similarly, and the results are the same). Consider a function $B(\pi_i)$ which is independent of the other coordinates and momenta. The average of $B(\pi_i)$ over an ensemble restricted to those microstates where the coordinate x_i satisfies min $(|x_i - r_1|, |x_i - r_2|) < d$ is given by

$$\langle B(\pi_i) \rangle_{IC} = \frac{\int_{-\infty}^{\infty} B(\pi_i) \, \text{prob}_{IC} \, (\pi_i) \, d^3\pi_i}{\int_{-\infty}^{\infty} \text{prob}_{IC} \, (\pi_i) \, d^3\pi_i} \qquad (10)$$

where prob_{IC} (π_i) is the probability density that the solvent atom has momentum π_i and is in the inner core. Because the π_i term in the Hamiltonian separates out, prob_{IC} (π_i) is proportional to $\exp(-\beta\pi_i^2/2m_s)$, and the average of $B(\pi_i)$ has no position dependence, either on the reaction coordinate r or on other solvent atom coordinates x_j. For the particular case where B is the kinetic energy, this gives

$$\langle \pi_i^2/2m_s \rangle_{IC} = 3k_BT/2 \qquad (11)$$

The same result holds for the outer core solvent.

Accurate Thermodynamic Properties of the Six Isotopomers of Diatomic Hydrogen

Robert J. Le Roy,* **Steven G. Chapman,** and **Frederick R. W. McCourt**

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada (Received: April 20, 1989; In Final Form: August 1, 1989)

Tabulations of the thermodynamic properties of the six isotopomers of diatomic hydrogen have been generated from a knowledge of the ab initio nonadiabatic eigenvalues for all bound and quasibound levels of the ground electronic state. The new results for H_2, HD, and D_2 should be more accurate than the existing JANAF values generated from an eigenvalue spectrum obtained empirically by interpolating over and extrapolating beyond the available spectroscopic data. For the tritium isotopomers, the present results comprise the first comprehensive tabulation of the thermodynamic properties. Comparisons between ortho, para, equilibrium, and "frozen" (or "normal") results for the homonuclear systems are also presented.

I. Introduction

Although diatomic hydrogen is already one of the most thoroughly characterized molecular species, it remains topical because of its importance in many physical and chemical processes and because of its central role as a meeting ground for theory and experiment. It was one of the first systems for which detailed statistical mechanical calculations were employed to generate comprehensive tables of thermodynamic properties.[1] The landmark tabulations of Wooley et al.[1] were based on level energies obtained empirically by interpolating over and extrapolating beyond the available spectroscopic data, and many subsequent tabulations were generated in that same manner.[2] For diatomic hydrogen, however, this approach was superseded in 1973 when Kosloff et al.[3] reported more accurate thermodynamic property calculations based on a complete set of purely theoretical level energies. This was the first example of an accurate determination of macroscopic properties directly from first principles.[4] Moreover, it appears to have been the first such calculation to take proper account of the metastable nature of quasibound levels by integrating over the continua associated with finite line widths. However, as in the calculations of Wooley et al.,[1] Kosloff et al.[3] considered only the three common isotopomers, H_2, HD, and D_2.

In recent years, ab initio calculations of the properties of molecular hydrogen have continued to improve in both accuracy and range. In particular, there have been significant improvements in both the clamped-nuclei (simple Born–Oppenheimer) potential[5] and its adiabatic corrections.[6] Effective adiabatic eigenvalues obtained on combining these functions with older estimates of the relativistic and radiative corrections[7–9] have been corrected by using

a generalized representation of the nonadiabatic level shifts, yielding accurate nonadiabatic energies for all bound and quasibound vibration–rotation levels of the six isotopomers of ground-state hydrogen.[10,11] Since certain of these energies differ significantly from those used previously, thermodynamic properties calculated from them might be expected to be improved significantly over those reported earlier. These considerations, taken together with the fact that there existed *no* comprehensive tabulations of thermodynamic properties for the tritium isotopomers, motivated our work.

The present paper reports new calculations of the thermodynamic properties of all six isotopomers of the ground electronic state of diatomic hydrogen. In the following, section II describes the input data and outlines how our calculations have been performed. The results are then presented in section III, together with an examination of the differences between the present results and those of ref 3, and a discussion of questions such as the effect on the results of the improvements in the level energies and the effect of the finite width of the quasibound levels.

II. Methodology

A. The Input Energies. The level energies used in the present calculations are the nonadiabatic eigenvalues reported by Schwartz and Le Roy.[10,11] They were obtained by solving the radial Schrödinger equation for the best existing potential energy curves and adding nonadiabatic level shifts to the resulting eigenvalues. The latter corrections were based on directly calculated nonadiabatic level shifts for H_2, HD, and D_2[6] but were generalized both to allow extrapolation to the tritium isotopomers and to take centrifugal distortion effects into account.[10] As a result, the level energies calculated for HT, DT, and T_2 are believed to have the same accuracy as those for H_2, HD, and D_2, and unlike the input energies used by Kosloff et al.,[3] the accuracy of these level energies does not deteriorate with increasing rotational energy.

The maximum errors in the calculated level energies due to the computational procedures used to generate them are believed to be less than 0.02 cm^{-1}, and comparisons with the extensive (but

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(2) Chase, M. W., Jr.; Curnutt, J. L.; Downey, J. R., Jr.; McDonald, R. A.; Syverud, A. N.; Valenzuela, E. A. *J. Phys. Chem. Ref. Data* **1982**, *11*, 695.

(3) Kosloff, R.; Levine, R. D.; Bernstein, R. B. *Mol. Phys.* **1974**, *27*, 981. Erratum: *Ibid.* **1976**, *31*, 323.

(4) Unfortunately, the detailed results of Kosloff et al.[3] seem to have been overlooked in the 1982 revisions of the JANAF thermochemical tables.[2]

(5) Kołos, W.; Szalewicz, K.; Monkhorst, H. *J. Chem. Phys.* **1986**, *84*, 3278.

(6) Wolniewicz, L. *J. Chem. Phys.* **1983**, *78*, 6173.

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much less complete) experimental data[12–14] for the three common isotopomers H_2, HD, and D_2 confirm that their absolute errors are no larger than ca. 0.2 cm^{-1}.[10] However, because of the improved treatment of the nonadiabatic corrections, the energies of the higher rotational levels differ from those used by Kosloff et al.[3] by as much as several cm^{-1}. Thus, the present high-temperature results should be somewhat more accurate than were theirs.

In the existing JANAF thermochemical property calculations for diatomic hydrogen,[2] the input energies were obtained empirically by interpolating over and extrapolating beyond the sets of observed level energies. However, that data base was far from complete, especially for HD and D_2, and both the limits to the range of J values and the extrapolated energies of unobserved levels were much less reliable than those used here. For example, for H_2, Chase et al.[2] note that the maximum deviations of their input energies were ±400 cm^{-1}, some 3 orders of magnitude larger than the uncertainties associated with the input energies used here. Moreover, in the present case there is *no* uncertainty regarding the cutoff of the range of J values for each vibrational level. Thus, the results reported herein should be significantly more accurate than those of ref 2.

B. Treatment of Quasibound Levels. In general, an attractive potential energy curve may support both truly bound vibration–rotation levels which lie below the potential asymptote and "quasibound levels" which lie above that limit, but behind a potential energy barrier. While in principle part of the continuum, for most practical purposes the latter act as truly bound states. It is tempting to think that their inclusion in partition function sums should be based on a criterion such as a requirement that their predissociation lifetime be longer than the time between collisions. However, Smith[15] and Mies and Julienne[16] have explicitly pointed out that this would be fallacious and that not only the quasibound levels but also contributions due to temporary colliding pairs of free atoms should be included in the partition function sums used to calculate the thermodynamic properties. Fortunately, at the maximum temperature considered in the present case (10 000 K), $k_B T$ is approximately one-fifth of the diatom dissociation energy, so the effect of partition function contributions due to free colliding pairs should be negligible. As a result, the partition function sums used here include all of the bound and quasibound levels, but no attempt has been made to take account of the remainder of the continuum.

Following Smith,[15] we note that the nth energy moment of the partition function contribution for a truly bound level with vibrational and rotational quantum numbers v and J and energy $E_{v,J}$ is

$$z_n^b(v,J;T) = (2J + 1)[E_{v,J}]^n e^{-E_{v,J}/k_B T} \tag{1}$$

while that for a metastable level with eigenvalue $E_{v,J}$ and full width at half-maximum $\Gamma_{v,J}$ is

$$z_n^m(v,J;T) = \frac{2J + 1}{\pi} \int_D^\infty E^n \frac{\Gamma_{v,J}/2}{[E - E_{v,J}]^2 + \Gamma_{v,J}^2/4} e^{-E/k_B T} \, dE \tag{2}$$

where D is the energy threshold for the predissociation. An efficient numerical procedure for evaluating the integral appearing in this expression is outlined in the Appendix.

C. Calculation of the Thermodynamic Properties. By use of the above notation, the energy moments of the total internal molecular partition function may be written as

$$Z_n(T) = g_e \sum_v \sum_J g_{ns} z_n(v,J;T) \tag{3}$$

where g_e and g_{ns} are the electronic and nuclear spin degeneracies, respectively, and the sums run over all bound and quasibound vibration–rotation levels. For heteronuclear species, the factor

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(13) Bredohl, H.; Herzberg, G. *Can. J. Phys.* **1973**, *51*, 867.
(14) Dabrowski, I.; Herzberg, G. *Can. J. phys.* **1976**, *54*, 525.
(15) Smith, F. T. *J. Chem. Phys.* **1963**, *38*, 1304.
(16) Mies, F. H.; Julienne, P. S. *J. Chem. Phys.* **1982**, *77*, 6162.

TABLE I: Reference Energies Associated with Thermodynamic Property Calculations

| | $(H°_{298.15} - E°_0)/(kJ \ mol^{-1})$ | | | |
	para	ortho	equilib	$D°_0/cm^{-1}$
H_2	8.409 65	8.486 59	8.467 30	36 118.074
D_2	8.569 19	8.569 13	8.569 15	36 748.349
T_2	8.609 35	8.609 35	8.609 35	37 028.481
HD			8.508 80	36 405.778
HT			8.528 93	36 512.166
DT			8.589 21	36 881.271

g_{ns} is independent of J and may be moved outside the summations of eq 3. For homonuclear species, however, it is necessary to distinguish between ortho (symmetric) and para (antisymmetric) nuclear spin species. The implications of such considerations for the case of diatomic hydrogen are discussed in more detail below.

In the present work, the energy moments of the partition function for $n = 0, 1,$ and 2 (see eq 1–3) were calculated from the tabulated nonadiabatic energies for the vibration–rotation levels of each of the six isotopomers of diatomic hydrogen.[11] The molar thermodynamic properties of interest were then generated from the standard ideal-gas expressions

$$H(T) = N_A \frac{Z_1(T)}{Z_2(T)} + \frac{5}{2}RT \tag{4}$$

$$C_p = R\left(\left[\frac{Z_2(T)}{Z_0(T)} - \left(\frac{Z_1(T)}{Z_0(T)}\right)^2\right](k_B T)^{-2} + \frac{5}{2}\right) \tag{5}$$

$$G(T) = -RT \ln \{Z_0(T) \, Z_{tr}(T)\} \tag{6}$$

$$S(T) = [H(T) - G(T)]/T \tag{7}$$

where $N_A Z_{tr}(T)$ is the translational partition function for 1 mol of ideal-gas molecules, N_A is Avogadro's number, and R is the gas constant. Following the new IUPAC recommendation,[17] the ideal-gas standard-state pressure (SSP) used in calculating the entropy and Gibbs energy is taken to be $p° = 1$ bar (rather than 1 atm). If we use the current values of the physical constants,[18] the translational partition function for an ideal gas at this SSP may then be written

$$Z_{tr}°(T) = (M^3 T^5)^{1/2}/38.53986 \tag{8}$$

where the molecular masses M (in amu) were based on the 1985 mass table.[19]

Following standard conventions,[20,21] the quantities actually reported for the Gibbs energy and the enthalpy are $-(G° - E°_0)/T$ and $(H° - E°_0)$, respectively, where $E°_0$ is the ground-state energy of the species in question. In order to facilitate relating these results to the traditional quantities $-(G° - H°_{298.15})/T$ and $(H° - H°_{298.15})$, values of $(H°_{298.15} - E°_0)$ were calculated for each isotopic species. These quantities are presented in Table I, together with the ground-state dissociation energies of the six isotopomers.[10]

D. Spin Statistics. As has been pointed out above, nuclear spin degeneracy factors must be incorporated into the partition function sums for the homonuclear species. In particular, for H_2 and T_2, which are formed from particles with nuclear spin $I = \frac{1}{2}$, $g_{ns} = g_{ns}^{para} = 1$ for the even-J rotational levels and $g_{ns} = g_{ns}^{ortho} = 3$ for the odd-J levels, while for D_2, whose component nuclei have $I = 1$, $g_{ns} = g_{ns}^{ortho} = 6$ for the even-J levels and $g_{ns} = g_{ns}^{para} = 3$ for the odd-J levels. If the system is in complete equilibrium, including these factors in the partition function sums takes full account of spin statistical considerations. However, these species are often found with frozen nuclear spin state populations that differ from their equilibrium values. To account for the properties

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TABLE II: Low-Temperature Thermodynamic Properties for Ortho, Para, and Spin-Equilibrium H_2 (Reference Pressure $p° = 1$ bar)

T/K	$C_p°/$(J K⁻¹ mol⁻¹)			$S°/$(J K⁻¹ mol⁻¹)			$-[(G° - E°_0)/T]/$(J K⁻¹ mol⁻¹)			$[H° - E°_0]/$(kJ mol⁻¹)			$K(o|p)$
	para	ortho	equilib	para	ortho	equilib	para	ortho	equilib	para	ortho	equilib	
5	20.7863	20.7863	20.7863	32.6204	50.8893	32.6204	11.8342	−253.3809	11.8342	0.1039	1.5214	0.1039	0.0000
10	20.7863	20.7863	20.7871	47.0284	65.2972	47.0284	26.2421	−97.2310	26.2421	0.2079	1.6253	0.2079	0.0000
15	20.7863	20.7863	20.8983	55.4565	73.7253	55.4672	34.6702	−41.5556	34.6711	0.3118	1.7292	0.3119	0.0001
20	20.7863	20.7863	21.8627	61.4363	79.7052	61.5777	40.6501	−11.9521	40.6649	0.4157	1.8331	0.4183	0.0018
25	20.7863	20.7863	24.5150	66.0747	84.3435	66.7082	45.2884	6.8604	45.3698	0.5197	1.9371	0.5335	0.0098
30	20.7868	20.7863	28.5324	69.8645	88.1333	71.5203	49.0782	20.0997	49.3291	0.6236	2.0410	0.6657	0.0306
35	20.7904	20.7863	32.7017	73.0690	91.3375	76.2381	52.2824	30.0535	52.8373	0.7275	2.1449	0.8190	0.0690
40	20.8059	20.7863	35.8901	75.8459	94.1131	80.8281	55.0581	37.8914	56.0512	0.8315	2.2489	0.9911	0.1269
45	20.8503	20.7863	37.6087	78.2987	96.5614	85.1692	57.5068	44.2769	59.0482	0.9356	2.3528	1.1754	0.2037
50	20.9473	20.7865	37.9704	80.5000	98.7515	89.1608	59.6979	49.6168	61.8631	1.0401	2.4567	1.3649	0.2975
60	21.3973	20.7892	36.2451	84.3528	102.5415	95.9639	63.4946	58.1313	67.0013	1.2515	2.6646	1.7378	0.5246
70	22.2903	20.8025	33.5403	87.7123	105.7469	101.3488	66.7188	64.7104	71.5383	1.4695	2.8726	2.0867	0.7854
80	23.6195	20.8425	31.1561	90.7712	108.5269	105.6655	69.5366	70.0176	75.5437	1.6988	3.0807	2.4097	1.0596
90	25.2531	20.9298	29.3798	93.6454	110.9863	109.2266	72.0570	74.4356	79.0943	1.9430	3.2896	2.7119	1.3312
100	27.0002	21.0832	28.1532	96.3964	113.1987	112.2543	74.3543	78.2031	82.2626	2.2042	3.4996	2.9992	1.5887
110	28.6744	21.3145	27.3529	99.0495	115.2184	114.8972	76.4794	81.4776	85.1117	2.4827	3.7115	3.2764	1.8242
120	30.1337	21.6263	26.8683	101.6090	117.0858	117.2545	78.4676	84.3681	87.6938	2.7770	3.9261	3.5473	2.0333
130	31.2958	22.0127	26.6141	104.0690	118.8316	119.3937	80.3430	86.9527	90.0512	3.0844	4.1443	3.8145	2.2144
150	32.6655	22.9569	26.5561	108.6578	122.0454	123.1925	83.8175	91.4211	94.2229	3.7260	4.5936	4.3454	2.4955
200	32.3948	25.5602	27.4478	118.0994	129.0110	130.9392	91.2663	99.9738	102.4745	5.3666	5.8074	5.6929	2.8498
250	30.8826	27.4696	28.3449	125.1610	134.9378	137.1673	97.3710	106.3888	108.8100	6.9475	7.1373	7.0893	2.9582
298.15	29.9526	28.4609	28.8365	130.5121	139.8712	142.2068	102.3060	111.4071	113.8073	8.4097	8.4866	8.4673	2.9880
300	29.9283	28.4863	28.8492	130.6973	140.0474	142.3852	102.4805	111.5381	113.9830	8.4650	8.5393	8.5207	2.9886
350	29.4981	28.9417	29.0811	135.2735	144.4777	146.8522	106.8475	115.9732	118.3673	9.9491	9.9766	9.9697	2.9969
400	29.3345	29.1306	29.1816	139.1999	148.3565	150.7429	110.6518	119.7838	122.1764	11.4192	11.4291	11.4266	2.9991
450	29.2839	29.2112	29.2294	142.6514	151.7929	154.1831	114.0194	123.1531	125.5452	12.8844	12.8879	12.8870	2.9997
500	29.2794	29.2538	29.2602	145.7363	154.8730	157.2643	117.0396	126.1738	128.5658	14.3484	14.3496	14.3493	2.9999
600	29.3295	29.3263	29.3271	151.0780	160.2127	162.6046	122.2809	131.4153	133.8072	17.2783	17.2784	17.2784	3.0000

of such frozen spin state species, it is necessary to evaluate separate partition function sums over the levels associated with the symmetric and antisymmetric nuclear spin wave functions and to generate separate values of their thermodynamic properties. For H_2 and T_2, this approach yields

$$Z_n^{para}(T) = \sum_v \sum_{even\ J} z_n(v,J;T) \quad \text{and} \quad Z_n^{ortho}(T) =$$
$$3\sum_v \sum_{odd\ J} z_n(v,J;T) \quad (9)$$

while for D_2

$$Z_n^{para}(T) = 3\sum_v \sum_{odd\ J} z_n(v,J;T) \quad \text{and} \quad Z_n^{ortho}(T) =$$
$$6\sum_v \sum_{even\ J} z_n(v,J;T) \quad (10)$$

Substitution of these expressions into eq 4–7 yields values of the thermodynamic properties for the ortho and para forms of any of the homonuclear isotopomers. Similarly, the ortho–para equlibrium constant $K(o|p)$ may be calculated from the ratio of $Z_0^{ortho}(T)$ to $Z_0^{para}(T)$.

The most common frozen spin case is the so-called "normal" high-temperature ortho–para mixture in which the population ratio is simply defined by the factors g_{ns}^{ortho} and g_{ns}^{para}. Its enthalpy is defined by the expression

$$H_{norm}(T) = [g_{ns}^{para}H_{para}(T) + g_{ns}^{ortho}H_{ortho}(T)]/[g_{ns}^{para} + g_{ns}^{ortho}] \quad (11)$$

and values of C_p^{norm} may be generated from a precisely analogous expression. However, because the factors g_{ns}^{para} and g_{ns}^{ortho} were incorporated into our definitions of Z_n^{para} and Z_n^{ortho} (see eq 9 and 10), values of S_{norm} and $-G_{norm}/T$ must be generated from expressions of the form

$$S_{norm}(T) = [g_{ns}^{para}S_{para}(T) + g_{ns}^{ortho}S_{ortho}(T)]/[g_{ns}^{para} + g_{ns}^{ortho}] -$$
$$R[g_{ns}^{para} \ln (g_{ns}^{para}) + g_{ns}^{ortho} \ln (g_{ns}^{ortho})]/[g_{ns}^{para} + g_{ns}^{ortho}] \quad (12)$$

where the added terms prevent redundant counting of spin degeneracy factors.

It is conventional to assume that the thermodynamic properties of the "normal" species become identical with the equilibrium values in the high-temperature limit. This is true for the heat capacity and the enthalpy *but not* for the entropy or Gibbs energy.

For the latter, nuclear spin statistical effects cause the high-temperature equilibrium values of $S°$ and $-G°/T$ to exceed the "normal" values by the term $R \ln (g_{ns}^{ortho} + g_{ns}^{para})$. For all three homonuclear hydrogen species, this limiting high-temperature region is reached by $T = 300$ K, so independent results for the ortho and para species are not reported for higher temperatures.

Note that, unlike previous tabulations,[1-3] the nuclear spin degeneracy factors *are* included in the entropy and Gibbs energy values reported herein.

III. Results and Discussion

For the three homonuclear isotopomers of ground-state hydrogen, our calculated values of the low-temperature thermodynamic properties of the ortho, para, and spin-equilibrium species are presented in Tables II–IV. Higher temperature equilibrium result; or these three species are then reported in Table V, while result or the three heteronuclear isotopomers over the entire temperature range from 5 to 10 000 K are presented in Table VI.

As mentioned above, results for homonuclear species having the frozen high-temperature ("normal") spin populations may be readily generated from eq 11 and 12 (and their analogues for the other properties) and the ortho and para species results of Tables II–IV. However, aside from the additive constant for $S°$ and $-G°/T$ (mentioned above), for temperatures from 300 to 7000 K, the "normal" and equilibrium results are identical with the full precision of the present tabulations. As was pointed out by Kosloff et al.,[3] at the very highest temperatures considered, the discrete nature of the eigenvalue spectrum causes the equilibrium ortho/para ratios to deviate slightly from the "ideal" values defined by the spin degeneracy factor ratios. This leads to slight differences there (of up to a few units in the last decimal place quoted) between the predicted properties of equilibrium and "normal" systems. However, at such high temperatures, spin equilibration via the dissociation/recombination process becomes quite rapid, so that frozen "normal" spin populations will not be stable. As a result, all of the high-temperature results reported for the homonuclear isotopomers are for spin-equilibrium systems.

It is interesting to note that the heat capacities of these species cross the classical high-temperature harmonic oscillator value of $(9/2)R$ at temperatures between 2300 and 3200 K (depending on the isotopomer) and pass through a maximum value roughly $0.62R$ larger than this at ca. 7000 K, before beginning to descend

TABLE III: Low-Temperature Thermodynamic Properties for Ortho, Para, and Spin-Equilibrium D$_2$ ($p°$ = 1 bar)

T/K	$C_p°$/(J K^{-1} mol^{-1})			$S°$/(J K^{-1} mol^{-1})			$-[(G° - E°_0)/T]$/(J K^{-1} mol^{-1})			$[H° - E°_0]$/(kJ mol^{-1})			K(p|o)
	para	ortho	equilib	para	ortho	equilib	para	ortho	equilib	para	ortho	equilib	
5	20.7863	20.7863	20.7864	56.1532	59.5245	56.1532	35.3669	-104.2873	35.3669	0.1039	0.8191	0.1039	0.0000
10	20.7863	20.7863	20.9559	70.5612	73.9324	70.5832	49.7749	-18.3666	49.7772	0.2079	0.9230	0.2081	0.0003
15	20.7867	20.7863	22.1001	78.9893	82.3605	79.2597	58.2030	13.8991	58.2432	0.3118	1.0269	0.3152	0.0049
20	20.8038	20.7863	23.8079	84.9706	88.3404	85.8509	64.1830	31.7977	64.3504	0.4158	1.1309	0.4300	0.0203
25	20.9339	20.7865	25.2296	89.6232	92.9787	91.3249	68.8226	43.5873	69.2129	0.5200	1.2348	0.5528	0.0481
30	21.3566	20.7888	26.2301	93.4714	96.7687	96.0183	72.6187	52.1446	73.2987	0.6256	1.3387	0.6816	0.0852
35	22.2088	20.8004	27.0076	96.8217	99.9739	100.1217	75.8416	58.7543	76.8436	0.7343	1.4427	0.8147	0.1281
40	23.4937	20.8363	27.7166	99.8668	102.7534	103.7746	78.6568	64.0843	79.9857	0.8484	1.5468	0.9516	0.1733
45	25.0907	20.9160	28.3981	102.7240	105.2116	107.0788	81.1736	68.5200	82.8154	0.9698	1.6511	1.0919	0.2183
50	26.8171	21.0581	29.0290	105.4566	107.4221	110.1041	83.4661	72.3015	85.3951	1.0995	1.7560	1.2355	0.2611
60	29.9645	21.5704	30.0052	110.6360	111.3020	115.4898	87.5679	78.4868	89.9732	1.3841	1.9689	1.5310	0.3355
70	32.0286	22.3726	30.5183	115.4263	114.6841	120.1594	91.2105	83.4210	93.9596	1.6951	2.1184	1.8340	0.3919
80	32.8962	23.3661	30.6460	119.7717	117.7350	124.2464	94.5139	87.5224	97.4955	2.0206	2.4170	2.1401	0.4313
90	32.8979	24.4215	30.5365	123.6528	120.5480	127.8513	97.5402	91.0376	100.6722	2.3501	2.6559	2.4461	0.4575
100	32.4353	25.4285	30.3185	127.0976	123.1740	131.0579	100.3271	94.1213	103.5534	2.6770	2.9053	2.7504	0.4741
110	31.8080	26.3161	30.0759	130.1600	125.6403	133.9361	102.9027	96.8757	106.1869	2.9983	3.1641	3.0524	0.4844
120	31.1890	27.0525	29.8531	132.9007	127.9629	136.5433	105.2903	99.3705	108.6097	3.3132	3.4311	3.3520	0.4907
130	30.6569	27.6353	29.6679	135.3754	130.1522	138.9252	107.5109	101.6549	110.8514	3.6224	3.7046	3.6496	0.4945
150	29.9151	28.4079	29.4158	139.7057	134.1663	143.1513	111.5229	105.7273	114.8834	4.2274	4.2658	4.2402	0.4981
200	29.2753	29.0661	29.2056	148.1971	142.4561	151.5757	119.6846	113.9191	123.0551	5.7025	5.7074	5.7041	0.4999
250	29.1941	29.1695	29.1859	154.7175	148.9564	158.0895	126.0637	120.3003	129.4348	7.1635	7.1640	7.1637	0.5000
298.15	29.1967	29.1937	29.1957	159.8595	154.0966	163.2309	131.1185	125.3553	134.4898	8.5691	8.5692	8.5692	0.5000
300	29.1971	29.1944	29.1962	160.0401	154.2771	163.4115	131.2963	125.5331	134.6676	8.6231	8.6232	8.6232	0.5000

TABLE IV: Low-Temperature Thermodynamic Properties for Ortho, Para, and Spin-Equilibrium T$_2$ ($p°$ = 1 bar)

T/K	$C_p°$/(J K^{-1} mol^{-1})			$S°$/(J K^{-1} mol^{-1})			$-[(G° - E°_0)/T]$/(J K^{-1} mol^{-1})			$[H° - E°_0]$/(kJ mol^{-1})			K(o|p)
	para	ortho	equilib	para	ortho	equilib	para	ortho	equilib	para	ortho	equilib	
5	20.7863	20.7863	20.8842	46.2914	64.5603	46.3006	25.5051	-52.0780	25.5059	0.1039	0.5832	0.1040	0.0001
10	20.7867	20.7863	28.1661	60.6994	78.9682	62.2473	39.9131	10.2559	40.1446	0.2079	0.6871	0.2210	0.0282
15	20.8412	20.7863	37.4709	69.1326	87.3963	75.7651	48.3416	34.6594	49.8082	0.3119	0.7911	0.3894	0.1929
20	21.3354	20.7886	36.4560	75.1783	93.3763	86.5761	54.3284	48.6269	57.7202	0.4170	0.8950	0.5771	0.5037
25	22.7474	20.8124	32.5266	80.0722	98.0169	94.2863	59.0007	58.0580	64.3059	0.5268	0.9990	0.7495	0.8928
30	25.0035	20.9095	29.5619	84.4095	101.8185	99.9341	62.8793	65.0440	69.7951	0.6459	1.1032	0.9042	1.2974
35	27.5690	21.1416	27.8131	88.4565	105.0571	104.3464	66.2469	70.5343	74.4271	0.7773	1.2083	1.0472	1.6747
40	29.8713	21.5437	26.9090	92.2936	107.9044	107.9939	69.2650	75.0310	78.4013	0.9211	1.3149	1.1837	2.0007
45	31.5624	22.1100	26.5409	95.9164	110.4731	111.1379	72.0271	78.8285	81.8679	1.0750	1.4240	1.3172	2.2660
50	32.5575	22.8032	26.5042	99.2992	112.8376	113.9302	74.5873	82.1127	84.9370	1.2356	1.5362	1.4497	2.4722
60	32.9081	24.3577	26.9265	105.2926	117.1313	118.7934	79.2197	87.5982	90.1857	1.5644	1.7720	1.7165	2.7393
70	32.1585	25.8259	27.5427	110.3160	120.9992	122.9902	83.3138	92.0979	94.5788	1.8902	2.0231	1.9888	2.8762
80	31.2169	26.9966	28.0901	114.5479	124.5280	126.7052	86.9608	95.9344	98.3668	2.2070	2.2875	2.2671	2.9425
90	30.4491	27.8282	28.4939	118.1780	127.7590	130.0385	90.2325	99.2936	101.7039	2.5151	2.5619	2.5501	2.9737
100	29.9207	28.3722	28.7621	121.3568	130.7213	133.0555	93.1892	102.2904	104.6906	2.8168	2.8431	2.8365	2.9880
110	29.5892	28.7074	28.9286	124.1917	133.4425	135.8053	95.8811	105.0004	107.3961	3.1142	3.1286	3.1250	2.9946
120	29.3934	28.9050	29.0273	126.7571	135.9497	138.3271	98.3489	107.4764	109.8701	3.4090	3.4168	3.4148	2.9975
130	29.2826	29.0179	29.0841	129.1051	138.2682	140.6529	100.6257	109.7570	112.1497	3.7023	3.7065	3.7054	2.9989
150	29.1904	29.1162	29.1347	133.2876	142.4289	144.8191	104.7086	113.8423	116.2344	4.2869	4.2880	4.2877	2.9998
200	29.1659	29.1632	29.1639	141.6793	150.8139	153.2058	112.9526	122.0870	124.4790	5.7453	5.7454	5.7454	3.0000
250	29.1790	29.1790	29.1790	148.1887	157.3232	159.7151	119.3730	128.5075	130.8994	7.2039	7.2039	7.2039	3.0000
298.15	29.1997	29.1997	29.1997	153.3298	162.4642	164.8562	124.4539	133.5883	135.9803	8.6093	8.6093	8.6093	3.0000
300	29.2007	29.2007	29.2007	153.5104	162.6449	165.0368	124.6325	133.7670	136.1589	8.6634	8.6634	8.6634	3.0000

toward the limiting high-temperature value $(5/2)R$. As was explained in ref 3, this behavior is readily understood as being due to the truncation of the eigenvalue spectrum after a finite number of levels and the compression of the vibrational and rotational eigenvalue spectra near dissociation.

At temperatures below 4200 K, replacing the integrals over the quasibound levels in eq 2 by the direct sum terms of eq 1 has absolutely no effect on our tabulated results, while for higher temperatures, the effect remains small. For example, for H$_2$ at 6000 K it affects (decreases) the values of the four properties presented in Table V by 6, 1, 0, and 5 units in the last decimal place quoted, while at 10 000 K the analogous differences are only 16, 7, 2, and 58 units, respectively. This conclusion differs significantly (by 2 orders of magnitude!) from the observation of Kosloff et al.[3] that "At 6000 K the integration over the lineshape affects C_p in the second decimal place" (in their units of calories). The reason for this discrepancy is that, in their analogue of eq 2, Kosloff et al.[3] set the upper limit to the range of integration at the top of the barrier to predissociation, rather than allow it to extend into the continuum above the barrier. This truncation substantially reduces the contributions of the very broadest levels,

which lie nearest to the barrier maxima. However, Smith[15] and Mies and Julienne[16] have made it clear that this continuum *should* be included when calculating equilibrium properties of this type, so the present approach is more correct.

Detailed comparisons with the results of Kosloff et al.[3] show that all of their results for H$_2$ agree with ours to within a few units in the last decimal place they quote (0.0001 kcal mol^{-1} or cal mol^{-1} K^{-1}) with the discrepancies being largest at the highest temperatures. The magnitudes of these differences are in reasonable accord with the improvements in the level energies used in the present work. For HD and D$_2$, the analogous discrepancies are also very small at the lower temperatures (with one exception, see below), but they grow abruptly into the second decimal place, starting at around 3500 K for D$_2$ and 4500 K for HD. This probably reflects the fact that the eigenvalues they used were based on potentials that incorporated an empirical correction function in the 3–6-Å region (which affects the higher vibrational levels) determined by comparison with the H$_2$ data and used without modification for the other isotopomers.[22] Overall, therefore, the

(22) Le Roy, R. J.; Bernstein, R. B. *J. Chem. Phys.* 1968, *49*, 4312.

TABLE V: High-Temperature Thermodynamic Properties for Spin-Equilibrium Homonuclear Diatomic Hydrogen ($p° = 1$ bar)

	$C_p°/(\text{J K}^{-1}\text{ mol}^{-1})$			$S°/(\text{J K}^{-1}\text{ mol}^{-1})$			$-[(G° - E°_0)/T]/(\text{J K}^{-1}\text{ mol}^{-1})$			$[H° - E°_0]/(\text{kJ mol}^{-1})$		
T/K	H_2	D_2	T_2	H_2	D_2	T_2	H_2	D_2	T_2	H_2	D_2	T_2
100	28.1532	30.3185	28.7621	112.2543	131.0579	133.0555	82.2626	103.5534	104.6906	2.9992	2.7504	2.8365
200	27.4478	29.2056	29.1639	130.9392	151.5757	153.2058	102.4745	123.0551	124.4790	5.6929	5.7041	5.7454
298.15	28.8365	29.1957	29.1997	142.2068	163.2309	164.8562	113.8073	134.4898	135.9803	8.4673	8.5692	8.6093
300	28.8492	29.1962	29.2007	142.3852	163.4115	165.0368	113.9830	134.6676	136.1589	8.5207	8.6232	8.6634
350	29.0811	29.2146	29.2414	146.8522	167.9133	169.5408	118.3673	139.1036	140.6142	9.9697	10.0834	10.1243
400	29.1816	29.2440	29.3162	150.7429	171.8162	173.4499	122.1764	142.9541	144.4797	11.4266	11.5448	11.5881
450	29.2294	29.2926	29.4373	154.1831	175.2632	176.9093	125.5452	146.3562	147.8944	12.8870	13.0081	13.0567
500	29.2602	29.3686	29.6101	157.2643	178.3531	180.0194	128.5658	149.4041	150.9540	14.3493	14.4745	14.5327
600	29.3271	29.6221	30.0986	162.6046	183.7279	185.4585	133.8072	154.6898	156.2640	17.2784	17.4229	17.5167
700	29.4407	30.0116	30.7220	167.1331	188.3218	190.1438	138.2527	159.1739	160.7768	20.2163	20.4035	20.5569
800	29.6237	30.5060	31.4050	171.0755	192.3607	194.2904	142.1144	163.0748	164.7116	23.1689	23.4287	23.6630
900	29.8810	31.0622	32.0903	174.5788	195.9855	198.0292	145.5305	166.5335	168.2092	26.1435	26.5068	26.8380
1000	30.2048	31.6417	32.7433	177.7433	199.2881	201.4444	148.5960	169.6462	171.3644	29.1473	29.6419	30.0800
1100	30.5804	32.2165	33.3472	180.6394	202.3310	204.5939	151.3792	172.4810	174.2439	32.1862	32.8349	33.3850
1200	30.9914	32.7690	33.8965	183.3177	205.1581	207.5194	153.9305	175.0877	176.8964	35.2646	36.0845	36.7476
1300	31.4224	33.2896	34.3920	185.8152	207.8018	210.2525	156.2882	177.5036	179.3583	38.3851	39.3877	40.1625
1400	31.8609	33.7742	34.8375	188.1599	210.2868	212.8178	158.4819	179.7574	181.6576	41.5493	42.7412	43.6243
1500	32.2973	34.2223	35.2382	190.3730	212.6324	215.2353	160.5348	181.8716	183.8163	44.7573	46.1413	47.1285
1600	32.7246	34.6350	35.5996	192.4711	214.8544	217.5212	162.4659	183.8642	185.8521	48.0084	49.5845	50.6707
1700	33.1385	35.0150	35.9269	194.4676	216.9657	219.6894	164.2901	185.7497	187.7793	51.3017	53.0672	54.2473
1800	33.5362	35.3651	36.2247	196.3730	218.9772	221.7515	166.0199	187.5403	189.6098	54.6356	56.5865	57.8551
1900	33.9163	35.6883	36.4974	198.1965	220.8981	223.7175	167.6658	189.2458	191.3536	58.0084	60.1393	61.4914
2000	34.2784	35.9877	36.7485	199.9455	222.7363	225.5960	169.2363	190.8747	193.0191	61.4183	63.7233	65.1538
2100	34.6227	36.2660	36.9812	201.6263	224.4990	227.3947	170.7390	192.4342	194.6135	64.8635	67.3362	68.8405
2200	34.9498	36.5259	37.1981	203.2446	226.1922	229.1201	172.1799	193.9304	196.1431	68.3422	70.9759	72.5495
2300	35.2606	36.7695	37.4017	204.8051	227.8212	230.7782	173.5647	195.3687	197.6131	71.8529	74.6408	76.2796
2400	35.5564	36.9991	37.5940	206.3121	229.3910	232.3741	174.8980	196.7538	199.0285	75.3939	78.3293	80.0295
2500	35.8382	37.2164	37.7766	207.7693	230.9058	233.9125	176.1838	198.0898	200.3932	78.9637	82.0402	83.7981
2600	36.1072	37.4231	37.9511	209.1802	232.3696	235.3975	177.4259	199.3802	201.7112	82.5611	85.7723	87.5846
2700	36.3647	37.6208	38.1189	210.5477	233.7856	236.8330	178.6275	200.6284	202.9855	86.1848	89.5245	91.3881
2800	36.6118	37.8106	38.2810	211.8747	235.1573	238.2222	179.7913	201.8372	204.2193	89.8337	93.2962	95.2081
2900	36.8495	37.9938	38.4385	213.1637	236.4873	239.5683	180.9199	203.0092	205.4152	93.5068	97.0864	99.0442
3000	37.0791	38.1715	38.5923	214.4168	237.7784	240.8740	182.0157	204.1468	206.5755	97.2033	100.8947	102.8957
3100	37.3014	38.3446	38.7432	215.6363	239.0328	242.1419	183.0807	205.2520	207.7024	100.9224	104.7206	106.7625
3200	37.5173	38.5138	38.8918	216.8240	240.2529	243.3743	184.1167	206.3268	208.7980	104.6634	108.5635	110.6443
3300	37.7276	38.6800	39.0388	217.9817	241.4406	244.5734	185.1254	207.3730	209.8640	108.4256	112.4233	114.5408
3400	37.9331	38.8438	39.1847	219.1110	242.5978	245.7409	186.1084	208.3920	210.9021	112.2087	116.2995	118.4520
3500	38.1345	39.0056	39.3299	220.2135	243.7261	246.8784	187.0672	209.3855	211.9138	116.0121	120.1919	122.3777
3600	38.3322	39.1660	39.4747	221.2906	244.8272	247.9889	188.0029	210.3548	212.9006	119.8355	124.1005	126.3180
3700	38.5268	39.3252	39.6195	222.3435	245.9024	249.0724	188.9169	211.3011	213.8636	123.6785	128.0251	130.2727
3800	38.7185	39.4836	39.7643	223.3735	246.9533	250.1309	189.8101	212.2255	214.8041	127.5408	131.9656	134.2419
3900	38.9077	39.6412	39.9093	224.3817	247.9809	251.1657	190.6837	213.1292	215.7233	131.4221	135.9218	138.2256
4000	39.0946	39.7981	40.0544	225.3691	248.9865	252.1780	191.5385	214.0131	216.6220	135.3222	139.8938	142.2237
4100	39.2792	39.9544	40.1996	226.3367	249.9712	253.1688	192.3755	214.8781	217.5014	139.2409	143.8814	146.2364
4200	39.4614	40.1098	40.3446	227.2854	250.9358	254.1392	193.1954	215.7252	218.3622	143.1780	147.8846	150.2636
4300	39.6413	40.2643	40.4894	228.2161	251.8815	255.0903	193.9991	216.5551	219.2053	147.1331	151.9033	154.3053
4400	39.8187	40.4175	40.6336	229.1295	252.8089	256.0228	194.7872	217.3685	220.0315	151.1062	155.9374	158.3615
4500	39.9932	40.5691	40.7767	230.0263	253.7189	256.9375	195.5603	218.1662	220.8415	155.0968	159.9868	162.4320
4600	40.1647	40.7188	40.9184	230.9072	254.6122	257.8353	196.3192	218.9489	221.6360	159.1047	164.0512	166.5168
4700	40.3327	40.8660	41.0583	231.7728	255.4895	258.7168	197.0643	219.7170	222.4156	163.1296	168.1304	170.6157
4800	40.4968	41.0104	41.1957	232.6236	256.3513	259.5827	197.7963	220.4713	223.1809	167.1711	172.2243	174.7284
4900	40.6566	41.1514	41.3302	233.4603	257.1984	260.4335	198.5156	221.2122	223.9325	171.2288	176.3324	178.8547
5000	40.8116	41.2884	41.4612	234.2832	258.0312	261.2698	199.2228	221.9403	224.6709	175.3023	180.4544	182.9943
5100	40.9613	41.4209	41.5881	235.0929	258.8501	262.0921	199.9182	222.6560	225.3966	179.3909	184.5899	187.1468
5200	41.1052	41.5484	41.7103	235.8897	259.6557	262.9008	200.6023	223.3598	226.1101	183.4943	188.7384	191.3118
5300	41.2428	41.6703	41.8272	236.6740	260.4482	263.6965	201.2755	224.0521	226.8118	187.6118	192.8994	195.4887
5400	41.3736	41.7860	41.9384	237.4461	261.2282	264.4793	201.9382	224.7334	227.5021	191.7426	197.0723	199.6770
5500	41.4971	41.8951	42.0431	238.2064	261.9960	265.2498	202.5908	225.4039	228.1815	195.8862	201.2564	203.8762
5600	41.6128	41.9969	42.1410	238.9552	262.7518	266.0083	203.2335	226.0641	228.8502	200.0418	205.4511	208.0854
5700	41.7204	42.0911	42.2315	239.6927	263.4960	266.7550	203.8666	226.7143	229.5086	204.2085	209.6555	212.3041
5800	41.8193	42.1771	42.3141	240.4192	264.2288	267.4902	204.4906	227.3548	230.1572	208.3856	213.8690	216.5314
5900	41.9093	42.2547	42.3884	241.1348	264.9504	268.2142	205.1056	227.9859	230.7961	212.5721	218.0907	220.7666
6000	41.9900	42.3233	42.4541	241.8399	265.6612	268.9272	205.7120	228.6079	231.4257	216.7671	222.3196	225.0088
6500	42.2453	42.5242	42.6428	245.2126	269.0584	272.3343	208.6224	231.5905	234.4431	237.8365	243.5417	246.2930
7000	42.2439	42.4761	42.5862	248.3449	272.2096	275.4940	211.3492	234.3807	237.2639	258.9695	264.8022	267.6106
7500	41.9935	42.1853	42.2888	251.2522	275.1316	278.4233	213.9137	237.0013	239.9114	280.0387	285.9772	288.8390
8000	41.5222	41.6789	41.7772	253.9485	277.8390	281.1373	216.3327	239.4701	242.4043	300.9261	306.9515	309.8636
8500	40.8703	40.9969	41.0905	256.4470	280.3461	283.6502	218.6198	241.8018	244.7576	321.5308	327.6268	330.5869
9000	40.0827	40.1835	40.2725	258.7613	282.6669	285.9762	220.7864	244.0084	246.9837	341.7737	347.9265	350.9323
9500	39.2024	39.2813	39.3660	260.9052	284.8157	288.1297	222.8423	246.1004	249.0934	361.5979	367.7956	370.8447
10000	38.2676	38.3283	38.4085	262.8924	286.8065	290.1247	224.7957	248.0865	251.0957	380.9669	387.1994	390.2898

level energies used here[10,11] give rise to improvements of up to 0.0040 J mol^{-1} K^{-1} (or kJ mol^{-1}, for the enthalpy) for H$_2$ and of up to 0.05 and 0.18 (in those same units) for HD and D$_2$, re-spectively, relative to the results reported in ref 3.

The exception referred to above is the fact that the Kosloff et al.[3] values of $S°$ and $-G°/T$ for HD lie above ours at all tem-

TABLE VI: Thermodynamic Properties for Heteronuclear Diatomic Hydrogen ($p° = 1$ bar)

T/K	$C_p°$/(J K^{-1} mol^{-1})			$S°$/(J K^{-1} mol^{-1})			$-[(G° - E_0°)/T]$/(J K^{-1} mol^{-1})			$[H° - E°_0]$/(kJ mol^{-1})		
	HD	HT	DT	HD	HT	DT	HD	HT	DT	HD	HT	DT
5	20.7863	20.7863	20.7892	52.5685	52.7686	58.9238	31.7822	31.9823	38.1373	0.1039	0.1039	0.1039
10	20.7972	20.8216	21.7581	66.9774	67.1799	73.4860	46.1903	46.3905	52.5641	0.2079	0.2079	0.2092
15	21.1365	21.4942	25.3205	75.4503	75.7099	82.9341	54.6231	54.8306	61.1782	0.3124	0.3132	0.3263
20	22.4457	23.4185	28.4373	81.6848	82.1312	90.6878	60.6387	60.8799	67.6140	0.4209	0.4250	0.4615
25	24.5268	25.8636	29.7224	86.9093	87.6202	97.2011	65.3820	65.6903	72.8995	0.5382	0.5482	0.6075
30	26.6363	27.8900	29.9118	91.5722	92.5255	102.6465	69.3649	69.7614	77.4169	0.6662	0.6829	0.7569
35	28.2529	29.1466	29.7541	95.8075	96.9290	107.2472	72.8447	73.3337	81.3585	0.8037	0.8258	0.9061
40	29.2516	29.7402	29.5670	99.6519	100.8658	111.2077	75.9593	76.5338	84.8479	0.9477	0.9733	1.0544
45	29.7458	29.9172	29.4286	103.1298	104.3818	114.6817	78.7883	79.4363	87.9737	1.0954	1.1225	1.2019
50	29.9130	29.8863	29.3384	106.2747	107.5335	117.7773	81.3823	82.0913	90.8021	1.2446	1.2721	1.3488
60	29.8168	29.6553	29.2442	111.7247	112.9628	123.1167	85.9992	86.7984	95.7566	1.5435	1.5699	1.6416
70	29.6048	29.4606	29.2025	116.3049	117.5185	127.6212	90.0103	90.8703	99.9953	1.8406	1.8654	1.9338
80	29.4451	29.3440	29.1815	120.2469	121.4440	131.5192	93.5492	94.4523	103.6976	2.1358	2.1593	2.2257
90	29.3459	29.2783	29.1699	123.7088	124.8961	134.9555	96.7118	97.6470	106.9836	2.4297	2.4524	2.5175
100	29.2866	29.2405	29.1634	126.7973	127.9788	138.0285	99.5687	100.5288	109.9371	2.7229	2.7450	2.8091
110	29.2505	29.2176	29.1597	129.5868	130.7645	140.8079	102.1728	103.1529	112.6192	3.0155	3.0373	3.1008
120	29.2277	29.2032	29.1579	132.1309	133.3061	143.3450	104.5649	105.5613	115.0755	3.3079	3.3294	3.3923
130	29.2129	29.1938	29.1573	134.4697	135.6432	145.6789	106.7765	107.7866	117.3411	3.6001	3.6214	3.6839
150	29.1963	29.1836	29.1584	138.6488	139.8201	149.8513	110.7542	111.7859	121.4042	4.1842	4.2051	4.2671
200	29.1861	29.1800	29.1672	147.0460	148.2147	158.2408	118.8278	119.8941	129.6148	5.6436	5.6641	5.7252
250	29.1911	29.1875	29.1799	153.5591	154.7267	164.7505	125.1470	126.2336	136.0151	7.1030	7.1233	7.1838
298.15	29.2008	29.1984	29.1954	158.7015	159.8686	169.8914	130.1628	131.2624	141.0831	8.5088	8.5289	8.5892
300	29.2012	29.1989	29.1961	158.8821	160.0492	170.0720	130.3393	131.4394	141.2613	8.5628	8.5829	8.6432
350	29.2140	29.2129	29.2213	163.5513	164.5513	174.5743	134.7467	135.8563	145.7069	10.0232	10.0432	10.1036
400	29.2299	29.2311	29.2653	167.2864	168.4532	178.4789	138.5757	139.6925	149.5647	11.4843	11.5043	11.5657
450	29.2514	29.2574	29.3393	170.7303	171.8976	181.9298	141.9608	143.0832	152.9728	12.9463	12.9665	13.0306
500	29.2826	29.2974	29.4516	173.8138	174.9821	185.0264	144.9946	146.1215	156.0260	14.4096	14.4303	14.5002
600	29.3935	29.4398	29.8008	179.1613	180.3347	190.4245	150.2567	151.3909	161.3220	17.3427	17.3663	17.4615
700	29.5928	29.6864	30.2942	183.7060	184.8900	195.0538	154.7185	155.8590	165.8177	20.2913	20.3217	20.4652
800	29.8881	30.0363	30.8792	187.6758	188.8759	199.1365	158.5952	159.7420	169.7323	23.2645	23.3071	23.5234
900	30.2668	30.4678	31.5026	191.2173	192.4379	202.8094	162.0266	163.1804	173.2068	26.2717	26.3317	26.6423
1000	30.7058	30.9521	32.1251	194.4285	195.6727	206.1609	165.1086	166.2703	176.3370	29.3199	29.4024	29.8239
1100	31.1808	31.4623	32.7221	197.3772	198.6466	209.2510	167.9099	169.0802	179.1905	32.4140	32.5230	33.0665
1200	31.6708	31.9771	33.2808	200.1112	201.4063	212.1224	170.4808	171.6604	181.8166	35.5565	35.6950	36.3670
1300	32.1601	32.4819	33.7961	202.6656	203.9858	214.8070	172.8594	174.0489	184.2522	38.7482	38.9181	39.7212
1400	32.6377	32.9672	34.2677	205.0665	206.4109	217.3291	175.0750	176.2747	186.5257	41.9882	42.1907	43.1248
1500	33.0968	33.4279	34.6977	207.3341	208.7013	219.7082	177.1507	178.3608	188.6593	45.2751	45.5107	46.5734
1600	33.5334	33.8616	35.0896	209.4841	210.8726	221.9602	179.1049	180.3255	190.6708	48.6068	48.8754	50.0630
1700	33.9460	34.2679	35.4473	211.5296	212.9378	224.0984	180.9526	182.1836	192.5748	51.9810	52.2821	53.5902
1800	34.3343	34.6475	35.7747	213.4810	214.9074	226.1339	182.7059	183.9473	194.3831	55.3952	55.7281	57.1515
1900	34.6990	35.0021	36.0756	215.3472	216.7903	228.0763	184.3751	185.6267	196.1057	58.8470	59.2108	60.7442
2000	35.0414	35.3333	36.3532	217.1359	218.5942	229.9339	185.9688	187.2303	197.7510	62.3342	62.7277	64.3658
2100	35.3630	35.6433	36.6108	218.8534	220.3257	231.7139	187.4941	188.7653	199.3262	65.8546	66.2767	68.0142
2200	35.6656	35.9340	36.8509	220.5055	221.9906	233.4227	188.9573	190.2380	200.8375	69.4062	69.8557	71.6874
2300	35.9509	36.2076	37.0760	222.0973	223.5940	235.0658	190.3638	191.6536	202.2902	72.9872	73.4630	75.3839
2400	36.2206	36.4657	37.2881	223.6331	225.1405	236.6482	191.7182	193.0169	203.6890	76.5959	77.0967	79.1022
2500	36.4763	36.7103	37.4891	225.1169	226.6341	238.1745	193.0246	194.3318	205.0381	80.2308	80.7557	82.8411
2600	36.7197	36.9428	37.6806	226.5523	228.0785	239.6486	194.2867	195.6022	206.3411	83.8907	84.4384	86.5997
2700	36.9520	37.1648	37.8641	227.9425	229.4769	241.0742	195.5076	196.8310	207.6012	87.5744	88.1439	90.3770
2800	37.1747	37.3776	38.0407	229.2904	230.8324	242.4544	196.6902	198.0213	208.8215	91.2808	91.8711	94.1723
2900	37.3889	37.5825	38.2117	230.5987	232.1476	243.7923	197.8370	199.1755	210.0044	95.0090	95.6191	97.9849
3000	37.5958	37.7804	38.3779	231.8698	233.4251	245.0906	198.9503	200.2960	211.1524	98.7583	99.3873	101.8145
3100	37.7964	37.9726	38.5403	233.1058	234.6670	246.3516	200.0323	201.3848	212.2676	102.5280	103.1750	105.6604
3200	37.9915	38.1598	38.6996	234.3089	235.8756	247.5777	201.0847	202.4438	213.3520	106.3174	106.9817	109.5224
3300	38.1821	38.3428	38.8565	235.4809	237.0526	248.7710	202.1093	203.4748	214.4073	110.1261	110.8068	113.4002
3400	38.3688	38.5223	39.0116	236.6235	238.1999	249.9333	203.1077	204.4793	215.4352	113.9537	114.6501	117.2936
3500	38.5523	38.6990	39.1653	237.7384	239.3192	251.0664	204.0813	205.4588	216.4371	117.7998	118.5112	121.2025
3600	38.7330	38.8734	39.3180	238.8270	240.4118	252.1718	205.0314	206.4146	217.4144	121.6641	122.3898	125.1267
3700	38.9114	39.0458	39.4701	239.8907	241.4792	253.2512	205.9592	207.3479	218.3684	125.5463	126.2858	129.0661
3800	39.0879	39.2165	39.6218	240.9307	242.5228	254.3058	206.8659	208.2599	219.3003	129.4463	130.1989	133.0207
3900	39.2626	39.3858	39.7731	241.9483	243.5437	255.3369	207.7524	209.1516	220.2112	133.3638	134.1291	136.9904
4000	39.4357	39.5538	39.9241	242.9445	244.5429	256.3458	208.6198	210.0239	221.1020	137.2988	138.0761	140.9753
4100	39.6072	39.7206	40.0747	243.9204	245.5217	257.3335	209.4690	210.8778	221.9737	141.2509	142.0398	144.9752
4200	39.7771	39.8859	40.2249	244.8769	246.4808	258.3010	210.3007	211.7141	222.8271	145.2202	146.0201	148.9902
4300	39.9453	40.0498	40.3743	245.8148	247.4213	259.2493	211.1157	212.5336	223.6632	149.2063	150.0169	153.0202
4400	40.1115	40.2120	40.5227	246.7351	248.3439	260.1791	211.9148	213.3371	224.4825	153.2092	154.0300	157.0650
4500	40.2755	40.3721	40.6698	247.6383	249.2494	261.0915	212.6987	214.1251	225.2860	157.2285	158.0593	161.1247
4600	40.4370	40.5300	40.8152	248.5253	250.1384	261.9869	213.4679	214.8983	226.0741	161.2642	162.1044	165.1989
4700	40.5955	40.6850	40.9583	249.3967	251.0117	262.8663	214.2231	215.6574	226.8476	165.3158	166.1652	169.2876
4800	40.7505	40.8369	41.0988	250.2530	251.8699	263.7300	214.9648	216.4030	227.6070	169.3832	170.2413	173.3905
4900	40.9017	40.9851	41.2360	251.0948	252.7134	264.5789	215.6936	217.1354	228.3529	173.4658	174.3324	177.5073
5000	41.0486	41.1291	41.3694	251.9226	253.5429	265.4133	216.4099	217.8553	229.0858	177.5634	178.4382	181.6376
5100	41.1905	41.2683	41.4985	252.7369	254.3588	266.2338	217.1142	218.5631	229.8062	181.6753	182.5581	185.7810
5200	41.3269	41.4023	41.6226	253.5380	255.1614	267.0408	217.8070	219.2592	230.5145	185.8013	186.6917	189.9371
5300	41.4574	41.5305	41.7413	254.3265	255.9513	267.8348	218.4887	219.9441	231.2112	189.9405	190.8383	194.1054

TABLE VI (Continued)

T/K	$C_p°/(J\ K^{-1}\ mol^{-1})$			$S°/(J\ K^{-1}\ mol^{-1})$			$-[(G° - E_0°)/T]/(J\ K^{-1}\ mol^{-1})$			$[H° - E°_0]/(kJ\ mol^{-1})$		
	HD	HT	DT	HD	HT	DT	HD	HT	DT	HD	HT	DT
5400	41.5814	41.6523	41.8539	255.1026	256.7287	268.6161	219.1595	220.6181	231.8966	194.0925	194.9975	198.2852
5500	41.6984	41.7673	41.9600	255.8666	257.4941	269.3851	219.8200	221.2816	232.5713	198.2566	199.1686	202.4759
5600	41.8079	41.8749	42.0589	256.6190	258.2476	270.1420	220.4704	221.9350	233.2354	202.4320	203.3507	206.6769
5700	41.9095	41.9747	42.1503	257.3599	258.9897	270.8873	221.1111	222.5786	233.8895	206.6179	207.5433	210.8875
5800	42.0026	42.0663	42.2336	258.0896	259.7205	271.6211	221.7424	223.2127	234.5337	210.8136	211.7454	215.1067
5900	42.0870	42.1493	42.3085	258.8083	260.4403	272.3437	222.3646	223.8376	235.1684	215.0181	215.9563	219.3339
6000	42.1623	42.2232	42.3747	259.5163	261.1494	273.0553	222.9779	224.4535	235.7940	219.2307	220.1750	223.5681
6500	42.3931	42.4490	42.5639	262.9019	264.5396	276.4562	225.9204	227.4083	238.7927	240.3799	241.3533	244.8129
7000	42.3703	42.4234	42.5059	266.0443	267.6860	279.6099	228.6755	230.1743	241.5970	261.5814	262.5819	266.0907
7500	42.1007	42.1526	42.2065	268.9597	270.6051	282.5337	231.2652	232.7736	244.2299	282.7090	283.7357	287.2784
8000	41.6122	41.6638	41.6930	271.6623	273.3110	285.2423	233.7066	235.2237	246.7096	303.6456	304.6981	308.2614
8500	40.9449	40.9966	41.0052	274.1658	275.8176	287.7500	236.0139	237.5388	249.0509	324.2914	325.3697	328.9423
9000	40.1435	40.1955	40.1870	276.4840	278.1388	290.0712	238.1986	239.7307	251.2662	344.5681	345.6724	349.2449
9500	39.2510	39.3032	39.2811	278.6308	280.2884	292.2200	240.2709	241.8095	253.3658	364.4197	365.5500	369.1147
10000	38.3057	38.3578	38.3252	280.6203	282.2805	294.2107	242.2392	243.7839	255.3589	383.8103	384.9668	388.5177

peratures by approximately 0.07 cal mol⁻¹ K⁻¹ (or 0.3 J mol⁻¹ K⁻¹!). However, since our results for $T \leq 1000$ K agree exactly (to the 0.001 cal mol⁻¹ K⁻¹ quoted) with those in the current JANAF tables,[2] we are inclined to attribute this displacement to use of a slightly erroneous numerical constant in this part of the work of ref 3.

The existing JANAF tabulations for this system[2] were reported to three decimal places in units of calories and hence have a precision 40 times lower than that of the present results. To this precision, they are in essentially exact agreement with the present results at temperatures up to 1000 K. Above that point, discrepancies grow in which by 6000 K reach 10, 81, and 95 units in the last decimal place quoted in ref 2 for H_2, HD, and D_2, respectively. These differences are what one might expect to arise from the empirical extrapolation methods used to estimate the number and energies of unobserved levels. This further illustrates the advantages of the entirely ab initio approach pioneered by Kosloff et al.[3] and further applied here, in which there is no uncertainty regarding the number and very little regarding the energies of the unobserved levels.

Our final point concerns the magnitude of the effect on these results of possible errors in the input energies. Comparisons with experiment show that such errors are likely smaller than 0.05 cm⁻¹ for the lowest levels and 0.5 cm⁻¹ for the highly excited levels. As a test, the H_2 calculations reported above were repeated after arbitrarily lowering the $(v,J) = (0,2)$ and $(0,3)$ levels by 0.05 cm⁻¹ and, again, after lowering the energies of all twelve $v = 12$ levels by 0.2 cm⁻¹. The effect of the first of these changes on the calculated properties reached a maximum of 7 units in the last significant digit at around 300 K and died off rapidly for higher and lower temperatures. While superficially more drastic, the second type of eigenvalue modification had a much smaller effect on the calculated properties, changing the calculated values of H and C_p by at most 1 or 2 units in the last significant digit of the results for $T = 8000-10000$ K. Thus, it seems clear that the effect of further improvements in the input level energies will definitely be very small and at worst will affect only the last

significant digit in the present results.

In conclusion, we believe that the present paper provides some of the most accurate thermodynamic property tabulations available for *any* system. They are also noteworthy in that they are generated in an entirely ab initio manner. For the tritium isotopomers, this approach has proved essential, as the difficulty of making detailed spectroscopic measurements for those species[23,24] would have effectively precluded reliable calculations based purely on experimental level energies.

Appendix: Integration Technique

Our procedure for performing the numerical integration of eq 2 is based upon the substitution $y = \tan^{-1}\{[E - E_{v,J}]/((1/2)\Gamma_{v,J})\}$, which transforms eq 2 into

$$z_n(v,J;T) = \frac{2J + 1}{\pi} \int_{-\tan^{-1}((E_{v,J} - D)/\frac{1}{2}\Gamma_{v,J})}^{\pi/2} [(1/2)\Gamma_{v,J} \tan(y) + E_{v,J}]^n e^{-[(1/2)\Gamma_{v,J}\tan(y)+E_{v,J}]/k_B T}\ dy \quad (A1)$$

The integrand in this expression is well-behaved across the entire interval, so the integral may be evaluated by using a standard Gaussian quadrature formula. Since the integrand behaves very differently near vs far from the point $y = 0$, the domain was divided into the three segments: $[-\tan^{-1}\{(E_{v,J} - D)/((1/2)\Gamma_{v,J})\}, \tan^{-1}(-3)]$, $[\tan^{-1}(-3), \tan^{-1}(3)]$, and $[\tan^{-1}(3), \pi/2]$. To avoid having to introduce an arbitrary number of quadrature points and weights, an 8-point formula was always used, but each interval was repeatedly subdivided (with an 8-point quadrature being performed on each fragment, and the results summed), as necessary, until the desired convergence criterion (here, one part in 10^{-5}) was achieved.

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