ExoMol molecular line lists XIX: high accuracy computed hot line lists for H$_2^{18}$O and H$_2^{17}$O

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ABSTRACT
Hot line lists for two isotopologues of water, H$_2^{18}$O and H$_2^{17}$O, are presented. The calculations employ newly constructed potential energy surfaces (PES) which take advantage of a novel method for using the large set of experimental energy levels for H$_2^{16}$O to give high quality predictions for H$_2^{18}$O and H$_2^{17}$O. This procedure greatly extends the energy range for which a PES can be accurately determined, allowing accurate prediction of higher-lying energy levels than are currently known from direct laboratory measurements. This PES is combined with a high-accuracy, ab initio dipole moment surface of water in the computation of all energy levels, transition frequencies and associated Einstein A coefficients for states with rotational excitation up to $J = 50$ and energies up to 30 000 cm$^{-1}$. The resulting HotWat78 line lists complement the well-used BT2 H$_2^{16}$O line list (Barber et al., 2006, MNRAS, 368, 1087). Full line lists are made available in the electronic form as supplementary data to this article and at www.exomol.com.

Key words: molecular data; opacity; astronomical data bases: miscellaneous; planets and satellites: atmospheres; stars: low-mass; stars: brown dwarfs.

1 INTRODUCTION
Water spectra can be observed from many different regimes in the Universe, several of which are discussed further below. The spectrum of water, particularly at elevated temperatures, is rich and complex. A few years ago Barber et al. (2006) presented a comprehensive line list, known as BT2, which used well-established theoretical procedures to compute all the transitions of H$_2^{16}$O of importance in objects with temperatures up to 3000 K. BT2 contains about 500 million lines. A similar line list for HD$_2^{16}$O, known as VTT, was subsequently computed by Voronin et al. (2010).

The BT2 line list has been extensively used. It forms the basis of the most recent release of the HITMPEP high-temperature spectroscopic database (Rothman et al. 2010) and for the BT-Settl model (Allard 2014) for stellar and substellar atmospheres covering the range from solar-mass stars to the latest-type T and Y dwarfs. BT2 has been used to detect and analyse water spectra in objects as diverse as the Nova-like object V838 Mon (Banerjee et al. 2005), atmospheres of brown dwarfs (Rice et al. 2010), and M subdwarfs (Rajpurohit et al. 2014), and extensively for exoplanets (Tinetti et al. 2007, Birkby et al. 2013). Within the solar system BT2 has been used to show an imbalance between nuclear spin and rotational temperatures in cometary comae (Dello Russo et al. 2004, 2005) and assign a new set of, as yet unexplained, high energy water emissions in comets (Barber et al. 2009), as well as to model water spectra in the deep atmosphere of Venus (Bailey 2009).

Although BT2 was developed for astrophysical use, it has been applied to a variety of other problems including the calculation of the refractive index of humid air in the infrared (Mathar 2007), high speed thermometry and tomographic imaging in gas engines and burners (Kranendonk et al. 2007, Rein & Sanders 2010), as the basis for an improved theory...
of line-broadening (Bykov et al. 2008), and to validate the data used in models of the earths atmosphere and in particular simulating the contribution of weak water transitions to the so-called water continuum (Chesnokova et al. 2009).

There are several water line lists published in the literature (Viti et al. 1997; Partridge & Schwenke 1997; Barber et al. 2006; Mikhailenko et al. 2005). Two linelists have also been computed specifically for the isotopologues: Shirin et al. (2008) created the 3mol room-temperature line lists for H$_2^{16}$O, H$_2^{17}$O and H$_2^{18}$O based on the PES of Shirin et al. (2006); Tashkun created a number of line lists based on the work of Partridge & Schwenke (1997), see Mikhailenko et al. (2005). These are considered further below.

At present hot line lists are only published for H$_2^{16}$O and HD$^{16}$O. However isotopically-substituted water containing $^{18}$O or $^{17}$O provides important markers for a variety of astronomical problems (Nittler & Gaidos 2012). For example Matsura et al. (2014) recently detected H$_2^{18}$O in the emission-line spectrum of the luminous M-supergiant VY CMa. Astronomical spectra of water isotopologues (Neufeld et al. 2013) and their direct analysis in cometary dust particles (Fless et al. 2010) and carbonaceous chronodrites (Clayton & Mayeda 1984; Vollmer et al. 2008) have been used to determine formation mechanisms and constrain formation models. Water isotope ratios are also used to monitor stellar evolution (Abia et al. 2012) and to probe the atmosphere of Mars (Villanueva et al. 2015). The seemingly minor isotopologues of water can be important species in their own right, for example, H$_2^{18}$O being the fifth largest absorber of sunlight the earth’s atmosphere.

There is therefore a need for line lists equivalent to BT2 for H$_2^{17}$O and H$_2^{18}$O to aid spectroscopic studies, and it is these that are presented here. These lists form part of the ExoMol project (Tennyson & Yurchenko 2012) which aims to provide a comprehensive set of molecular line lists for studies of molecular line lists for exoplanet and other hot atmospheres.

Although our new line lists in some way mimic BT2, they also take advantage of a number of recent theoretical developments. In particular a IUPAC task group (Tennyson et al. 2014) used a systematic procedure (Furtenbacher et al. 2007) to derive empirical energy levels for all the main isotopologues of water (Tennyson et al. 2009, 2010, 2013, 2014). These levels are combined with a newly-developed procedure for enhancing the accuracy of calculations on isotopically substituted species, which is used for the first time here. This ensures that most of the key frequencies in our new line lists are determined with an accuracy close to experimental, even though many of them are yet to be observed. Furthermore, theoretical work on improving the accuracy and representation of the water dipole moment (Lodi et al. 2008, 2011) has improved the accuracy with which water transition intensities are predicted (Grechko et al. 2009). Some of these advances have already been used to create improved room temperature line lists for H$_2^{17}$O and H$_2^{18}$O (Lodi & Tennyson 2012) which were included in their entirety in the 2012 release of HITRAN (Rothman L. S. et al. 2013).

The paper is structured as follows: section 2 outlines our overall methodology and presents the derivation of potential energy surfaces (PES). The details of the calculation of the new line lists, along with comparison with previous line lists, are given in section 3. Section 4 discusses further improvement of the line list by the substitution of calculated energy levels with empirical ones, together with the procedure used to label energy levels with approximate vibrational and rotational quantum numbers. Our results are discussed in section 5.

### 2 POTENTIAL ENERGY SURFACES

The fitting of water (H$_2^{16}$O) PESs to experimental spectroscopic data has a long history. The first fitted PES giving near to experimental accuracy was PJT1 (Polyansky et al. 1994). Partridge & Schwenke (1997) constructed a fitted PES starting from a highly accurate ab initio calculation; all subsequent water potentials followed this procedure and have been based on ab initio studies of increasing sophistication. As a result there are several very good water PESs available (Shirin et al. 2003, 2008; Bubukina et al. 2011).

Here we need a PES which satisfies two criteria. First, it should be as accurate as the PES used for the BT2 line list with the calculated energies ranging up to 30 000 cm$^{-1}$. Second, the PES should be adapted to the calculation of energy levels of the two water isotopologues H$_2^{17}$O and H$_2^{18}$O. This second requirement is harder to fulfill, as the characterisation of the experimental energy levels of both H$_2^{17}$O and H$_2^{18}$O is significantly less extensive than for H$_2^{16}$O (Tennyson et al. 2014).

To take advantage of the accumulated knowledge on the spectrum H$_2^{16}$O in constructing a PES for H$_2^{17}$O and H$_2^{18}$O and following previous work (Zobov et al. 1996; Voronin et al. 2010; Bubukina et al. 2011), we decided to fit a Born-Oppenheimer (BO) mass-independent PES to the available data for H$_2^{16}$O and fix the adiabatic BO diagonal correction (BODC), mass-dependent surface to the ab initio value of Polyansky et al. (2003). Obviously this procedure requires the accuracy of predictions for H$_2^{17}$O and H$_2^{18}$O to be verified. This is done by comparing the calculated H$_2^{17}$O and H$_2^{18}$O energy levels to the available experimentally-determined ones (Tennyson et al. 2009, 2010).

We used the same fitting procedure as Bubukina et al. (2011). Nuclear motion calculations were performed with DVR3D (Tennyson et al. 2004). As elsewhere, in the fit the experimentally derived energies of H$_2^{16}$O for the $J = 0$, 2 and 5 rotational states by Tennyson et al. (2013) were used.

In the following our new empirical PES obtained using the fitting procedure described above will be referenced to as PES1, while the PES by Bubukina et al. (2011) will be referenced to as PES2. Tables 1 and 2 present a comparison between...
Table 1. Comparison of calculated $J=0$ term values for $H_2^{17}O$ using three potentials with experimental data. Experimental (obs) data is taken from Tennyson et al. (2009).

| $v_1$ | $v_2$ | $v_3$ | Observed | PES1 Obs.-Calc. | PES2 Obs.-Calc. | PES3 Obs.-Calc. |
|-------|-------|-------|-----------|----------------|----------------|----------------|
| 0 0 1 |      |       | 3748.318  | 3748.334       | -0.02          | 3748.326       | 3748.463       | -0.15 |
| 0 0 2 |      |       | 7431.076  | 7431.103       | -0.03          | 7431.059       | 7431.467       | -0.39 |
| 0 0 3 |      |       | 7419.532  | 7419.532       | -0.05          | 7419.251       | 7419.251       | -0.38 |
| 0 1 0 |      |       | 1591.326  | 1591.297       | 0.03           | 1591.342       | 1591.434       | -0.09 |
| 0 1 1 |      |       | 5320.251  | 5320.241       | 0.01           | 5320.251       | 5320.378       | -0.13 |
| 0 1 2 |      |       | 8982.869  | 8982.868       | 0.00           | 8982.844       | 8983.118       | -0.25 |
| 0 1 3 |      |       | 12541.227 | 12541.267      | -0.04          | 12541.207      | 12541.614      | -0.39 |
| 0 2 0 |      |       | 3144.980  | 3144.934       | 0.05           | 3144.993       | 3145.085       | -0.10 |
| 0 2 1 |      |       | 6857.273  | 6857.260       | 0.01           | 6857.266       | 6857.476       | -0.20 |
| 0 7 1 |      |       | 13808.273 | 13808.224      | 0.05           | 13808.371      | 13809.171      | -0.90 |
| 1 0 0 |      |       | 3653.142  | 3653.147       | 0.00           | 3653.121       | 3653.193       | -0.05 |
| 1 0 1 |      |       | 7238.714  | 7238.773       | -0.06          | 7238.726       | 7238.932       | -0.22 |
| 1 0 2 |      |       | 10853.505 | 10853.545      | -0.04          | 10853.504      | 10853.504      | -0.00 |
| 1 0 3 |      |       | 14296.280 | 14296.340      | -0.06          | 14296.265      | 14296.584      | -0.30 |
| 1 1 0 |      |       | 5227.706  | 5227.704       | 0.01           | 5227.704       | 5227.881       | -0.18 |
| 1 1 1 |      |       | 8792.544  | 8792.578       | -0.03           | 8792.546       | 8792.816       | -0.27 |
| 1 2 0 |      |       | 6764.726  | 6764.747       | -0.02           | 6764.722       | 6764.905       | -0.18 |
| 1 2 1 |      |       | 10311.202 | 10311.247      | -0.05           | 10311.199      | 10311.421      | -0.22 |
| 1 3 0 |      |       | 11792.822 | 11792.861      | -0.04           | 11792.834      | 11793.172      | -0.35 |
| 2 0 0 |      |       | 7193.246  | 7193.265       | -0.02           | 7193.257       | 7193.394       | -0.15 |
| 2 0 1 |      |       | 10598.476 | 10598.550      | -0.07           | 10598.483      | 10598.763      | -0.29 |
| 2 1 1 |      |       | 12132.993 | 12133.056      | -0.06           | 12132.984      | 12132.365      | 0.63  |
| 2 2 1 |      |       | 13631.500 | 13631.542      | -0.04           | 13631.489      | 13631.650      | -0.15 |
| 3 0 1 |      |       | 13812.158 | 13812.215      | -0.06           | 13812.170      | 13812.394      | -0.24 |
| 3 1 0 |      |       | 16797.168 | 16797.182      | -0.01           | 16797.177      | 16797.011      | 0.16  |
| 4 0 0 |      |       | 16875.621 | 16875.662      | -0.04           | 16875.643      | 16875.474      | 0.15  |

3 LINE LIST CALCULATIONS FOR $H_2^{17}O$ AND $H_2^{18}O$

The line list calculations were performed with the DVR3D program suite (Tennyson et al. 2004) using the PES1 and PES2 discussed above, and the ab initio dipole moment surfaces LTP2011S of Lodi et al. (2011). As for BT2, the highest rotational
Table 2. Comparison of calculated $J = 0$ term values for $\text{H}_2^{18}\text{O}$ using three potentials with experimental data. Experimental (obs) data is taken from Tennyson et al. (2009).

| $v_1$ | $v_2$ | $v_3$ | Observed | PES1 Obs.-Calc. | PES2 Obs.-Calc. | PES3 Obs.-Calc. |
|-------|-------|-------|-----------|-----------------|-----------------|-----------------|
| 0     | 0     | 1     | 3741.57   | 3741.581       | -0.01           | 3741.575        |
| 0     | 0     | 2     | 7418.72   | 7418.741       | -0.02           | 7418.759        |
| 0     | 0     | 3     | 10993.68  | 10993.734      | -0.05           | 10993.659       |
| 0     | 1     | 0     | 1588.28   | 1588.240       | 0.04            | 1588.271        |
| 0     | 1     | 1     | 5310.46   | 5310.443       | 0.02            | 5310.438        |
| 0     | 1     | 2     | 8967.57   | 8967.552       | 0.01            | 8967.519        |
| 0     | 1     | 3     | 13250.12  | 12520.153      | -0.03           | 12520.069       |
| 0     | 2     | 0     | 3139.05   | 3138.999       | 0.05            | 3139.038        |
| 0     | 2     | 1     | 6844.60   | 6844.580       | 0.02            | 6844.566        |
| 0     | 2     | 2     | 10483.22  | 10483.264      | -0.04           | 10483.212       |
| 0     | 3     | 0     | 4648.48   | 4648.435       | 0.04            | 4648.469        |
| 0     | 3     | 1     | 8341.11   | 8341.109       | 0.00            | 8341.114        |
| 0     | 3     | 2     | 11963.54  | 11963.580      | -0.04           | 11963.615       |
| 0     | 4     | 0     | 6110.42   | 6110.408       | 0.05            | 6110.400        |
| 0     | 4     | 1     | 9795.33   | 9795.354       | -0.02           | 9795.324        |
| 0     | 4     | 2     | 12520.12  | 12520.153      | -0.03           | 12520.069       |
| 1     | 0     | 0     | 3649.69   | 3649.688       | 0.05            | 3649.679        |
| 1     | 0     | 1     | 7228.88   | 7228.934       | -0.05           | 7228.888        |
| 1     | 0     | 2     | 10839.96  | 10839.986      | -0.03           | 10839.942       |
| 1     | 1     | 0     | 8799.72   | 8799.747       | -0.03           | 8799.707        |
| 1     | 1     | 1     | 12372.71  | 12372.723      | -0.02           | 12372.679       |
| 1     | 1     | 2     | 6755.51   | 6755.528       | -0.02           | 6755.483        |
| 1     | 1     | 3     | 10295.63  | 10295.673      | -0.04           | 10295.616       |
| 1     | 2     | 0     | 8249.04   | 8249.063       | -0.03           | 8249.024        |
| 1     | 2     | 1     | 11774.71  | 11774.742      | -0.03           | 11774.701       |
| 1     | 2     | 2     | 7185.88   | 7185.894       | -0.02           | 7185.879        |
| 1     | 3     | 0     | 10585.29  | 10585.357      | -0.07           | 10585.292       |
| 1     | 3     | 1     | 14188.97  | 14188.069      | -0.09           | 14187.985       |
| 2     | 0     | 0     | 8739.53   | 8739.530       | 0.00            | 8739.520        |
| 2     | 1     | 1     | 12116.80  | 12116.851      | -0.05           | 12116.833       |
| 2     | 2     | 0     | 10256.58  | 10256.604      | -0.02           | 10256.569       |
| 2     | 3     | 0     | 11734.53  | 11734.543      | -0.02           | 11734.517       |
| 3     | 0     | 0     | 10573.92  | 10573.955      | -0.04           | 10573.927       |
| 3     | 1     | 0     | 13795.40  | 13795.455      | -0.06           | 13795.410       |
| 3     | 1     | 1     | 12106.98  | 12107.025      | -0.05           | 12106.974       |
| 3     | 2     | 0     | 16775.38  | 16775.396      | -0.11           | 16775.385       |
| 4     | 0     | 1     | 16854.99  | 16855.126      | -0.14           | 16855.099       |

state, $J$, in the calculation was taken as $J = 50$ and the limiting energy as 30 000 cm$^{-1}$. Analysis using the $\text{H}_2^{16}\text{O}$ partition function (Vidler & Tennyson 2000) performed in BT2 suggests that these parameters are sufficient to cover all transitions longwards of 0.5 $\mu$m for temperatures up to 3000 K.

Wavefunctions were obtained by solving the nuclear Schrödinger equation using two-step procedure of calculation of rovibrational energies (Tennyson & Sutcliffe 1986). The calculations benefitted from recent algorithmic improvements (Tennyson & Yurchenko 2016), in particular in the method used to construct the final Hamiltonian matrices for $J > 0$ due to Azzam et al. (2016). Transition intensities were computed for $\Delta J = 0$ and 1 for all four symmetries and every $J \leq 50$. The matrix elements of the DMS were calculated using the program Dipole of the suite DVR3D and the actual spectrum for both isotopologues was generated with the program Spectra. About 500 million transitions were calculated for each isotopologue.

Figure 1 shows the distribution of the $\text{H}_2^{18}\text{O}$ lines in HotWat78. Using our calculations we provide the values of partition function for both isotopologues for wide range of temperatures, which are presented in the Table 5 as well as in the supplementary data on a grid of 1 K. We use the HITRAN convention (Fischer et al. 2003) and include the nuclear statistical weights $g_{ns}$ in to the partition function explicitly (Tennyson et al. 2016). The nuclear statistical weights for $\text{H}_2^{18}\text{O}$ are the same as for the main isotopologue, 1 and 3 for the para- and ortho-states, respectively. In case of $\text{H}_2^{17}\text{O}$, $g_{ns}$ are 6 (para) and 18 (ortho). For calculation of partition functions for $\text{H}_2^{18}\text{O}$ and $\text{H}_2^{17}\text{O}$ we used all available energy levels with applying the cut-off at 30000 cm$^{-1}$. © 2014 RAS, MNRAS 000, 1–8.
Table 3. Standard deviation in cm\(^{-1}\) with which our pseudo-experimental energy levels the of \(\text{H}_2^{17}\text{O}\) and \(\text{H}_2^{18}\text{O}\) predicted the observed ones compiled by [Tennyson et al. (2010)] as a function of rotational state, \(J\). \(N\) is number of levels used for calculation of the standard deviation.

| \(J\) | \(N_{\text{H}_2^{17}\text{O}}\) | \(N_{\text{H}_2^{18}\text{O}}\) | \(N_{\text{H}_2^{17}\text{O}}\) | \(N_{\text{H}_2^{18}\text{O}}\) |
|-------|-----------------|-----------------|-----------------|-----------------|
| 0     | 27              | 39              | 0.0058          | 0.0092          |
| 1     | 93              | 124             | 0.0056          | 0.0093          |
| 2     | 161             | 212             | 0.0071          | 0.0109          |
| 3     | 199             | 254             | 0.0074          | 0.0090          |
| 4     | 236             | 316             | 0.0118          | 0.0147          |
| 5     | 232             | 335             | 0.0103          | 0.0141          |
| 6     | 263             | 401             | 0.0100          | 0.0116          |
| 7     | 222             | 385             | 0.0138          | 0.0140          |
| 8     | 182             | 381             | 0.0146          | 0.0130          |
| 9     | 138             | 335             | 0.0123          | 0.0174          |
| 10    | 116             | 288             | 0.0130          | 0.0176          |
| 11    | 72              | 232             | 0.0080          | 0.0168          |
| 12    | 47              | 188             | 0.0111          | 0.0201          |
| 13    | 26              | 135             | 0.0083          | 0.0179          |
| 14    | 9               | 106             | 0.0096          | 0.0198          |
| 15    | 3               | 73              | 0.0150          | 0.0176          |
| 16    | 1               | 46              | 0.0066          | 0.0184          |
| 17    | 1               | 19              | 0.0015          | 0.0156          |
| 18    | 1               | 11              | 0.0015          | 0.0187          |

Table 4. Prediction of experimental energy levels of \(\text{H}_2^{18}\text{O}\). Experimental (obs) data is taken from [Makarov et al. (2015)].

| \(J\) | \(\text{Observed}\) | \(\text{Calculated}\) | \(\text{Obs.-Calc.}\) |
|-------|---------------------|----------------------|---------------------|
| 0     | 27476.33            | 27476.24             | 0.09                |
| 1     | 27497.03            | 27496.92             | 0.11                |
| 2     | 27510.64            | 27510.31             | 0.33                |
| 3     | 27517.09            | 27517.44             | -0.35               |
| 2     | 27537.12            | 27536.96             | 0.16                |
| 2     | 27546.82            | 27546.45             | 0.37                |
| 2     | 27509.55            | 27509.19             | 0.36                |
| 2     | 27545.66            | 27545.28             | 0.38                |

Figure 1. The distribution of the \(\text{H}_2^{18}\text{O}\) transitions per \(J\) in the line HotWat78 list.
Figure 2. Comparison between BT2 and HotWat78 for H$_2^{18}$O at the temperature $T=2000$ K, and comparison of HotWat78 with 3mol (Shirin et al. 2008) and HITRAN at $T=296$ K for H$_2^{18}$O and H$_2^{17}$O respectively.
4 IMPROVED PSEUDO-EXPERIMENTAL ENERGY LEVELS

The series of IUPAC papers on the various isotopologues of water (Tennyson et al. 2009, 2010, 2013, 2014) used measured transition frequencies to derive ro-vibrational energy levels using the so-called MARVEL (measured active rotation-vibration energy levels) procedure (Furtenbacher et al. 2007; Furtenbacher & Császár 2012). These energy levels can be used to generate pseudo-experimental values of the line frequencies in our line lists when the calculated energy level is substituted by the corresponding (pseudo-)experimental one. The comparison of these generated line frequencies with actual experimental ones demonstrate near-perfect coincidence. The number of generated pseudo-experimental lines is significantly higher than the number of the directly observed lines because line frequencies between pseudo-experimental levels can be predicted to high accuracy even when the lines have not been measured, as demonstrated by Tennyson et al. (2013). Less than 200 000 experimentally observed H$_2^{16}$O lines give rise to about 5 000 000 lines with pseudo-experimental frequencies generated in this way. Use of such a procedure provides significantly more accurate line lists than just the calculated ones. We therefore substituted our computed energy with those of Tennyson et al. (2009) where possible.

However as described in section 2, the procedure for fitting PES using H$_2^{16}$O data opens the way for us to further improve the accuracy of the calculated line lists. Looking at Table 6, we can see that the obs–calc residuals for a particular H$_2^{16}$O vibrational state are very similar to the residuals for the same states of H$_2^{17}$O and H$_2^{18}$O. The following procedure can be used to exploit this. First let us consider the idealised situation when all the residuals for energy levels of H$_2^{16}$O, $R_{v,J}(16)$, are exactly equal to those of H$_2^{18}$O, $R_{v,J}(18)$, where $(v,J)$ represent the vibrational and rotational quantum numbers. In this case we can predict the precise “estimated” value of an H$_2^{18}$O level, $E_{est}^{v,J}(18)$, from the empirically-determined levels of H$_2^{16}$O, $E_{obs}^{v,J}(18)$

$$E_{est}^{v,J}(18) = E_{calc}^{v,J}(18) + R_{v,J}(18) = E_{calc}^{v,J}(18) + R_{v,J}(16)$$

(1)

where $E_{calc}^{v,J}(18)$ is the corresponding calculated H$_2^{18}$O energy level. So even if the level of the H$_2^{18}$O isotopologue has yet to be observed, its pseudo-experimental value can be retrieved from the calculated level of H$_2^{16}$O using our calculations plus the residual for H$_2^{16}$O provided the experimental level of H$_2^{16}$O is known.

Table 6 shows that residuals for H$_2^{16}$O and H$_2^{18}$O are slightly different, we can therefore improve this procedure. We notice from the Table 6 that the H$_2^{16}$O and H$_2^{18}$O residuals differ by similar amounts. If we average this value:

$$\Delta R(18) = \frac{1}{N} \sum_{v=1}^{N} R_{v,0}(18) - R_{v,0}(16).$$

(2)
Table 5. Partition Function of H\textsubscript{2}\textsuperscript{17}O and H\textsubscript{2}\textsuperscript{18}O.

| T (K) | H\textsubscript{2}\textsuperscript{17}O | H\textsubscript{2}\textsuperscript{18}O |
|-------|------------|------------|
| 10    | 7.97970859 | 1.33159007 |
| 20    | 20.1629004 | 3.37074465 |
| 40    | 56.7292812 | 9.48860674 |
| 60    | 101.331587 | 16.9509639 |
| 80    | 153.237432 | 25.6357152 |
| 100   | 211.822453 | 35.4382143 |
| 200   | 587.053283 | 98.2237727 |
| 296   | 1052.12202 | 176.043783 |
| 300   | 1073.45356 | 179.613285 |
| 400   | 1654.78625 | 276.895547 |
| 500   | 2328.51505 | 389.655412 |
| 600   | 3099.26294 | 518.674912 |
| 800   | 4966.65892 | 831.352302 |
| 1000  | 7346.85187 | 1230.02825 |
| 1200  | 10357.5304 | 1734.46724 |
| 1400  | 14140.2160 | 2368.43292 |
| 1500  | 16371.1820 | 2742.40404 |
| 1600  | 18857.9004 | 3159.29345 |
| 1800  | 24694.5428 | 4137.93895 |
| 2000  | 31855.8230 | 5338.90908 |
| 2200  | 40570.4778 | 6800.61746 |
| 2400  | 51091.7815 | 8565.59949 |
| 2500  | 57116.1119 | 9576.29345 |
| 2600  | 63698.8388 | 10680.7274 |
| 2800  | 78697.3411 | 13197.3344 |
| 3000  | 96419.4218 | 16171.1873 |
| 3200  | 117222.299 | 19662.2543 |
| 3400  | 141485.523 | 23734.2409 |
| 3500  | 155038.487 | 26008.8411 |
| 3600  | 169606.832 | 28453.8904 |
| 3700  | 201996.792 | 33890.0829 |
| 3800  | 239070.969 | 40112.9028 |
| 3900  | 281250.969 | 47191.9028 |
| 4000  | 328941.890 | 55196.1417 |
| 4100  | 354979.000 | 59566.0429 |
| 4200  | 382541.321 | 64191.8753 |
| 4300  | 422425.403 | 72424.1299 |
| 4400  | 450116.119 | 80405.6885 |
| 4500  | 47736.3411 | 8565.59949 |
| 4600  | 51091.7815 | 9576.29345 |
| 4700  | 57116.1119 | 10680.7274 |
| 4800  | 63698.8388 | 13197.3344 |
| 4900  | 78697.3411 | 16171.1873 |
| 5000  | 96419.4218 | 19662.2543 |
| 5200  | 117222.299 | 23734.2409 |
| 5400  | 141485.523 | 26008.8411 |
| 5600  | 155038.487 | 28453.8904 |
| 5800  | 177697.341 | 33890.0829 |
| 6000  | 19662.2543 | 39196.1417 |

where \( N \) runs over the number of vibrational states for which \( J = 0 \) levels are known, which corresponds to 40 for H\textsubscript{2}\textsuperscript{17}O and 24 for H\textsubscript{2}\textsuperscript{18}O. Then we can use this average difference to further correct our estimated H\textsubscript{2}\textsuperscript{18}O energy levels using the revised formula:

\[
E_{\text{est}}^{v,j}(18) = E_{\text{calc}}^{v,J}(18) + R_{v,J}(16) + \Delta R(18).
\]

Calculating the observed values of energies of H\textsubscript{2}\textsuperscript{18}O using Eq. (1) gives a standard deviation for \( E_{\text{est}}^{v,j}(18) \) levels from the known experimental values, \( E_{\text{obs}}^{v,j}(18) \), of 0.009 cm\(^{-1}\). However, \( \Delta R(18) \) is 0.006 cm\(^{-1}\). If instead we use Eq. (3), then the standard deviation reduces to 0.003 cm\(^{-1}\). Although \( \Delta R(18) \) is evaluated for \( J = 0 \) only, this procedure still works for higher \( J \) values. For example it also results in a standard deviation of 0.003 cm\(^{-1}\) when applied to the \( J = 10 \) levels of the (010) state.

This procedure, which can clearly also be applied to H\textsubscript{2}\textsuperscript{17}O, leads to the generation of about 5 million transitions which involve the pseudo-experimental levels of H\textsubscript{2}\textsuperscript{17}O and H\textsubscript{2}\textsuperscript{18}O. It therefore provides a line list with much more accurate values of the frequencies of these transitions: in general better by about 0.005 cm\(^{-1}\) for H\textsubscript{2}\textsuperscript{17}O and somewhat worse for H\textsubscript{2}\textsuperscript{18}O, but still much more accurate than possible with variational calculations.

The reason this procedure can be applied to the construction of the pseudo-experimental values of the energy levels of minor isotopologues is that for the major water isotopologue H\textsubscript{2}\textsuperscript{16}O the number of energy levels known experimentally is
Table 6. Vibrational band origins, in cm$^{-1}$, for H$_2^{16}$O, H$_2^{17}$O and H$_2^{18}$O. Observed (obs) data is taken from Tennyson et al. (2013) and calculated results are given as observed minus calculated (o–c).

| (v$_1$,v$_2$,v$_3$) | H$_2^{16}$O | H$_2^{17}$O | H$_2^{18}$O |
|-------------------|-------------|-------------|-------------|
| (010)             | 1594.75     | 1591.33     | 1588.28     | 0.036 |
| (020)             | 3151.63     | 3144.98     | 3139.05     | 0.051 |
| (100)             | 3657.05     | 3653.14     | 3649.69     | 0.002 |
| (110)             | 5234.97     | 5227.71     | 5221.24     | 0.010 |
| (120)             | 6775.09     | 6764.73     | 6755.51     | 0.018 |
| (200)             | 7201.54     | 7193.25     | 7185.88     | 0.016 |
| (012)             | 9000.14     | 8982.87     | 8967.57     | 0.013 |
| (102)             | 10868.88    | 10853.51    | 10839.96    | 0.030 |
| (001)             | 3755.93     | 3748.32     | 3741.57     | 0.014 |
| (011)             | 5331.27     | 5320.25     | 5310.46     | 0.019 |
| (021)             | 6871.52     | 6857.27     | 6844.60     | 0.019 |
| (101)             | 7249.82     | 7238.71     | 7228.88     | 0.051 |
| (111)             | 8807.00     | 8792.54     | 8777.72     | 0.027 |
| (121)             | 10328.73    | 10311.20    | 10295.63    | 0.039 |
| (201)             | 10613.36    | 10598.48    | 10585.29    | 0.072 |
| (031)             | 11032.40    | 11011.88    | 10993.68    | 0.053 |
| (131)             | 11813.20    | 11792.82    | 11774.71    | 0.034 |
| (211)             | 12151.25    | 12132.99    | 12116.80    | 0.054 |
| (113)             | 12565.01    | 12541.23    | 12520.12    | 0.030 |
| (221)             | 13652.66    | 13631.50    | 13612.71    | 0.035 |
| (301)             | 13830.94    | 13812.16    | 13795.40    | 0.057 |
| (103)             | 14318.81    | 14296.28    | 14276.34    | 0.053 |

Results significantly higher, then that for H$_2^{17}$O and H$_2^{18}$O. For example the assignment of weak H$_2^{16}$O lines in various regions is available (Tolchenov et al. 2005, Polyansky et al. 1998, Scherman et al. 2002), where isotopologues data are not known. As a result very highly-excited bending (Polyansky et al. 1997, Zobov et al. 2005) and stretching energy levels (Maksyutenko et al. 2007, Grechko et al. 2009, Császár et al. 2010) are known, which form the basis upon which our pseudo-experimental energy levels are constructed.

5 RESULTS

The newly constructed H$_2^{17}$O and H$_2^{18}$O line lists are named HotWat78. The new HotWat78 line lists are calculated for J $\leq$ 50 and for the spectral range 0-30000 cm$^{-1}$. HotWat78 contains 519 461 789 lines for H$_2^{18}$O is 519 461 789 and 513 112 779 lines for H$_2^{17}$O. The new linelist is both the most complete and the most accurate one, see Tables 1 and 2. They are stored in the ExoMol format (Tennyson et al. 2013) which uses the compact storage of results originally developed for BT2. This involves using a states file (.states), see Table 7 and a transitions file (.trans), see Table 8. The energy levels in the states files are marked as ‘observed’ if the results are taken from the IUPAC compilation, ‘estimated’ if they are generated using Eq. (3) or as ‘calculated’, for which the results of the PES2 calculation are used.

The states file lists all the ro-vibrational levels for each J and for four C$_{2v}$ symmetries. It is common to further label the every level with (approximate) vibrational quantum numbers (v$_1$, v$_2$, v$_3$) which correspond to the symmetric stretch, bending and asymmetric stretch modes, respectively and the Rotational levels within each vibrational state by J, K$_a$, K$_c$, where again the projection quantum numbers K$_a$ and K$_c$ are approximate. DVR3D does not provide these approximate labels but there are several methods available for labeling water energy levels (Partridge & Schwenke 1997, Szidarovszky et al. 2012, Shirin et al. 2008). Here we label levels with J $\leq$ 20 and energies below 20 000 cm$^{-1}$. As our energy levels differ by less than 1 cm$^{-1}$ from those of Shirin et al. (2008), transferring the labels from this previous study proved to be straightforward. We note that the labels we use are based on the normal modes from a harmonic oscillator model. It is well known that the higher stretching states of water are better represented with a local-mode model (Child & Halonen 1984). However, there is a one-to-one correspondence between the two labelling schemes (Carleer et al. 1999); the use of normal mode labels are used for simplicity.

The accuracy of the present line lists can be established by the comparison with the previous line lists calculations. Two types of comparison could be made. The overall picture for the high temperature is that the coverage the HotWat78 H$_2^{17}$O and H$_2^{18}$O line lists should be very similar to BT2, but that both the predicted intensities and the line positions should be significantly better. Furthermore lines may shift by between a few cm$^{-1}$ to a few tens of cm$^{-1}$ between isotopologues. Figure 1 demonstrates that, as expected, the overall picture is very similar for BT2 (H$_2^{16}$O) and HotWat78 (H$_2^{17}$O and H$_2^{18}$O). Here we provide the comparison only for H$_2^{18}$O but for the H$_2^{17}$O it looks the same.

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Table 7. Extract from the final states file for H$_{2}^{17}$O.

| i | $E_{g_{rot}}$ | J | $K_a$ | $K_c$ | $\nu_1$ | $\nu_2$ | $\nu_3$ | S |
|---|--------------|---|-------|-------|--------|--------|--------|---|
| 1 | 0.000000     | 6 | 0     | 0     | 0      | 0      | 0      | A1|
| 2 | 1591.322876  | 6 | 0     | 0     | 0      | 1      | 0      | A1|
| 3 | 3144.980225  | 6 | 0     | 0     | 0      | 2      | 0      | A1|
| 4 | 3653.145752  | 6 | 0     | 0     | 1      | 0      | 0      | A1|
| 5 | 4657.115211  | 6 | 0     | 0     | 0      | 3      | 0      | A1|
| 6 | 5227.703129  | 6 | 0     | 0     | 0      | 1      | 0      | A1|
| 7 | 6121.557129  | 6 | 0     | 0     | 0      | 0      | 3      | A1|
| 8 | 6764.726562  | 6 | 0     | 0     | 0      | 1      | 2      | A1|
| 9 | 7193.246582  | 6 | 0     | 0     | 0      | 2      | 0      | A1|
|10 | 7431.093262  | 6 | 0     | 0     | 0      | 0      | 2      | A1|
|11 | 7527.489258  | 6 | 0     | 0     | 0      | 0      | 5      | A1|
|12 | 8260.781250  | 6 | 0     | 0     | 0      | 1      | 3      | A1|
|13 | 8749.905273  | 6 | 0     | 0     | 0      | 2      | 1      | A1|
|14 | 8853.288086  | 6 | 0     | 0     | 0      | 0      | 6      | A1|
|15 | 8982.860352  | 6 | 0     | 0     | 0      | 0      | 1      | A1|
|16 | 9708.538086  | 6 | 0     | 0     | 0      | 1      | 4      | A1|
|17 | 10068.091797 | 6 | 0     | 0     | 0      | 0      | 7      | A1|
|18 | 10269.661133 | 6 | 0     | 0     | 0      | 2      | 2      | A1|
|19 | 10501.35516  | 6 | 0     | 0     | 0      | 0      | 2      | A1|
|20 | 10586.49805  | 6 | 0     | 0     | 0      | 3      | 0      | A1|

$i$: State counting number.
$E$: State energy in cm$^{-1}$.
$g$: Total state degeneracy.
$J$: Total angular momentum.
$K_a$: Asymmetric top quantum number.
$K_c$: Asymmetric top quantum number.
$\nu_1$: Symmetric stretch quantum number.
$\nu_2$: Bending quantum number.
$\nu_3$: Asymmetric stretch quantum number.
$S$: State symmetry in C$_{2v}$.

Figures 2 and 3 illustrate the similarity of the HotWat78 line lists with the previous high accuracy H$_{2}^{17}$O and H$_{2}^{18}$O line lists (called 3mol) of Shirin et al. (2008) for these molecules at the room temperature. Figures 4 and 5 also provide a comparison with the HITRAN data for the room temperature for H$_{2}^{17}$O and H$_{2}^{18}$O. These figures only provide an overview, but a detailed line by line comparison confirms that all the calculations we present here are done correctly.

The present line lists are significantly more complete, but this is only apparent at higher temperatures, see Fig. 3. For the room temperature the previous line lists should look similar, as they indeed do, see Figures 2.

6 CONCLUSIONS

This paper reports hot line lists for H$_{2}^{17}$O and H$_{2}^{18}$O. These line lists represent significant improvement on both coverage and accuracy of the previous H$_{2}^{17}$O and H$_{2}^{18}$O line lists (Mikhailenko et al. 2005; Shirin et al. 2008). The predicted frequencies in these line lists have been significantly improved using information obtained from the corresponding H$_{2}^{16}$O empirical energy levels. This procedure can be adapted to give improved predictions of energy levels and transition frequencies for isotopologues of molecules for whom the empirical energy levels of the parent molecule are well-known.

The complete HotWat78 line lists for H$_{2}^{17}$O and H$_{2}^{18}$O can be downloaded from the CDS, via ftp://cdsarc.u-strasbg.fr/pub/cats/J/MNRAS/ or via http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/MNRAS/. The line lists together with auxiliary data including the potential parameters, dipole moment functions, and theoretical energy levels can be also obtained at www.exomol.com, where they form part of the enhanced Exomol database (Tennyson et al. 2016). The BT2 H$_{2}^{16}$O line list (Barber et al. 2006) is already available from these sources.

Finally we note that pressure-broadening has been shown to have a significant effect on water spectra in exoplanets (Tinetti et al. 2012). ExoMol, in common with other databases, assumes that pressure-broadening parameters for H$_{2}^{17}$O and H$_{2}^{18}$O are the same as those for H$_{2}^{16}$O. This assumption is built into the recently updated structure of the ExoMol database (Tennyson et al. 2016). Barton et al. (2016) have recently presented a comprehensive set of pressure-broadening parameters for H$_{2}^{18}$O lines which form the basis for the ExoMol pressure-broadening diet for water (Barton et al. 2016). These parameters, which are available on the ExoMol website, are also suitable for use with the HotWat78 line lists.
### Table 8. Extract from the transitions file for $\text{H}_2^{17}\text{O}$

| $f$  | $i$    | $A_{fi}$     |
|------|--------|--------------|
| 142344 | 150189 | 5.6651e-05   |
| 2235  | 2362   | 1.7434e-03   |
| 34497 | 35342  | 5.7700e-09   |
| 125681 | 114596 | 5.5394e-10  |
| 135143 | 128340 | 6.3329e-08   |
| 24055 | 16736   | 1.5208e-03   |
| 147918 | 137719 | 1.3405e-04   |
| 45027 | 45537   | 8.0306e-07   |
| 37457 | 31884   | 9.0168e-08   |
| 39192 | 43632   | 7.3676e-07   |
| 25153 | 26085   | 4.3393e-05   |
| 131146 | 124272 | 8.5679e-04   |
| 134840 | 128287 | 8.5680e-04   |
| 102017 | 106580 | 2.4131e-04   |
| 193489 | 187074 | 2.7697e-06   |
| 202910 | 204558 | 7.0571e-03   |
| 53725 | 50906   | 1.8345e-06   |
| 142862 | 135857 | 2.5908e-05   |

$f$: Upper state counting number.  
i: Lower state counting number.  
$A_{fi}$: Einstein-A coefficient in s$^{-1}$.

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