Water on the Sun: Line Assignments Based on Variational Calculations

Oleg L. Polyansky,* Nikolai F. Zobov,* Serena Viti,
Jonathan Tennyson,† Peter F. Bernath,† Lloyd Wallace

The infrared spectrum of hot water observed in a sunspot has been assigned. The high temperature of the sunspot (3200 K) gave rise to a highly congested pure rotational spectrum in the 10-micrometer region that involved energy levels at least halfway to dissociation. Traditional spectroscopy, based on perturbation theory, is inadequate for this problem. Instead, accurate variational solutions of the vibration-rotation Schrödinger equation were used to make assignments, revealing unexpected features, including rotational difference bands and fewer degeneracies than anticipated. These results indicate that a shift away from perturbation theory to first principles calculations is necessary in order to assign spectra of hot polyatomic molecules such as water.

The detailed interpretation of the infrared spectrum of hot water is one of the important unsolved problems in molecular spectroscopy (1). Spectroscopic data on hot water is required for the modeling of a wide variety of systems. In astronomy, water vapor is the most important source of infrared opacity in the spectra of oxygen-rich late-type stars (2, 3). For substellar objects such as brown dwarfs, water is the most abundant molecule after hydrogen (4, 5). Hot water is a primary product of the combustion of hydrocarbons and has been detected in emission from forest fires (6) and from the flame of, for example, an oxyacetylene torch (7). Other applications include the simulation of rocket plumes (8).

The infrared spectrum of the water molecule has been the subject of numerous studies, both experimental and theoretical. The results have been gathered in standard compilations (9, 10), which are widely used for modeling and spectral analysis. However, the spectrum of water at temperatures $T > 800°C$ remains poorly understood. In most of the sunspot spectrum ($T = 3000°C$), water could only be identified by comparison with a high-temperature laboratory spectrum, which derives from substantially cooler water ($T = 1550°C$) and hence is much less dense (1). Both spectra remain largely unassigned.

At its densest, the sunspot spectrum contains about 50 (water) lines per wave number. This density implies that calculations with an accuracy better than 0.01 cm^{-1} for a vast range of transitions are necessary to make assignments. Such accuracy is far beyond many of the standard approximations of theoretical molecular spectroscopy. Here we report the assignment of previously published spectra taken from emission in the laboratory (11, 12) ($T \sim 1550°C$, wave numbers $370 \leq \tilde{\nu} \leq 930$ cm^{-1}; $T \sim 1000°C$, $900 \leq \tilde{\nu} \leq 2000$ cm^{-1}) and from absorption in sunspots (13) ($T \sim 3000°C$, $750 \leq \tilde{\nu} \leq 1010$ cm^{-1}).

Traditional high-resolution spectroscopy is based on the separability of electronic, vibrational, and rotational motion. Vibrations are described in terms of harmonic oscillations, and rotations are treated as those of a rigid body (14). These zeroth-order models are used as the basis of perturbative expansions, which reproduce the

spectra of most (cool) molecules to very high accuracy. However, such a perturbative treatment diverges for water even for relatively low-lying levels (15). Alternative treatments are based on direct, variational solutions of the Schrödinger equation for the nuclear motion problem of small molecules such as water (16) and use exact nuclear-motion kinetic-energy operators, which do not separate vibrational and rotational motion. These direct variational approaches have found some previous success in the assignment of the spectra of floppy van der Waals molecules (17). However, they still usually rely on the (Born-Oppenheimer) separability of the nuclear and electronic motion of the system. Non–Born-Oppenheimer effects are known to be significant (at the ~1-cm^{-1} level) in hydrogen-containing molecules (18).

For this work, calculations were performed with the use of a high-quality, ab initio Born-Oppenheimer potential-energy surface (19). The mass-dependent adiabatic correction to the Born-Oppenheimer approximation, which is significant for rotationally excited water, was included (20). An approximate allowance for the nonadiabatic correction was included by the use of an H-atom mass midway between that of H and a bare proton (20). The nuclear motion calculations (21) used a discrete variable representation (DVR) of the vibrational wave function and the DVR3D program suite (22). Levels with rotational angular momentum J up to 33 were considered; levels with higher J are undoubtedly present in sunspots, but strong transitions lie largely outside the spectral window considered here. Dipole transition intensities were computed using ab initio dipole surfaces (23), and spectra were generated assuming thermal equilib-

O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK.
P. F. Bernath, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1, and Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA.
L. Wallace, National Optical Observatories, Post Office Box 26732, Tucson, AZ 85732, USA.

*Permanent address: Institute of Applied Physics, Russian Academy of Sciences, Nizhnii Novgorod, Russia 603600.
†To whom correspondence should be addressed. E-mail: j.tennyson@ucl.ac.uk, bernath@watsci.uwaterloo.ca

Table 1. Highest energy level E observed previously and assigned in this work as a function of vibrational state. For this work, calculated values of the energy levels are given. Note that besides a substantial increase in E, our results also give a substantial increase in K_a. Until now, transitions involving high K_a levels have proved particularly hard to assign. A full list of assigned transitions will be published elsewhere (36).

Band	Previous				This work		
	J	K_a	E (cm^{-1})	Ref.	J	K_a	E (cm^{-1})
(000)	35	1	11656	(7)	33	33	21111
(010)	30	2	10866	(25)	31	31	21223
(020)	15	3	6346	(28)	30	30	22340
(100)	30	1	12203	(7)	28	28	19552
(001)	34	1	14618	(7)	28	28	19514
(030)	14	2	7361	(26)	28	27	22243
(110)	15	6	8720	(10)	24	24	17995
(011)	30	1	13838	(7)	26	26	19723
(040)	12	1	7689	(29)	13	12	11512
(050)	–	–	–	–	4	4	9785

rium at the appropriate temperature.

Analysis of the sunspot spectra was undertaken in a number of steps. First, all transitions between energy levels known from previous work (7, 24–29) were assigned; such assignments, which we call trivial, form only a minor part of the spectrum. Second, the sunspot spectrum was divided into four echelons on the basis of intensity: strong transitions with 6 to 8% absorption, medium transitions with 4 to 6% absorption, weak absorptions with 2 to 4% absorption, and poorly resolved structure with <2% absorption. We concentrated on the strong and medium transitions but are confident that extension of our calculations to higher vibrational states will allow assignment of the weaker transitions. Third, the spectrum was analyzed in terms of branches. A branch was defined as a series of transitions involving common sets of levels each defined by $K_a = J - n$, where n is constant for each set of levels and K_a is the approximate projection of the total angular momentum J along the rotational axis with the smallest moment of inertia.

Our variational calculations are not completely accurate, largely as a result of residual errors in the Born-Oppenheimer potential. However, the errors vary slowly and systematically with J for a given branch, and it is therefore possible to step along members of the branch starting from low J transitions, which are generally well characterized, to the previously unassigned higher J lines. For transitions observed both in the laboratory ($T \sim 1000°C$) and in sunspots ($T \sim 3000°C$), we obtained a crude confirmation of each assignment by comparing the ratio of line intensities with that estimated from Boltzmann distributions at the appropriate temperatures. Previous studies of hot water assigned energy levels up to $\sim 11,000$ cm^{-1} above the ground state (7, 24–29). We found that in the sunspot spectrum, the strong transitions originated mainly from states in the 12,000 to 17,000 cm^{-1} region, although transitions involving states above 22,000 cm^{-1} were also successfully assigned. We have approximately doubled both the energy range for which assignments have been made and the number of experimentally known energy levels (see Table 1). Our assigned levels reach about halfway to dissociation. With the exception of the rotational difference bands discussed below, all of these transitions involved changes in rotational but not vibrational quantum numbers. Sample portions of the sunspot spectrum, with our assignments, are presented in Figs. 1 and 2.

Analysis of the laboratory spectra involved techniques similar to those described above for the sun; we assigned about 3000 out of the 4700 transitions observed in the 480- to 900-cm^{-1} region. Transitions with $\tilde{\nu} > 900$ cm^{-1} in the laboratory spectra were associated with changes in both vibrational (mostly by one quantum in the bending mode) and rotational quantum numbers. In this case, the variational calculations are generally less accurate (up to 3 cm^{-1} from the observations) than our predictions for the pure rotational transitions, but the errors remain systematic so that again assignments can be made. Because the sunspot spectrum is generally contaminated by telluric features at these frequencies, it cannot be used for confirming assignments. However, for vibrational bands, assignment of both P ($\Delta J = -1$) and R ($\Delta J = +1$) transitions involving a particular level can be used to confirm the assignments. Some 1750 transitions have been assigned to transitions between pure bending states: the (010)→(000), (020)→(010), (030)→(020), (040)→(030), and (050)→(040) bands (12). Transitions to the (050) state at 7542.39 ± 0.05 cm^{-1} had not previously been observed, although an inaccurate value of 7552 cm^{-1} had been inferred from a perturbative analysis (30).

Our assignments show that the spectrum of hot water displays a number of unexpected features. In particular, a number of rotational difference transitions (31) occur alongside the pure rotational
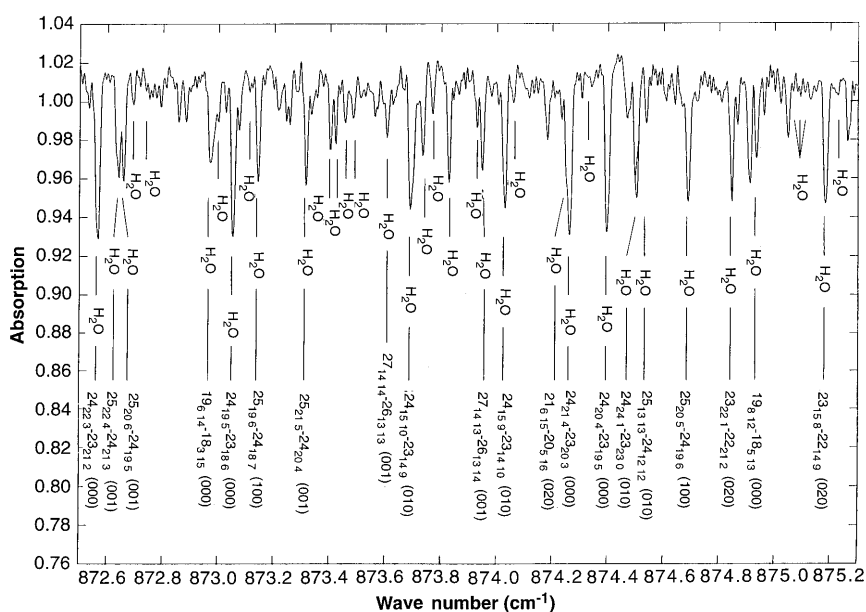

Fig. 1. Part of the sunspot spectrum of Wallace *et al.* (*13*). Features previously associated with water by comparison with laboratory spectra are labeled H_2O. Quantum number assignments, given as $J_{K_aK_c}$ (upper) − $J_{K_aK_c}$ (lower) for various vibrational states, are marked (K_c is the approximate projection of J along the rotational axis with the largest moment of inertia). This portion of the spectrum illustrates the congested nature of the sunspot spectrum.

Fig. 2. Part of the sunspot spectrum of Wallace *et al.* (*13*). The only feature previously associated with water by comparison with laboratory spectra is labeled H_2O; assignments for the features labeled SiO and OH are well known. This region of the spectrum is sensitive to higher water levels, and therefore, many of the lines that we assign are not seen in the cooler laboratory spectrum.
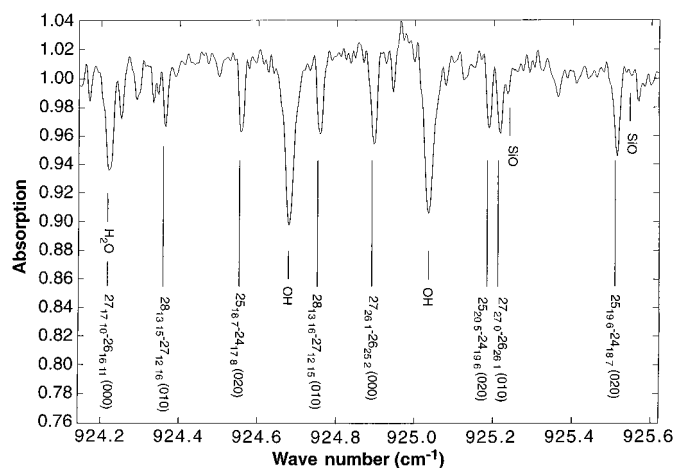
transitions of vibrationally excited states when the rotationally excited states of two nearby vibrational states interact and perturb each other. This interaction leads to a doubling of the number of observed transitions because the pure rotational transitions are augmented by cross transitions between the vibrational states (Fig. 3). A systematic series of transitions occurs between the symmetric stretching fundamental, (100), and the (020) bending state. In this case, there are strong interactions for all states with $K_a = 10$ and weaker ones with $K_a = 9$, 11, and 12. These interactions lead to a complete band of rotational difference transitions that arise from Fermi interactions (31). We found analogous rotational difference band structures for the polyads coupling to both (030) and (040) bending states. Understanding these interactions proved to be crucial in extending the assignments to high values of K_a.

The standard compilations of water lines (9, 10) contain many of the pure rotational transitions that accompany the rotational difference bands but none of the difference transitions. As these transitions are of similar strength, this is clearly a serious omission. There is nothing unique about water when it comes to these difference bands, and we anticipate that they will be a general feature of the spectra of all hot polyatomics. We note that the (Coriolis or Fermi) interactions that cause these transitions are a natural part of our full variational treatment of the problem but will only arise in perturbative treatments if appropriate terms are included in the effective Hamiltonian used. This calculation can often only be done once the empirical effect has been noted.
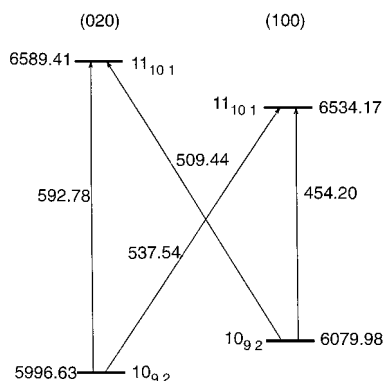
Fig. 3. Schematic diagram illustrating the rotational difference transitions between the (020) and (100) vibrational states and states with $J_{K_a K_c}$ equal to $10_{9\,2}$ and $11_{10\,1}$. Observed transition wave numbers and energy levels are given in wave numbers (cm^{-1}). Observation of any three transitions gives the wave number of the fourth. Its observation thus confirms the assignments of all four transitions.

Recent studies of highly excited rotational levels of H_2X (X = O, S, Se, or Te) molecules have concentrated on the tendency of the levels in these systems to form near-degenerate fourfold clusters (32). Such clustering has been observed for H_2Se and H_2Te, but not yet for water. Our assignments and extensive calculations suggest that neither clustering of the vibrational ground state (type I) nor clustering between the (100) and (001) stretching states (type II) occurs in water.

A number of higher levels of water show a more fundamental degeneracy splitting. It is a standard result of the rigid-rotor model that levels with even and odd Wang parity and high K_a are extremely, often indistinguishably, close. This behavior is well known spectroscopically (14). However, we found that for a number of levels, this degeneracy was lifted. In each case, the cause of this splitting was interaction with levels from a higher vibrational state. Again these Coriolis interactions can be included in standard perturbative analyses, but only on a case-by-case basis.

Although the work presented here concerns hot water, many of the characteristics of the spectrum will be common to the spectra of other light polyatomic molecules at high temperature. A full quantum mechanical treatment based on variational calculations will therefore be necessary for spectral analysis and modeling of such systems. This treatment is already the norm for much simpler diatomic systems, which display none of the spectral features described above, and for the H_3^+ molecule (33). This change represents a major shift away from analysis of high-resolution spectra on the basis of perturbation theory, which has underpinned the subject for more than half a century.

Variational calculations are computationally much more expensive than standard perturbative analysis (34) but also yield more information. Spectroscopic data and iterative variational calculations can be used to fit effective potentials for a given system. Such approaches are already in wide use for small molecules such as water (19, 35). They have been shown to give a much more compact representation of the data than the traditional vibrational state-by-vibrational state approaches based on perturbation theory and have vastly superior extrapolation properties (35).

REFERENCES AND NOTES

1. L. Wallace et al., Science 268, 1155 (1995).
2. F. Allard, P. H. Hauschildt, S. Miller, J. Tennyson, Astrophys. J. 426, L39 (1994).
3. K. H. Hinkle and T. G. Barnes, ibid. 227, 923 (1979).
4. T. Tsuji and K. Ohnaka, in Elementary Processes in Dense Plasmas, S. Ichimaru and S. Ogata, Eds. (Addison-Wesley, Reading, MA, 1995), p. 193.
5. B. R. Oppenheimer, S. R. Kulkarni, K. Mathews, T. Nakajima, Science 270, 1478 (1995).
6. H. Worden, R. Beer, C. P. Rinsland, J. Geophys. Res. 102, 1287 (1997).
7. J.-M. Flaud, C. Camy-Peyret, J.-P. Maillard, Mol. Phys. 32, 499 (1976).
8. Propulsion and Energetics Panel, Working Group 21, NATO AGARD (Advisory Group for Aerospace Research and Development) Advisory Rep. 287 (February 1993).
9. J.-M. Flaud, C. Camy-Peyret, R. A. Toth, Water Vapour Line Parameters from Microwave to Medium Infrared (Pergamon, Oxford, 1981).
10. L. S. Rothman et al., J. Quant. Spectrosc. Radiat. Transfer 48, 469 (1992).
11. O. L. Polyansky, J. R. Busler, B. Guo, K. Zhang, P. F. Bernath, J. Mol. Spectrosc. 176, 305 (1996).
12. O. L. Polyansky, N. F. Zobov, J. Tennyson, J. A. Lotoski, P. F. Bernath, ibid., in press.
13. L. Wallace, W. Livingston, P. F. Bernath, Natl. Solar Obs. Tech. Rep. 1994–01 (1994).
14. G. Herzberg, Molecular Spectra and Molecular Structure (Van Nostrand, New York, 1945), vol. 2.
15. O. L. Polyansky, J. Mol. Spectrosc. 112, 79 (1985).
16. Z. Bačić and J. C. Light, Annu. Rev. Phys. Chem. 40, 469 (1989).
17. R. J. Saykally and G. A. Blake, Science 259, 1570 (1993).
18. J. Tennyson and O. L. Polyansky, Phys. Rev. A 50, 314 (1994).
19. D. W. Schwenke, personal communication. Preliminary fit to the ab initio data of H. Partridge and D. W. Schwenke, [J. Chem. Phys. 106, 4618 (1997)].
20. N. F. Zobov, O. L. Polyansky, C. R. Le Sueur, J. Tennyson, Chem. Phys. Lett. 260, 381 (1996).
21. For more details on the nuclear motion calculations used here, see (12).
22. J. Tennyson, J. R. Henderson, N. G. Fulton, Comput. Phys. Commun. 86, 175 (1995).
23. W. Gabriel, E.-A. Reinsch, P. Rosmus, S. Carter, N. C. Handy, J. Chem. Phys. 99, 897 (1993).
24. J.-M. Flaud and C. Camy-Peyret, J. Mol. Spectrosc. 51, 142 (1974).
25. C. Camy-Peyret, J.-M. Flaud, J.-P. Maillard, G. Gueluchvili, Mol. Phys. 33, 1641 (1977).
26. J.-M. Flaud, C. Camy-Peyret, G. Guelachvili, J. Mol. Spectrosc. 65, 219 (1977).
27. C. Camy-Peyret, J.-M. Flaud, J.-P. Maillard, J. Phys. Lett. 41, L23 (1980).
28. R. A. Toth, J. Opt. Soc. Am. B 10, 1526 (1993).
29. _____, Appl. Opt. 33, 4851 (1994).
30. O. N. Ulenikov and G. A. Ushakova, J. Mol. Spectrosc. 117, 195 (1986).
31. O. L. Polyansky, J. Tennyson, P. F. Bernath, ibid., in preparation.
32. P. Jensen, G. Osmann, I. N. Kozin, in Vibration-Rotational Spectroscopy and Molecular Dynamics, D. Papoušek, Ed. (Advanced Series in Physical Chemistry 9, World Scientific, Singapore, 1997).
33. J. Tennyson, Rep. Prog. Phys. 58, 421 (1995).
34. The present calculations involved full diagonalization of many matrices of dimension 1000 and partial (iterative) diagonalization of matrices of dimension 150 × (J + 1). Each set of levels thus takes a few hours on a powerful workstation. In contrast, perturbative calculations are generally limited to matrices of dimension less than a 100 and can be performed on a personal computer.
35. O. L. Polyansky, P. Jensen, J. Tennyson, J. Chem. Phys. 101, 7651 (1994); ibid. 105, 6490 (1996).
36. O. L. Polyansky et al., J. Mol. Spectrosc., in preparation.
37. We thank S. Miller for helpful comments on this manuscript, and the U.K. Engineering and Physical Science Research Council, the U.K. Particle Physics and Astronomy Research Council, the North Atlantic Treaty Organization, the Royal Society, the Natural Sciences and Engineering Research Council of Canada, the Petroleum Research Fund, NASA, NSF, and the Russian Fund for Fundamental Studies, all of whom supported aspects of this project.

13 March 1997; accepted 16 May 1997