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Deuterated water: partition functions and equilibrium constants

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ABSTRACT

HDO and D_2O are thought to be present in significant quantities in the coldest regions of the Universe. Partition functions are calculated for these species and used to calculate temperature dependent equilibrium constants for the most important fractionation reactions involving water. HDO may also be a key indicator of the absence of deuterium burning in very low mass stars. The HDO partition function calculation is extended to high ($T \leqslant 6000$ K) temperatures for this purpose.

Key words: astrochemistry – molecular data – stars: low mass, brown dwarfs – ISM: general – ISM: kinematics and dynamics – ISM: molecules

1 INTRODUCTION

Deuterium was formed in the first few minutes after the Big Bang. As D is burnt rapidly in stellar interiors, the abundance of D has been reducing since this time. Deuterium burns in stars with masses greater than about 13 times that of Jupiter, which is one way of defining the boundary between a star and a planet (Burrows et al. 1997). The deuterium test has therefore been proposed (Bejar, Zapetero Osorio & Rebolo 1999; Chabrier et al. 2000) as a spectroscopic means of distinguishing between these objects. However, the practical realization of this test remains difficult (Pavlenko 2002).

Observations of very low temperature regions of the interstellar medium have shown that singly, doubly and even triply deuterated molecules can be very abundant (Loinard et al. 2001; Ceccarelli 2002). Water is the third most common molecule in the Universe after H_2 and CO. Its deuterated forms HDO and D_2O would therefore be expected to be present in regions of high deuteration. So far, however, although HDO has been observed in a number of locations (Jacq et al. 1990; Eberhardt et al. 1995; Encrenaz et al. 1995; Pardo et al. 2001), there have been no extraterrestrial observations of D_2O. One important point about HDO is that it has lower symmetry than undeuterated water and, as a consequence, has a significantly different vibration–rotation spectrum. This makes HDO a better candidate for deuterium test observations than other species likely to be present in very low mass stars or substellar objects.

Partition functions play a key role in determining temperature dependent properties of astronomical species (Irwin 1981; Sauval & Tatum 1984). In this paper, we present high accuracy, temperature-dependent partition functions for both D_2O and HDO. These partition functions are calculated using the method developed by Vidler & Tennyson (2000) who calculated the most accurate available temperature-dependent partition function for $H_2{}^{16}O$ by direct summation of the energy levels. For low temperatures, those up to about 500 K, the partition functions can be accurately determined by known experimental energy levels. At higher temperatures, where an accurate partition function is important for determining the abundance in the atmosphere of cool stars, the sum of known experimental energies is augmented with levels derived from variational nuclear motion calculations.

One application of the partition functions calculated here is that they can be used to derive temperature-dependent equilibrium constants for key reactions involved in low-temperature deuterium fractionation. Of course these constants are of limited direct usefulness in fractionation models since this process does not usually occur under conditions of thermodynamic equilibrium. However the equilibrium constant is also the ratio of the forward to the backward reaction rate. Often only one of these rates is known; for example the one for the exothermic process is usually more easily determined experimentally. This plus the equilibrium constant can therefore be used to determine the rate for the reverse process which is also essential for any fractionation model.

2 METHOD

2.1 Partition function

For a molecule, such as water, where the electronically excited states only lie at high energy, the internal partition function is determined by the vibration–rotation energy levels of the system. Given the vibration–rotation energy levels, E_i, of each isotopologue, the internal partition function, z_{int}, can be evaluated as a function of temperature, T, using the formula

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

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by explicit summation. In equation (1), J is the rotational quantum number, c_2 the second radiation constant and g_i is statistical weight which is given by nuclear spin statistics. Following the astronomers convention we use $g_i = 1/4$ and $3/4$ for para and ortho states of H_2O, $1/3$ and $2/3$ for para and ortho states of D_2O and 1 for all states of HDO. This correct treatment is important as it makes the partition function of HDO four times that of H_2O as T approaches zero. This behaviour is not always found in published comparisons of partition functions (Pavlenko 2002).

We have undertaken a systematic compilation of the known energy levels of HDO and D_2O, similar to that already presented for H_2O (Tennyson et al. 2001). These compilations comprised 5277 levels for HDO and 5638 levels for D_2O. The complete results of these compilations will be presented elsewhere. These compilations span rotational states up to those with $J = 30$ and vibrational states with energies about 10 000 cm^{-1} above the vibrational ground state, with a few higher vibrational states for HDO. Even within this range of vibrational and rotational energies, the lists are not complete. Even so these tabulations of low-lying levels are sufficient to determine the respective partition functions to much better than 0.1 per cent at temperatures below 600 K.

For HDO, the lowest level missing from the above compilation lies 6053 cm^{-1} above the vibrational ground state. To converge the sum in equation (1) for T above 1000 K for HDO, extra energy levels were added on the basis of theoretical calculations. Vibrational band origins were calculated using the DVR3D program (Tennyson, Henderson & Fulton 1995) and potential fit B of Shirin et al. (2003). For each vibrational state, the position of the missing rotational energy levels were estimated using a simple rigid rotor model with rotational constants $A = 22.97624\ \text{cm}^{-1}$, $B = 9.06019\ \text{cm}^{-1}$ and $C = 6.49789\ \text{cm}^{-1}$ (Martin, François & Gijbels 1991). Levels up to $J = 77$ were included in this fashion subject to the condition that the combined rotation-vibration energy was below the molecular dissociation energy, which was taken to be 41 088 cm^{-1}.

To test the accuracy of including these estimated energy levels in our summation, we recalculated the results replacing all experimental levels with $J > 28$ by calculated ones. For all temperatures this changed our calculated partition sum by less than 0.1 per cent, confirming the accuracy of our procedure.

Table 1 tabulates our values for the partition function. To aid their use in astronomical models we have fitted these partition functions to the standard form of Irwin (1981)

$$\log_{10}(z_{\text{int}}) = \sum_{n=0}^{6} a_n (\log_{10} T)^n; \tag{2}$$

the coefficients of these fits are given in Table 2.

The full partition function, z_{tot}, necessary for calculating equilibrium constants, can be written as

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

where z_{int} is the internal partition function discussed above and z_{trans} is the translational contribution. z_{trans} 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.

Table 1. Calculated internal partition functions as a function of temperature.

T(K)	HDO	D_2O
1	1.000	0.6667
5	1.035	0.7047
10	1.399	1.0144
20	2.945	2.2451
30	5.085	3.92623
40	7.617	5.92026
50	10.477	8.17571
60	13.629	10.6639
70	17.048	13.3648
80	20.715	16.2631
90	24.616	19.3464
100	28.736	22.6043
150	52.301	41.2490
200	80.198	63.3429
300	147.064	116.550
400	227.491	181.433
500	321.736	258.893
600	431.070	350.489
700	557.314	458.089
800	702.493	583.668
900	869.439	729.106
1000	1059.26	896.030
1500	2496	
2000	5101	
2500	9517	
3000	16559	
3500	27211	
4000	42592	
4500	63888	
5000	92278	
5500	128856	
6000	174574	

Table 2. Fitting coefficients for the polynomial fit (equation 2) of the internal partition functions.

	HDO	D_2O
a_0	−0.0055	−0.1700
a_1	0.5730	0.1377
a_2	−2.4839	−1.0382
a_3	3.4152	1.6888
a_4	−1.6782	−0.6905
a_5	0.3634	0.09022
a_6	−0.0287	

2.2 Equilibrium constants

For the reaction

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

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

$$K = \left(\frac{m_C m_D}{m_A m_B}\right)^{3/2} \frac{z_{\text{int}}^C z_{\text{int}}^D}{z_{\text{int}}^A z_{\text{int}}^B} \exp\left(-\frac{U}{kT}\right) \tag{6}$$

Table 3. Fractionation reactions considered in this work with associated enthalpies, U.

	Reaction	U/K
(a)	$D + H_2O \rightarrow H + HDO$	−889
(b)	$HD + H_2O \rightarrow H_2 + HDO$	−473
(c)	$H_2D^+ + H_2O \rightarrow H_3^+ + HDO$	−334
(d)	$D + HDO \rightarrow H + D_2O$	−440
(e)	$HD + HDO \rightarrow H_2 + D_2O$	−499
(f)	$H_2D^+ + HDO \rightarrow H_3^+ + D_2O$	−359

where U is the enthalpy of the reaction. The enthalpy of the reaction was calculated using

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

where E_0^X is the zero point energy of species X as measured on an absolute energy scale. Table 3 lists the six water fractionation reactions considered here along with our estimate of the enthalpy of each reaction.

The enthalpies were calculated using zero point energies for H_2O, HDO and D_2O of 4638.31 cm^{-1}, 4022.84 cm^{-1} and 3389.96 cm^{-1} respectively, as calculated using the potential of Shirin et al. (2003). It should be noted that the differences between the zero point energies are large, approximately 1000 K for the substitution of one hydrogen by a deuterium atom.

Other zero point energies were taken from the work of Ramanlal, Polyansky & Tennyson (2003) and Ramanlal & Tennyson (2004). It can be seen that all the reactions considered are exothermic by at least 300 K, so that significant fractionation can be expected at cold ISM temperatures.

In order to calculate the equilibrium constants, K, as a function of temperature it is necessary to have values for the partition function for all species involved in a particular reaction. We used the partition functions given above for HDO and D_2O, the H_2O partition function of Vidler & Tennyson (2000). Partition functions for H_3^+ and H_2D^+ were taken from Sidhu, Miller & Tennyson (1992), and those for other hydrogenic species were taken from Ramanlal & Tennyson (2004). Table 4 gives the equilibrium constants for each of the reactions tabulated in Table 3.

Table 4. Equilibrium constants, given as $\log_{10}K$, for the reactions given in Table 3, as a function of temperature.

T (K)	(a)	(b)	(c)	(d)	(e)	(f)
5	77.1022	40.8710	22.1967	78.5159	42.2848	23.6104
10	38.6665	20.3435	11.7622	38.9880	20.6650	12.0836
20	19.3593	9.9891	6.5251	19.2373	9.8671	6.4031
30	12.9201	6.5313	4.5296	12.6520	6.2632	4.2615
40	9.7103	4.8206	3.5028	9.3594	4.4696	3.1519
50	7.7855	3.8115	2.8582	7.3839	3.4099	2.4566
60	6.5047	3.1549	2.4175	6.0669	2.7171	1.9797
70	5.5902	2.6943	2.0959	5.1261	2.2302	1.6318
80	4.9045	2.3528	1.8507	4.4206	1.8688	1.3667
90	4.3713	2.0885	1.6574	3.8718	1.5891	1.1580
100	3.9446	1.8771	1.5012	3.4328	1.3653	0.9894
150	2.6673	1.2371	1.0272	2.1158	0.6856	0.4758
200	2.0248	0.9025	0.7835	1.4573	0.3350	0.2160
300	1.3851	0.5611	0.5419	0.7997	−0.0243	−0.0435
400	1.0662	0.3891	0.4218	0.4729	−0.2041	−0.1714
500	0.8761	0.2871	0.3508	0.2791	−0.3100	−0.2463

Table 5. Equilibrium constants for the atomization reactions $H_2O \leftrightarrow H + H + O$ and $HDO \leftrightarrow H + D + O$. The upper portion of the table gives $\log_{10} K$ in units m^{-6}, as an explicit function of temperature; the lower portion presents a fit of ln K to the form of equation (2).

T (K)	H_2O	HDO
500	35.7801	36.6555
600	19.6870	20.4372
700	8.1802	8.8423
800	−0.4577	0.1396
900	−7.1811	−6.6328
1000	−12.5686	−12.0590
1500	−28.7434	−28.3376
2000	−36.8264	−36.4634
2500	−41.6621	−41.3201
3000	−44.8713	−44.5419
3500	−47.1507	−46.8307
4000	−48.8493	−48.5381
4500	−50.1612	−49.8600
5000	−51.2032	−50.9135
5500	−52.0499	−51.7735
6000	−52.7510	−52.4894
a_0	47997.7	47873.5
a_1	−31712.7	−31542.6
a_2	8952.50	8877.05
a_3	−1378.41	−1362.16
a_4	121.509	119.624
a_5	−5.79209	−5.67809
a_6	0.116287	0.113446

In stellar atmospheres the amount of water present in the atmosphere is determined by the equilibrium with respect to dissociation into atoms, atomisation (Tsuji 1973). Given the atomisation energy and the partition functions for the atoms and molecules, it is possible to calculate this equilibrium constant as a function of temperature. We have calculated this for H_2O and HDO using: the H_2O partition function of Vidler & Tennyson (2000), HDO parition function given above, H and D atom partition functions set to the spin degeneracy value of 2, the temperature dependent partition function of atomic O given by Irwin (1981) and the atomisation energy for H_2O of 76720.5 cm^{-1} given by Irwin. This value was adjusted to 77336.0 cm^{-1} to allow for zero point energy effects in HDO. Finally translational partition functions were computed assuming perfect gases.

Our calculated equilibrium constants for atomisation are given in Table 5 where a fit to the functional form (2) is also presented. For H_2O these results are close to those of Irwin (1981), since they only differ in the partition function used for H_2O. The constant for HDO has, as far as we are aware, not been evaluated previously.

2.3 Discussion and conclusions

Fig. 1 compares our partition functions for HDO and D_2O as a function of temperature with that of H_2O (Vidler & Tennyson 2000). It can be seen that the HDO partition function is significantly larger than that of H_2O at all temperatures. This is in contrast to the results of Pavlenko (2002) who found $z(H_2O)$ to always be higher. It is easy to argue on physical grounds that HDO has more vibration–rotation states than H_2O at low energies, because these states are not constrained by the Pauli principle, and at high energies because the heavier D atom leads to an increased density of states. The problem with Pavlenko's results would appear to be caused by an

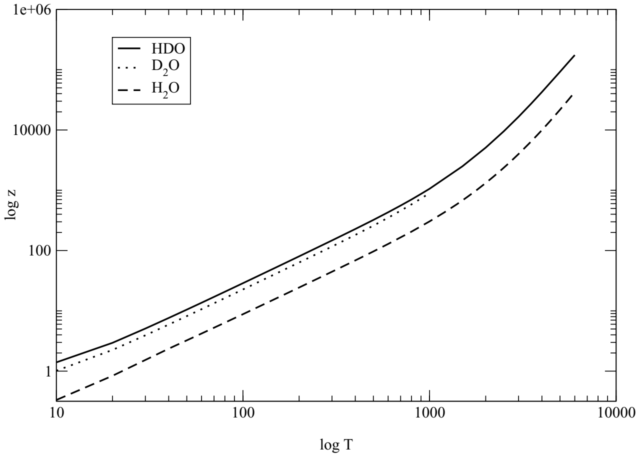

Figure 1. Comparison of HDO and D_2O internal partition functions, z, as a function of temperature, T, computed in this work with the H_2O partition function of Vidler & Tennyson (2000).

inconsistent treatment of nuclear spin statistics and the fact that the calculations of Partridge & Schwenke (1997), which he sums, do not provide enough levels for HDO to converge the partition sum at higher temperatures.

In contrast to this, we find surprisingly good agreement with the temperature-dependent values for z(HDO) given by Martin et al. (1992), despite the fact that they employed an, in principle, less accurate *ab initio* procedure. We obtain excellent agreement for the partition functions up to approximately 1000 K. Above this figure our partition is larger, although the difference is less than 2 per cent at 3000 K, the highest temperature for which they present results.

In summary, we present partition functions for deuterated water that are expected to be reliable over an extended energy range. These partition functions are used to compute equilibrium constants for key deuterium fractionation reactions. Although these constants cannot be used directly for modelling the chemistry in the non-thermal conditions found in much of the interstellar medium, they do allow reverse reaction rates to be calculated as a function of temperature for a process for which one reaction rate is known. This is useful because it is generally easier to measure reaction rates for exothermic reactions.

The partition function of HDO is also important for models of very low mass stars that have temperatures in the range 1000 to 3000 K. It may be possible to use the spectrum of HDO to determine the abundance of deuterium in these stellar and substellar species, and hence to have a practical realization of the deuterium test for distinguishing between objects massive enough to burn deuterium and those not capable of it.

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