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# Accurate partition function and thermodynamic data for water

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The partition function, $Q$, of $H_2{}^{16}O$ is calculated by explicit summation of about 10 500 experimental vibration-rotation energy levels and very high accuracy estimates are obtained for the specific heat capacity ($C_p$), the Gibbs enthalpy function (gef), the Helmholtz function (hcf) and the entropy ($S$) of gas phase water as a function of temperature. For temperatures above 600 K it is necessary to augment the sum with theoretical estimates of the energy levels. These are obtained from high accuracy variational calculations which are extended to dissociation using a model for rotational levels based on a Padé approximant. Estimates for the partition function and other thermodynamic quantities are obtained for temperatures up to 6000 K and temperature dependent error bars presented. All estimates are highly accurate with the exception of $C_p$ for $T>5000$ K, for which further work is required. © *2000 American Institute of Physics.* [S0021-9606(00)02045-6]

## I. INTRODUCTION

Water is ubiquitous: it is the most common polyatomic molecule in the Universe and fundamental to life. It is an important constituent of the Earth's atmosphere and a major product of most combustion processes. Accurate thermodynamic data on water is thus of great importance. Additionally, because water is both relatively simple and fundamental, it has become something of a benchmark system.

The traditional methods of calculating the partition function and related thermodynamic data for water has been to sum the result of effective Hamiltonian fits to experimental data.[1–4] However, such fits are unreliable for water at even moderate levels of excitation.[5] The traditional method therefore gives poor results at higher temperatures.[6] Other methods used include the use of high accuracy *ab initio* calculations to compare partition functions either via effective Hamiltonians[7] or by direct summation of rotation-vibration energy levels.[6,8] Recently there has been a series of alternative calculations aimed at the direct computation of partition functions via path integrals.[9,10]

A recent study by Harris *et al.*[6] computed a water partition function and other thermodynamic quantities over a wide temperature range ($T\leqslant 6000$ K) by explicit summation of calculated rotation-vibration energy levels. Harris *et al.* found that to obtain reliable results at high temperatures, particularly for the specific heat, it is necessary to explicitly consider every energy level in the system, something Harris *et al.* were only able to do rather approximately.

The high resolution spectrum of water is one of the most intensively studied. One product of these studies is tabulations of experimental energy levels, usually with an associated experimental error. Among other applications, these tabulated energy levels form the input for models which fit the parameters for effective Hamiltonians. To our knowledge these experimentally determined energy levels have never been used directly to compute partition functions. In part this is because the published tabulations are both disparate and incomplete.

Recently Tennyson *et al.*[11] have completed a systematic compilation of the empirical rotation-vibration energy levels of water. In this work we use some 10 500 of these energy levels to compute the low temperature partition function to high accuracy. This method allows the partition function and other data to be computed to the intrinsic accuracy of the experimental data, meaning reliable error bounds can be established. The low temperature results presented here agree with previous estimates[1] but are obtained with a much tighter error bound than previous studies.

For higher temperatures ($T>600$ K), there are insufficient observed energy levels to converge partition functions. However, the accuracy to which these higher energy levels are determined is less crucial. To compute high temperature partition functions we employ the procedures used by Harris *et al.*[6] but improve them by using more extensive calculations of the rotation-vibration energy levels and an improved model for the highest rotationally excited states. Our final summations include nearly a million energy levels.

## II. METHOD

### A. Formulation

Procedures for direct summation of energy levels to give the internal partition function, $Q_{\text{int}}$, and other thermodynamic quantities have been well documented elsewhere[6,7] and will only be outlined here.

Harris *et al.*[6] demonstrated that the practice of separating between rotational and vibrational partition functions leads to an overestimate of $Q_{\text{int}}$ at high temperature, so no such distinction is made here. Conversely, given the large energy required for electronic excitation, the electronic partition function was assumed to be unity at all temperatures considered.

The total partition function is assumed to be the product of internal and translational partition functions. Formulas for

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TABLE I. Rotational constants for the vibrational ground state in MHz [see Eq. (9)].

| | Polyansky (Ref. 5) | This work |
|---|---|---|
| $A$ | 835 838.592 160 | 842 078.600 889 |
| $B$ | 435 348.769 544 | 433 060.450 575 |
| $C$ | 278 139.834 584 | 277 276.747 182 |
| $\Delta_J$ | 37.618 7302 | 53.418 1083 |
| $\Delta_{JK}$ | −173.363 5582 | −271.955 2616 |
| $\Delta_K$ | 973.939 4806 | 752.987 5188 |

the translational partition function, based on the ideal gas model, have been given elsewhere.[1] For these we used a standard state pressure of 1 bar (= $10^5$ Pa)[12] as used in JANAF.[1] Fundamental constants and atomic masses were taken from the recommended IUPAC values.[13] Calculations were performed for the $H_2{}^{16}O$ isotopomer only.

The internal partition function, $Q_{\mathrm{int}}$, was evaluated using

$$Q_{\mathrm{int}}=\sum_i g_i(2J_i+1)\exp\left(-\frac{c_2E_i}{T}\right), \tag{1}$$

where $J_i$ is the rotational quantum number of the $i$th state which has energy $E_i$ relative to the $J=0$ ground state. $g_i$ is nuclear spin degeneracy factor which, following the astronomers' convention, was taken as $\frac{1}{4}$ for para states and $\frac{3}{4}$ for ortho states. The summation in (1) is not infinite but, at least in principle, runs over all the (bound) rotation-vibration energy levels of the system. Moments of the partition function are important for evaluating the thermodynamic quantities defined below. The internal contributions to these moments can be accurately evaluated by explicitly differentiating the sum (1) giving

$$Q'_{\mathrm{int}}=T\frac{dQ_{\mathrm{int}}}{dT}=\sum_i g_i(2J_i+1)\left(\frac{c_2E_i}{T}\right)\exp\left(-\frac{c_2E_i}{T}\right), \tag{2}$$

$$\begin{aligned}Q''_{\mathrm{int}}&=T^2\frac{d^2Q_{\mathrm{int}}}{dT^2}+2Q'_{\mathrm{int}}\\&=\sum_i g_i(2J_i+1)\left(\frac{c_2E_i}{T}\right)^2\exp\left(-\frac{c_2E_i}{T}\right),\end{aligned} \tag{3}$$

where the second radiation constant, $c_2$, is used for energies given in $\mathrm{cm}^{-1}$. Combining these with formulas for the translational partition function[1] one can obtain the following as a function of temperature:

(a) The Helmholtz function is

$$\mathrm{hcf}(T)=H(T)-H_0=RT\frac{Q'}{Q}-H_0, \tag{4}$$

where $H_0$ in the enthalpy reference which results in hcf equal to zero at the JANAF reference temperature of 298.15 K.[1] The precise value of $H_0$ is discussed below.

(b) The Gibbs enthalpy function is

$$\mathrm{gef}(T)=-\frac{[G(T)-H_0]}{T}=R\ln Q+\frac{H_0}{T}. \tag{5}$$

TABLE II. Calculated $H_2{}^{16}O$ internal partition function and moments as a function of temperature.

| $T$ (K) | $Q_{\mathrm{int}}$ | $Q'_{\mathrm{int}}$ | $Q''_{\mathrm{int}}$ |
|---|---|---|---|
| 10 | 0.332 093 6 | 0.302 151 8 | 1.161 134 |
| 20 | 0.837 236 2 | 1.286 145 | 3.288 287 |
| 40 | 2.354 260 | 3.386 883 | 8.042 009 |
| 60 | 4.204 690 | 6.016 460 | 14.772 37 |
| 80 | 6.358 008 | 9.185 971 | 22.801 03 |
| 100 | 8.788 355 | 12.799 31 | 31.868 85 |
| 200 | 24.353 99 | 36.097 85 | 90.307 24 |
| 300 | 44.530 53 | 66.596 39 | 168.2024 |
| 400 | 68.642 89 | 104.0501 | 268.9762 |
| 500 | 96.583 33 | 149.5118 | 399.183 |
| 600 | 128.5413 | 204.4224 | 565.3281 |
| 800 | 205.9478 | 349.1865 | 1036.448 |
| 1000 | 304.5798 | 553.9156 | 1758.363 |
| 1200 | 429.3154 | 838.0108 | 2824.526 |
| 1400 | 586.0270 | 1224.177 | 4343.094 |
| 1500 | 678.4539 | 1463.502 | 5310.418 |
| 1600 | 781.4782 | 1738.323 | 6439.341 |
| 1800 | 1023.295 | 2409.863 | 9258.888 |
| 2000 | 1319.996 | 3272.146 | 12 970.58 |
| 2200 | 1681.044 | 4362.899 | 17 769.12 |
| 2400 | 2116.921 | 5724.670 | 23 877.75 |
| 2500 | 2366.494 | 6521.911 | 27 501.56 |
| 2600 | 2639.205 | 7405.270 | 31 550.88 |
| 2800 | 3260.649 | 9458.213 | 41 076.76 |
| 3000 | 3995.27 | 11 943.2 | 52 779.7 |
| 3200 | 4858.42 | 14 926.3 | 67 021.0 |
| 3400 | 5866.89 | 18 480.5 | 84 199.0 |
| 3500 | 6431.26 | 20 496.4 | 94 023.1 |
| 3600 | 7038.94 | 22 685.6 | 104 745.8 |
| 3800 | 8394.37 | 27 628.2 | 129 121.6 |
| 4000 | 9954.54 | 33 401.0 | 157 806.7 |
| 4200 | 11 742.4 | 40 102.3 | 191 290.4 |
| 4400 | 13 782.2 | 47 834.7 | 230 058.2 |
| 4500 | 14 904.6 | 52 120.4 | 251 571.2 |
| 4600 | 16 099.8 | 56 703.6 | 274 578.9 |
| 4800 | 18 722.1 | 66 816.0 | 325 290.7 |
| 5000 | 21 677.3 | 78 278.4 | 382 588.9 |
| 5200 | 24 994.1 | 91 195.1 | 446 815.3 |
| 5400 | 28 702.2 | 105 666.5 | 518 249.1 |
| 5500 | 30 712.2 | 113 515.0 | 556 737.3 |
| 5600 | 32 831.2 | 121 787.3 | 597 100.7 |
| 5800 | 37 411.2 | 139 645.3 | 683 507.8 |
| 6000 | 42 471.8 | 159 320.0 | 777 534.1 |

(c) The entropy is

$$S(T)=R\frac{Q'}{Q}+R\ln Q. \tag{6}$$

(d) The specific heat at constant pressure is

$$C_p(T)=R\left[\frac{Q''}{Q}-\left(\frac{Q'}{Q}\right)^2\right]. \tag{7}$$

As $C_p$ is determined by the difference between the second moment and the square of the first moment, it is particularly sensitive to the accuracy of the partition function. In particular it is difficult to obtain reliable results for $C_p$ at high temperature.[6]

## B. Energy levels

Energy levels for evaluating sums (1)–(3) where obtained from three separate sources.

TABLE III. Calculated thermodynamic properties of $H_2{}^{16}O$ as a function of temperature.

| $T$ (K) | gef ($J K^{-1} mol^{-1}$) | hcf ($J mol^{-1}$) | $S$ ($J K^{-1} mol^{-1}$) | $C_p$ ($J K^{-1} mol^{-1}$) |
|---|---|---|---|---|
| 100 | 218.530 | −6615 | 152.384 | 33.301 |
| 200 | 191.892 | −3282 | 175.481 | 33.351 |
| 300 | 188.831 | 62 | 189.038 | 33.596 |
| 400 | 190.155 | 3452 | 198.784 | 34.262 |
| 500 | 192.681 | 6925 | 206.530 | 35.226 |
| 600 | 195.546 | 10 501 | 213.048 | 36.325 |
| 800 | 201.318 | 18 003 | 223.822 | 38.728 |
| 1000 | 206.734 | 26 003 | 232.737 | 41.287 |
| 1200 | 211.727 | 34 515 | 240.490 | 43.809 |
| 1400 | 216.340 | 43 513 | 247.420 | 46.124 |
| 1500 | 218.520 | 48 178 | 250.639 | 47.177 |
| 1600 | 220.624 | 52 946 | 253.715 | 48.157 |
| 1800 | 224.626 | 62 756 | 259.491 | 49.904 |
| 2000 | 228.383 | 72 890 | 264.828 | 51.394 |
| 2200 | 231.924 | 83 300 | 269.788 | 52.668 |
| 2400 | 235.274 | 93 946 | 274.418 | 53.766 |
| 2500 | 236.885 | 99 347 | 276.623 | 54.261 |
| 2600 | 238.454 | 104 797 | 278.761 | 54.724 |
| 2800 | 241.481 | 115 828 | 282.848 | 55.571 |
| 3000 | 244.368 | 127 019 | 286.708 | 56.326 |
| 3200 | 247.130 | 138 353 | 290.365 | 57.005 |
| 3400 | 249.776 | 149 816 | 293.840 | 57.614 |
| 3500 | 251.059 | 155 592 | 295.514 | 57.892 |
| 3600 | 252.317 | 161 394 | 297.149 | 58.152 |
| 3800 | 254.760 | 173 072 | 300.305 | 58.613 |
| 4000 | 257.113 | 184 833 | 303.322 | 58.986 |
| 4200 | 259.383 | 196 660 | 306.207 | 59.259 |
| 4400 | 261.574 | 208 529 | 308.968 | 59.418 |
| 4500 | 262.643 | 214 473 | 310.303 | 59.451 |
| 4600 | 263.693 | 220 418 | 311.610 | 59.451 |
| 4800 | 265.743 | 232 301 | 314.139 | 59.350 |
| 5000 | 267.727 | 244 149 | 316.557 | 59.111 |
| 5200 | 269.650 | 255 936 | 318.868 | 58.734 |
| 5400 | 271.514 | 267 634 | 321.076 | 58.225 |
| 5500 | 272.425 | 273 442 | 322.142 | 57.923 |
| 5600 | 273.322 | 279 218 | 323.182 | 57.591 |
| 5800 | 275.076 | 290 663 | 325.191 | 56.846 |
| 6000 | 276.779 | 301 950 | 327.104 | 56.003 |

TABLE IV. Estimated percentage error, as a function of temperature, in the computed internal partition function of Table II and the thermodynamic data of Table III. Blank entries have estimated errors less than 0.005%.

| $T$ (K) | $Q$ | gef | hcf | $S$ | $C_p$ |
|---|---|---|---|---|---|
| 3000 | | | | | 0.01 |
| 3500 | | | | | 0.01 |
| 4000 | | | | | 0.03 |
| 4500 | 0.06 | | 0.01 | 0.01 | 0.1 |
| 5000 | 0.1 | | 0.01 | 0.01 | 0.3 |
| 5500 | 0.3 | | 0.02 | 0.02 | ∼1 |
| 6000 | 0.3 | 0.01 | 0.06 | 0.03 | ∼2 |

Where possible experimentally determined rotational and vibrational energy levels were used. These levels were taken from the recent compilation of Tennyson *et al.*[11] The 10 488 energy levels spanning 97 vibrational states were summed in this fashion. For the ground vibrational state, rotational states up to $J=35$ are covered, although complete data was only available up to $J=27$. All the experimental levels used have an associated error which arises from the accuracy of high resolution spectra used to determine the data. This error is generally small, less than 0.01 $cm^{-1}$. This leads to very tight bounds on the low temperature data we compute.

At higher temperatures, the experimental data are insufficient to converge the sums (1)–(3). These data were therefore augmented by theoretical energy levels spanning higher energies.

As part of a study aimed at producing an improved opacity for models of cool stellar atmospheres, Viti[14] computed all the energy levels of $H_2{}^{16}O$ with $J \leqslant 42$ and $E_i \leqslant 30\,000$ $cm^{-1}$ using the spectroscopically determined PJT2[15]potential for water. This data set, called VT2,[14] provides a comprehensive and reliable set of energies although, of course, their accuracy is significantly less than that of the experimental levels. Once levels known from experiment had been removed, 205 228 VT2 levels were used in the sums. These levels are subject to systematic errors whose precise value is unknown. However, at higher temperatures convergence of the sums is probably the dominant source of error rather than statistical or systematic error due to individual energy levels.

Although the VT2 levels greatly increase the data available, they do not span all energies to dissociation. To account for these higher levels we employed a cruder model, adapted from one developed by Harris *et al.*[6]

It was assumed one could separate vibration and rotation energy levels:

$$E_{vr}=E_v+E_r. \tag{8}$$

Mussa and Tennyson[16] have computed all the vibrational band origins, $E_v$, of water up to dissociation for two separate potential energy surfaces. For the *ab initio* surface of Ho *et al.*[17] they obtained 1075 band origins. Sixty-two of these were replaced by values obtained from the experimental compilation;[11] in general these constituted the lowest lying levels. For the rotational energy levels, $E_r$, the Padé model of Polyansky[5] was used:

$$\begin{aligned} E_r(J,K) &= \frac{C_0^2}{C_0-C_1}, \\ C_0 &= \left(A-\frac{B+C}{2}\right)K^2+\left(\frac{B+C}{2}\right)J(J+1), \\ C_1 &= -\Delta_J[J(J+1)]^2-\Delta_{JK}K^2J(J+1)-\Delta_K K^4. \end{aligned} \tag{9}$$

As we wish to extrapolate to higher energies from known data, we employed the lowest order model as this should be the most stable. The model was parametrized using constants determined from the rotational levels of the vibrational ground state. Since there is now considerably more data available for this than was available to Polyansky,[5] these constants were redetermined using the levels given in Ref. 11 The resulting constants are given in Table I. This fit is not particularly accurate, the standard deviation is 229 $cm^{-1}$ for the 980 levels used, but this is an improvement on 525 $cm^{-1}$ given by the original constants. It should be noted that in (9) $K=K_a$ and no account is taken of splitting between levels with the same $K_a$ but different $K_c$.

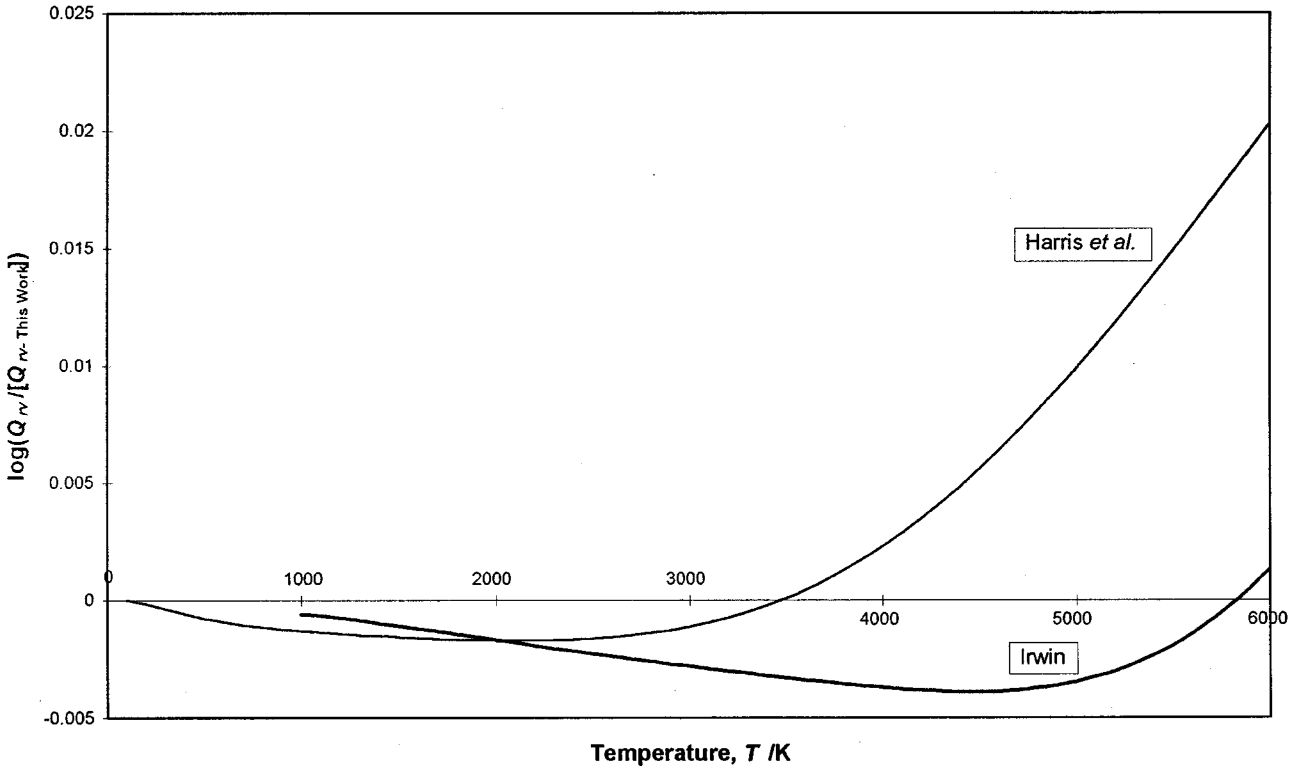

FIG. 1. Logarithm of the ratio of the internal partition function of Irwin (Ref. 19) and Harris *et al.* (Ref. 6) with the one calculated in this work as a function of temperature.

All energy levels, $E_{vr}$, up to the dissociation limit, $D_0$, which satisfied either $E_{vr}>30\,000$ cm$^{-1}$ or $J>42$, were retained. In practice two models were tested, one which used the *ab initio* value[17] for $D_0$ of 40 086 cm$^{-1}$, which gave 551 772 extra levels satisfying this criterion, and one with $D_0=41\,088$ cm$^{-1}$, the approximate experimental value,[18] which gave 640 685 extra levels for 1148 vibrational states. These models considered levels up to J = 82 and 84, respectively, the last $J$ for which the $K=0$ level of the ground vibrational state was below $D_0$. Unless otherwise stated, the following results used the experimental value for $D_0$.

### C. Results and discussion

Table II presents results obtained by explicit summation of 856 401 rotation-vibration energy levels. These values have been used to obtain the thermodynamic quantities presented in Table III. Strictly these results are for $H_2{}^{16}O$ only, while other tabulations, notably JANAF,[1] consider water in natural abundance. However, as demonstrated by Harris *et al.*[6] using the results of Martin *et al.*,[7] this distinction leads to only very minor differences which will be ignored in the discussion below.

In computing hcf and gef for Table III it is necessary to define a value for $H_0$, the enthalpy at the reference temperature $T=298.15$ K. Using the experimental energy levels we determine

$$H_0=9904.1\pm0.1\text{J mol}^{-1}, \tag{10}$$

where the error is given by the statistical error in the experimental data. This value is consistent with, but more accurate than, the JANAF value of 9904 J mol$^{-1}$ and can be compared with 9902 J mol$^{-1}$ computed *ab initio* by Martin *et al.*[7] and 9895 J mol$^{-1}$ computed by Harris *et al.*[6] using the VT2 energy levels.[12]

At low temperatures our results are entirely determined by the experimental levels: $Q_{\text{int}}$, hcf, gef, $S$ and $C_p$ are insensitive to inclusions of further levels for $T<600$ K, 600 K, 900 K, and 500 K, respectively. Within these temperature ranges the results are determined to very high accuracy: 1 part in $10^6$ or better for $Q_{\text{int}}$ and 2 parts in $10^5$ or better for the thermodynamic quantities. Up to 1000 K, our results are in complete agreement with the standard JANAF tabulation,[1] but are more precisely determined.

At higher temperatures the errors are, not surprisingly, larger and are to a greater extent as $T$ increases dominated by our use of approximate data to determine $E_{vr}$ via eq. (8). It is possible to estimate this error by substituting VT2 data with the approximate data. As levels with $J>42$ lie below 30 000 cm$^{-1}$, it is the cutoff at $J=42$ in Viti's energy levels which introduces the largest error. Table IV gives the estimated error for each quantity we compute for temperatures above 3000 K. Below 3000 K, all quantities are reproduced to better than 1 part in $10^4$. It can be seen that it is only for the specific heat at high temperatures that our model has any significant errors. These rise to about 2% at $T=6000$ K.

At high temperatures our results also show sensitivity to our choice of $D_0$. Using the *ab initio* $D_0$ reduces $Q_{\text{int}}$ to 42 335.9 at $T=6000$ K or by 0.3%; at $T=6000$ K $C_p$ is lowered to 55.16 J k$^{-1}$ mol$^{-1}$. This is a significant, almost

TABLE V. Coefficients of the fit to the internal partition function, $Q_{\mathrm{int}}$, given by Eq. (11).

| | Harris *et al.* (Ref. 6) | This work |
|---|---|---|
| $a_0$ | −14.238 480 506 262 7 | −14.087 469 157 417 9 |
| $a_1$ | 38.053 702 726 924 3 | 37.924 324 853 988 2 |
| $a_2$ | −42.649 044 013 388 9 | −42.681 797 873 178 9 |
| $a_3$ | 25.238 163 093 783 1 | 25.330 244 851 791 6 |
| $a_4$ | −8.056 218 790 085 96 | −8.108 512 629 355 32 |
| $a_5$ | 1.317 838 936 167 98 | 1.331 068 717 205 35 |
| $a_6$ | −0.086 022 746 786 300 4 | −0.087 298 105 109 575 7 |

2%, change which further increases the uncertainty in $C_p$ at the highest temperatures considered.

Figure 1 compares our internal partition function with other high temperature determinations due to Irwin[19] and Harris *et al.*[6] Irwin's results are actually a fit to the results of McBride *et al.*[3] using a functional form due to Sauvel and Tatum.[20] Below 4000 K the three methods give similar partition functions. Above this temperature the values of Harris *et al.*[6] are too high, which is consistent with their error analysis. Our results agree rather well with the cruder estimate of Irwin.[19]

Table V gives coefficients least squares fitted to our values for $Q_{\mathrm{int}}$ using the functional form

$$\log Q_{\mathrm{int}} = \sum_{i=0}^{6} a_i (\log T)^i. \tag{11}$$

This fit reproduces $\log Q_{\mathrm{int}}$ to within 0.3% for all $T$ considered. Although this is satisfactory, it is, for reasons which are unclear, less accurate than the fit achieved by Harris *et al.*[6] to their data.

Figure 2 compares our values of $C_p$ as a function temperature with other high temperature determinations. Below 2000 K our values for $C_p$ are within 0.3% of those given by JANAF.[1] For $T > 4000$ K there are significant differences between the different determinations. In this region the JANAF value is a single straight line extrapolation of what is already an unreliable value. Above $T = 4500$ K, both our value for $C_p$ and the previous less accurate value of Harris *et al.*[6] begin to decrease with temperature. This could be a consequence of increasing errors in both calculations. However, given that there are only a finite number of rotation-vibration energy levels associated with the ground electronic state of water, it is possible that this effect is due to the saturation of the energy levels of water. This situation, which leads to $C_p \to 0$ as $T \to \infty$, has been recently studied by Vigasin,[21] in the context of weakly bound complexes, who derived a mass-action law to account for the saturation effect.

## III. CONCLUSIONS

We have used a combination of explicit, experimentally determined energy levels, high accuracy theoretical calculations and, at high energy, model data to compute the partition function of water and related thermodynamic quantities as a function of temperature. This method gives the most accurate values for gas phase $H_2{}^{16}O$ at all the temperatures

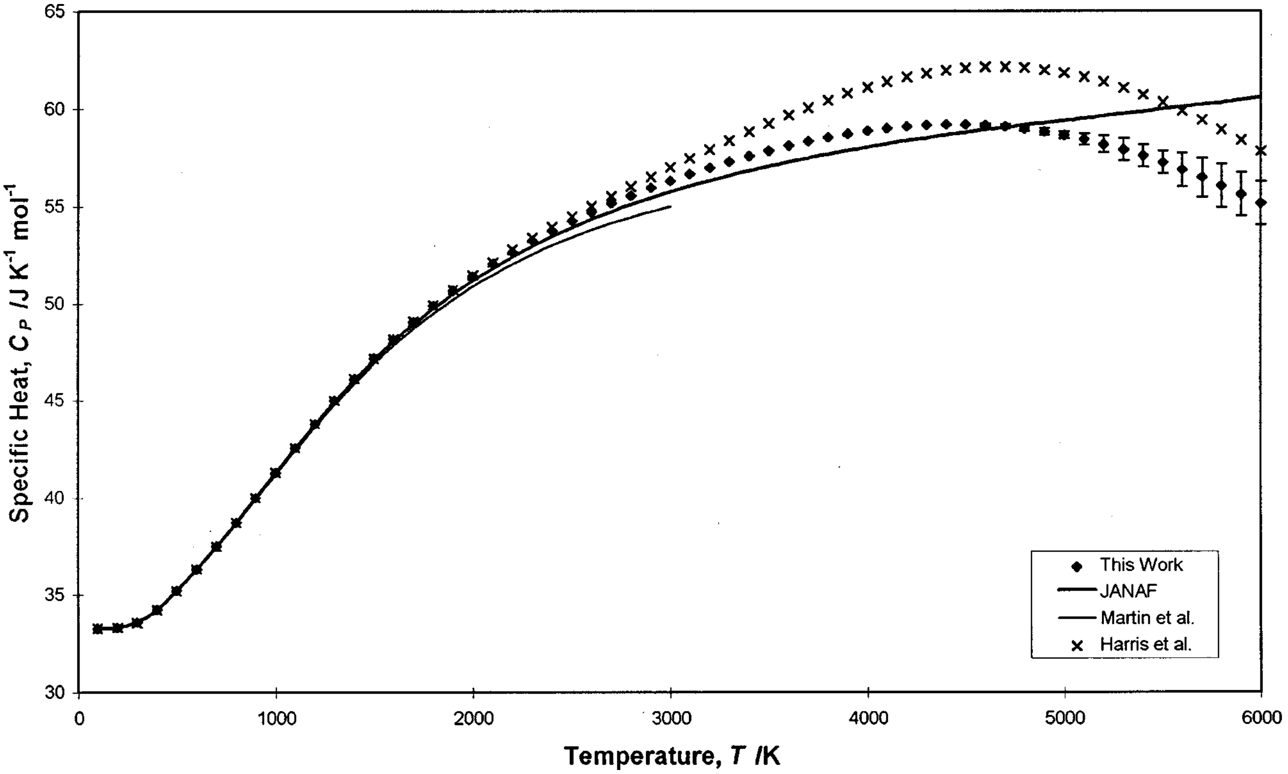

FIG. 2. Comparison of specific heat at constant pressure, $C_p$, computed in this with (with error bars) with that given in JANAF (Ref. 1), and computed by Martin *et al.* (Ref. 7) and Harris *et al.* (Ref. 6).

considered. Below 1000 K our values support those given in the standard JANAF tabulations,[1] although our error bars are very significantly smaller.

The determination of an accurate specific heat at high temperature remains a difficult problem and our values above 5000 K have a significant ($>1\%$) error. The effect of quasibound rotation-vibration states and saturation of the energy levels on these high energy results still need to be systematically studied.

## ACKNOWLEDGMENTS

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