Molecular line scattering and magnetic field effects: Resolution of an enigma

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Abstract. The linearly polarized solar spectrum that is produced by coherent scattering processes (also called “the second solar spectrum”) is full of polarizing features due to molecular transitions, in particular from MgH and C2. Their greatly different behavior in comparison with the observed polarization from atomic transitions has presented us with a new enigma: While the scattering polarization in atomic lines is very sensitive to magnetic fields via the Hanle effect and therefore exhibits polarization signatures that vary both spatially and with the solar cycle, the molecular polarization appears to be immune to the influence of magnetic fields. To clarify these issues we here develop a theoretical foundation for polarized molecular scattering, which can serve as a general tool for interpretations of the structures in the second solar spectrum. Intrinsic polarizabilities, line strengths, and effective Landé factors for the different transitions of the P, Q, and R branches of MgH and C2 are calculated. While the intrinsic polarizabilities remain significant, the effective Landé factors are close to zero for the majority of the lines, in contrast to the behavior of atomic lines. This resolves the enigma and indicates how the molecular lines may serve as immutable reference lines against which the atomic lines can be gauged when trying to determine long-term, solar-cycle variations of the magnetic fields via the Hanle effect.

Key words. polarization – scattering – Sun: magnetic fields – molecular processes – techniques: polarimetric

1. Introduction

Coherent scattering on the Sun produces a wealth of linearly polarized spectral structures that are poorly correlated with the familiar spectral lines in the ordinary intensity spectrum. The spectrum seen in Stokes Q/I (degree of linear polarization) has therefore been referred to as the “second solar spectrum” (Ivanov 1991) because of its entirely different appearance and information contents. One of the big surprises when the richness of the second solar spectrum was first uncovered (Stenflo & Keller 1996, 1997) was the prominence of molecular contributions. While the molecular lines on the quiet Sun are very inconspicuous and barely visible, they stand out and in many spectral regions dominate the appearance of the second solar spectrum. The center-to-limb variation of their polarization amplitudes is steeper than for most of the atomic lines (Stenflo et al. 1997).

The first and successful attempt to theoretically understand the observed molecular scattering polarization for the non-magnetic case was done by Rao & Rangarajan (1999), who did radiative-transfer modelling of two Q-branch lines of MgH, at 5165.92 and 5168.14 Å, simultaneously fitting the observed Stokes I and Q/I profiles with the oscillator strength, inelastic collision rate, and depolarizing elastic collision rate as free parameters. An intrinsic molecular polarizability \( W_2 \) of 0.4 as derived from the \( J \) quantum numbers of the transition was used. \( W_2 \) is the fraction of the scattering processes that occur as polarizing dipole-type scattering (while the remaining fraction, \( 1 - W_2 \), represents isotropic, unpolarized scattering).

Recently Faurobert & Arnaud (2002) made an empirical determination of the \( W_2 \) polarizability factors for nine C2 lines and two MgH lines. In contrast to previous observations they recorded with the THEMIS telescope the scattering polarization just outside the solar limb, where the radiation comes from an optically thin layer, which allows an interpretation without model-dependent radiative transfer. They found \( W_2 \) values of 0.41 and 0.46 for MgH, and between 0.13 and 0.26 for C2. These values should however be considered as tentative until confirmed by independent observations, because off-limb observations are notoriously sensitive to spurious effects due to stray-light and seeing (cf. Keller & Sheeley 1999). As we will see, their results agree for MgH with the theory presented in...
the present paper, but for $C_2$ they disagree by a factor of two.

Magnetic fields influence the scattering polarization via the Hanle effect. The main effect when observing near the Sun’s limb is Hanle depolarization, leading to reduced polarization amplitudes when magnetic fields are present. Due to this, the appearance of the second solar spectrum varies not only spatially, with the location on the Sun, but also temporally, with the phase of the solar cycle. Due to their different sensitivities to the Hanle effect, different spectral lines are affected to different degrees by the Hanle effect. This differential Hanle effect can be used for more model-independent diagnostics of spatially unresolved magnetic fields in parameter regimes not accessible with the ordinary Zeeman effect, e.g. weak, turbulent fields (Stenflo et al. 1998).

One striking and enigmatic feature found for the differential Hanle effect is that while the atomic lines exhibit large fluctuations of their depolarization factor, the molecular lines appear to be immune to the Hanle effect. When for instance comparing the Atlas of the Second Solar Spectrum (Gandorfer 2000) that was recorded near solar activity maximum with corresponding spectral sections recorded in 1995 near activity minimum, we find the same amplitudes for the molecular lines, while the atomic lines generally have substantially smaller amplitudes, and some depolarize the continuum rather than stand out above it. Figure 1 shows an example of a section of the Atlas with identifications of Q branch lines of MgH.

In addition to the 1-D $Q/I$ spectra from the Atlas recordings at IRSOL (Locarno) that we use as examples in the present paper we have performed vector polarimetric imaging of all four Stokes parameters ($I, Q/I, U/I, V/I$) in different magnetic regions on the Sun. These recordings (still unpublished) show pronounced signatures of both the Zeeman and Hanle effects with large spatial fluctuations along the spectrograph slit, like the Stokes recordings published for the Na I D$_2$ and D$_1$ lines (Stenflo et al. 2001), but these fluctuations are only present for the atomic lines. Both the Zeeman and Hanle effect are absent in the prominent MgH and $C_2$ molecular lines, which appear immune to the influence of magnetic fields.

The aim of the present paper is to present a theoretical foundation for the interpretation of molecular lines in the second solar spectrum and to resolve the enigmatic, contrasting behavior between atomic and molecular
lines: Why are the molecular lines strongly polarizing while at the same time being immune to magnetic fields?

2. Polarizabilities of scattering transitions

2.1. Atomic case

Radiative scattering can be regarded as a two-stage process: radiative absorption followed by spontaneous emission. If the initial and final levels of a scattering process are the same, we speak of Rayleigh scattering, while if they are different we are dealing with Raman scattering. We use the notation \( J \) for the total angular momentum quantum number of an atomic state, and \( \mu \) or \( m \) for the magnetic quantum numbers of a substate. Indices \( a, b, f \) are used to mark if a substate is an initial, intermediate, or final state of the scattering process. If we let index \( \beta \) symbolize the polarization state of the incident photons, \( \alpha \) that of the scattered photons, then the complex scattering amplitude from the initial to the final state is given by the Kramers-Heisenberg dispersion formula (Stenflo 1994, hereafter S94, pp. 121–122)

\[
w_{\alpha \beta} \sim \sum_b \frac{\langle f | \hat{p} \cdot e_\beta | b \rangle \langle b | \hat{p} \cdot e_\alpha | a \rangle}{\omega_f - \omega - i\gamma/2},
\]

where the sum is taken over all intermediate substates with quantum numbers \( J_b \) and \( m \). Through this sum the coherent superposition of both the different Zeeman sublevels \( m \) and of the different total angular momentum states \( J_b \) are taken into account. \( \omega \) is the frequency of the scattered radiation, \( h\omega_f \) the energy difference between the excited and final states, and \( \gamma \) the damping constant that accounts for the broadening of the excited state, while the initial state is assumed to be infinitely sharp. \( \hat{p} \) is the position operator, which is proportional to the dipole moment operator, and \( e_\alpha, e_\beta \) are the unit polarization vectors.

To describe the transformation of the incident to the scattered Stokes vector, we form the Mueller scattering matrix \( M \) as follows:

\[
M = TW T^{-1},
\]

where \( T \) and \( T^{-1} \) are purely mathematical transformation matrices without physical contents (S94, p. 41). The elements of the radiation coherency matrix \( W \) are formed by the products of the scattering amplitudes \( w_{\alpha \beta} \) in Eq. (1):

\[
W = w \otimes w^*,
\]

if the relative populations of the initial magnetic substates \( \mu_a \) are assumed to be equal (no initial-state atomic polarization). Since \( w_{\alpha \beta} \) is a tensor, the tensor product is used (S94, p. 39).

The polarizability \( W_2 \) of a scattering transition represents the fraction of the scattering processes that behave like dipole-type (polarizing) scattering, while the remaining fraction \( 1-W_2 \) behaves like isotropic, unpolarized scattering (S94, p. 183). \( W_2 \) is expressed via the elements of the \( W \) matrix and, hence, in terms of the amplitudes \( w_{\alpha \beta} \). Therefore, in order to calculate \( W_2 \), we need to clarify first the meaning of the matrix elements \( \langle f | \hat{p} \cdot e_\alpha | b \rangle \) and \( \langle b | \hat{p} \cdot e_\beta | a \rangle \).

The scalar products between the position operator and the linear unit polarization vectors give rise to the geometrical factors \( \varepsilon_{q-q'}^{\alpha \beta} \) and \( \varepsilon_q^\beta \) (S94, p. 48) through

\[
\hat{p} \cdot e_\alpha = \sum_q \hat{r}_q \varepsilon_{q-q'}^{\alpha \beta}.
\]

These factors are formed from the complex spherical vectors \( e_q \) through \( \varepsilon_{q-q'}^{\alpha \beta} = e_q \cdot e_\alpha \cdot e_\beta \), where \( q = 0, \pm 1 \).

\[
\langle f | \hat{p} \cdot e_\alpha | b \rangle = \langle J_f \mu_f | \sum_q \hat{r}_q \varepsilon_{q-q'}^{\alpha \beta} | J_b m \rangle.
\]

However, since \( q = \mu_f - m \), only one component of the sum contributes, so that

\[
\langle f | \hat{p} \cdot e_\alpha | b \rangle = \langle J_f \mu_f | \hat{r}_q | J_b m \rangle \varepsilon_{q-q'}^{\alpha \beta}.
\]

Similarly, for the second amplitude, we obtain:

\[
\langle b | \hat{p} \cdot e_\beta | a \rangle = \langle J_a \mu_a | \hat{r}_q | J_b m \rangle^* \varepsilon_{q-q'}^{\beta}.
\]

where \( q' = \mu_a - m \).

The matrix elements in the above expressions may be expanded via the Wigner-Eckart theorem (S94, p. 145):

\[
\langle J_f \mu_f | \hat{r}_q | J_b m \rangle = (-1)^{J_b+m_f+1} \sqrt{2J_f+1} \times \left( \frac{J_b}{-m} \frac{J_f}{\mu_f-q} \right) \langle J_f | \hat{r}_q | J_b \rangle,
\]

where the reduced matrix elements \( \langle J_f | \hat{r}_q | J_b \rangle \) and \( \langle J_a | \hat{r}_q | J_b \rangle^* \) can be directly related to the oscillator strengths of the transitions \( f_b \sigma \) and \( a_b \) (S94, pp. 192 and 199):

\[
\langle J_f | \hat{r}_q | J_b \rangle \sim (-1)^{r_b} \sqrt{J_f},
\]

\[
\langle J_a | \hat{r}_q | J_b \rangle^* \sim (-1)^{r_b} \sqrt{J_a}.
\]

Here, \( r_b \) and \( r_a \) are even or odd integers depending on the quantum numbers \( L, S \) and \( J \).

Thus, finally, we obtain the expanded expression of the scattering amplitude (S94, p. 174; Stenflo 1998):

\[
w_{\alpha \beta} \sim \sum_{J_b, m} (-1)^{r_b+r_b'} \sqrt{J_b J_f \sigma b \sqrt{(2J_f+1)(2J_a+1)}} \times \left( \frac{J_b}{-m} \frac{J_f}{\mu_f-q} \right) \left( \frac{J_a}{-m} \frac{J_a}{\mu_a-q'} \right) \times (-1)^{q-q'} \Phi_{mp} \varepsilon_{q-q'}^{\alpha \beta} \varepsilon_{q}^\beta,
\]

where

\[
\Phi_{mp} = \frac{2}{i} \frac{\omega_{mp} - \omega - i\gamma/2}{\omega_{mp} - \omega - i\gamma/2}.
\]
is the normalized profile function, and
\[
\omega_{m_f} = \frac{(E_m - E_{f})}{\hbar} = \omega_f + (g_b m - g_f f) \omega_L
\]
(14)
is the frequency of the transition between the magnetic sublevels \(m\) and \(f\) expressed via the Landé factors \(g_b\) and \(g_f\) of the intermediate and final \(J\)-states. \(\omega_L\) is the Larmor frequency.

2.2. Molecular case

Extending the theory of radiative scattering from atoms to diatomic molecules implies a basic change in the symmetry of the system – from the spherical symmetry of an atom to the axial symmetry of a diatomic molecule. The axial symmetry introduces a direction in which the total electronic orbital momentum and spin can be spatially quantized. Furthermore, a third angular momentum appears due to molecular rotation. Therefore the total angular momentum of a diatomic molecule is produced by three angular momenta and depends on how strongly they interact with each other. One can distinguish between a few coupling schemes for the three momenta with respect to how they combine with each other and the so-called internal axis. Independent of the coupling scheme, the total angular momentum quantum number conserves its values and is therefore always a good quantum number (assuming that there are no or only weak external perturbations, like from an external magnetic field). Because of this, molecular Zeeman sublevels are like atomic sublevels characterized by the quantum numbers \(J\) and \(m\), the total angular momentum and its magnetic projection. Therefore radiative scattering in lines of diatomic molecules is generally described by the same expressions as given for the atomic case in Sect. 2.1. The difference appears only in calculations of the line oscillator strength, the Landé factors and the sign of the interference terms, i.e., in \(r_{ab}\) and \(r_{pf}\) all of which also depend on the electronic quantum numbers that have no analogs in the atomic case. Leaving these parameters for the next section and the Appendix, let us here consider the main question of the polarizability of molecular scattering transitions when no interference is involved.

Since all the molecular lines considered here are weak without significant dispersion wings, interference will only be of significance between transitions with the same initial and final states, when the separation between the excited states is of the same order as the damping width, or smaller. This is not the case for the majority of the lines considered here. Although such interference can be neglected in the present work, we present the theory for it in the Appendix for the sake of completeness, to serve as a foundation for future applications.

As was noted in Sect. 2.1, the linear polarizability \(W_2\) of a scattering transition is expressed through the elements of the matrix \(W\), which are functions of the quantum numbers \(J_a\), \(J_b\), and \(J_f\). Due to the selection rule \(\Delta J = 0, \pm 1\), however, the complicated expressions for \(W_2\) can be reduced to simple ones for both Rayleigh and Raman scattering. The three sequences of transitions with \(\Delta J = -1, 0, +1\) form, respectively, P, Q, R rotational branches. In the Rayleigh scattering case, when \(J_f = J_a = J\) and \(\Delta J = J_b - J\), the absorption and subsequent emission occur in the same branch line. The polarizability of these scattering transitions is as follows (S94, p. 188–189):

\[
W_2(P \rightarrow P) = \frac{(J - 1)(2J - 3)}{10J(2J + 1)},
\]
(15)
\[
W_2(Q \rightarrow Q) = \frac{(2J - 1)(2J + 3)}{10J(J + 1)},
\]
(16)
\[
W_2(R \rightarrow R) = \frac{(J + 2)(2J + 5)}{10(J + 1)(2J + 1)},
\]
(17)

In the Raman scattering case, the absorption occurs in one branch and the emission in another. This case is exhausted by three transition types with \(J_a < J_f\). Denoting again \(J_a = J\), one obtains:

\[
W_2(Q \rightarrow P) = -\frac{2J - 1}{10(J + 1)},
\]
(18)
\[
W_2(R \rightarrow Q) = -\frac{2J + 5}{10(J + 1)},
\]
(19)
\[
W_2(R \rightarrow P) = \frac{1}{10},
\]
(20)

All the cases when \(J_a > J_f\) can always be converted to one of the cases above by reversing the direction of scattering, e.g., \(W_2(Q \rightarrow R) = W_2(R \rightarrow P)\), etc.

Although these expressions are formally identical to the expressions obtained for the atomic case, their physical meaning is quite different. In the case of atoms, a single line corresponds to a single electronic transition, and the polarization of the line is unambiguously determined by the quantum numbers of the electron levels involved in the scattering process. In the case of molecules, a single electronic transition leads to the appearance of lines with different states of polarization (all the lines in R, Q, and P branches in many vibrational bands). This happens because there is a difference of several orders of magnitude between the lifetime of an excited electronic state and the period of molecular rotation: while a molecule is in an excited state, it will execute an extremely large number of rotations (as well as a large number of vibrations, which however do not affect the polarization).

In Fig. 2 the polarizability \(W_2\) for the rotational branches is plotted for the Rayleigh scattering case and for the range of \(J\) numbers that are typical for molecular lines observed in the solar spectrum. It is interesting to note that the Q branch lines have four times larger polarizability for high \(J\) numbers, \(W_2\) rapidly increases and approaches the asymptotic value 0.4 for \(J > 7.5\). The opposite behaviour is seen for R branch lines, whose polarizability rapidly decreases and approaches from above
Fig. 2. The intrinsic polarizability $W_2$ for Rayleigh scattering in molecular lines for the P, Q, R rotational branches.

The asymptotic value 0.1. The same asymptotic value is reached from below for P branch lines, whose polarizability is the lowest, only between 0 and 0.1. The asymptotic limits for the polarizability with increasing rotation, i.e., with $J$ number, have a simple classical interpretation (Feofilov 1961). Absorption and emission in lines of P and R branches may, in this limit, be described in terms of linear oscillators that are aligned with the molecular axis and therefore rotate together with it. In contrast, the processes in Q branch lines can be described in terms of oscillators that are aligned with the rotational axis of the molecule, i.e., perpendicular to the molecular axis.

In Fig. 3 the polarizability $W_2$ is plotted for the Raman scattering case. Here only two types of scattering transitions are important, namely $Q \rightarrow P$ and $R \rightarrow Q$ for $J_a < J_f$ (or correspondingly $P \rightarrow Q$ and $Q \rightarrow R$ for $J_a > J_f$). The polarizability of these transitions vary with $J$ to rapidly approach the asymptotic value $-0.2$, starting from either 0.0 or $-0.4$. The significant difference with respect to the Rayleigh scattering case is that $W_2$ is negative. This means for instance that incoming light, which is linearly polarized perpendicular to the scattering plane, becomes polarized parallel to the scattering plane when emerging from the scattering event (S94, p. 189). Thus Raman scattering may reverse the state of the linear polarization, in contrast to Rayleigh scattering.

Let us finally note that the above polarization properties of the rotational branches are the same for all types of electronic transitions and all vibrational bands of diatomic molecules as long as $J$ is a good quantum number.

3. Molecular Landé factors and intensity factors

The axial symmetry of a diatomic molecule causes the emergence of new electronic quantum numbers not present in the atomic case: the projections $\Lambda$ and $\Sigma$ of the orbital angular momentum and spin on the internuclear axis. These projections can be defined if the electronic momenta are strongly coupled to the axis and to each other. This case, which implies strong spin-orbit coupling, is called Hund’s case (a) (cf. Herzberg 1950). The interaction of the electronic momenta with the rotation of the molecule may cause partial or complete decoupling from the internuclear axis. It is the spin that more often gets decoupled. This case of weak spin coupling is called Hund’s case (b). In this case the spin interacts stronger with rotation, and its projection onto the internuclear axis cannot be defined.

Since the magnetic moment of a molecule is determined by the electronic momenta, the expressions for the Zeeman effect depend on which spin coupling case applies. For pure Hund’s cases, the expressions for the Landé factors are rather simple, while for partial decoupling, perturbation calculations are needed (cf. Berdyugina & Solanki 2002).

The Zeeman effect in atomic and molecular lines differ in one fundamental respect. Since molecular rotation contributes to the total angular momentum, $J$ can have values much larger than what is possible in the atomic case, in which only the electronic angular momenta contribute to $J$. As $J$ increases, the relative contribution of rotation to $J$ also increases, while the magnetic moment of the molecule does not change significantly, since the rotational contribution to the magnetic moment is three
orders of magnitude smaller than the corresponding contribution of the electronic momenta. Therefore the ratio between the magnetic moment of a molecule and its total angular momentum rapidly decreases, which is reflected in the behaviour of the Landé factors.

Below we will consider the electronic transitions of MgH \(^{A2}\Pi - X^{2}\Sigma\) and \(C_2 d^{3}\Pi - a^{3}\Pi\), since numerous bands of each have been observed in the photospheric spectrum as well as in the second solar spectrum.

### 3.1. MgH \(^{A2}\Pi - X^{2}\Sigma\)

Berdyugina & Solanki (2002) have analysed the magnetic properties of this band system in the Zeeman regime (which is relevant also for the present problem) and concluded that the partial decoupling of the spin for the upper electronic state results in significant perturbations of the Zeeman-split rotational levels with \(J < 15.5\). The ground state is described by the pure Hund’s case (b), since for \(\Sigma\)-states \(\Lambda = 0\), and the spin is completely decoupled from the internuclear axis. Note, however, that the coupling of spin with rotation is also not very strong and can easily be destroyed by rather weak external magnetic fields. This would imply a transition to the Paschen-Back regime. For the ground electronic state of MgH, the field strength for which the Paschen-Back effect needs to be taken into account is only 280 G for the very first rotational levels. This value increases with rotation.

In Fig. 4 we give the Landé factors for the doublet rotational levels of the upper and lower states. For the upper state they have been calculated with the perturbation algorithm for partial spin decoupling described by Berdyugina & Solanki (2002). For the lower state they have been computed using the expression for the pure Hund’s case (b),

\[
g = \frac{1}{J(J+1)} \left\{ \frac{\Lambda^2}{2N(N+1)} \times \left[ J(J+1) + N(N+1) - S(S+1) \right] + J(J+1) - N(N+1) + S(S+1) \right\}, \tag{21}
\]

and inserting \(\Lambda = 0\) for the lower \(\Sigma\)-state. \(S\) is the spin quantum number (in our case \(S = 1/2\)), while \(N\) is the quantum number for the total angular momentum excluding spin. \(N\) can have the integral values \(N = 0, 1, \ldots\) (i.e., for the \(\Sigma\)-state \(N = 0, 1, \ldots\)). The total angular momentum including spin, \(J\), is then formed from \(N\) and \(S\) as follows: \(J = N + S, N + S - 1, \ldots, |N - S|\). Here we thus have \(J = N + 1/2\) and \(N - 1/2\), which leads to the doublet levels \(T_1\) and \(T_2\). Note that Eq. (21) with \(\Lambda = 1\) can also be used to accurately predict Landé factors for the upper, \(\Pi\)-state, levels with \(J > 15.5\), for which Hund’s case (b) becomes a good approximation.

One can see from Eq. (21) that there is a clear difference between the Zeeman splitting (or Landé factors) of atomic and molecular lines. While the Landé factor of an average atomic line is typically about unity, Landé factors of molecular lines are on average very close to zero (although exceptions exist, see Berdyugina & Solanki 2002). The explanation for this behavior was given in the beginning of this section. In contrast, the probability amplitudes of the Zeeman transitions are identical for the atomic and molecular lines as was concluded in Sect. 2.
Fig. 4. The Landé factors of the upper and lower multiplet sublevels $T'$ and $T''$ of MgH.

Fig. 5. The effective Landé factors for the rotational branches of the MgH lines: $R_1$ and $R_2$ – solid curves, $Q_1$ and $Q_2$ – dashed, $P_1$ and $P_2$ – dashed-dotted.

The behaviour of the Landé factors for both states of the MgH green system is that the splitting of the levels becomes independent of $J$ as $J$ increases, while the Landé factors rapidly approach zero (for details, see Berdyugina & Solanki 2002). As a consequence, the effective Landé factors for the very first rotational transitions are the largest, as shown in Fig. 5. The most magnetically sensitive lines are thus excited from the levels with $J < 10.5$. Note also the negative effective Landé factors, which are quite common for molecular transitions (Berdyugina & Solanki 2002).

In the second solar spectrum only MgH lines of the $Q_1$ and $Q_2$ branches are observed to be prominent.
To explain this, we have in Fig. 6 calculated for all rotational branches of the (0, 0) band the absorption intensity factors defined as follows:

\[ I_{J'0} = f_{J'0} N_{\text{max}} (2J'' + 1) \exp\left(-\frac{E_{J''}}{kT}\right), \]

(22)

where \( f_{J'0} \) is the absorption oscillator strength of the transition \( J'' \rightarrow J' \) and \( E_{J''} \) is the lower level excitation energy. They were calculated for the intermediate Hund’s case (for details, see Appendix) with molecular constants from Bernath et al. (1985) and the (0, 0) band oscillator strength, \( f_{00} = 0.161 \), from Kirby et al. (1979). The calculation has been done with the model of the solar atmosphere by Grevesse & Sauval (1999) for the layer where the number density of MgH reaches its maximum, \( N_{\text{max}} \), where the temperature is \( T = 5538 \) K. This maximum is located well below the temperature minimum because the molecular number density is proportional to the product of the number densities of the atoms that make up the molecules. It is clearly seen from Fig. 6 that the intensity of the Q branches is twice as large as that of the other branches. Combining this with the strong polarizability of the Q branches, we conclude that indeed only these lines should stand out in the observed second solar spectrum.

In our calculations Local Thermodynamic Equilibrium (LTE) and chemical equilibrium have been assumed. It has been shown that these assumptions are valid for molecular opacities in solar and stellar atmospheres, and no deviations from LTE level populations have been found observationally (cf. Johnson 1994). The most significant non-LTE effect on molecular opacities can arise from over-ionization of neutral atoms, which might reduce the pool from which molecules can be made. This effect will not occur for molecules composed of the abundant elements H, C, N, and O because of their large ionization potentials (11–15 eV). MgH might in principle be affected by over-ionization of Mg, whose ionization potential is 7.6 eV. The effect is however negligible for the Sun, since the difference in the Mg abundance determined from Mg I and Mg II lines is only 0.05 dex (Lambert & Luck 1978).

3.2. \( C_2 d^3 \Pi - a^3 \Pi \)

The magnetic properties of the Swan system of \( C_2 \) in the Zeeman regime have been investigated by Berdyugina & Solanki (2002). They concluded that both the upper and lower electronic states of the system are subject to intermediate spin coupling. However, deviations from the pure Hund’s case (b) due to incomplete spin decoupling are only seen for small \( J \), while lines with \( J \geq 10 \) are well described by case (b). Equation (21) can for instance be used for levels with higher \( J \) numbers. In general, the magnetic sensitivity of lines from this system is not very large as compared with for instance the MgH band system. The Zeeman regime is appropriate for the \( C_2 \) lines up to field strengths as large as 70 kG.

The triplet structure of the \( C_2 \) levels is caused by the three different combinations of \( N \) and \( S = 1 \), namely \( J = N + 1, N, \) and \( N - 1 \). They give rise to the three rotational terms \( T_1, T_2, \) and \( T_3 \). In Fig. 7 we present the Landé factors for the triplet terms of the upper (\( T' \)) and lower (\( T'' \)) states. For both states they were calculated using the perturbation algorithm for partial spin decoupling given by Berdyugina & Solanki (2002). The behaviour of the Landé factors is similar to that of the MgH lines, i.e., they are larger for smaller \( J \) and rapidly decrease as \( J \).
Table 1. Parameters for the Q1 and Q2 lines of MgH.

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<th>$W_2$</th>
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Increases. This is also reflected in the behaviour of the effective Landé factors of the lines shown in Fig. 8.

In the second solar spectrum, only the C2 lines of the P and R branches are clearly observed, while the lines of the Q branches are missing. Examples of the observed scattering polarization in the P and R branch lines are given in Figs. 9 and 10. This difference with respect to MgH can be understood if line strengths are taken into account. Since in the Swan system both the upper and lower electronic states have the same $\Lambda$, i.e., $\Delta \Lambda = 0$, the branches with $\Delta J = 0$, i.e., the Q branches, decrease very rapidly in intensity with increasing $J$ and are therefore most often not observed. This is clearly shown in Fig. 11, where the intensity factors $I_{J, P}$, for the $(0, 0)$ band of the Swan system calculated with Eq. (22) are presented. In this equation, $E_{J}$ and $f_{J, P}$ were calculated for the intermediate Hund's case (see appendix) using molecular constants from Huber & Herzberg (1979) and the $(0, 0)$ band oscillator strength, $f_{00} = 2.55 \times 10^{-2}$, from Cooper & Nicholls (1976). The calculation was again done with the model of the solar atmosphere by Grevesse & Sauval (1999) for the layer where the number density of C2 reaches its maximum, where the temperature is $T = 5440$ K. We can therefore conclude that C2 lines of the Q branches are not observed in the second solar spectrum because of their very low transition probabilities. Thus only lines of P and R branches are of interest. In Table 2 we list their wavelengths according to Phillips & Davis (1968), polarizabilities $W_2$ calculated for the effective Landé factors $g$.

From Fig. 11 we note that the intensity factors become very small for small values of $J$. This causes the P and R branch polarization to be very small or practically absent in lines with low $J$ values, as illustrated in Fig. 12 for R branch lines of C2. The observations thus confirm that the polarization amplitudes scale with the product between the intensity factors and $W_2$.

It is interesting to note that the polarization observed in the C2 P and R branch lines is stronger than the polarization in MgH Q branch lines, although, as was shown in Sect. 2.2, the theoretical polarizability of Q lines is on average 4 times larger as compared with P and R lines for any given molecule. This paradox is however resolved if we account for the relative C2 and MgH intensity factors. Due to the significantly different dissociation energies of C2 and MgH (6.11 eV and 1.27 eV, respectively), the maximum number density in the solar photosphere is 60 times larger for C2 than for MgH. The difference is however reduced by the smaller band oscillator strength of C2: $f_{00}(C_2)/f_{00}(MgH) = 0.16$. The final ratio of the intensity factors is therefore $I_{J, P}(C_2)/I_{J, P}(MgH) = 9.5$. This is clearly seen from Figs. 6 and 11. When we now account for the factor of four difference in the polarizabilities, we expect that the polarization in the C2 lines of the solar spectrum should be on average at least twice that of the MgH lines. This conclusion is consistent with the observations.

4. Resolution of the enigma and discussion

With the theoretical tools that we have now developed, we are able to clarify the enigmatic behavior of the molecular lines. The main puzzle, why the molecular lines seem to be immune to the Hanle effect, is resolved by the combination of significant intrinsic polarizability $W_2$ and very
small Landé factors. Most molecular lines have, in contrast to most atomic lines, large angular momentum quantum numbers $J$. When the electron spin $S$ remains small, the Landé factor goes asymptotically to zero as $J$ increases according to Eq. (21).

As molecular transitions with small $J$ are not immune to magnetic fields, it should in principle be possible to observe the Hanle effect for them. However, the intensity factors, which determine the effective strength of the lines as they appear in the solar spectrum, become small when $J$ is small. Since the polarization amplitudes scale with the intensity factors, the lines with significant Landé factors will have vanishing polarization signals. As a consequence all the molecular lines with strong scattering polarization are insensitive to magnetic fields.

The reason why we for MgH only see the Q branch lines in the second solar spectrum is two-fold: (1) the polarizability factor $W_2$ is four times larger for the Q branch.
Fig. 9. 17 Å section of the second solar spectrum, from the atlas of Gandorfer (2000) like in Fig. 1, but here illustrating the polarizing molecular lines from the P branch of C$_2$. The numbers in the brackets are the total angular momentum quantum numbers $J$ for the lower level of the transition. Note that while all the lines with high $J$ numbers have prominent polarization peaks, the three lines with small $J$ (2 and 3) marked in the lower right-hand corner of the diagram have no significant polarization. This behavior is explained by Fig. 11 below and in the text.

Fig. 10. Similar to Fig. 9, but this time illustrating the C$_2$ polarization of R branch lines with high $J$ number (given in the brackets for the lower level of the molecular transition).

than for the P and R branches. (2) The intensity factor, which determines the effective line strength, is about twice as large for the Q branch as compared with the P and R branches. The combination of these two factors means that the polarization amplitudes of Q branch lines are expected to be eight times larger than the amplitudes of the P and R branch lines. Therefore only the Q branch lines stand out in the observed spectrum.
The situation is different for the $C_2$ lines. Their Q branch lines are missing in the solar spectrum, because they have intensity factors that are almost zero, in contrast to the P and R branch lines. It may seem paradoxical that the observed polarization amplitudes of the $C_2$ P and R branch lines are often larger than the amplitudes of the MgH Q branch lines, although the intrinsic polarizability $W_2$ is four times smaller ($\approx 0.1$) and the band oscillator strength six times smaller for $C_2$ than for MgH. Both of these two large factors are however more than compensated for by an even larger factor in favor of $C_2$: due to the substantially higher dissociation energy for $C_2$ the number density in the solar atmosphere is about 60 times larger for $C_2$ than for MgH. When accounting for the difference in
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Table 2. Parameters for the P and R branch lines of C\(_2\).

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Table 2. continued.
oscillator strength we find that the intensity factors for C\textsubscript{2}
are larger than those of MgH by a factor of about ten. The
observations confirm that the polarization amplitudes do
indeed scale not only with the polarizability W\textsubscript{2}, but with
the product of W\textsubscript{2} with the respective intensity factors.

Recently Faurobert & Arnaud (2002) determined em-
pirical values for the polarizability factor W\textsubscript{2} for nine
C\textsubscript{2} lines and two MgH lines in the wavelength range
5157–5161 Å. The determinations were based on obser-
vations of the scattering polarization amplitudes just out-
side the solar limb, where the molecular lines stand out
in emission against a weak continuous background spec-
trum. Off-disk observations have the advantage that de-
pendence of the interpretation on radiative transfer can
be avoided, since the emitting layer is optically thin. The
disadvantage is however that such observations are no-
toriously sensitive to stray light, which has a multitude of
sources (seeing fluctuations, sky background, instrumen-
tal scattering). A large stray light background has to be
subtracted from the observations before an interpretation
of the spectral features is possible. Based on such obser-
vations, Faurobert & Arnaud (2002) find values for W\textsubscript{2}
of 0.41 and 0.46 for the two MgH lines, which is in good
agreement with the theoretical value of 0.40 according to
our Table 1. For the nine C\textsubscript{2} lines, however, they find val-
ues spread between 0.13 and 0.26, while according to our
Table 2 the theoretically predicted value is 0.09, smaller
by approximately a factor of two. It would be important
to clarify the nature of this discrepancy, by independent
and more extensive observations, as well as by theoretical
modelling of the scattering polarization in these lines.

With the theoretical foundation that we have de-velope
d here we now have an adequate tool for more system-
atic explorations and interpretations of the second solar
spectrum. Since the intensity factors depend on the phys-
ical conditions in the temperature minimum region of the
Sun, the absolute values of the polarization amplitudes
may be used to diagnose this region. The magnetic invari-
ance of the molecular lines makes them suitable to serve as
immutable reference lines against which the polarization
fluctuations in the atomic lines due to the Hanle effect
can be gauged and calibrated. This is of particular im-
portance if one wants to pursue a project to determine
the long-term, solar-cycle variations of the Hanle depo-
larization in atomic lines. By normalizing the polarization
scale to the immutable molecular lines, subtle, small drifts
that could possibly occur in the polarization scale of the
measurements could be eliminated.

**Acknowledgements.** The observations were carried out with
ZIMPOL at IRSOL (Istituto Ricerca Solari Locarno). The
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ZIMPOL system and provided the technical support. The
ZIMPOL development program and one of the authors
(A.G.) have been funded by the Swiss Nationalfonds, grant
no. 20-56853.99. IRSOL receives funding from the canton
of Ticino, the city of Locarno, ETH Zurich, and the Swiss
Nationalfonds.

### Table A.1. Sign of the phase factor for atomic transitions.

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<td>+</td>
</tr>
<tr>
<td>0</td>
<td>±*</td>
<td>±</td>
</tr>
<tr>
<td>–1</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

* Upper sign for transitions with \(J(J+1) \geq S(S+1) - L(L+1)\), lower sign if otherwise.

### Appendix A: Sign of the interference terms

#### A.1. Atomic lines

The sign of the interference terms is determined by the phase factor of the reduced matrix element

\[
\langle J''|\hat{\sigma}|J'\rangle = \langle L''S'\rangle|\hat{\sigma}|L'S'J'\rangle
\]

\[
= (-1)^{L''+S'+J'+1} \left\{ \begin{array}{ccc} L'' & L' & 1 \\ J' & J'' & S' \end{array} \right\}
\]

\[
\times \sqrt{2J'+1}\sqrt{2L''+1}\langle L''|\hat{\sigma}|L'\rangle.
\]

or, more specifically, by the sign of the product between the first factor on the right hand side (the power of \((-1)\)) and the 6-\(j\) symbol (594, p. 199). This sign is expressed in terms of the parameters \(r_{ab}\) and \(r_{ij}\) denoted here as \(r_{J'' J'}\),

where \(J''\) and \(J'\) are the quantum numbers of the lower and upper levels, respectively (cf. Eqs. (10) and (11)). The
sign is given in Table A.1.

#### A.2. Molecular lines

The sign of the interference terms for molecular transitions is also determined by the phase factor of the reduced matrix element as was concluded in Sect. 2.2. In diatomic molecular spectroscopy uniform and consistent conven-
tions for the electronic transition moments and the rota-
tional line intensities have been formulated by Whiting et al. (1980) following the definition given by Hougen
(1970). The expression for the reduced matrix element of a diatomic molecule is known to depend on the way the angular-momentum operators couple to form their resul-
tant, i.e., it is different for different Hund’s cases. It has
however not been thoroughly discussed whether the phase
factor of the molecular matrix elements is sensitive to the
angular momentum coupling scheme. Below we present an
extended discussion of the subject and try to explain in
general physical terms the behaviour of the sign that we
derive from the equations.

#### A.2.1. Hund’s case (a)

In Hund’s case (a), when the orbital angular momentum
and the spin are strongly coupled to each other and to
the internuclear axis, they have the projections \(\Lambda\) and \(\Sigma\), respectively, which together form the total electronic an-
gular momentum about the internuclear axis: \(\Omega = \Lambda + \Sigma\)
with quantum numbers $\Omega = |\Lambda + \Sigma|$. Then the total angular momentum $J$ is formed from $\Omega$ and the angular momentum of nuclear rotation, and has quantum numbers $J = \Omega, \Omega + 1, \Omega + 2, \ldots$. The matrix elements of a diatomic molecule in Hund’s case (a) are known expressions (e.g. Hougen 1970; Landau & Lifshits 1963). Here we present them in a more general form, in terms of the rotation group. Thus, if a molecular transition occurs between states described by Hund’s case (a), the reduced matrix element is the product of the Clebsch-Gordan coefficient and another reduced matrix element:

$$
\langle J''|\hat{P}|J'(a) = \langle J''\Omega''|l l J'\Omega'\rangle\langle v'|\hat{P}|v''\rangle
$$

$$
= (-1)^{J''+\Omega''+1}\sqrt{2J''+1}\left(\begin{array}{c} J'' \\ \Omega'' \\ J' \\ \Omega' \end{array}\right)
\times\langle v'|\hat{P}|v''\rangle.
$$

(A.2)

where $l = \Omega'' - \Omega'$. The matrix element $\langle v'|\hat{P}|v''\rangle$ represents the amplitude of the transition between vibrational states $v'$ and $v''$, i.e., it is proportional to the square root of the vibrational band oscillator strength, $\sqrt{f_{v'v''}}$. Note that it is symmetric with respect to the direction of the transition, and it is canceled out when forming the polarizability of the rotational transition within a given band is calculated. The sign of the interference term in this case is therefore determined by the phase factor of the Clebsch-Gordan coefficient, namely the power of $(-1)$ and the sign of the $3-j$ symbol. It is given in Table A.2 for different transition types.

The dependence of P and R branch transitions on the sign of $\Delta \Omega$ can be understood if we recall that in a classical interpretation they can be described in terms of linear oscillators that are aligned with the molecular axis and rotate together with it, while $\Omega$ is by definition oriented along this axis. In contrast, transitions in Q branches can be described in terms of oscillators that are perpendicular to the molecular axis, and their sign is not affected by the sign of $\Delta \Omega$. Furthermore, since in Hund’s case (a) only transitions with $\Delta \Sigma = 0$ are allowed, it is the sign of $\Delta \Lambda$ that determines the sign of $\Delta \Omega$ and, thus, the sign of the interference term.

### A.2.2. Hund’s case (b)

In Hund’s case (b), when the spin is decoupled from the internuclear axis, the projection $\Sigma$, and thus $\Omega$, is not determined. Therefore, firstly, the total angular momentum excluding spin $N$ is formed from $\Lambda$ and the rotation with quantum numbers $N = \Lambda, \Lambda + 1, \Lambda + 2, \ldots$, and, secondly, the total angular momentum $J$ is formed from $N$ and $S$ with quantum numbers $J = N + S, N + S - 1, \ldots, |N - S|$. In Hund’s case (b) only transitions with $\Delta N = 0$ are allowed. The resulting reduced matrix element for molecular transitions between states described by Hund’s case (b) is then

$$
\langle J''|\hat{P}|J'(b) = \langle -1\rangle_{N''+\Lambda''+1}\left(\begin{array}{c} N'' \\ \Lambda'' \\ J' \\ S \end{array}\right)
\times\langle v'|\hat{P}|v''\rangle.
$$

(A.3)

where $k = \Lambda'' - \Lambda'$. Here again, the reduced matrix element $\langle v'|\hat{P}|v''\rangle$ represents the amplitude of the transition between vibrational states $v'$ and $v''$. As in Hund’s case (a) it divides out when forming the polarizability $W_2$. The sign of the interference term in this case is thus determined by the power of $(-1)$ and the signs of the 6-j and 3-j symbols. The sign of the first row in Eq. (A.3) is the same as in the atomic case given by Eq. (A.1) with $L$ replaced by $N$, while the sign of the second row is the same as in Hund’s case (a) given by Eq. (A.2) and Table A.2, with $\Omega$ and $J$ replaced by $\Lambda$ and $N$, respectively.

Here we consider only transitions in the main rotational branches, for which $\Delta J = \Delta N$. Then the resulting signs of the transitions in the R and P branches are the same as in Hund’s case (a), while in the Q branches more complicated relations appear (see Table A.3). Taking into account that $J = N + S, \ldots, |N - S|$ for given $N$ and $S$, the signs of the corresponding Q branch transitions will be positive if $J \geq 0, \ldots, S$. This means that all but the first few Q branch transitions have positive sign as in Hund’s case (a).

Let us consider, for example, the MgH $A^2\Pi - X^2\Sigma$ system, for which $S = 1/2$ and $\Delta \Lambda = +1$. The first rotational transitions in the Q1 and Q2 branches arise from levels with $J_1 = 1.5$ and $J_2 = 0.5$, respectively, i.e., $N = 1$. The interference term of these transitions is positive, because $S(S + 1) - N(N + 1) < 0$. This is also valid for all the other transitions in the Q branches.

The resistance of the sign of the interference term in the P and R branches to change between cases (a) and (b) can be explained by the key role played by the sign of $\Delta \Lambda$. 

---

### Table A.2. Sign of the phase factor for molecular transitions with Hund’s case (a). Here, $\Delta \Omega = \Omega'' - \Omega'$ and $\Delta J = J' - J''$. 

<table>
<thead>
<tr>
<th>Branch</th>
<th>$\Delta J$</th>
<th>$(-1)^{J''+\Omega''+1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>$+1$</td>
<td>+</td>
</tr>
<tr>
<td>Q</td>
<td>$0$</td>
<td>+</td>
</tr>
<tr>
<td>P</td>
<td>$-1$</td>
<td>+</td>
</tr>
</tbody>
</table>

### Table A.3. Sign of the phase factor for molecular transitions with Hund’s case (b). Here, $\Delta \Lambda = \Lambda'' - \Lambda'$. 

<table>
<thead>
<tr>
<th>Branch</th>
<th>$\Delta J$</th>
<th>$(-1)^{J''+\Omega''+1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>$+1$</td>
<td>+</td>
</tr>
<tr>
<td>Q</td>
<td>$0$</td>
<td>+</td>
</tr>
<tr>
<td>P</td>
<td>$-1$</td>
<td>+</td>
</tr>
</tbody>
</table>

* Upper sign for transitions with $J(J+1) \geq S(S+1) - N(N+1)$, lower sign otherwise.
(cf. the explanations in Sect. A.2.1), and $A$ is a good quantum number for the case (b) coupling scheme. The decoupled spin however tries to affect the sign of the $Q$ branch transitions, which are associated with linear oscillators perpendicular to the molecular axis. The larger the spin value, the more the first transitions are affected, which means that the sign of their interference terms may be changed to become negative.

A.2.3. Intermediate Hund’s case (ab)

In the intermediate case between Hund’s cases (a) and (b), the spin is only partly decoupled from the internuclear axis. Then the reduced matrix element can only be calculated with perturbation theory. In general it can be expressed in terms of a linear combination of the unperturbed amplitudes, either through $\langle J''\vert \tilde{\hat{M}}\vert J'\rangle^{(a)}$ or $\langle J''\vert \tilde{\hat{M}}\vert J'\rangle^{(b)}$:

$$
\langle J''\vert \tilde{\hat{M}}\vert J'\rangle^{(ab)} = \sum_{\Sigma = -S}^{+S} \left( C^{(a)}_{\Sigma N} C^{(a)}_{\Sigma N'} \langle J''\vert \tilde{\hat{M}}\vert J'\rangle^{(a)} + C^{(b)}_{\Sigma N} C^{(b)}_{\Sigma N'} \langle J''\vert \tilde{\hat{M}}\vert J'\rangle^{(b)} \right),
$$

(A.4)

where $C^{(a)}_{\Sigma N}$ and $C^{(b)}_{\Sigma N}$ are the elements of the eigenvectors of the perturbation matrices that transform the case (a) or (b) wavefunctions into the intermediate case wavefunctions. Analytical expressions for $C^{(a)}_{\Sigma N}$ are given by Kovács (1969) for many electronic states. Practical information on the calculation of perturbation matrices for any electronic states can be found in the recent paper by Berdyugina & Solanki (2002).

Since the sign of the interference term for all the P and R branches and for most transitions in the $Q$ branches are identical for Hund’s cases (a) and (b), it is logical that it will conserve its value also in the intermediate case (recollecting that $A$ is a good quantum number for both cases). Only for the first few transitions in the $Q$ branches detailed calculations are needed. Depending on the value of the spin and on how strongly it is coupled to the internuclear axis, the sign for $Q$ branch transitions may be either positive or negative. These lines are however of very low intensity and are therefore not of practical interest.

Appendix B: Oscillator strengths of molecular lines

According to the convention of Whiting et al. (1980), the absorption oscillator strength of the molecular transition can be expressed via the reduced matrix element considered in Sect. A.2 in the same way as for atomic lines (cf. S94, p. 160):

$$
f_{J',J''} = \frac{8\pi^2 m_e v_{J',J''}}{3h} |\langle J''\vert \tilde{\hat{M}}\vert J'\rangle|^2,
$$

(B.1)

where $v_{J',J''}$ denotes the energy difference between the upper and lower rotational levels. According to the description given in Sect. A.2, the square of the reduced matrix element in the above expression can be written as a product of two factors. We then obtain

$$
f_{J',J''} = \frac{8\pi^2 m_e v_{J',J''}}{3h} |\langle J''\vert \tilde{\hat{M}}\vert J'\rangle|^2 \left( \frac{S_{J',J''}}{2J'' + 1} \right)
$$

$$
= f_{v'v''} \nu_{J',J''} \frac{S_{J',J''}}{2J'' + 1}
$$

(B.2)

where $f_{v'v''}$ is the ($v',v''$) band oscillator strength, $\nu_{v'v''}$ is the energy difference between the upper and lower vibrational states, and $S_{J',J''}$ is the dimensionless Hön-London factor. Note that $f_{v'v''}$ and $S_{J',J''}$ are symmetric with respect to the direction of the transition, i.e., they are the same for absorption and emission.

It is clear that the Hön-London factors are different for different coupling cases. In Hund’s case (a), simple analytical expressions can easily be obtained from Eq. (A.2) (they have been tabulated, e.g., by Kovács 1969 and Berdyugina & Solanki 2002). In Hund’s case (b), Hön-London factors for a given electronic transition can also be rather easily expressed via Eq. (A.3), and the final formulae look almost as simple as in Hund’s case (a) (cf. Schadee 1969). Analytical expressions for some electronic transitions governed by the intermediate Hund’s case (ab) have been obtained by Kovács, but they are rather complicated, and it is more practical to calculate them numerically with the expansion of Eq. (A.4). The normalization of the Hön-London factors should be done according to the convention of Whiting et al. (1980).

Finally note that for transitions between states with $\Lambda \neq 0$, the lines appear as close doublets because of the $\Lambda$-type doubling. The definition of the rotational line strength given by Whiting et al. (1980) implies that a $\Lambda$-doublet is composed of two rotational lines. Therefore, if such a doublet is not resolved in the observed spectra, the increase of absorption or emission in the blend is to be accounted for by adding the contributions from two rotational lines whose theoretical strengths are identical.

References

Hougen, J. T. 1970, The calculation of rotational energy levels and rotational line intensities in diatomic molecules, NBS Mon., 115


