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Deuterated hydrogen chemistry: partition functions, equilibrium constants and transition intensities for the H_3^+ system

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ABSTRACT

H_3^+ and the deuterated isotopomers are thought to play an important role in interstellar chemistry. The partition functions of H_3^+, D_2H^+ and D_3^+ are calculated to a temperature of 800 K by explicitly summing the ab initio determined rotation–vibration energy levels of the respective species. These partition functions are used to calculate the equilibrium constants for nine important reactions in the interstellar medium involving H_3^+ and its deuterated isotopomers. These equilibrium constants are compared with previously determined experimental and theoretical values. The Einstein *A* coefficients for the strongest dipole transitions are also calculated.

Key words: astrochemistry – molecular data – ISM: evolution – ISM: general – ISM: kinematics and dynamics – ISM: molecules.

1 INTRODUCTION

Deuterium chemistry in the interstellar medium has had renewed interest of late. This is due in part to recent observations of multiply deuterated species in the interstellar medium (Loinard et al. 2001; Ceccarelli 2002; Vastel, Phillips & Yoshida 2004). The cosmic abundance of deuterium with respect to hydrogen at low temperature is approximately 1.4×10^{-5} in the solar neighbourhood (Lemoine et al. 1999), but a much higher ratio is observed between molecules and their deuterium baring isotopomers in some environments. Molecules containing deuterium can become highly fractionated in the gas phase at low temperatures. This effect is thought to be primarily through reactions with H_2D^+. It was Stark, van der Tak & van Dishoeck (1999) who first detected H_2D^+ in the interstellar medium, and more recently Caselli et al. (2003). However modelling of interstellar deuterium chemistry by Roberts, Herbst & Millar (2003) suggest that that all the deuterated H_3^+ isotopomers have an effect on fractionation, i.e. the inclusion of D_3^+ and D_2H^+ enhances fractionation significantly.

The other mechanism by which deuterium fractionation can occur is via active grain chemistry: i.e. molecules that are stuck onto grains are deuterated by deuterium that accretes onto the grain mantle. Bacmann et al. (2003) suggest that, in prestellar cores, deuteration increases with increasing CO depletion. This would indicate that deuteration is primarily the product of gas-phase chemistry as CO depletion leads to an increase in $[H_2D^+]/[H_3^+]$ abundances (Dalgarno & Lepp 1984).

Hydrogenic gas-phase reactions involving H_3^+ and the deuterated isotopomers that are regarded to be significant in gas-phase deuteration are tabulated in Table 1. Within the thermodynamic equilibrium regime, the equilibrium constants *K* of these reactions can be calculated from the partition functions of the reactant and product species. It is not possibly to separate the forward and backward rates in these calculations, thus comparisons can only been made between the ratio of the forward k_f, and backward rates k_b:

$$K = \frac{k_\mathrm{f}}{k_\mathrm{b}}. \tag{1}$$

Experiments measuring both the forward and backward rates for the reactions of interest have been conducted by Adams & Smith (1981), Giles, Adams & Smith (1992) and most recently by Gerlich, Herbst & Roueff (2002). Both Adams and Smith and Giles et al. used a variable-temperature-selected ion flow arrangement (Smith, Adams & Alge 1982), while Gerlich et al. used a low-temperature multipole ion trap.

Previously, theoretical studies have concentrated on the H_3^+ partition functions and associated equilibrium constants for reactions of interest; most notably in Sidhu, Miller & Tennyson (1992) and Neale & Tennyson (1995). Sidhu et al. calculated the partition function of H_3^+ and H_2D^+ to a temperature of 2800 K. Sidhu et al. also calculated a number of equilibrium constants. Neale et al. calculated the high-temperature H_3^+ partition function, which extended to 10 000 K. We recalculate the H_3^+ partition function in order to compare with these previous calculations and verify our methodology. Herbst (1982) calculated partition functions using what was then rather limited experimental and calculated molecular data, and, from these, equilibrium constants were determined in a similar manner to this work.

Many attempts have been made to observe the deuterated species of H_3^+. To this end the Einstein *A* coefficients of the dipole transitions have been calculated. The strongest transitions have been selected and are tabulated here.

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Table 1. Calculated enthalpies for the reactions of interest.

	Reaction	Enthalpy/K
(a)	$H_3^+ + D \rightarrow H_2D^+ + H$	−597.8
(b)	$H_3^+ + HD \rightarrow H_2D^+ + H_2$	−231.8
(c)	$H_2D^+ + HD \rightarrow D_2H^+ + H_2$	−187.2
(d)	$D_2H^+ + HD \rightarrow D_3^+ + H_2$	−233.8
(e)	$H_3^+ + D_2 \rightarrow H_2D^+ + HD$	−153.0
(f)	$H_3^+ + D_2 \rightarrow D_2H^+ + H_2$	−340.2
(g)	$H_2D^+ + D_2 \rightarrow D_2H^+ + HD$	−108.4
(h)	$H_2D^+ + D_2 \rightarrow D_3^+ + H_2$	−342.2
(i)	$D_2H^+ + D_2 \rightarrow D_3^+ + HD$	−155.0

2 METHOD

2.1 Partition function

The partition function of H_2D^+ was taken from Sidhu et al. The internal partition functions, z_{int}, for H_3^+, D_3^+ and D_2H^+ were computed by explicitly summing the series

$$z_{\text{int}} = \sum_i (2J+1) g_i \exp\left(-\frac{c_2 E_i}{T}\right), \tag{2}$$

where J is the rotational quantum number, g_i is the nuclear spin degeneracy factor for state i, c_2 is the second radiation constant and E_i is the associated energy level relative to the $J = 0$ ground state in cm^{-1}. No distinction was made between rotational and vibrational energy levels. H_3^+ has only one bound electronic bound state, thus there was no electronic contribution to the partition functions. All the H_3^+ energy levels were taken relative to the $J = 0$ vibrational ground state.

The full partition function, z_{tot}, can be written as

$$z_{\text{tot}} = z^{\text{trans}} z_{\text{int}}, \tag{3}$$

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

$$\frac{z_C^{\text{trans}} z_D^{\text{trans}}}{z_A^{\text{trans}} z_B^{\text{trans}}} = \left(\frac{m_C m_D}{m_A m_B}\right)^{3/2}, \tag{4}$$

where m_X is the mass of species X.

2.2 Equilibrium constants

For the reaction

$$A + B \rightleftharpoons C + D, \tag{5}$$

the temperature-dependent equilibrium constant, $K(T)$, was calculated using the following:

$$K = \frac{z_{\text{tot}}^C z_{\text{tot}}^D}{z_{\text{tot}}^A z_{\text{tot}}^B} \exp\left(-\frac{U}{kT}\right), \tag{6}$$

where z_{tot} is the partition function incorporating translational motion and U is the enthalpy of the reaction. The enthalpy of the reaction was calculated using

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

where E_0^{X} is the zero-point energy of species X as measured on an absolute energy scale. Thus the enthalpies for reactions (b) to (i) were calculated in this way. The diatomic zero-point energies were calculated using the constants of Huber & Herzberg (1979) (Table 2) and equation (11). The zero-point energies of H_3^+ and isotopomers were taken from Ramanlal, Polyansky & Tennyson (2003). The ground state for H_3^+ is forbidden by the Pauli principle; the lowest state, $J = 1$, $K = 1$, lies some 64.123 cm^{-1} above this ground state (Ramanlal et al. 2003). Thus, for H_3^+, the so-called ‘rotational zero-point energy’ was used, which is 4425.823 cm^{-1}. For reaction (a) the difference in ionization energy between H and D was taken to be 46.4 K(Kelly 1987).

Table 2. Constants in cm^{-1} used to calculate diatomic partition functions, taken from Huber & Herzberg (1979).

	H_2	D_2	HD
B_e	60.853	30.443	45.655
α_e	3.06	1.0786	1.986
D_e	0.0471	0.01141	0.02605
ω_e	4401.21	3115.50	3813.15
$\omega_e x_e$	121.33	61.82	91.65
g_e	1	6	6
g_o	3	3	6
D_0^o	36118	36406	36749
$v_{\max}$	14	20	16

The diatomic partition functions needed for the equilibrium constants were calculated using the formula

$$z = \sum_{v,J} (2J+1) g_J \exp\left(-\frac{F_v + G_v - G_0}{kT}\right), \tag{8}$$

where

$$F_v = B_v J(J+1) - D_e J^2 (J+1)^2, \tag{9}$$

$$B_v = B_e = \alpha_e \left(v + \frac{1}{2}\right), \tag{10}$$

$$G_v = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2. \tag{11}$$

The constants used were taken from Huber & Herzberg (1979) and are tabulated in Table 2.

2.3 Energy levels

Energy levels for H_3^+, D_3^+ and D_2H^+ were determined using the DVR3D program suite of Tennyson et al. (2004) and the ultra-high accuracy ab initio procedure of Polyansky & Tennyson (1999), which was based on the electronic structure calculations of Cencek et al. (1998). The parameters used for the DVR3D program suite are the same as those outlined in Polyansky & Tennyson (1999). A total of $40 \times (J+1)$ levels were computed for each J, up to $J = 14$. This procedure gave at least 19 119 rotation vibration energy levels for each molecule and ensured that all energy levels up to 10 000 cm^{-1} were included.

D_2H^+ has C_{2v} symmetry, this symmetry is fully represent in the DVR3D program by the parity of the basis, even and odd; which means that energies with even ($g_e = 3$) and odd ($g_o = 6$) parity are easily easily identified. H_3^+ and D_3^+ have D_{3h} symmetry; this symmetry is not fully represented by the DVR3D program. Thus energies with E, A_1 and A_2 cannot be so easily identified. The A_1 and A_2 states are represented by DVR3D and have even and odd basis parity, respectively. The E symmetry energies are determined by the fact that they are degenerate across even and odd basis by parities. Thus the E symmetry states can be identified by examining by hand the complete list of energy levels for both even and odd basis parities.

For H_3^+ the nuclear degeneracy factors are 2, 0 and 4 for E, A_1 and A_2, respectively. For D_3^+ the the nuclear degeneracy factors are 8, 10 and 1 for E, A_1 and A_2, respectively.

There has been some confusion in the conventions used for the nuclear spin degeneracy factor g. In general astronomers use the nuclear spin degeneracy divided by its value for the dissociated atoms, while physicists use the nuclear spin degeneracy itself. Thus for example astronomers would take g for the E states of D_3^+ to be 8/27 while we have used eight. Both conventions are equally valid; however, it is important to be consistent when calculating equilibrium constants that the same convention has been used in calculating the partition functions for all the species in the reaction. Throughout this work the physicists' convention is used.

3 RESULTS AND DISCUSSION

3.1 Partition function

Table 3 presents the values obtained by the explicit summation of equation (2). It was found that at a temperature of 800 K the inclusion of the $J = 14$ energy levels only contributed 0.02, 0.77 and 0.35 per cent to the internal partition functions for H_3^+, D_3^+ and D_2H^+, respectively. Thus the partition functions are valid up to a temperature of 800 K.

Comparing the H_3^+ partition functions of this work and those of Sidhu et al. (Fig. 1) we see that the two works are in good agreement. There is some minor disagreement at higher temperatures where in any case the much more comprehensive partition function of Neale & Tennyson (1995) should be used. Fig. 2 shows the partition functions for D_2H^+ and D_3^+. There are no previous data for these partition functions but we would expect a similar accuracy to that obtained for H_3^+ (see Fig. 1).

The partition functions have been fitted to the standard formula, see Sauval & Tatum (1984), in the temperature range 5 to 800 K using the data in Table 3. The coefficients a_n for H_3^+, D_3^+ and D_2H^+ are tabulated in Table 4:

$$\log_{10}(z) = \sum_{n=0}^{6} a_n (\log_{10} T)^n. \qquad (12)$$

Table 3. Calculated internal partition functions as a function of a temperature. Powers of ten given in parenthesis.

$T(K)$	H_3^+	D_3^+	D_2H^+
5	5.8325(−08)	10.0022	6.0008
10	6.3491(−04)	10.2351	6.1281
20	0.0826	12.5729	7.8853
30	0.4654	16.3763	11.1196
40	1.1481	21.1870	15.0916
50	2.0197	26.9604	19.5932
60	2.9948	33.6025	24.5777
70	4.0243	40.9934	30.0255
80	5.0826	49.0277	35.9154
90	6.1579	57.6247	42.2237
100	7.2457	66.7263	48.9256
150	12.9039	118.6694	87.6098
200	19.0975	179.7917	133.6128
300	33.3860	325.2799	243.7791
400	50.0599	498.7918	375.2491
500	68.9696	701.1151	527.2953
600	90.1816	936.5854	701.5534
700	113.9581	1211.2871	901.0749
800	140.6995	1531.8784	1129.5545

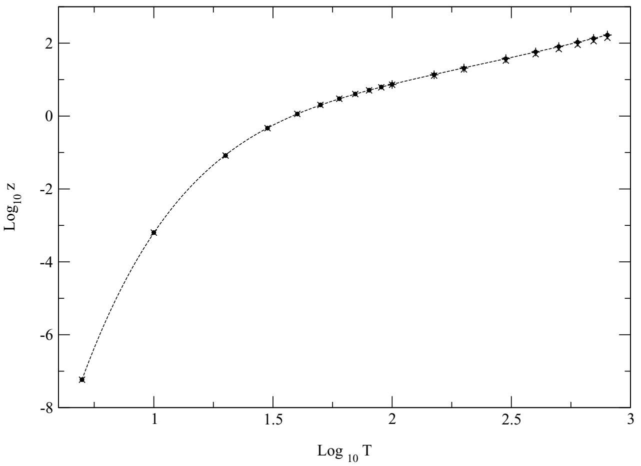

Figure 1. H_3^+ partition function, z, as a function of temperature, T. Crosses: this calculation; dashed curve: fit of equation (12) to our calculated data; circles: calculation of Sidhu et al. (1992); and pluses: calculation of Neale & Tennyson (1995).

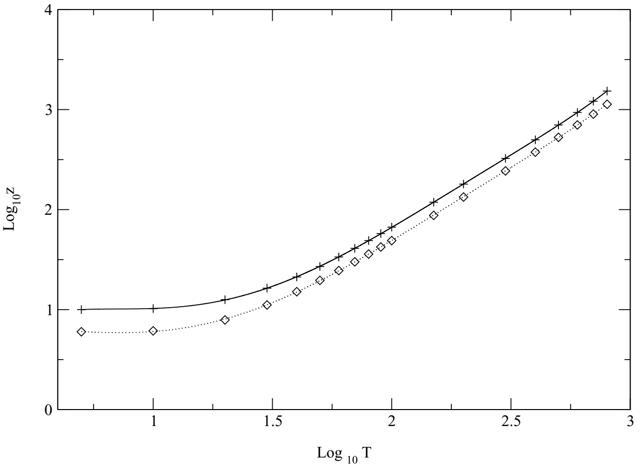

Figure 2. D_2H^+ and D_3^+ partition functions, z, as a function of temperature, T. Diamonds: D_2H^+ calculation; dashed curve: fit of equation (12) to D_2H^+ data; crosses: D_3^+ calculation; and solid curve: fit of equation (12) to D_3^+ data.

Table 4. Fitting coefficients for the polynomial fit (equation 12) of the partition functions in the temperature range 5 to 800 K.

	H_3^+	D_3^+	D_2H^+
a_0	−35.10102	−0.388363	−0.975341
a_1	72.2463	5.65495	7.92203
a_2	−66.3543	−8.53925	−13.5834
a_3	35.3938	5.83071	11.0576
a_4	−11.3756	−1.74965	−4.45541
a_5	2.06118	0.205985	0.890251
a_6	−0.160957	−0.00289176	−0.0704028

Our fit is never more than 1.35, 0.78 and 1.22 per cent from the calculated values of z for H_3^+, D_3^+ and D_2H^+, respectively.

3.2 Equilibrium constants

Table 5 gives the logarithm equilibrium constants, K, for the reactions tabulated in Table 1 as a function of temperature. The

Table 5. Equilibrium constants, K, for the reactions given in Table 1, as a function of temperature. The first line corresponds to reactants while the second line corresponds to products.

T (K)	H_3^++D H_2D^++H	H_3^++HD $H_2D^+ + H_2$	H_2D^++HD $D_2H^+ + H_2$	D_2H^++HD $D_3^+ + H_2$	$H_3^+ + D_2$ H_2D^++HD	$H_3^+ + D_2$ $D_2H^+ + H_2$	$H_2D^+ + D_2$ D_2H^++HD	$H_2D^+ + D_2$ $D_3^+ + H_2$	$D_2H^+ + D_2$ D_3^++HD
5	59.1951	26.5161	16.1410	19.6059	20.5256	36.6666	10.1505	29.7564	13.6154
10	29.2007	12.4148	8.0189	9.4544	9.8455	17.8644	5.4496	14.9040	6.8851
20	14.1069	5.2661	4.0622	4.3690	4.4023	8.4645	3.1984	7.5674	3.5052
30	9.3591	3.1640	2.5237	2.6552	2.8620	5.3857	2.2218	4.8770	2.3533
40	7.0102	2.1462	1.7791	1.8049	2.1178	3.8969	1.7507	3.5556	1.7765
50	5.6306	1.5816	1.3426	1.3131	1.7047	3.0473	1.4657	2.7787	1.4361
60	4.7257	1.2337	1.0659	0.9998	1.4456	2.5115	1.2777	2.2776	1.2117
70	4.0858	0.9997	0.8802	0.7841	1.2668	2.1471	1.1473	1.9314	1.0512
80	3.6116	0.8337	0.7465	0.6256	1.1377	1.8842	1.0505	1.6760	0.9296
90	3.2462	0.7093	0.6456	0.5030	1.0398	1.6854	0.9761	1.4792	0.8335
100	2.9563	0.6122	0.5664	0.4045	0.9632	1.5296	0.9174	1.3219	0.7555
150	2.1009	0.3270	0.3283	0.0973	0.7441	1.0724	0.7454	0.8426	0.5143
200	1.6813	0.1816	0.2021	-0.0694	0.6415	0.8436	0.6620	0.5925	0.3904
300	1.2660	0.0311	0.0676	−0.2472	0.5457	0.6133	0.5822	0.3350	0.2674
400	1.0602	−0.0445	−0.0014	−0.3386	0.5062	0.5048	0.5493	0.2108	0.2122
500	0.9374	−0.0893	−0.0421	−0.3927	0.4914	0.4493	0.5387	0.1460	0.1880
600	0.8569	−0.1179	−0.0687	−0.4274	0.4904	0.4217	0.5397	0.1123	0.1810
700	0.7999	−0.1380	−0.0866	−0.4507	0.4967	0.4101	0.5481	0.0974	0.1840
800	0.7579	−0.1523	−0.0997	−0.4668	0.5076	0.4079	0.5602	0.0934	0.1931

Table 6. A comparison of equilibrium constants with Giles et al. (1992).

	80K			300K		
	Giles et al. (Expt)	Giles et al. (Theory)	This work	Giles et al. (Expt)	Giles et al. (Theory)	This work
$H_3^+ + HD \rightarrow H_2D^+ + H_2$	3.8 (±0.6)	6.6	6.82	1.80 (±0.3)	2.0	1.07
$H_2D^+ + HD \rightarrow D_2H^+ + H_2$	1.7 (±0.3)	3.6	5.58	0.80 (±0.1)	0.8	1.17
$D_2H^+ + HD \rightarrow D_3^+ + H_2$	1.8 (±0.3)	2.0	4.22	0.40 (±0.1)	0.3	1.00
$H_3^+ + D_2 \rightarrow H_2D^+ + HD$	8.2 (±1.2)	13.2	13.73	5.20 (±0.8)	6.7	3.51
$H_3^+ + D_2 \rightarrow D_2H^+ + H_2$	9.2 (±1.4)	48.3	76.59	5.30 (±0.8)	5.1	4.10
$H_2D^+ + D_2 \rightarrow D_2H^+ + HD$	4.4 (±0.7)	7.2	11.23	1.90 (±0.3)	2.5	3.82
$H_2D^+ + D_2 \rightarrow D_3^+ + H_2$	4.4 (±0.7)	14.5	47.43	0.70 (±0.1)	0.8	2.16
$D_2H^+ + D_2 \rightarrow D_3^+ + HD$	1.7 (±0.3)	4.0	8.50	0.80 (±0.1)	1.0	1.85

equilibrium constants were calculated using the partition functions previously discussed. The H_2D^+ partition functions were taken from Sidhu et al. (1992).

There have been a few experiments where both the forward and backward reaction rates of interest have been measured, so that the equilibrium constant may be deduced for comparison. A comparison of the experimental data available to date is given in Tables 6, 7 and 8. Our calculations generally show approximate agreement with the experimental data. The notable exception is the recent experiment of Gerlich et al. (2002) for the reaction $H_3^+ + HD \rightarrow H_2D^+ + H_2$, which disagrees with our calculations by 12 orders of magnitude. Gerlich et al. measured the forward and backward rates at a low temperature, 10 K, using a low-temperature multipole ion trap. There have been no other experiments carried out at this low temperature, thus no direct experimental comparison can be made. Smith and Adams using standard extrapolation give an equilibrium constant of $1.7 \times 10^{+9}$ at 10 K, which is in better agreement with our own result. Most models use the the equilibrium constants of Adams & Smith (1981). The previously calculated value of Sidhu et al. used an enthalpy of 139.5 K; this enthalpy does not take into account the previously discussed rotational zero-point energy. Thus if an enthalpy of 231.8 K is used then an equilibrium constant of $7.1 \times 10^{+12}$, which is more consistent to our own, is obtained.

Table 7. A comparison of equilibrium constants with Adams & Smith (1981) and Herbst (1982) for the reaction $H_3^+ + HD \rightarrow H_2D^+ + H_2$.

T (K)	Adams and Smith	Herbst	This work
80	4.48 (±1.3)	5.9	6.82
200	2.35 (±0.7)	2.6	1.52
295	1.96 (±0.6)	2.1[a]	1.07[a]

[a] The theoretical value is actually at 300 K.

Table 8. A comparison of equilibrium constants at a temperature of 10 K for the reaction $H_3^+ + HD \rightarrow H_2D^+ + H_2$. Powers of ten are given in parentheses.

This Work	2.6(+12)
Gerlich et al. (2002)	7.14
Adams & Smith (1981)	1.5(+9)[a]
Sidhu et al. (1992)	7.1(+12)[b]

[a] This value is extrapolated from experimental data.
[b] This value uses the corrected enthalpy of 231.8 K.

A comparison of our equilibrium constants with those of Giles et al. (1992) for the reactions of interest are shown in Table 6. Giles et al. give relative errors of ±15 per cent for the equilibrium

Table 9. Einstein *A* coefficients for transitions from low-lying levels of H_2D^+. Powers of ten given in parenthesis.

J'	K'_a	K'_c		E'/cm^{-1}	J'	K'_a	K'_c		E'/cm^{-1}	$\omega_{if}(\mathrm{calc.})/\mathrm{cm}^{-1}$	$\omega_{if}(\mathrm{obs.})/\mathrm{cm}^{-1}$	A_{if}/s^{-1}
1	1	0	B_1	72.457	1	1	1	A_1	60.027	12.429	–	1.2186(−4)
1	0	1	A_2	45.698	0	0	0	A_1	0.000	45.698	–	4.0397(−3)
2	1	2	A_2	138.843	1	1	1	A_1	60.027	78.816	–	1.8762(−2)
2	0	2	A_1	131.638	1	0	1	A_2	45.698	85.94	–	3.0338(−2)
2	1	1	B_1	175.939	1	1	0	B_1	72.457	103.483	–	4.238(−2)
2	2	0	A_1	223.868	1	0	1	A_2	45.698	178.17	–	1.6643(−2)
0	0	0	A_1	2205.916	1	0	1	A_2	45.698	2160.218	2160.176[a]	17.545
1	1	0	B_1	2278.465	1	1	1	A_1	60.027	2218.438	2218.393[a]	10.372
1	0	1	A_2	2246.727	0	0	0	A_1	0.000	2246.727	2246.697[a]	1.8962
2	0	2	A_1	2318.377	1	0	1	A_2	45.698	2272.68	–	0.35157
0	0	0	A_2	2335.338	1	1	1	A_1	60.027	2275.31	2275.403[a]	145.65
1	0	1	A_1	2383.878	1	1	0	B_1	72.457	2311.421	2311.512[a]	83.419
1	1	0	B_1	2409.227	1	0	1	A_2	45.698	2363.529	–	78.984
2	2	0	A_1	2427.119	1	0	1	A_2	45.698	2381.421	2381.367[a]	3.058
1	1	1	A_2	2402.699	0	0	0	A_1	0.000	2402.699	2402.795[a]	60.938
2	0	2	A_2	2477.681	1	1	1	A_1	60.027	2417.654	2417.734[a]	29.82
2	1	2	A_1	2490.966	1	0	1	A_2	45.698	2445.268	2445.348[a]	58.586
2	2	1	B_1	2568.382	1	1	0	B_1	72.457	2495.925	2496.014[a]	60.067
2	2	0	A_2	2569.489	1	1	1	A_1	60.027	2509.461	2509.541[a]	48.476
0	0	0	A_1	2992.524	1	0	1	A_2	45.698	2946.826	2946.802[b]	53.167
1	1	0	B_1	3063.331	1	1	1	A_1	60.027	3003.304	3003.276[b]	27.509
1	0	1	A_2	3038.198	0	0	0	A_1	0.000	3038.198	3038.177[b]	20.353
2	1	2	A_2	3128.888	1	1	1	A_1	60.027	3068.86	3068.845[b]	20.088
2	0	2	A_1	3123.324	1	0	1	A_2	45.698	3077.626	3077.611[b]	24.757
2	1	1	B_1	3167.147	1	1	0	B_1	72.457	3094.69	3094.671[b]	19.302
2	2	0	A_1	3209.847	1	0	1	A_2	45.698	3164.149	–	1.5976
0	0	0	A_1	4287.61	1	0	1	A_2	45.698	4241.912	–	16.953
1	0	1	A_2	4331.45	0	0	0	A_1	0.000	4331.45	–	9.6306
2	1	2	A_2	4412.461	1	1	1	A_1	60.027	4352.434	4352.360[c]	14.871
2	0	2	A_1	4407.925	1	0	1	A_2	45.698	4362.227	–	15.45
0	0	0	A_2	4461.832	1	1	1	A_1	60.027	4401.805	–	88.628
2	1	1	A_2	4512.486	1	0	1	A_2	45.698	4466.788	–	0.41306
1	1	0	B_1	4536.348	1	0	1	A_2	45.698	4490.65	–	44.342
2	0	2	A_2	4555.88	1	1	1	A_1	60.027	4495.853	4495.881[c]	27.013
1	1	1	A_2	4512.558	0	0	0	A_1	0.000	4512.558	4512.567[c]	41.115
2	1	2	A_1	4563.405	1	0	1	A_2	45.698	4517.707	–	38.458
0	0	0	A_1	4602.746	1	0	1	A_2	45.698	4557.048	–	69.044
2	2	1	B_1	4677.548	1	1	0	B_1	72.457	4605.091	–	38.831
1	2	1	B_1	4677.74	1	1	1	A_1	60.027	4617.713	–	33.563
2	2	0	A_2	4691.531	1	1	1	A_1	60.027	4631.504	–	20.198
1	0	1	A_2	4657.859	0	0	0	A_1	0.000	4657.859	–	9.0071
2	0	2	A_1	4761.399	1	0	1	A_2	45.698	4715.701	–	7.7521
2	2	0	B_1	4845.211	1	0	1	A_2	45.698	4799.514	–	1.3349
0	0	0	A_1	5039.84	1	0	1	A_2	45.698	4994.142	–	10.723

[a] Frequencies of Foster et al. (1986).
[b] Frequencies of Kozin, Polyansky & Zobov (1988).
[c] Frequencies of Fárník et al. (2002).

constants. This relates to a much lower absolute value on the measured rate; Giles et al. state that certain systematic errors will cancel when taking the ratio of rates, thus producing lower error bounds. This may be rather optimistic. In general there is better agreement between our calculation and the experiment of Giles et al. at the higher temperature of 300 K. This is most probably due to the less demanding nature of measuring the reaction rates at the higher temperature. Giles et al. also calculate the equilibrium constants by calculating the partition functions of the reactant and product species, and also the enthalpy change for the reaction. These partition functions were obtained by explicitly summing the energy levels (see equation 2) as given by using the rigid rotor approximation and the relevant experimentally determined rotational constants. The rigid rotor approximation is problematic for the H_3^+ system and definitely inferior to our own ab initio energy level calculations. However, we are generally in better agreement with the theoretical equilibrium constants of Giles et al. than their experimentally derived equilibrium constants.

A comparison of equilibrium constants for the reaction $H_3^+ + HD \rightarrow H_2D^+ + H_2$ for a number of temperatures with those of Adams & Smith (1981) and Herbst (1982) are given in Table 7. Adams and Smith estimate their errors on the reaction rates to be ±20 per cent; this gives an error on the equilibrium constants of ±30 per cent. We are generally in good agreement with Adams and Smith. Herbst (1982) calculated the reaction constants using his calculated partition functions and reaction enthalpy. The partition functions for H_3^+ and H_2D^+ are determined from explicitly doing the sum as in equation (2). The energy levels are found by using the

Table 10. Einstein A coefficients for transitions from low-lying levels of D_2H^+. Powers of ten given in parenthesis.

J'	K'_a	K'_c		E'/cm^{-1}	J'	K'_a	K'_c		E'/cm^{-1}	$\omega_{if}(\mathrm{calc.})/\mathrm{cm}^{-1}$	$\omega_{if}(\mathrm{obs.})/\mathrm{cm}^{-1}$	A_{if}/s^{-1}
1	1	0	B_1	57.993	1	0	1	A_1	34.918	23.075	–	5.0911(−4)
1	1	1	A_2	49.255	0	0	0	A_1	0.000	49.255	–	3.3031(−3)
2	0	2	A_1	101.716	1	1	1	A_2	49.255	52.461	–	2.0702(−3)
2	1	2	A_2	110.259	1	0	1	A_1	34.918	75.341	–	1.0597(−2)
2	2	1	B_1	179.173	1	1	0	B_1	57.993	121.18	–	4.4504(−2)
2	2	0	A_1	182.074	1	1	1	A_2	49.255	132.819	–	4.4629(−2)
0	0	0	A_1	1968.146	1	1	1	A_2	49.255	1918.89	1918.908^a	52.175
1	0	1	A_1	1998.523	1	1	0	B_1	57.993	1940.53	1940.551^a	21.989
1	1	0	B_1	2027.034	1	0	1	A_1	34.918	1992.116	1992.130^a	28.48
2	0	2	A_1	2055.077	1	1	1	A_2	49.255	2005.821	2005.844^a	6.0891
1	1	1	A_2	2014.09	0	0	0	A_1	0.000	2014.09	2014.106^a	14.364
2	1	2	A_2	2062.923	1	0	1	A_1	34.918	2028.005	2028.024^a	9.9809
0	0	0	A_2	2078.435	1	0	1	A_1	34.918	2043.517	2043.515^a	21.728
1	1	1	A_1	2128.7	1	1	0	B_1	57.993	2070.707	2070.708^a	16.782
1	1	0	A_2	2136.248	1	1	1	A_2	49.255	2086.992	2086.990^a	12.135
2	2	1	B_1	2145.612	1	1	0	B_1	57.993	2087.619	2087.630^a	11.233
2	2	0	A_1	2149.555	1	1	1	A_2	49.255	2100.299	2100.307^a	5.9919
1	0	1	A_2	2118.589	0	0	0	A_1	0.000	2118.589	2118.588^a	14.303
2	1	2	A_1	2202.779	1	1	1	A_2	49.255	2153.524	2153.525^a	21.901
2	0	2	A_2	2194.064	1	0	1	A_1	34.918	2159.146	2159.145^a	19.827
2	1	1	B_1	2225.161	1	1	0	B_1	57.993	2167.168	2167.166^a	17.293
2	2	0	A_2	2257.594	1	0	1	A_1	34.918	2222.675	–	0.38661
0	0	0	A_1	2736.98	1	1	1	A_2	49.255	2687.724	–	86.183
1	0	1	A_1	2771.523	1	1	0	B_1	57.993	2713.53	–	44.856
1	1	0	B_1	2793.96	1	0	1	A_1	34.918	2759.042	2759.036^b	44.572
1	1	1	A_2	2785.338	0	0	0	A_1	0.000	2785.338	2785.332^b	31.182
2	0	2	A_1	2837.556	1	1	1	A_2	49.255	2788.3	2788.300^b	16.939
2	1	2	A_2	2845.72	1	0	1	A_1	34.918	2810.802	2810.800^b	29.412
2	2	1	B_1	2912.708	1	1	0	B_1	57.993	2854.716	2854.707^b	29.321
2	2	0	A_1	2915.616	1	1	1	A_2	49.255	2866.36	2866.350^b	22.136
0	0	0	A_1	3821.309	1	1	1	A_2	49.255	3772.054	–	6.5942
1	0	1	A_1	3851.977	1	1	0	B_1	57.993	3793.984	–	5.0848
1	1	0	B_1	3881.727	1	0	1	A_1	34.918	3846.809	3846.786^c	3.3258
2	0	2	A_1	3909.933	1	1	1	A_2	49.255	3860.677	3860.660^c	3.0475
1	1	1	A_2	3871.398	0	0	0	A_1	0.000	3871.398	3871.377^c	3.6663
2	1	2	A_2	3921.988	1	0	1	A_1	34.918	3887.07	3887.052^c	5.4261
2	2	1	A_1	4010.528	1	1	0	B_1	57.993	3952.535	–	3.6408
2	2	0	A_1	4013.18	1	1	1	A_2	49.255	3963.924	–	3.4514
0	0	0	A_1	4042.815	1	1	1	A_2	49.255	3993.56	3993.518^c	47.457
1	0	1	A_1	4058.521	1	1	0	B_1	57.993	4000.528	4000.494^c	42.9
0	0	0	A_2	4060.822	1	0	1	A_1	34.918	4025.904	4025.873^c	41.465
2	0	2	A_1	4097.094	1	1	1	A_2	49.255	4047.839	4047.840^c	21.275
1	1	1	A_2	4062.925	0	0	0	A_1	0.000	4062.925	4062.889^c	29.138
2	1	2	A_1	4097.933	1	0	1	A_1	34.918	4063.015	4062.983^c	26.675
1	1	0	A_2	4101.122	1	0	1	A_1	34.918	4066.204	4066.158^c	23.775
1	0	1	B_1	4119.147	1	1	1	A_2	49.255	4069.891	4069.859^c	20.300
2	2	1	B_1	4179.804	1	1	0	B_1	57.993	4121.811	–	24.474
1	1	1	A_2	4122.993	0	0	0	A_1	0.000	4122.993	–	1.3689(−3)
2	0	2	A_1	4214.033	1	1	1	A_2	49.255	4164.777	–	5.7652
2	2	0	A_2	4208.006	1	0	1	A_1	34.918	4173.088	–	0.92222
2	1	2	A_1	4229.853	1	1	1	A_2	49.255	4180.597	–	2.4239
2	2	1	A_2	4252.4	1	0	1	A_1	34.918	4217.482	–	1.3913
0	0	0	A_1	4648.808	1	1	1	A_2	49.255	4599.553	–	10.723
1	0	1	A_1	4673.469	1	1	0	B_1	57.993	4615.476	–	9.1384
0	0	0	A_2	4674.96	1	0	1	A_1	34.918	4640.042	–	13.692
2	0	2	A_1	4720.562	1	1	1	A_2	49.255	4671.307	–	4.6985
1	1	0	B_1	4706.784	1	0	1	A_1	34.918	4671.866	–	4.9443
1	1	1	A_2	4681.85	0	0	0	A_1	0.000	4681.85	–	7.1377
1	1	0	A_1	4732.173	1	1	1	A_2	49.255	4682.918	–	6.9989
2	1	2	A_2	4723.648	1	0	1	A_1	34.918	4688.73	–	6.6333
1	0	1	A_2	4727.065	0	0	0	A_1	0.000	4727.065	–	0.44733
2	2	1	B_1	4796.924	1	1	0	B_1	57.993	4738.931	–	6.7834
2	2	0	A_1	4798.798	1	1	1	A_2	49.255	4749.542	–	2.1769

Table 10 – *Continued.*

J'	K'_a	K'_c		E'/cm^{-1}	J'	K'_a	K'_c		E'/cm^{-1}	ω_{if}(calc.)/cm^{-1}	ω_{if}(obs.)/cm^{-1}	A_{if}/s^{-1}
2	0	2	A_2	4807.782	1	0	1	A_1	34.918	4772.864	–	0.87466
2	0	0	B_1	4852.274	1	0	1	A_1	34.918	4817.356	–	0.50311

[a] Frequencies of Polyansky & McKellar (1989).
[b] Frequencies of Kozin et al. (1988).
[c] Frequencies of Fárník et al. (2002).

Table 11. Einstein A coefficients for transitions from low-lying levels of D_3^+.

J'	$\nu'_1\nu'_2$	G$'$	U$'$		E'/ cm^{-1}	J'	$\nu'_1\nu'_2$	G$'$	U$'$		E'/ cm^{-1}	ω_{if}(calc.)/ cm^{-1}	ω_{if}(obs.)^a/ cm^{-1}	A_{if}/ s^{-1}
0	01	1	1	E'	1834.655	1	00	1	0	E'	32.324	1802.331	1802.349	264.18
1	01	0	−1	A'_2	1884.380	1	00	0	0	A1$'$	43.609	1840.770	1840.789	34.99
1	01	1	1	E'	1878.561	1	00	1	0	E'	32.324	1846.237	1846.256	141.96
1	01	0	1	A'_1	1888.048	0	00	0	0	A'_1	0.000	1888.048	1888.065	252.84
2	01	1	−1	E'	1955.981	1	00	1	0	E'	32.324	1923.657	1923.670	107.50
2	01	0	1	A'_2	1979.203	1	00	0	0	A'_2	43.609	1935.593	1935.609	24.65
2	01	1	1	E'	1968.077	1	00	1	0	E'	32.324	1935.753	–	119.38
1	02	3	2	A'_2	3646.285	1	00	0	0	A'_1	43.609	3602.676	3602.669	234.05
0	02	2	2	E'	3650.700	1	00	1	0	E'	32.324	3618.376	3618.371	231.47
2	02	4	2	E'	3662.342	1	00	1	0	E'	32.324	3630.018	3630.022	140.29
1	02	−3	−2	A'_1	3647.190	0	00	0	0	A'_1	0.000	3647.190	–	193.96
1	02	2	2	E'	3694.893	1	00	1	0	E'	32.324	3662.569	3662.557	114.64
2	02	−3	2	A'_2	3736.400	1	00	0	0	A'_2	43.609	3692.791	3692.785	17.29
2	02	2	2	E'	3783.234	1	00	1	0	E'	32.324	3750.909	3750.879	23.66

[a] Frequencies of Amano et al. Amano et al. (1994).

spectroscopic constants of Oka (1980, 1981) and Carney (1980), respectively. The constants of Huber & Herzberg (1979) were used to calculate the partition functions of HD and H_2. Our calculations are in good agreement with those of Herbst (1982).

3.3 Transition intensities

Using wavefunctions produced in the calculation of the energy levels outlined in Section 2.3 and additional wavefunctions calculated for H_2D^+ in the same manner, the DIPOLE3 program of Tennyson et al. (2004) and the dipole surface of Röhse et al. (1994), the transition intensities were calculated. The Einstein A_{if} coefficients were determined using

$$A_{if} = \frac{64\pi^4}{3c^3h}\omega^3\frac{S(f-i)g_i}{2J'+1}, \tag{13}$$

where the first fraction is set to 3.136186×10^{-7}, which also converts from a line strength in D^2 to an A_{if} coefficient in s^{-1}; $S(f-i)$ is the line strength in D^2, and ω is the transition frequency in cm^{-1}.

The transitions for H_2D^+, D_2H^+ and D_3^+ are given in Tables 9, 10 and 11, respectively; transitions are given up to $J = 5$ and a maximum frequency of 5000 cm^{-1}; transitions whose relative intensity is less than 0.0001 are neglected. The D_3^+ energy levels are labelled by the notation (ν_1, ν_2, J, G, U) (Watson, Foster & Mckellar 1987). The quantum numbers ν_1, ν_2, G and U were assigned by referring to the work of Amano et al. (1994) and by inspection. The H_2D^+ and D_2H^+ levels are assigned by hand using the standard quantum numbers J, K_a and K_c.

4 CONCLUSIONS

Partition functions for H_3^+ D_2H^+ and D_3^+ have been calculated. These have been used to calculate the equilibrium constants for the important gas-phase reactions involving H_3^+ and the deuterated isotopomers. In general ab initio calculations are easier to perform at very low temperatures because they require few levels, whereas very low-temperature experiments are extremely challenging. In addition, transition data have been calculated that should aid in the observation of deuterated isotopomers of H_3^+. It is hoped our data facilitate the understanding of deuterium chemistry in the interstellar medium.

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