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LABORATORY SPECTROSCOPY OF HOT WATER NEAR 2 MICRONS AND SUNSPOT SPECTROSCOPY IN THE H-BAND REGION

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ABSTRACT

The infrared spectrum of sunspots is analyzed in the H-band region (5540–6997 cm^{-1}) with the aid of a new, hot ($T = 1800$ K) laboratory emission spectrum of water covering 4878–7552 cm^{-1}. There are 682 lines in the sunspot spectrum and 5589 lines in the laboratory spectrum assigned quantum numbers corresponding to transitions due to $H_2{}^{16}O$ using a combination of previously known experimental energy levels for water and variational line lists. A further 201 unassigned lines common to both spectra can also be associated with water.

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

On-line material: color figure, machine-readable tables

1. INTRODUCTION

Water has been detected in a variety of astronomical objects from the ground as well as from satellite and airborne platforms. The first published observations of water were made in the near-infrared region (1.4, 1.7, and 2.7 μm) with the Stratoscope II instrument on a balloon (Woolf, Schwarzchild, & Rose 1964; Tsuji 2000a) and on the ground at 0.93 μm (Spinrad & Newburn 1965). Highly excited overtone bands ("steam bands") were detected in red giants. These steam bands were particularly strong in Mira variables such as o Ceti and R Leonis. Higher resolution spectra of R Leonis by Hinkle & Barnes (1979) revealed that the water vapor is formed in at least two separate circumstellar layers. The "warm" component (~1700 K) is near the photosphere and varies strongly with phase as compared to the cooler, overlying layer (~1100 K). Similar spectra of the Mira variable R Cas were recorded by Maillard et al. (1978) but never published in a journal article, and more recent *Infrared Space Observatory* (*ISO*) observations of o Ceti were presented by Yamamura, de Jong, & Cami (1999).

Jennings & Sada (1998) discovered pure rotational lines of water near 10 μm in the (non-Mira) early supergiants Betelgeuse (α Ori) and Antares (α Sco). Tsuji (2000a) has pointed out that these observations are consistent with the earlier disputed assignments by Woolf et al. (1964) and recent measurements with *ISO* (Tsuji 2000b). Tsuji (2001) has also found the 6 μm water band in several late-K and early-M giants with high surface temperatures (3600–4000 K). Such high temperatures are inconsistent with the presence of water in the stellar photosphere. Tsuji (2000a, 2000b, 2001) therefore suggests that the water is found in a warm circumstellar cloud ($T \sim 1500$ K) that he has dubbed the "MOLsphere."

The *ISO* satellite was able to detect water in a large number of additional sources, such as the star-forming region in Orion (Wright et al. 2000) and the Class 0 protostar L1448 (Nisini et al. 1999). Water is particularly prominent in oxygen-rich circumstellar outflows in, for example, NML Cyg (Justtanont et al. 1996) and W Hya (Barlow et al. 1996).

Water has also been detected by the techniques of radio astronomy, starting with the discovery of the 22 GHz maser transition by Cheung et al. (1969). Water masers are commonly associated with star-forming regions (Xiang & Turner 1995). All millimeter-wave transitions of water detectable from the ground are masing to some degree, although nonmasing HDO (Pardo et al. 2001) and $H_2{}^{18}O$ (Gensheimer, Mauersberger, & Wilson 1996) transitions can be observed.

The *Submillimeter Wave Astronomy Satellite* has detected thermal water emission from many sources using the low-lying 1_{10}–1_{01} ortho transition at 557 GHz (Melnick et al. 2000). Water abundances in dark molecular clouds were found to be very low, and water is not a strong coolant in these objects (Bergin et al. 2000a). Higher water abundances were found in Orion and other shocked regions. Water was even found unexpectedly in the circumstellar envelope of the carbon star IRC +10216. Melnick et al. (2001) speculated that this water could have originated from the evaporation of a belt of extrasolar comets.

The spectra of hot water have particular importance in determining the spectral energy distributions of dwarf stars. Water lines start to appear in early-M dwarfs (Leggett et al. 2000) and are prominent in the spectra of both L (Leggett et al. 2001) and T dwarfs (McLean et al. 2001), in which bands can be observed into the near-infrared (McLean et al. 2000). The recent classification schemes for the substellar T dwarfs (Burgasser et al. 2002; Geballe et al. 2002) are based largely on water and methane bands in the near infrared. Molecular opacity functions for water necessary for modeling even low-resolution spectral energy distributions of cool objects are calculated from millions of theoretical line positions (Allard, Hauschildt, & Schwenke 2000). These molecular opacities are ultimately based on an experimental list of line positions and energy levels.

In our own solar system, water has been detected on Venus (Encrenaz et al. 1995), Mars (Gurwell et al. 2000),

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and the giant planets (Bergin et al. 2000b). Cometary water can be detected by both millimeter-wave (Meier et al. 1998) and infrared techniques (Dell Russo et al. 2000). Although the surface of the Sun is too hot for water to exist, the umbrae of large sunspots (~3000 K) show complex infrared absorption bands attributed to hot water vapor (Wallace et al. 1995; Polyansky et al. 1997a).

The spectrum of water is particularly complicated due to a number of factors, including its asymmetric top structure and its lightness. This means that all vibrational bands have extensive and irregular rotational fine structures that cannot easily be assigned. In addition, the vibrational bands are strongly overlapped. The application of variational nuclear motion calculations to analyze the spectra of both hot and cold water vapor, instead of standard techniques based on perturbation theory, has led to the assignment of many spectra that could not previously be analyzed (Polyansky et al. 1997a, 1998; Polyansky, Tennyson, & Zobov 1999, hereafter ZVPT; Partridge & Schwenke 1997, hereafter PS). Both as a consequence of this and because of their atmospheric and astrophysical importance, water spectra have become a subject of renewed interest. This work has recently been reviewed by Bernath (2002).

In previous papers we have identified water lines in the K (Polyansky et al. 1997b; Zobov et al. 2000), L (Zobov et al. 2000), and N bands (Polyansky et al. 1997c) of sunspot spectra recorded with the Fourier transform spectrometer of the National Solar Observatory, along with the corresponding laboratory emission spectra (400–6000 cm^{-1}), including the 6 μm bending mode (Zobov et al. 1999). In the present paper we extend our work to the important H band (5540–6700 cm^{-1}) of the sunspot spectrum and provide a new matching laboratory spectrum of hot (1800 K) water from 4900–7500 cm^{-1}.

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; Zobov et al. 2000). The spectrometer was operated with a $\mathrm{CaF_2}$ window and beam splitter, a 5000 cm^{-1} high-pass optical 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 $\mathrm{CaF_2}$ windows. Water was vaporized and carried continuously into the tube by a flow of argon gas at room temperature. The tube was slowly pumped to stabilize the total pressure around 50 torr. A $\mathrm{CaF_2}$ lens was used to focus the emission into the entrance aperture of the spectrometer. The spectral region of 4000–9000 cm^{-1} was covered at a resolution of 0.02 cm^{-1}.

Line positions and intensities were determined using Voigt line shape functions with the WSPECTRA program of M. Carleer (Free University of Brussels). Measurement of the laboratory spectrum in the range 4878–7552 cm^{-1} gave 7395 emission lines, once artifacts due to the line-finding process had been removed. The lines were calibrated with the measurements of Toth (1994), and the wavenumber scale had an absolute accuracy of better than 0.001 cm^{-1}. The current data set overlaps with the previous line list derived for the 2500–6008 cm^{-1} region (Zobov et al. 2000). Comparison of our two line lists revealed a small calibration error of about 0.003 cm^{-1} at 5000 cm^{-1} in the data set of Zobov et al. (2000). The lines in the old data file (2500–6000 cm^{-1}) need to be multiplied by the factor 1.000000648 to bring them onto the wavenumber scale of Toth (1994). This correction does not affect any of the conclusions or numerical data printed in the paper by Zobov et al. (2000) and was corrected before the calculation of the term values by Tennyson et al. (2001). The recalibrated 2500–6008 cm^{-1} water line list can be obtained on-line.[6] The new laboratory spectrum spanning 4878–7552 cm^{-1} is given in Table 1.

The sunspot spectrum used for our analysis is part of a series of solar atlases (Wallace et al. 1996).[7] The spectrum that we have used in this study is that of a cold, dark sunspot umbra obtained by W. C. Livingston with the 1 m Fourier transform spectrometer at the McMath-Pierce telescope on Kitt Peak. This spectrum is in the archives of the National Solar Observatory and is identified by date and number: 1991 July 26 and 7, respectively. A first attempt at analysis of this spectrum by Wallace & Livingston (1992) has been substantially improved by Wallace, Hinkle, & Livingston

TABLE 1

List of Laboratory Emission Lines and Assignments

ω (cm^{-1})	Intensity	Width (mK)	J'	K_a'	K_c'	J''	K_a''	K_c''	$v_1'v_2'v_3'$–$v_1''v_2''v_3''$[a]
4878.17139.......	0.0007	12	...	...	...	...	...	...	...
4878.20273.......	0.0011	39	17	1	17	18	1	18	021–010
4879.32791.......	0.0011	33	15	1	15	16	1	16	031–020
4888.09515.......	0.0015	55	19	2	18	20	2	19	011–000
4893.00824.......	0.0009	24	17	3	15	18	3	16	021–010
4898.43577.......	0.0031	27	18	0	18	19	0	19	011–000
4903.08860.......	0.0019	19	14	0	14	15	0	15	031–020
4903.12953.......	0.0027	43	16	0	16	17	0	17	021–010
4903.45840.......	0.0012	33	16	3	13	17	3	14	021–010
4903.83654.......	0.0010	11	12	2	11	13	2	12	041–030

Note.—Table 1 is published in its entirety in the electronic edition of the Astrophysical Journal. A portion is shown here for guidance regarding its form and content.

[a] Normal mode notation.

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[6] Download from ftp://ftp.tampa.phys.ucl.ac.uk/pub/astrodata/water or http://bernath.uwaterloo.ca/H2O.

[7] Download from ftp://argo.tuc.noao.edu/pub/atlas.

TABLE 2

List of Sunspot Absorption Lines and Assignments

			Assigned Water Lines							Other Assignments	
ω (cm^{-1})	Intensity	Width (mK)	J'	K_a'	K_c'	J''	K_a''	K_c''	$v_1'v_2'v_3'$–$v_1''v_2''v_3''$[a]	Lab (cm^{-1})	Label[b]
5539.89715.......	0.0281	59.31	...	...	...	...	...	...	...	...	...
5540.03022.......	0.2851	75.01	18	0	18	17	0	17	021–010	...	...
5540.16178.......	0.1423	72.31	19	2	18	18	2	17	041–030	...	...
5540.29068.......	0.1067	71.58	13	6	8	12	6	7	041–030	...	...
5540.59335.......	0.0484	51.96	...	...	...	...	...	...	...	...	...
5540.67376.......	0.2840	80.97	...	...	...	...	...	...	...	5540.668	OH 4–2 P_{1e}15.5
5542.03019.......	0.0867	73.74	17	3	15	16	3	14	041–030	...	...
5542.16445.......	0.0696	100.55	...	...	...	...	...	...	...	...	...
5542.32717.......	0.3755	89.18	...	...	...	...	...	...	...	5542.326	OH 4–2 P_{2e}14.5
5542.52814.......	0.1286	121.41	...	...	...	...	...	...	...	...	...

Note.—Table 2 is published in its entirety in the electronic edition of the Astrophysical Journal. A portion is shown here for guidance regarding its form and content.

[a] Normal mode notation.

[b] H_2O means water line present in lab spectrum but quantum number assignment unknown. Other (atomic and diatomic) lines assignments use standard notation.

(2001), but many features remained unidentified. The lines in the 5540–6997 cm^{-1} region were measured with a derivative line finder giving a total of 3560 lines. All known nonwater lines (e.g., OH, CN, CO, etc.) were marked in the data file, and the line positions were calibrated by comparison with our laboratory spectrum. A calibration factor of 1.0000036 was applied to the measured sunspot lines, which amounts to a shift of $+0.022$ cm^{-1} near 6000 cm^{-1}. Table 2 gives the sunspot line positions.

3. LINE ASSIGNMENTS

Line assignments were made in a number of steps. The experimental term values for $H_2{}^{16}O$ derived by Tennyson et al. (2001) give an excellent starting point for assigning spectra containing transitions between previously observed energy levels. We usually call such transitions trivial. Analysis of the laboratory spectrum showed that the majority of transitions, 5547 out 7395, in this spectrum could be assigned in this fashion.

The sunspot is considerably hotter than the laboratory spectrum; as in previous studies, we assumed a temperature of 3200 K (Polyansky et al. 1997a, 1997b; Zobov et al. 2000). The sunspot also contains transitions due to other species. A total of 986 transitions can be assigned to known atomic and diatomic transitions. Notably, the region 5910–6300 cm^{-1} has many lines due to hot CO. This region contains a total of 1105 transitions. However, the laboratory spectrum, which has an average density of about 2 lines per cm^{-1}, shows very few water transitions in this region: 12 lines between 5910 and 6080 cm^{-1} and none between 6080 and 6270 cm^{-1}. The sparsity of water lines means that we have only made one assignment in this region.

Because of the hotter temperature, significantly fewer sunspot transitions could be trivially assigned. Analysis therefore proceeded by generating 3200 K spectra using two different variational line lists, the line list of PS, which was generated using a spectroscopically determined potential, and the line list of ZVPT, which was generated using ab initio quantum calculations. In each case, the line list represented the best available to us at the time. Experience has shown that the line list of PS is excellent for interpolating between known regions of the spectrum but must be used cautiously for extrapolations, while the ab initio line list of ZVPT has significantly larger residual errors for known transitions but extrapolates smoothly, which means that allowances can be made for these systematic errors (see Polyansky et al. 1997b).

There are 555 sunspot lines that could be assigned to water using trivial assignments. Using the line lists, a further 138 transitions, associated with 136 new energy levels, were assigned. This analysis also led to the assignment of 42 new transitions in the laboratory spectrum. As has been observed before (Zobov et al. 2000), the emission spectrum of hot water involves transitions in a very large number of vibrational bands. A total of 37 bands were identified in the sunspot and laboratory spectra, with a further 36 bands appearing only in the more extensive laboratory spectrum. The majority of these bands contain less than 10 transitions. Tables 1 and 2 contain assignments to the laboratory and sunspot data, respectively, while Table 3 summarizes the major bands observed in the sunspot spectrum. The new (i.e., nontrivial) assignments can be used to generate further water energy levels. The present data have been incorporated into an updated version of the energy levels of Tennyson et al. (2001). Results for the seven bands with a significant number of new levels as result of this work, which are (011), (021), (031), (041), (101), (111), and (201), are given in Table 4.

As has been observed before (Wallace et al. 1995), it is not actually necessary to make spectral assignments to identify sunspot lines as belonging to water. Detailed wavenumber matches between the sunspot and laboratory spectra allowed us to identify a further 201 sunspot lines due to water. These have been marked in Table 2 but remain to be assigned. This table contains a further 1709 lines that are yet to be assigned to any species, but it is likely that many of these lines are also due to hot water. Figure 1 presents a sample portion of the sunspot and laboratory spectra with assignments.

The University College London (UCL) and Nizhnii Novgorod groups are continuing their attempts to develop theoretical methods for analyzing the spectra of both hot and cold water. It is to be hoped that these will allow further

TABLE 3

SUMMARY OF WATER TRANSITIONS ASSIGNED IN THE 5540–6700 cm^{-1} REGION

Band	Origin	$E''(J=0)$	N(Sun)	N(Lab)
011–000.......	5331	0	169	879
200–000.......	7201	0	24	318
101–000.......	7250	0	80	540
111–010.......	7212	1595	36	315
012–010.......	7405	1595	142	661
031–010.......	6779	1595	30	262
031–020.......	5222	3152	46	389
041–020.......	6682	3152	27	117
201–100.......	6956	3657	26	170
012–001.......	5244	3756	15	273
300–001.......	6844	3756	11	85
041–030.......	5167	4667	11	193
051–030.......	6576	4667	15	15

NOTE.—This is a summary of water transitions assigned in the 5540–6700 cm^{-1} region of the sunspot spectrum of Wallace et al. 1996. 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 N(Lab) to the 4900–7500 cm^{-1} laboratory spectrum. For each band, the second column gives the calculated vibrational band origin in cm^{-1} (Tennyson et al. 2001) and the third column the energy of the lower vibrational state in cm^{-1}.

progress to be made on assigning water lines in both the sunspot and laboratory spectra discussed here. In the meantime, we have assigned a significant number of water transitions in the H band of a sunspot spectrum. We believe these lines will provide a useful observational tool for observing water in other warm objects.

4. CONCLUSIONS

Using a combination of new laboratory measurements and variational calculations, we have assigned 682 water lines in the H band of a sunspot spectrum and have identified a further 201 transitions, yet to be assigned, as being due to water. These transitions will occur in other hot objects containing water and have the advantage that they are amenable to ground-based observations, unlike the majority of water transitions, which are strongly obscured by water vapor in the Earth's atmosphere. Data on both sunspot and laboratory spectra have been made available electronically, as it is not practical to publish tabulations of over 10,000 transitions. This data form is, in any case, likely to be the most convenient for most workers.

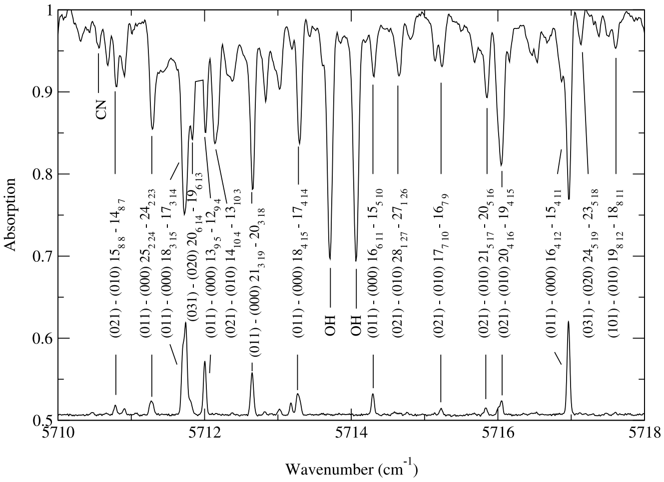

FIG. 1.—Sections of the sunspot umbra absorption spectrum and the laboratory emission spectrum in the H-window region with water assignments. The scale on the y-axis refers only to the sunspot spectrum. [*See the electronic edition of the Journal for a color version of this figure.*]

Finally, it should be noted that the Waterloo-Brussels collaboration has recently succeeded in recording a water emission spectrum covering an extended region including the H band at a temperature close to that of the sunspot. This spectrum contains a very large number of transitions and should aid with the assignment of the unassigned sunspot transitions, since the more extensive coverage and the absence of lines from other species (except OH) makes this spectrum considerably more amenable to theoretical analysis.

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TABLE 4

ENERGY LEVELS FOR WATER IN THE (011), (021), (031), (041), (101), (111), AND (201) BANDS

J	K_a	K_c	$v_1v_2v_3$[a]	Energy (cm^{-1})	Error (cm^{-1})	Number	Source
0	0	0	011	5331.267440	0.000774	4	L
1	0	1	011	5354.870432	0.000430	8	L
1	1	1	011	5369.762354	0.000436	8	L
1	1	0	011	5375.361669	0.000727	3	L
2	0	2	011	5400.736556	0.000392	16	L
2	1	2	011	5411.411057	0.000389	10	L
2	1	1	011	5428.171371	0.000370	14	L
2	2	1	011	5472.350488	0.000451	7	L
2	2	0	011	5473.655593	0.000397	10	L
3	0	3	011	5466.636808	0.000693	5	L

NOTE.—Table 4 is published in its entirety in the electronic edition of the Astrophysical Journal. A portion is shown here for guidance regarding its form and content.

[a] Normal mode notation.

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