Chemistry of TMC-1 with multiply deuterated species and spin chemistry of \( \text{H}_2 \), \( \text{H}_2^+ \), \( \text{H}_3^+ \) and their isotopologues

L. Majumdar\(^1,2\)\(^\star\), P. Gratier\(^1\), M. Ruaud\(^1\), V. Wakelam\(^1\), C. Vastel\(^3,4\), O. Sipilä\(^5\), F. Hersant\(^1\), A. Dutrey\(^1\), S. Guilloteau\(^1\)

\(^1\)Laboratoire d’astrophysique de Bordeaux, Univ. Bordeaux, CNRS, B18N, allée Geoffroy Saint-Hilaire, 33615 Pessac, France
\(^2\)Indian Centre For Space Physics, 43 Chalantika, Garia Station Road, Kolkata, 700084, India
\(^3\)Université de Toulouse, UPS-OMP, IRAP, Toulouse, France
\(^4\)CNRS, IRAP, 9 Av. Colonel Roche, BP 44346, F-31028 Toulouse Cedex 4, France
\(^5\)Max-Planck-Institute for Extraterrestrial Physics (MPE), Giessenbachstr. 1, D-85748 Garching, Germany

Accepted XXX. Received YYY; in original form ZZZ

ABSTRACT

Deuterated species are unique and powerful tools in astronomy since they can probe the physical conditions, chemistry, and ionization level of various astrophysical media. Recent observations of several deuterated species along with some of their spin isomeric forms have rekindled the interest for more accurate studies on deuterium fractionation. This paper presents the first publicly available chemical network of multiply deuterated species along with spin chemistry implemented on the latest state-of-the-art gas-grain chemical code ‘NAUTILUS’. D/H ratios for all deuterated species observed at different positions of TMC-1 are compared with the results of our model, which considers multiply deuterated species along with the spin chemistry of light hydrogen bearing species \( \text{H}_2 \), \( \text{H}_2^+ \), \( \text{H}_3^+ \) and their isotopologues. We also show the differences in the modeled abundances of non-deuterated species after the inclusion of deuteration and spin chemistry in the model. Finally, we present a list of potentially observable deuterated species in TMC-1 awaiting detection.

Key words: Astrochemistry, spectra, ISM: molecules, ISM: abundances, ISM: evolution, methods: statistical

1 INTRODUCTION

Until now (as of February 2016), almost 200 molecules have been detected in the interstellar medium or circumstellar shells (as listed by CDMS\(^1\)). In addition, several deuterated species have been detected in various astrophysical media. Among them there were several detections:

- in dark clouds: \( \text{DCO}^+ \) (van der Tak et al. 2009; Guelin et al. 1977), DNC (van der Tak et al. 2009; Turner & Zuckerman 1978), HDCO (Loren & Wootten 1985), \( \text{D}_2\text{CO} \) (Turner 1990);
- in pre-stellar cores: \( \text{D}_2\text{CO} \) (Bacmann 2004), \( \text{H}_2\text{D}^+ \) (Stark et al. 1999; Caselli et al. 2003; Vastel et al. 2006; Caselli et al. 2008; Parise et al. 2011), \( \text{D}_2\text{H}^+ \) (Vastel et al. 2004; Parise et al. 2011), \( \text{N}_2\text{D}^+ \) (Miettinen et al. 2012), \( \text{NHD}_2 \) (Roueff et al. 2000);
- towards low-mass and high-mass protostars: \( \text{D}_2\text{CO} \), HDCO (Bergman et al. 2011), DCOOCH\(_3\) (Demyk et al. 2010; Margulès et al. 2010), \( \text{HDO} \) (Coutens et al. 2012, 2014), \( \text{D}_2\text{O} \) (Vastel et al. 2010), OD (Parise et al. 2012);
- in protoplanetary disks: DCN, \( \text{DCO}^+ \) (van Dishoeck et al. 2003; Guilloteau et al. 2006; Qi et al. 2008; Öberg et al. 2015), \( \text{N}_2\text{D}^+ \) (Huang & Öberg 2015) and HD (Bergin et al. 2013), the main deuterium reservoir.

The detection of \( \text{ND}_3 \) in the Barnard 1 cloud (Lis et al. 2002) and \( \text{CD}_3\text{OH} \) in IRAS 16293-2422 (Parise et al. 2004) has shown the possibility of detecting multiply deuterated species in cold and high density regions. These observations opened new questions regarding the highest deuterium fractionation level that can occur in cold and high density regions. We have already entered into a new era of astrochemistry where powerful, high-sensitive, and high-resolution observational facilities like Atacama Large Millimetre Array (ALMA) are in operation. Thus, there is no doubt that many more singly and multiply deuterated species are going to be observed. By studying the chemistry of these deuterated species, we will be able to diagnose various cold and dense...
environments where stars are born (see for instance Albertsson et al. (2013) and references therein).

Deuterium chemistry in the gas phase is believed to be controlled by the isotopic exchange reactions between HD and H$_2^+$, as the reservoir of deuterium is initially locked in the form of HD, via the reaction

\[
\text{H}^+_2 + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2 + 232 \text{ K}. \tag{1}
\]

The above backward reaction is endothermic by 232 K and is thus negligible at low temperatures (less than 20 K). H$_2$D$^+$ can react with other abundant molecules (such as CO, N$_2$) to transfer D-atoms to other species (Ceccarelli et al. 2014). However, this reaction scheme becomes complicated if we consider nuclear spin states for the protonated species. Molecular hydrogen (H$_2$) has two distinct spin states under the permutation of identical protons. An ortho state (ortho-H$_2$) when the nuclear spin wave function is symmetric and a para state (para-H$_2$) when the nuclear spin wave function is antisymmetric. The energy difference between the rotational ground states of ortho-H$_2$ and para-H$_2$ is 170.5 K (Hugo et al. 2009). Consequently if we consider the reaction (1) in backward direction with ortho-H$_2$ and ortho-H$_2$D$^+$, the reaction becomes exothermic by about 24 K with para-H$_2$D$^+$ as one of the products. As a result, the ortho-to-para ratio of H$_2$ ($\text{H}_2(\text{opr(H}_2^\text{)})$ from now on in the text) becomes an important parameter in controlling the deuterium fractionation even at low temperature (Flower et al. 2006).

The study of deuterium chemistry is a challenging task. The reason is the unavailability of any public database which provides a network with detailed deuterium chemistry along with spin chemistry of important protonated species. In the past, many authors have studied deuteron fractionation by cloning reactions involving hydrogen-bearing species (Aikawa et al. 2012), Albertsson et al. (2013), Albertsson et al. (2014a), Das et al. (2015), Majumdar et al. (2014a), Majumdar et al. (2014b), Roberts & Millar (2000a), Roberts & Millar (2000b), Sipili et al. (2013), Taquet et al. (2014).

Among these studies, Roberts & Millar (2000a, b) reported one of the first gas-grain chemical models for deuteration, where the chemistry was limited to singly and a few doubly deuterated species along with surface chemistry only for H$_2$ and HD molecules. Aikawa et al. (2012) considered the chemistry of multiply deuterated species both in the gas phase and on the grain surface but without considering spin-state chemistry. Similar models were also published in Albertsson et al. (2013), Das et al. (2015), Majumdar et al. (2014a, b) where multiple deuteration was taken into account without considering spin-state chemistry. Sipili et al. (2013) and Taquet et al. (2014) reported deuteron fractionation models with gas-grain chemistry of deuterated species up to four atoms and the spin chemistry of H$_2$, H$_2^+$, H$_3^+$ and their deuterated isotopologues. More recently, Albertsson et al. (2014a) have considered deuterated species with 7 atoms whereas Sipili et al. (2015) have considered 6 atoms. Both works include spin chemistry. In many cases, deuteration was studied by restricting the number of atoms in the deuterated species, without studying spin chemistry or grain chemistry in detail. The main goal of the present paper is to present a more comprehensive deuteron fractionation model, which includes spin chemistry of H$_2$, H$_2^+$, H$_3^+$ and their deuterated isotopologues, the chemistry of multiply deuterated species and surface chemistry described in detail in Section 2. This network is the first of its kind to be made public (http://kida.obs.u-bordeaux1.fr/). This paper is structured as follows. In Section 2, we present our new deuteron fractionation model. We give a detailed description of our deuteronated network (deuspin.kida.uva.2016 from now in the rest of the text) along with its implementation in the gas-grain code NAUTILUS. We benchmark our model with the other published works. In Section 3, we discuss the general trends of deuterium chemistry. We compare our results with observations and discuss the effect of inclusion of deuspin.kida.uva.2016 on the predicted modelled abundances for several well observed non-deuterated species, and discuss some new observable deuterated species in dark clouds. Finally, in Section 4 we draw our conclusions.

2 CHEMICAL MODEL AND NETWORK

2.1 The NAUTILUS chemical model

To study deuteration together with spin chemistry, we use the NAUTILUS gas-grain chemical model (Rebousin et al. 2014; Ruaud et al. 2015; Wakelam et al. 2015b) under typical cold dense cloud conditions. NAUTILUS is a state-of-the-art chemical code, which can be applied to simulate various types of astronomical environments. Applications of this gas-grain chemical code have already been reported for dense clouds (Wakelam et al. 2015b), low-mass protostellar envelopes (Bottinelli et al. 2014; Majumdar et al. 2016), and the outer regions of protoplanetary discs (Dutrey et al. 2011). NAUTILUS computes the abundances of species (e.g. atoms, ions, radicals, molecules) as a function of time in the gas phase and on the surfaces of interstellar grains. All the equations and the chemical processes included in the model are described in detail in Ruaud et al. (2015). To include the effect of spin chemistry, we then modified all the variables in NAUTILUS relative to H$_2$ in terms of ortho-H$_2$ and para-H$_2$ (from now we will use o, p and m to represent ortho, para, and meta states 2 in the rest of the text).

In the model, several types of chemical reactions are considered in the gas phase by following the kida.uva.2014 chemical network of Wakelam et al. (2015a). These reactions can be classified in four categories: bimolecular reactions between neutral species, between charged species and between neutral and charged species, unimolecular reactions (i.e. photoreactions with direct UV photons and UV photons produced by the deexcitation of H$_2$ excited by the cosmic ray particles), and direct ionisation and dissociation by cosmic ray particles. Here the interstellar ice is modelled by a one phase rate equation approach (Hasegawa et al. 1992), i.e. there is no differentiation between the species in the mantle and on the surface. In our model, the gas and the grains are coupled to each other.

---

2 Here ortho, para and meta stand for different nuclear spin symmetries for a species. For example, H$_2$ has two spin states i.e. ortho (I=1 and g$_z$=3), para (I=0 and g$_z$=1) whereas D$_2^+$ has three spin states i.e. ortho (I=1,2 and g$_z$=16), para (I=0, g$_z$=1) and meta (I=3 and g$_z$=10). Among others, H$_2$O$^+$, H$_2$O$^+$, D$_2$O$^+$, H$_3$O$^+$, D$_3$O$^+$, H$_4$D$^+$, D$_4$H$^+$ have only ortho and para spin states. Here, I and g$_z$ stand for nuclear spin angular momenta and nuclear spin statistical weights respectively. See Hugo et al. (2009) for more details.
via four interaction processes: physisorption of gas phase species onto grain surfaces, diffusion of the accreted species, reaction at the grain surface, and evaporation to the gas phase. These evaporation processes can also be of various types. The evaporation mechanisms considered here are: thermal (which are inefficient at dense cloud conditions), induced by cosmic-rays (Hasegawa & Herbst 1993), and chemical as defined by Garrod et al. (2007). According to Wakelam et al. (2014), photodesorption induced by cosmic-ray secondary photons is less efficient than chemical desorption. We do not take into account the cosmic-ray induced diffusion mechanism (CRD) since for high visual extinction, effect of CRD is negligible (see Reboussin et al. 2014)

To simulate deuterium chemistry together with spin chemistry in dark clouds, the model is used with homogeneous physical conditions and integrated over 10^7 yrs. The initial elemental abundances reported in Table 1 are the same as in Hincelin et al. (2011) with deuterium and fluorine elemental abundances relative to hydrogen of 1.6 × 10^{-5} (Linsky et al. 2006) and 6.68 × 10^{-9} (Neufeld et al. 2005) respectively. The species are assumed to be initially in an atomic form as in diffuse clouds except for hydrogen and deuterium, which are initially in H_2 and HD forms respectively. All elements (e.g. C, S, Si, Fe, Na, Mg, Cl, and P) with an ionization potential lower than 13.6 eV are initially singly ionised. For our standard model, we have used a C/O ratio of 0.7 (i.e. the oxygen elemental abundance is 2.4 × 10^{-4}). The ortho-to-para H_2 ratio is initially set to its statistical value of 3. The model was run with a dust and gas temperature of 10 K, a total proton density of 2 × 10^4 cm^{-3}, a cosmic-ray ionization rate of 1.3 × 10^{-17} s^{-1}, and a visual extinction of 30 mag.

Figure 1. Gas-phase abundance of ortho and para H_2 with respect to n_H as a function of time.

Figure 2. Gas-phase abundance of ortho and para forms of H_3^+ with respect to n_H as a function of time.

Figure 3. Gas-phase abundance of various isotopologues of H_3^+ with respect to n_H as a function of time.

2.2 Developed chemical network from KIDA 2014

The initial gas-phase chemical network was adapted from the kida.uva.2014 network\(^3\) (Wakelam et al. (2015a), which includes 489 species composed of 13 elements (H, He, C, N, O, Si, S, Fe, Na, Mg, Cl, P, F) linked with 7509 reactions. Our starting network includes various updates of the HCN/HNC chemistry by Loison et al. (2014b), carbon chemistry by Loison et al. (2014a), branching ratios for reactions forming C_3H^+(0,1), C_4H^+(0,1), and C_5H_2^+(0,1) from Chabot et al. (2013) and also various new data sheets from KIDA database. This network has been extended to include the spin states of H_2, H_2^+ and H_3^+ and their deuterated isotopologues.

\(^3\) http://kida.obs.uj-bordeaux1.fr/
To add the spin states of $^2\text{H}_2$, $^2\text{H}_2^+$, $^2\text{H}_3^+$ into kida.uva.2014, we applied the method described by Sipilä et al. (2015) in which the branching ratios are calculated using Oka’s method (Oka 2004). In this method, selection rules for reactive collisions involving different spin species are derived using angular momentum algebra. Branching ratios resulting from this method correspond to pure nuclear spin statistical weights under the assumption that the nuclei are completely mixed in the reaction. Following Sipilä et al. (2015), we applied the same method to all reactions except charge-transfer reactions, where we assume that spin states are conserved. We have added an activation energy of 170 K to the $\gamma$ coefficient (of the temperature dependent rate coefficients $k(T) = \alpha(T/300)^n e^{-\gamma/T}$) for the reactions where $^2\text{H}_2$ is formed (see Albertsson et al. (2014a) for similar methods). The formation of $^2\text{H}_2$ and $^2\text{H}_2$ in reactions that involve species, whose spin states are not tracked (i.e., other than $^2\text{H}_2$, $^2\text{H}_2^+$, and $^2\text{H}_3^+$), is handled with the “recombination” approach described in detail in Sect. 2.3.1 of Sipilä et al. (2015). Our deuteration routine is similar to the one described in Albertsson et al. (2013) where deuterons are substituted for protons in the reactions, and branching ratios are calculated assuming complete scrambling. Here, we do not consider the spin chemistry of multiply deuterated species. For multiply deuterated species, the calculation of nuclear spin-state branching ratios is more complicated than for hydrogenated species since there is no one-to-one correspondence between angular momentum and symmetry representations. In the present work, we include the spin-state chemistry of the deuterated isotopologues involved in the $^2\text{H}_3^+ + \text{H}_2$ reaction system (which is essential in the present context) from Table III and IV of Hugo et al. (2009) complemented by important reactions involving light hydrogen and deuterium-bearing species ($^2\text{H}_2^+$, $^2\text{H}_2^+$, $^2\text{H}_2^+$, $^2\text{H}_3^+$, $^2\text{H}_3^+$, HD etc.) from Flower et al. (2004) and Walmsley et al. (2004). We also included dissociative recombination reactions for $^2\text{H}_2^+$ and its deuterated forms from Pagani et al. (2009). We have added all these important reactions as a supplementary file in the format of kida.uva.2014 network. In addition, we have added several important reactions from the literature: important reactions for deuterations from Albertsson et al. (2013) and water deuteration chemistry from Talukdar & Ravishankara (1996), Bergin et al. (1999). The entire network considered here is available on the KIDA4 website.

Our network for surface reactions and gas-grain interactions is based on the one from Garrod et al. (2007) with several additional processes from Ruaud et al. (2015). We extended our network to include deuteration by assuming statistical branching ratios (see for instance Taquet et al. (2014) for the same method). According to Taquet et al. (2013), although deuterated isotopologues have the higher mass, they seem to show similar binding energies to their hydrogenated counterpart. Therefore, by following these studies and also due to the unavailability of binding energies for deuterated species, we assume the same binding energies for all deuterated and non-deuterated species. Finally, we have nearly 7700 reactions on grain surface linked with the 111000 reactions in gas phase. If we sum up all these modifications, the despin.kida.uva.2016 network has the following characteristics:

- Spin chemistry of light hydrogen bearing species ($^2\text{H}_2$, $^2\text{H}_2^+$, $^2\text{H}_3^+$) essential to take into account the deuterium fractionation properly.
- Spin chemistry of $^2\text{H}_3^+$ + $^2\text{H}_2$ reacting system and their isotopologues from Hugo et al. (2009).
- Chemistry of multiply deuterated species.
- Extension of the kida.uva.2014 network to include full deuterium fractionation for species containing any of the 13 elements (H, He, C, N, O, Si, S, Fe, Na, Mg, Cl, P, F).
- All reactions are written in the the same format as in the KIDA database for the different types so that in future users can export this network easily without any confusion.

### 2.3 Benchmarking spin and deuterium chemistry

$^2\text{H}_2$, $^2\text{D}_2$, $^2\text{H}_3^+$, $^2\text{H}_2^+$, $^2\text{D}_2^+$, $^2\text{D}_3^+$ along with their spin isomers are the main species that dictate deuterium fractionation at low temperature (see for instance Ceccarelli et al. (2014) and references therein). In addition, deuterium fractionation strongly depends on the initial $\text{opr(H}_2)$ considered. Ortho and para $^2\text{H}_2$ are formed on the surfaces of interstellar

---

**Table 1. Initial abundances used in our model.**

| Element | Abundance relative to H |
|---------|-------------------------|
| $^2\text{H}_2$ | $3.75 \times 10^{-1}$ |
| $^2\text{H}_2$ | $1.25 \times 10^{-1}$ |
| He | $9 \times 10^{-2}$ |
| N | $6.2 \times 10^{-5}$ |
| O | $2.4 \times 10^{-4}$ |
| $\text{C}^+$ | $1.7 \times 10^{-4}$ |
| $\text{S}^+$ | $8 \times 10^{-8}$ |
| $\text{Si}^+$ | $8 \times 10^{-9}$ |
| Fe | $3 \times 10^{-9}$ |
| Na | $2 \times 10^{-9}$ |
| Mg | $7 \times 10^{-9}$ |
| P | $2 \times 10^{-10}$ |
| Cl | $1 \times 10^{-9}$ |
| F | $6.68 \times 10^{-9}$ |
| HD | $1.60 \times 10^{-5}$ |

---

4 [http://kida.obs.u-bordeaux1.fr/](http://kida.obs.u-bordeaux1.fr/)
Deuteration in cold cores

grains with a statistical ratio of 3:1 (Watanabe et al. 2010) and proton-exchange reactions in the gas phase then convert ortho-H$_2$ into para-H$_2$ (see Ceccarelli et al. (2014) and references therein for more discussions). In our model, we set an initial ratio of 3:1, in agreement with the experimental findings of Watanabe et al. (2010).

Before applying our model to a dense core (e.g. a TMC-1 like environment), we have benchmarked our model with other published works. The importance of spin-state chemistry is now widely accepted and has been tested in different stages of star formation process: diffuse clouds (Albertsson et al. 2013b), starless/prestellar cores (Pagani et al. (2009), Sipilä et al. (2013)) and protostellar systems (Taquet et al. (2013)). But in all cases spin-state chemistry was discussed to address particular issues by adopting various types of physical and chemical model making a direct comparison with our model very difficult. Two things can be compared though: the time scale for gas phase ortho-H$_2$ to para-H$_2$ conversion and abundance profiles for the two spin isomers of H$_2$. Fig. 1 shows the evolution of the ortho and para forms of H$_2$ in the gas-phase under dense core conditions. In our model, opr(H$_2$) becomes unity at around few times $10^5$ years and drops down to $10^{-3}$ or below after this. This is consistent with the result of Sipilä et al. (2013). Fig. 2 shows the evolution of the ortho and para forms of H$_3^+$. At $10^7$ years, the abundances of o-H$_3^+$ and p-H$_3^+$ are respectively $1.45 \times 10^{-09}$ and $1.73 \times 10^{-09}$. Sipilä et al. (2015) reported $2.00 \times 10^{-09}$ for o-H$_3^+$ under the same conditions.

To validate deuteron chemistry with associated spin chemistry, one basic test would be to compare the abundance profile of H$_3$D$^+$, D$_2$H$^+$, and D$_3^+$ with other models, since they are the major species controlling the deuteron fractionation. In order to perform a more realistic comparison, we ran our model with a similar initial opr(H$_2$)=$10^{-3}$ (i.e. kinetically equilibrated H$_2$ at low temperature, see Faure et al. (2013)) mentioned in Sipilä et al. (2015). Fig. 3 shows the abundances of all the isotopologues of H$_3$. At $10^7$ year, the abundances of o-H$_3$D$^+$, p-H$_3$D$^+$, o-D$_2$H$^+$, p-D$_2$H$^+$, o-D$_3^+$, p-D$_3^+$, m-D$_3^+$ are respectively $7.0 \times 10^{-10}$, $4.7 \times 10^{-10}$, $1.4 \times 10^{-10}$, $2.2 \times 10^{-11}$, $8.5 \times 10^{-12}$, $2.1 \times 10^{-13}$, $1.1 \times 10^{-13}$, in Fig. 3 of Sipilä et al. (2015), at $10^7$ year the reported abundances of o-H$_3$D$^+$ and p-D$_2$H$^+$ are respectively $4.0 \times 10^{-10}$ and $1.0 \times 10^{-11}$ under the same conditions, within a factor of 2 in agreement with our model. These differences are quite minor considering the differences in the starting networks (our work is based on kida.uva.2014 network whereas Sipilä et al. (2015) used osu_03_2008 network). But we have found the similar trend for all the isotopologues of H$_3$ as described in Sipilä et al. (2015) i.e. abundances are much higher at late times and this is attributed due to the depletion of their main reaction partners (e.g., CO) onto grain surfaces.

3 RESULTS AND DISCUSSION

3.1 General trends of deuteron chemistry

Using the model described above, we have investigated general trends of deuteron chemistry in the ISM. For this purpose, we selected two deuterated ions (DCO$^+$, N$_2$D$^+$) and several deuterated neutrals (NH$_2$D, DCN, DNC, HDCO, C$_2$D, C$_3$H$_2$D, C$_4$D, DC$_3$N, DC$_5$N, HDCS) as they have been observed in TMC-1 (see for instance Albertsson et al. 2013, and references therein). The abundances predicted by our model are shown in Fig. 4 as a function of time. Our model shows that the abundance of HCO$^+$ increases with time and its formation is very efficient after $10^6$ years due to the reaction between HOC$^+$ and o-H$_2$. Around this time, most of the gas phase H$_2$ is in the form of o-H$_2$. For DCO$^+$, we observe a very rapid fall in abundance between $10^6$ and $10^7$ years. Around this time, H$_2$O becomes an efficient destruction partner of DCO$^+$ since the formation of H$_2$O is very efficient (due to its highly abundant precursors H$_2$O$^+$ and o-H$_2$). After $10^6$ years, we observe an increase in abundance for DCO$^+$ due its efficient formation via the reaction o-H$_2$D$^+$ + CO. Since around this time o-H$_2$D$^+$ becomes highly abundant due to low opr(H$_2$). For the other deuterated ion N$_2$D$^+$, we observe a similar trend as with DCO$^+$. Between $10^5$ and $10^6$ years, N$_2$D$^+$ is destroyed efficiently by H$_2$O to form HDO$^+$. Similarly, after $10^6$ years, rapid formation of N$_2$D$^+$ is due to the efficient formation via the reaction of o-H$_2$D$^+$ + N$_2$.

Among the deuterated neutrals, we observe a slightly different behaviour for NH$_2$D and C$_2$H$_3$D as compared to deuterated ions. For NH$_3$ and NH$_2$D, we find an increase in the abundances after $10^6$ years. Around this time both NH$_3$ and NH$_2$D are formed via the dissociative recombination reactions of NH$_4^+$ and NH$_3$D$^+$. Both these ions are formed back again from various ion-molecular-chemical reactions of NH$_4$ and NH$_2$D by the ions HCO$^+$, H$_2$O$^+$. After $10^6$ years, the abundance of NH$_3$ drops quickly due its efficient depletion onto grain surface. But C$_3$H$_4$ and C$_3$H$_3$D show an increase in abundance in between $10^5$ and $10^6$ years due to their efficient formation via the barrier-less surface reactions s-H + s-C$_3$H$_4$ and s-H + s-C$_3$H$_3$D (here, ‘s’ represents species on the surface of grains). For the rest of the deuterated neutrals, we observe a general trend between $10^5$ and $10^6$ years i.e. abundances decrease. DNC, which is an isomer of DCN, shows a decrease in abundance around this time by several orders of magnitude. This is due to the efficient destruction of DNC by highly abundant p-H$_2^+$. HCN shows a peak in the abundance at $10^6$ year due to its high abundant precursors H$_2$CN$^+$ and p-H$_2$. HDCO is less destroyed than the other species at later times because its main destruction path is O + HDCO. DC$_2$N, DC$_5$N, HDCS, on the contrary, show a rapid fall in the abundance in between $10^5$ and $10^6$ years due to their efficient destruction by highly abundant p-H$_2^+$ and HCO$^+$. In Table 2, we have listed major reactions of production and destruction for these species at high and low opr(H$_2$) regimes.

3.2 Gas phase D/H ratios in TMC-1: comparison with observations and previous models

In the past, molecular D/H ratios observed towards TMC-1 were compared by various gas-grain chemical models (see for instance Roberts & Millar (2000b), Albertsson et al. (2013)). Roberts & Millar (2000b) have studied the chemical evolution with deuteron fractionation for temperatures 10–100 K and densities 3 × 10$^3$ – 3 × 10$^7$ cm$^{-3}$. They used a time-dependent gas-phase model based on the UMIST95 database. Their chemical network consists of >300 species linked by >5000 reactions, and only includes singly deuter-
Figure 4. Abundance with respect to \( n_H \) as a function of time of a selection of deuterated species observed in dense cores. Dotted lines correspond to non-deuterated species and solid lines correspond to deuterated species.

3.3 Effect of essential spin chemistry and deuteration on the observed non-deuterated species in TMC-1

One of the goals of this study is to quantify the effect of essential spin chemistry and deuteration on the abundances of non-deuterated species. For that, we have run two models: (1) with deuteration and spin chemistry (DS) and (2) without deuteration and spin chemistry (NoDS). We then focus on the gas-phase species observed in the cold core TMC-1. In Table 4, we report the observed abundances in TMC-1 collected by Agúndez & Wakelam (2013) together with the abundances predicted by our two models. To define the “chemical age” for TMC-1 for both models, we have calculated the mean confidence level following the prescription...
Table 2. Main reactions of production and destruction for observed deuterated species in TMC-1 cloud in the high and low opr(H$_2$) regimes. Here 10$^7$ yr corresponds to high opr(H$_2$) and 10$^6$ yr corresponds to low opr(H$_2$) regimes.

| Species | Formation ($10^7$ yr) | Destruction ($10^6$ yr) | Formation ($10^7$ yr) | Destruction ($10^6$ yr) |
|---------|-----------------------|------------------------|-----------------------|------------------------|
| NH$_2$D | NH$_3$D$^+$ + e$^-$ → H + NH$_2$D | H$_2$O$^+$ + NH$_2$D → NH$_3$D$^+$ + H$_2$O | NH$_3$D$^+$ + e$^-$ → H + NH$_2$D | H$^+$ + NH$_2$D → NH$_2$D$^+$ + H |
| HDCO   | O + CH$_2$D → HDCO + H | O + HDCO + H + CO + OD | → H + e-HDCO → HDCO | HCO$^+$ + HDCO → H$_2$CDO$^+$ + CO |
| DCN    | CH$_2$D$^+$ + HCN$^-$ → DCN + c-C$_2$H$_3$D$^+$ | CH$_3^+$ + DCN → C$_2$H$_4$D$^+$ | HDCN$^+$ + p-H$_2$ → p-H$_3^+$ + DCN | HCO$^+$ + HDCO → H$_2$CDO$^+$ + CO |
| DNC    | N + CHD → DNC + H | p-H$_3^+$ + DNC → H$_2$CN$^+$ + HD | C + NH$_2$D → DNC + H | HCO$^+$ + DNC → H$_2$CN$^+$ + HD |
| C$_4$D  | C + CHD → C$_3$D + H | C + C$_3$D → C$_2$D + CO | C$_2$H$_2$D$^+$ + e$^-$ → C$_2$D + H + H | C$_2$D + C$_3$ → C + D |
| C$_4$D  | C + c-C$_3$HD → C$_4$D + H | C + C$_3$D → C$_2$D + C | HCO$^+$ + C$_4$D → CH$_3$D + H | C + c-C$_3$HD → C$_4$D + H |
| DCO$^+$ | HCO$^+$ + D → DCO$^+$ + H | HCO$^+$ + D → DCO$^+$ + H | HCO$^+$ + D → DCO$^+$ + H | HCO$^+$ + D → DCO$^+$ + H |
| CH$_2$D$^+$ + O → DCO$^+$ + H | HCO$^+$ + D → DCO$^+$ + H | HCO$^+$ + D → DCO$^+$ + H | HCO$^+$ + D → DCO$^+$ + H |
| N$_2$D$^+$ | N$_2$H$^+$ + D → N$_2$D$^+$ + H | N$_2$D$^+$ + D → N$_2$D$^+$ + H | N$_2$D$^+$ + D → N$_2$D$^+$ + H | N$_2$D$^+$ + D → N$_2$D$^+$ + H |
| c-C$_3$H$_2$D$^+$ + e$^-$ → c-C$_3$H$_2$D + H | H + c-C$_3$H$_2$D → c-C$_3$H$_2$D + H | H + c-C$_3$H$_2$D → c-C$_3$H$_2$D + H | H + c-C$_3$H$_2$D → c-C$_3$H$_2$D + H |
| C$_3$H$_3$D$^+$ + H → c-C$_3$HD + N$_2$ | C + c-C$_3$D → C$_2$D + H | C + c-C$_3$D → C$_2$D + H | C + c-C$_3$D → C$_2$D + H |
| DC$_5$N | C + CHDCN → DC$_5$N + H | p-H$_3^+$ + DC$_5$N → HCN$_2$H$^+$ | p-H$_3^+$ + DC$_5$N → HCN$_2$H$^+$ | p-H$_3^+$ + DC$_5$N → HCN$_2$H$^+$ |
| HDCS   | S + CH$_2$D + H + HDCS | p-H$_3^+$ + H$_2$DCS$^+$ + H | S + CH$_2$D + H + HDCS | p-H$_3^+$ + H$_2$DCS$^+$ + H |

Deuteration in cold cores

Table 3. Comparison of observed D/H ratios for different positions of TMC-1 cloud with predictions from our model (T = 10 K, n$_H$ = 2 × 10$^7$ cm$^{-3}$, Time = 10$^6$ year), Roberts & Millar (2000a) and Albertsson et al. (2013).

| Species | Our model | Roberts & Millar (2000a) | Albertsson et al. (2013) | Observation | Observed Position & Refs. |
|---------|-----------|--------------------------|--------------------------|-------------|---------------------------|
| NH$_2$D/NH$_3$ | 4.3 × 10$^{-2}$ | 8.4 × 10$^{-2}$ | 5.2 × 10$^{-2}$ | 9.0 × 10$^{-3}$ | TMC1-N (4) |
| HDCO/H$_2$CO | 2.1 × 10$^{-2}$ | 4.2 × 10$^{-2}$ | 2.3 × 10$^{-2}$ | 5.9 × 10$^{-3}$ | TMC1-CP (2) |
| DCN/HNC | 0.4 × 10$^{-2}$ | 0.9 × 10$^{-2}$ | 2.4 × 10$^{-2}$ | 2.3 × 10$^{-2}$ | TMC1-CP (3) |
| D$_2$C/H$_2$C | 0.6 × 10$^{-2}$ | 1.5 × 10$^{-2}$ | 1.6 × 10$^{-2}$ | 1.5 × 10$^{-2}$ | TMC1-CP (2) |
| C$_2$D/C$_2$H | 0.4 × 10$^{-2}$ | 1.1 × 10$^{-2}$ | 1.5 × 10$^{-2}$ | 1.0 × 10$^{-3}$ | TMC1-CP (4) |
| C$_3$D/C$_3$H | 0.4 × 10$^{-2}$ | 0.4 × 10$^{-2}$ | 1.0 × 10$^{-2}$ | 4.0 × 10$^{-3}$ | TMC1-CP (5) |
| DCO$^+$/HCO$^+$ | 0.3 × 10$^{-2}$ | 1.9 × 10$^{-2}$ | 1.8 × 10$^{-2}$ | 2.0 × 10$^{-2}$ | TMC1-N (1) |
| N$_2$D$^+$/N$_2$H$^+$ | 0.2 × 10$^{-2}$ | 2.5 × 10$^{-2}$ | 0.8 × 10$^{-2}$ | 8.0 × 10$^{-2}$ | TMC1-N (1) |
| c-C$_3$HD/c-C$_3$H$_2$ | 1.6 × 10$^{-2}$ | 0.6 × 10$^{-2}$ | 1.3 × 10$^{-2}$ | 8.0 × 10$^{-2}$ | TMC1-CP (6) |
| C$_5$H$_3$D/C$_5$H$_4$ | 4.4 × 10$^{-2}$ | 8.3 × 10$^{-2}$ | 1.6 × 10$^{-2}$ | 5.4 × 10$^{-2}$ | TMC1-CP (7) |
| DC$_5$N/H$_2$CN | 0.7 × 10$^{-2}$ | 0.7 × 10$^{-2}$ | 0.9 × 10$^{-2}$ | 3.0 × 10$^{-2}$ | TMC1-CP (8) |
| DC$_5$N/H$_2$CN | 0.3 × 10$^{-2}$ | 2.3 × 10$^{-2}$ | 1.2 × 10$^{-2}$ | 1.3 × 10$^{-2}$ | TMC1-CP (9) |
| HDCS/H$_2$CS | 1.6 × 10$^{-2}$ | 4.0 × 10$^{-2}$ | 1.8 × 10$^{-2}$ | 2.0 × 10$^{-2}$ | TMC1-CP (10) |
| c-C$_2$D/c-C$_2$H | 0.5 × 10$^{-2}$ | - | - | 4.0 × 10$^{-2}$ | TMC1-C (11) |

References: 1: Tiné et al. (2000); 2: Turner (2001); 3: Wootten (1987); 4: Millar et al. (1989); 5: Turner (1989); 6: Bell et al. (1988); 7: Gerin et al. (1992); 8: Howe et al. (1994); 9: MacLeod et al. (1981); 10: Minowa et al. (1997); 12: Spezzano et al. (2013)

Positions: TMC1-CP ($\alpha_{J2000}$ = 04$^h$ 41$^m$ 31.88, $\delta_{J2000}$ = +25$^\circ$ 45$^\prime$ 27$^\prime$), TMC1-N ($\alpha_{J2000}$ = 04$^h$ 41$^m$ 21.01, $\delta_{J2000}$ = +25$^\circ$ 49$^\prime$ 58$^\prime$), TMC1-C ($\alpha_{J2000}$ = 04$^h$ 41$^m$ 16$^s$.1, $\delta_{J2000}$ = +25$^\circ$ 49$^\prime$ 43.8$''$).
of Garrod et al. (2007) to fit with the TMC-1 observations. First, we construct a log-normal distribution about each observational value, and then identify its defining standard deviation, $\sigma$, with an appropriate error factor ($\text{erfc}$) on the observed value. Finally, the "confidence", $\kappa_i$, that the modelled abundance ($X_{\text{model},i}$, for species $i$) is associated with the observed value ($X_{\text{obs},i}$) is defined as:

$$\kappa_i = \text{erfc} \left( \frac{\log (X_{\text{model},i}) - \log (X_{\text{obs},i})}{\sqrt{2}\sigma} \right)$$

where $\text{erfc}$ is the complementary error function ($\text{erfc} = 1 - \text{erf}$); $\kappa_i$ ranges between zero and unity. In our case, we define $\sigma = 1$, hence 1 standard deviation corresponds to one order of magnitude higher or lower than the observed value. Fig. 5 represents the mean confidence level calculated using the method described above. As it can be seen, the DS model (~37%) has a strong impact on the general confidence level as compared to the NoDS model (~45%) at its maximum. The use of the DS model suggests a best fit chemical age for TMC-1 of 10$^5$ year whereas the NoDS model gives 3 x 10$^6$ year. At the time of best agreement, for both the DS and NoDS models, ~50% and ~60% of the observed species in TMC-1 are reproduced within factor of 10. But all these estimates are very much dependent on the initial opr(H$_2$) and our estimates are only valid for the initial statistical ratio of 3:1. For example, in order to perform more realistic age estimates for TMC-1, it needs to be done in the context of parameter-space exploration with assumed opr(H$_2$) and this is out of scope of the current work. In Table 4, we have reported abundances for all the observed non-deuterated species using the above two models at their best chemical age.

By investigating closely, we found three types of differences: (1) DS model results differ from NoDS but in better agreement with the TMC-1 observation as compared to NoDS (Case I); (2) DS model results differ from NoDS but in less agreement with the TMC-1 observation as compared to NoDS (Case II); (3) differences between the two models and the observations are both within a factor of 10 (Case III). The differences between the agreements are caused by changes in the chemical time scales. This can be clearly seen from Fig. 6 where we have shown the most affected oxygen, nitrogen and sulphur bearing species for which the chemical time scales for reaching their peak have changed. Here we will focus on the detailed chemistry for Case I and Case II, which shows the effect of deuteration and ortho-para chemistry on the observed non-deuterated species. For Case I, we found molecules such as O$_2$, CH$_3$OH, C$_2$O, H$_2$C$_4$, HC$_5$N, C$_2$S, CH$_4^-$, CH$_5^-$ and for Case II, we found CH$_3$C$_2$H, NH$_3$, HCN, CH$_3$CN, CH$_2$CHCN, SO, SO$_2$. The rest of the species belong to Case III.

Among the Case I species, O$_2$ forms via the gas phase reaction O + OH in both models. But in model DS, as can be seen from Table 4, the abundance of OH is almost 10 times lower than in the NoDS model, which in turn produces less O$_2$. In the DS model, OH forms via the gas phase photodissociation of H$_2$O and by the neutral-neutral reaction O+ H$_2$CO→H + OH + CO which has an activation barrier while in the NoDS model, OH forms via the fast dissociative recombination of H$_2$O$^+$. CH$_3$OH forms via the dissociative recombination reaction of CH$_4$OH$^+$ in the gas phase at 10$^5$ years in the DS model whereas in the NoDS model, it forms via the surface reaction s-H + s-CH$_3$O and is destroyed rapidly via the barrier-less gas phase reaction CH$_3$OH + C. Reaction s-H + s-CH$_3$O becomes the main production reaction from 10$^6$ year in model DS i.e. well after the gas phase spin conversion of ortho to para H$_2$. C$_2$O is produced in model DS as well as in model NoDS via the gas phase reaction C + HCO. But we found that C$_2$O is more abundant in the DS model as compared to the NoDS model. This is due to the chemistry of HCO. HCO produced in the NoDS model via the grain surface reaction s-H + s- CO which has a high activation barrier of 2500 K and in the DS model, it is produced via the barrier-less reaction CH$_2$ + O. We produce less C$_4$H$_2$ in model DS due to the highly efficient destruction of this species via the barrier-less gas phase reaction C + s-H$_2$ whereas in the NoDS model, this destruction process is not very efficient. For HC$_5$N, we have better agreement with the observation and also it is more abundant in model DS than the NoDS. In both models, HC$_5$N forms via the dissociative recombination of H$_2$C$_4$N$^+$. But in model DS, HC$_5$N efficiently destroyed by p-H$_2$ to form H$_2$C$_4$N$^+$ which recombine again to form HC$_5$N. For C$_2$S, we observe that it is more abundant in DS model than NoDS model. This is due to the effect of the barrier-less gas phase reaction O + C$_2$S. This reaction destroys C$_2$S more rapidly in NoDS model as compared to the DS model. Among the anions, C$_2$H$^-$ and C$_3$H$^-$ both are efficiently produced in model DS as compared to NoDS. Since in model DS, the rate of production via the dissociative recombination reactions of C$_2$H and C$_3$H is very high due to high opr(H$_2$).

Among the case II species, CH$_3$C$_2$H is produced efficiently in model NoDS due to its formation on the surface via the barrier-less reaction s-H + s-CH$_2$CCH. Among the others, the chemistry of NH$_3$ and HCN is already been discussed in our earlier section. For CH$_3$CN, we observe a very high abundance in model DS as compared to the NoDS model. CH$_3$CN is produced by the dissociative recombination reaction of CH$_3$CNH$^+$ in both models but in model
Deuteration in cold cores

Figure 6. Abundance with respect to n_H for a selection of O, N, S bearing species and for two models: left panel: DS Model with spin and deuterium chemistry and right panel: NoDS model without spin and deuterium chemistry.

NoDS, it is destroyed by several other ion-molecule reactions with HCO^+, H_3^+, H_2 O^+, C^+ whereas in model DS, it is only destroyed by p-H_3^+ . We observe that CH_3 CHCN is less abundant in model DS since it is destroyed by several reactions of ortho and para H_3^+ to form C_3 H_3 NH^+ whereas in the NoDS model, it is destroyed mainly by HCO^+. SO is mainly produced by the neutral-neutral reaction S + OH in model DS and OH is among the highly affected species in model DS. This corresponds to the decrease in abundance of SO in model DS. For SO_2 , it is formed on the surface in DS model via the reaction s-O + s-SO whereas in model NoDS, it is formed by the neutral-neutral gas phase reactions OH + SO, O + SO. But its decrease in abundance in DS model is due to the efficient gas phase destruction reaction C + SO_2 . The decrease in the abundance of NS in model DS as compared to NoDS is due to the efficient destruction by the various atoms i.e. C, O, N.

3.4 Some new observable deuterated species in TMC-1 from our model

In Table 5, we list a set of potentially new observable deuterated species in TMC-1. For predicting the observability (in the frequency range of 73–180 GHz) of all the species (for which frequencies are known) listed in Table 5, we have used the CASSIS\(^5\) interactive spectrum analyser to calculate the line intensities under local thermodynamic equilibrium (LTE) conditions (though LTE might not be reasonable for some of those transitions at 10^4 cm\(^{-3}\), see for other alternatives in Liszt & Pety (2016)). For our calculations, we assume excitation temperature= 5 K (to take into account the fact that the populations of the molecular levels might not be at LTE), FWHM= 1 km/s, H_2 column density = 10^{22} cm\(^{-2}\) and no beam dilution to simulate typical dark cloud conditions. We list only the brightest transitions along with their Einstein coefficients and upper level energies in Table 5.

\(^5\) http://cassis.irap.omp.eu
Table 4. Effect of deuteration and spin chemistry on molecular abundances (relative to H$_2$) at best chemical age obtained by comparing the models to the observed values in TMC-1

| Species | TMC-1 | NoDS | DS | Species | TMC-1 | NoDS | DS |
|---------|-------|------|----|--------|-------|------|----|
| OH      | 3(-7) | 3.2(-8) | 2.6(-9) | *NH$_4$ | 2.45(-8) | 6.6(-9) | 3.7(-11) |
| H$_2$O  | <7(-8) | 3.1(-7) | 1.8(-5) | H$_2$N$^+$ | 2.8(-10) | 7.9(-11) | 7.5(-11) |
| *O$_2$  | <7.7(-8) | 7.3(-7) | 3.2(-9) | CN     | 7.4(-10) | 2.7(-8) | 9.4(-9) |
| CO      | 1.7(-4) | 6.0(-5) | 6.7(-5) | *HCN   | 1.1(-8) | 8.7(-8) | 2.6(-10) |
| HCO$^+$ | 9.3(-9) | 4.2(-9) | 1.0(-9) | HNC    | 2.6(-8) | 3.1(-8) | 4.8(-8) |
| H$_2$CO | 5(-8)  | 1.2(-8) | 14(-9) | *CH$_3$OH | 3.2(-9) | 7.3(-10) | 4.8(-9) |
| *CH$_3$OH | 3.2(-9) | 7.3(-10) | 4.8(-9) | *CH$_3$CN | 6(-10) | 4.2(-10) | 2.2(-7) |
| *C$_2$O | 6(-11) | 6.9(-13) | 2.1(-11) | CH$_3$CHCN | 1(-9) | 1.2(-11) | 1.3(-12) |
| CH$_2$O | 6(-10) | 9.0(-10) | 2.0(-10) | C$_2$N  | 6(-10) | 1.9(-9) | 8.6(-10) |
| CH$_3$CHO | 6(-10) | 2.3(-12) | 5.3(-12) | HCN   | 1.6(-8) | 1.0(-8) | 1.0(-7) |
| C$_5$O | 1(-10) | 7.7(-9) | 7.9(-10) | HNC$_3$ | 3.8(-11) | 4.1(-10) | 3.6(-10) |
| CH$_3$CHO | 2.0(-8) | 2.0(-9) | 3.5(-9) | C$_2$H | 7.2(-9) | 3.1(-9) | 15(-9) |
| C$_2$H | 103(-9) | 3.2(-9) | 2.8(-9) | C$_2$H$_3$ | 8.4(-11) | 2.4(-9) | 15(-9) |
| l-C$_2$H$_3$ | 5.8(-9) | 2.6(-8) | 2.6(-10) | C$_3$N  | 3.1(-11) | 2.1(-10) | 5.6(-11) |
| l-C$_3$N$_2$ | 2.1(-10) | 2.1(-8) | 9.2(-9) | CH$_3$C$_2$N | 7.4(-11) | 4.8(-13) | 5.1(-12) |
| CH$_3$C$_2$H | 6(-9) | 2.7(-10) | 8.4(-12) | HCN | 1(-9) | 3.9(-11) | 1.7(-10) |
| C$_2$H$_3$ | 7.1(-8) | 1.0(-9) | 8.0(-10) | C$_2$H$_3$ | 7.1(-8) | 1.0(-9) | 8.0(-10) |
| C$_2$HD | 8.0(-8) | 5.2(-10) | 1.0(-10) | H$_2$C$_4$ | 7(-10) | 2.7(-8) | 19(-11) |
| C$_3$H$_2$ | 5(-9) | 6.1(-11) | 3.8(-11) | C$_3$H | 4.1(-10) | 3.7(-11) | 3.7(-11) |
| C$_4$H$_2$ | 5(-9) | 6.1(-11) | 3.8(-11) | H$_2$S | 5.5(-10) | 4.5(-11) | 2.1(-10) |
| H$_2$C$_6$ | 4.7(-11) | 9.7(-11) | 6.8(-12) | C$_2$S | 2.9(-9) | 2.6(-9) | 2.2(-9) |
| C$_5$H$_5$ | 4.6(-11) | 9.3(-12) | 1.4(-11) | H$_2$CS | 7(-10) | 1.3(-10) | 2.1(-10) |
| C$_5$H$_4$ | 2.1(-12) | 8.1(-13) | 2.3(-12) | *CS$_2$ | 7(-9) | 6.8(-11) | 1.5(-9) |
| OCS | 2.2(-9) | 2.7(-10) | 6.0(-10) | C$_3$S | 1(-9) | 6.2(-10) | 4.7(-10) |
| NS | 8.0(-10) | 3.6(-11) | 1.6(-13) | *SO$_2$ | 3(-10) | 2.4(-10) | 2.4(-13) |

$\alpha(b)$ refers to $a \times 10^b$.

Abundances correspond to the positions TMC-1 $\alpha_{2000} = 04^h 41^m 8.88$, $\delta_{2000} = +25^\circ 41' 27''$ (cyanopolyyne peak). See Agundez & Wakelam (2013) for more details.

DS refers to modelled abundances with deuteration and spin chemistry taken into account.

NoDS refers to modelled abundances without deuteration and spin chemistry.

* Fig. 6 shows that the shift in the chemical time scale for the affected species (bold face) to reach the peak abundances.

Table 5. New set of observable gas phase deuterated species in TMC-1 awaiting detection (for example with the IRAM-30m telescope).

| Species | Line | $A_{ij}$ [s$^{-1}$] | $E_{up}$ [K] | Frequency [GHz] | n(x)/n(H) | Line Intensity [K] |
|---------|------|------------------|--------------|-----------------|-----------|-------------------|
| c-C$_3$D | 3 1 3 → 2 1 2 | 2.2(-7) | 9.41 | 116.73 (JPL) | 2.0(-10) | 0.18 |
| l-C$_3$HD | 4 0 4 → 3 0 3 | 4.05(-5) | 9.30 | 77.52 (CDMS) | 1.4(-10) | 0.055 |
| CH$_2$ND | 3 2 2 → 2 1 1 | 5.4(-6) | 8.43 | 117.08 (JPL) | 3.2(-11) | 0.005 |
| DNCC | 9 8 7 → 8 8 8 | 1.9(-8) | 19.01 | 79.20 (JPL) | 5.2(-11) | 0.019 |
| C$_4$HD | 9 0 9 → 8 0 8 | 4.11(-5) | 18.30 | 76.27 (CDMS) | 2.3(-9) | 0.13 |
| DNO | 2 0 2 → 1 0 1 | 5.0(-6) | 10.52 | 146.117 (JPL) | 1.7(-11) | 0.003 |

The table is limited to species with relative abundances $\geq 10^{-11}$.

$\alpha(b)$ refers to $a \times 10^b$. 

MNRAS 000, 000–000 (2015)
4 CONCLUSIONS

In this work, we present the first publicly available chemical network of multiply deuterated species along with spin chemistry of $\text{H}_2$, $\text{H}_3^+$, $\text{H}^+$ and their isotopologues. We also benchmarked our new model by comparing with existing works. Observed molecular D/H ratios at different positions of TMC-1 have been compared with our new comprehensive astrochemical model. By introducing an extensive description of deuteration along with nuclear spin state processes, we found that the chemical time scale for reaching the peak abundance of some non-deuterated species has changed by a factor of a few in some cases. Finally, we report a new set of potentially observable deuterated species in TMC-1.

ACKNOWLEDGEMENTS

LM, PG, MR, VW, FH thanks ERC starting grant (3DICE, grant agreement 336474) for funding during this work. PG postdoctoral position is funded by the INSU/CNRS. VW, AD, SG, FH also acknowledge the CNRS programme PCMI for funding of their research. We would like to thank the anonymous referee for constructive comments that helped to improve the manuscript.

REFERENCES

Agúndez M., Wakelam V., 2013, Chemical Reviews, 113, 8710
Aikawa Y., Wakelam V., Hersant F., Garrod R. T., Herbst E., 2012, ApJ, 760, 40
Albertsson T., Semenov D., Henning T., Herbst E., 2013, ApJS, 207, 27
Albertsson T., Semenov D., Henning T., 2014a, ApJ, 784, 39
Albertsson T., Indriolo N., Kreckel H., Semenov D., Crabtree K. N., Henning T., 2014b, ApJ, 787, 44
Bacmann A., 2004, Baltic Astronomy, 13, 402
Bell M. B., Avery L. W., Matthews H. E., Feldman P. A., Watson J. K. G., Madden S. C., Irvine W. M., 1988, ApJ, 326, 924
Bergin E. A., et al., 2013, ApJ, 770, L2
Bergin E. A., et al., 2015, ApJ, 808, 21
Bergman P., Parise B., Liseau R., Larsson B., 2011, A&A, 527, A39
Bottinelli S., Wakelam V., Caux E., Vidal T., Nakamura K., Ballesteros-Paredes J., Wakelam V., 2013, MNRAS, 437, 4004
Bottinelli S., Wakelam V., Caux E., Vidal T., Nakamura K., Ballesteros-Paredes J., Wakelam V., 2013, MNRAS, 437, 4004
Caselli P., van der Tak F. S. J., Ceccarelli C., 2014, A&A, 562, A56
Caselli P., van der Tak F. S. J., Ceccarelli C., Bacmann A., 2003, A&A, 403, L37
Caselli P., Vastel C., Ceccarelli C., van der Tak F. S. J., Crapsi A., Bacmann A., 2008, A&A, 492, 703
Ceccarelli C., Caselli P., Bockelée-Morvan D., Mousis O., Pizarrorollo S., Robert F., Semenov D., 2014, Protostars and Planets VI, pp 859–882
Chabot B., Bérou K., Gratier P., Jallat A., Wakelam V., 2013, ApJ, 771, 90
Coutens A., et al., 2012, A&A, 539, A132
Coutens A., et al., 2014, MNRAS, 445, 1299
Das A., Majumdar L., Sahu D., Gorai P., Sivaraman B., Chakrabarti S. K., 2015, ApJ, 808, 21
Demyk K., Bottinelli S., Caux E., Vastel C., Ceccarelli C., Kahane C., Castets A., 2010, A&A, 517, A17
Dutrey A., et al., 2011, A&A, 535, A104
Faure A., Hily-Blant P., Le Gal R., Rist C., Pineau des Forêts G., 2013, ApJ, 770, L2
Flower D. R., Pineau des Forêts G., Walmsley C. M., 2004, A&A, 427, 887
Flower D. R., Pineau des Forêts G., Walmsley C. M., 2006, A&A, 449, 621
Garrod R. T., Wakelam V., Herbst E., 2007, A&A, 467, 1103
Gerin M., Combes F., Whodarzak G., Encraenz P., Laurent C., 1992, A&A, 253, L29
Guelin M., Langer W. D., Snell R. L., Wootton H. A., 1977, ApJ, 217, L165
Guilloteau S., Piétu V., Dutrey A., Guelin M., 2006, A&A, 448, L5
Hasegawa T. I., Herbst E., 1993, MNRAS, 261, 83
Hasegawa T. I., Herbst E., Leung C. M., 1992, ApJS, 82, 167
Hincelin U., Wakelam V., Hersant F., Guilloteau S., Loison J. C., Honvault P., Troe J., 2011, A&A, 530, A61
Howe D. A., Millar T. J., Schilke P., Walmsley C. M., 1994, MNRAS, 267, 59
Huang J., Őberg K. I., 2015, ApJ, 809, L26
Hugo E., Asvany O., Schlemmer S., 2009, J. Chem. Phys., 130, 164302
Linsky J. L., et al., 2006, ApJ, 647, 1106
Lis D. C., Roueff E., Gerin M., Phillips T. G., Coudert L. H., van der Tak F. F. S., Schilke P., 2002, ApJ, 571, L55
Lis J. H., et al., 2016, ApJ, 821, 124
Loison J.-C., Wakelam V., Hickson K. M., Bergeat A., Mereau R., 2014a, MNRAS, 437, 930
Loison J.-C., Wakelam V., Hickson K. M., 2014b, MNRAS, 443, 398
Loren R. B., Wootten A., 1985, ApJ, 299, 947
MacLeod J. M., Avery L. W., Broten N. W., 1981, ApJ, 251, L33
Majumdar L., Das A., Chakrabarti S. K., 2014a, A&A, 562, A56
Majumdar L., Das A., Chakrabarti S. K., 2014b, ApJ, 782, 73
Majumdar L., Gratier P., Vidal T., Wakelam V., Loison J.-C., Hickson K. M., Caux E., 2016, MNRAS, 458, 1859
Margulès L., et al., 2010, ApJ, 714, 1120
Miettinen O., Harju J., Haikala L. K., Juvela M., 2012, A&A, 538, A137
Millar T. J., Bennett A., Herbst E., 1989, ApJ, 340, 906
Minowa H., Satoh M., Hirota T., Yamamoto S., Ohishi M., Kauf N., 1997, ApJ, 491, L63
Neufeld D. A., Wolfire M. G., Schilke P., 2005, ApJ, 628, 260
Öberg K. I., Furuya K., Loomis R., Aikawa Y., Andrews S. M., Qi C., van Dishoeck E. F., Wilner D. J., 2015, ApJ, 810, 112
Oka T., 2004, Journal of Molecular Spectroscopy, 228, 635
Pagani L., et al., 2009, A&A, 494, 623
Parise B., Castets A., Herbst E., Caux E., Ceccarelli C., Mukhopadhyay I., Tielens A. G. G. M., 2004, A&A, 416, 159
Parise B., Belloche A., Du F., Güsten R., Menten K. M., 2011, A&A, 526, A31
Parise B., et al., 2012, A&A, 542, L5
Qi C., Wilner D. J., Aikawa Y., Blake G. A., Hogerheijde M. R., 2008, ApJ, 681, 1396
Reboussin L., Wakelam V., Guilloteau S., Hersant F., 2014, MNRAS, 440, 3557
Roberts H., Millar T. J., 2000a, A&A, 361, 388
Roberts H., Millar T. J., 2000b, A&A, 364, 780
Roueff E., Tine S., Coudert L. H., Pineau des Forêts G., Falgarone E., Gerin M., 2000, A&A, 354, L63
Ruaud M., Loison J. C., Hickson K. M., Herbst E., 2000, A&A, 354, L165
Sipilä O., Caselli P., Harju J., 2015, A&A, 578, A55
Spezzano S., et al., 2013, ApJ, 769, L19
Stark R., van der Tak F. S. J., van Dishoeck E. F., 1999, ApJ, 521, L67
Talukdar R. K., Ravishankara A., 1996, Chemical Physics Letters, 253, 177
Taquet V., Peters P. S., Kahane C., Ceccarelli C., López-Sepulcre A., Toubin C., Duflot D., Wiesenfeld L., 2013, A&A, 550, A127

MNRAS 000, 000–000 (2015)
Taquet V., Charnley S. B., Sipilä O., 2014, ApJ, 791, 1
Tiné S., Roueff E., Falgarone E., Gerin M., Pineau des Forêts G., 2000, A&A, 356, 1039
Turner B. E., 1989, ApJ, 347, L39
Turner B. E., 1990, ApJ, 362, L29
Turner B. E., 2001, ApJS, 136, 579
Turner B. E., Zuckerman B., 1978, ApJ, 225, L75
Vastel C., Phillips T. G., Yoshida H., 2004, ApJ, 606, L127
Vastel C., Caselli P., Ceccarelli C., Phillips T., Wiedner M. C., Peng R., Houde M., Dominik C., 2006, ApJ, 645, 1198
Vastel C., et al., 2010, A&A, 521, L31
Wakelam V., Vastel C., Aikawa Y., Coutens A., Bottinelli S., Caux E., 2014, MNRAS, 445, 2854
Wakelam V., et al., 2015a, ApJS, 217, 20
Wakelam V., Loison J.-C., Hickson K. M., Ruaud M., 2015b, MNRAS, 453, L48
Walmsley C. M., Flower D. R., Pineau des Forêts G., 2004, A&A, 418, 1035
Watanabe N., Kimura Y., Kouchi A., Chigai T., Hama T., Pirronello V., 2010, ApJ, 714, L233
Wootten A., 1987, in Vardya M. S., Taraftlar S. P., eds, IAU Symposium Vol. 120, Astrochemistry. pp 311–318
van Dishoeck E. F., Thi W.-F., van Zadelhoff G.-J., 2003, A&A, 400, L1
van der Tak F. F. S., Müller H. S. P., Harding M. E., Gauss J., 2009, A&A, 507, 347