Partition Function and Thermodynamic Quantities for the H$_2^{17}$O and H$_2^{18}$O Isotopologues of Water

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Abstract

The internal partition function, \( Z_{\text{int}} \), for the \( \text{H}_2^{17}\text{O} \) and \( \text{H}_2^{18}\text{O} \) isotopologues of water are computed for the 100 – 1500K equilibrium temperature regime by the explicit summation of 2723 and 5131 experimentally determined accurate low-lying energy levels, respectively. These levels, compiled by using the MARVEL procedure, are supplemented by a semi-theoretical line list considered to be close to experimental accuracy, which covers levels up to total angular momentum number \( J = 20 \), and a maximum energy of 30,000cm\(^{-1}\). Further augmentation is required to achieve coverage of energy levels up to the dissociation limit, and this is attempted using an approximate method to estimate energy levels which could not be obtained otherwise.

By calculating a total partition function, various thermodynamic properties of each system can be derived as a function of temperature. The thermodynamic quantities of interest are the Heat Capacity at Constant Pressure \( (C_p) \), the Entropy, \( (S) \), the Gibbs Enthalpy function \( (\text{gef}) \), and the Helmholtz function \( (\text{hcf}) \). These are calculated as direct derivatives of the total partition function.

In the very low temperature regime where results are dependent only on the low-lying energy level data, the results can be considered to be very accurate to the precision quoted. Comparisons with other works show that the relatively small amounts of accurately determined data give rise to expanding uncertainties towards higher temperatures very quickly, where the use of approximate levels starts to dominate and affect the calculations.
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Introduction

The study of water in within the physical and chemical sciences has vast importance. This relatively simple molecule is the most abundant polyatomic found in the universe, and is regarded as fundamental ingredient for life on Earth. Moreover, it is observed throughout many areas in science; it has been observed in the atmosphere of the Sun (sunspots) and in protostar systems, and other extraterrestrial environments such as in comets, it has been attributed to the greenhouse effect and plays a key role in weathering systems, and is also a product of many combustion processes. A recently increasing area of interest concerns the field of extra solar planets and their habitability, where the presence of water can be modelled by various procedures. It is therefore of great interest to study the thermochemical properties of water, and have data readily available to be used for any thermodynamic computational procedure and modelling processes.

The standard (and most abundant) variation of the water molecule consists of two Hydrogen atoms, $^1$H, and a single Oxygen atom $^{16}$O. Both of these atoms have stable isotopic varieties, including $^{17}$O and $^{18}$O for oxygen. These are present in water molecules, and thus give rise to water isotopologues, isotopic variations of a particular molecule, $^{16}$O is present in 99.760%, $^{17}$O in 0.037%, and $^{18}$O in 0.200% of water molecules. As such, a great deal of work has been done in computing reliable thermodynamic parameters for H$_2^{16}$O. Works include those by Vidler and Tennyson, Harris et al, and Martin et al. HITRAN (High-Resolution Transmission molecular absorption database) was set up in the late 1960’s by the Air Force Cambridge Research Laboratories in an effort to compile a database of spectroscopic parameters that could be used in modelling and simulating of atmospheric transmission and absorption of light. The database includes data for water and its isotopologues. The majority of these works reference JANAF, which was originally set up to supply these types of data for modelling systems, and this work follows the standards indicated in the JANAF literature.

Since accurate data for H$_2^{16}$O is fairly abundant due to the works mentioned above, this work aims to produce some comparable results for H$_2^{17}$O and H$_2^{18}$O. The partition function, Z, plays a very important role in the thermodynamics of any system, whereby a number of thermochemical quantities can be derived from it. In this work, the partition function is computed by explicit summation of energy levels determined for the H$_2^{17}$O and H$_2^{18}$O isotopologues. Sources of this data include accurate measurements from purely experimental works, tabulated by MARVEL, and a
list of levels produced by a semi-theoretical fitting to experimental data. Further approximate levels can be produced by fitting to these data sets.

The standards of JANAF will be followed, whereby quantities are tabulated within the equilibrium temperature ranges of $100 \text{ – } 6000\text{K}$. The quantities of interest are the Gibbs Enthalpy function, the Helmholtz function, the Entropy, and Specific Heat at Constant Pressure.

The implications of this study will hopefully provide material to the literature which can be used directly in the studies of systems where water plays an important role. One particular interesting phenomenon that may be studied in more detail is that of *fractionation*, whereby the ratios of the different isotopologues of water will vary due to the environments and reaction rates (this is further discussed in the Background and Theory section).
**Background and Theory**

**The Partition Function**

A system which contains an ensemble of possible microscopic configurations can be described by the canonical ensemble model. In this picture there are a number of exact *microstates* in which the system can be found which can be uniquely defined (i.e. by some quantum labelling system) and which posses a definite energy.

If a microstate is labelled $s (= 1, 2, 3...)$, and its corresponding energy $E_s$, then the probability of finding the system in that particular state is proportional to a Boltzmann factor:

$$ P(E_s) \propto \exp\left(-\frac{E_s}{k_B T}\right) \quad (1) $$

Here, $k_B$ is Boltzmann’s constant, and $T$ is the temperature in Kelvin.

Since the system in question could reside in any one of these states, the probabilities must sum to unity:

$$ \sum P(E_s) = 1 \quad (2.1) $$

We can rewrite the equation using a proportionality constant, $C$:

$$ P(E_s) = C \exp\left(-\frac{E_s}{k_B T}\right) \quad (2.2) $$

We then see that:

$$ \sum P(E_s) = \sum C \exp\left(-\frac{E_s}{k_B T}\right) = C \sum \exp\left(-\frac{E_s}{k_B T}\right) = 1 $$

And so:

$$ C = \frac{1}{\sum \exp\left(-\frac{E_s}{k_B T}\right)} = \frac{1}{Z} \quad (3) $$

The quantity $Z$ is known as the partition function, a weighting factor which guarantees normalisation for the probability $P(E_s)$. In principle it is possible to explicitly compute this sum if all the details of the systems microscopic properties are known. In doing this for a certain equilibrium temperature, it is possible to determine the probabilities of finding the system in any of the microstates associated with it; number densities of the constituents within the system in a given
state can be computed for a given temperature and pressure if the partition function is known for those parameters. It is also an incredibly useful tool in thermodynamics as it can be used to compute such quantities as the expectation value of the total energy, which can be written in terms of the partition function, and hence through various thermodynamic relations can lead to the computation of many other quantities.
Physics of the Water Molecule

Internal Motion

The water molecule is a tri-atomic molecule where two separate chemical bonds connect the Hydrogen atoms to the Oxygen atom, subtending an angle of about 104.5 degrees\textsuperscript{13}. The molecule is described as an asymmetric top.

The rotation of the water molecule can be resolved into components about three perpendicular axes which dissect the centre of gravity of the molecule. A molecule described in this way will have three fundamental moments of inertia about each of these axes.

If the axes are labelled A, B and C, then the corresponding moments of inertia about them are labelled $I_A$, $I_B$, and $I_C$. The definition of an asymmetric top is a molecule where all these moments of inertia are different.\textsuperscript{†} Applying this axis convention to the water molecule gives its asymmetric top characterization.

![Figure 1: Labelling convention for the asymmetric top water molecule](image)

\textsuperscript{†}Molecules are divided into groups according to the relative values of these moments of inertia. In the case of water they are all different, but there are other cases where they may be equal to each other, or even negligible (zero).
From Fig. 1 it is also clear that there is only a single symmetric axis of rotation, defined here as the B-axis.

Each atom within the molecule can be referred to by specifying three coordinates in space, so for a molecule containing N atoms there are a total of 3N coordinate values, known as degrees of freedom. The water molecule can be described as having 3N = 9 degrees of freedom. Since the rotation of the water molecule has already been described by separating it into components about three axes, it is necessary for 3 degrees of freedom to be used to specify these axes.

As well as rotational motion, a molecule has translational and vibrational motion associated with it. Translational motion is described by the changes in position of the centre of mass of the molecule, due to the movement of the centre of mass between different coordinates. Since the position of the water molecule is described in 3-dimensional space, which is defined by three perpendicular axes, a further 3 degrees of freedom are necessary to define these coordinates.

With three degrees of freedom being used to describe rotational motion and another three used to describe translational motion, there are 9 – 6 = 3 degrees of freedom left. These correspond to internal vibration. The water molecule has 2 chemical bonds upon which the vibrations are described. The vibrational motion can be described as either a stretching or a bending of these bonds. For the water molecule there are three fundamental vibrational motions which are possible, which are known as the normal modes of vibration; two of them correspond to bond stretching, and one is a bond bending motion.

The three normal modes of vibration are labelled as $v_1$, $v_2$ and $v_3$. No matter how complex the vibration of the molecule is, it will still only be a superposition of the three fundamental modes of vibration, much like the superposition of rotational components of motion. The convention is to define vibrational modes about the symmetric axis that bisects the HOH angle. This axis, which has
already been defined here as the B-axis, is referred to as a C₂ axis\(^1\), referring to the order of symmetry of the molecule upon rotation about this axis. Thus the \(v_1\) and \(v_2\) modes are labelled symmetric, and the \(v_3\) mode anti-symmetric. All the vibrations of the molecule at rest must have a total momentum equal to zero; otherwise the centre of mass of the molecule will change and the motion will be a translation.

In order for a molecule to interact with electromagnetic radiation, it must posses a changing dipole moment\(^1\). Dipoles arise in molecules which have an uneven distribution of electrons between atoms, and hence a non-uniform distribution of positive and negative charge. Due to the non-linear structure of the water molecule, and the higher electronegativity of the Oxygen atom, an uneven distribution of electrons leads to this dipole phenomenon, and the molecule is said to be ‘polar’.

Rotational motion of a polar water molecule causes a periodic fluctuation in the dipole moment, as does the vibrational motion, (along the C₂ line of symmetry)\(^1\). The electric field due to the interacting radiation exerts a net torque on the dipole, exciting it or de-exciting the molecule between different energies.

The energies corresponding to rotation and vibration are quantized, due to restrictions placed on the solutions to the Schrodinger equation for the molecule. This gives rise to the spectra which are studied, where lines visible on the spectrum denote transitions between discrete ‘energy levels’. One of the most interesting aspects of this quantum description is the concept of ‘zero point energy’ which states that constituent atoms within a molecule can never be completely at rest relative to each other\(^1\) and hence are always vibrationally excited to a certain extent. The extent of the amount of energy the molecule can have is limited by dissociation. At a certain point the internal energy of the molecule will be sufficient enough to dissociate the constituent atoms from each other. There are two conventions for labelling the dissociation energy, either by \(D_e\) or by \(D_0\). The former convention includes the zero point energy in the value for the dissociation energy, and the latter is with the zero point energy subtracted. In this work the \(D_0\) convention will be used as the ground state will have a definition of zero energy. Vibration and rotational energy are not independent of each other, and hence mathematical methods for describing them must account for distortion, since approximations such as the rigid rotor and quantum harmonic oscillator will not suffice as energies corresponding to both of these motions increase.

There are also energy contributions due to the electrons found within the molecular structure, when it is found in excited electronic states. However it is important to note that
electronic excited states in the water molecule lie well above the dissociation energy\textsuperscript{19} and therefore we need only consider the ground electronic state.

The unit of measurement used for the energy values for each level in the water molecule is the wavenumber (cm\textsuperscript{-1}). It is commonly used in the analysis of spectra since energy is directly proportional to frequency, which is also proportional to inverse length by the constant speed of light.

**Quantum Numbers**

When the water molecule is found in a certain energy state, defined by its vibrational and rotational motion, it can be described by a combination of six quantum numbers; three corresponding to rotation, and three corresponding to vibration.

The three normal modes of vibration have quantum numbers $v_1$, $v_2$ and $v_3$, as described above.

The remaining three correspond to rotation: $J$ $K_a$ and $K_c$.

$J$ is the rotational quantum number, and it corresponds to the total angular momentum of the molecule. It can only take integral values from zero upwards, a restriction which arises out of solution to the Schrodinger equation, and the energy of the molecule is proportional to this number (which gives rise to the quantized energies described above)\textsuperscript{20}. For a given value of $J$ there is a $(2J+1)$-fold degeneracy. The total angular momentum of the molecule is a vector quantity, and the number of different directions which this vector can take is limited by the $2J+1$ degeneracy.

For molecules that are not diatomics, the quantum number $J$ is not enough to describe the rotation of the molecule, since there are components of rotation about more than one axis. It becomes increasingly difficult to analytically describe the internal motions describing rotation and vibration, and the usual method of approach is to treat an asymmetric top with the limiting geometries of a prolate and oblate symmetric top\textsuperscript{21}. The convention for a symmetric top, where the moments of inertia about two of the axes are equal and the remaining is different – the ‘top axis’. In this regime, the total angular momentum is defined by $J$, and the angular momentum about the top axis is defined by $K$. $K$ can be equal to or less than $J$, where rotation is completely about the top axis if $K=J$. 
For a prolate symmetric top, the configuration of the moments of inertia is $I_A < I_B = I_C$. For an oblate symmetric top, the configuration is $I_C > I_A = I_B$. Hence the assignment of the top axis differs for each.

Since there is no ‘top axis’ for an asymmetric top whereby this projection can be assigned, the method of characterising is by considering the two limiting cases of prolate and oblate. In this regime, the asymmetric top is considered to be a “near symmetric top” since, often as is the case two of the principle moments of inertia are very similar.

The number $K_a$ is the projection of rotational angular momentum $J$ onto the a-axis of the prolate top, and $K_c$ is the projection onto the c-axis of the oblate top. The $2J+1$ sublevels of a particular value of $J$ are labelled using $K_a$ and $K_c$, where, for the given value of $J$, $K_a = 0$ has the lowest energy and $K_a = J$ has highest energy. All combinations of $K_a$ and $K_c$ are possible to denote these sublevels.

It is important to note that $K_a$ and $K_c$ are not real quantum numbers, since they are not eigenvalues of the rotational Hamiltonian. Instead they refer to the idealized prolate and oblate limits of the asymmetric top molecule. However the rotation of an asymmetric top can be completely defined by $J$, $K_a$ and $K_c$.

**Ortho and Para Water**

There is an important consequence of quantum mechanics which leads to a further cause of degeneracy. The total molecular wavefunction can be described as a combination of individual wavefunctions:

\[
\Psi_{TOT} = \Psi_{Electronic}\Psi_{Nuclear}\Psi_{Rotational}\Psi_{Vibrational}
\] (4)

The Pauli Principle requires that total molecular wavefunctions must be antisymmetric with respect to interchange of identical fermions. In the case of the water molecule, this refers to the interchange of the Hydrogen nuclei about the axis of symmetry, and since these nuclei are fermions, they must obey this condition.

The wavefunction for the electronic ground state of the water molecule is symmetric, due to the nature of electron distribution about the axis of symmetry.
The nuclear wavefunction however can be either symmetric or antisymmetric. Within the water molecule, the two Hydrogen nuclei have an intrinsic angular momentum, commonly known as spin (nuclear spin). These spins can be either aligned or anti-aligned with each other, hence the possible combinations for two nuclei are summarised in four states. For a spin-1/2 particle, like the Hydrogen nucleus, the basis states span a 2-dimensional space (spin up or spin down). The tensor product of any pair of these basis states therefore spans a 4-dimensional space (in the standard bracket notation):

$$|s,m_s\rangle_1 |s,m_s\rangle_2 = |1/2,m_s\rangle_1 |1/2,m_s\rangle_2$$

(5)

This is the tensor product of the 2-dimensional spin states of particle 1 and 2, where \(m_s = -1/2\) or \(1/2\) for spin-1/2 particles\(^4\), the projection of spin on a defined axis. The product gives rise to four possible results for the total nuclear spin of the combined nuclear system. Three of these correspond to a total nuclear spin angular momentum of 1, together occupying a triplet state, and the other remaining state corresponds to a total nuclear spin angular momentum of 0, corresponding to a singlet state.

The triply degenerate spin configurations are symmetric with respect to the exchange of nuclei, and correspond to what is known as the ortho state, whereas the configuration corresponding to the singlet state is antisymmetric, and is known as the para state. At temperatures of 50K and above the ratio of ortho-water to para-water is 3:1\(^3\), i.e. the ortho state occurs three times as much as the para state since the vector associated with total nuclear spin = 1 has three possible orientations.

Since the ortho-water and para-water configurations each give rise to symmetric and antisymmetric nuclear wavefunctions, respectively, this puts constraints on the possible symmetry combinations of the rotational and vibrational wavefunctions.

The symmetry of a function with respect to reflection of all coordinates at the origin is called parity\(^2\). For a function \(f(x,y,z)\) to have even (positive) parity it must satisfy \(f(x,y,z) = +f(-x,-y,-z)\) (symmetric), and to have odd (negative) parity it must satisfy \(f(x,y,z) = -f(-x,-y,-z)\) (antisymmetric).

In the positive/negative regime, the total molecular wavefunction which is antisymmetric has negative parity, -1, and the electronic wavefunction component which is symmetric has positive

\(^4\) More generally, \(m_s = -s , -s+1 , ..., 0, ..., s-1 , s\)
parity, +1. Therefore the possible parity (symmetry) combinations can occur for the remaining wavefunction components are as follows:

<table>
<thead>
<tr>
<th>$\psi_{\text{tor}}$</th>
<th>$\psi_{\text{Electronic}}$</th>
<th>$\psi_{\text{Nuclear}}$</th>
<th>$\psi_{\text{Rotational}}$</th>
<th>$\psi_{\text{Vibrational}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>+1/-1</td>
<td>-1/+1</td>
</tr>
<tr>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>+1/-1</td>
<td>+1/-1</td>
</tr>
</tbody>
</table>

I.e. for the case of a symmetric nuclear wavefunction with even parity, the combination of rotational and vibrational wavefunctions must be between two wavefunctions of opposing parities, and in the case of an antisymmetric nuclear wavefunction with odd parity, the rotational-vibrational wavefunction combination must contain two wavefunctions with equivalent parities. Both of these symmetry configurations give rise to a total molecular (antisymmetric) wavefunction of odd parity.

The consequence of this is that if the nature of the rotational and vibrational wavefunctions are known then the parity of the nuclear wavefunction can be determined based on the constraints outlined above, and hence whether the wavefunction corresponds to the ortho configuration or the para configuration.

By analysis of the quantum numbers for rotation and vibration of a given energy level, this ‘reverse engineering’ technique can be used to determine the degeneracy of this level corresponding to the 3:1 ortho-para ratio. The following equation determines the configuration of the water molecule:

$$ \text{Mod}(K_a + K_c + v_3, 2) = 0 \text{ (para)}; = 1 \text{ (ortho)} $$

An energy level giving rise to an ortho-water configuration by this equation will have a 3-fold degeneracy due to the total nuclear spin states corresponding to the triplet, whereas energy levels giving rise to para-water will occur only once.

**Application of the Partition Function to the Water Molecule**

The energy levels of the water molecule are synonymous with the microstates described in the partition function; each energy level in the water molecule is defined by a definite energy value and a unique combination of six quantum numbers, i.e. a distinct microstate. For a system like the water molecule, the definition of the partition function already discussed corresponds to
microstates that are associated with internal sources of energy, and hence this partition function
should be formally referred to as an ‘internal’ partition function, \( Z_{\text{int}} \).

Explicitly:

\[
Z_{\text{int}} = Z_{\text{ro}} \cdot Z_{\text{vib}} \cdot Z_{\text{el}} \approx Z_{\text{ro/vib}} \cdot Z_{\text{el}} \quad (7)
\]

i.e. a product of individual partition functions corresponding to rotational energy, vibrational
energy and electronic energy. Here it is assumed that there is no coupling between energies from
excited electronic states and rotation/vibration energies. Also, the quantity \( Z_{\text{ro/vib}} \) is an approximate
form of the product between the individual partition functions owing to rotation and vibration
energies, found to be reliable at low temperatures\(^{19}\).

However the sum in the partition function needs to be adapted in order to account for the
degeneracy of energy levels in the water molecule. If a degeneracy weighting factor is defined then
the partition function can be expressed in terms of the energy levels, as opposed to individual
microstates:

\[
Z_{\text{int}} = \sum d_i \exp(-c_2 E_i / T) \quad (8)
\]

This has the energy level values \( E_i \) in terms of wavenumbers and \( c_2 \) is known as the second
radiation constant which deals with the conversion (which also incorporates the Boltzmann
constant); \( d_i \) is the degeneracy factor associated with the \( i^{th} \) energy level.

Since we are only dealing with the ground electronic state the contribution from the
electronic partition function is:

\[
Z_{\text{el}} = \sum d_0 \exp (0) \quad (9)
\]

Since there is no degeneracy in the ground state, \( d_0 = 1 \), and therefore \( Z_{\text{el}} = 1 \). This means
that \( Z_{\text{int}} = Z_{\text{ro/vib}} \), and the internal partition function is defined by the rotation-vibration energy
levels.

As previously discussed, degeneracy associated with these levels comes from two sources;
the \( 2J+1 \) – fold degeneracy of a level with a given \( J \), and from the nuclear spin degeneracy. These
can be defined from the quantum labels assigned to each level:

\[
d_i = (2J + 1)d_n \quad (10)
\]
If the $ith$ energy level corresponds to the an ortho-configuration based on Equation (6), then $d_n = 3/4$, and for para-configuration $d_n = 1/4$, ensuring that the partition function is weighted correctly based on the amounts of water that are found in each configuration.

An important point to mention is that due to the nature of the exponential factor within the internal partition function, the summation result is only dependent on low-lying energy values at low temperatures. The addition of higher energy values makes no contribution to the result since it will have truncated, and no loss of accuracy is observed; the partition function is said to have converged. As temperatures increase the result becomes more and more dependent on higher energy values. This has a consequence on the results of this work, depending upon the coverage of accurate data that is available.

The total partition function (per molecule) is taken to be a product of internal and translational partition functions:

$$Z_{tot} = Z_{int} \cdot Z_{trans}$$

$$Z_{trans} = \frac{\lambda^3 k_B T}{P}$$

$$\lambda = \sqrt{\frac{2\pi M k_B T}{h^2}}$$

$P$ is the pressure, $M$ is the mass of the molecule, $k_B$ is, again, Boltzmann’s constant, $T$ is the equilibrium temperature and $h$ is Planck’s constant.

**Computing the Thermodynamic Quantities of Interest**

From the partition function, it is possible to obtain expressions for various thermodynamic quantities, namely the Gibbs enthalpy function, the Helmholtz function, Entropy, and the Specific Heat at constant pressure. To do this it is necessary to compute the first and second derivatives of the partition function with respect to the equilibrium temperature, $T$. Instead of directly differentiating the total partition function, it is more reliable to express the derivatives in terms of the first and second moments of the partition function. The first and second moments of the internal partition function can be written by differentiating the sum in equation (8). In some cases the $d_n$-ortho = 3 and $d_n$-para = 1 convention is used.
The corresponding moments for the translational partition function can be expressed in the same way, by analytically differentiating equation (12):

\[ Z'_{\text{trans}} = 5 \lambda^3 k_B T \]
\[ Z''_{\text{trans}} = 35 \lambda^3 k_B T \]

The first and second moments of the total partition function are then given by the following equations:

\[ Z' = Z'_{\text{int}} \cdot Z_{\text{trans}} + Z'_{\text{int}} \cdot Z'_{\text{trans}} \]
\[ Z'' = Z''_{\text{int}} \cdot Z_{\text{trans}} + Z''_{\text{int}} \cdot Z''_{\text{trans}} + 2Z'_{\text{int}} \cdot Z'_{\text{trans}} \]

The thermodynamic quantities of interest can be defined in terms of these quantities.

The Gibbs enthalpy function and the Helmholtz function are expressed by:

\[ g e f (T) = -[G(T) - E_0]/T = R \ln Z \]
\[ h c f (T) = H(T) - E_0 = RTZ'/Z - E_0 \]

\( R \) is the ideal gas constant. These equations are expressed in terms of the reference point of the Helmholtz function, \( E_0 \), which is given as the enthalpy value at the reference temperature of 298.15 K, as in JANAF \(^8\) \([E_0 = H(298.15)]\). Therefore the Helmholtz function has a value of zero at 298.15 K, and therefore:

\[ E_0 = R \times 298.15 \times Z'/Z \]

The entropy and specific heat at constant pressure are given by the following expressions:

\[ S = R \left( T \frac{d \ln Z}{dT} + \ln Z \right) = R \left( \frac{Z'}{Z} + \ln Z \right) \]
\[ C_p = 2RT \frac{d \ln Z}{dT} + RT^2 \frac{d^2 \ln Z}{dT^2} = \frac{R}{Z} \left[ \frac{Z''}{Z} - \left( \frac{Z'}{Z} \right)^2 \right] \]  

(22)

**Isotope Effects**

Isotopic substitution of atoms within a molecule causes a change in the spectrum of the molecule\(^\text{29}\). These variations of molecules are the definition of an ‘isotopologue’, and are distinct in that their constituent atoms may have different neutron numbers to their proton numbers (an isotope). This shift in mass has an effect on the vibrational and rotational motion of the molecule.

In the case of a simple diatomic rigid rotor, the rotational energy is inversely proportional to the moment of inertia, which is in turn proportional to the reduced mass of the system. If the molecular system contains a heavier isotope then this will cause a reduction in the rotational energy. For vibrational motions, treating this simple diatomic as a harmonic oscillator, the energy is inversely proportional to the square root of the reduced mass, assuming that the spring-constant does not change with isotopic substitution (a valid assumption within the Born-Oppenheimer approximation)\(^\text{30}\).

In reality of course, the rigid rotor and harmonic oscillator approximations are in no way completely valid even for a diatomic molecule and more mathematical rigor is involved in the description of real motions. Also, for an asymmetric top like the water molecule, the mathematical description for these internal motions is much more complicated; however the same principles still apply. It would be expected that, for the water molecule, the moment of inertia about the axis dissecting the HOH angle would have negligible difference between isotopic substitutions of the Oxygen molecule since the contribution is mostly from the Hydrogen nuclei which go unchanged.

Within this work it is expected that the energies of the \( \text{H}_2^{17}\text{O} \) and \( \text{H}_2^{18}\text{O} \) isotopologues will be shifted to lower values compared to those for the corresponding quantum states of the \( \text{H}_2^{16}\text{O} \) molecule, with \( \text{H}_2^{18}\text{O} \) having the lowest of the three, given that it has the largest mass. Therefore, because of the nature of the negative exponential factor within the internal partition function, the \( \text{H}_2^{18}\text{O} \) molecule should have the largest value for the internal partition function, and \( \text{H}_2^{16}\text{O} \) the smallest, for a given equilibrium temperature.

However this is not the extent of the effects of isotopic substitution, as the presence of a heavier isotope within the molecule can actually alter its chemistry, and lead to an effect called *fractionation*\(^\text{31}\). In this phenomenon, the differences in mass lead to differences in abundance between the isotopic variations of a particular molecule. As discussed, the substitution of a less
massive isotope with a heavier one within a molecule leads to a reduction in energy, and the reduction of vibrational energies subsequently leads to a reduction in the zero point energy. Therefore at low temperatures a greater abundance of the heavier isotopologue is observed, as the energy required for dissociation will be greater. At higher temperatures the effect will not be as pronounced.

In many physical systems abundance ratios between the isotopic variations of a molecule can vary due to the discriminations of isotopologue mass that occur within chemical processes. A simple example can be described using the hydrologic cycle (water cycle) system on Earth. Phase changes such as evaporation and condensation separate the isotopic variations by mass discrimination, and thus abundances ratios vary in different parts of the cycle (i.e. sea water, clouds, etc.) since the chemical process involved in the phase change has favoured one isotopologue over the other. There has been plenty of work done on fractionation in climate studies and investigating the past of the hydrologic cycle. This phenomenon also has large implications in astronomical studies since these abundances can describe the nature of the extraterrestrial environments under investigation.
Method: Experimental Energy Levels

Origin of the Data

The experimentally derived, low-lying energy levels used in this work are those determined by Tennyson, et al\textsuperscript{10, 11} using the MARVEL (measured active rotational–vibrational energy levels) procedure\textsuperscript{9}. The process involves a rigorous algorithm whereby experimentally determined spectral transitions from a range of available sources are collated into a database. Each transition has a label for the upper and lower states between which the transition occurs, without which inversion of transitions into energy levels would not be possible. The labelling scheme uses the six quantum numbers $J, K_a, K_c, v_1, v_2$ and $v_3$.

‘Spectroscopic networks’ are then established whereby energy levels can be determined based on the connections between the transitions in the database (based on there upper/lower bounds), following appropriate selection rules, and constructed such that the lowest level has a value of zero. Tests are then performed in order to cleanse the database of any inaccuracies, since errors can arise from many places, for example poor transcription and wrong assignment of data.

Finally, the inversion from transitions to energy levels is computed by solving a set of linear equations. In fact, one of the benefits of the MARVEL procedure is that it can drastically reduce the volume of data in this way; on average about 10 energy levels can be used to reproduce about 40 lines\textsuperscript{9}. The overall scrutiny of the process provides a self-consistent set of results with appropriate margins of error.

Tennyson et al\textsuperscript{11} determined 2723 reliable energy levels for $\text{H}_2^{17}\text{O}$, and 5131 for $\text{H}_2^{18}\text{O}$ (‘reliable’ based on the MARVEL algorithm), which are the energy level lists used for this work (which will be referred to as MARVEL data). These final lists are actually updates to a previous set published in an earlier paper\textsuperscript{10}. Since the MARVEL procedure discriminates in favour of ‘purely experimental’ data, where not even results based on accurate Hamiltonians are considered\textsuperscript{10}, and given the dogmatic approach at deriving them, these energy levels are the most accurate data available.
Processing the MARVEL Data

The line lists for each isotopologue were presented in two sections, divided between the ortho and para states, a consequence of the MARVEL procedure ignoring ortho-para transitions, since they are predicted to be very weak and have actually yet to be observed. Each line in the MARVEL data represents an energy level, and contains eight columns:

- The first column contains a 3-digit number, which is an ordered combination of the three quantum numbers $v_1$, $v_2$ and $v_3$ (the normal vibrational modes), which together specify the vibrational mode of the level.

- The next three columns represent the $J$, $K_a$ and $K_c$ quantum numbers, respectively.

- The fifth column contains the value of the energy for the level, in wavenumbers (cm$^{-1}$), and the sixth column has an error on this value, in micro-wavenumbers ($10^{-6}$ cm$^{-1}$). The seventh column states the number of transitions to the energy level, which is taken to be a superficial measure of its accuracy. This is summed up in the final, eighth column, where a grade is assigned to the reliability of the result (e.g. A+, B, C etc). The only usable test of accuracy of course involves the numerical error that is assigned to the energy value.

The data was formatted into a standard arrangement using a version of the FORTRAN95 code. This involved the separation of the number in the first column into the constituent $v_1$, $v_2$ and $v_3$ numbers, which would be necessary for further processing. The standard layout of the ‘tidied-up’ lists was: $J$, $K_a$, $K_c$, $v_1$, $v_2$, $v_3$, Energy value (cm$^{-1}$), Uncertainty ($10^{-6}$ cm$^{-1}$). The final two columns in the MARVEL lists were ignored completely. Once each MARVEL list was standardised this way, para and ortho lists were combined for each isotopologue. The combined lists were then scanned in order to check that the number of rows in each matched the stated values of 2723 for H$_2^{17}$O, and 5131 for H$_2^{18}$O (Appendix: Program 1), which they did.

These lists cover up to $J = 17$ and $J = 18$ for H$_2^{17}$O and for H$_2^{18}$O, respectively, however not as a complete set (specifically towards higher $J$). At higher levels of $J$ there is less experimental coverage. However it is interesting to note at this point that convergence of the partition function at low temperature is still a possibility, since it will be dependent only on low-lying energy levels.
**Method: Theoretical Energy Levels**

**Origin of the Data**

The theoretical energy levels used in this work were produced by Shirin et al. The usual procedure for calculating energy levels theoretical is to create an *ab initio* "Potential Energy Surface" (PES).

In the Born-Oppenheimer Approximation, the nuclei of a molecule move within a potential which is generated by the various attractive and repulsive forces between the electrons within the atoms. In this approximation, it is assumed that the electronic and nuclear wavefunctions can be separated and the motions corresponding with each of them treated separately, and thus solution to the Schrodinger equation for the molecule is greatly simplified. The nuclear wavefunction can be further separated into those corresponding to rotation and vibration.

Essentially, the construction of a theoretical potential energy surface is performed by directly solving the Schrodinger equation in this way. To a first approximation the rigid-rotor and quantum harmonic oscillator solutions to the Schrodinger equation give values for rotational and vibrational energies. In reality, of course, these approximations can only be seriously considered at low energies, and break down due to the coupling of rotation and vibration, which distorts the idealized view of the molecule’s motion presented with these solutions.

For polyatomic molecules the procedure is also more complicated, since an energy ‘hyper-surface’ is generated, as opposed to a simple 1-dimensional PES of a diatomic. The dimension of a polyatomic PES is given as $3N - 6$. Therefore the water molecule has a 3-dimensional PES, and thee actually correspond to the degrees of freedom associated with vibration.

The construction of PES of polyatomics is an involved process. At higher energies it is expected that the solutions diverge from reality due to the distortion effects of rotation-vibration coupling, and hence coverage of theoretically determined energy levels can obviously only be trusted at relatively low energies.

The work of Shirin et al produced energy levels that were considered close to experimental accuracy, up to $J = 20$ for the three isotopic varieties of the water molecule. The calculations were

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**For linear polyatomics, the dimension is given by $3N - 5$**
performed using a semi-theoretical PES created by a high accuracy \textit{ab initio} PES fitted to experimentally determined results.

\textbf{Augmenting the MARVEL Data}

The theoretical data provided by Shirin et al were tabulated in a single line list. Each row contained 9 columns representing the six quantum numbers describing the internal motions of the molecules and the energies associated with them for each of the three forms of the molecule, i.e. with headings: $J$, $K_a$, $K_c$, $v_1$, $v_2$, $v_3$, Energy($H_2^{16}$O), Energy($H_2^{17}$O) and Energy($H_2^{18}$O). The energies are given in wavenumbers. The list contains 50039 energy levels for each isotopologue.

The purpose of these energy levels is to supplement the low lying experimental lists of $H_2^{17}$O and $H_2^{18}$O derived from the MARVEL procedure, therefore the column containing energy values for $H_2^{16}$O is unnecessary for this intention.

To augment the experimental data with this list a FORTRAN program (Appendix: Program 2) was used. This FORTRAN code was made to read in both lists for a specific isotopologue (i.e. neglecting the energy value column in the theoretical data for the opposing isotopologue where necessary) and compared. Levels in the theoretical data which had the same combination of quantum numbers that a corresponding level in the MARVEL data had were ignored. If an energy level in the theoretical PES data had no corresponding line in the MARVEL list then it was written to a new file. These lines in the new file were then added to the MARVEL data for the appropriate isotopologue.

Since the theoretical lists for both isotopologues have 50039 energy levels, then the final augmented list should also have 50039 levels, where 2723 theoretical energy levels for $H_2^{17}$O have been replaced by experimental values and 5131 theoretical levels replaced for $H_2^{18}$O. The final number count was checked with Program 1.

In summary, the theoretical lists are included to ‘fill in the gaps’ in the MARVEL data, since the MARVEL lists do not contain a complete set of energy levels. The overall aim is to guarantee MARVEL data is kept where ever possible to ensure that the essence of reality is still present in the calculations by using experimentally derived results. However even though the theoretical PES data does contain complete sets for each isotopologue, the coverage only includes values of $J$ up to and
including 20, and the highest energies computed are $29045.71432 \text{ cm}^{-1}$ for $\text{H}_2^{17}\text{O}$ and $28995.251119 \text{ cm}^{-1}$ for $\text{H}_2^{18}\text{O}$.

The inclusion of these highly accurate theoretical levels can help to converge the partition function at temperatures for which exclusive use of the MARVEL data could not, but as equilibrium temperatures increase in the partition function calculation, the result becomes more and more dependent on high-lying energy levels. Ideally it is necessary to have coverage up to dissociation in order to get convergence at these temperatures.
Method: Approximate Energy Levels

Previous work on the partition function for $H_2^{16}O$ by Harris et al\textsuperscript{19} and Vidler/Tennyson\textsuperscript{27} adopted a method presented by Polyansky\textsuperscript{36} as part of an effort to construct a list of approximate energy levels.

The basis of the approximation is to estimate energy levels for high $J$ (high energy) as:

$$E_{rv} = E_r + E_v$$  \hspace{1cm} (23)

i.e. as a combination of pure rotational energies and pure vibrational energies. With a source for each of these it is possible to compute the different combinations of these to produce energies for levels above those already provided by MARVEL and Shirin \textit{et al}, up to the limit of dissociation.

Purely vibrational levels are provided in the data produced by Shirin \textit{et al}\textsuperscript{12}, and can be used in this approximation. To produce purely rotational levels for high $J$ a slightly more involved process must be performed.

Polyansky’s Method

Perturbation theory can be used to calculate molecular energy levels, however it is a common trait that a calculated perturbation series begins to diverge, and for high values of $J$ this has been shown to be the case\textsuperscript{35}. Polyansky aimed to produce a convergent series in order to calculate energy levels for the ground state of water, where previous perturbation theory results for asymmetric tops had failed. This was done by using a Padé approximant. The Padé approximant method involves approximating a function by the ratio of two polynomials (a rational function). These polynomials are equivalent to certain order Taylor expansions of the function being approximated, whereby the rational function agrees with the original function to the highest order considered. Padé approximants are often used as substitutes for Taylor series’ of functions that do not converge.

Polyansky developed a one-dimensional approximation to an effective rotational Hamiltonian for asymmetric tops, and the work of Harris et al and Vidler/Tennyson adopted this method to a 1\textsuperscript{st}-order approximation, where the pure-rotational energy levels, $E_r$, are given by:
Here the number $J$ refers to the total angular momentum quantum number of the energy level, and $K = K_a$. The form that Polyansky represented was able to produce energy levels of the ground state of water to an accuracy no less than $8\text{cm}^{-1}$ compared to observed values, for levels up to $J = K = 20$. However, it must be noted that as a 1-dimensional approximation this method is rather crude in that it fails to take into account the splitting of energy levels that have the same value of $K_a$ but different values of $K_c$, i.e., levels with the same $K_a$ all have the same energy.

Polyansky fitted the constants in his full approximation to experimental data for the ground state of H$_2^{16}$O. In the 1$^{\text{st}}$-order approximation presented above the constants to be fitted are $A, B, C, \Delta_J, \Delta_{JK}$ and $\Delta_K$; a further eighteen constants were fitted in Polyansky’s complete approximation. It should be noted that the distinction between the constants $A$ and $B$ only becomes apparent at higher orders, and cannot be seen here.

Harris et al.$^{19}$ used the constants determined by Polyansky in their work, whereas Vidler and Tennyson re-fitted the constants to their newly obtained experimental data. The justification of this is that since the 1$^{\text{st}}$-order approximation was being used, along with more accurate data, the constants will have been different$^{27}$. This is the method of approach will be used in this work as well.

The method of fitting the constants to the experimental data involved a $\chi^2$ minimisation, whereby a functional form is fitted to data by varying certain parameters that give rise to a minimisation of a specific quantity. In this case the six constants described above are varied in order to fit the Polyansky function to the experimental MARVEL data. Pure rotational energy levels for each isotopologue in the experimental line lists were tabulated to carry out the fit, where the following quantity is minimised:

$$
\sum \left( \frac{E_e - E_a}{\Delta E_e} \right)^2
$$

$$
E_r = \frac{C_0^2}{C_0 - C_1}
$$

$$
C_0 = \left( A - \frac{B + C}{2} \right) K^2 + \left( \frac{B + C}{2} \right) J(J + 1)
$$

$$
C_1 = -\Delta_J[J(J + 1)]^2 - \Delta_{JK}K^2J(J + 1) - \Delta_K K^4
$$
In this sum $E_e$ is the pure-rotational experimental energy value in the MARVEL data, $\Delta E_e$ is its associated error, and $E_\alpha$ is the approximate pure-rotational energy value produced by the Polyansky function. The sum is over all available pure-rotational MARVEL levels. This procedure was carried out with Microsoft Excel, using the “Solver” tool. The quantity is minimised by taking the $J$ and $K_a$ of each level and implementing them into Polyansky’s equation [Equation (24)] along with some initial trial values for the six constants in order to produce an approximate value for each level, $E_\alpha$. The sum is then carried out and minimised to produce the appropriate values of $A, B, C, \Delta J, \Delta JK$ and $\Delta K$. Below are the constants used for each the $H_2^{17}$O and $H_2^{18}$O isotopologues compared to the Polyansky constants used for $H_2^{16}$O:

<table>
<thead>
<tr>
<th>Constant</th>
<th>Polyansky</th>
<th>This Work ($H_2^{17}$O)</th>
<th>This Work ($H_2^{18}$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>835838.592160</td>
<td>881395.069693</td>
<td>869090.096189</td>
</tr>
<tr>
<td>B</td>
<td>435348.769544</td>
<td>334789.818067</td>
<td>340628.236330</td>
</tr>
<tr>
<td>C</td>
<td>278139.834584</td>
<td>334789.818067</td>
<td>340628.236330</td>
</tr>
<tr>
<td>$\Delta J$</td>
<td>37.6187302</td>
<td>-56.952425</td>
<td>50.678643</td>
</tr>
<tr>
<td>$\Delta JK$</td>
<td>-173.3635582</td>
<td>-2255.671008</td>
<td>-1960.345558</td>
</tr>
<tr>
<td>$\Delta K$</td>
<td>973.939486</td>
<td>5954.865742</td>
<td>4469.599512</td>
</tr>
</tbody>
</table>

Table 1: Comparison of constants fitted to experimental data using Polyansky’s method, in MHz

Conversion of these constants into wavenumbers involves dividing them by 29979.245800 cm s$^{-1}$.

**Approximate Rotation-Vibration Energy Levels**

The aim of this effort was to attempt to produce a complete set of rotation-vibration energy levels for $J > 20$, and with $E > 29045.71432$cm$^{-1}$ for $H_2^{17}$O and $E > 28995.25119$cm$^{-1}$ for $H_2^{18}$O, up to the limit of dissociation. Vidler and Tennyson$^{27}$ were able to do this for $H_2^{16}$O up to a dissociation energy of 41088cm$^{-1}$, obtained from experimental observation (they also considered a theoretical result for comparison). They used some 980 pure-rotational experimental energy levels in their fitting of Polyansky’s constants$^{35}$. These constants were initially used to produce approximate rotational energy levels for the isotopologues in this work in order to test the procedure, before the new constants were fitted in this work according to the MARVEL data provided.

Like Harris et al, Vidler and Tennyson produced approximate levels within the interval of their available data up to dissociation. The limit of dissociation was taken to be 41008cm$^{-1}$ for Vidler/Tennyson and 39821.1cm$^{-1}$ for Harris et al. The maximum value of $J$ was taken to be that for which the $K_a = 0$ level still had energy below dissociation, since the $K_a = 0$ for a given $J$ is lowest in
energy. The calculations were truncated after this point. The maximum value of $J$ found by Harris et al\textsuperscript{19} was found to be $J = 71$, and for Vidler and Tennyson\textsuperscript{27} it was $J = 84$. The same method was adopted in this work.

However this approach turned out to be problematic using the constants fitted to the MARVEL data in this work for both isotopologues. The method as a whole is not entirely reliable as the accuracy of the rotational energy values produced in the Polyansky method are not of good quality (remembering that Polyansky originally stated that the method was only meant to be considered seriously up to $J = 20$). They are only used in an attempt to estimate and complete the line lists and ensure a complete set of energy levels up to dissociation, and to provide a means for estimating the partition function at higher temperatures. The approximation actually begins to fall apart at high values of $J$ even before dissociation, where $K = J$ levels begin to become to low after a certain high value of $J$\textsuperscript{19}. In this work it was observed that after a certain value of $J$ the energy levels produced by Polyansky’s method using MARVEL data disobeyed the rule of $K_a = 0$ having lowest energy and $K_a = J$ having highest energy for a given $J$. This was observed for $J \geq 19$ for $\text{H}_2^{17}\text{O}$ and $J \geq 25$ for $\text{H}_2^{18}\text{O}$.

The approximate rotational energy levels produced in this work for both isotopologues did not cover up to dissociation. Beyond the deviational characteristic of the computed energy values, the Polyansky method faltered such that it completely broke apart at certain values of $J$, where negative energy results surfaced for both isotopologues. This occurred after $J = 39$ for $\text{H}_2^{17}\text{O}$ and $J = 51$ for $\text{H}_2^{18}\text{O}$, and the calculations were arbitrarily truncated at this point. These are far from the maximum $J$ values found by Vidler/Tennyson and Harris et al. This is most likely due to the scarce coverage of pure-rotational levels provided by MARVEL which were needed to fit the data. For $\text{H}_2^{17}\text{O}$, 191 levels were used to fit the Polyansky constants, and 297 levels were used in the same procedure for $\text{H}_2^{18}\text{O}$. The greater coverage of MARVEL data for $\text{H}_2^{18}\text{O}$ can explain why the Polyansky method produced more approximate levels for this isotopologue. Vidler and Tennyson had 980 rotational levels to fit their constants, providing a much better fit up to dissociation before breakdown of the Polyansky method is observed.

Because of this it is obvious that any computed value of the partition function for $\text{H}_2^{17}\text{O}$ and $\text{H}_2^{18}\text{O}$ at higher temperatures will not be reliable at all even if the approximate levels produced were accurate, since a complete set of energy levels is required to compute the partition function at high temperatures. Also the fitting of the Polyansky constants to such limited amounts of pure-rotational MARVEL levels would have one expect the approximate energies calculated to deviate from reality much sooner causing anomalous results, and hence the upper limit of energy was kept at 41088 cm\textsuperscript{-1}. 
All possible combinations of Equation (23) are computed using the approximate rotation energies determined here and vibration energies supplied in the data from Shirin et al\textsuperscript{12}. The results that satisfy $29045.71432\text{cm}^{-1} < E_{\text{vp}} < 41088\text{cm}^{-1}$ and $21 < J \leq 39$ for $\text{H}_2^{17}\text{O}$ are kept, and similarly results that satisfy $28995.25119\text{cm}^{-1} < E_{\text{vp}} < 41088\text{cm}^{-1}$ and $21 < J \leq 51$ for $\text{H}_2^{18}\text{O}$ are kept. 41251 approximate levels are produced for $\text{H}_2^{17}\text{O}$ and 92305 levels are produced for $\text{H}_2^{18}\text{O}$. It is important to note that the choice of dissociation energy, $D_0$, is not entirely accurate. Even though $D_e$ is unaffected by the isotopic substitution, $D_0$ will be susceptible to change since the presence of the heavier isotope lowers the zero point energy, which increases the energy required for dissociation. This factor has been neglected since the nature of the procedure is only an approximation.
Computation and Error Analysis

FORTRAN Program

The calculation of the partition function was performed at several intervals over the course of this work using each of the data sets, and largely due to the ever-changing trial efforts in developing a suitable FORTRAN code. Ultimately, most calculations were performed with a single program (Appendix: Program 3). In this program the following actions are carried out (allowing for parameter changes to be applied for each isotopologue):

1) The augmented MARVEL line list (for a given isotopologue) and theoretical line lists provided by Shirin et al are read in;
2) Approximate rotational levels are produced within the appropriate intervals with Equation (24), by using Polyansky constants fitted to the appropriate isotopologue in Excel. These are combined with pure-vibrational energies from the list by Shirin et al using Equation (23);
3) The augmented MARVEL list previously read in is then combined with the newly calculated approximate levels;
4) Each of the energy levels in this combined list are then assigned with a nuclear degeneracy, given by Equation (6);
5) The enthalpy reference $E_0$ is then calculated by considering the partition function computation for the single reference temperature of 298.15 K [Equations (8), (11), (12), (13), (15), (17) and (20b) at $T = 298.15$ K];
6) The internal partition function and translational partition function, along with their moments are calculated [Equations (8), (12), (13), (14), (15) and (16)]. They are then combined to give a total partition function and its moments [Equations (11), (17) and (18)], from which the thermodynamic quantities of interest are derived [Equations (19), (20a), (21) and (22)]. This is performed over a DO loop, where equilibrium temperatures from 100K to 6000K are considered in increments of 100K;

The program also contains equations for the associated statistical uncertainties of these quantities, using the equation for statistical error combination:

$$\left(\Delta f\right)^2 = \left(\frac{\partial f}{\partial x}\right)^2 \left(\Delta x\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2 \left(\Delta y\right)^2 + \left(\frac{\partial f}{\partial z}\right)^2 \left(\Delta z\right)^2 \ldots$$  \hspace{1cm} (26)

[Where $f = f(x, y, z, ...)$]
Statistical errors given in this way arise due to the uncertainties of values used within the expressions, i.e. physical constants and uncertainties of the MARVEL energy levels. The values used for the physical constants used in the partition function equations were those recommended by IUPAC\textsuperscript{36}. Below is a table of the referenced values along with corresponding uncertainties:

<table>
<thead>
<tr>
<th>Physical Constant</th>
<th>Value</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Second Radiation constant</td>
<td>1.438769 m K</td>
<td>0.000012</td>
</tr>
<tr>
<td>Gas constant</td>
<td>8.314472 J/K mol</td>
<td>0.000015</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>1.3806504E-23 J/K</td>
<td>0.0000024E-23</td>
</tr>
<tr>
<td>Planck constant</td>
<td>6.62606896E-34 J s</td>
<td>Negligible</td>
</tr>
</tbody>
</table>

*Table 2: Physical constants and corresponding uncertainties, as by recommended by IUPAC*

For the translational partition function in particular, along with its moments [Equations (12), (15) and (16)], the molecular masses for the water isotopologues are also referenced from IUPAC\textsuperscript{37}, where the assumption of linear summation of constituent atomic masses is used. Below are their values and uncertainties (derived as a combination of individual uncertainties):

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>Mass</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}\textsuperscript{17}O</td>
<td>3.1574809E-26 kg</td>
<td>0.0000019E-26</td>
</tr>
<tr>
<td>H\textsubscript{2}\textsuperscript{18}O</td>
<td>3.3235397E-26 kg</td>
<td>0.0000020E-26</td>
</tr>
</tbody>
</table>

*Table 3: Isotopologue masses and uncertainties*

The value pressure used in the expressions for the translational partition function is that used in JANAF\textsuperscript{8}, which is a pressure of 100kPa.

One of the most important implications of the precision of these values is that any result that is calculated by using them can only be quoted to the same precision (significant figures). Any expression that contains a combination of values with different levels of precision can only yield an answer with the same precision as the least precise value. It is by this regime that uncertainties calculated later are deemed to be significant or negligible. From the parameters within each of the expressions, it can be seen that the total internal partition function and its moments can only be quoted to 7 significant figures, the Entropy and Specific Heat to 6 significant figures, and the Gibbs and Helmholtz functions to 5 significant figures.
**Compiling Results and Uncertainties**

Program 3 was run twice to produce results, once for H$_2^{17}$O and once for H$_2^{18}$O, where the changes of molecular mass and Polyansky constants were made appropriately for each isotopologue, as well as the input file of MARVEL data.

To ascertain the effect of the uncertainties in the MARVEL data on the final results, the internal partition function and its moments were computed twice more for each isotopologue; the uncertainties quoted in the MARVEL lists were added and subtracted to their corresponding energy values and then inputted into Equations (8), (13) and (14), and this produced lower and upper limits, respectively, for the internal partition function and its moments. The effect that this had was to produce error margins that were symmetric around the results, for example, for the internal partition function error margins were symmetric about the results to a maximum of 9 decimal places and minimum of 8 decimal places, for both isotopologues.

To the level of precision that results are quoted to, the MARVEL data is shown to have no effect on their values as the contribution from the MARVEL uncertainties is negligible to this degree. For the internal partition function and its moments, there is only significant error due to the uncertainty of the second radiation constant used within the equation. The uncertainty on the translational partition function is seen to be negligible, due to the error margins of the physical constants within the equation being significantly small. Therefore it does not contribute to uncertainty on the total partition function, and hence the thermodynamic quantities.

Even if the MARVEL data had a significant effect on the error margins of the results, then (coupled with the statistical error arising due to the physical parameters used throughout) it could only be regarded as a total error for the results that are exclusively dependent on the MARVEL data. For both H$_2^{17}$O and H$_2^{18}$O, the internal partition function is only dependent on the MARVEL data for T ≤ 200K. Above this, introduction of the theoretical data from Shirin et al begins to affect the results, since there is such little coverage of experimental MARVEL data, but these are negligible compared to the introduction of approximate levels.

The uncertainty of the enthalpy reference is estimated as 9904.3 ± 0.2 Jmol$^{-1}$ for H$_2^{17}$O and 9904.5 ± 0.1 Jmol$^{-1}$ for H$_2^{18}$O. The uncertainties are not based on a combination of statistical errors, since at a temperature of 298.15 K the partition function is not exclusively dependent on the MARVEL data (the MARVEL data will not have introduced a significant error anyway). Instead it is a slightly less rigorous estimate based on the difference between the values calculated only using MARVEL data and values calculated with augmented MARVEL data. Work on H$_2^{16}$O by Vidler and
Tennyson\textsuperscript{27} showed this value to be $9904.1 \pm 0.1 \text{ J mol}^{-1}$. JANAF\textsuperscript{8} quotes a value of $9904 \text{ J mol}^{-1}$, and Harris \textit{et al}.\textsuperscript{19} produced a value of $9895.4 \text{ J mol}^{-1}$.

At low temperatures, the uncertainties calculated as a result of statistical error combination can be regarded as total errors. It is quickly seen, however, that the introduction of approximate levels begins to dominate the total error on the results, along with the lack of convergence of the partition function.

**Effect of Approximate Levels**

Since the data provided by Shirin \textit{et al}.\textsuperscript{12} is considered to be close to experimental accuracy, their inclusion in the summation will have an effect that is negligible compared to that due to the presence of approximate levels. It is expected that for low temperatures the approximate levels will have no effect on the partition function or any of the other derived quantities, and only become important at higher temperatures. The degree of the effect they have needs to be quantified somehow.

The interest lies within the convergence of the partition function. As previously stated, low-lying levels suffice in the convergence at low temperatures, and this can be performed using the MARVEL/Shirin data. Higher-lying levels are needed to converge at higher temperatures, and these are provided by the approximate levels produced in the Polyansky method. Errors on results are expected to be larger at these temperatures, since the approximate levels are not at all accurate and as such can also lead to a lack of convergence, and especially since levels up to dissociation have not been considered in this work.

A method considered by Harris \textit{et al}. (also used by Vidler and Tennyson) was used in order to estimate errors introduced by the inclusion of approximate levels, and has also been used in this work. It must however be stated that the method does not contain a great deal of mathematical rigor. It involves testing the convergence of the results for varying amounts of approximate energy levels.

The main result includes MARVEL/Shirin levels up to and including $J = 20$ for both isotopologues. For $J \geq 21$ approximate levels are used, and it is at this $J = 20$ cut off point that errors start to become significantly large.
One can test the effect of the inclusion of the approximate levels by truncating the MARVEL/Shirin data at a particular value of J and performing the summation again with approximate levels from this point. In doing this in integer steps for the J cut off from 0 through to 20, a graph can be plotted to show the degree of convergence; the value of J from which approximate levels are used (the J cut off point) against the value of the quantity of interest. If the value of the thermodynamic quantity has converged by the J = 20 limit imposed by the MARVEL/Shirin data, then the result can be said to be independent of the approximate levels (this method is done by adapting Program 3).

![Convergence of Zint](image)

Figure 3: Convergence of the internal partition function for H$_2^{17}$O

The example graph in Fig. 3 shows the internal partition function as a function of the J value from which approximate levels are used, $J_{\text{CUT OFF}}$, (and below which MARVEL/Shirin data is used) for three different temperatures. Where the partition function has been computed exclusively by use of approximate levels, i.e. at $J_{\text{CUT OFF}} = 0$, an under-estimation of the internal partition function is observed (seen in the curves sloping from below). For each of the temperatures considered in the above graph, the results converge before the $J_{\text{CUT OFF}} = 20$ limit, and thus these results are not affected by the presence of the approximate levels. The errors associated with these results will be purely due to the statistical errors mentioned earlier.

However when convergence is not observed in this test for a given equilibrium temperature, it is apparent that the use of approximate levels has had consequences. Since the approximate levels do not span a complete set up to dissociation it is evident that convergence will not be possible for temperatures near to and including 6000K at all. However at lower temperature ranges lack of
convergence will not be due to an insufficient amount of energy levels, but instead due to the lack of accuracy of the approximate levels.

For temperatures beyond which convergence does not occur by the $J_{\text{cut off}} = 20$ limit, the curve created is extrapolated further to an estimated converged results. This is where the approach becomes less mathematically rigorous and more of a subjective interpretation. Nevertheless, attempts have been made to keep the process as systematic as possible. In the Microsoft Excel program it is possible to fit fairly simple functions to curves that have been produced by tabulating $x$- and $y$-axis values. These 'best fit' lines can be extended to intervals beyond the original data set, and thus in the effort to extrapolate the curves in these convergent tests semi-arbitrary data points were added to the data sets by fitting them along the extended functions fitted by Excel until the slopes of the curves were of zero-gradient, i.e. at the point of convergence. By doing this, the estimated error is taken to be the difference between the partition function value at the $J = 20$ cut off point, and the value at the estimated point of convergence.

A rough schematic of the idea is shown below:

![Figure 4: Estimating Errors due to approximate levels](image)

This difference is then quoted as a percentage error for the value of the quantity at the $J = 20$ cut off.

As well as testing convergence by varying the cut off of $J$ value, another convergence test was done which considered energy values as a cut off point instead. In increments of $1000\text{cm}^{-1}$ the
cut off point from which approximate levels were used ranged from 1000\,cm\(^{-1}\) up to dissociation, and the partition function and thermodynamic quantities were computed each time to test the effect this had on convergence. Total percentage errors due to approximate levels are then a combination of the percentage errors from each test.

At this point it is clear that the evaluation of results at temperatures near to and including 6000 K is clearly redundant, since the lack of a complete set of energy levels up to dissociation (coupled with the intrinsic inaccuracies of the approximate method) will produce very large errors, too large to be estimated with any reliability. The work of Harris \textit{et al}\(^{19}\) produced maximum percentage errors of 8\% for some of the thermodynamic quantities, and the later work of Vidler and Tennyson, which used more accurate data, produced percentage errors of a maximum value of 2\%.\(^{27}\) Therefore the decision was made to consider percentage errors in this work up to percentages of these magnitudes, which corresponded to a maximum temperature of 1500K for the internal partition function for each isotopologue. This is far from the coverage of the previous works which considered up to 6000K, but it is nevertheless a respectable amount considering the quantity of initial data included in the calculations.

The previous works on \(\text{H}_2^{16}\text{O}\) found the convergence test that truncated for energy values produced smaller errors, and were actually more sensitive to the J cut off convergence test\(^{19, 27}\). In this work, between the temperature ranges considered, the convergence tests found no significant error attributable to maximising/minimising the amount of approximate energy levels compared to the errors for J cut off test, whereas the previous works observed some significance. Unfortunately at this point this cannot be understood, but may have something to do with the erratic behaviour of the production of the approximate energy values due to the fit to the relatively small amounts of experimental data in this work compared to those of Vidler for example. Further work may be done on this with reference to the Polyansky constants produced in this work. However, this observation is still in accordance with the works of Vidler/Tennyson and Harris \textit{et al} in that convergence of results was more sensitive to changing J that Energy.
Results

Results are tabulated for the internal partition function along with its first and second moments, as well as for the Gibbs enthalpy and Helmholtz functions, and the Entropy and Specific Heat at constant pressure, all for equilibrium temperatures between 100 K and 1500 K. The results are also represented graphically, where the error margins shown are a combination of statistical error and error due to the use of approximate levels.

$H_2^{17}O$

<table>
<thead>
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<th>Temperature/K</th>
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<th>$Z''_{int}$</th>
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Table 4: Results for H2(17)O - (a)

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Table 5: Results for H$_2$(17)O - (b)

Figure 5: H$_2$(17)O - Internal Partition Function
**Figure 6: H$_2$(17)O - 1st Moment of Internal Partition Function**

**Figure 7: H$_2$(17)O - 2nd Moment of Internal Partition Function**
Figure 8: H2(17)O - Gibbs Enthalpy Function

Figure 9: H2(17)O - Helmholtz Function
Figure 10: H$_2$(17)O - Entropy

Figure 11: H$_2$(17)O - Specific Heat at Constant Pressure
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Table 6: Results for H\(^2\)O - (a)

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Table 7: Results for H2(18)O - (b)

Figure 12: H2(18)O - Internal Partition Function

Figure 13: 1st Moment of Internal Partition Function
Figure 14: H$_2$(18)O - 2nd Moment of Internal Partition Function

Figure 15: H$_2$(18)O - Gibbs Enthalpy Function
Figure 16: H2(18)O - Helmholtz Function

Figure 17: H2(18)O - Entropy
Below tables are listed presenting thermodynamic quantities at low temperatures. These are justified since it is seen that for low temperatures in the results computed above, convergence is seen at the very least at 100K.

\[ H_2^{17}O \]

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<tr>
<th>Temp./K</th>
<th>( Z_{\text{int}} )</th>
<th>( Z'_{\text{int}} )</th>
<th>( Z''_{\text{int}} )</th>
<th>( \text{gef} )/JKmol(^{-1})</th>
<th>( \text{hef} )/Jmol(^{-1})</th>
<th>( S )/JKmol(^{-1})</th>
<th>( C_p )/JKmol(^{-1})</th>
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Table 8: \( H_2^{17}O \) - Thermodynamic Quantities at Low Temperatures

\[ H_2^{18}O \]

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Table 9: \( H_2^{18}O \) - Thermodynamic Quantities at Low Temperatures

For \( H_2^{17}O \), \( Z_{\text{int}} \) and \( Z'_{\text{int}} \) are found to be unaffected by the use of approximate levels for \( T \leq 300 \) K, and \( T \leq 200 \) K in the case of \( Z''_{\text{int}} \), \( T \leq 600 \) K for gef, \( T \leq 200 \) for hcf, \( T \leq 500 \) for S and \( T \leq 300 \) for \( C_p \).
Similarly for H218O, $Z_{int}$ and $Z_{int}'$ are unaffected for $T \leq 400$ and $T \leq 300$ respectively, $T \leq 200$ for $Z_{int}''$, $T \leq 700$ for gef, $T \leq 300$ for hcf, $T \leq 400$ for S and $T \leq 300$ for $C_p$. Note that the precision of quoted results has been taken into account.
Evaluation and Discussion

The majority of works in the scientific literature have been attributed to the standard \( \text{H}_2^{16}\text{O} \) molecular variation, though the isotopologues considered in this work have also been regarded seriously. This work presents the first time that accurate MARVEL-produced data has been used in the calculation of the partition function for \( \text{H}_2^{17}\text{O} \) and \( \text{H}_2^{18}\text{O} \), which provides an interesting opportunity to compare with data produced by other methods (at low temperatures at least).

One of the first things to point out is a particular detail previously mentioned. Due to the lowering of energies from isotopic substitution, and the nature of the exponential factor within the partition sum, the value of the partition function for the \( \text{H}_2^{17}\text{O} \) and \( \text{H}_2^{18}\text{O} \) isotopologues should be greater than that of the \( \text{H}_2^{16}\text{O} \) variety, with \( \text{H}_2^{18}\text{O} \) being the largest of the three for a given equilibrium temperature. In comparison with the results produced by Vidler and Tennyson, this only seen to be the case for \( T \leq 1200\text{K} \) for \( \text{H}_2^{17}\text{O} \) and \( T \leq 1300\text{K} \) for \( \text{H}_2^{18}\text{O} \). This is a clear indication of the convergence problems due to the lack of more accurate high-lying levels used in the partition sum. Vidler and Tennyson had \(~200,000\) levels \(^{27}\) that were considered to be of good enough accuracy, compared to the 50039 (MARVEL-Shirin combination) levels used in this work. Their approximate levels also spanned up to dissociation, another aspect that was lacking in this work, and their total energy level coverage was greater than 800,000, whereas in this work only 91,290 levels were available for \( \text{H}_2^{17}\text{O} \) and 142,344 for \( \text{H}_2^{18}\text{O} \). It is still the case though that the consistency of \( \text{H}_2^{18}\text{O} \) having greater partition function values than \( \text{H}_2^{17}\text{O} \) is still observed in within this work. Below is a graph showing the differences between the partition function values for the isotopologues considered in this work and the values for the \( \text{H}_2^{16}\text{O} \) molecule derived by Vidler and Tennyson. The x-axis corresponds to a difference of zero. In the positive y-axis it is seen that the partition functions for \( \text{H}_2^{17}\text{O} \) and \( \text{H}_2^{18}\text{O} \) have higher values than \( \text{H}_2^{16}\text{O} \), but then fall below at 1200K and 1300K, respectively; \( \text{H}_2^{18}\text{O} \) always has a higher partition function value than \( \text{H}_2^{17}\text{O} \).
However the maximum differences from the Vidler/Tennyson data are around 0.9% for H$_2^{17}$O and 0.4% for H$_2^{18}$O, which both lie within the corresponding margins of error at those temperatures. For most of the results derived in this work, values corresponding to temperatures of around 1000K and under can be taken more seriously, considering that they will be majorly dependent on the MARVEL data, coupled with the high accuracy, semi-theoretical data provided by Shirin et al.

Within the HITRAN database numerous partition sums are tabulated for a variety of molecules of interest for the principle isotopic species and some of their isotopomers/isotopologues. The temperature ranges cover 70 – 3005K. Their methods included a variety of different calculative techniques for determining a partition function, including the direct summation approach, approximate methods that are similar to those used in this work, and the use of “sophisticated analytical developments”. For their work on the H$_2^{17}$O and H$_2^{18}$O isotopologues, energy levels were derived from the Watson (Molecular) Hamiltonian, which produced energy levels to around 7000cm$^{-1}$. This meant that their partition functions only converged by this method for the low temperature regimes; for higher temperatures an analytical formula by Watson was used. Below are graphical representations showing the differences between partition sums in this work and the corresponding values taken from the HITRAN database.
Figure 20: Graph of difference line between results from this work and those from HITRAN [H2(17)O]

Figure 21: Graph of difference line between results from this work and those from HITRAN [H2(18)O]

The comparisons show that, for both isotopologues convergence of the partition function has not been observed in the HITRAN data for $T \leq 700$K. Beyond this temperature however the partition sums calculated in this work appear to fall below the values determined in HITRAN. Note that these graphs exaggerate the difference; the maximum differences amount to 1.8% for both isotopologues, which actually falls within the estimated margins of error calculated for both of them. It is above 700K that the introduction of approximate levels begins to affect the value of the partition function, explained previously in the error analysis section. In HITRAN, low-lying levels were produced by a Schrodinger equation solution, whereas higher-lying energy levels were computed...
from a mixture of an approximate method akin to that discussed in this work, and by using various cited analytical approaches. It would make sense that at low temperatures, the partition functions in this work would be more accurate than those of HITRAN, where they would be dependent largely on the Hamiltonian solution, and this can explain why at temperatures under 700K the partition functions of HITRAN do not converge to a high enough value to match those computed in this work. The nature of the deviations above 700K seen in the above graphs will be down to a mixture of the inaccuracies of the approximate levels produced in this work, and the reliability of the approximate and analytical coupled methods used in HITRAN.

Coverage of thermodynamic data for the two isotopologues studied in this work has also been made by Martin et al.\textsuperscript{28} Their method was \textit{ab initio}, with the aim of producing an anharmonic potential energy surface for the water molecule to derive various spectroscopic parameters for isotopomers of water, and derived some thermodynamic quantities by a hybrid method that combined an analytic approach with a direct summation process.\textsuperscript{28} Listed are the Gibbs Enthalpy function, Helmholtz function, Specific Heat at Constant Pressure, and the Entropy, for both H\textsubscript{2}\textsuperscript{17}O and H\textsubscript{2}\textsuperscript{18}O. The enthalpy reference was not standardised as H(298.15K) = E\textsubscript{0}, as in JANAF, but corrections to the Helmholtz function value at the reference temperature (setting it to zero) organised it into the system used in this work. Below are comparisons between this work and that of Martin et al, for the Helmholtz function, the Entropy, and the Specific Heat for both isotopologues.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure22.png}
\caption{Graph of difference line between results from this work and those from Martin et al [H2(17)O]}
\end{figure}
Figure 23: Graph of difference line between results from this work and those from Martin et al [H2\(17\)O]

Figure 24: Graph of difference line between results from this work and those from Martin et al [H2\(17\)O]
$H_2^{18}O$

Figure 25: Graph of difference line between results from this work and those from Martin et al [H2(18)O]

Figure 26: Graph of difference line between results from this work and those from Martin et al [H2(18)O]
Figure 27: Graph of difference line between results from this work and those from Martin et al [H2(18)O]

Again the comparisons show that the results in this work begin to deviate after about 700K, a consequence of the use of approximate levels (an incomplete set). The values obtained for the Specific Heat by Martin et al fall within the error margins of the values found in this work, for both isotopologues, with maximum differences of 5% for both isotopologues at the limits of the temperature range considered. The maximum difference between the entropy values in the two works is 0.3% for $H_2^{17}O$ and 0.4% for $H_2^{18}O$, and that of the Helmholtz function values is 1.4% for both. It should be noted that the values for the Specific Heat obtained in this work are susceptible to large errors due to their dependence on the square of the first moment of the partition function, and also on the second moment, and convergence issues with these quantities will therefore be amplified in the Specific Heat results. However the comparisons show that the same sort of characteristic variation occurs as a function of temperature, and at higher temperatures (within the range considered) it is still present, only deviated due to use of approximate methods. What is also observed is that there are instances where the values of Entropy and Specific Heat converge to higher values that those of Martin et al, and then drop below after a certain temperature, a characteristic that can almost certainly be attributed to approximate levels beginning to become significant at those temperatures. It is somewhat speculative, but in such a small temperature range it is most likely a certainty that the functions derived in this work are the ones that falter at these temperatures since there are not enough accurate energy levels to maintain the results at higher temperatures.

One of the biggest drawbacks in this work (apart from the fact that accurate energy level data was sparse) was that the fitting of the Polyansky constants did not produce values up to
dissociation, and near the highest J limits considered the values tended to grow in anomaly. Further work could be done considering this either by using Polyansky's constants, as did Harris et al\textsuperscript{19}, or by the re-fitted constants of Vidler and Tennyson\textsuperscript{27}. These constants were originally fitted for H\textsubscript{2}O, but given their intrinsic approximate nature it may be considered a reasonable suggestion and may be of interest to pursue this in the future (in fact Vidler's constants were used in preliminary tests during this work). Reliable and accurate spectroscopic data would of course improve the study tremendously, and updates of MARVEL data can lead to further persuasion. As well as ensuring low temperature results are as accurate as possible, an increase in MARVEL-type data would also help to produce better fits in the approximate methods that were considered in this work, and therefore better coverage of approximate energy levels.

Since the data provided by Shirin et al was considered to be close to experimental accuracy, extension of that data would also improve the results at higher temperatures. Ideally purely experimental data would be desired up to those types of ranges, but the limitations of spectroscopic measurements could mean that these would be far off, and \textit{ab initio} calculations should still be regarded.
Conclusion

The internal partition functions for the $\text{H}_2^{17}\text{O}$ and $\text{H}_2^{18}\text{O}$ isotopologues of water have been explicitly computed using 2723 and 5131 highly accurate energy levels, respectively. These are each augmented to an amount of 50039 levels by supplementary, close-to-experimentally accurate data. In all, 91,290 levels were used on the computation for $\text{H}_2^{17}\text{O}$ and 142,344 for $\text{H}_2^{18}\text{O}$, where the accurate data has been augmented by an approximate method using a Padé approximant. From these calculations, the Gibbs Enthalpy function, Helmholtz function, Entropy and Specific Heat are calculated for each as a function of temperature, ranging from 100K to 1500K at a standard JANAF pressure of 100kPa.

The original aim of the work was to produce results up to the temperature of 6000K, but the lack of accurate data compared to previous works, along with an approximate method that could not be extrapolated to higher lying energy levels meant that few results could be considered to be useful. For $T \leq 700K$, where approximate levels don’t play a major role in producing results, computed values may be taken seriously, and at very low temperatures where the values are not affected by the introduction of approximate levels at all, results can be deemed to be very accurate to the precision quoted.

This work provides a first in the use of highly accurate data to compute these thermodynamic values, and has proved to be of interest in comparing with ab initio results and can be used as a bench mark for the future when work in this field is taken forward. This can be performed if more accurate data becomes available; either by MARVEL or some other method, and work in producing more accurate potential energy surfaces to higher degrees of energy can further help the process.

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References


5) The International Association for the Properties of Water and Steam (IAPWS). (2001). Guideline on the Use of Fundamental Physical Constants and Basic Constants of Water. Gaithersburg, Maryland, USA.


14) Ibid., p. 92.

15) Ibid., p. 93.
16) Ibid., pp. 8-9.
17) Ibid., pp. 93-94.
18) Ibid., p. 75.
20) Ibid. 13, at p. 44.
21) Ibid., p. 66.
23) Ibid., p. 388
25) Ibid. 22, at p. 250
29) Ibid. 24, at p. 151.
30) Ibid., p. 159.
33) Ibid. 24, at pp. 125-126.
34) Ibid., pp. 138-140.
Appendix

FORTRAN Programs

Program 1: Counter

```fortran
program count
    implicit none
    integer:: N, a

    open(10,File="list.txt")

    N=0
    do 10
        read(10,*,iostat=a)
        if(a==-1)exit
        N=N+1
    10 continue

    print *, N

end program
```

Program 2: Replace

```fortran
program replace
    implicit none
    integer:: N,M,a,ij,match
    integer,allocatable:: Jt(:),Kat(:),Kct(:),v1t(:),v2t(:),v3t(:),&
                        Je(:),Kae(:),Kce(:),v1e(:),v2e(:),v3e(:)
    double precision,allocatable:: E16t(:),E17t(:),E18t(:),E17e(:),E18e(:),dEe(:)

    open(10,File="theo161718.txt") !this one must be larger file, ie theoretical (labels are denoted with 't')
    open(11,File="expdata.txt") !this is the smaller file, ie experimental (labels are denoted with 'e')
    open(12,File="theonew.txt") !this is the new file of theoretical levels which are not found in the experimental list

    N=0
    do
        read(10,*,iostat=a)
        if(a==-1)exit
        N=N+1
    end do

    M=0
    do
        read(11,*,iostat=a)
        if(a==-1)exit
        M=M+1
    end do

    Allocate(Jt(N),Kat(N),Kct(N),v1t(N),v2t(N),v3t(N),E16t(N),E17T(N),E18t(N))

    rewind(10)
```

59
do i=1,N
read(10,*)Jt(i),Kat(i),Kct(i),v1t(i),v2t(i),v3t(i),E16t(i),E17t(i),E18t(i)
end do

close(10)

Allocate(Je(M),Kae(M),Kce(M),v1e(M),v2e(M),v3e(M),E17e(M),dEe(M))

rewind(11)
do i=1,M
read(11,*)Je(i),Kae(i),Kce(i),v1e(i),v2e(i),v3e(i),E17e(i),dEe(i)
end do
close(11)

do i=1,N
Do j=1,M
if(Jt(i).EQ.Je(j) .and. Kat(i).EQ.Kae(j) .and. Kct(i).EQ.Kce(j) .and. & v1t(i).EQ.v1e(j) .and. v2t(i).EQ.v2e(j) .and. v3t(i).EQ.v3e(j))then
match=1
exit
else
match=0
end if
end do
if(match==0)then
write(12,100)Jt(i),Kat(i),Kct(i),v1t(i),v2t(i),v3t(i),E18t(i)
100 format(I2.1,4x,I2.1,4x,I2.1,4x,I2.1,4x,I2.1,4x,I2.1,4x,f15.6)
end if
end do
end program

Program 3: Results

program resulter
implicit none
integer::i,n,M,O,y,x,Jp,Kap,Kcp,Jt,Kat,Kct,v1t,v2t,v3t,T,match,Ka,Kc,v1,v2,v3
integer,allocatable:: Jpa(:),Kapa(:),Kcpa(:),v1ta(:),v2ta(:),v3ta(:),Jau(:),Kaau(:),& Kcau(:),v1au(:),v2au(:),v3au(:),J(:) ! a's denote ARRAYS, au's denote from AUGMENTED file double precision ::
double precision, allocatable:: ETOTa(:),g(:),Eau(:),E(:),dEau(:) ! au's denote from the augmented list
open(10,file="theo161718.txt")
open(11)
open(12,file="exptheodata.txt")
open(13)
open(14,file="results.txt")

! Approximate data denoted by 'p'
! Theoretical data denoted by 't'
n="number"! J level for which the Ka=0 level is still bound
M=0
!
! VIDLER CONSTANTS (H2(16)o)
!A=28.08871866
!B=14.44534174  
!C=9.248956729  
!dJ=0.001781836  
!dJK= -0.009071451  
!dK=0.02511696

!H2(17)O  
!A=29.40017489343030000  
!B=11.16738627451170000  
!C=11.16738627451170000  
!dJ= -0.00189972840385545  
!dJK= -0.07524108589577940  
!dK=0.19863294031042800

!H2(18)O  
!A=28.98972515810090000  
!B=11.36213494503860000  
!C=11.36213494503860000  
!dJ=0.00169045758562199  
!dJK= -0.06539008923190100  
!dK=0.14908979171266200

Do  
Read (10,*),Jt,Kat,Kct,v1t,v2t,v3t,E16t,E17t,E18t  
if(x==-1)exit  
M=M+1  
DO Jp=21,n  
DO Kap=0,Jp  
DO Kcp=(Jp-Kap),(Jp-Kap+1)  
IF(Kcp>Ja)EXIT  
if(Jt.NE.0)exit  
C0=((A-((B+C)/2))*(Kap**2))+(((B+C)/2)*(Jp*(Jp+1)))  
C1=-(dJ*((Jp*(Jp+1))**2))-(dJK*(Kap**2)*(Jp*(Jp+1)))-(dK*(Kap**4))  
Er=(C0**2)/(C0-C1)

ETOT=Er+E18t  
if(ETOT<"MaxEnergy")EXIT  
IF(ETOT>"Dissociation")EXIT

write(11,*),Jp,Kap,Kcp,v1t,v2t,v3t,ETOT  
end do  
end do  
end do

rewind(11)  
M=0  
read(11,*,iostat=x)  
if(x==-1)exit  
M=M+1  
enddo

O=0  
do  
read(12,*,iostat=x)  
if(x==-1)exit  
O=O+1  
enddo
allocate(Jpa(m),Kapa(m),Kcpa(m),v1ta(m),v2ta(m),v3ta(m),ETOTa(m))

rewind(11)

do i=1,M
read(11,*)Jpa(i),Kapa(i),Kcpa(i),v1ta(i),v2ta(i),v3ta(i),ETOTa(i)
write(13,*)Jpa(i),Kapa(i),Kcpa(i),v1ta(i),v2ta(i),v3ta(i),ETOTa(i)
end do
close(11)

allocate(Jau(o),Kaau(o),Kcau(o),v1au(o),v2au(o),v3au(o),Eau(o),dEau(o))

rewind(12)

do i=1,O
read(12,*)Jau(i),Kaau(i),Kcau(i),v1au(i),v2au(i),v3au(i),Eau(i),dEau(i)
write(13,*)Jau(i),Kaau(i),Kcau(i),v1au(i),v2au(i),v3au(i),Eau(i)
end do
close(12)

rewind(13)
M=0

do
read(13,*,iostat=x)
if(x==-1)exit
M=M+1
enddo

! allocating the needed arrays
allocate(J(m),E(m),g(m))

! reading the arrays
rewind(13)

do i=1,M
read(13,*)J(i),Ka,Kc,v1,v2,v3,E(i)
! Defining value of g
IF (MOD(Ka+Kc+v3,2)==0) then
   g(i)=0.25 !Para
else if (MOD(Ka+Kc+v3,2)==1) then
   g(i)=0.75 !Ortho
end if
enddo
close(13)

! Necessary constants

c2=1.438769 ! Second radiation constant UNCERTAINTY = 0.000012
delc2=0.000012
R=8.314472 ! Avogadro constant UNCERTAINTY = 0.000015
delR=0.000015
k=1.3806504E-23 ! Boltzmann constant UNCERTAINTY = 0.0000024E-23
delk=0.0000024E-23
h=6.62606896E-34 ! Planck constant UNCERTAINTY = 0.00000033E-34 THIS IS TAKEN TO BE NEGLIGIBLE

PI=2.D0*DASIN(1.D0) ! Pi
! Defining Translational Partition Function required quantities
M17=3.1574809E-26 ! Mass of (17)\text{O} molecule UNCERTAINTY = 0.0000019E-26
M18=3.3235397E-26 ! Mass of (18)\text{O} molecule UNCERTAINTY = 0.0000020E-26
P=10**5 ! (1 bar) ! Pressure

! SIGNIFICANT FIGURES!

! THE INTERNAL PARTITION FUNCTION, ALONG WITH ITS 1ST AND 2ND MOMENTS, CAN ONLY BE COMPUTED TO 7 SIGNIFICANT FIGURES, DUE TO c2.
! FOR TRANSLATIONAL PARTITION FUNCTION, MAXIMUM PRECISION IS 6 SIG FIGS, DUE TO PRESSURE

! THE OVERALL TOTAL PT CAN ONLY BE QUOTED TO 6 SIG FIGS ALSO

! ALL THERMODYNAMIC QUANTITIES CAN BE QUOTED TO 6 SIG FIGS
! HOWEVER, GEF AND HEF, WHICH DEPEND ON H_0 CAN ONLY BE QUOTED TO 5 SIG FIGS

! UNCERTAINTIES!

! UNCERTAINTIES DUE TO MARVEL DATA HAVE BEEN FOUND TO BE NEGLIGIBLE AT THE DEGREE OF PRECISION QUOTED FOR THE INTERNAL PARTITION FUNCTION
! THIS IS ALSO TRUE FOR THE TRANSLATIONAL PARTITION FUNCTION

! HOWEVER THE INTERNAL PARTITION FUNCTION HAS STATISTICAL UNCERTAINTY DUE TO c2. -> THIS IS TAKEN TO BE UNCERTAINTY ON TOTAL PT

! STATISTICAL UNCERTAINTIES FOR THERMODYNAMIC QUANTITIES ARE CALCULATED THROUGH UNCERTAINTIES ON INITIAL VALUES

! Calculating H_0 Enthalpy Reference!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
Zint_H=0
dZint_H=0
do x=1,M
! Internal PF
Zint_H=Zint_H+g(x)*((2*J(x))+1)*exp(-E(x)*c2/275)
dZint_H=dZint_H+g(x)*((2*J(x))+1)*(c2*E(x)/275)*exp(-E(x)*c2/275)
end do

! Translational PF
Ztran_H=((2*PI*M18*k*275)/(h**2))**(1.5))*((k*275)/P)
dZtran_H=(2.5)*((2*PI*M18*k*275)/(h**2))**(1.5))*((k*275)/P)

! Total PF
Z_H=Ztran_H*Zint_H
dZ_H=(Ztran_H*dZint_H)+(Zint_H*dZtran_H)
!
!
H_0=R*298.15*(dZ_H/Z_H)
!
!
print*, H_0
!
delH_0="number"
! MAXIMUM OF 5 SIGNIFICANT FIGURES DUE TO ABSOLUTE TEMPERATURE
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!!!

! computing the Internal/Translational Partition Function for several values of T
do i=50,90,10
  T=0+i
  Zint=0
  delZint=0
  dZint=0
  deldZint=0
  d2Zint=0
  deld2Zint=0
  do x=1,M
    ! Internal PF
    Zint=Zint+g(x)*((2*J(x))+1)*exp(-E(x)*c2/T)
    del1=del1+((-(E(x)/T)*g(x)*((2*J(x))+1)*exp(-E(x)*c2/T))
    dZint=dZint+g(x)*((2*J(x))+1)*(c2*E(x)/T)*exp(-E(x)*c2/T)
    del2=del2+((E(x)/T)*g(x)*((2*J(x))+1)*exp(-E(x)*c2/T))
    d2Zint=d2Zint+g(x)*((2*J(x))+1)*((c2*E(x)/T)**2)*exp(-E(x)*c2/T)
  end do
  delZint=SQRT((del1**2)*(0.000012**2))
  deldZint=SQRT((del2**2)*(0.000012**2))
  deld2Zint=SQRT((del3**2)*(0.000012**2))

  ! Translational PF
  Ztran=((2*PI*M18*k*T)/(h**2))**(1.5)*((k*T)/P)
  dZtran=(2.5)*(((2*PI*M18*k*T)/(h**2))**(1.5))*((k*T)/P)
  d2Ztran=(8.75)*(((2*PI*M18*k*T)/(h**2))**(1.5))*((k*T)/P)

  !ALL OF THESE HAVE NEGLIGIBLE UNCERTAINTIES

  ! Total PF
  Z=Ztran*Zint
  delZ=SQRT(((Ztran**2)*(delZint**2))+((Zint**2)*(0)))
  dZ=(Ztran*dZint)+(Zint*dZtran)
  delZ=SQRT(((Ztran**2)*(delZint**2))+((Zint**2)*(0)))
  d2Z=(Ztran*d2Zint)+(Zint*d2Ztran)+2*(dZtran*dZint)
  deldZ=SQRT(((Ztran**2)*(deldZint**2))+(((d2Ztran)**2)*(delZint**2))

  !gef
  GEF=R*log(Z) +((H_0)/T)
  delGEF=SQRT(((log(Z)**2)*(delR**2))+(((R/Z)**2)*(delZ**2))+((1/T)**2)*(delH_0**2))

  ! hef
  HEF=R*T*(dZ/Z)-H_0
  delHEF=SQRT(((T*(dZ/Z)**2)*(delR**2))+((R*T*(1/Z)**2)*(delZ**2))+((R*T*(-dZ/(Z**2)))**2)*(delZ**2))+((-1**2)*(delH_0**2)))
! Entropy
S=(R*(dZ/Z))+(R*log(Z))
delS =SQRT(((dZ/Z)+log(Z)**2)*(delR**2))+(((R/Z)**2)*(deldZ**2))+(((R*(-dZ/(Z**2)))+(R/Z)**2)* (delZ**2))

! Specific Heat at constant pressure
Cp=R*((d2Z/Z) -((dZ/Z)**2))
delCp =SQRT(((d2Z/Z) -((dZ/Z)**2))**2)*(delR**2))+(((R/Z)**2)*(deld2Z**2))+(((R*(-2*dZ/(Z**2)))**2)* (deldZ**2))+(((R*(d2Z/(Z**2))+(2*(dZ**2))/(Z**3)))**2)*(delZ**2))

write(14,100) T,Zint,dZint,d2Zint,Gef,HEF,S,Cp
100 format(I4.3,4x,f20.10,4x,f20.10,4x,f20.10,4x,f20.10,4x,f20.10,4x,f20.10)
enddo

! THIS PROGRAM AUGMENTS THE EXPERIMENTAL/THEORETICAL LEVELS WITH APPROXIMATE LEVELS WITH |j|>20
! DEcimal points. Remember through propagation of results decimal points can be to no further accuracy than the original data
!MAXIMUM THEO E17 = 29045.71432 CM-1
!MAXIMUM THEO E18 = 28995.251119 CM-1

end program

Additional Results

Results for H$_2^{17}$O up to 6000K

Table 10: Results - H$_2$(17)O

<table>
<thead>
<tr>
<th>T</th>
<th>Zint</th>
<th>Zint'</th>
<th>Zint''</th>
<th>gef</th>
<th>hef</th>
<th>S</th>
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