Polarizability Factors for Molecular Bands

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Abstract. The polarimetric properties of resonance scattering in molecular bands are studied in detail for the general case where both the lower and upper electronic states of the molecule are described in the intermediate coupling scheme between Hund’s cases (a) and (b). Starting from the diagonalization of the atomic Hamiltonian, and introducing suitable numerical coefficients for the description of the energy eigenvectors, we give semi-analytical expressions for the polarizability factors under the hypothesis of the absence of atomic polarization in the lower electronic state. Similar expressions are also given for the Einstein coefficients, and the Landé factors of all the lines pertaining to a molecular band. This allows to provide approximate expressions for the linear polarization observed at the solar limb in weak molecular lines and for its modification due to the Hanle effect.

1. Introduction

It is well known that the polarimetric properties of atomic resonance lines are characterized by two line polarizability factors, $W_1$ and $W_2$, given by (Landi Degl’Innocenti 1984; Landi Degl’Innocenti & Landolfi 2004)

$$W_K(J_\ell, J_u) = 3(2J_u + 1) \left\{ \frac{1}{J_u} \frac{1}{J_u} \frac{K}{J_\ell} \right\}^2,$$  \hspace{1cm} (1)

where $J_\ell$ 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 in compact form complicated results arising in resonance scattering problems. 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 $\Omega$ to the $j$-th Stokes parameter of the radiation incident along the direction $\Omega'$, can be expressed through the compact equation

$$P_{ij}(\Omega, \Omega') = \sum_{KQ} W_K(J_\ell, J_u) (-1)^Q T^K_Q(i, \Omega) T^{-K}_{-Q}(j, \Omega'),$$  \hspace{1cm} (2)

where $T^K_Q$ is the irreducible tensor of the polarization unit vectors introduced by Landi Degl’Innocenti (1984). Similarly, the effect of a magnetic field on the scattered polarization (Hanle effect) can be easily accounted for by the following, simple modification of Eq. (2) (Landi Degl’Innocenti 1985)

$$P_{ij}(\Omega, \Omega'; B) = \sum_{KQ} W_K(J_\ell, J_u) (-1)^Q \frac{1}{1 + iHQ} T^K_Q(i, \Omega) T^{-K}_{-Q}(j, \Omega'),$$  \hspace{1cm} (3)
where \( H = 2\pi \nu_L g_u \tau_u \) is a quantity proportional to the magnetic field intensity (\( \nu_L \) is the Larmor frequency), and to the Landé factor, \( g_u \), and lifetime, \( \tau_u \), of the upper level.

Under a number of simplifying assumptions, illustrated in Sect. 3, Eqs. (2) and (3)—as well as similar equations typically encountered in resonance scattering problems—hold also for molecular lines, provided that the factors \( W_1 \) and \( W_2 \) are replaced by suitable quantities, \( W_1 \) and \( W_2 \), which can be referred to as generalized polarizability factors. Such factors have already been derived in previous papers for the spinless molecule (Landi Degl’Innocenti, Landi Degl’Innocenti, & Landolfi 1997), and for the molecule with spin in the pure coupling regime of Hund’s case (b) (Landi Degl’Innocenti 2003). In this paper we present a collection of formulae for diagonalizing the molecular Hamiltonian, and for expressing Einstein coefficients, polarizability factors, and Landé factors of all lines pertaining to a molecular band in the intermediate regime between Hund’s cases (a) and (b). We also show how such formulae can be combined to derive an approximate expression for the linear polarization that can be expected from weak molecular lines in the second solar spectrum. Apart from notations, the material concerning the matrix diagonalization and the Einstein coefficients is by no means original (see, e.g., a modern discussion in Brown & Carrington 2003), and is repeated here only for completeness. The formal derivation of the formulae presented here can be found in Landi Degl’Innocenti (2006).

2. Eigenvalues and Eigenvectors of the Molecular Hamiltonian

In many cases, molecules cannot be described by either one of the coupling schemes referred to as Hund’s cases (a) and (b). It then becomes necessary to consider the intermediate coupling scheme where the molecular part of the Hamiltonian, resulting from nuclear rotation and from spin-orbit interaction, is approximated, to lowest order, by

\[
H_{\text{mol}} = H_{\text{rot}} + H_{\text{so}} = B_e R^2 + A_e \Lambda \mathbf{n} \cdot \mathbf{S}.
\]

Apart from standard symbols commonly adopted in molecular spectroscopy, in Eq. (4), \( \mathbf{R} \) is the angular momentum due to nuclear rotation, and \( \mathbf{n} \) is the unit vector directed along the internuclear axis. We recall that \( \mathbf{R} \) combines with the total orbital electronic angular momentum, \( \mathbf{L} \), to give the angular momentum \( \mathbf{N} \) (i.e., the total orbital angular momentum due to the nuclei and to the electrons). In turn, \( \mathbf{N} \) combines with \( \mathbf{S} \) to give the total angular momentum \( \mathbf{J} \) of the molecule (with exclusion of the nuclear spin), so that \( \mathbf{J} = \mathbf{N} + \mathbf{S} = \mathbf{R} + \mathbf{L} + \mathbf{S} \).

To treat the intermediate coupling scheme it is possible to use the basis eigenfunctions of either case (a) or case (b). The Hamiltonian \( H_{\text{so}} \) is diagonal on the first basis, whereas the Hamiltonian \( H_{\text{tot}} \) is diagonal on the second basis.

The eigenfunctions of Hund’s case (a) are given, in compact notations, by

\[
|\gamma \Lambda; \nu; \Omega \Sigma J M \rangle = \sqrt{\frac{2J+1}{4\pi}} D_{M \Omega}^J(\phi, \theta, 0)^* |\Sigma \Sigma \rangle_{\text{mol}} |\gamma \Lambda; \nu \rangle.
\]

The meaning of the various quantum numbers is the following: \( \gamma \) specifies the molecular configuration of the optical electron(s); \( \Lambda \) is the projection of the
orbital angular momentum, $L$, on the internuclear axis $n$; $v$ is the nuclear vibrational number; $J$ is the total angular momentum; $M$ is the projection of $J$ along the quantization axis; $\Omega$ is the projection of $J$ along $n$; $S$ is the electron spin; $\Sigma$ is the projection of $S$ along $n$. Finally, $|SS\rangle_{mol}$ is the spin eigenvector defined in the rotating (or molecular) reference system ($\xi$, $\eta$, $\zeta$), $\zeta$ being directed along the internuclear axis. The three quantum numbers $\Lambda$, $\Omega$, and $\Sigma$ are not independent, being $\Omega = \Lambda + \Sigma$. The matrix elements of the Hamiltonian on this basis are given by the expressions

$$
\langle \Lambda; v; \Omega'SJM | H_{so} | \Lambda; v; \Omega'SJM \rangle = \delta_{\Omega\Omega'} A_e \Lambda \Sigma , 
$$

(6)

$$
\langle \Lambda; v; \Omega'SJM | H_{rot} | \Lambda; v; \Omega'SJM \rangle = B_e (\delta_{\Omega\Omega'} B - 2M) ,
$$

(7)

where

$$
B = J(J + 1) + S(S + 1) - \Lambda^2 + \Delta ,
$$

(8)

$$
\Delta = \langle \Lambda | L_2^2 + L_y^2 | \Lambda \rangle ,
$$

(9)

$$
\mathcal{M} = (-1)^{S-J+\Lambda} \sqrt{J(J+1)(2J+1)S(S+1)(2S+1)} \times \sum_q \left( \! \begin{array}{ccc} J & J & 1 \\ \Omega & -\Omega' & q \end{array} \! \right) \left( \! \begin{array}{ccc} N & S & 1 \\ M & -\Sigma & q \end{array} \! \right) .
$$

(10)

These equations allow to compute the matrix elements of the Hamiltonian, which can then be diagonalized. The diagonalization can be performed analytically only in the case of doublet terms, otherwise it has to be performed by means of numerical methods. Introducing the quantum number $\omega$ to denote the eigenvectors, these can be written in the form

$$
|\Lambda; v; \omega SJM\rangle = \sum_{\Omega} C^{\omega}_{\Omega} |\Lambda; v; \Omega SJM\rangle ,
$$

(11)

where the real coefficients $C^{\omega}_{\Omega}$ can be found numerically from the same algorithm that diagonalizes the Hamiltonian.

Similarly, the eigenfunctions of Hund’s case (b) are given, in compact notations, by

$$
|\Lambda; v; N SJM\rangle = \sum_{M_N M_S} (-1)^{N-S-M} \sqrt{2J+1} \left( \! \begin{array}{ccc} N & S & J \\ M_N & M_S & -M \end{array} \! \right) \times \sqrt{\frac{2N+1}{4\pi}} D^N_{M_N\Lambda}(\phi, \theta, 0)^* |SM_S\rangle |\Lambda; v\rangle ,
$$

(12)

where the quantum numbers $M_N$ and $M_S$ are the projections on the quantization axis of the angular momenta $N$ and $S$, respectively. The matrix elements of the Hamiltonian on this basis are given by the expressions

$$
\langle \Lambda; v; N SJM | H_{so} | \Lambda; v; N' SJM \rangle = A_e \Lambda (-1)^{J+S+N+N'-\Lambda} \times \sqrt{(2N+1)(2N'+1)S(S+1)(2S+1)} \left( \! \begin{array}{ccc} N & N' & 1 \\ \Lambda & -\Lambda & 0 \end{array} \! \right) \left( \! \begin{array}{ccc} N & S & J \\ N' & S & J \end{array} \! \right) .
$$

(13)

$$
\langle \Lambda; v; N SJM | H_{rot} | \Lambda; v; N' SJM \rangle = \delta_{NN'} B_e [N(N+1) - \Lambda^2 + \Delta] ,
$$

(14)
Similarly to the former case, these equations allow to diagonalize the Hamiltonian. Introducing the quantum number \( n \) to denote the eigenvectors, these can be expressed in the form

\[
|\gamma \Lambda; v; nSJ\rangle = \sum_N C^v_n \ |\gamma \Lambda; v; NSJM\rangle .
\]  

(15)

\section{Einstein Coefficients, Polarizability Factors, and Landé Factors}

In order to evaluate the polarizability factors of molecular lines, it is necessary to derive first the Einstein coefficients for spontaneous de-excitation. To this purpose, we consider the well-known expression that relates such 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, in standard notations, by

\[
A_{ab} = \frac{64\pi^4}{3\hbar c^3} \bar{\nu}^3 \sum_q \langle a|d_q|b\rangle^2 ,
\]  

(16)

where \( \langle a|d_q|b\rangle \) is the matrix element of the spherical component of the dipole operator. Our aim is to apply this equation to a molecular band, namely to the lines of the band, \( \gamma_a\Lambda_u; v_u; \omega_uSJ_u \rightarrow \gamma_\ell\Lambda_\ell; v_\ell; \omega_\ellSJ_\ell \), pertaining to the upper electronic state \((\gamma_u\Lambda_u)\), and the vibrational level \( v_\ell \), 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 functions either those of case (a) or of case (b). Using basis (a), one gets

\[
A(\gamma_u\Lambda_u; v_u; \omega_uSJ_u \rightarrow \gamma_\ell\Lambda_\ell; v_\ell; \omega_\ellSJ_\ell) = A_{\text{band}} \sum_{\Omega_u, \Omega_\ell} C^\omega_u_{\Omega_u} C^{\omega_\ell}_{\Omega_\ell} C^\Lambda_u_{\Omega_u} C^{\Lambda_\ell}_{\Omega_\ell} \times (2J_\ell + 1) (-1)^{\Omega_\ell - \Omega_u} \left( \begin{array}{cc} J_u & J_\ell \\ \Omega_u & -\Omega_\ell \end{array} \right) \left( \begin{array}{cc} J_u & J_\ell \\ \Omega_u' & -\Omega_\ell' \end{array} \right) \left( \begin{array}{c} 1 \\ \Delta \Lambda \end{array} \right) ,
\]  

(17)

where \( \Delta \Lambda = \Lambda_\ell - \Lambda_u \), and where, in terms of an “average” frequency, \( \bar{\nu} \), for all the lines of the band,

\[
A_{\text{band}} = \frac{64\pi^4}{3\hbar c^3} \bar{\nu}^3 \langle v_u|v_\ell\rangle^2 |D_{\text{uf}}|^2 ,
\]  

(18)

\( D_{\text{uf}} \) being the “internal” dipole matrix-element defined by (\( d_q \) are the spherical components of the dipole operator in the molecular frame)

\[
D_{\text{uf}} = \langle \gamma_u\Lambda_u|\hat{d}_p|\gamma_\ell\Lambda_\ell\rangle , \quad (p = \Lambda_\ell - \Lambda_u) .
\]  

(19)

Using the eigenfunctions of case (b), one gets

\[
A(\gamma_u\Lambda_u; v_u; n_uSJ_u \rightarrow \gamma_\ell\Lambda_\ell; v_\ell; n_\ellSJ_\ell) = A_{\text{band}} \sum_{N_u, N_\ell, \Omega_u, \Omega_\ell} C^{n_u}_{N_u} C^{n_\ell}_{N_\ell} C^\Lambda_u_{\Omega_u} C^{\Lambda_\ell}_{\Omega_\ell} \times (2J_\ell + 1) \sqrt{(2N_u + 1)(2N_\ell + 1)(2N_u' + 1)(2N_\ell' + 1)} \times \left( \begin{array}{c} N_u \\ N_\ell \\ -\Lambda_\ell \\ \Delta \Lambda \end{array} \right) \left( \begin{array}{c} N_u' \\ N_\ell' \\ \Lambda_\ell \\ -\Delta \Lambda \end{array} \right) \left\{ \begin{array}{ccc} J_\ell & J_u & 1 \\ N_u & N_\ell & S \end{array} \right\} \left\{ \begin{array}{ccc} J_\ell & J_u & 1 \\ N_u' & N_\ell' & S \end{array} \right\} .
\]  

(20)
We now pass to the determination of the polarizability factors. 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 \(b\). We assume that: \(i\) the radiation field is the same for all transitions \(c \rightarrow a\) that contribute to pump the upper level; \(ii\) all levels \(c\) are unpolarized, and \(iii\) they are populated according to their statistical weight; \(iv\) stimulated emission can be neglected. With these assumptions, the effective polarizability factor of the line, \(W_K(a, b)\), is given by

\[
W_K(a, b) = \frac{\sum_c A(a \rightarrow c) w_{JaJa}^{(K)} w_{JaJb}^{(K)}}{\sum_c A(a \rightarrow c) w_{JaJa}^{(K)}},
\]

(21)

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

\[
w_{JJ'}^{(K)} = (-1)^{1+J+J'} \sqrt{3(2J+1)} \left\{ \begin{array}{ccc} 1 & 1 & K \\ J & J' & K \end{array} \right\}.
\]

(22)

Substituting into Eq. (21) the expression of the Einstein coefficients given by either Eq. (17) or Eq. (20), and performing the sums by means of Racah algebra, one gets the following results for the polarizability factors

\[
W_K(\omega_{\ell J_\ell}, \omega_{uJ_u}) = 3(2J_u + 1) \left( \begin{array}{ccc} 1 & 1 & K \\ \Delta \Lambda & -\Delta \Lambda & 0 \end{array} \right) \left\{ \begin{array}{ccc} 1 & 1 & K \\ J_u & J_u & J_\ell \end{array} \right\} \times \sum_{\Omega_u} (-1)^{\Omega_u + J_\ell + \Delta \Lambda} (C_{\Omega_u}^{\omega_u})^2 \left( \begin{array}{ccc} J_u & J_u & K \\ \Omega_u & -\Omega_u & 0 \end{array} \right),
\]

(23)

\[
W_K(n_{\ell J_\ell}, n_{uJ_u}) = 3(2J_u + 1) \left( \begin{array}{ccc} 1 & 1 & K \\ \Delta \Lambda & -\Delta \Lambda & 0 \end{array} \right) \left\{ \begin{array}{ccc} 1 & 1 & K \\ J_u & J_u & J_\ell \end{array} \right\} \times (-1)^{S - J_\ell - \Lambda_\ell + K} \sum_{N_uN'_u} C_{N_u}^{n_u} C_{N'_u}^{n_u} \sqrt{(2N_u + 1)(2N'_u + 1)} 
\times \left( \begin{array}{ccc} N_u & N'_u & K \\ \Lambda_u & -\Lambda_u & 0 \end{array} \right) \left\{ \begin{array}{ccc} N_u & N'_u & K \\ J_u & J_u & S \end{array} \right\}.
\]

(24)

These equations show 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 \(\omega_\ell\) (see Eq. [23]) or \(n_\ell\) (see Eq. [24]). This property is strictly connected with assumptions \(i\), \(ii\), and \(iii\).

It is well known that electronic states having \(\Lambda \neq 0\) present the phenomenon of quasi-degeneracy known as \(\Lambda\)-doubling. An analysis of the influence of \(\Lambda\)-doubling on the polarizability factors shows that for all transitions except those of the form \(\Pi-\Sigma\) (in the usual notation of molecular spectroscopy where the upper state is written first and the lower state second), the expressions given in the former section for the polarizability factors are still valid. For \(\Pi-\Sigma\) transitions,
on the contrary, the expressions of the polarizability factors must be modified into the following ones

\[
W_K(N_\ell J_\ell p_\ell, \omega_u J_u \pi_u) = 3(2J_u + 1) \left\{ \frac{1}{J_u} \frac{1}{J_u} \frac{K}{J_\ell} \right\} \sum_{\Omega_u} (-1)^{K+1+\Omega_u+J_\ell} \\
\times \left[ (C_{\Omega_u}^{\omega_u})^2 \begin{pmatrix} 1 & 1 & K \\ 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} J_u & J_u & K \\ \Omega_u & -\Omega_u & 0 \end{pmatrix} \right. \\
+ (-1)^{S+J_u-\pi_u-p_\ell} C_{\Omega_u}^{\omega_u} C_{\Omega_u}^{\omega_u} \begin{pmatrix} 1 & 1 & K \\ 1 & 1 & -2 \end{pmatrix} \begin{pmatrix} J_u & J_u & K \\ \Omega_u & 2 - \Omega_u & -2 \end{pmatrix} \right],
\tag{25}
\]

\[
W_K(N_\ell J_\ell p_\ell, n_u J_u \pi_u) = (-1)^{S-J_\ell} 3(2J_u + 1) \left\{ \frac{1}{J_u} \frac{1}{J_u} \frac{K}{J_\ell} \right\} \sum_{N_u N_u'} C_{N_u}^{n_u} C_{N_u'}^{n_u} \\
\times \sqrt{(2N_u + 1)(2N_u' + 1)} \left\{ \frac{N_u}{J_u} \frac{N_u'}{J_u} \frac{K}{S} \right\} \left[ \begin{pmatrix} 1 & 1 & K \\ 1 & -1 & 0 \end{pmatrix} \left( J_u & J_u & K \right) \right. \\
+ (-1)^{N_u'-\pi_u-p_\ell} \left( \begin{array}{ccc} 1 & 1 & K \\ 1 & 1 & -2 \end{array} \right) \left( \begin{array}{ccc} N_u & N_u' & K \\ 1 & 1 & -2 \end{array} \right) \right],
\tag{26}
\]

where \(\pi_u\) is the parity of the upper state, and \(p_\ell\) is 0 or 1 according to whether the lower state is a \(\Sigma^+\) or a \(\Sigma^-\) state, respectively. It has also to be remarked that for homonuclear molecules the phenomenon of \(\Lambda\)-doubling is not present and no complications arise for the evaluation of the polarizability factors.

Finally, we pass to the expressions for the Landé factors. In the weak-field limit (Zeeman regime), the problem of finding Landé factors of molecular states in intermediate coupling has already been solved either analytically in the case of doublets (Hill 1929) or numerically for arbitrary multiplets (Berdyugina & Solanki 2002). We give here, without formal proof, the relevant equations for the Landé factors using the same formalism as that employed throughout the paper. We have (\(\Lambda\)-doubling is irrelevant as far as Landé factors are concerned)

\[
g_{\omega J} = \sum_{\Omega \Omega' \Omega''} C_{\Omega}^{\omega} C_{\Omega'}^{\omega'} \left[ \frac{\Omega \Lambda}{J(J+1)} \delta_{\Omega \Omega'} + 2 \sqrt{(2J+1)S(S+1)(2S+1)} \right] \\
\times (-1)^{J-S-\Lambda} \sum_{q} \left( J \Omega J \Omega' q \right) \left( S S -\Sigma' q \right),
\tag{27}
\]

\[
g_{nJ} = \sqrt{\frac{2J+1}{J(J+1)}} \sum_{N N'} C_{N}^{n} C_{N'}^{n} (-1)^{J+S+\Lambda+1} \\
\times \left[ \Lambda \sqrt{(2N+1)(2N'+1)} \left( \begin{array}{ccc} N & N' & 1 \\ \Lambda & -\Lambda & 0 \end{array} \right) \left( J N J S \right) \right. \\
+ 2 \delta_{N N'} (-1)^{N-S} \sqrt{S(S+1)(2S+1)} \left( J S J N \right) \\
\left. + 2 \delta_{N N'} (-1)^{N-S} \sqrt{S(S+1)(2S+1)} \left( J S J N \right) \right].
\tag{28}
\]
4. Polarization in Solar Molecular Bands

The results collected in the previous Sections can be suitably applied to the interpretation of the polarization signal detected in weak molecular bands when observing close to the solar limb. For a weak line characterized by the generalized polarizability factor $W_2$, 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)

$$\left(\frac{Q}{I}\right)_{\text{line}} = \frac{3k^A_L}{4k^{(c)}_\nu} W_2 w \frac{S_L}{B_P} \phi(\nu_0 - \nu) ,$$

where $k^A_L$ is the frequency integrated absorption coefficient of the line, $k^{(c)}_\nu$ is the continuous absorption coefficient, $w$ is the 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 $\nu_0$ of the line. The various quantities $k^{(c)}_\nu$, $w$, $S_L$, and $B_P$, and the shape of the profile $\phi$ 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 symbols $\ell$ and $u$ stand, respectively, for “lower” and “upper” level of the transition)

$$k^A_L = \frac{c^2}{8\pi\nu^2} N_{\text{mol}} \frac{1}{Z(T_{\text{exc}})} \exp \left(-\frac{E_\ell}{k_B T_{\text{exc}}} \right)(2J_u + 1) A(u \rightarrow \ell) ,$$

where $N_{\text{mol}}$ is the total number density of molecules in the lower electronic state, $T_{\text{exc}}$ 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

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

Taking into account this result, the polarization signal in the various lines of the band can be expressed through the equation

$$\left(\frac{Q}{I}\right)_{\text{line}} = K \mathcal{P}_{\text{line}} \phi(\nu_0 - \nu)$$

where $K$ is a constant for all the lines of the band, given by

$$K = \frac{3c^2}{32\pi\nu^2 k^{(c)}_\nu w} \frac{S_L}{B_P} A_{\text{band}} N_{\text{mol}} \frac{1}{Z(T_{\text{exc}})}$$

and where

$$\mathcal{P}_{\text{line}} = \exp \left(-\frac{E_\ell}{k_B T_{\text{exc}}} \right)(2J_u + 1) W_2 \frac{A(u \rightarrow \ell)}{A_{\text{band}}} .$$
Some numerical results for the MgH band that is observed around 5100 Å in the second solar spectrum are shown Fig. 1. The rotational constants and the fine structure data of the two vibro-electronic states, $A^2\Pi$ and $X^2\Sigma$, are taken from Bernath (1985).

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References
Berdyugina, S. V., & Solanki, S. K. 2002, 
Hill, E. L. 1929, Phys.Rev., 34, 1507
Landi Degl’Innocenti, E. 1984, Solar Phys., 91, 1