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A HIGH-TEMPERATURE PARTITION FUNCTION FOR H_3^+

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ABSTRACT

H_3^+ is the main supplier of electrons to metal-free stars below ~8000 K. To describe H_3^+ properly it is important to know its partition function. Previous determinations of this function are based on extrapolations from lower temperatures. A new partition function is presented that is calculated by explicit ab initio computation of levels lying up to 15,000 cm^{-1} above the ground state and with $J \leq 20$. The effect of *all* other bound levels of H_3^+, which is significant at higher temperatures, is included using a simple model based on Padé approximants. The new partition function is very significantly larger (up to a factor of 100 in some cases) than previous estimates above 3000 K.

Subject headings: molecular data — stars: atmospheres

1. INTRODUCTION

The simple molecular ion H_3^+ is rapidly formed by the reaction

$$H_2 + H_2^+ \rightarrow H_3^+ + H. \tag{1}$$

H_3^+ is thus to be expected in any active environment containing molecular hydrogen (Dalgarno 1994; Miller, Lam, & Tennyson 1994). So far, however, most studies of H_3^+ have concerned themselves with relatively cool environments; perhaps the hottest considered seriously has been the remnant of SN 1987A, for which it was necessary to allow for temperatures up to 3000 K (Miller et al. 1992). However, it is apparent that H_3^+ is also an important constituent of cool stars with low metallicity.

In metal-free stars the main source of opacity is generally believed to be H^-. Electrical neutrality demands that the H^- must be balanced by a corresponding population of positive ions. Below ~8000 K and at higher pressures, H_3^+ is thought to be the major source of electrons. Because of this, the H_3^+ partition function becomes crucial in any attempt to model cool stars of low metallicity (Bergeron, Saumon, & Wesemael 1995; Allard & Hauschildt 1995).

Accurate previous partition functions for H_3^+ have been largely concerned with substellar temperatures (Tennyson & Sutcliffe 1984; Sidhu, Miller, & Tennyson 1992). Chandra, Gaur, & Pande (1991) presented a function for the temperature range 500–8000 K. This partition function was derived from a small set of calculated H_3^+ energy levels and is suspect at higher temperatures. In this work we present an H_3^+ partition function that we believe to be accurate over the temperature range 500–8000 K.

Our partition function was calculated by summing energy levels explicitly calculated using high-accuracy ab initio methods augmented by levels computed using a simple model. H_3^+ is an equilateral triangle at equilibrium but can reach linear geometries with excitation energies as low as 12,000 cm^{-1}. Above linearity, calculations predict that there is a significant increase in the density of vibrational states (Berblinger et al. 1994). To obtain an accurate partition function at 8000 K, it is necessary to account, approximately, for *every* bound state of the H_3^+ system. Our partition function is more than an order of magnitude larger than that presented by Chandra et al. (1991) over much of the temperature range they consider. Use of this new partition function is likely to have a profound effect on models of metal-free stars.

2. CALCULATIONS

As before (Sidhu et al. 1992), the internal partition functions, z, for H_3^+ were computed by explicitly summing the series:

$$z = \sum_i (2J+1) g_i \exp\left(-\frac{E_i}{kT}\right), \tag{2}$$

where J is the rotational quantum number, g_i is the nuclear spin degeneracy factor for state i, and E_i is the associated energy level. In the low-energy region (defined below), our calculation made no distinction between vibration and rotation energy levels. Because H_3^+ has only one bound electronic state, no electronic contribution to the partition function was considered. All energies were taken relative to the $J = 0$ level of the vibrational ground state, which for H_3^+ has a statistical weight of zero.

Calculations were performed using the DVR3D program suite of Tennyson, Henderson, & Fulton (1995), the spectroscopically determined effective H_3^+ potential energy surface of Dinelli, Polyansky, & Tennyson (1995), and nuclear masses for the hydrogens. Calculations were performed in scattering coordinates (r_1, r_2, θ), with the body-fixed z-axis taken to be parallel to the r_1 coordinate. Discrete variable representation (DVR) grids with 36, 40, and 32 points in the r_1, r_2, and cos θ coordinates, respectively, were used. These grids were based on the use of Morse oscillator-like functions for the r_1 coordinate and spherical oscillator functions for the r_2 coordinate. Associate Legendre polynomials were used for the angular coordinate. See Henderson, Tennyson, & Sutcliffe (1993) and Tennyson (1993) for further details of this procedure.

As states of A_1 symmetry have zero statistical weight ($g_{A_1} = 0$), "even" symmetry calculations which give these states were not attempted. Unfortunately, for technical reasons (Tennyson & Sutcliffe 1984), the H_3^+ energies with $E(g_E = 2)$ and $A_2(g_{A_2} = 4)$ symmetry could not be separately identified in the "odd" symmetry calculations. This problem was addressed by Sidhu et al. (1992), who found that the high-temperature approximation (Miller, Tennyson, & Sutcliffe 1990) of using $g = 8/3$ for all levels introduced an error of less than 0.2% for temperatures above 200 K. For temperatures below 500 K, we recommend the use of the partition function of Sidhu et al. (1992), who hand-corrected the nuclear spin degeneracy factors for their 33 lowest levels.

We computed energies for all states up to 15,000 cm^{-1} above the ground state and with rotational angular momentum, $J \leq 20$. In the first "vibrational" step of the calculation, the lowest 700 energy solutions were selected from a 3000 dimension secular problem, and the lowest $500 \times (J+1)$ solutions were used to solve the full ro-vibrational problem (see Tennyson et al. 1995). The wave functions generated in the course of these calculations will be used to create a comprehensive H_3^+ line list.

The energy levels generated by these calculations are much more comprehensive than any previous treatment. Nonetheless, tests showed that at temperatures above ~4000 K the truncation of our energy-level expansion introduced by the energy and J cutoffs causes the partition function to be significantly underestimated. The lowest level with $J = 21$ lies only some 9000 cm^{-1} above the H_3^+ ground state. To compensate for these truncation effects, a simple model to introduce the effective contribution from levels at higher energies and/or higher J values was used.

Effective Hamiltonians, based on perturbation theory expansions, have often been used to fit rotational data for polyatomic molecules, but many do not extrapolate reliably. For this work we used an effective Hamiltonian given as a low-order, diagonal Padé approximant (Polyansky 1985), which is better behaved than simple series representations (Polyansky & Tennyson 1992):

$$E_{gs}(J, K) = \frac{C_0^2}{C_0 - C_1}, \tag{3}$$

$$C_0 = BJ(J+1) + (C-B)K^2,$$

$$C_1 = -D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4.$$

The parameters B, C, D_J, D_{JK}, and D_K were obtained by fitting the 112 ground-state energies with $J \leq 20$ that could be identified in our line list. Final parameter values, in cm^{-1}, were

$$B = 43.5140230459771686,$$

$$C = 20.6255176280631680,$$

$$D_J = 0.0379840980260718816,$$

$$D_{JK} = -0.0609709667247304021,$$

$$D_K = 0.0256312415531191225. \tag{4}$$

These reproduced our data with a standard deviation of 4.9 cm^{-1}. Although a better fit could be obtained with a more flexible model, this model is adequate for our purposes.

The Padé formula gives a simple means of including rotational levels with $J > 20$ that belong to the ground vibrational state. However, these form only a small portion of the states missing from our sum. To model the rotational levels associated with the higher vibrational states, we assumed that the rotational structure of these states was the same as that for the ground state. This means that the energy of the (J, K) level associated with vibrational state ν is given by

$$E_\nu(J, K) = E_\nu(J=0) + E_{\mathrm{gs}}(J, K), \tag{5}$$

where $E_\nu(J=0)$ is the νth vibrational band origin. This model thus employs the approximation (Sauval & Tatum 1984; Zhang, Day, & Truhlar 1993) that represents the partition function as a product of vibrational and rotational partition functions. In particular, the model neglects the complications introduced into the structure of the H_3^+ rotational levels by the vibrational angular momentum (Watson 1984).

One further correction had to be made to this model: vibrational states of E symmetry have twice as many rotational levels, on average, as those with A_1 or A_2 symmetry. Components of the E states appear in both "even" and "odd" calculations; simply including both of these automatically introduces the required factor of 2. This procedure obviates the need to worry about symmetry assignments in the lists of band origins. These were taken from the present calculation up to 27,600 cm^{-1}. Above this, the band origins of Henderson et al. (1993) were used. These extend all the way to dissociation.

Although other models are discussed for test purposes below, our best partition function calculation used all levels explicitly calculated in the range defined by $E \leq 15{,}000$ cm^{-1} and $J \leq 20$. Outside this range, levels calculated using the model above were used provided these levels did not lie above dissociation of the H_3^+ molecule, defined as $E = 35{,}000$ cm^{-1} or $J = 46$ (Miller & Tennyson 1988). In our final (largest) calculation, the summation ran over a total of 187,115 levels, of which 5418 came from our ab initio calculation and the remainder from our extrapolation model.

3. RESULTS

It is necessary to consider the validity of the model proposed to deal with the levels not explicitly included in our calculation. For this purposes we consider two regimes: high rotational states, $J > 20$, and high energies, $E > 15{,}000$ cm^{-1}.

To test the model for extrapolation on rotational excitation we considered a partition function, z_J, calculated (*a*) only with levels below 15,000 cm^{-1} and (*b*) with rotational states less than or equal to J. As shown in Table 1, at the highest temperatures considered z_{16} is some 20% less than z_{20}. However, if z_{16} is corrected for the effects of rotational levels with $J = 16$–20 using the model described above, the resulting extrapolated partition function, z_{ext}, is within 2% of z_{20} at 10,000 K and is less than 1% in error at 4000 K.

To test the model for extrapolation to higher energies, we considered a partition function, z_E, calculated (*a*) only with levels below E cm^{-1} and (*b*) with rotational states $J \leq 20$. As shown in Table 2, $z_{10{,}000}$ seriously underestimates $z_{15{,}000}$ at even quite low energies. At 4000 K, it is more than 30% too low. If $z_{10{,}000}$ is corrected using the extrapolation procedure described above, the resulting partition function, z_{ext}, is within 3% of the true value even at 10,000 K.

It is clear that our model extrapolation procedure works very satisfactorily. Our final test is to consider the effect of including progressively more high-lying levels in the sum; see Table 3. In this case, because of the dissociation limit, $z_{35{,}000}$ includes all possible H_3^+ bound states, and it is not necessary to demonstrate convergence with increasing cutoff energy. For $T < 3000$ K, $z_{25{,}000}$ and $z_{35{,}000}$ are insignificantly different, but at $T > 3000$ K, the higher energy levels become increasingly important.

Column (6) of Table 3, $z_{35{,}000}$, represents our best estimate of

TABLE 1

H_3^+ PARTITION FUNCTIONS, z, AS A FUNCTION OF TEMPERATURE, T

T (K)	z_{15}	$z_{\rm ext}$	z_{20}
100	7.360	7.360	7.360
150	13.599	13.599	13.599
200	20.726	20.726	20.726
300	37.608	37.608	37.608
400	57.649	57.649	57.649
500	80.579	80.579	80.579
600	106.393	106.393	106.393
700	135.330	135.331	135.331
800	167.812	167.819	167.819
900	204.388	204.414	204.415
1000	245.683	245.759	245.762
1200	345.179	345.595	345.614
1400	472.127	473.645	473.731
1600	632.761	637.028	637.305
1800	833.568	843.537	844.249
2000	1081.047	1101.362	1102.926
2200	1381.394	1418.656	1421.695
2400	1740.166	1803.037	1808.406
2600	2161.986	2261.147	2269.930
2800	2650.347	2798.318	2811.815
3000	3207.520	3418.385	3438.088
3500	4905.640	5342.647	5385.317
4000	7025.369	7793.556	7870.782
4500	9524.475	10727.827	10851.290
5000	12344.758	14078.610	14259.164
5500	15423.154	17770.136	18017.290
6000	18698.755	21727.333	22049.049
6500	22116.532	25881.200	26283.882
7000	25628.858	30171.229	30659.825
7500	29195.733	34546.032	35124.198
8000	32784.301	38962.985	39633.254
8500	36368.060	43387.371	44151.331
9000	39925.978	47791.368	48649.819
9500	43441.621	52153.002	53106.100
10000	46902.373	56455.194	57502.571

NOTES—Values for z_J were calculated using energy levels up to J. $z_{\rm ext} = z_{15}$, plus the extrapolation for $16 \le J \le 20$. Only levels up to 15,000 cm^{-1} were included in all cases.

TABLE 2

H_3^+ PARTITION FUNCTIONS, z, AS A FUNCTION OF TEMPERATURE, T

T (K)	$z_{10,000}$	$z_{\rm ext}$	$z_{15,000}$
100	7.360	7.360	7.360
150	13.599	13.599	13.599
200	20.726	20.726	20.726
300	37.608	37.608	37.608
400	57.649	57.649	57.649
500	80.579	80.579	80.579
600	106.393	106.393	106.393
700	135.331	135.331	135.331
800	167.819	167.819	167.819
900	204.413	204.415	204.415
1000	245.751	245.761	245.762
1200	345.464	345.607	345.614
1400	472.729	473.684	473.731
1600	633.050	637.101	637.305
1800	830.959	843.614	844.249
2000	1069.526	1101.329	1102.926
2200	1350.172	1418.281	1421.695
2400	1672.761	1801.942	1808.406
2600	2035.850	2258.797	2269.930
2800	2437.006	2794.027	2811.815
3000	2873.120	3411.332	3438.088
3500	4092.937	5324.416	5385.317
4000	5452.250	7757.319	7870.782
4500	6899.202	10666.600	10851.290
5000	8391.550	13985.878	14259.164
5500	9897.123	17640.194	18017.290
6000	11392.507	21555.427	22049.049
6500	12861.285	25663.525	26283.882
7000	14292.384	29904.861	30659.825
7500	15678.701	34228.832	35124.198
8000	17016.023	38593.481	39633.254
8500	18302.216	42964.658	44151.331
9000	19536.610	47315.001	48649.819
9500	20719.563	51622.919	53106.100
10000	21852.126	55871.634	57502.571

NOTES—Values of z_E were calculated using energy levels up to E cm^{-1}. $z_{\rm ext} = z_{10,000}$, plus the extrapolation for energies up to 15,000 cm^{-1}. Only levels with $J \le 20$ were included in all cases.

the H_3^+ high-temperature partition function. The tests described above suggest that this partition function should be within 5% of the true value in the temperature range 500–8000 K. It is likely that, if anything, our partition function is slightly on the low side.

We have fitted our partition function to a standard formula (Sauval & Tatum 1984) by calculating it at 35 temperatures in the range 100–10,000 K. Our fit is never more than 1% from our calculated value of $\log_{10}(z)$ for 500 K $\le T \le$ 8000 K. It is given by

$$\log_{10}(z) = \sum_{n=0}^{6} a_n (\log_{10} T)^n, \tag{6}$$

where

$$\begin{aligned} a_0 &= 78.6233962485680706, \\ a_1 &= -134.822002886523251, \\ a_2 &= 88.4482694968956480, \\ a_3 &= -25.9274134010262429, \\ a_4 &= 2.60233376654769222, \\ a_5 &= 0.224167420795110400, \\ a_6 &= -0.0452550693680233290. \end{aligned} \tag{7}$$

For ease of use, the energy zero of the fit was taken to be the lowest allowed state of H_3^+, i.e., the $J = 1$, $K = 1$ state, which lies 64.126 cm^{-1} above the spin-forbidden $J = 0$ state.

4. DISCUSSION AND CONCLUSIONS

Figure 1 makes a comparison of our H_3^+ partition functions with previous estimates. This shows that we obtain good agreement with the results of Sidhu et al. (1992) over most temperatures they consider, although, as anticipated by these authors, their partition function is somewhat too low at their highest temperatures. Conversely, for $T > 1000$ K, the partition function of Chandra et al. (1991) is systematically too low. This error increases rapidly with temperature, and by 8000 K they get only ~1% of our value!

The large difference between our partition function and that of Chandra et al. is not entirely due to the leveling off of their partition function with temperature, which is undoubtedly caused by omission of energy levels. The upward curvature of

TABLE 3

H_3^+ PARTITION FUNCTIONS, z, AS A FUNCTION OF TEMPERATURE, T

T (K) (1)	$z_{15,000}$ (2)	$z_{20,000}$ (3)	$z_{25,000}$ (4)	$z_{30,000}$ (5)	$z_{35,000}$ (6)
100	7.360	7.360	7.360	7.360	7.360
150	13.599	13.599	13.599	13.599	13.599
200	20.726	20.726	20.726	20.726	20.726
300	37.608	37.608	37.608	37.608	37.608
400	57.649	57.649	57.649	57.649	57.649
500	80.579	80.579	80.579	80.579	80.579
600	106.393	106.393	106.393	106.393	106.393
700	135.331	135.331	135.331	135.331	135.331
800	167.819	167.819	167.819	167.819	167.819
900	204.415	204.415	204.415	204.415	204.415
1000	245.762	245.762	245.762	245.762	245.762
1200	345.620	345.616	345.616	345.616	345.616
1400	473.766	473.751	473.751	473.751	473.751
1600	637.453	637.461	637.466	637.466	637.466
1800	844.724	845.052	845.092	845.094	845.094
2000	1104.154	1105.925	1106.147	1106.161	1106.162
2200	1424.402	1430.571	1431.479	1431.559	1431.565
2400	1813.685	1830.449	1833.401	1833.741	1833.777
2600	2279.277	2317.716	2325.751	2326.916	2327.070
2800	2827.138	2904.851	2923.861	2927.215	2927.755
3000	3461.683	3604.211	3644.403	3652.808	3654.411
3500	5441.751	5918.523	6099.370	6152.489	6166.740
4000	7980.128	9157.143	9719.196	9932.181	10005.957
4500	11034.960	13412.393	14775.031	15404.511	15670.501
5000	14537.981	18712.576	21486.354	22987.730	23731.476
5500	18410.238	25031.037	30000.520	33062.690	34790.358
6000	22572.625	32300.799	40388.230	45940.155	49431.188
6500	26951.869	40429.339	52650.268	61842.761	68178.249
7000	31483.342	49310.927	66730.109	80900.495	91465.603
7500	36111.895	58835.837	82528.296	103156.050	119620.123
8000	40791.581	68896.638	99916.038	128576.098	152856.539
8500	45484.829	79392.139	118746.852	157065.205	191281.611
9000	50161.400	90229.598	138865.831	188480.131	234904.289
9500	54797.314	101325.719	160116.644	222643.122	283649.199
10000...	59373.838	112606.842	182346.547	259353.500	337371.359

NOTES—Values of z_E were calculated using energy levels up to E cm^{-1}. Levels up to $J = 46$ were used in all calculations.

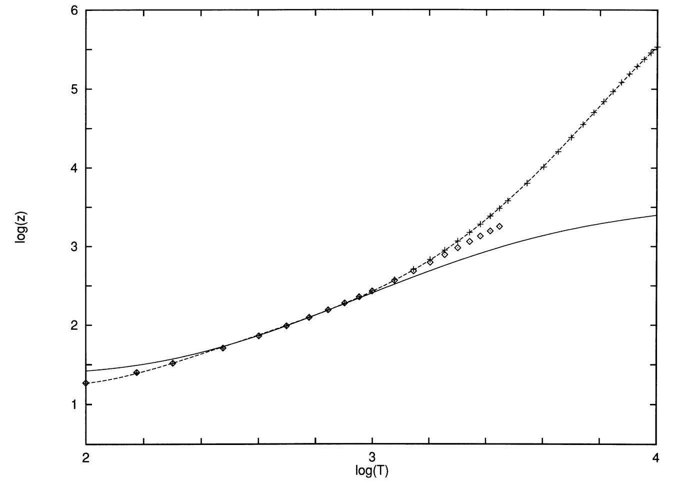

FIG. 1.—H_3^+ partition function, z, as a function of temperature, T. *Pluses*, this calculation; *dashed curve*, fit of eq. (6) to our calculated data; *diamonds*, calculation of Sidhu et al. (1993); *solid curve*, fit of Chandra et al. (1991).

our partition function increases rapidly above ~2500 K. As can be seen from Table 3, this increase is caused by the large number of vibrational states in the region above in which H_3^+ is allowed to go linear. Even at 10,000 K, the lowest of these states is at ~$2kT$, but their density means that together they make a major contribution to the partition function. Without this contribution it is not possible to obtain a reliable high-temperature partition function.

In conclusion, we have calculated an H_3^+ partition function we believe to be reliable over the temperature range 500–8000 K. Above 4000 K, this partition is an order of magnitude larger than previous estimates. It is likely that employing our larger values in models for cool stars of low metallicity will lead to fundamental changes in the model of these stars.

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