

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 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 enthalpy, the entropy, and the isobaric heat capacity of the individual nuclear-spin-equilibrated isotopologues 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

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the thermochemical functions are reported, in 1 K increments, in the supplementary material. © 2017 AIP Publishing LLC for the National Institute of Standards and Technology. [<http://dx.doi.org/10.1063/1.4983120>]

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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 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 2005¹⁶ to make the old equation conform to the ITS-90¹⁷ temperature scale, it kept employing the ideal-gas FH data. The results of FH¹⁵ also form the basis of the JANAF (Joint Army, Navy, and Air Force) tables of D₂¹⁶O.¹⁸ The dimensionless data of FH¹⁵ were converted to become the JANAF tables using a universal molar gas constant $R = 8.31441(26) \text{ J mol}^{-1} \text{ K}^{-1}$, 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 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 provide 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^{6,15,23,24} 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 comes close to the accuracy of the present investigation, which heavily builds upon achievements in the fourth age of quantum chemistry.²⁵

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 dataset comprises all the available experimental energy levels, obtained via a measured active rotational-vibrational energy levels (MARVEL)^{26–29} analysis of the experimental rovibrational transitions,²² while the second dataset contains first-principles computed levels determined as part of the present study.

2.1. MARVEL energy levels

The most complete and probably most accurate source of bound measured rovibrational energy levels of D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O 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 12269, 338, and 3351 for D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O, 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 D₂O 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 (PESs). 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 D₂¹⁶O, the PoKaZaTeL global adiabatic PES,³¹ developed for H₂¹⁶O 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 dataset 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 H₂¹⁶O, 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 D₂¹⁶O 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 H₂¹⁶O bound-state rovibrational energy levels with $J = 0–68$ took several months of supercomputer time.³¹ For D₂¹⁶O, 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 H₂¹⁶O. To perform the computations of D₂¹⁶O 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 D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O 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 possible and in this way we obtain what is called hereafter the hybrid database.

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	0–3 000	0.1
		3 000–5 000	0.5
	PES-P ³¹	5 000–15 000	1.0
		0–15 000	2.0
		15 000–25 000	5.0
		25 000–30 000	10.0
		30 000–35 000	100.0
		35 000–40 000	250.0
D ₂ ¹⁷ O, D ₂ ¹⁸ O	PES-S ³⁰	0–3 000	0.1
		3 000–5 000	0.5
	PES-P ³¹	5 000–15 000	1.0
		0–15 000	3.0
		15 000–25 000	7.5
		25 000–30 000	15.0
		30 000–35 000	150.0
		35 000–40 000	375.0
		Above 40 000	750.0

In the cases of D₂¹⁷O and D₂¹⁸O, due to the lack of explicitly computed energies above 15 000 cm⁻¹, we need to determine an approximate rovibrational energy level set beyond this energy. We decided to employ for this purpose the D₂¹⁶O energy levels computed with PES-P. We calculate the ratio between the D₂¹⁶O and D₂¹⁷O and the D₂¹⁶O and D₂¹⁸O energy levels as a function of J , up to $J = 40$. The left and the right panels of Fig. 1 show the ratios as a function of J for D₂¹⁷O and D₂¹⁸O, respectively. As J is a good quantum number available from the first-principles computations, these ratios can be used to scale the D₂¹⁶O energy levels and obtain those of D₂¹⁷O and D₂¹⁸O. As expected, the scale factors are close to 1.0 for both isotopologues.

Above $J = 40$, we use an average factor to scale the D₂¹⁶O energy levels to obtain the corresponding levels of D₂¹⁷O and D₂¹⁸O. We scale the energies not only below but also above the D_0 of D₂¹⁶O, so that more bound states are obtained up to the first dissociation limit for D₂¹⁷O and D₂¹⁸O than for D₂¹⁶O. Ref. 43 gives D_0 values for all isotopologues of water; the D_0 values employed here for D₂¹⁷O and D₂¹⁸O were obtained by correcting D_0 of D₂¹⁶O of Ref. 40 with differences calculated in Ref. 43, yielding $D_0(\text{D}_2^{17}\text{O}) = 41\,869\text{ cm}^{-1}$ and $D_0(\text{D}_2^{18}\text{O}) = 41\,873\text{ cm}^{-1}$. The average scale factors used are 0.996 283 and 0.992 842 for D₂¹⁷O and D₂¹⁸O, respectively. Using the average scale factors, we finally arrived at 3 013 166 and 3 038 803 rovibrational energy levels for D₂¹⁷O and D₂¹⁸O, respectively. The final D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O 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 D₂¹⁷O and D₂¹⁸O (note the large uncertainties employed for energy levels above 35 000 cm⁻¹, Table 1).

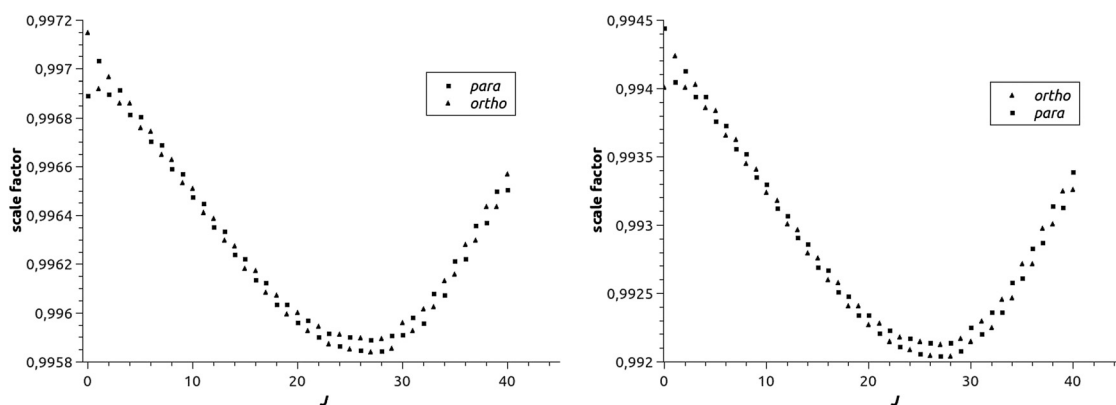


FIG. 1. Ratio of the $D_2^{16}O$ and $D_2^{17}O$ (left panel) and $D_2^{16}O$ and $D_2^{18}O$ (right panel) energy levels as a function of the rotational quantum number J .

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 atoms 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 study⁴⁸ can be found in I. Values of the molecular masses used in this study are $3.324916944 \times 10^{-26}$ kg, $3.491671120 \times 10^{-26}$ kg, and $3.657729650 \times 10^{-26}$ 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 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)^{49,50} of the molecule cannot be connected by transitions measured by traditional techniques of high-resolution spectroscopy. As emphasized in Subsection 2.4, the nuclear spin statistics, and consequently the degeneracy factors of Eq. (1), also depends on the nuclear spin I of the non-commuting nucleus. In the present case, the D nucleus is a boson with spin 1 and $I(^{16}O) = I(^{18}O) = 0$ and $I(^{17}O) = 5/2$, explaining the degeneracy factors of Table 2.

Note that for the three D_2O isotopologues, due to the fact that $I(D) = 1$, 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

TABLE 2. Nuclear spin degeneracy factors of $D_2^{16}O$, $D_2^{17}O$, and $D_2^{18}O$

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.

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 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.

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 $D_2^{16}O$ molecule. Since this technique most likely overestimates the uncertainty contribution, we used the results for the $D_2^{16}O$ molecule in the cases of $D_2^{17}O$ and $D_2^{18}O$. 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 that 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.

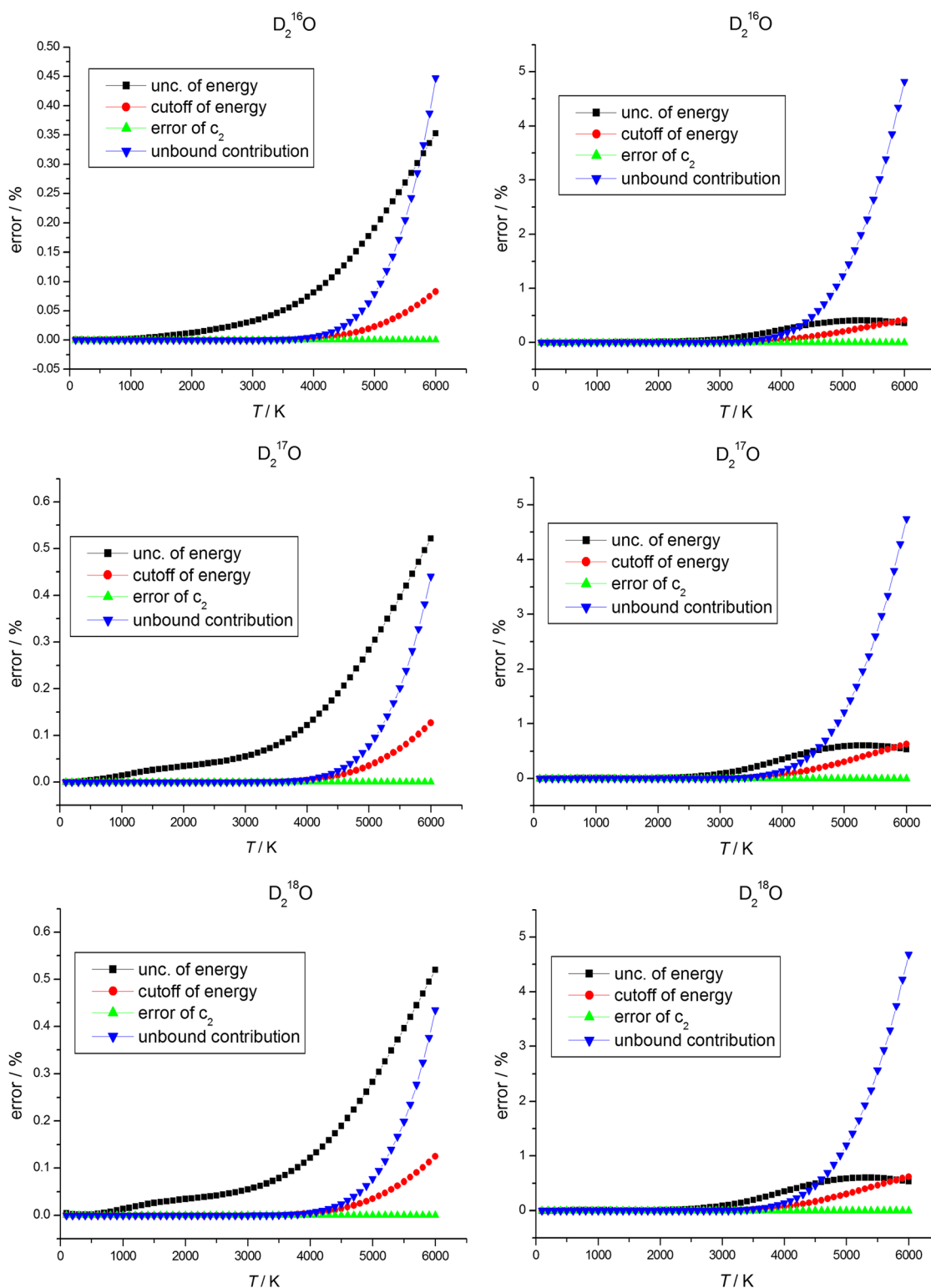


FIG. 2. The individual uncertainty contributions of $Q_{\text{int}}(T)$ (left panel) and $C_p(T)$ (right panel) of $D_2^{16}O$ (first row), $D_2^{17}O$ (second row), and $D_2^{18}O$ (third row).

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 is much larger than the uncertainty of energy levels

of $H_2^{16}O$, 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 $D_2^{16}O$ 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 $Q_{\text{int}}^{\text{tot}}$ and $Q_{\text{int}}^{\text{cutoff}}$ where the 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 below 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 ($1.438\,777\,36(83) \times 10^{-2} \text{ m K}$) 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 sizable 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 values 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,⁴⁸ 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 material](#) to this paper. Table 6

TABLE 3. The temperature-dependent nuclear-spin-equilibrated internal partition function, $Q_{\text{int}}(T)$, 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	$Q_{\text{int}}(T)$	$Q'_{\text{int}}(T)$	$Q''_{\text{int}}(T)$
100	203.437(3)	300.805(2)	750.952(3)
200	570.081(4)	851.998(3)	2 141.878(8)
298.15	1 039.136(6)	1 577.002(6)	4 077.37(2)
300	1 048.939(6)	1 592.554(6)	4 120.61(2)
400	1 632.887(8)	2 554.16(1)	6 912.96(4)
500	2 330.08(1)	3 791.40(2)	10 767.8(1)
600	3 154.99(2)	5 367.78(4)	15 988.2(2)
700	4 126.10(3)	7 358.73(9)	22 943.2(5)
800	5 265.34(4)	9 851.2(2)	32 050(1)
900	6 597.73(7)	12 942.2(3)	43 765(2)
1000	8 151.1(1)	16 737.7(6)	58 592(4)
1100	9 955.8(2)	21 353(1)	77 081(7)
1200	12 044.8(3)	26 913(2)	99 842(11)
1300	14 453.6(5)	33 555(3)	127 546(17)
1400	17 220.3(7)	41 425(4)	160 929(26)
1500	20 386(1)	50 682(6)	200 799(37)
1600	23 993(2)	61 500(8)	248 035(52)
1700	28 089(2)	74 063(11)	303 596(72)
1800	32 723(3)	88 573(15)	368 521(98)
1900	37 949(4)	105 243(21)	443 931(132)
2000	43 821(5)	124 304(27)	531 041(176)
2100	50 399(7)	146 001(36)	631 154(231)
2200	57 747(8)	170 599(46)	745 671(302)
2300	65 931(11)	198 377(59)	876 096(393)
2400	75 021(14)	229 634(75)	1 024 034(507)
2500	85 093(17)	264 686(95)	1 191 201(653)
2600	96 223(21)	303 870(120)	1 379 423(838)
2700	108 496(26)	347 543(151)	1 590 642(1 075)
2800	121 997(33)	396 081(189)	1 826 915(1 379)
2900	136 818(40)	446 818(237)	2 090 415(1 768)
3000	153 056(49)	509 364(296)	2 383 435(2 267)
3100	170 810(60)	574 970(369)	2 708 380(2 904)
3200	190 187(73)	647 162(460)	3 067 770(3 715)
3300	211 295(89)	726 423(574)	3 464 231(4 741)
3400	234 252(108)	813 262(715)	3 900 491(6 033)
3500	259 175(131)	908 205(889)	4 379 374(7 647)
3600	286 191(159)	1 011 801(1 103)	4 903 787(9 654)
3700	315 431(193)	1 124 619(1 365)	5 476 720(12 135)
3800	347 028(233)	1 247 249(1 686)	6 101 225(15 190)
3900	381 123(282)	1 380 297(2 075)	6 780 394(18 940)
4000	417 861(340)	1 524 388(2 548)	7 517 394(23 541)
4100	457 393(409)	1 680 163(3 118)	8 315 392(29 182)
4200	499 873(492)	1 848 279(3 806)	9 177 646(36 130)
4300	545 460(590)	2 029 406(4 636)	10 107 338(44 692)
4400	594 319(706)	2 224 225(5 635)	11 107 654(55 249)
4500	646 618(843)	2 433 433(6 840)	12 181 919(68 359)
4600	702 530(1 006)	2 657 730(8 296)	13 333 573(84 794)
4700	762 231(1 198)	2 897 832(10 060)	14 564 939(104 760)
4800	825 903(1 425)	3 154 458(12 199)	15 880 826(130 245)
4900	893 729(1 693)	3 428 334(14 799)	17 283 265(161 579)
5000	965 898(2 011)	3 720 196(17 963)	18 775 197(199 802)
5100	1 042 601(2 389)	4 030 781(21 812)	20 360 698(247 075)
5200	1 124 033(2 836)	4 360 834(26 491)	22 043 310(305 414)
5300	1 210 392(3 369)	4 711 104(32 170)	23 825 486(376 108)
5400	1 301 878(4 003)	5 082 344(39 045)	25 707 939(459 020)
5500	1 398 695(4 758)	5 475 316(47 340)	27 701 470(563 337)
5600	1 501 050(5 657)	5 890 781(57 310)	29 802 534(685 556)
5700	1 609 150(6 727)	6 329 509(69 241)	32 012 311(826 479)
5800	1 723 208(7 999)	6 792 280(83 458)	34 344 308(998 804)
5900	1 843 438(9 508)	7 279 882(100 322)	36 796 103(1 200 524)
6000	1 970 056(11 294)	7 793 107(120 231)	39 363 667(1 428 102)

TABLE 4. The temperature-dependent nuclear-spin-equilibrated internal partition function, $Q_{\text{int}}(T)$, 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	$Q_{\text{int}}(T)$	$Q'_{\text{int}}(T)$	$Q''_{\text{int}}(T)$
100	1 230.214(7)	1 819.116(5)	4 541.42(1)
200	3 447.54(2)	5 152.76(6)	12 955.3(3)
298.15	6 284.66(8)	9 540.1(3)	24 677(2)
300	6 343.96(9)	9 634.2(4)	24 939(2)
400	9 877.4(3)	15 458(1)	41 867(4)
500	14 097.9(6)	22 957(2)	65 252(9)
600	19 094(1)	32 516(4)	96 933(17)
700	24 978(2)	44 594(7)	139 150(32)
800	31 883(3)	59 719(11)	194 430(55)
900	39 961(5)	78 477(18)	265 547(87)
1000	49 381(7)	101 513(27)	355 547(129)
1100	60 328(10)	129 527(38)	467 786(181)
1200	73 001(14)	163 279(53)	605 970(246)
1300	87 615(19)	203 596(71)	774 182(324)
1400	104 403(25)	251 372(92)	976 911(417)
1500	123 611(32)	307 580(117)	1 219 075(529)
1600	145 505(41)	373 268(147)	1 506 041(666)
1700	170 367(51)	449 568(182)	1 843 652(836)
1800	198 499(62)	537 699(224)	2 238 245(1 052)
1900	230 222(76)	638 970(275)	2 696 674(1 328)
2000	265 876(91)	754 784(336)	3 226 339(1 682)
2100	305 824(109)	886 643(411)	3 835 206(2 139)
2200	350 450(130)	1 036 151(502)	4 531 832(2 726)
2300	400 159(155)	1 205 020(614)	5 325 392(3 482)
2400	455 381(184)	1 395 070(753)	6 225 699(4 453)
2500	516 570(218)	1 608 237(925)	7 243 230(5 703)
2600	584 204(259)	1 846 574(1 139)	8 389 143(7 313)
2700	658 787(306)	2 112 258(1 404)	9 675 296(9 389)
2800	740 849(363)	2 407 588(1 735)	11 114 255(12 067)
2900	830 948(431)	2 734 994(2 148)	12 719 301(15 521)
3000	929 669(512)	3 097 036(2 665)	14 504 428(19 963)
3100	1 037 626(610)	3 496 406(3 311)	16 484 328(25 656)
3200	1 155 463(727)	3 935 931(4 118)	18 674 383(32 913)
3300	1 283 851(869)	4 418 568(5 124)	21 090 618(42 105)
3400	1 423 494(1 039)	4 947 410(6 375)	23 749 686(53 663)
3500	1 575 125(1 246)	5 525 680(7 923)	26 668 804(68 086)
3600	1 739 507(1 495)	6 156 727(9 831)	29 865 707(85 944)
3700	1 917 435(1 795)	6 844 024(12 170)	33 358 608(107 894)
3800	2 109 734(2 155)	7 591 163(15 021)	37 166 104(134 691)
3900	2 317 260(2 588)	8 401 850(18 479)	41 307 025(167 194)
4000	2 540 898(3 106)	9 279 894(22 650)	45 800 643(206 443)
4100	2 781 565(3 723)	10 229 205(27 654)	50 666 215(253 635)
4200	3 040 204(4 456)	11 253 781(33 632)	55 923 535(310 321)
4300	3 317 788(5 324)	12 357 707(40 747)	61 591 943(378 267)
4400	3 615 319(6 348)	13 545 139(49 186)	67 690 767(459 610)
4500	3 933 823(7 552)	14 820 301(59 175)	74 240 165(557 328)
4600	4 274 354(8 963)	16 187 475(70 981)	81 260 967(675 510)
4700	4 637 989(10 613)	17 650 997(84 925)	88 767 272(815 823)
4800	5 025 831(12 537)	19 215 245(101 396)	96 788 084(988 326)
4900	5 439 003(14 779)	20 884 640(120 863)	105 335 722(1 195 720)
5000	5 878 650(17 387)	22 663 631(143 891)	114 427 930(1 444 135)
5100	6 345 940(20 418)	24 556 708(171 161)	124 089 255(1 745 553)
5200	6 842 057(23 940)	26 568 381(203 485)	134 341 002(2 111 750)
5300	7 368 205(28 033)	28 703 191(241 819)	145 197 936(2 550 998)
5400	7 925 606(32 791)	30 965 699(287 285)	156 664 345(3 063 814)
5500	8 515 498(38 324)	33 360 512(341 190)	168 805 034(3 701 226)
5600	9 139 135(44 763)	35 892 240(405 020)	181 598 712(4 446 075)
5700	9 797 788(52 258)	38 565 538(480 472)	195 052 408(5 303 681)
5800	10 492 742(60 984)	41 385 109(569 471)	209 247 097(6 346 507)
5900	11 225 296(71 144)	44 355 710(674 183)	224 168 167(7 565 059)
6000	11 996 765(82 969)	47 482 113(796 988)	239 791 330(8 939 979)

TABLE 5. The temperature-dependent nuclear-spin-equilibrated internal partition function, $Q_{\text{int}}(T)$, of D_2^{18}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	$Q_{\text{int}}(T)$	$Q'_{\text{int}}(T)$	$Q''_{\text{int}}(T)$
100	206.475(9)	305.334(5)	762.277(8)
200	578.65(1)	864.917(8)	2 174.80(2)
298.15	1 054.92(2)	1 601.70(1)	4 144.60(4)
300	1 064.88(2)	1 617.51(1)	4 188.66(4)
400	1 658.22(2)	2 596.31(3)	7 036.1(1)
500	2 367.24(3)	3 857.37(7)	10 972.2(4)
600	3 206.88(6)	5 465.9(2)	16 308(1)
700	4 196.2(1)	7 499.3(4)	23 422(3)
800	5 357.6(2)	10 046.7(9)	32 740(5)
900	6 716.9(3)	13 207(2)	44 732(10)
1000	8 302.5(6)	17 090(3)	59 911(16)
1100	10 145.7(9)	21 813(4)	78 846(24)
1200	12 280(1)	27 504(6)	102 162(34)
1300	14 742(2)	34 304(9)	130 549(46)
1400	17 571(3)	42 364(12)	164 768(61)
1500	20 809(4)	51 847(16)	205 648(79)
1600	24 500(5)	62 932(21)	254 099(102)
1700	28 692(6)	75 809(26)	311 109(131)
1800	33 436(8)	90 685(33)	377 749(167)
1900	38 786(10)	107 782(41)	455 179(213)
2000	44 801(12)	127 335(51)	544 652(273)
2100	51 541(15)	149 601(64)	647 516(351)
2200	59 071(18)	174 849(79)	765 220(450)
2300	67 460(22)	203 371(98)	899 316(578)
2400	76 780(27)	235 472(121)	1 051 466(743)
2500	87 109(32)	271 482(150)	1 223 444(955)
2600	98 527(39)	311 749(186)	1 417 141(1 227)
2700	111 119(47)	356 639(231)	1 634 564(1 579)
2800	124 975(56)	406 543(286)	1 877 841(2 032)
2900	140 190(67)	461 872(356)	2 149 221(2 617)
3000	156 862(81)	523 060(444)	2 451 074(3 368)
3100	175 096(97)	590 562(553)	2 785 888(4 331)
3200	195 000(117)	664 857(689)	3 156 266(5 557)
3300	216 688(140)	746 446(859)	3 564 921(7 111)
3400	240 280(169)	835 852(1 071)	4 014 670(9 063)
3500	265 898(204)	933 621(1 332)	4 508 425(11 498)
3600	293 673(246)	1 040 319(1 655)	5 049 187(14 512)
3700	323 739(296)	1 156 535(2 050)	5 640 032(18 215)
3800	356 236(357)	1 282 876(2 531)	6 284 105(22 733)
3900	391 308(430)	1 419 969(3 115)	6 984 584(28 211)
4000	429 106(517)	1 568 458(3 819)	7 744 722(34 821)
4100	469 784(621)	1 729 005(4 663)	8 567 769(42 764)
4200	513 502(745)	1 902 285(5 671)	9 457 061(52 298)
4300	560 424(891)	2 088 988(6 870)	10 415 857(63 716)
4400	610 721(1 064)	2 289 816(8 291)	11 447 412(77 374)
4500	664 566(1 267)	2 505 483(9 972)	12 555 115(93 766)
4600	722 136(1 505)	2 736 712(11 958)	13 742 468(113 570)
4700	783 614(1 783)	2 984 233(14 302)	15 011 844(137 065)
4800	849 187(2 107)	3 248 786(17 068)	16 368 099(165 920)
4900	919 044(2 484)	3 531 114(20 335)	17 813 305(200 585)
5000	993 379(2 923)	3 831 969(24 196)	19 350 434(242 082)
5100	1 072 389(3 433)	4 152 104(28 765)	20 983 590(292 403)
5200	1 156 274(4 025)	4 492 281(34 176)	22 716 331(353 507)
5300	1 245 238(4 713)	4 853 262(40 588)	24 551 123(426 777)
5400	1 339 485(5 511)	5 235 814(48 189)	26 488 683(512 304)
5500	1 439 227(6 440)	5 640 710(57 195)	28 539 810(618 574)
5600	1 544 673(7 519)	6 068 724(67 853)	30 700 950(742 745)
5700	1 656 038(8 774)	6 520 638(80 448)	32 973 266(885 707)
5800	1 773 540(10 235)	6 997 238(95 299)	35 370 243(1 059 521)
5900	1 897 396(11 935)	7 499 323(112 766)	37 889 432(1 262 615)
6000	2 027 828(13 912)	8 027 690(133 247)	40 526 766(1 491 773)

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	33.299 595(9)	33.299 571(6)	33.299 60(7)	180.012 02(2)	195.585 62(1)	181.326 54(3)	3.308 004(9)	3.308 073(4)	3.308 15(3)
200	33.453 69(1)	33.457 0(5)	33.459 34(1)	203.119 53(2)	218.693 7(1)	204.434 93(2)	6.642 458(8)	6.642 62(1)	6.642 76(4)
298.15	34.261 13(2)	34.274(1)	34.285 15(7)	216.602 69(3)	232.179 9(4)	217.923 64(3)	9.959 477(7)	9.960 43(9)	9.961 21(3)
300	34.282 80(2)	34.296(1)	34.307 17(7)	216.814 69(3)	232.392 0(4)	218.135 78(3)	10.022 880(7)	10.023 86(9)	10.024 65(3)
400	35.642 87(5)	35.664(1)	35.683 0(3)	226.856 27(3)	242.438 6(7)	228.186 69(8)	13.516 657(3)	13.519 4(2)	13.521 71(2)
500	37.195 5(1)	37.222(1)	37.247 1(8)	234.974 23(5)	250.562(1)	236.314 9(2)	17.157 538(5)	17.162 7(3)	17.167 20(3)
600	38.853 1(2)	38.883(2)	38.914(2)	241.900 95(9)	257.494(1)	243.251 9(4)	20.959 24(2)	20.967 2(5)	20.974 5(1)
700	40.572 7(5)	40.603(3)	40.639(3)	248.018 9(1)	263.616(2)	249.379 6(7)	24.930 25(6)	24.941 3(8)	24.951 9(3)
800	42.290 9(8)	42.320(4)	42.358(4)	253.549 2(2)	269.151(2)	254.919(1)	29.073 7(1)	29.088(1)	29.102 1(7)
900	43.946(1)	43.971(5)	44.011(5)	258.626 7(3)	274.231(3)	260.004(2)	33.386 3(2)	33.403(2)	33.421(1)
1000	45.494(2)	45.514(5)	45.555(5)	263.338 1(5)	278.945(3)	264.722(2)	37.859 3(4)	37.878(2)	37.901(2)
1100	46.912(2)	46.929(4)	46.969(6)	267.741 7(7)	283.351(4)	269.132(3)	42.480 7(6)	42.502(3)	42.528(2)
1200	48.195(3)	48.208(4)	48.248(5)	271.879 5(9)	287.490(4)	273.274(3)	47.237 1(8)	47.260(3)	47.290(3)
1300	49.345(3)	49.358(3)	49.395(5)	275.783(1)	291.395(4)	277.182(4)	52.115(1)	52.139(3)	52.173(3)
1400	50.373(4)	50.386(2)	50.422(4)	279.479(1)	295.091(5)	280.881(4)	57.102(2)	57.127(4)	57.165(4)
1500	51.291(5)	51.305(2)	51.339(4)	282.986(2)	298.599(5)	284.392(4)	62.186(2)	62.212(4)	62.254(4)
1600	52.112(5)	52.128(1)	52.160(4)	286.323(2)	301.937(5)	287.732(4)	67.357(2)	67.385(4)	67.430(4)
1700	52.846(6)	52.866(2)	52.896(3)	289.505(2)	305.120(5)	290.916(5)	72.606(3)	72.635(4)	72.683(5)
1800	53.507(6)	53.529(2)	53.558(4)	292.544(3)	308.161(5)	293.959(5)	77.924(4)	77.955(4)	78.006(5)
1900	54.102(7)	54.129(3)	54.156(5)	295.453(3)	311.071(5)	296.871(5)	83.305(4)	83.339(4)	83.393(6)
2000	54.642(8)	54.673(4)	54.699(6)	298.242(3)	313.862(5)	299.663(5)	88.743(5)	88.779(5)	88.836(6)
2100	55.134(9)	55.169(6)	55.194(7)	300.921(4)	316.541(6)	302.344(6)	94.232(6)	94.272(5)	94.331(7)
2200	55.58(1)	55.622(8)	55.65(1)	303.496(4)	319.118(6)	304.922(6)	99.768(7)	99.812(6)	99.873(8)
2300	56.00(1)	56.04(1)	56.06(1)	305.976(5)	321.600(6)	307.405(7)	105.347(8)	105.395(7)	105.459(9)
2400	56.38(1)	56.42(1)	56.45(2)	308.367(5)	323.993(7)	309.799(7)	110.966(9)	111.018(8)	111.08(1)
2500	56.73(1)	56.78(2)	56.80(2)	310.676(6)	326.304(7)	312.111(8)	116.62(1)	116.68(1)	116.75(1)
2600	57.06(2)	57.11(2)	57.14(2)	312.908(6)	328.538(8)	314.345(9)	122.31(1)	122.37(1)	122.44(1)
2700	57.37(2)	57.42(3)	57.44(3)	315.067(7)	330.699(9)	316.51(1)	128.03(1)	128.10(1)	128.17(2)
2800	57.66(2)	57.71(3)	57.73(3)	317.159(8)	332.79(1)	318.60(1)	133.78(2)	133.86(2)	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(2)	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(3)	145.53(3)
3100	58.41(4)	58.47(6)	58.49(6)	323.07(1)	338.71(1)	324.52(2)	151.20(3)	151.29(3)	151.37(3)
3200	58.63(5)	58.69(7)	58.71(7)	324.92(1)	340.57(2)	326.38(2)	157.05(3)	157.15(4)	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(5)	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(6)
3500	59.18(8)	59.2(1)	59.3(1)	330.20(2)	345.85(3)	331.66(3)	174.73(5)	174.84(7)	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(8)	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(2)
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)

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 material](#) also contains the same information for the three isotopologues, all at 1 K increments.

3.2. Comparison with previous results

Figure 3 shows the difference between our $D_2^{16}O$ $Q_{\text{int}}(T)$ partition function and that of Hewitt *et al.*,⁶ who only considered temperatures below 1000 K. At low temperatures, the agreement between the two studies is excellent, although it would appear that the calculations of Hewitt *et al.* give a partition function which is too low above 600 K, probably due to incomplete lists of energy levels.

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 water can be traced back to the work of Kell.⁵¹ An analysis⁵² 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 determined⁵³ 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

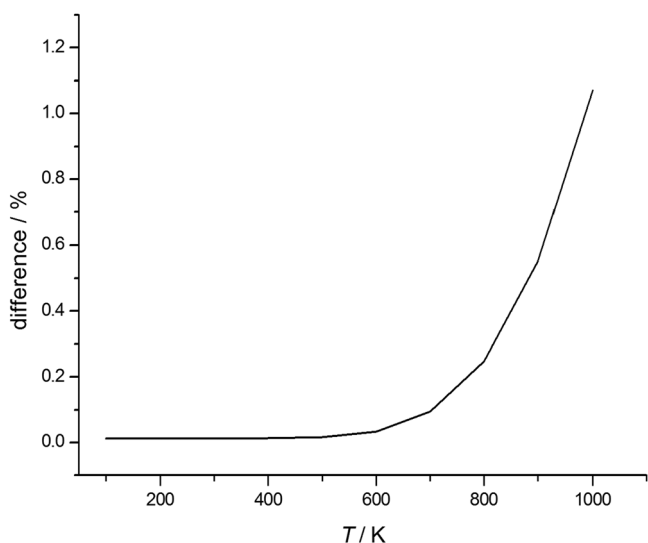


FIG. 3. Comparison of the present $Q_{\text{int}}(T)$ values of $D_2^{16}O$ with those of Hewitt *et al.*,⁶ defined with respect to the present values.

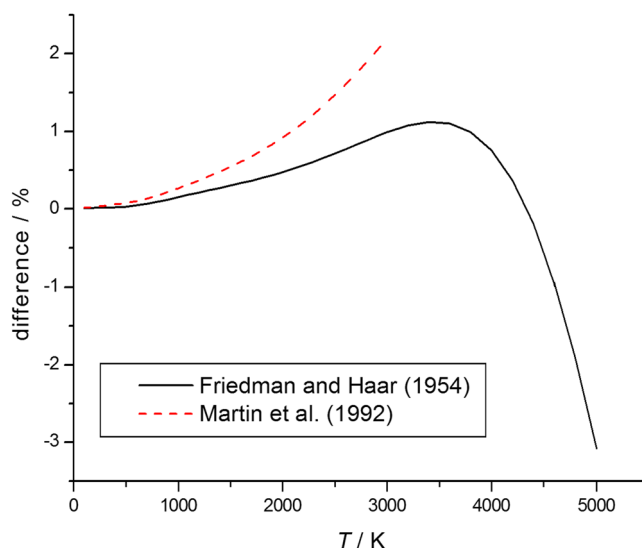


FIG. 4. Comparison of the present $C_p(T)$ values of $D_2^{16}O$ with those of Friedman and Haar (FH)¹⁵ (solid black curve) and Martin *et al.*²³ (dashed red curve).

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

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

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 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

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(3)	33.299 59(1)
200	571.188(4)	33.453 71(1)
298.15	1 041.155(6)	34.261 18(3)
300	1 050.977(6)	34.282 85(3)
400	1 636.06(1)	35.642 96(6)
500	2 334.61(2)	37.195 6(1)
600	3 161.14(3)	38.853 2(3)
700	4 134.14(5)	40.572 8(5)
800	5 275.61(8)	42.291 1(8)
900	6 610.6(1)	43.946(1)
1000	8 167.0(2)	45.494(2)
1100	9 975.3(3)	46.912(2)
1200	12 068.4(4)	48.195(3)
1300	14 481.9(6)	49.345(3)
1400	17 254.0(9)	50.374(4)
1500	20 425(1)	51.292(5)
1600	24 040(2)	52.112(5)
1700	28 144(2)	52.847(6)
1800	32 788(3)	53.507(6)
1900	38 023(4)	54.103(7)
2000	43 907(5)	54.642(8)
2100	50 498(7)	55.134(9)
2200	57 861(9)	55.58(1)
2300	66 061(11)	56.00(1)
2400	75 169(14)	56.38(1)
2500	85 260(18)	56.73(1)
2600	96 413(22)	57.06(2)
2700	108 709(27)	57.37(2)
2800	122 237(33)	57.66(2)
2900	137 088(41)	57.92(3)
3000	153 358(50)	58.18(3)
3100	171 147(61)	58.41(4)
3200	190 562(74)	58.63(5)
3300	211 713(90)	58.83(6)
3400	234 714(110)	59.01(7)
3500	259 687(133)	59.18(8)
3600	286 757(162)	59.33(9)
3700	316 054(196)	59.5(1)
3800	347 714(237)	59.6(1)
3900	381 877(286)	59.6(1)
4000	418 688(345)	59.7(2)
4100	458 299(416)	59.8(2)
4200	500 863(500)	59.8(2)
4300	546 541(599)	59.8(3)
4400	595 497(717)	59.7(3)
4500	647 900(857)	59.7(4)
4600	703 923(1 022)	59.6(4)
4700	763 743(1 217)	59.5(5)
4800	827 541(1 447)	59.4(6)
4900	895 502(1 719)	59.2(7)
5000	967 815(2 042)	59.1(8)
5100	1 044 671(2 423)	58.9(9)
5200	1 126 265(2 877)	59(1)
5300	1 212 795(3 415)	58(1)
5400	1 304 464(4 056)	58(1)
5500	1 401 474(4 819)	58(2)
5600	1 504 032(5 727)	58(2)
5700	1 612 347(6 807)	58(2)
5800	1 726 633(8 091)	57(2)
5900	1 847 102(9 612)	57(2)
6000	1 973 972(11 412)	57(3)

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

Table 7 contains the recommended $Q_{\text{int}}(T)$ partition function and $C_p(T)$ 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 compared to ordinary water, it behaves less as a quantum system at the lowest temperatures than $\text{H}_2^{54,55}$ or H_2^{16}O .^{21,56} Nevertheless, as Fig. 5 shows, the qualitative picture is the same as for H_2^{16}O , except that 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 . Quasi-bound 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 plus the uncertainties of the

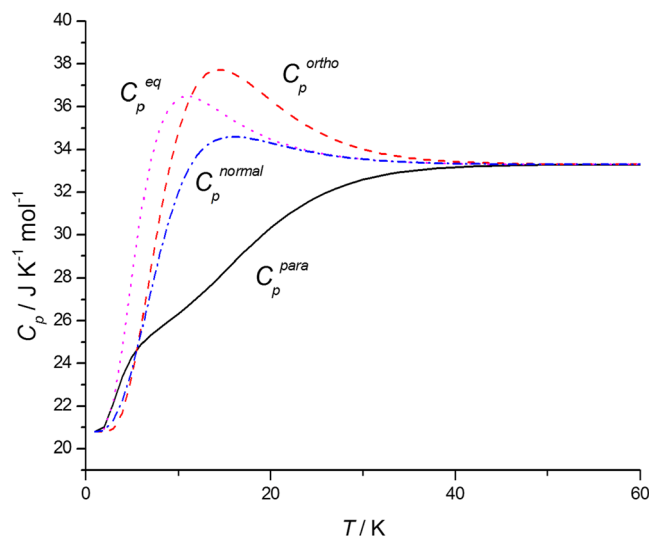


FIG. 5. The *ortho*- D_2^{16}O (dashed red curve), the *para*- D_2^{16}O (solid black curve), the nuclear-spin-equilibrated D_2^{16}O (dotted magenta curve), and the normal mixture D_2^{16}O (dashed-dotted blue curve) isobaric heat capacities at low temperatures, below 60 K.

computed values should also be taken into account. It must also be emphasized that measurements will not show any maximum; C_p of a sample will continue to rise with temperature, but an increasing amount will be due to dissociation products and less to intact water molecules.

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*-D₂¹⁶O, *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: 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 slightly “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 allow 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 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.

Supplementary Material

See [supplementary material](#) for listings of various temperature-dependent thermochemical quantities.

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