

Polarization properties of resonance scattering in molecular bands

The intermediate (a-b) coupling regime^{*}

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ABSTRACT

The polarimetric properties of the phenomenon of resonance scattering in molecular bands are analyzed in detail for the general case where both the lower and upper electronic states of the molecule are described in the coupling scheme intermediate between Hund’s cases (a) and (b). A semi-analytical expression is derived for the line polarizability factor in the special case where atomic polarization is neglected in the lower electronic state, and particular attention is devoted to clarifying the role played by the phenomenon of Λ -doubling, which turns out to be particularly relevant in the case of $\Pi - \Sigma$ transitions. The expression for the line polarizability factor is derived for both cases where the energy eigenvectors are expressed as a linear combination of the eigenvectors relative to Hund’s case (a) and of those relative to Hund’s case (b). Such expressions are then combined with the corresponding expressions of the Einstein coefficient and of the Landé factors to obtain an estimate of the linear polarization signals to be expected in molecular bands observed at the solar limb either in the quiet atmosphere or in magnetic regions. Illustrative results are shown for the bands of MgH and of C₂ around 5100 Å.

Key words. molecular processes – scattering – polarization

1. Introduction

Systematic measurements of linear polarization in the solar spectrum, observed over the disk at close distances from the limb, have revealed the unexpected existence of strong polarization signals in molecular bands (Stenflo & Keller 1996; Gandorfer 2000, 2002). This phenomenon, an obvious manifestation of resonance scattering in an astrophysical context, has motivated a revival of interest in the theoretical study and modeling of resonance polarization in molecular lines (see, e.g., the proceedings of the workshop “Solar Polarization 3” edited by Trujillo Bueno & Sánchez Almeida 2003). This research field has received little attention in the literature since some pioneering work dating back to the end of the 1930s (see the section on polarization of resonance fluorescence in Herzberg 1950). However, a collection of results on the same topics, based on the use of Wigner symbols, is found in Zare (1988).

The concept of a polarizability factor was introduced in the literature to characterize the polarization properties of the continuous radiation scattered by anisotropic classical particles (Chandrasekhar 1950) and of the resonance line radiation scattered by atoms (Hamilton 1947). In a more modern perspective, we now know that atomic resonance lines can be characterized, from the point of view of their polarimetric properties, by two coefficients, W_1 and W_2 , that can be called “line polarizability factors” and that are given by the expression (Landi Degl’Innocenti 1984; Landi Degl’Innocenti & Landolfi 2004)

$$W_K = 3(2J_u + 1) \left\{ \begin{matrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{matrix} \right\}^2 = \frac{\left\{ \begin{matrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{matrix} \right\}^2}{\left\{ \begin{matrix} 1 & 1 & 0 \\ J_u & J_u & J_\ell \end{matrix} \right\}^2}, \quad (1)$$

where J_ℓ and J_u are the angular momentum quantum numbers of the lower and upper level of the transition, respectively.

The polarizability factors are well suited for expressing complicated results arising in resonance scattering problems in compact form. For instance, the quantum-mechanical scattering phase matrix for a two-level atom with unpolarized lower level, relating the i th Stokes parameter of the radiation scattered into the direction $\mathbf{\Omega}$ to the j th Stokes parameter of the radiation incident along the direction $\mathbf{\Omega}'$, can be expressed through the compact equation (Landi Degl’Innocenti 1984)

$$P_{ij}(\mathbf{\Omega}, \mathbf{\Omega}') = \sum_{KQ} W_K (-1)^Q \mathcal{T}_Q^K(i, \mathbf{\Omega}) \mathcal{T}_{-Q}^K(j, \mathbf{\Omega}'), \quad (2)$$

^{*} Appendices are only available in electronic form at <http://www.aanda.org>

where \mathcal{T}_Q^K is the irreducible tensor of the polarization unit vectors introduced in the same paper. Similarly, the effect of a magnetic field (Hanle effect) on the scattered polarization in resonance lines can be easily accounted for by a simple modification of the same equation, namely (Landi Degl'Innocenti 1985)

$$P_{ij}(\mathbf{\Omega}, \mathbf{\Omega}'; \mathbf{B}) = \sum_{KQ} W_K(J_\ell, J_u) (-1)^Q \frac{1}{1 + iHQ} \mathcal{T}_Q^K(i, \mathbf{\Omega}) \mathcal{T}_{-Q}^K(j, \mathbf{\Omega}'), \quad (3)$$

where $H = 2\pi\nu_L g_u \tau_u$ is a quantity proportional to the magnetic field intensity (ν_L is the Larmor frequency) and to the Landé factor, g_u , and lifetime, τ_u , of the upper level.

The former equations, as well as similar equations typically encountered in resonance scattering problems, also hold for molecular lines, provided the line polarizability factors, W_1 and W_2 , are substituted by suitable quantities, \mathcal{W}_1 and \mathcal{W}_2 , that can be referred to as *generalized polarizability factors*. Such quantities can be introduced under a series of restrictive hypotheses that are however well satisfied for weak molecular bands in stellar atmospheres (Landi Degl'Innocenti et al. 1997; Landi Degl'Innocenti 2003).

Consider a particular molecular line corresponding to the transition between the upper level a and the lower level b . In a typical resonance scattering process taking place in a stellar atmosphere, level a is pumped by the radiative transitions ending into level a and originating from a set of several lower levels, $\{c\}$, the set obviously including level b itself. Supposing: i) that the radiation field is the same¹ for all the transitions $c \rightarrow a$ that contribute to pump the upper level, ii) that all the levels c are unpolarized, iii) that the same levels are populated according to their statistical weight, and iv) that stimulated emission can be neglected, the effective polarizability factor of the line, $\mathcal{W}_K(b, a)$, is given by²

$$\mathcal{W}_K(b, a) = \frac{\sum_c A(a \rightarrow c) w_{J_a J_c}^{(K)}}{\sum_c A(a \rightarrow c)} w_{J_a J_b}^{(K)}, \quad (4)$$

where $A(a \rightarrow c)$ is the Einstein coefficient for spontaneous emission from level a to level c ; J_a , J_b , and J_c are, respectively, the angular momenta of levels a , b , and c ; and $w_{JJ'}^{(K)}$ is the symbol introduced in Landi Degl'Innocenti (1984), defined by

$$w_{JJ'}^{(K)} = (-1)^{1+J+J'} \sqrt{3(2J+1)} \begin{Bmatrix} 1 & 1 & K \\ J & J & J' \end{Bmatrix} = \begin{Bmatrix} 1 & 1 & K \\ J & J & J' \end{Bmatrix}. \quad (5)$$

Generalized polarizability factors have already been derived in previous papers for the spinless molecule (Landi Degl'Innocenti et al. 1997) and for the molecule with spin in the pure coupling regime Hund's (b) (Landi Degl'Innocenti 2003). In the present paper their expression will be derived in the intermediate regime between Hund's cases (a) and (b).

The concept of polarizability factor is also very useful for the interpretation of the second solar spectrum. For a weak molecular line characterized by the generalized polarizability factor \mathcal{W}_2 , it can indeed be shown that the ratio Q/I , for an observation at the extreme limb, is approximately given by the expression (Landi Degl'Innocenti & Landolfi 2004)

$$\left[\frac{Q}{I} \right]_{\text{line}} = \frac{3}{4} \frac{k_L^A}{k_\nu^{(c)}} \mathcal{W}_2 w \frac{S_L}{B_P} \phi(\nu_0 - \nu), \quad (6)$$

where k_L^A is the frequency integrated absorption coefficient of the line, $k_\nu^{(c)}$ is the continuous absorption coefficient at line frequency, w is the corresponding anisotropy factor of the continuous radiation at the top layers of the solar atmosphere, S_L is the line source function, B_P is the source function in the continuum (supposed in LTE), and finally $\phi(\nu_0 - \nu)$ is a profile (normalized to unity in frequency) centered at the frequency ν_0 of the line. The various quantities $k_\nu^{(c)}$, w , S_L , and B_P , and the shape of the profile ϕ can be considered constant for all the lines of the band. On the other hand, the frequency integrated line absorption coefficient relative to a single line can be related to the Einstein coefficient of the corresponding transition through the standard equation (the indices u and ℓ denote, respectively, the upper and lower level of the transition)

$$k_L^A = \frac{c^2}{8\pi\nu_0^2} \mathcal{N}_{\text{mol}} \frac{\exp\left(-\frac{E_\ell}{k_B T_{\text{exc}}}\right)}{Z(T_{\text{exc}})} (2J_u + 1) A(u \rightarrow \ell), \quad (7)$$

where \mathcal{N}_{mol} is the overall number density of molecules in the lower electronic state, T_{exc} is the excitation temperature that controls the distribution of molecules among the various rotational levels, and $Z(T_{\text{exc}})$ is the corresponding partition function given by

$$Z(T_{\text{exc}}) = \sum_\ell (2J_\ell + 1) \exp\left(-\frac{E_\ell}{k_B T_{\text{exc}}}\right). \quad (8)$$

¹ Formally, this implies that the radiation field for all the transitions is characterized by the same radiation field tensor J_Q^K ; see Landi Degl'Innocenti & Landolfi (2004) for the definition of this tensor.

² The formal proof of this equation can be easily obtained from the general theory of optical pumping presented in Landi Degl'Innocenti & Landolfi (2004).

Also, it has to be remarked that the effect of a turbulent, unimodal magnetic field on the same quantity, $[Q/I]_{\text{line}}$, can be obtained (neglecting collisional depolarization in the upper level) by performing a formal substitution in Eq. (6):

$$\mathcal{W}_2 \rightarrow \mathcal{W}_2 \frac{1}{5} \left(1 + \frac{2}{1+H^2} + \frac{2}{1+4H^2} \right), \quad (9)$$

where H is defined previously (see first line after Eq. (3)).

As shown by the different equations that we have just mentioned, a complete analysis of the polarimetric properties of molecular bands, including the effect of a magnetic field, requires the knowledge, for each line pertaining to the branch, of the polarizability factor, of the Einstein coefficient, and of the Landé factor of the upper level. In the present paper we will go through the derivation of all these quantities for a molecular band whose upper and lower electronic states are described in the intermediate coupling scheme between Hund's cases (a) and (b). This will imply some heavy repetition with respect to standard material that is already published in the scientific literature, since various papers and text-books have been devoted in the past to the problem of the diagonalization of the molecular Hamiltonian and to the derivation of the Einstein coefficients and of the Landé factors for molecular bands in the intermediate regime. However, since the notations employed differ from author to author, and since the applications of molecular spectroscopy to polarimetry appear to be particularly delicate in as far as sign conventions are concerned, we feel it necessary to reconsider the full theoretical scheme, starting from the diagonalization of the atomic Hamiltonian, to avoid any possibility of confusion or misinterpretation of the symbols employed and to furnish the reader with a self-contained formalism that can be directly used for further applications. We also have to stress that, when dealing with the intermediate regime, one can choose to work either with the basis eigenfunctions of Hund's case (a) or with the basis eigenfunctions of Hund's case (b). Here, we prefer to develop our calculations for both bases with the aim of providing the unique possibility of directly checking the numerical results obtained (which obviously have to be independent of the chosen basis). To improve the readability of the paper, the revision of the older results for the diagonalization of the molecular Hamiltonian, for the Einstein coefficients, and for the Landé factors is collected in the Appendix. The main body of the paper contains only the original part of the investigation on polarizability factors.

2. Generalized polarizability factors

To find the polarizability factors in the intermediate regime, we rely on the results contained in Appendix B and apply Eq. (4) with the expression of the Einstein coefficients given by Eq. (B.14) or, alternatively, by Eq. (B.23). In both cases, the sum of the Einstein coefficients appearing in the denominator of Eq. (4) simply gives A_{band} (see Eqs. (B.17) and (B.24)), while the sums appearing in the numerator can be performed by means of Racah algebra. When using the eigenfunctions of Hund's case (a) we have, in shortened notations³,

$$\mathcal{W}_K(\omega_\ell J_\ell, \omega_u J_u) = \mathcal{S} w_{J_u J_\ell}^{(K)}, \quad (10)$$

where

$$\begin{aligned} \mathcal{S} = & \sum_{\omega_\ell J_\ell} \sum_{\Omega_u \Omega'_u \Omega_\ell \Omega'_\ell} C_{\Omega_u}^{\omega_u} C_{\Omega_\ell}^{\omega_\ell} C_{\Omega'_u}^{\omega_u} C_{\Omega'_\ell}^{\omega_\ell} (2J_\ell + 1) (-1)^{\Omega'_u - \Omega_u} \begin{pmatrix} J_u & J_\ell & 1 \\ \Omega_u & -\Omega_\ell & \Delta\Lambda \end{pmatrix} \begin{pmatrix} J_u & J_\ell & 1 \\ \Omega'_u & -\Omega'_\ell & \Delta\Lambda \end{pmatrix} \\ & \times (-1)^{1+J_\ell+J_u} \sqrt{3(2J_u+1)} \begin{Bmatrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{Bmatrix}. \end{aligned} \quad (11)$$

To perform this sum, one starts by summing over ω_ℓ . Due to the orthonormality properties of the coefficients $C_{\Omega_\ell}^{\omega_\ell}$, this brings a Kronecker-delta of the form $\delta_{\Omega_\ell \Omega'_\ell}$, implying $\delta_{\Omega_u \Omega'_u}$. One then has

$$\mathcal{S} = \sum_{J_\ell \Omega_u \Omega_\ell} \left[C_{\Omega_u}^{\omega_u} \right]^2 (2J_\ell + 1) \sqrt{3(2J_u+1)} (-1)^{1+J_\ell+J_u} \begin{pmatrix} J_u & J_\ell & 1 \\ \Omega_u & -\Omega_\ell & \Delta\Lambda \end{pmatrix}^2 \begin{Bmatrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{Bmatrix}. \quad (12)$$

Performing next the sum over J_ℓ thanks to the Racah algebra equation

$$\sum_f (-1)^{f+\phi} (2f+1) \begin{pmatrix} d & b & f \\ -\delta & \beta & \phi \end{pmatrix} \begin{pmatrix} a & e & f \\ \alpha & -\epsilon & -\phi \end{pmatrix} \begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix} = (-1)^{d+e+\delta-\epsilon} \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix} \begin{pmatrix} d & e & c \\ \delta & \epsilon & \gamma \end{pmatrix}, \quad (13)$$

one finally gets

$$\mathcal{W}_K(\omega_\ell J_\ell, \omega_u J_u) = 3(2J_u+1) \begin{pmatrix} 1 & 1 & K \\ \Delta\Lambda & -\Delta\Lambda & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{Bmatrix} \left[\sum_{\Omega_u} (-1)^{\Omega_u+J_\ell+\Delta\Lambda} \left[C_{\Omega_u}^{\omega_u} \right]^2 \begin{pmatrix} J_u & J_u & K \\ \Omega_u & -\Omega_u & 0 \end{pmatrix} \right]. \quad (14)$$

This equation shows that the polarizability factor does not depend on the coupling scheme that describes the lower electronic state (Hund's case (a), (b), or intermediate), and that, moreover, it does not depend on the quantum number ω_ℓ . This property is strictly

³ As indices for the lower level we use only ω_ℓ and J_ℓ instead of the full set of quantum numbers $(\gamma_\ell, \Lambda_\ell, \nu_\ell, \omega_\ell, S, J_\ell)$, and use similar terms for the upper level.

connected with assumptions i), ii), and iii) itemized in Sect. 1. The same equation, particularized to the case where the upper electronic state is in pure Hund's case (a), gives

$$\mathcal{W}_K(\omega_\ell J_\ell, \Omega_u J_u) = 3(2J_u + 1)(-1)^{\Omega_u + J_\ell + \Delta\Lambda} \begin{pmatrix} 1 & 1 & K \\ \Delta\Lambda & -\Delta\Lambda & 0 \end{pmatrix} \begin{pmatrix} J_u & J_u & K \\ \Omega_u & -\Omega_u & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{Bmatrix}, \quad (15)$$

and, for a spinless molecule ($\omega_\ell = \Lambda_\ell$, $\Omega_u = \Lambda_u$), we recover the result of Landi Degl'Innocenti et al. (1997)

$$\mathcal{W}_K(\Lambda_\ell J_\ell, \Lambda_u J_u) = 3(2J_u + 1)(-1)^{J_\ell + \Lambda_\ell} \begin{pmatrix} 1 & 1 & K \\ \Delta\Lambda & -\Delta\Lambda & 0 \end{pmatrix} \begin{pmatrix} J_u & J_u & K \\ \Lambda_u & -\Lambda_u & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{Bmatrix}. \quad (16)$$

On the other hand, the polarizability factor can also be obtained by using the eigenfunctions of Hund's case (b). One gets, in shortened notations

$$\mathcal{W}_K(n_\ell J_\ell, n_u J_u) = \mathcal{S}' w_{J_u J_\ell}^{(K)}, \quad (17)$$

where

$$\begin{aligned} \mathcal{S}' = & \sum_{n_\ell J_\ell} \sum_{N_u N_\ell N'_u N'_\ell} C_{N_u}^{n_u} C_{N_\ell}^{n_\ell} C_{N'_u}^{n_u} C_{N'_\ell}^{n_\ell} (2J_\ell + 1) \sqrt{(2N_u + 1)(2N_\ell + 1)(2N'_u + 1)(2N'_\ell + 1)} \\ & \times \begin{pmatrix} N_u & N_\ell & 1 \\ \Lambda_u & -\Lambda_\ell & \Delta\Lambda \end{pmatrix} \begin{pmatrix} N'_u & N'_\ell & 1 \\ \Lambda_u & -\Lambda_\ell & \Delta\Lambda \end{pmatrix} \begin{Bmatrix} J_\ell & J_u & 1 \\ N_u & N_\ell & S \end{Bmatrix} \begin{Bmatrix} J_\ell & J_u & 1 \\ N'_u & N'_\ell & S \end{Bmatrix} (-1)^{1+J_\ell+J_u} \sqrt{3(2J_u + 1)} \begin{Bmatrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{Bmatrix}. \end{aligned} \quad (18)$$

This sum can be reduced by first summing over n_ℓ , then over J_ℓ by means of the Racah-algebra formula

$$\sum_j (-1)^{-j-a-b+e-f-i} (2j+1) \begin{Bmatrix} j & g & c \\ a & f & i \end{Bmatrix} \begin{Bmatrix} j & g & c \\ e & d & h \end{Bmatrix} \begin{Bmatrix} j & d & h \\ b & i & f \end{Bmatrix} = (-1)^{c+d-g-h} \begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} \begin{Bmatrix} a & b & e \\ h & g & i \end{Bmatrix}, \quad (19)$$

and finally over N_ℓ by means of Eq. (13). One finally finds the expression

$$\begin{aligned} \mathcal{W}_K(n_\ell J_\ell, n_u J_u) = & (-1)^{S-J_\ell-\Lambda_\ell+K} 3(2J_u + 1) \begin{pmatrix} 1 & 1 & K \\ \Delta\Lambda & -\Delta\Lambda & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{Bmatrix} \\ & \times \left[\sum_{N_u N'_u} C_{N_u}^{n_u} C_{N'_u}^{n_u} \sqrt{(2N_u + 1)(2N'_u + 1)} \begin{pmatrix} N_u & N'_u & K \\ \Lambda_u & -\Lambda_u & 0 \end{pmatrix} \begin{Bmatrix} N_u & N'_u & K \\ J_u & J_u & S \end{Bmatrix} \right]. \end{aligned} \quad (20)$$

This equation, particularized to the case where the upper electronic state is in pure Hund's case (b), gives (Landi Degl'Innocenti 2003)

$$\mathcal{W}_K(n_\ell J_\ell, N_u J_u) = (-1)^{S-J_\ell-\Lambda_\ell+K} 3(2J_u + 1)(2N_u + 1) \begin{pmatrix} 1 & 1 & K \\ \Delta\Lambda & -\Delta\Lambda & 0 \end{pmatrix} \begin{pmatrix} N_u & N_u & K \\ \Lambda_u & -\Lambda_u & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{Bmatrix} \begin{Bmatrix} N_u & N_u & K \\ J_u & J_u & S \end{Bmatrix}, \quad (21)$$

which brings one again to Eq. (16) in the case of the spinless molecule ($S = 0$, $N_u = J_u$).

3. Complications introduced by Λ -doubling

It is well known that electronic states having $\Lambda \neq 0$ present the phenomenon of quasi-degeneracy known as Λ -doubling⁴. This typical phenomenon of molecular spectroscopy is described in detail in several monographs (Herzberg 1950; Landau & Lifchitz 1967; Kovács 1969; Brown & Carrington 2003, and references therein), as well as in individual papers where the relevance of Λ -doubling on Einstein coefficients is pointed out (see, e.g., Whiting & Nicholls 1974; Whiting et al. 1980). Given the important role that Λ -doubling plays in resonance polarization, we feel that it is necessary to review the main physical facts so as to make the definitions concerning the different symmetry operators that are met in the physics of diatomic molecules clear.

Besides the quantum numbers introduced in Appendix A, the energy eigenstates of a diatomic molecule are characterized by a further quantum number, namely the eigenvalue of the parity operator, P , which transforms all the coordinates of the electrons, \mathbf{r}_i , into $-\mathbf{r}_i$, and which acts in the same way on the coordinates of the two nuclei ($\mathbf{R}_1 \rightarrow -\mathbf{R}_1$, $\mathbf{R}_2 \rightarrow -\mathbf{R}_2$). Since this operator obviously commutes with the Hamiltonian, and since its square is the identity operator, its eigenvalues are ± 1 , and the states can be divided into two categories, "positive" or "negative", according to whether the eigenvalue of P is $+1$ or -1 , respectively. To denote the parity of a state we can introduce the supplementary quantum number π (with possible values 0 and 1) so that the parity is, by definition, $(-1)^\pi$. Positive states are those with $\pi = 0$ and negative states are those with $\pi = 1$. Looking for the common eigenvectors of the Hamiltonian and of the operator P , we have, however, to distinguish between states having $\Lambda = 0$ (Σ states) and states having $\Lambda \neq 0$. Σ states are already eigenvectors of the operator P . This means that an eigenfunction such as those defined in Eqs. (A.14) or (A.25) already has, for $\Lambda = 0$, a well defined parity. Indeed, particularizing Eq. (A.25) to Σ states, one has

$$|\gamma\Sigma; \mathbf{v}; nSJM\rangle = \delta_{nN} |\gamma\Sigma; \mathbf{v}; NSJM\rangle, \quad (22)$$

and it turns out that

$$P |\gamma\Sigma; \mathbf{v}; NSJM\rangle = (-1)^{N+p} |\gamma\Sigma; \mathbf{v}; NSJM\rangle, \quad (23)$$

⁴ This statement is indeed contradicted in the case of homonuclear molecules, see Sect. 3.1.

where $p = 0$ for Σ^+ states and $p = 1$ for Σ^- states. It then results that, for Σ states⁵,

$$\pi = N + p. \quad (24)$$

On the other hand, for states having $\Lambda \neq 0$, one can directly construct eigenfunctions of a given parity by considering linear combinations of the form

$$|a, \pi\rangle = \frac{1}{\sqrt{2}} [|a\rangle + (-1)^\pi P|a\rangle], \quad (25)$$

where $|a\rangle$ is a vector such as those defined either in Eq. (A.14) or in Eq. (A.25), with $\Lambda \neq 0$. Indeed, by applying the operator P to both sides of Eq. (25), one gets⁶

$$P|a, \pi\rangle = (-1)^\pi |a, \pi\rangle, \quad (26)$$

which shows that the eigenvector with $\pi = 0$ is positive, whereas the eigenvector with $\pi = 1$ is negative. Note also that the states $|a\rangle$ and $P|a\rangle$ are orthogonal, so that the states $|a, \pi\rangle$ are indeed normalized. So, either for Σ states, or for states having Λ different from zero, we can always identify a state with the symbol $|a, \pi\rangle$, where $|a\rangle$ is a state such as those defined either in Eq. (A.14) or in Eq. (A.25). For Σ states, there is only a formal addition of the parity quantum number to the eigenvector. On the contrary, for all other states Π , Δ , Φ , etc., the vector $|a, \pi\rangle$ is obtained by means of Eq. (25).

Let us now analyze the consequences of Λ -doubling on the results that we have obtained in Appendix B and in Sect. 2. First of all, we consider a matrix element of the dipole operator, d_q , between any two states having defined parity. Taking into account that $Pd_q = -d_qP$, one gets the following series of equalities

$$\langle a, \pi_a | d_q | b, \pi_b \rangle = \langle a, \pi_a | P^2 d_q | b, \pi_b \rangle = -\langle a, \pi_a | Pd_qP | b, \pi_b \rangle = (-1)^{\pi_a + \pi_b + 1} \langle a, \pi_a | d_q | b, \pi_b \rangle. \quad (27)$$

This equation shows that the matrix element of the dipole operator is zero unless the two states have different parity, a statement summarized in the general selection rule valid for electric dipole transitions

$$\text{positive} \rightarrow \text{negative}, \quad \text{negative} \rightarrow \text{positive}. \quad (28)$$

It is now possible to express the Einstein coefficient for spontaneous de-excitation between states of definite parity in terms of the Einstein coefficients derived in Appendix B, where parity considerations have been overlooked a priori. With the help of some algebra, it is possible to show that the Einstein coefficient for spontaneous de-excitation is given by the equation

$$A(a, \pi_a \rightarrow b, \pi_b) = \frac{1}{2} [1 + (-1)^{\pi_a + \pi_b + 1}] A(a \rightarrow b), \quad (29)$$

which, besides reaffirming the selection rule on the parity quantum number expressed by Eq. (28), allows us to directly use the results obtained in Appendix B. The formal proof of this equation is rather tedious since it implies the necessity of distinguishing between $\Sigma - \Sigma$ transitions, $\Sigma - \Pi$ (or $\Pi - \Sigma$) transitions and all other transitions⁷. Here we just prove Eq. (29) for these last ones. Evaluating the dipole matrix element between the two states $|a, \pi_a\rangle$ and $|b, \pi_b\rangle$ one gets

$$\langle a, \pi_a | d_q | b, \pi_b \rangle = \frac{1}{2} \left\{ \langle a | d_q | b \rangle + (-1)^{\pi_a} \langle a | Pd_q | b \rangle + (-1)^{\pi_b} \langle a | d_q P | b \rangle + (-1)^{\pi_a + \pi_b} \langle a | Pd_q P | b \rangle \right\}. \quad (30)$$

With easy transformation this equation can be cast in the form

$$\langle a, \pi_a | d_q | b, \pi_b \rangle = \frac{1}{2} [1 + (-1)^{\pi_a + \pi_b + 1}] \left\{ \langle a | d_q | b \rangle + (-1)^{\pi_a} \langle a | Pd_q | b \rangle \right\}. \quad (31)$$

It can be easily shown that the matrix element $\langle a | Pd_q | b \rangle$ is zero. This is due to the fact that the ‘‘internal’’ electronic matrix element $\langle \gamma_\ell - \Lambda_\ell | d_q | \gamma_u \Lambda_u \rangle$ is zero, since d_q is the spherical component of a tensor of rank 1, whereas $-\Lambda_\ell$ differs from Λ_u by at least 2 (recall that Λ_ℓ and Λ_u are both positive integers different from zero). In conclusion, one has

$$\langle a, \pi_a | d_q | b, \pi_b \rangle = \frac{1}{2} [1 + (-1)^{\pi_a + \pi_b + 1}] \langle a | d_q | b \rangle, \quad (32)$$

from which Eq. (29) easily follows.

Turning to the problem of finding the polarizability factors, we have to formally generalize Eq. (4) by writing, with self-evident notations,

$$\mathcal{W}_K(b\pi_b, a\pi_a) = \frac{\sum_{c\pi_c} A(a, \pi_a \rightarrow c, \pi_c) w_{J_a J_c}^{(K)}}{\sum_{c\pi_c} A(a, \pi_a \rightarrow c, \pi_c)} w_{J_a J_b}^{(K)}. \quad (33)$$

⁵ This equation obviously holds also for the eigenfunctions of Eq. (A.14), since they describe the same physical states as the eigenfunctions of Eq. (A.25). In this case, however, the parity quantum number should preferably be written in the form $\pi = \omega + p$, by formally identifying the quantum number ω with N .

⁶ Here we adopt the convention according to which the vector $|a\rangle$ corresponds to $\Lambda > 0$ and $P|a\rangle$ to $\Lambda < 0$.

⁷ Here we adopt the usual molecular spectroscopy convention of denoting transitions by writing the upper state first and the lower state second.

Considering first the transitions that do not involve Σ states in the lower level, namely the transitions of the form $\Sigma - \Pi$, $\Pi - \Pi$, $\Pi - \Delta$, $\Delta - \Pi$, $\Delta - \Delta$, $\Delta - \Phi$, etc., it is easily seen that the extrasum over π_c appearing in Eq. (33) does not alter the general results that we have obtained in Sect. 2. This is because once the parity of level a , π_a , has been specified, for any c level there is always one and only one parity value π_c , namely the one satisfying the equation

$$\text{mod}(1 + \pi_a + \pi_c, 2) = 0, \quad (34)$$

which contributes to the sums appearing in the numerator and in the denominator with the usual Einstein coefficient $A(a \rightarrow c)$. This implies that, for these transitions, Eqs. (14) and (20) are valid irrespective of the presence of the phenomenon of Λ -doubling. In other words, there is no complication introduced by Λ -doubling for these transitions.

The same result also holds for $\Sigma - \Sigma$ transitions. Indeed, in this case, the sums over π_c do not need to be explicitly performed because each level c has an assigned parity value, and one has, recalling Eqs. (29), (24), and (B.26),

$$A(a, \pi_a \rightarrow c, \pi_c) = \frac{1}{2} \left[1 + (-1)^{1+N_a+p_a+N_c+p_c} \right] A_{\text{band}} (2J_c + 1)(2N_a + 1)(2N_c + 1) \begin{pmatrix} N_a & N_c & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \left\{ \begin{matrix} J_c & J_a & 1 \\ N_a & N_c & S \end{matrix} \right\}^2. \quad (35)$$

The presence of the first 3-j symbol, whose lower row is composed of null elements, implies that the sum $(N_a + N_c + 1)$ has to be an even number, which in turn implies that the sum $(p_a + p_c)$ also has to be an even number, to have an allowed transition. This is satisfied only for $\Sigma^+ \rightarrow \Sigma^+$ and $\Sigma^- \rightarrow \Sigma^-$ transitions, for which we simply have

$$A(a, \pi_a \rightarrow c, \pi_c) = A(a \rightarrow c). \quad (36)$$

This proves the statement that has been anticipated. The only novelty found by introducing our considerations on the parity operator is the appearance of a new selection rule on the parity of the Σ states.

The case of a $\Pi - \Sigma$ transition, that is the most complicated and the only one where Λ -doubling is indeed important for determining the polarizability factor, remains to be analyzed. To treat this case, we recall Eq. (B.23) and particularize it for the case of the transition $\Pi - \Sigma$

$$A(\gamma_u \Pi; \mathbf{v}_u; n_u S J_u \rightarrow \gamma_\ell \Sigma; \mathbf{v}_\ell; N_\ell S J_\ell) = A_{\text{band}} \sum_{N_u N'_u} C_{N_u}^{n_u} C_{N'_u}^{n_u} (2J_\ell + 1) (2N_\ell + 1) \sqrt{(2N_u + 1)(2N'_u + 1)} \\ \times \begin{pmatrix} N_u & N_\ell & 1 \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} N'_u & N_\ell & 1 \\ 1 & 0 & -1 \end{pmatrix} \left\{ \begin{matrix} J_\ell & J_u & 1 \\ N_u & N_\ell & S \end{matrix} \right\} \left\{ \begin{matrix} J_\ell & J_u & 1 \\ N'_u & N_\ell & S \end{matrix} \right\}. \quad (37)$$

Introducing the parity quantum numbers, we then have, recalling Eqs. (29) and (24),

$$A(\gamma_u \Pi; \mathbf{v}_u; n_u S J_u; \pi_u \rightarrow \gamma_\ell \Sigma; \mathbf{v}_\ell; N_\ell S J_\ell; \pi_\ell) = \frac{1}{2} \left[1 + (-1)^{1+\pi_u+N_\ell+p_\ell} \right] A_{\text{band}} \sum_{N_u N'_u} C_{N_u}^{n_u} C_{N'_u}^{n_u} (2J_\ell + 1) (2N_\ell + 1) \\ \times \sqrt{(2N_u + 1)(2N'_u + 1)} \begin{pmatrix} N_u & N_\ell & 1 \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} N'_u & N_\ell & 1 \\ 1 & 0 & -1 \end{pmatrix} \left\{ \begin{matrix} J_\ell & J_u & 1 \\ N_u & N_\ell & S \end{matrix} \right\} \left\{ \begin{matrix} J_\ell & J_u & 1 \\ N'_u & N_\ell & S \end{matrix} \right\}. \quad (38)$$

The factor in square brackets shows that, once the parity of the upper level, π_u , is fixed, some of the transitions to the possible lower levels are forbidden. In other words, the upper level is pumped only by certain transitions, not by all the possible ones. This is the novel physical fact introduced by Λ -doubling in the $\Pi - \Sigma$ transition. We now pass to the determination of the polarizability factor by performing, as indicated in Eq. (33), the following sums

$$\mathcal{S} = \sum_{N_\ell J_\ell} A(\gamma_u \Pi; \mathbf{v}_u; n_u S J_u; \pi_u \rightarrow \gamma_\ell \Sigma; \mathbf{v}_\ell; N_\ell S J_\ell; \pi_\ell), \quad (39)$$

$$\mathcal{S}' = \sum_{N_\ell J_\ell} A(\gamma_u \Pi; \mathbf{v}_u; n_u S J_u; \pi_u \rightarrow \gamma_\ell \Sigma; \mathbf{v}_\ell; N_\ell S J_\ell; \pi_\ell) w_{J_u J_\ell}^{(K)}. \quad (40)$$

These two sums can be done using the same methods as those of Sect. 2 and observing that

$$(-1)^{1+\pi_u+N_\ell+p_\ell} \begin{pmatrix} N_u & N_\ell & 1 \\ 1 & 0 & -1 \end{pmatrix} = (-1)^{\pi_u+N_u+p_\ell} \begin{pmatrix} N_u & N_\ell & 1 \\ -1 & 0 & 1 \end{pmatrix}. \quad (41)$$

For the first sum one gets

$$\mathcal{S} = \frac{1}{2} A_{\text{band}}, \quad (42)$$

and, from the evaluation of the second sum, one obtains the result

$$\mathcal{W}_K(N_\ell J_\ell p_\ell, n_u J_u \pi_u) = (-1)^{S-J_\ell} 3(2J_u + 1) \left\{ \begin{matrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{matrix} \right\} \sum_{N_u N'_u} C_{N_u}^{n_u} C_{N'_u}^{n_u} \sqrt{(2N_u + 1)(2N'_u + 1)} \left\{ \begin{matrix} N_u & N'_u & K \\ J_u & J_u & S \end{matrix} \right\} \\ \times \left[\left(\begin{matrix} 1 & 1 & K \\ 1 & -1 & 0 \end{matrix} \right) \begin{pmatrix} N_u & N'_u & K \\ 1 & -1 & 0 \end{pmatrix} + (-1)^{N'_u - \pi_u - p_\ell} \begin{pmatrix} 1 & 1 & K \\ 1 & 1 & -2 \end{pmatrix} \begin{pmatrix} N_u & N'_u & K \\ 1 & 1 & -2 \end{pmatrix} \right]. \quad (43)$$

From Eq. (38) it can be remarked that, for a line to have its Einstein coefficient different from zero, the quantity $(1 + \pi_u + p_\ell + N_\ell)$ has to be even. This implies that the sign factor appearing in Eq. (43) can also be written in the form

$$(-1)^{N'_u - \pi_u - p_\ell} = (-1)^{N'_u + N_\ell + 1}. \quad (44)$$

We also remark that, when the upper state is in pure Hund's case (b), Eq. (43) reduces to

$$\begin{aligned} \mathcal{W}_K(N_\ell J_\ell p_\ell, N_u J_u \pi_u) &= (-1)^{S - J_\ell} 3(2J_u + 1)(2N_u + 1) \begin{Bmatrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{Bmatrix} \begin{Bmatrix} N_u & N_u & K \\ J_u & J_u & S \end{Bmatrix} \\ &\times \left[\begin{pmatrix} 1 & 1 & K \\ 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} N_u & N_u & K \\ 1 & -1 & 0 \end{pmatrix} + (-1)^{N_u - \pi_u - p_\ell} \begin{pmatrix} 1 & 1 & K \\ 1 & 1 & -2 \end{pmatrix} \begin{pmatrix} N_u & N_u & K \\ 1 & 1 & -2 \end{pmatrix} \right], \end{aligned} \quad (45)$$

which coincides with the result of Landi Degl'Innocenti (2003).

Finally, it is also possible to express the result of Eq. (43) in an alternative form, using the development in series of the eigenfunctions of Hund's case (a) for the upper level. Starting from Eq. (B.14), particularized to the case of the transition Π - Σ , one obtains, after some Racah algebra, the following expression:

$$\begin{aligned} \mathcal{W}_K(N_\ell J_\ell p_\ell, \omega_u J_u \pi_u) &= 3(2J_u + 1) \begin{Bmatrix} 1 & 1 & K \\ J_u & J_u & J_\ell \end{Bmatrix} \sum_{\Omega_u} (-1)^{K+1+\Omega_u+J_\ell} \left[[C_{\Omega_u}^{\omega_u}]^2 \begin{pmatrix} 1 & 1 & K \\ 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} J_u & J_u & K \\ \Omega_u & -\Omega_u & 0 \end{pmatrix} \right. \\ &\left. + (-1)^{S+J_u-\pi_u-p_\ell} C_{\Omega_u}^{\omega_u} C_{2-\Omega_u}^{\omega_u} \begin{pmatrix} 1 & 1 & K \\ 1 & 1 & -2 \end{pmatrix} \begin{pmatrix} J_u & J_u & K \\ \Omega_u & 2-\Omega_u & -2 \end{pmatrix} \right]. \end{aligned} \quad (46)$$

3.1. Homonuclear molecules

In the case of homonuclear molecules, or, more generally, in the case where the molecule is composed of two ions having equal nuclear charge, there is another symmetry property that enters into play because the Hamiltonian of the molecule is invariant with respect to the interchange of the two nuclei ($\mathbf{R}_1 \leftrightarrow \mathbf{R}_2$). With the symbol E , we denote the operator that consists in exchanging the two nuclei, and we observe that, being $E^2 = 1$, the eigenvalues of the operator E are ± 1 . We next observe that, from the point of view of the electronic wave-function, the interchange of the two nuclei corresponds to the transformation of the rotating-frame coordinates ($\xi \rightarrow -\xi, \eta \rightarrow -\eta, \zeta \rightarrow -\zeta$), and electronic states can thus be classified as even (*gerade*) or odd (*ungerade*) according to whether they do not change or change sign, respectively, under this transformation. From this definition, it is now possible to relate the eigenvalue of the parity operator, P , to the eigenvalue of the exchange operator, E , acting on a given eigenvector of the molecular Hamiltonian. To this end we observe that the parity operator involves the inversion of all the coordinates of the particles (electrons and nuclei) and can thus be considered as the product of the operator E (exchange of the nuclei) times the operator that inverts the coordinates of the electrons. Introducing the quantum number e to denote the eigenvalues of the operator E according to the equation

$$E|a\rangle = (-1)^e |a\rangle, \quad (47)$$

one gets

$$e = \text{mod}(\pi - s, 2), \quad (48)$$

where $s = 0$ for even (*gerade*) electronic states and $s = 1$ for odd (*ungerade*) states.

According to the standard lexicon of molecular spectroscopy, terms with $e = 0$ are called symmetric (with respect to the exchange of the nuclei), while terms with $e = 1$ are called antisymmetric. It follows that for even (*gerade*) electronic states, positive terms are symmetric and negative terms are antisymmetric. Vice versa, for odd (*ungerade*) electronic states, positive terms are antisymmetric and negative terms are symmetric.

On the other hand, a general theorem on the exchange symmetry of identical particles states that the coordinate wave-function of a system composed of two identical particles is symmetric or antisymmetric according to whether the total spin (obtained by adding the spins of the two particles) is either even or odd. It follows that, for strictly homonuclear molecules (i.e., molecules composed of two identical isotopes of the same element), some terms are, in general, forbidden or, in other words, inexistent. If we consider, for instance, the molecule C_2 (more precisely the molecule $C^{12}C^{12}$), since both nuclei have spin equal to zero, the only allowed terms have to be symmetric. This implies that for even (*gerade*) electronic states there are only positive terms and for odd (*ungerade*) electronic states, there are only negative terms. For this molecule, the Λ -doubling phenomenon is therefore absent.

4. Polarization in solar molecular bands

The theory developed in the previous sections can be suitably applied to the interpretation of the polarization signal detected in molecular bands when observing close to the solar limb. We have, however, to remark that our previous results on the polarizability factors are based on assumptions i), ii), iii), and iv) that are itemized in Sect. 1. A discussion is in order about their applicability to the interpretation of the polarimetric observations performed at the solar limb.

Since the different transitions that contribute to pump a given upper level fall at wavelengths that are very close in the spectrum (typically at distances of the order of one or a few \AA), and since the same transitions are characterized by nearly equal Einstein coefficients (and oscillator strengths), assumption i) is generally well verified unless, by chance, one of the transitions overlaps with an atomic transition. In this case, the blend between the molecular line and the atomic one prevents the applicability of Eq. (4),

especially when the atomic line is particularly strong. Assumption ii) is more delicate because it implies that depolarizing collisions are efficient enough to destroy any atomic polarization that can be induced in the lower levels by the pumping mechanism. Unfortunately, depolarizing collision rates for molecular levels are poorly known and one can only rely on order of magnitude estimates based on the classical theory of the Van der Waals interaction between molecules and neutral hydrogen atoms. These estimates bring us to the conclusion that, at the typical depths where the weakest of the molecular bands are formed, collisional depolarization is an efficient mechanism to destroy atomic polarization in the molecular levels pertaining to the ground electronic state. Finally, assumption iii) is well verified when assumptions i) and ii) are, and assumption iv) is also well verified for molecular bands in the visible or in the near UV region of the solar spectrum.

Three molecular bands have been found to produce significant polarimetric signals in the solar spectrum (Stenflo & Keller 1996; Gandorfer 2000, 2002). In order of increasing wavelength, these are: the CN band shorter than 3900 Å, and the C₂ and MgH bands in the interval 4900–5200 Å. Previous work on the interpretation of the last two bands, though based on less sophisticated theoretical approaches that do not account for intermediate coupling, has been presented by Mohan Rao & Rangarajan (1999), Berdyugina et al. (2002), and Faurobert & Arnaud (2002, 2003).

The C₂ and MgH bands are particularly weak in the Fraunhofer spectrum so that the linear polarization signal in each line can be suitably described by Eq. (6), which, taking into account Eqs. (7) and (8), can be expressed in the form (in the notations of Appendix B.2)

$$\left[\frac{Q}{I}\right]_{\text{line}} = \mathcal{K} \mathcal{P}_{\text{line}} \phi(v_{n_u J_u, n_\ell J_\ell} - \nu), \quad (49)$$

where \mathcal{K} is a constant for all the lines of the band that is given by

$$\mathcal{K} = \frac{3c^2}{32\pi^2 \bar{\nu}^2 k_v^{(c)}} w \frac{S_L}{B_P} A_{\text{band}} \frac{N_{\text{mol}}}{Z(T_{\text{exc}})}, \quad (50)$$

and where

$$\mathcal{P}_{\text{line}} = \exp\left(-\frac{E_{n_\ell J_\ell}}{k_B T_{\text{exc}}}\right) (2J_u + 1) \mathcal{W}_2(n_\ell J_\ell, n_u J_u) \frac{A(n_u J_u \rightarrow n_\ell J_\ell)}{A_{\text{band}}}. \quad (51)$$

In the following we give, in the form of graphs, some numerical results for these two bands.

4.1. Numerical results for the MgH band

The lines of the MgH molecule that are observed in the second solar spectrum originate from the transition between the vibrational level $v_u = 0$ of the excited electronic state, $A^2\Pi$, and the vibrational level $v_\ell = 0$ of the ground electronic state, $X^2\Sigma^+$. The band covers an interval of about 200 Å centered at approximately 5100 Å. The rotational constants and the fine structure data of the two vibro-electronic states can be found in Bernath et al. (1985). In particular, the constant $Y = A_e/B_e$ of the upper level is given by these authors as 5.74535. Since we are facing a $\Pi - \Sigma$ transition, the relevant expressions to be used to compute $\mathcal{P}_{\text{line}}$ are given by Eqs. (29) and (B.23) for the Einstein coefficient and by Eq. (43) for the generalized polarizability factor. The numerical results for $\mathcal{P}_{\text{line}}$ are shown in Fig. 1 (upper-left panel) in the absence of magnetic fields. With the exception of a very few lines, the polarization is positive in all three branches (whose maxima are found in the order P, Q, R for decreasing wavelength). However, the polarization signals in the P and R branches are much weaker than those in the Q-branch, as confirmed by the observations of the second solar spectrum of Gandorfer (2000). It has to be remarked that the polarization signal reaches a maximum value for the lines of the Q-branch that are found around 5160 Å, a fact that is also well confirmed by observations. The upper-right panel of Fig. 1 shows the results – formally obtained by performing in Eq. (51) the transformation implied by Eq. (9) and using the values of the Landé factors as derived in Appendix C – in the presence of a unimodal, turbulent magnetic field of 40 G. One can notice the overall reduction of the polarization signal due to the Hanle effect. The lower panels present a detail of the band around 5175 Å. At this larger value of the resolution of the figure, the doublet structure of the band is clearly visible. The figure also shows that the two components of each doublet are almost equally affected by the turbulent magnetic field (having nearly equal Landé factors and Einstein coefficients).

4.2. Numerical results for the C₂ band

The lines of the C₂ molecule that are observed in the second solar spectrum originate from the transition between the vibrational level $v_u = 0$ of the upper electronic state, $A^3\Pi_g$, and the vibrational level $v_\ell = 0$ of the lower electronic state, $X^3\Pi_u$ ⁸. The band covers an interval of about 400 Å centered at approximately 5000 Å. The rotational constants and the fine structure data of the two vibro-electronic states can be found in Phillips & Davis (1968). In particular, the constant Y is given by these authors as -9.40 for the upper level and -10.7 for the lower level. The transition is $\Pi - \Pi$ and there is no Λ -doubling because the molecule is a homonuclear one. The expressions to be used to compute $\mathcal{P}_{\text{line}}$ are given by Eq. (B.14) for the Einstein coefficient and by Eq. (14) for the generalized polarizability factor (alternatively, one can use Eqs. (B.23) and (20)). The numerical results for $\mathcal{P}_{\text{line}}$ in the absence of magnetic fields are shown in Fig. 2 (upper-left panel). The Q-branch produces a very weak, negative polarization signal,

⁸ The spectroscopic denomination given here is the one employed by Herzberg (1950) and by Phillips & Davis (1968). Huber & Herzberg (1979) refer to the same states as $d^3\Pi_g$ and $a^3\Pi_u$, respectively.

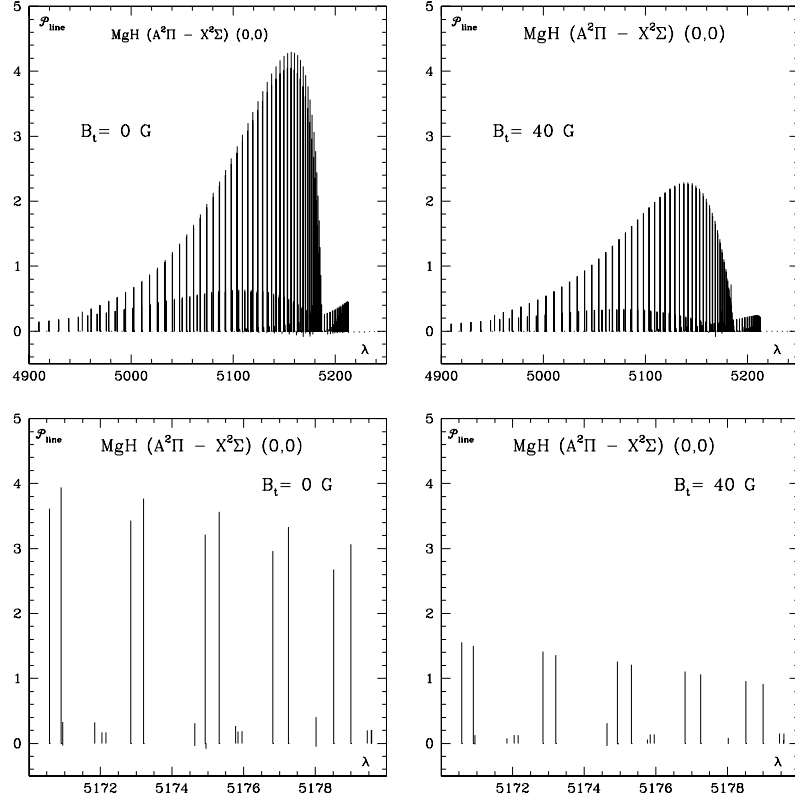


Fig. 1. The quantity $\mathcal{P}_{\text{line}}$ is plotted as a function of the line wavelength for the (0, 0) band of the transition $A^2\Pi - X^2\Sigma$ of the MgH molecule. The upper panels cover a wavelength interval of the order of 300 Å, whereas the lower panels show a detail of the band in a much smaller wavelength interval, of the order of 10 Å. The left panels give the fractional polarization in the absence of magnetic fields. The right panels are obtained assuming a unimodal, turbulent magnetic field of 40 G.

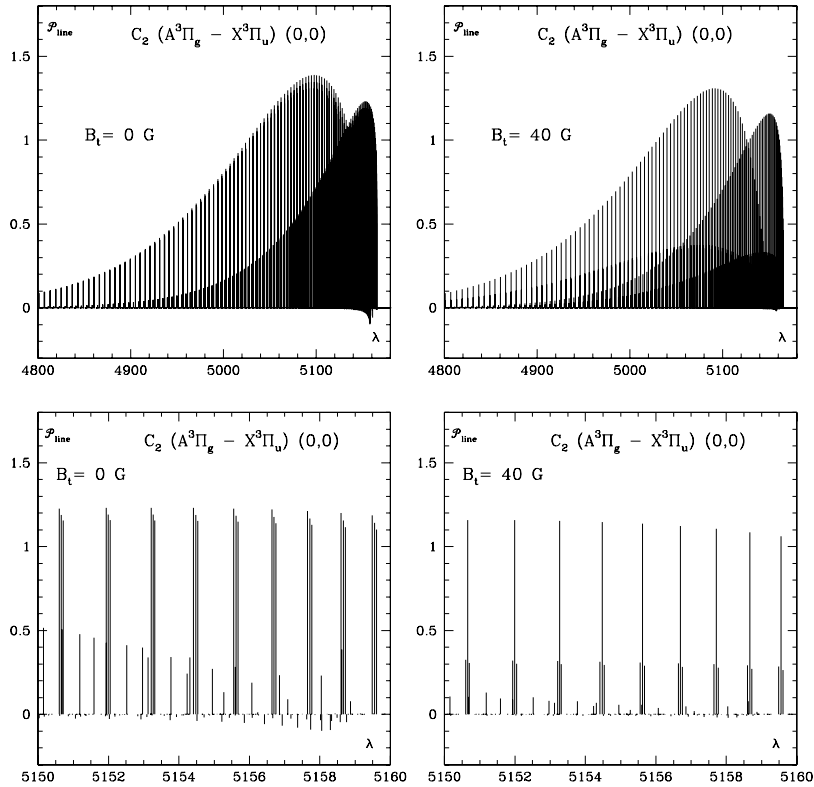


Fig. 2. The quantity $\mathcal{P}_{\text{line}}$ is plotted as a function of the line wavelength for the (0, 0) band of the transition $A^3\Pi_g - X^3\Pi_u$ of the C₂ molecule. The upper panels cover a wavelength interval of the order of 400 Å, whereas the lower panels show a detail of the band in a much smaller wavelength interval, of the order of 10 Å. The left panels give the fractional polarization in the absence of magnetic fields. The right panels are obtained assuming a unimodal, turbulent magnetic field of 40 G. See the text for further details.

whereas the polarization is positive and quite large in both the P and R branches. The maxima of the polarization peaks are found around 5150 Å in the P-branch and around 5100 Å in the R-branch. These features are well confirmed by observations (Gandorfer 2000). In the upper-right panel of Fig. 2 the Hanle effect due to a unimodal, turbulent magnetic field of 40 G is shown. Due to a lack of resolution of the figure, the band appears to be almost unaffected by the magnetic field. The real situation is better shown in the lower panels of the figure, which refer to a smaller wavelength interval centered around 5155 Å. The band is indeed structured in triplets and it happens that one component of the triplets has a Landé factor that is much smaller than the Landé factor of the other two components, and thus results in being almost insensitive to a turbulent field of 40 G. This phenomenon is quite remarkable and has been proposed and used as a diagnostic tool of tangled magnetic fields by Trujillo Bueno (2003). Examples of applications can also be found in Berdyugina & Fluri (2004) and in Trujillo Bueno et al. (2004).

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References

- Asensio Ramos, A., & Trujillo Bueno, J. 2003, in *Solar Polarization 3*, ed. J. Trujillo Bueno, & J. Sánchez Almeida, ASP Conf. Ser., 307, 195
- Asensio Ramos, A., & Trujillo Bueno, J. 2006, *ApJ*, 636, 548
- Berdyugina, S. V., & Solanki, S. K. 2002, *A&A*, 385, 701
- Berdyugina, S. V., & Fluri, D. M. 2004, *A&A*, 417, 775
- Berdyugina, S. V., Stenflo, J. O., & Gandorfer, A. 2002, *A&A*, 338, 1062
- Bernath, P. F., Black, J. H., & Brault, J. W. 1985, *ApJ*, 298, 375
- Brown, J. M., & Carrington, A. 2003, *Rotational Spectroscopy of Diatomic Molecules* (Cambridge Univ. Press)
- Budó, A. 1935, *Zeitschr. Phys.*, 96, 219
- Chandrasekhar, S. 1950, *Radiative Transfer*, Clarendon Press, Oxford
- Faurobert, M., & Arnaud, J. 2002, *A&A*, 382, L17
- Faurobert, M., & Arnaud, J. 2003, *A&A*, 412, 555
- Gandorfer, A. 2000, *The Second Solar Spectrum*, Vol. 1 (vdf Hochschulverlag AG an der ETH Zürich)
- Gandorfer, A. 2002, *The Second Solar Spectrum*, Vol. 2 (vdf Hochschulverlag AG an der ETH Zürich)
- Hamilton, D. R. 1947, *ApJ*, 106, 457
- Herzberg, G. 1950, *Molecular Spectra and Molecular Structure* (Van Nostrand, Toronto)
- Hill, E. L. 1929, *Phys. Rev.*, 34, 1507
- Huber, K. P., & Herzberg, G. 1979, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold Co., New York
- Kovács, I. 1969, *Rotational Structure in the Spectra of Diatomic Molecules* (London: Adam Hilger Ltd)
- Landau, L., & Lifchitz, E. 1967, *Mécanique Quantique* (Moscou: Éditions Mir)
- Landi Degl'Innocenti, E. 1984, *Sol. Phys.*, 91, 1
- Landi Degl'Innocenti, E. 1985, *Sol. Phys.*, 99, 1
- Landi Degl'Innocenti, E. 2003, in *Solar Polarization 3*, ed. J. Trujillo Bueno, & J. Sánchez Almeida, ASP Conf. Ser., 307, 164
- Landi Degl'Innocenti, E., & Landolfi, M. 2004, *Polarization in Spectral Lines* (Dordrecht: Kluwer Acad. Publ.)
- Landi Degl'Innocenti, E., Landi Degl'Innocenti, M., & Landolfi, M. 1997, in *Forum THÉMIS*, ed. N. Mein, & S. Sahal-Bréchet, Publications de l'Observatoire de Paris, 59
- Mohan Rao, D., & Rangarajan, K. E. 1999, *ApJ*, 524, L139
- Phillips, J. G., & Davis, S. P. 1968, *Berkeley Analyses of Molecular Spectra*, Vol. 2 (Berkeley: Univ. of California Press)
- Schadee, A. 1978, *J. Quant. Spec. Radiat. Transf.*, 19, 517
- Stenflo, J. O., & Keller, C. U. 1996, *Nature*, 382, 588
- Trujillo Bueno, J. 2003, in *Solar Polarization 3*, ed. J. Trujillo Bueno, & J. Sánchez Almeida, ASP Conf. Ser., 307, 195
- Trujillo Bueno, J., & Sánchez Almeida, J. 2003, *Solar Polarization 3*, ASP Conf. Ser., 307
- Trujillo Bueno, J., Shchukina, N., & Asensio Ramos, A. 2004, *Nature*, 430, 236
- Varshalovich, D. A., Moskalev, A. N., & Khersonskii, V. K. 1988, *Quantum Theory of Angular Momentum* (Singapore: World Scientific)
- Whiting, E. E., & Nicholls, R. W. 1974, *ApJS*, 27, 1
- Whiting, E. E., Schadee, A., Tatum, J. B., Houghen, J. T., & Nicholls, R. W. 1980, *J. Mol. Spectr.*, 80, 249
- Zare, R. N. 1988, *Angular Momentum* (New York: John Wiley & Sons)

Online Material

Appendix A: Eigenvalues and eigenvectors of the molecular Hamiltonian in the intermediate (a-b) coupling case

As detailed in classical textbooks such as Herzberg (1950), Landau & Lifchitz (1967), and Kovács (1969), in many cases molecules cannot be described either in the coupling scheme referred to as Hund's case (a) or in the alternative scheme called Hund's case (b). It is then necessary to consider the intermediate coupling scheme where the part of the Hamiltonian resulting from nuclear rotation and from spin-orbit interaction, is given, to lowest order approximation⁹, by

$$H_{\text{mol}} = H_{\text{rot}} + H_{\text{s-o}}, \quad (\text{A.1})$$

where

$$H_{\text{rot}} = B_e R^2, \quad H_{\text{s-o}} = A_e \Lambda \mathbf{n} \cdot \mathbf{S}. \quad (\text{A.2})$$

In these equations, the quantities B_e and A_e are the rotational and spin-orbit molecular constants, respectively, \mathbf{R} is the angular momentum due to nuclear rotation, Λ is the projection of the electronic orbital angular momentum along the internuclear axis, denoted by the unit vector \mathbf{n} , and \mathbf{S} is the electron spin. The two angular momenta \mathbf{R} and \mathbf{L} (this last one being the total orbital electronic angular momentum) combine to give the angular momentum \mathbf{N} (that is the total orbital angular momentum due to the nuclei and to the electrons). This last angular momentum combines in turn with the spin \mathbf{S} to give the total angular momentum \mathbf{J} of the molecule (with exclusion of the nuclear spin), so that $\mathbf{J} = \mathbf{N} + \mathbf{S} = \mathbf{R} + \mathbf{L} + \mathbf{S}$. When $B_e \ll A_e$ (in principle when the constant B_e is zero), one gets the pure coupling case Hund's (a), whereas when $A_e \ll B_e$ (in principle when $A_e = 0$ or when $\Lambda = 0$), one gets the pure case Hund's (b).

To deal with the intermediate case it is possible to use either the eigenfunctions of case (a) or the eigenfunctions of case (b). The Hamiltonian $H_{\text{s-o}}$ is diagonal on the former, whereas the Hamiltonian H_{rot} is diagonal on the latter. In the following, we proceed with the diagonalization of the total Hamiltonian by using the eigenfunctions of both cases

A.1. Diagonalization of the Hamiltonian using the eigenfunctions of Hund's case (a)

The eigenfunctions of case (a) are given, in compact notations, by the expression

$$|\gamma\Lambda; \mathbf{v}; \Omega S J M\rangle = \sqrt{\frac{2J+1}{4\pi}} \mathcal{D}_{M\Omega}^J(\phi, \theta, 0)^* |S\Sigma\rangle_{\text{mol}} |\gamma\Lambda; \mathbf{v}\rangle. \quad (\text{A.3})$$

The meaning of the quantum numbers appearing here is the following: γ is a collection of quantum numbers that specifies the molecular configuration of the optical electron(s), Λ is the projection of the orbital angular momentum \mathbf{L} on the internuclear axis, \mathbf{v} is the nuclear vibrational quantum number, J is the total angular momentum, M is its projection along the quantization axis, Ω is the projection of \mathbf{J} along the internuclear axis, S is the electron spin, and Σ is its projection along the internuclear axis. Finally, the symbol $|S\Sigma\rangle_{\text{mol}}$ is the spin eigenvector defined in the rotating (or molecular) reference system. The three quantum numbers Λ , Ω , and Σ are not independent, being

$$\Omega = \Lambda + \Sigma. \quad (\text{A.4})$$

For fixed Λ , S , and J , the quantum number Ω spans the interval $(\Omega_{\text{min}}, \Omega_{\text{max}})$ where

$$\Omega_{\text{min}} = \max(-J, \Lambda - S), \quad \Omega_{\text{max}} = \min(J, \Lambda + S). \quad (\text{A.5})$$

The Hamiltonian H_{mol} has to be diagonalized on this basis. As anticipated, the spin-orbit Hamiltonian is diagonal, and has matrix elements of the form

$$\langle \gamma\Lambda; \mathbf{v}; \Omega S J M | H_{\text{s-o}} | \gamma\Lambda; \mathbf{v}; \Omega' S J M \rangle = \delta_{\Omega\Omega'} A_e \Lambda \Sigma. \quad (\text{A.6})$$

The rotational Hamiltonian can be cast in the form

$$H_{\text{rot}} = B_e R^2 = B_e (\mathbf{J} - \mathbf{L} - \mathbf{S})^2 = B_e (J^2 + L^2 + S^2 - 2\mathbf{J} \cdot \mathbf{L} - 2\mathbf{J} \cdot \mathbf{S} + 2\mathbf{L} \cdot \mathbf{S}). \quad (\text{A.7})$$

The calculation of its matrix elements is more complicated. Introducing the components of the different angular momenta on the rotating reference system (ξ, η, ζ) having the ζ axis directed along the internuclear axis, and taking into account that the terms linear in L_ξ and L_η bring no contribution to the matrix element, this can be computed by substituting the rotational Hamiltonian with its equivalent form

$$H'_{\text{rot}} = B_e (J^2 + L_\xi^2 + L_\eta^2 + L_\zeta^2 + S^2 - 2J_\zeta L_\zeta + 2L_\zeta S_\zeta - 2\mathbf{J} \cdot \mathbf{S}). \quad (\text{A.8})$$

All the operators in braces are diagonal on this basis, except for the last one, and one gets

$$\langle \gamma\Lambda; \mathbf{v}; \Omega S J M | H'_{\text{rot}} | \gamma\Lambda; \mathbf{v}; \Omega' S J M \rangle = \delta_{\Omega\Omega'} B_e [J(J+1) + S(S+1) - \Lambda^2 + \Delta] - 2B_e \mathcal{M}, \quad (\text{A.9})$$

⁹ In principle, further terms can be added to H_{mol} , such as, for instance, a term of the form $-D_e R^4$, which accounts for the distortion of the molecule with increasing rotation, terms of the form $A_D R^2 (\mathbf{n} \cdot \mathbf{S})(\mathbf{n} \cdot \mathbf{L})$, accounting for centrifugal corrections to the spin-orbit interaction, and further terms accounting for spin-rotation interaction and for Λ -doubling interactions. All these corrective terms are in general important for determining the exact wavelengths of the transitions, but they have little influence – except in some very special cases – on the determination of Einstein coefficients, Landé factors, and generalized polarizability factors.

where¹⁰

$$\Delta = \langle \gamma\Lambda | L_\xi^2 + L_\eta^2 | \gamma\Lambda \rangle, \quad (\text{A.10})$$

and

$$\mathcal{M} = \langle \gamma\Lambda; \mathbf{v}; \Omega S JM | \mathbf{J} \cdot \mathbf{S} | \gamma\Lambda; \mathbf{v}; \Omega' S JM \rangle. \quad (\text{A.11})$$

The matrix element \mathcal{M} can be computed through standard methods of Racah algebra. First one writes

$$\mathbf{J} \cdot \mathbf{S} = \sum_q (-1)^q \hat{J}_{-q} \hat{S}_q, \quad (\text{A.12})$$

where \hat{J}_q and \hat{S}_q are the spherical components of the vectors \mathbf{J} and \mathbf{S} in the rotating (or molecular) reference system. Then one applies the Wigner-Eckart theorem twice, also taking into account that the operators \hat{J}_q act contravariantly with respect to the rotation matrices (see, e.g., Varshalovich et al. 1988). One thus obtains

$$\mathcal{M} = (-1)^{S-J+\Lambda} \sqrt{J(J+1)(2J+1)S(S+1)(2S+1)} \sum_q \begin{pmatrix} J & J & 1 \\ \Omega & -\Omega' & q \end{pmatrix} \begin{pmatrix} S & S & 1 \\ \Sigma & -\Sigma' & q \end{pmatrix}. \quad (\text{A.13})$$

Equations (A.6), (A.9-11), and (A.13) allow us to compute all the matrix elements of the Hamiltonian H_{mol} , which can thus be diagonalized. The diagonalization can be performed analytically only in the case of doublet terms, otherwise it has to be performed by means of standard numerical methods¹¹. Introducing the quantum number ω to denote the eigenvectors, these can be written in the form

$$|\gamma\Lambda; \mathbf{v}; \omega S JM\rangle = \sum_{\Omega} C_{\Omega}^{\omega} |\gamma\Lambda; \mathbf{v}; \Omega S JM\rangle, \quad (\text{A.14})$$

where the real coefficients C_{Ω}^{ω} can be found numerically from the same algorithm that diagonalizes the Hamiltonian.

A.2. Diagonalization of the Hamiltonian using the eigenfunctions of Hund's case (b)

The eigenfunctions of Hund's case (b) are given, in compact notations, by the following expression

$$|\gamma\Lambda; \mathbf{v}; NS JM\rangle = \sum_{M_N M_S} (-1)^{N-S-M} \sqrt{2J+1} \begin{pmatrix} N & S & J \\ M_N & M_S & -M \end{pmatrix} \sqrt{\frac{2N+1}{4\pi}} \mathcal{D}_{M_N \Lambda}^N(\phi, \theta, 0)^* |S M_S\rangle |\gamma\Lambda; \mathbf{v}\rangle, \quad (\text{A.15})$$

where the quantum numbers M_N and M_S are the projections on the quantization axis of the angular momenta N and S , respectively. For J , S , and Λ fixed, N can span in the interval (N_{\min}, N_{\max}) , with

$$N_{\min} = \max(|J - S|, \Lambda), \quad N_{\max} = J + S. \quad (\text{A.16})$$

Obviously, the eigenfunctions now introduced are not independent of those relative to Hund's case (a), since they span the same Hilbert space. Indeed, it can be shown that

$$\langle \gamma\Lambda; \mathbf{v}; \Omega S JM | \gamma\Lambda; \mathbf{v}; NS JM \rangle = (-1)^{N-S-\Omega} \sqrt{2N+1} \begin{pmatrix} N & S & J \\ \Lambda & \Sigma & -\Omega \end{pmatrix}, \quad (\text{A.17})$$

an equation that allows us to express the eigenfunctions of each basis as a linear combination of the eigenfunctions of the other.

On the basis of Hund's case (b), the Hamiltonian H_{rot} is diagonal and its matrix elements can be easily computed by observing that

$$H_{\text{rot}} = B_e R^2 = B_e (\mathbf{N} - \mathbf{L})^2 = B_e (N^2 + L^2 - 2\mathbf{N} \cdot \mathbf{L}) = B_e (N^2 + L_\xi^2 + L_\eta^2 + L_\zeta^2 - 2N_\xi L_\xi - 2N_\eta L_\eta - 2N_\zeta L_\zeta). \quad (\text{A.18})$$

Taking into account that the linear terms in L_ξ and L_η bring no contribution to the matrix element, one obtains

$$\langle \gamma\Lambda; \mathbf{v}; NS JM | H_{\text{rot}} | \gamma\Lambda; \mathbf{v}; N' S JM \rangle = \delta_{NN'} B_e [N(N+1) - \Lambda^2 + \Delta], \quad (\text{A.19})$$

where Δ is the quantity introduced in Eq. (A.10).

The evaluation of the matrix elements of the spin-orbit interaction on this basis is more complicated. This can be done either using the Weyl theorem or recalling the general expressions of Racah algebra for the matrix elements of irreducible tensors. Following this second alternative, we form from the scalar product $(\mathbf{n} \cdot \mathbf{S})$ the irreducible tensor of rank 0, T_0^0 , defined by

$$T_0^0 = -\frac{1}{\sqrt{3}} \mathbf{n} \cdot \mathbf{S}, \quad (\text{A.20})$$

¹⁰ The quantity Δ is independent of the quantum numbers Ω and J and it appears only on the diagonal of the matrix. As such, its explicit value only results in an overall shift of all the levels pertaining to the electronic state $(\gamma\Lambda)$ and is totally inessential for determining the eigenvectors.

¹¹ Approximate analytical expressions can also be found for the case of triplets (Budó 1935; Kovács 1969).

and we observe that the operator \mathbf{n} acts only on the orbital part of the wave-function, while \mathbf{S} acts only on its spin part. Next, we use the Wigner-Eckart theorem to obtain

$$\langle \gamma\Lambda; \mathbf{v}; NSJM | T_0^0 | \gamma\Lambda; \mathbf{v}; N'SJM \rangle = \langle \gamma\Lambda; \mathbf{v}; NSJ | \mathbf{T}^0 | \gamma\Lambda; \mathbf{v}; N'SJ \rangle, \quad (\text{A.21})$$

and we use the standard relations to express the reduced matrix element of \mathbf{T}^0 in terms of the reduced matrix elements of the vectors \mathbf{n} and \mathbf{S} , namely

$$\langle \gamma\Lambda; \mathbf{v}; NSJ | \mathbf{T}^0 | \gamma\Lambda; \mathbf{v}; N'SJ \rangle = (-1)^{J+N'+S+1} \sqrt{\frac{(2N+1)(2S+1)}{3}} \left\{ \begin{matrix} N & N' & 1 \\ S & S & J \end{matrix} \right\} \langle N\Lambda | \mathbf{n} | N'\Lambda \rangle \langle S | \mathbf{S} | S \rangle. \quad (\text{A.22})$$

Finally, we substitute the expressions for the reduced matrix elements

$$\langle N\Lambda | \mathbf{n} | N'\Lambda \rangle = (-1)^{N-\Lambda} \sqrt{2N'+1} \begin{pmatrix} N & N' & 1 \\ \Lambda & -\Lambda & 0 \end{pmatrix}, \quad \langle S | \mathbf{S} | S \rangle = \sqrt{S(S+1)}, \quad (\text{A.23})$$

to obtain the final expression for the spin-orbit Hamiltonian

$$\begin{aligned} \langle \gamma\Lambda; \mathbf{v}; NSJM | H_{s-o} | \gamma\Lambda; \mathbf{v}; N'SJM \rangle &= A_e \Lambda (-1)^{J+S+N+N'-\Lambda} \sqrt{(2N+1)(2N'+1)S(S+1)(2S+1)} \\ &\times \begin{pmatrix} N & N' & 1 \\ \Lambda & -\Lambda & 0 \end{pmatrix} \left\{ \begin{matrix} N & N' & 1 \\ S & S & J \end{matrix} \right\}. \end{aligned} \quad (\text{A.24})$$

Equations (A.19) and (A.24) allow us to compute all the matrix elements of the Hamiltonian H_{mol} , which can thus be diagonalized. Similarly to what was done in the former section, we introduce the quantum number n to denote the eigenvectors, which can thus be expressed in the form

$$|\gamma\Lambda; \mathbf{v}; nSJM \rangle = \sum_N C_N^n |\gamma\Lambda; \mathbf{v}; NSJM \rangle. \quad (\text{A.25})$$

Obviously, the eigenvectors given in this equation have to coincide with those expressed by Eq. (A.14), and a correspondence can be established within the quantum numbers ω and n .

Appendix B: The Einstein coefficients

To evaluate the polarizability factors of molecular lines, it is necessary to first derive the Einstein coefficients for spontaneous de-excitation. Again, we stress that the material contained in this appendix is not new. Expressions for the Einstein coefficients in Hund's cases (a) and (b), as well as in the intermediate regime have been given by several authors and are collected, for instance, in Kovács (1969) or in Brown & Carrington (2003). Here we proceed with the notations introduced in Appendix A, and we refer to the well known expression that relates the Einstein coefficient to the wave-functions of the upper and lower levels between which the electric-dipole transition takes place. In Dirac's notation, the Einstein coefficient for spontaneous de-excitation, A_{ab} , from the non-degenerate upper level $|a\rangle$ to the non-degenerate lower level $|b\rangle$ is given by the equation

$$A_{ab} = \frac{64\pi^4}{3hc^3} \nu_{ab}^3 \sum_i |(d_i)_{ab}|^2 = \frac{64\pi^4}{3hc^3} \nu_{ab}^3 \sum_q |(d_q)_{ab}|^2, \quad (\text{B.1})$$

where h is Planck's constant, c is the speed of light, ν_{ab} is the frequency of the transition between the upper and lower levels, and where $(d_i)_{ab}$ and $(d_q)_{ab}$ are, respectively, the matrix elements of the Cartesian and spherical coordinates of the dipole operator \mathbf{d} . Our aim is to apply this equation to a molecular band, namely to the various transitions that originate between the vibrational level \mathbf{v}_u , pertaining to the upper electronic state ($\gamma_u\Lambda_u$), and the vibrational level \mathbf{v}_ℓ , pertaining to the lower electronic state ($\gamma_\ell\Lambda_\ell$), both levels being in intermediate coupling between Hund's cases (a) and (b). The calculations can be performed by using as basis eigenfunctions either those of case (a) or those of case (b). This is done in succession in the following subsections.

B.1. Expression of the Einstein coefficient using the eigenfunctions of Hund's case (a)

By means of the notations introduced in Appendix A, the upper and lower level involved in the transition can be written in the following form (see Eq. (A.14))

$$|\gamma_u\Lambda_u; \mathbf{v}_u; \omega_u S J_u M_u \rangle = \sum_{\Omega_u} C_{\Omega_u}^{\omega_u} |\gamma_u\Lambda_u; \mathbf{v}_u; \Omega_u S J_u M_u \rangle, \quad |\gamma_\ell\Lambda_\ell; \mathbf{v}_\ell; \omega_\ell S J_\ell M_\ell \rangle = \sum_{\Omega_\ell} C_{\Omega_\ell}^{\omega_\ell} |\gamma_\ell\Lambda_\ell; \mathbf{v}_\ell; \Omega_\ell S J_\ell M_\ell \rangle, \quad (\text{B.2})$$

so that we have, for the matrix element of the operator d_q

$$\langle \gamma_u\Lambda_u; \mathbf{v}_u; \omega_u S J_u M_u | d_q | \gamma_\ell\Lambda_\ell; \mathbf{v}_\ell; \omega_\ell S J_\ell M_\ell \rangle = \sum_{\Omega_u\Omega_\ell} C_{\Omega_u}^{\omega_u} C_{\Omega_\ell}^{\omega_\ell} \langle \gamma_u\Lambda_u; \mathbf{v}_u; \Omega_u S J_u M_u | d_q | \gamma_\ell\Lambda_\ell; \mathbf{v}_\ell; \Omega_\ell S J_\ell M_\ell \rangle. \quad (\text{B.3})$$

The evaluation of the matrix element contained in the right-hand side can be performed by recalling the definition of the eigenfunctions of Eq. (A.3), and by observing that the operator d_q acts only on the orbital variables of the electrons, and neither on the spin

variables, nor on the nuclear vibrational eigenfunctions. Moreover, one can substitute the spherical components d_q , relative to the laboratory frame, with the spherical components \hat{d}_p relative to the molecular frame by means of the equation

$$d_q = \sum_p \hat{d}_p \mathcal{D}_{qp}^1(\phi, \theta, 0)^*. \quad (\text{B.4})$$

Observing finally that the operator \hat{d}_p acts only on the electron coordinates (ξ, η, ζ) one thus obtains¹²

$$\langle \gamma_u \Lambda_u; \mathbf{v}_u; \Omega_u S J_u M_u | d_q | \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; \Omega_\ell S J_\ell M_\ell \rangle = \delta_{\Sigma_u \Sigma_\ell} \langle \mathbf{v}_u | \mathbf{v}_\ell \rangle \sum_p \langle \gamma_u \Lambda_u | \hat{d}_p | \gamma_\ell \Lambda_\ell \rangle \sqrt{(2J_u + 1)(2J_\ell + 1)} \mathcal{J}, \quad (\text{B.5})$$

where the integral \mathcal{J} , given by

$$\mathcal{J} = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \mathcal{D}_{M_u \Omega_u}^{J_u}(\phi, \theta, 0) \mathcal{D}_{M_\ell \Omega_\ell}^{J_\ell}(\phi, \theta, 0)^* \mathcal{D}_{qp}^1(\phi, \theta, 0)^*, \quad (\text{B.6})$$

can be easily evaluated through the Weyl theorem to yield

$$\mathcal{J} = (-1)^{M_\ell - \Omega_\ell + q - p} \begin{pmatrix} J_u & J_\ell & 1 \\ M_u & -M_\ell & -q \end{pmatrix} \begin{pmatrix} J_u & J_\ell & 1 \\ \Omega_u & -\Omega_\ell & -p \end{pmatrix}. \quad (\text{B.7})$$

One can then observe that the ‘‘internal’’ dipole matrix-element $\langle \gamma_u \Lambda_u | \hat{d}_p | \gamma_\ell \Lambda_\ell \rangle$ is zero unless $p = \Lambda_u - \Lambda_\ell$, which also implies, being $\Sigma_u = \Sigma_\ell$ because of the presence of the Kronecker-delta, that $p = \Omega_u - \Omega_\ell$. Moreover, such a matrix-element is independent of the various quantum numbers Ω , S , and J , which means that it is a characteristic quantity for the full band. Introducing then the notation

$$D_{u\ell} = \langle \gamma_u \Lambda_u | \hat{d}_p | \gamma_\ell \Lambda_\ell \rangle, \quad (\text{B.8})$$

and substituting Eqs. (B.5) and (B.7) into Eq. (B.3), one obtains

$$\begin{aligned} \langle \gamma_u \Lambda_u; \mathbf{v}_u; \omega_u S J_u M_u | d_q | \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; \omega_\ell S J_\ell M_\ell \rangle &= \sum_{\Omega_u \Omega_\ell} C_{\Omega_u}^{\omega_u} C_{\Omega_\ell}^{\omega_\ell} D_{u\ell} \langle \mathbf{v}_u | \mathbf{v}_\ell \rangle (-1)^{M_u - \Omega_u} \sqrt{(2J_u + 1)(2J_\ell + 1)} \\ &\times \begin{pmatrix} J_u & J_\ell & 1 \\ M_u & -M_\ell & -q \end{pmatrix} \begin{pmatrix} J_u & J_\ell & 1 \\ \Omega_u & -\Omega_\ell & \Delta\Lambda \end{pmatrix}, \end{aligned} \quad (\text{B.9})$$

where

$$\Delta\Lambda = \Lambda_\ell - \Lambda_u. \quad (\text{B.10})$$

To find the Einstein coefficient we now have to proceed to evaluate the square moduli of the matrix elements just derived and to sum over q . However, since the molecular levels are degenerate with respect to the magnetic quantum number, a further sum is in order, namely a sum over the magnetic quantum numbers of the lower level. With self-evident notations one has

$$A(\gamma_u \Lambda_u; \mathbf{v}_u; \omega_u S J_u \rightarrow \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; \omega_\ell S J_\ell) = \frac{64\pi^4}{3hc^3} \bar{\nu}^3 |\langle \mathbf{v}_u | \mathbf{v}_\ell \rangle|^2 |D_{u\ell}|^2 \mathcal{S}, \quad (\text{B.11})$$

where

$$\mathcal{S} = \sum_{M_\ell q \Omega_u \Omega_\ell \Omega'_\ell} C_{\Omega_u}^{\omega_u} C_{\Omega_\ell}^{\omega_\ell} C_{\Omega_u}^{\omega_u} C_{\Omega'_\ell}^{\omega_\ell} (2J_u + 1)(2J_\ell + 1) (-1)^{\Omega'_\ell - \Omega_u} \begin{pmatrix} J_u & J_\ell & 1 \\ M_u & -M_\ell & -q \end{pmatrix}^2 \begin{pmatrix} J_u & J_\ell & 1 \\ \Omega_u & -\Omega_\ell & \Delta\Lambda \end{pmatrix} \begin{pmatrix} J_u & J_\ell & 1 \\ \Omega'_\ell & -\Omega'_\ell & \Delta\Lambda \end{pmatrix}. \quad (\text{B.12})$$

The sum over M_ℓ and q is easily performed and simply gives a factor $(2J_u + 1)^{-1}$. Finally, one can introduce an overall Einstein coefficient for the whole band by neglecting the slight dependence of the single transitions on frequency. Defining

$$A_{\text{band}} = \frac{64\pi^4}{3hc^3} \bar{\nu}^3 |\langle \mathbf{v}_u | \mathbf{v}_\ell \rangle|^2 |D_{u\ell}|^2, \quad (\text{B.13})$$

where $\bar{\nu}$ is an ‘‘average’’ frequency for all the lines of the band, one gets the final expression

$$\begin{aligned} A(\gamma_u \Lambda_u; \mathbf{v}_u; \omega_u S J_u \rightarrow \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; \omega_\ell S J_\ell) &= A_{\text{band}} \sum_{\Omega_u \Omega'_\ell \Omega_\ell \Omega'_\ell} C_{\Omega_u}^{\omega_u} C_{\Omega_\ell}^{\omega_\ell} C_{\Omega_u}^{\omega_u} C_{\Omega'_\ell}^{\omega_\ell} (2J_\ell + 1) (-1)^{\Omega'_\ell - \Omega_u} \\ &\times \begin{pmatrix} J_u & J_\ell & 1 \\ \Omega_u & -\Omega_\ell & \Delta\Lambda \end{pmatrix} \begin{pmatrix} J_u & J_\ell & 1 \\ \Omega'_\ell & -\Omega'_\ell & \Delta\Lambda \end{pmatrix}. \end{aligned} \quad (\text{B.14})$$

An important property that is worth noticing concerns the sum of all the Einstein coefficients relative to the transitions originating from a common upper level, or, in other words, the sum \mathcal{S}' defined by

$$\mathcal{S}' = \sum_{\omega_\ell J_\ell} A(\gamma_u \Lambda_u; \mathbf{v}_u; \omega_u S J_u \rightarrow \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; \omega_\ell S J_\ell). \quad (\text{B.15})$$

¹² Note that the scalar product $\langle \mathbf{v}_u | \mathbf{v}_\ell \rangle$ appearing in Eq. (B.5) is responsible for the so-called Franck-Condon principle (see Herzberg 1950).

Substituting the expression in Eq. (B.14) for A , taking into account the orthonormality properties of the coefficients $C_{\Omega_\ell}^{\omega_\ell}$, namely

$$\sum_{\omega_\ell} C_{\Omega_\ell}^{\omega_\ell} C_{\Omega'_\ell}^{\omega_\ell} = \delta_{\Omega_\ell \Omega'_\ell}, \quad \sum_{\Omega_\ell} C_{\Omega_\ell}^{\omega_\ell} C_{\Omega_\ell}^{\omega'_\ell} = \delta_{\omega_\ell \omega'_\ell}, \quad (\text{B.16})$$

observing that the first Kronecker-delta implies a similar delta over Ω_u , and summing over Ω_ℓ and J_ℓ (which entails the disappearance of the 3-j symbols), one gets

$$S' = A_{\text{band}} \sum_{\Omega_u} C_{\Omega_u}^{\omega_u} C_{\Omega_u}^{\omega_u} = A_{\text{band}}. \quad (\text{B.17})$$

The results now obtained imply that all the upper levels share the same lifetime, $1/A_{\text{band}}$, irrespective of the coupling scheme necessary to describe both the lower and the upper electronic states.

Equation (B.14) can obviously be used to derive the expressions of the Einstein coefficients in particular cases. For instance, when both the electronic states, upper and lower, are described by pure Hund's case (a), one has

$$C_{\Omega_u}^{\omega_u} = \delta_{\omega_u \Omega_u}, \quad C_{\Omega_\ell}^{\omega_\ell} = \delta_{\omega_\ell \Omega_\ell}, \quad (\text{B.18})$$

and one gets the well known equation (Kovács 1969; Brown & Carrington 2003)

$$A(\gamma_u \Lambda_u; \mathbf{v}_u; \Omega_u S J_u \rightarrow \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; \Omega_\ell S J_\ell) = A_{\text{band}} (2J_\ell + 1) \begin{pmatrix} J_u & J_\ell & 1 \\ \Omega_u & -\Omega_\ell & \Delta\Lambda \end{pmatrix}^2. \quad (\text{B.19})$$

B.2. Expression of the Einstein coefficient using the eigenfunctions of Hund's case (b)

By means of the notations introduced in Appendix A, the upper and lower levels involved in the transition can be written in the form (see Eq. (A.25))

$$|\gamma_u \Lambda_u; \mathbf{v}_u; n_u S J_u M_u\rangle = \sum_{N_u} C_{N_u}^{n_u} |\gamma_u \Lambda_u; \mathbf{v}_u; N_u S J_u M_u\rangle, \quad |\gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; n_\ell S J_\ell M_\ell\rangle = \sum_{N_\ell} C_{N_\ell}^{n_\ell} |\gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; N_\ell S J_\ell M_\ell\rangle, \quad (\text{B.20})$$

so that we have, for the matrix element of the operator d_q ,

$$\langle \gamma_u \Lambda_u; \mathbf{v}_u; n_u S J_u M_u | d_q | \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; n_\ell S J_\ell M_\ell \rangle = \sum_{N_u N_\ell} C_{N_u}^{n_u} C_{N_\ell}^{n_\ell} \langle \gamma_u \Lambda_u; \mathbf{v}_u; N_u S J_u M_u | d_q | \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; N_\ell S J_\ell M_\ell \rangle. \quad (\text{B.21})$$

The calculation of this matrix element can be performed along the same lines as those followed in the former section. After some Racah algebra we obtain the expression

$$\begin{aligned} \langle \gamma_u \Lambda_u; \mathbf{v}_u; n_u S J_u M_u | d_q | \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; n_\ell S J_\ell M_\ell \rangle &= \sum_{N_u N_\ell} C_{N_u}^{n_u} C_{N_\ell}^{n_\ell} D_{u\ell} \langle \mathbf{v}_u | \mathbf{v}_\ell \rangle (-1)^{J_u + J_\ell - S + 1 + M_u - \Lambda_u} \\ &\times \sqrt{(2J_u + 1)(2J_\ell + 1)(2N_u + 1)(2N_\ell + 1)} \begin{pmatrix} J_u & J_\ell & 1 \\ M_u & -M_\ell & -q \end{pmatrix} \begin{pmatrix} N_u & N_\ell & 1 \\ \Lambda_u & -\Lambda_\ell & \Delta\Lambda \end{pmatrix} \left\{ \begin{matrix} J_\ell & J_u & 1 \\ N_u & N_\ell & S \end{matrix} \right\}, \end{aligned} \quad (\text{B.22})$$

from which, taking the square modulus, and summing over q and M_ℓ , we get the final result

$$\begin{aligned} A(\gamma_u \Lambda_u; \mathbf{v}_u; n_u S J_u \rightarrow \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; n_\ell S J_\ell) &= A_{\text{band}} \sum_{N_u N_\ell} C_{N_u}^{n_u} C_{N_\ell}^{n_\ell} C_{N'_u}^{n_u} C_{N'_\ell}^{n_\ell} (2J_\ell + 1) \sqrt{(2N_u + 1)(2N_\ell + 1)(2N'_u + 1)(2N'_\ell + 1)} \\ &\times \begin{pmatrix} N_u & N_\ell & 1 \\ \Lambda_u & -\Lambda_\ell & \Delta\Lambda \end{pmatrix} \begin{pmatrix} N'_u & N'_\ell & 1 \\ \Lambda_u & -\Lambda_\ell & \Delta\Lambda \end{pmatrix} \left\{ \begin{matrix} J_\ell & J_u & 1 \\ N_u & N_\ell & S \end{matrix} \right\} \left\{ \begin{matrix} J_\ell & J_u & 1 \\ N'_u & N'_\ell & S \end{matrix} \right\}, \end{aligned} \quad (\text{B.23})$$

where A_{band} is defined in Eq. (B.13).

Similarly to what was found in the former section, also in this case it is possible to prove that

$$\sum_{n_\ell J_\ell} A(\gamma_u \Lambda_u; \mathbf{v}_u; n_u S J_u \rightarrow \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; n_\ell S J_\ell) = A_{\text{band}}. \quad (\text{B.24})$$

Finally, considering the particular case when both the upper and lower electronic levels are in pure Hund's (b) coupling, being

$$C_{N_u}^{n_u} = \delta_{N_u n_u}, \quad C_{N_\ell}^{n_\ell} = \delta_{N_\ell n_\ell}, \quad (\text{B.25})$$

one gets the familiar expression (Kovács 1969)

$$A(\gamma_u \Lambda_u; \mathbf{v}_u; N_u S J_u \rightarrow \gamma_\ell \Lambda_\ell; \mathbf{v}_\ell; N_\ell S J_\ell) = A_{\text{band}} (2J_\ell + 1)(2N_u + 1)(2N_\ell + 1) \begin{pmatrix} N_u & N_\ell & 1 \\ \Lambda_u & -\Lambda_\ell & \Delta\Lambda \end{pmatrix}^2 \left\{ \begin{matrix} J_\ell & J_u & 1 \\ N_u & N_\ell & S \end{matrix} \right\}^2. \quad (\text{B.26})$$

Appendix C: Landé factors

To find the modification of resonance polarization due to the presence of a magnetic field, it is necessary to find the expressions for the Landé factors in the intermediate coupling regime between Hund's cases (a) and (b). This problem has already been solved either analytically in the case of doublets (Hill 1929) or numerically for arbitrary multiplets (Berdyugina & Solanki 2002)¹³. We give here, without formal proof, the relevant equations for the Landé factors using the same formalism as that employed throughout the whole paper. We have (Λ -doubling is irrelevant as far as Landé factors are concerned)

$$g_{\omega J} = \sum_{\Omega \Omega'} C_{\Omega}^{\omega} C_{\Omega'}^{\omega} \left[\frac{\Omega \Lambda}{J(J+1)} \delta_{\Omega \Omega'} + 2 \sqrt{\frac{(2J+1)S(S+1)(2S+1)}{J(J+1)}} (-1)^{J-S-\Lambda} \sum_q \begin{pmatrix} J & J & 1 \\ \Omega & -\Omega' & q \end{pmatrix} \begin{pmatrix} S & S & 1 \\ \Sigma & -\Sigma' & q \end{pmatrix} \right], \quad (\text{C.1})$$

$$g_{nJ} = \sqrt{\frac{2J+1}{J(J+1)}} \sum_{NN'} C_N^n C_{N'}^n (-1)^{J+S+\Lambda+1} \left[\Lambda \sqrt{(2N+1)(2N'+1)} \begin{pmatrix} N & N' & 1 \\ \Lambda & -\Lambda & 0 \end{pmatrix} \begin{pmatrix} J & J & 1 \\ N & N' & S \end{pmatrix} \right. \\ \left. + 2\delta_{NN'} (-1)^{N-\Lambda} \sqrt{S(S+1)(2S+1)} \begin{pmatrix} J & J & 1 \\ S & S & N \end{pmatrix} \right]. \quad (\text{C.2})$$

In the case of pure coupling (Hund's case (a) or (b), respectively) these expressions reduce to the well known results that can be found either in Herzberg (1950) or in Landau & Lifchitz (1967), namely

$$g_{\Omega J} = \frac{\Omega(\Lambda + 2\Sigma)}{J(J+1)}, \quad (\text{C.3})$$

$$g_{NJ} = \frac{J(J+1) + N(N+1) - S(S+1)}{2J(J+1)N(N+1)} \Lambda^2 + \frac{J(J+1) + S(S+1) - N(N+1)}{J(J+1)}. \quad (\text{C.4})$$

It is quite interesting to observe that *the sum of the Landé factors of a given multiplet is independent of the coupling scheme*. Indeed, taking into account the orthonormality properties of the coefficients C_N^n and C_{Ω}^{ω} , one gets, for a fixed J

$$\sum_{\omega} g_{\omega J} = \sum_{\Omega} \left[\frac{\Omega \Lambda}{J(J+1)} + 2 \sqrt{\frac{(2J+1)S(S+1)(2S+1)}{J(J+1)}} (-1)^{J-S-\Lambda} \begin{pmatrix} J & J & 1 \\ \Omega & -\Omega & 0 \end{pmatrix} \begin{pmatrix} S & S & 1 \\ \Sigma & -\Sigma & 0 \end{pmatrix} \right], \quad (\text{C.5})$$

or, alternatively

$$\sum_n g_{nJ} = \sqrt{\frac{2J+1}{J(J+1)}} \sum_N (-1)^{J+S+\Lambda+1} \left[\Lambda(2N+1) \begin{pmatrix} N & N & 1 \\ \Lambda & -\Lambda & 0 \end{pmatrix} \begin{pmatrix} J & J & 1 \\ N & N & S \end{pmatrix} \right. \\ \left. + 2(-1)^{N-\Lambda} \sqrt{S(S+1)(2S+1)} \begin{pmatrix} J & J & 1 \\ S & S & N \end{pmatrix} \right]. \quad (\text{C.6})$$

¹³ The paper by Hill (1929) and a further paper by Schadee (1978) also provide analytical results for the Paschen-Back regime, still in the case of doublets. The numerical treatment of the Paschen-Back regime in the more general case of multiplets is described in Asensio Ramos & Trujillo Bueno (2003, 2006).