j'j}^M\ , \tag{3.8}$$

$$\Delta_{j'j}^M=\mathrm{Im}(R_{j'j})=\mathrm{Im}[W_{j'j}(\omega_{j'j})]\ , \tag{3.9}$$

$$\Gamma_{j'j}^M=\mathrm{Re}(R_{j'j})=\mathrm{Re}[W_{j'j}(\omega_{j'j})]\ . \tag{3.10}$$

Equations (3.5) and (3.7) show that the Markovian secular contribution $\alpha_0^M(\omega)$ is given by an additive superposition of Lorentzian lines with half-width $\Gamma_{j+1,j}^M$ and shifted in $\Delta_{j+1,j}^M$ respect to the pure rotational frequencies $\omega_{j+1,j}$. This is the well-known result of those spectral theories in which non-Markovian and nonadditivity line effects are not taken into account. Equation (3.6) and (3.7) show that the Markovian interference contribution $\alpha_1^M(\omega)$ takes into account the overlapping effects between the, now, main Lorentzian transition line $j\rightarrow j+1$ and the two adjacent Lorentzian lines $j+1\rightarrow j+2$, $j-1\rightarrow j$, and the antiresonant Lorentzian line $j+1\rightarrow j$, which are given, respectively, by the factors $\Lambda_{j+2,j+1}^M(\omega)\Lambda_{j+1,j}^M(\omega)$, $\Lambda_{j,j-1}^M(\omega)\Lambda_{j+1,j}^M(\omega)$, and $\Lambda_{j,j+1}^M(\omega)\Lambda_{j+1,j}^M(\omega)$.

In order to study the influence of the memory effects, we now focus our attention on the far-infrared spectra of HCl dissolved in dense Ar at $T=162.5$ K and at Ar densities of 100, 200, 300, 400, and 480 amagat. For this system the values of the stochastic parameters involved in the theory, λ and t_c, are obtained using a fit procedure between the experimental spectral results [12] and the theoretical DAC, obtained from the TTOC framework, Eq. (2.8). The good agreement obtained from the fit procedure can be checked in Fig. 1 and the fitted values of λ and t_c are collected in Table I. In Fig. 1, the theoretical TTOC values have been normalized to unity for each density. This normalization, as well as the fitted values of λ and t_c, will be used in all following computations.

As a first step in our study on the memory effects, it seems illustrative to visualize for any frequency the differences between the theoretical DAC, $\alpha(\omega)$, and the theoretical Markovian DAC, $\alpha^M(\omega)$. To this end, we introduce the band shape function $K_M(\omega)$ defined as

$$K_M(\omega)=\alpha(\omega)-\alpha^M(\omega) \tag{3.11}$$

which accounts for deviations from the Markovian limit of the total theoretical DAC, $\alpha(\omega)$, by retaining the interference effects. $K_M(\omega)$ is plotted in Fig. 2 (dotted lines) for HCl-Ar at the five Ar densities here considered. A glance at this figure shows that (i) the differences between Markovian and non-Markovian expressions are very small in all frequency ranges at all densities; (ii) the memory effects increase when the Ar density increases, and (iii) for fixed Ar density, $K_M(\omega)$ is positive for low frequencies ($\omega<75$ cm^{-1}) and negative for high frequencies ($\omega>75$ cm^{-1}), exhibiting extreme values in the 45–65- and 85–125-cm^{-1} frequency ranges. At the highest frequencies $K_M(\omega)\rightarrow 0$.

A quantitative analysis of the memory effects can be deduced from the parameter

$$D_M=\int|\alpha(\omega)-\alpha^M(\omega)|d\omega\Big/\int\alpha(\omega)d\omega\ . \tag{3.12}$$

The values obtained for this parameter are given in Table I and plotted in Fig. 3 as a function of the Ar density [the integrals appearing in (3.12) were performed over the experimental available range of frequencies: 0–200 cm^{-1}]. The smallness of the reported values proves that the corrections on the calculated profiles due to memory effects are not very significant for the HCl-Ar system at the densities under study, although, as expected, the memory effects are more relevant as the density increases, showing a linear behavior with the Ar density.

In Fig. 2, it is observed that $K_M(\omega)\rightarrow 0$ for the higher frequencies at all Ar densities considered. Then, for these higher frequencies it is verified that $\alpha(\omega)\approx\alpha^M(\omega)$. Such a behavior can be understood by analyzing the way in which the Markovian limit is reached. Introducing the reduced parameters, $\tilde{t}_c=(2\pi Bc)t_c$ and $\tilde{\lambda}=\lambda/(Bhc)$, the Markovian condition (3.3) becomes

$$\tfrac{2}{3}\tilde{\lambda}^2\tilde{t}_c^2\ll 1\ . \tag{3.13}$$

We check this condition in Table I. Although at some of the reported densities the HCl-Ar system does not fulfill this condition, the corresponding non-Markovian corrections are not important. One concludes that condition (3.13) is a very conservative estimate of the range of the validity of the Markovian expressions. This is due to the fact that each off-diagonal matrix element $\sigma_{j+1,j}(t)$ [see Eqs. (2.4) and (3.1)] has its own j-dependent relaxation time, while in writing condition (3.13) we assumed that the inverse of $\frac{2}{3}\hbar^{-2}\lambda^2 t_c$ was a j-independent time characterizing the relaxation of $\sigma(t)$. From Eq. (3.7), an adequate parameter measuring the relaxation of $\sigma_{j+1,j}(t)$ should be the inverse of the half-width $\Gamma_{j+1,j}^M$ corresponding to the transition line $j \rightarrow j+1$. Thus the Markovian condition (3.13) should be replaced by

$$\tilde{\Gamma}^{M}_{j+1,j}\tilde{t}_c \ll 1 \qquad (3.14)$$

with $\tilde{\Gamma}^{M}_{j+1,j} = \Gamma^{M}_{j+1,j}/B$. Note that $\tilde{\Gamma}^{M}_{j+1,j} \rightarrow \frac{2}{3}\tilde{\lambda}^{2}\tilde{t}_c$ when $t_c \rightarrow 0$ [from Eqs. (3.10) and (2.12)] and so condition (3.14) becomes condition (3.13) in this limit. Behavior of $\tilde{\Gamma}^{M}_{j+1,j}\tilde{t}_c$ versus j is plotted in Fig. 4, where the reported

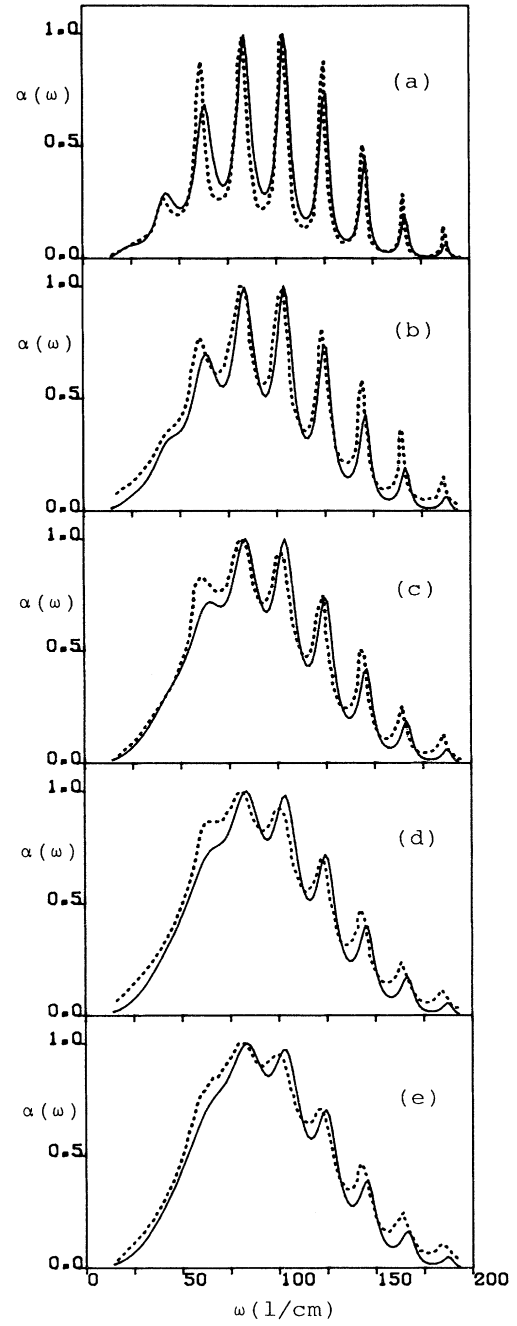

FIG. 1. Dipolar absorption coefficients for HCl in dense Ar at $T = 162.5$ K and at five different densities: (a) $\rho = 100$ amagat; (b) $\rho = 200$ amagat; (c) $\rho = 300$ amagat; (d) $\rho = 400$ amagat; (e) $\rho = 480$ amagat. Experimental spectra of Frenkel, Gravesteyn, and van der Elsken [12] (· · · ·). Theoretical TTOC spectra (——), obtained by Eq. (2.8) with values for the parameters λ^2 and t_c collected in Table I. For each density, the corresponding $\alpha(\omega)$ has been normalized to unity.

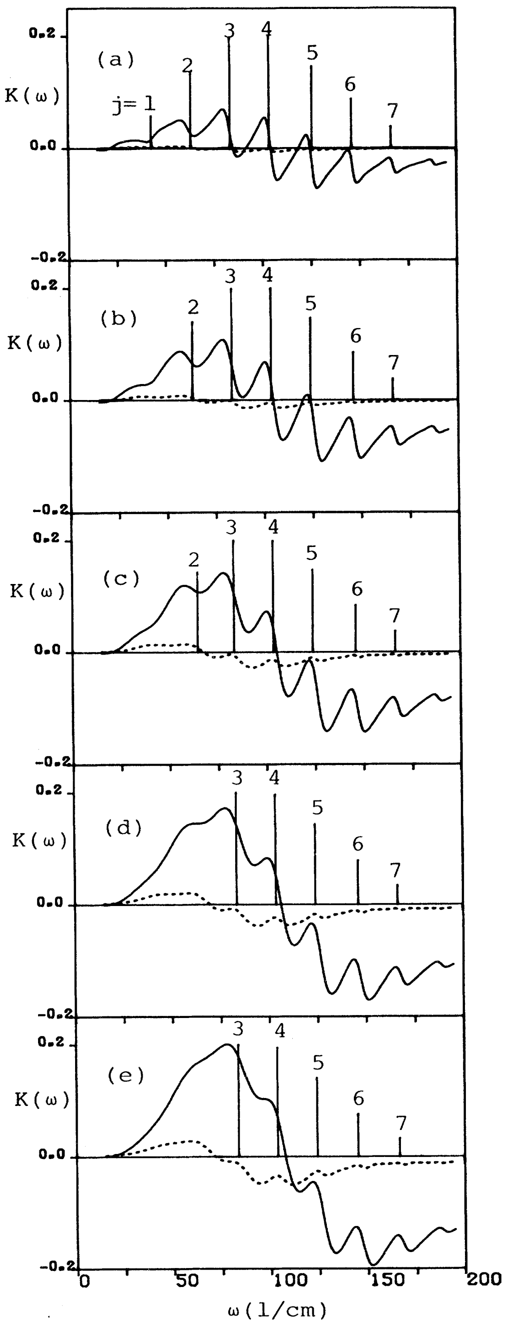

FIG. 2. Band shape functions $K_M(\omega)$ (· · · ·) and $K_I(\omega)$ (——) accounting for memory and nonadditivity effects for the HCl in dense Ar at $T = 162.5$ K and at different densities: (a) $\rho = 100$ amagat; (b) $\rho = 200$ amagat; (c) $\rho = 300$ amagat; (d) $\rho = 400$ amagat; (e) $\rho = 480$ amagat. $K_M(\omega)$ and $K_I(\omega)$ are obtained from Eqs. (3.11) and (4.2), respectively, with parameters in Table I. Vertical lines indicate the positions and the relative intensities of some well-resolved theoretical rotation lines.

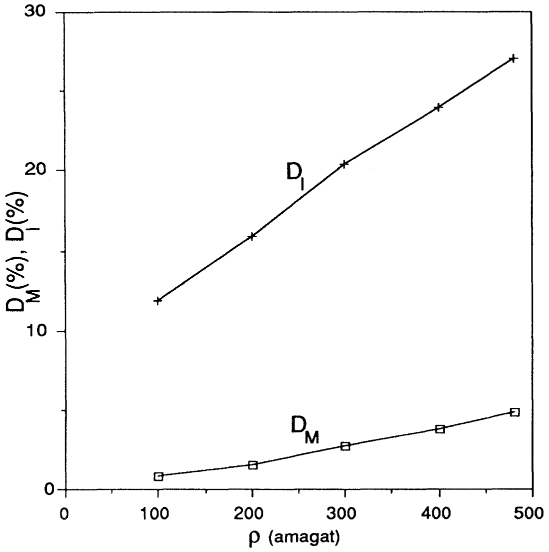

FIG. 3. Parameters D_M, Eq. (3.12), and D_I, Eq. (4.3), measuring memory and nonadditivity effects, respectively, for the HCl-Ar system at $T=162.5$ K vs the Ar density.

values must be compared to unity, accordingly Eq. (3.14). In this figure, it is observed that the high rotational transitions fulfill condition (3.14) better than the low ones, and so the basic resonances are closer to the Markovian shape when j increases, giving the obtained behavior $K_M(\omega)\rightarrow 0$ for high frequencies. Besides, the increasing importance of the memory effects when the Ar density increases can also be understood from the values of the Markovian condition $\tilde{\Gamma}^M_{j+1,j}\tilde{t}_c \ll 1$. In this figure, it is observed that, at fixed j, $\tilde{\Gamma}^M_{j+1,j}\tilde{t}_c$ gets its maximum deviation from Markovian condition when the density gets the maximum value of 480 amagat. At this density, the system presents the biggest memory effects. Such a behavior is corroborated by previous studies of some of us, where values of the Markovian condition $\tilde{\Gamma}^M_{j+1,j}\tilde{t}_c$ greater than those reported here were obtained for the same system but at higher densities, using both the stochastic model considered in this work and a dynamical quasiharmonic model [14]. For example, for HCl in liquid Ar at 105 K, $\tilde{\Gamma}^M_{1,0}t_c$ was found to be greater than 0.7 with both models [9,14], whereas the greatest value here obtained for the same parameter is less than 0.4.

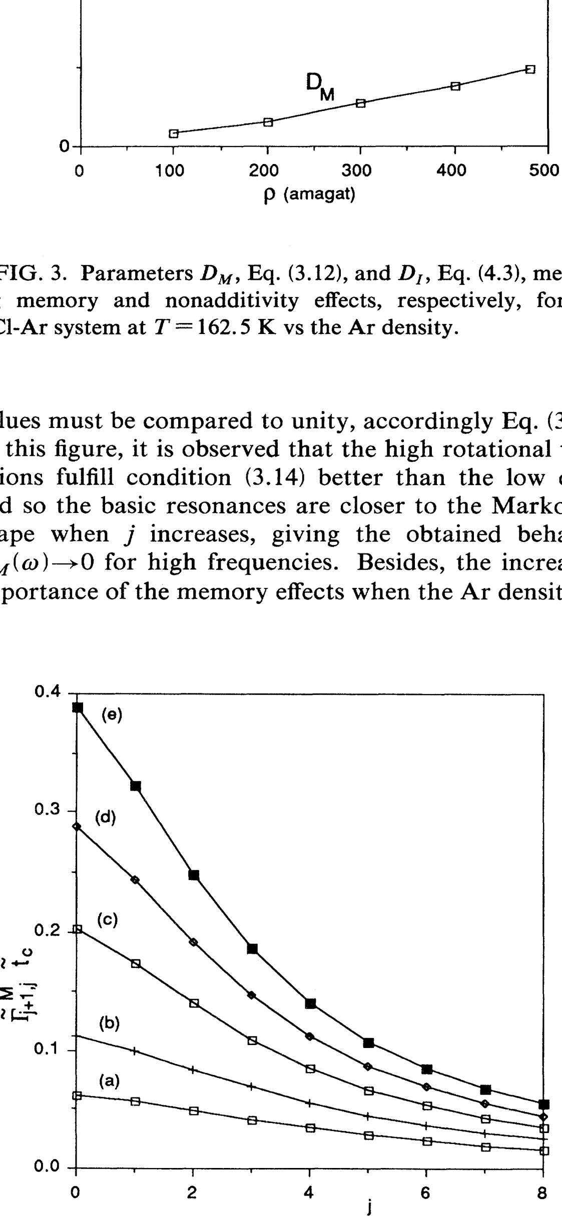

FIG. 4. Reduced parameter $\tilde{\Gamma}^M_{j+1,j}\tilde{t}_c$, Eq. (3.14), vs the rotational quantum number j for HCl in Ar dense at $T=162.5$ K: (a) $\rho=100$ amagat; (b) $\rho=200$ amagat; (c) $\rho=300$ amagat; (d) $\rho=400$ amagat; (e) $\rho=480$ amagat.

IV. NONADDITIVITY EFFECTS

The existence of cross correlations between different transition lines, due to the off-diagonality of the TTOC relaxation superoperator $W(t)$ or its Markovian limit R introduces nonadditivity effects with reference to the additive superposition of basic resonances of the secular contribution. In the study of these effects we follow the same procedure as the one used in the preceding for the memory effects: first, we present a qualitative analysis, and then we present a quantitative one.

In order to account for the spectral modifications for each frequency, due to the line coupling effects in the pure rotational infrared spectrum, we introduce a band shape function $K_I(\omega)$ defined as

$$K_I(\omega)=\alpha(\omega)-\alpha_0(\omega) \tag{4.1}$$

which, assuming the smallness of the memory effects obtained in Sec. III for all frequencies and densities, becomes

$$K_I(\omega)\approx\alpha^M(\omega)-\alpha_0^M(\omega) \tag{4.2}$$

as the appropriate Markovian band function which takes into account the mixing or nonadditivity effects.

For our system, $K_I(\omega)$ is plotted in Fig. 2 (solid line), where the importance of overlapping effects should be obtained from deviations from zero [note that $\alpha(\omega)$ is always less than unity and, thus, the computed values of $K_I(\omega)$ are numerically significant]. A first glance at this figure shows that the mixing effects are very important for all considered densities and that they become more relevant when the Ar density increases. In all cases, the interference contribution, as a whole, implies an enhancement of the absorption (i.e., constructive interference) in the low-frequency side and a reduction of the absorption (i.e., destructive interference) in the high-frequency side (note that the intensity transfer must be conservative in the absence of induction absorption). This pattern is sometimes explained as super-Lorentzian (sub-Lorentzian) behavior in the low (high) part of the spectrum [1–3].

A closer inspection of Fig. 2 reveals some other noticeable facts. At low densities (100, 200 amagat), the band shape function $K_I(\omega)$ vanishes ($K_I=0$) near the centers of stronger lines, $j=3,4,5$ (see Fig. 1) while deviations from zero occur only for weaker lines, $2>j>6$, presenting its extremal values into the windows between lines (troughs). Moreover, the observed oscillatory behavior of $K_1(\omega)$ gradually disappears when going from low densities to high densities (400, 480 amagat), especially in the low-frequency side. Such a behavior is in remarkable agreement with the results reported by Bulanin *et al* [1] for the $R(2)$-$R(10)$ rotational lines of the CO-H_2 system at $T=78$ K (see Fig. 9 in Ref. [1]), using a theory of line mixing based on Markov approximation and on the strong collision model. The existence of these oscillations in vibration-rotation bands was later confirmed by Cousin *et al.* [2] studying the CO_2-N_2 and CO_2-CO_2 systems at 296 K with the exponential-gap law model.

We recall attention to the fact that the factor $K_M(\omega)$ [Eq. (3.12) and dotted lines in Fig. 2] in accounting for the memory effects, presents a very similar qualitative behavior to $K_I(\omega)$ although the numerical values are much less significant. This fact shows the stronger importance of the nonadditivity effects in studying the spectrum of small polar diatomic molecules dissolved in dense nonpolar media in contrast with the smaller quantitative importance of the memory effects.

The quantitative study of the nonadditivity effects is made from the parameter

$$D_I=\int|\alpha^M(\omega)-\alpha_0^M(\omega)|d\omega\Big/\int\alpha^M(\omega)d\omega$$
$$=\int|K_I(\omega)|d\omega\Big/\int\alpha^M(\omega)d\omega \qquad (4.3)$$

which gives a measure of the influence of these effects. The values obtained for this parameter given in Table I and plotted in Fig. 3, showing the importance of the nonadditivity effects at all Ar densities considered here [the integrals appearing in (4.3) are also performed over the reported experimental range of frequencies]. As can be seen in this figure, D_I varies approximately linearly with the Ar density and the interference effects are much more relevant than the corresponding memory effects for all densities.

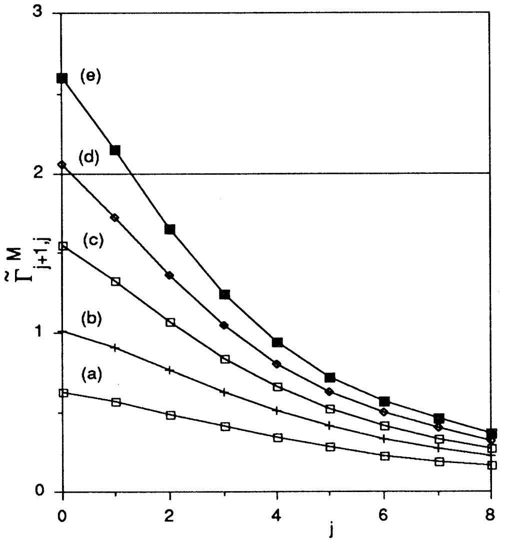

FIG. 5. Same as Fig. 4, but for the reduced half-widths $\tilde{\Gamma}^M_{j+1,j}$.

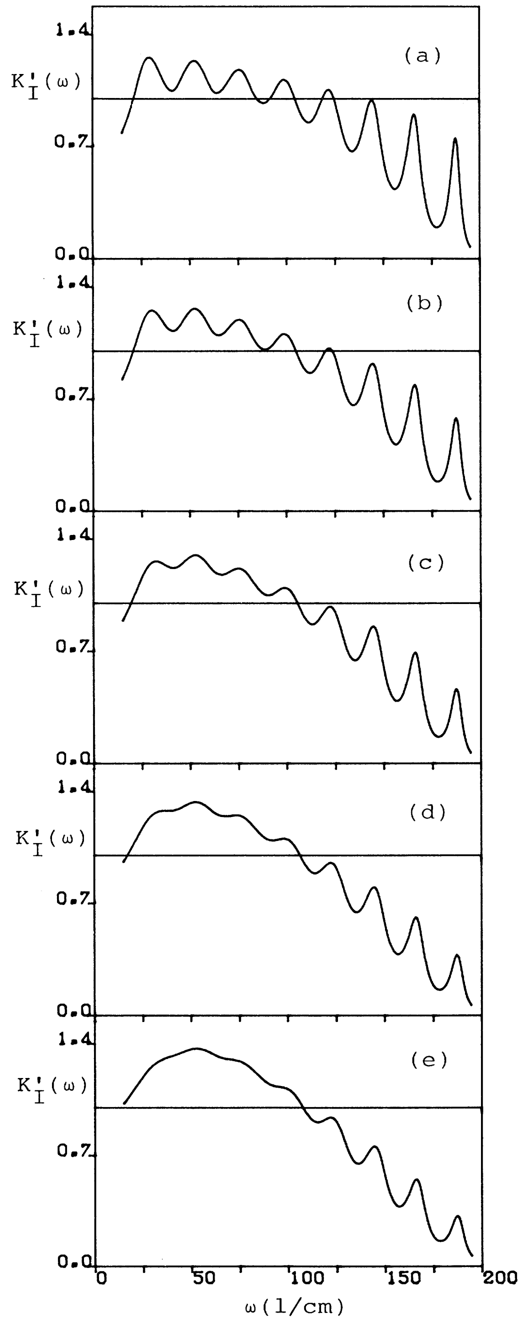

FIG. 6. The band-correction function $K_I'(\omega)$, Eq. (4.6), for the far-infrared spectra of HCl in dense Ar at $T=162.5$ K with parameters given in Table I: (a) $\rho=100$ amagat; (b) $\rho=200$ amagat; (c) $\rho=300$ amagat; (d) $\rho=400$ amagat; (e) $\rho=480$ amagat.

Some conclusions on the j dependence of the nonadditivity effects can be obtained from Eq. (2.10). This equation shows that the interference contribution depends on the overlapping between two resonances through the products $\Lambda_{fi}(\omega)\Lambda_{f'i'}(\omega)$, i.e., the importance of these effects is related to the linewidths of the resonances and to the distance between them. In the TTOC non-Markovian theory, a simple relation between widths and resonance distances is not easy to obtain since the widths, given by $\text{Re}W_{fi,f'i'}(\omega)$, are ω dependent [see Eq. (2.11)]. However, in the Markovian limit, each basic resonance $\Lambda_{fi}(\omega)$ becomes a Lorentzian line $\Lambda_{fi}^{M}(\omega)$ given by Eq. (3.7). From this equation it is obvious that

$$\text{Re}\Lambda_{j'j}^{M}(\omega)=\Gamma_{j'j}^{M}/\{[\omega-(\omega_{j'j}+\Delta_{j'j}^{M})]^2 +(\Gamma_{j'j}^{M})^2\} . \tag{4.4}$$

So, each Lorentzian line is centered at $\omega_{j'j}+\Delta_{j'j}^{M}$, having a half-width given by the ω-independent parameter $\Gamma_{j+1,j}^{M}$. On the other side, the shifts $\Delta_{j'j}^{M}$ are much less than the corresponding $\Gamma_{j+1,j}^{M}$, for all Ar densities considered. Then, from Eq. (4.4) the distance between two adjacent resonances is $|\omega_{j+2,j+1}-\omega_{j+1,j}|=2B$ (cm^{-1}) and therefore a sufficient condition to neglect the overlapping between resonances is

$$\tilde{\Gamma}_{j+1,j}^{M} \ll 2 . \tag{4.5}$$

Behavior of $\tilde{\Gamma}_{j+1,j}^{M}$ versus j is plotted in Fig. 5. A simple analysis of the numerical deviations of $\tilde{\Gamma}_{j+1,j}^{M}$ from 2 shows that (a) the low j-rotational transitions present strong overlapping while the high j-rotational transitions present weak overlapping and (b) these effects increase as the Ar density grows. In agreement with the above behavior, previous studies of the far-infrared absorption coefficient of HCl and DCl in rare-gas liquids and liquid SF$_6$ have found that the interference contribution is greater than those here obtained for HCl in dense fluid Ar. $\tilde{\Gamma}_{1,0}^{M}$ was found to be approximately 4 for HCl in Ar liquid [9,14] and 8 for HCl and DCl in liquid SF$_6$ [11], while in the present work for HCl in dense Ar, $\tilde{\Gamma}_{1,0}^{M}$ is always less than 2.7.

In the analysis of vibration-rotation spectra, it is a common practice to use a dimensionless band-correction shape in order to account for the spectral modifications due to the line coupling effects which is different from the one we use. Some authors [1–3] introduce a dimensionless band-correction function, $K_I'(\omega)$, defined as the ratio of the calculated absorption coefficient to the Lorentz absorption. In our notation, $K_I'(\omega)$ is

$$K_I'(\omega)=\alpha^{M}(\omega)/\alpha_0^{M}(\omega) . \tag{4.6}$$

For completeness, we have plotted $K_I'(\omega)$ for our system in Fig. 6, where the importance of overlapping effects should now be obtained from deviations from unity. All essential qualitative characteristics above mentioned on the behavior of $K_I(\omega)$, solid lines in Fig. 2, can be checked also in Fig. 6. In comparing Fig. 6 in this work with the results obtained by these authors for vibration-rotation bands, it must be taken into account that our results agree qualitatively with those when only the R branch is considered. No quantitative agreement is expected since the systems studied are different.

V. SUMMARY

Applying a non-Markovian theory we have obtained the dipolar absorption coefficient of HCl in dense Ar at $T=162.5$ K and at five Ar densities: 100, 200, 300, 400, and 480 amagat. The spectrum is given by a sum of two terms. The first one, called the secular contribution, appears as an additive superposition of basic resonances which become Lorentzian in the Markovian limit. The second one, called the interference contribution, incorporates a correcting factor due to the existence of cross correlations between rotational transitions. This nonadditivity effect arises from the off-diagonality of the superoperator describing the rotational relaxation of the diatomic molecule.

Both secular and interference contributions are given in terms of time correlation functions of the intermolecular potential. Assuming that the time evolution of this potential is described by an Ornstein-Uhlenbeck stochastic process, these correlation functions present an exponential time decay, and so the calculated spectra depend on only two phenomenological parameters: the mean-square interaction strength λ^2 and its correlation time t_c. These parameters are obtained by fitting to the experimental spectra of Frenkel, Gravesteyn, and van der Elsken [12].

We have presented a numerical analysis of the influence of both non-Markovian and nonadditivity effects for the system under study. We conclude that the former are not very significant, while the latter are very important in the calculation of the theoretical spectra, inducing an important increase in the absorption (super-Lorentzian behavior or constructive interference) for the low-frequency side and an important decrease (sub-Lorentzian behavior or destructive interference) in the high-frequency side, even for the low Ar densities considered here.

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