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Angular-momentum coupling in spectroscopic relaxation cross sections: Consequences for line coupling in bending bands

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In the classical limit and within the infinite-order sudden approximation (IOSA), the tetradic collisional spectroscopic cross sections are transformed into a dyadic supermatrix. Each element of this matrix is expressed in terms of generalized state-to-state cross sections, each row or column corresponding to a given spectroscopic branch. These generalized cross sections are convenient both for *ab initio* calculations, including possible energy corrections to IOSA, and for modeling. One of the main advantages of the present approach is to give a clear understanding of the line-coupling mechanism and of its spectral consequence on complex systems, whatever the type of spectroscopy (infrared absorption, isotropic or anisotropic Raman scattering) and whatever the nature of the observed vibrational transition (stretching or bending band). To illustrate this point, the strong-collision model is used to calculate explicitly the generalized state-to-state cross sections. This model allows one to justify, on a first and simple physical basis, the origin of the *ad hoc* decoupling "factor of 2" previously introduced to fit the infrared Q-branch profiles for bending bands.

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The phenomenon of collisional transfer of intensity due to line mixing has an increasing importance for atmospheric monitoring and combustion diagnostics [1,2]. Calculation of infrared (IR) or Raman band profiles thus requires the knowledge of the whole matrix of line-broadening and line-coupling cross sections. Although accurate calculations are now feasible for line broadening, line-coupling cross sections have received much less attention. For simple systems such as CO-He, accurate coupled-channel scattering calculations of line-coupling cross sections have been performed [3], providing a fairly good account of the collapsed infrared band at high pressure [4]. For more complex systems, development of accurate approximate methods is required. For isotropic Raman Q branches of stretching bands, several models have been proposed which allow a convenient description of the observed profiles for a larger number of systems [1]. However, their extension to IR and anisotropic Raman branches is still problematic since each line no longer corresponds to a single rotational line; such an extension is usually achieved by identifying a given line with its initial rotational level.

If bending bands are considered, an *ad hoc* weighting factor must be introduced [5] to account for the modification of the rotational energy transfer. In CO_2, a "factor of 2" was necessary to fit the data [5,6]. A similar adjustment has been introduced for other systems [2,7]. A recent theoretical study [8] of CO_2-He within the infinite-order sudden approximation (IOSA) has allowed rationalization of this *ad hoc* weighting procedure and has also indicated its approximate nature. This is due to the fact that the IOSA properly accounts for the angular-momentum coupling (vibration-rotation photon) and thus does not require the equating of line-coupling cross sections with state-to-state cross sections. Unfortunately, the IOSA becomes less accurate for high rotational lines, so that, even for a light perturber like He, only a qualitative agreement with observed IR spectra is achieved [9]. Corrections accounting for the rotational energy-level spacing and the finite duration of collisions [e.g., energy corrected sudden (ECS) [10]] must be introduced to obtain a quantitative agreement. Such corrections are convenient for state-to-state but not for spectroscopic cross sections (except, for isotropic Raman cross sections [11]).

One of the main advantages of the IOSA is to propose a convenient factorization [12] of generalized cross sections into dynamical terms and spectroscopic coefficients. The IOS factorization applied to symmetric-top molecules leads to [13]

$$\sigma^{Kl_il_f}_{j_ij_f,j_i'j_f'}=\left(\frac{[j_i']}{[j_i]}\right)^{1/2}\sum_L [L]F^{Kl_il_fL}_{j_ij_f,j_i'j_f'}Q_L\ , \tag{1}$$

where the Q_L are the IOS collisional factors and the spectroscopic coefficients $F^{Kl_il_fL}_{j_ij_f,j_i'j_f'}$ are defined by

$$F^{Kl_il_fL}_{j_ij_f,j_i'j_f'}=(-1)^{K+l_i+l_f}[j_ij_i'j_fj_f']^{1/2}\times\begin{pmatrix} j_i & L & j_i' \\ l_i & 0 & -l_i\end{pmatrix}\begin{pmatrix} j_f & L & j_f' \\ -l_f & 0 & l_f\end{pmatrix}\begin{Bmatrix} j_i & j_f & K \\ j_f' & j_i' & L\end{Bmatrix}\ . \tag{2}$$

In Eqs. (1) and (2), K is the tensor rank for the radiation-matter coupling, $[j]=2j+1$, the large parentheses denote the usual 3-j angular-momentum-coupling symbols, and the large curly brackets denote a 6-j symbol. For the sake of simplicity, only $M_i=M_f=0$ has been retained in Eq. (2), since low-lying bending modes are still nearly linear [8]. The spectroscopic cross sections for $j_ij_f\rightarrow j_i'j_f'$ transitions [Eq. (1)] are not expressed in terms of $j\rightarrow j'$ state-to-state cross sections but

TABLE I. Collisional spectroscopic cross-section supermatrix $\sigma^{100}_{j_i j_f, j_i' j_f'}$ for an IR stretching band.

	P	R
P	$\frac{1}{2}(\Gamma^0_{j_i j_i'}+\Gamma^1_{j_i j_i'})$	$-\frac{1}{2}(\Gamma^0_{j_i j_i'}-\Gamma^1_{j_i j_i'})$
R	$-\frac{1}{2}(\Gamma^0_{j_i j_i'}-\Gamma^1_{j_i j_i'})$	$\frac{1}{2}(\Gamma^0_{j_i j_i'}+\Gamma^1_{j_i j_i'})$

in terms of the IOS collisional factors Q_L. As discussed above, an explicit expression of the $\sigma^{Kl_i l_f}_{j_i j_f, j_i' j_f'}$ cross sections as a function of the $j \rightarrow j'$ ones would be very useful. In particular, it would make it possible to establish simple relations between collisional spectroscopic cross sections for stretching or bending bands and appropriate state-to-state ones. The calculation of IR, isotropic, or anisotropic Raman band profile would thus be reduced to the *ab initio* calculation, or the modeling, of these state-to-state cross sections. The *ad hoc* adjustments required for modeling the bending bands would be rendered unnecessary; this is the aim of the present Brief Report.

Transforming the product of a 3-j and a 6-j symbol into a linear combination of three 3-j symbols [14], the spectroscopic cross sections are then expressed in the required form:

$$\sigma^{Kl_i l_f}_{j_i j_f, j_i' j_f'} = (-1)^{j_f + j_f'}[j_f j_f']^{1/2} \times \sum_l \begin{pmatrix} j_i & K & j_f \\ l+l_f & -l & -l_f \end{pmatrix} \times \begin{pmatrix} j_i' & K & j_f' \\ l+l_f & -l & -l_f \end{pmatrix} \tilde{\Gamma}^{l_i l_f + l}_{j_i j_i'} , \tag{3}$$

where the generalized state-to-state cross sections $\tilde{\Gamma}^{ll'}_{jj'}$ are given by

$$\tilde{\Gamma}^{ll'}_{jj'} = (-1)^{l+l'}[j'] \sum_L [L] \begin{pmatrix} j & L & j' \\ l & 0 & -l \end{pmatrix} \begin{pmatrix} j & L & j' \\ l' & 0 & -l' \end{pmatrix} Q_L . \tag{4}$$

These cross sections contain all the system-dependent collision information ($\tilde{\Gamma}^{ll'}_{jj'} = \sigma^{0ll'}_{jj,j'j'}$) and describe the state-to-state rotational cross sections in the various pairs of vibrational modes. The Q_L factors are related to these state-to-state cross sections by $Q_L = \tilde{\Gamma}^{00}_{L0}$. In Eq. (4) the two 3-$j$ symbols properly account for the angular-momentum coupling. By using the same transformation for the 3-j and 6-j symbols as above, the usual state-to-state cross sections [15]

$$\Gamma^K_{jj'} = (-1)^K [j'][jj']^{1/2} \sum_L [L] \begin{Bmatrix} j & j & K \\ j' & j' & L \end{Bmatrix} \times \begin{pmatrix} j & L & j' \\ 0 & 0 & 0 \end{pmatrix}^2 Q_L \tag{5}$$

can be related to the $\tilde{\Gamma}^{0l}_{jj'}$ ones by

$$\Gamma^K_{jj'} = (-1)^{j+j'}[jj']^{1/2} \sum_l \begin{pmatrix} j & K & j \\ l & -l & 0 \end{pmatrix} \begin{pmatrix} j' & K & j' \\ l & -l & 0 \end{pmatrix} \tilde{\Gamma}^{0l}_{jj'} . \tag{6}$$

The $\Gamma^K_{jj'}$ cross sections have a simple physical meaning through their direct connection with the specific spectroscopic cross sections [$\Gamma^K_{jj'} = \sigma^{K00}_{jj,j'j'}$; cf. Eqs. (3) and (5)]. For the usual spectroscopic situations where $K=0,1,2$, Eq. (6) leads to

$$\Gamma^0_{jj'} = \tilde{\Gamma}^{00}_{jj'}, \quad \Gamma^1_{jj'} = \tilde{\Gamma}^{01}_{jj'} , \tag{7}$$

$$\Gamma^2_{jj'} = \tfrac{1}{4}\tilde{\Gamma}^{00}_{jj'} + \frac{3}{([j-1][j+1][j'-1][j'+1])^{1/2}} \tilde{\Gamma}^{01}_{jj'} + 3 \left[\frac{(j-1)(j+2)(j'-1)(j'+2)}{[j-1][j+1][j'-1][j'+1]} \right]^{1/2} \tilde{\Gamma}^{02}_{jj'} . \tag{8}$$

For most molecules, terms of order $1/j$ are negligible ($T \gg T_{\text{rot}}$ limit) and Eq. (8) becomes

$$\Gamma^2_{jj'} = \tfrac{1}{4}\tilde{\Gamma}^{00}_{jj'} + \tfrac{3}{4}\tilde{\Gamma}^{02}_{jj'} . \tag{9}$$

Equations (3) and (4) allow one to obtain the collisional spectroscopic cross sections in terms of the generalized state-to-state cross sections $\tilde{\Gamma}^{ll'}_{jj'}$ for a given spectroscopic band. For an IR stretching band ($l_i = l_f = 0$), the relevant expression is

$$\sigma^{100}_{j_i j_f, j_i' j_f'} = (-1)^{j_f + j_f'}[j_f j_f']^{1/2} \times \left\{ \begin{pmatrix} j_i & 1 & j_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_i' & 1 & j_f' \\ 0 & 0 & 0 \end{pmatrix} \tilde{\Gamma}^{00}_{j_i j_i'} + [1+(-1)^{j_i + j_i' + j_f + j_f'}] \begin{pmatrix} j_i & 1 & j_f \\ 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} j_i' & 1 & j_f' \\ 1 & -1 & 0 \end{pmatrix} \tilde{\Gamma}^{01}_{j_i j_i'} \right\} . \tag{10}$$

In the $T \gg T_{\text{rot}}$ limit, the tetradic IR cross sections $\sigma^{100}_{j_i j_f, j_i' j_f'}$ may be transformed into a *supermatrix of rank 2,* each element of this matrix being a dyadic state-to-state cross section [16] $\tilde{\Gamma}^{00}_{j_i j_i'}$ and $\tilde{\Gamma}^{01}_{j_i j_i'}$ [or $\Gamma^0_{j_i j_i'}$ and $\Gamma^1_{j_i j_i'}$ from Eq. (7)] (see Table I).

The rows and columns of the supermatrix correspond to the IR branches P and R, and its elements are the line-broadening and the line-coupling cross sections. The P-P and R-R elements describe, for $j_i' = j_i$, the P and R line broadening (and line shifting), and, for $j_i' \neq j_i$, the line coupling inside the considered band. The P-R elements describe the coupling between lines belonging to the two branches.

Let us examine now the case of an IR bending band ($l_i = 0$, $l_f = 1$). The spectroscopic cross sections are thus defined

TABLE II. Collisional spectroscopic cross-section supermatrix $\sigma^{101}_{j_i j_f, j_i' j_f'}$ for an IR bending ($l_i=0$, $l_f=1$) band.

	P	Q	R
P	$\frac{1}{6}\Gamma^0_{j_i j_i'}+\frac{1}{2}\Gamma^1_{j_i j_i'}+\frac{1}{3}\Gamma^2_{j_i j_i'}$	$\frac{\sqrt{2}}{3}(\Gamma^0_{j_i j_i'}-\Gamma^2_{j_i j_i'})$	$\frac{1}{6}\Gamma^0_{j_i j_i'}-\frac{1}{2}\Gamma^1_{j_i j_i'}+\frac{1}{3}\Gamma^2_{j_i j_i'}$
Q	$\frac{\sqrt{2}}{3}(\Gamma^0_{j_i j_i'}-\Gamma^2_{j_i j_i'})$	$\frac{1}{3}\Gamma^0_{j_i j_i'}+\frac{2}{3}\Gamma^2_{j_i j_i'}$	$\frac{\sqrt{2}}{3}(\Gamma^0_{j_i j_i'}-\Gamma^2_{j_i j_i'})$
R	$\frac{1}{6}\Gamma^0_{j_i j_i'}-\frac{1}{2}\Gamma^1_{j_i j_i'}+\frac{1}{3}\Gamma^2_{j_i j_i'}$	$\frac{\sqrt{2}}{3}(\Gamma^0_{j_i j_i'}-\Gamma^2_{j_i j_i'})$	$\frac{1}{6}\Gamma^0_{j_i j_i'}+\frac{1}{2}\Gamma^1_{j_i j_i'}+\frac{1}{3}\Gamma^2_{j_i j_i'}$

by [Eq. (3)]

$$\sigma^{101}_{j_i j_f, j_i' j_f'}=(-1)^{j_f+j_f'}[j_f j_f']^{1/2}\left\{\begin{pmatrix} j_i & 1 & j_f \\ 0 & 1 & -1 \end{pmatrix}\begin{pmatrix} j_i' & 1 & j_f' \\ 0 & 1 & -1 \end{pmatrix}\tilde{\Gamma}^{00}_{j_i j_i'}+\begin{pmatrix} j_i & 1 & j_f \\ 1 & 0 & -1 \end{pmatrix}\begin{pmatrix} j_i' & 1 & j_f' \\ 1 & 0 & -1 \end{pmatrix}\tilde{\Gamma}^{01}_{j_i j_i'}\right.$$
$$\left.+\begin{pmatrix} j_i & 1 & j_f \\ 2 & -1 & -1 \end{pmatrix}\begin{pmatrix} j_i' & 1 & j_f' \\ 2 & -1 & -1 \end{pmatrix}\tilde{\Gamma}^{02}_{j_i j_i'}\right\} . \tag{11}$$

In the $T \gg T_{\mathrm{rot}}$ limit, the rank-3 supermatrix is, from Eqs. (7), (9), and (11), shown in Table II.

The role of the vibrational angular momentum $l_f=1$ in the excited vibrational mode is clearly apparent through a comparison between Tables I and II.

An ECS calculation of the $(11^10)_I \leftarrow (00^00)$ CO_2 band profile has been performed using the present approach [17] $(v_1 v_2^{l_2} v_3)_I$ denotes the vibrational band of higher energy in the Fermi dyad). The results are in good quantitative agreement with experiment. In the present case the approach is used within the strong-coupling (SC) model [18,19] to obtain simple analytical expressions for the various line couplings. The SC state-to-state cross sections are [18,19]

$$\Gamma^K_{jj'}=\tau_j^{-1}[\delta_{jj'}-\xi_K\tau_{j'}^{-1}\langle\tau^{-1}\rangle^{-1}\rho_{j'}] , \tag{12}$$

with $\xi_K=\pi^{-1}\int_0^\pi d\alpha P_K(\cos\alpha)$ ($\xi_0=1$, $\xi_1=0$, and $\xi_2=\frac{1}{4}$). In Eq. (12), τ_j^{-1} is the collisional frequency and $\langle\tau^{-1}\rangle$ its Boltzmann average. The line coupling inside the IR bending Q branch is thus given by $-1/2\tau_j^{-1}\tau_{j'}^{-1}\langle\tau^{-1}\rangle^{-1}\rho_{j'}$ [cf. Table II and Eq. (12)]. Since the rotational energy state-to-state cross sections are defined by $\sigma_{j\to j'}=-\Gamma^0_{jj'}(1-\delta_{jj'})$, apart from the sign, they are twice the infrared SC Q-line couplings. This corresponds well with the *ad hoc* decoupling "factor of 2" introduced previously [2,5,6]. It is easy now to put forward the qualitative explanation of the factor 2 obtained. Spectral exchange inside the IR Q branch depends on the reorientation of angular-momentum vector **J** during the collision. Bending vibration defines a plane, with respect to which the reorientation of **J** must be symmetrical, and the corresponding probability density must be dependent on $\cos^2\alpha$, where α is the collisional angular shift of **J**. It may be checked by the substitution of a uniform asymptotic expansion for the 6-j symbol in Eq. (5) which results in $\cos^2\alpha$ as a leading term for the Q-Q supermatrix element in Table II. The SC model offers a simple straightforward opportunity to average this $\cos^2\alpha$ over different types of collisions with "factor of 2" being reproduced. Notice that the use of another collisional model (such as ECS) leads to a different value close, but not equal, to 2 [17].

The present analysis also predicts a decoupling factor for the P and R branches, 2 for a stretching band and 4 for a bending band within the SC model. Although the SC model is generally not convenient for a very accurate description of band profiles [19], it permits a simple explanation for the angular-momentum effects on the spectral narrowing.

This approach may be easily extended to vibrational transitions between bending modes and to anisotropic Raman scattering. The Raman cross sections are then transformed into a supermatrix of rank 5 in terms of the $\tilde{\Gamma}^{ll'}_{jj'}$. Starting from the present formalism, various applications will be developed to account for the collisional energy transfers of intensity as well inside a given branch (e.g., Q) as between various branches (e.g., Q-P, Q-R, or P-R). These applications will allow one to get a better understanding of the different spectral modifications observed, following the type of the vibrational band and the nature of the spectroscopy used.

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