The pure rotation spectrum of the hydroxyl radical and the solar oxygen abundance

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Summary. Observations of pure rotation $^2\Pi$ (0—0) lines of the hydroxyl radical in the solar photospheric spectrum provide a new and independent determination of the solar oxygen abundance. These OH lines with the Holweger—Müller model atmosphere give log $e(O) = 8.84$ which is within 0.08 dex of the abundance provided by the [O i] lines and the same model.

It is pointed out that a detection of the CH pure rotation lines would permit a determination of the O/C abundance ratio with a much reduced sensitivity to the model atmosphere uncertainties. Selected combinations of atomic and molecular (not including the OH pure rotation lines) lines give log $e(O)/e(C) = 0.23 \pm 0.03$ dex.

1 Introduction

Examination of high-resolution solar spectra in the 825—960 cm$^{-1}$ (10.4—12.1 µm) interval enabled Goldman et al. (1981) to identify pure rotational transitions of the hydroxyl (OH) radical with solar absorption lines. In this paper, we present a quantitative interpretation of the OH lines, which offer several attractive attributes as a potential indicator of the solar oxygen abundance: the $f$-values are known with good accuracy; the excitation of the vibronic structure of the $^2\Pi$ ground state of OH is surely close to local thermodynamic equilibrium (LTE); and the dissociation energy of the OH molecule, an important factor influencing the molecular density in the solar atmosphere, is determined to a precision of about 2 meV. Since published determinations of the solar O abundance rely primarily on the two weak [O i] lines at 6300 and 6353 Å (Lambert 1978), new abundance indicators such as the OH pure rotational transitions deserve a thorough consideration.

The principal ingredients of an abundance analysis are (i) the solar equivalent widths, (ii) the $f$-values of the lines and (iii) the model solar atmosphere. After a discussion of items (i) and (ii), we present in Section 4 the oxygen abundance derived directly from the OH pure rotational lines. Tests conducted with a variety of model atmospheres show that the uncertainty of the O abundance is dominated by the atmosphere-related uncertainties. In principle, the effect of the latter may be eliminated almost completely by extracting the O/C abundance ratio from combinations of atomic and molecular lines of oxygen and carbon.
Figure 1. The solar spectrum from 900 to 910 cm$^{-1}$. Photospheric OH pure rotational lines are identified below the upper spectrum which was recorded from a high altitude balloon. A quartet from each of the vibrational levels $v = 0$, 1, and 2 is present.
2 Observations

The equivalent widths used for the quantitative analysis of the solar OH lines are derived from two sets of data. The first set is the spectra obtained on 1981 March 23 during a balloon flight with a Fourier transform spectrometer. The spectral resolution was about 0.02 cm$^{-1}$. The entrance aperture of the spectrometer passed the central 8 arcmin of the 32 arcmin solar disc. As demonstrated in fig. 1 of Goldman et al. (1981), telluric and solar lines are readily distinguished because spectra were obtained at several airmasses. On spectra obtained at the maximum altitude reached by the balloon (33 km) and the minimum zenith angle of the Sun, the telluric molecules contribute very few lines. Eight 'high Sun' (solar zenith angle < 82°) were coadded for improved signal-to-noise ratio.

The second set of spectra were recorded with the same spectrometer system on 1980 December 5 at the South Pole (altitude 2.9 km, zenith angle 67.7°). The small rate of

Table 1. Solar pure rotation OH $^2\Pi$ (0–0) lines.

<table>
<thead>
<tr>
<th>Line*</th>
<th>Observed $\sigma_0$ (cm$^{-1}$)</th>
<th>$W_0$ (mK)†</th>
<th>$E''$ (eV)$\dagger$</th>
<th>Calculated $A$ (s$^{-1}$)</th>
<th>log gf</th>
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<tbody>
<tr>
<td>$R_{3f}$ (23.5)</td>
<td>814.321</td>
<td>1.29</td>
<td>1.300</td>
<td>236.9</td>
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<td>1.401</td>
<td>258.5</td>
<td>-1.542</td>
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<td>$R_{1e}$ (25.5)</td>
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<td>2.065</td>
<td>392.2</td>
<td>-1.377</td>
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</table>

* The line classifications specify $J$ for the lower level. The parity of this lower level is denoted by the subscript $e$ or $f$ (Brown et al. 1975).
† 1 milliKayser = 10$^{-3}$ cm$^{-1}$.
‡ $E''$ is the excitation potential of the lower level.
change of the solar zenith angle with time allowed the coadding of 25 spectral scans, resulting
in high signal-to-noise ratio.

The 760—960 cm\(^{-1}\) region of the South Pole coadded spectra and the balloon combined
spectra is displayed in an atlas by Blatherwick et al. (1982). This region covers the OH lines
used in the present study. Fig. 1 shows an expansion of the 900—910 cm\(^{-1}\) frame from the
South Pole atlas. Representative OH lines from \( ^2\Pi \,(0—0), \ ^2\Pi \,(1—1) \) and \( ^2\Pi \,(2—2) \) can be
seen in this figure. A complete table of observed line positions and identifications is given in
the atlas. It is apparent that while the signal-to-noise ratio is higher on the South Pole
spectra, the OH lines are more isolated on the balloon spectra. The equivalent widths of the
OH lines were derived from both sets of data.

With a \( ^2\Pi \) ground state, the pure rotational spectrum of the OH radical consists of
quartets with common quantum numbers \( N'' \) and \( N' \, (= N'' + 1) \). Line frequencies and
parameters relevant to a quantitative analysis are taken from Goldman et al. (1983). The
spectral window scanned by the spectrometer includes OH \( ^2\Pi \,(0—0) \) lines from \( N'' = 22 \) to
32.

Table 1 gives details of the isolated OH lines analysed here. The equivalent width \( W_e \) are
accurate to about \( \pm 5 \) per cent. This estimate is based on the resolution and signal-to-noise
ratio of the spectra and is confirmed by the scatter in the \( W_e \) measurements within each
quartet. The weaker \( ^2\Pi \,(1—1) \) and \( ^2\Pi \,(2—2) \) lines are excluded from this analysis because
their \( W_e \)'s are significantly less accurate.

3 The oscillator strengths

Strengths of pure rotational transitions are customarily specified in terms of the permanent
(rotationless) electric dipole moment \( \mu \). Meerts & Dynamus (1973) measured \( \mu = 1.6676 \pm
0.0009 \) Debye for the \( ^2\Pi_{1/2}, J = 9/2 \) levels. They note that an earlier less accurate measure-
ment (Powell & Lide 1965) for the \( ^2\Pi_{3/2}, J = 7/2 \) levels gives a similar result: \( \mu = 1.667 \pm
0.010 \) D. By combining the RKR potential function for the \( ^2\Pi_{1/2} \) state with an \textit{ab initio}
calculation of the electric dipole moment function (Stevens et al. 1974), we find that
vibration—rotation interaction is small for the pure rotational transitions. We estimate that
the effective electric dipole moment increases by about 1.4 per cent between \( J = 9/2 \) and
the high \( J \) values of the solar lines. Then, we adopt \( \mu = 1.691 \) D in the calculations of the
\( gf \)-values.

Einstein \( A \)-values are given by a standard expression

\[
A(J+1,J) = 3.136 \times 10^{-7} \sigma^3 \mu^2 S \,[s^{-1}]
\]

where \( \sigma \) is the line frequency in cm\(^{-1}\), \( \mu \) is the electric dipole moment in Debyes and \( S \) is the
rotational linestrength (see Somerville 1978) where

\[
S = \frac{(2J-1)(2J+3)}{4(J+1)(2J+1)} \quad \text{for} \quad R_1(J)
\]

\[
= \frac{(2J+1)^2(2J+5)}{4(J+1)(2J+3)} \quad \text{for} \quad R_2(J).
\]

The \( gf \)-values for a line are given by another standard expression

\[
gf = 1.499 g_{J'} \, A/\sigma^2
\]

where \( g_{J'} = (2J' + 1) \) is the statistical weight of the upper level. Table 1 lists both the \( A \) and
\( gf \)-values for which the uncertainties are unlikely to exceed \( \pm 0.02 \) dex.
This $g\ell$-value applies to a single component of the resolved A-doublet $R_{1e}(J) + R_{1f}(J)$. The OH rotational levels are subject to a small hyperfine splitting such that each single component consists of three hyperfine components. Examination of the molecular constants and energy levels (see, for example, Beaudet & Poynter 1978) shows that the hyperfine components are split by less than 0.0025 cm$^{-1}$ or 0.8 km s$^{-1}$. Since the strongest of the solar OH lines are only slightly saturated and the thermal velocities exceed the hyperfine splitting, we ignore the hfs in the computation of the solar O abundance.

Analysis of the OH lines also requires the dissociation energy for which we adopt $D_0^\text{OH} = 4.392 \pm 0.002$ eV (Carlone & Dalby 1969). The 2meV uncertainty translates to a negligible (0.002 dex) abundance uncertainty.

4 The abundance analysis

Our initial analysis employed the model atmosphere constructed by Holweger & Müller (1974). This model, which provides an excellent fit to the solar continuous spectrum and many features of the Fraunhofer lines, appears to be superior to other published models — see the comments by Lambert (1978), Lambert & Luck (1978), Blackwell, Shallis & Simmons (1980), Biémont et al. (1981). Our calculations employ a microturbulent velocity of 1.0 km s$^{-1}$ but a change of $\pm 0.5$ km s$^{-1}$ changes the mean by less than 0.01 dex. When the line sample is run through the program LINES (Sneden 1974), the mean O abundance is log $e$(O) = 8.84 with a rms error of $\pm 0.03$ dex. The lines from the four series of levels $1e, 2f, 2e$ and $2f$ give identical mean values to within 0.01 dex. The scatter in the abundances provided by individual lines appears to be dominated by the $W_0$ measurement uncertainties. The abundance is not correlated with the excitation potential $E''$ (see Fig. 2). The mean abundance is 0.08 dex smaller than the value recommended by Lambert (1978) from an analysis of the two weak [O I] lines at 6300 and 6363 Å. The difference between the OH and [O I] lines is pleasingly small in light of the fact that the temperature and pressure sensitivities of the atomic and molecular lines are quite different. This sensitivity is revealed when alternative model atmospheres are used in the analysis of the OH lines.

Table 2 gives the O abundance for the five empirical models examined by Lambert (1978) in his CNO abundance study. The models HM, A and VAL all provide tolerable fit to the observed continuous spectrum but the O abundance from OH span 0.30 dex for this trio. Since the models have not been severely tested on their ability to reproduce spectral features such as the OH lines formed near the top of the photosphere and the comparison with the continuous spectrum checks primarily the temperature and not the gas pressure profile, the factor of 2 spread in the O abundance is not too surprising.

The OH infrared lines do offer a partial test of the models. For example, the VAL model yields a correlation between abundance and excitation potential (Fig. 2) that points to a lack of correspondence between the model and the true solar atmosphere. In fact, all of the tested empirical models apart from the Holweger–Müller model show a significant correlation. Such a correlation identifies a defective model atmosphere but the absence of a correlation does not guarantee that a model is accurate. An additional attractive feature of the Holweger–Müller model is the close agreement between the O abundance estimate provided from the OH pure rotational and the ultraviolet $A-X$ system lines (Lambert 1978). This abundance difference, which is just 0.04 dex, increases to 0.24 dex for the VAL model.

Insensitivity to the model atmosphere is best achieved by pairing of the OH infrared lines with other molecular lines in the same spectral interval. Of course, a combination of molecules provides not an elemental abundance but a ratio of such abundances. The line absorption coefficient for a molecule $XY$ may be written

$$\kappa_1 \propto e(X) e(Y) P_2^Z h(T) \exp \left[(D_0^\text{XY} - E'')/kT\right]$$

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Table 2. The oxygen abundance and related quantities.

<table>
<thead>
<tr>
<th>Lines</th>
<th>Quantity †</th>
<th>Model atmosphere*</th>
<th>Principal sources of uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HM</td>
<td>A</td>
</tr>
<tr>
<td>OH Rot.</td>
<td>log ε(O)</td>
<td>8.84</td>
<td>8.62</td>
</tr>
<tr>
<td>OH A−X</td>
<td>O/C</td>
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<td>0.21</td>
</tr>
<tr>
<td>CH $A-X$</td>
<td>[O I] 6300, 6363 Å</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>[C I] 8727 Å</td>
<td>0.27</td>
<td>0.31</td>
</tr>
<tr>
<td>O1 permitted CH A−X</td>
<td>O/C</td>
<td>0.13</td>
<td>0.07</td>
</tr>
<tr>
<td>C2 Swan</td>
<td>[O I] 6300, 6363 Å</td>
<td>0.13</td>
<td>0.07</td>
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* The model atmospheres are: HM = Holweger & Müller (1974); A = Allen (1976, private communication); VAL = Vernazza et al. 1976; HSRA = Gingerich et al. (1971); AL = Ayers & Linsky (1976).
† O/C = log [$\varepsilon(O)/\varepsilon(C)$].
Pure rotation spectrum of the hydroxyl radical

Figure 2. Oxygen abundance versus excitation potential of the lower state. Results are shown for the model atmospheres constructed by Holweger–Müller (1974) and Vernazza et al (1976).

where \( h(T) \) is a slowly-varying function of temperature with a rather similar variation for similar molecules and the atoms \( X \) and \( Y \) are assumed to be predominantly neutral in the solar atmosphere. Then, the \( \kappa_f \) ratio for two molecules \( XY \) and \( AB \) may be written

\[
\frac{\kappa_f(XY)}{\kappa_f(AB)} = \frac{e(X) e(Y)}{e(A) e(B)} \exp \left\{ \frac{[(D_0^X - E^X)_{XY} - (D_0^A - E^A)_{AB}]}{kT} \right\}.
\]

This ratio is independent of the gas pressure, \( P_g \), and the temperature dependence can be minimized by selection of molecules with similar dissociation energies \( D_0^X \). If the lines of the molecules \( XY \) and \( AB \) occur at widely differing wavelengths, a model atmosphere dependence will be introduced through the differences in the continuous opacity.

A pairing of \( OH \) and \( CH \) pure rotational lines is an obvious source of the \( O/C \) abundance ratio with minimal dependence on the choice of a model atmosphere. Unfortunately, the \( CH \) pure rotational transitions are not yet detectable. We expect the \( CH \) lines to be about a factor of 20 weaker than the \( OH \) \( ^2 \Pi \) lines on account of the lower \( C \) abundance, the lower dissociation energy of \( CH \) and the smaller electric dipole moment (\( \mu = 1.46 \pm 0.06 \, \text{D} \) for \( CH \) \( ^2 \Pi \), Phelps & Dalby 1966). With a predicted \( W_o \approx 0.05 \, \text{mK} \), the \( CH \) lines are masked by noise on the currently available spectra. [An analogous attempt to extract the \( O/C \) ratio from the vibration–rotation (\( V–R \)) spectra of \( OH \) and \( CH \) was also thwarted by the non-detectability of the \( CH \) lines. Weak lines attributable to the \( OH \) \( ^2 \Pi \) \( V–R \) lines are identified successfully on the new atlas of the solar spectrum (Delbouille et al 1981) with the observed \( W_o 's \) in good agreement (about \( \pm 0.05 \, \text{dex} \) with predictions based on the Holweger–Müller model (Lambert, Brown, Hinkle & Johnson 1982, in preparation). The \( CH \) \( ^2 \Pi \) \( V–R \) lines are below the current detection limit: Lie, Hinze & Liu (1973) provide \textit{ab initio} predictions for
the CH line strengths.] Although several electronic transitions provide many CH lines in the blue, the pairing of these lines with the infrared OH lines does not yield a model-independent estimate of the O/C ratio because of the differences in the continuous opacity between the blue and the infrared. For example, the Holweger–Müller (HM) and Vernazza, Avrett & Loeser (VAL) models give log $e(\text{O})/e(\text{C}) = 0.17$ and $-0.06$ respectively from a pairing of the OH pure rotational transitions with the CH $A^2\Delta - X^2\Pi$ lines discussed by Lambert (1978). The 0.23 dex difference is only slightly less than the 0.30 dex spread in the directly deduced O abundances.

In Table 2, we present several model-insensitive estimates of the O/C ratio as provided by combinations of atomic and molecular lines — see Lambert (1978) for the abundance estimates used in the derivation of the O/C ratio. The OH pure rotational transitions are not considered for these estimates because of the large wavelength difference between these newly discovered lines and other lines. The principal sources of uncertainty affecting the O/C estimates are succinctly identified in Table 2. Construction of the abundance ratios reduces somewhat the model atmosphere dependence; for example, the C abundance provided from the CH $A-X$ lines ranges over 0.18 dex for the five models but the O/C ratio from the $[\text{O} \text{I}]$, CH $A-X$ and C$_2$ Swan lines spans just 0.06 dex. [The C abundances derived by combining the CH and C$_2$ lines alone are spread over only 0.03 dex. This pairing gives log $e(\text{C}) = 8.79$ for the HM model but note our comments on the dissociation energy $D_0^\text{C}_2$. A pairing of the OH pure rotational lines with the CO first-overtone vibration–rotation lines also provides a C abundance with a very slight model dependence: log $e(\text{C}) = 8.79$ for the HM model with a range of only 0.07 dex over the five tested models in spite of the large difference between the dissociation energies of CO and OH. This C abundance is about 0.1 dex larger than that obtained from independent analyses of the $[\text{C} \text{I}]$ and CH lines. Such a difference is indicative of a small systematic error.]

Three of the four estimates of the O/C ratio are in remarkably good agreement. The discrepant result involves the C$_2$ Swan system. [The CH $f$-values are not the source of significant error. A recent measurement (Becker, Brenig & Tatarezyk 1980) of the $A^2\Delta$ state's radiative lifetime gave $\tau = 537.5 \pm 5$ ns in excellent agreement with the measurement $\tau = 534 \pm 5$ ns (Brzozowski et al. 1976) adopted by Lambert 1978.] The C$_2$ dissociation energy is a possible source of error. In their compilation of molecular constants, Huber & Herzberg (1979) recommend $D_0^\text{C}_2 = 6.21$ eV on the basis of thermochemical determinations and disregard the spectroscopic values which led Lambert (1978) to employ $D_0^\text{C}_2 = 6.11$ eV. If the higher value were adopted, the O/C ratios involving the C$_2$ Swan system would be increased by about 0.10 dex and brought close to the values provided by the other three line combinations. [Also, the C abundance provided by the CH/C$_2$ combination would be reduced to log $e(\text{C}) = 8.69$, a result quite insensitive to the choice of a model atmosphere.] Clearly, a thorough reinvestigation of the C$_2$ dissociation energy is now desired. If the C$_2$ Swan system is omitted, the result log $e(\text{O})/e(\text{C}) = 0.23 \pm 0.03$ dex is provided by the remaining three model-insensitive line pairings.

5 Concluding remarks

In this paper, we have shown that the recently discovered rotational transitions of the $X^2\Pi$ state of OH can provide useful information on the solar O abundance. The basic molecular data for the transitions are known to high accuracy. The O abundance derived from the best empirical model atmosphere is within 0.08 dex of the previously recommended abundance based on two $[\text{O} \text{I}]$ lines (Lambert 1978). This level of agreement demonstrates that the solar O abundance is now well determined. Parkinson (1977) noted
that coronal X-ray lines from flares indicated a low abundance log $e(O) = 8.45$. Our confirmation of the higher photospheric abundance suggests that, as Veck & Parkinson (1981) propose, the coronal abundances are affected by ambipolar and magnetic diffusion.

Unfortunately, the O abundance from the OH infrared lines is rather sensitive to the choice of a model atmosphere. We noted that this sensitivity is effectively eliminated by combining observations of two similar molecules with transitions at similar wavelengths; i.e. OH and CH rotational lines would give an accurate estimate of the O/C abundance ratio. Additional improvements to solar infrared spectra may lead to the detection of the weaker CH lines and so to a precise estimate of the O/C ratio. Our current best estimate for the O/C ratio is obtained from three different combinations of atomic and molecular lines: $e(O)/e(C) = 1.70 \pm 0.12$. Inclusion of the $C_2$ Swan system in an O/C and a C abundance (from CH and $C_2$) determination suggests that the dissociation $D_0 = 6.21 \text{ eV}$ (Huber & Herzberg 1979) is to be preferred to the lower spectroscopic estimate adopted earlier (Lambert 1978). The insensitivity to the model atmosphere of those abundance ratios obtained from selected combinations of lines appears not to have been fully recognized before.

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