THE ASTROPHYSICAL JOURNAL, 489:L205–L208, 1997 November 10

K-BAND SPECTRUM OF WATER IN SUNSPOTS

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Received 1997 August 4; accepted 1997 September 12; published 1997 October 13

ABSTRACT

The infrared spectrum of a sunspot, published in the form of an atlas by Wallace & Livingston, is analyzed in the 2.17–1.96 μm (4600–5100 cm^{-1}) region where most of the transitions are due to hot water. Assignments are made using variational nuclear motion calculations based on a high-level ab initio electronic surface for water, with allowance for both adiabatic and nonadiabatic corrections to the Born-Oppenheimer approximation. 485 new lines are assigned to transitions in 10 vibrational bands. Only two of these vibrational bands have been previously identified. Newly assigned bands include the (061)–(050) and (071)–(060) vibrational transitions, for which even the lower vibrational levels had not been previously characterized. Assignments are made to levels as high as ~17,000 K above the origin.

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

1. INTRODUCTION

It has long been believed that water is one of the most important astronomical molecules in cool sources. 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 1979). 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). Telluric absorption, however, makes the detection of water difficult from the surface of the Earth.

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). In 1996 the infrared and far-infrared spectrometers on the *ISO* satellite were used to show that both solid water (Schutte et al. 1996) and gaseous water (van Dischoek & Helmich 1996) are ubiquitous in the Galaxy.

The infrared lines of hot water pass through the Earth's atmosphere because these highly excited transitions are shifted away from telluric absorptions of cooler water. The near-infrared *K*-band water lines in sunspots have been known for some time, most notably from the work of Hall (1970). Benedict made some water line assignments in Hall's spectra, but this work was never completed and published. The most complete analysis previous to the work reported here is the work of Wallace & Livingston (1992) based on the French laboratory measurements (Flaud, Camy-Peyret, & Maillard 1976; Camy-Peyret et al. 1977). In our earlier work (Wallace et al. 1995) we were able to demonstrate that hot water was responsible for the dense lines in the *M* band (10–20 μm) sunspot spectrum by direct comparison with a laboratory spectrum (Polyansky et al. 1996). The line assignments in this *M*-band spectrum are the subject of another paper (Polyansky et al. 1997c), and we report here on our *K*-band assignments.

2. SPECTRAL ANALYSIS

Wallace & Livingston (1992) have published a spectral atlas of a dark sunspot umbra in the wavenumber range 1970–8640 cm^{-1} (1.6–5.1 μm). This spectrum shows spectral features that are due to a variety of neutral atoms and diatomic molecules; the only known polyatomic species is water, which contributes the largest number of transitions (Wallace et al. 1996). Wallace & Livingston were able to assign 892 water absorption features on the basis of previously observed laboratory spectra (Flaud et al. 1976; Camy-Peyret et al. 1977). The majority of these transitions lie in the *L* band (3–4 μm).

Our previous analysis of water absorption spectra in sunspots (Polyansky et al. 1997b, 1997c) concentrated on the *M* atmospheric window (10–20 μm). This work demonstrated the efficacy of variational nuclear motion calculations for making line assignments. The *M*-band studies allowed us to significantly extend the number of water energy levels that have been experimentally determined (Polyansky et al. 1997b, hereafter Paper I). Initially, we hoped to assign sunspot water transitions in the *K* band (~2 μm) simply on the basis of energy level differences in our new set of water energy levels; we generally denote such spectral assignments "trivial." Although it was possible to make some new trivial assignments, particularly in the *L* band where the ν_3 antisymmetric stretching fundamental of H_2O dominates, this was not possible in the *K* band.

We concentrate on the 4600–5100 cm^{-1} region where the water features are densest and least contaminated by telluric effects and absorptions that are due to other species. For water, this region corresponds to one in which absorption leads to simultaneous excitation of one quantum in the bend and one

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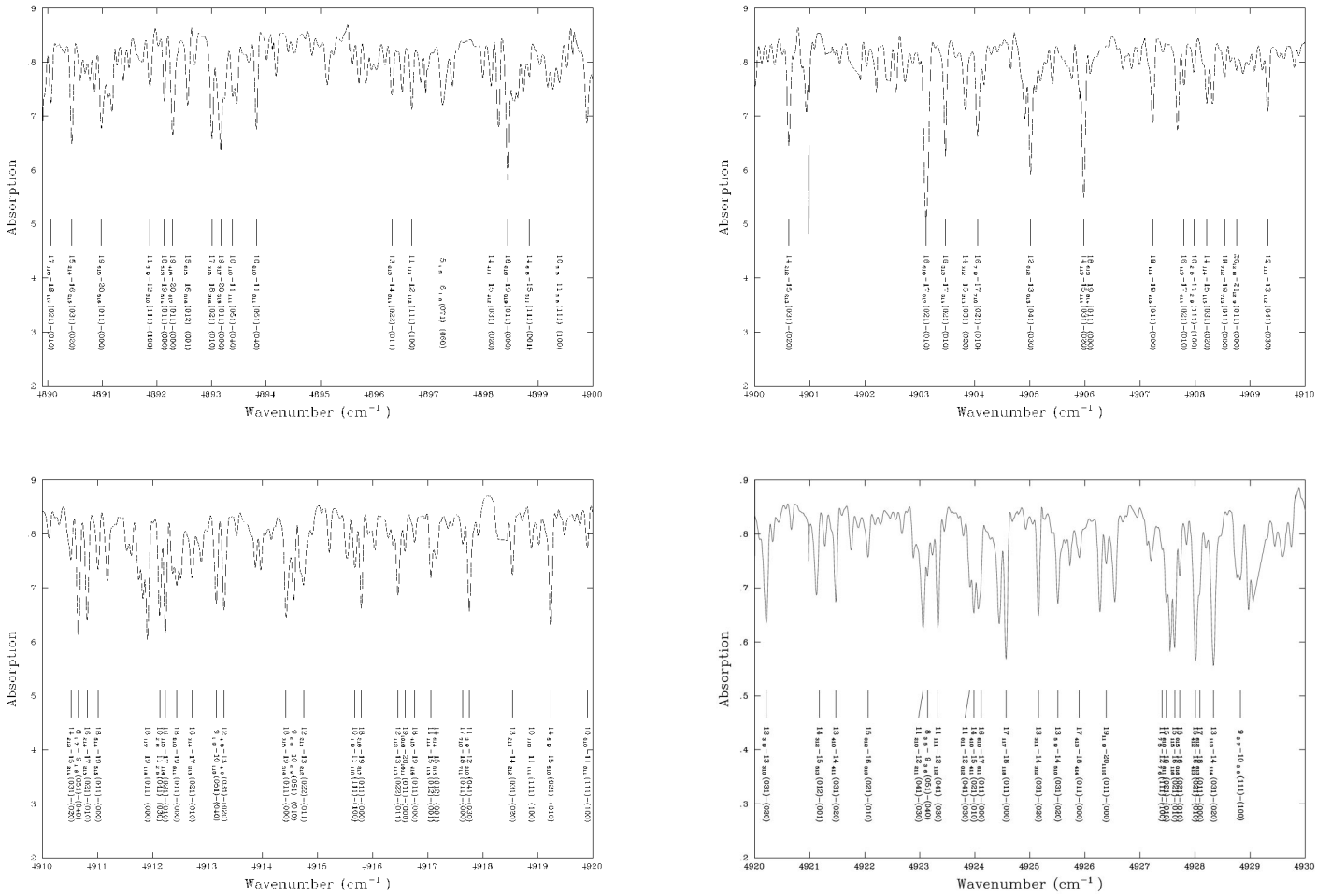

FIG. 1.—Part of the sunspot spectrum of Wallace & Livingston (1992). Newly assigned water transitions are labeled using standard notation $J_{K_aK_c}$ for rotational levels and $(v_1v_2v_3)$ for vibrational levels.

in the antisymmetric stretch. As will be shown below, the bands we assign have the general form $(v_1, v_2 + 1, v_3 + 1) - (v_1, v_2, v_3)$. Although the water spectrum is relatively dense in this spectral region, it should be emphasized that this only corresponds to about 5 lines per cm^{-1}, in contrast to the *M*-band spectrum, where up to 50 water absorption features per cm^{-1} can sometimes be seen. This means that the *K*-band water assignments can be made with a lower level of computational accuracy in line predictions.

In the absence of trivial assignments, we decided to perform a systematic spectral analysis of this region using the available line lists and the technique of analyzing branches used successfully for assigning the *M*-band spectrum. For this work the branches were assigned by following transitions with low K_a for which $K_c = J$ and $K_c = J - 1$. Branches with $K_c = J - 2$ are lower in intensity and so far have not been analyzed. It is to be expected that transitions involving states $J \sim K_a$, that is low K_c, should also be strong, as they are in the *M*-band spectrum. However, for the bands considered here these transitions lie largely outside the spectral window for which good sunspot spectra are available.

Two line lists were used to aid our assignments. Our ab initio line list described below and the recently published list of Partridge & Schwenke (1997, hereafter PS), which is based on an ab initio potential energy surface that has been further refined by fits to spectroscopic data. Our line list was calculated using a very high quality, ab initio Born-Oppenheimer (BO) potential energy surface (Schwenke 1996, private communication). The mass-dependent adiabatic correction to the BO approximation, which has been shown to be significant for rotationally excited water, was included using another mass-dependent ab initio adiabatic surface (Zobov et al. 1996). An approximate allowance for nonadiabatic corrections was included by the use of an H atom mass midway between that of H and a bare proton (Zobov et al. 1996). The nuclear motion calculations were performed with the DVR3D program suite (Tennyson, Henderson, & Fulton 1995), which uses an exact (Born-Oppenheimer) kinetic energy operator and a discrete variable representation (DVR) of the vibrational wave functions. Rotational levels up to $J = 33$ were considered. Further details of these calculations are given in Paper I.

Except for two bands, there are no laboratory data available to start our assignment procedure using branches, so that the initial low *J* assignments were made by direct comparison with the line lists. PS's line list, which is outstandingly accurate at low *J*, was particularly useful in this respect. Branches were then followed to higher *J* by allowing for small systematic differences in the error between the predicted and observed lines. As *J* increased, the line positions deviated in a smooth and predictable way from the predictions. For this step our ab initio line list was generally more systematic and reliable than that of PS. An illustration of how the errors behave along a

TABLE 1

SUMMARY OF WATER TRANSITIONS

Band	E^{max} (cm^{-1})	$J\ K_a\ K_c$	$E(J = 0)$ (cm^{-1})	N
011–000	13842	30 0 30	5335–0	144
021–010	14820	29 1 29	6876–1596	103
031–020	15315	27 1 27	8379–3154	119
041–030	15882	25 1 25	9839–4670	26
051–040	16066	22 0 22	11249–6138	14
061–050	15959	18 0 18	12592–7546	22
071–060	15309	11 1 11	13841–8874	6
012–001	13659	22 1 22	9007–3758	20
022–011	12784	15 0 15	10529–5335	14
111–100	13850	23 1 23	8813–3660	17

NOTES.—Summary of water transitions assigned in the 4600–5100 cm^{-1} region of the sunspot spectrum of Wallace & Livingston 1992. Given are the number of transitions, N, for a particular band, the highest calculated energy level involved, E^{max}, and corresponding rotational assignment. The calculated vibrational band origin, $E(J = 0)$, are given for both vibrational states involved in each band.

branch is given in Figure 2, which will be discussed in detail below.

So far, 485 transitions have been assigned in the 4600–5100 cm^{-1} region, a sample of which is given in Figure 1. It can be seen that these assignments include all of the strong absorption features in the spectral region of interest. The results of these assignments are summarized in Table 1. 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). Indeed, there have been no previous observations of transitions involving the (061), (071), (060), and (022) vibrational states, and transitions to the (050) state were only recently assigned in the laboratory in a study performed as part of our coordinated attack on the sunspot spectrum (Polyansky et al. 1997a).

3. DISCUSSION AND CONCLUSIONS

We have used two line lists in making our assignments, and it is worthwhile comparing them. Some comparisons have already been made in Paper I, where it was found that PS's line list gave superb predictive results for low J levels but suffered from problems with artificial splittings between quasi-degenerate levels for higher J. Calculations by us suggested that this was due to lack of variational convergence in PS's high J calculations.

One contrasting feature between PS's and our line list is that PS's contains a full set of vibrational and rotational labels, whereas ours only gives rigorous symmetry labels. Comparisons in Paper I showed that PS's labels are reliable up to about 15,000 cm^{-1} but are occasionally rather wild above this.

An important aspect of our work is the technique of following a series of similar transitions along a branch. Figure 2 compares typical behavior of our line list with PS's as J increases along a branch. For all J our results give a systematic error for each branch that is quite large, ~2–3 cm^{-1}, and it is this aspect that PS sought to improve by performing their fits to spectroscopic data. As a result, for low J, PS's line list gives very little residual error. However, as J increases along a branch, the change in the error of our calculations is small and smooth; conversely, for PS's line list the changes become large and erratic. The density of water lines in the K band requires that transitions be predicted to better than 0.1 cm^{-1} for assignments to be made with confidence. This is clearly possible using our line list once the overall "branch error" has been removed, but not using PS's results.

This Letter demonstrates the utility of line lists generated

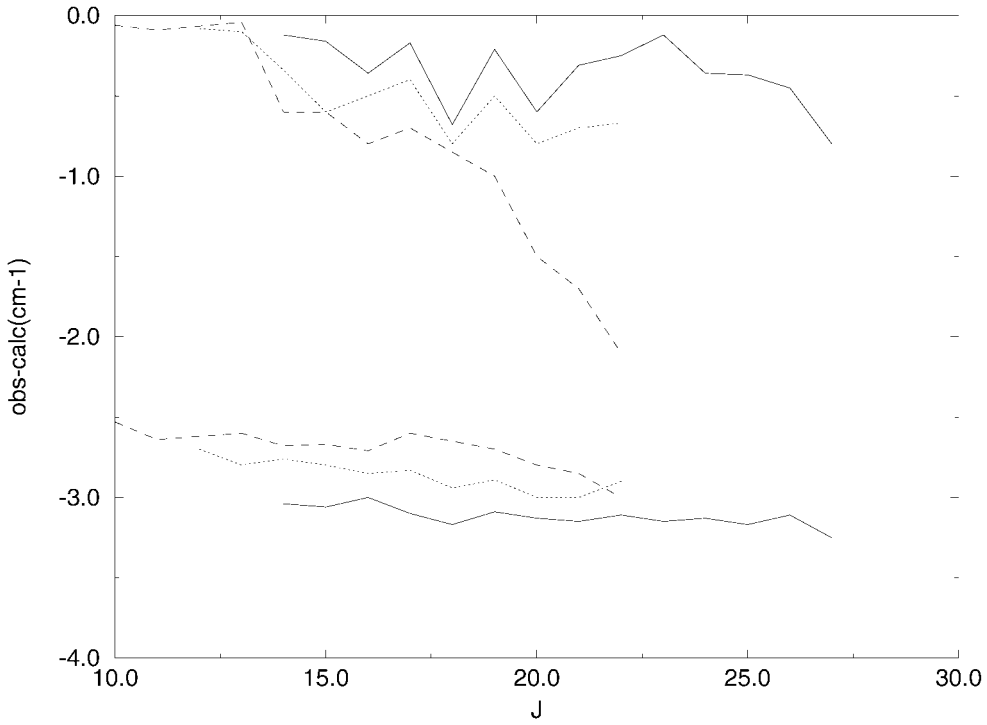

FIG. 2.—Comparison of typical band errors ($O - C$) for the newly assigned water line list. *Solid lines*, (031)–(020) $J = K_c$; *dotted lines*, (041)–(030) $J = K_c$; *dashed lines*, (051)–(040) $J = K_c$. Upper three lines obtained using Partridge & Schwenke (1997) line list; lower three lines obtained using our ab initio line list.

using variational nuclear motion calculations in making spectral assignments for a complicated and seemingly unassignable spectrum. However, it should be noted that despite the accuracy of these line lists, particularly the PS list at low J, these assignments cannot in general be made by simple spectral matching of the observations with the predictions. In many cases correct assignments do not correspond to the nearest features when synthetic and observed spectra are compared.

In making assignments we have used line positions and line strengths provided by variational calculations. It is not possible for us to present all these data in this Letter, but a full line list containing observed frequencies, assignments, and calculated line strengths for all our newly assigned water transitions is currently being prepared for publication. In the meantime, frequencies and assignments are available from the authors on request.

We thank H. Partridge and D. W. Schwenke for supplying their potential energy surface prior to publication. The authors acknowledge NATO grant 5-2-05/CRG951293 for making the experimental-theoretical collaboration possible. N. F. Z. thanks the Royal Society for funding his visit the University College London. The work of O. L. P. was supported in part by the Russian Fund for Fundamental Studies. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). Acknowledgment is made to the Petroleum Research Fund for partial support of this work. Support was also provided by the NASA Laboratory Astrophysics Program, the UK Engineering and Science Research Council and the UK Particle Physics and Astronomy Research Council.

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