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Non-Markovian energy-corrected sudden model for the rototranslational spectrum of N_2

J. V. Buldyreva* and L. Bonamy
Laboratoire de Physique Moléculaire, UMR CNRS 6624, Université de Franche-Comté, 25030 Besançon Cedex, France

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A model generalizing the isotropic-scattering-energy-corrected sudden (ECS) relaxation matrix to arbitrary rank spectra is developed on the basis of a theoretical expression proposed by A.P. Kouzov [*Spectral Line Shapes*, 14th International Conference on Spectral Line Shapes, State College, PA, 1998, edited by R. M. Herman, AIP Conf. No. 467 (AIP, Woodbury, NY, 1999), Vol. 10, p. 497] for the case of non-Markovian collisions. The constructed matrix obeys all known general relations obtained from first principles: both matrix and Ben-Reuven [Phys. Rev. **141**, 34 (1966)] symmetries as well as the double-sided sum rules. In the framework of the present formalism the usual *ad hoc* detailed balance factor is replaced by a more physical one. Without any additional parameter with respect to the Markovian ECS, this model gives a reasonable description of the N_2 anisotropic depolarized spectrum in the whole frequency range up to the far wing. [S1050-2947(99)08507-8]

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I. INTRODUCTION

Light scattering from molecular gases provides important information about angle-dependent intermolecular forces. Due to wide atmospheric and diagnostic applications it has been intensively studied both experimentally and theoretically [1,2]. But, in contrast to the atomic case, the depolarized light scattering by a molecular gas *a priori* involves the allowed and induced polarizabilities of the molecules. The present paper is devoted to the study of the allowed molecular spectra only. It will be shown indeed that the opportunity offered by the available experimental absolute intensities in the case of N_2 allows us to confirm that the induced spectra are almost negligible not only in the core of the spectra (as expected) but even in the far wings.

The description of the central part of isotropic ($r=0$) and anisotropic ($r=2$) light scattering spectra involves only the frequency-independent Markovian (impact) limit of the relaxation matrix $\Gamma^{(r)}$. This approach is justified by the fact that for a photon energy nearly equal to the molecular resonance frequencies the energy defect can be neglected. The ''three participants'' situation (two colliding molecules plus one photon), which takes place in the spectroscopic study, is then simplified to the usual scattering theory (two colliding molecules). On the contrary, the treatment of spectral wings needs the introduction of the frequency dependence of the relaxation matrix $\Gamma^{(r)}(\omega)$ due to the significant increase (or decrease) of the rototranslational energy by the extra photon energy during the transition process.

In general, the matrix elements of $\Gamma^{(r)}(\omega)$ characterize the coupling between two optical transitions $i\rightarrow f$ and $i'\rightarrow f'$ from the initial $i(i')$ to the final $f(f')$ states of the active molecule and thus need four indices $\Gamma^{(r)}_{if,i'f'}(\omega)$. The expression for the spectral density $\tilde{S}^{(r)}(\omega)$ can be written as [3–5]

$$\tilde{S}^{(r)}(\omega)=\frac{1}{\pi}\,\mathrm{Re}\sum_{if,i'f'}A^{(r)}_{if}[i(\omega-L_s)+n\Gamma^{(r)}(\omega)]^{-1}_{if,i'f'}A^{(r)}_{i'f'}. \tag{1}$$

Here $A^{(r)}_{if}$ are the components of the associated rth rank irreducible spherical coupling tensor in the line-space basis (for the optical transition $i\rightarrow f$)

$$A^{(r)}_{if}=(-1)^{J_i}[J_iJ_f]^{1/2}\begin{pmatrix} J_i & r & J_f\\ 0 & 0 & 0\end{pmatrix}n_{if},$$

where $[abc\cdots]\equiv(2a+1)(2b+1)(2c+1)\cdots$ and $(:::)$ is a $3J$ symbol. n_{if} is the norm of the line-space vectors (the transition operators $|f\rangle\langle i|$), obtained with the symmetrized form of the scalar product [5]

$$n_{if}=[(\rho_i+\rho_f)/2]^{1/2},$$

where $\rho_i=Z^{-1}_{\mathrm{rot}}\exp[-\beta BJ_i(J_i+1)]$ with $\beta=(kT)^{-1}$ and B is the rotational constant of the active molecule. The squared values of $A^{(r)}_{if}$ give the intensities of separate lines. L_s is the Liouville operator for the free active molecule leading, in the basis used, to the diagonal matrix of proper rotational transition frequencies ω_{fi}.

For low density values n of the perturbing molecules, Eq. (1) leads to a spectrum consisting of isolated lines described by the diagonal elements of $\Gamma^{(r)}$, whose real and imaginary parts represent linewidths and line shifts. At high densities, the lines overlap and the observed band shapes are greatly modified. Consequently, the off-diagonal elements must also be known, since they are responsible for the transfer of intensity between lines.

The infinite-order sudden (IOS) approximation [6], which is obtained by neglecting the molecular rotation during the collision, allows us to construct the entire $\Gamma^{(r)}$ matrix from its diagonal. But, in this approach, two fundamental relations (the sum rules and the detailed balance) are lost. The energy-corrected sudden (ECS) model [7] consists first in reintroducing, at least approximately, the effect of molecular rotation and then in imposing the sum rules and the detailed

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*Permanent address: Institute of Physics, Saint Petersburg University, Peterhof, Saint Petersburg 198904, Russia.

balance relation. This model leads to a reasonable theoretical interpretation of numerous experimental spectra [8–11].

For the past several years, experimental techniques have allowed the spectral intensities to be measured in the very far wings. For example, the anisotropic depolarized Raman spectrum of N_2 at high pressure has been observed by Le Duff and Teboul [12] up to 620 cm^{-1}. This wide frequency domain needs the theoretical description to be essentially non-Markovian and the entire relaxation matrix $\Gamma^{(2)}(\omega)$ must be known. For sufficiently high rotational energy states the Massey parameter $\eta=\omega_{fi}\tau_c$, where τ_c is the mean collision duration, is large. This means that the collisions are adiabatic. The interaction picture becomes static and the perturbation theory (PT) approximation becomes valid since the smallness condition of the rotational perturbation in comparison with the considered energy gap $\hbar\omega_{fi}$ can be satisfied. Such a calculation was realized by Fu *et al.* [13], who demonstrated that the observed intensities in the far wing are essentially due to the allowed rototranslational spectrum and not to induced effects.

But the actual description of the spectrum is incomplete. At low frequencies the Markovian (ω-independent) ECS model leads to a good description [7–11], while at high frequencies the PT treatment (including the ω dependence) is available [5,13]. The analysis of the relaxation matrix in these two limiting approaches [5] demonstrates the presence of a common structure. This indicates the possibility of unified treatment for the whole frequency range.

Recently, a general non-Markovian extension of the relaxation matrix in the frame of the ECS approach was proposed by Kouzov [14] by incorporating incomplete collisions in the Fano-Mori formalism together with complete ones. It should be noted that a non-Markovian relaxation matrix can be obtained within the completed collisions scheme [15], but the sum rules fail. In Ref. [14] the relaxation matrix is expressed through the collisional superoperator [3] with the full Hamiltonian

$$H=H_R+H_B+V,$$

where H_R is the rotational Hamiltonian (which is neglected in the IOS approach), H_B is the bath Hamiltonian (including the isotropic part of the interaction potential), and V stands for the anisotropic part of the interaction. The specific choice of the bath basis as the eigenbasis of H_B+V at a fixed molecular axis orientation in the laboratory frame greatly simplifies the calculation. The relaxation matrix is then completely defined by the correlation functions characterizing the intracollisional dynamics. The relaxation matrix obtained is symmetric, so that the sum rules are double sided and the Ben Reuven relation [16] accounting for the time-reversal symmetry is respected.

In Sec. II, starting from the general expression of Ref. [14] we put it in a concrete ECS form. This is done by preserving the main assumptions of the usual impact ECS model [7] developed for the isotropic scattering case and without introducing any additional parameter. The important particular case of the Q_{iso} branch is discussed separately in Sec. III. The detailed balance factor obtained in the framework of the actual model improves the *ad hoc* factor previously introduced by De Pristo *et al.* [7]. Finally, the calculation of the N_2 rototranslational spectrum in the whole frequency range, including the far wing, is presented and discussed in Sec. IV. The concluding section is devoted to summarizing remarks.

II. ECS MODEL FOR THE RELAXATION MATRIX

It should be recalled that the ECS model was proposed by De Pristo *et al.* [7] for calculating the rotational transition probability $\Gamma_{JJ'}$ for going from state J to state J'. The main result of this model was to obtain $\Gamma_{JJ'}$ simply by correcting the corresponding IOS expression by a multiplicative J-dependent adiabaticity factor Ω_J accounting for the effect of molecular rotation during the collision. This aproximation for the relaxation matrix will be preserved in the present non-Markovian extension of the ECS model.

To do this, we start from the general expression for the off-diagonal matrix element [14]

$$\begin{aligned}\Gamma^{(r)}_{if,i'f'}(\omega)=&-[1+\exp(-\beta\hbar\omega)]/2n_{if}n_{i'f'}\\ &\times\sum_L [L]F^{Lr}_{if,i'f'}[\rho_i\Phi_L(\omega-\omega_{f'i})\\ &+\rho_{i'}\Phi^*_L(\omega-\omega_{fi'})],\end{aligned} \tag{2}$$

where the symmetrized Percival-Seaton coefficient is introduced,

$$\begin{aligned}F^{Lr}_{if,i'f'}=&[J_iJ_fJ'_iJ'_f]^{1/2}\begin{pmatrix}J'_i & L & J_i\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}J_f & L & J'_f\\ 0 & 0 & 0\end{pmatrix}\\ &\times\begin{Bmatrix}J_i & J_f & r\\ J'_f & J'_i & L\end{Bmatrix}.\end{aligned}$$

Here the quantity in braces is a $6J$ symbol. The correlation functions $\Phi_L(\omega)$ characterize the intracollisional dynamics and satisfy the Boltzmann relation [17]

$$\Phi_L(-\omega)=\exp(-\beta\hbar\omega)\,\Phi_L(\omega). \tag{3}$$

Notice that Eq. (2) ensures the fundamental symmetry property

$$\Gamma^{(r)}_{if,i'f'}(\omega)=\Gamma^{(r)}_{i'f',if}(\omega), \tag{4}$$

the time-reversal symmetry (the Ben-Reuven relation [16])

$$\Gamma^{(r)}_{if,i'f'}(\omega)=\Gamma^{(r)*}_{fi,f'i'}(-\omega), \tag{5}$$

and also the double-sided sum rules

$$\begin{aligned}-\sum_{i'f'\neq if}\Gamma^{(r)}_{if,i'f'}(\omega)A^{(r)}_{i'f'}=&-\sum_{i'f'\neq if}A^{(r)}_{i'f'}\Gamma^{(r)}_{i'f',if}(\omega)\\ &=\Gamma^{(r)}_{if,if}(\omega)A^{(r)}_{if}.\end{aligned} \tag{6}$$

In fact Eq. (6) allows the diagonal elements to be calculated once the off-diagonal ones are known.

From a practical standpoint, it is easier to operate with classical even functions $\Phi^{\mathrm{class}}_L(\omega)$ instead of the quantum ones appearing in Eq. (2). Due to Eq. (3), this can be achieved by identifying the quantum asymmetry factor consistent with Eq. (2),

$$\mathrm{Re}\,\Phi_L(\omega)=\frac{2}{1+\exp(-\beta\hbar\omega)}\Phi_L^{\mathrm{class}}(\omega). \tag{7}$$

Concerning the imaginary part of $\Phi_L(\omega)$, previous studies [8,10] of the isotropic and anisotropic vibrational Raman Q branches have shown that the influence of the imaginary part of the relaxation matrix is expected to be small, and will be neglected here. Taking into account the even parity of $\Phi_L^{\mathrm{class}}(\omega)$ and the Boltzmann distribution of the populations one obtains

$$\Gamma^{(r)}_{if,i'f'}(\omega)=-\frac{1+\exp(-\beta\hbar\omega)}{4n_{if}n_{i'f'}}\sum_L [L]F^{Lr}_{if,i'f'}\times\left[\frac{\rho_i\Phi_L^{\mathrm{class}}(\omega-\omega_{f'i})}{1+\exp[-\beta\hbar(\omega-\omega_{f'i})]}+\frac{\rho_{i'}\Phi_L^{\mathrm{class}}(\omega-\omega_{fi'})}{1+\exp[-\beta\hbar(\omega-\omega_{fi'})]}\right]. \tag{8}$$

Now we assume that all the classical correlation functions have the same time dependence; this allows the $\Phi_L^{\mathrm{class}}(\omega)$ to be factorized into L- and ω-dependent parts

$$\Phi_L^{\mathrm{class}}(\omega)=Q'_L\Omega(\omega).$$

Furthermore, the correlation function $\Omega(\omega)$ will be identified with the adiabaticity factor of De Pristo *et al.* [7],

$$\Omega(\omega)=\left(1+\frac{b_c^2}{12\,n\,\overline{v^2}}\omega^2\right)^{-n},\quad n=2 \tag{9}$$

where the characteristic interaction length b_c is a fitted parameter. This choice leads directly to the traditional adiabaticity factor $\Omega_L=\Omega(\omega_{L0})$ [7]. Here the situation is getting complicated by the presence of $\omega_{f'i}$ and $\omega_{fi'}$. To overcome this difficulty, we separate these frequencies into their optical and collisional parts

$$\Omega(\omega-\omega_{f'i})=[\Omega(\omega-\omega_{fi}+\omega_{ff'})+\Omega(\omega-\omega_{f'i'}+\omega_{ii'})]/2, \tag{10}$$

$$\Omega(\omega-\omega_{fi'})=[\Omega(\omega-\omega_{fi}-\omega_{ii'})+\Omega(\omega-\omega_{f'i'}-\omega_{ff'})]/2. \tag{11}$$

The presence of both optical transitions ω_{fi} and $\omega_{f'i'}$ is justified by the symmetry condition of the relaxation matrix [cf. Eq. (4)].

The full implementation of the original ECS approach [7] consists now in replacing each collisional frequency $\omega_{kk'}$ ($kk'=ii'$ or ff') by the frequency $\overline{\omega}_{kk'}$ of the transition from the upper level to the closest one consistent with the symmetry of the interaction potential

$$\overline{\omega}_{kk'}=\begin{cases}\omega_{k,k-\delta}, & k>k'\\ 0, & k=k'\\ -\omega_{k',k'-\delta}, & k<k'\end{cases} \tag{12}$$

with $\delta=2$ for N_2. Under all the above mentioned remarks, the final non-Markovian ECS expression for the off-diagonal relaxation matrix element can be factorized into its impact limit and an ω-dependent correction factor

$$\begin{aligned}\Gamma^{(r)}_{if,i'f'}(\omega)={}&\Gamma^{(r)\mathrm{impact}}_{if,i'f'}\frac{1+\exp(-\beta\hbar\omega)}{\{[1+\exp(-\beta\hbar\omega_{fi})][1+\exp(-\beta\hbar\omega_{f'i'})]\}^{1/2}}\\&\times\left[2\frac{\Omega(\overline{\omega}_{ii'})+\Omega(\overline{\omega}_{ff'})}{\rho_i+\rho_{i'}}\right]^{-1}\left[\frac{\Omega(\omega-\omega_{fi}+\overline{\omega}_{ff'})+\Omega(\omega-\omega_{f'i'}+\overline{\omega}_{ii'})}{\rho_{i'}+\rho_i\exp[-\beta\hbar(\omega-\omega_{f'i'})]}\right.\\&\left.+\frac{\Omega(\omega-\omega_{fi}-\overline{\omega}_{ii'})+\Omega(\omega-\omega_{f'i'}-\overline{\omega}_{ff'})}{\rho_i+\rho_{i'}\exp[-\beta\hbar(\omega-\omega_{fi})]}\right],\end{aligned} \tag{13}$$

where the impact limit

$$\Gamma^{(r)\mathrm{impact}}_{if,i'f'}=-\frac{1}{2}\frac{(\rho_i\rho_{i'})^{1/2}}{\rho_i+\rho_{i'}}[\Omega(\overline{\omega}_{ff'})+\Omega(\overline{\omega}_{ii'})]\times\sum_L [L]F^{Lr}_{if,i'f'}Q'_L \tag{14}$$

is obtained by setting $\omega=\omega_{fi}$ or $\omega_{f'i'}$ depending on the considered term.

As easily verified, this final expression respects all necessary relations [Eqs. (4) and (5)]. Concerning the sum rules of Eq. (6), they are automatically verified since, as already mentioned, they are used to calculate the diagonal elements. To make clear the physical meaning of the Q'_L coefficients, the isotropic scattering case is of particular interest.

III. MARKOVIAN LIMIT FOR Q_{iso}

A previous theoretical study of the isotropic Raman rovibrational Q_{iso} branch [8] has shown that the vibrational effects are limited to a global shift of the whole branch. For this Q_{iso} branch ($r=0$, $i=f=J$, $i'=f'=J'$) in the Markovian approximation ($\omega=\omega_{fi}=\omega_{f'i'}=0$), the off-diagonal matrix element of Eq. (14), in traditional nonsymmetrized form, is

TABLE I. Basic rates Q_L parameters [Eq. (16)] and adiabaticity factor Ω parameters [Eq. (9)] for the ECS-P and ECS-EP models with different detailed balance factors for pure N_2.

Model	Detailed balance factor	A (295 K) mK/amagat	N	α	γ	n	b_c(Å)
ECS-EP	De Pristo	51.24	1.178	0.7556	0.5183	1	0.8217
	De Pristo	33.02	1.302	0.7474	0.5870	2	0.7486
	Ben Reuven	29.28	1.145	0.7929	0.5963	1	0.9235
	Ben Reuven	29.94	1.161	0.7939	0.6318	2	0.8239
ECS-P	De Pristo	78.30	0.9379	1.200	0	2	0.7829
	Ben Reuven	53.34	0.9634	1.069	0	2	1.045

$$\tilde{\Gamma}_{JJ'} \equiv \left(\frac{[J']\rho_{J'}}{[J]\rho_J}\right)^{1/2} \Gamma^{(0)}_{JJ,J'J'}(0)$$
$$= -\frac{[J']\rho_{J'}}{\rho_J+\rho_{J'}}\Omega_{J_>}\sum_L [L]\begin{pmatrix} J & L & J' \\ 0 & 0 & 0 \end{pmatrix}^2 Q'_L, \qquad (15)$$

where $J_> = \max(J,J')$. It differs from the original De Pristo *et al.* expression [7] by the detailed balance factor $\rho_{J'}/(\rho_J + \rho_{J'})$ instead of $\rho_{J>}/\rho_J$. But it can be verified that these factors are identical in both limiting cases $J \gg J'$ and $J \ll J'$.

Nevertheless, this expression of the off-diagonal matrix elements allows the basic transition rates to be identified,

$$Q_L \equiv \tilde{\Gamma}_{L0} = \frac{\Omega_L}{1+\rho_L/\rho_0} Q'_L .$$

The use of this alternative (known as Ben-Reuven's) detailed balance factor needs a new determination of the basic rates Q_L. The usual procedure has been used here by introducing either the exponential-polynomial (ECS-EP) modeling of the L dependence of the Q_L [18],

$$Q_L = A(T)[L(L+1)]^{-\alpha}\exp[-\gamma\beta B L(L+1)],$$
$$A(T) = A(T_0)\left(\frac{T}{T_0}\right)^{-N}, \qquad (16)$$

where T_0 is a reference temperature, or the polynomial (ECS-P) modeling ($\gamma = 0$) [8]. This procedure consists in minimizing the mean square deviation between the theoretical linewidths and the experimental linewidths obtained from low-pressure measurements on isolated $Q_{\mathrm{iso}}(J)$ lines [19,20]. The theoretical linewidths $\tilde{\Gamma}_{JJ}$ are obtained through the sum rule [Eq. (6)] which reads in the particular case of a $Q_{\mathrm{iso}}(J)$ line

$$\tilde{\Gamma}_{JJ} = -\sum_{J' \neq J} \tilde{\Gamma}_{JJ'} .$$

The optimized Q_L parameters A, N, α, γ corresponding to the two detailed balance factors are collected in Table I for pure N_2. The values of the parameter b_c for the adiabaticity factor are also presented for the two values $n = 1$ and 2.

IV. APPLICATION TO THE N_2 ROTOTRANSLATIONAL SPECTRUM

The measurements far from the band center can be realized only at high pressures. It may be thought that the resulting spectrum is the superposition of a collision-induced spectrum and of the allowed rototranslational one. Nevertheless, it was demonstrated [13] by a full quantum perturbation calculation in the case of N_2, that beyond 350 cm^{-1}, the measured intensity is only due to the allowed spectrum. This situation provides a test for the non-Markovian model developed above. It should be noticed that due to Eq. (5) the spectral density $\tilde{S}^{(r)}(\omega)$ defined by Eq. (1) is symmetric with respect to the frequency, while the observed spectral density $S^{(r)}(\omega)$ is asymmetric and satisfies the Boltzmann relation [5]

$$S^{(r)}(-\omega) = \exp(-\beta\hbar\omega) S^{(r)}(\omega). \qquad (17)$$

$S^{(r)}(\omega)$ can be related to $\tilde{S}^{(r)}(\omega)$ by introducing a quantum asymmetry factor. In general, the choice of this factor is not unique and influences greatly the calculated shape at high frequencies. Here, due to the accepted symmetric form of the scalar product, one has

$$S^{(r)}(\omega) = \frac{2}{1+\exp(-\beta\hbar\omega)} \tilde{S}^{(r)}(\omega). \qquad (18)$$

The full relaxation matrix for O-Q-S branches was calculated by Eq. (13) with different parametrizations for Q_L and $\Omega(\omega)$ (cf. Table I) and substituted in Eq. (1). Then, the resulting spectra are corrected by the quantum asymmetry factor of Eq. (18). Finally, the calculated spectra are related to the absolute cross section $V\partial^2\sigma/\partial\Omega\partial\omega$ (cm^6) measured by Le Duff and co-workers [12,21,22] by

$$V\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = \frac{4k_0 k^3 \gamma^2}{15 n_0}\frac{1}{\rho} S^{(2)}(\omega). \qquad (19)$$

The proportionality factor is obtained by comparing the definitions of the double differential cross sections from Refs. [13,21]. Notice that, here, the wave numbers k and k_0, associated, respectively, with the scattered and the incident radiations ($k_0 = 1.2212 \times 10^{-3}$ Å^{-1}) are nearly equal. γ is the anisotropic polarizability of N_2 ($\gamma = 4.823$ a.u. [13]) and n_0 is the density of molecules under normal conditions. This leads to $4k_0^4\gamma^2/15n_0 = 1.1283 \times 10^{-48}$ cm^5. The division by ρ

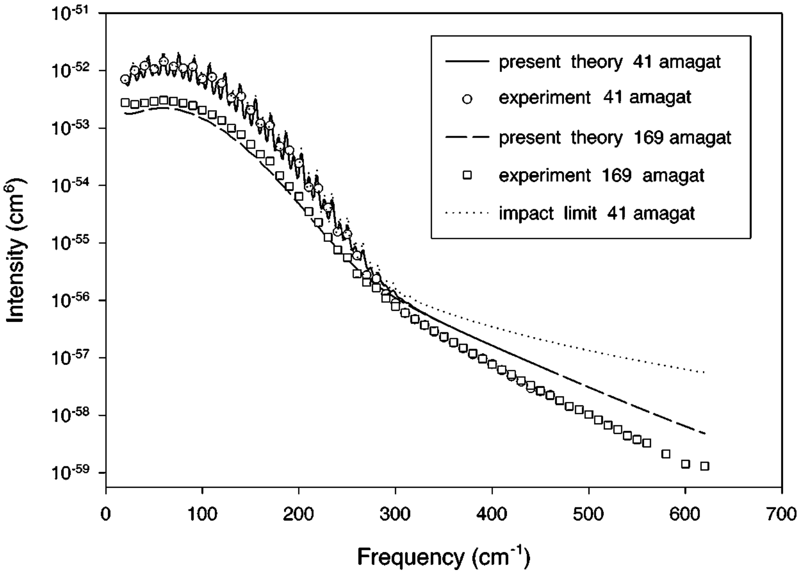

FIG. 1. Calculated and measured absolute cross sections for the anisotropic depolarized Raman spectrum of N_2 at 41 and 169 amagats.

$=n/n_0$ (the amagat density) in Eq. (19) is made to clearly show that the limiting behavior of the spectral function for high ω values,

$$\tilde{S}^{(r)}(\omega) \simeq \frac{n}{\pi} \sum_{if,i'f'} \frac{A_{if}^{(r)*}}{\omega-\omega_{fi}} \Gamma^{(r)}_{if,i'f'}(\omega) \frac{A^{(r)}_{i'f'}}{\omega-\omega_{f'i'}}, \qquad (20)$$

which is proportional to the density, is actually reached beyond 350 cm^{-1}.

The testing of various ECS-P and ECS-EP parametrizations showed that the spectral profiles are very sensitive to the choice of the model in the region of intermediate frequencies 200–300 cm^{-1} and in the far wing (different slopes of the theoretical curves). This means that this wide frequency range study leads to a good discrimination between the different ECS-P and ECS-EP models. It should be recalled that for the isotropic Q-branch case at room temperature [23], when only about 20 lines are visible, the set of experimental linewidths is too poor to favor one of the models.

Here the best results were obtained with the ECS-P model using the Ben Reuven balance. Both calculated curves (at 41 and 169 amagats) and the corresponding experimental values [22] are shown in Fig. 1 for the whole frequency range (20–620 cm^{-1}). The measured intensity in the far wing is actually proportional to the squared density. Up to 400 cm^{-1} the measurements are excellently reproduced by the theory. Increasing overestimation occurs and reaches a factor of 4 at 600 cm^{-1}. Notice that this disagreement can be reduced by a factor of 2 (for these high ω values) if, instead of using the quantum asymmetry factor of Eq. (18), one uses

$$S^{(r)}(\omega)=\tilde{S}^{(r)}(\omega), \quad \omega>0 \quad \text{and} \quad \text{Eq. (17) for } \omega<0$$

by analogy with the empirical observation of De Pristo *et al.* [7] concerning the relaxation matrix. Recall that in the PT calculation of Ref. [13] the disagreement with respect to experiment in this frequency domain was also of this order of magnitude. The overestimation of intensities at high frequencies in our model may be attributed to the lack of validity of

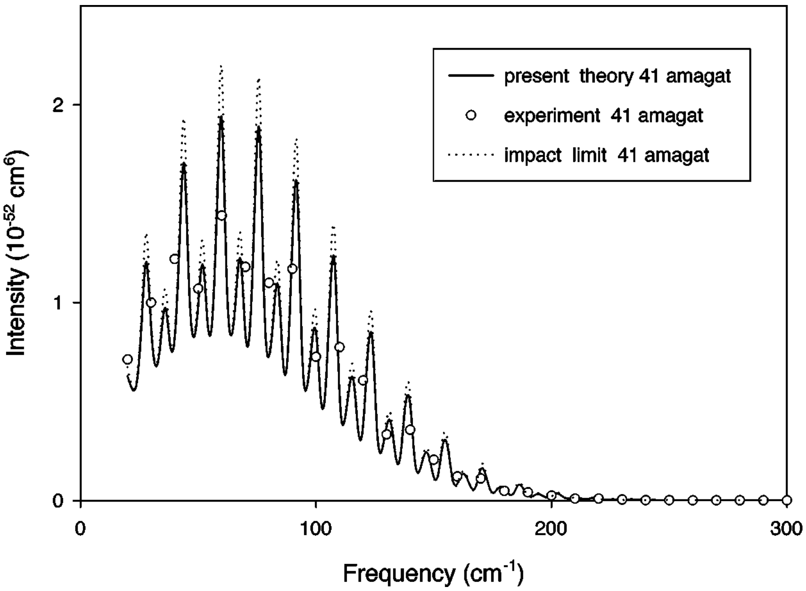

FIG. 2. Calculated and measured rotational structures of N_2 S branch at 41 amagats.

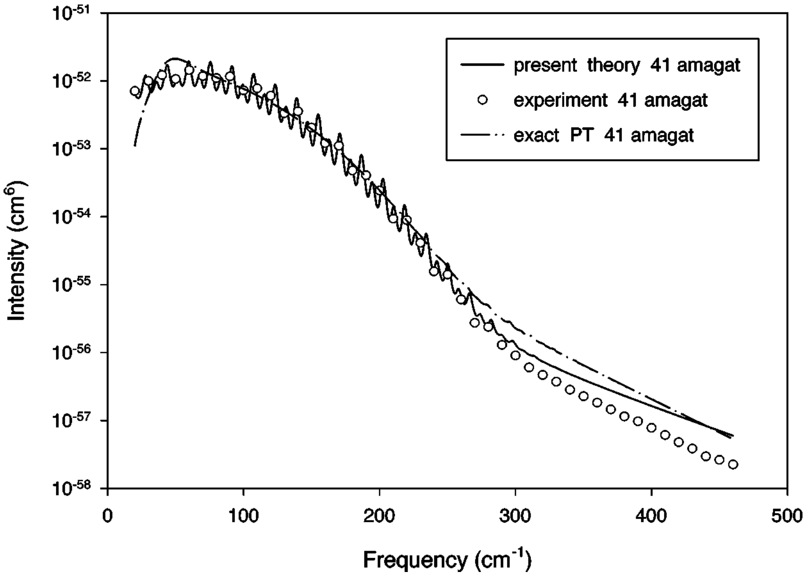

FIG. 3. Absolute intensities in N_2 far wing at 41 amagats. The PT calculation is done with the exact expression for the spectral function.

the adiabaticity factor $\Omega(\omega)$ in Eq. (9) which remains Lorentzian even for high-energy defects $\hbar\omega$. Notice that the correct (Gaussian) behavior of this factor for high ω values could be ensured by using another modeling (expressed through a Bessel function [24]), while in the Markovian limit $(\omega \to 0)$ it should still yield the correct Lorentzian behavior. This modification is actually studied, but it needs the introduction of a new parameter to describe separately the ω dependence of the adiabaticity factor at low and high frequencies.

The calculated intensities beyond 350 cm^{-1} overestimate the measured ones. This confirms that the contribution of the induced spectrum is really of minor importance. The dotted curve of Fig. 1 represents the spectral behavior in the impact limit. It clearly shows that the impact description is adequate for low frequencies (till ≈ 300 cm^{-1}), but in the far wing it disagrees with experiment by one order of magnitude, since the participation of the extra photon energy in the energy balance of the scattering process can no longer be neglected.

At 41 amagats the usual rotational structure of the *S* branch is still visible (Fig. 2). Unfortunately, the low experimental resolution (8 cm^{-1}) [12], needed for measuring the very low intensities in the wing, is not sufficient to reproduce these intensity variations. The result of our PT calculations is also plotted in Fig. 3. PT matrix elements were obtained in the same way as in Ref. [13] but, here, the general spectral density expression of Eq. (1) was used instead of the high-frequency limit of Eq. (20). It is clear that in this PT calculation the diagonal matrix elements for the first few lines are overestimated, so that the rotational structure is smoothed out. Nevertheless, at intermediate frequencies such calculated PT intensities are quite reasonable.

V. CONCLUSION

In the preceding sections, starting from the general theoretical expression of Ref. [14], we proposed a concrete non-Markovian ECS model for the relaxation matrix associated with the arbitrary rank *r* irreducible coupling tensor. The constructed matrix obeys all the known general relations: symmetry (imposed by the detailed balance), double-sided sum rules, and time-reversal equation. It is remarkable that the actual model is built without introducing any new additional parameter. Reasonable description in the whole frequency range, not only in the far wing, was achieved. The present model shows that the role of the induced spectrum is certainly not important, even at high frequencies, as it was already shown in the second-order PT calculation [13]. Moreover, if the resolvent operator $[i(\omega - L_s) + n\Gamma^{(r)}(\omega)]^{-1}$ is not developed, the PT calculation reasonably reproduces the measured intensities even at intermediate frequencies.

The detailed balance factor of De Pristo *et al.* [7], which was introduced empirically, appears as an appropriate alternate approximation for the Ben Reuven balance factor used in the present model.

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[1] F.R. McCourt, J.J.M. Beenaker, W.F. Kohler, and I. Kuscer, *Nonequilibrium Phenomena in Polyatomic Gases* (Clarendon Press, Oxford, 1990), Chaps. 10 and 11.
[2] A.I. Burshtein and S.I. Temkin, *Spectroscopy of Molecular Rotation in Gases and Liquids* (Cambridge University Press, Cambridge, England, 1994).
[3] D. Forster, in *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (Benjamin, London, 1975).
[4] H. Mori, Prog. Theor. Phys. **33**, 423 (1965).
[5] A.P. Kouzov and J.V. Buldyreva, Chem. Phys. **221**, 103 (1997).

[6] R. Goldflam, S. Green, and D.J. Kouri, J. Chem. Phys. **67**, 4149 (1977).

[7] A.E. De Pristo, S.D. Augustin, R. Ramaswamy, and H. Rabitz, J. Chem. Phys. **71**, 850 (1979).

[8] L. Bonamy, J. Bonamy, D. Robert, B. Lavorel, R. Saint-Loup, R. Chaux, J. Santos, and H. Berger, J. Chem. Phys. **89**, 5568 (1988).

[9] L. Bonamy, J. Bonamy, S. Temkin, D. Robert, and J.M. Hartman, J. Chem. Phys. **98**, 3747 (1993).

[10] L. Bonamy, J. Bonamy, D. Robert, S.I. Temkin, G. Millot, and B. Lavorel, J. Chem. Phys. **101**, 7350 (1994).

[11] L. Bonamy and F. Emond, Phys. Rev. A **51**, 1235 (1995).

[12] Y. Le Duff and V. Teboul, Phys. Lett. A **157**, 44 (1991).

[13] Yi. Fu, A. Borysow, and M. Moraldi, Phys. Rev. A **53**, 201 (1996).

[14] A.P. Kouzov, in *Spectral Line Shapes*, 14th International Conference on Spectral Line Shapes, State College, PA, 1998, edited by R. M. Herman, AIP Conf. Proc. No. 467 (AIP, Woodbury, NY, 1999), Vol. 10, p. 497; and private communication.

[15] U. Fano, Phys. Rev. **141**, 34 (1966).

[16] A. Ben-Reuven, Phys. Rev. **141**, 34 (1966).

[17] L.D. Landau and E.M. Lifshitz, *Theoretical Physics*, Statistical Physics Vol. 5 (Nauka, Moscow, 1976).

[18] G. Millot, J. Chem. Phys. **93**, 8001 (1990).

[19] B. Lavorel, G. Millot, R. Saint-Loup, C. Wenger, H. Berger, J.P. Sala, J. Bonamy, and D. Robert, J. Phys. (Paris) **47**, 417 (1986).

[20] L.A. Rahn and R.E. Palmer, J. Opt. Soc. Am. B **3**, 1164 (1986).

[21] Y. Le Duff, T. Bancewicz, and W. Glaz, in *Collision- and Interaction-Induced Spectroscopy*, edited by G.C. Tabisz and N.M. Neuman (Kluwer Academic Publishers, Dordrecht, 1995), pp. 423–440.

[22] Y. Le Duff (private communication).

[23] G.J. Rosasco, W. Lempert, W.S. Hurst, and A. Fein, Chem. Phys. Lett. **97**, 435 (1983).

[24] P.A. Egelstaff and P. Schofield, Nucl. Sci. Eng. **12**, 260 (1962); G. Birnbaum and E.R. Cohen, Can. J. Phys. **54**, 593 (1976).