

# The spectroscopy of water vapour: Experiment, theory and applications

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The recent spectroscopy of water vapour in the ground electronic state is reviewed. Experimental advances from the microwave to the near ultraviolet spectral regions are surveyed. On the theoretical front, new approaches to the calculation of vibration–rotation energy levels are covered. Water spectroscopy finds extensive application in astronomy, atmospheric science and combustion research. An illustrative summary of these applications is presented.

## 1. Introduction

Water is the most important molecule for without it life on earth would not be possible. Water vapour, for example, makes the Earth habitable through the greenhouse effect<sup>1</sup> that provides some 30 K of heating.<sup>2</sup> Although highly variable in concentration, the infrared-active water molecule is the third most abundant atmospheric species. Water is also probably the third most abundant molecule in the Universe (after H<sub>2</sub> and CO) and can be detected in many of the objects in our solar system including our Sun,<sup>3</sup> and more generally in cool stars. During the formation of stars from molecular clouds, radiation from water vapour helps remove the excess energy generated by gravitational collapse.<sup>4</sup> Water is a primary product of combustion of hydrocarbon fuels. As a light, very asymmetric top, water is also of intrinsic spectroscopic interest.

In view of the general interest in the spectroscopy of water vapour and the important applications in atmospheric science, astronomy and combustion, water has been studied for a long time. The electronic spectrum in the vacuum ultraviolet is diffuse because of predissociation<sup>5</sup> so the pure rotational transitions in the millimetre wave region and the vibration–rotation transitions in the infrared have been studied the most. Early infrared work on the fundamental bands by Plyler<sup>6</sup> and on the overtones, seen as atmospheric lines in the solar spectrum, by Mecke<sup>7</sup> dates from the early 1930's.

More recently the discovery of hot water vapour in sunspots<sup>3</sup> led to new theoretical approaches<sup>8</sup> to the prediction of water spectra. This article surveys the recent advances in the experimental and theoretical spectroscopy of water on the ground state potential surface.

## 2. Advances in theory

Our understanding of the energy levels of water vapour is based on the traditional Born–Oppenheimer<sup>9,10</sup> separation of electronic and nuclear motion. The nuclear motion on the water potential energy surface is further separated into vibrational and rotational parts by making the rigid rotor approximation for rotation and neglecting Coriolis coupling. The harmonic approximation is then made for the potential function for vibrational motion. The resulting normal mode and rotational wavefunctions (although symmetric top wavefunc-

tions are more convenient in practice) are then used as basis functions for the treatment of a more realistic Hamiltonian that contains anharmonic potential terms, Coriolis coupling, vibration–rotation coupling, centrifugal distortion, *etc.*<sup>11</sup> Various energy level correction terms are derived<sup>11</sup> using perturbation theory and the usual constants such as  $x_{rs}$  (vibrational anharmonicity) or  $\alpha_A$  (vibration–rotation interaction constant for *A*-axis) or  $\Delta_J$  (a quartic centrifugal distortion constant in the Watson A-reduction) are related back to these added terms in the full Hamiltonian.

The traditional zeroth order model of vibrational motion is based on normal modes.<sup>10</sup> A better zeroth order picture, however, for the stretching overtones is the local mode model,<sup>12,13</sup> and recent work<sup>14</sup> has used local model labels. The usual  $\nu_1\nu_2\nu_3$  vibrational quantum numbers for symmetric stretch, bend and antisymmetric stretching modes are replaced by  $nm^\pm\nu_2$ , in which  $n$  and  $m$  are the number of quanta of OH stretch in each bond and  $\nu_2$  is the usual bending mode quantum number. The  $\pm$  refer to the positive and negative linear combination of the basis functions, *viz.*

$$|nm\pm\rangle = \frac{1}{\sqrt{2}}(|nm\rangle \pm |mn\rangle), \quad \text{for } n > m,$$

and

$$|nm+\rangle = |mn\rangle, \quad \text{for } n = m.$$

The  $\pm$  signs (symmetric/antisymmetric) are thus also symmetry labels for the operation of exchanging the nuclear displacements, and  $+$  is usually not indicated in the symmetric case of  $n = m$ .

As the bending mode character increases, however, Rose and Kellman<sup>15</sup> predict that the vibrational modes become “chaotic” and neither the local mode nor the normal mode models are appropriate. This problem of assigning vibrational quantum numbers has not been confirmed yet experimentally because only highly-excited stretching modes are known.<sup>14</sup> Another interesting prediction is that as the bending energy approaches the barrier to linearity ( $11\,105^{16} \pm 5 \text{ cm}^{-1}$  or  $11\,119^{17} \pm 15 \text{ cm}^{-1}$ ) the vibrational intervals will be disturbed and will show a discontinuity.<sup>17</sup> This well-known effect associated with quasilinearity<sup>5</sup> has recently been named “quantum monodromy”.<sup>18</sup> For H<sub>2</sub>O the effects should be noticeable for the 080 level and strong for the 0100 level (in normal mode notation), although at the moment the 060 level is highest reliably known pure bending state.<sup>14</sup>

The vibrational Hamiltonian can be reformulated based on concepts drawn from the theory of continuous groups (Lie algebras).<sup>19</sup> This “algebraic” or vibron model has a potential advantage over the more conventional normal mode or local mode models for water in that it can represent large amplitude motion with fewer parameters.<sup>20–22</sup> The symmetry and structure imposed by the Lie algebra reduces the number of free parameters in the model. However, the vibron model has yet to be widely adopted.

The rotational energy levels of the water molecule are particularly difficult to calculate because water is so light. Water displays “anomalous centrifugal distortion” and the usual Watson formulation<sup>11,23</sup> of the rotational Hamiltonian as sums of powers of rotational angular momentum operators diverges. At modest  $J$  values the contributions of the higher order terms in the Watson Hamiltonian increase in size<sup>24</sup> rather than decrease as appropriate for a perturbation expansion. This fact does not prevent the use of the Watson Hamiltonian in the sense that given enough terms (and enough patience), the experimental energy levels can still be reproduced. The utility of the spectroscopic constants, however, is compromised and they cannot be used, for example, to predict reliably new energy levels.

There are a number of mathematical tricks that can be applied to diverging power series to make them converge.<sup>24–26</sup> One method is to represent the power series as a rational fraction of two polynomials called a Padé approximant.<sup>24</sup> The coefficients in the original series

$$f(x) = \sum_{i=0}^{\infty} a_i x^i$$

are combined to form the  $a_i$ ,  $b_i$  coefficients in the new  $f[m,n]$  approximation with

$$f[m,n] = \frac{\sum_{i=0}^m a_i x^i}{\sum_{i=0}^n b_i x^i}.$$

This Padé approximant for  $f(x)$  has improved convergence properties and this technique has been applied by Polyansky<sup>24</sup> to the representation of the energy levels of water.

Other approaches are possible such as the Borel method<sup>24,26</sup> and a related scheme due to Pickett *et al.*<sup>27</sup> The “generating function method” also achieves improved convergence by using non-polynomial forms.<sup>28,29</sup> When these non-polynomial forms are expanded in a Taylor series, the regular Watson Hamiltonian is recovered.

The basic problem with water is that the rotationally-excited levels can undergo large geometric distortions, particularly in the bond angle. The bending motion and the rotational motion thus interact strongly and are difficult to separate. A very useful approximation is to formulate a 4-dimensional bending–rotation Hamiltonian along the lines originally proposed by Bunker and co-workers.<sup>30</sup> There have been numerous variations on this theme by Bunker and co-workers.<sup>31</sup> Coudert<sup>32</sup> has carried out a very successful set of bending–rotation calculations with a formalism based on some earlier work by Makarewicz.<sup>33</sup> With a relatively modest number of parameters, Coudert was able to achieve spectroscopic accuracy in his fitting of the rotational levels for the 000 and 010 vibrational levels.<sup>32</sup>

The ultimate method for the calculation of the vibration–rotation energy levels is to solve exactly the full six dimensional problem (3 vibrations and 3 rotations) for a particular potential energy surface. For a given co-ordinate system an exact kinetic energy operator can be derived.<sup>34–37</sup> Thus with a dipole moment surface (empirical<sup>38</sup> or *ab initio*<sup>39</sup>) any line in any band can in principle be calculated to arbitrary precision.<sup>40</sup> The problem is, however, obtaining a potential of sufficient

accuracy (ignoring for the moment the breakdown of the Born–Oppenheimer approximation and the neglect of various relativistic effects). The primary disadvantage of the full 6-dimensional approach (apart from the longer computation time) compared to the pure rotation calculations (3 dimensions) or the bending–rotation calculations (4 dimensions) is that spectroscopic accuracy has not yet been achieved.

There are three kinds of potential surfaces that are currently used: empirical, adjusted *ab initio* and *ab initio*. Empirical potentials are derived by fitting the parameters in a flexible potential function. A popular form is Jensen’s power series expansion,

$$V(\Delta r_1, \Delta r_3, \bar{\rho}) = V_0(\bar{\rho}) + \sum_j F_j(\bar{\rho}) y_j + \sum_{j \leq k} F_{jk}(\bar{\rho}) y_j y_k + \dots$$

in which  $y_j = 1 - \exp(-a_j \Delta r_j)$  is a Morse co-ordinate and  $\bar{\rho}$  is the supplement of the bond angle.<sup>41–42</sup> The term  $V_0(\bar{\rho})$  and each  $F(\bar{\rho})$  is further expanded in terms of the large amplitude co-ordinate  $\cos \bar{\rho}$  as, for example

$$V_0(\bar{\rho}) = \sum f_0^{(i)} (\cos \bar{\rho}_e - \cos \bar{\rho})^i.$$

The dipole moment surface<sup>43</sup> can be expanded in a similar fashion as a function of the displacements  $\Delta r_i$  and  $\cos \bar{\rho}$ . Solving the vibration–rotation Schrödinger equation, computing the line intensities, comparing the predictions to experiment and then correcting the potential parameters (iterating as necessary) leads to an empirical potential surface.<sup>38,42,44,45</sup> This procedure has been carried out by several groups and, for example, Polyansky *et al.*<sup>44</sup> determined a potential surface (PJT1) that reproduces a set of experimental line positions with  $J \leq 14$  with a standard deviation of  $0.36 \text{ cm}^{-1}$ . This PJT1 surface was improved<sup>45</sup> by using additional potential terms and the consideration of more experimental data yielding a standard deviation of  $0.25 \text{ cm}^{-1}$ .

An *ab initio* potential surface for water is derived by solving the electronic Schrödinger equation on a grid of points each with a particular value of the two bond lengths and the bond angle.<sup>39,46–48</sup> State-of-the-art calculations such as those of Partridge and Schwenke<sup>48</sup> start with very large single particle basis sets (up to h functions on the O atom) and include extensive electron correlation of all electrons including the 1s O core. The *ab initio* potential points are then fitted to a parameterized potential function. The components of the dipole moment are analogously fitted to a parameterized dipole moment surface.<sup>48–49</sup> Calculation of line positions using the Partridge and Schwenke<sup>48</sup> *ab initio* surface shows errors of typically a few  $\text{cm}^{-1}$  ( $< 10 \text{ cm}^{-1}$ ), significantly worse than the purely empirical surface of, for example, Polyansky *et al.*<sup>45</sup> However, small empirical adjustments can be made to the *ab initio* potential surface by comparison with experiment.<sup>48</sup> This adjustment of the *ab initio* surface improves the agreement with experiment by about two orders of magnitude, *i.e.*, to within about  $0.05 \text{ cm}^{-1}$ .

The adjusted *ab initio* potential surface of Partridge and Schwenke<sup>48</sup> is currently the best surface available and has largely replaced the purely empirical surfaces. The purely empirical surfaces available to date are not very reliable for either interpolation within the range of data or extrapolation beyond the range of observations. The adjusted *ab initio* surface of Partridge and Schwenke<sup>48</sup> is superb for interpolation but because of the empirical adjustment is erratic for extrapolation. The fully *ab initio* surface of Partridge and Schwenke, however, extrapolates more smoothly. It is this smooth evolution of errors that allowed the assignment of the very high temperature water spectrum recorded in sunspots.<sup>8,40</sup>

A few comments are in order about the calculation of energy levels from the full six dimensional vibration–rotation Hamiltonian. This type of calculation is now almost routine<sup>36</sup> and computer programs are readily available.<sup>50</sup> The general

approach is variational, so that sets of basis functions are used to set up a Hamiltonian matrix, which is then diagonalized to yield eigenvalues and eigenvectors. Often the basis functions for the vibrational co-ordinates are replaced by a “discrete variable representation” (DVR) and this DVR method<sup>36,50–52</sup> yields wavefunctions represented pointwise on a grid of internal co-ordinates.

The water molecule is a favourite testing ground of new methods for solving the vibration–rotation Schrödinger equation. For example, Carrington and co-workers<sup>53</sup> have tested the Lanczos algorithm for rapidly determining highly-excited rovibrational energy levels. Carrington and co-workers<sup>53</sup> confirm, for example, that water in contrast to H<sub>2</sub>S and H<sub>2</sub>Se, will not show a four-fold clustering of energy levels.<sup>12,44,54</sup> Very recently, Li and Guo<sup>55</sup> used the Lanczos algorithm to compute all of the possible bound vibrational levels (1054 levels, 576 symmetric and 478 antisymmetric) with the adjusted *ab initio* surface of Partridge and Schwenke.<sup>48</sup> The highly-excited vibration–rotation levels of water obtained by calculation<sup>55–57</sup> are useful for computing stellar opacities in astronomy<sup>58,59</sup> and for the derivation of thermochemical properties at high temperatures.<sup>60</sup>

State-of-the-art *ab initio* potential surfaces from water are now of sufficient quality that the breakdown of the Born–Oppenheimer approximation and the effects of relativity limit the accuracy of the derived vibration–rotation energy levels. Corrections to the Born–Oppenheimer approximation can be derived by perturbation theory and lead to a “diagonal” (or adiabatic) first order correction of the form,<sup>61,62</sup>

$$E^{(1)} = \Delta V_{\text{ad}} = \langle \psi | \hat{T}_{\text{N}} | \psi \rangle$$

in which  $\hat{T}_{\text{N}}$  is the nuclear kinetic energy operator neglected in the electronic structure calculation (“clamped nuclei”) used to derive the ground state electronic wavefunction  $\psi$ . This adiabatic correction term is relatively easily calculated by modern electronic structure programs<sup>62</sup> and constitutes a small mass-dependent change to the potential surface. Unfortunately the diagonal correction is not dominant<sup>62</sup> and the non-adiabatic correction (defined as the difference between the full correction and the adiabatic correction) is comparable in magnitude. Zobov *et al.*<sup>62</sup> noticed, however, that the use of hydrogen masses half way between atomic and nuclear masses gave better agreement with experiment. Electrons cannot follow the nuclei perfectly so this empirical mass adjustment gives part of the non-adiabatic correction.

The non-adiabatic correction is difficult to calculate because (using perturbation theory) it has matrix elements between the ground state and all possible excited electronic states.<sup>63</sup> Moreover, the non-adiabatic correction destroys the concept of a potential surface because it involves a mixing of electronic states, not just a potential shift on a single surface like the adiabatic correction. Schwenke<sup>63</sup> has made a recent breakthrough in the first *ab initio* calculation of the non-adiabatic corrections for water. He has evaluated *ab initio* the terms in the Bunker and Moss<sup>64</sup> form of the correction. The method recovers about 90% of the non-adiabatic correction and the residual part seems amenable to empirical scaling.<sup>63</sup>

The use of the non-relativistic Schrödinger equation to derive a water potential also leads to non-negligible errors in the vibration–rotation energy levels of water. There are three main relativistic corrections that need to be considered: mass–velocity, Darwin and spin–orbit terms.<sup>65</sup> The mass–velocity term<sup>65</sup> is due to the increase in mass for a moving electron and has the form, in atomic units,

$$\hat{H}_{\text{MV}} = -\frac{1}{8c^2} \sum \hat{\mathbf{p}}_i^4$$

with  $\hat{\mathbf{p}}_i$  the momentum operator. The one electron and two electron Darwin terms<sup>65</sup> arise from a smearing of the electron

positions at high speeds and are, in atomic units,

$$\hat{H}_{\text{D}} = \hat{H}_{\text{D1}} + \hat{H}_{\text{D2}} = \frac{\pi}{2c^2} \sum_{i,K} Z_K \delta(r_{iK}) - \frac{\pi}{2c^2} \sum_{i \neq j} \delta(r_{ij})$$

in which  $i$  and  $j$  are electron indices,  $K$  is a nuclear index and  $\delta$  is the usual Dirac delta function. For the light closed-shell water molecule, the spin–orbit contribution is negligible.<sup>65</sup> Surprisingly, for water the mass–velocity and one electron Darwin terms have about the same effect on the vibration–rotation energy levels as the adiabatic and non-adiabatic corrections.<sup>66</sup> The two electron Darwin term<sup>67</sup> is about an order of magnitude smaller and is comparable to a number of other neglected terms. Even more surprising is that the Lamb shift resulting from quantum electrodynamics is about the same size as the two electron Darwin term.<sup>68</sup> The Lamb shift can be estimated simply from the one electron Darwin correction and contributes about 0.5 cm<sup>−1</sup> to the vibration–rotation energy levels.<sup>68</sup>

### 3. Advances in experiment

The water molecule is a popular target for testing new experimental techniques. For example, the shape of the water molecule undergoing a “laser-induced Coulomb explosion” after irradiation with a high power femtosecond laser pulse has been studied.<sup>69</sup> A femtosecond pulse can be rectified to produce terahertz radiation and the far infrared spectrum of hot water in a flame was recorded.<sup>70,71</sup> Finally the Doppler-tagging technique has been used to study the photodissociation of water at high resolution.<sup>72</sup> A new value of the bond dissociation energy ( $D_0$ ) of H–OH was determined as 41151 ± 5 cm<sup>−1</sup> (see also Ruscic *et al.*<sup>73</sup> and Joens<sup>74</sup>).

The water molecule has been difficult to study in the microwave and submillimetre range because the rotational constants<sup>75</sup> ( $A_0 = 835839.10$  MHz or 27.880591 cm<sup>−1</sup>,  $B_0 = 435347.353$  MHz or 14.5216246 cm<sup>−1</sup> and  $C_0 = 278139.826$  MHz or 9.27774594 cm<sup>−1</sup>) are so large that the spectrum is sparse. A few new water lines have been measured by traditional millimetre wave methods<sup>76–78</sup> and Johns<sup>79</sup> and others<sup>80,81</sup> have analysed far infrared Fourier transform spectra. The major advance, however, has been the application of laser-mixing technology to generate widely tunable terahertz radiation. Matsushima *et al.*<sup>75</sup> covered the 0.5–5 THz (17–167 cm<sup>−1</sup>) region with a tunable far infrared (TuFIR) source based on mixing two CO<sub>2</sub> lasers and a microwave oscillator with a metal–insulator–metal (MIM) point contact diode. Some 140 water lines were measured with a claimed precision of better than 50 kHz.<sup>75</sup> Chen *et al.*<sup>27</sup> also measured a number of new water lines using a terahertz spectrometer based on mixing two semiconductor diode lasers in a GaAs photomixer with a special submillimetre wave antenna structure. The water lines were measured with a precision of about 250 kHz and all of the existing data was combined in a grand fit using Pickett’s modification of the Watson Hamiltonian to improve convergence.<sup>27</sup> Intensities of the lines were also computed by Chen *et al.*<sup>27</sup> using the power series expansion of the dipole moment due to Muentzer and co-workers.<sup>82,83</sup> These predicted pure rotational line positions and intensities for the 000 and 010 vibrational levels (see <http://spec.jpl.nasa.gov/>) are the best current estimates. It remains only to extend these precise terahertz measurements to higher vibrational and rotational levels by using heated water samples and several groups are contemplating such work.

The pure rotational transitions of water extend into the mid infrared region, particularly for heated samples. High quality cold spectra recorded with a Fourier transform spectrometer are available.<sup>79–81,84</sup> It was, however, the spectrum of a sun-

spot in the 10 micron atmospheric window that resulted in a major advance in our knowledge of highly-excited pure rotational transitions.<sup>3</sup> Wallace *et al.*<sup>3</sup> noted that the dense absorption spectrum of the sunspot (nearly 50 lines  $\text{cm}^{-1}$ ) matched that of a laboratory emission spectrum of hot water. This proved that there was “Water on the Sun” but the line density was so high that the spectrum seemed “unassignable” by conventional techniques.<sup>3</sup> Indeed such hot pure rotational and bending mode spectra had already been recorded (but largely unassigned) using a methane–oxygen flame.<sup>85</sup> By using the unadjusted *ab initio* potential of Partridge and Schwenke and six-dimensional variational calculations of the energy levels Polyansky *et al.* were able to assign most of the strong lines.<sup>8</sup> The assignment method relies on the smooth variation of errors and confirmation of tentative assignments by combination differences.<sup>8,40</sup>

The most recent infrared spectra of room temperature water vapour are due largely to Toth,<sup>84,86–90</sup> who built on the earlier work of Flaud and co-workers.<sup>91</sup> The Giessen group also recorded a new spectrum in the 2500–4500  $\text{cm}^{-1}$  region and used the generating function method of Tyuterev to fit their data.<sup>92</sup>

The greatest progress on the infrared spectrum of water was made with the interpretation of new hot water emission spectra. At Waterloo emission spectra covering 400–6000  $\text{cm}^{-1}$  were recorded with the water at about 1500 °C.<sup>93–95</sup> The pioneering spectra of hot water were recorded some 25 years ago by Maillard and co-workers using an oxy-acetylene torch in the 2800–9100  $\text{cm}^{-1}$  region.<sup>96,97</sup> Some more limited hot absorption spectra are also now available.<sup>98,99</sup> Lanquetin and co-workers<sup>100,101</sup> also have recently analysed their new hot emission spectra of a low pressure methane-oxygen flame. In this work, Coudert extended his 4-dimensional bending-rotation Hamiltonian<sup>32,102–104</sup> to fit the 100 and 001 stretching levels and the 020 bending overtone. The Waterloo spectra are largely responsible for the dramatic increase in the number of known vibration–rotation energy levels, particularly for high  $J$  and high  $K_a$ . Line intensities, however, are best derived from absorption spectra of hot samples and much work remains.

Another complementary approach for locating highly-excited water energy levels is the study of overtone spectra. Overtone spectra of water favour low rotational levels of mainly stretching modes. Because high overtone spectra are so weak, a number of new highly sensitive laser techniques have been applied. Intracavity laser absorption spectroscopy is capable of yielding both line positions and intensities,<sup>105,106</sup> but care with calibration is needed. Antipov *et al.*<sup>107</sup> measured the optoacoustic spectrum of water near 590 nm with a dye laser. Naus *et al.*<sup>108</sup> have applied cavity ringdown spectroscopy to water vapour in the 555–604 nm region. Wong and Hall<sup>109</sup> have demonstrated near-shot-noise-limited frequency modulation spectroscopy near 16 940  $\text{cm}^{-1}$  with a dye laser. Two tone frequency modulation<sup>110</sup> of a GaAlAs diode laser near 12 240  $\text{cm}^{-1}$  was also successful. These laser-based techniques generally offer superb sensitivity but suffer from the disadvantage of relatively narrow spectral coverage. One interesting laser-based technique that may offer wider coverage is the detection of faint laser-induced vibration–rotation “fluorescence” with a Fourier transform spectrometer.<sup>111</sup>

The main progress, however, in overtone spectroscopy of water has been made with long path absorption cells coupled with high resolution Fourier transform spectrometers. Broad spectral coverage, reliable line positions and intensities are achieved at the expense of somewhat reduced sensitivity as compared to a cavity ringdown experiment.<sup>108</sup> By using a White-type multiple reflection cell with a base path of 50 m, improved visible<sup>112</sup> and near ultraviolet<sup>113</sup> spectra of water were recorded. About 20 new vibrational levels were located and the number of lines were nearly tripled over the previous

work. In the near infrared region several groups have made similar measurements of the water overtones.<sup>114–120</sup>

The great flurry of experimental work has led to a doubling of the number of known vibration–rotation energy levels of water (12 248 energy levels) tabulated in the recent paper of Tennyson *et al.*<sup>14</sup> Some 101 vibrational band origins are now known<sup>14</sup> of the  $\sim 1000$  supported by the ground state potential. The highest excited vibrational level is 80<sup>0</sup> (701 in normal mode notation) at 25 120  $\text{cm}^{-1}$ , more than halfway to the dissociation limit<sup>72</sup> of 41 151  $\text{cm}^{-1}$ . For the 000 vibrational level the 33<sub>33,0</sub> rotational state has 21 105  $\text{cm}^{-1}$  of rotational energy.<sup>14</sup> Highly-excited bending levels are much more difficult to locate because bending overtones are weak relative to the stretches. Note that a few high vibration–rotation levels of the 070, 080 and 0100 pure bending states have been tentatively assigned through their perturbations.<sup>121</sup> Clearly, more highly-excited vibration–rotation levels need to be found. One interesting possibility is to use an infrared water laser based on the recombination of  $\text{H}_3\text{O}^+$  with electrons for this purpose.<sup>122</sup>

The interpretation of the new experimental data depends heavily on the use of non-traditional methods of analysis. To some extent, the particular scheme used to represent the vibration–rotation energy levels is a matter of taste but the variational 6-dimensional approach is very powerful and generally applicable.

#### 4. Applications in astronomy

The main problem with the astronomical spectroscopy of water is the massive blanket of telluric water vapor. Atmospheric absorption has largely blocked the detection of cool water from the ground. Historically, three types of ground-based water observations are possible: masers, isotopomers and “steam bands”. Maser transitions between highly-excited levels (*e.g.*, 6<sub>16</sub>  $\rightarrow$  5<sub>23</sub> at 22 GHz) can be detected by radio techniques.<sup>123</sup> Water masers are typically seen in mass-losing, late-type stars and are often associated with star formation.<sup>124</sup> While kinematics can be readily extracted from maser data, the determination of abundances is extremely difficult. The non-masing  $\text{H}_2^{18}\text{O}$ <sup>125</sup> and HDO<sup>126</sup> isotopomers can also be detected by submillimetre radio techniques, but strong chemical isotope fractionation makes the inference of normal water abundances difficult.

Water is a light molecule with large rotational constants so that transitions between highly-excited levels are often shifted away from transitions between lower energy levels. This means that rotational and vibration–rotation transitions associated with hot water can penetrate the Earth’s atmosphere. (Note that the vacuum ultraviolet spectra of diffuse interstellar clouds recorded with the Copernicus satellite using bright stars as light sources has yielded upper limits for water column densities based on electronic transitions.)<sup>127,128</sup> The overtone spectra of hot water vapour (“steam bands”) can be detected in many cool stars. For example, Spinrad *et al.*<sup>129</sup> found the stellar water band at 928 nm to be strong in M-type stars, particularly Mira variables.<sup>130</sup>

M-type stars are the coolest kind of normal oxygen-rich stars (*i.e.*,  $[\text{O}]/[\text{C}] > 1$ ) and have surface temperatures in the range of 3500 K to about 2000 K. Stars are classified in a “two-dimensional” scheme based on surface temperature, *i.e.*, black body “colour” designated by letters (*e.g.*, M for coolest, oxygen-rich stars) and on size (or more correctly luminosity) as dwarfs, giants and supergiants. M-type stars are classified by the presence of the metal oxides TiO and VO in the near infrared spectra.<sup>131</sup> Mira variables are red giant stars whose luminosity varies with an irregular period of about a year.<sup>131</sup> Water can also be seen in non-Mira M-giants and supergiants such as  $\alpha$ -Ori (Betelgeuse) and  $\alpha$ -Sco (Antares).<sup>132</sup>

The original identifications<sup>133</sup> were based on the balloon-borne Stratosphere II observations of 1.4  $\mu\text{m}$  and 1.9  $\mu\text{m}$  water bands in 1964. Water is relatively weak in these sources but can also be seen near 13  $\mu\text{m}$  through pure rotational transitions,<sup>132</sup> particularly in oxygen-rich circumstellar outflows.<sup>134,135</sup> The water is not found in the photospheres of the M-supergiants but in a circumstellar cloud ( $T \sim 1500$  K, *c.f.* “cool” layer in Miras)<sup>130</sup> dubbed the “MOLsphere” by Tsuji.<sup>136,137</sup> The pure rotational water lines in the far infrared spectra ( $\sim 40$   $\mu\text{m}$ ) of  $\mu$ -Cep recorded by the Infrared Space Observatory (ISO) satellite<sup>138</sup> appear in emission.<sup>136</sup>

The solution to the telluric water interference problem is to record spectra from satellites. The ISO satellite<sup>138</sup> has found water in a large number of sources including star-forming regions such as Orion.<sup>139</sup> Very recently, the first data from the Submillimeter Wave Astronomy Satellite<sup>140</sup> (SWAS) has been published. SWAS can detect water using the low-lying  $1_{10}-1_{01}$  transition at 557 GHz. SWAS found<sup>141</sup> rather low gas-phase water abundances in cold dark molecular clouds but elevated abundances were found in warm regions around young stars or in hot shocked regions (*e.g.*, in the Orion nebula).

Water is also present in the photosphere of M-dwarf stars.<sup>142,143</sup> As the surface temperature of the dwarf drops below about 2000 K, hydrogen burning in the core is no longer possible and the objects are called brown dwarfs. There are two types of brown dwarfs, L and T, both of which show prominent water bands.<sup>143</sup> In the temperature range of about 1200–1800 K, the L dwarfs have strong FeH and CrH bands<sup>143,144</sup> but with weak TiO bands. As the temperature drops even lower the metal hydrides disappear and the near infrared spectra of T dwarfs (“methane brown dwarf”) are dominated by hot water and hot methane.<sup>145</sup> At the end of this series (M, L and T) are giant planets similar to Jupiter, which is known to contain water.<sup>146</sup>

An important advance in the spectroscopy of hot water occurred as a result of the detection of water vapor in sunspots. At 5800 K, the Sun’s photosphere is too hot for water to exist. Temperatures as low as  $\sim 3000$  K, however, are found in sunspots. We noticed a large number of unassigned lines in two sunspot atlases prepared by Wallace *et al.*<sup>147</sup> It was suspected that these lines were due to hot water but the available laboratory data were inadequate to confirm this. We, therefore, recorded new laboratory emission spectra of hot water at 1800 K in the infrared region. Comparison of the laboratory emission spectra of  $\text{H}_2\text{O}$  and the sunspot absorption spectra identified most of the unassigned sunspot lines<sup>3</sup> as  $\text{H}_2\text{O}$  lines.

Only a small fraction of the new water lines could be assigned quantum numbers. It is the anomalous centrifugal distortion that makes the assignment of quantum numbers very difficult in the dense spectra. We began a collaboration with the theoreticians Polyansky and Tennyson to apply more sophisticated approaches to the problem.<sup>8</sup>

The hot water lines in the laboratory and in the sunspot have been assigned by direct calculation of the infrared spectra starting with the *ab initio* Partridge and Schwenke<sup>48</sup> potential energy surface. So far we have recorded laboratory emission spectra in 400–6000  $\text{cm}^{-1}$  region<sup>93–95</sup> and made assignments in the sunspot spectrum in the N band (10–13  $\mu\text{m}$ )<sup>93</sup> as well as the L band (3–4  $\mu\text{m}$ )<sup>95</sup> and the K-band (2.0–2.3  $\mu\text{m}$ ).<sup>94,148</sup> An important application of hot water work is the calculation of molecular water opacities<sup>149</sup> for various cool objects. Reliable potential and dipole surfaces are needed to compute millions of transitions to reproduce the low resolution infrared spectra of M-type stars and brown dwarfs.<sup>58,59,149,150</sup>

In addition to our Sun, water vapour has been identified in many other objects in our solar system including Venus,<sup>151</sup> Mars,<sup>152</sup> the giant planets,<sup>146</sup> and notably in comets.<sup>153,154</sup> Comets are “icy snowballs” that are believed to be remnants of the primordial solar nebula. Infrared<sup>153</sup> and millimetre

wave<sup>154</sup> emission spectra of water are observed when the ice is vaporized by solar radiation. Water was discovered<sup>155</sup> by SWAS in a carbon-rich circumstellar cloud of dust and molecules around an old star called IRC +10216. Because water vapour should not be present in such an object, it was speculated that the water originated from the vaporization of a cloud of comets surrounding the star.<sup>155</sup>

## 5. Applications in atmospheric science

Water vapour is crucial for the energy balance of the earth.<sup>2</sup> Not only is it the most important absorber of out-going thermal radiation (greenhouse gas) but water is responsible for about 70% of the atmospheric absorption of in-coming solar radiation.<sup>156</sup> There is a major problem in our understanding of this balance because the calculated average atmospheric absorption is about 25% ( $25 \text{ W m}^{-2}$ ) less than observed.<sup>156,157</sup> Water is the obvious suspect for this “missing absorber.” In atmospheric science the line parameters that are collected together in the HITRAN<sup>158</sup> and GEISA<sup>159</sup> databases are widely used for the computation of atmospheric transmission. It has been suggested that errors in the water line intensities,<sup>160,161</sup> missing weak water lines,<sup>162</sup> water dimers,<sup>163</sup> water continuum<sup>164</sup> and clouds<sup>165</sup> are all possible contributors to the missing absorber problem. Several groups are re-measuring, extending and improving the water line parameters<sup>114–116,166</sup> in the near infrared, visible and near UV. Interestingly, Mlawer *et al.*<sup>167</sup> claim that there is no missing molecular absorber but that aerosol scattering is not quite correct in the atmospheric transmission models (see also Lubin *et al.*).<sup>168</sup>

The calculation of atmospheric transmission requires more than just line positions and intensities. Nearly as important are the pressure broadening coefficients due to air, self-broadening coefficients, air-induced line shift parameters and the temperature dependence of the air-broadening parameters. The temperature dependence of the absorption line intensities can be deduced from the known lower state energies and a reliable partition function. Although much data on water has been accumulated, the situation is still far from satisfactory and a number of groups are working on the problem.<sup>114–116,166,169,170</sup> This type of measurement is plagued by systematic errors so that large numbers of carefully recorded and analysed spectra by different groups are required.

One of the major experimental and theoretical problems in the atmospheric spectroscopy of water is the “continuum.” When atmospheric infrared spectra are simulated by a collection of lines that are each represented by a Voigt lineshape function (the convolution of a Gaussian from Doppler broadening and a Lorentzian from pressure broadening<sup>10</sup>) the results are in poor agreement with long path observations. The discrepancies are attributed to an underlying unstructured water continuum absorption.<sup>171–173</sup> It is generally (although not universally<sup>174</sup>) accepted that the continuum is due to the failure of all commonly used lineshape functions in the far wing region. The far wing region is often somewhat arbitrarily defined as more than 25  $\text{cm}^{-1}$  from line centre.<sup>175,176</sup> Clough, Kneizys and Davis<sup>176</sup> (“CKD”) have devised a widely-used semi-empirical lineshape function for water that has been adjusted to give reasonable agreement with laboratory experiments and atmospheric observation. The summation of the far wing lineshape contributions of all of the lines then produces the continuum. There are two contributions to this continuum—a self-broadened (“wet”) part due to water–water collisions and a water-foreign gas (“dry”) part due to water-air collisions.

Tipping and Ma<sup>175,177</sup> have developed a collision theory to account for the water continuum and their model is in good agreement with the available data. Better experimental data are required, however, and work is in progress, for example, using cavity ringdown techniques.<sup>178</sup>

The atmosphere is opaque over most of the far infrared region mainly because of water absorption lines.<sup>179</sup> A good part of this far infrared opacity is due to the water continuum which has an empirical  $\nu^2$  frequency dependence.<sup>179,180</sup> Pardo *et al.*<sup>180</sup> were able to determine both the wet and dry water continuum up to 1100 GHz from Fourier transform measurements with the Caltech Submillimeter Observatory on Mauna Kea, Hawaii. The pure rotational water line parameters are available from HITRAN,<sup>158</sup> GEISA,<sup>159</sup> the JPL catalog<sup>181</sup> and the Smithsonian Astrophysical Observatory linelist.<sup>182</sup>

In the infrared region, atmospheric transmission spectra using the Sun as a source are recorded routinely at many sites using high resolution Fourier transform spectrometers as part of the Network for the Detection of Stratospheric Change (NDSC).<sup>183</sup> Needless to say these spectra are dominated by water absorption even for high, dry sites. For global coverage, measurements using the Sun as a source (solar occultation) have also been made from orbit using the ATMOS instrument on the Space Shuttle.<sup>184,185</sup> Thermal emission measurements are possible looking downwards<sup>186,187</sup> (nadir) or at the limb of the earth.<sup>187,188</sup>

Long path measurement of atmospheric water can be made with diode lasers in the mid and near infrared<sup>189</sup> and these systems find application as humidity sensors.<sup>190</sup> Fourier transform spectrometers can record broadband spectra using infrared glowers as sources.<sup>191</sup> The interpretation of all atmospheric water spectra is critically dependent on the line parameters, which are not yet satisfactory particularly in the 3 micron stretching region.

Water overtones in the near infrared, visible and even near UV region appear in solar spectra recorded from the ground.<sup>7</sup> For example, Harder and Braut<sup>192</sup> measured water lines at 442 nm with a Fourier transform spectrometer during sunset at Kitt Peak. Similar measurements were made near 900 nm by Smith and Newnham<sup>193</sup> to test the various sets of atmospheric line parameters currently available in the near infrared. A new set of water line parameters is also available for the visible and near UV.<sup>166</sup>

Global coverage of water vapour columns and vertical profiles are best made with satellite instruments. These humidity data are crucial inputs to weather forecast models. Weather sounders (*e.g.*, TOVS<sup>194</sup>) typically monitor the up-welling radiance as measured through infrared bandpass filters as well as with microwave emission channels. Water vapour selectively absorbs the thermal emission of the earth. The filters and microwave channels are carefully chosen to select a specific set of water lines in order to probe different parts of the atmosphere. For example, the high J lines in the wings of the  $\nu_2$  band can sense water in the warmer, lower part of the troposphere. Combining microwave and infrared data improves the humidity profiles (modelled as 3 to 5 layers, typically) because microwave radiances are much less affected by clouds which block infrared radiation.<sup>194</sup> A new generation of sounders such as IASI (Infrared Atmospheric Sounding Interferometer) will improve the vertical resolution and the accuracy by recording higher resolution ( $0.5\text{ cm}^{-1}$ ) nadir-looking spectra.<sup>195</sup>

Recently, the Global Ozone Monitoring Experiment (GOME),<sup>196</sup> a set of four low resolution UV-visible spectrographs on the ERS-2 satellite, has been able to provide global water columns using water overtones near 700 nm.<sup>197</sup> GOME measures backscattered sunlight from the Earth and the water bands appear in absorption.<sup>196</sup>

## 6. Applications in combustion science

The combustion of hydrocarbon fuels leads primarily to the production of hot water and hot carbon dioxide. Infrared spectra of flames were first recorded in the 1890's by Julius and by

Paschen, and they clearly show "steam" bands.<sup>198</sup> The early French work on the highly-excited energy levels of water was carried out by recording the infrared emission spectrum of an oxyacetylene torch with a Fourier transform spectrometer.<sup>96,97</sup> Although such an atmospheric pressure flame is both bright and hot (nearly 3000 K), the lines show pressure-broadened widths of typically  $0.1\text{ cm}^{-1}$ . Narrower lines can be obtained by operating the flames at reduced pressure.<sup>101</sup>

The observation, however, of hot water produced by combustion is rarely carried out for purely spectroscopic purposes. Most work has a more practical goal of monitoring, detecting or understanding the combustion process. For example, Worden *et al.*<sup>199</sup> used a high resolution Fourier transform spectrometer on an aircraft to record spectra of forest fires. Some hot water lines appeared in emission and they were identified by comparison with the sunspot absorption spectrum.<sup>3</sup> Rocket plumes also contain prominent hot water signatures in the infrared.<sup>200</sup> Fourier transform spectroscopy has been used to monitor jet engine exhaust both on the ground<sup>201</sup> and in flight.<sup>202</sup>

The latest in spectroscopic techniques have been used to detect hot water in combustion environments. Cheville and Grischowsky<sup>70,71</sup> measured hot water lines in a propane-air flame by terahertz time-domain spectroscopy. Tunable diode laser absorption spectroscopy can be used on water in cylindrically-symmetric flames to deduce concentration and temperature *via* tomographic techniques.<sup>203</sup> Two-colour, laser-induced grating spectroscopy<sup>204</sup> (related to degenerate four wave mixing) on the third stretching overtone near 717 nm was used to obtain a line image of water in a methane-air flame. Coherent anti-stokes Raman spectroscopy (CARS) can detect water in a rocket plume.<sup>205</sup> Finally, Xie *et al.*<sup>206</sup> were able to obtain cavity ringdown spectra of water near 815 nm produced in a propane-air torch and a methane-air flat burner.

## 7. The future

Progress on the spectroscopy of water has been remarkable in the past 5 years. The use of new experimental techniques such as cavity ringdown spectroscopy with, for example, hot sources could lead to another doubling of the number of known energy levels. These methods can be extended further into the UV to detect the  $9\nu_{\text{O-H}}$  and  $10\nu_{\text{O-H}}$  overtone levels. The ultimate goal of measuring vibration-rotation levels up to the dissociation limit does not seem so distant now. On the theoretical front, extensive variational calculations that include non-adiabatic, relativistic and even Lamb-shift corrections are now possible over the entire ground state potential surface. The variational calculation of energy levels has revolutionized and revived the interpretation of water spectra. With only a little tweaking, calculations of line positions and intensities of nearly spectroscopic accuracy up to the dissociation limit are now feasible.

### Note added in proof

B. Ruscic *et al.*<sup>207</sup> recommend the value of  $41\,128 \pm 24\text{ cm}^{-1}$  for the dissociation energy  $D_0(\text{H-OH})$  of water.

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