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Partition functions and equilibrium constants for H_3^+ and H_2D^+

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Abstract. Partition functions for H_3^+ and H_2D^+ are calculated by explicit summation of ab initio rotation–vibration energy levels for temperatures up to 2800 K. Estimates of the errors are given. A previously proposed high temperature approximation to the nuclear spin statistics of H_3^+ is tested and found to be reliable. Equilibrium constants are given as a function of temperature for the main H_3^+ forming reaction $H_2+H_2^+\rightarrow H_3^++H$ and reactions responsible for deuterium fractionation $H_3^++D\rightarrow H_2D^++H$ and $H_3^++HD\rightarrow H_2D^++H_2$. Comparisons are made with data previously used for modelling.

Key words: molecular data – molecular partition function – interstellar molecules – equilibrium constant

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: its emission spectrum has been observed in Jupiter (Drossart et al. 1989), it is a constituent in solar models (Patch 1969; Lynski 1970), it is known to play a crucial role (Herbst & Klemperer 1973; Suzuki 1979; Lequeux & Roueff 1991) in ion–molecule reaction schemes for the production of interstellar molecules. Data on H_3^+ are thus important for modelling in a variety of astrophysical situations.

Although H_3^+ has yet to be observed in the interstellar medium (Black et al. 1990), there has been a tentative sighting of H_2D^+ (Phillips et al. 1985). Such a sighting is possible because of D fractionation effects (Brown & Rice 1986; Millar et al. 1989) from the reactions

$$H_3^++D\rightarrow H_2D^++H \tag{2}$$

and

$$H_3^++HD\rightarrow H_2D^++H_2, \tag{3}$$

which lead to very great enhanced abundances of H_2D^+ in cold environments.

In this paper we report partition functions for H_3^+ and H_2D^+ for temperatures up to 2800 K. These partition functions and approximate ones for H_2, H_2^+ and HD are combined to give equilibrium constants for reactions (1)–(3).

Previous, approximate, estimates of the partition function of H_3^+ have been given by Patch (1968) and Tennyson & Sutcliffe (1984). However the former are not accurate and the latter only covered a very limited temperature range. Very recently more accurate partition functions for H_3^+ in the temperature range 500–8000 K have been given by Chandra et al. (1991).

The partition functions presented in this work are based on accurate calculations of the rotation–vibration levels of H_3^+ (Majewski et al. 1989) and H_2D^+ (Miller et al. 1989). These calculations use an ab initio potential energy surface (Meyer et al. 1986) of near spectroscopic accuracy (Miller & Tennyson 1987) and a large list of energy levels. The resulting constants are thus expected to be of high accuracy.

2. Method

Internal partition functions, z, for H_3^+ and H_2D^+ were computed by explicitly summing the series:

$$z=\sum_i (2J+1)g_i\exp\left(-\frac{E_i}{kT}\right) \tag{4}$$

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. The calculation made no distinction between vibration and rotation energy levels. As 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, even though for H_3^+ this state has a statistical weight of zero.

The temperature-dependent equilibrium constant, $K(T)$, for the reaction

$$A+B\rightarrow C+D \tag{5}$$

was calculated from the formula

$$K=\frac{z'_C z'_D}{z'_A z'_B}\exp\left(-\frac{U}{kT}\right), \tag{6}$$

where the enthalpy of the reaction is given by

$$U=E_0^C+E_0^D-E_0^A-E_0^B \tag{7}$$

and E_0^Q is the zero point energy of species Q measured on a common (absolute) energy scale.

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Absolute energies were taken from accurate ab initio calculations for H_2^+ (Bates et al. 1953) and H_3^+ (Meyer et al. 1986). As the H_3^+ dissociation energy was taken relative to dissociation into H_2+H^+, the dissociation energy of H_2 was not required. The difference in binding energies of H and D was taken to be 43 K. The diatomic zero point energies were calculated using constants from Huber & Herzberg (1979) and the formulae given below. This gave values of U for reactions (1)–(3), respectively, of $-16\,300$ K, -509 K and -139.5 K.

Note that in (6) it is necessary to consider the translational contribution to the full partition function, z'. This can be written as

$$z' = z^{\mathrm{trans}} z, \tag{8}$$

where z is often known as the internal partition function. z^{trans} can be estimated using the perfect gas model. As all the reactions considered in this work conserve the number of particle in the system, the ratio of their translational partition functions is given by a simple mass factor (Hayman 1967)

$$\frac{z_{\mathrm{C}}^{\mathrm{trans}} z_{\mathrm{D}}^{\mathrm{trans}}}{z_{\mathrm{A}}^{\mathrm{trans}} z_{\mathrm{B}}^{\mathrm{trans}}} = \left(\frac{m_{\mathrm{C}} m_{\mathrm{D}}}{m_{\mathrm{A}} m_{\mathrm{B}}}\right)^{3/2}, \tag{9}$$

where m_{Q} is the mass of species Q.

For H_3^+ we used a list of energy levels (Majewski et al. 1989; Kao et al. 1991) which extended to $J=12$ and covered at least the lowest 10 vibrational states of the molecule. This list includes all the states of H_3^+ up 5000 cm^{-1} above E_0 (1 K $=0.695$ cm^{-1}) and many states above this energy. This list is considerably more extensive than that used by Chandra et al. (1991). Unfortunately, for technical reasons to do with the rotation–vibration calculations (Tennyson & Sutcliffe 1984), the H_3^+ energies with E ($g_{\mathrm{E}}=2$) and A_2 ($g_{\mathrm{A}_2}=4$) symmetry were not separately identified on the list (A_1 states, for which $g_{\mathrm{A}_1}=0$, were not included on the list).

For H_2D^+ we use a list of energies (Miller et al. 1989; Tennyson et al. 1991) which extended to $J=30$. This covered the lowest 16 vibrational states of the molecule for $J=0$, reducing to 6 for $J=30$. As H_2D^+ is heavier than H_3^+ it is necessary to consider more levels, however our data set for H_2D^+ is more complete and covers all levels 5500 cm^{-1} above E_0. For H_2D^+ separate lists of even ($g_{\mathrm{e}}=1$) and odd ($g_{\mathrm{o}}=3$) symmetry levels were used.

For the calculation of equilibrium constants, diatomic partition functions were calculated using the formula

$$z = \sum_{v,J} (2J+1) g_J \exp\left(-\frac{F_v + G_v - G_0}{kT}\right), \tag{10}$$

where

$$F_v = B_v J(J+1) - D_{\mathrm{e}} J^2 (J+1)^2,$$

$$B_v = B_{\mathrm{e}} - A_{\mathrm{e}}(v+\tfrac{1}{2}),$$

$$G_v = \omega_{\mathrm{e}}(v+\tfrac{1}{2}) - \omega_{\mathrm{e}} x_{\mathrm{e}}(v+\tfrac{1}{2})^2. \tag{11}$$

The constants were taken from Huber & Herzberg (1979).

As a test of our diatomic partition functions and absolute energies, we considered the reaction

$$H_2 + D^+ \rightarrow HD + H^+. \tag{12}$$

Smith et al. (1982) measured both forward and backward reaction rates for this reaction at two temperatures. Taking the ratio of these constants gives an equilibrium constant which is directly comparable to ours. The results are given in Table 1. Although large experimental uncertainties make a close comparison difficult, we note that the ratio of our results and the observed constants are in close agreement.

Table 1. Observed (Smith et al. 1982) and calculated (this work) equilibrium constant for the reaction $H_2+D^+ \rightarrow HD+H^+$

T (K)	Observed	Calculated
205	20 (+12, −8)	12.6
295	10 (+5, −3.3)	6.8

3. Results and discussion

Our best partition functions were obtained by using all the levels in our data sets in the sum (4). As the individual levels used are of very high accuracy, the major source of error at all but the lowest energies must be the truncation of high lying levels from the list. To assess the accuracy of our computed partition functions we therefore tried a number of methods of omitting higher levels from our calculations. Omitting alternatively the higher rotational or vibrational levels from the sum showed that for H_3^+ the omission of rotationally excited levels with $J>12$ was the major source of error at higher temperatures whereas for H_2D^+ the omission of higher vibrational states was more serious.

To get quantitative estimates of the error we defined a cut-off energy. Levels lying above this energy were then omitted from the sum. Varying this cut-off energy showed the sensitivity of our partition functions to omitting higher levels and allowed error estimates to be made by plotting $\log z$ against cut-off energy. Table 2 summarizes our estimated errors a function of temperature. It should be noted that as the error is caused by omission of levels and hence terms from sum (4), our computed partition functions should always give a *lower bound* to the exact partition function.

Table 3 gives our calculated partition functions as a function of temperature. For H_3^+ $\log_{\mathrm{e}}(z) \rightarrow -\infty$ as $T \rightarrow 0$ because occupation of the $J=0$ ground state is forbidden. For H_3^+ the partition functions were computed by hand assigning the appropriate symmetries and hence statistical weight. An alternative high temperature approximation, used by Miller et al. (1990), is to assign all states a degeneracy $g=8/3$. We found that this gave very good results, with an error relative to the partition function calculated with the correct degeneracy factors of only 0.2% above 200 K. Indeed, if the lowest 33 levels were weighted correctly then nearly the entire error disappears.

Table 2. Approximate errors in the logarithm of our calculated partition functions for H_3^+ and H_2D^+ as a function of temperature

Error	H_3^+	H_2D^+
<0.1%	<850 K	<700 K
<1.0%	<1100 K	<900 K
>10%	>1800 K	>1350 K

Table 3. Partition functions, z, for H_3^+ and H_2D^+ as a function of temperature

T (K)	$\log_e(z)$	
	H_3^+	H_2D^+
5	-16.65	$6.2\,(-6)^a$
10	-7.360	$6.0\,(-3)$
20	-2.492	0.072
30	-0.7638	0.7665
40	0.1390	1.2422
50	0.7044	1.6192
60	1.0999	1.9200
70	1.3982	2.1673
80	1.6358	2.3763
90	1.8329	2.5570
100	2.0015	2.7163
150	2.6118	3.3163
200	3.0321	3.7384
300	3.6276	4.3371
400	4.0548	4.7663
500	4.3896	5.103
600	4.6672	5.385
700	4.9072	5.630
800	5.121	5.851
900	5.316	6.055
1000	5.496	6.245
1200	5.822	6.595
1400	6.113	6.912
1600	6.372	7.200
1800	6.605	7.461
2000	6.813	7.698
2200	6.999	7.914
2400	7.166	8.110
2600	7.317	8.290
2800	7.453	8.455

[a] Powers of ten given in parenthesis

Comparing our H_3^+ partition function with previous calculations shows that the partition function of Patch (1968) differs greatly from ours both in magnitude and behaviour as a function of temperature and thus cannot be considered reliable. Conversely, the limited results of Tennyson & Sutcliffe (1984) were generated using a method similar to one used here but using a much smaller dataset. However, during the course of this work it became apparent that Tennyson and Sutcliffe had omitted the factor of $(2J+1)$ in Eq. (4). Our partition functions are in agreement with theirs if we also omit this factor. The best previously available partition function, due to Chandra et al. (1991) agrees very well with ours at their lowest temperature (500 K) but is lower than ours by 6% at 1000 K and nearly a factor of 2 at our highest temperature of 2800 K. This can be attributed to their use of a much smaller set of energy levels. Since we consider the error in the logarithm of our partition function already to be greater than 10% at this temperature, values of Chandra et al. at even higher temperatures must seriously underestimate the actual partition functions. (It should be noted that their H_3^+ partition function uses the $J=1$ level as its energy zero; we have allowed for this in making our comparison).

Table 4 gives equilibrium constants for reactions (1), (2) and (3) as a function of temperature. Table 5 compares the equilibrium constants for reactions (2) and (3) with those assumed by Millar et al. (1989) (hereafter MBH). They actually give forward and backward reaction rates for the reactions. For reaction (3) their forward rate comes from the extrapolation of the high-temperature data of Smith et al. (1982) and the reverse rates were estimated theoretically by Herbst (1982). For reaction (2) MBH use the estimates of Adams & Smith (1985), which give a temperature-dependent equilibrium constant of $K=\exp(+632/T)$.

The agreement with MBH's values for reaction (3) is within 20% except at 10 K, where our equilibrium constant is nearly twice theirs. Considering that their estimate is a mixture of extrapolated experiment and approximate theory, this level of agreement must be regarded as most satisfactory.

For reaction (2) the agreement between our results and the rather cruder estimate MBH took from Smith & Adams (1985) is less satisfactory. Our equilibrium constant is a factor of 100 lower at 10 K. In fact, the two estimates cross at about 160 K with our equilibrium constant being higher for higher temperatures. We note that if the 92 K H_3^+ rotational energy is included, our

Table 4. Equilibrium constants, K, as a function of temperature for reactions:
(1) $H_2+H_2^+ \rightarrow H_3^+ + H$
(2) $H_3^+ + D \rightarrow H_2D^+ + H$
(3) $H_3^+ + HD \rightarrow H_2D^+ + H_2$

T (K)	$\log_{10}(K)$		
	(1)	(2)	(3)
5		51.54	19.03
10		25.38	8.910
20		12.30	3.856
30	259.2	8.080	2.312
40	194.5	6.050	1.626
50	155.6	4.861	1.260
60	129.7	4.082	1.043
70	111.3	3.533	0.903
80	97.21	3.126	0.806
90	86.37	2.811	0.735
100	77.70	2.561	0.679
150	51.66	1.819	0.512
200	38.63	1.451	0.421
300	25.58	1.083	0.321
400	19.04	0.899	0.279
500	15.10	0.790	0.238
600	12.47	0.718	0.218
700	10.59	0.667	0.205
800	9.178	0.721	0.196
900	8.067	0.604	0.191
1000	7.182	0.584	0.188
1200	5.849	0.557	0.186
1400	4.893	0.543	0.189
1600	4.169	0.535	0.193
1800	3.601	0.532	0.198

Table 5. Comparison of our equilibrium constants, *K*, for reactions (2) and (3) with those used by Millar et al. (1989) (MBH). (Powers of ten in parenthesis)

T (K)	Reaction (2)		Reaction (3)	
	MBH	This work	MBH	This work
10	2.8(+27)	2.4(+25)	4.7(+8)	8.1(+8)
30	1.4(+9)	1.2(+8)	170	205
50	3.1(+5)	7.3(+4)	16	18
70	8.3(+3)	3.4(+3)	7.0	8.0

enthalpy of reaction is −611 K compared to their value of −632 K. However Smith and Adams arbitrarily set their pre-exponential factor to unity which could clearly be improved.

4. Conclusions

We have calculated partition functions for the astrophysically important ion H_3^+ and its monodeuterated isotopomer H_2D^+. These partition functions are substantially more accurate than any previously available. We have used these partition functions to calculate equilibrium constants for reactions involving H_3^+ as a function of temperature.

It is rate constants rather than equilibrium constants which provide the basic input for most astrophysical models. However, as the equilibrium constant is simply the ratio between forward and reverse reaction rates, our constants can be used to convert one constant into the others. As for the 3 reactions considered, the forward reaction is usually taken to proceed at near the Langevin value, the equilibrium constant can provide a direct estimate of the reverse reaction rate.

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