

Collisional coupling between hyperfine and Stark components of molecular spectra

S. Belli, G. Buffa, and O. Tarrini

Dipartimento di Fisica dell'Università, Piazza Torricelli 2, I-56126 Pisa, Italy

(Received 8 July 1996)

A theoretical treatment, based on a tensorial expansion of the scattering matrix, is presented for collisional coupling between hyperfine and Stark components of molecular spectral lines. This treatment also describes the dependence of collisional broadening of well-resolved components on F and M_F quantum numbers. The case of molecules with a large dipole moment is discussed in detail and simple selection rules are obtained for collisional coupling by using our treatment of the relaxation matrix within a perturbative expansion of the scattering matrix. The existing experimental results are explained. [S1050-2947(97)02701-7]

PACS number(s): 33.70.Jg, 34.10.+x

I. INTRODUCTION

As is well known, when the rotational momentum \mathbf{J} of a molecule is coupled to the nuclear spin \mathbf{I} of one of its atoms, a quadrupole hyperfine structure of the states is present. Each component corresponds to different values of the quantum number F eigenvalue of total angular momentum $\mathbf{F}=\mathbf{I}+\mathbf{J}$.

A few studies deal with collisional broadening and a shift of hyperfine components [1–7]. Some theoretical predictions about the dependence on F and M_F of the collisional broadening of the single components were given in Ref. [1]. No F dependence was observed for the $J=1\leftarrow 0$ rotational line of the symmetric top molecules CH_3Cl [2] and CH_3CN [3,4]. On the contrary, a relevant hyperfine variation was observed and theoretically explained for the $J=4\leftarrow 3$, $K=3$ rotational line of CH_3I [5]. The problem was also discussed theoretically in Ref. [6] for the particular case of linear molecules colliding with an atom.

The frequency spread of the hyperfine structure depends on the molecule and on the rotational transition. In some cases the frequency distance between the components is so small that they cannot be resolved. In other cases they are resolved at low pressures and overlapped at higher pressures. Anyhow, a simplifying assumption is implicitly or explicitly used in almost all existing collisional line-shape studies: the spectrum is treated as the sum of noninterfering hyperfine components. This may lead to unreliable conclusions when collisional coupling is present. Indeed, due to coherent amplitude transfer between lines, when some collision-broadened lines are overlapping, the resulting spectrum can be different from the simple sum of the individual Lorentzian shapes. This effect was discussed in many experimental and theoretical studies [7–13], but the case of hyperfine lines is almost unexplored. No general indication can be found in the literature. Some works [3,4,6,14] have shown that collisional coupling between hyperfine components should be small in particular spectra. In Ref. [7] the collisional line shape of rotational transitions of the CHF_2Cl asymmetric-top molecule was studied. A negligible collisional coupling between hyperfine components of a single rotational transition was observed, while coupling, in some cases, was relevant between hyperfine components of different rotational transitions. Some hints were given in that paper on the theoretical explanation of the phenomenon.

We present here a general treatment of the problem that

also includes the possible presence of a static electric or magnetic field splitting the hyperfine lines into components with different values of the hyperfine magnetic quantum number M_F . Since the particular case $I=0$ is included, our treatment also describes, for a molecule without hyperfine structure, the dependence of collisional broadening and coupling on the magnetic quantum number M_J .

In Sec. II the general dependence of collisional broadening and coupling on hyperfine and magnetic quantum numbers is obtained from the symmetry properties of the scattering matrix and its expansion in terms of tensorial operators on the separate degrees of freedom of the colliding molecules. It is supposed that the nuclear spin \mathbf{I} has a negligible influence on the collisional dynamics. Both cases of the presence and absence of static field are considered. In Sec. III the theory is adapted to the standard perturbative approximation, obtaining results that can be used within any of the different perturbative models [15–17] commonly used in the literature. In Sec. IV the case of molecules interacting during collisions mainly by their dipole moment is considered and simple selection rules are obtained, allowing one to evaluate in which cases collisional coupling between hyperfine and Stark components must be taken into account.

II. HYPERFINE DEPENDENCE OF THE RELAXATION MATRIX

The present section is devoted to disentangling the dependence of the relaxation matrix from hyperfine (F and M) and from nonhyperfine (α and J) quantum numbers of the states $\alpha J, FM$ of the absorbing molecule, where $M=M_F$ is the component of \mathbf{F} along the quantization axis and α summarizes all quantum numbers other than J , F , and M . We first suppose that the presence of a static field completely resolves the M degeneration of the states (linear Stark effect or Zeeman effect). Then we treat the case when degeneration in the sign of M occurs (quadratic Stark effect). Finally, we consider the zero-field case. In the present work we assume that the perturbation energy due to the external static field is sufficiently small with respect to the spacing between the unperturbed rotational and hyperfine levels so that, at the same order of approximation, F can be treated as a good quantum number.

A spectral transition

$$l = l_f \leftarrow l_i = \alpha_f J_f, F_f M_f \leftarrow \alpha_i J_i, F_i M_i$$

is represented by the line vector

$$|l\rangle = |\alpha_f J_f, F_f M_f\rangle \langle \alpha_i J_i, F_i M_i|,$$

where $\epsilon = M_f - M_i = 0, \pm 1$ labels the polarization of the radiating field. Within the impact approximation [18], the collisional broadening Γ_{ll} of isolated lines l and the collisional coupling $\Gamma_{ll'}$ between lines l, l' are linear with the number density n of the perturbing molecules. $\Gamma_{ll'}$ are the elements

$$\Gamma_{l,l'} = (\Gamma_{l,l}^i + \Gamma_{l,l}^f) \delta_{l,l'} + \Gamma_{l,l'}^{i,f}, \quad (2.1a)$$

$$\Gamma_{l,l}^i = n \langle \langle \mathbf{q} | \mathbf{r} | \langle \alpha_i J_i, F_i M_i | T | \alpha_i J_i, F_i M_i \rangle | \mathbf{r} \rangle | \mathbf{q} \rangle \rangle_{q,r}, \quad (2.1b)$$

$$\Gamma_{l,l}^f = n \langle \langle \mathbf{q} | \langle \alpha_f J_f, F_f M_f | T^\dagger | \alpha_f J_f, F_f M_f \rangle | \mathbf{r} \rangle | \mathbf{q} \rangle \rangle_{q,r}, \quad (2.1c)$$

$$\Gamma_{l,l'}^{i,f} = -n \left\langle \sum_{r'} \int d\mathbf{q}' \langle \mathbf{q} | \langle \mathbf{r} | \langle \alpha_i J_i, F_i M_i | T | \alpha_i' J_i', F_i' M_i' \rangle | \mathbf{r}' \rangle | \mathbf{q}' \rangle \langle \mathbf{q}' | \langle \mathbf{r}' | \langle \alpha_f' J_f', F_f' M_f' | T^\dagger | \alpha_f J_f, F_f M_f \rangle | \mathbf{r} \rangle | \mathbf{q} \rangle \right\rangle_{q,r}, \quad (2.1d)$$

where $\langle \rangle_{q,r}$ stands for the thermal average on bath parameters, which are the internal states of the perturber \mathbf{r} and the momentum \mathbf{q} of relative translational motion of colliding molecules. From Eq. (2.1a) we can see that the relaxation matrix can be decomposed into two ‘‘single-state,’’ or ‘‘outer,’’ terms and one ‘‘double-state,’’ or ‘‘middle,’’ term. The single-state terms $\Gamma_{l,l}^i$ and $\Gamma_{l,l}^f$ are diagonal in the space of the lines and account for the collisional relaxation of the two states l_i and l_f considered separately. The double-state term $\Gamma_{l,l'}^{i,f}$ involves both initial and final states of the line and is given by a correlated product of collisional matrix elements $\langle l_i | T | l_i' \rangle$ and $\langle l_f' | T^\dagger | l_f \rangle$. Its diagonal part $\Gamma_{l,l}^{i,f}$ is usually negative and decreases the contribution of semiadiabatic collisional transitions $l_i \mathbf{q}, \mathbf{r} \rightarrow l_i \mathbf{q}', \mathbf{r}'$ and $l_f \mathbf{q}, \mathbf{r} \rightarrow l_f \mathbf{q}', \mathbf{r}'$ to the relaxation of the single line l . Its off-diagonal part $\Gamma_{l,l'}^{i,f} (1 - \delta_{l,l'})$ accounts for the rate of amplitude transfer between different lines and hence for collisional coupling.

As we will show in the following, any hyperfine and magnetic dependence is restricted to the double-state part of the relaxation matrix. Hence the F and M dependence of pressure broadening of line l comes from $\Gamma_{l,l}^{i,f}$ while collisional coupling between lines l and l' , and its F and M dependence, comes from $\Gamma_{l,l'}^{i,f}$.

By rotational invariance we can put the T matrix in the tensorial form [19]

$$T = \sum_k \sum_{\lambda, \nu} C_k R_{\lambda}^{\dagger \nu}(k) Q_{\lambda}^{\nu}(k), \quad (2.2a)$$

$$Q_{\lambda}^{\nu}(k) = \sum_{\lambda_1, \lambda_2, \nu_1, \nu_2} \langle \lambda \nu | \lambda_1 \nu_1 \lambda_2 \nu_2 \rangle^1 \tau_{\lambda_1}^{\nu_1}(k)^2 \tau_{\lambda_2}^{\nu_2}(k), \quad (2.2b)$$

of a relaxation matrix Γ in the space of the line vectors $|l\rangle$. Since no data can be found in literature for the hyperfine dependence of the imaginary part of the relaxation matrix, we consider here only the real part of $\Gamma_{ll'}$. However our treatment can be extended with no modification to the imaginary part, whose diagonal elements represent the collisional shift of the lines.

$\Gamma_{ll'}$ can be expressed in terms of T -matrix elements describing the collisional transitions from the initial and final states of the lines l_i and l_f ,

where C are scalar operators, R are tensors in the space of translational states, and τ are tensors in the spaces of internal degrees of absorbing (1) and perturbing (2) molecules, as denoted by the presubscript. The label k accounts for the presence of many terms with the same tensorial degrees λ , λ_1 , and λ_2 .

A relevant simplification is obtained by assuming that the hyperfine energy is small in comparison to the other energies involved (translational and rotational energy) and that the nuclear spin states $|IM_I\rangle$ are not influenced appreciably by collisional forces. In this case the scalars C_k in Eq. (2.2) do not depend on F and ${}^1\tau$ operates only on the space of vectors $|JM_J\rangle$. The matrix elements of ${}^1\tau$ in the coupled representation $|JFM_F\rangle$ can be related directly to the matrix elements in the uncoupled representation $|JM_J M_I\rangle$ by means of the Racah coefficients of the unitary transformation between the two-vector basis:

$$\begin{aligned} & \langle \alpha J, FM | {}^1\tau_{\lambda_1}^{\nu_1} | \alpha' J', F' M' \rangle \\ &= \langle FM | \lambda_1 \nu_1 F' M' \rangle \langle \alpha J | {}^1\tau_{\lambda_1} | \alpha' J' \rangle \\ & \quad \times [(2J' + 1)(2F + 1)]^{1/2} W(JI\lambda_1 F'; FJ'). \end{aligned} \quad (2.3)$$

At this point, by using in Eq. (2.1) the tensor decomposition (2.2) for T and resorting to (2.3) for the matrix elements of tensors ${}^1\tau$ operating in the space of internal degrees of the absorber, the above-mentioned F and M dependence of the relaxation matrix $\Gamma_{ll'}$ is obtained. In fact, performing for the diagonal terms of T in Eqs. (2.1b) and (2.1c) a thermal average on the directions of \mathbf{q} and \mathbf{r} , only scalar operators

$R_0^0(k)$, ${}^1\tau_0^0(k)$, and ${}^2\tau_0^0(k)$ are left in the single-state relaxation terms. Hence the effective T matrix for the calculation of Γ_{ll}^i and Γ_{ll}^f becomes

$$T_0 = \sum_k C_k R_0^0(k) {}^1\tau_0^0(k) {}^2\tau_0^0(k). \quad (2.4)$$

Moreover, using the rotational invariance of the scalar operators τ_0 and remembering that for the Racah coefficients the identity

$$W(JIOF; FJ) = [(2J+1)(2F+1)]^{-1/2}$$

holds, Eq. (2.3) yields

$$\langle \alpha' J' F' M' | {}^1\tau_0^0 | \alpha J F M \rangle = \langle \alpha' J' | {}^1\tau_0 | \alpha J \rangle \delta_{JJ'} \delta_{FF'} \delta_{MM'}. \quad (2.5)$$

Hence

$$\Gamma_{ll}^i = n \left\langle \sum_k C_k \langle \alpha_i J_i | {}^1\tau_0(k) | \alpha_i J_i \rangle \langle r | {}^2\tau_0(k) | r \rangle \times \langle q | R_0(k) | q \rangle \right\rangle_{q,r}, \quad (2.6a)$$

$$\Gamma_{ll}^f = n \left\langle \sum_k C_k \langle \alpha_f J_f | {}^1\tau_0(k) | \alpha_f J_f \rangle \langle r | {}^2\tau_0(k) | r \rangle \times \langle q | R_0(k) | q \rangle \right\rangle_{q,r}. \quad (2.6b)$$

Equation (2.6) proves that, because of the average on the directions of bath variables \mathbf{q} and \mathbf{r} , the single-state collisional broadening terms Γ_{ll}^i and Γ_{ll}^f do not depend on the hyperfine and magnetic quantum numbers F and M .

By similar considerations, based on the tensorial properties of the operators τ and R under rotations and on the orientational averages on \mathbf{q} and \mathbf{r} , the double-state term in Eq. (2.1d) becomes

$$\Gamma_{l,l'}^{i,f} = -n \left\langle \sum_{\lambda_1, k, j} \Pi_{k,j}(q, r) \langle \alpha_i J_i | {}^1\tau_{\lambda_1}(k) | \alpha_i' J_i' \rangle \times \langle \alpha_f J_f | {}^1\tau_{\lambda_1}(j) | \alpha_f' J_f' \rangle \Phi_{l,l'}^{\lambda_1} \right\rangle_{q,r}, \quad (2.7a)$$

where $\Pi(q, r)$ describes the contribution to $\Gamma_{l,l'}^{i,f}$ of each type of collision with given values of bath variables q and r and is given by

$$\Pi_{k,j}(q, r) = \sum_{\lambda, \lambda_2, r'} \int dq' C_k C_j \langle q | R_\lambda(k) | q' \rangle \langle q | R_\lambda(j) | q' \rangle \times \langle r | {}^2\tau_{\lambda_2}(k) | r' \rangle \langle r | {}^2\tau_{\lambda_2}(j) | r' \rangle. \quad (2.7b)$$

$\Phi_{l,l'}^{\lambda_1}$ in (2.7a) is given by

$$\begin{aligned} \Phi_{l,l'}^{\lambda_1} &= [(2J_i' + 1)(2J_f' + 1)(2F_i + 1)(2F_f + 1)]^{1/2} \\ &\times W(J_i I \lambda_1 F_i'; F_i J_i') W(J_f I \lambda_1 F_f'; F_f J_f') \\ &\times \langle F_i M_i | \lambda_1 \nu_1 F_i' M_i' \rangle \langle F_f M_f | \lambda_1 \nu_1 F_f' M_f' \rangle. \end{aligned} \quad (2.7c)$$

The presence of the geometric factor $\Phi_{l,l'}^{\lambda_1}$ comes from the correlated product in Eq. (2.1d) of the two matrix elements

$$\langle \alpha_f J_f, F_f M_f | {}^1\tau_{\lambda_1}^{\nu_1} | \alpha_f' J_f', F_f' M_f' \rangle, \quad (2.8a)$$

$$\langle \alpha_i J_i, F_i M_i | {}^1\tau_{\lambda_1}^{\nu_1} | \alpha_i' J_i', F_i' M_i' \rangle \quad (2.8b)$$

representing the collisional transitions between the final and initial states of the two lines induced by ${}^1\tau_{\lambda_1}^{\nu_1}(k)$ and ${}^1\tau_{\lambda_1}^{\nu_1}(j)$. Because of the directional average on the bath variables \mathbf{q} and \mathbf{r} , only scalar products of tensors for each degree of freedom are left in the double-state relaxation term (2.1d). Hence we have the same tensorial indices λ_i and ν_i for ${}^1\tau(k)$ and ${}^1\tau(j)$ in (2.8) and in the expression (2.7c) of $\Phi_{l,l'}^{\lambda_1}$. The matrix elements (2.8) are different from zero only if $\Delta M_i = M_i' - M_i$ and $\Delta M_f = M_f' - M_f$ are both equal to ν_1 . Hence collisional coupling is possible only if

$$\Delta M_i = \Delta M_f. \quad (2.9)$$

We point out that Eqs. (2.6) and (2.7) describe completely the dependence of relaxation matrix Γ on F and M and give two important results. First, the single-state terms Γ_{ll}^i and Γ_{ll}^f are independent of F and M . Second, the dependence of the double-state term $\Gamma_{l,l'}^{i,f}$ is due to the geometric factors $\Phi_{l,l'}^{\lambda_1}$, which are a simple product of Clebsch-Gordan and Racah coefficients.

We consider now the case of the quadratic Stark effect. The observed lines are a superimposition of two components $|l_M\rangle, |l_{-M}\rangle$ degenerate in the sign of M . According to the ‘‘effective-line’’ model described in Ref. [11] for representing degenerate spectra, the line vector basis appropriate for describing such Stark lines is

$$|\bar{l}_M\rangle = A_M |l_M\rangle + A_{-M} |l_{-M}\rangle. \quad (2.10)$$

In fact, $|\bar{l}_M\rangle$ is the average of two degenerate components

$$|l_M\rangle = |\alpha_f J_f, F_f M_f\rangle \langle \alpha_i J_i, F_i M_i |,$$

$$|l_{-M}\rangle = |\alpha_f J_f, F_f - M_f\rangle \langle \alpha_i J_i, F_i - M_i |,$$

weighted with normalized amplitude factors

$$A_M = 1/\sqrt{2}, \quad A_{-M} = (-1)^{1-F_f+M_f}/\sqrt{2},$$

where the factor $(-1)^{1-F_f+M_f}$ follows from the symmetry property of $A_M \propto \langle F_f M_f | 1 \epsilon F_i M_i \rangle$ under sign inversion $M \rightarrow -M$.

In this representation it is straightforward to obtain the relaxation matrix in the form

$$\Gamma_{\bar{l}_M \bar{l}'_M} = \Gamma_{l_M l'_M} + \Gamma_{l_M l'_M} (-1)^{1-F_f+F_i}. \quad (2.11)$$

Due to the selection rule (2.9), the second term on the right-hand side of Eq. (2.11) is different from zero only if $\epsilon = M_f - M_i = M'_f - M'_i = 0$.

By Eqs. (2.1a), (2.6), (2.7), and (2.11) the relaxation matrix $\Gamma_{\bar{l}_M \bar{l}'_M}$ in the space of the M -sign degenerate lines can be obtained. The single-state terms $\Gamma_{\bar{l}_M \bar{l}_M}$ and $\Gamma_{\bar{l}_M \bar{l}_M}^f$ are still given by Eq. (2.6). Moreover, since the M dependence of $\Gamma_{l,l'}^{if}$ in Eq. (2.7) is contained in the factor $\Phi_{l,l'}^{\lambda_1}$, the same equations can be extended to the double degenerate relaxation terms $\Gamma_{\bar{l}_M \bar{l}'_M}^{if}$ provided that Eq. (2.7c) for $\Phi_{l,l'}^{\lambda_1}$ is changed to

$$\begin{aligned} \Phi_{\bar{l}_M \bar{l}'_M}^{\lambda_1} &= [(2J'_i + 1)(2J'_f + 1)(2F_i + 1)(2F_f + 1)]^{1/2} \\ &\times W(J_i I \lambda_1 F'_i; F_i J'_i) W(J_f I \lambda_1 F'_f; F_f J'_f) \\ &\times [\langle F_i M_i | \lambda_1 \nu_1 F'_i M'_i \rangle \langle F_f M_f | \lambda_1 \nu_1 F'_f M'_f \rangle \\ &+ (-1)^{1-F_f+F_i} \langle F_i M_i | \lambda_1 - \mu_1 F'_i - M'_i \rangle \\ &\times \langle F_f M_f | \lambda_1 - \mu_1 F'_f - M'_f \rangle], \end{aligned} \quad (2.12)$$

where $M_f + M'_f = M_i + M'_i = \mu_1$.

Let us extend now our treatment to the case of zero static field, where all M components

$$l_M = \alpha_f J_f, F_f M_f \leftarrow \alpha_i J_i, F_i M_i$$

merge into a single line

$$\bar{l} = \alpha_f J_f, F_f \leftarrow \alpha_i J_i, F_i.$$

The appropriate vector basis [11] representing such degenerated spectral transitions is

$$|\bar{l}\rangle = \sum_M A_M |l_M\rangle, \quad (2.13a)$$

where the average of the degenerate components $|l_M\rangle$ is weighted with the normalized amplitude factors

$$A_M = \left(\frac{3}{2F_f + 1} \right)^{1/2} \langle F_f M_f | 1 \epsilon F_i M_i \rangle. \quad (2.13b)$$

In this vector basis, the relaxation matrix becomes

$$\Gamma_{\bar{l}, \bar{l}'} = \sum_{M, M'} A_M \Gamma_{l_M l'_M} A_{M'}. \quad (2.14)$$

At this point, all the considerations already given for the case of M quantum numbers degenerate only in sign can be extended to the case of complete M degeneracy, leading to

conclude that Eqs. (2.1a), (2.6), and (2.7) are still valid for the matrix elements $\Gamma_{\bar{l}, \bar{l}'}$ if Eq. (2.7c) is replaced by

$$\begin{aligned} \Phi_{\bar{l}, \bar{l}'}^{\lambda_1} &= \sum_{M_i, M'_i} A_M \Phi_{l, l'}^{\lambda_1} A_{M'} = [(2J'_i + 1)(2J'_f + 1)(2F_i + 1) \\ &\times (2F_f + 1)(2F'_i + 1)(2F'_f + 1)]^{1/2} \\ &\times W(J_i I \lambda_1 F'_i; F_i J'_i) W(J_f I \lambda_1 F'_f; F_f J'_f) \\ &\times W(1 F_i F'_i \lambda_1; F_f F'_f). \end{aligned} \quad (2.15)$$

III. PERTURBATIVE CALCULATIONS

So far we have derived general expressions of the relaxation matrix by using symmetry properties and rotational invariance of the scattering matrix. However, an exact calculation of the scattering matrix T and of the tensorial operators τ and R in Eq. (2.2), in general is not easily realized. Further simplifying hypotheses are needed in order to obtain more practical and computable expressions.

A remarkable simplification is obtained if weak collisions, dominated by the long-range part of interaction potential V , are treated by a perturbative expansion in V . This type of collision gives an important contribution both to the single-state relaxation terms $\Gamma_{l,l}^i$ and $\Gamma_{l,l}^f$ and to the double-state term $\Gamma_{l,l'}^{if}$ in Eq. (2.1). On the other hand, strong collisions, occurring when molecules come very close, give a large contribution to the single-state terms, but only a negligible contribution to the double-state term, which is bilinear in T . In fact, for short impact parameters b , the T -matrix elements have rapidly oscillating phase factors and the correlated product $\langle l_i | T(b) | l'_i \rangle \langle l'_i | T^\dagger(b) | l'_i \rangle$ in Eq. (2.1d) averages to zero when integrated on b . On the contrary, such fluctuating phase factors are not present in Eqs. (2.1b) and (2.1c) for the single-state terms. This kind of difference between strong and weak collision was observed in Ref. [7] by studying the collisional broadening and coupling effects on some rotational CHF_2Cl lines for self-collisions and for collisions with N_2 and O_2 molecules. A clear correlation was found between the coupling to broadening ratio and the long-range part of intermolecular interaction, which is very different for the three perturbers considered. The lowering of the interaction range, and hence of the importance of weak collisions, produced a strong decrease of the coupling to broadening ratio. This confirms that strong collisions have a large broadening effect but give only a small contribution to collisional coupling and to the double-state part of the relaxation matrix. Since any hyperfine dependence is contained in this part, we can focus our attention on weak collisions only and resort to a lowest-order perturbative expansion in V . This amounts to assuming for the scattering matrix elements in Eq. (2.1d),

$$\langle l_i | T | l'_i \rangle \langle l'_i | T^\dagger | l_f \rangle \approx \frac{\delta(E' - E)}{\hbar^2} \langle l_i | V | l'_i \rangle \langle l'_i | V^\dagger | l_f \rangle, \quad (3.1)$$

where $\delta(E' - E)$ provides energy conservation for incoming and outgoing collisional states.

The long-range interaction V can be written as a sum

$$V = \sum_s V_s, \quad (3.2a)$$

where each term V_s is characterized by a particular value of the three tensor degrees λ , λ_1 , and λ_2 and of the exponent m describing the dependence of V_s on the intermolecular distance d :

$$V_s = C_s \sum_\nu \frac{Y_{\lambda(s)}^{*\nu}(\hat{d})}{d^{m(s)}} \sum_{\nu_1, \nu_2} \langle \lambda(s) \nu | \lambda_1(s) \nu_1 \lambda_2(s) \nu_2 \rangle^1 \tau_{\lambda_1(s)}^{\nu_1} \tau_{\lambda_2(s)}^{\nu_2}, \quad (3.2b)$$

where $Y(\hat{d})$ is a spherical harmonic of the angular direction of \hat{d} . By use of Eqs. (3.1) and (3.2), Eq. (2.7) yields

$$\Gamma_{l,l'}^{i,f} \simeq -\frac{n}{\hbar^2} \sum_{\lambda_1, s} \langle \Pi(s, q, r) \langle \alpha_i J_i | \tau_{\lambda_1(s)} | \alpha'_i J'_i \rangle \times \langle \alpha_f J_f | \tau_{\lambda_1(s)} | \alpha'_f J'_f \rangle \Phi_{l,l'}^{\lambda_1(s)} \rangle_{q,r}, \quad (3.3a)$$

$$\Pi(s, q, r) = C_s^2 \sum_{r'} \int dq' \left| \left\langle q \left\| \frac{Y_{\lambda(s)}(\hat{d})}{d^{m(s)}} \right\| q' \right\rangle \right|^2 \times | \langle r | \tau_{\lambda_2(s)} | r' \rangle |^2 \delta(E' - E), \quad (3.3b)$$

where the transition $r, q \rightarrow r', q'$ is connected by energy conservation to the transition $l \rightarrow l'$.

For a particular interaction V , with tensor order λ_1 in the internal space of the absorbing molecule, the hyperfine dependence of $\Gamma_{l,l'}^{i,f}$ is contained in the geometric factor $\Phi_{l,l'}^{\lambda_1}$ given by (2.7c) if all M_F quantum numbers are resolved, by (2.12) in case of quadratic Stark effect or by (2.15) in the absence of a static field.

Within the limit of validity of the second-order perturbative treatment, Eq. (3.3) allows one to calculate collisional coupling between different hyperfine lines and, if the case $l=l'$ is considered, to calculate also the hyperfine dependence of collisional broadening. If a dipole-dipole interaction is assumed ($\lambda_1 = \lambda_2 = 1$) and the model of Ref. [15] is used, Eq. (3.3) reduces to the method of calculation described in detail and experimentally verified in Ref. [5] for self-collisional broadening of the hyperfine and Stark resolved hyperfine, components of the $J=4 \leftarrow 3$, $K=3$ rotational line of CH_3I . However, Eq. (3.3) can be used for any kind of long-range interaction and with any of the different perturbative calculation models [15–17] commonly used in the literature, independently of the particular choice adopted for collisional trajectories or for interpolation between weak and strong collisions.

It is worthwhile noting that if Eqs. (3.3), and (2.7c) or (2.12) are used with $I=0$, $F=J$, and $M=M_J$, the M_J dependence of collisional broadening and coupling of the Stark resolved lines of a molecule without hyperfine structure is obtained. Such a procedure, with the assumption of a dipole-dipole interaction and of the approximations given in Ref. [15], gives the treatment exposed in detail and experimentally verified in Ref. [20] for self-broadening of the Stark components of CH_3F lines $J=3 \leftarrow 2$, $K=1, 2$.

IV. DIPOLE INTERACTION

We specialize now the perturbative treatment obtained in Sec. III to the particular case of molecules with an electric-dipole moment large enough to play a predominant role in the long-range part V . Namely, we suppose that in Eq. (3.2) $\lambda_1=1$ and ${}^1\tau_{\lambda_1}^{\nu_1}$ is the dipole moment of the absorbing molecule $\mu_1^{\nu_1}$:

$$V = \sum_s V_s = \sum_{s,\nu} C_s \frac{Y_{\lambda(s)}^{*\nu}(\hat{d})}{d^{m(s)}} \sum_{\nu_1, \nu_2} \langle \lambda(s) \nu | 1 \nu_1 \lambda_2(s) \nu_2 \rangle \mu_1^{\nu_1} \tau_{\lambda_2(s)}^{\nu_2}. \quad (4.1)$$

As a consequence, Eq. (3.3) becomes

$$\Gamma_{l,l'}^{i,f} \simeq -\frac{n}{\hbar^2} \sum_s \langle \Pi(s, q, r) \langle \alpha_i J_i | \mu | \alpha'_i J'_i \rangle \times \langle \alpha_f J_f | \mu | \alpha'_f J'_f \rangle \Phi_{l,l'}^1 \rangle_{q,r} = -\sum_s \langle \Pi(s, q, r) \langle l_i | \mu | l'_i \rangle \langle l_f | \mu | l'_f \rangle \rangle_{q,r}, \quad (4.2a)$$

$$\Pi(s, q, r) = \sum_{r'} C_s^2 \int dq' \left| \left\langle q \left\| \frac{Y_{\lambda(s)}(\hat{d})}{d^{m(s)}} \right\| q' \right\rangle \right|^2 \times | \langle r | \tau_{\lambda_2(s)} | r' \rangle |^2 \delta(E' - E). \quad (4.2b)$$

$\Phi_{l,l'}^1$ can be obtained by (2.7c) in the presence of a static field

$$\Phi_{l,l'}^1 = [(2J'_i + 1)(2J'_f + 1)(2F_i + 1)(2F_f + 1)]^{1/2} \times W(J_i I 1 F'_i; F_i J'_i) W(J_f I 1 F'_f; F_f J'_f) \times \langle F_i M_i | 1 \nu_1 F'_i M'_i \rangle \langle F_f M_f | 1 \nu_1 F'_f M'_f \rangle \quad (4.3a)$$

and by (2.15) in the opposite case

$$\Phi_{l,l'}^1 = [(2J'_i + 1)(2J'_f + 1)(2F_i + 1)(2F_f + 1)(2F'_i + 1) \times (2F'_f + 1)]^{1/2} W(J_i I 1 F'_i; F_i J'_i) \times W(J_f I 1 F'_f; F_f J'_f) W(1 F_i F'_i 1; F_f F'_f). \quad (4.3b)$$

Equation (4.3a) holds for cases of both the linear and the quadratic Stark effect because when the dipolar interaction and the perturbative expansion are adopted, the Clebsch-Gordan coefficients $\langle F_i M_i | 1 - \mu_1 F'_i - M'_i \rangle$ and $\langle F_f M_f | 1 - \mu_1 F'_f - M'_f \rangle$ in Eq. (2.12) vanish.

Fortunately, in many cases Eqs. (4.2) and (4.3) predict zero or very small values for $\Gamma_{l,l'}^{i,f}$, and one has not to worry about the hyperfine or Stark structure in collisional line-shape studies. In other cases collisional coupling cannot arise between any two hyperfine components but only between particular pairs. By looking at Eq. (4.2a) it is simple to see when the hyperfine structure must be taken into account and when this is not the case. The hyperfine-structure-dependent part of relaxation $\Gamma_{l,l'}^{i,f}$ is proportional to the product of two dipole matrix elements, which are well-known quantities. However, involved here are not the usual elements $\langle l_i | \mu | l_f \rangle$ and $\langle l'_i | \mu | l'_f \rangle$ describing the intensities of lines l and l' , but the matrix elements $\langle l_i | \mu | l'_i \rangle$ and $\langle l_f | \mu | l'_f \rangle$ between initial and final states of the two lines. For this reason here and in the following we use Δ to denote difference between lines l and l' ; for instance, $\Delta M_i = M'_i - M_i$.

Before giving a detailed discussion of the selection rules that can be deduced from Eqs. (4.2) and (4.3), we recall here the selection rule (2.9) obtained in Sec. II, which holds exactly and independently of perturbative approximation and interaction type. When different values of the polarization quantum number ϵ are present in the radiation, Eq. (2.9) allows one to reduce the calculation of the relaxation matrix to the Liouville subspaces with fixed values of ϵ and to exclude collisional coupling between lines with different values of $M_f - M_i = \epsilon$. For instance, if the resolution in M is due to a linear Stark effect and the polarization of radiation is perpendicular to the static field, the two Stark components $M_i \rightarrow M_i + 1$ and $M_i - F_i \rightarrow M_i - F_i - 1$ of the hyperfine transition $F_i \rightarrow F_f = F_i + 1$ are degenerate. However, collisional coupling between them is excluded.

The selection rules

$$\Delta J_i = 0, \pm 1; \quad \Delta J_f = 0, \pm 1 \quad (4.4a)$$

are obtained from the reduced matrix moments present in Eq. (4.2a). For molecules with parity splitting another selection rule is obtained. In this kind of molecule, such as ammonia, the rotational states are split into two different energy levels with different parity; a symmetric level s and an antisymmetric one a . Dipole transitions are allowed only between states of different parity: there are as and sa lines, but neither aa nor ss lines. In this case collisional coupling is possible only between hyperfine components of lines with different parity: an as line can interfere with an sa line but not with another as line.

The selection rules

$$\Delta F_i = 0, \pm 1; \quad \Delta F_f = 0, \pm 1 \quad (4.4b)$$

are a consequence of the Racah coefficient in Eqs. (4.3). The same coefficients are very small, in case of large J values, unless the relations

$$\Delta F_i = \Delta J_i, \quad \Delta F_f = \Delta J_f \quad (4.4c)$$

hold, which can be used as approximate selection rules when J is large. For the case of M resolved lines, the additional selection rules

$$\Delta M_i = 0, \pm 1; \quad \Delta M_f = 0, \pm 1 \quad (4.4d)$$

come from the Clebsch-Gordan coefficients in Eq. (4.3b).

Further specific selection rules are obtained for different kind of molecules. We discuss separately linear, symmetric and asymmetric-top molecules. For linear and symmetric top molecules the frequency distance between lines with different J values is usually much larger than the spread of the hyperfine structure. Therefore, collisional interference between hyperfine components of lines with different J is rarely a problem of interest because it may arise only when the lines are so broadened that the hyperfine structure completely disappears. For this kind of molecules, we restrict our discussion to interference between lines with equal J values, namely, we assume $\Delta J_i = \Delta J_f = 0$, a restriction that we do not extend to the case of asymmetric-top molecules because their spectrum is less ordered and lines with different J may have close frequencies.

A. Linear molecules

For a linear molecule the selection rule of the dipole moment operator is $\Delta J = \pm 1$ and no coupling is expected between the hyperfine components of the same rotational line $\Delta J_i = \Delta J_f = 0$. For the same reason $\Gamma_{l,l'}^{i,f} \approx 0$ in Eq. (4.2a) and no hyperfine-structure-dependence is expected for collisional broadening. Our conclusions on this point are in agreement with that found by Green [6] who studied the case of HCN perturbed by a noble-gas atom and concluded that the hyperfine effects on the collisional line shape are, in that case, null or very small.

B. Symmetric-top molecules

The rotational state of a symmetric-top molecule is described by the two quantum numbers J and K . While lines with different J values have usually very different frequencies, the K structure for a given J value may have a frequency spread comparable to, or even smaller than, the hyperfine spread. However, the dipole selection rules for a symmetric-top molecule are $\Delta J = 0, \pm 1$ and $\Delta K = 0$, so that from Eq. (4.2a) one can see that collisional coupling between lines with different K values vanishes. We may restrict ourselves to the case $J_i = J'_i, J_f = J'_f, K_i = K'_i, \text{ and } K_f = K'_f$.

Equation (4.2a) yields

$$\Gamma_{l,l'}^{i,f} \approx -n \left\langle \Pi(q,r) \frac{K_i K_f}{[J_i(J_i+1)J_f(J_f+1)]^{1/2}} \Phi_{l,l'}^1 \right\rangle_{q,r} \quad (4.5)$$

This explains the null result obtained in Refs. [2–4] for $K_i = K_f = 0$. At fixed J , the effect is expected to increase with

K . However, for large- J values a very small collisional coupling is expected between two different hyperfine components of a rotational transition. Indeed, in this case we have $\Delta J_i = \Delta J_f = 0$, but either $\Delta F_i \neq 0$ or $\Delta F_f \neq 0$, which contradicts the approximate selection rule (4.4c). On the contrary, a relevant collisional coupling can exist between the Stark components of a hyperfine line, provided that condition (4.4d) holds.

C. Asymmetric-top molecules

The rotational state of an asymmetric-top molecule is denoted by J and by the two pseudoquantum numbers K_a and K_c . The selection rules for J are, as usual, $\Delta J = 0, \pm 1$, while the selection rules for K_a and K_c depend on the orientation of μ with respect to the principal axis of inertia of the molecule [21]. If the dipole is in the direction of the axis of least inertia ($\mu = \mu_a$) only transitions are allowed that conserve the parity (even or odd) of K_a and change the parity of K_c . Vice versa, if μ is in the direction of the axis of maximum inertia ($\mu = \mu_c$) the allowed transitions conserve the parity of K_c and change the parity of K_a . Finally, if μ is in the direction of the axis of intermediate inertia ($\mu = \mu_b$) only transitions are allowed that change the parity of both K_a and K_c .

On the whole, by parity considerations, transitions that conserve both K_a and K_c are forbidden for any direction of the dipole moment. As a consequence, if the hyperfine components of a single rotational line are considered, the reduced matrix elements in (4.2a) are zero. This conclusion is in agreement with the results of Ref. [7] where no collisional coupling between hyperfine components of a single rotational transition was observed for the asymmetric rotor CHF_2Cl .

On the contrary, collisional coupling is possible between the hyperfine components of two different rotational transitions, provided that the aforementioned selection rules for K_a and K_c are satisfied together with (4.4a) and (4.4b). If J is large, also condition (4.4c) must be considered. Indeed, in Ref. [7] pairs of closely lying CHF_2Cl rotational transition were studied having the same J values but different K_a or K_c values. In that case $J > 18$ and, in agreement with the selection rule (4.4c), collisional coupling was observed only between hyperfine components with the same quantum numbers: $\Delta F_i = \Delta F_f = 0$.

V. CONCLUSION

We developed a theoretical treatment for collisional coupling between hyperfine components of molecular spectra and for the dependence of collisional broadening of individual lines on hyperfine quantum numbers F and M_F . The cases of both the presence and absence of a static field resolving the quantum numbers M_F , were considered. Our treatment extends also to collisional coupling and broadening of Stark resolved lines of a molecule without hyperfine structure.

We have shown that the relaxation matrix can be decomposed into two single-state terms and one double-state term. The single-state terms are diagonal in the space of the lines and account for the collisional relaxation of their initial and final states, considered separately. The double-state term involves both initial and final states. Its diagonal part decreases the contribution of collisions that are adiabatic in the internal degrees of the absorber to the relaxation of a single line, while its off-diagonal part accounts for collisional coupling. By using the symmetry properties of the scattering matrix and by supposing that the nuclear spin I has a negligible influence on the collisional dynamics we have shown that the single state terms are independent on F and M_F , while, for a collisional interaction of given tensor rank in the space of the absorbing molecule, the dependence of the double-state term can be expressed by a simple product of Clebsch-Gordan and Racah coefficients.

Our treatment was adapted to the perturbative models commonly used in the literature and the case of rotational lines of molecules with a large electric-dipole moment was discussed in detail. The double-state part of relaxation matrix is in this case proportional to the product of the dipole moment matrix elements $\langle l_i | \mu | l'_i \rangle$ and $\langle l_f | \mu | l'_f \rangle$ between initial and final states of the lines. Simple selection rules were derived, allowing one to understand whether or not collisional coupling between hyperfine and Stark components is expected. As far as the coupling between hyperfine components of the same rotational transition is concerned, we have shown that only a small effect is expected for linear and asymmetric-top molecules, while for symmetric-top molecules the effect grows with K for a fixed J and becomes negligible for large J values. For asymmetric-top molecules a relevant collisional coupling may occur only between the hyperfine components of different rotational transitions. All the data in the literature may be explained by the present treatment.

-
- [1] L. Carenini, thesis, University of Pisa, Italy, 1982 (unpublished).
- [2] R. C. Ham and S. L. Coy, *J. Chem. Phys.* **74**, 5453 (1981).
- [3] G. Buffa, D. Giulietti, M. Lucchesi, M. Martinelli, and O. Tarrini, *Nuovo Cimento D* **10**, 511 (1988).
- [4] J. Haekel and H. Mäder, *J. Quant. Spectrosc. Radiat. Transfer* **41**, 9 (1989).
- [5] G. Buffa, A. Di Lieto, P. Minguzzi, O. Tarrini, and M. Tonelli, *Phys. Rev. A* **37**, 3790 (1988).
- [6] S. Green, *J. Chem. Phys.* **88**, 7331 (1988).
- [7] G. Cazzoli, L. Cludi, G. Cotti, C. Degli Esposti, G. Buffa, and O. Tarrini, *J. Chem. Phys.* **102**, 1149, (1995); *J. Quant. Spectrosc. Radiat. Transfer* **52**, 847, (1994).
- [8] A. Ben-Reuven, *Phys. Rev. Lett.* **14**, 349 (1965); *Phys. Rev.* **145**, 7 (1966).
- [9] G. Buffa, A. Di Giacomo, and O. Tarrini, *Nuovo Cimento B* **20**, 281 (1974).
- [10] P. W. Rosenkranz, *IEEE Trans. Antennas Propagat.* **23**, 498 (1975).
- [11] G. Buffa and O. Tarrini, *Phys. Rev. A* **16**, 1612 (1977).
- [12] M. O. Bulanin, A. B. Dokuchaev, M. V. Tonkov, and N. N. Filippov, *J. Quant. Spectrosc. Radiat. Transfer* **31**, 3790 (1988).
- [13] J. Boissoles, C. Boulet, L. Bonamy, and D. Robert, *J. Quant.*

- Spectrosc. Radiat. Transfer **42**, 509 (1989).
- [14] G. Buffa, O. Tarrini, and M. Inguscio, Appl. Opt. **26**, 3066 (1987).
- [15] P. W. Anderson, Phys. Rev. **76**, 647 (1949); C. T. Tsao and I. Curnutte, J. Quant. Spectrosc. Radiat. Transfer **2**, 41 (1962).
- [16] J. S. Murphy and J. E. Boggs, J. Chem. Phys. **47**, 691 (1967).
- [17] D. Robert and J. Bonamy, J. Phys. (Paris) **40**, 923 (1979).
- [18] M. Baranger, Phys. Rev. **111**, 481 (1958); U. Fano, *ibid.* **131**, 259 (1963); A. Di Giacomo, Nuovo Cimento **34**, 473 (1964).
- [19] A. Di Giacomo, Nuovo Cimento B **44**, 140 (1966).
- [20] G. Buffa, A. Di Lieto, P. Minguzzi, O. Tarrini, and M. Tonelli, Phys. Rev. A **34**, 1065 (1986).
- [21] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (Dover, New York, 1975), Chap. 4.