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Hot Water on the Sun: Assignments via *ab initio* Line Lists

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Abstract:

Sunspot infrared absorption spectra have recently been reported which are highly congested with spectral lines thought to be due to water. We have completed a theoretical interpretation of these spectra using a new accurate *ab initio* water linelist (Polyansky et al. 1997a). This treatment led to vibration-rotation quantum number assignments for individual lines of both sunspot ($T \sim 3200$ K) and water laboratory measurements ($T \sim 1800$ K). We have assigned $\sim$ 1300 sunspot lines and $\sim$ 3000 laboratory lines in the M band (Polyansky et al. 1997b) and $\sim$ 500 sunspot lines in the K band (Polyansky et al. 1997c).

1. Introduction

The infrared spectrum of water is one of the most important of all molecules due to the multitude of applications, not only in Astronomy.

It has long been believed that water is one of the most important astronomical molecules in "cool" (400–4000K) sources. However the spectrum of water is very complicated and the spectrum of hot water remains poorly understood. Detailed, line-by-line data on hot water are required for radiative transport models of many hot systems. For example the water molecule is the most important source of infrared opacity in the spectra of oxygen rich late-type stars (Allard et al. 1994; Gustaffson & Jorgensen 1994). Mira variables show strong infrared water bands (Hinkle & Barnes 1974). For substellar objects such as brown dwarfs, water is predicted to be the most abundant molecule after H_2 (Tsuji & Ohnaka 1995; Fegley & Lodders 1996). Water is also the primary mother molecule in comets (Mumma et al. 1986).

Interstellar water was discovered by Cheung et al. (1969) in dark clouds on the basis of the 22 GHz maser transition. More recently millimeter and submillimeter wave rotational transitions of water and its isotopomers have been studied in dark clouds and star-forming regions (Cernicharo et al. 1994; Gensheimer et al. 1996).

The detection of water from Earth is difficult because of telluric absorption. However, the infrared lines of hot water pass through the Earth's atmosphere because these highly excited transitions are shifted away from telluric absorp-

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tions of cooler water. Also, with the advent of the ISO satellite, in 1996, infrared and far infrared spectrometers were used to show that both solid water (Schutte et al. 1996) and gaseous water (van Dischoek & Helmich 1996) are ubiquitous in the Galaxy.

Recently water has also been found in the spectra of the sunspots (Wallace et al. 1995) by using hot laboratory spectra. By using a combination of high-level *ab initio* calculation and careful spectral analysis we have assigned a large number of new transitions in both these spectra. This assignment procedure represents a significant shift away from traditional, perturbation theory-based, methods of spectral assignment. In this paper we discuss i) a new linelist, ZVPT, computed to assign water in the sunspots and in the laboratory; ii) assignments of the M and K band of the sunspots spectra.

2. Water in the Sunspots

In 1970, Hall identified water lines in sunspots in the K window (Hall 1970). The sunspot spectra were originally considered unassignable. Benedict made some water line assignments in Hall's spectra but this work was never completed and published. The next successful attempt to perform a complete analysis of the sunspot was by Wallace & Livingston (1992) who published a spectral atlas of a dark sunspot umbra in the region 1970–8640 cm^{-1} (1.16 to 5.1 μm) They obtained umbral spectra with the 1-meter Fourier transform spectrometer on Kitt Peak. They found that the spectra contained large absorption bands of water vapour. This is not very surprising considering that the temperature of the sunspots is $\sim$ 3200K. They identified many absorption features within the L window using the French laboratory measurements (Flaud et al. 1976; Camy-Peyret et al. 1977).

Later, Wallace et al. (1995, 1996) were able to demonstrate that hot water was responsible for the dense lines in the M band (10–20 μm) sunspot spectrum (again collected in an atlas, Wallace et al. 1994).

These bands were assigned to pure rotation and vibration-rotation transitions of water by comparing them to high-temperature laboratory emission spectra (Wallace et al. 1995). Polyansky et al. (1996), assigned transitions involving high rotational quantum numbers J and K_a to an emission spectrum recorded at 1800 K in the M window. The methods used to assign these laboratory spectra are perturbational. In some cases their procedure gave more than one candidate per line. They underline that this is due to the limitation of the perturbational methods point out that more accurate variational calculations are needed for better assignments.

The laboratory measurements were made at lower temperature than the sunspots. Therefore they contained a significantly lower density of lines. To tackle the high density of lines in the sunspot spectrum, up to 50 lines per cm^{-1} in the M window, an entirely new method of assignment is required.

3. The Method

Water is a triatomic asymmetric top molecule. For an asymmetric top, each vibrational level contains $2J+1$ sublevels of energy for each value of the rotational angular momentum, J.

A program suite, DVR3D (Tennyson et al. 1995) was developed to calculate *ab initio* the quantized energy levels, the *all* dipole transitions (following rigorous symmetry rules), and hence the line positions and intensities of each transition. This suite employs the Discrete Variable Representation (DVR) technique (Bačič & Light 1986). The suite is divided into 3 subprograms:

- DVR3DRJ calculates the vibrational states in Radau coordinates
- ROTLEV3B produces the rotationally excited energy levels and wavefunctions
- DIPOLE3 computes dipole transitions intensities

For a much fuller description refer to Tennyson et al. (1995). An additional program, SPECTRA (Tennyson et al. 1993), is used to synthesize spectra from the linelist generated by dipole. These programs have been updated during the course of this work (Viti 1997). The method has been employed to produce various water linelists. These include VTP1 (Viti et al. 1997) and the new linelist, ZVPT.

4. The Computation of a New Line List, ZVPT

For low vibrational states, the accuracy of a previously calculated water linelist using variational methods (Viti et al. 1997) is limited by the choice of the potential surface. We computed a new linelist employing the very high quality *ab initio* Born–Oppenheimer (BO) potential energy surface by Partridge & Schwenke (PS, Schwenke 1996). We corrected the PS potential surface for the mass-dependent adiabatic correction to the BO approximation. This correction was included by addition of a mass-dependent *ab initio* adiabatic surface (Zobov et al. 1996). An approximate allowance for the non-adiabatic correction was included by the use of a H atom mass of 1.007551 amu, mid-way between that of H and a bare proton (Zobov et al 1996) and an O atom of 15.990526 amu.

For the construction of the dipoles we used the dipole surface by Gabriel et al (1993).

We used a DVR grid of 40 points based on Gauss-(associated) Legendre polynomials in the θ coordinate. For the radial coordinates we used a DVR grid of 21 points with radial basis set parameters of $r_e = 2.06a_0$, $D_e = 0.14E_h$ and $\omega_e = 0.014E_h$, where r_e is the equilibrium radius, D_e is the dissociation energy and ω_e is the fundamental frequency of the Morse oscillator-like functions upon which the DVR is based (Tennyson et al. 1995). This number of grid points is sufficient to obtain good convergence for low-lying vibrational levels (Fulton 1994).

In the first 'vibrational' step we diagonalised a series of final secular problems of dimension 1000 from which we retained the lowest 500 eigenvalues and eigenvectors. For given J, the full ro-vibrational problem was solved using a basis of the $150 \times (J+1)$ lowest solutions from the first step. The number of eigenvalues obtained varied with J with no fixed rule. We computed eigenvalues with energies of up to at least 18000 cm^{-1} for $J \leq 25$; for $J = 25$ this corresponds to the lowest 500 eigenvalues for each symmetry block. For the 25 $\leq J \leq 33$, eigenenergies up to 23000 cm^{-1} were computed corresponding to 320 eigenvalues per symmetry block for $J = 33$. These criteria ensured that we covered all the energy levels belonging to the (000), (100), (010), (020), (001), (030) vibrational states and of course, low K_a states of many higher vibrational bands are also included. Temperature dependent spectra were generated using an adapted version of program SPECTRA which uses full nuclear spin statistics.

ZVPT is less accurate than linelists based on spectroscopically determined potentials: VTP1 (Viti et al. 1997) and PS (Partridge & Schwenke 1997). However it is more systematic in its inaccuracy: the error increases slowly and systematically with J within the same branch, where a branch is a set of levels where either K_a or K_c are constant (Polyansky et al. 1997c).

5. Applications: Spectral Analysis of the Sunspot Spectra

With the aid of ZVPT we have been able to assign the infrared spectrum of hot water in a sunspot. This was done using intensity information in the calculations and spectra, and by following branches so that systematic errors in the calculations were removed. The atlases, published by Wallace et al. (1994, 1995, 1996), cover from mid–to near infrared. Many regions are affected by Telluric and other species (such as SiO) absorption. We have concentrated on M and K bands. The regions were most of the assignments where made are: i) 750–1010 cm^{-1} (10–13 μm) and ii) 4600–5100 cm^{-1} (2.17–1.96 μm), where the spectrum is dominated by hot water absorption. In total, we have a assigned 1687 sunspot lines in the M window and 485 in the K window.

Figs. 1 to 5 show such assignments for several regions of the spectrum.

Figure 1 shows the region 771.5–775.5 cm^{-1} where transitions belonging to three distinct vibrational bands can be observed.

The region covered by Figure 2 is 841–849.5 cm^{-1}. We have an example of the so called “splitting”: two high K_a transitions, which one would expect to be strongly overlapped, are instead split, presumably by Coriolis interactions with levels of a different vibrational state (Polyansky et al. 1997d).

In Figure 3, the region 872.5–875.3 cm^{-1} is shown. With this figure we illustrate the congested nature of the sunspot spectrum.

Figure 4 (924.2–925.6 cm^{-1}) shows a region of the spectrum that is sensitive to higher water levels and therefore many of the lines that we assign are not seen in the cooler laboratory spectrum. Figures 1– 4 are examples of assignments in the M window.

Figure 5 (4890–4930 cm^{-1}) is an example of the transitions assigned in the K window. It can be seen that these assignments include all of the strong absorption features in the spectral region of interest. Of the 10 vibrational bands for which transitions have been assigned, only (011) − (000) and (021) − (010) have been observed previously in the laboratory or in space (Rothman et al. 1992).

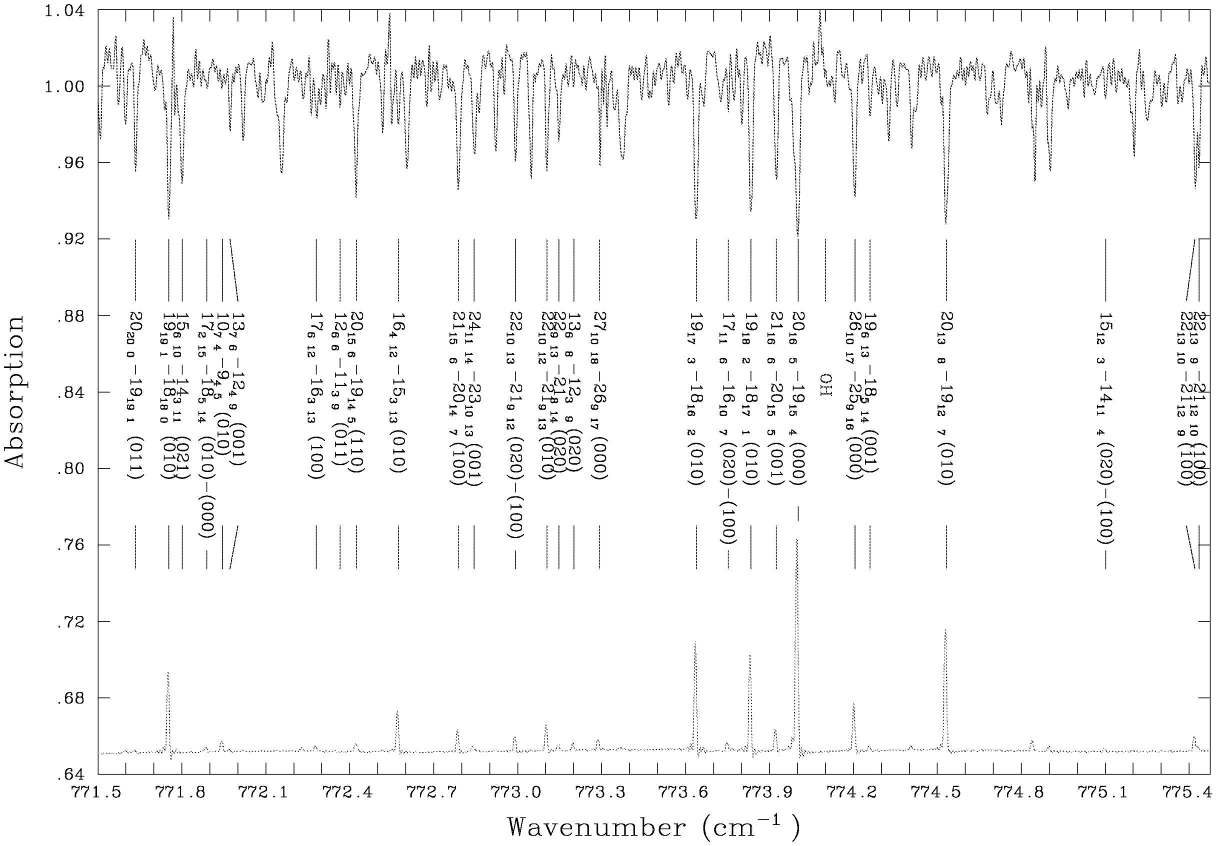

Figure 1. Top: part of the sunspot spectrum of Wallace et al.(1995). The region covered is from 771.5 to 775.5 cm^{-1}. Quantum number assignments, given as $J_{K_aK_c}$ (upper)–$J_{K_aK_c}$ (lower) for various vibrational states (labelled using standard notation ($v_1v_2v_3$)), are marked. Bottom: the corresponding part of the laboratory spectrum (Polyansky et al. 1996). For convenience, we have normalized the intensity.

Full details of the assignments can be found in be found in Polyansky et al. (1997a, 1997b, 1997c).

6. Conclusion

We demonstrate the utility of linelists generated using variational nuclear motion calculations in making spectral assignments for complicated spectra which are unassignable using traditional methods.

ZVPT should have many applications both in astronomy, in molecular spectroscopy and elsewhere. It is not possible for us to publish the entire linelist in this paper but ZVPT will shortly be freely available on the WWW.

ZVPT is currently still being used to assign further water lines observed in laboratory and in sunspots.

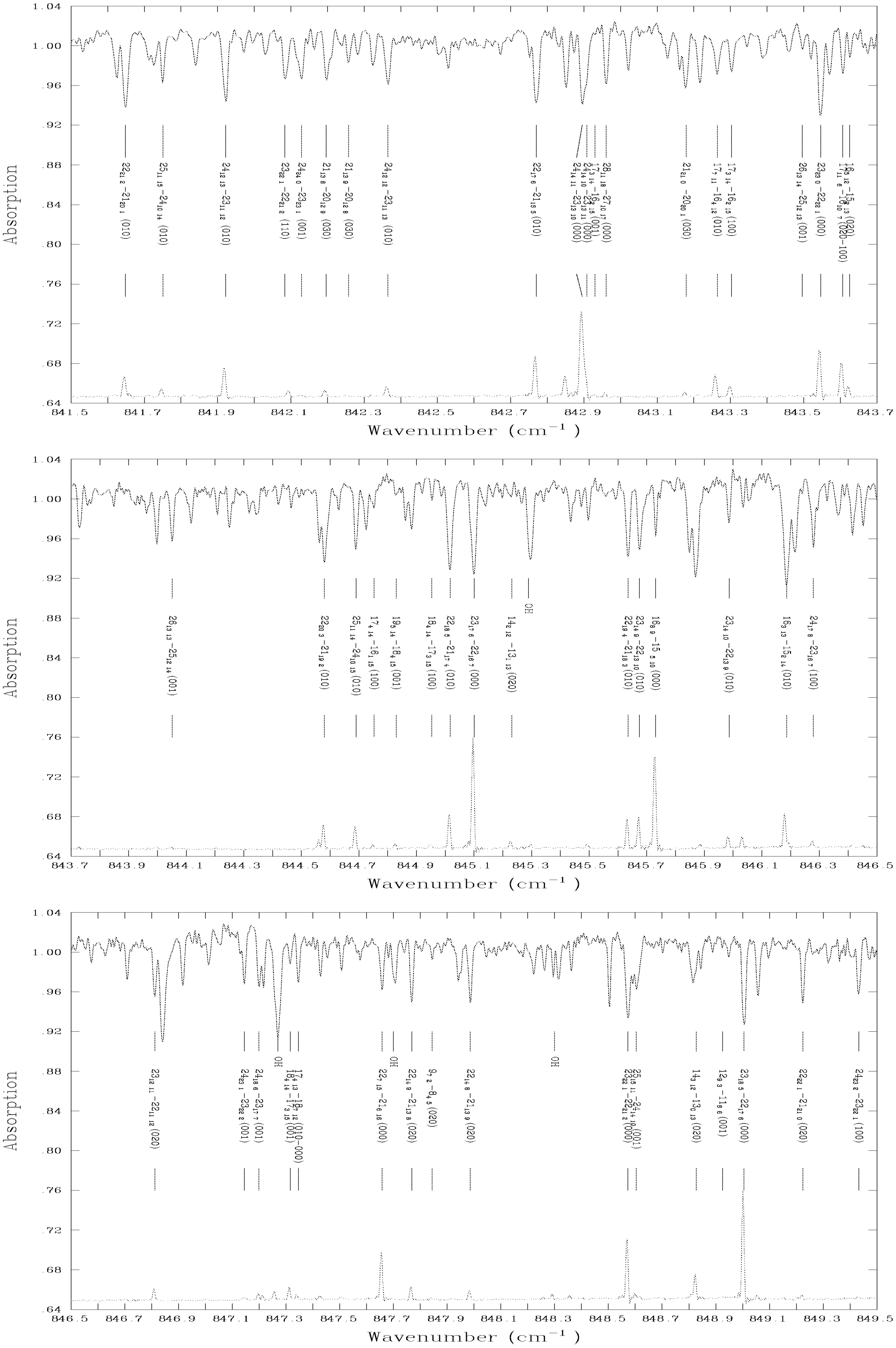

Figure 2. Top: part of the sunspot spectrum of Wallace et al.(1995) from 841.5 to 849.5 cm^{-1}. Bottom: the corresponding laboratory spectrum.

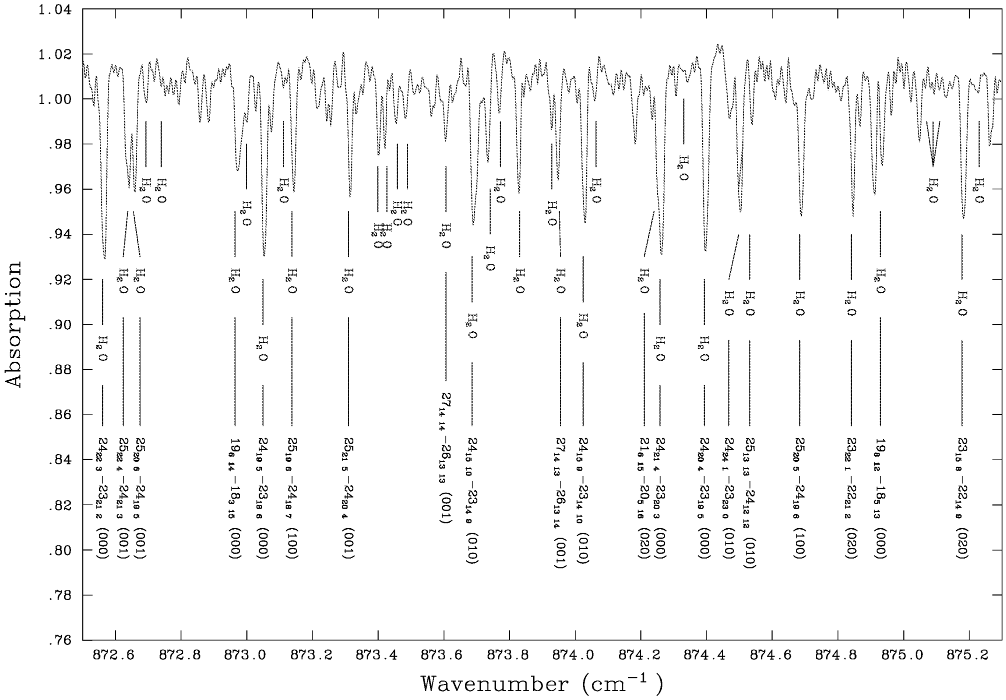

Figure 3. Part of the sunspot spectrum of Wallace et al. from 872.5 to 875.3 cm^{-1} region. Features previously associated with water by comparison with laboratory spectra are labeled H_2O.

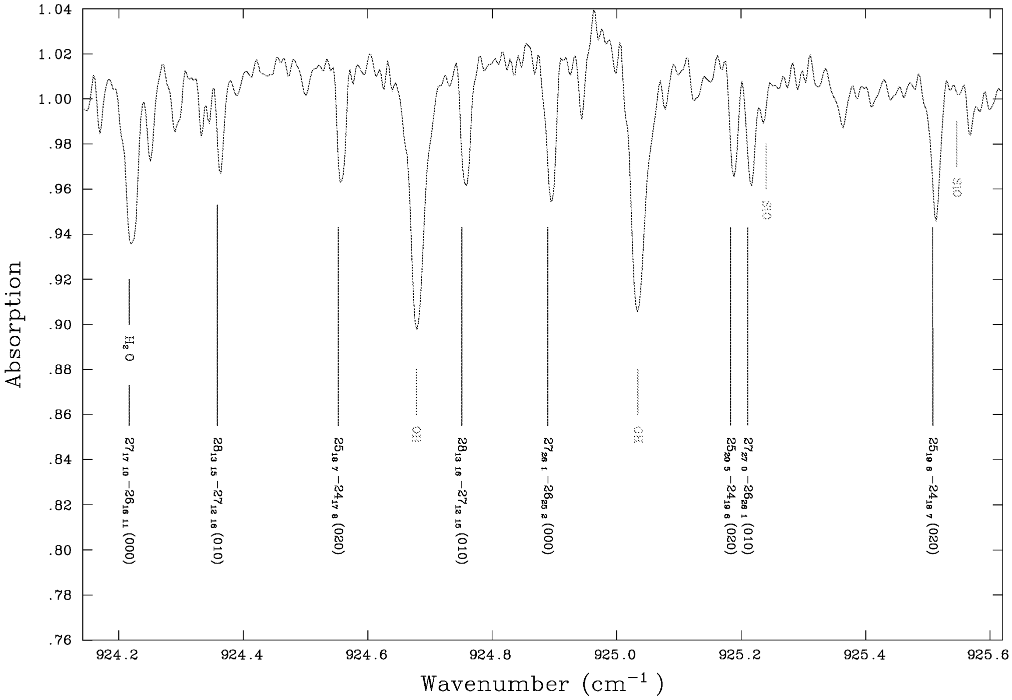

Figure 4. Part of the sunspot spectrum of Wallace et al. from 984.2 to 925.6 cm^{-1}. The only feature previously associated with water by comparison with laboratory spectra is labeled "H_2O". Assignments for the features of "SiO" and "OH" are well known.

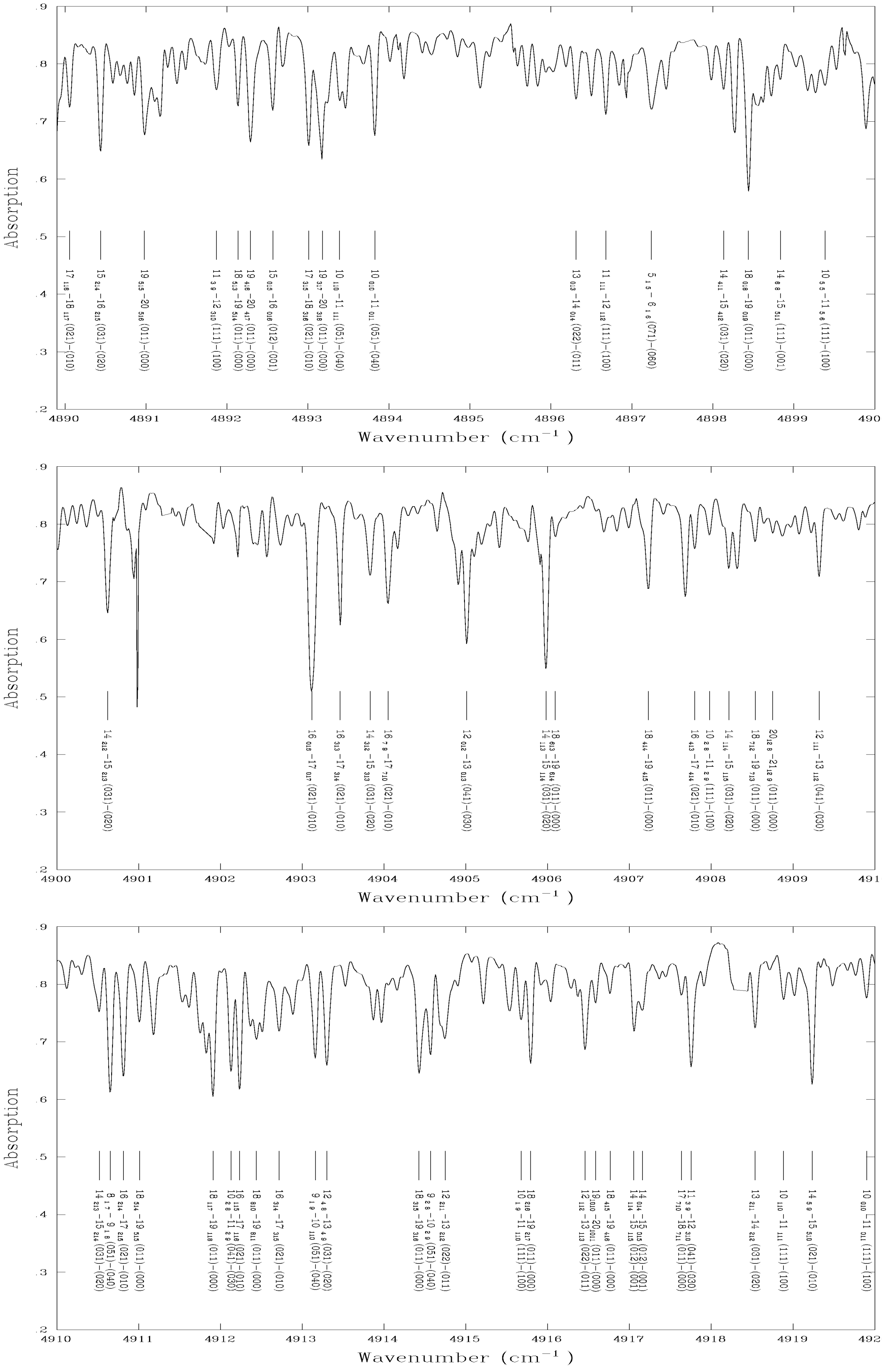

Figure 5. Part of the sunspot spectrum of Wallace et al. from 4890 to 4900 cm^{-1}.

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