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Rotational-angular-momentum relaxation mechanisms in the energy-corrected-sudden scaling theory

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In calculating the infrared (IR) band shape for bending modes, the angular-momentum coupling between vibration, rotation, and radiation must be taken into account. The accuracy of the energy-corrected-sudden (ECS) model has been proved through many recent applications in isotropic Raman Q-branch profiles. Furthermore, this model is based on the physical infinite-order-sudden (IOS) approximation, which allows inclusion of the other relaxation mechanisms required when considering other spectroscopic branches, such as IR Q-bending bands. To include, in a consistent way, the role of the vibrational angular momentum in the rovibrational relaxation matrix, the relaxation of the rotational angular momentum $\mathbf{J}$ and of its associated higher-order tensors $[\mathbf{J}]^{(2)},\ldots$ (basically absent in the IOS approximation) is enforced in the present ECS model. Application to the 2076.86 cm^{-1} infrared rovibrational band of $^{12}C^{16}O_2$ leads to the determination of the $[\mathbf{J}]^{(2)}$ relaxation time in agreement with previous values obtained from different measurements. The present theory may be applied to other spectroscopic bands, such as the anisotropic Raman ones.

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I. INTRODUCTION

The calculation of the infrared (IR) bending band shapes requires one to take into account the vibrational angular-momentum coupling with the coupling of the photon and with the rotational coupling. An *ab initio* theoretical study [1] of CO$_2$-He accounting for such a coupling has allowed a quantitative interpretation of observed spectra within the infinite-order-sudden (IOS) approximation.

It has also been shown [2] that in the classical limit and within the IOS approximation, the tetradic collisional spectroscopic cross sections can be transformed into a dyadic supermatrix. Thus the use of the simple strong collision model has led to a clear understanding of the strong modifications introduced by the vibrational angular momentum in the IR bending band shapes [2].

For most molecular systems, the IOS approximation is too crude to obtain sufficient accuracy for a quantitative comparison with experiments. Therefore, the energy-corrected-sudden (ECS) model [3], which accounts for both rotational level spacing and a finite duration of collisions, must be considered. This was done in Ref. [4] for the $(11\,^10)_{\mathrm{I}}\leftarrow(00\,^00)$ band of $^{12}C^{16}O_2$ where the three numbers are the quantum numbers associated to the three vibrational modes of a linear triatomic molecule, the superscript refers to the degeneracy of the bending mode and the underscript refers to the Fermi dyad. In this study the diagonal contribution $(\tau_j^{ll'})^{-1}$, which rigorously appears in the formal expression of the dyadic $\tilde{\Gamma}_{jj'}^{ll'}$ cross sections, was assumed, in a first approximation, to be ll' independent. In spite of a reasonable agreement between ECS calculated spectra and experimental data, a degree of discrepancy remains.

The aim of the present paper is to account for this dependence on the vibrational angular momentum in $(\tau_j^{ll'})^{-1}$. It will be done here on a physical basis through the introduction of the $\mathbf{J}$ rotational-angular-momentum relaxation (and of the higher-order tensors $[\mathbf{J}]^{(2)},\ldots$ associated with $\mathbf{J}$).

Such a relaxation is basically absent in the IOS approximation [5]. The ECS corrections introduce [6,7] a possible relaxation of $\mathbf{J}$, but somewhat as an artifact. The requirement of these relaxation mechanisms would allow one to define $(\tau_j^{ll'})^{-1}$ in terms of the known physical relaxation times characterizing the $\mathbf{J},[\mathbf{J}]^{(2)},\ldots$ correlation functions.

Section II is devoted to the theoretical developments. After the definition of a generalized IOS sum rule that is valid whatever the excitation degree of vibrational angular momentum, an ECS model, including consistently the rotational-angular-momentum relaxation mechanisms, is proposed. Calculations of the $(11\,^10)_{\mathrm{I}}\leftarrow(00\,^00)$ $^{12}C^{16}O_2$ bending band at moderate densities (i.e., several bars) using the present theory are presented in Sec. III. Comparison of the resulting value for the $[\mathbf{J}]^{(2)}$ relaxation time and those previously obtained from the Senftleben viscomagnetic effect [8] and from Rayleigh scattering [9], and concluding remarks are given in the last section.

II. THEORY

In linear spectroscopies the spectral function is given, in the impact approximation at density n and mean relative velocity $\bar{v}$, by

$$I^{Kl_il_f}(\omega)=\mathrm{Re}\sum_{j_ij_f,j_i'j_f'}\rho_{j_i}\theta_{j_ij_f}^{Kl_il_f}[i(\omega-\omega^0)+n\bar{v}\sigma^{Kl_il_f}]^{-1}_{j_ij_f,j_i'j_f'}\theta_{j_i'j_f'}^{Kl_il_f}\ , \tag{1}$$

where K is the rank of the radiation-matter coupling tensor ($K=1$ for infrared absorption and $K=0$ or 2 for isotropic or anisotropic Raman scattering), l_i and l_f are, respectively, the initial and final vibrational angular momenta. The reduced matrix elements of the radiation-matter coupling tensor are given by

$$\theta_{j_i j_f}^{K l_i l_f} = (-1)^{j_f + l_f}[j_f]^{1/2} \begin{pmatrix} j_i & K & j_f \\ l_i & l_f - l_i & -l_f \end{pmatrix} , \tag{2}$$

where $[j]=2j+1$ and ( ) is the usual $3j$ angular-momentum coupling symbol. The elements of the diagonal matrix ω^0 are the line frequencies of the free molecule

$$\omega^0_{j_i j_f, j_i' j_f'} = \omega^0_{j_i j_f} \delta_{j_i j_i'} \delta_{j_f j_f'} . \tag{3}$$

It has been shown [2] how the tetradic spectroscopic cross sections $\sigma^{K l_i l_f}_{j_i j_f, j_f' j_f'}$ can be expressed as a linear combination of dyadic cross sections $\tilde{\Gamma}^{l_i l_i'}_{j_i j_i'}$, which no longer depend on the nature of the spectroscopic probe used. Here, this is expressed as

$$\sigma^{K l_i l_f}_{j_i j_f, j_i' j_f'} = \sum_{l_i'} \theta^{K l_i' l_f}_{j_i j_f} \theta^{K l_i' l_f}_{j_i' j_f'} \tilde{\Gamma}^{l_i l_i'}_{j_i j_i'} , \tag{4}$$

where the range of the l_i' values is governed by the selection rule implied in the $\theta^{K l_i' l_f}$ matrix elements $l_f - K \le l_i' \le l_f + K$. The identification $\tilde{\Gamma}^{ll'}_{jj'} = \sigma^{0ll'}_{jj,j'j'}$ shows that the $\tilde{\Gamma}^{ll'}$ matrices are generalized rovibrational state-to-state cross sections. It should be noted that Burshtein, Storozev, and Strekalov [5] introduced the relaxation operators Γ^K appropriate for a tensor of rank K as $\Gamma^K_{jj'} \equiv \sigma^{K00}_{jj,j'j'}$.

The fundamental sum rule is obtained when the exact value of the initial derivative of the time correlation function associated with $I^{K l_i l_f}(\omega)$ is considered [10]:

$$\sum_{j_i' j_f'} \sigma^{K l_i l_f}_{j_i j_f, j_i' j_f'} \theta^{K l_i l_f}_{j_i' j_f'} = 0 . \tag{5}$$

In the present formalism this leads to the sum rules

$$\sum_{j'} \tilde{\Gamma}^{ll}_{jj'} = 0 . \tag{6}$$

The generalized dynamic cross sections are given in the ECS approximation [4] by

$$\tilde{\Gamma}^{ll'}_{jj'} = \frac{\delta_{jj'}}{\tau_j^{ll'}} + \frac{\rho_{j_>}}{\rho_j} \Omega_{j_>} [j_<](-)^{l+l'} \times \sum_{L\neq 0} [L] \begin{pmatrix} j & L & j' \\ l & 0 & -l \end{pmatrix} \begin{pmatrix} j & L & j' \\ l' & 0 & -l' \end{pmatrix} \frac{Q_L}{\Omega_L} \equiv \frac{\delta_{jj'}}{\tau_j^{ll'}} - \Delta^{ll'}_{jj'} , \tag{7}$$

where the Q_L are the basis state-to-state cross sections, since it is easily verified that $Q_L = \tilde{\Gamma}^{00}_{L0}$.

It should be stressed here that, in contrast with Ref. [4], the ll' dependence of the diagonal part of $\tilde{\Gamma}^{ll'}$ should be accounted for. This is the main goal of this article.

At this stage we must emphasize that, except for $(\tau_j^{ll})^{-1}$, it is not possible to obtain all the diagonal parts $(\tau_j^{ll'})^{-1}$ from first principles. Thus it is necessary to particularize our study. Here, we will mainly focus our interest on infrared transitions ($K=1$) between $l_i=0$ and $l_f=1$ states, so that only the cross sections $\tilde{\Gamma}^{0l}$ for $l=0$, 1, and 2 have to be considered, since in this case, Eq. (4) may be explicated as

$$\sigma^{101}_{j_i j_f, j_i' j_f'} = \theta^{101}_{j_i j_f} \theta^{101}_{j_i' j_f'} \tilde{\Gamma}^{00}_{j_i j_i'} + \theta^{111}_{j_i j_f} \theta^{111}_{j_i' j_f'} \tilde{\Gamma}^{01}_{j_i j_i'} + \theta^{121}_{j_i j_f} \theta^{121}_{j_i' j_f'} \tilde{\Gamma}^{02}_{j_i j_i'} , \tag{8}$$

which leads, in the particular case of the isolated Q branch, to

$$\sigma^{101}_{jj,j'j'} = \tfrac{1}{2} \tilde{\Gamma}^{00}_{jj'} + [j(j-1)j'(j'-1)]^{-1} \tilde{\Gamma}^{01}_{jj'} + \frac{1}{2} \left[\frac{(j-1)(j+2)(j'-1)(j'+2)}{j(j+1)j'(j'+1)} \right]^{1/2} \tilde{\Gamma}^{02}_{jj'} , \tag{9}$$

which, in the high-j limit, reduces to $\sigma^{101}_{jj,j'j'} = \frac{1}{2}(\tilde{\Gamma}^{00}_{jj'} + \tilde{\Gamma}^{02}_{jj'})$. Finally, we are only interested in $(\tau_j^{0l})^{-1}$ for $l=0$, 1, and 2, which will be determined by introducing new generalized sum rules and the convenient phenomenological relaxation times.

A. The exact IOS sum rules

The expression of the IOS cross sections is well known:

$$(\tilde{\Gamma}^{0l}_{jj'})^{\mathrm{IOS}} = [j'](-)^l \times \sum_L [L] \begin{pmatrix} j & L & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & L & j' \\ l & 0 & -l \end{pmatrix} Q_L , \tag{10}$$

where it is convenient to include the $L=0$ term in the summation, in contrast with the case of the ECS approximation [Eq. (7)]. In the case of the $l=0$ cross sections, the orthonormality of the $3j$ symbols leads to

$$\sum_{j'} (\tilde{\Gamma}^{00}_{jj'})^{\mathrm{IOS}} = \sum_L [L] Q_L = 0 , \tag{11}$$

where the last equality insures the sum rule [Eq. (6)] for $l=0$. It is shown in the Appendix that, in the IOS approximation, one has the exact general sum rules

$$\sum_{j'} (\tilde{\Gamma}^{0l}_{jj'})^{\mathrm{IOS}} X^l_{j'} = 0 , \tag{12}$$

with the coefficients X^l_j,

$$X^l_j = \left[\frac{(j+l)!}{(j-l)!} \right]^{1/2} = [E_j(E_j - E_1) \cdots (E_j - E_{l-1})]^{1/2} , \tag{13}$$

where $E_j = j(j+1)$ is the *reduced* rotational energy. Notice that the sum rule for the case $l=1$ was already obtained by Burshstein, Storozev, and Strekalov [5] (since $\tilde{\Gamma}^{01} \equiv \Gamma^1$), who concluded that the angular momentum does not relax in the IOS approximation.

B. Introduction of macroscopic relaxation times

As shown in the preceding section, exact IOS sum rules [Eq. (12)] hold not only for the $l=0$ case (isotropic Raman scattering for stretching vibrational modes), but also for $l\neq 0$ (isotropic Raman scattering for bending modes, IR absorption, anisotropic Raman scattering, etc.). For most molecular systems, the IOS approximation is too crude, and a quantitative comparison with experiments requires ECS corrections [3] accounting for both rotational level spacing and finite duration of collisions. This ECS model allows one to get the $(\tau_j^{00})^{-1}$ cross sections from the exact sum rule [Eq. (6)] by using the ECS expressions $\tilde{\Gamma}^{00}_{jj'}$ [Eq. (7)].

The determination of the off-diagonal part of $\tilde{\Gamma}^{01}_{jj'}, \tilde{\Gamma}^{02}_{jj'}, \ldots$ (i.e., $-\Delta^{01}_{jj'}, -\Delta^{02}_{jj'}, \ldots$ with $j'\neq j$) tied to the IR or anisotropic Raman scattering spectroscopies [$\sigma^{100}_{j_ij_f,j_i'j_f'}, \sigma^{101}_{j_ij_f,j_i'j_f'}, \sigma^{200}_{j_ij_f,j_i'j_f'}, \ldots$ cf. Eq. (4)] is directly deduced from Eq. (7). The only modification with respect to $\tilde{\Gamma}^{00}_{jj'}$ is due to the angular-momentum coupling factor, through the $3j$ symbol. The diagonal contributions $-\Delta^{01}_{jj}, -\Delta^{02}_{jj}, \ldots$ are similarly determined. The leading contributions $\tau_j^{0l}(l=1,2)$ were previously obtained [4] by assuming that they are l independent and thus equal to τ_j^{00}, which was already determined from the isotropic Raman cross sections $\sigma^{000}_{jj,j'j'}$.

In such an ECS model, in contrast with the IOS one [5], the rotational angular momentum relaxes. But no clear physical constraint is introduced to control this relaxation mechanism. It has been shown [7] that for some particular choice for the rotational energy dependence of the basis rates $Q_L \equiv \tilde{\Gamma}^{00}_{L0}$ (an inverse power law), a divergence of the corresponding rotational-angular-momentum correlation function appears for the nitrogen gas. This divergence disappears for another choice, such as an exponential law.

To avoid such an artifact of the relaxation matrix, an improved ECS model is proposed here by enforcing the rotational angular momentum **J**, the symmetric traceless tensor of rank 2 $[\mathbf{J}]^{(2)}, \ldots,$ *to relax exponentially with a characteristic macroscopic time* (j independent). So, the off-diagonal cross sections $\tilde{\Gamma}^{0l}_{jj'}$ are still expressed through the same ECS procedure as previously [4], but the diagonal part is now determined through these physical relaxation properties. The derivation of the convenient expression for the diagonal elements $\tilde{\Gamma}^{0l}_{jj}$ is thus similar for each tensor rank $[\mathbf{J}]^{(l)}$ as explicated below.

1. Determination of $\tilde{\Gamma}^{01}_{jj'}$ from the relaxation of the rotational angular momentum *J*

The macroscopic time relaxation $\tau_{\mathbf{J}}$ of the rotational angular momentum **J** is defined by the time derivative of the normalized correlation function $\Phi_{\mathbf{J}}(t)$,

$$\frac{\partial \Phi_{\mathbf{J}}(t)}{\partial t} = -\tau_{\mathbf{J}}^{-1}\Phi_{\mathbf{J}}(t) \;, \tag{14}$$

with

$$\Phi_{\mathbf{J}}(t) = \frac{\langle \mathbf{J}(0)\cdot\mathbf{J}(t)\rangle}{\langle \mathbf{J}^2\rangle} = \sum_{jj'} \rho_j E_j^{1/2} (e^{-\Gamma^1 t})_{jj'} E_{j'}^{1/2} \Big/ \sum_j \rho_j E_j \;. \tag{15}$$

The relaxation matrix $\Gamma^1_{jj'}$ is such that [cf. Eq. (4)]

$$\Gamma^1_{jj'} \equiv \sigma^{100}_{jj,j'j'} = \tilde{\Gamma}^{01}_{jj'} \tag{16}$$

and satisfies, through Eqs. (14) and (15), the relation

$$\sum_{j'} \tilde{\Gamma}^{01}_{jj'} E_{j'}^{1/2} = E_j^{1/2} \tau_{\mathbf{J}}^{-1} \;, \tag{17}$$

whatever j. Accounting for the inverse relaxation time $\tau_{\mathbf{J}}^{-1}$ in $(\tau_j^{01})^{-1}$ leads to [cf. Eq. (7)]

$$(\tau_j^{01})^{-1} = (\tilde{\tau}_j^{01})^{-1} + \tau_{\mathbf{J}}^{-1} \;, \tag{18}$$

where $(\tilde{\tau}_j^{01})^{-1}$ is defined from the sum rule [Eq. (12) for $l=1$] and from Eqs. (13) and (17):

$$(\tilde{\tau}_j^{01})^{-1} = \sum_{j'} E_{j'}^{1/2} \Delta^{01}_{jj'} / E_j^{1/2} \;. \tag{19}$$

Since the relaxation time $\tau_{\mathbf{J}}$ is known from measurements of nuclear spin relaxation [11], Eqs. (18) and (19) through Eq. (7) fully determine the $\tilde{\Gamma}^{01}_{jj'}$ cross sections. As explained above, the other diagonal contributions $-\Delta^{01}_{jj}$ are directly deduced from $\tilde{\Gamma}^{00}_{jj'}$ as well as the off-diagonal ones $-\Delta^{01}_{jj'}$ $(j'\neq j)$.

The calculation of IR bending bands or anisotropic Raman scattering profiles requires the additional determination of the $\tilde{\Gamma}^{02}_{jj}$ cross sections. This is done by using a procedure similar to that for $\tilde{\Gamma}^{01}_{jj}$ but tied to $[\mathbf{J}]^{(2)}$ instead of **J**.

2. Determination of $\tilde{\Gamma}^{02}_{jj'}$ from the relaxation of the symmetric traceless tensor $[J]^{(2)}$

Consider the correlation function

$$\phi_{[\mathbf{J}]^{(2)}}(t) = \sum_{jj'} \rho_j A_j^{(2)} (e^{-\Gamma^2 t})_{jj'} A_{j'}^{(2)} \Big/ \sum_j \rho_j (A_j^{(2)})^2 \;, \tag{20}$$

where

$$\Gamma^2_{jj'} = \sum_l \theta^{20l}_{jj} \theta^{20l}_{j'j'} \tilde{\Gamma}^{0l}_{jj'} \tag{21}$$

is the relaxation matrix for the second-rank tensor $[\mathbf{J}]^{(2)}$. The modulus of this tensor is given by [12]

$$A_j^{(2)} = [\tfrac{2}{3} E_j (E_j - 3/4)]^{1/2} \;. \tag{22}$$

This correlation function appears in the description of the viscomagnetic effect [9,12].

To insure an exponential relaxation of $\phi_{[\mathbf{J}]^{(2)}}(t)$, with a characteristic time $\tau_{[\mathbf{J}]^{(2)}}$, we must impose the sum rule [similar to Eq. (17)]

$$\sum_{j'} \Gamma^2_{jj'} A_{j'}^{(2)} = A_j^{(2)} / \tau_{[\mathbf{J}]^{(2)}} \;, \tag{23}$$

whatever j. Using Eq. (21), this equation may be developed into

$$\frac{1}{\tau_{[\mathbf{J}]^{(2)}}}[E_j(E_j-3/4)]^{1/2}=\frac{1}{4}\left[\frac{E_j}{E_j-3/4}\right]^{1/2}\sum_{j'}\tilde{\Gamma}^{00}_{jj'}E_{j'}+\frac{3}{4}\frac{1}{(E_j-3/4)^{1/2}}\sum_{j'}\tilde{\Gamma}^{01}_{jj'}E_{j'}^{1/2}$$
$$+\frac{3}{4}\left[\frac{E_j-2}{E_j-3/4}\right]^{1/2}\sum_{j'}\tilde{\Gamma}^{02}_{jj'}[E_{j'}(E_{j'}-2)]^{1/2}\ . \qquad (24)$$

The first term in the right-hand side of Eq. (24) is easily calculated since the $\tilde{\Gamma}^{00}$ matrix is assumed to be already known from isotropic Raman Q-branch experimental data. We introduce the individual energy relaxation times

$$\frac{1}{\tau_j^E}=\sum_{j'}\tilde{\Gamma}^{00}_{jj'}E_{j'}\ . \qquad (25)$$

The second term is also already known, through Eq. (17). Concerning the third term [cf. Eq. (7)] one can introduce the decomposition

$$\frac{1}{\tau_j^{02}}=\frac{1}{\tilde{\tau}_j^{02}}+\frac{1}{\bar{\tau}_j^{02}}\ , \qquad (26)$$

where $(\tilde{\tau}_j^{02})^{-1}$ is defined by

$$\frac{1}{\tilde{\tau}_j^{02}}=\sum_{j'}\Delta^{02}_{jj'}[E_{j'}(E_{j'}-2)]^{1/2}/[E_j(E_j-2)]^{1/2}\ , \qquad (27)$$

$(\bar{\tau}_j^{02})^{-1}$ is thus easily deduced from Eq. (24) using Eqs. (25)–(27):

$$\frac{1}{\bar{\tau}_j^{02}}=\frac{4}{3}\frac{1}{\tau_{[\mathbf{J}]^{(2)}}}$$
$$+[3(E_j-2)]^{-1}\left[\frac{5}{\tau_{[\mathbf{J}]^{(2)}}}-\frac{1}{\tau_j^E}-\frac{3}{\tau_{\mathbf{J}}}\right]\ . \qquad (28)$$

Equations (25)–(28), through Eq. (7), determine the $\tilde{\Gamma}^{02}_{jj'}$ cross sections, since, as explained above, the other diagonal contributions $-\Delta^{02}_{jj}$ are directly deduced from $\tilde{\Gamma}^{00}_{jj'}$ as well as from the off-diagonal ones $-\Delta^{02}_{jj'}$ $(j'\neq j)$. The relaxation time $\tau_{[J]^{(2)}}$ can be obtained from the Senftleben viscomagnetic effect [8] or from depolarized Rayleigh light scattering [9].

III. CALCULATION RESULTS AND COMPARISON WITH EXPERIMENTAL DATA

A. Data used and computational procedure

The basis transition rates Q_L are modelized [13] by the exponential-power law

$$Q_L=A(T)\exp(-\beta BL(L+1)/kT)[L(L+1)]^{-\gamma}\ , \qquad (29)$$

and the adiabatic factor by [3]

$$\Omega_L=(1+\omega^2_{L,L-2}l_c^2/24v^{-2})^{-2}\ . \qquad (30)$$

The numerical values of the different parameters are those given in Ref. [13]; namely,

$$A(295\ \mathrm{K})=0.0341\ \mathrm{cm}^{-1}/\mathrm{amagat},\quad \beta=0.0275\ ,$$
$$\gamma=0.8435,\quad l_c=1.75\ \text{Å}\ .$$

This allows the off-diagonal elements of the $\tilde{\Gamma}^{0l}_{jj'}$ cross sections to be calculated (for $l=0$, 1, and 2). Then the diagonal parts $(\tilde{\tau}_j^{01})^{-1}$ and $(\tilde{\tau}_j^{02})^{-1}$ are obtained through Eqs. (19) and (27). The $(\tau_{\mathbf{J}})^{-1}$ contribution is almost negligible since it goes to zero at high-j values. In the present study, the measured value of [11] has been used ($\tau_{\mathbf{J}}^{-1}/2\pi cn=0.046$ cm^{-1}/amagat). Concerning the $(\tau_{[\mathbf{J}]^{(2)}})^{-1}$ relaxation time in Eq. (28), it is clear that its value greatly determines the diagonal part of the relaxation matrix $\tilde{\Gamma}^{02}$. So, due to the approximate nature of the theories and experiments used to evaluate this parameter[8], we have chosen here to consider it as a free parameter. This is possible since $(\tau_{[\mathbf{J}]^{(2)}})^{-1}$ is diagonal and j independent, so the results of the diagonalization procedure introduced in Ref. [14] will not be altered by the introduction of this parameter. The relevant relaxation matrix can be written as

$$n\bar{v}\sigma^{101}_{jj,j'j'}=nW^{101}_{jj'}+\tfrac{2}{3}(\tau_{[\mathbf{J}]^{(2)}})^{-1}\delta_{jj'}\ , \qquad (31)$$

where the diagonal j-independent contribution $(\tau_{[\mathbf{J}]^{(2)}})^{-1}$ in Eq. (31) has been explicated and the high j limit of $(\theta^{101}_{jj})^2$ equal to $\frac{1}{2}$ has been retained in connection with the diagonalization procedure discussed just above. Now, the M matrix, which diagonalizes $nW^{101}-i\omega^0$, is introduced:

$$\sum_{j'}(nW^{101}_{jj'}-i\omega^0_j\delta_{jj'})M_{j'k}=M_{jk}\Lambda_k\ . \qquad (32)$$

The spectral function for the infrared Q branch (assumed to be uncoupled to P and R branches) becomes

$$I^{101}_Q(\omega)=\mathrm{Re}\sum_k Z_k\Big/[i\omega+\Lambda_k+\tfrac{2}{3}(\tau_{[\mathbf{J}]^{(2)}})^{-1}]\ , \qquad (33)$$

where the complex weights Z_k are given by

$$Z_k=\left[\sum_j \rho_j\theta^{101}_{jj}M_{jk}\right]\left[\sum_{j'}M^{-1}_{kj'}\theta^{101}_{j'j'}\right]\ . \qquad (34)$$

Finally, this theoretical expression of the IR bending Q-branch profile is fitted to the experimental spectrum by a least-squares procedure which optimizes two parameters: (i) an overall frequency shift (accounting for a possible imaginary part of the transition matrix that is discarded in the ECS approximation); (ii) the additive j-independent linewidth $\frac{2}{3}(\tau_{[\mathbf{J}]^{(2)}})^{-1}/2\pi c$.

TABLE I. Symmetric traceless tensor $[\mathbf{J}]^{(2)}$ relaxation time obtained from various physical properties.

Property	$(\tau_{[\mathbf{J}]^{(2)}})^{-1}/2\pi cn$ (cm^{-1}/amagat)
From Rayleigh scattering [9]	0.061
From Senftleben viscomagnetic effect [8]	0.040
This work: from IR Q branch $p=1.46$ atm	0.039
$(11\,^10)_I \leftarrow (00\,^00)$ $p=2.95$ atm	0.045

Notice that the absolute value of the absorbance is obtained through

$$K_Q^{101}(\omega)=\pi^{-1}S_v^{101}I_Q^{101}(\omega)\ ,$$

where $S_v^{101}=4155\times10^{-24}$ cm^{-1}/molecule cm^{-2} is the experimental value [15] of the integrated intensity of the considered band.

B. IR Q-band-shape calculation at moderate densities

Moderate densities are to be understood here as the range of density values high enough to suppress the rotational structure of the Q branch, but low enough to consider this Q branch as isolated from the P and R branches.

In this case, the minimization procedure can be applied to the two experimental situations already used in Ref. [4]. The resulting values for the relaxation time of CO_2 at room temperature are given in Table I. It is important to note that, as shown in Fig. 1 for one of these situations, the quality of the calculated Q-branch profile is within the experimental uncertainties. The fitted values from the $(11\,^10)\leftarrow(00\,^00)$ CO_2 bending band are in remarkable agreement with the Senftleben viscomagnetic effect and remain consistent with the Rayleigh data, since, as discussed in Ref. [9], the connection of experiment with $\tau_{[\mathbf{J}]^{(2)}}$ is more intricate.

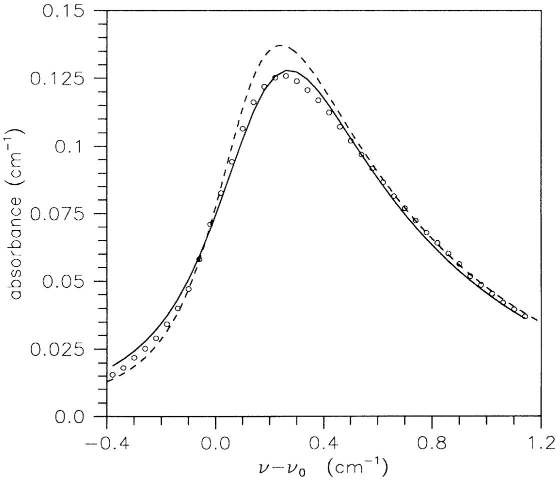

FIG. 1. Pure CO_2 Q branch at room temperature for $P=2.95$ bars in absolute scale: ○, experimental; — — —, previous result [4]; ——, present result. The frequencies are detuned by the pure vibrational frequency ($\nu_0=2076.86$ cm^{-1}).

IV. CONCLUSION

The introduction of an exponential relaxation for the rotational angular momentum $\mathbf{J}$ and for the symmetric traceless tensor $[\mathbf{J}]^{(2)}$ has led to a significant improvement of the ECS model for calculating IR bending bands. The fitted value for the relaxation time $\tau_{[\mathbf{J}]^{(2)}}$ has been found in agreement with previous determinations, in particular those coming from the Senftleben viscomagnetic effect.

The present calculation has been limited to moderate densities in order to avoid having to take into account the Q-P and Q-R line couplings. Furthermore, in the higher-density range (i.e., several tens of bars), these interbranch couplings make it necessary not only to explicate and to diagonalize the 3×3 supermatrix $\sigma^{101}_{j_1,j_f,j_i',j_f'}$ but also to introduce the Herman-Wallis vibration-rotation interaction, which is negligible for the Q branch. This interaction has to be included not only for the line intensities as usual [15], but also for the collisionally induced rotational energy transfer [cf. Eqs. (4) and (5)]. These extensions of the present theoretical model as well as other possible applications (such as anisotropic Raman scattering, which also implies the $\tilde{\Gamma}^{02}_{jj'}$ cross sections [16]) will be developed in a further study.

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APPENDIX: THE IOS SUM RULES

By introducing the usual Legendre polynomials $P_L(x)$ [satisfying $P_L(1)=1$] and the normalized Legendre functions,

$$\bar{P}_j^l(x)=\left[\frac{[j]}{2}\frac{(j-l)!}{(j+l)!}\right]^{1/2}(1-x^2)^{l/2}P_j^{(l)}(x)\ , \tag{A1}$$

where $P_j^{(l)}(x)$ is the lth derivative of $P_j(x)$, the IOS cross sections can be written as

$$(\tilde{\Gamma}^{0l}_{jj'})^{\mathrm{IOS}}=(-)^l\tfrac{1}{2}[j']\left[\frac{(j-l)!(j'-l)!}{(j+l)!(j'+l)!}\right]^{1/2}$$
$$\times\sum_L[L]Q_L\int_{-1}^{1}dx(1-x^2)^lP_j^{(l)}(x)$$
$$\times P_L(x)P_{j'}^{(l)}(x)\ . \tag{A2}$$

Let us calculate the quantity

$$C_j^l=\sum_{j'}(\tilde{\Gamma}_{jj}^{0l})^{\mathrm{IOS}}\left[\frac{(j'+l)!}{(j'-l)!}\right]^{1/2}=(-)^l\left[\frac{(j-l)!}{(j+l)!}\right]^{1/2}\sum_L[L]Q_L\int_{-1}^{1}dx(1-x^2)^lP_j^{(l)}(x)\tfrac{1}{2}\sum_{j'}[j']P_{j'}^{(l)}(x)\ . \tag{A3}$$

The j' summation becomes

$$\tfrac{1}{2}\sum_{j'}[j']P_{j'}^{(l)}(x)=\frac{d^l}{dx^l}\frac{1}{2}\sum_{j'}[j']P_{j'}(x)P_{j'}(1)=\frac{d^l}{dx^l}\delta(x-1)\ , \tag{A4}$$

where δ is the Dirac function for the definition space of $x\in[-1,1]$, due to the completeness of the Legendre polynomials on this domain, so that

$$C_j^l=\left[\frac{(j-l)!}{(j+l)!}\right]^{1/2}\sum_L[L]Q_L\left[\frac{d^l}{dx^l}[(1-x^2)^lP_j^{(l)}(x)P_L(x)]\right]_{x=1}\ . \tag{A5}$$

It is clear that all the derivatives of $(1-x^2)^l$ contain $(1-x^2)$ as a factor except the lth; this leads to

$$C_j^l=\left[\frac{(j-l)!}{(j+l)!}\right]^{1/2}\sum_L[L]Q_LP_j^{(l)}(1)P_L(1)\left[\frac{d^l}{dx^l}(1-x^2)^l\right]_{x=1}\ , \tag{A6}$$

where $P_j^{(l)}(1)=0$ for $l\neq0$, so that: $C_j^l=0$ whatever l and j. For $l=0$, it should be recalled that the condition $C_j^0=\sum_L[L]Q_L=0$ is imposed by the usual sum rule. Notice that

$$X_j^l\equiv[(j+l)!/(j-l)!]^{1/2}=[E_j(E_j-E_1)\cdots(E_j-E_{l-1})]^{1/2}\ \text{with}\ E_j=j(j+1)\ . \tag{A7}$$

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