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Calculated high-temperature partition function and related thermodynamic data for $H_2{}^{16}O$

Gregory J. Harris, Serena Viti, Hamse Y. Mussa, and Jonathan Tennyson
Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom

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The partition function, Q, of water is calculated by explicit summation of $\sim$200 000 vibration–rotation levels computed using variational nuclear motion calculations. Temperatures up to 6000 K are studied. Estimates are obtained for the heat capacity (C_p), the Gibbs enthalpy factor (gef), the Helmholtz function (hcf), and the entropy (S) of gas-phase water as a function of temperature. To get converged results at higher temperatures it is necessary to augment the accurate list of energy levels. This is done using estimates for all the vibrational band origins to dissociation and rotational levels calculated using Padé approximants. The widely used method of computing the internal partition function as the product of vibrational and rotational partition functions is tested and found to overestimate the partition function by up to 10%. The present estimates of $Q(T)$, $C_p(T)$, gef(T), hcf(T), and $S(T)$ are probably the most accurate available for water at temperatures, T, above 2000 K. Errors, as a function of temperature, are estimated in each case. © *1998 American Institute of Physics.* [S0021-9606(98)02141-2]

I. INTRODUCTION

Data on the thermodynamic behavior of water at high temperature is important for modeling combustion, exhaust gases, and the atmosphere of cool stars to give but a few of the examples. This data is very difficult to obtain from laboratory measurements and standard compilations[1,2] rely heavily on theoretical estimates.

In principle, it should be possible to determine the internal partition function of water, and hence other thermodynamic properties, by explicit summation of the energy levels of the system. However, despite very significant advances in analyzing water spectra, only about 8000 energy levels of $H_2{}^{16}O$ have thus far been determined from experimental data.[3] This is far too few levels to give an accurate partition function at temperatures greater than a few hundred Kelvin. At higher temperatures it is, therefore, necessary to resort to theoretically determined energy levels to get the sums to converge.

There are two aspects which determine the accuracy of theoretically determined energy levels: The accuracy of the potential-energy surface used and the reliability of the model used to determine the levels from a given surface. Both of these steps have been the subject of systematic investigations.[4–7] Since these studies, there have been major advances in the determination of very high accuracy effective potential-energy surfaces for water from spectroscopic data.[8–10] Furthermore, variational nuclear motion calculations have been developed to the point where large-scale computations of energy levels, and associated transition data, have been performed.[10–12] In this paper we use energy levels obtained from very extensive variational calculations[13] on a high accuracy spectroscopically determined potential[9] to determine the partition function of $H_2{}^{16}O$ up to 6000 K. Corresponding estimates for other important thermodynamic properties are also obtained.

A corresponding study by Neale and Tennyson[14] on the astronomically important H_3^+ molecular ion found that the previous estimate of the H_3^+ partition function was an order of magnitude too low at high temperature! Too much careful work has been performed on the water system for gross errors of this sort to be likely, but the results presented here should still represent a significant improvement over previous estimates of the data in the high temperature ($T > 2000$ K) region.

II. METHOD

A. General considerations

It is standard to express the partition function, Q, as a product of translational and internal contributions

$$Q = Q_{\text{trans}} Q_{\text{int}}. \tag{1}$$

Here we follow the universal assumption that the translational partition function can be obtained from the perfect gas formula.[6] We, therefore, concentrate on the internal partition function which itself is usually expressed as a product

$$Q_{\text{int}} = Q_{vr} Q_e \approx Q_r Q_v Q_e, \tag{2}$$

where Q_e represents the contribution from excited electronic states to the partition function. As for water excited electronic states lie well above the dissociation energy of the system, Q_e is assumed to be unity. Martin *et al.*[6,15] found this to be a safe approximation for water but not for other systems, such as NH_2, which have low-lying electronic states. It is also common to assume that the vibration–rotation partition function Q_{vr} can be expressed as a product of separate vibrational and rotational partition functions, Q_v and Q_r, respectively. This is an approximation we test below.

The vibration–rotation partition function as a function of temperature, T, can be obtained by explicit summation of the vibration–rotation energy levels of the system

$$Q_{vr}=\sum_i g_i \exp\left(-\frac{E_i}{kT}\right), \tag{3}$$

where k is Boltzmann's constant. The energy of the ith level relative to the vibration–rotation ground state is given by E_i and its degeneracy by g_i. For water in a state of total rotational angular momentum, J, g_i is given by $(2J+1)$ times the nuclear spin factor, g_n.

For $H_2{}^{16}O$ the nuclear spin states are occupied in a 3:1 ratio corresponding to the so-called ortho and para states. Results given below used $g_n=\frac{3}{4}$ and $\frac{1}{4}$, respectively, for the ortho and para nuclear spin degeneracy factors. This factor is the one generally employed by astronomers although workers in some other areas use nuclear spin degeneracy factors of 3 and 1. The difference between the two conventions is whether a separated H-atom is assumed to have a nuclear spin degeneracy factor of 2 or 1.

In principle the sum in Eq. (3) runs over *all* vibration–rotation states of the molecule. In practice it has usually been necessary to truncate this sum according to some suitable criterion. Below we explore methods of, at least approximately, accounting for *all* truly bound vibration–rotation states in the molecule. This raises the question of what, if any, role is played by the quasi-bound states of the molecule. Since we have essentially no information about these states, we have simply neglected them and neglected any energy level which lies above dissociation. A similar procedure was used by Irwin to derive high-temperature partition functions for diatomics.[16]

In order to obtain temperature-dependent estimates of various thermodynamic quantities it is necessary to obtain the first and second derivative of the partition function with respect to temperature. In principle these could be obtained by differentiating $Q(T)$, but a numerically more reliable procedure is to analytically differentiate the right-hand-side of Eq. (3) and then perform the summation. One can write the first and second moments of the partition function as[6]

$$Q'=T\frac{dQ}{dT}=\sum_i g_i\left(\frac{E_i}{kT}\right)\exp\left(-\frac{E_i}{kT}\right), \tag{4}$$

$$Q''=T^2\frac{d^2Q}{dT^2}+2Q'=\sum_i g_i\left(\frac{E_i}{kT}\right)^2 \exp\left(-\frac{E_i}{kT}\right). \tag{5}$$

In terms of these quantities, the internal contribution to the ideal gas thermodynamic functions Gibbs enthalpy function (gef) and the Helmholtz function (hcf), are given by the expressions[1,6]

$$\text{gef}(T)=-\frac{[G(T)-E_0]}{T}=R\ \ln Q-\frac{E_0}{T}, \tag{6}$$

$$\text{hcf}(T)=H(T)-E_0=RT\frac{Q'}{Q}-E_0, \tag{7}$$

where the functions are expressed, as in JANAF,[1] relative to a the reference point of the Helmholtz function at a temperature of 298.15 K [i.e., $H(298.15)$]. In our calculations, the reference, E_0, was found to have a value of 9895.4 J mol^{-1}. This can be compared with 9904 J mol^{-1} used by JANAF[1] and 9902 J mol^{-1} by Martin *et al.*[6] Differences of this magnitude have some effect on the results at low temperatures ($T\leqslant 1000$ K) but are negligible at the higher temperatures which are our main concern here. It is not possible to determine an exact value for E_0 from the data of Woolley,[4] so in comparisons presented below his results for $G(T)$ and $H(T)$ were shifted using a value of $E_0=9902$ J mol^{-1}.

Corresponding expressions for the entropy (S) and specific heat at constant pressure (C_p) are[6]

$$S(T)=R\frac{Q'}{Q}+R\ \ln Q, \tag{8}$$

$$C_p(T)=R\left[\frac{Q''}{Q}-\left(\frac{Q'}{Q}\right)^2\right]. \tag{9}$$

Expressions for the translational contribution to the partition function, and other thermodynamic properties, for an ideal gas are standard.[1] It should be noted that the specific heat depends on the difference between the second moment and the square of the first moment. This makes this property particularly sensitive to convergence of any summation used to estimate the partition function. The results presented below illustrate this behavior.

B. Energy levels

The main source of energy levels for the summations (3)–(5) is a calculation by Viti and Tennyson.[13,17] This calculation was performed to produce a comprehensive linelist, VT2, of water transitions suitable for modeling radiative transport in the atmosphere of cool stars and other hot bodies. The results of the calculation will be presented elsewhere[17] and only a brief summary is given here.

The VT2 linelist was generated by performing nuclear motion calculations on the experimentally determined potential-energy surface of Polyansky, Jensen, and Tennyson,[9] known as PJT2. The calculations were performed in Radau coordinates using a full discrete variable representation (DVR) of the vibrational coordinates as implemented in the DVR3D program suite.[18] The calculation produced estimates for all $H_2{}^{16}O$ energy levels below 30 000 cm^{-1} above the ground state up to a given value of the total rotational angular momentum, J. In this work we used energy levels for all rotational states with $J\leqslant 35$, giving a list of about 200 000 levels. The PJT2 potential reproduced all the experimentally determined energy levels with $J\leqslant 14$ known at the time of its construction with a standard deviation of only 0.6 cm^{-1}. Low-lying levels, which are particularly important for determining properties at low temperature, are reproduced much better than this.

As will be discussed below, the VT2 linelist does not contain enough energy levels to fully converge the partition function at higher temperatures. It was not considered worthwhile to extend the comprehensive nuclear motion calculations to higher energies. These calculations are computationally expensive and the absence of a reliable potential-energy surface at these high energies makes it hard to justify such calculations. Instead an alternative procedure, used successfully for H_3^+,[14] was employed.

For high energy or rotational angular momentum, energy levels were obtained as

$$E_{vr}=E_v+E_r. \tag{10}$$

Estimates for the higher vibrational band origins, E_v, were obtained from the recent calculation of Mussa and Tennyson (MT).[19] MT computed *all* the vibrational band origins of $H_2{}^{16}O$ for the *ab initio* potential of Ho *et al.*[20] These calculations were performed with a parallel version of the DVR3D program, PDVR3D.[21] MT obtained 1053 bound vibrational states with $J=0$ below 39 821.1 cm^{-1}, of which 631 lie at energies 30 000 cm^{-1} or more above the ground state. In fact MT have also performed some calculations which obtained *all* the bound states for certain rotationally excited states of water. However, these calculations are at present limited and we only used their $J=0$ results. A full description of MT's calculations will be presented elsewhere.[19]

To obtain energy estimates, E_r, for rotationally excited levels not in the VT2 linelist, we used a simple, effective Hamiltonian expression for the rotational energy levels

$$\begin{aligned} E(J,K)&=\frac{C_0^2}{C_0-C_1},\\ C_0&=\left(A-\frac{B+C}{2}\right)K^2+\left(\frac{B+C}{2}\right)J(J+1), \\ C_1&=-\Delta_J[J(J+1)]^2-\Delta_{JK}K^2J(J+1)-\Delta_K K^4. \end{aligned} \tag{11}$$

This Padé approximant form, which is due to Polyansky,[22] has the advantage over standard forms that it does not diverge at high values of J. It is, however, fairly crude and makes no allowance for splitting between levels with the same value of K $(=K_a)$ but differing in K_c. Such splittings are small, especially for most high J states. We used the constants fitted by Polyansky[22] for the ground state of water. These constants have the feature that levels with $K=J$ are too low at high J and, in fact, converge to a value below the dissociation energy. We, therefore, arbitrarily truncated our calculations at $J=71$, the last value of J for which the $K=0$ level is bound.

C. Summation procedure and error analysis

Our temperature-dependent partition function is obtained using a sum of the form of Eq. (3) but split into two regions. For levels lying below some energy cutoff, $E^{\max}$ and rotational cutoff, $J^{\max}$, the VT2 levels were used. For levels outside this range, the E_{vr} value estimated above were used. The sum over estimated levels was truncated such that only energy levels for which $E_{vr}<D_0$ were included. For this work we used a value for the dissociation energy, D_0, of 39 821.1 cm^{-1}. This value was estimated from the results of Ho *et al.*[20] and is approximately 1000 cm^{-1} lower than the accepted experimental value. This difference arises because the *ab initio* data fitted by Ho *et al.* is, of course, not exact. Our high-temperature ($T\sim 6000$ K) results almost certainly show some sensitivity to the choice of D_0, but this is not something that we have explored.

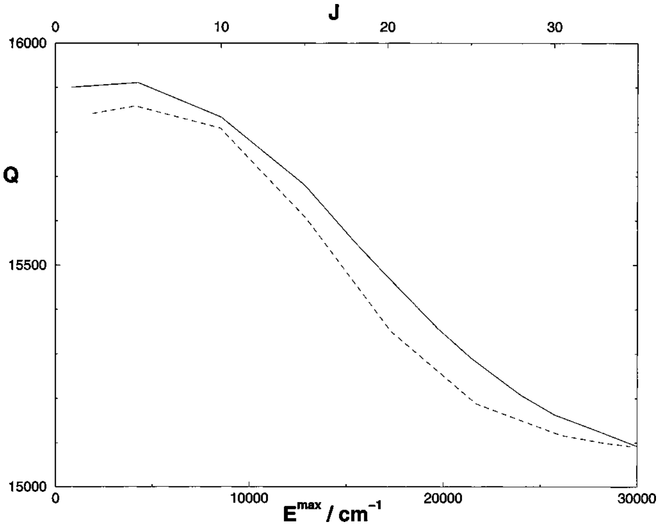

FIG. 1. Convergence of our calculation for the internal partition function, Q_{vr}, at $T=4500$ K as function of truncating the levels included in the sum by energy, $E^{\max}$, solid curve and lower scale, and rotational state, $J^{\max}$, dashed curve and upper scale. See text for details.

Our best results are obtained using the values $E^{\max}=30\,000$ cm^{-1} and $J^{\max}=35$ which specify the limits of the VT2 energy levels used here. However, to help estimate the error introduced by using the approximate E_{vr} energy levels a series of calculations were performed which tested the effect of reducing either $E^{\max}$ or $J^{\max}$. Figure 1 illustrates the convergence of our partition function at $T=4500$ K as a function of varying $E^{\max}$ or $J^{\max}$. Table I summarizes the estimated percentage error for the partition function and other computed thermodynamic properties as a result of these tests. No results are presented in Table I for $T<3000$ K as the use of approximate energy levels at high energy or J introduces no significant error in any of the quantities we compute at these temperatures.

While truncation of summation (3) will usually lead to an underestimate of the partition function, and associated quantities, especially at higher temperatures, this was not found to be so for our calculations which used approximate E_{vr} energy levels. Lowering of $J^{\max}$, to which our results were more sensitive than $E^{\max}$, led to an overestimate of the partition functions at all temperatures. This appears to be a

TABLE I. Estimated percentage error as a function of temperature, due to approximation of higher levels. See text for details.

$T=$	3000 K	4500 K	6000 K
Q_{int}	0	2	6
Q'_{int}	0	5	8
Q''_{int}	2	7	8
hef	0.8	3	2
gef	0	0.1	0.3
S	0.1	0.5	0.8
C_p	1	4	[a]

[a] For C_p at $T=6000$ K the error is too large to be estimated reliably.

TABLE II. Internal partition, Q_{vr}, from this work and Irwin (Ref. 2). The vibrational partition function, Q_v, the rotational partition function, Q_r, and the internal partition function given as the simple product of these are also given for comparison.

	This work				Irwin (Ref. 2)
T/K	Q_v	Q_r	$Q_v \times Q_r$	Q_{vr}	Q_{vr}
100	1.000 00	8.788 26	8.788 26	8.788 23	
200	1.000 01	24.3453	24.3455	24.3453	
300	1.000 48	44.4734	44.4947	44.4931	
400	1.003 24	68.3434	68.5648	68.5518	
500	1.010 33	95.4919	96.4783	96.4132	
600	1.022 66	125.632	128.479	128.268	
700	1.040 35	158.581	164.980	164.455	
800	1.063 24	194.219	206.501	205.403	
900	1.091 12	232.461	253.643	251.617	
1000	1.123 85	273.245	307.086	303.670	304.073
1100	1.161 33	316.523	367.588	362.203	362.676
1200	1.203 49	362.253	435.968	427.918	428.437
1300	1.250 31	410.400	513.127	501.575	502.122
1400	1.301 75	460.932	600.018	583.987	584.547
1500	1.357 83	513.822	697.683	676.023	676.574
1600	1.418 54	569.044	807.212	778.608	779.119
1700	1.483 91	626.573	929.778	892.718	893.147
1800	1.553 99	686.384	1066.63	1019.39	1019.68
1900	1.628 82	748.454	1219.10	1159.72	1159.79
2000	1.708 47	812.758	1388.57	1314.85	1314.63
2100	1.793 00	879.271	1576.53	1486.01	1485.38
2200	1.882 49	947.964	1784.53	1674.49	1673.30
2300	1.977 03	1018.81	2014.22	1881.63	1879.73
2400	2.076 71	1091.77	2267.29	2108.87	2106.06
2500	2.181 63	1166.82	2545.57	2357.72	2353.75
2600	2.291 90	1243.92	2850.94	2629.76	2624.33
2700	2.407 62	1323.03	3185.35	2926.69	2919.42
2800	2.528 92	1404.12	3550.91	3250.27	3240.70
2900	2.655 90	1487.13	3949.67	3602.38	3589.94
3000	2.788 69	1572.04	4383.93	3984.98	3968.99
3100	2.927 42	1658.78	4855.95	4400.17	4379.77
3200	3.072 20	1747.33	5368.15	4850.13	4824.30
3300	3.223 17	1837.64	5923.03	5337.18	5304.69
3400	3.380 45	1929.67	6523.15	5863.76	5823.14
3500	3.544 16	2023.37	7171.15	6432.43	6381.93
3600	3.714 45	2118.70	7869.81	7045.89	6983.46
3700	3.891 42	2215.62	8621.91	7706.95	7630.21
3800	4.075 22	2314.10	9430.47	8418.59	8324.77
3900	4.265 95	2414.10	10 298.4	9183.88	9069.84
4000	4.463 76	2515.58	11 228.9	10 006.1	9868.22
4100	4.668 75	2618.53	12 225.3	10 888.5	10 722.8
4200	4.881 05	2722.89	13 290.6	11 834.7	11 636.7
4300	5.100 77	2828.66	14 428.3	12 848.2	12 613.0
4400	5.328 03	2935.81	15 642.1	13 932.9	13 654.9
4500	5.562 94	3044.32	16 935.4	15 092.5	14 766.0
4600	5.805 60	3154.16	18 311.8	16 331.0	15 949.7
4700	6.056 11	3265.33	19 775.2	17 652.5	17 209.6
4800	6.314 59	3377.80	21 329.4	19 061.2	18 549.6
4900	6.581 12	3491.57	22 978.4	20 561.3	19 973.6
5000	6.855 80	3606.63	24 726.3	22 157.1	21 485.8
5100	7.138 71	3722.98	26 577.3	23 853.0	23 090.3
5200	7.429 95	3840.60	28 535.5	25 653.4	24 791.5
5300	7.729 59	3959.49	30 605.2	27 562.9	26 594.1
5400	8.037 72	4079.66	32 791.2	29 586.0	28 502.6
5500	8.354 40	4201.10	35 097.7	31 727.1	30 522.1
5600	8.679 71	4323.82	37 529.5	33 990.8	32 657.6
5700	9.013 72	4447.81	40 091.3	36 381.7	34 914.3
5800	9.356 48	4573.08	42 787.9	38 904.3	37 297.7
5900	9.708 06	4699.64	45 624.4	41 563.0	39 813.4
6000	10.0685	4827.50	48 605.7	44 362.4	42 467.2

TABLE III. Gibbs enthalpy function, gef, in J K^{-1} mol^{-1} as a function of temperature, T. Results from Woolley (Ref. 4), JANAF (Ref. 1), and Martin *et al.* (Ref. 6) are given for comparison.

T/K	[a]	[b]	[c]	[d]	[e]
100	218.33	218.53	218.61		
200	191.73	191.89	191.98	191.77	191.77
300	188.68	188.83	188.92	188.71	188.71
400	190.01	190.15	190.24	190.04	190.04
500	192.53	192.68	192.76	192.57	192.57
600	195.40	195.55	195.63	195.43	195.43
700	198.31	198.46	198.54	198.35	198.35
800	201.17	201.32	201.39	201.21	201.21
900	203.93	204.08	204.15	203.97	203.97
1000	206.58	206.73	206.80	206.62	206.62
1100	209.13	209.28	209.35		
1200	211.58	211.73	211.79		
1300	213.93	214.08	214.13		
1400	216.19	216.34	216.39		
1500	218.37	218.52	218.56		
1600	220.47	220.62	220.66		
1700	222.51	222.65	222.69		
1800	224.47	224.62	224.65		
1900	226.38	226.52	226.55		
2000	228.23	228.37	226.85	228.26	228.28
2100	230.03	230.16	230.18		
2200	231.77	231.90	231.91		
2300	233.47	233.60	233.60		
2400	235.12	235.25	235.25		
2500	236.73	236.86	236.85		
2600	238.30	238.42	238.40		
2700	239.84	239.95	239.92		
2800	241.33	241.44	241.41		
2900	242.80	242.89	242.85		
3000	244.23	244.32	244.27	244.23	244.33
3100	245.63	245.71			
3200	247.00	247.07			
3300	248.34	248.40			
3400	249.65	249.70			
3500	250.94	250.98			
3600	252.21	252.23			
3700	253.45	253.45			
3800	254.66	254.66			
3900	255.86	255.84			
4000	257.04	256.99		256.97	257.14
4100	258.19	258.13			
4200	259.33	259.25			
4300	260.14	260.34			
4400	261.55	261.42			
4500	262.63	262.48			
4600	263.69	263.52			
4700	264.74	264.55			
4800	265.77	265.56			
4900	266.79	266.55			
5000	267.79	267.53		267.60	267.82
5100	268.78	268.49			
5200	269.75	269.44			
5300	270.71	270.37			
5400	271.65	271.29			
5500	272.56	272.19			
5600	273.49	273.09			
5700	274.39	273.97			
5800	275.28	274.84			
5900	276.16	275.69			
6000	277.02	276.54		276.75	276.98

[a] This work.
[b] JANAF (Ref. 1).
[c] Martin *et al.* (Ref. 6).
[d] Woolley, ''1982 version'' (Ref. 4).
[e] Woolley, ''1984 version'' (Ref. 4).

general problem with effective Hamiltonian representations of rotational motion and should be remembered when comparing with previous results, all of which used effective Hamiltonians for all energy levels.

It should be noted that the errors referred to in Table I only refer to errors introduced due to our use of energy estimates to top up the incomplete VT2 energy levels. Other, systematic errors, due to such factors as the (minor) inaccuracies in the VT2 levels or value of the dissociation energy, are harder to estimate. However, one would expect errors introduced by any inaccuracy in the VT2 levels to be most significant at lower temperatures, where the partition function and other properties are more strongly dependent on the correct representation of relatively few levels. As demonstrated below, at low temperature our results are in very good agreement with previous estimates, especially those due to Woolley.[4] This suggests that there is no significant problem with the accuracy of the VT2 levels.

III. RESULTS AND DISCUSSION

Tables II–VI give the main results of this work. Comparison is made with the available high temperature data from previous work. It should be noted that the JANAF[1] results quoted in Tables III–VI are for water in its natural abundance whereas our results, as well as those quoted from Woolley,[4] Irwin,[2] and Martin *et al.*,[6] are for pure $H_2{}^{16}O$. In practice this only leads to very minor differences; a direct measure of these differences for $T \leqslant 3000$ K is given by Martin *et al.*[6] Martin *et al.* found that the differences depend only very weakly on temperature and are less than 0.01 J K^{-1} mol^{-1} for gef and S, 0.001 J K^{-1} mol^{-1} for C_p, and 0.06 kJ mol^{-1} for hcf. Compared with other differences between the various calculations discussed below, these differences are negligible.

There seems to be little published data on the high-temperature partition function of water available in the literature. The most extensive appears to be due to Irwin[2] who produced a fit based on the partition function data of McBride *et al.*[23] updated with modern (JANAF[1]) physical constants. Irwin's fit is only valid for 1000 K$\leqslant T \leqslant$6000 K, but in this range the agreement with our internal partition function is remarkable. Table II shows that over this range the two partition functions agree to within the error estimates of both works and at most temperatures, much better than this.

Of course the Gibbs enthalpy function, gef, can also be used to give a measure of the partition function. Comparisons, see Table III, with previous work suggest that our (and Irwin's) partition function is somewhat lower at high temperature than those of the other studies discussed here. Reasons for this are given below.

For some applications it is useful to have the partition function as a function of temperature represented in analytic form. We have, therefore, fitted our results to the following function:[24]

$$\log Q_{vr} = \sum_{i=0}^{6} a_i (\log T)^i. \tag{12}$$

A fit in the range $T=100$ to 6000 K in steps of 100 K gave $a_0=-14.238\,480\,506\,262\,7$, $a_1=38.053\,702\,726\,924\,3$, $a_2=-42.649\,044\,013\,388\,9$, $a_3=25.238\,163\,093\,783\,1$, $a_4=-8.056\,218\,790\,085\,96$, $a_5=1.317\,838\,936\,167\,98$, and $a_6=-0.086\,022\,746\,786\,300\,4$. This functional form reproduces Q_{vr} to within 0.1% over the entire range, and log Q_{vr} to better than 0.02%.

Tables III, IV, V, and VI give results for the Gibbs enthalpy function (gef), the Helmholtz function (hcf), the entropy (S), and specific heat (C_p), respectively. In general our results are in good agreement with previous studies up to intermediate temperatures ($T\leqslant 2000$ K), with particularly good agreement being obtained with the results of Woolley to about 4000 K. In general the agreement between the various results for C_p are worse than for the other quantities, although our results remain in excellent accord with those of Woolley up to 4000 K.

In order to discuss the differences between the various models considered here, it is necessary to understand how the results of the previous works quoted were constructed. The JANAF[1] data is the standard input for many models. Therefore, considerable care has been taken in making this compilation. The 1985 JANAF compilation for gas-phase water quoted here used preliminary results due to Woolley (see below) for $S(T)$ and $C_p(T)$ below 2000 K. Between 2000 and 5000 K, C_p was obtained from the calculations of Friedman and Haar.[25] Friedman and Haar's 1954 calculation represented a pioneering use of electronic computers but cannot be considered accurate by today's standards. Above 5000 K JANAF's C_p is simply a linear extrapolation of the Friedman and Haar data. It is not explicitly stated how the other data for gaseous water given in JANAF was obtained.

Martin *et al.*[6] used various potential-energy surfaces to obtain constants which were then used to compute separate vibrational and rotational partition functions. The vibrational partition function used harmonic plus leading anharmonic terms to represent the vibrations; the rotational partition function used a conventional rigid-rotor based effective Hamiltonian expansion. It is well-known that such expansions are divergent for water at relatively low J.[22] Martin *et al.* ''best'' results, which are the ones quoted here, were based on constants from their own *ab initio* calculations. Strongly suggestive of cancellation of errors is that they obtained significantly worse results when they used a more accurate, empirically determined, potential due to Jensen.[26]

Table II compares our partition (Q_{vr}) with one calculated from the same energy level data but as a product of vibrational and rotational partition functions ($Q_v\times Q_r$). It shows that this product is not reliable except at the lowest temperatures. Indeed at 3000 K, Q_{vr} is 10% less than $Q_v\times Q_r$. This error is enough to account for the differences between our data and Martin *et al.*, although it should be noted that their perturbative treatment of rotational motion is also likely to have led to an overestimate of the rotational partition function.

Woolley's[4] and Topper *et al.*[7] are the only previous studies which appear not to have assumed that the partition function can be represented as a product of vibrational and rotational parts. Woolley recognized that the rotational ex-

TABLE IV. Helmholtz function, hcf, in kJ K^{-1} mol^{-1} as a function of temperature, T.

T/K	[a]	[b]	[c]	[d]	[e]
100	−6606	−6615	−6613		
200	−3275	−3282	−3281	−3280	−3280
300	67	62	62	64	64
400	3454	3452	3449	3454	3454
500	6925	6925	6919	6727	6727
600	10 500	10 501	10 492	10 503	10 503
700	14 190	14 192	14 182	14 194	14 194
800	18 000	18 002	17 983	18 004	18 005
900	21 936	21 939	21 911	21 939	21 941
1000	26 000	26 000	25 965	26 001	26 005
1100	30 191	30 191	30 145		
1200	34 509	34 506	34 448		
1300	38 949	38 942	38 870		
1400	43 504	43 493	43 403		
1500	48 169	48 151	48 042		
1600	52 936	52 908	52 779		
1700	57 799	57 758	57 605		
1800	62 750	62 693	62 515		
1900	67 782	67 706	67 500		
2000	72 891	72 790	72 555	72 086	73 034
2100	78 071	77 941	77 673		
2200	83 317	83 153	82 850		
2300	88 625	88 421	88 079		
2400	93 992	93 741	93 356		
2500	99 415	99 108	98 677		
2600	104 892	104 520	104 037		
2700	110 420	109 973	109 434		
2800	115 998	115 464	114 864		
2900	121 626	120 990	120 325		
3000	127 302	126 549	125 812	126 930	127 653
3100	133 025	132 139			
3200	138 795	137 757			
3300	144 610	143 403			
3400	150 471	149 073			
3500	156 375	154 768			
3600	162 321	160 485			
3700	168 308	166 222			
3800	174 334	171 980			
3900	180 395	177 757			
4000	186 490	183 552		184 891	185 848
4100	192 615	189 363			
4200	198 766	195 191			
4300	204 939	201 034			
4400	211 130	206 892			
4500	217 334	212 764			
4600	223 545	218 650			
4700	229 760	224 548			
4800	235 973	230 458			
4900	242 178	236 380			
5000	248 371	242 313		245 294	246 061
5100	254 545	248 258			
5200	260 697	254 215			
5300	266 820	260 184			
5400	272 911	266 164			
5500	278 965	272 157			
5600	284 978	278 161			
5700	290 946	284 177			
5800	296 864	290 204			
5900	302 731	296 244			
6000	308 544	302 295		307 659	307 871

[a] This work.

[b] JANAF (Ref. 1).

[c] Martin *et al.* (Ref. 6).

[d] Woolley, ''1982 version'' (Ref. 4).

[e] Woolley, ''1984 version'' (Ref. 4).

TABLE V. Entropy, S, in J K^{-1} mol^{-1} as a function of temperature, T.

T/K	a	b	c	d	e
100	152.26	152.38	152.48		
200	175.35	175.48	175.57	175.37	175.37
300	188.90	189.04	189.12	188.93	188.93
400	198.64	198.78	198.86	198.67	198.67
500	206.38	206.53	206.60	206.42	206.42
600	212.89	213.05	213.11	212.94	212.94
700	218.58	218.73	218.79	218.62	212.62
800	223.66	223.82	223.87	223.71	223.71
900	228.30	228.45	228.50	228.34	228.35
1000	232.58	232.73	232.77	232.62	232.62
1100	236.57	236.73	236.75		
1200	240.33	240.48	240.49		
1300	243.88	244.03	244.03		
1400	247.26	247.40	247.39		
1500	250.48	250.62	250.59		
1600	253.55	253.69	253.65		
1700	256.50	256.69	256.57		
1800	259.33	259.45	256.38		
1900	262.05	262.16	262.08		
2000	264.67	264.76	264.67	264.66	264.80
2100	267.20	267.28	267.17		
2200	269.64	269.70	269.57		
2300	272.00	272.04	271.90		
2400	274.28	274.31	274.14		
2500	276.49	276.50	276.32		
2600	278.64	278.62	278.42		
2700	280.73	280.68	280.46		
2800	282.76	282.68	282.43		
2900	284.73	284.61	284.35		
3000	286.66	286.50	286.21	286.54	286.88
3100	288.53	288.33			
3200	290.36	290.12			
3300	292.15	291.85			
3400	293.90	293.55			
3500	295.62	295.20			
3600	297.29	296.81			
3700	298.93	298.38			
3800	300.54	299.91			
3900	302.11	301.42			
4000	303.66	302.88		303.19	303.60
4100	305.17	304.32			
4200	306.65	305.72			
4300	308.10	307.10			
4400	309.53	308.44			
4500	310.92	309.76			
4600	312.28	311.06			
4700	313.62	312.32			
4800	314.93	313.57			
4900	316.21	314.79			
5000	317.46	315.99		316.66	317.03
5100	318.68	317.17			
5200	319.88	318.32			
5300	321.04	319.46			
5400	322.18	320.58			
5500	323.29	321.68			
5600	324.38	322.76			
5700	325.43	323.82			
5800	326.46	324.87			
5900	327.47	325.90			
6000	328.44	326.92		328.02	328.30

[a] This work.
[b] JANAF (Ref. 1).
[c] Martin *et al.* (Ref. 6).
[d] Woolley, ''1982 version'' (Ref. 4).
[e] Woolley, ''1984 version'' (Ref. 4).

TABLE VI. Heat capacity at constant pressure, C_p, in J K^{-1} mol^{-1} as a function of temperature, T.

T/K	a	b	c	d	e
100	33.294	33.299	33.303		
200	33.332	33.349	33.339	33.350	33.350
300	33.571	33.596	33.578	33.596	33.596
400	34.239	34.262	34.237	34.262	34.262
500	35.208	35.226	35.193	35.226	35.226
600	36.315	36.325	36.283	36.324	36.326
700	37.492	37.495	37.443	37.494	37.498
800	38.723	38.721	38.658	38.719	38.727
900	39.993	39.987	39.909	39.982	39.999
1000	41.278	41.268	41.173	41.259	41.291
1100	42.553	42.536	42.423		
1200	43.795	43.768	43.634		
1300	44.986	44.945	44.788		
1400	46.114	46.054	45.876		
1500	47.173	47.090	46.889		
1600	48.160	48.050	47.828		
1700	49.078	48.935	48.692		
1800	49.929	49.749	49.486		
1900	50.718	50.496	50.212		
2000	51.452	51.180	50.875	51.309	51.756
2100	52.136	51.823	51.481		
2200	52.776	52.408	52.034		
2300	53.380	52.947	52.537		
2400	53.953	53.444	52.996		
2500	54.500	53.904	53.414		
2600	55.026	54.329	53.795		
2700	55.536	54.723	54.141		
2800	56.033	55.089	54.455		
2900	56.519	55.430	54.740		
3000	56.996	55.748	54.997	56.394	56.824
3100	57.466	56.044			
3200	57.928	56.323			
3300	58.381	56.583			
3400	58.824	56.828			
3500	59.255	57.058			
3600	59.671	57.276			
3700	60.067	57.480			
3800	60.441	57.675			
3900	60.788	57.859			
4000	61.104	58.033		59.312	59.330
4100	61.385	58.199			
4200	61.627	58.357			
4300	61.827	58.507			
4400	61.981	58.650			
4500	62.087	58.787			
4600	62.143	58.918			
4700	62.147	59.044			
4800	62.098	59.164			
4900	61.997	59.275			
5000	61.844	59.390		61.425	61.040
5100	61.639	59.509			
5200	61.384	59.628			
5300	61.081	59.746			
5400	60.732	59.864			
5500	60.340	59.982			
5600	59.907	60.100			
5700	59.438	60.218			
5800	58.934	60.335			
5900	58.400	60.453			
6000	57.838	60.571		63.268	62.556

[a] This work.
[b] JANAF (Ref. 1).
[c] Martin *et al.* (Ref. 6).
[d] Woolley, ''1982 version'' (Ref. 4).
[e] Woolley, ''1984 version'' (Ref. 4).

pansions are potentially divergent and treated these in tandem with the bending motion. He parameterized his expressions using empirically derived constants. He used two different sets of constants to give two sets of results, the ''1982'' and ''1984'' versions. Rather than claiming one set to be superior, he states that the two sets give an error estimate for his procedure. For this reason we quote both sets of his results.

Woolley's procedure for treating nuclear motion would seem to be significantly better than the others with which we compare. It is, therefore, not surprising that we obtain much better agreement with his results. However there is one aspect of Woolley's work which is somewhat surprising. His sums include a very large number of vibrational states, over 13 000 at the highest temperatures. Our explicit $J=0$ calculations suggest that water has a little over a 1000 bound vibrational states. Although it is possible that this figure is an underestimate, it cannot be an order of magnitude too low. It would appear that Woolley ignored the possibility that water dissociates. Woolley's high-temperature data, he quotes results up to 10 000 K cannot, therefore, be considered reliable.

From these comparisons it is reasonable to suppose that our estimates of the high-temperature behavior of the various thermodynamic functions of water considered here are much the most accurate available. The hardest property to treat is the specific heat, C_p, which is obtained as the difference between first and second derivates of the partition function. For this reason C_p is particularly sensitive to convergence of the partition function. Above 4500 K we were unable to estimate an error in our value for C_p because of the sensitivity to convergence. Indeed our value of C_p begins to drop above 4700 K. This feature is almost certainly an artifact of our calculation and work clearly remains to be done to determine accurately the specific heat of water at very high temperature.

IV. CONCLUSIONS

We have used a large, accurately determined dataset of vibration–rotation energy levels for water to determine the partition function and related thermodynamic properties for steam at high temperatures. Our calculations show that previous approximations, particularly the separation of vibrational and rotational partition functions, and the use of effective Hamiltonian expansions for rotational motions, leads to overestimates of the partition function at high temperature. The results presented here, therefore, represent a significant improvement on previous data, although work remains to be done obtaining accurate high-temperature values for the specific heat of water.

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