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Indirect dephasing model and librovibrational spectra of diatomics trapped in rare gas matrices. Application to the case of CO/Ar

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In the present work, the theoretical scheme applied to the study of hindered rotation of molecular impurity in rare gas matrices [J. Chem. Phys. **77**, 1757 (1982)] is extended to librational motion. The librational motions are considered as the intermediate modes in the process of vibrational dephasing. The effect of libron–phonons coupling is formally calculated for a three dimensional lattice. The case of CO dispersed in Ar is examined within the frame of a simple cubic lattice. Despite the oversimplified model, the computed temperature dependence of the vibrational absorption band adequately reproduces the observed experimental trend.

I. INTRODUCTION

Direct dephasing processes are responsible in many cases for the broadening of vibrational modes in liquid and solid media. In the infrared area, they are the consequence of adiabatic fluctuations of the vibrational energy levels coupled to a thermal bath.[1–6] In some cases however, other degrees of freedom are involved. They correspond usually to low frequency modes coupled to both vibrational and thermal bath modes. The importance of these contributions has been discussed by Fischer and Laubereau[7] and later reformulated by various authors.[8–13]

In the present work we consider the case of vibrational dephasing through librational modes perturbed by the phonon modes of a three dimensional lattice.

The effects of vibrational dephasing on the band shape of the IR absorption band ($v = 0 \rightarrow v = 1$) are displayed by calculating the coefficient of absorption within the framework of the linear response theory following a procedure developed for the case of the hindered rotation of HCl in Ar[14] (Hereafter referred to as I.) General formulas are derived for a molecular impurity embedded in a three dimensional lattice and the role of librational anharmonicity is discussed.

These formal results are tentatively applied to the case of CO trapped in Ar,[15–21] using a rather drastic approximation for the intermolecular potential. Our work differs from previous interpretations[22–24] since emphasis is placed on the role of phonon coupling and special attention is paid to the temperature dependence of the absorption line within the vibrational region. Recent results seems to rule out the possibility of hindered rotation, the strong absorption observed at 2138.56 cm^{-1} by Dubost *et al.*[21] is attributed to the vibrational transition $v = 0 \rightarrow v = 1$, whereas the superposed broad feature is attributed to a librovibrational transition $v = 0$, $l = 1 \rightarrow v = 1$, $l = 1$, its dependence on temperature may result from a strong interaction between the librational and lattice modes.

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II. THEORY

A. Model

Basically, our model consists of a diatomic molecule embedded in a cfc perfect lattice, the host molecule occupying a substitutional site. It is assumed that the dilution of the trapped species is very high and that bulk properties are little affected by the impurities. In particular, lattice modes as well as their density of states remain unchanged by molecular inclusion. Inside its cage, the molecular impurity is assumed to librate around some symmetry axis as is strongly suggested by the spectral analysis mentioned above.[21,25] But since several symmetry axes exist in a cage the question arises if the molecule may jump from one axis to an other. According to the frequency of this jumping mode, it can eventually be coupled to the librational mode and be responsible for serious perturbations. Tunnel effects may also be invoked. In the absence of experimental confirmation of such effects, we assume that vibrational and jumping time scale are very different. Consequently, the residence time of the molecule in the vicinity of a given axis is assumed to be so long that the phonon–libration interaction may be dealt with in a referential system which assumes this axis as the z axis. The molecular center of mass is at the center of the cage which is taken as the origin of the coordinate system.

Inside this system the molecular dipole moment has projections along the coordinate axes given by

$$M_\mu = M(r)\mathbf{u} \cdot \mathbf{\mu} \equiv M(r)\Phi_\mu(\theta,\phi), \tag{1}$$

where $\mathbf{\mu}$ (100, 010, 001) and $\mathbf{u}$ are unit vectors on the coordinate axis and the internuclear axis. r is the internuclear distance and Φ_μ the director cosine which depend on the angular coordinates θ,ϕ of the molecular axes (Fig. 1).

The Hamiltonian associated with the molecular impurity and the host crystal is split into three parts:

$$H = H_M + H_B + V. \tag{2}$$

H_M, H_B, and V represent the molecule, the bath, and the interaction, respectively.

The molecular impurity is considered as a multilevel system and its Hamiltonian is projected into a subspace of
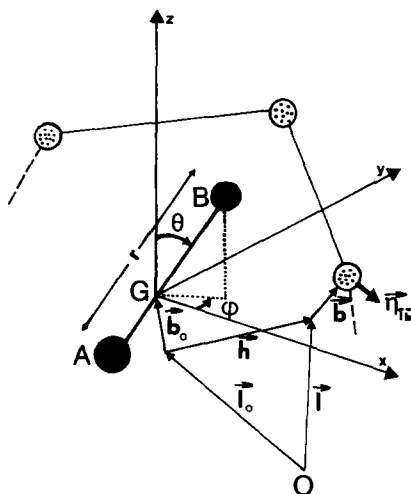
FIG. 1. Geometrical arrangements of the molecular impurity A–B and cage atoms in the host lattice. The molecule A–B lies inside the unit cell l_0 at site b_0. Nearest neighbors are inside the unit cell l at site b, and $h = l - l_0$.

vibrational and librational states $|vl\rangle$ (Fig. 2). If these states are uncoupled, then

$$H_M = \sum_{v,l}(E_v + \mathcal{E}_l)|vl\rangle\langle vl|. \tag{3}$$

The bath Hamiltonian represents a cfc lattice

$$H_B = \sum_{\tau}\hbar\omega_{\tau}(a_{\tau}^+ a_{\tau} + 1/2). \tag{4}$$

$\hbar$ is the Plank's constant, τ is a symbol which represents both the wave vector $\mathbf{k}$ and the mode p ($\tau \equiv \mathbf{k},p$ and $-\tau \equiv -\mathbf{k},p$), a_{τ}^+ and a_{τ} are the creation and annihilation operators for a given τ (vector $\mathbf{k}$ and mode p). More attention must be paid to the construction of the interaction term V. Within the framework of the previously discussed hypothesis (libration around one axis only), V depends essentially on R, θ and η_{lb} (the displacements of atom b in the unit cell l). V can be expanded in a Taylor series with respect to these variables. If the interactions are restricted to one phonon process, the relevant contributions are $\theta\eta_{lb}$, $r^2\theta\eta_{lb}$, and $r^2\theta$. This latter term is a pure dephasing contribution leading only to a shift of both vibrational and librational levels. The magnitude of this contribution is small and will be neglected in what follows. The $r^2\theta\eta_{lb}$ term is a mixture of pure dephas-
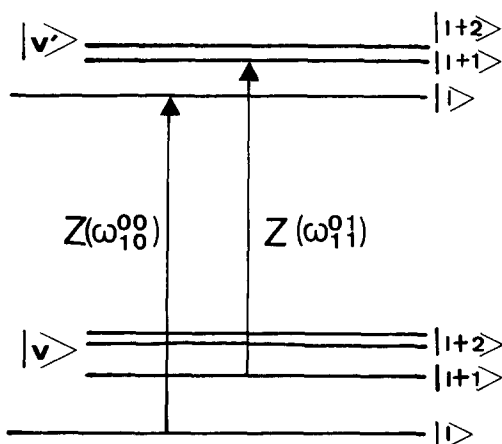

FIG. 2. Energy levels of the vibro-librational molecular system. Vertical arrows designate the transitions considered.

ing of vibrational mode via the libron–phonon exchange. The dependence of the exchange librational mode on the lattice mode is also expressed by the direct coupling term $\theta\eta_{lb}$. Direct coupling of vibrational and lattice modes is neglected since this would require the participation of multiphonon processes which are rather inefficient at the temperature considered.[26] V is then reduced to the sum of two terms

$$V(r\theta\eta_{lb}) = \theta\sum_{l,b}\left(\frac{\partial^2 V}{\partial\theta\partial\eta_{lb}}\right)\eta_{lb}$$

$$+ \frac{1}{2}r^2\theta\sum_{lb}\left(\frac{\partial^4 V}{\partial r^2\partial\theta\partial\eta_{lb}}\right)\eta_{lb}. \tag{5}$$

A more convenient expression for later calculations is obtained by using weighted coordinates (μ and I are the reduced mass and moment of inertia of the diatom impurity)

$$R = (\mu)^{1/2}r, \quad \Theta = (I)^{1/2}\theta. \tag{6}$$

as well as creation and annihilation operators. These are related to the displacement vectors η_{lb} through the relation

$$\eta_{lb} = i(\hbar/2m_bN)^{1/2}\sum_{\tau}(\omega_{\tau})^{-1/2}$$

$$\times\epsilon_{-\tau}(b)e^{-i\mathbf{k}\cdot\mathbf{l}}(a_{-\tau} - a_{\tau}^+), \tag{7}$$

where $\epsilon_{\tau}(b)$ is the eigenvector of the dynamic matrix associated to the imperturbed lattice and m_b the mass of atom b in the unit cell l (Fig. 1). It is also convenient to define the vectors $\mathbf{D}_{lb}^{(n)}$, $n = 2,4$.

$$\mathbf{D}_{lb}^{(2)} = \left(\frac{\partial^2 V}{\partial\Theta\partial\eta_{lb}}\right)_0 \quad\text{and}\quad \mathbf{D}_{lb}^{(4)} = \left(\frac{\partial^4 V}{\partial R^2\partial\Theta\partial\eta_{lb}}\right)_0. \tag{8}$$

then the summations in Eq. (5) are readily transformed

$$\sum_{lb}\mathbf{D}_{lb}^{(n)}\cdot\eta_{lb} = i(\hbar/2\pi)^{1/2}\sum_{\tau}e^{-i\mathbf{k}\cdot\mathbf{l}_0}\sum_b(m_b\omega_{\tau})^{-1/2}$$

$$\times\left(\sum_h \mathbf{D}_{l_0+h,b}^{(n)}\cdot\epsilon_{-\tau}(b)e^{-i\mathbf{k}\cdot\mathbf{h}}\right)(a_{-\tau} - a_{\tau}^+)$$

$$= i(N)^{-1/2}\sum_{\tau}\Lambda_{\tau}^{(n)}(a_{-\tau} - a_{\tau}^+) \tag{9}$$

with

$$\Lambda_{\tau}^{(n)} = \sum_b(\hbar/2m_b\omega_{\tau})^{1/2}\sum_h\{\mathbf{D}_{l_0+h,b}^{(n)}\epsilon_{-\tau}(b)e^{-i\mathbf{k}\cdot\mathbf{h}}\}e^{-i\mathbf{k}\cdot\mathbf{l}_0}. \tag{10}$$

In this expression $\mathbf{h} = \mathbf{l} - \mathbf{l}_0$, where $\mathbf{l}$ designates any unit cell, whereas $\mathbf{l}_0$ refers to the unit cell containing the molecular impurity (Fig. 2). The summation over $\mathbf{h}$ is usually restricted to the nearest neighbor shell surrounding the impurity. Taking into account these successive transformations, the interaction operator becomes

$$V = i\Theta N^{-1/2}\sum_{\tau}(\Lambda_{\tau}^{(2)} + 2^{-1}\cdot R^2\Lambda_{\tau}^{(4)})(a_{-\tau} - a_{\tau}^+). \tag{11}$$

Projecting into the subspace $|vl\rangle$ leads to the expression

$$V = iN^{-1/2}\sum_{\tau}\sum_{\substack{vv'\\ll'}}\langle l\Theta l'\rangle$$

$$\times\{\delta_{vv'}\Lambda_{\tau}^{(2)} + \langle vR^2v'\rangle\Lambda_{\tau}^{(4)}\}(a_{-\tau} - a_{\tau}^+)|vl\rangle\langle v'l'| \tag{12}$$

under the assumption that the vibrational mode is purely harmonic, $\langle vR^2v' \rangle \equiv \langle R^2 \rangle_{vv'} = \langle R^2 \rangle_{vv} \delta_{vv'}$ and, consequently, Eq. (12) is reduced to

$$V = iN^{-1/2} \sum_{\tau} \sum_{vll'} \langle l\Theta l' \rangle \{ \Lambda_{\tau}^{(2)} + \langle R^2 \rangle_{vv} \Lambda_{\tau}^{(4)} \}$$

$$\times (a_{-\tau} - a_{\tau}^+) |vl\rangle \langle vl'|. \tag{13}$$

B. Absorption coefficient. Generality

Following I, the absorption coefficient is given by

$$\sigma(\omega) = (4\pi/\hbar)\omega |f_0|^2 \sum_{\mu,\nu} e_\mu e_\nu \, \text{Im} \, G_{\mu\nu}(\omega), \tag{14}$$

where ω, f_0, and e_μ ($\mu = x, y, z$) are, respectively, the frequency, electric field, and polarizability vector of the incoming wave. All these quantities are interconnected by the relation: $\epsilon(t) = ef_0 \exp i\omega t + \text{c.c.}$ As for Im $G_{\mu\nu}(\omega)$, it is the imaginary part of the function $G_{\mu\nu}(\omega) = \langle\langle M_\mu, M_\nu \rangle\rangle$ which is the solution of the set of coupled equations given in Eq. (4) in I. Finally M_μ are the components of the total dipole moment operator. Assuming the isotropy of light and averaging over the e_μ, only the M_z component is left. If the dependence of M_z over the lattice coordinates is neglected and if it is projected into the $|vl\rangle$ subspace, then

$$M_z = \sum_{\substack{vv' \\ ll'}} |vl\rangle \langle vl M_z v'l' \rangle \langle v'l'| \tag{15}$$

so that $G_{zz}(\omega)$ is developed over a set of $Z(\omega|_{v'l'}^{vl})$ functions

$$G_{zz}(\omega) = \sum_{\substack{vv'\bar{v}\bar{v}' \\ ll'\bar{l}\bar{l}'}} M_z(_{v'l'}^{vl}) M_z(_{\bar{v}\bar{l}}^{\bar{v}'\bar{l}'}) \cdot Z(\omega|_{v'l'}^{vl}), \tag{16}$$

where

$$Z(\omega|_{v'l'}^{vl}) = \langle\langle |vl\rangle\langle v'l'|, \bar{p} \rangle\rangle \tag{17}$$

and $\bar{p} = |\bar{v}\bar{l}\rangle\langle\bar{v}'\bar{l}'|$. This projector plays a passive role in the formation of the set of Eq. 4 in I, written for the $Z(\omega|_{ll'}^{vv'})$ functions. It is only present as a constant term, which for the first equation ($n = 0$), is readily calculated through the formula

$$(\hbar/2\pi)\langle [|vl\rangle\langle v'l'|, |\bar{v}\bar{l}\rangle\langle\bar{v}'\bar{l}'|] \rangle$$

$$= (\hbar/2\pi)Sp[|vl\rangle\langle v'l'|, |\bar{v}\bar{l}\rangle\langle\bar{v}'\bar{l}'|]e^{-\beta H}. \tag{18}$$

H is the Hamiltonian given in Eq. (2) and $\beta = 1/kT$, k is Boltzmann's constant, and T the absolute temperature. When $H = H_M + H_B$, this reduces to $(N_v n_l - N_{v'} n_{l'}) \times \delta_{v'\bar{v}} \delta_{v\bar{v}'} \delta_{l\bar{l}'}$, where N_v and n_l are the populations of the uncoupled states $|v\rangle$ and $|l\rangle$. If the interaction term is included in the Hamiltonian, some of the $|v\rangle$ and $|l\rangle$ states may be coupled and selection rules removed. Evaluation of these constants may be performed by a perturbation calculation. (The notation $p = |vl\rangle\langle v'l'|$, $p^* = |v'l'\rangle\langle vl|$, $\bar{p} = |\bar{v}\bar{l}\rangle\langle\bar{v}'\bar{l}'|$... will sometimes be used.)

A crude approximation consists, as in I, of neglecting all terms above the zero order. Under these conditions the Z functions depend only on four indices v,l,v',l' and the coefficient of absorption can then be reduced to

$$\sigma(\omega) = (4\pi/\hbar)\omega |f_0|^2 \sum_{\substack{vv' \\ ll'}} |M_z(_{v'l'}^{vl})|^2 \, \text{Im} \, Z(\omega_{v'l'}^{vl}), \tag{19}$$

where each function Z can be considered as associated with a transition $vl \rightarrow v'l'$.

C. Equation of motion of the $Z(\omega|_{v'l'}^{vl})$

The first equation generated from the master equation (4) in I is ($p = |v'l'\rangle\langle vl|$):

$$\hbar\omega \ll |vl\rangle\langle v'l'|,p\rangle\rangle = (\hbar/2\pi)C(_{v'l'}^{vl})$$

$$+ \langle\langle [|vl\rangle\langle v'l'|,H],p\rangle\rangle. \tag{20}$$

When the commutator is worked out, new functions of higher order are generated. In particular, from the first commutator we obtain the function $\langle\langle Q_\tau |vl\rangle\langle v'l'|,p\rangle\rangle$ and $\langle\langle P_{-\tau} |vl\rangle\langle v'l'|,p\rangle\rangle$ for which an equation similar to Eq. (20) is written and which, in turn, provides new functions $\langle\langle Q_\tau Q_{\tau'} vl\rangle\langle v'l'|,p\rangle$ and $\langle\langle P_{-\tau}Q_{\tau'} |vl\rangle\langle v'l'|,p\rangle\rangle$ as well as $\langle\langle Q_{\tau'} P_{-\tau} |vl\rangle\langle v'l'|,p\rangle\rangle$. At this stage, use is made of the random phase approximation (RPA) to uncouple the equation. The essence of the procedure is outlined in the following example:

$$\langle\langle (a_{-\tau} - a_\tau^+)(a_{-\tau'} - a_{\tau'}^+) |vl\rangle\langle v'l'|,p\rangle\rangle$$

$$= \langle (a_{-\tau} - a_\tau^+)(a_{-\tau'} - a_{\tau'}^+)\rangle \langle\langle |vl\rangle\langle v'l'|,p\rangle\rangle$$

$$= (n_\tau + \tfrac{1}{2})\delta_{\tau,-\tau'} \langle\langle |vl\rangle\langle v'l'|,p\rangle\rangle, \tag{21}$$

where

$$n_\tau \equiv n(\omega_\tau) = (e^{\beta\hbar\omega_\tau} - 1)^{-1}. \tag{22}$$

For a given $v \rightarrow v'$ transition, the equation may be conveniently written in the $(1 \times 1')$ subspace. For later purposes we introduce some new notations:

$$\hbar\Omega_{ll'} = E_{v'} - E_v + \mathscr{E}_{l'} - \mathscr{E}_l, \tag{23}$$

$$Z_{ll'} = Z(\omega|_{v'l'}^{vl}), \tag{24}$$

$$Q_{ll'} = \langle\langle (a_{-\tau} - a_\tau^+) |vl\rangle\langle v'l'|,p\rangle\rangle, \tag{25}$$

$$P_{ll'} = \langle\langle (a_{-\tau} + a_\tau^+) |vl\rangle\langle v'l'|,p\rangle\rangle. \tag{26}$$

Each of these functions satisfies an equation of motion which contains a constant term later designated by $C_{ll'}^Z$, $C_{ll'}^Q$, and $C_{ll'}^P$. Finally two more quantities need to be introduced:

$$m(ll') = \langle l\Theta l' \rangle = m(l'l), \tag{27}$$

$$\Gamma_\tau(v) = N^{-1/2}(\Lambda_\tau^{(2)} + \langle R^2 \rangle_{vv} \Lambda_\tau^{(4)}). \tag{28}$$

Using these notations and after application of the RPA approximation, the set of Eq. (4) in I is reduced to a 3×3 system for the unknown functions Z, Q, and P:

$$\hbar(\omega - \Omega_{ll'})Z_{ll'} = C^Z + i\sum_{\tau L} \{\Gamma_\tau(v')Q_{lL}m(Ll') - \Gamma_\tau(v)m(lL)Q_{Ll'}\},$$

$$\hbar(\omega - \Omega_{ll'})Q_{ll'} = \hbar\omega_\tau P_{ll'} - i(2n_\tau + 1)\sum_L \{\Gamma_{-\tau}(v')Z_{lL}m(Ll') - \Gamma_{-\tau}(v)m(lL)Z_{Ll'}\}, \tag{29}$$

$$\hbar(\omega - \Omega_{ll'})P_{ll'} = \hbar\omega_\tau Q_{ll'} - i\sum_L \{\Gamma_{-\tau}(v')Z_{lL}m(Ll') + \Gamma_{-\tau}(v)m(lL)Z_{Ll'}\}.$$

The functions P and Q can be eliminated by substitution, a procedure leading to the formation of a linear system of equations for the $(1 \times 1')$ functions $Z_{ll'}$.

$$\hbar(\omega - \Omega_{ll'})Z_{ll'} = C^Z + \hbar^{-1}\sum_{\tau L}\alpha_\tau^+ (lL)\Gamma_\tau(v')\Gamma_{-\tau}(v')\sum_{\bar{L}}m(\bar{L}L)Z_{\bar{l}\bar{L}}m(Ll')$$

$$- \hbar^{-1}\sum_{\tau L}\alpha_\tau^-(lL)\Gamma_\tau(v')\Gamma_{-\tau}(v)\sum_{\bar{L}}m(l\bar{L})Z_{\bar{L}L}m(Ll')$$

$$- \hbar^{-1}\sum_{\tau L}\alpha_\tau^+(Ll')\Gamma_\tau(v)\Gamma_{-\tau}(v')\sum_{\bar{L}}m(lL)Z_{L\bar{L}}m(\bar{L}l')$$

$$+ \hbar^{-1}\sum_{\tau L}\alpha_\tau^-(Ll')\Gamma_\tau(v)\Gamma_{-\tau}(v)\sum_{\bar{L}}m(lL)Z_{\bar{L}l'}m(L\bar{L}), \tag{30}$$

where

$$\alpha_\tau^\pm(L\bar{L}) = \frac{(2n_\tau + 1)(\omega - \Omega_{L\bar{L}}) \pm \omega_\tau}{(\omega - \Omega_{L\bar{L}})^2 - \omega_\tau^2}$$

$$= \frac{n_\tau + (1/2)(1 \pm 1)}{\omega - \Omega_{L\bar{L}} - \omega_\tau} + \frac{n_\tau + (1/2)(1 \mp 1)}{\omega - \Omega_{L\bar{L}} + \omega_\tau}.$$

The $Z_{ll'}$ functions involved in this linear system belong to a subspace of the functional (1×1) space defined by the structure of the matrix. When the dipole moment is represented in the basis of harmonic functions, each function with indices ll' generate eight functions: $l \pm 1, l' \pm 1; l, l' \pm 2; l \pm 2, l'$. In a space of finite dimensions, $l = l_1$ and $l' = l_2$, the dimension of the system is $l_1 \times l_2$. All functions in the system are weighted by factors depending on the matrix elements $m(ll')$ which in their turn depend on the librational anharmonicity. The mixing of the function $Z_{ll'}$ is then monitored by the librational anharmonicity. Each function corresponds to a transition $vl \to v'l'$ whose profile is proportional to $\omega\, \mathrm{Im}\, Z_{ll'}$. In the absence of coupling, $Z_{ll'} \simeq (\omega - \Omega_{ll'})^{-1}$ and the profile reduces to a Dirac delta function. If the coupling is weak, a zero order solution is provided by keeping only the diagonal terms of Eq. (30),

$$Z_{ll'} = C^z\Big[\hbar(\omega - \Omega_{ll'}) + \hbar^{-1}\sum_\tau \{[\alpha_\tau^+(ll')\Gamma_\tau(v)\Gamma_\tau(v')$$

$$+ \alpha_\tau^-(ll')\Gamma_\tau(v')\Gamma_\tau(v)]m(ll)m(l'l')$$

$$- \sum_L [\alpha_\tau^+(lL)\Gamma_\tau(v')\Gamma_\tau(v')m(l'L)m(Ll')$$

$$+ \alpha_\tau^-(Ll')\Gamma_\tau(v)\Gamma_\tau(v)m(lL)m(Ll)]\}\Big]^{-1}. \tag{32}$$

Even in this simple approximation the band profile cannot be reduced to a simple form like the Lorentzian one. This limit is reached only when the summations over τ are independent of ω. Using formula (28), analytical expressions can be derived for products such as

$$\Gamma_\tau(\bar{v})\Gamma_\tau(\bar{v}') = N(\Lambda_\tau^{(2)}\Lambda_{-\tau}^{(2)} + \langle R^2\rangle_{\bar{v}\bar{v}}\Lambda_\tau^{(4)}\Lambda_{-\tau}^{(2)}$$

$$+ \langle R^2\rangle_{\bar{v}'\bar{v}'}\Lambda_\tau^{(2)}\Lambda_{-\tau}^{(4)}$$

$$+ \langle R^2\rangle_{\bar{v}\bar{v}}\langle R^2\rangle_{\bar{v}'\bar{v}'}\Lambda_\tau^{(4)}\Lambda_{-\tau}^{(4)}), \tag{33}$$

where $\bar{v}\,\bar{v}'$ designate either $v,v;v,v';v',v$ or v',v'. The expressions so derived are valid for any type of crystals and numerical calculations can be performed if both the dynamical matrix eigenvectors and second (or fourth) derivatives of the interaction potential are known. These latter constants are rather difficult to obtain since they require a high quality intermolecular potential. Practically, calculations can only be achieved within the framework of some approximation such as a continuum-like approximation where all derivatives may be considered as identical

$$\mathbf{D}_{lb}^{(i)} = \mathbf{D}^{(i)}. \tag{34}$$

In such a case, and for the cfc, crystal, manageable expressions are obtained (m = mass of the Ar atom):

$$\Lambda_\tau^{(i)}\Lambda_{-\tau}^{(i)} = \hbar(2Nm\omega_\tau)^{-1}(\mathbf{D}^{(i)} \cdot \mathbf{F}_\tau)(\mathbf{D}^{(i)} \cdot \mathbf{F}_{-\tau}), \tag{35}$$

$$\sum_{i \neq j}\Lambda_\tau^{(i)}\Lambda_{-\tau}^{(j)}$$

$$= \hbar(2Nm\omega_\tau)^{-1}[(\mathbf{D}^{(i)} \cdot \mathbf{F}_\tau) \cdot (\mathbf{D}^{(j)} \cdot \mathbf{F}_\tau) + \text{c.c.}] \tag{36}$$

with

$$\mathbf{F}_\tau = \sum_{b=0}^{3} f_k(\mathbf{b})\boldsymbol{\epsilon}_\tau^*(\mathbf{b}) \tag{37}$$

and a form factor $f_k(\mathbf{b})$ given by

$$f_k(\mathbf{b}) = (1 - e^{-i\mathbf{k}\cdot\mathbf{b}_\alpha})(1 - e^{-i\mathbf{k}\cdot\mathbf{b}_\beta}), \tag{38}$$

where $\mathbf{b}_\alpha$ and $\mathbf{b}_\beta$ are unit vectors in the $\alpha\beta$ plane which contains the vectors **1,2**, and **3**, respectively. **0** designates the origin of the cell. Further simplifications can be obtained when the case of a simple cubic crystal is considered since then $p = 1,2,3$, and the three eigenvectors are reduced to the three unit vectors $(1,0,0)$, $(0,1,0)$, and $(0,0,1)$, respectively. Under these conditions Eq. (32) reduces to

$$Z_{ll'} = C^Z\Big[\hbar(\omega - \Omega_{ll'}) + (2mN)^{-1}\sum_\tau \omega_\tau^{-1}g_\tau^2\Big\{[C_p(vv')$$

$$\times \alpha_\tau^+(ll') + C_p(v'v)\alpha_\tau^-(ll')]m(ll)m(l'l')$$

$$- \sum_L [C_p(v'v')\alpha_\tau^+(lL)m(l'L)m(Ll')$$

$$+ C_p(vv)\alpha_\tau^-(Ll')]m(lL)m(Ll)\Big\}\Big]^{-1} \tag{39}$$

with

$$g_\tau \equiv g_k = 1 + 2\sum_\alpha \cos \mathbf{k} \cdot \mathbf{1}_\alpha. \tag{40}$$

$\mathbf{1}_\alpha$ is the unit vector along the α direction ($\alpha = x,y,z$), and

$$C_p(\bar{v},\bar{v}') = (\mathbf{D}^{(2)} + \langle R^2\rangle_{\bar{v}\bar{v}}\mathbf{D}^{(4)})\boldsymbol{\epsilon}_\tau^*(\mathbf{D}^{(2)}$$

$$+ \langle R^2\rangle_{\bar{v}'\bar{v}'}\mathbf{D}^{(4)})\boldsymbol{\epsilon}_\tau. \tag{41}$$

The $C_p(\bar{v},\bar{v}')$ constants reflect the nature of the interactions terms included in the interaction potential [Eq. (5)] and, as could be expected, their vibrational dependance is entirely governed by the $\mathbf{D}^{(4)}$ term.

D. Absorption coefficient in the special case of a simple cubic lattice environment. A simulation of the case of CO/Ar

According to formula (19) the main ingredient in the expression of the absorption coefficient is the imaginary part of the $Z_{ll'}(\omega)$ function. In the special case considered here $Z_{ll'}(\omega)$ is given by Eq. (39) which can be written

$$Z_{ll'}(\omega) = C^z[\hbar(\omega - \Omega_{ll'}) + \phi(\omega|_{v'l'}^{vl})]^{-1}, \qquad (42)$$

where $\phi(\omega|_{v'l'}^{vl})$ is the third term in the denominator of Eq. (39). Im $Z_{ll'}(\omega)$ may be readily obtained by application of the limiting procedure:

$$\text{Im } Z_{ll'}(\omega) = \lim_{\epsilon \to +0}\{Z_{ll'}(\omega + i\epsilon) - Z_{ll'}(\omega - i\epsilon)\} \qquad (43)$$

and use of the asymptotic formula

$$\lim_{\epsilon \to +0}(x \pm i\epsilon - x_0)^{-1} = P(x - x_0)^{-1} \mp i\pi\delta(x - x_0), \qquad (44)$$

which gives the decomposition of the function $(x - x_0)^{-1}$ at the pôle x_0. P denotes the Cauchy's principal value. For $\phi(\omega)$ this procedure is applied to the function $\alpha_{kp}^{\pm}(ll')$ as given by Eq. (31). As a result

$$\phi(\omega \pm i\epsilon) = \phi_R(\omega) \mp i\pi\phi_I(\omega) \qquad (45)$$

and

$$\sigma(\omega) = (8\pi/\hbar)|f|^2\omega\sum_{\substack{vl \\ v'l'}}|M_z(_{v'l'}^{vl})|^2 C^z(_{v'l'}^{vl})\phi_I(\omega|_{v'l'}^{vl})$$

$$\times\{[\hbar(\omega - \Omega_{ll'}) + \phi_R(\omega|_{v'l'}^{vl})]^2 + \phi_I^2(\omega|_{v'l'}^{vl})\}^{-1} \qquad (46)$$

assuming a continuous distribution of states in space, i.e., a Debye approximation with $\omega_k = vk$ where v is the constant velocity of sound and the cutoff frequency is $\omega_D = vk_D$.

$$\phi_I(\omega|_{v'l'}^{vl}) = 9(8m\omega_D^3)^{-1}\int_0^{\omega_D} g_k^2 \, d\Omega$$

$$\times\left[C(vv')m(ll)m(l'l')\int_0^{\omega_D}\omega_k(2n_k + 1)\{\delta(\omega - \Omega_{ll'} - \omega_k) + \delta(\omega - \Omega_{ll'} - \omega_k)\}d\omega_k\right.$$

$$+ \sum_L C(v'v')m(l'L)m(Ll')\int_0^{\omega_D}\omega_k(n_k + 1)\{\delta(\omega - \Omega_{lL} - \omega_k) + \omega_k n_k\delta(\omega - \Omega_{lL} + \omega_k)\}d\omega k$$

$$+ \left.\sum_L C(vv)m(lL)m(Ll)\int_0^{\omega_D}\omega_k n_k\{\delta(\omega - \Omega_{Ll'} - \omega_k) + \omega_k(n_k + 1)\delta(\omega - \Omega_{Ll'} + \omega_k)\}d\omega_k\right]. \qquad (47)$$

In this expression, the result of the spatial integration over the form factor g_k^2 has been assumed to be independent of $|\mathbf{k}|$ and consequently taken out of the integration over ω_k. This is based on the fact that g_k^2 is a bounded function which may safely be assumed to vary slowly with $|\mathbf{k}|$. Then the factor

$$s = \int g_k^2 \, d\Omega \qquad (48)$$

will be hereafter considered as constant, and

$$C(vv') = \sum_p C_p(vv') = \sum_{\alpha = x, y, z}(D_\alpha^{(2)} + \langle R^2\rangle_{vv}D_\alpha^{(4)})(D_\alpha^{(2)}$$

$$+ \langle R^2\rangle_{v'v'}D_\alpha^{(4)}) = C(v'v), \qquad (49)$$

where the $D_\alpha^{(i)}$ ($i = 2,4$) are the components of the $\mathbf{D}(i)$ vectors, and in particular

$$C(vv) = |\mathbf{D}^{(2)} + \langle R^2\rangle_{vv}D^{(4)}|^2 \qquad (50)$$

the value of the integral (47) is under the controle of: (a) the form factor g_k^2 which, depends on the geometrical arrangement of the nearest neighbors around the molecular impurity; (b) the magnitude of the coupling factors $C(\bar{v},\bar{v}')$, and (c) the anharmonicity of the librator. Temperature dependence occurs through the populations n_r. A similar expression is obtained for $\phi_R(\omega|_{v'l'}^{vl})$ by replacing the $\pi\delta$ symbols by the corresponding Cauchy's principal values.

A thorough numerical analysis based on expression (39) or (46) would be relevant only if a set of data could be provided for the potential constants occurring in Eq. (41). This requires numerical values for the second and fourth derivatives of the interaction potential which are not actually available. It is however possible to examine some simple cases and pursue the analysis up to its final goal if some more approximations are introduced and reasonable values are attributed to the potential constant and, above all, if the result can be controlled by some experimental data. The case of CO diluted in Ar has been thoroughly studied experimentally and appears as a good test of our calculations since the most recent results seem to definitely confirm that the rotation is strongly hindered, i.e., that the CO molecule librates in its cage.[21] A rather drastic approximation consists of assuming that the librational motion is harmonic. This is not essential and Eq. (47) is valid for any type of librational motion. However this assumption leads to a simplified formula for $\phi_I(\omega)$, very convenient for numerical calculations and allowing a rapid test of the model consistency. Then under this assumption the summation over L is restricted to a few terms and the matrix elements are reduced to

$$m(L,L \pm 1) = m(L \pm 1,L)$$

$$= (2\gamma)^{-1/2}[L + (1/2)(1 \pm 1)]^{1/2}, \qquad (51)$$

where $\gamma = \omega_L/\hbar$, and

$$\phi_I(\omega_{v'l'}^{vl}) = 9(16m\omega_D^3\gamma)^{-1}\int_0^{\omega_D}(\{C(v'v')l'\omega_k(n_k+1) + C(vv)(l+1)\omega_k n_k\}\delta[\omega - \omega_v - (l'-l-1)\omega_L - \omega_k]$$

$$+ \{C(v'v')l'\omega_k n_k + C(vv)(l+1)\omega_k(n_k+1)\}\delta[\omega - \omega_v - (l'-l-1)\omega_L + \omega_k]$$

$$+ \{C(v'v')(l'+1)\omega_k(n_k+1) + C(vv)l\omega_k n_k\}\delta[\omega - \omega_v - (l'-l+1)\omega_L - \omega_k]$$

$$+ \{C(v'v')(l'+1)\omega_k n_k + C(vv)l\omega_k(n_k+1)\}\delta[\omega - \omega_v - (l'-l+1)\omega_L + \omega_k])d\omega_k. \tag{52}$$

In particular for the transition $v=0, l=0 \rightarrow v=1, l=0$ and $v=0, l=1 \rightarrow v=1, l=1$, the corresponding imaginary contributions become, using the short hand notation:

$$a = 9(16m\omega_D^3\gamma)^{-1} \tag{53}$$

as well as $\omega_0 = \omega_v + \omega_L$ and $\omega_1 = \omega_v - \omega_L$ (note that $\omega_0 > \omega_1$ and $\omega_0 > \omega_L$):

$$\phi_I(\omega|_{10}^{00}) = \begin{cases} s\cdot a\cdot C(00)(\omega-\omega_1)n(\omega-\omega_1) & \cdots \omega_1-\omega_D < \omega < \omega_0-\omega_D \\ \left. \begin{array}{l} s\cdot a\cdot C(00)(\omega-\omega_1)n(\omega-\omega_1) \\ + s\cdot a\cdot C(11)(\omega_0-\omega)n(\omega_0-\omega) \end{array}\right\} & \cdots \omega_0-\omega_D < \omega < \omega_1+\omega_D \quad (54) \\ s\cdot a\cdot C(11)(\omega_0-\omega)n(\omega_0-\omega) & \cdots \omega_1+\omega_D < \omega < \omega_0+\omega_D \end{cases}$$

$$\phi_I(\omega|_{11}^{01}) = \begin{cases} 2s\cdot a\cdot C(00)(\omega-\omega_1)n(\omega-\omega_1) + s\cdot aC(11)(\omega_1-\omega)n(\omega_1-\omega) & \cdots \omega_1-\omega_D < \omega < \omega_0-\omega_D \\ \left. \begin{array}{l} 2s\cdot a\cdot C(00)(\omega-\omega_1)n(\omega-\omega_1) + s\cdot aC(11)(\omega_1-\omega)n(\omega_1-\omega) \\ + 2s\cdot a\cdot C(11)(\omega_0-\omega)n(\omega_0-\omega) + s\cdot aC(00)(\omega-\omega_0)n(\omega-\omega_0) \end{array}\right\} & \cdots \omega_0-\omega_D < \omega < \omega_1+\omega_D \quad (55) \\ 2s\cdot a\cdot C(11)(\omega_0-\omega)n(\omega_0-\omega) + s\cdot aC(00)(\omega-\omega_0)n(\omega-\omega_0) & \cdots \omega_1+\omega_D < \omega < \omega_0+\omega_D \end{cases}$$

all through relations from Eq. (52) to Eq. (55) a simple property of the $n(\omega)$ function has been used, i.e.: $-\omega[n(-\omega)+1] = \omega n(\omega)$. Calculation of the real part $\phi_R(\omega)$ cannot be so easily reduced to a simple analytic form and involves the evaluation of lengthy integrals. Since it can be admitted that the magnitude of the dynamical shift is small (14) and rather ω independent only a typical value for $\omega = \omega_v$ is given below.

$$\phi_R(\omega_v|_{10}^{00})$$

$$= s\cdot a[C(0,0) - C(1,1)]$$

$$\times\left[\oint_0^{\omega_D}\frac{\omega_k n_k}{\omega_L - \omega_k}d\omega_k + \int_0^{\omega_D}\frac{\omega_k(n_k+1)}{\omega_L + \omega_k}d\omega_k\right], \tag{56}$$

$$\phi_R(\omega_v|_{11}^{01})$$

$$= s\cdot a[C(00) - C(1,1)]$$

$$\times\left[\oint_0^{\omega_D}\frac{\omega_k(n_k-1)}{\omega_L - \omega_k}d\omega_k + \int_0^{\omega_D}\frac{\omega_k(n_k+2)}{\omega_L + \omega_k}d\omega_k\right], \tag{57}$$

where $\oint$ designates the principal value of the integral. At $\omega = \omega_v$ the broadening terms $\phi_I(\omega_v{}_{11}^{00})$ and $\phi_I(\omega_v{}_{11}^{01})$ are, respectively, equal to $s\cdot a\cdot[C(0,0)+C(1,1)]\omega_L n(\omega_L)$. It is worth noticing that the frequency shift is proportional to the difference $[C(0,0)-C(1,1)]$, whereas the line broadening depends on the sum $C(0,0)+C(1,1)$. Furthermore, using Eqs. (56) and (57) it is easily deduced that

$$\phi_R(\omega_v|_{10}^{00}) - \phi_R(\omega_v|_{11}^{01})$$

$$= s\cdot a[C(0,0) - C(1,1)]$$

$$\times\left[2\omega_D + \omega_L \ln\left(\frac{\omega_D - \omega_L}{\omega_D + \omega_L}\right)\right]. \tag{58}$$

If all component of the $\mathbf{D}^{(i)}$ vectors are positive it can be inferred from Eq. (50) that $C(0,0) > C(1,1)$ and consequently the larger the frequency shift, the higher the l level.

III. RESULTS AND DISCUSSION

A numerical investigation has been undertaken in order to check that, despite the series of approximations introduced to simplify the analytical derivation, the use of a reasonable set of constants leads to the determination of band profiles which may roughly reproduce the experimental trend.

Both contributions $\phi_I(\omega|_{10}^{00})$ and $\phi_I(\omega_{11}^{01})$ given in formulas (54) and (55) have been calculated by assuming successively that $C(00) = C(11)$ and $C(00) \neq C(11)$. Arbitrarily, the ratio $C(00)/C(11)$ has been chosen equal to 2
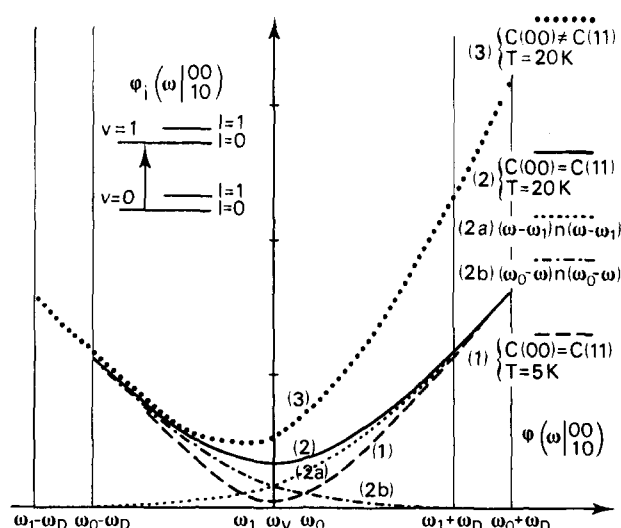

FIG. 3. Contribution ϕ_I [transition 00→01, see Eq. (54)] as a function of ω over the interval $\omega_v - \omega_L - \omega_D < \omega < \omega_v + \omega_L + \omega_D$.

FIG. 4. Contribution ϕ_I [transition $01 \rightarrow 11$, see Eq. (55)] as a function of ω over the interval $\omega_v - \omega_L - \omega_D < \omega < \omega_v + \omega_L + \omega_D$.
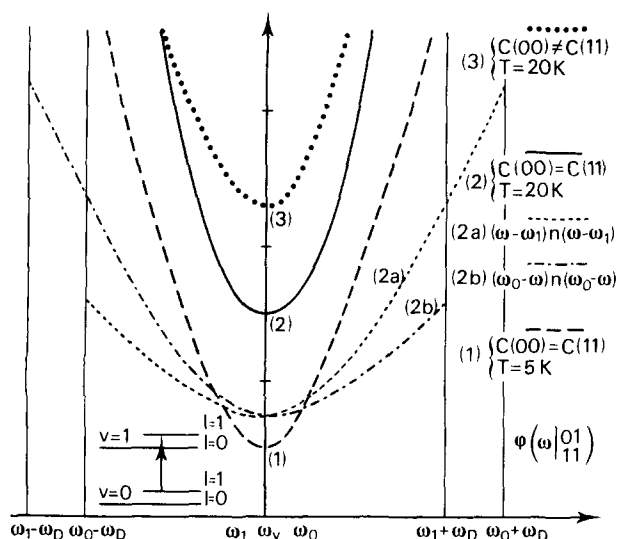
(in this first part of the calculation). In Figs. 3 and 4. The variations of the contributions are given on a rather large interval of frequencies extending between $\pm (\omega_D + \omega_L)$ around the unperturbed vibrational frequency ω_v. In both Figs. 3 and 4, the curves 2(a) and 2(b) represent the variation of the functions which are the main ingredients entering into formulas (54) and (55), i.e.: $(\omega - \omega_1)n(\omega - \omega_1)$ and $(\omega_0 - \omega)n(\omega_0 - \omega)$ at $T = 20$ K. In each case, curves 1, 2, and 3 represent the variation of the functions $\phi_I(\omega_{10}^{00})$ as given by formula (54) (Fig. 3) or $\phi_I(\omega_{11}^{01})$, from formula (55) (Fig. 4). Curves 1 and 2 correspond to the case $C(00) = C(11)$ at temperature 5 and 20 K, respectively. Finally, the case $C(00) \neq C(11)$ at $T = 20$ K is illustrated by the curve 3. In all cases whatever the temperature, $\phi_I(\omega_{11}^{01})$ is always larger than $\phi_I(\omega_{11}^{01})$.

Each contribution increases with temperature and these are larger for $C(00) \neq C(11)$ than for $C(00) = C(11)$. Finally the various contributions are unsymmetrical with respect to the $\omega = \omega_v$ axis, the $\phi_I(\omega)$ being slightly larger than $\phi_I(-\omega)$. The effect is more pronounced for the pure vibrational term $\phi_I(\omega_{10}^{00})$ than for the libro vibrational contribution $\phi_I(\omega_{11}^{01})$.

In order to compare with experimental spectra and, in particular, to check if temperature effects are at least qualitatively reproduced it is necessary to draw the curves corresponding to the Im $Z(\omega)$ function [formulas (43) and (46)]. Estimations of the $C(00)$ constant and of the ratio $C(00)/C(11)$ are then required. Since significant information is provided by the experimental spectrum only in a small frequency region centered in ω_v, we restrict our investigation to the domain, $\omega_v - \omega_L < \omega < \omega_v + \omega_L$. In this interval it is easily deduced from Eqs. (54) and (55) that:

$$\phi_I(\omega|_{10}^{00}) = 2\pi c \cdot s \cdot a \cdot C(00) \cdot (y_1 + x y_0), \qquad (59)$$

$$\phi_I(\omega|_{11}^{01}) = 2\pi c \cdot s \cdot a \cdot C(00)\{(2 + x)y_1$$
$$+ (2x + 1)y_0 + x \cdot (\omega - \omega_1) + (\omega_0 - \omega)\}, \qquad (60)$$

where s and a are given by Eqs. (48) and (53). Moreover $x = C(00)/C(11)$, and y_0, y_1 designate, respectively, the functions $(\omega_0 - \omega) n(\omega_0 - \omega)$ and $(\omega - \omega_1) n(\omega - \omega_1)$. The estimation of the coefficient $C(0,0)$ relies on the value of force constants such as $(\partial^2 V |\partial\theta\partial\eta_{lib})_e$ appearing in $\mathbf{D}^{(2)}$, the leading term in $C(vv)$, as can be seen in formula (50). Assuming isotropic interactions, the unique value involved is chosen equal to 10^{-5} mdyn. This in the range of values determined by ab initio calculations for similar quadratic force constants in hydrogen bonded complexes.[27] As for the $\mathbf{D}^{(4)}$ term, in order to emphasize its role, the calculations in Eqs. (59) and (60) have been performed by taking $x = 1,5$, a value certainly too large [it is equivalent to admitting that $\langle R^2 \rangle_{00}\mathbf{D}^{(4)} \simeq 3.10 \mathbf{D}^{(2)}$ in Eq. (50)] but which permits magnifying the nonsymmetrical effects due to the $\mathbf{D}^{(4)}$ contribution. The other quantities required are the lattice cutoff frequency and the librational frequency taken equal to 80 and 11.4 cm^{-1}, respectively. As for the geometrical factor s [see Eq. (40)] it can be deduced from an estimate of the lower and upper bounds of the integral (48). A reasonable guess leads to $s = 1/3$.

With this set of data it is then possible to draw the various curves representing the variation of $\sigma(\omega)$ as given by Eq. (46) but assuming that on the frequency interval considered, the factor

$$(8\pi/\hbar)|f_0|^2\omega|M_Z(_{v'l'}^{vl})|^2 C^Z(_{v'l'}^{vl})$$

remains constant and the summation over $v,l,v'l'$ is restricted to both transitions $(00 \rightarrow 10)$ and $(01 \rightarrow 11)$. Furthermore, a first calculation has been performed by taking $\phi_R(\omega_{v'l'}^{vl}) = 0$. Under these conditions the variation of the sum of both contributions $Z(_{01}^{00})$ and $Z(_{11}^{01})$ has been represented in Fig. 5 assuming that the ratio $x = C(00)/C(11)$ may take two different values, i.e., 1.5 and 1.05. Shifting from the first to the second value has a very moderate effect on the band shape. The evolution of the band profiles with
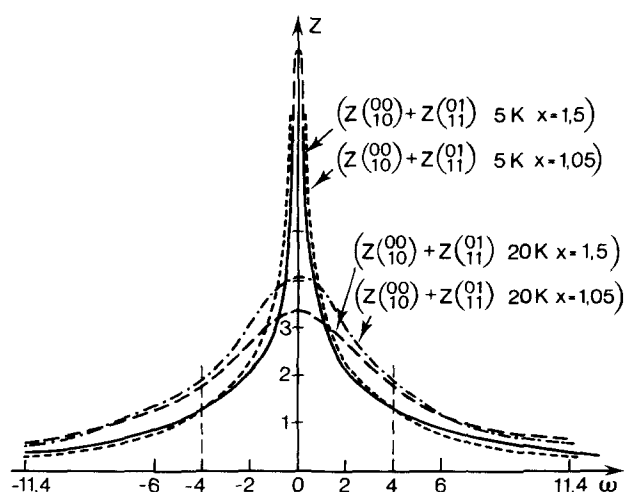

FIG. 5. Absorption coefficients (arbitrary unit) around the ω_v central frequency (interval $\omega_v - \omega_L < \omega < \omega_v + \omega_L$) for temperature $T = 5$ and 20 K. Curves are given for two different values of the ratio $x = C(11)|C(00)$: 1.5 and 1.05.

temperature reproduces well enough the observed experimental trend.[21]

Primarily applied to the hindered rotational case,[14] our model, when extended to the case of libration, still gives consistent results with respect to experimental data despite some drastic approximations used to preserve the analytical character of our analysis. This may bring some support for extending our work in various directions: (i) perform a more rigorous treatment of the fundamental equation of motion, removal of such approximations as Debye approximation or sphericalization procedure which ignore many of the specific features of the physical problem; (ii) study intermediate situations between free rotation and librational motion, where jumping or tunneling between residence sites may occur and play some role in the band shaping mechanism.

Finally, it must be admitted that even if the present model allows finding a consistent set data which reproduce well enough the temperature dependence of the infrared spectrum of CO embedded in an Ar matrix, the adjustment over the observed spectrum does not permit a unique determination of the coupling constant involved. This reinforces the need for reliable intermolecular potentials to test the validity of the models proposed to explain the mechanism responsible for band broadening due to matrix trapping. {In the course of writing of this paper, an article by I. L. Garzon and co-workers [J. Chem. Phys. **83**, 4311 (1985)] was published using analogous method. Some of their applications concern the case of CO embedded in Ar. Though a more general form is adopted by the authors for the interaction Hamiltonian, their conclusions are close to our results. A particularity of our work is to offer a detailed discussion and comparison of the contributions to both transitions $v = 0$, $l = 0 \rightarrow v = 1$, $l = 0$ and $v = 0$, $l = 1 \rightarrow v = 1$, $l = 1$.}

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