

Recommended ideal-gas thermochemical functions for heavy water and its substituent isotopologues

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Accurate temperature-dependent ideal-gas internal partition functions, $Q_{\text{int}}(T)$, and several derived thermochemical functions are reported for heavy water, with an oxygen content corresponding to the isotopic composition of the Vienna Standard Mean Ocean Water (VSMOW), and its constituent isotopologues, D_2^{16}O , D_2^{17}O , and D_2^{18}O , for temperatures between 0 and 6000 K. The nuclear-spin-dependent partition functions are obtained by the direct summation technique, involving altogether about 16 000 measured and more than nine million computed bound rovibrational energy levels for the three molecules. Reliable standard uncertainties, as a function of temperature, are estimated for each thermochemical quantity determined, including the Gibbs energy function, the enthalpy, the entropy, and the isobaric heat capacity of the individual *ortho* and *para* nuclear-spin isomers, as well as of their nuclear-spin-equilibrated mixture and of heavy water. The accuracy of the heavy-water ideal-gas $C_p(T)$ is unprecedented, below 0.01% up to 1800 K. All the thermochemical functions are reported, in 1 K increments, in the supplementary material to this paper.

Keywords: bound and unbound states; heavy water; ideal-gas thermochemical quantities; nuclear motion theory; partition function

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1. Introduction

Despite the low cosmological abundance of deuterium, $D_2^{16}O$ has been detected in the interstellar medium.¹ $D_2^{16}O$ is particularly prevalent in the environments of low-mass star-forming regions, where its gas-phase abundance can be surprisingly large² and where analysis of ratios of *ortho* and *para* species point to formation at very low temperatures.³ Fractionation effects are important for the production of $D_2^{16}O$ in these environments.^{4–6} On earth, D_2O is used as a substitute for ordinary water in various fields of science and technology utilizing neutron scattering and related experimental and testing techniques. Following the recommendation of the International Association for the Properties of Water and Steam (IAPWS),⁷ “heavy water” is defined⁸ here as “water whose hydrogen content is pure 2H and whose oxygen has the isotopic composition of the Vienna Standard Mean Ocean Water (VSMOW)”.^{9–11} The terrestrial and extraterrestrial applications mentioned often require knowledge of a range of thermodynamic properties of heavy water as well as of its constituent isotopologues. The thermodynamic properties of heavy water have particular importance in the nuclear power industry.^{12–14} Consequently, IAPWS⁷ developed an international standard equation of state (EOS) for the thermodynamic properties of heavy water and adopted it in 1984. This EOS is based on a publication of Hill *et al.*,¹³ who fitted a polynomial to the ideal-gas heat capacity of heavy water calculated by Friedman and Haar (FH) in 1954.¹⁵ Although the 1984 IAPWS recommendation was slightly revised in 2005,¹⁶ to make the old equation conform to the ITS-90¹⁷ temperature scale, it kept employing the ideal-gas FH data. The results of FH¹⁵ form also the basis of the JANAF (Joint Army, Navy, and Air Force) tables of $D_2^{16}O$.¹⁸ The dimensionless data of FH¹⁵ have been converted to become the JANAF tables using a universal molar gas constant $R = 8.314\ 41(26)\ J\ mol^{-1}\ K^{-1}$, the value of this physical constant available in 1973.¹⁹ Furthermore, the FH data for isobaric heat capacities between 4000 and 5000 K were extrapolated linearly (except with a term in T^{-2}) to obtain the JANAF data up to 6000 K. JANAF can be considered as the most widely employed present-day general reference for thermochemical data.

Any standard EOS requires a formulation of the ideal-gas thermodynamic functions in order to compute properties of the real fluid, such as heat capacity, enthalpy, and entropy (sometimes called “caloric properties”), as well as properties such as the speed of sound in the given phase and the Joule–Thomson coefficient.²⁰ The EOS is typically written as a function of temperature and density. Part of the EOS is based on the ideal-gas contribution depending on properties of single molecules, while the residual part reflects intermolecular interactions. The ideal-gas contribution to the EOS requires an expression for the isobaric heat capacity of the ideal gas.

In 2012, IAPWS began an effort to develop a new heavy-water standard, which would take advantage of recent developments in EOS methodology and of new data. Since our molecular knowledge of heavy water, and therefore our ability to compute its ideal-gas thermodynamics, has greatly advanced compared to 1954, it is highly desirable to have new,

more accurate ideal-gas heat-capacity values to use in the new formulation. An inaccurate ideal-gas heat capacity would force the other fitted terms in the EOS to be distorted in order to fit experimental data for caloric properties. It is also desirable to have good estimates of the uncertainty in these heat capacities, in order to estimate the uncertainty in caloric properties calculated from the EOS – the uncertainty of the FH¹⁵ results is unclear and FH did not provide quantitative uncertainty estimates. Moreover, a clear disadvantage of the FH calculations is that they only concern D₂¹⁶O, the most abundant heavy-water constituent. Clearly, both the IAPWS and the JANAF heavy-water data are ready for a substantial revision.

Several of the present authors published a study in this journal on the determination of highly accurate ideal-gas thermochemical functions for H₂¹⁶O between 0 and 6000 K.²¹ In that study, hereafter referred to as **I**, it was shown that a limited set of highly accurate experimental rovibrational energy levels combined with a full set of first-principles computed energy levels up to (and beyond) dissociation provides the basis for highly accurate ideal-gas thermochemical functions up to rather high temperatures, 6000 K being the reported limit. For H₂¹⁶O the uncertainty in the internal partition function, $Q_{\text{int}}(T)$, below 600 K, where all the rovibrational energy levels needed to compute a fully converged $Q_{\text{int}}(T)$ are available experimentally, is less than 10⁻⁴ %. The uncertainty grows slowly as the temperature increases. Some of the present authors have also been involved in the determination of experimental rotational-vibrational energy levels on the ground electronic states of D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O.²² Hereby, in response to the interest in improving the quality of the IAPWS and JANAF data, we extend the ideal-gas thermochemical study of H₂¹⁶O to three deuterated isotopologues of water, D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O, which must be considered during the computation of thermodynamic properties of heavy water in the ideal-gas state.

Finally, note that there are only a very limited number of studies^{15,23–25} known to us on the ideal-gas $Q_{\text{int}}(T)$ and related thermochemical functions of any of the three heavy-water isotopologues. None of these studies come close to the accuracy of the present investigation, which heavily builds upon achievements in the fourth age of quantum chemistry.²⁶

2. Methodological Details

In what follows we compute ideal-gas thermochemical functions for the three isotopologues of heavy water employing a protocol advocated in **I**. According to that recommendation, two types of rovibrational energy level sets are utilized for computing $Q_{\text{int}}(T)$ for D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O. The first data set comprises all the available experimental energy levels, obtained via a measured active rotational-vibrational energy levels (MARVEL)^{27–29} analysis of the experimental rovibrational transitions,²² while the second data set contains first-principles computed levels determined as part of the present study.

Table 1. Uncertainties of the first-principles computed rovibrational energy levels of the three heavy-water isotopologues within the hybrid databases

Molecule	PES	Energy range / cm^{-1}	Uncertainty / cm^{-1}
D_2^{16}O	PES-S ³⁰	0–3000	0.1
		3000–5000	0.5
		5000–15000	1.0
	PES-P ³¹	0–15000	2.0
		15000–25000	5.0
		25000–30000	10.0
		30000–35000	100.0
		35000–40000	250.0
		above 40000	500.0
$\text{D}_2^{17}\text{O}, \text{D}_2^{18}\text{O}$	PES-S ³⁰	0–3000	0.1
		3000–5000	0.5
		5000–15000	1.0
	PES-P ³¹	0–15000	3.0
		15000–25000	7.5
		25000–30000	15.0
		30000–35000	150.0
		35000–40000	375.0
		above 40000	750.0

2.1. MARVEL energy levels

The most complete and probably most accurate source of bound measured rovibrational energy levels of D_2^{16}O , D_2^{17}O , and D_2^{18}O is the MARVEL database,^{22,32} obtained as part of an IUPAC-sponsored research effort.^{22,33–36} The number of validated energy levels in the published IUPAC database of measured rovibrational transitions and energy levels is 12 269, 338, and 3351 for D_2^{16}O , D_2^{17}O , and D_2^{18}O , respectively. The uncertainty of the MARVEL energy levels is between 10^{-6} and 10^{-2} cm^{-1} , each energy level carries its own uncertainty.

The labeling scheme employed for the rovibrational states of the D_2O isotopologues employs six quantum numbers: v_1 , v_2 , and v_3 are approximate normal-mode quantum numbers describing the vibrations (symmetric stretch, bend, and antisymmetric stretch, respectively), while the exact J rotational quantum number and the approximate K_a and K_c values are used for the description of the rotations.³⁷

2.2. First-principles energy levels

The first-principles bound rovibrational energy levels of the three isotopologues of heavy water utilized in this study were computed using two different potential energy surfaces (PES). For all three isotopologues, we used the best, semi-theoretical heavy-water PES,³⁰ hereby called PES-S, and the D2FOPI³⁸ variational nuclear-motion code to obtain the bound rovibrational energy levels up to 15 000 cm^{-1} and/or up to $J = 40$. The reason to employ this cutoff value is that the accurate, empirical PES-S was fitted only up to this value and it does not dissociate correctly.

In the case of D_2^{16}O , the PoKaZaTeL global adiabatic PES,³¹ developed for H_2^{16}O and hereby called PES-P, and the DVR3D nuclear-motion code³⁹ were used to determine all bound rovibrational energy levels up to the first dissociation limit ($D_0 = 41\,864.7\text{ cm}^{-1}$).⁴⁰ This data set contains slightly more than 3 000 000 energy levels and the largest rotational quantum number is $J = 98$. The accuracy of the energy levels computed with PES-P for H_2^{16}O , for which it was developed, is better, on average, than 1 cm^{-1} , even near the first dissociation limit. We could expect a similar though lower level of accuracy for the D_2^{16}O levels when using PES-P if the variational nuclear motion computations were highly converged (the kinetic energy operator employed is exact within the Born–Oppenheimer approximation). However, for the calculation of partition functions we do not need the same high level of accuracy as required for spectroscopic problems, especially not for the high-lying states (though we must ensure²¹ that the correct number of states is involved during the direct evaluation of the internal partition function). The converged computations of the H_2^{16}O bound-state rovibrational energy levels with $J = 0 - 68$ took several months of supercomputer time.³¹ For D_2^{16}O , the dissociation energy is somewhat larger and the maximum J value at which computations are required, as well as the level density, are much higher than for H_2^{16}O . To perform the computations of D_2^{16}O in a reasonable amount of time, with an accuracy deemed sufficient for the determination of the partition function, we chose to use different basis sets during the DVR3D computations for the different J values. With increasing J and increase of the energy we decreased the size of the basis and thus decreased the accuracy of the computed levels. Note that the energy levels with $J > 75$ were computed with a version of the DVR3D and ROTLEV programs modified to do high- J computations.^{41,42}

Table 1 lists the average accuracies, representing two standard deviations, estimated for the different energy regions for D_2^{16}O , D_2^{17}O , and D_2^{18}O for the two PESs.

2.3. The hybrid database

To ensure the highest possible accuracy of our energy level sets, we replaced the first-principles energy levels with MARVEL energies whenever it is possible and this way we obtain what is called hereafter the hybrid database.

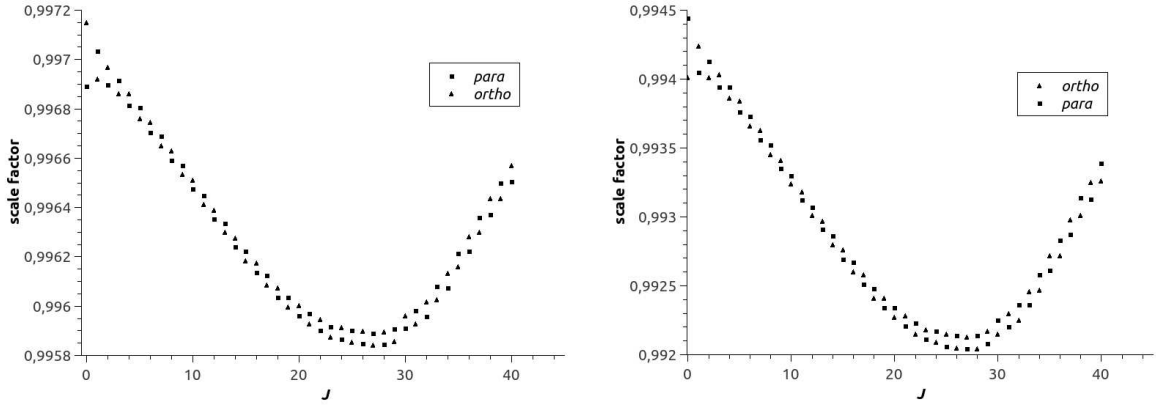


Figure 1. Ratio of the $D_2^{16}O$ and $D_2^{17}O$ (left panel) and $D_2^{16}O$ and $D_2^{18}O$ (right panel) energy levels as a function of the rotational quantum number J .

In case of $D_2^{17}O$ and $D_2^{18}O$, due to the lack of explicitly computed energies above $15\,000\text{ cm}^{-1}$, we need to determine an approximate rovibrational energy level set beyond this energy. We decided to employ for this purpose the $D_2^{16}O$ energy levels computed with PES-P. We calculate the ratio between the $D_2^{16}O$ and $D_2^{17}O$, and the $D_2^{16}O$ and $D_2^{18}O$ energy levels as a function of J , up to $J = 40$. The left and the right panels of Figure 1 show the ratios as a function of J for $D_2^{17}O$ and $D_2^{18}O$, respectively. As J is a good quantum number available from the first-principles computations, these ratios can be used to scale the $D_2^{16}O$ energy levels and obtain those of $D_2^{17}O$ and $D_2^{18}O$. As expected, the scale factors are close to 1.0 for both isotopologues.

Above $J = 40$, we use an average factor to scale the $D_2^{16}O$ energy levels to obtain the corresponding levels of $D_2^{17}O$ and $D_2^{18}O$. We scale the energies not only below but also above the D_0 of $D_2^{16}O$, so that more bound states are obtained up to the first dissociation limit for $D_2^{17}O$ and $D_2^{18}O$ than for $D_2^{16}O$. Ref. 43 gives D_0 values for all isotopologues of water, the D_0 values employed here for $D_2^{17}O$ and $D_2^{18}O$ were obtained by correcting D_0 of $D_2^{16}O$ of Ref. 40 with differences calculated in Ref. 43, yielding $D_0(D_2^{17}O) = 41\,869$ and $D_0(D_2^{18}O) = 41\,873\text{ cm}^{-1}$. The average scale factors used are 0.996 283 and 0.992 842 for $D_2^{17}O$ and $D_2^{18}O$, respectively. Using the average scale factors we finally arrived at 3 013 166 and 3 038 803 rovibrational energy levels for $D_2^{17}O$ and $D_2^{18}O$, respectively. The final $D_2^{16}O$, $D_2^{17}O$, and $D_2^{18}O$ hybrid databases contain 3 055 717, 3 084 456, and 3 110 893 energy levels up to $J = 98$, respectively.

This procedure does not ensure that we have the complete set of rovibrational states very close to the dissociation limit. This minor shortcoming of the present treatment is reflected in the somewhat increased uncertainties at the highest temperatures for $D_2^{17}O$ and $D_2^{18}O$ (note the large uncertainties employed for energy levels above $35\,000\text{ cm}^{-1}$, Table 1).

2.4. Thermochemical quantities

As usual,^{20,44–46} the total partition function is assumed to be the product of the internal and the translational partition functions. As also well known,^{23,47} the internal partition function, Q_{int} , of a free molecule is written as

$$Q_{\text{int}} = g_s \sum_i g_i (2J_i + 1) \exp\left(\frac{-c_2 E_i}{T}\right), \quad (1)$$

where $c_2 = hc/k_B$ is the second radiation constant, J_i is the rotational quantum number, E_i is the rotational-vibrational energy level given in cm^{-1} (the zero is taken as the ground vibrational state), T is the thermodynamic temperature in K, g_s is a state-independent nuclear-spin degeneracy factor for atoms not exchanged under rotation,⁴⁵ g_i is the nuclear-spin degeneracy factor for identical atom interchanged under rotation, and the index i runs over all possible rovibronic energies considered. The definitions of further thermochemical functions and the numerical values of the constants employed in this study can be found in **I**. Values of the molecular masses used in this study are $3.324\,916\,944 \times 10^{-26}$ kg, $3.491\,671\,120 \times 10^{-26}$ kg, and $3.657\,729\,650 \times 10^{-26}$ kg for D_2^{16}O , D_2^{17}O and D_2^{18}O , respectively.

2.5. Nuclear spin degeneracy factor

In the case of a triatomic molecule where two identical nuclei can be exchanged, like the case of the three isotopologues of heavy water, there are two separate rovibrational energy level sets corresponding to two distinct molecules. The two sets are called *ortho* and *para*. These distinct principal components of the spectroscopic network (SN)^{48,49} of the molecule cannot be connected by transitions measured by traditional techniques of high-resolution spectroscopy. As emphasized in the previous subsection, the nuclear spin statistics, and consequently the degeneracy, factors of Eq. (1) also depend on the nuclear spin I of the non-commuting nucleus. In the present case, the D nucleus is a boson with spin 1 and $I(^{16}\text{O})=I(^{18}\text{O})=0$ and $I(^{17}\text{O})=5/2$, explaining the degeneracy factors of Table 2.

Note that for the three D_2O isotopologues, due to the fact that $I(\text{D})=1$, the ground, $J=0$ state is *ortho* (with one of six symmetric spin states, $I=0$ or 2) and $J_{K_a K_c} = 1_{01}$ is the lowest-energy rotational state of *para* symmetry (with one of three antisymmetric spin states, $I=1$). At the lowest temperatures the equilibrium composition (*e*- D_2O) is pure *ortho*, and for “normal” D_2O (*n*- D_2O), where “normal” means the equilibrated composition at the high-temperature limit, the *ortho-para* ratio (OPR) is 2:1.

2.6. Uncertainty analysis

We just briefly summarize the most important sources of uncertainty of the computed thermochemical functions, identified in **I**, before going into a detailed uncertainty quantification analysis for the isobaric heat capacity.

Table 2. Nuclear spin degeneracy factors of D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O.

Molecule	Spectroscopic notation ^a	Degeneracy factor
<i>ortho</i> -D ₂ ¹⁶ O	$v_3 + K_a + K_c$ even	6
<i>para</i> -D ₂ ¹⁶ O	$v_3 + K_a + K_c$ odd	3
<i>ortho</i> -D ₂ ¹⁷ O	$v_3 + K_a + K_c$ even	36
<i>para</i> -D ₂ ¹⁷ O	$v_3 + K_a + K_c$ odd	18
<i>ortho</i> -D ₂ ¹⁸ O	$v_3 + K_a + K_c$ even	6
<i>para</i> -D ₂ ¹⁸ O	$v_3 + K_a + K_c$ odd	3

^a v_3 is the antisymmetric OD stretch quantum number, K_a and K_c are the standard asymmetric-top rotational quantum numbers.

Figure 2 shows the individual uncertainty contributions of $Q_{\text{int}}(T)$ (left panel) and $C_p(T)$ (right panel) in the case of the heavy water isotopologues. It can be seen that above 4500 K the largest uncertainty of $C_p(T)$ comes from the consideration of the unbound states. In **I** the contribution of the unbound states was estimated based on a simple model which overestimated this contribution by a factor of around two for bound states and a similar overestimation was assumed for the unbound states. In this study we employed the same technique to determine the contribution of the unbound states of the D₂¹⁶O molecule. Since this technique most likely overestimates the uncertainty contribution, we used the results of D₂¹⁶O molecule in cases of D₂¹⁷O and D₂¹⁸O. Furthermore, the uncertainty of the contribution was assumed to be the same as its value. This type of uncertainty is close to zero up to 4000 K, but above this temperature this contribution dominates. The situation is different in the case of $Q_{\text{int}}(T)$, where the largest source of uncertainty (almost in the whole temperature range) is the uncertainty of the energy levels.

We employed the “two extrema” method (see **I**) to determine the uncertainty of the partition function (and the thermochemical functions) which comes from the uncertainty of the energy levels. We also determined this type of uncertainty using the common error propagation formula, but since the uncertainty of the energy levels of the heavy-water molecules are much larger than the uncertainty of energy levels of H₂¹⁶O, the analytical formula provided artificially small uncertainties. Figure 2 shows that this type of uncertainty is smaller than 0.5% even at high temperatures. In the case of $Q_{\text{int}}(T)$, this contribution is the dominant part of the total uncertainty in the whole temperature range (except for D₂¹⁶O above 5500 K), since the uncertainties of the first-principles computed energy levels are considerably larger (see Table 1). In the case of $C_p(T)$ this type of uncertainty is almost negligible above 5000 K.

The third type of uncertainty is the uncertainty about the number of bound energy levels. We estimated this type of uncertainty with the differences of the $Q_{\text{int}}^{\text{tot}}$ and $Q_{\text{int}}^{\text{cutoff}}$ where the

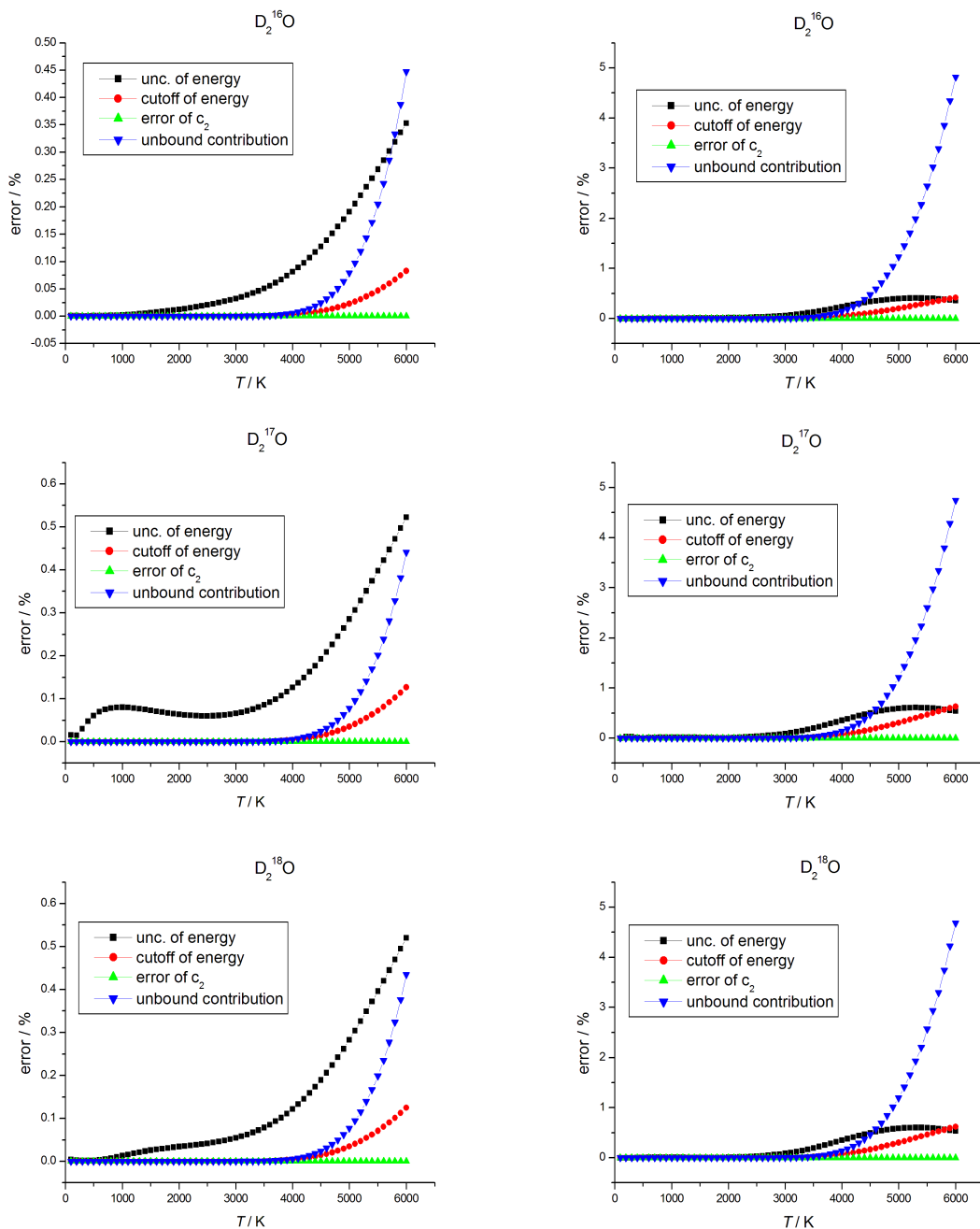


Figure 2. The individual uncertainty contributions of $Q_{\text{int}}(T)$ (left panel) and $C_p(T)$ (right panel) of D_2^{16}O (first row), D_2^{17}O (second row), and D_2^{18}O (third row).

cutoff value (*i.e.*, the inclusion of the energy levels only up to this value) is $D_0 - 500 \text{ cm}^{-1}$ in the case of D_2^{16}O , and $D_0 - 750 \text{ cm}^{-1}$ for the other two isotopologues (*i.e.*, we reduced the dissociation limit with the largest uncertainty). Figure 2 shows that this type of uncertainty is also smaller than 0.5% and it is negligible under 4000 K.

The fourth source of uncertainty in computed thermochemical functions comes from the uncertainties of the physical constants employed. Although such uncertainties are usually

considered to be negligible, the uncertainty of c_2 ($1.438\,777\,36(83) \times 10^{-2}$ m K) cannot simply be neglected, as shown in **I**. But in the case of the heavy-water isotopologues, the effect of the uncertainty of c_2 is negligible even at lower temperatures, since (a) the MARVEL database of the heavy-water molecules is not as complete as the MARVEL database of H_2^{16}O , so there are first-principles computed energy levels (with sizeable uncertainties) at relatively low energies, and (b) the uncertainties of the experimental energy levels are larger in the case of heavy water than they are for H_2^{16}O . An adjustment of $C_p(T)$ in case that the value of R and c_2 are changed is

$$C_{p,\text{new}}(T) = C_{p,\text{old}}(T) \left[\frac{R_{\text{new}}}{R_{\text{old}}} - \frac{\partial \ln C_p}{\partial \ln T} \left(\frac{c_{2,\text{new}}}{c_{2,\text{old}}} - 1 \right) \right]. \quad (2)$$

The dependence of our computed heat capacity values on the uncertainty of R can be masked by reporting $C_p(T)/R$ values. This practice is followed in the present study. However, it is to be noted that the values of the second radiation constant c_2 are very closely correlated to R and, consequently, any change of R must be accompanied by a corresponding adjustment of c_2 . As a consequence of the close covariance of R and c_2 , a simple form can be derived for the combined contribution of the uncertainties of c_2 and R to the standard uncertainty of C_p ,

$$\left| 1 + \frac{\partial \ln C_p}{\partial \ln T} \right| u_r(R) C_p, \quad (3)$$

where $u_r(R)$ is the relative standard uncertainty of the universal gas constant. In the proposed re-definition of the SI system,⁵⁰ both R and c_2 will become exact constants and their uncertainties will be transformed into the uncertainty of the temperature scale.

3. Results and Discussion

3.1. The partition and the thermochemical functions

The values of Q_{int} , Q'_{int} , and Q''_{int} of D_2^{16}O , D_2^{17}O , and D_2^{18}O are presented in Tables 3–5, respectively, in 100 K intervals up to 6000 K. The full set of results at 1 K increments is given in the supplementary material⁵¹ to this paper. Table 6 lists the following thermochemical functions at different temperatures for the three isotopologues: isobaric heat capacity, $C_p(T)$, entropy, $S(T)$, and standard enthalpy, $H^\circ(T)$. The supplementary material⁵¹ also contains the same information for the *ortho* and *para* forms of the three isotopologues and the most important thermochemical functions, all at 1 K increments.

3.2. Comparison with previous results

Figure 2 shows the difference between our D_2^{16}O $Q_{\text{int}}(T)$ partition function and that of Hewitt *et al.*,²⁴ who only considered temperatures below 1000 K. At low temperatures the agreement between the two studies is excellent although it would appear that Hewitt *et al.*'s calculations give a partition function which is too low above about 600 K, probably due to incomplete lists of energy levels.

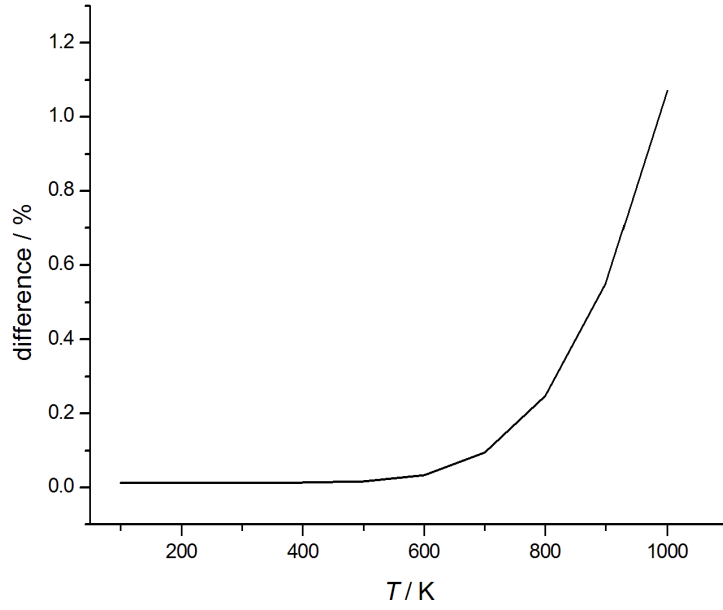


Figure 3. Comparison of the present $Q_{\text{int}}(T)$ values of D_2^{16}O with those of Hewitt *et al.*, defined with respect to the present values.

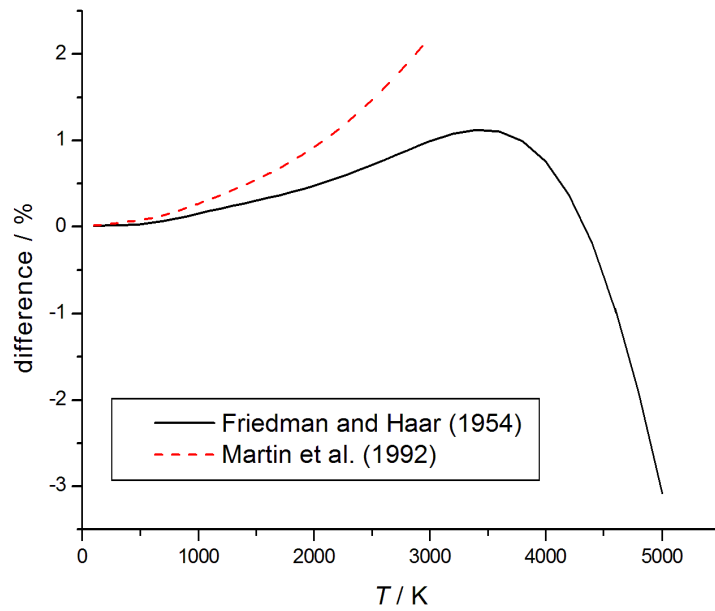


Figure 4. Comparison of the present $C_p(T)$ values of D_2^{16}O with those of Friedman and Haar (FH) (full, black curve) and Martin *et al.* (dashed, red curve).

Table 3. The temperature-dependent nuclear-spin-equilibrated internal partition functions, $Q_{\text{int}}(T)$, of D_2^{16}O and its first two moments, $Q'_{\text{int}}(T)$ and $Q''_{\text{int}}(T)$. The standard uncertainties associated with the data are given in parentheses.

T/K	$Q_{\text{int}}(T)$	$Q'_{\text{int}}(T)$	$Q''_{\text{int}}(T)$	T/K	$Q_{\text{int}}(T)$	$Q'_{\text{int}}(T)$	$Q''_{\text{int}}(T)$
100	203.437(3)	300.805(2)	750.952(3)	3100	170810(60)	574970(370)	2708380(2904)
200	570.081(4)	851.998(3)	2141.878(8)	3200	190187(74)	647162(461)	3067770(3715)
298.15	1039.136(6)	1577.002(6)	4077.37(2)	3300	211295(89)	726423(574)	3464231(4741)
300	1048.939(6)	1592.554(7)	4120.61(2)	3400	234252(109)	813262(715)	3900491(6032)
400	1632.887(9)	2554.16(2)	6912.96(7)	3500	259175(132)	908205(889)	4379374(7647)
500	2330.08(1)	3791.40(4)	10767.8(2)	3600	286191(160)	1011801(1103)	4903787(9653)
600	3154.99(2)	5367.78(8)	15988.2(4)	3700	315431(193)	1124619(1366)	5476720(12134)
700	4126.10(4)	7358.7(2)	22943.2(9)	3800	347028(234)	1247249(1686)	6101225(15190)
800	5265.34(7)	9851.2(3)	32050(2)	3900	381123(282)	1380297(2076)	6780394(18940)
900	6597.7(1)	12942.2(5)	43765(3)	4000	417861(340)	1524388(2548)	7517394(23540)
1000	8151.1(2)	16737.7(8)	58592(5)	4100	457393(410)	1680163(3118)	8315392(29181)
1100	9955.8(3)	21353(1)	77081(8)	4200	499873(492)	1848279(3807)	9177646(36129)
1200	12044.8(4)	26913(2)	99842(12)	4300	545460(590)	2029406(4636)	10107338(44691)
1300	14453.6(6)	33555(3)	127546(18)	4400	594319(707)	2224225(5635)	11107654(55249)
1400	17220.3(9)	41425(4)	160929(27)	4500	646618(844)	2433433(6840)	12181919(68358)
1500	20386(1)	50682(6)	200799(38)	4600	702530(1007)	2657730(8297)	13333573(84793)
1600	23993(2)	61500(9)	248035(53)	4700	762231(1199)	2897832(10060)	14564939(104759)
1700	28089(2)	74063(12)	303596(73)	4800	825903(1426)	3154458(12199)	15880826(130245)
1800	32723(3)	88573(16)	368521(99)	4900	893729(1694)	3428334(14800)	17283265(161579)
1900	37949(4)	105243(21)	443931(133)	5000	965898(2012)	3720196(17963)	18775197(199802)
2000	43821(5)	124304(28)	531041(177)	5100	1042601(2389)	4030781(21812)	20360698(247075)
2100	50399(7)	146001(36)	631154(232)	5200	1124033(2837)	4360834(26491)	22043310(305414)
2200	57747(9)	170599(47)	745671(303)	5300	1210392(3370)	4711104(32170)	23825486(376108)
2300	65931(11)	198377(60)	876096(393)	5400	1301878(4004)	5082344(39045)	25707939(459020)
2400	75021(14)	229634(76)	1024034(507)	5500	1398695(4759)	5475316(47340)	27701470(563336)
2500	85093(18)	264686(96)	1191201(653)	5600	1501050(5658)	5890781(57310)	29802534(685556)
2600	96223(22)	303870(121)	1379423(838)	5700	1609150(6728)	6329509(69241)	32012311(826479)
2700	108496(27)	347543(152)	1590642(1075)	5800	1723208(8000)	6792280(83458)	34344308(998803)
2800	121997(33)	396081(190)	1826915(1379)	5900	1843438(9509)	7279882(100322)	36796103(1200524)
2900	136818(41)	449881(237)	2090415(1768)	6000	1970056(11294)	7793107(120231)	39363667(1428102)
3000	153056(50)	509364(296)	2383435(2267)				

Figure 4 compares our values of D_2^{16}O $C_p(T)$ with data from Friedman and Haar (FH)¹⁵ and Martin *et al.*²³ The figure suggests that the results of FH are reasonable for temperatures up to about 4000 K, while those of Martin *et al.* systematically underestimate the heat capacity starting at the lowest temperatures.

3.3. Isotopic composition of heavy water

As mentioned above, IAPWS⁷ defines “heavy water”⁸ as a mixture of water isotopologues whose hydrogen content is pure ^2H (D) and whose oxygen content has the isotopic composition of VSMOW.^{9–11} The convention of using VSMOW’s oxygen composition for heavy

Table 4. The temperature-dependent nuclear-spin-equilibrated internal partition functions, $Q_{\text{int}}(T)$, of D_2^{17}O and its first two moments, $Q'_{\text{int}}(T)$ and $Q''_{\text{int}}(T)$. The standard uncertainties associated with the data are given in parentheses.

T/K	$Q_{\text{int}}(T)$	$Q'_{\text{int}}(T)$	$Q''_{\text{int}}(T)$	T/K	$Q_{\text{int}}(T)$	$Q'_{\text{int}}(T)$	$Q''_{\text{int}}(T)$
100	1230.2(2)	1819.1(1)	4541.4(3)	3100	1037626(712)	3496406(3347)	16484328(25596)
200	3447.5(5)	5153(1)	12955(8)	3200	1155463(830)	3935931(4151)	18674383(32848)
298.15	6285(2)	9540(6)	24677(25)	3300	1283851(973)	4418568(5154)	21090618(42036)
300	6344(2)	9634(6)	24939(25)	3400	1423494(1144)	4947410(6402)	23749686(53590)
400	9877(5)	15458(13)	41867(45)	3500	1575125(1351)	5525680(7947)	26668804(68010)
500	14098(9)	22957(22)	65252(65)	3600	1739507(1601)	6156727(9852)	29865707(85865)
600	19094(13)	32516(31)	96933(89)	3700	1917435(1901)	6844024(12188)	33358608(107813)
700	24978(19)	44594(41)	139150(117)	3800	2109734(2263)	7591163(15037)	37166104(134607)
800	31883(25)	59719(53)	194430(150)	3900	2317260(2696)	8401850(18493)	41307025(167109)
900	39961(32)	78477(66)	265547(190)	4000	2540898(3214)	9279894(22660)	45800643(206357)
1000	49381(40)	101513(80)	355547(237)	4100	2781565(3831)	10229205(27663)	50666215(253548)
1100	60328(48)	129527(97)	467786(291)	4200	3040204(4564)	11253781(33639)	55923535(310234)
1200	73001(57)	163279(116)	605970(354)	4300	3317788(5432)	12357707(40750)	61591943(378180)
1300	87615(67)	203596(137)	774182(426)	4400	3615319(6456)	13545139(49188)	67690767(459525)
1400	104403(78)	251372(160)	976911(512)	4500	3933823(7659)	14820301(59175)	74240165(557244)
1500	123611(90)	307580(187)	1219075(615)	4600	4274354(9070)	16187475(70979)	81260967(675428)
1600	145505(103)	373268(218)	1506041(742)	4700	4637989(10719)	17650997(84921)	88767272(815744)
1700	170367(118)	449568(253)	1843652(902)	4800	5025831(12643)	19215245(101390)	96788084(988250)
1800	198499(133)	537699(295)	2238245(1106)	4900	5439003(14884)	20884640(120855)	105335722(1195648)
1900	230222(150)	638970(344)	2696674(1371)	5000	5878650(17490)	22663631(143882)	114427930(1444066)
2000	265876(169)	754784(403)	3226339(1714)	5100	6345940(20520)	24556708(171151)	124089255(1745489)
2100	305824(191)	886643(476)	3835206(2159)	5200	6842057(24040)	26568381(203474)	134341002(2111689)
2200	350450(215)	1036151(565)	4531832(2736)	5300	7368205(28132)	28703191(241808)	145197936(2550942)
2300	400159(242)	1205020(675)	5325392(3481)	5400	7925606(32887)	30965699(282723)	156664345(3063762)
2400	455381(274)	1395070(811)	6225699(4443)	5500	8515498(38418)	33360512(341177)	168805034(3701178)
2500	516570(310)	1608237(980)	7243230(5684)	5600	9139135(44854)	35892240(405007)	181598712(4446031)
2600	584204(353)	1846574(1191)	8389143(7286)	5700	9797788(52346)	38565538(480459)	195052408(5303640)
2700	658787(402)	2112258(1453)	9675296(9354)	5800	10492742(61070)	41385109(569458)	209247097(6346469)
2800	740849(461)	2407588(1781)	11114255(12025)	5900	11225296(71227)	44355710(674170)	224168167(7565024)
2900	830948(530)	2734994(2191)	12719301(15472)	6000	11996765(83048)	47482113(796975)	239791330(8939948)
3000	929669(613)	3097036(2705)	14504428(19909)				

water can be traced back to the work of Kell.⁵² An analysis⁵³ of these batches provided an isotopic abundance of $a_{18} = N(^{18}\text{O})/N(^{16}\text{O}) = 2005.20 \times 10^{-6}$ with a standard uncertainty of $u_{18} = 0.45 \times 10^{-6}$. Later, the isotopic abundance $a_{17} = N(^{17}\text{O})/N(^{16}\text{O})$ was determined⁵⁴ as 379.9×10^{-6} with a standard uncertainty of $u_{17} = 0.8 \times 10^{-6}$. These isotopic abundances have been cited in a NIST report¹⁰ and, recently, re-affirmed¹¹ for the new VSMOW2 definition. The corresponding values⁸ of molar fractions, x , of the individual isotopologues are as follows: 0.997 620 6, 0.000 379 0, and 0.002 000 4 for D_2^{16}O , D_2^{17}O , and D_2^{18}O , respectively. These molar fractions are obtained as

$$x_{16} = \frac{1}{1 + a_{17} + a_{18}}, \quad x_{17} = \frac{a_{17}}{1 + a_{17} + a_{18}}, \quad x_{18} = \frac{a_{18}}{1 + a_{17} + a_{18}}. \quad (4)$$

Table 5. The temperature-dependent nuclear-spin-equilibrated internal partition functions, $Q_{\text{int}}(T)$, of D_2^{18}O and their first two moments, $Q'_{\text{int}}(T)$ and $Q''_{\text{int}}(T)$. The standard uncertainties associated with the data are given in parentheses.

T/K	$Q_{\text{int}}(T)$	$Q'_{\text{int}}(T)$	$Q''_{\text{int}}(T)$	T/K	$Q_{\text{int}}(T)$	$Q'_{\text{int}}(T)$	$Q''_{\text{int}}(T)$
100	206.475(9)	305.334(5)	762.277(8)	3100	175096(102)	590562(557)	2785888(4329)
200	578.65(1)	864.917(8)	2174.80(2)	3200	195000(122)	664857(693)	3156266(5556)
298.15	1054.92(2)	1601.70(2)	4144.60(6)	3300	216688(146)	746446(863)	3564921(7108)
300	1064.88(2)	1617.51(2)	4188.66(6)	3400	240280(175)	835852(1074)	4014670(9060)
400	1658.22(3)	2596.31(5)	7036.1(3)	3500	265898(209)	933621(1336)	4508425(11495)
500	2367.24(5)	3857.4(2)	10972(1)	3600	293673(251)	1040319(1658)	5049187(14508)
600	3206.9(1)	5465.9(5)	16308(3)	3700	323739(302)	1156535(2053)	5640032(18211)
700	4196.2(2)	7499(1)	23422(6)	3800	356236(363)	1282876(2534)	6284105(22729)
800	5357.6(4)	10047(2)	32740(10)	3900	391308(436)	1419969(3118)	6984584(28206)
900	6716.9(7)	13207(3)	44732(15)	4000	429106(523)	1568458(3821)	7744722(34817)
1000	8303(1)	17090(5)	59911(23)	4100	469784(627)	1729005(4665)	8567769(42760)
1100	10146(2)	21813(7)	78846(32)	4200	513502(751)	1902285(5673)	9457061(52293)
1200	12280(2)	27504(9)	102162(42)	4300	560424(897)	2088988(6872)	10415857(63712)
1300	14742(3)	34304(12)	130549(55)	4400	610721(1070)	2289816(8293)	11447412(77369)
1400	17571(4)	42364(16)	164768(70)	4500	664566(1273)	2505483(9974)	12555115(93761)
1500	20809(5)	51847(20)	205648(89)	4600	722136(1511)	2736712(11960)	13742468(113565)
1600	24500(7)	62932(25)	254099(111)	4700	783614(1789)	2984233(14303)	15011844(137061)
1700	28692(9)	75809(31)	311109(139)	4800	849187(2113)	3248786(17069)	16368099(165915)
1800	33436(10)	90685(38)	377749(175)	4900	919044(2491)	3531114(20336)	17813305(200580)
1900	38786(13)	107782(46)	455179(220)	5000	993379(2929)	3831969(24197)	19350434(242078)
2000	44801(15)	127335(56)	544652(280)	5100	1072389(3439)	4152104(28765)	20983590(292399)
2100	51541(18)	149601(69)	647516(356)	5200	1156274(4031)	4492281(34176)	22716331(353503)
2200	59071(22)	174849(84)	765220(455)	5300	1245238(4718)	4853262(40589)	24551123(426773)
2300	67460(26)	203371(103)	899316(582)	5400	1339485(5517)	5235814(48189)	26488683(512300)
2400	76780(31)	235472(126)	1051466(746)	5500	1439227(6445)	5640710(57195)	28539810(618571)
2500	87109(37)	271482(155)	1223444(957)	5600	1544673(7524)	6068724(67854)	30700950(742742)
2600	98527(43)	311749(191)	1417141(1229)	5700	1656038(8780)	6520638(80448)	32973266(885705)
2700	111119(51)	356639(235)	1634564(1580)	5800	1773540(10241)	6997238(95298)	35370243(1059518)
2800	124975(61)	406543(291)	1877841(2033)	5900	1897396(11940)	7499323(112766)	37889432(1262613)
2900	140190(72)	461872(361)	2149221(2616)	6000	2027828(13917)	8027690(133247)	40526766(1491771)
3000	156862(86)	523060(448)	2451074(3367)				

The properties of heavy water in the ideal gas state are obtained as properties of a mixture of ideal gas components. The components are the individual isotopologues D_2^{16}O , D_2^{17}O , and D_2^{18}O , for which, as usual in thermochemistry, we assume nuclear-spin equilibration. Of particular importance for this study is the isobaric heat capacity, which can be obtained as

$$C_p = x_{16}C_{p,16} + x_{17}C_{p,17} + x_{18}C_{p,18}. \quad (5)$$

The uncertainties of the isotopic abundances result in a contribution to the uncertainty of the thermodynamic properties of heavy water. The abundances a_{17} and a_{18} have been determined independently and, therefore, can be assumed to be uncorrelated. However, the

Table 6. Thermochemical functions of $D_2^{16}O$, $D_2^{17}O$, and $D_2^{18}O$; the standard uncertainties associated with the data are given in parentheses.

T/K	$C_p(T) / J K^{-1} mol^{-1}$			$S(T) / J K^{-1} mol^{-1}$			$H(T) / kJ mol^{-1}$		
	$D_2^{16}O$	$D_2^{17}O$	$D_2^{18}O$	$D_2^{16}O$	$D_2^{17}O$	$D_2^{18}O$	$D_2^{16}O$	$D_2^{17}O$	$D_2^{18}O$
100	33.299595(9)	33.2996(3)	33.29960(7)	180.01202(2)	195.5856(2)	181.32654(3)	3.308004(9)	3.3081(1)	3.30815(3)
200	33.45369(1)	33.457(9)	33.45934(1)	203.11953(2)	218.694(3)	204.43493(2)	6.642458(8)	6.6426(3)	6.64276(4)
298.15	34.26113(4)	34.27(1)	34.2851(2)	216.60269(3)	232.180(7)	217.92364(5)	9.959477(6)	9.960(1)	9.96121(3)
300	34.28280(4)	34.30(1)	34.3072(2)	216.81469(3)	232.392(7)	218.13578(5)	10.022880(6)	10.024(1)	10.02465(3)
400	35.6429(1)	35.664(5)	35.6830(9)	226.85627(5)	242.439(9)	228.1867(2)	13.516657(2)	13.519(2)	13.52171(2)
500	37.1955(3)	37.22210(2)	37.247(2)	234.9742(1)	250.56(1)	236.3149(5)	17.15754(2)	17.163(2)	17.1672(2)
600	38.8531(5)	38.883(3)	38.914(3)	241.9010(2)	257.494(9)	243.252(1)	20.95924(6)	20.967(2)	20.9745(5)
700	40.5727(7)	40.603(5)	40.639(5)	248.0189(3)	263.616(9)	249.380(2)	24.9303(1)	24.941(2)	24.9519(9)
800	42.2909(9)	42.320(6)	42.358(5)	253.5492(4)	269.151(8)	254.919(2)	29.0737(2)	29.088(1)	29.102(1)
900	43.946(1)	43.971(7)	44.011(5)	258.6267(5)	274.231(7)	260.004(3)	33.3863(3)	33.4030(5)	33.421(2)
1000	45.494(2)	45.514(7)	45.555(5)	263.3381(7)	278.945(6)	264.722(3)	37.8593(5)	37.8783(2)	37.901(2)
1100	46.912(2)	46.929(8)	46.969(4)	267.7417(8)	283.351(6)	269.132(4)	42.4807(7)	42.5015(9)	42.528(3)
1200	48.195(3)	48.208(8)	48.248(4)	271.880(1)	287.490(5)	273.274(4)	47.2371(9)	47.260(2)	47.290(3)
1300	49.345(3)	49.358(7)	49.395(3)	275.783(1)	291.395(5)	277.182(5)	52.115(1)	52.139(2)	52.173(4)
1400	50.373(4)	50.386(7)	50.422(2)	279.479(2)	295.091(4)	280.881(5)	57.102(2)	57.127(3)	57.165(4)
1500	51.291(4)	51.305(6)	51.339(1)	282.986(2)	298.599(4)	284.392(5)	62.186(2)	62.212(4)	62.254(4)
1600	52.112(5)	52.128(5)	52.1598(7)	286.323(2)	301.937(3)	287.732(5)	67.357(2)	67.385(4)	67.430(4)
1700	52.846(5)	52.866(3)	52.8959(8)	289.505(2)	305.120(3)	290.916(5)	72.606(3)	72.635(5)	72.683(4)
1800	53.507(6)	53.529(2)	53.558(1)	292.544(3)	308.161(3)	293.959(5)	77.924(3)	77.955(5)	78.006(4)
1900	54.102(7)	54.1291(6)	54.156(2)	295.453(3)	311.071(3)	296.871(5)	83.305(4)	83.339(5)	83.393(4)
2000	54.642(8)	54.673(3)	54.699(4)	298.242(3)	313.862(3)	299.663(5)	88.743(5)	88.779(5)	88.836(5)
2100	55.134(9)	55.169(6)	55.194(6)	300.921(4)	316.541(3)	302.344(5)	94.232(6)	94.272(4)	94.331(5)
2200	55.58(1)	55.622(9)	55.646(8)	303.496(4)	319.118(3)	304.922(6)	99.768(6)	99.812(4)	99.873(6)
2300	56.00(1)	56.04(1)	56.06(1)	305.976(5)	321.600(4)	307.405(6)	105.347(8)	105.395(3)	105.459(7)
2400	56.38(1)	56.42(2)	56.45(1)	308.367(5)	323.993(4)	309.799(7)	110.966(9)	111.018(1)	111.084(8)
2500	56.73(1)	56.78(2)	56.80(2)	310.676(6)	326.304(5)	312.111(7)	116.62(1)	116.6789(6)	116.75(1)
2600	57.06(2)	57.11(2)	57.14(2)	312.908(6)	328.538(6)	314.345(8)	122.31(1)	122.374(3)	122.44(1)
2700	57.37(2)	57.42(3)	57.44(3)	315.067(7)	330.699(7)	316.507(9)	128.03(1)	128.101(6)	128.17(1)
2800	57.66(2)	57.71(4)	57.73(3)	317.159(8)	332.792(8)	318.60(1)	133.78(2)	133.857(9)	133.93(2)
2900	57.92(3)	57.98(4)	58.00(4)	319.186(9)	334.82(1)	320.63(1)	139.56(2)	139.64(1)	139.72(2)
3000	58.18(3)	58.23(5)	58.26(5)	321.15(1)	336.79(1)	322.60(1)	145.37(2)	145.45(2)	145.53(3)
3100	58.41(4)	58.47(6)	58.49(6)	323.07(1)	338.71(1)	324.52(1)	151.20(3)	151.29(2)	151.37(3)
3200	58.63(5)	58.69(8)	58.71(7)	324.92(1)	340.57(2)	326.38(2)	157.05(3)	157.15(3)	157.23(4)
3300	58.83(6)	58.89(9)	58.91(9)	326.73(1)	342.37(2)	328.19(2)	162.92(3)	163.03(4)	163.11(5)
3400	59.01(7)	59.1(1)	59.1(1)	328.49(2)	344.14(2)	329.95(2)	168.82(4)	168.92(5)	169.01(5)
3500	59.18(8)	59.2(1)	59.3(1)	330.20(2)	345.85(2)	331.66(3)	174.73(5)	174.84(6)	174.93(7)
3600	59.33(9)	59.4(1)	59.4(1)	331.87(2)	347.52(3)	333.34(3)	180.65(6)	180.77(7)	180.86(8)
3700	59.5(1)	59.5(2)	59.5(2)	333.50(2)	349.15(3)	334.96(3)	186.59(7)	186.71(9)	186.81(9)
3800	59.6(1)	59.6(2)	59.6(2)	335.09(3)	350.74(4)	336.55(4)	192.54(8)	192.7(1)	192.8(1)
3900	59.6(1)	59.7(2)	59.7(2)	336.64(3)	352.29(4)	338.10(4)	198.50(9)	198.6(1)	198.7(1)
4000	59.7(2)	59.8(2)	59.8(2)	338.15(3)	353.80(5)	339.62(5)	204.5(1)	204.6(1)	204.7(1)
4100	59.8(2)	59.8(3)	59.8(3)	339.62(4)	355.28(5)	341.09(5)	210.4(1)	210.6(2)	210.7(2)
4200	59.8(2)	59.8(3)	59.8(3)	341.06(4)	356.72(6)	342.53(6)	216.4(1)	216.6(2)	216.7(2)
4300	59.8(3)	59.8(3)	59.8(3)	342.47(5)	358.12(7)	343.94(7)	222.4(2)	222.5(2)	222.6(2)
4400	59.7(3)	59.8(4)	59.8(4)	343.84(5)	359.50(7)	345.31(7)	228.4(2)	228.5(3)	228.6(3)
4500	59.7(4)	59.7(4)	59.7(4)	345.18(6)	360.84(8)	346.66(8)	234.3(2)	234.5(3)	234.6(3)
4600	59.6(4)	59.6(5)	59.6(5)	346.49(7)	362.15(9)	347.97(9)	240.3(3)	240.5(3)	240.6(3)
4700	59.5(5)	59.5(5)	59.5(5)	347.77(7)	363.4(1)	349.2(1)	246.3(3)	246.4(4)	246.5(4)
4800	59.4(6)	59.4(6)	59.4(6)	349.03(8)	364.7(1)	350.5(1)	252.2(3)	252.4(4)	252.5(4)
4900	59.2(7)	59.2(7)	59.2(7)	350.2(1)	365.9(1)	351.7(1)	258.1(4)	258.3(5)	258.4(5)
5000	59.1(8)	59.1(8)	59.0(8)	351.4(1)	367.1(1)	352.9(1)	264.0(5)	264.2(6)	264.3(6)
5100	58.9(9)	58.9(9)	58.8(9)	352.6(1)	368.3(2)	354.1(2)	269.9(5)	270.1(6)	270.2(6)
5200	59(1)	59(1)	59(1)	353.8(1)	369.4(2)	355.2(2)	275.8(6)	276.0(7)	276.1(7)
5300	58(1)	58(1)	58(1)	354.9(2)	370.5(2)	356.3(2)	281.7(7)	281.8(8)	281.9(8)
5400	58(1)	58(1)	58(1)	356.0(2)	371.6(2)	357.4(2)	287.5(8)	288(1)	287.7(9)
5500	58(2)	58(2)	58(2)	357.0(2)	372.7(2)	358.5(2)	293(1)	293(1)	294(1)
5600	58(2)	58(2)	58(2)	358.1(2)	373.7(3)	359.5(3)	299(1)	299(1)	299(1)
5700	58(2)	57(2)	57(2)	359.1(3)	374.7(3)	360.6(3)	305(1)	305(1)	305(1)
5800	57(2)	57(2)	57(2)	360.1(3)	375.7(3)	361.6(3)	311(2)	311(2)	311(2)
5900	57(2)	57(2)	57(2)	361.1(3)	376.7(4)	362.5(4)	316(2)	316(2)	317(2)
6000	57(3)	57(3)	57(3)	362.0(4)	377.7(4)	363.5(4)	322(2)	322(2)	322(2)

Table 7. The $Q_{\text{int}}(T)$ partition function and the $C_p(T)$ isobaric heat capacity of heavy water determined in this study.

T / K	$Q_{\text{int}}(T)$	$C_p(T) / \text{J K}^{-1} \text{mol}^{-1}$
100	203.832(5)	33.29960(1)
200	571.19(1)	33.4537(2)
298.15	1041.16(4)	34.2612(2)
300	1050.98(4)	34.2829(2)
400	1636.06(9)	35.6430(2)
500	2334.6(2)	37.1956(3)
600	3161.1(3)	38.8532(5)
700	4134.1(4)	40.5728(7)
800	5275.6(5)	42.291(1)
900	6610.6(6)	43.946(1)
1000	8167.0(8)	45.494(2)
1100	9975(1)	46.912(2)
1200	12068(1)	48.195(3)
1300	14482(1)	49.345(3)
1400	17254(2)	50.374(4)
1500	20425(2)	51.292(4)
1600	24040(3)	52.112(5)
1700	28144(3)	52.847(5)
1800	32788(4)	53.507(6)
1900	38023(5)	54.103(7)
2000	43907(6)	54.642(8)
2100	50498(8)	55.134(9)
2200	57861(10)	55.58(1)
2300	66061(12)	56.00(1)
2400	75169(15)	56.38(1)
2500	85260(19)	56.73(1)
2600	96413(23)	57.06(2)
2700	108709(28)	57.37(2)
2800	122237(34)	57.66(2)
2900	137088(42)	57.92(3)
3000	153358(51)	58.18(3)
3100	171147(62)	58.41(4)
3200	190562(75)	58.63(5)
3300	211713(92)	58.83(6)
3400	234714(111)	59.01(7)
3500	259687(135)	59.18(8)
3600	286757(163)	59.33(9)
3700	316054(197)	59.5(1)
3800	347714(238)	59.6(1)
3900	381877(287)	59.6(1)
4000	418688(347)	59.7(2)
4100	458299(417)	59.8(2)
4200	500863(501)	59.8(2)
4300	546541(600)	59.8(3)
4400	595497(718)	59.7(3)
4500	647900(858)	59.7(4)
4600	703923(1023)	59.6(4)
4700	763743(1218)	59.5(5)
4800	827541(1448)	59.4(6)
4900	895502(1720)	59.2(7)
5000	967815(2043)	59.1(8)
5100	1044671(2424)	58.9(9)
5200	1126265(2878)	59(1)
5300	1212795(3416)	58(1)
5400	1304464(4057)	58(1)
5500	1401474(4820)	58(2)
5600	1504032(5728) ¹⁹	58(2)
5700	1612347(6808)	58(2)
5800	1726633(8091)	57(2)
5900	1847102(9613)	57(2)
6000	1973972(11413)	57(3)

molar fractions are interrelated. Therefore, when determining the uncertainty based on the uncertainties of molar fractions, their covariance matrix should also be considered. An easier way is relating the contribution to the uncertainty of the isobaric heat capacity directly to the uncertainties of the abundances,

$$\left[\left(\frac{\partial x_{16}}{\partial a_{17}} C_{p,16} + \frac{\partial x_{17}}{\partial a_{17}} C_{p,17} + \frac{\partial x_{18}}{\partial a_{17}} C_{p,18} \right)^2 u_{17}^2 + \left(\frac{\partial x_{16}}{\partial a_{18}} C_{p,16} + \frac{\partial x_{17}}{\partial a_{18}} C_{p,17} + \frac{\partial x_{18}}{\partial a_{18}} C_{p,18} \right)^2 u_{18}^2 \right]^{1/2}, \quad (6)$$

where the partial derivatives are obtained from Eq. (4). This results in the expression

$$x_{16} \cdot \left\{ [-C_{p,16} + (1 + a_{18}) C_{p,17} - a_{18} C_{p,18}]^2 u_{17}^2 + [-C_{p,16} - a_{17} C_{p,17} + (1 + a_{17}) C_{p,18}]^2 u_{18}^2 \right\}^{1/2}. \quad (7)$$

Table 7 contains the recommended $Q_{\text{int}}(T)$ partition function and the $C_p(T)$ of heavy water. We note that the uncertainty which comes from the uncertainties of the abundances (using Eq. (7)) is negligible, as the uncertainties of $Q_{\text{int}}(T)$ and $C_p(T)$ are larger by at least two orders of magnitude.

3.4. Low-temperature limit

Due to the heavier mass and the larger moments of inertia of heavy water over ordinary water, it behaves less as a quantum system at the lowest temperatures than $\text{H}_2^{55,56}$ or H_2^{16}O .^{21,57} Nevertheless, as Fig. 5 shows the qualitative picture is the same as for H_2^{16}O , just the (nearly) complete equilibration happens at a much lower temperature, below 50 K.

3.5. On the maximum in C_p

Similarly to the case of H_2^{16}O ,²¹ Table 7 shows a clear maximum, at about 4100 K, of the $C_p(T)$ function of heavy water. As tested, one does not qualitatively change this feature by adding the quasi-bound states to the energy-level set. There is only a shift of the maximum to (slightly) higher T . Quasibound states will make a much bigger contribution than the excited electronic states, as all the low-lying electronic excited states of water are dissociative so they do not contribute in a model with only sums over (quasi-)bound states. Having a maximum in the $C_p(T)$ function is a feature and not a problem and it just means that the structure in $C_p(T)$ is definitional and due to our choice of treating the various dissociated systems separately.

4. Summary and Conclusions

Temperature-dependent ideal-gas internal partition functions, $Q_{\text{int}}(T)$, have been determined, in the range of 0 to 6000 K, for the following molecules: *ortho*- and *para*- D_2^{16}O ,

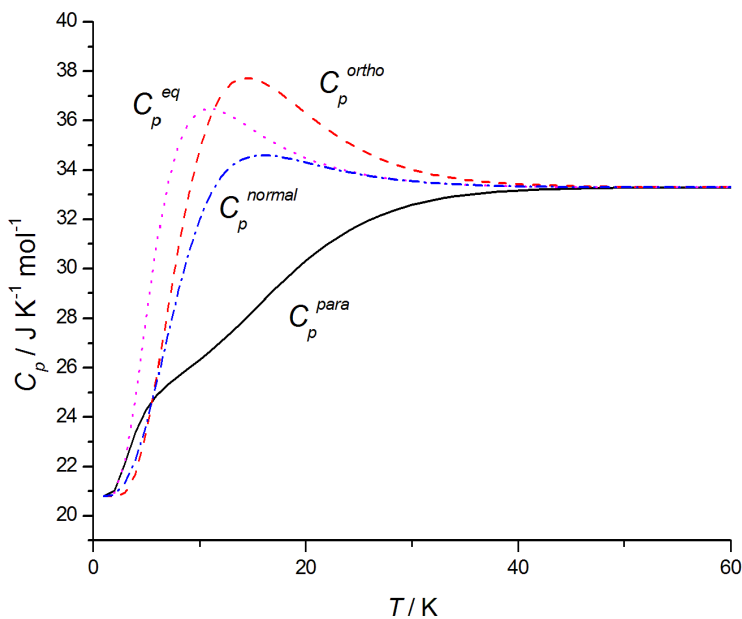


Figure 5. The *ortho*-D₂¹⁶O (dashed, red curve), the *para*-D₂¹⁶O (full, black curve), the nuclear-spin-equilibrated D₂¹⁶O (magenta, dotted curve), and the normal mixture D₂¹⁶O (blue, dash dotted curve) isobaric heat capacities at low temperatures, below 100 K.

ortho- and *para*-D₂¹⁷O, and *ortho*- and *para*-D₂¹⁸O. The $Q_{\text{int}}(T)$ values are based on the use of the explicit summation technique. A large number of experimentally known energy levels (12 269, 338, and 3351 for D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O, respectively) and an almost complete set of first-principles energy levels, over three million for each isotopologue, have been utilized during the explicit summation. These ideal-gas internal partition functions and their first two moments were then employed to obtain the following thermochemical functions in the same temperature range: Gibbs energy function, enthalpy, entropy, and isobaric heat capacity. Approximately two standard deviation uncertainties have also been determined for all these quantities. These uncertainties are much smaller than ever determined before for these molecules. Above about 3000 K the contribution coming from unbound states gives the largest percentage of the overall uncertainty, while at the highest temperatures the uncertainty in the energy level density is the other factor which significantly affects the overall uncertainties. Following the accepted practice in thermochemistry, nuclear-spin-equilibrated thermochemical functions have also been obtained for D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O. These functions were then combined to provide partition and caloric functions for heavy water, defined according to the IAPWS convention. All the data obtained are given in the supplementary material with 1 K increments.

Four sources of uncertainty of the values of the thermochemical functions determined have been identified, namely the uncertainty of the energy levels, the uncertainty of the number of energy levels (this becomes an issue close to dissociation), the approximate consideration of

the effect of unbound states, and the uncertainty of the physical constants employed. At this point it must also be mentioned that “real” heavy water, especially as used in industry, might not match the “official” VSMOW oxygen isotope abundances. The procedures for purifying heavy water typically also make the oxygen abundances a little “heavier”, but this is almost never measured. Thus, this is an additional (small) source of uncertainty in applying the “heavy water” heat capacities determined in this study to real systems. The isotopologue-dependent data presented here allows users to construct accurate thermodynamic data for other compositions as needed.

The large amount of data supplied in this study should serve well the purposes of the International Association for the Properties of Water and Steam (IAPWS) seeking to produce a new Equation of State (EOS) for heavy water, replacing their 1984 recommendation, slightly revised in 2005, based on ideal-gas data obtained in 1954 by Friedman and Haar (FH).¹⁵ The FH data form also the basis of the JANAF tables of heavy water.¹⁸ Replacing the IAPWS and JANAF data with the new, high-quality data of the present study is highly recommended.

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