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Water on the Sun: the Sun yields more secrets to spectroscopy

JONATHAN TENNYSON and OLEG L. POLYANSKY

Analysis of sunlight, which started the discipline of spectroscopy, has been the key to a number of major scientific discoveries. Sunspots, which are much cooler than most of the Sun's surface, have particularly rich and complicated spectra which has long been thought to be due to very hot water. The challenge of analysing this spectrum has stimulated the development of new theoretical procedures based on full quantum mechanical treatments of the vibrational and rotational motion of the water molecule. The result has been the identification of novel spectral features and a deeper understanding of how excited molecules such as superheated water behave. This work has applications ranging from the models of cool star atmospheres and rocket exhausts to the possible automated detection of forest fires. Perhaps the most interesting result is the insight given to understanding how our own atmosphere absorbs sunlight, and the possible consequences that this may have for modelling the greenhouse effect.

1. Spectroscopy and the Sun

In 1814 Fraunhofer allowed a beam of sunlight from a narrow opening in his shutters to pass through a prism and to be projected onto a white wall. What Fraunhofer saw was not only the colours of the rainbow, which had been observed in this manner since Newton, but also 'almost countless strong and weak vertical lines' [1], see figure 1. By this observation of sunlight was the discipline of spectroscopy born.

It took half a century to establish the link between the many lines in the solar spectrum and the chemical composition of the Sun. This was done by Bunsen and Kirchhoff who associated absorption features in the solar spectrum with emission lines from hot atoms observed in the laboratory [1]. It took a further half century, and the radical change in thinking represented by the adoption of quantum mechanics, to explain the source of these many transitions. Most of the Fraunhofer lines are now known to be associated with absorption of light by atoms in the outer layer of the Sun's photosphere. Some of the transitions are associated with diatomic molecules, notably CH, in the

Sun's photosphere. The remaining absorptions are caused by molecules such as water and oxygen in the Earth's atmosphere which also absorb sunlight. Such spectral analysis of light, possible both at visible and non-visible wavelengths, yields the vast majority of our knowledge not only about the rest of the Universe but also about the internal structure of atoms and molecules.

Study of the solar spectrum has revealed many other secrets. The most famous example is the discovery of the element helium. Helium was identified in the Sun from a spectral line recorded by a number of groups during the solar eclipse of 1868. It was nearly three decades before Ramsay succeeded in isolating helium in the laboratory and demonstrating a spectral match using a discharge tube [1].

This article is concerned with the analysis of sunlight not in the visible portion of the spectrum but at somewhat longer wavelengths in the infrared. We are not concerned with infrared radiation from the whole of the Sun but only from very much cooler regions called sunspots. Sunspots themselves have an interesting place in scientific history. These dark blemishes on the Sun's surface were originally observed by the Chinese some two thousand years ago. In the West, Galileo was responsible for the original observations which disproved the then widely held Ptolemaic theory of astronomy. Ptolemy had proposed that while all on Earth was corrupt and changing, heavenly bodies such as the Sun were symmetric and perfect. Dark patches on the face of the Sun, see figure 2, simply did not fit in with the picture of perfection.

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Figure 1 Spectrum of the Sun at visible wavelengths obtained using the UCLES high resolution echelle spectrometer. Each row in the spectrum is a different order of the echelle and thus sunlight of a different wavelength or colour. Clearly visible are the many absorption lines now known as the Fraunhofer lines. It was the observation of these lines by Fraunhofer that was the first hint that spectra contained any such information. This led directly to the use of spectroscopy as a sensitive probe of atomic and molecular structure. UCLES is now mounted on the Anglo-Australian Telescope. (Picture courtesy of Francisco Diego, University College London).

2. Textbook molecular spectra

The standard, textbook view of molecular spectra is to consider molecules as rather rigid. Within this view, rotation is the motion of a rigid body rotating about three rotation axes and vibrations are very small amplitude oscillations about the equilibrium structure of the molecule. In this model vibrational and rotational motion do not interact; the vibrations are the solutions of the well-known harmonic oscillator problem, known as normal modes.

In the harmonic oscillator–rigid rotor model it is possible to build the entire vibration–rotation spectrum of the molecule with only a very small amount of

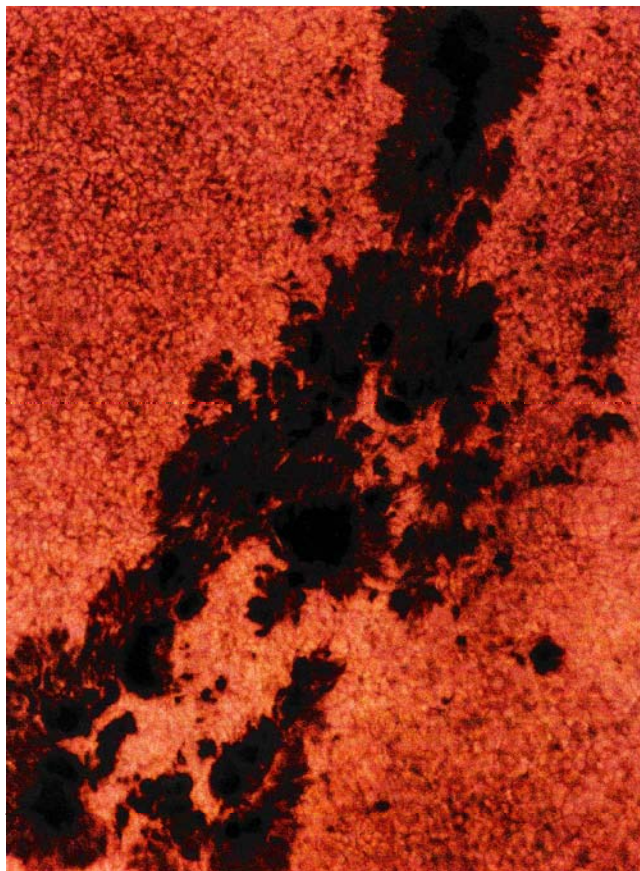


Figure 2 Chain of sunspots. The feather-like features surrounding each sunspot, or umbra, are known as penumbra. Water forms increasingly in these penumbra and is the most abundant species after molecular hydrogen in the sunspots. (Picture courtesy of NASA).

information about the molecule: its equilibrium structure and a set of force constants. If a molecule is deformed, for instance by stretching one of its bonds, then the force constants give the strength of the force pulling the molecule back towards its equilibrium structure. In quantum mechanical treatments it is more usual to talk in terms of the molecular potential, which is discussed further in section 4. The force constants are simply the second derivatives of the potential energy surface at the equilibrium structure of the molecule.

Spectra calculated within the harmonic oscillator model have a number of general properties. For example all the levels of a particular normal mode of vibration are evenly spaced and transitions between these levels always involve changing the vibrational quantum number by one quantum only.

A molecule which is not linear can rotate about three different, perpendicular axes. In the case of water, the moments of inertia and hence rotor constants about each of

these three rotational axes is different. The lack of symmetry in the rotational motions of such molecules means that they are called asymmetric tops. It is not possible to obtain analytic solutions for the rigid rotor model for asymmetric top molecules. The solutions of this model are, however, well-known [2] and have a number of generic features. One of these which is found in spectra of asymmetric top molecules is that levels with high rotational excitation appear in increasing proportion as degenerate pairs.

Molecules are not rigid, indeed hydrogen containing molecules are far from rigid, so no-one uses the harmonic oscillator–rigid rotor model for detailed numerical work on small molecules. Instead this model is used as the starting point for a series of expansions based upon Perturbation Theory. Despite the fact that the vibrations and the rotations of a given molecule are governed by the same potential, it is standard practice to treat these motions using independent expansions.

Analysis based upon perturbation theory expansions has been the bedrock of high resolution molecular spectroscopy for over fifty years. It has had many major successes and any gathering of high resolution spectroscopists always involves the display of the latest sets of spectroscopic parameters obtained from perturbation theory based expansions.

However it has long been known that this approach has its problems. This is particularly true for high values of the rotational angular quantum number, J . Some spectra, notably that of water, have proved very difficult to analyse within perturbation theory despite many years of effort by talented scientists. Indeed it has been shown [3] that standard expansions based on the rigid rotor model are formally divergent for $J > 14$ for the vibrational ground state of water, and for even lower J for higher vibrational states. Under these circumstances it is desirable to find alternative methods of describing how the nuclei in the water molecule move when excited.

A number of groups are working on more accurate methods of treating the nuclear motion problem, based on the Variational Principle, see section 4. However it was observations performed in sunspots which provided the final impetus for the development of these alternative theoretical techniques.

3. Sunspots and hot water

Sunspots are centres of intense solar magnetic activity. They have been well documented in the West since the time of Galileo and are known to occur in 22-year cycles. Indeed it has been claimed that the level of sunspot activity can have a profound effect on the weather here on Earth.

In visible light (don't look directly!) sunspots appear as dark patches on the Sun, see figure 2. This is because they

are significantly cooler than the rest of the Sun's atmosphere. While the atmosphere of the Sun is about 5500°C, sunspots can be as cool as 3000°C. This difference in temperature results in significant changes in the chemistry of the different regions of the Sun's atmosphere.

At a temperature of 5500°C, only a few simple molecules form, comprising of two atoms only. A number of diatomics, including the OH radical are well known in the Sun's atmosphere. Anything more complicated is simply blasted apart under the constant bombardment of hot, high velocity atoms. However as the temperature cools, these collisions become less energetic and it is possible for molecules with many atoms, such as the triatomic water molecule, to form. At temperatures around 3500°C about half of the OH has reacted with hydrogen to form water. Water is well known as an important constituent of cool, oxygen rich stars [4]. The complicated way in which water absorbs the starlight in these systems profoundly alters the structure of the stars atmosphere.

For nearly three decades solar astronomers have speculated (see [5] for example) that water might well be a significant constituent of sunspots. Hall, as part of his PhD studies [6], recorded a detailed atlas of sunspot spectra. Benedict made some identifications of water in the near infrared but never completed or published his work [7].

Wallace and co-workers [8] compiled several atlases of solar spectra using the excellent Fourier transform spectrometer at the Kitt Peak Solar Observatory in Arizona. This spectrometer worked at very high resolution and was sensitive to changes in the wavelength of the incoming sunlight as small as 1 part in 250 000. The atlases contained spectra of both the normal solar atmosphere and of sunspots. These were recorded at infrared wavelengths in the windows where the Earth's own atmosphere does not blot out all the incoming radiation. As atmospheric water is the species largely responsible for absorbing this radiation, it is very difficult to observe water in astronomical bodies from Earth. However, as we show below, the spectrum of hot water is very different from the cold water vapour found in the Earth's atmosphere. This means that hot water can be readily seen through the windows in the Earth's atmosphere.

Astronomers label these windows in the Earth's atmosphere using letters. The region which originally caught our attention was the N-window [7,9]. This window in Earth's atmosphere at infrared wavelengths (10 – 20 μm) is in a gap between the pure rotational spectrum of atmospheric water and the spectrum associated with excitation of its bending fundamental band. The water in sunspots is much hotter and under these conditions pure rotational transitions occur throughout the N-window region. Wallace and co-workers [8] also recorded spectra in the so-called L-window, which is at wavelengths near 4 μm , and the K-window, at wavelengths in the 2 – 2.5 μm region.

Like Hall and Benedict, Wallace *et al.* found that sunspots had much more complicated infrared spectra than the main body of the Sun. They too thought that water was the likely culprit but were unable to prove it. To help resolve this problem, Bernath and co-workers recorded spectra of hot water in his laboratory at the University of Waterloo in Canada. It is possible to record spectra of very hot water in flames [10,11], but Bernath's method was to

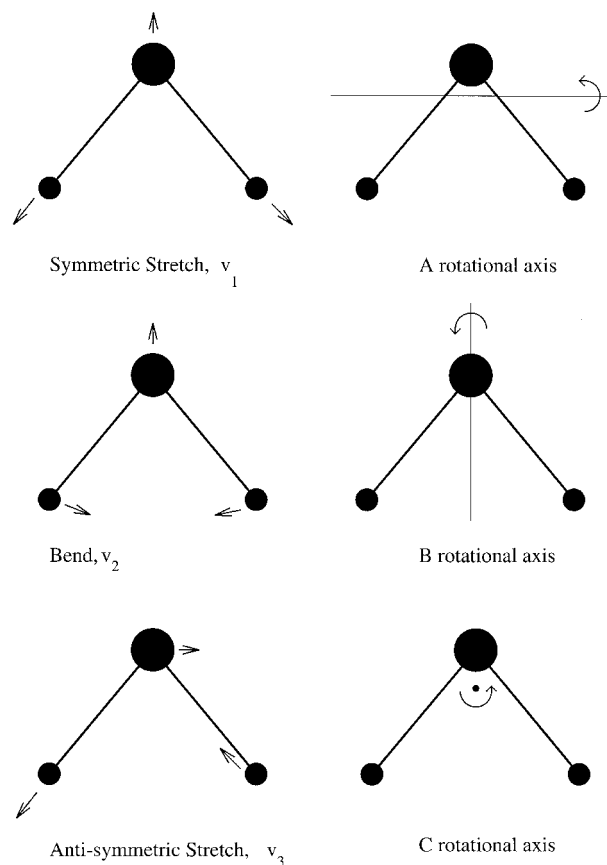


Figure 3 Vibrational and rotational motions of the water molecule. Water has three vibrational degrees of freedom and its vibrational states are usually designated (v_1, v_2, v_3) where there are v_i quanta in vibrational mode v_i . In this notation the vibrational ground state is $(0,0,0)$. Rotational motion occurs about each of the three rotational axes depicted. By convention the axes are labelled so that the rotational constant A is biggest and C smallest. The rotational states of angular momentum J are split into $2J+1$ sub-states according to which axis the molecule rotates about. By convention these sub-states are known by the projection of J onto the A axis, designated K_A , and the C axis, designated K_C . Each state is labelled as $J_{K_A K_C}$. Thus for a given vibrational state and rotational quantum number, the lowest level is $J_{0,0}$ and the highest $J_{J,0}$. In fact the only rigorous quantum numbers of the vibration-rotation levels of water are J , the parity of the asymmetric stretch, i.e. whether v_3 is even or odd, and the rotational parity given by whether the difference between K_A and K_C is even or odd. All other labels are only approximate.

heat steam until it glowed and then to record the resulting emission.

The standard procedure for recording molecular spectra is to detect absorption of light as a function of frequency. In an absorption spectrum, transitions are observed as a dip in the intensity of the light at the resonant frequency of each transition or absorption line. In the case of the sunspot, the continuous radiation source is the centre of the Sun itself and it is against this that a complicated absorption spectrum can be seen. Conversely, Bernath has developed a technique for recording molecular spectra by heating them and recording their thermal emission spectra [12]. Emission spectra are seen as peaks against a null (or black body) background.

It is hard to record a laboratory emission spectrum at very high temperature as parts of the apparatus, such as the windows on the cells containing the superheated steam, are liable to melt. Bernath's experiment was limited to temperatures below 1600°C , significantly lower than that

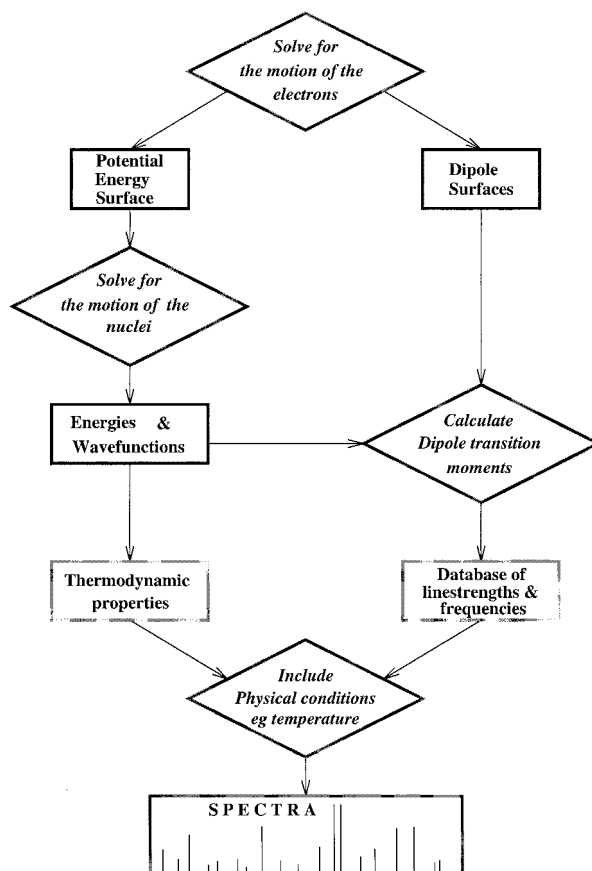


Figure 4 Flow diagram showing the steps (in diamonds) and data (in rectangles) involved in calculating an infrared spectrum using first principles quantum mechanics. In our work on water we have used the DVR3D program suite [16], to perform the calculations from the potential energy and dipole surfaces onwards.

found in the sunspot. As water, or any molecule, is heated the number of energy levels which are populated increases.

The increase in populated levels gives a corresponding increase in the number of possible spectral transitions and

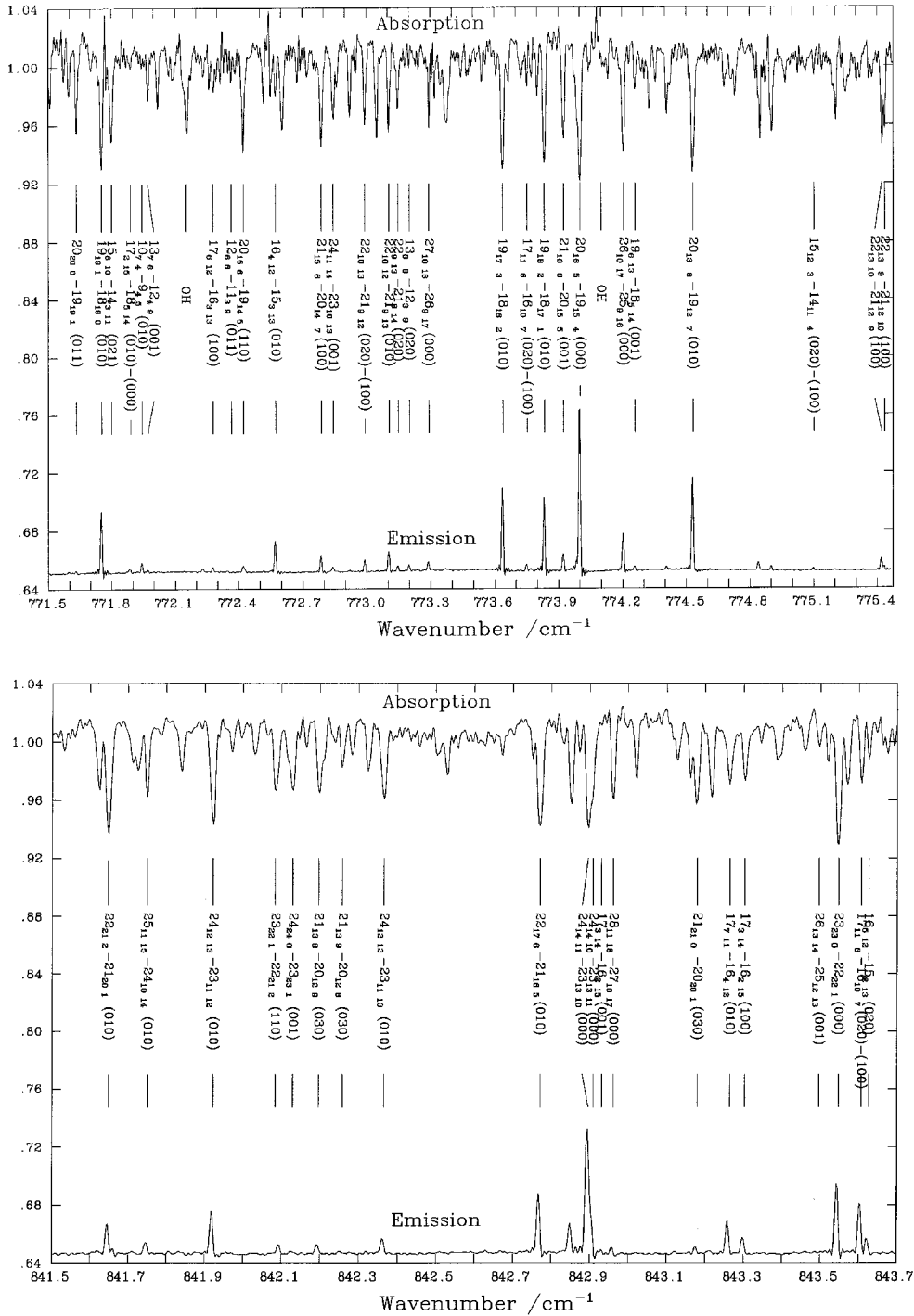


Figure 5 Two sample portions of the sunspot absorption spectrum (upper trace) and laboratory emission spectrum (lower trace). The vertical scale belongs to the sunspot absorption spectrum. Unity corresponds to no absorption of sunlight, 0.96 to absorption of 4% of the light. The strength of the laboratory emissions was not recorded on an absolute scale. Quantum number assignments, given as $J_{K_a K_c}$ (upper) – $J_{K_a K_c}$ (lower) for various vibrational states, are marked. The spectra illustrate the congested nature of the whole sunspot spectrum in the 10–20 μm region. Transitions which also involve a change in vibrational quantum numbers are part of the rotational difference bands, see figure 6. (Figures courtesy of Serena Viti, University College London.).

hence in the complexity of the spectrum. At the lower temperature used by Bernath, the spectrum of water is much simpler, 10 lines per cm^{-1} rather than 50 lines per cm^{-1} found in the sunspot†. Despite this drawback, there are thousands of places where peaks in the laboratory emission spectrum coincide exactly with dips in the sunspot absorption spectrum, see figure 5. This could be taken a clear signature that water is present in sunspots [7].

The confirmation that water was present in sunspots did not mean that the spectrum of hot water in either the laboratory or sunspots was understood. Indeed few of the transitions that were confidently associated with water had assignments giving either the vibrational or the rotational quantum numbers of the levels involved. It is necessary to understand why analysis of the spectrum of hot water presents such a problem.

4. The vibrating and rotating water molecule

As a bent three atom (triatomic) molecule, water has three vibrational and three rotational degrees of freedom. These are depicted in figure 3. As an asymmetric top molecule, the degeneracy of the vibrational and rotational states of the system is lifted leading to many allowed transitions and spectra with little or no readily discernible structure.

Figure 3 also gives schematically the normal modes of vibration for water. In practice these modes only approximately represent the true vibrational motions of the water molecule even at low levels of excitation. Indeed, at higher energies the local mode model, where vibrational excitation is localized in a single OH bond rather than being shared equally, gives a better model for the stretching motions. The normal mode to local mode transition is a manifestation of mixing between vibrational states. The need to consider mixing with excited bending states as well leads to the concept of 'polyads'.

The symmetric and asymmetric stretch vibrate with similar fundamental frequencies, 3657 cm^{-1} and 3756 cm^{-1} respectively. The bending fundamental, 1595 cm^{-1} , is nearly half this so that states with $2n$ quanta of bend lie close in energy, and to mix with, states with n quanta of stretch. Here n is the polyad number. A polyad is a group of states which are close in energy. In perturbation theory-based analysis it is often necessary to consider all (observable) members of a polyad simultaneously. In water each polyad is made up of the states which interact with the $(n,0,0)$ stretching state. Thus the $n=3$ polyad comprises the vibrational states $(3,0,0)$, $(2,0,1)$, $(1,0,2)$, $(0,0,3)$, $(2,2,0)$, $(0,2,2)$, $(1,4,0)$, $(0,4,1)$ and $(0,6,0)$ where the notation for labelling vibrational states is explained in the caption to figure 3. For water it is

possible to get good representations of the vibrational structure by considering individual polyads up to $n=4$. However for $n=5$ upwards the polyads begin to overlap and this concept becomes decreasingly useful.

More difficult to represent than the vibrational structure of water are the rotational energy levels of the system. Standard treatments, which have been outstandingly successful for many molecules, use the rigid rotor model as the starting point for perturbation expansions. In this model, the molecule only changes in response to rotational motion via centrifugal distortion terms which appear as second-order perturbations. A number of features of the rigid rotor model of molecular rotations are well established in molecular spectra. For example, as the rotational quantum number increases, levels with J_{J0} and J_{J1} become increasingly quasi-degenerate, where again the notation is explained in the caption to figure 3. The levels J_{0J} and J_{1J} behave similarly. As J is further increased many intermediate pairs of sub-levels also become quasi-degenerate. Indeed recent work on H_2X molecules, of which water should be a prime example, has shown that symmetry considerations lead to circumstances where clusters of four quasi-degenerate levels should be found if J is sufficiently high, see the review in [13].

The interactions between rotational and vibrational motions are governed by Coriolis forces. For molecules such as water, where Coriolis forces are important, the perturbative analysis of the rotational levels must normally be performed simultaneously for all members of a vibrational polyad. Even when this is done however, water is a well known and well documented awkward case.

An alternative, and increasingly popular, method of reproducing molecular spectra is by direct solution of the underlying quantum mechanical equations of the problem. To do this completely from first principles it is necessary to consider both how the electrons and how the nuclei move. A standard step in such treatments, known as the Born–Oppenheimer approximation, is to assume that the light electrons can relax instantaneously to any movement by the heavy and slow nuclei. Within this approximation the two motions are treated separately. For high accuracy it is usual for both these steps to use procedures based on the Variational Principle, which gives energy level estimates which approach the exact energies systematically from above [14]. Figure 4 gives the steps involved in the first principles calculation of a molecular spectrum.

The electronic structure problem of many electron systems such as water has received considerable attention from quantum chemists. A major difficulty here is that even the best calculations on a molecule with as many electrons as water gives absolute energies many thousands of cm^{-1} above the true energy of the system. For

† cm^{-1} are standard spectroscopy units. Technically they represent the wavenumber of the transitions but are often treated as energy frequency units through the relationship $E = h\nu$ ($8065\text{ cm}^{-1} \approx 1\text{ eV}$).

calculations of the vibration–rotation spectra this is not necessarily a problem. What is important for these studies is not the absolute electronic energy of the system but how this energy varies as the bond lengths and bond angles of the molecule are changed. The latest quantum chemical methods can compute very good estimates of the electronic wavefunction and relative electronic energy for a specified set of atomic positions. Such a calculation is then repeated at a series of molecular geometries to define the electronic energy at a grid of points. These points can then be used to define a potential energy (hyper)surface on which the nuclei move, usually by fitting to some assumed functional form such as Morse potentials for the stretching coordinates.

In water the potential energy surface has three dimensions corresponding to the three vibrational degrees of freedom. An outstanding example of this procedure is the recent electronic structure calculation of Partridge and Schwenke [15].

There are a number of methods available for getting very accurate energy levels and wavefunctions for the vibrational and rotational motion of a triatomic molecule on a given potential energy surface. The method favoured by us

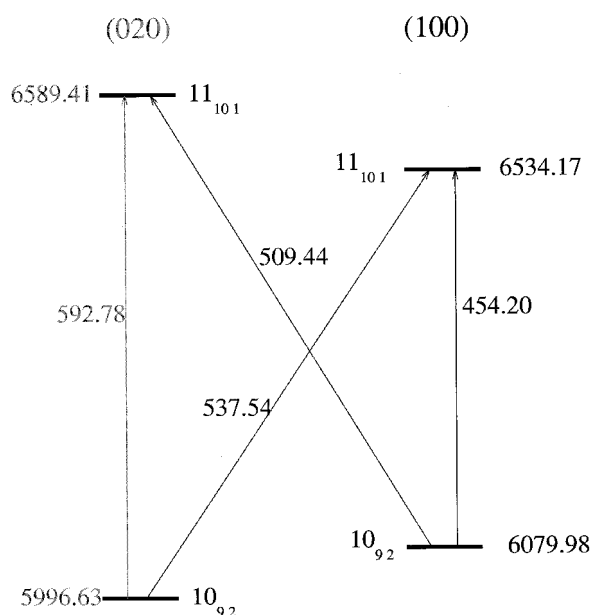


Figure 6 Schematic diagram illustrating the rotational difference transitions band between the (020) and (100) vibrational states and states with $J_{K_a K_c}$ equal to 10_{92} and 11_{101} . Observed transition wavenumbers and energy levels are given in cm^{-1} . Observation of any three transitions gives the wavenumber of the fourth. Its observation thus confirms the assignments of all four transitions. The ‘cross transitions’ between rotational levels associated with the (020) and (100) vibrational states occur because of mixing between these states, a process known as intensity stealing. Such transitions recur throughout the water spectrum.

[16] is based on using grid representations of the vibrational wavefunctions known as the Discrete Variable Representation or DVR. Rotational motion can be represented by Wigner rotation matrices which, unlike any finite representation of vibrational motion, form a complete set for the problem. In practical applications involving rotational excitation it is usual to treat the problem in two steps, utilizing the solutions of an effective vibrational problem as a starting point to solve the full vibration–rotation nuclear motion problem. This procedure gives the energy levels necessary for estimating the transition frequencies in the spectrum. For water it is possible to solve for motions of the nuclei to much higher accuracy than for motions of the electrons.

Knowing the frequencies for a set of transitions belonging to a given molecule allows it to be identified by its spectrum. However most practical applications of spectroscopy want more than this. A spectrum can be used as a diagnostic of both the temperature of the system and the amount of a particular molecule present in the sample, whether it is the atmosphere of a star or the inside of an internal combustion engine. To obtain this information it is necessary to know how probable a particular transition is. The driving force behind all strong molecular transitions are dipole moments. The strength of pure rotational transitions are determined by the size of the permanent dipole moment of the molecule. Vibrational transition strengths depend on changes in this dipole moment. Water has a permanent dipole which points along the B rotational axis (see figure 3). Excitation of any of the vibrational modes leads to a change in the dipole. Stretching motions lead to larger changes in the dipole than bending motion, so these transitions are stronger.

Electronic structure calculations usually yield values for the dipole moment vector at each geometry. These can be used to calculate the probability of a given vibration–rotation transition occurring. As discussed below this information is vital for analysing highly complex spectra of hot species.

Variational methods for predicting and assigning molecular spectra are computationally much more costly than the traditional perturbation theory based procedures. These methods treat vibrational and rotational motion using the same potential, meaning, for example, that improvements derived from studying vibrational motions can lead to greatly improved estimates of rotational levels [17]. Because of this, and because of the reliability of first principles electronic structure calculations, variational calculations also show much better extrapolation properties than perturbation expansions. Furthermore all resonant interaction between vibrational states are automatically included in variational calculation based on the use of exact nuclear motion kinetic energy operators, such interactions can only be treated perturbatively on a case by case basis.

Localized interactions with vibrational states that are not usually seen in the spectrum are almost impossible to predict using perturbation theory.

5. Analysing the sunspot spectrum

The sunspot spectrum recorded by Wallace *et al.* [8], portions of which are shown in figure 5, is extremely complicated. However, all the features, even the low amplitude structure which appears to be noise, is reproducible. This structure is all due to processes genuinely occurring in the sunspot being monitored. The sunspot spectrum has some 50 identifiable features per cm^{-1} . So how does one set about modelling such a spectrum?

Superficially it would appear that in order to interpret individual transitions in the sunspot spectrum it should be necessary to reproduce them with an accuracy of 0.01 cm^{-1} or better. This level of accuracy is simply unachievable with present day theoretical tools. For example, the first principles potential energy surface of Partridge and Schwenke [15] mentioned above only reproduces the fundamental frequencies of water with an accuracy of 2 to 3 cm^{-1} . Indeed the Born–Oppenheimer approximation itself is only valid at the 1 cm^{-1} level for molecules which contain the light hydrogen atom [18]. However a full frontal attack is not the way to address the problem.

A combination of two factors makes the spectrum interpretable. The first is that not all transitions are equally probable. Inspection of the spectrum, see figure 5, clearly shows that some features are very much stronger than others. Strong features are less common, and, by concentrating on these, the density of transitions is significantly reduced. The second factor is theoretical. As discussed above, the absolute accuracy of transition frequencies predicted using first principles quantum mechanics is not high enough for identifying individual lines. However, it transpires that if these calculations are performed carefully enough—which means using the best potential energy surface available from electronic structure calculations, including allowance for the failure of the Born–Oppenheimer approximation [18] and nuclear motion calculations which are performed to uniform high accuracy—then the errors behave in a systematic and, under certain circumstances, predictable fashion.

The technique used to give quantum number assignments to the strong transitions in the sunspot spectrum involved following branches in a spectrum. These branches are defined as transitions which differ in only one key quantum number. For example, transitions $20_{200} - 19_{191}$, $21_{210} - 20_{201}$ and $22_{220} - 21_{211}$ can all be described as a single branch defined by $K_a = J - \ell$ where in this example $\ell = 0$ (remember that levels with J_{J0} and J_{J1} are essentially degenerate for high J). It transpires that the error in the

predicted frequency only varies by very small amounts along a branch. Accurate estimates of the branch errors can be obtained from well known transitions involving low J states. The branch is then followed through the spectrum allowing quantum number assignments to be made.

This technique was originally applied to the sunspot spectrum recorded in the so-called N-window [9]. Figure 5 shows a portion of the N-window sunspot spectrum with quantum number assignments. The laboratory emission spectrum is given for comparison.

Analysis of the sunspot spectra and the associated laboratory emission spectra have significantly increased our knowledge of the water molecule. In particular we have built up a large stack not only of new observed transitions, but also new energy levels for the system which can be used for both further spectral analysis and for modelling. Given a set of selection rules which govern which levels in the water molecules are linked by transitions, tables of measured energy levels can be used to make predictions of possible new transitions. We generally designate new assignments made in this fashion as ‘trivial’ as they do not involve the large scale quantum mechanical calculations described above. Trivial assignments do not give new energy levels for further assignments, but they do serve to confirm that the previously analysed transitions were assigned correctly.

Following our success with the N-window, we turned our attention to the K-window. Originally we anticipated that it would be possible to assign many of the unassigned features in these spectra to particular water transitions using the trivial assignment technique. However analysis of the K-band showed that this was not so for two reasons. First the limited spectral window meant that many of the trivial transitions did not lie in the window. Second, it turned out that most K-band transitions involved high-lying vibrational states for which no data was available. Indeed in a number of cases transitions were between vibrational states neither of which had been previously observed. The K-band spectrum was therefore analysed using a procedure very similar to that described for the N-window [19]. This analysis was easier because the density of transitions is lower but complicated by frequent gaps in the spectrum, due to absorption features from the Earth’s atmosphere, which makes following branches harder. A similar analysis of the so called L-window (at $\sim 3000 \text{ cm}^{-1}$) is currently under way.

A number of new, and unexpected, features of the water spectrum have been discovered. A new type of transition, rotational difference bands [20] which are explained in figure 6, have been identified. It transpires that these transitions, which occur in whole series following branches for which $K_a = 9, 10, 11$ and 12, had been overlooked in previous analysis leading to serious omissions from standard databases of water transitions used for such

things as modelling the Earth's atmosphere (see below). Furthermore, we found numerous cases where the structure of quasi-degenerate levels, so standard in the spectra of rotationally excited molecules is broken, presumably by Coriolis interactions with nearby states. Strong evidence was also found that water did not form the four-fold clusters of levels found in similar molecules such as H_2Se .

This process of assigning transitions of water in various spectra may look like an advanced form of book-keeping which attaches handy labels to a lot of data. However it is not possible to use information gleaned about the spectrum of water to model water spectra in different environments without these labels or assignments. For example the strong temperature dependence of the water absorptions can only be obtained with a knowledge of both the energy of the lower state of the molecule and its total rotational quantum number, J . Water is such a common and fundamental system that understanding its spectroscopic properties at high temperature has important consequences, only some of which are we starting to appreciate.

6. Water in other hot environments

The water molecule is ubiquitous both here on Earth and, as is becoming increasingly apparent as astronomers reveal more and more of what is about us, elsewhere in the Universe. Thus the infrared spectrum of water is arguably the most important of all molecules because of its multitudinous applications. Detailed, line-by-line data on gas phase water are required for understanding or modelling many and varied systems.

Broadly speaking the demand for data on hot water can be broken down into two types. The first are applications where monitoring of one or more spectral lines reveals important information about a particular environment; the second type of application involves modelling the way light travels through an environment which, in principle, requires information on *all* spectral lines involved.

Hot water is a major product of nearly all combustion processes; it is one of the primary products of hydrocarbon combustion and essentially the sole product of burning hydrogen in pure oxygen. Individual transitions of hot water can easily be detected in flames such as those from an oxyacetylene torch [11]. Data on water is thus needed for modelling a variety of processes in flames and exhausts [21]. It is particularly important for modelling exhaust processes in hydrogen burning rockets. Transitions of hot water are being used by a number of research groups to try to monitor and optimize the performance of internal combustion engines. These experiments not only give spatial information on the distribution of water but also on the local temperature.

Hot water emissions from forest fires have been detected from overflying aircraft [22]. This leads to the interesting

idea that geo-stationary satellites, tuned to appropriate frequencies of hot water transitions, could be used to monitor large tracts of forest to give early warning of forest fires. It must surely beat standing on a watchtower with a pair of binoculars!

Just as water is important for modelling combustion and exhaust processes, those who want to monitor the movements and even identification of ships, aircraft, helicopters and tanks think this can be done by looking remotely for hot water emissions from their exhaust gases [21].

In astronomy, water vapour is the most important absorber of infrared starlight in the atmosphere of oxygen-rich cool stars [14]. For objects smaller than stars, usually known as brown dwarfs, water is the most abundant molecule after hydrogen. Including line-by-line water absorption in a model remains a difficult task because of the sheer volume of data required [14,15]. It might appear that how light travels through superheated steam should be something that can be easily determined by laboratory observation. However at higher temperatures this is a difficult experiment to perform.

The best attempt to address this problem was by Ludwig [10] who, as a NASA employee, was interested in data for models of rocket exhausts. He burnt hydrogen in pure oxygen in an especially constructed combustion tube 5 m long and 2 m in diameter. By shining light of different frequencies through this tube he tried to determine how much light was absorbed by water as a function of both frequency and temperature. Unfortunately he was unable to do this at high resolution and had to collect his results in relatively large, 25 cm^{-1} , frequency bins.

Figure 7 compares Ludwig's measured water absorption profile with ones synthesized using lists of individual water transition frequencies and probabilities—linelists. The HITRAN linelist [23] has been compiled over many years for modelling the absorption of light by water in the Earth's atmosphere. This linelist gives a thorough representation of room temperature water vapour in infrared regions of the electromagnetic spectrum and contains over 30 000 water transitions. The MT linelist [24] is a computed one; actually it was a precursor to the ones used above to assign sunspot spectra. It contains over 6 million water transitions.

At room temperature HITRAN and the MT linelist give similar results which differ markedly from that obtained using Ludwig's data. The difference is that the linelists give a spiky structure, while Ludwig's data predict essentially continuous absorption over the region of the water rotational transitions. Any atmosphere modelled using Ludwig's data will behave very differently because the blanket absorption will simply trap light over a wide range of wavelengths. In reality, the gaps in the absorptions, which are correctly represented in the other models, allow much of the light to pass through unhindered. At higher

temperatures similar differences persist, but at these temperatures there are insufficient lines in the HITRAN database to model the behaviour of water. Indeed the latest calculation of over 300 million water transitions [15] makes even the MT linelist seem rather modest!

However water does not have to be hot for the information obtained from analysing sunspot spectra to be important.

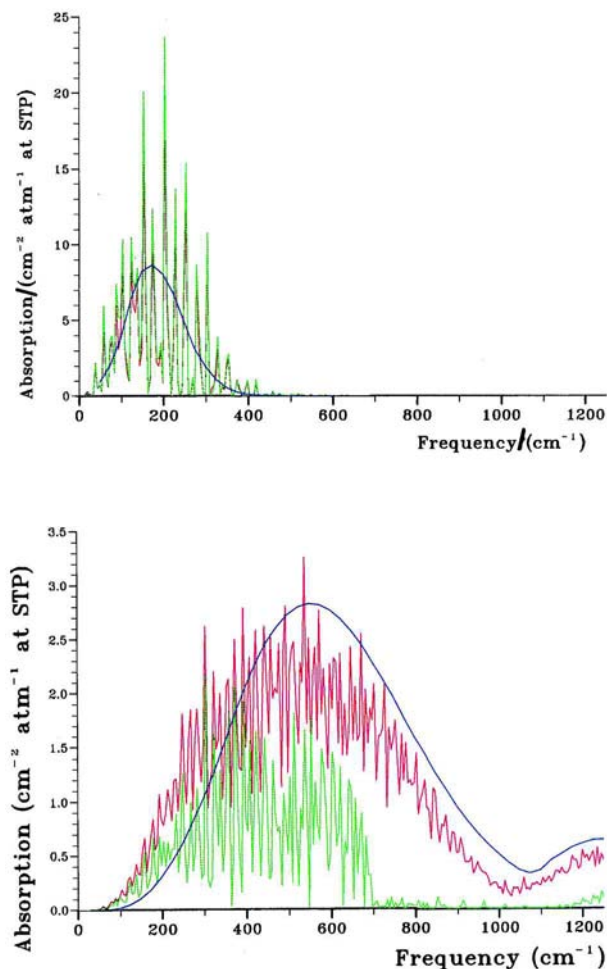


Figure 7 Model absorption profiles of water at 300 K (upper figure) and 3000 K (lower figure) [24]. The blue curves come from measurements by Ludwig [10]; the green curves were obtained using the atmospheric database HITRAN [23] which is a compilation of measured lines; the red curves were obtained using a calculated list of 6 million water lines due to Miller and Tennyson (MT) [24]. The 300 K figure demonstrates that the measurements of Ludwig, which only obtained absorptions in 25 cm^{-1} bins, were too coarse to reproduce the pronounced structure present in the spectrum. At high temperature, lower figure, the HITRAN database contains too few lines to model the complete water spectrum. (Figures courtesy of Jeremy Schryber, University College London.)

7. Water in a cold climate

Atmospheric physicists have long suspected that there is a problem with their radiation budget: less sunlight seems to be transmitted through a cloud-free atmosphere than is predicted. Recently six independent studies have combined satellite data and ground based measurements to confirm that some 8% less sunlight is reaching ground level than is predicted by the most up-to-date atmospheric models [25]. Put another way, this ‘blue skies anomaly’ means that nearly 50% more sunlight is absorbed in a cloud free atmosphere than any model can account for. This discrepancy is large and potentially very significant: at ground level it represents a difference of between 25 and 30 W m^{-2} . This is some five times larger than most worst case predictions of the greenhouse effect ($\sim 5\text{ W m}^{-2}$). Similar discrepancies between theory and observation have been also been found in studies which used aircraft to monitor sunlight above and below clouds [26].

A number of possible causes for this anomaly have been postulated: these include absorption of sunlight in the atmosphere by water clusters or small aerosols (micro-droplets) or the scattering of sunlight back out of the Earth’s atmosphere by microscopic dust particles. Another possibility which needs to be considered is absorption by the many weak transitions of water which lie in the near infrared and visible region of the spectrum. Despite the fact that water already accounts for some 70% of known atmospheric absorption, near infrared and visible features are poorly represented in atmospheric databases such as HITRAN [23] and hence in models of the Earth’s atmosphere. Water transitions in this region are numerous but weak. This means that they are very difficult to both see and to interpret. Indeed the very weak absorptions can only be observed in the laboratory using exceptional techniques which allow radiation to travel through very long paths (maybe kilometres) of water vapour. Of course such path lengths arise naturally in the Earth’s atmosphere.

This problem, involving as it does, water vapour at room temperature or below may seem somewhat remote from the behaviour of highly excited water molecules in the furnace of the Sun. However there is a direct link via the vibrational states involved. The atmospheric spectrum of water is largely governed by absorption of sunlight by various (low J) rotational states of the vibrational ground state. In the near infrared and optical region ($12\,000 - 22\,000\text{ cm}^{-1}$), this absorption leads directly to highly excited vibrational states in the $n = 4$, the $n = 5$ and, perhaps, the $n = 6$ polyads. Such vibrational states are the ones we have analysed, sometimes for the first time, in the sunspot spectrum. Clearly this information is directly transferable although it should be noted that the sunspot spectrum involves states with much higher levels of rotational excitation than is found in atmospheric water vapour.

One problem with applying our assignment method to the atmospheric water vapour spectrum is that there is a, perhaps understandable, reluctance amongst spectroscopists to publish their spectra without quantum number assignments. This means that although we know, from hearsay evidence, many such spectra have been recorded few are available in the scientific literature for us to analyse. However, in 1986 Mandin *et al.* [27] published a very high quality, but only partially analysed, laboratory near infrared water spectrum, again recorded using the excellent instrumentation available at Kitt Peak. This work identified 2745 transitions of which some 800 remained unassigned after a thorough analysis using perturbation theory.

We have been able to analyse these unassigned transition using a mixture of the trivial and linelist assignment procedures described above. Thus far we have successfully assigned about 700 of the unassigned transitions [28]. One feature of this spectrum, not generally found in the sunspot spectra we have analysed so far, is that several transitions to the same upper state can often be identified. The lower states in the spectrum correspond to the levels of water occupied at room temperature, all of which are well known. Knowledge of a transition frequency and the lower state energies can be used to predict new frequencies of transitions to the same upper state. Finding these transitions in the spectrum confirms the assignment. Interestingly we have assigned transitions to a number of vibrational states not previously observed in the laboratory but found, by us, in sunspots.

Among the new vibrational bands that we have assigned in near infrared spectrum are (170)–(000) and (071)–(000). These transitions, which gain intensity for a few rotational levels only by resonant interaction with nearby ‘bright’ states, involve changes of 8 vibrational quanta—a long way indeed from $\Delta v = 1$ restriction of the harmonic oscillator model!

So far in this article when we have mentioned water we have always implicitly referred to the molecule composed of two normal hydrogen atoms and the mass 16 isotope of oxygen. However the natural abundance of the mass 18 isotope of oxygen is relatively high, about 0.5%. This means that when analysing weak spectra of naturally occurring water one should not neglect the possibility that some of the transitions will actually be due to the H_2^{18}O molecule. This is a system we have yet to do serious work on, but it is likely that many, maybe most, of the transitions we have yet to assign in Mandin *et al.*’s near infrared water vapour spectrum belong to this species. Presumably a certain amount of the ‘grass’ that we have yet to analyse in the various sunspot spectra does too.

8. Does the Sun hold further secrets?

The identification of water in sunspots and the consequent advance in the theory of water spectroscopy is undoubt-

edly important. However this work is a long way from being complete. Even a cursory inspection at the sunspot spectrum, such as the portions shown in figure 5, shows that the majority of the features in this spectrum await proper quantum number assignments. Such analysis will undoubtedly lead to further new insights into the spectroscopy of water as well as providing a wealth of new data for other applications. However this analysis is unlikely to be completed without further new theoretical developments.

In particular it will be necessary to improve the way the quantum mechanical models used represent both the motions of the electrons and the way these motions couple to the motions of the nuclei in the molecule. This will involve questioning approximations which have up until now always been assumed to be valid. For example, it has always been assumed that in light molecules such as water the electrons move relatively slowly and relativistic effects could therefore be safely ignored. However, there are recent indications that the relativistic motions of the electrons in the water molecule significantly alter the shape of the water potential [29].

For centuries observations of the Sun have revealed information which has led to fundamental new scientific developments. So does the Sun hold further secrets? While it is not possible to predict serendipitous discoveries, it would be foolish to suggest that continued sunspot observations will not lead to further advances. We would certainly be interested if anyone could provide detailed sunspot infrared spectra in the many spectral regions obscured from ground level observations by the Earth’s atmosphere.

However there is already a long-standing set of solar observations which are causing much scientific debate and head scratching. Neutrinos are light (perhaps massless) particles produced in most nuclear reactions and in huge quantities by the Sun. Neutrinos are extremely hard to detect. However all measurements of the flux of electron neutrinos reaching Earth from the Sun finds many fewer than predicted by solar models. There are a number of possible solutions to the solar neutrino problem [30], one of which is that neutrinos change their type as they travel from the Sun to Earth. This can only happen if neutrinos have a mass. At present the ‘standard model’ of particle physics assumes neutrinos with no mass. It could well be that another set of solar observations will cause the text books to be re-written.

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