NEW EXTENDED DEUTERIUM FRACTIONATION MODEL: ASSESSMENT AT DENSE ISM CONDITIONS AND SENSITIVITY ANALYSIS

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ABSTRACT

Observations of deuterated species are useful in probing the temperature, ionization level, evolutionary stage, chemistry, and thermal history of astrophysical environments. The analysis of data from the Atacama Large Millimeter Array and other new telescopes requires an elaborate model of deuterium fractionation. This paper presents a publicly available chemical network with multi-deuterated species and an extended, up-to-date set of sources. Two cases of initial abundances are considered: (1) atomic except for H2 and HD, and (2) molecular from a prestellar core. We reproduce the observed D/H ratios of many deuterated molecules, and sort the species according to their sensitivity to temperature gradients and initial abundances. We find that many multiply deuterated species produced at 10 K retain enhanced D/H ratios at temperatures ≤ 100 K. We study how recent updates to reaction rates affect calculated D/H ratios, and perform a detailed sensitivity analysis of the uncertainties of the gas-phase reaction rates in the network. We find that uncertainties are generally lower in dark cloud environments than in warm infrared dark clouds and that uncertainties increase with the size of the molecule and number of D-atoms. A set of the most problematic reactions is presented. We list potentially observable deuterated species predicted to be abundant in low- and high-mass star-formation regions.

Key words: astrochemistry – circumstellar matter – ISM: clouds – ISM: molecules – methods: numerical – molecular processes – stars: protostars

Online-only material: color figures

1. INTRODUCTION

The life cycle of molecules covers a wide range of environments, starting from the sparse interstellar medium (ISM), which eventually evolves into stars and planets. As molecular hydrogen cannot be easily observed in the cold ISM, other molecular tracers are employed to probe the relevant physical conditions and chemical composition. More than 170 molecules have been observed in the ISM to date,3 ranging from diatomic species to the fullerenes C60 and C70 (Cami et al. 2010) and including deuterated species. A variety of deuterated species have been detected in various astrophysical environments, including molecular clouds: DCO+ (van der Tak et al. 2009; Guelin et al. 1977), DNC (van der Tak et al. 2009; Turner & Zuckerman 1978), H2D+ (Parise et al. 2011; Stark et al. 1999), HDCO (Loren & Wootten 1985), D2CO (Turner 1990), HD2+ (Parise et al. 2011), HDO (Phillips et al. 1973); pre-stellar cores: D2CO (Bacmann 2004), H2D+ (Caselli et al. 2003, 2008; Vastel et al. 2006), HD2+ (Vastel et al. 2012), N2D+ (Miettinen et al. 2012), NHD2 (Roueff et al. 2000); hot cores/corinos: D2CO, HDCO (Bergman et al. 2011), DCOOCH3 (Demyk et al. 2010; Margulés et al. 2010), HD2+ (Vastel et al. 2004), HDO, NH2D (Jacq et al. 1990); warm protostellar envelopes: DCO+, HDCO (Parise et al. 2009), HDO (Jørgensen & van Dishoeck 2010; Liu et al. 2011), OD (Parise et al. 2012); protoplanetary disks: DCN, DCO+ (van Dishoeck et al. 2003; Guillemou et al. 2006; Qi et al. 2008) and comets: CH3D (Bonev et al. 2009; Gibb et al. 2012), HDCO (Kuan et al. 2008), HDO (Villanueva et al. 2009; Hartogh et al. 2011; Gibb et al. 2012). For comprehensive reviews, we refer the reader to Roueff & Gerin (2003) and Bergin et al. (2007). The study of deuterium chemistry has proven useful to constrain the ionization fraction, density and thermal history of the ISM and protoplanetary disks (e.g., Geiss & Reeves 1981; Aikawa & Herbst 2001; Crapsi et al. 2005; Willacy 2007; Őberg et al. 2012).

Still, many more deuterated species of key importance remain to be detected. Upon the completion of the high-sensitive, high-resolution Atacama Large Millimeter Array (ALMA), we will be able to, for the first time, detect and spatially resolve emission lines of numerous new complex and rare-isotope molecules. In order to analyze these rich observational data, new astrochemistry models including isotope-exchange reactions and state-to-state processes will be required. The main goal of the present paper is to present and provide a new extended, public deuterium fractionation model, and to explore its validity and accuracy.

The implementation of deuterium chemistry is a challenging task though because of a limited number of accurately determined rate coefficients of relevant reactions, and the sheer number of hydrogen-dominated reactions in astrochemical networks. Previous studies used the available limited set of reaction data, substituted with “educated guesses” for missing reaction rates, and cloned data from similar reactions involving hydrogen-bearing species (e.g., Herbst 1982; Brown et al. 1988; Rodgers & Millar 1996; Charnley et al. 1997; Turner 2001; Aikawa et al. 2003, 2012; Sipilä et al. 2013). In many cases only mono- and double-deuterated species were considered. We follow the general approach, but abandon the restriction on the total number of deuterons in chemical species.

The redistribution of elemental deuterium, initially locked mainly in HD, is initiated by fast ion–molecule reactions with

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4 http://www.astrochymist.org/astrochymist_mole.html
polyatomic ions, such as H$_3^+$ (and H$_2$D$^+$, HD$_2^+$, D$_3^+$). Due to zero-point vibrational energy differences between modes with D and H, and the lack of a ground rotational state for H$_3^+$, the backward reactions between H$_2$ and H$_3^+$ isotopologues are endothermic, with barriers of ~100–300 K, leading to the initial enrichment of abundances of the H$_3^+$ isotopologues at ~20–30 K. In a similar way, other ions such as CH$_3$D$^+$ and C$_2$HD$^+$ allow deuterium fractionation to proceed effectively at warmer temperatures of ~30–80 K because of larger endoergicities for the backward reactions (e.g., Millar et al. 1989; Roueff et al. 2005; Parise et al. 2009). These deuterated ions react further with abundant molecules such as CO and N$_2$, transferring deuterium atoms to new molecules. These findings have been proven both observationally and theoretically (see, e.g., Bacmann et al. 2002, 2003; Roberts et al. 2003; van der Tak 2006; Roberts & Millar 2006; Caselli et al. 2008). The initial gas-phase deuterium enrichment of H$_3^+$ is even more pronounced in cold, dense regions, where some destructive neutral species, especially CO, become severely depleted onto dust grain surfaces. The disso- ciative recombination of abundant H$_3^+$ isotopologues leads to a high flux of D atoms (<10%–30% compared to H) sticking to dust grains, which further react with surface species such as CO forming abundant multi-deuterated complex (organic) ices such as formaldehyde and methanol. These molecules can later desorb into the gas-phase due to non-thermal desorption or due to the gradual warm-up of the environment by a forming protostar.

The physical environment plays an important role in deuterium fractionation. In one of the first theoretical studies of deuterium fractionation, Solomon & Wolff (1973) estimated the D/H ratio for HCN in Orion, albeit erroneously assuming that fractionation is driven solely by neutral–neutral processes involving HD and atomic D. The ion–molecule fractionation route was first proposed by Watson (1974) and Watson (1976), who used it to constrain the interstellar D/H elemental ratio. Güsten et al. (1977) used observations of DCO$^+$ to constrain the electron abundance in dark clouds, while Herbst (1982) showed that the DCO$^+$/HCO$^+$ ratio can be used as a sensitive measure of the gas kinetic temperature in the ISM. Dalgarno & Lepp (1984) studied the D/H ratio of HCO$^+$, considering cold and warm ISM conditions, and illustrated the role of depletion (and thus the density of the environment) for deuterium fractionation processes.

The first complete gas-phase model of deuterium chemistry in a dense cold cloud was undertaken by Millar et al. (1989), while Brown & Millar (1989) explored grain-surface deuteration processes. More recently, Roberts & Millar (2000b) studied deuterium chemistry over a wide range of physical parameters, by varying density, temperature, initial abundances and freeze-out. They found that if freeze-out is present, molecular D/H ratios can become very high, e.g., >1%–10%, and gas-phase chemistry can produce abundant mono- and multi-deuterated molecules.

Not only are the current physical properties of the environment important for chemical evolution, but so is the evolutionary history. Taquet et al. (2012) have considered a two-stage model to study deuterium chemistry in prestellar cores, with a gas-phase steady-state phase followed by the formation and evolution of grain mantles and surface deuterium fractionation. With such a simple approach they have reproduced high observed abundances of the isotopologues of formaldehyde and methanol. Taquet et al. (2012) have concluded that D and H abstraction and substitution reactions on dust surfaces are crucial for attaining the observed high D/H ratios. The role of abstraction reactions for deuterium fractionation has been intensively investigated in the laboratory (see, e.g., Nagaoka et al. 2005; Hidaka et al. 2009; Hama et al. 2012).

Cazaux et al. (2011) have studied the chemistry of formaldehyde and water by modeling the formation of ices in translucent clouds, and later following the chemical evolution as the cloud collapses to eventually form a Class I protostellar object. Their results show that the degree of deuteration of formaldehyde is sensitive to the initial D/H ratios of gaseous molecules attained before the collapse phase, while the degree of deuteration of water depends strongly on the dust temperature during the water ice formation. Intriguingly, Coutens et al. (2012) have observed deuterated water vapor in the low-mass protostar IRAS 16293–2422 and found that the water D/H ratio is lower than for other deuterated species detected in the same source. This observational trend continues toward more evolved hot cores/corinos (e.g., Parise et al. 2004; Bacmann et al. 2012) and suggests that the water may have formed relatively early, in a warm dilute ISM environment, while the depletion of CO at a later, cold and dense core stage allows for efficient surface synthesis of highly deuterium-enriched complex ices. An alternative explanation could be efficient abstraction and substitution reactions of H atoms by D atoms for organic ices like formaldehyde and methanol during cold prestellar cloud phase, which would not be as effective for water ice. A detailed one-dimensional chemical-hydrodynamical model of the prestellar core collapse and the formation of a protostar, coupled to the gas–grain chemistry and deuterium fractionation, has been developed by Aikawa et al. (2012). They have found that due to initially high D/H ratios accumulated in the cold phase, large (organic) molecules and carbon chains remain strongly deuterated even at later, warmer conditions.

While physical properties, such as temperature and density, and surface chemistry can have a significant effect on deuterium fractionation, smaller effects can be derived from other global properties such as metallicity and ionization fields. In order to understand the influence of metallicity and ionization one needs to study deuterated species on a more global scale. Bayet et al. (2010) have conducted an observational survey of deuterated species in extragalactic star-forming regions and studied the influence of density, temperature, far-UV radiation field, cosmic-ray ionization and metallicity on the D/H ratios for ~20 deuterated species. Without modeling any particular source, they have compared the predicted column densities with those derived from the current limited set of observational data in external galaxies and found an overall reasonable agreement. Bayet et al. (2010) have provided a list of key deuterated species in extragalactic environments to be searched for with ALMA.

ALMA is a truly revolutionary observational facility not only for extragalactic and cosmological studies, but also for observations of the Milky Way ISM, the analysis of which requires better chemical tools. In this paper we present a new up-to-date, extended, multi-deuterated chemical network and assess its reliability by modeling the deuterium fractionation in various phases of the ISM and comparing the results with observed D/H ratios of a variety of mono-, doubly, and triply deuterated species in distinct astrophysical environments. A list of the most promising, deuterated species potentially detectable with ALMA in the local Milky Way ISM is provided. Also, we report a detailed sensitivity analysis to understand and to quantify the intrinsic error bars in calculated abundances of deuterated species in several representative astrophysical environments.
We isolate the most problematic gas-phase reactions with uncertain rate coefficients to be studied in the laboratory or theoretically, and quantify the associated uncertainties in modeled abundances. The User Manual and the new deuterium network are freely available online.

The remainder of the paper is structured as follows. In Section 2 we present our new deuterium chemistry model. We give a detailed description of the construction of our deuterium network and our choice of the relevant reaction rates and branching ratios. We also discuss error propagation based on uncertainties in rate coefficients. In Section 3 this model is used to calculate abundances and D/H ratios under a wide range of physical conditions. We discern general trends in D/H ratios with temperature, density, and initial abundances, and divide the species according to whether temperature or initial abundance influences D/H ratios more strongly. A sensitivity analysis is performed to quantify intrinsic uncertainties in modeled abundances due to uncertainties in reaction rate data. A list of the most problematic reactions for deuterium chemistry is presented. We then discuss our results and compare them with recent observations and theoretical studies in Section 4. Conclusions follow in Section 5. Appendix A contains updated and added reactions, Appendix B shows dominant reaction pathways for selected deuterated species, and Appendix C lists deuterium fractionation rate coefficients in cold dark environments.

2. MODEL

2.1. Parameter Space

In this work we are primarily concerned with providing a new extended deuterium network and assessing its capacity to model chemistry under both static cold and warm conditions in the ISM. We do not consider evolutionary models such as those pertaining to low-mass and high-mass star formation separately, although the static conditions we consider arise from evolutionary processes. The evolution of the ISM begins from fragmentation of turbulent, mainly atomic clouds with kinetic temperatures up to $\sim 100$ K and densities of $\sim 10^{10}$ cm$^{-3}$. The denser clumps evolve into starless molecular cores (Bergin & Tafalla 2007) with temperatures of 8–15 K and densities of $\sim 10^{3}–10^{6}$ cm$^{-3}$ (Snow & McCall 2006; André et al. 2009; Launhardt et al. 2010; Nielbock et al. 2012). Some of these gravitationally bound cores may begin contracting, first isothermally, and then with increasing internal densities and temperatures. Then a central hydrostatic object forms, which starts heating up the surrounding gas. Protostars with a mass greater than 8 solar masses are generally referred to as high-mass protostellar objects (HMPOs). The collapsing envelope material can then reach temperatures of several hundred Kelvin closer to the central star, and peak densities of $\sim 10^{9}$ cm$^{-3}$, conditions which define a “hot core” or, for low-mass protostars, a hot “corino” (van Dishoeck 2006). In this paper we concentrate on the evolutionary stages ranging from a cold molecular cloud to the warm envelopes of protostars. We choose a wide parameter space with a grid of 1000 points covering temperatures between 5 and 150 K and densities of $10^{3}–10^{6}$ cm$^{-3}$, and assume the standard ISM dust and a fixed $A_V = 10$ mag, meaning that the photochemistry is only driven by secondary UV photons. Assuming a fixed $A_V$ reduces the problem to two dimensions, which is easier to analyze and visualize.

5 http://mpia.de/PSF/codes.php

2.2. Chemical Model

We have utilized the gas–grain chemical model “ALCHEMY” developed by Semenov et al. (2010), where a detailed description of the code and its performance is presented. The code is optimized for modeling the time-dependent evolution of large chemical networks, including both gas-phase and surface species. In this paper we added a large set of reactions involving deuterated species. A few features of the “ALCHEMY” model are summarized below.

The self-shielding of H$_2$ from photodissociation was calculated using Equation (37) from Draine & Bertoldi (1996). The shielding of CO by dust grains, H$_2$, and its self-shielding was calculated using the precomputed table of Lee et al. (1996, Table 11). We consider cosmic-ray particles (CRP) as the only external ionizing source, using a CRP ionization rate for H$_2$, $ζ_{CR} = 1.3 \times 10^{-17}$ s$^{-1}$ (Herbst & Klumper 1973), appropriate for molecular cloud environments and which has been utilized in several previous studies (such as Wakelam et al. 2006; Vasyunin et al. 2008; Druard & Wakelam 2012). The gas–grain interactions include dissociative recombination and neutralization of ions on charged grains, sticking of neutral species and electrons to uniformly sized 0.1 $\mu$m dust grains with a sticking coefficient of 1 and release of ices by thermal, CRP-, and UV-induced desorption, such that at high temperatures the surface population will be low as thermal desorption takes over. We do not allow H$_2$ and its isotopologues to stick to grains. We assume a UV photodesorption yield of $10^{-3}$ (e.g., Öberg et al. 2009a, 2009b). With our fixed visual extinction, the photon field derives from secondary electron excitation of molecular hydrogen followed by fluorescence.

We assume that each 0.1 $\mu$m spherical silicate grain provides $1.88 \times 10^6$ sites (Biham et al. 2001) for surface recombination that proceeds solely through the classic Langmuir–Hinshelwood mechanism (e.g., Hasegawa et al. 1992). The grain surface topology, the presence of high- and low-energy binding sites, grain sizes and shapes are all separate parameters that may severely impact the chemistry. An accurate study of this impact will require a detailed treatment of the microscopic physics of molecules on various solid surfaces, which is far beyond the scope of the present study. For further reading we recommend papers by Perets & Biham (2006), Cuppen et al. (2009), and Vasyunin & Herbst (2013a, 2013b), where some of these issues have already been addressed.

Upon a surface recombination, we assume there is a 5% probability for the products to leave the grain due to the conversion of some of the exothermicity of reaction into breaking the surface-adsorbate bond (Garrod et al. 2007). We do not find significant differences (less than a factor of two) in D/H ratios and abundances of essential species, such as H$_2^+$, water, and ammonia from varying this probability between 1% and 10%. However, we found a significant variation in ice abundances of formaldehyde and methanol of up to a factor of 6 at lower temperatures ($\lesssim 25$ K) when considering higher desorption probabilities $\geq 5\%$. Interestingly, ice abundances increase with the desorption probability and we find that this is due to a much more efficient formation of formaldehyde and methanol at intermediate times. Due to more intense gas–grain interactions precursor species of H$_2$CO and CH$_3$OH are able to form more readily in the gas phase and later stick to grains. Consequently, formaldehyde and methanol are formed faster via surface processes. Following experimental studies on the formation of molecular hydrogen on dust grains by Katz et al. (1999), we adopt the standard rate equation approach...
to the surface and ice chemistry without quantum-mechanical tunneling through the potential walls of the surface sites. We also do not consider competition kinetics between activation and diffusive barriers (Garrod & Pauly 2011).

A typical run, with relative and absolute tolerances of $10^{-5}$ and $10^{-25}$, utilizing the original gas–grain network without deuterium chemistry ($\sim$7000 reactions, $\sim$700 species) takes 1–5 s for 1 Myr of evolution with a Xeon 3.0 GHz CPU. With our new, almost ten-fold larger deuterium network, the same run takes approximately an order of magnitude longer to calculate. The linear dependence of the CPU time versus species number in the model is due to the advanced numerical scheme implemented in the ALCHEMIC code, which generates and uses sparse Jacobi matrices.

2.3. Initial Abundances

As input data, reaction rate coefficients and physical properties need to be specified, as do initial abundances. We have chosen to implement two different initial abundance sets and calculate the chemical evolution with the new deuterium network for 1 Myr.

For the first set, hereafter referred to as the “Primordial” model, we utilized the “low metals” abundances of Graedel et al. (1982) and Lee et al. (1998). Initially all deuterium is located in HD, with D/H = 1.5 × 10$^{-5}$ (Stancil et al. 1998; Linsky 2003); see Table 1. The abundances in the second set, the “Evolution” model, were calculated with our deuterium chemistry model, assuming a TMC1-like environment: $T = 10$ K and $n_{H} = 10^{4}$ cm$^{-3}$, at $t = 1$ Myr. Under such conditions elemental deuterium from HD is efficiently redistributed to other molecules, leading to their high initial D/H fractionation. These final abundances at 1 Myr are used as input in the Evolution model (see Table 2). The Evolution model serves as a simple example of a two-stage chemical model with physical conditions that can change dramatically at 1 Myr, unless the evolutionary model is run strictly under TMC-1 conditions.

2.4. Deuterium Fractionation Chemistry

As a first step toward creating a consistent network with deuterium fractionation, we undertook a thorough search in the literature for updates to the reaction rates of the original non-deuterated network. We utilized the latest osu.2009 gas-phase chemical network and incorporated all essential updates as of 2012 December, adopted from Horn et al. (2004), Chabot et al. (2010), Hamberg et al. (2010a), Wakelam et al. (2010b), Laas et al. (2011), as well as those reported in the KInetic Database for Astrochemistry (KIDA). Further, to allow for the synthesis of the few complex molecules in our network such as methanol (CH$_3$OH), methyl formate (HCOOCH$_3$), and dimethyl ether (CH$_3$OCH$_3$), an extended list of surface reactions and photodissociation of ices was adopted from Garrod & Herbst (2006). Several tens of gas-phase photoreaction rates were updated using the new calculations of van Dishoeck et al. (2006).

Next, we applied a cloning routine to this updated network (as described in Rodgers & Millar 1996), and added all additional primal isotope exchange reactions for H$_3^+$ as well as CH$_3^+$ and C$_2$H$_5^+$ from Roberts & Millar (2000b), Gerlich et al. (2002), Roberts et al. (2004), and Roueff et al. (2005). In this cloning routine all reactions bearing hydrogen atoms are considered to have deuterated analogs, and “cloned” accordingly (assuming the same rate coefficient if no laboratory data are available). In cases where the position of the deuterium atom is ambiguous, we apply a statistical branching approach. In the resulting network we do not yet distinguish between the ortho/para states of molecules, and leave this for a separate paper.

A typical example of the outcome of the cloning procedure is presented for the reaction between C$^+$ and CH$_3$:

$$
C^+ + CH_3 \rightarrow C_2H^+ + H_2 \Rightarrow \begin{cases} C^+ + CHD_2 \rightarrow C_2D^+ + HD \\ C^+ + CHD_2 \rightarrow C_2H^+ + D_2 \end{cases}
$$

(1)

The single ion–molecule reaction of C$^+$ with CH$_3$ is cloned into two separate channels for CHD$_2$. Moreover, the branching of these two new channels is not equal. To visualize this, we label the two deuterium atoms in CHD$_2$ as D$_a$ and D$_b$. For the first reaction, which forms C$_2$D$^+$, D$_a$ can be placed on either product and D$_b$ can be placed on the other, hence we have two possibilities: C$_2$D$_a^+$ + HD$_b$ or C$_2$D$_b^+$ + HD$_a$. For the second channel, which forms C$_2$H$^+$, both deuterons have to be placed on D$_a$ and we only have one possibility. This analysis assumes that the deuterons on D$_2$ are indistinguishable, which is in agreement with the Pauli exclusion principle. Alternatively, we could initially assume that they are distinguishable, but because

Table 1

| Species | H$_2$ | H | HD | He | C | N | O |
|---------|------|---|----|----|---|---|---|
| $n_{H}$ | 0.499 | 2.00 × 10$^{-3}$ | 1.50 × 10$^{-5}$ | 9.75 × 10$^{-2}$ | 7.86 × 10$^{-5}$ | 2.47 × 10$^{-5}$ | 1.80 × 10$^{-4}$ |

| Species | S | Si | Na | Mg | Fe | P | Cl |
|---------|---|----|----|----|----|---|---|
| $n_{H}$ | 9.14 × 10$^{-8}$ | 9.74 × 10$^{-9}$ | 2.25 × 10$^{-9}$ | 1.09 × 10$^{-8}$ | 2.74 × 10$^{-9}$ | 2.16 × 10$^{-10}$ | 1.00 × 10$^{-9}$ |

Table 2

| Species | H$_2$ | He | H | HD | C | N | O |
|---------|------|---|---|----|---|---|---|
| $n_{H}$ | 0.500 | 9.76 × 10$^{-2}$ | 2.32 × 10$^{-4}$ | 9.57 × 10$^{-6}$ | 1.02 × 10$^{-8}$ | 8.75 × 10$^{-8}$ | 1.45 × 10$^{-6}$ |

| Species | S | Si | Na | Mg | Fe | P | Cl |
|---------|---|----|----|----|----|---|---|
| $n_{H}$ | 2.00 × 10$^{-9}$ | 7.00 × 10$^{-11}$ | 6.37 × 10$^{-11}$ | 3.70 × 10$^{-10}$ | 6.07 × 10$^{-11}$ | 5.72 × 10$^{-12}$ | 1.64 × 10$^{-10}$ |

| Species | H$_2$O (ice) | CO (ice) | CO | CH$_4$ (ice) | NH$_3$ (ice) | O$_2$ | N$_2$ |
|---------|-------------|----------|----|-------------|------------|-----|-----|
| $n_{H}$ | 9.90 × 10$^{-5}$ | 3.91 × 10$^{-5}$ | 1.85 × 10$^{-5}$ | 1.66 × 10$^{-5}$ | 1.30 × 10$^{-5}$ | 7.04 × 10$^{-6}$ | 3.78 × 10$^{-6}$ |

| Species | O$_2$ (ice) | D | N$_2$ (ice) | HDO (ice) | C$_2$H$_2$ (ice) | HNO (ice) | D$_2$ |
|---------|-------------|---|------------|----------|----------------|---------|-----|
| $n_{H}$ | 2.29 × 10$^{-6}$ | 1.81 × 10$^{-6}$ | 1.26 × 10$^{-6}$ | 1.08 × 10$^{-6}$ | 7.68 × 10$^{-7}$ | 7.25 × 10$^{-7}$ | 7.07 × 10$^{-7}$ |

6 http://kida.obs.u-bordeaux1.fr/ as of 2012 December 26.
7 http://www.strw.leidenuniv.nl/~ewine/photo/
half of the D₂ rotational-nuclear spin states are missing, the simple argument about 2/3 and 1/3 branching ratios remains valid.

To limit the size of the network we have restricted the cloning process to avoid any -OH endgroups. Observations of deuterated species suggest that fractionation of species with -OD endgroups is less important in low-mass protostars, but may still be important for high-mass protostars. For example, Parise et al. (2006) conducted a survey of deuterated formaldehyde and methanol in a sample of seven low-mass class 0 protostars, and found CH₃OD/CH₃DOH ≲ 0.1. A hypothesis of rapid conversion of CH₃OD into CH₃OH in the gas-phase due to protonation reactions that would affect only species for which deuterium is bound to the electronegative oxygen has been suggested by Charnley et al. (1997) and Osamura et al. (2004). We conducted a small study using a version of our deuterium network where -OH endgroups were cloned and found no significant changes in the resulting time-dependent molecular abundances.

Added and updated reactions are found in Tables 12 and 13. The resulting chemical network consists of ~55,000 reactions connected by ≥1900 species, to our knowledge the most extended network for deuterium chemistry to date.⁸

### 2.5. Analysis of Reaction Updates

Given the large size of the network with uncertainties in the adopted rate coefficients, reaction barriers, and branching ratios, it is educational to estimate how these uncertainties propagate in time-dependent modeled abundances. Before performing a detailed sensitivity analysis, as in our study of disk chemistry uncertainties (Vasyunin et al. 2008), it is of interest to characterize the influence of the reaction rate updates on the calculated abundances and the D/H ratios. This may help us to highlight the significance of recent laboratory astrochemistry activities, both for deuterated and undeuterated species, in providing more accurate astrochemical data to the community.

First, we studied the effects of introducing deuterium chemistry into our model on abundances of un-deuterated species by comparing abundances throughout the parameter space to a non-deuterated version of the network. We found that species with relative abundance > 10⁻²⁵ show mean values in abundance variations between the two networks within a factor of 0.95–1.05. Since we did not find any particularly large variations in abundances for H-bearing species, we conclude that the results from our updated analysis are a pure effect of updated reaction rates and not caused by the additional pathways created by the cloning routine.

In order to separate the effect that recent updates have had on abundances, we generated an additional network by cloning an outdated network restricted to the reaction rate updates up until 2005. We then studied the impact of updated reaction rate coefficients by comparing the calculated time-dependent abundances between the "old" chemical network and the "new" network in the two-dimensional parameter space discussed in Section 2.1. In addition to the D/H abundance ratios, we will emphasize the differences in these ratios between the models, which we calculated by dividing the respective D/H ratios in the updated 2012 network by those from the outdated 2005 network, and will denote this ratio as R(D/H). The results have been obtained with the Primordial model only. In this comparison, we have excluded minor species with relative abundances below 10⁻²⁵. It should be noted that the R(D/H) ratios may remain unchanged when absolute abundances of species and their isotopologues in the updated and outdated networks increase in unison.

We list in Table 3 the arithmetic mean value calculated over the parameter grid (T = 5–150 K, n_H = 10⁵–10¹⁰ cm⁻³) of R(D/H) ratios for all species with fractional abundances ≥ 10⁻²⁵ for which the mean value of R(D/H) ratios have changed by more than a factor of five. Among the listed species, we find light hydrocarbons (e.g., CH₂D₂, CH₃D₂), ions (CH₄D⁺, HD₂O⁺), and simple organic molecules (e.g., DCOOH, D₂CO), as well as key molecules such as doubly deuterated water and ammonia. Multi-deuterated species appear to be more affected by the updates than their singly deuterated analogs, as there are more intermediate pathways involved in their chemistry, as is most evident by comparing HD₂O⁺ and H₂DO⁺ in Table 3.

There are also several species affected by the abundances that do no show any variance in D/H ratios, i.e., both deuterated and undeuterated species are similarly affected by updates. The abundances of CH₂D⁺ and CHD₂⁺ provide good examples of such behavior. These species show a coherent increase (within a factor of 1.1 between un-deuterated species and isotopologues) in their gas-phase abundances at 1 Myr and at high temperatures (≥ 100 K) and densities (n_H ≥ 10⁷ cm⁻³). As a result, their R(D/H) values remain close to unity. We identified the coherent increase in abundance as originating from an update taken from KIDA in the rate coefficient for the slow radiative association reaction forming CH₂⁺ via CH₂⁺ colliding with H₂. The rate coefficient of this reaction was lowered by almost two orders of magnitude, from 1.30 × 10⁻¹⁴ cm³ s⁻¹ to 4.10 × 10⁻¹⁶ cm³ s⁻¹ (at room temperature; see Wakelam et al. 2010b). We note that the older value was based on a misinterpretation of the original literature, which used 300 K in the formula for the rate coefficient but was intended only for temperatures up to 50 K (Herbst 1985). The same D/H ratio variation is transferred to HD₂O⁺ and H₂DO⁺ through the ion–neutral reaction with CH₂⁺ and its isotopologues reacting with free oxygen atoms. The abundances of the CH₂ isotopologues derive from the dissociative recombination of CH₂⁺ (and its isotopologues) as well as from ion–molecule reactions with CO, so CH₂⁺ is directly affected by the updated reaction rate. It then transfers its D/H ratio variation into C₂H₂D₂ through CH₂D₂ reacting with CH. Another route involves the intermediary reaction between CH₂D₂ and S⁺ to form HD₂S⁺, which later dissociatively recombines into D₂CS, which in turn reacts with CH₂D₂.

On the other hand, the deuterated analog of this radiative association reaction does not occur; instead CH₂⁺ + HD produces CH₂D⁺ and H₂, and the corresponding rate constant is the same in the outdated and new networks (Millar et al. 1989). This slows down production of the key ion, CH₂⁺, while deuterated isotopologues of CH₂⁺ and CH₂⁺ are produced with almost the

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⁸ Publicly available at: http://mpia.de/PSF/codes.php

### Table 3

| Species         | R(D/H) | Species         | R(D/H) |
|-----------------|--------|-----------------|--------|
| HD₂O⁺           | 24.3   | CHD₃            | 8.5    |
| CH₂D₂           | 8.5    | CH₃D            | 8.1    |
| CH₂D⁺           | 7.9    | CH₃D₂           | 7.3    |
| CD₃             | 7.0    | H₂DO⁺           | 5.9    |
| HD₂CS⁺          | 5.4    | D₂CS            | 5.3    |

**Note:** Includes only species with fractional abundances > 10⁻²⁵.
same rate, consequently affecting D/H ratios of the gas-phase species listed in Table 3. It does not affect abundant organic species such as methanol and formaldehyde however, as they are mainly formed by surface hydrogenation of CO ice.

We find that there is a particularly large variance in abundances for the two sulfur-bearing species, C2S and C2S+, which show an increase in abundance by a factor of 187 and 26, respectively, compared with the non-deuterated network. We are not concentrating on the chemistry of sulfur-bearing molecules in this study because their chemistry is still poorly understood and often restricted to a few pathways. But the additional pathways that the cloning routine generates has a stronger effect on these two species as pathways reducing their abundances proceed much slower than their formation pathways.

2.6. Error Propagation in Deuterium Fractionation Chemistry

We studied the impact of uncertainties in reaction rate coefficients on the resulting chemical abundances, and how they propagate throughout the chemical evolution. Two separate environments were chosen for this study, representing dark clouds (T = 10 K, n_H = 10^4 cm^{-3}; Nielbock et al. 2012) and lukewarm infrared dark clouds (IRDCs; T = 25 K, n_H = 10^3 cm^{-3}; Vasyunina et al. 2012). In these and all subsequent runs mentioned in this paper, we use the Primordial initial conditions unless stated to the contrary. We chose to concentrate on the uncertainties of the rate coefficients of the gas-phase reactions. Including variations in surface chemistry rates is a tricky problem as these depend on surface mobility, binding and diffusion energies of reactants, and properties of the surface itself (porosity, irregularities, etc.). Recently, Taquet et al. (2012) have studied the importance of deuterium fractionation on dust surfaces, using a multi-layered ice mantle model and quantified it a challenging task to find a very precise correlation between the rate uncertainties and uncertainties in the molecular abundances of a particular species. Since for many deuterated species the set of primal pathways easily exceeds several reactions, the relative contribution of each individual reaction to the final uncertainty is likely to be small, <10%. To isolate the most problematic reactions for several key observed species, we conducted a sensitivity analysis using the same cross-correlation method as implemented by Vasyunin et al. (2008). We selected a handful of molecules, including their isotopologues and isomers, viz., H3+, H2O, HCN, HCO+, and CH3OH, and for each of these species we calculated time-dependent linear correlation coefficients between the abundances and the rate coefficients for all the 10,000 network realizations and for each of our 30 logarithmically taken time steps. The linear correlation coefficients c_L(i, j, t) at specific density, i, and temperature, j, points and at time t are calculated by:

$$c_L(i, j, t) = \frac{\Sigma(x^s(i, j, t) - x^s(i, j, t))}{\Sigma(x^s(i, j, t) - x^s(i, j, t))^2} \Sigma(\alpha^s - \alpha^s)^2$$ (3)

with $x^s(i, j, t)$ being the molecular abundance for species $s$ and iteration $l$, and $x^s(i, j, t)$ and $\alpha^s$ signifying the standard (mean) abundances and rate coefficients for species $s$, respectively. Because key reactions can vary through time evolution, we calculate and use cumulative correlation coefficients in our results, for which we integrated the absolute values of time-dependent linear correlation coefficients over the 30 logarithmic taken time steps taken over 1 Myr. In our results in the next section, we restrict discussion to the cumulative correlation coefficients, designated as c.

3. RESULTS

3.1. Sensitivity Analysis

We have determined that 10,000 realizations of the network may not be adequate for results of our sensitivity analysis to fully converge. For correlation coefficients c < 0.1 we sometimes still see small variations when we compare our results with a model containing only 9000 realizations. Therefore, we also ran a separate set of simulations with 20,000 realizations for a dark cloud environment, but found the same result with only minor deviations for the reactions with low correlation coefficients, c < 0.1. All correlation coefficients should stop fluctuating with size as soon as the number of the network realizations exceeds the number of reactions in the network, which is ~50,000. Running the sensitivity analysis code with so many realizations, however, would be prohibitively time consuming. Therefore, below we consider reactions with c > 0.1 in our discussion.

Table 4 lists the subset of reactions with cumulative correlation coefficients c > 0.1, which are the most problematic for the chemical evolution of the following species (and their isotopologues and isomers): H3+, HCO+, HCN, H2O, CH3OH, H2O+, CH3+, C2H2+, and CO. Because there are several additional key reactions with 0.05 < c < 0.1, we list them extensively in Table 11, including also reactions with c > 0.05 for the same set of species.

As can clearly be seen, ion–neutral processes dominate Table 4, accompanied by a few dissociative recombinantation and neutral–neutral reactions as well as cosmic ray ionization of the two critical species: H2 and He. The last process may require more detailed description in astrochemical models, such as recently presented in Rimmer et al. (2012) and Glassgold et al.
Reaction Uncertainty

than estimated. Also, isomerization reactions for HOC + and coefficients are only an approximation, and can, in fact, be larger the table are produced by our cloning procedure, so their error may become important. Many of the deuterated reactions in dense cores, for which uncertainties in the gas-phase chemistry fraction of these species is still present in the gas in the center of not be strongly affected by the uncertainties. However, a small bimolecular reactions are connected to the chemical evolution of two for this group of processes. Approximately half of the DOC+ with reaction rate uncertainties of a factor of two possess strong correlation coefficients (0.3–0.4).

We find it clear that fractionation channels of the H3+ and CH3+ isotopologues require further study, as do reactions involving the isotopologues of H3+ reacting with CO, water, OH, and their isotopologues, forming the initial steps toward more complex molecules. Reactions with H3+ and H2D+ are both well represented in the list and initiate the ion–molecule chemistry, while HD2+ and D3+ are often not abundant enough to have a significant effect in our models. H3+ and H2D+ react with CO to form the isotopologues of HCO+, with OH and OD to form ionized water (H2O+, HDO+) as well as the water isotopologues, which strongly affect water abundances and D/H ratios. We also see many other interconnecting reactions among our set of key species. Several dissociative recombination reactions, which proceed very rapidly, show strong correlations. While their reaction rates can be accurately determined (Florescu-Mitchell & Mitchell 2006) the products and branching ratios of these reactions are not precisely known (see, e.g., Hamberg et al. 2010b; Geppert et al. 2006).

3.2. Uncertainties

After calculating time-dependent abundances for all the realizations of the chemical network with varied reaction rate coefficients, and for each considered physical model, we fit Gaussians to the resulting abundance distributions at 1 Myr for all species. We carefully checked that such an approximation could be applied to the abundance distributions and found it to be the case for almost all species. In Figure 1, we show examples of abundance distributions, with their Gaussian fits, for H3D+ and DCOOH in dark cloud and warm IRDC environments, respectively, both showing good fits. From the Gaussian fits, we then determined the FWHM (2σ) of these distributions and used the 1σ values to quantify the spread in abundances, which we henceforth refer to as the abundance uncertainties. We also applied the same procedure for the calculated D/H ratios, and show examples of the resulting D/H ratio distributions in Figure 2 for water and formic acid in the same two regions. We find good fits to all these distributions with estimated 1σ values of factors of 1.9 and 2.9 for the abundance distribution of water and formic acid, respectively, while the values for D/H ratios are a factor of 1.4 and 3.2, respectively.
In Figure 3, we plot the 1σ abundance uncertainties for deuterated species with up to three D-atoms at 1 Myr as a function of the number of atoms for both environments. There are two major trends visible in this plot. First, the abundance uncertainties are in general lower in the case of the IRDCs models compared with cold dark clouds.

At such a low temperature (10–20 K) many reactions with barriers cannot proceed, lowering the overall chemical complexity and thus the cumulative rate uncertainties. One would expect uncertainties to be the lowest for dark clouds, but we suggest that as D/H ratios and abundances of deuterated species are also higher in colder environments, more reactions can occur to increase uncertainties. Second, there is a strong trend of increasing abundance uncertainties with the number of atoms in species. This is obvious as the more atoms a species has, the more reaction pathways lead to its production and destruction from initial composition, and thus the higher is the accumulating effect of their uncertainties on modeled abundances (see also the discussion in Vasyunin et al. 2008).

In general, using the 1σ confidence level, the abundances and column densities of species made of $\leq 3$ atoms (e.g., CO, HCO$^+$, DCO$^+$) are uncertain by factors 1.5–5, those for species made of 4–7 atoms are uncertain by a factor of 1.5–7, and those for more complex species made of >7 atoms are uncertain by a factor of 2–10. The uncertainties for D- and H-bearing species are very similar in dark cloud environments. In warm IRDCs the typical uncertainties of larger H-bearing species (>4 atoms) are approximately a factor of two lower compared to D-bearing species, as de-fractionation begins at these elevated temperatures (25 K). Our estimates for the abundance uncertainties for deuterated species are comparable to the abundance uncertainties of un-deuterated species in protoplanetary disks (Vasyunin et al. 2008), as well as diffuse and dark dense clouds (e.g., Vasyunin et al. 2004; Wakelam et al. 2010a). Chemically simple species containing Mg, Na, and Si tend to have high uncertainties reaching up to three orders of magnitude in abundances because their chemical pathways remain poorly investigated. Also large molecular species, whether they are rather abundant hydrocarbons (C$_n$H$_m$ with $n, m \gtrsim 4$), with fractional abundances up to $10^{-9}$–$10^{-7}$, or complex and less abundant organic species (e.g., methyl formate, dimethyl ether), have large error bars in the computed abundances. For this latter group, the uncertainties can reach more than one order of magnitude.

In addition to the abundance uncertainties, we also determine uncertainties in the resulting D/H ratios, as shown in Figure 4. Overall, the uncertainties in D/H ratios are lower when compared with the uncertainties of the corresponding H- and D-bearing isotopologues. This is because abundances of the individual isotopologues are often affected by the rate uncertainties in the same way, given that a majority of the deuterium fractionation processes are cloned, thus inheriting the rate of the “ancestor” reaction. We find the same trends as for the abundance uncertainties, but only a hint of increasing uncertainties with number of atoms. Uncertainties for D/H ratios are generally about half of one order of magnitude, but may vary between a factor of 2 and 10. As in the case of the abundance uncertainties, we find the largest D/H uncertainties for large hydrocarbons (C$_n$H$_m$, with $n, m \gtrsim 4$), complex organics, and species containing Mg, Na, and Si.

The question remains how the uncertainties compare between deuterated and un-deuterated species. To illustrate the overall relative uncertainties between deuterated species and their undeuterated analogs, we plot in Figure 5 the ratios of abundance uncertainties of up to triply deuterated species and their undeuterated analogs as a function of the number of atoms. Note that these relative uncertainties are not the same as the uncertainties in D/H ratios; the former can be labeled as...
u(D)/u(H), while the latter can be labeled as u(D/H), where u stands for uncertainty. Hence, the u(D)/u(H) ratio allows us to compare the relative errors between deuterated and un-deuterated species.

A majority of deuterated species show larger abundance uncertainties with respect to their un-deuterated analogs. There are two major reasons for this behavior. First, the majority of reactions with deuterated species originate from our cloning procedure, and thus have larger assumed uncertainties. Second, to produce a deuterium isotopologue of a molecule, additional chemical pathways (e.g., isotope exchange processes) are required, increasing the accumulation of rate uncertainties. For many hydrocarbons (C\textsubscript{m}H\textsubscript{n}, C\textsubscript{m}H\textsubscript{n}^+ with m, n = 2, 3) the abundance uncertainties of their deuterated isotopologues are comparable to those of the main isotopologues (with ratios of ~0.7–2). These hydrocarbons form through ions of hydrocarbons reacting with H\textsubscript{2} or smaller neutral hydrocarbons, such as CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{2}, and their reactions originate purely from the cloning procedure.

For a limited number of species, the abundance uncertainties of their deuterated isotopologues are even smaller than for the main isotopologues (with ratios of ~0.7–0.9; see Figure 5), e.g., C\textsubscript{2}D\textsuperscript{+} and D\textsuperscript{-}. These are simple radicals and ions produced by a limited set of reactions, with relatively well-known rate coefficients and thus small uncertainties. The relevant deuterium fractionation chemistry is also limited and has comparably low uncertainties (~0.7–1.1). Note that the spread in abundance uncertainties ratios appears to decrease with increasing number of atoms in species, getting closer to unity. This effect in Figure 5 occurs because we plot only species with relative abundances exceeding 10\textsuperscript{-25} (with respect to hydrogen), whose numbers decrease substantially with size. If we also add species with such low abundances, this feature disappears and the trend in the uncertainties between small and large molecules is similar.

For HD and D\textsubscript{2}, we find that the ratio of their abundance uncertainties to that of H\textsubscript{2} can reach very large values, ~1000 and ~10,000, respectively. This effect occurs because abundances of H\textsubscript{2} are very well constrained (uncertainties are ~10\textsuperscript{-5}), while HD and D\textsubscript{2} have typical values of abundance uncertainties up to one order of magnitude.

Finally, in Figure 6 we plot the abundance uncertainties of deuterated species as a function of number of D-atoms, once again restricted to species with relative abundances > 10\textsuperscript{-25}. We see an increase in uncertainty with number of D-atoms, as expected from the increasing number of reactions involved for subsequently adding more D-atoms. We also notice a wider spread in uncertainties for species with lower levels of deuteration because smaller species, such as OD, HDO, and DCO\textsuperscript{+}, often have lower uncertainties because there are not as many steps involved in their formation compared to larger species. Larger multiply deuterated species cannot have these low uncertainties as there are too many steps involved in their formation. Once again we also find that dark clouds have a larger spread in uncertainties than warm IRDCs. Again we argue that this difference occurs because dark cloud environments overall have higher abundances of deuterated species which are processed through more reactions.

### 3.3. General Trends in D/H Distributions

In this section, we discuss general trends in the modeled D/H ratios in our two-dimensional parameter space (see Section 2.1). The computed D/H fractionation ratios at the final time of 1 Myr are shown in Figure 7 for the Primordial (left panels of each separate block) and Evolution model (right panels of each separate block), which were introduced in Section 2.3, as functions of density and temperature for the following key gaseous molecules: H\textsubscript{2}DO\textsuperscript{+}, H\textsubscript{2}D\textsuperscript{+}, HDO, D\textsubscript{2}O, ND, ND\textsubscript{3}, DCOOH, and DCN. For most species, the D/H ratios can reach high values of ≥ 10\textsuperscript{-3} at T ≤ 30–80 K. At higher temperatures, ≥ 100 K, the computed D/H ratios begin to approach the elemental ratio of ≈ 1.5 × 10\textsuperscript{-5}. The higher D/H ratios of ≥ 0.1 have been observed for many species in the ISM, such as CH\textsubscript{2}DOH, D\textsubscript{2}CO (Ceccarelli 2002), D\textsubscript{2}O (Butner et al. 2007), H\textsubscript{2}D\textsuperscript{+} (Caselli et al. 2003), HDO (Liu et al. 2011), NH\textsubscript{3}D (Hatchell 2003; Roueff et al. 2005), and NH\textsubscript{2}D (Roueff et al. 2005). For comparison of our model results with observations, see Section 4.1.

We isolate species that are either mostly sensitive to kinetic temperature or initial abundances, the former referring to the standard temperature dependence for deuterium fractionation, and the latter referring to the difference between the initial abundances in the primordial and evolutionary models. We note that usually species for which D/H ratios depend more strongly on the initial abundances also show (a weaker) temperature dependence, because the release of CO and other radicals...
decreases the abundances of the H$_3^+$ isotopologues which lowers the efficiency of transferring D atoms to other species. These two groups are listed in Table 5. The temperature-dependent species can be further divided into two subgroups by the temperature where D/H ratios decrease most sharply, and hence where deuterium fractionation becomes less pronounced: (1) at low temperatures, $T \sim 20$–40 K (related to the fractionation via H$_3^+$ isotopologues) and (2) at higher temperatures $T \sim 80$ K (related to the fractionation via CH$_2$D$^+$ and C$_2$HD$^+$).

The left two columns of Figure 7 show species that demonstrate a strong dependence of D/H ratios on the initial abundances while the right two columns show species with a strong temperature gradient for D/H ratios and no distinct dependence on initial abundances. We define here a strong dependence on initial abundance as their evolution is significantly slower unless the physical conditions are changed. In Figure 8 we show the evolution of D/H ratios at three separate times of $10^4$, $10^5$, and $10^6$ yr, and at a density $n_H = 10^4$ cm$^{-3}$ as a function of temperature for H$_2$D$^+$, CH$_3$D$^+$ and HDO. We discuss the specific case for the evolution of HDO later and begin with the two ions (two top panels) which are highly reactive, with fast chemical timescales associated with ion–neutral reactions and dissociative recombinations. Thus, the chemical “memory” of the pristine state of the fast-evolving deuterated species is completely lost at the final considered time of 1 Myr, with no apparent differences between abundances computed with the two distinct initial abundance sets.

We find that the majority of neutral species, which includes several H-, C-, O-, and S-bearing species, show a dependence on the initial abundance as their evolution is significantly slower compared to ions. These are predominantly neutral species consider production of deuterated molecules by surface chemistry). Therefore, we do not discuss the distribution of D/H for ices separately.

The placement of species in different groups can be explained by the relative pace of their chemical evolution. If steady-state abundances are reached by 1 Myr in the primordial stage, then they remain at steady state throughout the evolutionary model unless the physical conditions are changed. In Figure 8 we show the evolution of D/H ratios at three separate times of $10^4$, $10^5$, and $10^6$ yr, and at a density $n_H = 10^4$ cm$^{-3}$ as a function of temperature for H$_2$D$^+$, CH$_3$D$^+$ and HDO. We discuss the specific case for the evolution of HDO later and begin with the two ions (two top panels) which are highly reactive, with fast chemical timescales associated with ion–neutral reactions and dissociative recombinations. Thus, the chemical “memory” of the pristine state of the fast-evolving deuterated species is completely lost at the final considered time of 1 Myr, with no apparent differences between abundances computed with the two distinct initial abundance sets.

We find that the majority of neutral species, which includes several H-, C-, O-, and S-bearing species, show a dependence on the initial abundance as their evolution is significantly slower compared to ions. These are predominantly neutral species consider production of deuterated molecules by surface chemistry). Therefore, we do not discuss the distribution of D/H for ices separately.
Ions constitute the majority of species for which calculated D/H ratios are only dependent on temperature (see Figure 7, right two columns). Species such as the H$_3^+$ isotopologues that are sensitive to freeze-out (or specifically, the freeze-out of CO), “daughter” molecules such as DCO$^+$, as well as (ionized) light hydrocarbons related to CH$_2$D$^+$ and C$_2$HD$^+$, all show a strong temperature dependence. From the exact gas kinetic temperature, labeled the critical temperature, at which the D/H ratios start to approach the elemental value, we can separate these species into two subgroups. The deuterated species formed via low-temperature fractionation channels involving isotopologues of H$_3^+$ have a critical temperature of 20–30 K, whereas other deuterated species synthesized via high-temperature fractionation channels involving CH$_2$D$^+$ and C$_2$HD$^+$ show a higher critical temperature of $\sim$80 K (Parise et al. 2009). Most multi-deuterated species belong exclusively to the low-temperature group as do the majority of ions, which inherit the temperature dependence from the H$_3^+$ isotopologues via proton/deuteron transfer reactions. The best example of such species is H$_2$D$^+$, shown in Figure 7. It shows a D/H turnover point at 20 K, after which the fractionation ratios decrease smoothly and reach levels of $\sim$10$^{-5}$ at temperatures of $\sim$100 K.

There are only a few species that show a dependence on temperature where deuterium fractionation is reduced at $T \sim$ 80 K. Those are directly synthesized from deuterated light hydrocarbon ions such as CH$_2$D$^+$, which retain high D/H ratios at elevated temperatures, e.g., DCN and CH$_2$D$_2$. HDCS is unique in showing no clear difference between the two models at least within our defined temperature range, as its chemical evolution depends almost equally on the two distinct deuterium fractionation routes (via H$_3^+$ and light hydrocarbon isotopologues) via the formation of the ion H$_2$DCS$^+$.

Also, we find that the overall sensitivity of the calculated D/H ratios to density is weak, except for species sensitive to the freeze-out of CO and other radicals, i.e., H$_2$D$^+$, HD$^+$, and their direct dissociative recombination products. These species experience a rapid decrease in fractionation ratios toward lower densities of $<10^4$ cm$^{-3}$, at which CO cannot severely deplete onto the dust grains even after 1 Myr of evolution. However, if we would follow the evolution of our chemical model beyond 1 Myr, at some moment the CO depletion can become severe enough for low-density regions to allow high D/H ratios for the H$_3^+$ isotopologues (if the adopted non-thermal desorption rate is not too high).

To understand in more detail the differences between the evolution of deuterated molecules, we have analyzed the chemistry of several key isotopologues. We considered four distinct astrophysical environments: densities of $10^4$ and $10^5$ cm$^{-3}$, and temperatures of 10 and 80 K for both the Primordial and Evolution initial abundance sets. We list key formation and destruction pathways for the assorted species and their main reactants in Tables 14–18 in Appendix B.

4. DISCUSSION

In recent years, it has been realized that the ortho/para ratio of H$_2$ and other species in a source can strongly affect the degree of deuterium fractionation. For example, the backward endothermic reaction between o-H$_2$ and H$_2$D$^+$ can proceed far more rapidly at low temperatures such as 10 K than the corresponding reaction involving p-H$_2$, and so reduce the degree of deuterium fractionation if there is a sufficient amount of o-H$_2$ (e.g., Flower & Pineau-Des-Forets 1990; Pagani et al. 1992, 2013; Flower et al. 2006; Sipilä et al. 2010). The fraction
Table 6
Observable Deuterated Species with ALMA in Dark Clouds

| Species | \( n(x)/n(H_2) \) \( \times 10^{-12} \) | Line | Frequency (GHz) | Line Flux (mK) | ALMA Band |
|---------|-------------------------------|------|----------------|----------------|-------------|
| D_2CO   | 1.05                          | 3 0 3 → 2 0 2 | 174.413 | 33.48 | 5 |
|         |                               | 4 0 4 → 3 0 3 | 231.410 | 28.48 | 6 |
|         |                               | 5 0 5 → 4 0 4 | 287.486 | 14.99 | 7 |
| D_2O    | 53.6                          | 1 1 1 → 1 0 1 | 316.800 | 1899.80 | 7 |
|         |                               | 2 0 2 → 1 1 1 | 468.247 | 853.66 | 8 |
|         |                               | 2 1 1 → 2 0 2 | 403.562 | 198.18 | 8 |
| D_2S    | 0.0634                        | 2 2 0 → 1 1 1 | 669.787 | 1.40  | 9 |
| DCN     | 5.21                          | 1 → 0       | 115.271 | 6648.00 | 3 |
|         |                               | 2 → 1       | 230.538 | 5272.00 | 6 |
|         |                               | 3 → 2       | 345.796 | 3860.00 | 7 |
| DCO^+   | 16.04                         | 2 → 1       | 144.077 | 2196.40 | 4 |
|         |                               | 4 → 3       | 288.144 | 2054.53 | 7 |
|         |                               | 5 → 4       | 360.170 | 801.50  | 7 |
| DNC     | 11.01                         | 2 → 1       | 152.610 | 1047.68 | 4 |
|         |                               | 4 → 3       | 305.207 | 866.60  | 7 |
|         |                               | 6 → 5       | 457.776 | 66.33   | 8 |
| H_2DO^+ | 29.93                         | 1 0 1 1 → 2 1 1 0 | 250.914 | 9.84  | 6 |
| HDCO    | 24.69                         | 4 0 4 → 3 0 3 | 256.586 | 616.96 | 6 |
|         |                               | 2 0 2 → 1 0 1 | 128.813 | 513.23 | 4 |
|         |                               | 3 1 2 → 2 1 1 | 201.341 | 853.66 | 5 |
| HDCS    | 0.7897                        | 5 0 5 → 4 0 4 | 154.885 | 4.12  | 4 |
|         |                               | 3 0 3 → 2 0 2 | 92.982  | 3.12  | 3 |
|         |                               | 6 0 6 → 5 0 5 | 185.693 | 3.05  | 5 |
| HDS     | 1.630                         | 2 0 2 → 1 0 1 | 477.764 | 25.62 | 8 |
|         |                               | 1 0 1 → 0 0 0 | 244.556 | 18.22 | 6 |
|         |                               | 1 1 0 → 1 0 1 | 195.559 | 9.05  | 5 |
| ND      | 27.03                         | 1 0 1 2 → 0 1 2 3 | 491.934 | 294.70 | 8 |
|         |                               | 1 0 1 2 → 0 1 1 2 | 491.969 | 124.38 | 8 |
|         |                               | 1 0 1 1 → 0 1 2 2 | 491.917 | 123.84 | 8 |
| ND_3    | 0.96                          | 2 0 0 → 1 0 1 | 614.933 | 73.05 | 9 |
|         |                               | 2 1 1 → 1 1 0 | 618.125 | 60.59 | 9 |
|         |                               | 2 1 0 → 1 1 1 | 614.968 | 59.74 | 9 |
| NH_2D   | 29.67                         | 1 1 0 1 → 0 0 0 0 | 494.455 | 10000.00 | 8 |
|         |                               | 1 1 0 0 → 1 1 0 0 | 85.926  | 870.34 | 3 |
|         |                               | 1 0 1 1 → 0 0 0 1 | 332.782 | 732.35 | 7 |
| NHD_2   | 14.60                         | 2 1 1 0 → 1 0 1 1 | 699.224 | 874.07 | 9 |
|         |                               | 2 1 1 1 → 1 0 1 0 | 709.350 | 456.67 | 9 |
|         |                               | 1 1 1 0 → 0 0 0 0 | 335.514 | 40.68 | 7 |

Notes. The table is limited to species with relative abundances > \( 10^{-12} \). Species detected unambiguously or in a preliminary manner in the specific environments are marked in boldface. Parameters for line flux calculations: 10 K, \( 10^4 \) cm\(^{-3} \), 10\(^{22} \) cm\(^{-2} \).

^ a DCN should be observable, but is not listed in CDMS or RADEX; instead, calculated RADEX values for HCN are listed.

of \( H_2 \) in its ortho levels is small but not well known, however, and can only be obtained by careful analysis of reduced fractionation levels in specific sources. Given the complexity and huge size of our chemical network, with many reactions containing ortho and para reactants, we chose not to include the different states of deuterated and non-deuterated species for the moment, and leave this to a separate study. Thus, our network is rather accurate for modeling dense, cold ISM phases, where \( H_2 \) mainly exists in its para state (e.g., Pagani et al. 2009) and higher temperature phases where the degree of fractionation is in any case low.

Another important effect concerning deuterium fractionation that is not fully treated by our approach is the evolution of physical conditions, such as a steady warm-up phase of a protostellar envelope leading to the formation of a hot core/corino. Our simple evolutionary model, where we simulate a TMC-1 environment for 1 Myr and use these final abundances as the initial abundances for the modeling is only a “poor man’s” approach for such a study (see, e.g., Cazaux et al. 2011; Aikawa et al. 2012). Certainly this abrupt change from TMC-1 temperature and density to other temperatures and densities does not catch the gradual evolution of the physical conditions from one phase to the next. As we showed in Section 3, D/H ratios for a large number of the deuterated species are mainly dependent on temperature, while density has an effect on the evolution of a limited number of species. The gradual increase in temperature throughout the collapse of a dark cloud and the formation of a (proto)star will undoubtedly affect the evolution of some deuterated species in ways uncatchable by our approach. Examples include the release of key ice species into the gas-phase or the steady increase in mobility of surface radicals, which produce complex organic molecules (Garrod et al. 2008). However, the effects on predicted D/H ratios are likely to be only minor as the final stages of collapse are rapid, so that deuterium fractionation of the gas-phase species stays until the material winds up in the actual protostar or in the protoplanetary disk surrounding it (Aikawa et al. 2008, 2012).
Table 7
Observable Deuterated Species with ALMA in Infrared Dark Clouds

| Species     | n(x)/n(H$_2$) ($\times 10^{-11}$) | Line     | Frequency (GHz) | Line Flux (mK) | ALMA Band |
|-------------|---------------------------------|----------|----------------|----------------|-----------|
| C$_2$D      | 0.039                           | 11 12 → 10 11 | 97.140          | 2.36           | 3         |
|             |                                 | 12 13 → 11 12 | 105.971         | 2.35           | 3         |
|             |                                 | 10 11 → 9 10  | 88.308          | 2.25           | 3         |
|             | 0.045                           | 2 1 2 → 1 1 1 | 490.012         | 44.05          | 8         |
|             |                                 | 1 0 1 → 0 0 0 | 278.692         | 10.68          | 7         |
|             |                                 | 2 1 1 → 2 1 2 | 201.754         | 1.62           | 5         |
| CH$_2$D$^+$ | 0.0038                          | 9 0 9 → 8 0 8 | 156.281         | 7.47           | 4         |
|             |                                 | 10 0 10 → 9 0 9 | 173.639        | 6.73           | 5         |
|             |                                 | 6 0 6 → 5 0 5  | 104.198         | 6.00           | 3         |
| D$_2$CO     | 0.011                           | 5 0 5 → 4 0 4 | 287.486         | 63.48          | 7         |
|             |                                 | 6 0 6 → 5 0 5  | 342.522         | 48.67          | 7         |
|             |                                 | 3 0 3 → 2 0 2  | 174.413         | 45.25          | 5         |
| D$_2$O      | 3.10                            | 1 1 0 → 0 0 0 | 317.800         | 30000.00       | 7         |
|             |                                 | 2 0 2 → 1 0 1  | 468.247         | 30000.00       | 8         |
|             |                                 | 2 1 1 → 1 0 0  | 403.562         | 24681.37       | 8         |
| DCN$^a$     | 0.38                            | 1 → 0    | 88.634          | 21800.00       | 3         |
|             |                                 | 2 → 1    | 177.258         | 20590.00       | 5         |
|             |                                 | 3 → 2    | 265.886         | 19040.00       | 6         |
| DCO$^a$     | 47.09                           | 5 → 4    | 360.170         | 30000.00       | 7         |
|             |                                 | 3 → 2    | 216.113         | 30000.00       | 6         |
|             |                                 | 6 → 5    | 432.189         | 30000.00       | 8         |
| DNC         | 0.81                            | 3 → 2    | 228.910         | 24216.75       | 6         |
|             |                                 | 6 → 5    | 457.776         | 14474.58       | 8         |
|             |                                 | 2 → 1    | 152.610         | 11600.74       | 4         |
| DOC$^a$     | 0.00062                         | 3 → 2    | 229.149         | 15.36          | 6         |
|             |                                 | 5 → 4    | 318.885         | 15.26          | 7         |
|             |                                 | 6 → 5    | 458.237         | 9.15           | 8         |
| H$_2$DO$^+$ | 3.39                            | 1 0 1 → 2 1 0 | 250.914         | 2582.00        | 6         |
|             |                                 | 3 1 0 → 2 2 1 1 | 649.653        | 368.10         | 9         |
|             |                                 | 3 3 0 → 2 2 0 1 | 632.902        | 342.59         | 9         |
| HDCO        | 0.10                            | 5 0 5 → 4 0 4 | 319.770         | 629.27         | 7         |
|             |                                 | 3 0 3 → 2 0 2 | 192.893         | 502.15         | 5         |
|             |                                 | 4 1 3 → 3 1 2 | 268.292         | 426.06         | 6         |
| HDCS        | 0.0065                          | 7 0 7 → 6 0 6 | 216.662         | 6.88           | 6         |
|             |                                 | 5 0 5 → 4 0 4 | 154.885         | 6.46           | 4         |
|             |                                 | 8 0 8 → 7 0 7 | 247.488         | 5.69           | 6         |
| HDS         | 0.018                           | 1 1 1 → 0 0 0 | 389.041         | 70.17          | 8         |
|             |                                 | 2 0 2 → 1 0 1 | 477.764         | 62.06          | 8         |
|             |                                 | 3 0 3 → 2 0 2 | 691.498         | 45.74          | 9         |
| ND          | 0.16                            | 1 0 1 → 0 1 2 3 | 491.934        | 357.79         | 8         |
|             |                                 | 1 0 1 → 0 1 2 2 | 491.969        | 150.99         | 8         |
|             |                                 | 1 0 1 → 0 1 2 2 | 491.917        | 150.36         | 8         |
| ND$_3$      | 0.0080                          | 2 1 1 → 1 1 0 | 618.125         | 125.84         | 9         |
|             |                                 | 2 1 0 → 1 1 1 | 614.968         | 124.41         | 9         |
|             |                                 | 1 0 1 → 0 0 0 | 309.909         | 68.34          | 7         |
| NH$_2$D     | 27.15                           | 1 1 0 → 0 0 0 0 | 494.455        | 30000.00       | 8         |
|             |                                 | 2 0 2 → 1 0 1 1 | 649.916        | 17102.87       | 9         |
|             |                                 | 1 1 1 → 1 0 1 1 | 85.926         | 16766.37       | 3         |
| NHD$_2$     | 0.45                            | 1 1 0 → 0 0 0 0 | 388.652         | 4199.24        | 8         |
|             |                                 | 2 1 1 → 1 0 1 0 | 709.350         | 3739.42        | 8         |
|             |                                 | 2 0 2 → 1 1 0 1 | 410.491         | 296.35         | 8         |

Notes. The table is limited to with relative abundances > $10^{-12}$. Species detected unambiguously or in a preliminary manner in the specific environments are marked in boldface. Parameters for line flux calculations: 25 K, $10^7$ cm$^{-3}$, $10^{24}$ cm$^{-2}$.

$^a$ DCN should be observable, but is not listed in CDMS or RADEX; instead, calculated RADEX values for HCN are listed.

4.1. Observations

In Tables 6–8 we list the most abundant, (potentially) observable deuterated species with ALMA in dark clouds, IRDCs, and HMPOs, respectively. In order to predict the observability of molecules in these different environments we use the Cologne Database of Molecular Spectroscopy (CDMS; Müller et al. 2001, 2005) to calculate line fluxes under local thermal equilibrium (LTE) conditions for various deuterated molecules with transitions observable by ALMA. For these estimates we assume the following parameters for the different environments: for dark clouds temperature 10 K, number density $10^4$ cm$^{-3}$ and...
Table 8
Observable Deuterated Species with ALMA in High-mass Protostellar Objects

| Species | \(n(x)/n(H_2) \times 10^{-11}\) | Line       | Frequency (GHz) | Line Flux (mK) | ALMA Band |
|---------|-----------------------------|------------|----------------|----------------|------------|
| C4D     | 0.95                        | 23 24 → 22 23 | 203.104        | 28.13          | 5          |
|         |                             | 22 23 → 21 22 | 194.275        | 27.98          | 5          |
|         |                             | 24 25 → 23 24 | 211.932        | 27.96          | 6          |
|         | 0.018                       | 42 -1 43 → 41 42 | 112.462       | 1.97           | 3          |
|         |                             | 41 -1 42 → 40 41 | 109.856        | 1.97           | 3          |
|         |                             | 41 1 42 → 40 1 41 | 109.816        | 1.97           | 3          |
| D2CO    | 0.0017                      | 8 0 8 → 7 0 7 | 499.596        | 2.44           | 8          |
|         |                             | 11 0 11 → 10 1 10 | 605.672       | 2.21           | 9          |
|         |                             | 7 0 7 → 6 0 6 | 396.517        | 2.18           | 8          |
| D2CS    | 0.000658                    | 12 0 12 → 11 0 11 | 337.599       | 1.79           | 7          |
|         |                             | 14 0 14 → 13 0 13 | 392.631       | 1.78           | 8          |
|         |                             | 11 0 11 → 10 0 10 | 309.916       | 1.71           | 7          |
| D2O     | 1.87                        | 2 1 1 → 2 0 2 | 403.562        | 5768.78        | 8          |
|         |                             | 2 2 2 → 3 1 1 | 692.444        | 3398.71        | 9          |
|         |                             | 2 0 2 → 1 0 1 | 468.247        | 3344.45        | 8          |
| DCN     | 0.21                        | 1 → 0       | 88.634         | 71760.00       | 3          |
|         |                             | 2 → 1       | 177.258        | 70430.00       | 5          |
|         |                             | 3 → 2       | 265.886        | 68680.00       | 6          |
|         |                             | 9 → 8       | 648.193        | 75000.00       | 9          |
|         | 23.91                       | 6 → 5       | 432.189        | 75000.00       | 8          |
|         |                             | 5 → 4       | 360.170        | 75000.00       | 7          |
| DCS     | 0.0023                      | 12 → 11     | 432.338        | 5.49           | 8          |
|         |                             | 10 → 9      | 360.307        | 5.27           | 7          |
|         |                             | 13 → 12     | 468.347        | 5.23           | 8          |
| DNC     | 0.41                        | 9 → 8       | 686.553        | 70428.88       | 9          |
|         |                             | 6 → 5       | 457.776        | 6233.04        | 8          |
|         |                             | 4 → 3       | 305.206        | 3003.38        | 7          |
| H2DO+   | 2.27                        | 3 3 1 0 → 2 2 1 1 | 649.653       | 2352.22        | 9          |
|         |                             | 3 3 0 0 → 2 2 0 1 | 632.902       | 2258.85        | 9          |
|         |                             | 4 1 3 0 → 3 0 3 1 | 716.959       | 1629.36        | 9          |
| HDCO    | 0.093                       | 10 0 10 → 9 0 9 | 625.688       | 136.82         | 9          |
|         |                             | 7 0 7 → 6 0 6 | 444.229        | 134.73         | 9          |
|         |                             | 8 1 8 → 7 1 7 | 491.937        | 129.31         | 8          |
| HDCS    | 0.56                        | 13 0 13 → 12 0 12 | 400.766       | 151.96         | 8          |
|         |                             | 11 0 11 → 10 0 10 | 339.646       | 148.23         | 7          |
| ND      | 3.70                        | 10 1 2 → 0 1 2 3 | 491.934       | 911.92         | 8          |
|         |                             | 10 1 2 → 0 1 1 2 | 491.969       | 384.82         | 8          |
|         |                             | 10 1 1 → 0 1 2 2 | 491.917       | 383.23         | 8          |
| ND3     | 0.0031                      | 2 1 1 → 1 0 0 | 618.125        | 4.24           | 9          |
|         |                             | 2 1 0 → 1 0 0 | 614.968        | 4.20           | 9          |
|         |                             | 1 0 1 → 0 0 0 | 309.909        | 1.14           | 7          |
| NH2D    | 25.07                       | 1 1 0 1 → 0 0 0 0 | 494.455       | 8876.12        | 8          |
|         |                             | 3 3 0 0 → 3 2 2 1 | 618.142       | 5010.99        | 9          |
|         |                             | 2 2 0 1 → 2 1 2 0 | 475.890       | 4998.31        | 9          |
| NHD2    | 0.37                        | 2 1 1 1 → 1 0 1 0 | 709.350       | 301.28         | 9          |
|         |                             | 1 1 0 1 → 0 0 0 0 | 388.652       | 158.40         | 8          |
|         |                             | 3 1 2 1 → 2 2 0 0 | 672.370       | 40.29          | 9          |

Notes. The table is limited to species with relative abundances > \(10^{-12}\). Species detected unambiguously or in a preliminary manner in the specific environments are marked in boldface. Parameters for line flux calculations: 75 K, 10^5 cm^{-3}, 10^24 cm^{-2}.  

\(^a\) DCN should be observable, but is not listed in CDMS or RADEX; instead, calculated RADEX values for HCN are listed.

H\(_2\) column density \(10^{22}\) cm\(^{-2}\) (Launhardt et al. 2013), for warm IRDCs 25 K, \(10^5\) cm\(^{-3}\) and \(H_2\) column density \(10^{24}\) cm\(^{-2}\) (e.g., Rathborne et al. 2008), and for HMPOs 75 K, \(10^5\) cm\(^{-3}\) and column density \(10^{24}\) cm\(^{-2}\) (e.g., Beuther et al. 2007; Rodón et al. 2008). There are known differences in \(H_2\) column densities between interferometry and single-dish observations (Vasyunina et al. 2009). While we concentrate here on the higher end of column densities for our calculations, the calculated line fluxes can be adopted to the lower column densities by simply dividing them by 10.

For dark clouds and warm IRDCs we implement the atomic initial abundances, while for HMPOs we implemented instead the Evolution model (with initially high D/H ratios). Line intensities for a few molecules (e.g., DCO\(^+\)) can also be estimated using the non-LTE molecular radiative transfer tool RADEX (van der Tak et al. 2007). Because RADEX and
our calculations using CDMS gave different results than we scaled the CDMS calculations to match RADEX values for linear molecules (e.g., DCO⁺). We look for transitions in bands 3–9 for ALMA (84–720 GHz with gaps between bands; see science.nrao.edu/facilities/alma/observing) and consider a line sensitivity limit of 1 mK for all bands. In Tables 6–8 are only the three strongest transitions listed, while a full list is available upon request from the authors.

Amongst these listed species are tracers (through D/H ratios) of initial abundances (e.g., D₂CO, HDO, NH₂D, CH₂D⁺) and temperature (D₂O, DCO⁺, DCN, D₂S) as we have listed in Table 5. A few ions are observable with ALMA, such as DCO⁺, H₂DO⁺, CH₂D⁺. We find that tracers of ionization in the cold ISM regions with high depletion, H₂D⁺ and HD₂⁺, will be hard to detect with ALMA, as found by Chapillon et al. (2011) for protoplanetary disks. We note that all isotopologues of ammonia are easily observable in the all three ISM environments. The metastable doublet lines of NH₃ are used to constrain gas temperature (e.g., Ho & Townes 1983; Maret et al. 2009). We think that using the relative abundances of the minor NH₃ isotopologues one could also discern the previous temperature history of the environment. We determine that several sulfur-bearing species, such as HDCS, D₂CS, HDS, should be observable by ALMA, and as sulfur chemistry is not yet well understood, observations of these species could serve as proxies for future studies. Finally we note that the HDO lines are expected to be observable with ALMA, but it is not included in CDMS, and we could not calculate its line intensities assuming LTE. On the other hand, water has a complex level structure, with some of the lines that are masing and many that become highly optically thick, and the escape probability non-LTE method of RADEX is not capable of modeling its line intensities reliably. For estimation of the water line fluxes one has to perform a full line radiative transfer modeling for each individual object.

For deuterated ices we only list the most abundant species in Table 9 and do not try to predict their observability. Amongst the deuterated ices we find that several polyyenes (CₙH₂, with n > 4) are abundant, especially at temperatures > 10 K. These species have been observed in the solar system such as in Titan’s atmosphere (e.g., Tansby et al. 2009), but should also be abundant in ices in interstellar space. Several organics such as deuterated formic acid and hydroxylamine (both singly and doubly deuterated) are abundant, even among the most abundant at higher temperatures (≥ 25 K). Also both ammonia and water (singly and doubly deuterated) show high abundances.

### Table 9
Fractional Abundances and D/H Ratios: Deuterated Ices

| Dark Clouds | Warm IRDCs | HMPOs |
|-------------|------------|-------|
| Species     | Abundance  | D/H Ratio | Species     | Abundance  | D/H Ratio | Species     | Abundance  | D/H Ratio |
| HDO         | 3.90 x 10⁻⁷| 4.26 x 10⁻³| HDO         | 6.77 x 10⁻⁸| 2.94 x 10⁻³| HDO         | 8.68 x 10⁻⁷| 1.27 x 10⁻²|
| CH₃D        | 1.41 x 10⁻⁷| 8.70 x 10⁻³| HDO₂       | 4.06 x 10⁻⁹| 1.78 x 10⁻³| NH₂D        | 1.68 x 10⁻⁷| 2.21 x 10⁻²|
| NH₃D        | 6.75 x 10⁻⁸| 6.14 x 10⁻³| NH₂D⁺      | 2.48 x 10⁻⁹| 7.40 x 10⁻³| D₂O         | 1.11 x 10⁻⁸| 1.63 x 10⁻⁴|
| C₃H₄D      | 5.38 x 10⁻⁹| 9.61 x 10⁻³| C₃H₄⁺      | 6.62 x 10⁻¹⁰| 7.75 x 10⁻⁴| D₂O₂        | 5.01 x 10⁻⁹| 7.95 x 10⁻⁵|
| CH₃D₂       | 1.89 x 10⁻⁹| 1.17 x 10⁻⁴| D₂O⁺       | 4.68 x 10⁻¹⁰| 1.15 x 10⁻⁵| H₂D₂OH      | 3.14 x 10⁻⁹| 1.68 x 10⁻³|
| DNO         | 1.72 x 10⁻⁹| 1.06 x 10⁻¹| CHDCO⁺     | 2.77 x 10⁻¹⁰| 1.83 x 10⁻⁵| NH₃D₂       | 2.65 x 10⁻⁹| 3.29 x 10⁻⁴|
| D₂O         | 1.05 x 10⁻⁹| 1.15 x 10⁻⁵| DČN        | 2.30 x 10⁻¹⁰| 1.04 x 10⁻⁵| GCN         | 2.45 x 10⁻⁹| 1.25 x 10⁻²|
| HDS         | 6.72 x 10⁻¹⁰| 1.15 x 10⁻²| DCOOH⁺     | 1.72 x 10⁻¹⁰| 4.31 x 10⁻²| CH₃D⁺       | 9.96 x 10⁻¹⁰| 1.72 x 10⁻²|
| NH₂D        | 2.48 x 10⁻¹⁰| 2.25 x 10⁻⁵| DNC         | 1.57 x 10⁻¹⁰| 1.11 x 10⁻²| D₂O₂⁺       | 8.15 x 10⁻¹⁰| 1.29 x 10⁻²|
| DCN         | 1.73 x 10⁻¹⁰| 5.90 x 10⁻⁵| CH₃D       | 1.53 x 10⁻¹⁰| 1.09 x 10⁻¹| DCN         | 9.64 x 10⁻¹⁰| 1.29 x 10⁻²|

**Notes:** The table is limited for each environment to 10 species or species with relative abundances >10⁻¹². Dark clouds: 10 K, 10⁵ cm⁻³; warm IRDCs: 25 K, 10⁶ cm⁻³; HMPOs: 75 K, 10⁵ cm⁻³.

Uncertainties for the predicted abundances are factors of ~1.5–5 for species made of ≤3–4 atoms and ≥1.5–10 for more complex ones. Apart from the estimated abundance and D/H ratio uncertainties due to the errors in the rate coefficients, we also have error bars associated with the exact estimation of physical properties of the observed environment (uncertainties in dust emissivity, temperature, poorly known dust-to-gas mass ratio, etc.) Also, many of the published observed D/H values are based on measurements made from several sources, for which derived physical properties can differ significantly.

We now discuss how our model results compare with assorted observations. A more extensive comparison of our model results to observations of deuterated species can be found in Table 19, van Dishoeck et al. (1995) observed several deuterated species toward the protobinary source IRAS 16293, namely, DCO⁺, DCN, C₂D, HDS, HDCO, NH₂D, detected in the different regions around the protostar. The first region is the warm and dense inner core (T ≥ 80 K, n_H₂ ≥ 10⁷ cm⁻³) found to be rich with organic molecules, the second is the circumbinary envelope with T ~ 40 K and n_H₂ ~ 10⁶–10⁷ cm⁻³, where molecules such as DCO⁺ and HDCO where found, and the third is the colder, low-density outer part of the envelope with T ~ 10–20 K and n_H₂ ~ 10⁴–10⁵ cm⁻³ with radicals such as CN, C₂H, and C₂H₂. We find good agreement between our calculated values and those derived for all observed species. As an example, HDCO shows a D/H ratio of 0.13 in our Evolution
model compared with the observed value of 0.14, and for DCN the D/H ratio is 0.027 compared with the observed ratio of 0.013. The worst agreement we find is for C2D and DCO+ with a difference of a factor of ∼5 in the D/H ratios, which is still acceptable agreement. Uncertainties for these species range between factors of 2–5, with largest uncertainties for C2D and DCN. Considering these uncertainties, our predicted D/H values are in agreement with the IRAS 16293 observations.

Caselli et al. (2003) detected ortho-H2D+ toward the prestellar core L1544, with derived abundances of $7.2 \times 10^{-10}$ and $3.2 \times 10^{-10}$ at the peak and off-peak positions, respectively. For our Primordial model with a core density $n_{H_2} = 10^5 \text{ cm}^{-3}$, a temperature of 7 K, and an appropriate equilibrium $\alpha/\rho$ ratio of 3:1 taken from Walmsley et al. (2004), we find reasonable agreement with calculated abundances of $0.7–4.8 \times 10^{-10}$ in the core (peak position) and $2.3–4.2 \times 10^{-10}$ at the off-peak position, with a lower density, assuming a density of $10^4–10^5 \text{ cm}^{-3}$. We however find a higher abundance at the off-peak position; there are several possible reasons for the discrepancy such as incorrect treatment of the ortho–para species in the network or the lack of a detailed physical model. A detailed study is not within the scope of this paper but we note that abundances are within a factor of 2–3 of observed abundances.

Stark et al. (2004) observed H2D+, DCO+, HCO+, HDO and H2O toward the protostar IRAS 16293 (A and B) as well as the cold prestellar object IRAS 16293 E. They measured the H2D+ abundance to be $2 \times 10^{-9}$ in the cold, outer envelope with $n_{H_2} = 10^4–10^5 \text{ cm}^{-3}$ and $T < 20 \text{ K}$, where our Evolution model predicts a similar abundance of $\sim 10^{-9}$. In the inner envelope the temperature is higher, depleting the H2+ isotopologues as CO returns to the gas phase, and the abundance decreases to $\sim 10^{-12} \text{ cm}^{-3}$. The temperature in the inner envelope is not well constrained, but with a central density of $10^4–10^5 \text{ cm}^{-3}$.

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Table 11

| Reaction | Uncertainty | Reaction | Uncertainty |
|----------|-------------|----------|-------------|
| H2O + CRP → H2O + e- | 2.00 | He+ CRP → He+ + e- | 2.00 |
| H2+ isotopologues | | | |
| H2+ + e- | H + H + H | 2.00 | H2D+ + e- | D + H + H | 2.00 |
| HD2+ + e- | D + D + H | 2.00 | H2D+ + HD | D2+ + H2 | 1.25 |
| H2D+ + HD | HD+ + H2 | 1.25 | HD+ + HD | D2+ + H2 | 1.25 |
| HD2+ + H2 | H2+ + HD | 2.00 | HD+ + H2 | H2D+ + HD | 2.00 |
| D2+ + H2 | H2+ + D | 2.00 | H2+ + D | H2D+ + H | 2.00 |
| H2D+ + D | HD+ + H | 2.00 | HD+ + D | D2+ + H | 2.00 |
| H2+ + CO | HCO+ + H2 | 1.25 | H2D+ + CO | DCO+ + H2 | 1.25 |
| HD2+ + CO | DCO+ + HD | 1.25* | D2+ + CO | DCO+ + D2 | 1.25* |
| H2+ + OH | H2O+ + H2 | 2.00 | H2D+ + OH | H2O+ + HD | 2.00 |
| H2+ + OD | H2O+ + HD | 2.00 |
| HCO+ isotopologues | | | |
| HCO+ + CO | HCO+ + H2 | 1.25 | HCO+ + e- | HCO+ + H2 | 1.25 |
| HD2CO+ + CO | HCO+ + D | 1.25 | HD2CO+ + e- | CO + D | 1.25* |
| HCO+ + H2 | HCO+ + H2 | 1.25 | HCO+ + e- | CO + H | 1.25 |
| DCO+ + CO | CO + D | 2.00 | DCO+ + CO | DCO+ + D | 2.00 |
| H2CN+ + CO | H2CN+ + HD | 2.00 | H2CN+ + e- | H2CN+ + HD | 2.00 |
| H2CN+ + CO | H2CN+ + HD | 2.00 | H2CN+ + e- | H2CN+ + HD | 2.00 |
| H2CN+ + HD | HD2CN+ + H2O | 2.00 | H2CN+ + e- | H2CN+ + HD | 2.00 |
| HD2CN+ + CO | C2N+ + HD | 2.00 | C2N+ + D | C2N+ + D | 2.00* |
| HD2CN+ + CO | C2N+ + HD | 2.00 | C2N+ + D | C2N+ + D | 2.00* |
| C+ + NH3 | H2CN+ + H | 2.00 | NH2 + O | HNO + H | 2.00 |
| N + CN | C + N2 | 2.00 |
| H2O+ isotopologues | | | |
| H2O+ + e- | H2O + H | 1.25* | H2DO+ + e- | HDO + H | 1.25* |
| HD2O+ + e- | D2O + H | 1.25* | HD2O+ + e- | OH + H | 1.25 |
| H2O+ + HD | H2O+ + H2 | 1.25 | H2O+ + HD | H2O+ + HD | 1.25* |
| H2+ + HDO | H2DO+ + H2 | 1.25* | H2+ + O | H2O+ + H | 1.40 |
| HCO+ + H2O | H2O+ + CO | 1.50 | HCO+ + HDO | H2DO+ + CO | 1.50* |
| DCO+ + H2O | H2DO+ + CO | 1.50* | DCO+ + HDO | H2DO+ + CO | 1.50* |
| HCO+ + D2O | H2DO+ + CO | 1.50* |

Note. An asterisk alongside the uncertainty signifies a reaction resulting from cloning the network.
| Reaction                                      | α          | β           | γ           | References |
|----------------------------------------------|------------|-------------|-------------|------------|
| C+ + H₂ → CH₂⁺                               | 2.00 × 10⁻¹⁶ | -1.30       | -23         | 1          |
| C+ + HCOOH → HCO⁺ + OH + C                  | 8.00 × 10⁻¹⁰ | -0.50       | 0           | 5          |
| C₂H⁺ + H₂ → C₂H₃⁺                           | 2.90 × 10⁻¹⁴ | -1.50       | 0           | 1          |
| CH₂⁺ + H₂O → CH₂OH⁺                         | 5.50 × 10⁻¹² | -1.70       | 0           | 3          |
| CH⁺ + H₂ → CH₃⁺                             | 3.78 × 10⁻¹⁶ | -2.30       | 22          | 4          |
| CH₂O₂⁺ + CH₃OH → H₂C₂O₂⁺ + H₂O             | 2.00 × 10⁻⁹  | -0.50       | 2810        | 5          |
| CH₂OH⁺ + H₂COOH → HCOOH⁺ + CH₃OH            | 3.63 × 10⁻⁹  | -0.50       | 685         | 5          |
| CH⁺ + HCOOH → HCOOH⁺ + CH₄                 | 3.00 × 10⁻⁹  | -0.50       | 0           | 5          |
| H₂CN⁺ + C₂H₂ → CH₄H⁺ + CH₂                  | 3.30 × 10⁻¹⁶ | -2.00       | 0           | 4          |
| H₂CN⁺ + HCOOH → HCOOH⁺ + H₂O + H₂           | 1.40 × 10⁻⁹  | -0.50       | 0           | 5          |
| H⁺ + O → OH⁺ + H₂                          | 7.98 × 10⁻¹⁰ | -0.156      | -1.41       | 1          |
| H⁺ + O → H₂O⁺ + H                          | 3.42 × 10⁻¹⁰ | -0.156      | -1.41       | 1          |
| H₂CO⁺ + HCOOH → HCOOH⁺ + H₂CO              | 2.00 × 10⁻⁹  | -0.50       | 0           | 5          |
| H₂O⁺ + C₂H₄ → C₂H₂OH⁺                       | 1.90 × 10⁻¹⁴ | -2.80       | 0.25        | 4          |
| H₂CO⁺ + H₂CO → H₂C₂O₂⁺                     | 8.15 × 10⁻¹⁵ | -3.00       | 0           | 6          |
| H₂S⁺ + HCOOH → HCOOH⁺ + H₂S                 | 2.00 × 10⁻⁹  | -0.50       | 0           | 5          |
| HCOOH⁺ + C₂H₄OH → CH₂OH⁺ + HCOOH            | 2.29 × 10⁻⁹  | -0.50       | 0           | 5          |
| H⁺ + HCOOH → HCO⁺ + OH + He                 | 9.00 × 10⁻¹⁰ | -0.50       | 0           | 5          |
| NH⁺ + HCOOH → HCOOH⁺ + N₂                   | 1.70 × 10⁻⁹  | -0.50       | 0           | 5          |
| C + O₂ → CO + O                             | 1.28 × 10⁻⁹  | -0.32       | 0           | 4          |
| C + OH → CO + H                             | 1.15 × 10⁻¹⁰ | -0.34       | 0           | 4          |
| C₁ + O → CO + C                             | 2.00 × 10⁻¹⁰ | -0.12       | 0           | 1          |
| C₁ + OCS → CO + C₂S                         | 1.00 × 10⁻¹⁰ | 0.00        | 0           | 4          |
| C₂H + N → C₂H⁺ + N                         | 1.00 × 10⁻¹⁰ | 0.18        | 0           | 1          |
| C₂H + O → CO + CH                           | 1.00 × 10⁻¹⁰ | 0.00        | 0           | 1          |
| C₂H + O → C₂H⁺ + CO                         | 1.00 × 10⁻¹⁰ | 0.00        | 0           | 1          |
| C₂O + O → C₂ + O₂                           | 1.00 × 10⁻¹⁰ | 0.00        | 0           | 1          |
| CH + OCS → H + CO + CS                      | 4.00 × 10⁻⁴  | 0.00        | 0           | 4          |
| CH + SO → H + OCS                           | 1.10 × 10⁻¹⁰ | 0.00        | 0           | 4          |
| CH + SO → CO + HS                           | 9.00 × 10⁻¹¹ | 0.00        | 0           | 4          |
| CH₂ + H → CH₂⁺ + H                          | 2.20 × 10⁻¹⁰ | 0.00        | 0           | 1          |
| CH₂ + CH → C₂H₃⁺ + H                         | 1.06 × 10⁻¹⁰ | -1.04       | 0           | 4          |
| CN + N → C + N₂                             | 1.00 × 10⁻¹⁰ | 0.00        | 0           | 1          |
| CN + O → CO + N                             | 2.60 × 10⁻¹¹ | -0.12       | 0           | 1          |
| CN + O₂ → OCN + O                           | 1.99 × 10⁻¹¹ | -0.63       | 0           | 4          |
| H₂ + CH → CH₂⁺ + H                         | 1.20 × 10⁻⁹  | 0.00        | 0           | 4          |
| HNO + O → NO + OH                           | 3.77 × 10⁻¹¹ | -0.08       | 0           | 1          |
| NH + O → NO + H                             | 6.60 × 10⁻¹¹ | 0.00        | 0           | 1          |
| NH₂ + O → HNO + H                           | 6.39 × 10⁻¹¹ | -0.10       | 0           | 1          |
| NH₂ + O → NH + OH                           | 7.10 × 10⁻¹² | -0.10       | 0           | 1          |
| NH₃ + CN → HCN + NH₂                         | 2.77 × 10⁻¹¹ | -0.85       | 0           | 1          |
| O + C₂S → CO + CS                           | 1.00 × 10⁻¹⁰ | 0.00        | 0           | 4          |
| O + OCS → CO + CS                           | 1.00 × 10⁻¹⁰ | 0.00        | 0           | 4          |
| O + OH → O₂ + H                             | 4.00 × 10⁻¹¹ | 0.00        | 0           | 4          |
| S + C₂O → CO + CS                           | 1.00 × 10⁻¹⁰ | 0.00        | 0           | 4          |
| S + HCO → H + OCS                           | 8.00 × 10⁻¹¹ | 0.00        | 0           | 4          |
| S + HCO → CO + HS                           | 4.00 × 10⁻¹¹ | 0.00        | 0           | 4          |
| C₂H⁺ + e⁻ → C₂ + CH                         | 6.00 × 10⁻⁹  | -0.50       | 0           | 2          |
| C₂H⁺ + e⁻ → C₂H + C                         | 9.90 × 10⁻⁸   | -0.50       | 0           | 2          |
| C₂H⁺ + e⁻ → C₂ + H                          | 1.95 × 10⁻⁷   | -0.50       | 0           | 2          |
| C₂H₂⁺ + e⁻ → C₂ + CH₂                      | 1.44 × 10⁻⁸   | -0.50       | 0           | 2          |
| C₂H₂⁺ + e⁻ → C₂H + CH                      | 1.44 × 10⁻⁸   | -0.50       | 0           | 2          |
| C₂H₂⁺ + e⁻ → C₂H⁺ + C                     | 8.64 × 10⁻⁸   | -0.50       | 0           | 2          |
| C₂H₂⁺ + e⁻ → C₂H + H                       | 1.66 × 10⁻⁷   | -0.50       | 0           | 2          |
| C₂H₂⁺ + e⁻ → C₂ + H₂                      | 8.28 × 10⁻⁸   | -0.50       | 0           | 2          |
| C₂H⁺ + e⁻ → C₂ + H                        | 1.74 × 10⁻⁷   | -0.50       | 0           | 2          |
| C₂H⁺ + e⁻ → C₂H + C                        | 7.80 × 10⁻⁸   | -0.50       | 0           | 2          |
| C₂H⁺ + e⁻ → C₂H + C₂                     | 4.80 × 10⁻⁸   | -0.50       | 0           | 2          |
| C⁺ + e⁻ → C⁺ + C                            | 3.90 × 10⁻⁸   | -0.50       | 0           | 2          |
| C⁺ + e⁻ → C⁺ + C₂                        | 2.61 × 10⁻⁷   | -0.50       | 0           | 2          |
| C⁺ + e⁻ → C⁺ + C₃                        | 1.80 × 10⁻⁷   | -0.30       | 0           | 2          |
| C⁺ + e⁻ → C⁺ + C₄                        | 2.20 × 10⁻⁷   | -0.30       | 0           | 2          |
| C⁺ + e⁻ → C⁺ + C₅                        | 1.60 × 10⁻⁶   | -0.30       | 0           | 2          |
| C⁺ + e⁻ → C⁺ + C₆                        | 2.30 × 10⁻⁸   | -0.30       | 0           | 2          |
| C⁺ + e⁻ → C⁺ + C₇                        | 4.37 × 10⁻⁷   | -0.30       | 0           | 2          |
Table 12
(Continued)

| Reaction | α       | β        | γ  | References |
|----------|---------|----------|----|------------|
| C7++ e−  | → C4+C3 | 1.84 × 10−6 | −0.50 | 0 | 2         |
| C7++ e−  | → C7+C  | 6.00 × 10−8 | −0.30 | 0 | 2         |
| C6++ e−  | → C6+C2 | 2.00 × 10−8 | −0.30 | 0 | 2         |
| C5++ e−  | → C5+C3 | 1.80 × 10−6 | −0.30 | 0 | 2         |
| C4++ e−  | → C4+C4 | 1.20 × 10−7 | −0.30 | 0 | 2         |
| C3++ e−  | → C3+C2 | 1.20 × 10−7 | −0.30 | 0 | 2         |
| C2++ e−  | → C2+C  | 1.32 × 106  | −0.30 | 0 | 2         |
| C10+ + e−| → C3+C4 | 5.60 × 10−7 | −0.30 | 0 | 2         |
| C10+ + e−| → C6+C4 | 2.00 × 10−8 | −0.30 | 0 | 2         |
| C10+ + e−| → C7+C3 | 1.40 × 10−6 | −0.30 | 0 | 2         |
| C10+ + e−| → C8+C5 | 5.00 × 10−7 | −0.30 | 0 | 2         |
| C9+ + e− | → C2+N  | 2.00 × 10−8 | −0.60 | 0 | 1         |
| C9+ + e− | → CN+C  | 3.80 × 10−7 | −0.60 | 0 | 1         |
| H3+ + e− | → H+H+H | 5.44 × 10−8 | −0.50 | 0 | 3         |
| HC5NH+ + e−| → C5N+H2 | 8.00 × 10−8 | −0.70 | 0 | 1         |
| HCN+ + e−| → C7+H  | 1.20 × 10−7 | −0.70 | 0 | 1         |
| HCN+ + e−| → HCN+H | 9.20 × 10−7 | −0.70 | 0 | 1         |
| HCN+ + e−| → HCN+C2H | 4.40 × 10−7 | −0.70 | 0 | 1         |
| HCN+ + e−| → CN+H+H | 9.06 × 10−8 | −0.65 | 0 | 1         |
| C3H + CRPHOT | → C2+H | 5.27 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C+CH | 1.24 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C2H+C | 2.15 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C2+CH | 1.30 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C1+H | 4.23 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C1+H+H | 2.99 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C3+H2 | 1.56 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C2H++ | 1.50 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C3H+CH | 2.60 × 10−15 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C2+CH2 | 1.95 × 10−15 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C3+C | 1.00 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C2+C2 | 2.99 × 10−15 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C4+H | 3.77 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C1+C | 1.69 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C2H+C2 | 1.04 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C4+C | 1.69 × 10−15 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C3+C2 | 1.13 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C3+C | 1.17 × 10−15 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C2+C2 | 1.43 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C3+C3 | 1.04 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C4+C | 1.30 × 10−16 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C5+C | 2.47 × 10−15 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C4+C3 | 1.04 × 10−14 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C7+C | 3.9 × 10−16 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C6+C2 | 1.30 × 10−16 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C5+C3 | 1.17 × 10−15 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C4+C4 | 7.80 × 10−16 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C7+C2 | 7.80 × 10−16 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C6+C3 | 8.58 × 10−15 | 0.00 | 0 | 2         |
| C3H + CRPHOT | → C5+C4 | 3.64 × 10−15 | 0.00 | 0 | 2         |
| CH + PHOTON | → CH+ + e−| 7.60 × 10−10 | 0.00 | 3.80 | 4         |
| CH + PHOTON | → C+H | 9.20 × 10−10 | 0.00 | 1.72 | 4         |
| C2H + PHOTON | → C2+H | 8.10 × 10−10 | 0.00 | 1.7  | 2         |
| C2H + PHOTON | → CH+C | 1.90 × 10−10 | 0.00 | 1.7  | 2         |
| C2H + PHOTON | → C3+H | 6.50 × 10−10 | 0.00 | 1.7  | 2         |
| C2H + PHOTON | → C2H+C | 3.30 × 10−10 | 0.00 | 1.7  | 2         |
| C2H + PHOTON | → C2+CH | 2.00 × 10−11 | 0.00 | 1.7  | 2         |
\[ \sim 10^6 \text{ cm}^{-3} \] we find the best agreement at temperatures \( \approx 30 \text{ K} \), with an abundance of \( 1.2 \times 10^{-12} \), and the agreement worsens if the temperature is increased, as more CO returns to the gas phase and the overall deuterium fractionation ceases. DCO\(^+\) and HCO\(^+\) were observed with abundances \( 2 \times 10^{-11} \) and \( < 1 \times 10^{-9} \), respectively, which agree with our model values from 17 to 26 K with DCO\(^+\) abundances \( 8.4 \times 10^{-11} \sim 8.2 \times 10^{-11} \) and HCO\(^+\) abundances \( 4.7 \times 10^{-10} \sim 1.1 \times 10^{-9} \), leading to a D/H ratio of 0.078–0.18. HDO and H\(_2\)O were observed with abundances \( 3 \times 10^{-10} \) and \( 3 \times 10^{-7} \sim 4 \times 10^{-9} \) respectively, which agree reasonably well with our modeled abundances of \( 5.9 \times 10^{-12} \sim 6.3 \times 10^{-11} \) and \( 9.9 \times 10^{-10} \sim 1.7 \times 10^{-8} \), respectively. Lastly, HDO, DCO\(^+\) and HCO\(^+\) were also observed in the prestellar core object IRAS 16293 E. From estimated temperatures \( 16–25 \text{ K} \) and densities \( 1.1–1.6 \times 10^6 \text{ cm}^{-3} \), we estimate DCO\(^+\) abundances to be \( 7 \times 10^{-11} \sim 2.9 \times 10^{-9} \) and HCO\(^+\) abundances \( 8.9 \times 10^{-11} \sim 1.1 \times 10^{-9} \), leading to a D/H ratio 0.26–0.79. This agrees well with the observed abundances of \( 5.0 \times 10^{-11} \) and \( 1.0 \times 10^{-10} \) for DCO\(^+\) and HCO\(^+\) with a D/H ratio 0.5. We find the same agreement for HDO with an observed abundance \( 2 \times 10^{-10} \) comparable to our modeled abundance range of \( 3.0–7.5 \times 10^{-10} \).

Coutens et al. (2012) observed multiple lines of HDO and H\(_2\)\(^18\)O toward IRAS 16293A with an estimated D/H \( \sim 0.034 \) in the hot corino region and D/H \( \sim 0.005 \) in the outer envelope, utilizing a standard isotopic ratio of H\(_2\)\(^18\)O/H\(_2\)\(^16\)O \( = 500 \). In order to reproduce the observed line emission, they added an outer absorbing layer with an H\(_2\)O column density.

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**Table 12**

(Continued)

| Reaction | \( \alpha \) | \( \beta \) | \( \gamma \) | References |
|----------|--------------|------------|------------|------------|
| \( \text{C}_2\text{H}_4 \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5 \text{O}^+ \) | \( \ldots \) | \( \ldots \) | \( \ldots \) | 7 |
| \( \text{H}_2\text{CO}^+ + \text{CH} \rightarrow \text{C}_2\text{H}_2 \text{O}^+ \) | \( \ldots \) | \( \ldots \) | \( \ldots \) | 4 |
| \( \text{HCO}^+ + \text{CH}_4 \rightarrow \text{CH}_3\text{OCH}_4^+ \) | \( \ldots \) | \( \ldots \) | \( \ldots \) | 4 |
| \( \text{C}_3\text{H}_3^+ + \text{e}^– \rightarrow \text{C}_3^+ + \text{CH} \) | \( \ldots \) | \( \ldots \) | \( \ldots \) | 2 |
| \( \text{C}_6^+ + \text{e}^– \rightarrow \text{C}_6^+ + \text{C} \) | \( \ldots \) | \( \ldots \) | \( \ldots \) | 2 |
| \( \text{C}_6^+ + \text{PHOTON} \rightarrow \text{C}_6^+ + \text{C}_2 \) | \( \ldots \) | \( \ldots \) | \( \ldots \) | 2 |
| \( \text{C}_6^+ + \text{CRPHOT} \rightarrow \text{C}_6^+ + \text{C}_2 \) | \( \ldots \) | \( \ldots \) | \( \ldots \) | 2 |
| \( \text{HNO} + \text{O} \rightarrow \text{NO}_2 + \text{H} \) | \( \ldots \) | \( \ldots \) | \( \ldots \) | 1 |
| \( \text{O} + \text{NH} \rightarrow \text{OH} + \text{N} \) | \( \ldots \) | \( \ldots \) | \( \ldots \) | 1 |
| \( \text{NH}_2 + \text{O} \rightarrow \text{NO} + \text{H}_2 \) | \( \ldots \) | \( \ldots \) | \( \ldots \) | 1 |
| \( \text{NH}_3 + \text{CN} \rightarrow \text{NH}_2 \text{CN} + \text{H} \) | \( \ldots \) | \( \ldots \) | \( \ldots \) | 1 |

**Note.** Cosmic ray-induced photoionization: \( k = \alpha (\text{CR}) \); photoreactions: \( k = \alpha e^{-\gamma A_i} \); ion–neutral reactions (Kooji formula): \( k = \alpha (T/300)^{\beta} e^{-\gamma/T} \).

**References.** (1) Wakelam et al. 2010b; (2) Chabot et al. 2010; (3) Roberts et al. 2004; (4) KIDA database; (5) Laas et al. 2011; (6) Garrod & Herbst 2006; (7) Horn et al. 2004.
### Table 13

**Added and Updated Deuteron Reactions**

| Reaction | $\alpha$ | $\beta$ | $\gamma$ | References |
|----------|---------|---------|---------|------------|
| $\text{C}_2\text{D} + \text{H}$ $\rightarrow$ $\text{C}_2\text{H} + \text{D}$ | $5.00 \times 10^{-11}$ | $0.50$ | $832$ | 9 |
| $\text{C}_2\text{H} + \text{D}$ $\rightarrow$ $\text{C}_2\text{D} + \text{H}$ | $5.00 \times 10^{-11}$ | $0.50$ | $250$ | 9 |
| $\text{C}_2\text{H}_2^+ + \text{HD}$ $\rightarrow$ $\text{C}_2\text{H}_2^+ + \text{H}_2$ | $1.00 \times 10^{-9}$ | $0.00$ | $0$ | 5 |
| $\text{C}_2\text{H}_2^+ + \text{H}_2$ $\rightarrow$ $\text{C}_2\text{H}_2^+ + \text{H}_2$ | $2.50 \times 10^{-9}$ | $0.00$ | $550$ | 5 |
| $\text{CH}_2^+ + \text{D}_2$ $\rightarrow$ $\text{CH}_2^+ + \text{D}_2$ | $4.40 \times 10^{-10}$ | $0.00$ | $0$ | 3 |
| $\text{CH}_2^+ + \text{D}_2$ $\rightarrow$ $\text{CH}_2^+ + \text{D}_2$ | $6.60 \times 10^{-10}$ | $0.00$ | $0$ | 3 |
| $\text{CH}_2^+ + \text{HD}$ $\rightarrow$ $\text{CH}_2^+ + \text{HD}$ | $1.30 \times 10^{-9}$ | $0.00$ | $0$ | 3 |
| $\text{CH}_2^+ + \text{HD}$ $\rightarrow$ $\text{CH}_2^+ + \text{H}_2$ | $8.70 \times 10^{-10}$ | $0.00$ | $370$ | 3 |
| $\text{CH}_3^+ + \text{H}_2$ $\rightarrow$ $\text{CH}_3^+ + \text{H}_2$ | $1.60 \times 10^{-9}$ | $0.00$ | $0$ | 3 |
| $\text{CH}_3^+ + \text{H}_2$ $\rightarrow$ $\text{CH}_3^+ + \text{D}_2$ | $4.40 \times 10^{-10}$ | $0.00$ | $400$ | 3 |
| $\text{CH}_3^+ + \text{D}_2$ $\rightarrow$ $\text{CH}_3^+ + \text{D}_2$ | $6.60 \times 10^{-10}$ | $0.00$ | $0$ | 3 |
| $\text{CH}_3$ $\rightarrow$ $\text{CH}_3$ | $1.20 \times 10^{-9}$ | $0.00$ | $0$ | 3 |
| $\text{CH}_3$ $\rightarrow$ $\text{CH}_3$ | $1.60 \times 10^{-9}$ | $0.00$ | $400$ | 3 |
| $\text{CHD}$ $\rightarrow$ $\text{CHD}$ | $2.00 \times 10^{-9}$ | $0.00$ | $0$ | 3 |
| $\text{CHD}$ $\rightarrow$ $\text{CHD}$ | $2.00 \times 10^{-9}$ | $0.00$ | $0$ | 3 |
| $\text{CD}_2^+ + \text{H}_2$ $\rightarrow$ $\text{CD}_2^+ + \text{H}_2$ | $1.00 \times 10^{-9}$ | $0.00$ | $107$ | 2 |
| $\text{CD}_2^+ + \text{H}_2$ $\rightarrow$ $\text{CD}_2^+ + \text{D}_2$ | $1.00 \times 10^{-9}$ | $0.50$ | $500$ | 9* |
| $\text{HCN} + \text{H}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
| $\text{HCN}$ $\rightarrow$ $\text{HCN}$ | $1.00 \times 10^{-10}$ | $0.50$ | $500$ | 9* |
of $1.23 \times 10^{13} \text{ cm}^{-2}$. Depending on the exact choice of density and temperatures, our models give for the cold envelope ($n_H \sim 10^5 \text{ cm}^{-3}$, $T \lesssim 30 \text{ K}$) $D/H$ ratios of $\sim 0.01-0.1$, for both sets of initial abundances, in agreement with observations. For hot cores ($n_H \sim 10^8 \text{ cm}^{-3}$, $T \sim 150 \text{ K}$) the Primordial model estimates the $D/H$ ratio to be $0.0001-0.001$, while the Evolution model predicts that the $D/H$ ratio is $\sim 0.0001-0.01$. Although our evolutionary model is a poor solution and does not account for the gradual warm-up of the environment, our predicted $D/H$ ratios from the Evolution model are in agreement with those.
estimated by Coutens et al. (2012), albeit only with upper limits of our estimates.

The radical OD was observed for the first time outside of the solar system by Parise et al. (2012) along the line of sight toward the low-mass protostar IRAS 16293A. They also observed HDO and found a high OD/HDO ratio of $\sim$10–100. Parise et al. (2012) compared their observations to the modeled values of OH/H$_2$O and found their calculated values to be too low. The agreement was slightly better when they implemented a simple evolutionary model with increasing temperature with time, but the result was still lower than observations, with the highest modeled values reaching 5.7. Studying the chemical evolution in our Primordial model for temperatures $T < 30$ K and densities $n_H = 10^4$–$10^6$ cm$^{-3}$, we find that the large OD/HDO ratio is mainly due to the efficient reaction $OH + D \rightarrow OD + H$, as originally suggested by Millar et al. (1989). Via this reaction, the OD/HDO ratios can reach values approximately one order of magnitude larger than OH/H$_2$O. Furthermore, toward temperatures $\sim 30$ K the OD/HDO ratios can even be as high as two orders of magnitude. Thus, our model is in agreement with the observed OD/HDO ratios from Parise et al. (2012), without the need for a warm-up phase.

### 4.2. Earlier Models

Roberts & Millar (2000a, 2000b) have investigated the chemical evolution with deuterium fractionation for temperatures 10–100 K and densities $3 \times 10^3$–$3 \times 10^6$ cm$^{-3}$ on a less resolved grid, consisting of only 100 points. They used a time-dependent chemical gas-phase model based on the UMIST'95 database (Millar et al. 1997). Their resulting network consists of $\sim 300$ species linked by $>5000$ reactions, but only includes singly deuterated species and limited surface chemistry for H$_2$ and HD. We compared the results between our models for a number of species, including DCO$^+$, HDCO, DCN, DNC, and DC$_5$N, looking at the distribution of D/H fractionation ratios and time-dependent abundances at $10^5$ yr, and we found good agreement between our models. We also studied the molecular abundances under conditions typical of the TMC-1 environment in our Primordial model and under these conditions we found that the quantitative agreement in the D/H ratios is better than an order of magnitude for all species, with the worst agreement for NH$_2$D where the ratio between the two models is 0.14. The comparison for D/H values is shown in Table 10. The intrinsic uncertainty in the abundance of DC$_5$N as predicted in our sensitivity analysis is very large, $\sim$1–1.5 orders of magnitude, and is comparable to the difference between our and Roberts’ & Millar’s model. We note however that our modeled D/H ratios show a better agreement with the observations of DC$_5$N and HC$_5$N in TMC-1 by MacLeod et al. (1981) than calculated values by Roberts & Millar. Roberts & Millar (2000a) expanded their study to include doubly deuterated species, allowed species to freeze onto grains and looked at a different selection of species. We compared their predictions with our results for singly and doubly deuterated isotopologues of NH$_3$, H$_2$O, H$_2$CO, and found reasonably good agreement for all singly deuterated species. In our model, NH$_2$D shows enhanced D/H ratios ($\sim 10^{-3}$–$10^{-1}$) up to temperatures of 30–40 K, while the enhanced D/H ratios in the model of Roberts & Millar only appear up to 20–30 K. For the doubly deuterated species D$_2$O, NH$_2$D, and D$_2$CO, we predict D/H ratios similar to Roberts & Millar up to temperatures of $\sim 50$ K, with values $\sim 10^{-3}$–$10^{-1}$, while at larger temperatures our models diverge. Our model predicts a strong decrease in the respective D/H ratios to $\sim 10^{-5}$, while the D/H ratios of Roberts & Millar decrease more smoothly and do not reach the same value until at $\sim 100$ K.

In the study of Roberts et al. (2004), the chemical evolution in a sample of prestellar cores using two subsets of the Rate99 and osu.2003 chemical networks was compared. With the networks limited to include species with six or fewer carbon atoms and no surface chemistry, Roberts et al. (2004) used the chemical models to successfully explain observations of the CO depletion, and its relevance to the D$_2$CO and HDCO fractionation ratios. If we compare the calculated fractionation ratios between the steady state abundances of Roberts et al. (2004; see their Table 5)
Table 16
Most Essential Formation and Destruction Pathways for HCN, HNC, DCN, and DNC

| Reaction               | $\alpha$  | $\beta$  | $\gamma$ | Accuracy | References | Estimated by |
|------------------------|-----------|-----------|-----------|-----------|------------|--------------|
| H$_2$CN$^+$ + e$^-$   |           |           |           |           |            | M            |
| H$_2$CN$^+$ + e$^+$   |           |           |           |           |            |              |
| C$_2$H$^+$ + e$^-$    |           |           |           |           |            |              |
| C$_2$H$^+$ + e$^+$    |           |           |           |           |            |              |
| CH$_3$ + N            |           |           |           |           |            | T            |
| CH$_3$ + H$^+$        |           |           |           |           |            |              |
| HNC + H$^+$           |           |           |           |           |            |              |
| HD$_2$O$^+$ + H$^+$   |           |           |           |           |            |              |
| H$_2$ + O$_2$         |           |           |           |           |            |              |

Table 17
Most Essential Formation and Destruction Pathways for H$_2$O, HDO, and D$_2$O

| Reaction               | $\alpha$  | $\beta$  | $\gamma$ | Accuracy | References | Estimated by |
|------------------------|-----------|-----------|-----------|-----------|------------|--------------|
| H$_2$O$^+$ + e$^-$    |           |           |           |           |            | M            |
| H$_2$O$^+$ + HCN      |           |           |           |           |            |              |
| H$_2$O$^+$ + HNC      |           |           |           |           |            |              |
| OH (ice) + H (ice)    |           |           |           |           |            |              |
| OD (ice) + H (ice)    |           |           |           |           |            |              |
| OH (ice) + D (ice)    |           |           |           |           |            |              |
| H$_2$O + H$^+$        |           |           |           |           |            |              |
| H$_2$O + H$_2$        |           |           |           |           |            |              |
| H$_2$DO$^+$ + e$^-$   |           |           |           |           |            |              |
| HD$_2$O$^+$ + e$^+$   |           |           |           |           |            |              |
| HD$_2$O$^+$ + H$^+$   |           |           |           |           |            |              |
| HD$_2$O + H$^+$       |           |           |           |           |            |              |
| HD$_2$O$^+$ + HCN     |           |           |           |           |            |              |
| HD$_2$O + HNC         |           |           |           |           |            |              |
| HD$_2$O + H$_2$       |           |           |           |           |            |              |
| HD$_2$O$^+$ + CO      |           |           |           |           |            |              |
| HD$_2$O$^+$ + D$_2$   |           |           |           |           |            |              |
| HD$_2$O$^+$ + HD      |           |           |           |           |            |              |
| HD$_2$O + C$^+$       |           |           |           |           |            |              |
| HD$_2$O$^+$ + H$^+$   |           |           |           |           |            |              |
| OD (ice) + D (ice)    |           |           |           |           |            |              |
| D$_2$O$^+$ + e$^-$    |           |           |           |           |            |              |
| D$_2$O$^+$ + HCN      |           |           |           |           |            |              |
| D$_2$O$^+$ + HNC      |           |           |           |           |            |              |
| HD$_2$O + H$_2$       |           |           |           |           |            |              |
| HD$_2$O$^+$ + HD      |           |           |           |           |            |              |
| HD$_2$O$^+$ + H$_2$   |           |           |           |           |            |              |
| HD$_2$O + H$_2$       |           |           |           |           |            |              |

Notes. T, theoretical/calculated; C, cloned; ?, no listing for estimation method, most likely theoretical; ion-neutral reactions (Kozi formula): $k = \alpha(T/300)^\beta e^{-\gamma/T}$. Pathways extracted at 1 Myr from four points with $T = 10$ or $100$ K and densities $= 10^4$ and $10^5$ cm$^{-3}$ in the Primordial model.

References. (1) Wakelam et al. 2010b; (2) OSU: http://www.physics.ohio-state.edu/~eric/; (3) Garrod & Herbst 2006; (4) Roueff et al. 2005; (5) Schilke et al. 1992.

Table 18
Most Essential Formation and Destruction Pathways for H$_2$O, HDO, and D$_2$O

| Reaction               | $\alpha$  | $\beta$  | $\gamma$ | Accuracy | References | Estimated by |
|------------------------|-----------|-----------|-----------|-----------|------------|--------------|
| H$_2$O$^+$ + e$^-$    |           |           |           |           |            | M            |
| H$_2$O$^+$ + HCN      |           |           |           |           |            |              |
| H$_2$O$^+$ + HNC      |           |           |           |           |            |              |
| OH (ice) + H (ice)    |           |           |           |           |            |              |
| OD (ice) + H (ice)    |           |           |           |           |            |              |
| OH (ice) + D (ice)    |           |           |           |           |            |              |
| H$_2$O + H$^+$        |           |           |           |           |            |              |
| H$_2$O + H$_2$        |           |           |           |           |            |              |
| H$_2$DO$^+$ + e$^-$   |           |           |           |           |            |              |
| HD$_2$O$^+$ + e$^+$   |           |           |           |           |            |              |
| HD$_2$O$^+$ + H$^+$   |           |           |           |           |            |              |
| HD$_2$O + H$^+$       |           |           |           |           |            |              |
| HD$_2$O$^+$ + HCN     |           |           |           |           |            |              |
| HD$_2$O + HNC         |           |           |           |           |            |              |
| HD$_2$O + H$_2$       |           |           |           |           |            |              |
| HD$_2$O$^+$ + CO      |           |           |           |           |            |              |
| HD$_2$O$^+$ + D$_2$   |           |           |           |           |            |              |
| HD$_2$O$^+$ + HD      |           |           |           |           |            |              |
| HD$_2$O + C$^+$       |           |           |           |           |            |              |
| HD$_2$O$^+$ + H$^+$   |           |           |           |           |            |              |
| OD (ice) + D (ice)    |           |           |           |           |            |              |
| D$_2$O$^+$ + e$^-$    |           |           |           |           |            |              |
| D$_2$O$^+$ + HCN      |           |           |           |           |            |              |
| D$_2$O$^+$ + HNC      |           |           |           |           |            |              |
| HD$_2$O + H$_2$       |           |           |           |           |            |              |
| HD$_2$O$^+$ + HD      |           |           |           |           |            |              |
| HD$_2$O + H$_2$       |           |           |           |           |            |              |
| HD$_2$O$^+$ + H$_2$   |           |           |           |           |            |              |
| HD$_2$O + H$_2$       |           |           |           |           |            |              |

Notes. M, laboratory measurement; C, cloned; ?, no listing for estimation method, most likely theoretical; ion-neutral reactions (Kozi formula): $k = \alpha(T/300)^\beta e^{-\gamma/T}$. Pathways extracted at 1 Myr from four points with $T = 10$ or $100$ K and densities $= 10^4$ and $10^5$ cm$^{-3}$ in the Primordial model.

References. (1) Jensen et al. 2000; (2) OSU: http://www.physics.ohio-state.edu/~eric/; (3) Garrod & Herbst 2006.
and our models for a TMC-1 environment, the D/H ratios for the majority of key species such as H2D+, N2D+, DCO+, and HDO agree reasonably well. However, we found significant discrepancies for D2O, HD2+, D3+, and NHD2. The reason why our D/H ratios for doubly deuterated species differ from those of Roberts et al. (2004) appears to be twofold. First, they have not considered surface chemistry and assumed that all atomic D that freezes out is immediately returned to the gas as HD. In contrast, in our model, the accreted deuterium atoms are incorporated in surface species and do not easily return to the gas phase. Second, they use only steady-state abundances while we use time-dependent abundances at 1 Myr.

Walmsley et al. (2004) studied steady-state chemistry in a completely depleted, low-mass prestellar core, with an emphasis on explaining observations of ortho-H2D+ toward L1544 by Caselli et al. (2003). While our model does not yet include nuclear-spin state chemistry, we compared the calculated abundances of the H3+ isotopologues at densities of nH = 10^3, 10^6, 10^9 cm^-3, T = 10 K assuming a cosmic ray ionization rate ζ = 3 × 10^-17 s^-1 (note that at such conditions para-H2 will be the dominant form of molecular hydrogen and thus fractionation will proceed with a high efficiency as assumed in our model). For both the Primordial and Evolution models we found good overall agreement for the D/H ratios of the H3+ isotopologues and the electron abundances. The only difference occurs at high densities of ~10^9 cm^-3, where the HD2+ and D3+ abundances are one and two orders of magnitude lower in our model, respectively. We could not find out whether this difference increases at higher densities. The likely reason for such a discrepancy is the lack of surface chemistry and the assumption of complete freeze-out in the Walmsley et al. (2004) model. Even at such high densities and 10 K, the depletion is not complete in our model, so that the H3+ isotopologues can still be destroyed by ion–molecule reactions in addition to dissociative recombination with electrons or negatively charged grains. Moreover, in our model, atomic D released upon dissociative recombination can stick to a grain and be incorporated in the surface molecules. At n_H > 10^7 cm^-3 and after 1 Myr of evolution, a substantial fraction of the gas-phase reservoir of the elemental D can be chemically “transferred” to ices, unable to directly come back to the gas phase. Consequently, it will increase surface fractionation and abundances of deuterated ices.

5. CONCLUSIONS

We present an extended, publicly available chemical network for deuterium fractionation, with the most up-to-date reaction rate coefficients from laboratory measurements and theoretical studies. The new deuterium chemistry model does not yet include nuclear-spin state processes and is better suitable for cold ISM environments, T < ~10–20 K. In this paper, we have tested this network by performing a benchmarking study of deuterium chemistry under dense ISM conditions with two distinct initial abundance sets. The limits of accuracy of the network have been investigated with a sensitivity analysis. The most problematic reactions for the chemical evolution of H3+, HCO+, HOC+, HCN, HNC, H2O, CH3OH, H3O+, CH3+, C2H5+, and their isotopologues as well as CO are listed or presented.
### Table 19
Listings of Observed Interstellar Deuterated Species

| Species          | Class I | Class O/I | Spatial Scale | References | Model     |
|------------------|---------|-----------|--------------|------------|-----------|
| D/H              | <4 × 10⁻⁴ |          | 1′:8         | 1          | 10⁻³–10⁻² |
| ...              | ≤2.7 × 10⁻⁵ |          |              | 2          | ...       |
| ...              | 2.2 × 10⁻⁵ |          |              | 3          | ...       |
| ...              | ≤0.14    |          |              | 4          | ...       |
| HD/H₂            | 0.74–8.6 × 10⁻⁶ | 40 × 30 | 5            | <10⁻⁴      |           |
| ...              | 1.32–14.83 × 10⁻⁶ |          |              | 6          | ...       |
| ND/NH            | 0.3–1.0  | 41(ND), 22(NH) | 7          | 10⁻⁴–10⁰  |           |
| OD/OH            | ≤2.5 × 10⁻³ |          | 1′:8        | 8          | 10⁻²–10⁰  |
| C₂D/C₂H         | 0.01     | 33        |              | 9          | 10⁻³–10⁻² |
| ...              | 0.18     | 20        |              | 10         | ...       |
| D₂O/H₂O         | 0.008–0.015 | 5 × 10⁻⁵ | 11          | <10⁻⁵–10⁻³ |           |
| DCN/HCN          | 0.012–0.11 |          |              | 13         | ...       |
| ...              | 0.013    | 20        |              | 10         | ...       |
| ...              | 0.023    | 14        |              | 15         | ...       |
| DCO⁺/HCO⁺        | 0.007–0.081 |        |              | 13         | 10⁻²–10⁰  |
| ...              | 0.02–0.18 | 20        |              | 16         | ...       |
| ...              | 0.006–0.04 | 25–57    | 17          | ...        |           |
| ...              | 0.0086–0.015 |        |              | 20         | ...       |
| ...              | 0.031–0.059 | 30–96   | 18          | ...        |           |
| ...              | ≤0.03    |           |              | 4          | ...       |
| ...              | 0.04–1 × 10⁻² | 13²     | 19          | 10⁻⁴–10⁻²  |           |
| DNC/HNC          | <0.014   | 10–30    | 13          | 10⁻³–10⁻¹  |           |
| ...              | 0.02–0.09 | ~20      |              | 21         | ...       |
| ...              | 0.008–0.122 |        |              | 17–20³     | 22        | ...       |
| ...              | 0.015–0.03 |          |              | 20         | ...       |
| H₂D⁺/H₃⁺         | <3 × 10⁻³ | 13²     | 19          | 10⁻⁴–10⁻²  |           |
| HDO/H₂O          | 0.014–0.058 |        |              | 23         | 10⁻³–10⁻² |
| ...              | ≥0.01    | 10–30    | 24          | ...        |           |
| ...              | ≥6 × 10⁻⁴ | 3.1 × 2.5 | 25          | ...        |           |
| ...              | 2.94 × 10⁻⁵ | 1.5 × 1.5 | 11          | ...        |           |
| ...              | 0.03     | 10–33    | 26          | ...        |           |
| ...              | 0.6–5 × 10⁻⁴ |        |              | 27         | ...       |
| ...              | ≥0.01    | 20       | 28          | ...        |           |
| HDO/H₂O (solid)  | 0.005–0.02  |        |              | 29         | 10⁻³–10⁻¹ |
| ...              | 8 × 10⁻⁴–10⁻² |        |              | 30         | ...       |
| HDS/H₂S          | 0.05–0.15 |          | 20          | 10         | 10⁻²–10⁻¹ |
| N₂D⁺/N₂H⁺        | 0.016–0.051 |        |              | 31         | 10⁻²–10⁰  |
| ...              | 0.01–0.16 | 10–20    | 32          | ...        |           |
| ...              | 0.03–0.04 | 26.4²    | 33          | ...        |           |
| ...              | 0.11     | 44       | 34          | ...        |           |
| ...              | 0.08–0.14 | 18³      | 35          | ...        |           |
| ...              | 0.02–0.52 | 11³      | 36          | ...        |           |
| ...              | ~0.1     | 9–26³    | 37          | ...        |           |
| ...              | 0.08–0.35 | 20       | 16          | ...        |           |
| ...              | 0.005–0.014 |        |              | 38         | 10⁻⁴–10⁻² |
| ...              | 0.033–0.271 |        |              | 39         | ...       |
| ...              | 0.003–0.027 |        |              | 40         | ...       |
| D₂CO/H₂CO        | 0.11–0.19 | 27³      | 41          | 10⁻³–10⁻²  |           |
| ...              | 0.40     |          | 42          | ...        |           |
| ...              | 0.01–0.1  | 17       | 43          | ...        |           |
| ...              | ≤0.07    | 22       | 44          | ...        |           |
| ...              | 2.05–3.3 × 10⁻² |        | 45          | ...        |           |
| ...              | 0.01–0.04 | 20–60    | 46          | ...        |           |
| ...              | 0.022–1.04 |        | 47          | 10⁻³–10⁻³  |           |
| ...              | 0.02–0.4  |          | 48          | ...        |           |
| ...              | 0.03–0.16 |          | 49          | ...        |           |
| D₂CS/H₂CS        | 0.333    |          |              | 50         | 10⁻³–10⁻¹ |
| HDCO/H₂CO        | 0.092–0.122 |        |              | 41         | 10⁻³–10⁻¹ |
| ...              | 0.015    |          | 10          | ...        |           |
| ...              | 0.07–4.3 | 10–30    | 47          | 10⁻³–10⁻²  |           |
| ...              | 0.09–2.6 | 20–60    | 45          | ...        |           |
| Species          | Sources | Spatial Scale | References | Model    |
|-----------------|---------|---------------|------------|----------|
| HDCS/H$_2$CS    | 0.333   |               | 42         | $10^{-2}$–$10^{-1}$ |
| ...             | 0.015–0.025 | >-60          | 51         | $10^{-2}$–$10^{-1}$ |
| ND$_2$/NH$_3$   | 1.1–6.5 × 10$^{-4}$ | 22$^a$       | 52         | $<10^{-3}$–$10^{-3}$ |
| ...             | 8 × 10$^{-4}$ | 25            | 53         | ...      |
| ...             | 9.35 × 10$^{-4}$ | 25            | 54         | $<10^{-5}$–$10^{-4}$ |
| NH$_2$D/NH$_3$  | 0.1–0.8 | 7             | 55         | $10^{-4}$–$10^{-2}$ |
| ...             | 0.07–0.42 | ~20           | 57         | ...      |
| ...             | 0.02–0.1 | 20            | 16         | ...      |
| ...             | 0.025–0.18 | 18          | 56         | ...      |
| ...             | <0.02   | 20            | 10         | ...      |
| ...             | <0.1    | 7             | 55         | $10^{-4}$–$10^{-2}$ |
| ...             | 0.071   | ~20           | 57         | ...      |
| ...             | 0.06–0.1 | 22            | 44         | ...      |
| ...             | 0.04–0.33 | 37           | 58         | ...      |
| ...             | 0.06–0.1 | 20            | 10         | ...      |
| ...             | 0.06    | 20            | 28         | ...      |
| ...             | 2.6–17.3 × 10$^{-2}$ | 20–60       | 45         | ...      |
| NH$_2$D/NH$_3$  | 0.03–0.27 | 22$^a$       | 52         | $10^{-4}$–$10^{-1}$ |
| ...             | ∼5 × 10$^{-3}$ | 22           | 44         | ...      |
| ...             | 0.02–0.4 | 59            | ...        | $<10^{-5}$–$10^{-3}$ |
| C$_2$HD/C$_2$H$_2$ | 0.05–0.15 | 1.7$^a$     | 60         | ...      |
| C$_3$D/C$_3$H    | 4.30 × 10$^{-3}$ | 1.7$^a$   | 61         | $10^{-3}$–$10^{-1}$ |
| ...             | 0.0043–0.023 | 17–28   | 62         | ...      |
| C$_3$HD/C$_3$H$_2$ | 0.013–0.051 | 17–28 | 62         | $10^{-3}$–$10^{-1}$ |
| CD$_2$OH/CH$_3$OH | 0.001–0.028 | 15        | 63         | $<10^{-5}$–$10^{-2}$ |
| CH$_2$DNC/CH$_3$CN | 0.04–0.18  | 40–60     | 64         | $10^{-3}$–$10^{-1}$ |
| ...             | 0.1–0.22 | 40           | 65         | ...      |
| ...             | 0.05–0.06 | 27$^b$      | 66         | ...      |
| CH$_2$DOH/CH$_3$OH | ≥0.01    | 27$^b$     | 67         | $10^{-2}$–$10^{-1}$ |
| ...             | 0.05–0.30 | 68          | ...        | ...      |
| ...             | 0.05–0.95 | 47          | ...        | ...      |
| ...             | 0.60–1.2  | 69          | ...        | ...      |
| CH$_2$OD/CH$_3$OH | 0.008–0.076 | 40–60 | 64         | $10^{-4}$–$10^{-2}$ |
| ...             | 0.02–0.06 | 40–60     | 69          | ...      |
| ...             | ≤0.1     | 20          | 10         | ...      |
| CHD$_2$OH/CH$_3$OH | 0.06–0.51  | 10–30    | 47         | $10^{-3}$–$10^{-9}$ |
| ...             | 0.1–0.3  | 11–30      | 69         | ...      |
| DC$_3$N/HC$_3$N  | 0.010–0.020 | 70        | ...        | $10^{-3}$–$10^{-2}$ |
| DC$_3$N/HC$_3$N  | 0.006–0.016 | 70        | ...        | $10^{-4}$–$10^{-3}$ |
| DC$_3$N/HC$_3$N  | 0.018–0.036 | 70        | ...        | $10^{-4}$–$10^{-3}$ |
| ...             | 0.013–0.019 | 72        | ...        | ...      |
| DCOOCH$_3$/HCOOCH$_3$ | 0.02–0.06  | 73        | 71         | $10^{-3}$–$10^{-1}$ |
| ...             | ~0.15    | 9–33       | 71         | ...      |

Notes. Young stellar object IR classification—I: pre-protostellar objects; O/I: embedded/revealed protostellar sources.

$^a$ Full-width half-maximum (FWHM).

$^b$ Half-power beam width (HPBW).

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in the appendices. Ion–neutral and dissociative recombination reactions dominate the list, accompanied by a smaller number of neutral–neutral reactions and the cosmic ray ionization of H₂ and He.

In general, using the 1σ confidence level, the abundances and column densities of species made of \( \leq 3 \) atoms (e.g., CO, HCO\(^+\), DCO\(^+\)) are uncertain by factors 1.5–5.0, those for species made of 4–7 atoms are uncertain by a factor of 1.5–7, and those for more complex species made of >7 atoms are uncertain by a factor of 2–10. For D/H ratios the uncertainties are, for the same different ranges of molecule sizes, a factor of 1.6–5, 1.6–10, and 2.5–10, respectively.

Despite certain limitations of our model, it successfully explains the observed D/H ratios in dark clouds (10 K and \( 10^4 \) cm\(^{-3}\)), prestellar cores (\( T \leq 10 \) K, \( n \sim 10^4 \) cm\(^{-3}\)), and protostellar envelopes (cold, \( T \sim 30 \) K, \( n_{HI} \sim 10^5 \) cm\(^{-3}\) and warm, \( T \sim 150 \) K, \( n_{HI} \sim 10^8 \) cm\(^{-3}\)), for many key species including water, methanol, ammonia, and many hydrocarbons. Our results show good agreement with previous model studies by Roberts & Millar (2000a, 2000b), Roberts et al. (2004), and Walmsley et al. (2004). We also list the dominant formation and destruction pathways for DCO\(^+\), DCN, and isotopologues of H\(_2\)\(^+\) and water in Appendix B. Finally, in Tables 6–8 we have listed the most abundant, potentially detectable deuterated species in cold cores, and warm IRDCs and HMPOs, which can be searched for with ALMA.

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APPENDIX A

UPDATED AND ADDED REACTIONS TO CHEMICAL NETWORK

In this appendix, we list problematic reactions and rate coefficients (Table 11) identified in our sensitivity analysis for isotopologues and isomers of water, H\(_2\)\(^+\), HCO\(^-\) and HCN, as well as added and updated non-deuterated (Table 12) and deuterated (Table 13) reactions to our network. The added and updated reactions have been collected from several literature references as well as newly announced values (as of 2012 December 26) reported in theKIDA (http://kida.obs-u-bordeaux1.fr/).

APPENDIX B

DOMINANT FORMATION AND DESTRUCTION PATHWAYS FOR DEUTERATED SPECIES

In this appendix, we list the dominant pathways identified for isotopologues and isomers of the selected species H\(_3\)\(^{+}\), HCO\(^+\), HCN, H\(_2\)O as well as species involved in the formation of these essential species (Tables 14–18). The intention is to help with future comparisons with our model.
