

Conservation of resonance frequency in the collisional transitions between spectral lines

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Collisional transitions between molecular lines give rise to relevant modifications of the spectral distribution of absorption. We discuss here the consistency of such a coupling effect with the conservation of resonance frequency for the scattered lines, a requirement that, in the frame of the usually adopted impact approximation models, should follow from the conservation of energy in the collisions. This problem, leads either to the need for a more appropriate theoretical treatment of collisional coupling or to the existence of a decoupling between well resolved lines which could heavily affect the line shape in the far wings. A check allowing discrimination between these two events could be obtained by measurement of the microwave far wing absorption of deuterated ammonia.

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I. IMPACT APPROXIMATION

In order to extend some concepts of the usual scattering theory, such as energy conservation, to collisional transitions between lines, we recall here some basic points of the impact approximation theory [1] usually adopted in the literature for the treatment of the frequency-dependent relaxation operator $\langle M_c(\nu) \rangle$ in the space of the lines introduced by Fano [2], which describes the perturbing effect of the surrounding thermal bath on the spectra.

Within the impact approximation, the interaction of the absorbing (or emitting) molecule with the other perturbing molecules of the gas is described by sudden uncorrelated collisions. Assuming this interaction scheme one usually omits the frequency dependence of $\langle M_c(\nu) \rangle$ which would be induced by correlation between collisions or by their non-negligible duration. Moreover, the collisional regime is binary, as is usually the case for densities up to several tenths of amagats, so that $\langle M_c \rangle$ is linear with the number density n of the perturbers,

$$\langle M_c(\nu) \rangle \approx \langle M_c \rangle = n \langle m \rangle. \quad (1.1)$$

$\langle m \rangle$ is an operator [2] in the space of lines which describes the average contribution of a binary collision to relaxation. It can be expressed [1] in terms of transition matrix elements $T_{\alpha\alpha'}$ between the states of the colliders.

The impact model has proved to be valid for microwave spectra and in general is applicable in a frequency range where the duration τ of the collision is negligible with respect to the inverse of the distance between the line peak ν_0 and photon frequency:

$$|\nu - \nu_0| \ll \frac{1}{2\pi\tau}. \quad (1.2)$$

In the opposite case, the short time details of collisional dynamics should be considered.

In the ordinary space of molecular wave vectors, the effect of collisions is described by the scattering matrix S ,

$$S_{\alpha'\alpha} = \delta_{\alpha'\alpha} - 2\pi i T_{\alpha'\alpha}(E) \delta(E' - E), \quad (1.3)$$

where the transition matrix $T(E)$ obeys the Lippmann-Schwinger equation

$$T(E) = V + \frac{1}{E - H_0 + i\epsilon} T(E) \quad (\epsilon \rightarrow 0) \quad (1.4)$$

and describes the dynamics of the collision between a pair of molecules. V is the collisional potential, H_0 is the unperturbed Hamiltonian of the colliding pair, and its eigenvalues E and E' are the energy of the “ingoing” state $|\alpha\rangle$ and the “outgoing” state $|\alpha'\rangle$, respectively. The δ function $\delta(E' - E)$ expresses energy conservation in the collision. Each state $|\alpha\rangle$ is composed of the internal states of the two molecules (absorber a and perturber p) and of the wave vector \mathbf{k} of the relative motion:

$$|\alpha\rangle \equiv |a, p, \mathbf{k}\rangle. \quad (1.5)$$

The matrix element

$$\langle a', p', \mathbf{k}' | T(E) | a, p, \mathbf{k} \rangle \delta(E' - E) \quad (1.6)$$

gives the amplitude of a collisional transition between the ingoing state $|a, p, \mathbf{k}\rangle$ with energy $E = E_a + E_p + E_k$ and the outgoing state $|a', p', \mathbf{k}'\rangle$ with energy $E' = E'_a + E'_p + E'_k$.

Computable approximations for the scattering matrix elements (1.6) are obtained [3] by resorting in Eq. (1.4) to a perturbative expansion of $T(E)$ in terms of V :

$$\begin{aligned} T(E) &= T_1(E) + T_2(E) + \dots, \\ T_1(E) &= V, \\ T_2(E) &= V \frac{1}{E - H_0 + i\epsilon} V, \\ &\dots \end{aligned} \quad (1.7)$$

Since molecular transitions, rather than single molecular states, are the spectroscopic observables, spectral quantities, such as resonance frequencies ν_0 and linewidths Γ , are better treated in the Liouville subspace of the lines [2] whose vector basis $|\ell\rangle\rangle = |\ell_i\rangle\langle\ell_f|$ corresponds to dipolar transitions

$\ell_i \rightarrow \ell_f$ between two states of the absorbing molecule. Appropriate Liouville operators $S_{\ell\ell'}$ and $T_{\ell\ell'}$ in this subspace can be obtained describing the scattering between line vectors; just as $S_{\alpha'\alpha}$ and $T_{\alpha'\alpha}$ describe this process in the ordinary space. An operator $m_{\ell\ell'}(p, \mathbf{k})$ can be defined [1] which represents the contribution to the relaxation matrix $\langle \mathbb{M}_c \rangle_{\ell\ell'}$ of a collision occurring at given values of the thermal bath parameters p and \mathbf{k} . The Liouville scattering matrix $S(p, \mathbf{k})$ and the relaxation operator $m(p, \mathbf{k})$ can be expressed in terms of the ordinary scattering matrix S :

$$m_{\ell\ell'}(p, \mathbf{k}) = \langle \langle \ell | m(p, \mathbf{k}) | \ell' \rangle \rangle = \delta_{\ell\ell'} - S_{\ell\ell'}(p, \mathbf{k}), \quad (1.8a)$$

$$\begin{aligned} S_{\ell\ell'}(p, \mathbf{k}) &= \langle \langle \ell | S(p, \mathbf{k}) | \ell' \rangle \rangle \\ &= \sum_{p'} \int d\mathbf{k}' \langle \ell_i, p, \mathbf{k} | S | \ell'_i, p', \mathbf{k}' \rangle \\ &\quad \times \langle \ell'_f, p', \mathbf{k}' | S^\dagger | \ell_f, p, \mathbf{k} \rangle. \end{aligned} \quad (1.8b)$$

The relaxation operator $\langle m \rangle$ of Eq. (1.1) is obtained by averaging $m(p, \mathbf{k})$ over the bath variables:

$$\langle m \rangle = \langle f(p, \mathbf{k}) m(p, \mathbf{k}) \rangle_{p, \mathbf{k}}, \quad (1.9)$$

where $nf(p, \mathbf{k})$ is the probability per unit time that the absorber has a collision at given values of p and \mathbf{k} . The average over these variables is indicated by $\langle \rangle_{p, \mathbf{k}}$.

The diagonal term $\langle m \rangle_{\ell\ell}$ describes the relaxation of a single line ℓ having Lorentzian shape

$$F_\ell(\nu) = I_\ell \frac{\Gamma_\ell}{(\nu - \nu_\ell - \Delta_\ell)^2 + \Gamma_\ell^2}, \quad (1.10)$$

with line intensity

$$I_\ell = \rho_\ell |\langle \ell_f | \boldsymbol{\mu} | \ell_i \rangle|^2 \quad (1.11)$$

and resonance frequency

$$\nu_\ell = [E(\ell_f) - E(\ell_i)]/h. \quad (1.12)$$

The collisional width Γ_ℓ and collisional shift Δ_ℓ are, respectively, the real and imaginary parts of the relaxation matrix element $\langle \mathbb{M}_c \rangle_{\ell\ell}$,

$$\Gamma_\ell + i\Delta_\ell = \langle \mathbb{M}_c \rangle_{\ell\ell} = n \langle m \rangle_{\ell\ell}. \quad (1.13)$$

Equations (1.8) and (1.3) allow one to express the diagonal part of $\langle m \rangle$, and hence the relaxation parameters Γ_ℓ and Δ_ℓ of isolated lines ℓ , in terms of matrix elements of the transition operator $T(E)$ in the ordinary space of collider states $|\ell, p, \mathbf{k}\rangle$:

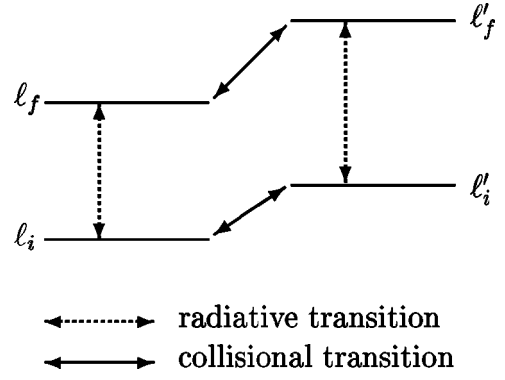


FIG. 1. Schematic representation of collisional coupling effect.

$$\begin{aligned} \langle m \rangle_{\ell\ell} &= \left\langle f(p, \mathbf{k}) \left(\langle \ell_i, p, \mathbf{k} | T(E) | \ell_i, p, \mathbf{k} \rangle \right. \right. \\ &\quad - \langle \ell_f, p, \mathbf{k} | T^\dagger(E) | \ell_f, p, \mathbf{k} \rangle \\ &\quad + \sum_{p'} \int d\mathbf{k}' \langle \ell_i, p, \mathbf{k} | T(E) | \ell_i, p', \mathbf{k}' \rangle \\ &\quad \times \langle \ell_f, p', \mathbf{k}' | T^\dagger(E) | \ell_f, p, \mathbf{k} \rangle \\ &\quad \left. \left. \times 2\pi i \delta(E'_p + E'_k - E_p - E_k) \right) \right\rangle_{p, \mathbf{k}}. \end{aligned} \quad (1.14)$$

The Dirac function $\delta(E'_p + E'_k - E_p - E_k)$ in the third term, bilinear in $T(E)$, follows from energy conservation $\delta(E' - E)$ in the scattering matrix element $S_{\alpha'\alpha}$ of Eq. (1.3). In the semiadiabatic transitions $\ell, p, \mathbf{k} \rightarrow \ell', p', \mathbf{k}'$ energy is transferred only between translation and internal degrees of the perturber.

The perturbative expansion (1.7) of $T(E)$ in terms of V and a classical treatment of relative motion in the collision allow the semiclassical calculations commonly used in the literature for Γ_ℓ and Δ_ℓ to be obtained.

In the case we will study, the shift effect is small in any case and therefore the imaginary part of the relaxation matrix $\langle \mathbb{M}_c \rangle$ will be neglected in the following.

II. COLLISIONAL COUPLING

The off-diagonal part $\langle \mathbb{M}_c \rangle_{\ell\ell'}$ of the relaxation matrix accounts for the collisional transitions between spectral lines, an effect receiving growing attention in recent decades and usually called collisional coupling [1,2,4–10]. A good bibliography can be found in Ref. [11]. Collisional coupling between a pair of molecular lines $\ell = \ell_i \rightarrow \ell_f$ and $\ell' = \ell'_i \rightarrow \ell'_f$ occurs when, as shown in Fig. 1, collision induced transitions between the initial and final states, $\ell_i \leftrightarrow \ell'_i$ and $\ell_f \leftrightarrow \ell'_f$, produce an amplitude transfer between ℓ and ℓ' .

The off-diagonal relaxation terms $\langle \mathbb{M}_c \rangle_{\ell\ell'}$ can be obtained from Eqs. (1.1), (1.8), and (1.9):

$$\begin{aligned}
 \langle \mathbb{M}_c \rangle_{\ell\ell'} &= n \langle f(p, \mathbf{k}) m_{\ell\ell'}(p, \mathbf{k}) \rangle_{p, \mathbf{k}} \\
 &= -n \left\langle f(p, \mathbf{k}) \sum_{p'} \int d\mathbf{k}' \langle \ell_i, p, \mathbf{k} | S | \ell'_i, p', \mathbf{k}' \rangle \right. \\
 &\quad \left. \times \langle \ell'_f, p', \mathbf{k}' | S^\dagger | \ell_f, p, \mathbf{k} \rangle \right\rangle_{p, \mathbf{k}}. \quad (2.1)
 \end{aligned}$$

When off-diagonal relaxation occurs, the line shape is more complicated than a simple sum of Lorentzians and, in the Liouville formalism, is given by [2,5,10]

$$F(\nu) = \frac{1}{\pi} \text{Im} \left\langle \left\langle \boldsymbol{\mu} \left| \frac{1}{\nu - (\mathbb{L}_0 + i \langle \mathbb{M}_c \rangle)} \right| \boldsymbol{\mu} \right\rangle \right\rangle, \quad (2.2)$$

where the scalar product is defined by $\langle\langle A|B \rangle\rangle = \text{Tr}\{\rho A^\dagger B\}$. $\boldsymbol{\mu}$ is the molecular dipole moment whose representation in the Liouville space is given by

$$|\boldsymbol{\mu}\rangle = \sum_{\ell} \mu_{\ell} |\ell\rangle, \quad (2.3)$$

where $\mu_{\ell} = \langle \ell_f | \boldsymbol{\mu} | \ell_i \rangle$ is the amplitude of the line. \mathbb{L}_0 is the Liouville time evolution operator in absence of collisions, whose eigenvectors are the spectral lines with eigenvalues the resonance frequencies:

$$\frac{i}{\hbar} \frac{\partial}{\partial t} |\ell\rangle = \mathbb{L}_0 |\ell\rangle = \nu_{\ell} |\ell\rangle.$$

In the region of line peaks the effect of collisional coupling is not simply described and requires a diagonalization of the non-Hermitian effective Liouville operator $\mathbb{L}_0 + i \langle \mathbb{M}_c \rangle$. Fortunately, a simpler approach can be used when the spread of the eigenvalues of \mathbb{L}_0 is negligible in the denominator of Eq. (2.2). This is the case when the frequency distance between the lines is far smaller than their collisional width,

$$\Gamma_{\ell} \gg |\nu_{\ell} - \nu_{\ell'}|, \quad (2.4a)$$

or when the spectrum is observed in the far wing region,

$$|\nu - \nu_{\ell}| \gg |\nu_{\ell} - \nu_{\ell'}|. \quad (2.4b)$$

In both these cases absorption is well described by an effective line [12]

$$\bar{F}(\nu) = \bar{I} \frac{\Gamma}{(\nu - \bar{\nu})^2 + \bar{\Gamma}}. \quad (2.5a)$$

The intensity, frequency, and width of the effective line are

$$\bar{I} = \sum_{\ell} I_{\ell} = \sum_{\ell} \rho_{\ell} |\mu_{\ell}|^2, \quad (2.5b)$$

$$\bar{\nu} = \sum_{\ell} I_{\ell} \nu_{\ell} / \bar{I}, \quad (2.5c)$$

$$\bar{\Gamma} = \sum_{\ell, \ell'} (I_{\ell} I_{\ell'})^{1/2} \langle \mathbb{M}_c \rangle_{\ell\ell'} / \bar{I}. \quad (2.5d)$$

Separation of diagonal and off-diagonal terms in the right-hand side of Eq. (2.5d) yields

$$\bar{\Gamma} = \Gamma_{\text{av}} + \Gamma_{\text{coup}}, \quad (2.6a)$$

$$\Gamma_{\text{av}} = \sum_{\ell} I_{\ell} \langle \mathbb{M}_c \rangle_{\ell\ell} / \bar{I} = \sum_{\ell} I_{\ell} \Gamma_{\ell} / \bar{I}, \quad (2.6b)$$

$$\Gamma_{\text{coup}} = \sum_{\ell, \ell'; \ell \neq \ell'} (I_{\ell} I_{\ell'})^{1/2} \langle \mathbb{M}_c \rangle_{\ell\ell'} / \bar{I}, \quad (2.6c)$$

and makes it clear that the effective width $\bar{\Gamma}$ is not the weighted average Γ_{av} of the width of the resolved components because a (usually negative) term Γ_{coup} must be added as a consequence of the collisional coupling effect.

III. ENERGY CONSERVATION AND FREQUENCY CONSERVATION

In the space of ordinary wave vectors each collision is described by a S matrix that is subject to energy conservation between ingoing and outgoing molecular states, as expressed by the δ function $\delta(E' - E)$ in Eq. (1.3). We denote by $\Delta E_a = E(a') - E(a)$, by $\Delta E_p = E(p') - E(p)$, and by $\Delta E_k = E(k') - E(k)$ the energy changes of the internal degrees of the absorber, of the perturber, and of translation, respectively. The S -matrix element (1.3) for the collisional transition $a, p, \mathbf{k} \rightarrow a', p', \mathbf{k}'$ becomes

$$\begin{aligned}
 \langle a', p', \mathbf{k}' | S | a, p, \mathbf{k} \rangle &= -2\pi i \langle a', p', \mathbf{k}' | T(E) | a, p, \mathbf{k} \rangle \\
 &\quad \times \delta(\Delta E_a + \Delta E_p + \Delta E_k) \quad (3.1)
 \end{aligned}$$

and therefore vanishes unless

$$\Delta E_a + \Delta E_p + \Delta E_k = 0. \quad (3.2)$$

In the Liouville space of the lines the contributions of each collision to the relaxation matrix $\langle m \rangle$ and $\langle \mathbb{M}_c \rangle$ involve two S -matrix elements, as can be seen from Eqs. (1.8) and (1.9). Energy conservation must hold for both of them. When the off-diagonal components $\langle m \rangle_{\ell\ell'}$ and $\langle \mathbb{M}_c \rangle_{\ell\ell'}$ are considered, this raises the problem that is the object of this paper. Looking at Eq. (2.1), one can see that the energy change in the same transition $p, \mathbf{k} \rightarrow p', \mathbf{k}'$ of the thermal bath must compensate two different energy changes of the absorber: that of the transition $\ell_i \rightarrow \ell'_i$ between the two initial states of the coupling lines and that of the transition $\ell_f \rightarrow \ell'_f$ between their final states.

No problem exists for diagonal terms $\ell = \ell'$. In this case, energy conservation imposes just

$$\Delta E_p + \Delta E_k = 0 \quad (3.3)$$

for both the transitions in Eqs. (1.8b) and (1.14). But the situation is different for the off-diagonal terms $\langle M_c \rangle_{\ell\ell'}$ in Eq. (2.1), receiving contributions from correlated products of S -matrix elements

$$\langle \ell_i, p, \mathbf{k} | S | \ell'_i, p', \mathbf{k}' \rangle \langle \ell'_f, p', \mathbf{k}' | S^\dagger | \ell_f, p, \mathbf{k} \rangle \quad (3.4)$$

where $\ell \neq \ell'$. From energy conservation in the first S -matrix element we have

$$\Delta E_i = E(\ell'_i) - E(\ell_i) = -\Delta E_p - \Delta E_k. \quad (3.5a)$$

The same energy balance holds for the second S -matrix element of Eq. (3.4):

$$\Delta E_f = E(\ell'_f) - E(\ell_f) = -\Delta E_p - \Delta E_k. \quad (3.5b)$$

Since

$$\Delta \nu = \nu_{\ell'} - \nu_\ell = (\Delta E_f - \Delta E_i)/h, \quad (3.6)$$

Eqs. (3.5) yield frequency conservation

$$\Delta \nu = \nu_{\ell'} - \nu_\ell = 0 \quad (3.7)$$

for the two coupling spectral transitions.

Equations (1.8), (1.3), and (3.5) allow the off-diagonal part of the relaxation matrix $\langle M_c \rangle$ to be expressed in terms of matrix elements of the transition operator $T(E)$ in the ordinary space of colliders states:

$$\begin{aligned} \langle M_c \rangle_{\ell\ell'} &= n \langle m \rangle_{\ell\ell'} \\ &= n \left\langle f(p, \mathbf{k}) \left(\sum_{p'} \int d\mathbf{k}' \langle \ell_i, p, \mathbf{k} | T(E) | \ell'_i, p', \mathbf{k}' \rangle \right. \right. \\ &\quad \times \langle \ell'_f, p', \mathbf{k}' | T^\dagger(E) | \ell_f, p, \mathbf{k} \rangle \\ &\quad \left. \left. \times 2\pi i \delta(\Delta E_\ell + \Delta E_p + \Delta E_k) \right) \right\rangle_{p, \mathbf{k}}, \quad (3.8a) \end{aligned}$$

$$\Delta E_\ell = \Delta E_i = \Delta E_f. \quad (3.8b)$$

Energy conservation is formally described by the function $\delta(E' - E)$ in the expression (1.3) of the scattering matrix $S_{\alpha'\alpha}$; likewise the conservation (3.7) of resonance frequency in collisional transitions between spectral lines is described by the function $\delta(\nu_{\ell'} - \nu_\ell)$ in the Liouville scattering matrix $S_{\ell\ell'}$ of Eq. (1.8), which we express in the form

$$\begin{aligned} S_{\ell\ell'}(p, \mathbf{k}) &= \langle \langle \ell | S(p, \mathbf{k}) | \ell' \rangle \rangle = \delta_{\ell\ell'} - m_{\ell\ell'}(p, \mathbf{k}), \\ m_{\ell\ell'}(p, \mathbf{k}) &= -2\pi i T_{\ell\ell'}(p, \mathbf{k}) \hbar^{-1} \delta(\nu_{\ell'} - \nu_\ell). \quad (3.9) \end{aligned}$$

The Liouville transition matrix $T_{\ell\ell'}(p, \mathbf{k})$ plays in the space of lines the same role as the transition matrix $T_{\alpha\alpha'}$ of Eq. (1.8b) in the ordinary space. From Eqs. (1.8), (1.3), and (3.9), the expression of the off-diagonal coupling part $T_{\ell\ell'}(p, \mathbf{k})$ in terms of transition matrix elements between molecular states becomes

$$\begin{aligned} T_{\ell\ell'}(p, \mathbf{k}) &= \sum_{p'} \int d\mathbf{k}' \langle \ell_i, p, \mathbf{k} | T(E) | \ell'_i, p', \mathbf{k}' \rangle \\ &\quad \times \langle \ell'_f, p', \mathbf{k}' | T^\dagger(E) | \ell_f, p, \mathbf{k} \rangle \\ &\quad \times \delta(\Delta E_\ell + \Delta E_p + \Delta E_k). \quad (3.10) \end{aligned}$$

According to Eqs. (3.7)–(3.10), collisional coupling between separated lines would be strictly forbidden, in complete disagreement with a large number of experimental results. However, due to collisional interaction with bath molecules, the energy levels E_ℓ and resonance frequencies ν_ℓ of the absorber are both affected by an indeterminacy of the order of the linewidth Γ_ℓ , which is the inverse of the time T elapsing between two successive collisions experienced by the absorber, $\Gamma = 1/2\pi T$. The restrictions on collisional transitions imposed by energy and frequency conservation are consequently weakened: the limitations on the energy and frequency differences, δ_E and δ_ν ,

$$\begin{aligned} |\delta_E| &= |E' - E| \lesssim \hbar\Gamma, \\ |\delta_\nu| &= |\nu_{\ell'} - \nu_\ell| \lesssim \Gamma, \quad (3.11) \end{aligned}$$

take the place of the classical $\delta(E' - E)$ and $\delta(\nu_{\ell'} - \nu_\ell)$ functions in Eqs. (1.3) and (3.9) for the scattering matrix S and S . This means that when the indeterminacy caused by collisions of the resonance frequencies is taken into account, coupling does not violate frequency conservation, provided that the lines are not well resolved. As a consequence, the density dependence should be different for diagonal and off-diagonal relaxation matrix elements of the relaxation operator $\langle M_c \rangle$. Denoting by v the average relative velocity in the collisions, the cross section

$$\sigma_{\ell\ell'} = 2\pi \langle M_c \rangle_{\ell\ell'} / nv \quad (3.12)$$

describes the averaged relaxation efficiency of a single collision. The diagonal elements $\sigma_{\ell\ell}$ are independent of n and this leads to a linear density dependence of $\langle M_c \rangle_{\ell\ell}$, which has been accurately checked in many experimental studies. If energy conservation hinders collisional coupling, $\sigma_{\ell\ell'}$ should be density independent only when the lines overlap, but should go to zero at low pressures when the lines are well resolved, giving rise to decoupling. One might think that such a nonlinear dependence of $\langle M_c \rangle_{\ell\ell'}$ should already have been observed. However, as we will discuss in the next section, such an effect is not easily disentangled in the usual cases. On the contrary, it could be clearly observed, if it exists, in an experiment that we propose in order to decide which one of the two following hypotheses is true: (i) the theory of collisional coupling must be better formulated; or (ii) when lines are well separated decoupling occurs.

IV. FAR WING ABSORPTION OF ND₃

Particularly suitable for this kind of investigation is the microwave spectrum of ammonia, the same spectrum that provided the first evidence of the collisional coupling effect [5]. Both isotopic species NH₃ and ND₃ are symmetric top

molecules whose rotational states, defined by the quantum numbers J and K , are split into symmetric (+) and antisymmetric (-) parity states. The inversion transitions

$$\ell_{J,K,+} \equiv J,K,+ \rightarrow J,K,-$$

have a frequency depending on J and K , with an average value ν_0 of approximately 1.6 GHz for ND₃ and approximately 23 GHz for NH₃. Due to pressure broadening, the different inversion transitions merge into a single inversion line ℓ_{+-} . For the case of ND₃ this occurs at pressures of some hundreds of pascals. When the pressure is raised to still higher values, a strong coupling can be observed between the positive frequency inversion transition ℓ_{+-} , which has resonance frequency ν_0 and corresponds to photon emission, and the negative frequency inversion transition ℓ_{-+} , which has resonance frequency $-\nu_0$ and corresponds to photon absorption. When ℓ_{+-} and ℓ_{-+} merge into a unique Debye profile, the linewidth is reduced by collisional coupling approximately by a factor of 4 for NH₃ and approximately by a factor of 5 for ND₃. The problem in this case is simply described in a Liouville space of dimension 2 by the relaxation matrix [5]

$$\langle \mathbb{M}_c \rangle = \begin{pmatrix} \Gamma & -\xi \\ -\xi & \Gamma \end{pmatrix}, \quad (4.1)$$

where Γ is the collisional broadening of both absorption and emission lines and ξ is their collisional coupling parameter. The effective time evolution operator $L_0 + i\langle \mathbb{M}_c \rangle$ in Eq. (2.2) is in this case easily diagonalized, yielding the line shape

$$F_c(\nu) = 2I \frac{(\Gamma - \xi)\nu^2 + (\Gamma + \xi)(\nu_0^2 + \Gamma^2 - \xi^2)}{(\nu^2 - \nu_0^2 - \Gamma^2 + \xi^2)^2 + 4\nu^2\Gamma^2}, \quad (4.2a)$$

very different from the simple sum of two Lorentzians, one at frequency ν_0 (absorption) and the other at frequency $-\nu_0$ (emission):

$$F_0(\nu) = I \left[\frac{\Gamma}{(\nu - \nu_0)^2 + \Gamma^2} + \frac{\Gamma}{(\nu + \nu_0)^2 + \Gamma^2} \right]. \quad (4.2b)$$

In Fig. 2 a comparison is performed between F_c and F_0 for different values of the overlap ratio Γ/ν_0 , a parameter depending linearly on the gas pressure. We used $\xi = \frac{3}{4}\Gamma$, which is a reasonable value for the inversion spectrum of ammonia. Figure 2(a) shows that, when $\Gamma \ll \nu_0$ and the two lines are well resolved, collisional coupling has a negligible effect in the frequency region of the line peaks. The effect is larger for higher values of the overlap ratio. When, on increasing the pressure, the lines are partially overlapping [Figs. 2(b) and 2(c)], they attract each other, while, at still higher pressures, when they merge into a single profile, the linewidth is reduced by collisional coupling [Fig. 2(d)]. According to Eqs. (2.5) and (2.6), in the high pressure limit $\Gamma \gg \nu_0$, the shape is given by a single Debye profile with a width reduced from Γ to $\Gamma - \xi$.

Collisional coupling was introduced by Ben-Reuven [5] just in order to explain this (at that time anomalous) effect,

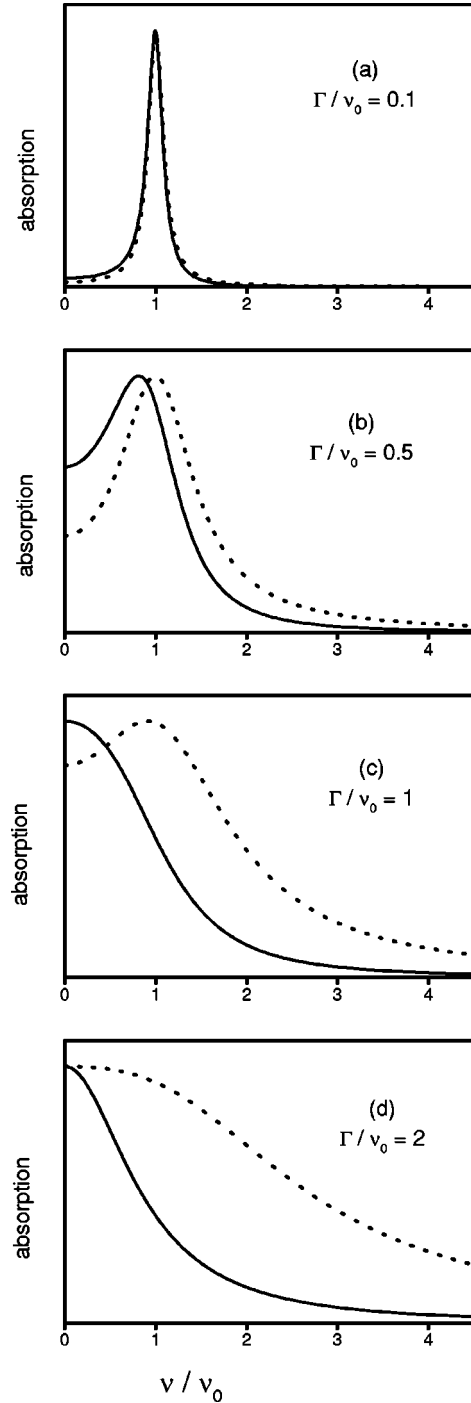


FIG. 2. Collisional coupling between two lines, one at frequency ν_0 and the other at frequency $-\nu_0$. It is assumed that the relaxation matrix is given by Eq. (4.1) and $\xi = (3/4)\Gamma$. The line shape is plotted versus ν/ν_0 for four different values of the overlap ratio Γ/ν_0 either taking (solid line) or not taking (dotted line) collisional coupling into account.

which had been observed by Bleaney and Loubser for NH₃ [13] and by Birnbaum and Maryott for ND₃ [14]. Coupling was later observed for many other molecules and for ammonia also between the two parity components ($+\rightarrow-$ and $-\rightarrow+$) of the far infrared rotational transitions [15,16] and of the infrared rotovibrational transitions [17–21].

We denote by $\bar{\Gamma}$ the ND_3 linewidth obtained when collisional coupling is taken into account and by Γ_{av} the same quantity in the absence of this effect. The same notation is extended to the corresponding cross sections $\sigma = 2\pi\Gamma/nv$ and radii $r = \sigma^{1/2}/\pi$. Quite reliable theoretical calculations are available for \bar{r} and r_{av} . Indeed, the broadening parameter of isolated lines can be obtained by the commonly used semiclassical methods [22]. Then, by performing the average in Eq. (2.6a) one has [23]

$$r_{\text{av}} = 15.1 \times 10^{-8} \text{ cm.} \quad (4.3a)$$

The effective line method of Eqs. (2.5) and (2.6) can be used to take the collisional coupling effect into account, yielding [12,23]

$$\bar{r} = 6.6 \times 10^{-8} \text{ cm,} \quad (4.3b)$$

in reasonable agreement with the measured value $r = 6.9 \times 10^{-8} \text{ cm}$ [14].

On the whole, we have seen that collisional coupling has been well studied in the case of the ammonia inversion spectrum. Modification of the line shape is very large and theoretical treatment is particularly simple because the Liouville space is essentially of dimension 2. However, the existing studies look at absorption peaks; as a consequence, as shown by Fig. 2(a), the coupling effect is small in the case of well resolved lines, which is of interest for the present discussion. Decoupling is not easily examined in that frequency region.

The far wing line shape, which is more suitable for the problem we are interested in, has been studied for other molecules but in this case also a firm conclusion is not easily obtained. Analysis of the spectra is complicated by the large number of off-diagonal terms in a relaxation matrix of large dimension. In some cases a deviation from the line shape forecast by the impact approximation was observed, but this was ascribed to the effect of finite duration of the collisions [24,25].

In contrast, the problem could be easily solved by observing the far wing absorption of deuterated ammonia. Indeed, while condition (2.4a) is false when the lines are well resolved, condition (2.4b) is always true in the far wings. If collisional coupling is not hindered by energy conservation, the far wing absorption should be characterized at any pressure by \bar{r} of Eq. (4.3b). In the opposite case, at low pressures the far wing absorption should be characterized by r_{av} of Eq. (4.3a).

As an example, we choose $\nu = 18 \text{ GHz}$. Results of calculations performed at this frequency are shown in Fig. 3, where the absorption α , divided by p^2 , is reported versus pressure p . The solid line includes the collisional coupling effect, that is to say, uses Eqs. (2.5a) and (4.3b). The dotted line neglects the collisional coupling effect, that is to say, it is simply the sum of the Lorentzian shapes of all the positive and negative frequency inversion lines. If energy conservation has no effect on collisional coupling, absorption should be described in any case by the solid line. If, on the contrary, decoupling is present, the solid line might be reliable only at high pressure, while at low pressure absorption might follow

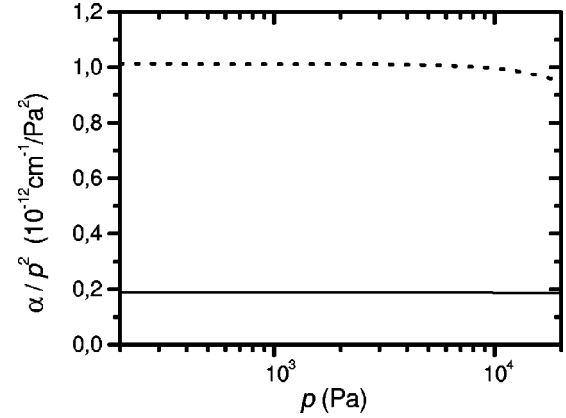


FIG. 3. Dependence on the pressure p for the ND_3 absorption α at 18 GHz, divided by p^2 . Solid line takes collisional coupling into account, dotted line omits this effect.

the dotted line, which is higher by approximately a factor of 5. The transition from solid line to dotted line should occur in the pressure range 10^3 – 10^4 Pa. Indeed, at a pressure of 10^3 Pa, the average linewidth is approximately 200 MHz, much lower than the average inversion frequency $\nu_0 \approx 1.6 \text{ GHz}$. The two inversion components are well resolved and collisional coupling might be hindered by resonance frequency conservation. At pressures of the order of 10^4 Pa, all the positive frequency and negative frequency lines merge into a single absorption profile and collisional coupling should be allowed by the indeterminacy of the resonance frequency of the broadened spectral components.

On the whole, from Fig. 3 one can see that if resonance frequency conservation affects collisional coupling, this should be clearly observed in the microwave far wing of the ND_3 inversion spectrum. A number of reasons make this situation particularly suitable for the purpose.

(1) Collisional coupling is very large. Absorption is changed approximately by a factor of 5, larger by far than the errors involved in the semiclassical calculation of linewidths, which usually do not exceed 10–20%.

(2) Both conditions required by impact approximation are well satisfied. The collisional regime is binary up to 10^6 Pa, while the pressure range of interest is 10^3 – 10^4 Pa. Moreover, the frequency distance from line peak ($\nu - \bar{\nu} = 18 \text{ GHz}$) is small in comparison to the inverse of the duration of a collision ($1/\tau \approx r/v \approx 500 \text{ GHz}$) and condition (1.2) is well respected.

(3) Contribution from the wings of transitions other than inversion is negligible: the nearest rotational line $J=0 \rightarrow 1$ has low intensity and is quite distant.

V. CONCLUSIONS

The impact approximation is usually adopted to treat the collisional coupling effect, which consists of a coherent amplitude transfer between two molecular transitions. We have shown that within this approximation the requirement of energy conservation in the space of molecular states is reflected in the requirement of frequency conservation for the cou-

pling transitions. Hence, collisional coupling between transitions at different frequencies should be possible only when they are not well resolved and because of the indeterminacy in the resonance frequencies of the broadened lines. We suggest an experimental check, consisting in a measurement of the ND₃ absorption at 18 GHz and in the pressure range

10³–10⁴ Pa. This check should show either that the theoretical framework commonly used to describe collisional coupling should be modified, or that a decoupling effect exists which was never considered, but which could be relevant for the far wings of molecular lines. For the case of ND₃, absorption could be changed by a factor of 5.

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