USING LABORATORY SPECTROSCOPY TO IDENTIFY LINES IN THE *K*- AND *L*-BAND SPECTRUM OF WATER IN A SUNSPOT

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ABSTRACT

The infrared spectrum of a sunspot is analyzed in the *L*-band region 3.1–4.0 μm (2497–3195 cm^{-1}) and 2.02–2.35 μm (4251–4962 cm^{-1}) in the *K* band. A new laboratory emission spectrum covering 2500–6000 cm^{-1} is analyzed to help make the assignments. Quantum number assignments are made using linelists computed using variational calculations, assisted by tabulations of experimental energy levels. There are 1207 new H$_2^{16}$O lines assigned in the *L* band and 508 new lines in the *K* band. Vibrational band origins of 11242.8 ± 0.1 cm^{-1} and 12586 ± 1 cm^{-1} are obtained for the (051) and (061) states.

Subject headings: molecular data — sunspots — infrared: solar system — infrared: stars

1. INTRODUCTION

Recent observations have lent strong support to the widely held supposition that water is the third most abundant molecule in the Universe after hydrogen and carbon monoxide. Molecular hydrogen is hard to detect because it lacks a dipole-allowed infrared or microwave spectrum. In contrast, water has extensive infrared and submillimeter wave spectra, but is hard to observe from the ground because of the blanketing effect of telluric water vapor.

The *Infrared Space Observatory* (*ISO*) satellite yielded many detections of water spectra in the infrared, several in unexpected locations (van Dishoeck 1997). For example, in the massive star-forming region Orion IRc2, gaseous water is seen in both emission and absorption along with ice bands (van Dishoeck et al. 1998). Some of the observations are of water vapor at temperatures significantly higher than 300 K. At higher temperatures the infrared spectrum of water shifts into the atmospheric windows through which high quality ground-based observations can be performed. It is astronomically important to have good spectroscopic data on water in these spectral regions. The infrared spectrum of hot water is complicated and until recently much of it could not be properly analyzed.

Hot water is known to be an important opacity source in cool oxygen-rich stars (Hinkle & Barnes, 1979; Allard et al. 1994; Flaud et al. 1997) and brown dwarfs (Geballe et al. 1996; Allard et al. 1997). That water could also be observed in sunspots has been known for some time (Hall 1970). Wallace et al. (1996) reported on the preparation of a series of detailed spectral atlases of sunspots. In particular, Wallace & Livingston (1992) presented the sunspot spec-

trum in the range 1.16 –5.1 μm, in which they were able to identify some water transitions in both the K and L bands using energy levels obtained from the measurements of Flaud et al. (1976) and Camy-Peyret et al. (1977).

Wallace et al. (1995) made a direct comparison between a laboratory emission spectrum in the 400–900 cm^{-1} region and the *N*-band sunspot spectrum. They showed that the dense forest of lines, up to 50 lines per cm^{-1}, in the *N*-band region were mainly due to water vapor. Line assignments for both the laboratory and sunspot *N*-band spectra were achieved by Polyansky et al. (1997a, 1997c) using theoretical techniques based on variational nuclear motion calculations. In subsequent, work Polyansky et al. (1997b) performed an initial analysis of the *K*-band spectrum of Wallace & Livingston (1992). They assigned 487 new lines to transitions in 10 vibrational bands in 2.17–1.96 μm (4600–5100 cm^{-1}) region. This analysis left many unassigned lines in both *L* and *K* bands. To make progress on the sunspot spectrum, we have recorded a new, hot laboratory emission spectrum of water in the range 1.67–4.0 μm (2500–6000 cm^{-1}), covering both the *K* and *L* bands. We have analyzed this spectrum together with the sunspot spectra. We report the assignment of 90% of the 8482 laboratory emission lines, along with 1153 water lines in the *L*-band sunspot spectrum and 882 water lines in the *K*-band sunspot spectrum.

2. LABORATORY EXPERIMENT

The line positions were taken from an emission spectrum recorded with the Bruker IFS 120 HR Fourier transform spectrometer at the University of Waterloo (Bernath 1996). The spectrometer was operated with a CaF$_2$ window and beamsplitter, a 6666 cm^{-1} low-pass filter, and a liquid nitrogen-cooled InSb detector. The 1 m × 5 cm diameter alumina tube was heated by a furnace up to about 1500 °C. The ends of the tube were sealed with water-cooled CaF$_2$ windows. Water was vaporized and carried continuously into the tube by a flow of the dry hydrogen gas at room

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temperature. The tube was slowly pumped to stabilize the total pressure around 30 torr. The partial pressure of water was estimated to be 0.5–1 torr. The thermal emission of the water vapor was focussed by a 45 degree off-axis parabolic mirror ($f = 15$ cm) into the entrance aperture of the spectrometer. The spectral region of 1800–7000 cm^{-1} was covered at a resolution of 0.02 cm^{-1}. A total of 275 scans were co-added in 138 min of integration.

The use of hydrogen as a buffer gas resulted in an order of magnitude improvement in the signal-to-noise ratio (S/N) over our previous efforts using no carrier gas, and the reason for this is not completely clear. Water vapor reacts with the alumina walls of the tube at 1500 °C so that a steady flow of water into the cell is required. Perhaps the H$_2$ reacts with water decomposition products such as OH to reform H$_2$O or the H$_2$ may slow down the decomposition of H$_2$O. When the experiment was repeated with Ar as a carrier gas, the signal improved nearly as much suggesting that it is just the flow of buffer gas that carries more water into the cell.

Measurement of the laboratory spectrum in the range 2500–6008 cm^{-1} gave 8482 emission lines once artifacts due to the line-finding process had been removed. The lines were calibrated with the measurements of Toth (1993) and have an absolute accuracy better than 0.001 cm^{-1}. The HITRAN database (Rothman et al. 1998) contains a similar number of water lines in this spectral range. HITRAN is a low-temperature database and many of the lines present do not have significant intensity at 1773 K; conversely the laboratory spectrum contains many hot lines that are not present in HITRAN. We identified 1743 H$_2^{16}$O lines in our new spectrum that were already in HITRAN.

3. SPECTRAL ANALYSIS

Together with the laboratory spectrum, we performed a detailed analysis of the sunspot umbra spectrum of Wallace & Livingston (1992), which covers the wavenumber range 1970–8640 cm^{-1} (1.6–5.1 μm). This spectrum is considerably hotter than the laboratory spectrum with an assumed water temperature of 3200 K, derived from the spectrum of SiO (Campbell et al. 1995; Wallace et al. 1995). In this work we concentrated on two regions: 2497–3195 cm^{-1} (3.1–4.0 μm), which covers the L band, and 4251–4962 cm^{-1} (2.02–2.35 μm) in the K band. Measurements of these regions showed, respectively, 2737 and 3133 clearly resolved absorption features.

The infrared sunspot spectrum contains features due to a variety of neutral atoms and diatomic molecules. Lines due to the diatomics OH, HCl, CO, and HF can be identified in the region of interest. Water is the only identified polyatomic species and it contributes the largest number of transitions (Wallace et al. 1995). Wallace & Livingston (1992) assigned 161 lines in the 2497–3195 cm^{-1} region and 126 lines in the 4251–4962 cm^{-1} region as being due to water on the basis of laboratory spectra (Flaud et al. 1976; Camy-Peyret et al. 1977). Polyansky et al. (1997b) assigned an additional 465 transitions in the 4600–4962 cm^{-1} region of the spectrum. Most of the transitions assigned prior to this work correspond to ones associated with relatively low-lying states of water.

Our technique for assigning spectra of hot water has been well documented (Polyansky et al. 1997a, 1997b, 1997c, 1999; Zobov et al. 1999) and will only be outlined here. The task is tackled in two stages. First, we make all possible "trivial" assignments, those for transitions between states whose energy levels have already been experimentally determined. We maintain lists of experimental energy levels for this purpose, based on previous experimental studies (Chevillard et al. 1989; Flaud et al. 1997; Lanquetin 1997) and our own work. During this work we found that six of the levels quoted by Chevillard et al. (1989) and rather more of those due to Lanquetin (1997) were not correct. The levels presented by Lanquetin et al. (1999) all agree with previously published data.

In contrast to our work on the N-band sunspot spectrum, a large number of lines studied here could be identified using trivial assignments. This is a by-product of our work on spectra of hot water at other wavelengths and serves to confirm these previous assignments.

Transitions that could not be assigned trivially were analyzed using linelists computed using variational nuclear motion calculations. As before (Polyansky, Zobov, & Tennyson 1999; Polyansky et al. 1997b; Zobov et al. 1999), two linelists were used: "PS" (Partridge & Schwenke 1997), which used a potential energy function empirically modified using spectroscopic data, and "ZVPT" (Polyansky et al. 1999), which is based on a high-accuracy ab initio potential with explicit allowance for the failure of the Born-Oppenheimer approximation. Comparisons of the linelists have been made elsewhere (Polyansky et al. 1997b, 1997c, 1999); in essence PS is very accurate for interpolating between known levels, whereas ZVPT is more reliable for extrapolation. Synthetic spectra were generated using the linelists at a temperature of 1800 K for the laboratory spectrum and 3200 K for the sunspot. The linelists need to be used carefully when making assignments since neither is accurate enough for direct-frequency comparisons alone to be reliable. Assignments can be supported by intensity comparisons and, where possible, confirmed using combination differences.

Our initial focus was on the laboratory spectrum because it does not suffer from the problems of limited spectral coverage, omitted portions due to telluric effects and absorptions by other species. We found no significant emission due to OH in the laboratory spectrum (see Fig. 1). Of the 8482 lines measured in the laboratory, we assigned 7603 of them to transitions involving H$_2^{16}$O. There were 6880 lines assigned from previously known data either because they are in HITRAN or on the basis of trivial assignments. Of the 723 new line assignments, 296 were confirmed by combination differences, meaning that more than one transition in the spectrum involved the same upper state. These assignments can be regarded as secure.

In analyzing the umbral L-band spectrum, we first removed lines that could be associated with other molecules known to be present in sunspots. There were 192 OH lines that could be identified in the 2497–3195 cm^{-1} region using the data of Mélen et al. (1995). An additional 10 transitions due to HCl had already been identified by Wallace & Livingston (1992). Second, we assigned lines either by comparison with the laboratory spectrum or using trivial assignments; 1153 water lines were assigned in this fashion. Finally, 54 additional water lines were assigned by direct comparison with the linelists. As the water in the sunspot spectrum is hotter than in the laboratory one, extra lines are to be expected.

A similar procedure was applied to the K-band umbral spectrum where 127 CO lines and six HF lines were identi-
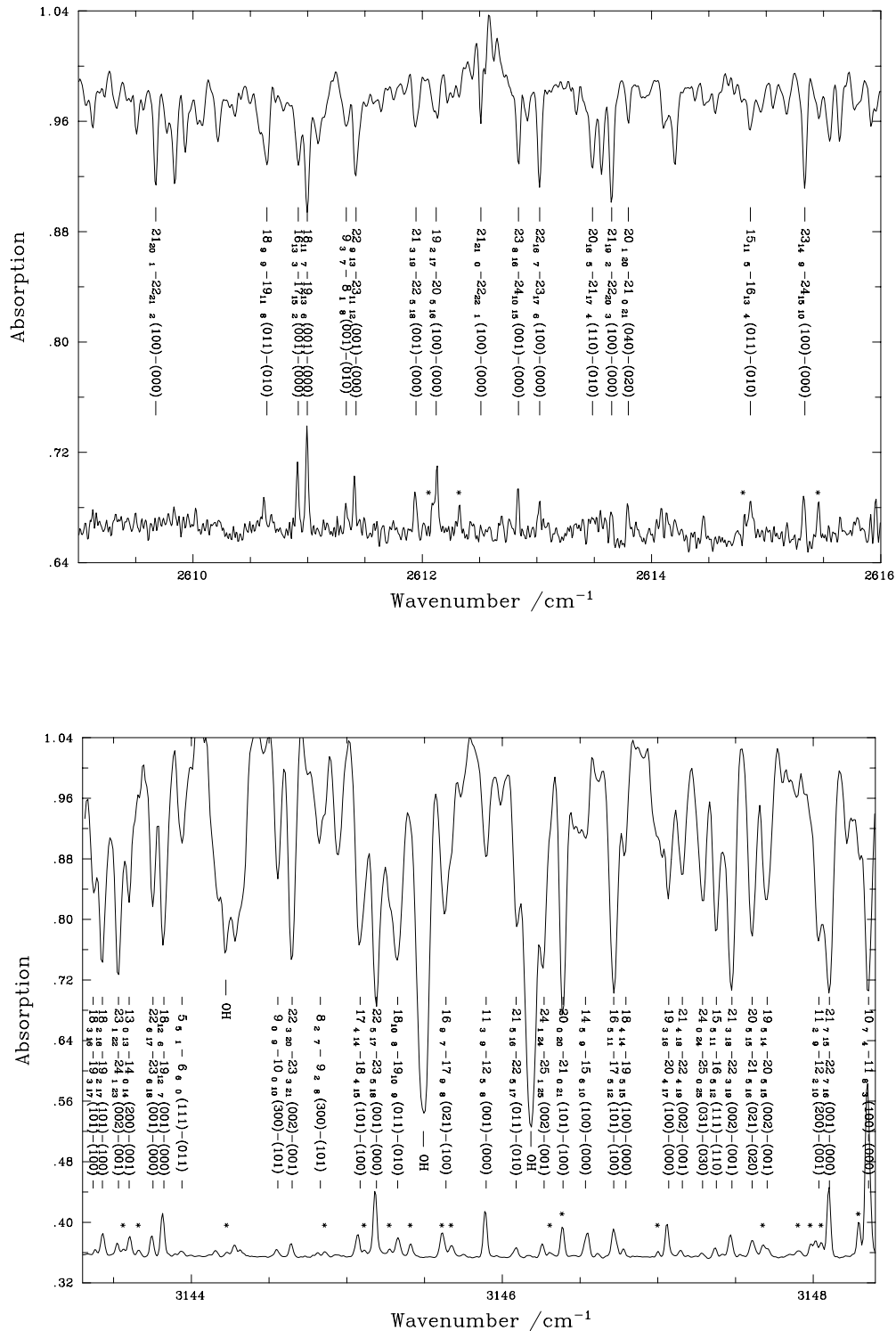
FIG. 1.—Two sections of the sunspot umbra absorption spectrum and the laboratory emission spectrum in the L-window region. The scale on the y-axis refers only to the sunspot spectrum. Asterisks mark lines assigned in the laboratory spectrum that are absent in the measured sunspot spectrum.

fied by Wallace & Livingston (1992) in the 4251–4962 cm^{-1} region. There were 868 water lines assigned in this region. This is an increase of 508 from previous studies when an allowance is made for five transitions we found to have been misassigned previously.

The L-band spectrum contains transitions that involve 44 distinct vibrational bands, although for 17 of these bands fewer than four lines were assigned. In the K band, transitions belonging to 39 distinct vibrational bands could be identified, although 21 bands involved three or fewer lines.

Tables 1 and 2 give a summary of the *L*- and *K*-band assignments, respectively. A summary of assignments to the laboratory spectrum is given for comparison: this spectrum contains 70 distinct vibrational bands, 26 with three or fewer lines. As in our recent analysis of a laboratory spectrum of hot water in the 933–2500 cm^{-1} region (Zobov et al. 1999), many of the vibrational bands are difference transitions that appear to be prevalent in spectra of hot water. The hotter sunspot spectra give a higher proportion of lines starting from the higher vibrationally excited states, particularly in the *K* band.

All the vibrational states observed here had been observed in previous studies. However, very few transitions had been previously observed that involved the (051) and (061) vibrational states. The vibrational band origins for these states were unknown. We have not observed transitions to the *J* = 0 level of either of these states, but it is possible to use the linelists to estimate the experimental band origin (Polyansky et al. 1998). This procedure gives band origins of 11242.8 cm^{-1} for (051) and 12586 cm^{-1} for (061) with an error of one unit in the last digit.

Figure 1 gives two illustrative portions of the *L*-band sunspot absorption spectrum, the laboratory emission spectrum and the associated assignments. We have successfully assigned the strong features in both spectra, but there are a number of weaker lines that remain to be analyzed. The

TABLE 1

WATER TRANSITIONS IN THE 2497–3195 cm^{-1} REGION OF THE SUNSPOT SPECTRUM

Band	Origin	$E''(J = 0)$	N(Sun)	N(Lab)
020–000......	3152	0	62	371
100–000......	3657	0	194	762
001–000......	3756	0	208	1300
001–010......	2161	1595	23	67
030–010......	3072	1595	91	306
110–010......	3730	1595	83	290
011–010......	3737	1595	111	858
011–020......	2180	3152	12	24
040–020......	2962	3152	71	175
120–020......	3623	3152	10	32
021–020......	3720	3152	26	315
120–100......	3118	3657	4	12
200–100......	3544	3657	29	77
101–100......	3593	3657	38	231
021–001......	3116	3756	7	12
200–001......	3446	3756	24	76
101–001......	3494	3756	34	78
002–001......	3689	3756	20	259
021–030......	2205	4667	8	11
050–030......	2876	4667	26	51
031–030......	3707	4667	6	78
111–110......	3572	5235	9	53
111–011......	3476	5331	9	11
012–011......	3669	5331	8	82
031–040......	2240	6134	4	2
201–200......	3412	7202	5	13
300–101......	3350	7250	6	14

NOTE.—Summary of water transitions assigned in the 2497–3195 cm^{-1} region of the sunspot spectrum of Wallace & Livingston 1992. Given are the number of transitions assigned, N(Sun), to the major vibrational bands in the sunspot spectrum and the number of laboratory transitions assigned to this band, N(lab). For each band, "Origin" gives the calculated vibrational band origin in cm^{-1} and $E''(J = 0)$ the energy of the lower vibrational state in cm^{-1}.

TABLE 2

WATER TRANSITIONS IN THE 4251–4962 cm^{-1} REGION OF THE SUNSPOT SPECTRUM

Band	Origin	$E''(J = 0)$	N(Sun)	N(Lab)
100–000......	3657	0	170	762
001–000......	3756	0	78	1300
110–000......	5235	0	4	28
011–000......	5331	0	129	689
110–010......	3640	1595	8	290
011–010......	3737	1595	56	858
021–010......	5277	1595	111	526
021–020......	3720	3151	10	315
031–020......	5222	3151	107	317
111–100......	5150	3657	62	54
012–001......	5244	3756	30	91
041–030......	5167	4667	115	73
121–110......	5094	5325	11	10
022–011......	5193	5331	20	25
051–040......	5109	6134	48	36
061–050......	5044	7542	27	4
071–060......	4965	8871	7	...

NOTE.—Summary of water transitions assigned in the 4251–4962 cm^{-1} region of the sunspot spectrum of Wallace & Livingston 1992. Columns are as in Table 1.

higher resolution of the laboratory spectrum can also be seen.

4. DISCUSSION AND CONCLUSIONS

Using a combination of new laboratory measurements and variational calculations, we have extended the number of assigned water lines in both the *L* and *K* bands of the sunspot spectrum. These transitions can be used to monitor water in other astronomical objects. The transitions have the significant advantage that, unlike most of the infrared spectrum of water, their wavelengths lie in atmospheric windows.

It is not practical to publish tabulations of over 14,000 lines. We therefore supply this data electronically, which is more useful for most applications. The data take the form of three files corresponding to the laboratory, *L*- and *K*-band spectra. Each file contains a list of all measured lines and an estimate of the relative intensity, followed by an assignment where available. They can be obtained by an anonymous ftp from ftp.tampa.phys.ucl.ac.uk and looking in "directory/pub/astrodata/water/lwin" or by sending email to the authors (JT).

The linelists contain accurate transition frequencies and some crude experimental assessment of the relative transition intensity. We have accurate theoretical estimates of the line strength for all the water transitions that have been assigned. For the quantitative simulation of astronomical spectra, it is preferable to use the theoretical line intensities. We are constructing complete linelists that include these line strengths, but this is a considerable undertaking. Data for individual transitions can be supplied by the authors if required. We are also preparing a revised list of water energy levels.

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