there is no particular reason, from the point of view of atomic physics[4] , that may substantiate the statement by Berdyugina et al. (2002) according to which molecular lines should be "immune" to the Hanle effect.

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Discussion

J.O. STENFLO: Our observations show that the molecular lines are immune to the Hanle effect, in contrast to the atomic lines. The main signature of the Hanle effect is spatial variations of the scattering polarization along the spectrograph slit, which are seen in atomic lines but not in moleculare lines. Do you have an explanation for this "enigma"?

E. LANDI DEGL'INNOCENTI: Unfortunately, I do not think that there is a simple explanation for this behavior. According to my opinion, this is a further example of those mysteries that we still do not understand in the second solar spectrum, but which urgently need to be clarified before the observations of resonance polarization at the solar limb may really become a useful diagnostic tool for the study of solar magnetism.

[4]Indeed, there is another physical process that may contribute to decrease the life-time τ of the molecular levels. This is the phenomenon of *predissociation* that can take place when a level has an energy larger that the dissociation energy of the molecule. In this case, it is possible to have a radiationless transition from the level itself to a continuous state, leading to the dissociation of the molecule. This phenomenon does not seem to be important for the MgH molecule and can be excluded for the Swan bands of the C_2 molecule.

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Molecules as Diagnostics of Solar and Stellar Magnetic Fields

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Abstract. We present an overview of the recent advances in using molecular lines for studying solar and stellar magnetic fields. The synthetic Stokes profiles of various molecular species in the presence of magnetic fields have been compared with profiles observed in sunspots. The agreement between the theory and observations is remarkable. Introducing molecular lines into the inversion of sunspot spectra leads to significant improvements in the deduced magnetic field vector. The high temperature sensitivity of molecular lines allows for high-contrast imaging of small-scale magnetic fields in the solar photosphere and the fine structure of sunspots. Furthermore, the process of coherent scattering in molecular lines in the presence of a magnetic field (the Hanle effect) allows us to investigate spatially unresolved solar magnetic fields. We show also how molecular lines can be used for studying magnetic fields in spatially unresolved spots on the surfaces of cool active stars.

1. Introduction

Most of the results of observational solar physics are based on the analysis of radiation emitted or absorbed in atomic spectral lines. For investigations of the cool gas on the Sun, however, molecules offer significant advantages and can lead to important new insights. Already in the early 1900s molecules have been recognized as important diagnostics of the sunspot atmosphere (cf. Hale et al. 1906). More recently, the study of CO lines has unveiled the extremely inhomogeneous structure of the solar chromosphere (Ayres & Testerman 1981; Solanki, Livingston & Ayres 1994; Ayres & Rabin 1996).

Molecules have been the source of several surprises in polarimetric surveys of solar radiation. For instance, in sunspots, where the Stokes V profiles of almost all atomic lines are nearly antisymmetric and exhibit the same polarity, many Stokes V profiles of molecular lines have strange shapes, and some have the op-

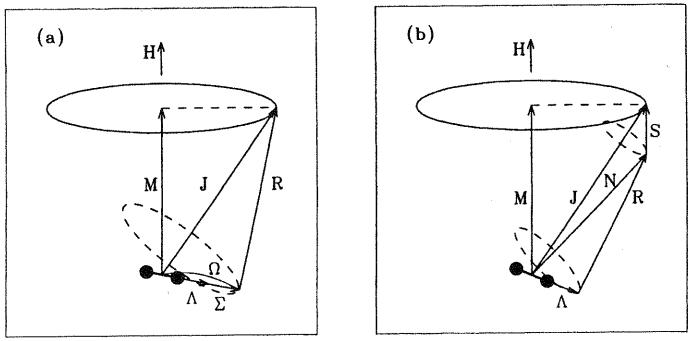

Figure 1. Vector diagrams of a diatomic molecule, denoted by the dumbell shape near the bottom of each frame, in a magnetic field in Hund's case (a) and (b). Solid ellipses indicate the precession of **J** in the magnetic field, **H**. In both cases **J** has the same meaning, although is obtained differently.

posite polarity as compared with atomic or other molecular lines (e.g. Nicholson 1938; Harvey 1973, 1985; Rüedi et al. 1995). In the photosphere, if observed at the solar limb, molecular lines produce surprisingly strong polarization signals due to coherent scattering (Stenflo & Keller 1996; Gandorfer 2000).

We present some of the results obtained with recent advances in the theory of the molecular Zeeman and Hanle effects. At the same time we point out the potential of molecular diagnostics for the future, in particular for the detection of magnetic fields in starspots.

2. The molecular Zeeman effect

The magnetic splitting of energy levels in the case of molecules occurs due to the same fundamental causes as in atoms. If the molecule possesses a non-zero magnetic moment, the external magnetic field interacts with the magnetic moment and causes a precession of the total angular momentum, **J**, about the field direction (Herzberg 1950). The space quantization of **J** results in $2J+1$ magnetic components with different energies. The largest contribution to the magnetic moment of a diatomic molecule is due to the magnetic moment associated with the orbital and spin angular momenta of the electrons. If they are zero or small, the contributions from the rotational motion of the molecule and the spins of nuclei should be taken into account.

The energies of the magnetic components depend on how the electronic angular momenta are coupled to the rotation of the molecule.

In *Hund's case (a)* the electronic angular momenta, both spin and orbital, are strongly coupled to the internuclear axis with projections Λ and Σ, respectively (Fig. 1, left panel). Thus, the splitting is determined only by the quantum numbers of the transitions and independent of the molecular constants. This

behaviour is analogous to the Zeeman effect of atomic lines. In this case, the splitting and strengths of the Zeeman components are described by rather simple analytical expressions (e.g. Berdyugina & Solanki 2002).

In *Hund's case (b)*, the orbital angular momentum of the electrons is coupled to the internuclear axis, whereas the spin is coupled to the rotational axis (Fig. 1, right panel). It often also happens that the spin-rotational coupling is so weak that these two angular momenta are uncoupled even by a small field. This is the molecular analogue of the atomic Paschen-Back effect. Computation of the splitting and strengths of the Zeeman components in the Paschen-Back effect can be done only numerically (Schadee 1978).

It often happens that one of the states or even both are in an intermediate coupling case, i.e. between Hund's cases (a) and (b). Actually, a molecule in slow rotation generally is well described by case (a), whereas for increased rotation case (b) provides a better approximation. Thus, as the molecule gradually passes from a state of slow rotation (with low values of the rotational quantum number J) to one of increased rotation (with higher values of J), the uncoupling of the spin momentum from the molecular axis and its coupling to rotation also takes place *gradually*. Hence, the Zeeman splitting of levels also gradually changes from Hund's case (a) to (b) as J increases. This transition is treated as a first order perturbation of the pure Hund's cases.

Recently, we performed the perturbation calculation of the molecular Zeeman effect for the intermediate case (a-b) for a number of molecules and deduced general properties of the molecular Zeeman effect (Berdyugina & Solanki 2002)[1]. The most important are the following. Magnetic splitting of rotational levels is symmetrical and proportional to the field strength for a given total angular momentum number J. In Hund's case (a), it is larger for low J and rapidly decreases with increasing J. In Hund's case (b), for large J values the splitting of the levels becomes approximately independent of J and other quantum numbers. The splitting then approaches the splitting due to the normal Zeeman effect. For both cases, effective Landé factors of molecular transitions rapidly approach zero. For the intermediate case, in contrast with the pure cases, absolute values of the effective Landé factors of the transitions can *increase* as J increases. An interesting finding is that the effective Landé factors of lines in different rotational branches can be of opposite sign, implying opposite polarization sign in lines of the same band. Moreover, for the intermediate case, the sign of the effective Landé factor can change with J within a given rotational branch. Such properties open the possibility for novel diagnostics of solar and stellar magnetic fields with molecular lines.

3. Diagnostics of sunspot magnetic fields

High temperature sensitivity makes molecular bands attractive for probing the structure of the coolest parts of sunspot umbrae. As the first step in such a study, a comparison of observed and synthetic Stokes parameters of molecular lines

[1] As kindly pointed out by E. Landi Degl'Innocenti the *effective* Landé factors given and plotted in that paper are all too large by a factor of 2. They, in fact, represent the average splitting in units of the normal Zeeman splitting.

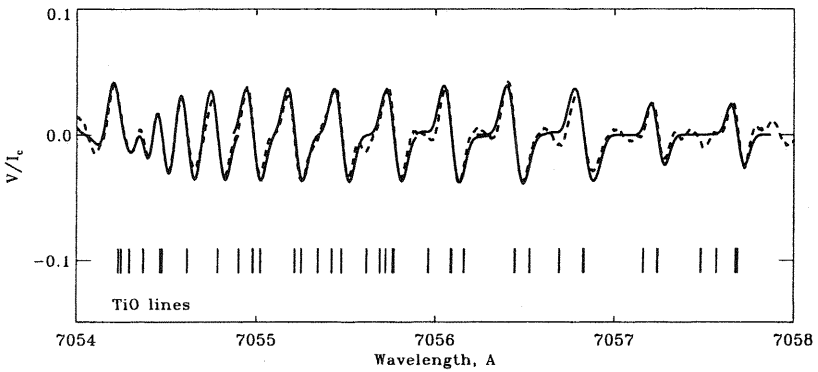

Figure 2. Calculated (solid line) and observed (dashed line) Stokes V of the TiO $\gamma(0,0)R_3$ band head in a sunspot. For the synthesis a field strength of 3000 G and a filling factor of 0.75 for an angle between the magnetic vector and the line of sight of 0° is assumed. Vertical dashes indicate positions of lines included in the spectral synthesis.

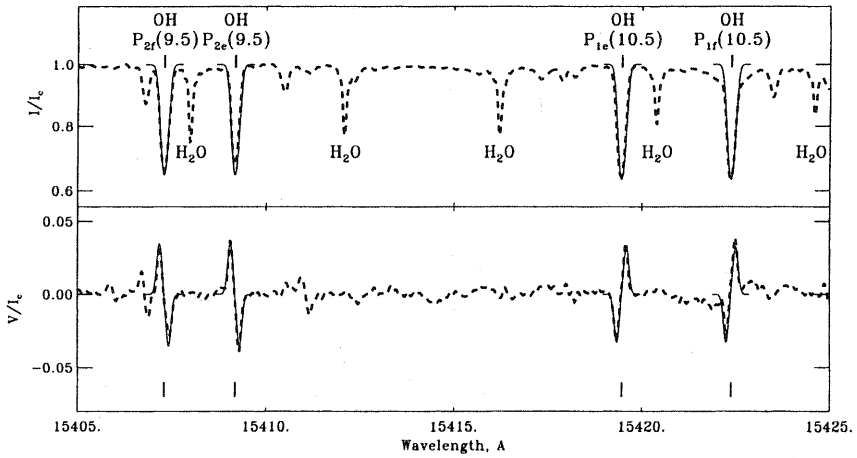

Figure 3. Stokes I and V spectra of the two pairs of OH lines pointed out by Harvey (1985). Dashed lines: spectra observed in a sunspot, solid lines: synthesized. The field strength is 2.5 kG, and the filling factor is 0.8. Note that the magnetic field in the spot is directed away from the observer and, thus, the reversed polarization is present in the left pair of lines. The weaker reversed-polarity V profiles at 15407.0 Å and 15411.4 Å are also due to OH.

should be made. For this purpose, we performed radiative transfer calculations with an extended and improved version of the code STOPRO (Solanki et al. 1992; Frutiger et al. 2000), which solves the set of radiative transfer equations in the formulation given by Rees et al. (1989). This code has been updated to enable computations of lines of diatomic molecules in the presence of a magnetic field, i.e. calculate the wavelength shifts of the Zeeman components and their theoretical strengths as well as molecular number densities.

The first example is the TiO $(0,0)R_3$ band head of the γ-system in the visual spectrum of sunspot umbrae at λ 7054.4 Å (Wallace et al. 1998). In this band head, lines of low rotational numbers coincide with those of high numbers, and, thus, the amplitude in Stokes V increases, resulting in a measurable signal (Berdyugina et al. 2000b). With reasonable values of the field strength (3000 G) and filling factor (0.75), we found an excellent agreement between the observed and calculated Stokes V (Fig. 2). We conclude, therefore, that the approach we use is appropriate.

In the spectrum of a sunspot umbra Harvey (1985) discovered that Stokes V profiles of OH lines of the same band and of approximately the same strength exhibit opposite polarities. A portion of an FTS (Fourier Transform Spectrometer) spectrum of a sunspot umbra is plotted in Fig. 3, where 4 OH lines from the (2,0) band are marked. The complete data set is described and discussed by Rüedi et al. (1995). Note that the pair on the right has V profiles of opposite polarity compared with that on the left. The fact that two lines each have V profiles of the same polarity, the V profiles are antisymmetric and all lines are otherwise similar cannot be explained any other way than that they have equal but opposite effective Landé factors (Berdyugina & Solanki 2002).

Using the theoretical Zeeman patterns calculated as described by Berdyugina & Solanki (2001), we carried out the forward spectral synthesis of Stokes parameters of OH transitions. The calculations revealed that reversed polarity is exhibited by the lines belonging to the P_2 sub-branch ($g_{\rm eff} < 0$), while the P_1 transitions have normal polarity ($g_{\rm eff} > 0$). We found also that the same occurs for the R_1 and R_2 transitions and such a behavior is typical for all OH lines from the Meinel system and pure rotational transitions in the ground state. As a model umbra we used a radiative equilibrium atmosphere tabulated by Kurucz (1993) having $T_{\rm eff}$ = 3750K and $\log g$ = 4.5, into which we introduced a height-independent magnetic field of an appropriate strength. The synthetic profiles are overplotted on the observed profiles in Fig. 3. The correspondence is gratifying.

The synthesis of Zeeman-split OH lines also helps to improve the diagnostic capability of atomic lines. In sunspots, strong OH lines from the (3,1) band are observed in the vicinity of the Zeeman sensitive Fe I 15648.5 Å line and are blended with Fe I 15652.9 Å. Together, these two Fe I lines are the premier infrared diagnostics of the solar magnetic field (e.g. Solanki et al. 1992) and are being increasingly widely used. Inverting the Stokes parameters of the blending OH lines along with the Fe I lines greatly improves the reliability of magnetic, thermal and dynamic quantities deduced from these lines in sunspot umbrae.

With the inversion code described by Frutiger et al. (2000), we carried out the inversion of Stokes parameters observed in the central part of an umbra where the strength of molecular lines was the largest. These observations are

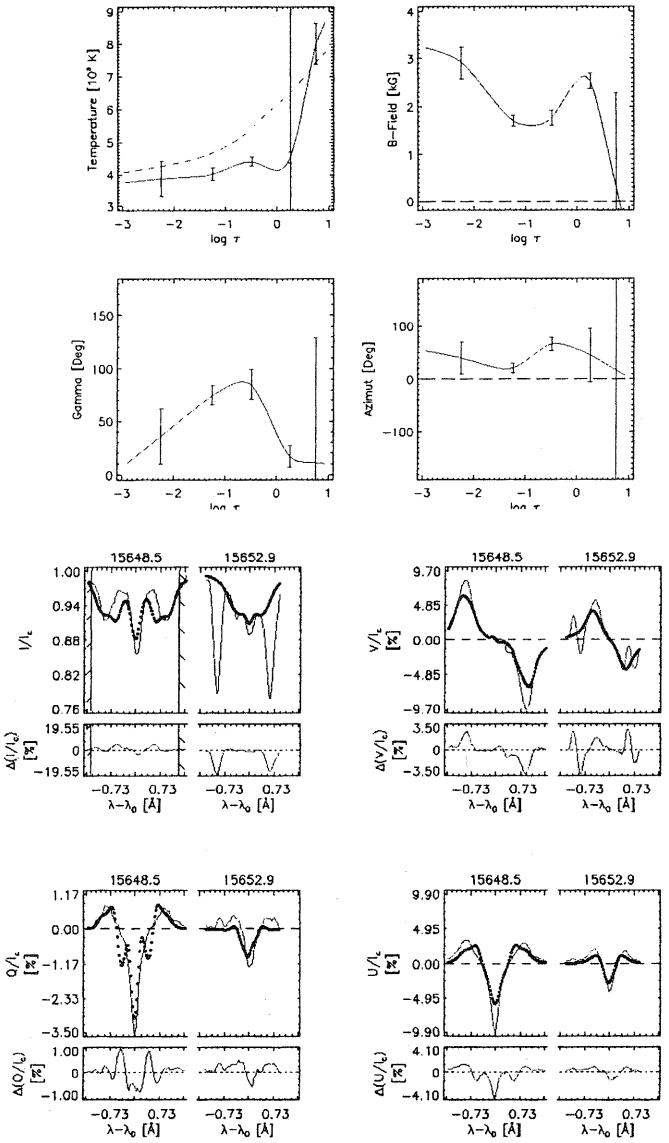

Figure 4. The umbral atmosphere deduced from the inversion of Fe I profiles only (upper 4 panels) and the corresponding fits (dots) to the observed Stokes profiles (solid lines; lower 4 panels). In the atmosphere plots, the solid curves represent the magnetic component of the model, while the dashed curve shows the temperature distribution in the non-magnetic component.

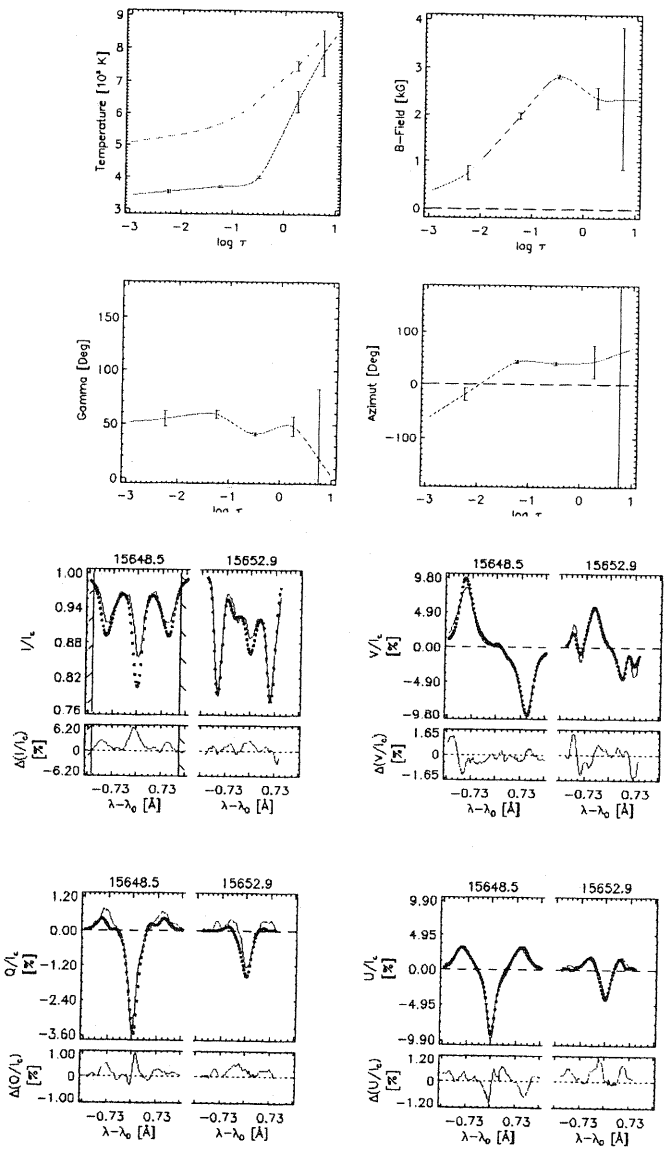

Figure 5. The same as Fig. 4 for the inversion including both Fe I and OH lines.

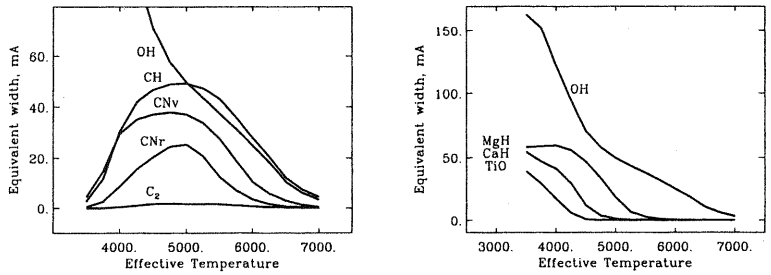

Figure 6. Equivalent widths of a sample of molecular lines observed in solar and sunspot spectra for the models of stellar atmospheres by Kurucz (1993).

fully described by Mathew et al. (2003). Our simplified model included two components, one magnetic and one nonmagnetic. The first represents the umbra itself, while the second describes the contribution from the photospheric stray light. Two inversions were carried out, one disregarding the blending OH lines, the other including them. As the Fe I and OH lines are formed in different parts of the umbral atmosphere, the effect of including the OH lines was largest in the upper layers, at optical depths $\log\tau \leq -1$. Without OH lines, the nonmagnetic component is too cool, the field strength in the magnetic component grows unreasonably towards smaller optical depths and the vector of the field changes its direction with respect to the line of sight (Fig. 4). Also, the fit to the Stokes parameters is not satisfactory (Fig. 4). If the OH lines are included in the calculations, the behaviour of the magnetic component is more reasonable, i.e. the field strength smoothly drops towards higher layers and the field direction corresponds well to the observed position of the sunspot on the solar disk. Also, the nonmagnetic component becomes as hot as the photosphere (Fig. 5). Finally, the fit to the profiles becomes acceptable for such a simple model (Fig. 5). Further calculations are needed to test if this result is robust.

4. Imaging of small-scale magnetic fields in the solar photosphere and the fine structure of sunspots

When the solar photosphere is imaged in G-band radiation, it reveals the presence of the so-called G-band bright points, which correspond to small-scale magnetic structures within intergranular lanes (cf. Berger & Title 2001 and references therein). It was shown recently by Steiner, Hauschildt, & Bruls (2001) and Sánchez Almeida et al. (2001) that the observed high contrast of the G-band bright points can be explained by the dissociation process of the CH molecule, which contributes the most in the G-band absorption. The high temperature of the small-scale magnetic structures reduces the number of CH molecules via dissociation, and the features look brighter.

Similar effects can be observed with other molecular bands. In Fig. 6 we present calculations of the equivalent widths of a sample of molecular lines observed in solar and sunspot spectra for different models of stellar atmospheres (Kurucz 1993). Molecular lines which are strongest at about 5000 K (left panel in Fig. 6) are useful for studying temperature inhomogeneities and imaging of small-scale magnetic fields in the solar photosphere. In addition to CH, these are CN and OH lines. Their dissociation equilibrium is similar to that of CH and one should expect a similar effect of brightening in their bands. In fact, this was already observed in the CN violet band at 3880Å.

Molecular lines which are strongest at about 3500 K (right panel in Fig. 6) are useful for studying temperature inhomogeneities in sunspots. For instance, umbral dots would be seen at higher contrast if observed in the TiO or OH band heads. An experiment recently made with the filter centred at the TiO 7054Å band head has confirmed this expectation (Berger et al. 2003).

5. Diagnostics of turbulent magnetic fields via molecular Hanle effect

The linearly polarized solar spectrum that is produced by coherent scattering processes and called "the second solar spectrum" is full of polarizing features due to molecular transitions, in particular from MgH (Fig. 7) and C_2, which behave very differently as compared to atomic transitions. 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 insensitive to the magnetic field variations. To clarify these issues, we developed recently a theoretical foundation for polarized molecular scattering (Berdyugina, Stenflo, & Gandorfer 2002), which can serve as a general tool for interpretations of the structures in the second solar spectrum.

We found that the main reason why the molecular lines seem to be invariant in scattering polarization is the combination of significant intrinsic polarizability W_2 and very small Landé factors (Fig. 7). Most molecular lines have, in contrast with 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. As molecular transitions with small J are sensitive 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, is 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 possess low sensitivity to magnetic fields. On the other hand, Trujillo Bueno (2003) reported that the observed difference in scattering amplitudes between pairs of C_2 lines can be explained when a weak turbulent magnetic field is included in the calculations. If this is true, then these lines should show variable polarization signals, which is of particular interest for both the theory and observations.

Molecular lines with low magnetic sensitivity and strong scattering polarization can serve as reference lines against which the polarization fluctuations in the atomic lines due to the Hanle effect can be calibrated. This is of particular importance if one wants to pursue a project to determine the long-term, solar-cycle variations of the Hanle depolarization in atomic lines.

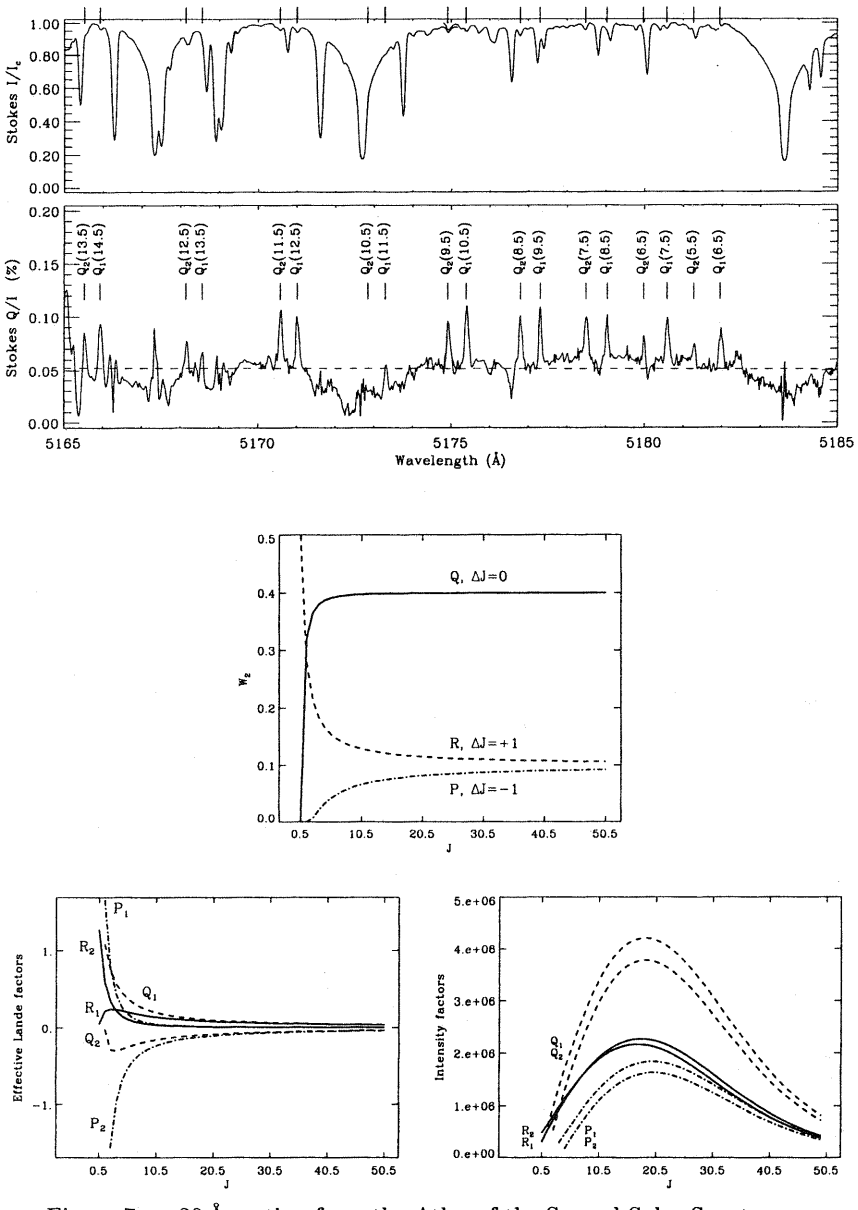

Figure 7. 20 Å section from the Atlas of the Second Solar Spectrum (Gandorfer 2000) showing polarization signals from the MgH Q branch lines (top panel). The other panels are plots of the intrinsic polarizability W_2, effective Landé factors, and intensity factors for MgH lines.

6. Diagnostics of magnetic fields in spatially unresolved starspots

For stars with magnetic activity, such as T Tauri stars, solar-type G-K dwarfs, RS CVn- and FK Com-type stars, molecular lines provide evidence of cool spots on their surfaces. These stars show strong photometric and spectroscopic variability which is interpreted as caused by cool spots with strong magnetic fields. If the effective temperature of the stellar photosphere is high enough, molecular lines can be formed only in cool starspots. The first detection of molecular bands from starspots was reported by Vogt (1979) for a star whose spectral type K2 was not compatible with the observed presence of TiO and VO bands. From the relative strengths and overall appearance of the molecular features, an equivalent spectral type of the spot spectrum was estimated as late as M6. A comparison of photometric variations with TiO band strengths provided very reliable estimates of unspotted stellar magnitudes (Berdyugina et al. 1998, 1999).

Since TiO lines are formed only in starspots on the surfaces of G-K giants and subgiants, polarization observations in these lines can provide measurements of magnetic fields directly in spatially unresolved spots. As shown by our calculations, the TiO lines at 7055Å are rather strongly magnetically sensitive (Fig. 2). Estimates of the Stokes V signal from starspots in these lines have been obtained by Berdyugina (2002) for the spot distribution on the RS CVn-type star IM Peg observed in 1997, which is shown in Fig. 8. The stellar image was obtained from simultaneous inversions of 6 atomic lines observed at 11 rotational phases. The total spot coverage was found to be 13%. This was confirmed by a comparison of the calculated and observed TiO spectra. In order to see a pure contribution of the TiO band, synthetic spectra including only TiO lines were calculated from the image of IM Peg. These are shown in the bottom left plot in Fig. 8 (thick dashed lines). One can clearly see band heads formed in two spots observed in the phase interval 0.3 to 0.8 (thick and thin solid lines,respectively). The band heads appear at different Doppler shifts and change their relative strengths as the star rotates and the spots move across the stellar disk.

In order to calculated TiO Stokes V profiles, it was assumed that the spots possessed a uniform radial magnetic field of 3 kG, while other surface regions were free of magnetic field. Unfortunately, the spatial resolution of the images does not allow to figure out if the large starspots are uniform or made of smaller spots, whose polarities could be different. One can assume, however, that spots of one polarity dominate the stellar disk at the time of observations. The resulting profiles for the observed phases are shown in the bottom right plot of Fig. 8. The most interesting thing is that the sign of the feature at the band head indicates clearly the polarity of the spot: it is positive for the positive field and vise versa. The peak polarization of this feature is about 0.3% for the largest spot. Such a signal can be recorded if the signal-to-noise ratio in the observations is higher than 300. Another important finding is that Stokes V signals from spots at different Doppler shifts (different limb angles) can be successfully added and result in a stronger combined signal. This calculation shows, therefore, that a reasonably strong polarization signal can be recorded from starspots in the TiO band. It will be stronger for more compact spots (with small Doppler shifts across) and for stars with smaller projected rotational velocities. As soon as such observations are available, inversions of line profiles can provide information about physical conditions in spatially unresolved starspots.

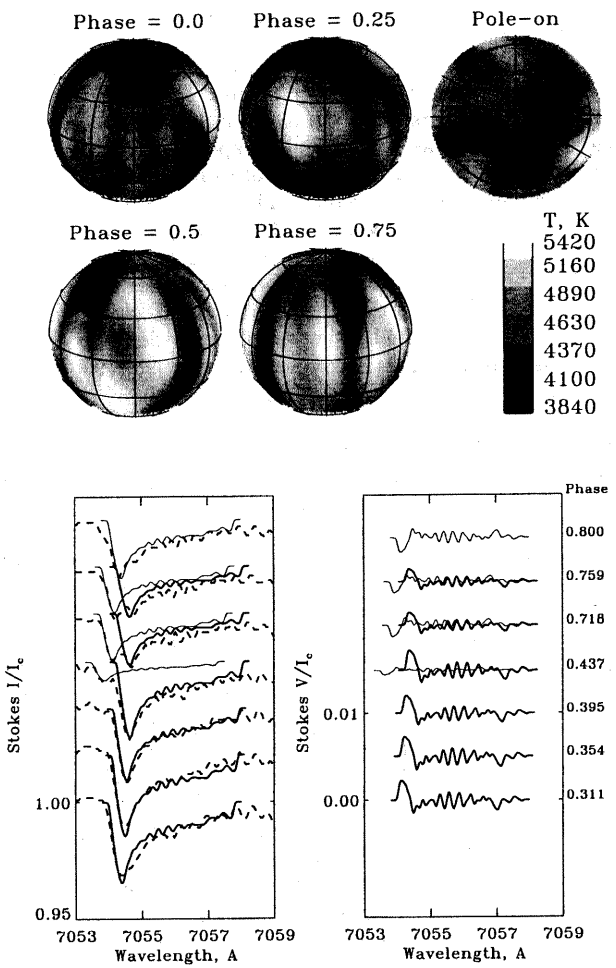

Figure 8. The image of the RS CVn-type star IM Peg showing the spot distribution on the stellar surface in December 1997 (Berdyugina et al. 2000a) together with the TiO band Stokes I and V calculated for the image under the assumption that starspots possess a uniform radial magnetic field of 3 kG (Berdyugina 2002). Thick dashed lines in the left panel represents the calculation fitting the observations in terms of pure TiO absorption in starspots visible at a given phase, while the contribution from individual spots in the model is indicated by solid lines. The magnetic field is assumed to be directed away from the stellar surface in the spot at phase 0.3 (thick solid line) and towards the stellar interiors in the spot at phase 0.8 (thin solid line).

7. Conclusions

The present overview demonstrates that *molecular lines are magnetically sensitive* and provide new, useful information on magnetic fields in the Sun and stars.

We find that strong Zeeman signals are expected for molecular transitions with intermediate case spin coupling (e.g. TiO, FeH). Also, negative Landé factors are found to be common for molecular lines, and unusual Stokes V signatures of infrared OH lines is the natural outcome of molecular properties. Stokes polarimetry with pairs of negative and positive Zeeman-split OH lines offers advantages for assessing instrumental effects (I,Q,U to V cross-talk) or magneto-optic effects in the solar atmosphere.

Molecular lines are excellent diagnostics of cooler parts of sunspots. Simultaneous inversion of the Fe I and OH lines improves the reliability of magnetic, thermal and dynamic quantities deduced from these lines in sunspot umbrae. Imaging in molecular bands is useful for studying small-scale structures in sunspot umbrae and penumbrae (e.g. in TiO, MgH).

Molecular lines show strong and invariable scattering polarization. The combination of significant intrinsic polarizability and very small Landé factors reduces the sensitivity of molecular lines to the Hanle effect.

Molecular lines are unique diagnostics of starspot interiors. They provide evidence for cool spots on stellar surfaces and are very useful for determining starspot filling factors. Inversions of Stokes profiles of molecular lines can provide information on temperature structure, magnetic and velocity fields inside spatially unresolved starspots.

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Discussion

VAN BALLEGOOIJEN: Are there any observations of polar spots on active stars using molecular spectroscopy?

BERDYUGINA: We have some observations of active stars with presumably polar spots on their surfaces in the TiO band at 7054 Å. These observations will be analysed in order to check whether the recovered spot distribution with a polar spot satisfies the observed TiO absorption. This will be a test for existence of polar spots. From the example shown in this presentation it is clear that not all active stars possess polar spots. This is confirmed by a good fit of the observed TiO band with the spectrum calculated using the spot distribution on the surface of IM Peg recovered with the surface imaging technique applied to atomic lines.

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Non-equilibrium Chemistry and Molecular Spectropolarimetry

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Abstract. We investigate the reliability of the assumption of instantaneous chemical equilibrium (ICE) for calculating the molecular number densities in the solar atmosphere, showing that the time scales needed to reach the equilibrium concentrations may be larger than the dynamical time scales mainly in regions with relatively low density and temperature. The spectral line polarization of diatomic molecules produced either by the Zeeman effect or by scattering processes is also investigated in detail. We show that the splitting and strengths of the Zeeman components can be easily obtained by numerical diagonalization of the effective Hamiltonian, which allows us to include any coupling term in the description of the molecule. We demonstrate that the Zeeman patterns of some IR lines of CN observed in sunspots explain the curious antisymmetric shape of their Stokes Q and U profiles. We verify that our multilevel molecular models for interpreting scattering polarization observations in MgH, C_2 and CN lines are sufficiently realistic. For instance, we have been able to explain the regular pattern of the Q/I scattering polarization peaks produced by CN in the UV, as shown in the recent observations of the second solar spectrum reported by Stenflo (2003) and by Gandorfer during this workshop.

1. Introduction

The modeling of polarization signatures in molecular lines is important for two reasons. Firstly, the molecular Zeeman effect (Crawford 1934; Herzberg 1950; Schadee 1978) can be used as a sensitive diagnostic tool of the physical conditions in strongly magnetized regions of stellar atmospheres, including sunspots and starspots (e.g., the overview by Berdyugina et al. in this volume). On the other hand, the modeling of scattering polarization in molecular lines taking into account the Hanle effect offers a novel diagnostic tool for weak magnetic fields in the solar photosphere (Trujillo Bueno 2003). In this contribution, we focus on several key problems of molecular physics in the solar atmosphere: the effect of the finite reaction times for the establishment of the molecular concentrations in our dynamic Sun, the molecular Zeeman effect in OH and CN lines and scattering polarization in CN lines.

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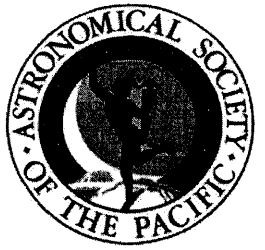

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