Intensity factors in molecular spectra

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The interest in precise knowledge of the intensity factors for investigating molecular structure is pointed out and illustrated by some typical recent examples. Diatomic intensity factors are derived. Starting from pure coupling-case wave functions, the intensity factors related to transitions between states belonging to a_α, a_β, $b_{\beta J}$, $b_{\beta S}$, and $b_{\beta N}$ coupling cases, in the spin-forbidden or spin-allowed hypothesis, are derived. Cases are considered for which hyperfine structure is fully observed, partially observed, or absent.

I. INTRODUCTION

The basic formula for studying diatomic line intensities[1,2] can be summarized in a simple expression:

$$I(i \to f) = f(\nu)\mathfrak{N}(i)m(i \to f), \tag{1}$$

where $f(\nu)$ is equal to $k\nu^4$ for an emission line and to $k'\nu$ for an absorption one; ν is the frequency of the line, k and k' are constants dependent upon the characteristics of the experimental apparatus. $\mathfrak{N}(i)$ is the number of particles in the initial level i, and could be called the "statistical part of the formula." Its evaluation is not always easy[3] and the usual Boltzmann approximation is often rough because of imprecise knowledge of the real emission or absorption processes. $m(i \to f)$, the intensity factor, related to the probability for the transition $i \to f$, is the square modulus of the matrix element of the operator connecting the initial and final states. In this paper only the most frequent of the possible operators is considered, the electric dipole moment operator $\vec{M}$.

It is a common fact that when a molecular elementary (rotational or even hyperfine) level is perturbed, the strongest effect is often concentrated in the intensities of the corresponding spectral lines. Therefore intensities in molecular spectra may often provide a very sensitive means of investigation. For instance, a very simple calculation shows that when considering the transitions from two initial levels a and b to the same final level x, a very slight perturbation between a and b leads to a *second-order* energy correction and line shift, while the wave functions of the initial levels, and hence, the intensity factors $m(a \to x)$, $m(b \to x)$ and the intensity of each line, show a *first-order* correction. This emphasizes the importance of the quantum factor m in the intensity formula. Three examples in the recent literature may be mentioned where the role played by m in an intensity study is predominant. Firstly, the study of the $^3\phi \to X\,^3\Delta$ transition of NbN,[4] where the use of hyperfine intensity factors unambiguously demonstrates a slight hyperfine effect in the excited $^3\phi$ state and provides some ideas on the molecular bonding. Secondly the hyperfine analysis of the $B\,^2\Sigma \to X\,^2\Sigma$ system of LaO,[5] where a detailed study of the intensity ratios, involving only a knowledge of m, allows an accurate determination of the weak spin-rotation interaction parameter, unavailable by the usual line-position analysis. Finally, a recent intensity analysis[6] of the emission spectrum of ScO gives a good example of the high sensitivity of intensity to a slight mixing of states; the method used to evaluate the mixing effect on intensity gives an idea of the fruitful connection existing between intensity and line-position investigations but essentially gives us the opportunity of justifying the somewhat detailed attention exercised in deriving the diatomic pure coupling-case wave functions[7-10]: In the (almost unavoidable) case of mixing of states the calculation of m is made by a linear combination of wave functions which is incompatible with any phase-factor error.

In the following, the aim is to present the basic algebraic expressions of the intensity factors related to transitions between theoretical pure coupling-case states. Expressions suitable for actual molecular problems can be obtained by using procedures analogous to those presented in Refs. 5 and 6.

Section II is devoted to some general considerations concerning the background of our calculations and the problems of symmetry and parity selection rules. In Sec. III, the wave-function notations and the calculation of the basic case $a_\alpha \to$ case a_α and $a_\beta \to a_\beta$ intensity factors are presented. Sections IV and V are devoted, respectively, to $b \to a$ and $b \to b$ intensity factors.

II. GENERAL REMARKS

All the following calculations will be made using a set of "case a" wave functions[11] as a reference basis. Thus $m(i \to f)$ has the following basic form[12]:

$$m(i\to f)=|\langle(L')\Lambda'S'\Sigma',\Omega'J'M_J'|M_R|(L)\Lambda S\Sigma,\Omega JM_J\rangle|^2, \tag{2}$$

where the primed wave function corresponds to the final state, M_J' and M_J are the components of J' and J along the Z axis of the laboratory frame of reference, and M_R is a component of the electric dipole moment $\vec{M}$ in this frame.[13] The matrix element involved in this expression is related to the reduced matrix element of $\vec{M}$ by the Wigner-Eckart theorem[14]:

$$\langle(L')\Lambda'S'\Sigma',\Omega'J'M_J'|M_R|(L)\Lambda S\Sigma,\Omega JM_J\rangle = (-1)^{J'-M_J'}\begin{pmatrix} J' & 1 & J \\ -M_J' & R & M_J\end{pmatrix} \times\langle(L')\Lambda'S'\Sigma',\Omega'J'||\vec{M}||(L)\Lambda S\Sigma,\Omega J\rangle. \tag{3}$$

If we assume that there is no external field and if we are not concerned with a particular polarization of the light, we have to evaluate $\sum_{M_J',M_J,R} m(i\to f)$ which reduces to[10]

$$|\langle(L')\Lambda'S'\Sigma',\Omega'J'||\vec{M}||(L)\Lambda S\Sigma,\Omega J\rangle|^2.$$

Our second remark is related to "Krönig symmetrization." A better representation of a molecular level is given by the two eigenfunctions of the symmetry operator σ_V,[11] each associated with a Λ-component of the elementary level (if $\Lambda\neq 0$)

$$|(L)\Lambda S\Sigma,\Omega JM_J\pm\rangle = (1/\sqrt{2})[|(L)\Lambda S\Sigma,\Omega JM_J\rangle \pm|(L)-\Lambda S-\Sigma,-\Omega JM_J\rangle], \tag{4}$$

with

$$\sigma_V|(L)\Lambda S\Sigma,\Omega JM_J\rangle=(-1)^{\epsilon+L-\Lambda+S-\Sigma}(-1)^{J-\Omega} \times|(L)-\Lambda S-\Sigma,-\Omega JM_J\rangle,$$

and $\epsilon=0$ or $+1$ "if the electronic state of the molecule correlates with a united atom state of even or odd parity, respectively."[11] Thus, in fact we have to evaluate $\langle\Psi'\xi'|M_R|\Psi\xi\rangle$, where ξ' and ξ represent + or −. This matrix element can be written

$$\langle\Psi'\xi'|M_R|\Psi\xi\rangle=\tfrac{1}{2}[\langle+\phi'|M_R|+\phi\rangle +(\xi 1)(\xi'1)\langle-\phi'|M_R|-\phi\rangle +(\xi 1)\langle+\phi'|M_R|-\phi\rangle +(\xi'1)\langle-\phi'|M_R|+\phi\rangle], \tag{5}$$

where $|\pm\phi\rangle$ stands for $|(L)\pm\Lambda S\pm\Sigma,\pm\Omega JM_J\rangle$. Using

$$\sigma_V^\dagger\sigma_V=I, \tag{6}$$

this can be easily reduced to

$$\langle\Psi'\xi'|M_R|\Psi\xi\rangle=\tfrac{1}{2}[1+(\xi 1)(\xi'1)(-1)^{\eta-\eta'+1}] \times[\langle+\phi'|M_R|+\phi\rangle +(\xi 1)\langle+\phi'|M_R|-\phi\rangle], \tag{7}$$

where

$$\eta=\epsilon+L+\Lambda+S+\Sigma+J+\Omega. \tag{8}$$

The parity of $|\Psi\xi\rangle$ is easily shown to be $(\xi 1)(-1)^{\eta}$, and $(\xi'1)(-1)^{\eta'}$ that of $|\Psi'\xi'\rangle$; thus the first bracket on the right-hand side of Eq. (7) gives the well-known selection rule $+\not\leftrightarrow+$, $-\not\leftrightarrow-$, $-\leftrightarrow+$, $+\leftrightarrow-$. The second matrix element of the second bracket is nonvanishing if $\Omega+\Omega'\leq 1$ in the case of spin-forbidden transitions, and if $\Lambda+\Lambda'\leq 1$ in the case of a spin-allowed one, which gives, with the usual corresponding selection rules $|\Omega-\Omega'|\leq 1$ and $|\Lambda-\Lambda'|\leq 1$; Ω and $\Omega'=0,\frac{1}{2},1$; or Λ and $\Lambda'=0,1$. This must be taken into account in the calculations, above all in the most frequent cases of $\Pi\leftrightarrow\Pi$ and $\Pi\leftrightarrow\Sigma$ transitions. In almost all cases[15] if $\langle+\phi'|M_R|+\phi\rangle$ exists, then $\langle+\phi'|M_R|-\phi\rangle$ vanishes and conversely; consequently, when the parity selection rule is verified, the relation (7) reduces often to

$$\langle\Psi'\xi'|M_R|\Psi\xi\rangle=\langle+\phi'|M_R|+\phi\rangle$$

or

$$\langle\Psi'\xi'|M_R|\Psi\xi\rangle=(\xi 1)\langle+\phi'|M_R|-\phi\rangle. \tag{9}$$

Note that, in the following, the expressions of Σ-state wave functions (belonging to case b coupling scheme) will be already Krönig symmetrized.[16]

Therefore, each transition must be studied carefully as a particular case, using the parity information obtainable about the corresponding states,[10,17] the coefficients of mixing, the factors of Herman and Wallis and a degeneracy factor 2 when Λ components are not separated.[2] The following intensity factors are basic and correspond to ideal wave functions, thus they should not generally be used without the corrections mentioned above.

We are very indebted to the works of Edmonds[14] and Yutsis *et al.*[18] on angular momentum theory; several references will be made to these books in the following. The notations Ed(ξ) and Y(η) will, respectively, refer to equation number (ξ) in the Edmonds book and equation number (η) in that of Yutsis *et al.*

III. WAVE FUNCTIONS AND BASIC $a_\alpha\to a_\alpha$ AND $a_\beta\to a_\beta$ INTENSITY FACTORS

A. "Hyperfine" diatomic wave functions

The method for deriving molecular wave functions in complex hyperfine coupling cases has already been presented[7,8,10] We give here our notations and the expansions we use for the functions

$$|\underset{(a_\beta)}{(L)\Lambda S\Sigma\Omega, IJ\Omega FM_F}\rangle$$

or

$$|\underset{(a_\beta)}{(L)\Lambda S\Sigma I, \Omega JFM_F}\rangle = \sum_{\Sigma_I, \Omega_F} (-1)^{I+\Sigma_I}(-1)^{I-F+\Omega}\hat{J}^{1/2} \begin{pmatrix} I & F & J \\ -\Sigma_I & \Omega_F & -\Omega \end{pmatrix} |\underset{(a_\alpha)}{(L)\Lambda S\Sigma I\Sigma_I, \Omega_F FM_F}\rangle. \tag{10}$$

Henceforth, $\hat{A}$ will denote $2A+1$:

$$|\underset{(b_{\beta J})}{(L)\Lambda SN\Lambda IJFM_F}\rangle = \sum_{\Sigma,\Omega} (-1)^{S+\Sigma}(-1)^{S-J+\Lambda}\hat{N}^{1/2} \begin{pmatrix} S & J & N \\ -\Sigma & \Omega & -\Lambda \end{pmatrix} |\underset{(a_\beta)}{(L)\Lambda S\Sigma I, \Omega JFM_F}\rangle, \tag{11a}$$

and similarly

$$|\underset{(b)}{(L)\Lambda SN\Lambda JM_J}\rangle = \sum_{\Sigma,\Omega} (-1)^{S+\Sigma}(-1)^{S-J+\Lambda}\hat{N}^{1/2} \begin{pmatrix} S & J & N \\ -\Sigma & \Omega & -\Lambda \end{pmatrix} |\underset{(a)}{(L)\Lambda S\Sigma, \Omega JM_J}\rangle, \tag{11b}$$

$$|\underset{(b_{\beta S})}{(L)\Lambda(SI)GN\Lambda FM_F}\rangle = \sum_J (-1)^{S+I+F+N}[\hat{G}\hat{J}]^{1/2} \begin{Bmatrix} S & I & G \\ F & N & J \end{Bmatrix} |\underset{(b_{\beta J})}{(L)\Lambda SN\Lambda IJFM_F}\rangle, \tag{12}$$

$$|\underset{(b_{\beta N})}{(L)\Lambda IN\Lambda SKFM_F}\rangle = \sum_J (-1)^{I+J+S+K}[\hat{J}\hat{K}]^{1/2} \begin{Bmatrix} I & F & J \\ S & N & K \end{Bmatrix} |\underset{(b_{\beta J})}{(L)\Lambda SN\Lambda IJFM_F}\rangle. \tag{13}$$

In the last $b_{\beta N}$ coupling case, K is the quantum number associated with the momentum $\vec{K}$ which arises from the coupling of $\vec{N}$ and $\vec{I}$. The coupling of $\vec{K}$ and $\vec{S}$ gives the total angular momentum $\vec{F}$.

B. $a_\alpha \to a_\alpha$ intensity factor

We calculate

$$M(a_\alpha, a_\alpha) = \langle\langle (L')\Lambda' S'\Sigma' I'\Sigma_I'\Omega_F' F' \| \vec{M} \| (L)\Lambda S\Sigma I\Sigma_I \Omega_F F\rangle$$

or

$$M(a_\alpha, a_\alpha) = (-1)^{M_F'-F'} \begin{pmatrix} F' & 1 & F \\ -M_F' & R & M_F \end{pmatrix}^{-1} \langle (L')\Lambda' S'\Sigma' I'\Sigma_I'\Omega_F' F' M_F' | M_R | (L)\Lambda S\Sigma I\Sigma_I \Omega_F FM_F\rangle. \tag{14}$$

It is convenient to write M_R in terms of $\vec{M}$ components in the molecule fixed frame of reference xyz[10]

$$M_R = \sum_{s=0,\pm1} \mu_s \mathfrak{D}_{sR}^{(1)}(\omega), \tag{15}$$

where ω is the set $\{\alpha, \beta, \gamma\}$ of Euler angles giving the position of the molecule in the laboratory frame of reference XYZ. Therefore

$$M(a_\alpha, a_\alpha) = (-1)^{M_F'-F'} \begin{pmatrix} F' & 1 & F \\ -M_F' & R & M_F \end{pmatrix}^{-1} \sum_{s=0,\pm1} \langle (L')\Lambda' S'\Sigma' I'\Sigma_I' | \mu_s | (L)\Lambda S\Sigma I\Sigma_I\rangle \langle \Omega_F' F' M_F' | \mathfrak{D}_{sR}^{(1)}(\omega) | \Omega_F FM_F\rangle, \tag{16}$$

by separating the rotational part, which depends on $\{\alpha, \beta, \gamma\}$, and the nonrotating one.

The rotating matrix element is calculated using symmetric-top molecule wave functions[14]

$$|\Omega_F FM_F\rangle \longleftrightarrow \phi(F)[(2F+1)/8\pi^2]^{1/2}\mathfrak{D}_{\Omega_F M_F}^{(F)}(\omega), \tag{17}$$

where $\phi(F)$ is a phase factor which depends only on F. Therefore, we obtain

$$\langle \Omega_F' F' M_F' | \mathfrak{D}_{sR}^{(1)}(\omega) | \Omega_F FM_F\rangle = \phi^*(F')\phi(F)\frac{[\hat{F}'\hat{F}]^{1/2}}{8\pi^2} \int_{\alpha=0}^{2\pi}\int_{\beta=0}^{\pi}\int_{\gamma=0}^{2\pi} \mathfrak{D}_{\Omega_F' M_F'}^{(F')*}(\omega)\mathfrak{D}_{sR}^{(1)}(\omega)\mathfrak{D}_{\Omega_F M_F}^{(F)}(\omega)\,d\alpha\,\sin\beta\,d\beta\,d\gamma, \tag{18}$$

and thus, using Ed(4.6.2),

$$\langle \Omega'_F F' M'_F | \mathfrak{D}^{(1)}_{sR}(\omega) | \Omega_F F M_F\rangle = \phi^*(F')\phi(F)(-1)^{\Omega'_F - M'_F}[\hat{F}'\hat{F}]^{1/2}\begin{pmatrix} F' & 1 & F \\ -\Omega'_F & s & \Omega_F \end{pmatrix}\begin{pmatrix} F' & 1 & F \\ -M'_F & R & M_F \end{pmatrix}. \tag{19}$$

Finally, we obtain

$$M(a_\alpha, a_\alpha) = \phi^*(F')\phi(F)(-1)^{\Omega'_F - F'}[\hat{F}'\hat{F}]^{1/2} \sum_{s=0,\pm 1} \begin{pmatrix} F' & 1 & F \\ -\Omega'_F & s & \Omega_F \end{pmatrix} \langle\langle L'\rangle \Lambda' S' \Sigma' I' \Sigma'_I | \mu_s | \langle L\rangle \Lambda S \Sigma I \Sigma_I\rangle. \tag{20}$$

The operator $\vec{\mathrm{M}}$ depends essentially upon the electronic repartition around the nuclei and, in several cases, only upon the orbital motion of the electrons. Thus we can make the assumption that μ_s is diagonal in I and Σ_I. Therefore, we have for brevity's sake

$$\begin{aligned}\langle\langle L'\rangle \Lambda' S' \Sigma' I' \Sigma'_I | \mu_s | \langle L\rangle \Lambda S \Sigma I \Sigma_I\rangle &= \delta_{I'I}\delta_{\Sigma'_I\Sigma_I}\langle\langle L'\rangle \Lambda' S' \Sigma' I' \Sigma'_I | \mu_s | \langle L\rangle \Lambda S \Sigma I \Sigma_I\rangle \\ &= \delta_{I'I}\delta_{\Sigma'_I\Sigma_I}\langle\langle L'\rangle \Lambda' S' \Sigma' | \mu_s | \langle L\rangle \Lambda S \Sigma\rangle. \end{aligned} \tag{21}$$

We could call this assumption "nuclear-spin-allowed (NSA) hypothesis." We do not know any nuclear-spin-forbidden (NSF) case. If the matrix element of μ_s is diagonal in S and Σ we have in the same way

$$\begin{aligned}\langle\langle L'\rangle \Lambda' S' \Sigma' | \mu_s | \langle L\rangle \Lambda S \Sigma\rangle &= \delta_{S'S}\delta_{\Sigma'\Sigma}\langle\langle L'\rangle \Lambda' S' \Sigma' | \mu_s | \langle L\rangle \Lambda S \Sigma\rangle \\ &= \delta_{S'S}\delta_{\Sigma'\Sigma}\langle\langle L'\rangle \Lambda' | \mu_s | \langle L\rangle \Lambda\rangle, \end{aligned} \tag{22}$$

which is the case of spin-allowed (SA) transition. If this matrix element is not diagonal in S and/or Σ, the transition is spin forbidden (SF). These definitions are well known and are only given here in order to specify our notations.

With the NSA hypothesis, we get

$$M(a_\alpha, a_\alpha) = \delta_{I'I}\delta_{\Sigma'_I\Sigma_I}\phi^*(F')\phi(F)(-1)^{\Omega'_F - F'}[\hat{F}'\hat{F}]^{1/2} \sum_{s=0,\pm 1} \begin{pmatrix} F' & 1 & F \\ -\Omega'_F & s & \Omega_F \end{pmatrix} \langle\langle L'\rangle \Lambda' S' \Sigma' | \mu_s | \langle L\rangle \Lambda S \Sigma\rangle. \tag{23}$$

Therefore, if we assume that $s = \Omega'_F - \Omega_F$, the corresponding intensity factor is given by

$$m(a_\alpha \to a_\alpha) = \delta_{I'I}\delta_{\Sigma'_I\Sigma_I}\hat{F}'\hat{F}\begin{pmatrix} F' & 1 & F \\ -\Omega'_F & s & \Omega_F \end{pmatrix}^2 |\langle\langle L'\rangle \Lambda' S' \Sigma' | \mu_s | \langle L\rangle \Lambda S \Sigma\rangle|^2. \tag{24}$$

C. $a_\beta \to a_\beta$ intensity factor

By use of Eq. (10), we obtain the reduced matrix element of $\vec{\mathrm{M}}$,

$$\begin{aligned} M(a_\beta, a_\beta) = {} & \delta_{I'I}\phi^*(F')\phi(F)[\hat{F}'\hat{F}\hat{J}'\hat{J}]^{1/2}(-1)^{-I'+F'-\Omega'}(-1)^{I-F+\Omega} \\ & \times \sum_{\Sigma'_I\Omega'_F}\sum_{\Sigma_I\Omega_F}\sum_s \delta_{\Sigma'_I\Sigma_I}(-1)^{-I'-\Sigma'_I}(-1)^{I+\Sigma_I}(-1)^{\Omega'_F - F'}\begin{pmatrix} I' & F' & J' \\ -\Sigma'_I & \Omega'_F & -\Omega' \end{pmatrix} \\ & \times \begin{pmatrix} I & F & J \\ -\Sigma_I & \Omega_F & -\Omega \end{pmatrix}\begin{pmatrix} F' & 1 & F \\ -\Omega'_F & s & \Omega_F \end{pmatrix}\langle\langle L'\rangle \Lambda' S', \Sigma' | \mu_s | \langle L\rangle \Lambda S \Sigma\rangle, \end{aligned} \tag{25}$$

which reduces to

$$M_{\mathrm{SF}}(a_\beta, a_\beta) = \delta_{I'I}\phi^*(F')\phi(F)(-1)^{F+\Omega'+I+1}[\hat{F}'\hat{F}\hat{J}'\hat{J}]^{1/2}\begin{pmatrix} J' & 1 & J \\ -\Omega' & s & \Omega \end{pmatrix}\begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix}\langle\langle L'\rangle \Lambda' S' \Sigma' | \mu_s | \langle L\rangle \Lambda S \Sigma\rangle, \tag{26}$$

using Ed(6.2.8) and assuming $s = \Omega' - \Omega$. The subscript SF specifies the spin forbidden type of the transition. In the case of spin allowed transition, the expression of $M(a_\beta, a_\beta)$ is

$$M_{\mathrm{SA}}(a_\beta, a_\beta) = \delta_{I'I}\delta_{S'S}\delta_{\Sigma'\Sigma}\phi^*(F')\phi(F)(-1)^{F+\Omega'+I+1}[\hat{F}'\hat{F}\hat{J}'\hat{J}]^{1/2}\begin{pmatrix} J' & 1 & J \\ -\Omega' & s & \Omega \end{pmatrix}\begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix}\langle\langle L'\rangle \Lambda' | \mu_s | \langle L\rangle \Lambda\rangle \tag{27}$$

with $s = \Lambda' - \Lambda$. In each case, the square modulus of M yields the corresponding intensity factor. For instance, we have in the SF case

$$m_{\mathrm{SF}}(a_\beta \to a_\beta) = \delta_{I'I}\hat{F}'\hat{F}\hat{J}'\hat{J}\begin{pmatrix} J' & 1 & J \\ -\Omega' & s & \Omega \end{pmatrix}^2 \begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix}^2 |\langle(L')\Lambda'S'\Sigma'|\mu_s|(L)\Lambda S\Sigma\rangle|^2. \tag{28}$$

It is obvious that the knowledge of M is much more important than that of m because of the phase problem already mentioned. Therefore in the following we shall only give M. Next, we shall systematically derive the expression of the intensity factor when no hyperfine splitting is observed; firstly, in the final state; secondly, in the initial state (when it does not belong to the same coupling case as the final state); and thirdly, when no hyperfine components are observed at all. Next, other cases depending on the characteristics of more complicated coupling cases will be studied.

For instance, in the present case, we obtain the intensity factor corresponding to the case when no hyperfine effect is observed in the final state by summing m over F',

$$\sum_{F'} |M(a_\beta, a_\beta)|^2 = \delta_{I'I}\hat{F}\hat{J}'\hat{J}\begin{pmatrix} J' & 1 & J \\ -\Omega' & s & \Omega \end{pmatrix}^2 \times |\langle(L')\Lambda'S'\Sigma'|\mu_s|(L)\Lambda S\Sigma\rangle|^2 \times \sum_{F'} \hat{F}' \begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix}^2 \tag{29}$$

or

$$\sum_{F'} |M(a_\beta, a_\beta)|^2 = \delta_{I'I}\hat{F}\hat{J}'\begin{pmatrix} J' & 1 & J \\ -\Omega' & s & \Omega \end{pmatrix}^2 \times |\langle(L')\Lambda'S'\Sigma'|\mu_s|(L)\Lambda S\Sigma\rangle|^2. \tag{30}$$

Similarly if no hyperfine effect is observed in both states the intensity factor is, using $\sum_F \hat{F} = \hat{I}\hat{J}$.

$$\sum_{F,F'} |M(a_\beta, a_\beta)|^2 = \delta_{I'I}\hat{I}\hat{J}\hat{J}'\begin{pmatrix} J' & 1 & J \\ -\Omega' & s & \Omega \end{pmatrix}^2 \times |\langle(L')\Lambda'S'\Sigma'|\mu_s|(L)\Lambda S\Sigma\rangle|^2. \tag{31}$$

D. $a \to a$ intensity factor

The "classical" (i.e., without nuclear spin $\vec{I}$) $M_c(a, a)$ is easily obtained by analogy with $M(a_\alpha, a_\alpha)$,

$$M_c(a, a) = \phi^*(J')\phi(J)(-1)^{\Omega'-J'}[\hat{J}'\hat{J}]^{1/2} \times \begin{pmatrix} J' & 1 & J \\ -\Omega' & s & \Omega \end{pmatrix}\langle(L')\Lambda'S'\Sigma'|\mu_s|(L)\Lambda S\Sigma\rangle, \tag{32}$$

and leads to the usual degeneracy expression

$$\sum_{F,F'} |M(a_\beta, a_\beta)|^2 = \delta_{I'I}(2I+1)|M_c(a, a)|^2, \tag{33}$$

which may be considered as a verification of our expressions.

In the following, we shall omit $\delta_{I'I}$ and also the phase factors $\phi^*(F')$, $\phi(F)$, $\phi^*(J')$, and $\phi(J)$ which have no influence on the final expression of the intensity factors.

IV. $b \to a$ INTENSITY FACTORS

A. Classical $b \to a$ transition

Equations (11b) and (32) lead to

$$M_c(b, a) = (-1)^{J'-\Omega'}(-1)^{S-J+\Lambda}[\hat{J}'\hat{J}\hat{N}]^{1/2}B(J', J), \tag{34}$$

with

$$B(J', J) = \sum_{\Sigma,\Omega,s} (-1)^{S+\Sigma}\begin{pmatrix} S & J & N \\ -\Sigma & \Omega & -\Lambda \end{pmatrix}\begin{pmatrix} J' & 1 & J \\ -\Omega' & s & \Omega \end{pmatrix} \times \langle(L')\Lambda'S'\Sigma'|\mu_s|(L)\Lambda S\Sigma\rangle, \tag{35}$$

which reduces to

$$B_{\mathrm{SA}}(J', J) = \delta_{S'S}\delta_{\Sigma'\Sigma}\langle(L')\Lambda'|\mu_s|(L)\Lambda\rangle \times \sum_{\Sigma,\Omega} (-1)^{S+\Sigma}\begin{pmatrix} S & J & N \\ -\Sigma & \Omega & -\Lambda \end{pmatrix}\begin{pmatrix} J' & 1 & J \\ -\Omega' & s & \Omega \end{pmatrix}, \tag{36}$$

if the transition is spin allowed and assuming $s = \Lambda' - \Lambda$.

B. $b_{\beta J} \to a_\beta$ transition

Following the same procedure we obtain from Eqs. (11a) and (26), we have

$$M(b_{\beta J}, a_\beta) = (-1)^{F+\Omega'+I+1}(-1)^{S-J+\Lambda}[\hat{F}'\hat{F}\hat{J}'\hat{J}\hat{N}]^{1/2} \times \begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix}B(J', J). \tag{37}$$

Using Ed(6.2.9.), we obtain

$$\sum_{F'} |M(b_{\beta J}, a_\beta)|^2 = \hat{F}\hat{J}'\hat{N}|B(J', J)|^2, \tag{38}$$

$$\sum_{F} |M(b_{\beta J}, a_\beta)|^2 = \hat{F}'\hat{J}\hat{N}|B(J', J)|^2, \tag{39}$$

$$\sum_{FF'} |M(b_{\beta J}, a_\beta)|^2 = \hat{I}\hat{J}'\hat{J}\hat{N}|B(J', J)|^2 = \hat{I}|M_c(b, a)|^2. \tag{40}$$

C. $b_{\beta S} \to a_\beta$ transition

Starting from Eqs. (12) and (37), we obtain

$$M(b_{\beta S}, a_\beta) = (-1)^{N-1}[\hat{F}'\hat{F}\hat{J}'\hat{N}\hat{G}]^{1/2} \times \sum_J (-1)^{\Omega'+\Lambda-J}\hat{J}\begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix} \times \begin{Bmatrix} S & I & G \\ F & N & J \end{Bmatrix} B(J', J). \tag{41}$$

Using Ed(6.2.9) leads to

$$\sum_{F'} |M(b_{\beta S}, a_\beta)|^2 = \hat{F}\hat{J}'\hat{N}\hat{G} \times \sum_J \hat{J}\begin{Bmatrix} S & I & G \\ F & N & J \end{Bmatrix}^2 |B(J', J)|^2. \tag{42}$$

The definition of the $12j$ coefficient of the second kind [Y(A.6.12)] gives

$$\sum_F |M(b_{\beta S}, a_\beta)|^2 = \hat{F}'\hat{J}'\hat{N}\hat{G} \sum_{J, J_1} (-1)^{J_1-J}\hat{J}_1\hat{J} \times \begin{bmatrix} I & I & J & J_1 \\ S & J' & S & J' \\ G & N & F' & 1 \end{bmatrix} B^*(J', J_1)B(J', J). \tag{43a}$$

The use of Y(A.6.47) leads to another form ensuring of the positive sign of the expression

$$\sum_F |M(b_{\beta S}, a_\beta)|^2 = \hat{F}'\hat{J}'\hat{N}\hat{G} \times \sum_g \hat{g}\left| \sum_J (-1)^{J'-J}\hat{J}\begin{Bmatrix} 1 & G & g \\ J & S & N \\ J' & I & F' \end{Bmatrix} B(J', J)\right|^2. \tag{43b}$$

Directly from Eq. (42) we obtain

$$\sum_{F', F} |M(b_{\beta S}, a_\beta)|^2 = \frac{\hat{J}'\hat{N}\hat{G}}{\hat{S}} \sum_J \hat{J}|B(J', J)|^2 = \frac{\hat{G}}{\hat{S}} \sum_J |M_c(b, a)|^2. \tag{44}$$

Let us consider the case when the "G components" are not observed; starting from Eq. (43a) and using Y(A.6.21), we obtain

$$\sum_{F, G} |M(b_{\beta S}, a_\beta)|^2 = \hat{F}'\hat{N} \sum_J \hat{J}|B(J', J)|^2 = \frac{\hat{F}'}{\hat{J}'} \sum_J |M_c(b, a)|^2 \tag{45}$$

and

$$\sum_{F', F, G} |M(b_{\beta S}, a_\beta)|^2 = \hat{I}\hat{J}'\hat{N} \sum_J \hat{J}|B(J', J)|^2 = \hat{I} \sum_J |M_c(b, a)|^2. \tag{46}$$

D. $b_{\beta N} \to a_\beta$ transition

The calculations are similar to those of the preceding case; here we only give the results

$$M(b_{\beta N}, a_\beta) = (-1)^{F+\Omega'+I+1}(-1)^{2S+I+K+\Lambda}[\hat{F}'\hat{F}\hat{J}'\hat{K}\hat{N}]^{1/2} \times \sum_J \hat{J}\begin{Bmatrix} I & F & J \\ S & N & K \end{Bmatrix}\begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix} B(J', J), \tag{47}$$

$$\sum_{F'} |M(b_{\beta N}, a_\beta)|^2 = \hat{F}\hat{J}'\hat{N}\hat{K} \sum_J \hat{J}\begin{Bmatrix} I & F & J \\ S & N & K \end{Bmatrix}^2 \times |B(J', J)|^2, \tag{48}$$

$$\sum_F |M(b_{\beta N}, a_\beta)|^2 = \hat{F}'\hat{J}'\hat{N}\hat{K} \sum_{J, J_1} \hat{J}_1\hat{J}\begin{bmatrix} S & 1 & K & F' \\ N & N & J' & J' \\ J & I & J_1 & I \end{bmatrix} \times B^*(J', J_1)B(J', J), \tag{49}$$

$$\sum_{F', F} |M(b_{\beta N}, a_\beta)|^2 = \hat{J}'\hat{K} \sum_J \hat{J}|B(J', J)|^2 = \frac{\hat{K}}{\hat{N}} \sum_J |M_c(b, a)|^2, \tag{50}$$

$$\sum_{F, K} |M(b_{\beta N}, a_\beta)|^2 = \hat{F}'\hat{N} \sum_J \hat{J}|B(J', J)|^2 = \frac{\hat{F}'}{\hat{J}'} \sum_J |M_c(b, a)|^2, \tag{51}$$

$$\sum_{F, F', K} |M(b_{\beta N}, a_\beta)|^2 = \hat{I}\hat{J}'\hat{N} \sum_J \hat{J}|B(J', J)|^2 = \hat{I} \sum_J |M_c(b, a)|^2. \tag{52}$$

V. $b \to b$ INTENSITY FACTORS

A. Classical $b \to b$ transition

Equations (11b) and (34) lead to

$$M_c(b, b) = (-1)^{S+J-\Lambda}[\hat{J}'\hat{J}\hat{N}'\hat{N}]^{1/2}C(J', J), \tag{53}$$

where

$$C(J', J) = \sum_{\Sigma,\Omega} \sum_{\Sigma',\Omega'} \sum_{s} (-1)^{S+\Sigma} \begin{pmatrix} S' & J' & N' \\ -\Sigma' & \Omega' & -\Lambda' \end{pmatrix} \times \begin{pmatrix} S & J & N \\ -\Sigma & \Omega & -\Lambda \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -\Omega' & s & \Omega \end{pmatrix} \times \langle (L')\Lambda' S' \Sigma' | \mu_s | (L)\Lambda S \Sigma \rangle \tag{54}$$

in the more-general case of spin-forbidden hypothesis. When the transition is spin allowed, Eq. (22) and Ed(6.2.8) lead to

$$C_{\mathrm{SA}}(J', J) = (-1)^{N-\Lambda}(-1)^{N'-\Lambda'} \begin{Bmatrix} N & 1 & N' \\ J' & S & J \end{Bmatrix} \times \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix} \langle (L')\Lambda' | \mu_s | (L)\Lambda \rangle, \tag{55}$$

assuming $s = \Lambda' - \Lambda$ and omitting $\delta_{S'S}$.

In the following, both cases will be studied, first, by considering the general spin forbidden case, and next, by restricting the formula to the spin allowed case using the subscript SA.

B. $b_{\beta J} \to b_{\beta J}$ transition

Equation (37) and (11a) lead to

$$M(b_{\beta J}, b_{\beta J}) = (-1)^{S-J+\Lambda}(-1)^{F+I-J'-1}[\hat{F}'\hat{F}\hat{J}'\hat{J}\hat{N}'\hat{N}]^{1/2} \begin{pmatrix} J & 1 & J' \\ F' & 1 & F \end{pmatrix} C(J', J), \tag{56a}$$

$$M_{\mathrm{SA}}(b_{\beta J}, b_{\beta J}) = (-1)^{S-J}(-1)^{F+I-J'-1}(-1)^{N-N'+\Lambda'} \times [\hat{F}'\hat{F}\hat{J}'\hat{J}\hat{N}'\hat{N}]^{1/2} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix} \begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix} \begin{Bmatrix} N & 1 & N' \\ J' & S & J \end{Bmatrix} \langle (L')\Lambda' | \mu_s | (L)\Lambda \rangle, \tag{56b}$$

$$\sum_{F'} |M(b_{\beta J}, b_{\beta J})|^2 = \hat{F}\hat{J}'\hat{N}'\hat{N} |C(J', J)|^2 = \frac{\hat{F}}{\hat{J}} |M_c(b, b)|^2, \tag{57}$$

$$\sum_{F, F'} |M(b_{\beta J}, b_{\beta J})|^2 = \hat{I}\hat{J}\hat{J}'\hat{N}'\hat{N} |C(J', J)|^2 = \hat{I} |M_c(b, b)|^2. \tag{58}$$

The SA formulas are easily derived using Eq. (55).

C. $b_{\beta S} \to b_{\beta J}$ transition

Equation (56) and (12) give

$$M(b_{\beta S}, b_{\beta J}) = (-1)^{N-1}(-1)^{2S'-\Lambda}[\hat{F}'\hat{F}\hat{J}'\hat{G}\hat{N}'\hat{N}]^{1/2} \sum_{J} (-1)^{J-J'}\hat{J} \begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix} \begin{Bmatrix} S & I & G \\ F & N & J \end{Bmatrix} C(J', J). \tag{59a}$$

In the case of SA transition, the use of Biedenharn and Elliott sum-rule relationship [Ed. (6.2.12)] yields the simplest expression

$$M_{\mathrm{SA}}(b_{\beta S}, b_{\beta J}) = (-1)^{N+\Lambda'}(-1)^{S+G+I}(-1)^{F+F}[\hat{F}'\hat{F}\hat{J}'\hat{G}\hat{N}'\hat{N}]^{1/2} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix} \begin{Bmatrix} N & 1 & N' \\ F' & G & F \end{Bmatrix} \begin{Bmatrix} F' & N' & G \\ S & I & J' \end{Bmatrix} \langle (L')\Lambda' | \mu_s | (L)\Lambda \rangle. \tag{59b}$$

In the general SF case, we obtain

$$\sum_{F'} |M(b_{\beta S}, b_{\beta J})|^2 = \hat{F}\hat{J}'\hat{G}\hat{N}'\hat{N} \sum_{J} \hat{J} \begin{Bmatrix} S & I & G \\ F & N & J \end{Bmatrix}^2 |C(J', J)|^2, \tag{60a}$$

$$\sum_{F} |M(b_{\beta S}, b_{\beta J})|^2 = \hat{F}'\hat{J}'\hat{G}\hat{N}'\hat{N} \sum_{J, J_1} (-1)^{J-J_1}\hat{J}_1\hat{J} \begin{bmatrix} I & I & J & J_1 \\ S & J' & S & J' \\ G & N & F' & 1 \end{bmatrix} C^*(J', J_1)C(J', J), \tag{61a}$$

$$\sum_{F,F'} |M(b_{\beta S}, b_{\beta J})|^2 = \frac{\hat{G}}{\hat{S}} \hat{J}'\hat{N}'\hat{N} \sum_J \hat{J}\,|C(J',J)|^2 = \frac{\hat{G}}{\hat{S}} \sum_J |M_c(b,b)|^2, \tag{62a}$$

and in the SA case, we have

$$\sum_{F'} |M_{SA}(b_{\beta S}, b_{\beta J})|^2 = \hat{F}\hat{J}'\hat{G}\hat{N}'\hat{N} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix}^2 \begin{bmatrix} G & G & N' & N' \\ N & S & N & S \\ F & 1 & I & J \end{bmatrix} |\langle (L')\Lambda' | \mu_s | (L)\Lambda\rangle|^2, \tag{60b}$$

$$\sum_{F} |M_{SA}(b_{\beta S}, b_{\beta J})|^2 = \hat{F}'\hat{J}'\hat{G}\hat{N} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix}^2 \begin{Bmatrix} F' & N' & G \\ S & I & J' \end{Bmatrix}^2 |\langle (L')\Lambda' | \mu_s | (L)\Lambda\rangle|^2, \tag{61b}$$

$$\sum_{F,F'} |M_{SA}(b_{\beta S}, b_{\beta J})|^2 = \frac{\hat{G}}{\hat{S}} \hat{J}'\hat{N} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix}^2 |\langle (L')\Lambda' | \mu_s | (L)\Lambda\rangle|^2 = \frac{\hat{G}}{\hat{S}} \sum_J |M_{c,SA}(b,b)|^2. \tag{62b}$$

When the "G components" are not observed, one can obtain some improvements of the formulas

$$\sum_{F,G} |M(b_{\beta S}, b_{\beta J})|^2 = \hat{F}'\hat{N}'\hat{N} \sum_J \hat{J}\,|C(J',J)|^2 = \frac{\hat{F}'}{\hat{J}'} \sum_J |M_c(b,b)|^2, \tag{63}$$

$$\sum_{F,F'G} |M(b_{\beta S}, b_{\beta J})|^2 = \hat{I}\hat{J}'\hat{N}'\hat{N} \sum_J \hat{J}\,|C(J',J)|^2 = \hat{I} \sum_J |M_c(b,b)|^2, \tag{64}$$

and analogous expressions for the SA case.

D. $b_{\beta N} \to b_{\beta J}$ transition

The calculations are similar to those of the preceding case:

$$M(b_{\beta N}, b_{\beta J}) = (-1)^{2S+\Lambda}(-1)^{2I}(-1)^{K+F-J'-1}[\hat{F}'\hat{F}\hat{J}'\hat{K}\hat{N}'\hat{N}]^{1/2} \sum_J \hat{J} \begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix} \begin{Bmatrix} I & F & J \\ S & N & K \end{Bmatrix} C(J',J), \tag{65a}$$

and, using Ed(6.4.3),

$$M_{SA}(b_{\beta N}, b_{\beta J}) = (-1)^{2I+\Lambda}(-1)^{K+F-J'-1}(-1)^{N-\Lambda}(-1)^{N'-\Lambda'}[\hat{F}'\hat{F}\hat{J}'\hat{K}\hat{N}'\hat{N}]^{1/2} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix} \begin{Bmatrix} J' & I & F' \\ S & K & F \\ N' & N & 1 \end{Bmatrix} \langle (L')\Lambda' | \mu_s | (L)\Lambda\rangle, \tag{65b}$$

$$\sum_{F'} |M(b_{\beta N}, b_{\beta J})|^2 = \hat{F}\hat{J}'\hat{K}\hat{N}'\hat{N} \sum_J \hat{J} \begin{Bmatrix} I & F & J \\ S & N & K \end{Bmatrix}^2 |C(J',J)|^2, \tag{66a}$$

$$\sum_{F} |M(b_{\beta N}, b_{\beta J})|^2 = \hat{F}'\hat{J}'\hat{K}\hat{N}'\hat{N} \sum_{J,J_1} \hat{J}_1\hat{J} \begin{bmatrix} S & 1 & K & F' \\ N & N & J' & J' \\ J & I & J_1 & I \end{bmatrix} C^*(J',J_1)C(J',J), \tag{67a}$$

$$\sum_{F'} |M_{SA}(b_{\beta N}, b_{\beta J})|^2 = \hat{F}\hat{J}'\hat{K}\hat{N}'\hat{N} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix}^2 \begin{bmatrix} K & N' & K & N' \\ I & F & 1 & J' \\ N & N & S & S \end{bmatrix} |\langle (L')\Lambda' | \mu_s | (L)\Lambda\rangle|^2, \tag{66b}$$

$$\sum_{F} |M_{SA}(b_{\beta N}, b_{\beta J})|^2 = \hat{F}'\hat{J}'\hat{K}\hat{N}'\hat{N} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix}^2 \begin{bmatrix} N & J' & N & J' \\ K & 1 & F' & S \\ I & I & N' & N' \end{bmatrix} |\langle (L')\Lambda' | \mu_s | (L)\Lambda\rangle|^2. \tag{67b}$$

In both SA and SF cases, we have

$$\sum_{F,K}|M(b_{\beta N}, b_{\beta J})|^2=\frac{\hat{F}'}{\hat{J}'}\sum_J|M_c(b,b)|^2, \tag{68}$$

$$\sum_{F',F}|M(b_{\beta N}, b_{\beta J})|^2=\frac{\hat{K}}{\hat{N}}\sum_J|M_c(b,b)|^2, \tag{69}$$

$$\sum_{F,F',K}|M(b_{\beta N}, b_{\beta J})|^2=\hat{I}\sum_J|M_c(b,b)|^2. \tag{70}$$

E. $b_{\beta S}\rightarrow b_{\beta S}$ transition

Equations (59a) and (12) yield

$$M(b_{\beta S}, b_{\beta S})=(-1)^{F'+I-S'}(-1)^{N'+N+\Lambda-1}[\hat{F}'\hat{F}\hat{N}'\hat{N}\hat{G}'\hat{G}]^{1/2} \times\sum_{J',J}(-1)^{J-J'}\hat{J}'\hat{J}\begin{Bmatrix}S' & I & G'\\ F' & N' & J'\end{Bmatrix}\begin{Bmatrix}S & I & G\\ F & N & J\end{Bmatrix}\begin{Bmatrix}J & 1 & J'\\ F' & I & F\end{Bmatrix}C(J',J), \tag{71a}$$

and in the case of SA transition, the use of Ed(6.2.12) and Ed(6.2.9) gives

$$M_{\mathrm{SA}}(b_{\beta S}, b_{\beta S})=\delta_{GG'}(-1)^{\Lambda'}(-1)^{F+G}(-1)^{N+N'}[\hat{F}'\hat{F}\hat{N}'\hat{N}]^{1/2}\begin{pmatrix}N & 1 & N'\\ \Lambda & s & -\Lambda'\end{pmatrix}\begin{Bmatrix}G & F & N\\ 1 & N' & F'\end{Bmatrix}\langle(L')\Lambda'|\mu_s|(L)\Lambda\rangle, \tag{71b}$$

leading to the selection rule $\Delta G=0$.

The summation over F' does not lead to great simplification of the formula in the case of SF transition. Using Y(A.6.12) or Y(A.6.47) we obtain

$$\sum_{F'}|M(b_{\beta S},b_{\beta S})|^2=\hat{F}\hat{N}'\hat{N}\hat{G}'\hat{G}\sum_{J,J'}\sum_{J_1,J_1'}(-1)^{J'-J_1}\hat{J}_1'\hat{J}_1\hat{J}'\hat{J}\begin{Bmatrix}S & I & G\\ F & N & J_1\end{Bmatrix}\begin{Bmatrix}S & I & G\\ F & N & J\end{Bmatrix}\begin{bmatrix}I & I & J' & J_1'\\ S' & J & S' & J_1\\ G' & N' & F & 1\end{bmatrix}C^*(J_1',J_1)C(J',J) \tag{72a}$$

or

$$\sum_{F'}|M(b_{\beta S},b_{\beta S})|^2=\hat{F}\hat{N}'\hat{N}\hat{G}'\hat{G}\sum_g\hat{g}\left|\sum_{J,J'}(-1)^{J'-J}\hat{J}'\hat{J}\begin{Bmatrix}S & I & G\\ F & N & J\end{Bmatrix}\begin{Bmatrix}1 & G' & g\\ J' & S' & N'\\ J & I & F\end{Bmatrix}C(J',J)\right|^2, \tag{73}$$

with the SA hypothesis, we get a more simple expression

$$\sum_{F'}|M_{\mathrm{SA}}(b_{\beta S}, b_{\beta S})|^2=\delta_{GG'}\hat{F}\hat{N}'\begin{pmatrix}N & 1 & N'\\ \Lambda & s & -\Lambda'\end{pmatrix}^2 \times|\langle(L')\Lambda'|\mu_s|(L)\Lambda\rangle|^2 =\delta_{GG'}\frac{\hat{F}}{\hat{J}}\sum_{J'}|M_{c,\mathrm{SA}}(b,b)|^2. \tag{72b}$$

The summation over F and F' leads to improvements of the formula only in the SA case

$$\sum_{F,F'}|M_{\mathrm{SA}}(b_{\beta S}, b_{\beta S})|^2=\delta_{GG'}\hat{G}\hat{N}'\hat{N}\begin{pmatrix}N & 1 & N'\\ \Lambda & s & -\Lambda'\end{pmatrix}^2 \times|\langle(L')\Lambda'|\mu_s|(L)\Lambda\rangle|^2, =\delta_{GG'}\frac{\hat{G}}{\hat{S}}\sum_{J,J'}|M_{c,\mathrm{SA}}(b,b)|^2. \tag{74}$$

When the "G components" are not observed in one of the states, the SF formula becomes

$$\sum_{F',G'}|M(b_{\beta S}, b_{\beta S})|^2 =\hat{F}\hat{N}'\hat{N}\hat{G}\sum_{J,J'}\hat{J}'\hat{J}\begin{Bmatrix}S & I & G\\ F & N & J\end{Bmatrix}^2|C(J',J)|^2. \tag{75}$$

The SA formula is easily derived from Eq. (72b). Finally, in both the SF and SA cases, we have

$$\sum_{F,F',G'}|M(b_{\beta S}, b_{\beta S})|^2=\frac{\hat{G}}{\hat{S}}\sum_{J,J'}|M_c(b,b)|^2, \tag{76}$$

$$\sum_{F,F',G,G'}|M(b_{\beta S}, b_{\beta S})|^2=\hat{I}\sum_{J,J'}|M_c(b,b)|^2. \tag{77}$$

F. $b_{\beta N} \to b_{\beta N}$ transition

Similarly, we obtain the following formulas:

$$M(b_{\beta N}, b_{\beta N}) = (-1)^{2S+\Lambda}(-1)^{K+K'}(-1)^{F+S'-I-1}[\hat{F}'\hat{F}\hat{K}'\hat{K}\hat{N}'\hat{N}]^{1/2} \sum_{J,J'} \hat{J}'\hat{J} \begin{Bmatrix} I & F' & J' \\ S' & N' & K' \end{Bmatrix} \begin{Bmatrix} I & F & J \\ S & N & K \end{Bmatrix} \begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix} C(J', J), \quad (78a)$$

$$M_{SA}(b_{\beta N}, b_{\beta N}) = (-1)^{N-N'+\Lambda'}(-1)^{K'-K}(-1)^{F+S-I-1}[\hat{F}'\hat{F}\hat{K}'\hat{K}\hat{N}'\hat{N}]^{1/2}$$

$$\times \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix} \begin{Bmatrix} 1 & F' & F \\ S & K & K' \end{Bmatrix} \begin{Bmatrix} N' & K' & I \\ K & N & 1 \end{Bmatrix} \langle (L')\Lambda' | \mu_s | (L)\Lambda \rangle . \quad (78b)$$

Formulas analogous to Eqs. (72)–(77) are available, but are not given here for brevity's sake, and because of the rare occurrence of $b_{\beta N}$ coupling case.

G. $b_{\beta S} \to b_{\beta N}$ transition

Here too, some difficulties arise in the reduction of the formulas. We give the most important relations with obvious notations and without comments:

$$M(b_{\beta S}, b_{\beta N}) = (-1)^{N+\Lambda-1}(-1)^{I+K'}[\hat{F}'\hat{F}\hat{K}'\hat{G}\hat{N}'\hat{N}]^{1/2}$$

$$\times \sum_{J'} \hat{J}' \begin{Bmatrix} I & F' & J' \\ S' & N' & K' \end{Bmatrix} \sum_{J} (-1)^{J-S'} \hat{J} \begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix} \begin{Bmatrix} S & I & G \\ F & N & J \end{Bmatrix} C(J', J), \quad (79a)$$

$$M_{SA}(b_{\beta S}, b_{\beta N}) = (-1)^{F'+F}(-1)^{N+\Lambda'}(-1)^{2S}(-1)^{2I}$$

$$\times [\hat{F}'\hat{F}\hat{K}'\hat{G}\hat{N}'\hat{N}]^{1/2} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix} \begin{Bmatrix} G & F & N \\ 1 & N' & F' \end{Bmatrix} \begin{Bmatrix} G & F' & N' \\ K' & I & S \end{Bmatrix} \langle (L')\Lambda' | \mu_s | (L)\Lambda \rangle . \quad (79b)$$

$$\sum_{F'} |M(b_{\beta S}, b_{\beta N})|^2 = \hat{F}\hat{K}'\hat{G}\hat{N}'\hat{N} \sum_{J_1', J_1} \sum_{J', J} (-1)^{J-J_1} \hat{J}_1'\hat{J}_1\hat{J}'\hat{J} C^*(J_1', J_1) C(J', J)$$

$$\times \begin{Bmatrix} S & I & G \\ F & N & J_1 \end{Bmatrix} \begin{Bmatrix} S & I & G \\ F & N & J \end{Bmatrix} \begin{bmatrix} S' & 1 & K' & F \\ N' & N' & J & J_1 \\ J' & I & J_1' & I \end{bmatrix}, \quad (80a)$$

$$\sum_{F'} |M_{SA}(b_{\beta S}, b_{\beta N})|^2 = \hat{F}\hat{K}'\hat{G}\hat{N}'\hat{N} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix}^2 \begin{bmatrix} F & S & 1 & K' \\ N & N & I & I \\ G & N' & G & N' \end{bmatrix} \times |\langle (L')\Lambda' | \mu_s | (L)\Lambda \rangle|^2 . \quad (80b)$$

$$\sum_{F} |M(b_{\beta S}, b_{\beta N})|^2 = \hat{F}'\hat{K}'\hat{G}\hat{N}'\hat{N} \sum_{J_1', J_1} \sum_{J', J} (-1)^{J'-J_1'}(-1)^{J-J_1} \hat{J}_1'\hat{J}_1\hat{J}'\hat{J}$$

$$\times C^*(J_1', J_1) C(J', J) \begin{Bmatrix} I & F' & J_1' \\ S' & N' & K' \end{Bmatrix} \begin{Bmatrix} I & F' & J' \\ S' & N' & K' \end{Bmatrix} \begin{bmatrix} I & I & J & J_1 \\ S & J' & S & J' \\ G & N & F' & 1 \end{bmatrix}, \quad (81a)$$

$$\sum_{F} |M_{SA}(b_{\beta S}, b_{\beta N})|^2 = \hat{F}'\hat{K}'\hat{G}\hat{N} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix}^2 \begin{Bmatrix} G & F' & N' \\ K' & I & S \end{Bmatrix}^2 |\langle (L')\Lambda' | \mu_s | (L)\Lambda \rangle|^2 . \quad (81b)$$

$$\sum_{F,F'} |M_{SA}(b_{\beta S}, b_{\beta N})|^2 = \frac{\hat{G}}{\hat{I}} \hat{K}'\hat{N} \begin{pmatrix} N & 1 & N' \\ \Lambda & s & -\Lambda' \end{pmatrix}^2 |\langle (L')\Lambda' | \mu_s | (L)\Lambda \rangle|^2 ,$$

$$= \frac{\hat{G}}{\hat{S}\hat{I}} \frac{\hat{K}'}{\hat{N}'} \sum_{J,J'} |M_{c,SA}(b,b)|^2 , \quad (82)$$

$$\sum_{F;F,K'} |M(b_{\beta S}, b_{\beta N})|^2 = \frac{\hat{G}}{\hat{S}} \sum_{J,J'} |M_c(b,b)|^2, \quad (83)$$

$$\sum_{F',F,G} |M(b_{\beta S}, b_{\beta N})|^2 = \frac{\hat{K}'}{\hat{N}'} \sum_{J,J'} |M_c(b,b)|^2, \quad (84)$$

$$\sum_{F',F,G,K'} |M(b_{\beta S}, b_{\beta N})|^2 = \hat{I} \sum_{J,J'} |M_c(b,b)|^2. \quad (85)$$

VI. CONCLUSION

With new experimental techniques, like saturated absorption, interference spectrometers, and spectroscopy by Fourier transform, a great deal of accurate data in intensity investigation will probably be available in the near future, and, as seen in the introduction, such results may provide valuable information on the quantum behavior of molecules.

Intensity investigation is a very powerful tool for interpreting molecular structure. The formulas presented in this paper, combined with the data obtained from the usual line-position analysis, should provide a way to use this powerful tool to the utmost.

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[12]Except when specified, in our notation the quantum numbers Λ and Ω have *positive* values.

[13]We do not specify if M_R is a cartesian or a spherical component. In the following, we shall use spherical components.

[14]A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U.P., Princeton, N. J., 1960).

[15]One exception is, e.g., a spin-forbidden transition with $\Lambda \neq 0$ and $\Omega = 0$.

[16]This gives rise, e.g., to a factor $\sqrt{2}$ in the symmetrized expression of the Π(case a) $\rightarrow \Sigma$(case b) matrix element of M_R.

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