

A high-accuracy computed water line list

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ABSTRACT

A computed list of H₂¹⁶O infrared transition frequencies and intensities is presented. The list, BT2, was produced using a discrete variable representation two-step approach for solving the rotation–vibration nuclear motions. It is the most complete water line list in existence, comprising over 500 million transitions (65 per cent more than any other list) and it is also the most accurate (over 90 per cent of all known experimental energy levels are within 0.3 cm^{−1} of the BT2 values). Its accuracy has been confirmed by extensive testing against astronomical and laboratory data.

The line list has been used to identify individual water lines in a variety of objects including comets, sunspots, a brown dwarf and the nova-like object V838 Mon. Comparison of the observed intensities with those generated by BT2 enables water abundances and temperatures to be derived for these objects. The line list can also be used to provide an opacity for models of the atmospheres of M dwarf stars and assign previously unknown water lines in laboratory spectra.

Key words: line: identification – molecular data – radiation mechanisms: general – comets: general – stars: low-mass, brown dwarfs – infrared: general.

1 INTRODUCTION

Water is the most abundant molecule in the Universe after H₂ and CO. It is present in many astrophysical environments including the atmospheres of M dwarfs (Allard et al. 1994), brown dwarfs (Allard et al. 1996), K and M giants and supergiants (Jennings & Sada 1998; Tsuji 2001; Ryde et al. 2002) and oxygen-rich asymptotic giant branch stars (Barlow et al. 1996). It occurs in sunspots (Wallace & Livingston 1992; Polyansky et al. 1997), nova outflows (Banerjee et al. 2005), Mira variables (Hinkle & Barnes 1979), T Tauri eruptive variables (Shiba et al. 1993), dark molecular clouds (Gensheimer, Mauersberger & Wilson 1996), young stellar objects (Carr, Tokunaga & Najita 2004), comets (Mumma et al. 1996; Dello Russo et al. 2000), the interstellar medium (Cernicharo et al. 1994), masers (Cheung et al. 1969; González-Alfonso et al. 1995) and planetary atmospheres. An accurate water line list is thus essential for interpreting spectra from all of these sources and in modelling stellar atmospheres at temperatures up to 4000 K.

The importance of water has given rise to many laboratory investigations of its spectrum. Ludvig (1971), Camy-Peyret et al. (1977) and Bernath (1996) all investigated hot water line positions. However, technical problems and the huge number of transitions (many of which appear blended) mean that only in the region of 80 000 (out of a total of more than a billion) transitions are known experi-

mentally and there are few hot water lines for which intensities have been determined.

The spectrum of water, which extends over a wide wavelength range from millimetre to near-ultraviolet, is due to quantized changes in the rotation–vibration energy of the atomic nuclei moving in the electronic potential well. Essentially, the water molecule is only able to absorb or emit in its ground electronic state as the energy of the first stable excited electronic state is above the dissociation energy. In practice, some emissions do occur from short-lived excited electronic states. The possibility of detecting vacuum ultraviolet water absorption lines in diffuse interstellar clouds has been considered by Smith et al. (1981), and they provide wavelengths, oscillator strengths and detection limits.

Water is a triatomic asymmetric top molecule. Its rotation–vibration spectrum is more complicated than those of most other triatomic molecules. In common with all non-linear triatomic molecules, H₂O has six degrees of internal freedom (three of rotation and three of vibration). However, the lightness of the hydrogen atoms means that the rotation constants are large, and this gives rise to an open spectrum that extends over a wide frequency range. Moreover, the ‘floppy’ nature of the molecule means that the movement of the hydrogen atoms is generally anharmonic and consequently transitions involving changes of more than one vibrational quantum number often occur. Also, since many of the vibrational frequencies are nearly resonant with other frequencies, it is common for vibrational bands to overlap and for states to interact in ways that cannot easily be predicted by perturbation theory but are amenable to a variational approach.

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The importance of the H₂O molecule in astronomy and the complexity of its spectrum have created a great deal of interest in the possibility of generating the spectrum synthetically. Previous synthetic line lists include: MT (Miller et al. 1994), VT1 (Viti, Tennyson & Polyansky 1997), VT2 (Viti 1997), PS, otherwise called AMES (Partridge & Schwenke 1997), and SCAN (Jørgensen et al. 2001). All previous synthetic line lists have suffered from a number of problems that are discussed below. The most successful attempts have employed similar variational nuclear motion procedures to that used in producing the BT2 water line list. However, for reasons detailed in the next section, none of the earlier lists is considered to be satisfactory. We have addressed these problems and consequently the BT2 line list is an accurate tool for astronomers working in a variety of fields.

2 BACKGROUND TO THE CALCULATIONS

2.1 Variational techniques

Variational techniques represent the best approach to solving the nuclear motion problem (Tennyson 1992), and they are examined in detail in Bačić & Light (1989). Here we use a discrete variable representation (DVR).

In a DVR, the wavefunctions are defined by a complete set of weighted, orthogonal grid points, each wavefunction having a different set of weightings. This method is capable of generating accurate solutions, the accuracy being determined by the number and appropriateness of the points. It is efficient for a large number of situations. The DVR approach has the advantage that the potential matrix elements are diagonal, and hence are easily evaluated. Even more important is the fact that the dipoles can be reduced to a similar form (Tennyson et al. 2004).

The current work is not unique in employing a DVR approach to solve the nuclear motion problem for water (see e.g. Viti et al. 1997). However, improved physics, in the form of a highly accurate potential energy surface (PES), the methodology embodied in the DVR3D program suite and increases in computational power have made it possible to produce a line list that is more complete and more accurate than any previous list, even those employing similar methodologies.

The DVR3D approach generates four rotation–vibration symmetry blocks for the H₂O molecule, which we label ee, eo, oe and oo. The first e/o term is the vibrational basis symmetry ‘*q*’ and the second, e/o is the standard quantum number ‘*p*’, the rotational parity. These symmetry blocks are not the same as the C_{2v}(M) symmetry blocks Γ_{rv} : A₁, A₂, B₁, B₂, but are related to them (see standard texts on molecular spectroscopy, such as Bunker & Jensen 2005).

The nuclear permutation operation in which the two identical protons comprising the hydrogen nuclei are interchanged gives rise to two non-degenerate states of the molecule: ortho (O) and para (P). The nuclear spins may couple symmetrically or antisymmetrically. The antisymmetric coupling that gives rise to the O form of the H₂O molecule is triply degenerate, whilst the symmetric coupling, which gives rise to the P form of the molecule, is non-degenerate.

For any *J*, apart from *J* = 0, there are two ortho and two para symmetry blocks (in the case of *J* = 0 there is one O and one P block). There are two possible arrangements, depending on whether *J* is odd or even and these are detailed in Table 1.

The difference in degeneracies of the O and P states impacts on the partition function of the molecule as well as on line intensity. Also,

Table 1. Symmetry blocks.

	<i>J</i> even				<i>J</i> odd			
<i>q</i>	e	e	o	o	e	e	o	o
<i>p</i>	e	o	e	o	e	o	e	o
O/P	P	O	O	P	O	P	P	O
Code	1	3	4	2	3	1	2	4

q is the vibrational basis symmetry and *p* is the rotational parity. These are labelled as either symmetric (e), or antisymmetric (o) states. O/P = ortho/para. The ‘Code’ is the notation for symmetry used in the Levels File (Table 2).

the fact that O–P and P–O transitions are forbidden has spectroscopic consequences.

2.2 PES and the energy levels

The energies of the quantized rotation–vibration states are the eigenvalue solutions that satisfy the Schrödinger equation for the oxygen and two hydrogen nuclei moving within the electronic potential. However, the electronic potential within which the charged nuclei are moving is itself a function of the actual internuclear geometry. Therefore, in order to solve for the nuclear motion, it is necessary to have an accurate model of how the potential varies with the nuclear geometry. The problem is rendered tractable by adopting the Born–Oppenheimer approximation which separates the nuclear and electronic motions and has as its basis the fact that, due to their lightness, the electrons may be considered to react immediately to any changes in the nuclear geometry. The most accurate PESs are computed using an *ab initio* starting point, with the resulting surface being empirically adjusted to improve the agreement between the computed energies and experimental data (Partridge & Schwenke 1997).

We used the PES fit B of Shirin et al. (2003), which is based on a highly accurate *ab initio* surface with adjustments for electronic relativistic and adiabatic (also known as the Born–Oppenheimer diagonal correction) effects and fitted to the available experimental data. At the time of writing, this surface is the most accurate available and it is the single most important factor affecting the accuracy of our results.

Non-adiabatic corrections to the Born–Oppenheimer approximation are also important in the case of water (Schwenke 2003). However, a full theoretical non-adiabatic adjustment to the PES has been shown to produce no significant benefits compared to simplified approaches (Tennyson et al. 2002). These authors examine two such approaches: using separate reduced masses for the vibrational and rotational motions (this systematically overcorrects bending motions and undercorrects stretches), and a simplified version of the full correction which includes only terms that scale with the kinetic energy terms in θ and r . The latter approach is preferred and the adjustment is effected through the DVR3D program rather than changes to the PES.

2.3 Transition intensities

The intensities of the allowed transitions between rotation–vibration states are determined by the dipole transition moments for these pairs of states, $\langle \psi' | \bar{\mu} | \psi'' \rangle$, where ψ' and ψ'' are the wavefunctions of the two states, and $\bar{\mu}$ is the electronic dipole moment vector. Therefore, in order to calculate intensities, a dipole moment surface (DMS) is required.

The line strength, S_{if} of transitions between states i and f having angular momenta J' and J'' , respectively is

$$S_{if} = (2J' + 1)(2J'' + 1)|\langle \psi' | \bar{\mu} | \psi'' \rangle|^2. \quad (1)$$

Line strength is independent of temperature. In the SI system it has units of (C m)².

The parameter computed by the DVR3D program suite is the Einstein A coefficient, A_{if} , for each transition. This is the coefficient of spontaneous emission between the upper and lower states. It is related to the dipole transition moment for the pair of states and to J for the upper state. A_{if} is independent of temperature, relates to a single molecule, has units of s⁻¹ and in SI units (Bernath 2005), is given by

$$A_{if} = \frac{16\pi^3}{3\epsilon_0 c^3 h} \nu^3 \frac{S_{if}}{(2J' + 1)}. \quad (2)$$

The quantity usually derived from observation is the line intensity, I , which has units of cm molecule⁻¹. I is temperature dependent and in emission is related to A_{if} by the expression

$$I = \frac{C g_i (2J' + 1)}{Q_{\text{vm}}(T) \nu^2} \exp\left(\frac{-hcE''}{kT}\right) \left[1 - \exp\left(\frac{-hc\nu}{kT}\right)\right] A_{if}, \quad (3)$$

where ν is the frequency in cm⁻¹, E'' is the energy of the lower rotational–vibrational level in cm⁻¹. $Q_{\text{vm}}(T)$ is the internal electronic ground-state partition function and is dimensionless, and g_i is the nuclear spin degeneracy and carries only one subscript since transitions between different nuclear spin states are not allowed (Miani & Tennyson 2004). Boltzmann constant, k , has units of J K⁻¹ and the constant C has the value $(8\pi c)^{-1} = 1.3271 \times 10^{-12}$ s cm⁻¹.

Since the BT2 line list includes A_{if} for each transition, the above equation enables the line intensities to be computed at any given temperature.

Unlike the PES, where the most accurate are *ab initio* surfaces that have been fitted to the available experimental data, in the case of DMS, limitations on the accuracy of experimental line strengths means that at the current time the most accurate surfaces are purely *ab initio* (Lynas-Gray, Miller & Tennyson 1995). Two such DMS were tested in the intensity part of our calculations. Our initial BT1 line list was computed using the same PES as BT2 and a preliminary DMS of Lynas-Gray et al. (in preparation). The line positions in BT1 are identical to those in BT2 (the same PES having been used for both). However, we observed that the Einstein A coefficients of the weaker lines generated using the DMS of Lynas-Gray et al. were often too large when compared with experiment. This part of the computation was therefore repeated using the DMS of Schwenke & Partridge (2000). The results, which are contained in BT2, show much better agreement between the computed strengths of weak lines and experiment. The Einstein A coefficients of the stronger lines in BT1 and BT2 generally agree to within 2 per cent and both agree reasonably well with experimental values. In addition to being superior to the surface of Lynas-Gray et al. that we tested, the DMS of Schwenke and Partridge (2000) represents a major improvement on the earlier DMS of Partridge & Schwenke (1997) and from our analysis, as well from the same authors, is the most accurate in existence.

3 CALCULATING THE LINE LIST

The BT1 and BT2 line lists were computed using the DVR3D suite of programs (Tennyson et al. 2004) on three Sun 5 Microsystem V880 mainframe computers: Enigma and Ra which are clustered

using high-speed interconnections, each having eight processors and 32 GB of RAM and 432 GB of disk storage and PSE, which has 24 processors and 96 GB of RAM and 1296 GB of disk storage at UCL Hiperspace computing centre. The final ‘DIPOLE’ stage of the suite was amenable to parallelization with little time penalty. Other parts of the program were run on single processors, which avoided coding problems and was more efficient in computer time. The total number of processor hours employed in generating the BT1 line list (including the preliminary convergence testing which is discussed below) was 55 000 h and a further 10 000 h were used in repeating the ‘DIPOLE’ runs to generate BT2 and in testing the outputs.

DVR3D calculates the bound rotation–vibration energy levels, the wavefunctions on a grid in three dimensional space, and the dipole transition strengths of the allowed transitions. The final part of the DVR3D suite, ‘SPECTRA’ is able to compute temperature-dependent spectra over any selected frequency range, convolved with either the natural linewidth or some other selected profile, such as that given by the resolving power of a particular spectrometer. DVR3D uses an exact (within the Born–Oppenheimer approximation) kinetic energy operator. The program uses a DVR with two radial and one angular coordinate for the nuclear motion problem (vibrational and rotational motions being treated separately).

In establishing the working parameters for our calculations, we aimed to provide a line list that would be complete and accurate at the temperatures of late series K-series stars (up to 4000 K) and at wavelengths down to 0.8 μm . Preliminary calculations showed that in order to achieve this it would be necessary to include all states lying at energies up to 30 000 cm⁻¹ relative to the ground state of the system. Previous workers (Miller et al. 1994; Partridge & Schwenke 1997) selected lower energy cut-offs.

Our cut-off for the total angular momentum was $J = 50$. We calculate that the highest value of J which has rotational–vibrational energies of less than 30 000 cm⁻¹ is 58. However, we also estimate that by terminating our calculation at $J = 50$ we omit less than 500 levels out of a total of more than 505 million and none of the omitted levels has an energy less than 23 490 cm⁻¹, with the majority being at energies above 28 000 cm⁻¹. Consequently, even at a temperature of 4000 K these missing levels contribute less than 0.02 per cent of the total partition function. Moreover, by omitting J values above 50 we saved in the region of 8000 processor hours.

In order to generate accurate eigenvalues, it is essential that all calculations are fully converged within the limitations imposed by computing power and time. The lack of convergence in earlier lists has already been noted (Polyansky et al. 1997).

DVR3D has the option of using Jacobi or Radau coordinates. The latter was selected as being more appropriate for water. Our Radau grid is defined in terms of two radial coordinates, r_1 and r_2 , each with 28 points, and one angular coordinate, θ having 44 points. These numbers are determined by convergence testing at $J = 20$. The eigenvalue solutions are particularly sensitive to the number of radial points, r_n . However, the computation time rises very rapidly as this number is increased, so the selection of r_n represents a compromise and is the principal factor impacting on convergence.

The angular grid points are arrived at using associated Legendre polynomials for the underlying basis sets, whilst the radial grid points are set up using Morse oscillator-like underlying basis sets, which are defined in terms of parameters, r_e , ω_e and D_e . These must be entered into ‘DVR3DRJZ’, the first module of the DVR suite. The parameters have physical counterparts which are, respectively, the equilibrium bond length, harmonic frequency and dissociation energy of the water molecule. However, the parameters

in the Morse oscillator function differ from the physical values and must be determined by empirical testing.

Although in principle DVR3D is not strictly a variational method, in practice it is found that the variational principle does apply; this fact is employed in obtaining values for r_e , ω_e and D_e . The method is to alter the three parameters in a systematic manner until DVR3DRZ generates a set of pure vibrational states (the $J = 0$, para states), the sum of whose energies is a minimum (251 eigenvalues were employed). We conducted this part of the process manually.

The investigation was complicated by the existence of local minima, which are not global minima for the three variables. The set of parameters giving this result was: $r_e = 2.05$, $\omega_e = 0.008$ and $D_e = 0.20$ all in atomic units (the equivalent dissociation energy is $43\,895\text{ cm}^{-1}$). A good choice of these parameters (which are a function of the system and of the particular energy range that is of interest) is fundamental to the accuracy of the ensuing calculations. The eigenvalues are particularly sensitive to r_e and ω_e and it was observed that differences of as little as 0.05 in the first of these two parameters and 0.002 in the second could affect the energy levels by in the region of 0.01 cm^{-1} for states with energies in the region of $10\,000\text{ cm}^{-1}$. Larger deviations in these basis functions from their determined optimum values produced correspondingly greater errors and in the case of states with energies over $20\,000\text{ cm}^{-1}$, a bad choice of parameters could easily result errors in the individual levels in excess of 20 cm^{-1} . Consequently, considerable time was spent in determining the values of the Morse oscillator-like basis set.

Two other inputs are required by the vibrational module, DVR3DRZ. These are the maximum size of the intermediate Hamiltonian, which we chose after testing as 2500 and the number of eigenvectors to be saved for use in the rotational module, 'ROTLEV3B', the optimum value for which was found by testing to be 700.

ROTLEV3B also requires one variable to be determined; this is IBASS, the size of the Hamiltonian in the rotation module. IBASS varies with J . Its value was established by convergence testing at $J = 20$ as being $530 \times (J + 1 - p)$, where p is the rotational parity and has the value 0 for even-parity states and 1 for odd-parity states. Hamiltonians of this size are expensive in terms of computing time at high J values. Nevertheless, it was easy to demonstrate that lower values of IBASS produce results that are not converged. This is significant, as earlier workers using similar DVR techniques have used lower IBASS values. Viti et al. (1997), for example, used $200 \times (J + 1 - p)$, and PS used an even lower effective number, particularly at high J .

In selecting the various parameters referred to above, we regularly tested for convergence. We estimate that our choice of $r_n = 28$ accounted for approximately half of our total convergence error, which we estimated as being less than 0.01 cm^{-1} at $10\,000\text{ cm}^{-1}$ and in the region of 0.02 cm^{-1} at $20\,000\text{ cm}^{-1}$.

4 RESULTS

The BT2 water line list is available electronically in compressed form at <http://www.tampa.phys.ucl.ac.uk/ftp/astrodata/water/BT2/> and also at <ftp://cdsarc.u-strasbg.fr/cats/VI/119>. The data are in two parts. The first, the 'Levels File' is a list of 221 097 energy levels, ordered by J and symmetry block. About 25 000 of these energy levels have been labelled with the appropriate angular momentum (J, K_a, K_c) and vibrational (v_1, v_2, v_3) quantum numbers. An extract from the Levels File with an explanation of the contents of each of the 11 columns in the file is given in Table 2.

The second part of BT2 is the 'Transitions File'. This has 505, 806, 202 entries. Each transition references upper and lower energy

Table 2. Extract from the BT2 Levels File.

A	B	C	D	E	F	G	H	I	J	K
2284	2	2	5	3885.718 672	0	0	1	2	2	1
2285	2	2	6	4777.145 956	0	3	0	2	1	1
2286	2	2	7	5332.258 064	1	1	0	2	1	1
2287	2	2	8	5472.371 851	0	1	1	2	2	1
2288	2	2	9	6254.694 085	0	4	0	2	1	1
2289	2	2	10	6876.917 089	1	2	0	2	1	1
2290	2	2	11	7027.396 535	0	2	1	2	2	1
2291	2	2	12	7293.201 639	2	0	0	2	1	1
2292	2	2	13	7376.617 020	1	0	1	2	2	1
2293	2	2	14	7536.864 373	0	0	2	2	1	1

A: row in file; B: J ; C: symmetry (1–4: see Table 1); D: row in block; E: ν in cm^{-1} ; F, G, H: v_1, v_2, v_3 ; I, J, K: J, K_a, K_c .

Table 3. Extract from BT2 Transitions File.

A	B	C
1000	239	9.671E+01
1001	239	1.874E+00
1002	239	4.894E−03
1003	239	1.140E−04
1004	239	1.707E−02
1005	239	8.473E−08
1006	239	6.535E−04
1007	239	7.157E+00
1008	239	6.403E−06
1009	239	9.861E−05

A, B: row numbers in the Levels File. The identification of A as an upper level is not necessary because upper and lower levels can be identified from Level(A) – Level(B). C: A_{if} (s^{-1}).

levels in the Levels File and gives the Einstein A_{if} coefficient for the transition. An extract from the Transitions File is given in Table 3.

In uncompressed form the BT2 Transitions File is 12.6 GB of data. Therefore, in order to facilitate use of the list, the transitions have been ordered by frequency and separated into 16 smaller files, each representing a specific frequency range.

In addition to the files containing the actual line list, the ftp sites contain a FORTRAN program, SPECTRA-BT2.F90, that will enable users to generate emission or absorption spectra from BT2 by specifying various parameters including temperature, frequency range, cut-off intensity and linewidth. There is also a facility to generate spectra with full rotational–vibrational assignments if required. The method of using SPECTRA-BT2.F90 is detailed in a 'readme-spectra' file and there are also examples of a job file and an output file. It will be seen that the job file requires the partition function Q_{vm} for H_2O at the required temperature. The program has the ability to calculate $Q_{\text{vm}}(T)$; alternatively the value may be inserted manually. It should be noted that the O/P degeneracies included in SPECTRA-BT2.F90 are 3 and 1, which are four times the numbers commonly adopted by astronomers. Consequently, if $Q_{\text{vm}}(T)$ is to be inserted manually, the value to be employed is the 'spectroscopic' value which is four times the 'astronomical value' given in Vidler & Tennyson (2000).

4.1 Comparing the BT2 and PS line lists

Several water line lists are in regular use by astronomers and the most accurate list previously is that of PS. Table 4 compares BT2

Table 4. Comparison of BT2 and PS (Partridge & Schwenke 1997) with 14 889 experimentally determined energy levels.

Within (cm ⁻¹)	BT2 (per cent)	PS (per cent)
0.1	48.7	59.2
0.3	91.4	85.6
1.0	99.2	92.6
3.0	99.9	96.5
5.0	100	97.0
10.0	100	98.1

Table 5. Distribution of levels in the BT2 and PS (Partridge & Schwenke 1997) disagreeing with experiment by more than 2 cm⁻¹ by frequency.

Level energy (cm ⁻¹)	Number in range	BT2 no.	PS no.
20 000–26 300	575	9	334
15 000–20 000	2813	10	105
10 000–15 000	6323	8	58
7000–10 000	3263	3	9
<7000	1914	0	0
Total	14 889	30	506

and PS energy levels with known experimental values (Tennyson et al. 2001). It will be seen from this table that although the PS list is more accurate than BT2 in the cases where agreement with experiment is better than 0.1 cm⁻¹, this is not the case generally. Specifically, based on a sample of 14 889 levels, whilst 99.9 per cent of the BT lines are within 3.0 cm⁻¹ of experiment, 3.5 per cent of the PS lines are outside this range. Other line lists (MT, VT2, SCAN) perform significantly worse than this.

Examining deviations from experiment by energy is even more revealing, for it is seen that PS is increasingly unreliable above 10 000 cm⁻¹, which is the region with the greatest number of transitions (Table 5).

4.2 Labelling the levels

As with observed water lines, the production of a synthetic line list prompts the question of how to assign quantum numbers to the transitions. The BT2 line list contains over 505 million transitions, but the DVR3D suite only provides data on J and the symmetry block of each energy level. Since each individual line is a transition between two energy states, the problem reduces to one of labelling the 221 097 energy levels, but this is still a large task.

Many papers have been devoted to assigning quantum numbers to energy levels that have been deduced from experimental line frequencies (e.g. Zobov et al. 2000). So far, less than 15 000 experimentally determined levels have been labelled with their three rotational and three vibrational quantum numbers, even though much effort has been expended on the task. 25 870 levels in the BT2 list have been labelled using methodologies detailed below. BT2 labels 270 of the 416 levels which have $J = 0$ and energies below 30 000 cm⁻¹. However, the proportion labelled is less at higher J values.

The process of labelling BT2 started by identifying particular energies with experimental levels that have already been determined.

In addition, we have labelled many of the energy levels that are unknown experimentally, using several different methods. A large number of vibrational states for $J = 0$ have been labelled by visual inspection of the nodal structure of the wavefunction as described in Mussa & Tennyson (1998). This method has the disadvantage that observations can only easily be made on two-dimensional sections of the three-dimensional wavefunction and the procedure can be misleading. In addition, Mussa and Tennyson observed that at energies in the region of our 30 000 cm⁻¹, a high proportion of the wavefunctions are irregular with no identifiable nodal structure.

A second method involved examining the A_{if} coefficients for pure rotational transitions between an unlabelled vibrational state and a known vibrational state; the strongest transitions being those where standard selection rules are obeyed. We found this method (see Tolchenov et al. 2005) to be useful for $J < 10$.

A third method that was found to be useful in labelling higher- J states involved the use of an algorithm to identify sets of levels within the same parity block having the same K_a, v_1, v_2, v_3 quantum numbers, but different values of J and K_c . The method was originally developed for labelling the energy levels of the HCN and HNC isomers (Barber, Harris & Tennyson 2002). However, because of the density of the energy levels in water, an extra term was introduced when labelling the water levels. The algorithm used in this case was

$$E_{J_n} \cong 4E_{J_{n-1}} - 6E_{J_{n-2}} + 4E_{J_{n-3}} - E_{J_{n-4}}. \quad (4)$$

However, when resonance between levels caused the behaviour pattern to be erratic, or no $E_{J_{n-4}}$ value existed, the original, simpler algorithm was used:

$$E_{J_n} \cong 3E_{J_{n-1}} - 3E_{J_{n-2}} + E_{J_{n-3}}, \quad (5)$$

where E_{J_n} is the energy of the state in the same symmetry block having $J = n$ and the same set of K_a, v_1, v_2, v_3 quantum numbers.

The results of the labelling exercise are included in the BT2 Level File. This means that when synthetic spectra are generated many of the transitions are fully labelled. This feature is useful when generating synthetic spectra for astronomical or laboratory applications as is discussed in the next section.

4.3 Completeness

If we compare the partition function $Q(T)$ for water computed at a particular temperature using the BT and PS line lists with the most accurately known value at this temperature, it is possible to estimate the completeness of the line lists and the amounts of opacity that are missing in spectra generated by the two line lists at the selected temperature.

A calculation of the partition function of water at 3000 K using the 221 097 energy levels in BT2 yields a value that is 99.9915 per cent of the Vidler & Tennyson (2000) value, which indicates that levels missing from BT2 only contribute about 85 parts in a million to the partition function of water at this temperature, the reason being that there is a diminishingly small probability of states above 30 000 cm⁻¹ being occupied at this temperature. For comparison, the PS line list, which has 28 000 cm⁻¹ cut-off gives a partition function at 3000 K that is only 99.493 per cent of the value of Vidler & Tennyson (2000).

Although the exclusion of levels above 30 000 cm⁻¹ does not materially affect the completeness of the BT2 list, it does affect absorption at shorter wavelengths. If we consider a photon of wavelength 1 μm (energy 10 000 cm⁻¹). This is able to be absorbed by a water molecule in a particular rotation–vibration eigenstate provided that there is another eigenstate exactly 10 000 cm⁻¹ above this

lower state into which the molecule may be excited. It follows that since the BT2 line list has an upper cut-off of $30\,000\text{ cm}^{-1}$, none of the energy levels in the list above $20\,000\text{ cm}^{-1}$ is capable of being excited by a $1\text{-}\mu\text{m}$ photon, since there is no corresponding upper level.

If we examine the extent to which $Q(3000\text{ K})$ computed from BT2, but excluding all levels above $20\,000\text{ cm}^{-1}$, falls short of the value of Vidler & Tennyson (2000) we will have an indication (this is an upper limit as it takes no account of blending effects) of the opacity that has been excluded by adopting a $30\,000\text{ cm}^{-1}$ cut-off. Performing the calculation gives a shortfall of 0.83 per cent.

In the case of PS, only energy levels below $18\,000\text{ cm}^{-1}$ are able to absorb a $1\text{-}\mu\text{m}$ photon, and computing $Q(3000\text{ K})$ using only PS states up to $18\,000\text{ cm}^{-1}$ shows that these comprise only 98.37 per cent of the Vidler value. Hence, it will be seen that the opacity deficit at $1\text{ }\mu\text{m}$ is in the region of twice as great in the PS list as in BT and the ratio increases at shorter wavelengths.

5 SAMPLE APPLICATIONS

Although BT2 shows good agreement with experimentally known lines, this is not a sufficient test of its accuracy as the PES used to generate BT2 was fitted to the known experimental data (this is also true of the PS line list).

The most effective way of checking the accuracy of a line list is to test its ability to predict or identify previously unknown lines in astronomical or laboratory spectra. BT2 has been used successfully as outlined below. It should be noted here that some of the earlier spectroscopic applications used BT1 as they predate BT2. However, the line positions of the two lists are identical, and the intensities of the strong lines are similar for the two lists.

5.1 Astronomical spectra

5.1.1 Brown dwarf spectral fitting

A synthetic spectrum generated at 1500 K using BT1 was able to reproduce the previously unknown absorption feature observed at $1.554\text{ }\mu\text{m}$ in the spectrum of the early T dwarf ϵ Indi Ba, discovered by Volk et al. (2003), as being a blend of six water lines with no individual line contributing more than 25 per cent of intensity (Smith et al. 2003).

BT2 has been used to model J -band, high-resolution spectra of five ultracool dwarfs from M6 to L0 and to identify individual features in these spectra (Lyubchik et al., in preparation).

5.1.2 Comet 153P/Ikeya–Zhang (2002 C1)

BT1 was used to compute the frequencies and Einstein A coefficients of the 64 transitions (up to $J = 7$) that make up each of the seven hot bands of water detected in Comet 153P/Ikeya–Zhang. Dello Russo et al. (2004) applied these data in determining the rotational temperature of the comet on three dates.

5.1.3 Temperatures of comet forming regions in early solar nebula

The hot-band transitions identified by BT1 in Dello Russo et al. (2004) were classified into ortho and para using the symmetry information contained within the BT2 energy file (see column C in Table 1). Transitions between different nuclear spin parities can be ignored (Miani & Tennyson 2004). Dello et al. (2005) were able to deduce the primordial O/P water composition of three comets:

C/1999 H1, C/1999 S4 and C/2001 A2 and hence the temperatures of the different regions of the early solar nebula in which the comets were formed. The normal O/P ratio is 3:1, but since the lowest ortho level lies 23.8 cm^{-1} ($\sim 34\text{ K}$) above the ground state (which is a para state), the O/P ratio is subnormal at temperatures below $\sim 50\text{ K}$. A comparison of the Einstein A coefficients in BT2 with those actually used in BT1 shows that the results of Dello Russo et al. (2004) would have been the same had the later line list been used.

5.1.4 Detection of water lines in nova-like object V838 Mon

Synthetic spectra generated by BT2 were used to identify absorption features observed in the $1.73\text{--}1.75\text{ }\mu\text{m}$ region of the spectrum of the nova-like object, V838 Mon on five separate dates as being due to blended water lines. Quantum numbers were assigned to the 17 strong transitions that comprise the five absorption features (Banerjee et al. 2005). 16 of the lines were found to be in the (0 0 0)–(0 1 1) band. This is the first time that individual water lines have been identified in a nova-like outflow region.

In addition, BT2 was used to compute the theoretical intensities of the five absorption features as a function of temperature and column density (assuming local thermodynamic equilibrium LTE). The results indicated that the water features were arising from a cool $\sim 750\text{--}900\text{ K}$ region around V838 Mon that was cooling at a rate of $\sim 100\text{ K yr}^{-1}$. Column densities computed for the five dates also showed a reduction with time.

5.1.5 Sunspot spectra

Following their assignment of high-temperature laboratory water lines in which extensive use was made of BT2 (see ‘Laboratory Spectra’ below), Coheur et al. (2005) revisited the sunspot absorption spectrum in the $9.89\text{--}12.95\text{ }\mu\text{m}$ region of Wallace et al. (1995) which had been partially assigned by Polyansky et al. (1997) and Zobov et al. (1999). Coheur et al. (2005) used their high-temperature laboratory assignments to identify a substantial number of previously unassigned sunspot lines.

5.2 Laboratory spectra

Hot water spectra have been analysed in the laboratory over the last 30 yr. Methods generally involve high-resolution Fourier transform spectrometry of vapour which may be at an elevated temperature, such as in an oxy-acetylene flame (Camy-Peyret et al. 1977; Coheur et al. 2005).

The BT2 line list has already been used on a number of occasions to analyse spectra generated at both high and low temperatures at various wavelengths and this has added considerably to the existing data base of experimentally known energy levels and transitions.

Coheur et al. (2005) working with experimental spectra generated at 3000 K in the $5\text{--}20\text{ }\mu\text{m}$ region labelled about 600 previously unidentified levels using the BT2 line list. The identification of these levels was an important factor in their subsequent assignment of 8500 of the 10 100 lines that they observed in the $0.385\text{--}1.081\text{ }\mu\text{m}$ region. Most of the states that were labelled by Coheur et al. (2005) were either high- J states having low bending modes or else lower- J states with higher bending modes. These states had defied earlier analysis because the previous line lists used in earlier work were unable to accurately predict the energies of states above $15\,000\text{ cm}^{-1}$ or to treat accurately the high bending mode states, even those below $15\,000\text{ cm}^{-1}$.

They note that whilst the agreement between BT2 and observation is generally within 0.1 cm^{-1} for the energy levels that they observe for low- J states, the disagreement can be as great as 0.8 cm^{-1} for some of the very high- J states. Nevertheless, they comment that since for a given vibrational and K_a state the difference between the BT2 list and experiment increases smoothly with J , they are able to use BT2 to predict the positions of unknown higher- J levels with an accuracy of 0.02 cm^{-1} . This is considerably less than the experimentally determined linewidths (full widths at half-maximum) which were in the range $0.05\text{--}0.10 \text{ cm}^{-1}$ due to broadening at 1 atm and $T = 3000 \text{ K}$.

In a follow-up paper analysing the $2\text{--}5 \mu\text{m}$ region Zobov et al. (2006) use BT2 to label approximately 700 previously unidentified rotational–vibrational energy levels for water, observed in laboratory torch spectra.

Tolchenov et al. (2005) analysed long-path-length room temperature spectra. They use three separate line lists in their work. However, only the BT2 list is found to be reliable over all transition frequencies and in the case of lines having frequencies above $16\,000 \text{ cm}^{-1}$ it is the only one that they use. In addition, Tolchenov et al. (2005) encounter difficulties with the labelling adopted in previous studies, finding, for example, that in some cases different states have been labelled with the same quantum numbers. They therefore undertake a systematic relabelling exercise using the BT2 energies. These labels are incorporated into the BT2 list for states with $J \leq 9$.

Dupré et al. (2005) found BT2 similarly reliable for predictions of long-path-length room temperature spectra in the near-ultraviolet. They observed 62 R-branch transitions in the 8ν polyad and were able to determine 36 energy levels, previously unknown experimentally.

6 CONCLUSION

We present a new synthetic water line list which gives the energies of 221 097 states with cut-offs of $J = 50$ and $E = 30\,000 \text{ cm}^{-1}$. 25 870 of the lower energy levels have been labelled with a full set of three rotational and three vibrational quantum numbers. BT2 lists 505, 806, 202 transitions. It has been extensively tested against experimental observations and also compared with other lists. It has been shown to be the most complete and accurate water line list in existence.

We make our results freely available in electronic form via <http://www.tampa.phys.ucl.ac.uk/ftp/astrodata/water/BT2> and also via <ftp://cdsarc.u-strasbg.fr/cats/VI/119>, in the hope that BT2 line list will be a valuable tool for astronomers in both spectroscopy and atmospheric modelling applications.

One of the problems facing the modellers of the atmospheres of cool stars and brown dwarfs is the disagreement between observation and model. Nevertheless, considerable progress has been made in recent years in such areas as convection, molecular abundances, non-LTE effects and dust (Hauschildt, Allard & Baron 1999; Tsuji 2002; Alexander et al. 2003). At the same time, there have been advances in computing the opacity effects of the various species that are included in the models.

At the temperature of late M dwarfs (2500 K), water is by far the most important contributor to stellar atmospheric opacity, typically contributing over 60 per cent of all opacity in the infrared. It is also an extremely important contributor to the opacity of L and T brown dwarfs, although at these lower temperatures (down to 900 K), methane and ammonia play an increased role.

As part of our ongoing work in applying BT2 we plan to compare observed M dwarf spectra with synthetic spectra produced with the Phoenix model (Hauschildt et al. 1999) using several water line

lists, including BT2 (Barber et al., in preparation). This is an extension of work already conducted on modelling oxygen-rich cool stars. Jones et al. (2005) compare the CO 2–0 bands in the $2.297\text{--}2.210 \mu\text{m}$ region of several M dwarfs and an L dwarf with opacity calculations using the PS and BT line lists and conclude that for this particular wavelength range: ‘while the Partridge–Schwenke line list is a reasonable spectroscopic match [for the BT line list] at 2000 K, by 4000 K it is missing around 25 per cent of the water vapour opacity’.

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