

Deuterated interstellar and circumstellar molecules: D/H ratio and dominant formation processes

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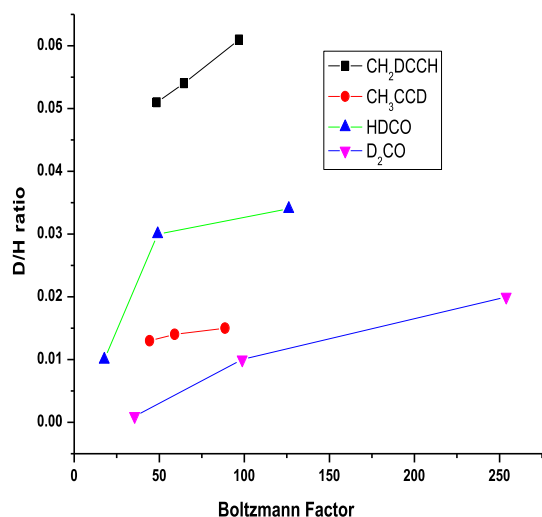
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Abstract: There are several constraints associated with the different models used in accounting for the D/H ratio observed of singly and multiply deuterated interstellar and circumstellar molecular species. Thermodynamically, the most distinctive difference between a molecule and its deuterated analogue is the zero point energy (ZPE). Applying high level quantum chemical calculations, the ZPE for all H-containing and their corresponding D-analogues for all interstellar/circumstellar molecular species considered in this study are determined. From the difference in the ZPE between the H-containing and the corresponding D-analogue, Boltzmann factor is computed for all the systems using the excitation temperature/molecular cloud temperature for the known D-molecules and a range of temperature for others. From the results, there is a direct correlation between the Boltzmann factors and the D/H ratios. Pronounced deuterium fractionation occurs at larger values of Boltzmann factor resulting in the observed high D/H ratios. Increased deuterium fractionation at low temperature suggests that grain surface reactions are the major formation processes for deuterated molecules. This implies that at lower temperature (higher Boltzmann factor), the exchange reaction involving deuterium or deuterium fractionation is much pronounced resulting in the distribution and redistribution of deuterium among various species. The implications of these results and the possibility of detecting more D-molecules are discussed.

Graphic abstract



Keywords: Abundance; Molecules; Astrochemistry; Interstellar medium; Deuterium

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1. Introduction

In the early part of the 20th century, space was considered as chemically barren. The discoveries of NH₃, H₂O, H₂CO, CO, CH₃OH, etc., in the 1960's and early 1970's in quick succession from different astronomical sources changed this perception [1–5]. These discoveries ignited a strong interest among researchers on what molecules could be seen in space and what could be learned from these molecules. Today, over 200 different molecular species have been detected from different astronomical sources [6–8]. These molecules are not only opening up a new research field; molecular astrophysics/astrochemistry, but have also increased the body of knowledge and interest in other related fields. That these molecules are excellent

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probes of the physical conditions in space is one of the driving forces for increased interest in astronomy. The field of astrobiology thrives on the discoveries of biologically related molecules in space.

Among these interstellar and circumstellar molecules, various isotopologues of H, C, N, O and S containing molecular species have also been detected. Deuterated molecules are the most detected isotopologues of all interstellar and circumstellar isotopologues. This is quite amazing considering the cosmic D/H ratio which is only of the order of 10^{-5} . Studies of deuterated molecules from both astronomical observation and theoretical modeling serve as the most appropriate test of ion–molecule processes for the formation and destruction of many interstellar species [9a, b, 10, 11]. The origin of deuterium in the interstellar space is traced to the Big Bang. It is believed to have been produced in large quantities as part of the primordial Big Bang Nucleosynthesis [12]. Despite the low D/H ratio ($\approx 10^{-5}$), the reported D/H ratios for different deuterated molecules detected from different astronomical sources are far higher than the cosmic or elemental D/H ratio. D/H ratio ranging from 0.04 to 0.18 is reported for CH_3CCD ; 0.054 for CH_2DCCH ; 0.001–0.03 for D_2CO ; ≈ 0.003 for NH_2D ; 8×10^{-4} for ND_3 ; 0.0007–1.0 for DCN ; > 0.003 –0.05 for HDO [9a, 10, 11, 13–19, 20]. These high D/H ratios are reported for all known deuterated molecules notwithstanding the low cosmic D/H ratio. The observed D/H ratios for different deuterated molecules set a high possibility for many other deuterated isotopologues of interstellar and circumstellar molecules to be detectable.

Accounting for the high D/H ratios has been a major concern of many studies for decades including models and space observatory missions; for instance the Far Ultraviolet Spectroscopic Explorer (FUSE) [12] among others. While the models are still trying to account for the high ratios reported for singly deuterated molecules on the bases of ion–molecule chemistry, deuterium fractionation processes, cold grain surface processes and some gas-phase processes [9a, 15, 21] and references therein]. D/H ratios for multiple deuterated species were predicted by various models to be very low such that their astronomical detection was not in view. According to Turner [11] “An overall prediction of ion–molecule chemistry is that while many species may be singly deuterated in detectable quantities, none will be doubly or multiply deuterated to similar degree”. The detection of D_2CO with $\text{D}_2\text{CO}/\text{H}_2\text{CO}$ ratio of ≈ 0.003 led to the conclusion that gas-phase chemistry cannot account for the observed high $\text{D}_2\text{CO}/\text{H}_2\text{CO}$ ratio [11, 21].

HD is the main reservoir of deuterium in the interstellar medium and it is also one of the earliest detected deuterated molecules [22]. Deuterium fractionation is a temperature dependent process [23–26]; the main reaction for this process is



The forward reaction is exothermic at the low temperature of the molecular clouds, thereby allowing the redistribution of deuterium resulting in the enhanced D/H ratio while at high temperature, the reverse reaction becomes favourable, thus, destroying the H_2D^+ and suppressing the deuterium enhancement; the reverse reaction is said to require an additional energy of about 232 K which is not easily achievable considering the conditions in the molecular clouds, thus the forward reaction keeps thriving [17, 27–29]. In accordance with Le Châtelier’s principle, as the H_2D^+ ion is being depleted via successive reactions with neutral molecules; the forward reaction is further enhanced. The depletion of H_2D^+ results in the transfer and subsequent incorporation of deuterium in the newly species. The dependence on temperature by fractionation process has been reported for a number of systems. In the $\text{N}_2\text{D}^+/\text{N}_2\text{H}^+$ system, major fractionation occurs before 15 K (with maximum at 13 K) while at above 15 K, deuterium fractionation drops drastically as the temperature approaches 30 K [17, 28–31].

Thermodynamically, the most conspicuous difference between a molecule and its deuterated analogue is in the zero point energy (ZPE) with the deuterated molecule having a lower ZPE. From the ZPE difference between a molecule and its deuterated analogue; the Boltzmann factor (E/kT) for a particular system (say DX/HX) can be determined using the determined using the temperature of the molecular cloud/rotational temperature from which DX was observed. The calculated Boltzmann factor gives insight about the nature or level of fractionation leading to the formation of DX . Boltzmann factor of 1 (or ≈ 1) implies no major fractionation, thus, the cosmic ratio of D/H ($\approx 10^{-5}$) will be expected for such system while for larger values of Boltzmann factor, notable and major fractionation will occur which will result in very high D/H ratio above the cosmic ratio. In order to address the several constraints associated with different models used in accounting for the D/H ratio observed in different deuterated interstellar and circumstellar molecular species, the present work aims at determining the Boltzmann factor for all the H-containing interstellar/circumstellar molecules considered in this study using the ZPE of the H-and their corresponding D-analogues computed from high level quantum chemical simulations. Apart from accounting for the observed D/H ratios of the known deuterated molecules, the results obtained are also used in setting the pace of what should be expected regarding the D/H ratios for other systems depending on the prevailing conditions that will lead to their formation.

The dominant formation processes for deuterated molecules and the possibility of more deuterated molecules are also discussed within the limit of the results obtained. The methodology employed in this work is briefly discussed in the next section while the results obtained based on the discussed methodology are presented and discussed in Sect. 3.

2. Methodology

Advances in computational and theoretical methods have made it possible to study systems, reactions and predict parameters which would have been either impossible or very difficult to study experimentally. For the present work, the GAUSSIAN 09 suit of programs [32] is employed for all quantum chemical simulations reported here. Achieving high accurate results at less computational cost is a major consideration for every computational study. In this regard, the compound models are the best candidates. Among these compound models, the G4 method has proven to be very reliable in predicting thermodynamic parameters to a very high level of accuracy [33, 34].

The high accuracy of the G4 method coupled with our previous experience on the use of this method made it the right choice for the present work [35–40]. A brief summary of the different methods used at various steps of calculations in the G4 compound method is shown in Table 3 in the appendix. In comparison with other compound methods like G4MP2, W1U and W2U, the table also shows the various steps of calculations in these methods [33, 34, 41].

The ZPE is obtained from the optimized structures of all the systems under consideration, all the structures are found to be stable with no imaginary frequency as shown from the frequency calculations. For all the known deuterated molecules, the reported temperature or rotational temperature of the molecular cloud from which they are detected are used in computing the Boltzmann factor while for the D/H systems whose D-analogues are not yet detected; a range of temperature is used in computing the Boltzmann factor. Delta T (ΔT) in all the tables in this study is obtained as the difference in the zero point energy (ZPE) of a molecule and its D-analogue expressed in terms of temperature.

3. Results and discussion

There are over 200 known interstellar and circumstellar molecular species, not less than 132 of these species contain at least an atom of H. This is not surprising with atoms of H making up about 89% of the gas in the interstellar

medium (ISM) and molecular hydrogen (H_2) being the most abundant molecules species in ISM [1–5].

Note less than 132 of the H-containing and their corresponding deuterated analogues are considered in this study. Over 20 deuterated molecules have been detected from different astronomical sources [9a, b, 10, 11]. 22 of these molecules with reported D/H ratio and the excitation temperature in the astronomical source where they are detected are examined. In Table 1, the ZPE, the excitation temperature (indicated as source temp), Boltzmann factor, E/kT (obtained by dividing the value of ΔT in column 3 by the source temp. in column 4), D/H ratio and reference to the reported values are presented. These molecules are arranged in ascending order of the number of atoms and are discussed in the same manner together with the ones presented in subsequent tables. The tables containing the Boltzmann factor for D-analogues of H-containing diatomic to trideca-atomic species and the corresponding ZPE are presented in the appendix as Tables 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15, respectively.

For H-containing interstellar and circumstellar species whose deuterated analogues are not known, four sets of temperature; 10, 100, 500 and 1000 K have been adopted in determining the Boltzmann factor for such systems. This temperature range spans from what could be expected in the cold molecular clouds (≈ 10 K) as reported for most species in Table 1 to those in the very hot cores. As a justification of the choice of this temperature range, Table 2 in the appendix summarizes the different component of the interstellar medium. Table 4 in the appendix shows the diatomic H-containing molecules and their corresponding D-analogues; their ZPE and the Boltzmann factor for the four sets of temperature considered.

There are at least 14 H-containing known interstellar/circumstellar species of which at least 5 (CH^+ , OH^+ , SH^+ , HCl^+ , ArH^+) are ions. They contain some of the rare species among interstellar molecules; the only known noble gas, Ar- and Li-containing species are in this group. HD is a known deuterated species among the diatomic species [22]. This is not surprising considering the abundance of H_2 with respect to other diatomic species. The Boltzmann factor for the HD/ H_2 system is almost unity (1.010–0.903) using the reported temperature at the source from which HD was observed while the D/H ratio is 10^{-6} , a value that is close to the cosmic D/H ratio ($\approx 10^{-5}$). Thus, at high temperature no major deuterium fractionation occurs, hence the D/H ratio would likely reflect the cosmic or elemental D/H ratio as observed here. From Table 4 in the appendix, if the deuterium fractionation processes that will lead to the formation of the D-analogues of these diatomics are to occur as part of the low temperature grain surface processes, pronounced deuterium fractionation that

Table 1 Known D-molecules, their excitation temperature, Boltzmann factor (E/kT) and D/H ratio

Molecule	ZPE (kcal/mol)	* ΔT (K)	Source temp. (k)	E/kT	D/H ratio	References
H ₂	6.4	–				
HD	5.5	430.1	423–473	1.0–0.9	10 ⁻⁶	21
H ₂ O	13.4	–				
HDO	11.6	906.3	100	9.1	0.014–0.058	36
D ₂ O	9.8	1838.2	100	18.3	1.7 * 10 ⁻³ (D ₂ O/HDO) 5 * 10 ⁻⁵ (D ₂ O/H ₂ O)	37
N ₂ H ⁺	10.4	–				
N ₂ D ⁺	8.6	874.4	< 20 > 20	< 43.7 > 43.7	0.3–0.8 < 0.04	10
H ₃ ⁺	12.8	–				
H ₂ D ⁺	11.7	582.9	18	32.4	< 0.003	47
HCO ⁺	10.3	–				
DCO ⁺	8.6	857.7	< 20 > 20	< 42.9 > 42.9	0.04–3.4 < 0.01–0.6	10
C ₂ H	8.0	–				
C ₂ D	6.7	671.3	20	33.6	0.01	48
HCN	10.4	–				
DCN	8.6	898.1	< 20 > 20	< 44.9 > 44.9	7 * 10 ⁻⁴ –0.018 \approx 1.0	10
HNC	9.3	–				
DNC	7.7	807.4	< 20 > 20	< 40.4 > 40.4	0.7–1.3 0.006–0.24	10
H ₂ S	9.5	–				
HDS	8.1	661.6	20	33.1	0.1	48
D ₂ S	6.8	1343.0	12	(56.8) 111.9	0.011 (D ₂ S/HDS)	43
H ₂ CS	15.5	–				
HDCS	13.7	902.2	\approx 10	90.2	0.300	38
D ₂ CS	11.9	1819.2	\approx 10	181.9	0.111 (D ₂ CS/H ₂ CS) 0.333 (D ₂ CS/HDCS)	38
NH ₃	21.6	–				
NH ₂ D	19.7	954.9	10.8–14.6	65.4–88.4	0.04–0.33	44
NHD ₂	17.7	1931.6	24	80.4	0.03	45
ND ₃	15.7	2929.8	5–10	293.0–586.0	8 * 10 ⁻⁴	15
l-C ₃ H	11.5	–				
l-C ₃ D	9.9	812.8	13.9	58.5	0.048	46
H ₂ CS	15.5	–				
HDCS	13.7	902.2	18 50	50.1 18.0	0.02–0.06 0.01–0.03	18,19
D ₂ CS	11.9	1819.2	18 50	101.1 36.4	0.01–0.03 0.001–0.01	18,19
c-C ₃ H ₂	18.5	–				
c-C ₃ HD	16.7	918.9	12.3	74.7	0.071	46
C ₄ H	15.2	–				
C ₄ D	13.5	869.3	10	86.9	0.0043	42
HC ₃ N	16.6	–				
DC ₃ N	14.9	889.2	10	89.9	0.05	40
CH ₃ OH	32.1	–				
CH ₂ DOH	30.1	1011.4	12.3	82.2	0.030	46

Table 1 continued

Molecule	ZPE (kcal/mol)	* ΔT (K)	Source temp. (k)	E/kT	D/H ratio	References
CHD ₂ OH	28.1	2015.9	47	42.9	0.060	49
CD ₃ OH	26.1	3030.9	85	35.7	0.014	49
CH ₃ CN	28.4	–				
CH ₂ DCN	26.5	981.4	240	4.1	≥ 0.005	13
H ₂ C ₄	22.4	–				
HDC ₄	20.7	876.9	12.3	71.3	0.030	46
HC ₅ N	23.3	–				
DC ₅ N	21.5	888.6	10	88.9	0.006–0.016	41
CH ₃ CCH	34.8	–				
CH ₃ CCD	33.0	894.3	10	89.4	0.04–0.18	9
CH ₂ DCCH	32.8	977.3	10	97.7	0.079–0.17	9
HCOOCH ₃	38.9	–				
HCOOCH ₂ D	36.8	1012.7	110	9.2	0.04 \pm 0.02	39

NH_3D^+ has been detected with a column density of $1.1 \pm 0.2 * 10^{12} \text{ cm}^{-2}$ [14]. The hydrogenated analogue, NH_4^+ is not detected (it's a spherical top with no permanent dipole moment), hence the D/H ratio cannot be determined

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

will result in D/H ratio higher than the cosmic or elemental D/H ratio is the most probable event.

But at temperature close to the range where HD is observed, the Boltzmann factor will tend towards unity signifying no pronounced deuterium fractionation; therefore, D/H ratio close to the cosmic D/H ratio would be expected. That only HD is the only observed D-analogues of the diatomic species could be due to interstellar abundances of these species. Since most of them are radicals/ions, they are not very stable; thus, their D-analogues may not be very abundant.

The triatomic species constitute the highest number of known deuterated molecules. Of the 20 H-containing triatomic species presented in Table 5 in the appendix, 8 (indicated with bold typeface in Table 5) have their corresponding D-analogues as known interstellar/circumstellar species [10, 42, 43, 44, 45, 46]. From Table 1, the Boltzmann factor for these detected deuterated species ranges from 9 to 97.054 with reported excitation or molecular cloud temperature in the range of 5–100 K.

Under these conditions, major deuterium fractionation which will culminate in D/H ratio far higher than the cosmic D/H ratio should be expected and this is evident from the results. For the singly deuterated species, the D/H ratio ranges from $7 * 10^{-4}$ to ≈ 1 and $5 * 10^{-5}$ to 0.011 for the doubly deuterated species. These trends are anticipated for other triatomic species if they are observed under similar conditions. From Table 5, if the fractionation processes leading to the formation of these species are to occur

at temperature above 500 K where the Boltzmann factor will be approaching unity, then D/H ratio in the range of the cosmic D/H ratio will be expected. The observed D/H ratios signal grain surface reactions as the dominant processes leading to the formation of these species. The trends of the D/H ratios noted here are anticipated for other triatomic species if they are formed and observed under similar conditions.

There are about 20 H-containing tetra-atomic interstellar/circumstellar molecular species. The ZPE of these species and their corresponding D-analogues together with the Boltzmann factor for all the systems considered here are depicted in Table 6 in the appendix. Of these 20 species, 4 (H₂CS, H₂CO, NH₃ and l-HC₃) have their deuterated analogues as known molecular species in space [15, 18, 19, 47, 48–50]. Ammonia is one of the very few molecules with triply deuterated analogues. The periodic trend between O and S is noted here with the O-containing molecules (H₂CO) having its S-analogue (H₂CS) also deuterated to the same level. This is also the case of H₂O and H₂S in the previous part (Tables 1, 5). The reported source temperature (excitation/molecular cloud temperature) where these triatomic species are observed ranges from 5 to 50 K (Table 1). This range is far below the temperature (* ΔT in Table 6 in the appendix) at which the Boltzmann factor for these species should be unity. The high values of the Boltzmann factor results in high D/H ratios. The D/H ratio increase with Boltzmann factor, as the

Boltzmann factor approaches unity, the D/H ratio approaches the cosmic D/H ratio (see HD, Table 1).

Against the predictions of various models which did not envisage the detectability of multiply deuterated species due to the low abundances predicted for them, these species have been detected with very high D/H ratios (0.001–0.333 for doubly deuterated species and 8×10^{-4} for triply deuterated ammonia). From the Boltzmann factor and the conditions surrounding the observations of these molecules, these ratios are not surprising. At the reported source temperature for these species, there is no doubt that there is very high level of deuterium fractionation, thus resulting in the high D/H ratios of these species. This temperature range further supports the grain surface processes as the dominant mechanisms for the formation of deuterated molecules. The observed D/H ratio can easily be foreseen for other D-analogues tetra-atomic species if the same conditions here dominate their formation processes.

Only a handful of all the interstellar and circumstellar molecules are cyclic. Whether this will be the trend among the isotopologues remains to be seen. However, that of the three deuterated species with 5 atoms, one is cyclic is a good omen in this direction. The number of H-containing molecules with 5 atoms (19) is almost as those with 4 and 3 atoms (20 each). These molecules and their corresponding D-analogues are presented in Table 7 in the appendix with the predicted parameters for the respective systems. DC₄, c-C₃HD and DC₃N are the known D-molecules of these series [51, 52, 50]. The D/H ratio for these molecules ranges from 0.0045 to 0.071 far above the cosmic D/H ratio which is consistent with the Boltzmann factors for these molecules that are also far from unity.

From Table 7, achieving a Boltzmann factor of unity which will suppress deuterium fractionation and lead to the cosmic D/H ratio for these molecules will mean a process or processes occurring at very high temperature ($*\Delta T$). However, it is clear from the present results, that the processes that led to the formation of the observed penta-atomic species are largely cold temperature processes occurring on the surface of the interstellar dust grains surfaces.

Molecules with 6 atoms and above are regarded as complex in interstellar chemistry parlance, as the complexity increases, the number of known molecules decreases as compared to the non-complex molecules (those with 2–5 atoms). CH₃OH, CH₃CN and H₂C₄ are the hexa-atomic molecules with known D-analogues out of the 16 H-containing hexa-atomic molecules displayed in Table 8 in the appendix. CH₃OH is another molecule after NH₃ with triply deuterated analogue [53, 50, 54] and references therein]. The D/H ratio reported for these molecules ranges from 0.005 to 0.06 with least value corresponding to the least Boltzmann factor (4.061) among all the systems (Table 1). The source temperature and the Boltzmann factor for these molecules

would not have suggested anything less than high D/H ratio above the cosmic D/H ratio because under these conditions, exchange reactions among D-containing molecules are highly exothermic, thus the deuterium get distributed and redistributed among different species leading to the observed high D/H ratio.

From Table 8 in the appendix, this range of ratio is expected for other complex (with 6 atoms discussed here) species since most of the main species (H-analogues) are grain surface products except where other formation processes (very high temperature) prevail.

All the known interstellar and circumstellar molecules with seven atoms contain at least an atom of H. Of the 9 species in this series, two of their deuterated analogues have been detected in space. For HC₅N, it is the only possible deuterated analogue of it (DC₅N) that has been detected while for CH₃CCH, two of its isotopomers (CH₃CCD and CH₂DCCH) have been detected [9a, 53]. As would be expected, the position of substitution of the D-atom has an effect on the entire system as it is observed in the two isotopomers.

Table 9 in the appendix shows the H-containing hepta-atomic species, their D-analogues, ZPE and the Boltzmann factor. The D/H ratio for DC₅N ranges from 0.006 to 0.016 at the reported source temperature of 10 k. The observation of the two isotopomers under the same conditions allows one to test the dependence of the D/H ratio on the Boltzmann factor for similar systems. As in previous cases, D/H ratio increases with increasing value of Boltzmann factor.

The source temperature and the Boltzmann factor for these systems rightly support the high D/H ratio reported for these systems, since under these conditions, major deuterium fractionation is expected to occur which is believed to culminate in D/H ratio higher than the cosmic D/H ratio. By all considerations, the dominance of grain surface reactions as the prevailing formation processes for these molecules cannot be ruled out.

There are about 12 interstellar/circumstellar molecules with 8 atoms (Table 10 in the appendix). All of these molecules contain at least an atom of H. HCOOCH₂D is the only D-analogue of these species with 8 atoms [55]. This is probably the largest deuterated molecule detected till date. The detection of HCOOCH₂D can largely be traced to the high abundance of its main isotopologue; methyl formate. The high abundance of methyl formate in many astronomical sources has earned it the name “interstellar weed”. It is more abundant than its isomers; acetic acid and glycolaldehyde.

Its high abundance in comparison to its isomers has been traced to interstellar hydrogen bonding where its isomers are found to be highly bonded to the surface of the interstellar dust grains thereby reducing their abundance while methyl formate is the least affected isomer of the C₂H₄O₂

isomeric group with respect to interstellar hydrogen bonding [40]. The D/H ratio reported for HCOOCH_2D (0.04 ± 0.02) is far above the cosmic D/H ratio, the Boltzmann factor and other conditions surrounding its detection support this ratio.

In Tables 11, 12, 13, 14, and 15 in the appendix, we present H-containing interstellar and circumstellar molecules comprising of 9–13 atoms. Their deuterated analogues, ZPE and Boltzmann factor are also presented. From available literature, there is currently no known deuterated interstellar or circumstellar species in this series. The discussion in this section will only be limited to what could be expected based on what is known.

Permanent dipole moment plays an important role in the astronomical detection of molecular species. The intensities of rotational transitions are known to scale with the square of the dipole moment, the higher the dipole moment, the higher the intensity of the lines. Interstellar chemistry processes are also affected by thermodynamic effects [35–40]. As it is discussed in the energy, stability and abundance (ESA) relationship, the astronomical detection of a molecule is also a function of its abundance. The higher the interstellar abundance of a species the higher its chances of being detected as compared to similar specie with low abundance. As seen in all the cases of the known D-molecules, the main isotopologue should be highly abundant for the detection of its D-analogue to be anticipated. Despite the abundance of these species, the availability of accurate laboratory measurement of the rotational transitions/rest frequencies of these D-isotopologues is a crucial issue. As in most cases, even when there is overwhelming evidence of the present of the D-analogue in a detectable form, its astronomical search will still be dependent on the availability of accurate laboratory measurements.

Table 16 shows specific examples of Boltzmann factor and D/H ratio for different systems. Figure 1 depicts the dependence of D/H ratio on the Boltzmann factor. It is obvious from the figure that the D/H ratio increases as the Boltzmann factor increases. This is traceable to the low temperature processes which dominate the formation of these species in the interstellar medium under which there is a very high enhancements of deuterium fractionation, thus, resulting in very high D/H ratio.

Knowing the right candidates for astronomical searches is vital in reducing the number of unsuccessful astronomical searches considering the time, energy and resources involved in these projects. With respect to the deuterated molecules examined in this study, with the availability of accurate spectroscopic parameters required for their astronomical searches coupled with a good choice of the molecular cloud(s) for the searches, some of the deuterated

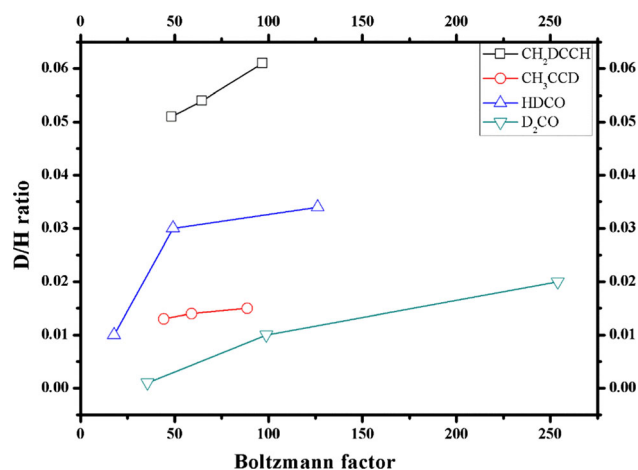


Fig. 1 Dependence of D/H ratio on Boltzmann factors

molecular that are yet to be astronomically observed could serve as good candidates for astronomical searches with the possibility of successful observation as highlighted in the results of this study.

4. Conclusion

A total of 132 H-containing interstellar and circumstellar molecules and their corresponding deuterated analogues with atoms ranging from 2 to 13 have been examined with the aim of investigating the D/H ratios and the dominant formation processes for the known deuterated molecules and what could be expected for others. The Boltzmann factor computed for each of these systems using the ZPE obtained from high level quantum chemical simulations shows a direct correlation with the D/H ratio reported for various known deuterated molecules.

As the Boltzmann factor approaches unity, the D/H ratio also approaches the cosmic D/H ratio while at higher Boltzmann factor, the D/H ratio increases to various orders of magnitude above the cosmic D/H ratio. This implies that at lower temperature (higher Boltzmann factor), the exchange reaction involving deuterium or deuterium fractionation is much pronounced leading to the distribution and redistribution of deuterium among various species, thus resulting in the high D/H ratio while at very high temperature (Boltzmann factor approaching unity), there will be no major fraction, thus the D/H ratio will probably reflect the cosmic D/H ratio as observed in the case of HD.

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Appendix

See Tables 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 and 16.

Table 2 Different components of the interstellar matter and their characteristics

Component	Number density (cm ⁻³)	Temperature (K)	Major constituents	Main detection technique
Molecular clouds (dark nebulae)	Up to 10 ⁶	10–20	H ₂ , many molecules, ice-coated dust grains.	Radio and infrared emissions and absorptions
Intergalactic coronal gas	≈ 10 ⁻³	10 ⁶ –10 ⁷	H ⁺ , C ³⁺ , N ⁴⁺ , O ⁵⁺	UV absorption, X-ray emission
Neutral and ionized medium	0.2–0.5	6–10 × 10 ³	H, H ⁺ , He, He ⁺	21 cm emission of H, H α emission
Ionized diffuse clouds (Emission nebulae, HII regions)	10 ² –10 ⁴	8 × 10 ³	H ⁺ , He ⁺ , O ⁺ , C ⁺ , N ⁺ , CH ⁺ , H ₃ ⁺ , HCO ⁺	Hα emission
Neutral diffuse clouds (reflection nebulae, HI regions)	20–50	50–100	H, He, H ₂ , H ₃ ⁺ , C ⁺ , CO, CN, OH, NH, C ₂ , dust	21 cm emission of H atoms

Table 3 Different methods for different calculations in compound methods

Calculation	G4	G4MP2
Geometry optimization	B3LYP/6–31G(2df,p)	B3LYP/6–31G(2df,p)
ZPE	B3LYP/6–31G(2df,p) Scaled by 0.9854	B3LYP/6–31G(2df,p) Scaled by 0.9854
Single-point calculations	MP4/6–31G(d) modified by corrections from additional calcs. (with MP4 and other methods)	CCSD(T)/6–31G(d) modified by corrections from additional calcs. (with MP2 and other methods)
Energy	MP4/6–31G(d) and the corrections from previous step	CCSD(T)/6–31G(d) and the corrections from previous step./6–31G(d)
Core correlation	Higher level correction terms	Higher level correction terms
Calculation	W1U	W2U
Geometry optimization	B3LYP/cc-pVTZ	CCSD(T)/cc-pVQZ
ZPE	B3LYP/cc-pVTZ	CCSD(T)/cc-pVTZ
Single-point calculations	CCSD(T)/aug-cc-pVDZ	CCSD(T)/aug-cc-pVTZ
Energy	SCF/aug-pVDZ	SCF/aug-pVQZ
Core correlation	CCSD/MT	CCSD/MT

Table 4 Boltzmann factor (E/kT) for D-analogues of H-containing diatomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ K)	E/kT (at $T = 100$ k)	E/kT (at $T = 500$ k)	E/kT (at $T = 1000$ K)
H ₂	6.4	–	–	–	–	–
HD	5.5	430.1	43.0	4.3	0.9	0.4
HCl	4.2	–	–	–	–	–
DCl	3.0	600.3	60.0	6.0	1.2	0.6
NH	4.7	–	–	–	–	–
ND	3.4	637.6	63.8	6.4	1.3	0.6
OH	5.3	–	–	–	–	–
OD	3.8	723.4	72.3	7.2	1.4	0.7
OH ⁺	4.4	–	–	–	–	–
OD ⁺	3.2	598.1	59.8	6.0	1.2	0.6
HF	5.9	–	–	–	–	–
DF	4.3	813.8	81.4	8.1	1.6	0.8
LiH	2.0	–	–	–	–	–
LiD	1.5	256.7	25.7	2.6	0.5	0.3
CH	4.0	–	–	–	–	–
CD	2.9	538.1	53.8	5.4	1.1	0.5
CH ⁺	4.0	–	–	–	–	–
CD ⁺	2.9	537.1	53.7	5.4	1.1	0.5
SH	3.8	–	–	–	–	–
SD	2.7	542.5	54.2	5.4	1.1	0.5
SH ⁺	3.6	–	–	–	–	–
SD ⁺	2.6	516.6	51.7	5.2	1.0	0.5
SiH	2.9	–	–	–	–	–
SiD	2.1	407.4	40.7	4.1	0.8	0.4
HCl ⁺	3.8	–	–	–	–	–
DCI ⁺	2.7	537.1	53.7	5.4	1.1	0.5
ArH ⁺	3.8	–	–	–	–	–
ArD ⁺	2.7	540.6	54.1	5.4	1.1	0.5

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Table 5 Boltzmann factor (E/kT) for D-analogues of H-containing triatomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ K)	E/kT (at $T = 100$ K)	E/kT (at $T = 500$ K)	E/kT (at $T = 1000$ K)
H₂O	13.4	–	–	–	–	–
HDO	11.6	906.3	90.6	9.1	1.8	0.9
D₂O	9.8	1838.2	183.8	18.4	3.7	1.8
H ₂ O ⁺	11.7	–	–	–	–	–
HDO ⁺	10.1	786.6	78.7	7.9	1.6	0.8
H₂S	9.5	–	–	–	–	–
HDS	8.1	661.6	66.2	6.6	1.3	0.7
D₂S	6.8	1343.0	134.3	13.4	2.7	1.3
HCN	10.4	–	–	–	–	–
DCN	8.6	898.1	89.8	9.0	1.8	0.9
HNC	9.3	–	–	–	–	–
DNC	7.7	807.4	80.7	8.1	1.6	0.8
NH ₂	11.9	–	–	–	–	–
NDH	10.3	797.0	79.7	8.0	1.6	0.8
CH ₂	11.6	–	–	–	–	–
CHD	10.1	759.8	76.0	8.0	1.5	0.8
HCO	8.9	–	–	–	–	–
DCO	7.3	798.3	79.8	8.0	1.6	0.8
HCO⁺	10.3	–	–	–	–	–
DCO⁺	8.6	857.7	85.8	8.6	1.7	0.9
HOC ⁺	8.4	–	–	–	–	–
DOC ⁺	6.9	753.1	75.3	7.5	1.5	0.7
HCS ⁺	9.2	–	–	–	–	–
DCS ⁺	7.4	902.5	90.2	9.0	1.8	0.9
H₃⁺	12.8	–	–	–	–	–
H₂D⁺	11.7	582.9	58.3	5.8	1.2	0.6
H ₂ Cl	4.6	–	–	–	–	–
HDCl	3.3	634.4	63.4	6.3	1.3	0.6
H ₂ Cl ⁺	7.2	–	–	–	–	–
HDCl ⁺	6.2	515.7	51.6	5.2	1.0	0.5
AlOH	6.9	–	–	–	–	–
AlOD	5.4	786.6	78.7	7.9	1.6	0.8
HO ₂	7.6	–	–	–	–	–
DO ₂	6.0	791.7	79.2	7.9	1.6	0.8
C₂H	8.0	–	–	–	–	–
C₂D	6.7	671.3	67.1	6.7	1.3	0.7
HNO	9.0	–	–	–	–	–
DNO	7.3	874.7	87.5	8.7	1.7	0.9
HCP	8.9	–	–	–	–	–
DCP	7.1	898.1	89.8	9.0	1.8	0.9
N₂H⁺	10.4	–	–	–	–	–
N₂D⁺	8.6	874.4	87.4	8.7	1.7	0.9

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Table 6 Boltzmann factor (E/kT) for D-analogues of H-containing tetra-atomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ K)	E/kT (at $T = 100$ K)	E/kT (at $T = 500$ K)	E/kT (at $T = 1000$ K)
NH ₃	21.6	–	–	–	–	–
NH ₂ D	19.7	954.9	95.5	9.5	1.9	0.9
NHD ₂	17.7	1931.6	193.2	19.3	3.9	1.9
ND ₃	15.7	2929.8	293.0	29.3	5.9	2.9
H ₂ CO	16.7	–	–	–	–	–
HDCO	14.9	889.2	88.9	8.9	1.8	0.9
D ₂ CO	13.1	1790.5	179.0	17.9	3.6	1.8
H ₂ CS	15.5	–	–	–	–	–
HD ₂ CS	13.7	902.2	90.2	9.0	1.8	0.9
D ₂ CS	11.9	1819.2	181.9	18.2	3.6	1.8
HNCO	13.0	–	–	–	–	–
DNCO	11.4	810.6	81.1	8.1	1.6	0.8
HNCS	11.4	–	–	–	–	–
DNCS	9.8	800.2	80.0	8.0	1.6	0.8
H ₂ CN	15.8	–	–	–	–	–
HDCN	14.1	854.8	85.5	8.5	1.7	0.8
CH ₃	18.6	–	–	–	–	–
CH ₂ D	17.0	813.8	81.4	8.1	1.6	0.8
PH ₃	15.0	–	–	–	–	–
PH ₂ D	13.6	690.9	69.1	6.9	1.4	0.7
MgC ₃ H	11.1	–	–	–	–	–
MgC ₃ D	9.3	900.3	90.0	9.0	1.8	0.9
H ₂ O ₂	16.6	–	–	–	–	–
HDO ₂	14.6	1032.9	103.3	10.3	2.1	1.0
HSCN	10.6	–	–	–	–	–
DSCN	9.2	724.1	72.4	7.2	1.4	0.7
HOCN	13.6	–	–	–	–	–
DOCN	11.7	967.2	96.7	9.7	1.9	1.0
HCNO	12.0	–	–	–	–	–
DCNO	10.6	723.8	72.4	7.2	1.4	0.74
HC ₂ N	11.5	–	–	–	–	–
DC ₂ N	9.9	819.4	81.9	8.2	1.6	0.8
HCNH ⁺	17.6	–	–	–	–	–
DCNH ⁺	15.8	890.2	89.0	8.9	1.8	0.9
HOCO ⁺	12.7	–	–	–	–	–
DOCO ⁺	11.2	752.8	75.3	7.5	1.5	0.7
H ₃ O ⁺	20.584	–	–	–	–	–
H ₂ DO ⁺	18.7	925.5	92.5	9.2	1.8	0.9
l-C₃H	11.5	–	–	–	–	–
l-C₃D	9.9	812.8	81.3	8.1	1.6	0.8
c-C ₃ H	12.0	–	–	–	–	–
c-C ₃ D	10.1	921.4	92.1	9.2	1.8	0.9
C ₂ H ₂	16.8	–	–	–	–	–
C ₂ HD	15.1	887.3	88.7	8.9	1.8	0.9

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Bold indicates molecules that have their corresponding D-analogues as known interstellar/circumstellar species

Table 7 Boltzmann factor (E/kT) for D-analogues of H-containing penta-atomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ K)	E/kT (at $T = 100$ K)	E/kT (at $T = 500$ K)	E/kT (at $T = 1000$ K)
CH ₄	28.1	0	0	0	0	0
CH ₃ D	26.3	920.5	92.0	9.2	1.8	0.9
SiH ₄	19.5	0	0	0	0	0
SiH ₃ D	18.2	671.7	67.2	6.7	1.3	0.7
CH ₂ NH	25.0	0	0	0	0	0
CHD ₂ NH	23.1	960.9	96.1	9.6	1.9	1.0
NH ₂ CN	21.4	0	0	0	0	0
NHDCN	19.4	1007.6	100.8	10.1	2.0	1.0
CH ₂ CO	19.9	0	0	0	0	0
CHDCO	18.2	870.9	87.1	8.7	1.7	0.9
HCOOH	21.3	0	0	0	0	0
DCOOH	19.1	1070.8	107.1	10.7	2.1	1.1
CH ₄ ⁻	15.1	–	–	–	–	–
CH ₃ D ⁻	13.6	749.0	74.9	7.5	1.5	0.7
HC(O)CN	16.6	–	–	–	–	–
DC(O)CN	14.7	965.7	96.6	9.7	1.9	1.0
HNCNH	18.8	–	–	–	–	–
DHCNH	17.2	820.1	82.0	8.2	1.6	0.8
CH ₃ O	22.8	–	–	–	–	–
CH ₂ DO	20.1	1340.8	134.1	13.4	2.7	1.3
NH ₄ ⁺	31.0	–	–	–	–	–
NH ₃ D ⁺	28.9	1025.3	102.5	10.2	2.0	1.0
HC₃N	16.6	–	–	–	–	–
DC₃N	14.9	889.2	88.9	8.9	1.8	0.9
HC ₂ NC	16.3	–	–	–	–	–
DC ₂ NC	14.6	870.9	87.1	8.7	1.7	0.9
HNC ₃	15.8	–	–	–	–	–
DNC ₃	14.1	834.6	83.5	8.3	1.7	0.8
CH ₂ CN	19.5	–	–	–	–	–
CHDCN	17.7	887.3	88.7	8.9	1.8	0.9
l-C ₃ H ₂	18.5	–	–	–	–	–
l-C ₃ HD	16.8	839.0	83.9	8.4	1.7	0.8
c-C₃H₂	18.5	–	–	–	–	–
c-C₃HD	16.7	918.9	91.9	9.2	1.8	0.9
C₄H	15.2	–	–	–	–	–
C₄D	13.5	869.3	86.9	8.7	1.7	0.9
H ₂ COH ⁺	25.4	–	–	–	–	–
HDCOH ⁺	23.5	974.8	97.5	9.7	1.9	1.0

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Bold indicates molecules that have their corresponding D-analogues as known interstellar/circumstellar species

Table 8 Boltzmann factor (E/kT) for D-analogues of H-containing hexa-atomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ K)	E/kT (at $T = 100$ K)	E/kT (at $T = 500$ K)	E/kT (at $T = 1000$ K)
CH₃OH	32.1	–	–	–	–	–
CH₂DOH	30.1	1011.4	101.1	10.1	2.0	1.0
CHD₂OH	28.1	2015.9	201.6	20.2	4.0	2.0
CD₃OH	26.1	3030.9	303.1	30.3	6.1	3.0
CH ₃ SH	28.8	–	–	–	–	–
CH ₂ DSH	26.8	988.4	98.8	9.9	2.0	1.0
C ₂ H ₄	32.0	–	–	–	–	–
C ₂ H ₃ D	30.1	960.9	96.1	9.6	1.9	1.0
H₂C₄	22.4	–	–	–	–	–
HDC₄	20.7	876.9	87.7	8.8	1.7	0.9
HNCHCN	24.9	–	–	–	–	–
DNCHCN	22.8	1058.2	105.8	10.6	2.1	1.1
SiH ₃ CN	20.7	–	–	–	–	–
SiH ₂ DCN	19.3	717.1	71.7	7.2	1.4	0.7
CH₃CN	28.4	–	–	–	–	–
CH₂DCN	26.5	981.4	98.1	9.8	2.0	1.0
CH ₃ NC	28.3	–	–	–	–	–
CH ₂ DNC	26.3	1001.0	100.1	10.0	2.0	1.0
H ₂ CCNH	27.5	–	–	–	–	–
HDCCNH	25.7	911.3	91.1	9.1	1.8	0.9
HC ₄ N	18.3	–	–	–	–	–
DC ₄ N	16.6	862.1	86.2	8.6	1.7	0.9
c-H ₂ C ₃ O	23.8	–	–	–	–	–
c-HDC ₃ O	21.9	922.4	92.2	9.2	1.8	0.9
HCCC(O)H	23.3	–	–	–	–	–
DCCC(O)H	21.5	905.7	90.6	9.1	1.8	0.9
HC(O)NH ₂	28.4	–	–	–	–	–
DC(O)NH ₂	26.5	980.5	98.1	9.8	2.0	1.0
H(CC) ₂ H	23.4	–	–	–	–	–
H(CC) ₂ D	21.7	889.2	88.9	8.9	1.8	0.9
HC ₅	18.2	–	–	–	–	–
DC ₅	16.6	842.5	84.2	8.4	1.7	0.8
HC ₃ NH ⁺	24.2	–	–	–	–	–
DC ₃ NH ⁺	22.4	920.2	92.0	9.2	1.8	0.9

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Bold indicates molecules that have their corresponding D-analogues as known interstellar/circumstellar species

Table 9 Boltzmann factor (E/kT) for D-analogues of H-containing hepta-atomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ K)	E/kT (at $T = 100$ K)	E/kT (at $T = 500$ K)	E/kT (at $T = 1000$ K)
CH ₂ CH(OH)	35.3	–	–	–	–	–
CHDCH(OH)	33.3	1008.6	100.9	10.1	2.0	1.0
c-C ₂ H ₄ O	35.9	–	–	–	–	–
c-C ₂ H ₃ D	33.9	1031.3	103.1	10.3	2.1	1.0
HC(O)CH ₃	34.7	–	–	–	–	–
HC(O)CH ₂ D	32.8	967.2	96.7	9.7	1.9	1.0
CH ₂ CH(CN)	31.9	–	–	–	–	–
CHDCH(CN)	29.9	997.2	99.7	10.0	2.0	1.0
CH₃CCH	34.8	–	–	–	–	–
CH₂DCCH	32.8	977.3	97.7	9.8	1.9	1.0
CH₃CCD	33.0	894.3	89.4	8.9	1.8	0.9
CH ₃ NH ₂	40.1	–	–	–	–	–
CH ₂ DNH ₂	38.1	1003.5	100.3	10.0	2.0	1.0
HC₅N	23.3	–	–	–	–	–
DC5N	21.5	888.6	88.9	8.9	1.8	0.9
HC ₆	21.9	–	–	–	–	–
DC ₆	20.2	871.9	87.2	8.7	1.7	0.9
HC ₆ [–]	21.2	–	–	–	–	–
DC ₆ [–]	19.8	737.0	73.7	7.4	1.5	0.7

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Bold indicates molecules that have their corresponding D-analogues as known interstellar/circumstellar species

Table 10 Boltzmann factor (E/kT) for D-analogues of H-containing octa-atomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ K)	E/kT (at $T = 100$ K)	E/kT (at $T = 500$ K)	E/kT (at $T = 1000$ K)
CH ₃ COOH	38.7	–	–	–	–	–
CH ₃ COOD	36.6	1090.4	109.0	10.9	2.2	1.1
HCOOCH₃	38.9	–	–	–	–	–
HCOOCH₂D	36.8	1012.7	101.3	10.1	2.0	1.0
HOCH ₂ C(O)H	37.9	–	–	–	–	–
HOCH ₂ C(O)D	35.9	1018.4	101.8	10.2	2.0	1.0
H ₃ C ₄ N	34.9	–	–	–	–	–
H ₂ DC ₄ N	32.9	978.9	97.9	9.8	1.9	1.0
CH ₂ CHCHO	38.5	–	–	–	–	–
CH ₂ CDCHO	36.5	1011.1	101.1	10.1	2.0	1.0
CH ₂ C ₂ HCN	34.4	–	–	–	–	–
CHDC ₂ HCN	32.6	954.0	95.4	9.5	1.9	0.9
H ₂ C ₆	29.0	–	–	–	–	–
HDC ₆	27.3	884.5	88.4	8.8	1.8	0.9
CH ₃ CHNH	42.9	–	–	–	–	–
CH ₃ CDNH	41.0	977.3	97.7	9.8	1.9	1.0
(NH ₂) ₂ CO	38.372	–	–	–	–	–
NH ₂ CONHD	36.3	1017.1	101.7	10.2	2.0	1.0
NH ₂ CH ₂ CN	39.7	–	–	–	–	–
NHDCH ₂ CN	37.6	1063.2	106.3	10.6	2.1	1.1
HC ₇	44.5	–	–	–	–	–
DC ₇	23.4	10,619.7	102.0	106.2	21.2	10.6
HC ₆ H	29.5	–	–	–	–	–
DC ₆ H	27.8	878.8	87.9	8.8	1.8	0.9

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Bold indicates molecules that have their corresponding D-analogues as known interstellar/circumstellar species

Table 11 Boltzmann factor (E/kT) for D-analogues of H-containing nona-atomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ K)	E/kT (at $T = 100$ K)	E/kT (at $T = 500$ K)	E/kT (at $T = 1000$ K)
(CH ₃) ₂ O	49.9	–	–	–	–	–
CH ₃ OCH ₂ D	47.9	1002.6	100.3	10.0	2.0	1.0
CH ₃ CH ₂ CN	46.5	–	–	–	–	–
CH ₃ CHDCN	44.5	1036.7	103.7	10.4	2.1	1.0
CH ₃ CH ₂ OH	50.0	–	–	–	–	–
CH ₃ CHDOH	48.0	1046.2	104.6	10.5	2.1	1.0
CH ₃ C(O)NH ₂	45.9	–	–	–	–	–
CH ₂ DC(O)NH ₂	44.0	968.5	96.8	9.7	1.9	1.0
CH ₃ CH ₂ SH	46.8	–	–	–	–	–
CH ₃ CHDSH	44.7	1043.0	104.3	10.4	2.1	1.0
CH ₃ C ₄ H	41.2	–	–	–	–	–
CH ₂ DC ₄ H	39.3	977.3	97.7	9.8	1.9	1.0
HC ₇ N	30.1	–	–	–	–	–
DC ₇ N	28.4	883.9	88.4	8.8	1.8	0.9
CH ₃ CHCH ₂	49.9	–	–	–	–	–
CH ₂ CHCH ₂	48.0	984.6	98.5	9.8	2.0	1.0
HC ₈	29.0	–	–	–	–	–
DC ₈	27.2	875.0	87.5	8.7	1.7	0.9
HC ₈ [–]	28.3	–	–	–	–	–
DC ₈ [–]	26.8	744.9	74.5	7.4	1.5	0.7

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Table 12 Boltzmann factor (E/kT) for D-analogues of H-containing deca-atomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ K)	E/kT (at $T = 100$ K)	E/kT (at $T = 500$ K)	E/kT (at $T = 1000$ K)
(CH ₃) ₂ CO	52.3	–	–	–	–	–
CH ₃ COCH ₂ D	50.3	1002.3	100.2	10.0	2.0	1.0
HOCH ₂ CH ₂ OH	53.1	–	–	–	–	–
HOCH ₂ CHDOH	51.0	1049.0	104.9	10.5	2.1	1.0
CH ₃ CH ₂ CHO	52.8	–	–	–	–	–
CH ₂ DCH ₂ CHO	50.8	1000.7	100.1	10.0	2.0	1.0
CH ₃ C ₄ CN	41.3	–	–	–	–	–
CH ₂ DC ₄ CN	39.4	977.7	97.8	9.8	1.9	1.0

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Table 13 Boltzmann factor (E/kT) for D-analogues of H-containing undeca-atomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ k)	E/kT (at $T = 100$ K)	E/kT (at $T = 500$ K)	E/kT (at $T = 1000$ K)
HC ₉ N	37.5	–	–	–	–	–
DC ₉ N	35.7	881.7	88.2	8.8	1.8	0.9
CH ₃ C ₆ H	47.6	–	–	–	–	–
CH ₂ DC ₆ H	45.7	977.7	97.8	9.8	1.9	1.0
CH ₃ CH ₂ OCHO	56.8	–	–	–	–	–
CH ₂ DCH ₂ OCHO	54.8	998.5	99.8	1.0	2.0	1.0
CH ₃ OC(O)CH ₃	56.1	–	–	–	–	–
CH ₂ DOC(O)CH ₃	54.1	987.8	98.8	9.9	2.0	1.0

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Table 14 Boltzmann factor (E/kT) for D-analogues of H-containing dodeca-atomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ K)	E/kT (at $T = 100$ K)	E/kT (at $T = 500$ K)	E/kT (at $T = 1000$ K)
C ₂ H ₅ OCH ₃	67.7	–	–	–	–	–
CH ₂ DCH ₂ OCH ₃	65.7	1001.3	100.1	10.0	2.0	1.0
iso-C ₃ H ₇ CN	64.2	–	–	–	–	–
iso-C ₃ H ₆ DCN	62.2	1012.7	101.3	10.1	2.0	1.0
C ₃ H ₇ CN	64.4	–	–	–	–	–
C ₃ H ₆ DCN	62.4	1002.9	100.3	10.0	2.0	1.0
C ₆ H ₆	62.9	–	–	–	–	–
C ₆ H ₅ D	54.1	4386.2	438.6	43.9	8.8	4.4

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Table 15 Boltzmann factor (E/kT) for D-analogues of H-containing trideca-atomic species and the corresponding ZPE

Molecule	ZPE (kcal/mol)	* ΔT (K)	E/kT (at $T = 10$ K)	E/kT (at $T = 100$ K)	E/kT (at $T = 500$ K)	E/kT (at $T = 1000$ K)
HC ₁₁ N	42.8	–	–	–	–	–
DC ₁₁ N	41.0	883.5	88.3	8.8	1.8	0.9

*The difference in the ZPE of a molecule and its D-analogue expressed in terms of temperature

Table 16 The dependence of D/H ration on Boltzmann factor

Boltzmann factor	CH ₂ DCCH/CH ₃ CCH ^a
96.9	0.061
64.6	0.054
48.4	0.051
Boltzmann factor	CH ₃ CCD/CH ₃ CCH ^a
88.7	0.015
59.1	0.014
44.3	0.013
Boltzmann factor	HDCO/H ₂ CO ^b
126.1	0.034
49.1	0.03
17.7	0.01
Boltzmann factor	D ₂ CO/H ₂ CO ^b
254.0	0.02
98.8	0.01
35.6	0.001

^aGerin et al. [56]

^bRoberts and Millar [19]

References

1. A C Cheung, D M Rank, C H Townes, D D Thornton and W J Welch *Phys Rev Lett* **25** 1701 (1968)
2. A C Cheung, D M Rank, C H Townes, D D Thornton and W J Welch *Nature* **221** 626–628 (1969)
3. L E Synder, D Buhl, B Zuckerman and P Palmer *Phys Rev Lett* **22** 679 (1969)
4. R W Wilson, K B Jefferts and A A Penzias *ApJ* **161** L43 (1970)
5. J A Ball, C A Gottlieb, A E Lilley and H E Radford *ApJ* **162** L203 (1970)
6. C P Endres, S Schlemmer, P Schilke, J Stutzki and H S P Müller *J. Mol. Spectrosc* **327** 95 (2016)
7. http://www.astrochymist.org/astrochymist_ism.html. Accessed in September 2018.
8. E E Etim and E Arunan *Planex Newsletter* **5** 16 (2015)
9. (a) A J Markwick, S B Charnley, H M Butner and T J Millar *ApJ* **627** L117 (2005). (b) G Wlodarczak *Journal of Molecular Structure* **347** 131 (1995)
10. B E Turner and B Zuckerman *ApJ* **225** L75 (1978)
11. B E Turner *ApJ* **362** L29 (1990)
12. S Lacour, M K Andre and P Sonnentrucker *A&A* **430** 967 (2005)
13. M Gerin, F Combes and G Wlodarczak *ApJ* **259** L35 (1992a)
14. J Cernicharo, B Tercero and A Fuente *ApJ* **771** L10 (2013)
15. D C Lis, E Roueff and M Gerin *ApJ* **571** L55 (2002)
16. K B Jefferts, A A Penzias and R W Wilson, *ApJ* **179** L57 (1973)
17. J E Lee and E A Bergin *ApJ* **799** 104 (2015)
18. H Roberts, G A Fuller, T J Millar, J Hatchell and J V Buckle *A&A* **381** 1026 (2002)
19. H Roberts and T J Millar *A&A* **471** 849 (2007)
20. T J Millar *Astronomy and Geophysics* **46**, 2, 2.29–2.32 (2005) <https://doi.org/10.1111/j.1468-4004.2005.46229.x>
21. C Ceccarelli *Planetary and Space Science* **50** 1267 (2002)
22. L Spitzer, J F Drake and E B Jenkins *ApJ* **181** L116 (1973)
23. V Taquet, C Ceccarelli and C Kahane *ApJL* **748** L3
24. M Emprechtinger, P Caselli, N H Volgenau, J Stutzki and M C Wiedner *A&A* **493** 89 (2009)

25. L Dore, P Caselli, S Beninatil, T Bourke, P C Myers and G Cazzoli *A&A* **413** 1177 (2004)
26. B Parise, C Ceccarelli, A G G M Tielens, A Castets, E Caux, B Lefloch and S Maret *A&A* **453** 949 (2006)
27. D Rehder, *Chemistry in Space*. Wiley, Weinheim, Germany (2010)
28. T J Millar, H Roberts, A J Markwick and S B Charnley *Philos. Trans. R. Soc. Lond.* **358** 2535 (2000)
29. A G G M Tielens *A&A* **119** 177 (1983)
30. S Kong, P Caselli, J C Tan, V Wakelam and O. Sipila, Submitted, [arXiv:1312.0971\[astro-ph.SR\]](https://arxiv.org/abs/1312.0971) (2015)
31. P M Solomon and N J Woolf *ApJ* **180** L89 (1973)
32. M J Frisch, G W Trucks and H B Schlegel *G09:RevC.01*, Gaussian, Inc., Wallingford CT (2009)
33. L A Curtiss, P C Redfern and K Raghavachari *JChPh* **126** 084108 (2007a)
34. L A Curtiss, P C Redfern and K Raghavachari, *JChPh* **127** 124105 (2007b)
35. E E Etim and E Arunan *European Physical Journal Plus* **131** 448 (2016)
36. E E Etim and E Arunan, *Advances in Space Research* **59** 1161 (2017)
37. E E Etim, P Gorai, A Das, S K Chakrabarti and E Arunan *The Astrophysical Journal* **832** 144 (2016)
38. E E Etim, E J Inyang, O A Ushie, I E Mbakara, C Andrew and U Lawal *FUW Trends in Science and Technology Journal* **2** 665 (2017)
39. E E Etim, G Gorai, A Das and E Arunan *Astrophysics and Space Science* **363** 6 (2018a)
40. E E Etim, P Gorai, A Das, S K Chakrabarti and E Arunan, *Advances in Space Research* **61** 2870–2880 (2018b)
41. J M L Martin and G de Oliveira *J Chem Phys* **111** 1843 (1999)
42. A Coutens, C Vastel, and E Caux *A&A* **539** 132 (2012)
43. H M Butner, S B Charnley and C Ceccarelli *ApJ* **659** L137 (2007)
44. C Vastel, T G Phillips, C Ceccarelli and J Pearson *ApJ* **593** L97 (2003)
45. R Stark, F van der Tak and E F van Dishoeck *ApJ* **521** L67 (1999)
46. E van Dishoeck, G A Blake, D J Jansen and T D Groesbeck *ApJ* **447** 760 (1995)
47. N Marcelino, J Cernicharo, E Roueff, M Gerin and R Mauersberger *ApJ* **620** 308 (2005)
48. J Hatchell *A&A* **403** L25 (2003)
49. L Loinard, A Castets, C Ceccarelli, E Caux and A G G M Tielens *ApJ* **552** L163 (2001)
50. N Sakai, T Sakai, T Hirota and S Yamamoto *ApJ* **702** 1025 (2009)
51. D A Howe, T J Millar, P Schike and C M Walmsley *Mont. Not. R. Astron. Soc.* **267** 59 (1994)
52. J M Macleod, L W Avery and N W Broten *ApJ* **251** L33 (1981)
53. B E Turner *ApJ* **347** L39 (1989)
54. B Praise, A Castets and E Herbst *A&A* **416** 159 (2004)
55. L H Coudert, B J Drouin and B Tercero *ApJ* **779** 119 (2013)
56. M Gerin, F Combes, G Wlodarczak, P Encrenaz and C Laurent *ApJ* 253 L29 (1992b)

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