Reconstructing the history of water ice formation from HDO/H$_2$O and D$_2$O/HDO ratios in protostellar cores

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ABSTRACT

Recent interferometer observations have found that the D$_2$O/HDO abundance ratio is higher than that of HDO/H$_2$O by about one order of magnitude in the vicinity of low-mass protostar NGC 1333–IRAS 2A, where water ice has sublimated. Previous laboratory and theoretical studies show that the D$_2$O/HDO ice ratio should be lower than the HDO/H$_2$O ice ratio, if HDO and D$_2$O ices are formed simultaneously with H$_2$O ice. In this work, we propose that the observed feature, D$_2$O/HDO > HDO/H$_2$O, is a natural consequence of chemical evolution in the early cold stages of low-mass star formation as follows: 1) majority of oxygen is locked up in water ice and other molecules in molecular clouds, where water deuteration is not efficient; and 2) water ice formation continues with much reduced efficiency in cold prestellar/protostellar cores, where deuteration processes are highly enhanced as a result of the drop of the ortho-para ratio of H$_2$, the weaker UV radiation field, etc. Using a simple analytical model and gas-ice astrochemical simulations, which traces the evolution from the formation of molecular clouds to protostellar cores, we show that the proposed scenario can quantitatively explain the observed HDO/H$_2$O and D$_2$O/HDO ratios. We also find that the majority of HDO and D$_2$O ices are likely formed in cold prestellar/protostellar cores rather than in molecular clouds, where the majority of H$_2$O ice is formed. This work demonstrates the power of the combination of the HDO/H$_2$O and D$_2$O/HDO ratios as a tool to reveal the past history of water ice formation in the early cold stages of star formation, and when the enrichment of deuterium in the bulk of water occurred. Further observations are needed to explore if the relation, D$_2$O/HDO > HDO/H$_2$O, is common in low-mass protostellar sources.

Key words. astrochemistry – ISM: molecules – ISM: clouds – stars: protostars

1. Introduction

The degree of deuterium fractionation in molecules in general, and that of water in particular, depends on its formation environments. This characteristic enables us to gain insights into the water trail from its formation in molecular clouds to, ultimately, the delivery to planets by comparing the deuterium fractionation in objects at different evolutionary stages (e.g., recent reviews by Ceccarelli et al. 2014; van Dishoeck et al. 2014).

It is well established that water is formed on grain surfaces in molecular clouds. At dust temperatures lower than 100–150 K, water is predominantly present on the surfaces of dust grains as ice (Fraser et al. 2001). There has been no clear detection of HDO ice in the interstellar medium (ISM), and the deuteration of water ice is not well-constrained (HDO/H$_2$O < (2–5)×10$^{-3}$; Dartois et al. 2003; Parise et al. 2003). Instead, there have been numerous observational studies on the deuteration of water vapor, which may reflect that of water ice through thermal and non-thermal desorption of ice.

In particular, recent interferometer and single-dish observations have quantified the degree of deuteration of water vapor in four low-mass protostellar sources, IRAS 16293-2422, NGC 1333–IRAS 2A, IRAS 4A, and IRAS 4B (Jørgensen & van Dishoeck 2010; Liu et al. 2011; Coutens et al. 2012, 2013, 2014; Persson et al. 2013, 2014; Taquet et al. 2013). The interferometer observations provide the emission from the inner hot regions (T > 100 K), where water ice is sublimated, while the single-dish observations, including the Herschel Space Observatory, provide the integrated emission from larger spatial scales (Jørgensen & van Dishoeck 2010; Coutens et al. 2012). The combination of the two types of the observations have revealed that 1) the gaseous HDO/H$_2$O ratio in the inner hot regions (∼10$^{-3}$) is lower than that in the cold outer envelopes by more than one order of magnitude; and 2) the gaseous D$_2$O/HDO ratio is much higher than the HDO/H$_2$O ratio (∼10$^{-2}$ versus ∼10$^{-3}$) in the inner hot regions of NGC 1333–IRAS 2A (Coutens et al. 2014) and at least one other source (A. Coutens, priv. comm.).

Water deuteration in low-mass protostellar sources has also been studied using physical and astrochemical models (e.g., recent work by Aikawa et al. 2012; Taquet et al. 2014; Wakelam et al. 2014). These studies adopt one-dimensional gravitational collapse models, which describe the physical evolution of collapsing prestellar cores to protostellar sources, with detailed gas-ice chemical networks. The models successfully reproduce observed feature #1, the radial gradient of the HDO/H$_2$O ratio, by gas-phase ion-neutral chemistry in the outer cold regions and sublimation of ice in the inner hot regions. The models, however, tend to overpredict the HDO/H$_2$O ratio in the inner hot regions by a factor of several or more compared to the observations. Furthermore, in contrast to the observed feature #2, all models predict that the gaseous D$_2$O/HDO ratio in the inner hot regions is lower than or comparable to the HDO/H$_2$O ratio. Coutens et al. (2014) have proposed that, either there is something missing in the current understanding of deuterium
chemistry on icy grain surfaces, or that water formation at high temperatures ($T_{\text{gas}} > 200$–$300$ K) through reactions $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ and $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ play a role in the inner quiescent regions, following sublimation of ice. In the latter case, the $\text{D}_2\text{O}/\text{HDO}$ ratio reflects that in ice, while the HDO/$\text{H}_2\text{O}$ ratio is diluted by the additional formation of $\text{H}_2\text{O}$ vapor, so that the $\text{D}_2\text{O}/\text{HDO}$ ratio can be higher than the HDO/$\text{H}_2\text{O}$ ratio. However, it requires that a large amount of oxygen is in atomic form rather than in molecules in the high density inner regions.

In this paper, we propose an alternative scenario that can account for the higher $\text{D}_2\text{O}/\text{HDO}$ ratio compared with HDO/$\text{H}_2\text{O}$ by the combination of cold deuterium chemistry and sublimation of ice without the need for the enhanced $\text{H}_2\text{O}$ formation in hot gas. This paper is organized as follows. In Sect. 2, the proposed scenario is presented through a simple analytical model. In Sect. 3, we simulate the gas-ice chemical evolution in star-forming cores with a numerical model to verify the scenario. We briefly discuss molecular oxygen and the ortho-to-para ratio of $\text{H}_2$, the deuteration of methanol, and thermally induced $\text{H–D}$ exchange reactions in ice in Sect. 4. Our findings are summarized in Sect. 5.

### 2. Scenario

We assume that both the HDO/$\text{H}_2\text{O}$ and $\text{D}_2\text{O}/\text{HDO}$ gas ratios in the inner hot regions around protostars reflect those in ice. In this subsection we denote the HDO/$\text{H}_2\text{O}$ ratio as $f_{\text{D1}}$, while we denote the $\text{D}_2\text{O}/\text{HDO}$ ratio as $f_{\text{D2}}$.

We first note that previous laboratory and theoretical studies show that $f_{\text{D2}}$ should be lower than $f_{\text{D1}}$, if $\text{H}_2\text{O}$, HDO, and $\text{D}_2\text{O}$ ices are formed via grain surface reactions at the same time. Let us assume that they all are formed via sequential reactions of atomic hydrogen/deuterium with atomic oxygen. These reactions have no activation energy barrier (Allen & Robinson 1977). If the surface reactions distribute deuterium statistically (or, in other words, mass-independently), the following relation holds (Rodgers & Charnley 2002):

$$f_{\text{D2}}/f_{\text{D1}}\text{statistic} = 0.25.$$  \hspace{1cm} (1)

Laboratory experiments have demonstrated that there are other formation pathways of water ice: sequential surface reactions initiated by reactions of $\text{O}_2$ with atomic hydrogen (Toppolo et al. 2008; Miyauchi et al. 2008; Mokrane et al. 2009), and the reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ (Oba et al. 2012). These pathways include reactions with activation energy barriers, and thus proceed through quantum tunneling (Oba et al. 2012, 2014). The barrier-mediated reactions favor hydrogenation over deuteration, because deuterium is twice heavier than hydrogen (Oba et al. 2014). In addition, once water is formed, it does not efficiently react with atomic deuterium to be deuterated at low temperatures, unlike formaldehyde and methanol (Nagaoka et al. 2005). At warm temperatures (>70 K), $\text{H–D}$ exchange reaction, $\text{H}_2\text{O} + \text{D}_2\text{O} \rightarrow 2\text{HDO}$, is thermally activated, and the $f_{\text{D2}}/f_{\text{D1}}$ ratio can be lowered (e.g., Lamberts et al. 2015, see also Sect. 4.3). Taken together, $0.25$ is the upper limit of the $f_{\text{D2}}/f_{\text{D1}}$ ratio.

The above constraint, $f_{\text{D2}}/f_{\text{D1}} \leq 0.25$, can be directly applied to the compositions of ice in the ISM, if $\text{H}_2\text{O}$, HDO, and $\text{D}_2\text{O}$ ices are predominantly formed simultaneously (Butner et al. 2007). However, in the sequence of star formation, they are not necessarily formed at the same evolutionary stage (Dartois et al. 2003). The onset of the water ice mantle formation requires a threshold extinction, above which the photodesorption rate of water ice is lower than the formation rate of water ice and its precursors (e.g., Tielens 2005). The $\text{H}_2\text{O}$ ice-formation rate decreases with time since elemental oxygen is locked into O-bearing molecules. Later, in the evolution, at higher extinction and densities, CO freezes out and the products of its hydrogenation, such as formaldehyde ($\text{H}_2\text{CO}$) and methanol ($\text{CH}_3\text{OH}$), are thought to be the main constituent of the outer layers of the ice mantle (e.g., Pontopiddan 2006; Oberg et al. 2011). On the other hand, the formation rates of HDO and $\text{D}_2\text{O}$ ices do not necessarily decrease together with that of $\text{H}_2\text{O}$ ice; deuteration fractionation is more efficient at later times, as CO is frozen out, the ortho-to-para nuclear spin ratio of $\text{H}_2$ ($\text{OPR(H)}$) decreases, and interstellar UV radiation is heavily shielded (e.g., Caselli & Ceccarelli 2012, and references therein).

Infrared observations show that $\text{H}_2\text{O}$ ice starts to become abundant in molecular clouds above a threshold line-of-sight extinction, depending on environments, e.g., $\sim$3 mag for Taurus dark clouds (Whittet 1993; Boogert et al. 2015, and references therein). The scenario we propose is that, in contrast to $\text{H}_2\text{O}$ ice, HDO and $\text{D}_2\text{O}$ ices are mainly formed at the later stages of star formation, i.e., in cold prestellar and protostellar cores, where deuteration fractionation processes would be more efficient than in ambient molecular clouds. Then, taking the layered structure of ice mantles into consideration, HDO and $\text{D}_2\text{O}$ are mainly present in the CO/$\text{CH}_3\text{OH}$-rich outer layers, rather than in the $\text{H}_2\text{O}$-dominated inner layers. Assuming complete sublimation of the ice mantles in the inner hot regions of low-mass protostars, the gaseous $\text{D}_2\text{O}/\text{HDO}$ ratio directly reflects that in the outer layers of the ice mantles, while the gaseous HDO/$\text{H}_2\text{O}$ ratio is much lower than that in the outer layers because of the dilution by the abundant $\text{H}_2\text{O}$ in the inner layers. Thus, the gaseous $\text{D}_2\text{O}/\text{HDO}$ ratio can be higher than the HDO/$\text{H}_2\text{O}$ ratio in the vicinity of protostars. A schematic view of the layered ice structure in our scenario is shown in Fig. 1. Our scenario is essentially similar to that proposed by Dartois et al. (2003) for HDO enhancement. They suggest that water ice is formed without deuteration enrichment, followed by the additional water formation with high levels of deuteration fractionation at later times. The motivation behind their scenario was to explain the upper limits of the icy HDO/$\text{H}_2\text{O}$ ratio in the cold outer envelope of protostars, which are lower than the D/H ratios of other gaseous species.

![Fig. 1. Schematic view of our scenario and the layered ice structure. Stage I) The main formation stage of $\text{H}_2\text{O}$ ice. Water deuteration is not efficient, $f_{\text{D2}} < f_{\text{D1}} < 10^{-3}$. The majority of oxygen is locked in O-bearing molecules in this stage. Stage II) CO/$\text{CH}_3\text{OH}$-rich outer ice layers are formed, while the formation of water ice continues with much reduced efficiency, compared to Stage I. Nevertheless, the formation of HDO and $\text{D}_2\text{O}$ ices is more efficient in Stage I, owing to the enhanced deuteration processes, $10^{-3} < f_{\text{D2}} < f_{\text{D1}}$.](image-url)
Gas-ice chemical simulations of collapsing prestellar cores to the formation of protostars to explore if condition #2 is fulfilled.

Based on the two stage model, we find that there are two regimes at the same $[\text{HDO}]_1$-II. Above the dashed line of Fig. 2, where $\alpha \beta > 1$, the difference between $[\text{HDO}]_1$-II and $[\text{HDO}]_2$ is more than a factor of two, i.e., the HDO/H$_2$O ratio that is established at the main formation stage of H$_2$O ice is mostly hidden by water ice additionally formed at later times. Below the dashed line, on the other hand, $[\text{HDO}]_1$-II and $[\text{HDO}]_2$ are similar. The former corresponds exactly to our scenario, where HDO and D$_2$O ices are predominantly formed after the main formation stage of H$_2$O ice. The latter is the case where H$_2$O and HDO ices are formed together, while D$_2$O ice is mainly formed after the main formation stage of H$_2$O and HDO ices. For the same $[\text{HDO}]_2/[\text{HDO}]_1$-II, the latter case requires more significant freeze out of oxygen, especially atomic oxygen and CO; water ice can be formed from CO gas through CO + He$^+$ → C$^+$ + O. Which regime is more likely in the ISM, or in other words, does the HDO/H$_2$O ratio in the hot gas directly reflect the HDO/H$_2$O ice ratio at the main formation stage of H$_2$O ice? Numerical simulations are needed to answer this question.

3. Numerical simulation

3.1. Model description

We simulate water deuteration from a prestellar core to a protostellar core adopting one-dimensional radiation hydrodynamics simulations of Masunaga & Inutsuka (2000). Initially the core has an isothermal hydrostatic structure with a fixed outer boundary of 4 × 10$^4$ AU from the core center. The total mass of the core is 3.9 M$_\odot$, which is greater than the critical mass for gravitational instability. The protostar is born at 2.5 × 10$^5$ yr after the beginning of the collapse, corresponding to 1.4$t_\text{ff}$, where $t_\text{ff}$ is the free-fall time of the initial central density of hydrogen nuclei ~6 × 10$^3$ cm$^{-3}$. After the birth of the protostar, the model further follows the physical evolution for 9.3 × 10$^4$ yr.

Fluid parcels are traced in the hydrodynamics simulation, and we perform gas-ice chemical simulations along the stream lines to obtain the radial distribution of molecules in the protostellar envelope. This approach is the same as Aikawa et al. (2012). For simplicity, we set the temperature as 10 K when the temperature in the original data is lower than 10 K. We adopt a rate equation method and the chemistry is described by a three-phase model, which consists of gas, a chemically active icy surface, and inert ice mantles (Hasegawa & Herbst 1993b). The top four monolayers of ice mantles are assumed to be chemically active, following Vasyunin & Herbst (2013). We refer to all of the layers including both the ice surface and the inert ice mantle as the bulk ice mantle. We take into account gas-phase reactions, interaction between gas and (icy) grain surface, and surface reactions. For non-thermal desorption processes, we consider stochastic heating by cosmic-rays (Hasegawa & Herbst 1993a), photodesorption (Westley et al. 1995), and chemical desorption (Garrod et al. 2007). Our chemical reaction network is originally based on Garrod & Herbst (2006). The network has been extended to include high-temperature gas-phase reactions from Harada et al. (2010), mono, doubly, and triply deuterated species (Aikawa et al. 2012; Furuya et al. 2013), and nuclear spin states of H$_2$, H$^+_3$, and their isotopologues (Hincelin et al. 2014). The rate coefficients for the H$_2$ + H$^+_3$ system are taken from Hugo et al. (2009). More details can be found in Paper I.

We consider six sets of the initial abundances for the collapse model, which are summarized in Table 1. In the sets labeled

![Fig. 2](image-url)
“MC”, the molecular abundances are adopted from Paper I. In Paper I, a one-dimensional shock model (Bergin et al. 2004; Hassel et al. 2010) was used to study the chemical evolution during the formation and growth of a molecular cloud via the accumulation of H1 gas. Note that the evolution of the molecular cloud is dominated by ram pressure that is due to the accretion flow rather than self-gravity, which is in contrast with our collapse model. The time it takes for the column density of the molecular cloud reaches 1 mag (MC1), or 3 mag (MC3). In all three sets, H2O1 c ei s ~ 10 mag (MC1), or 3 mag (MC3). We adopt the abundances when the flux of FUV photons that is induced by cosmic-rays is set to be 3 × 10^{-6} s^{-1}, while the flux of FUV photons that is induced by cosmic-rays is set to be 3 × 10^{-6} s^{-1}. In these settings, photochemistry is not important for water ice.

Before the onset of the collapse, we assume that the prestellar core keeps its hydrostatic structure for some time. We consider three cases in which the elapsed time before the onset of the collapse is 0 yr (labeled “A”), 10^{6} yr (corresponding to 5.61 ff, labeled “B”), or 3 × 10^{6} yr (16 ff, “C”). Our fiducial model is MC2B; i.e., the initial molecular abundance is set by the cloud-formation model at the epoch when the column density reaches 2 mag, and the duration of the static prestellar phase is 10^{6} yr.

3.2. Results

3.2.1. Fiducial model

Figure 3 shows the temporal variation of molecular abundances and abundance ratios in the fiducial model (MC2B) along the stream line of a fluid parcel. The fluid parcel is initially at 10^{5} AU from the core center and finally reaches 5 AU. Figure 4 shows the fractional composition and the D/H ratios in the active surface ice layers in the fluid parcel as a function of the number of ice layers in total. We note that surface layers become part of the inert ice mantle with the growth of ice. Initially, most oxygen is locked up in CO and water ice with bulk ice ratios of HDO/H2O > D2O/HDO of ~10^{-3}. In the static phase and during the collapse at T < 20 K, the environment is favorable for deuteration: the low temperature, 10−20 K, and the relatively low OPR(H2), ~10^{-3}, and the weak UV radiation field. During those periods, corresponding to layers ~70−90 in Fig. 4, a small amount of additional water ice (the total abundance of ~5 × 10^{-6}) is formed with HDO/H2O > D2O/HDO ≥ 10^{-2}. The source of oxygen

Table 1. Initial abundances of selected species with respect to hydrogen nuclei.

<table>
<thead>
<tr>
<th>Species</th>
<th>MC1</th>
<th>MC2</th>
<th>MC3</th>
<th>AT1</th>
<th>AT2</th>
<th>AT4</th>
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Notes. a(b) means a × 10^{-b}. o-H2 indicates ortho-H2, while p-H2 indicates para-H2. iX indicates species X in the bulk ice mantle. – indicates that abundances are less than 10^{-15}.
CH3OH in the surface ice layers. The visual extinction for calculating photodissociation ratios of HDO and D2O in the outer layers of the ice mantle, CO. The additional water ice formation increases the concentration of H2CO and methanol are abundant, as shown in Fig. 4. Table 2 summarizes the results from our grid of the models with variations in the initial abundances and the elapsed time before the onset of the collapse. In general, the models labeled MC predict a higher D2O/HDO ratio than HDO/H2O ratio at 10^5 yr in the static phase.

The top panel of Fig. 5 shows radial profiles of the abundances of H2O, HDO, and D2O at 9.3 × 10^4 yr after the protostellar birth, while the lower panel shows radial profiles of the HDO/H2O and D2O/HDO ratios.

The additional water ice formation increases the concentration of H2CO and CH3OH in the surface ice layers, and gaseous molecules, respectively.

for the formation of the water ice is gaseous atomic oxygen and CO. The additional water ice formation increases the concentration of HDO and D2O in the outer layers of the ice mantle, where CO and methanol are abundant, as shown in Fig. 4. The D2O/HDO ratio in the bulk ice becomes similar to that in the surface layers with time, while the HDO/H2O ratio in the bulk ice remains much lower than that in the surface layers owing to the abundant H2O in the inert ice mantle. The D2O/HDO ratio in the bulk ice becomes larger than the HDO/H2O ratio in 10^5 yr in the static phase.

The additional water ice formation increases the concentration of H2CO and CH3OH in the surface ice layers, and gaseous molecules, respectively.
The enhancement factor of the $\text{HDO}/\text{H}_2\text{O}$ ratio, $\epsilon_{\text{D}_1}$, is also listed in Table 2. In general, $\epsilon_{\text{D}_1}$ is larger than 2 in models labeled MC. Therefore, the HDO/$\text{H}_2\text{O}$ ice ratio that is established at the main formation phase of $\text{H}_2\text{O}$ ice is mostly hidden by the additional formation of highly deuterated water ice at later times.

The models labeled AT tend to predict lower $\text{D}_2\text{O}/$HDO ratios than HDO/$\text{H}_2\text{O}$ ratios at $T > 150$ K, in agreement with previous numerical studies (e.g., Aikawa et al. 2012). In these models, the gradient of deuterium fractionation seems not to be large enough. This is because the initial OPR($\text{H}_2$) is high ($\sim 5 \times 10^{-5}$) and the collapse begins immediately. The time required for the OPR($\text{H}_2$) to reach steady state is longer than the free-fall timescale (Flower et al. 2006); the OPR($\text{H}_2$) is higher than $2 \times 10^{-4}$ during the simulation, which reduces the efficiency of the overall deuteration processes, and prevents the enrichment of deuterated water in ice.

The order of $10^{-4}$. With the low initial OPR($\text{H}_2$) of $10^{-4}$, deuterium fractionation is already efficient at the main formation stage of $\text{H}_2\text{O}$ ice while, with the high initial OPR($\text{H}_2$) of $\geq 10^{-2}$, the efficiency of the overall deuterium fractionation is reduced during the cold prestellar core phase. Among the models labeled AT, only models with a high initial OPR($\text{H}_2$) and a very long static phase (AT1C and AT2C) predict higher $\text{D}_2\text{O}/\text{HDO}$ than HDO/$\text{H}_2\text{O}$ ratios.

4. Discussion

4.1. $\text{O}_2$ and ortho-para ratio of $\text{H}_2$

In the simulations of the collapsing core, the critical parameters controlling the HDO/$\text{H}_2\text{O}$ and $\text{D}_2\text{O}/$HDO ratios in the hot gas around protostars are the OPR($\text{H}_2$) and the amount of oxygen, i.e., atomic oxygen and CO, which is available for water ice formation. Here we briefly compare our model predictions with the observationally derived $\text{O}_2$ abundance and OPR($\text{H}_2$) toward low-mass protostars. Although the abundance of atomic oxygen in the cold outer envelopes is hard to constrain via observations, we can partly verify the oxygen chemistry in our models by comparing the predicted $\text{O}_2$ abundance with that derived from observations.

Yıldız et al. (2013) derived an upper limit of $\text{O}_2$ gas abundance $\lesssim 10^{-8}$ toward NGC 1333–IRAS 4A, assuming a constant abundance in the envelope. Brünken et al. (2014) derived the OPR($\text{H}_2\text{D}^+$) of $\sim 0.1$ in the cold outer envelope of IRAS 16293-2422, which corresponds to an OPR($\text{H}_2$) of $2 \times 10^{-4}$ in their best fit model. In general, the models that predict a higher $\text{D}_2\text{O}/$HDO than HDO/$\text{H}_2\text{O}$ ratio in the gas phase at $T > 150$ K reproduce the observations of $\text{O}_2$ and OPR($\text{H}_2$) better than the other models. Our fiducial model, for example, is consistent with the upper limit of the $\text{O}_2$ abundance and the OPR($\text{H}_2$) that is derived from the observations, as shown in Fig. 5 and Table 2. Unless a very long static phase (16Gy) is assumed, the models labeled AT tend to overpredict the $\text{O}_2$ abundance, implying that the majority of oxygen should be locked up in molecules such as water and CO before the prestellar core stage (Yıldız et al. 2013; Bergin et al. 2000).

In summary, our models labeled MC reproduce reasonably well the observations of the water deuterium fractionation, the $\text{O}_2$ abundance, and the OPR($\text{H}_2$), simultaneously. This strengthens our scenario. However, these observed values are measured in different sources and it is unclear whether the higher $\text{D}_2\text{O}/$HDO ratio compared with HDO/$\text{H}_2\text{O}$, the low $\text{O}_2$ abundance, and the low OPR($\text{H}_2$) are general chemical features of low-mass protostellar sources.

4.2. Water deuteration versus methanol deuteration

In the inner hot regions ($T \gtrsim 100$ K) of low-mass protostellar sources, formaldehyde, and methanol show higher levels of deuterium fractionation than water. For example, the $\text{CH}_3\text{OD}/\text{CH}_3\text{OH}$ ratio ($\gtrsim 10^{-2}$; Parise et al. 2006) is much higher than the HDO/$\text{H}_2\text{O}$ ratio ($\sim 10^{-3}$; e.g., Persson et al. 2014). This difference is thought to reflect the different epochs of their formation, i.e., water ice is formed in an earlier stage of star formation than formaldehyde and methanol ices (Cazaux et al. 2011; Taquet et al. 2012). We note that the scenario implicitly assumes that $\text{H}_2\text{O}$ and HDO ices are formed at the same evolutionary stage.

In our scenario, $\text{H}_2\text{O}$ ice is mainly formed in molecular clouds, while HDO and $\text{D}_2\text{O}$ ices are mainly formed at later
times when CO and methanol are the main constituent of the surface layers of the ice. In other words, H2O ice is formed at an earlier stage of star formation than deuterated water, formaldehyde, and methanol ices. This naturally leads to the following reaction, where water ice has sublimated (Coutens et al. 2014). In this study, we have proposed that the observed feature is a natural consequence of chemical evolution in the early cold stages of the H–D exchange reaction, where water ice has sublimated (Coutens et al. 2014), who showed that the D2O emission peak is located at the peak of the continuum emission as well as the H18O/D18O ratio in the ISM. Ratajczak et al. (2009) experimentally demonstrated that the thermally activated H–D exchange between CD18O and H2O occurs efficiently in mixed ice at T > 120 K, while the exchange does not occur in the case of segregated ice, even at higher temperatures on a laboratory timescale. As noted in Ratajczak et al. (2009), this implies that the H/D exchange occurs only between closely interacting molecules in ice. In the experiments of Lamberts et al. (2015), mixed ices with the mixing ratio of (H2O:D2O) ~ (1:1) were used, which ensures that each D2O has at least one neighbour of H2O. In our scenario, however, D2O is mainly present in the CO/CH3OH-rich outer-layers, i.e., significant fraction of D2O would not be neighbored by H2O molecules, and it may be the limiting factor of the H/D exchange by Reaction (5) in the ISM.

### 4.3. Thermally induced H–D exchange reactions

Laboratory experiments have shown that thermally activated H–D exchanges between hydrogen-bonded molecules in mixed ices occur efficiently at warm temperatures of ≥70 K (Ratajczak et al. 2009; Faure et al. 2015; Lamberts et al. 2015). This type of reaction is not included in our chemical network. In particular, for the present study, Lamberts et al. (2015) experimentally studied the thermally activated H–D exchange reactions,

\[
\text{H}_2\text{O} + \text{D}_2\text{O} \rightarrow 2\text{HDO},
\]

in mixed amorphous ices. In equilibrium, the ratio of the D2O/HDO ratio to the HDO/H2O ratio is given as kSB/kSF, where kSB and kSF are the reaction rate coefficient of Reaction (5) in the backward direction and the forward direction, respectively. Lamberts et al. found that the activation energy barrier of the forward reaction is 3840 ± 125 K, which is much smaller than the binding energy of water on a water substrate, 5700 K (Fraser et al. 2001). Although the activation barrier for the backward reaction has not been measured in a laboratory, the backward reaction is energetically less favorable than the forward reaction, i.e., likely kSB/kSF < 1 (Collier et al. 1984; Lamberts et al. 2015). Taken together, the D2O/HDO ice ratio can be lowered during the warm-up of ices in in-falling protostellar envelopes (Lamberts et al. 2015).

To check the impact of the H–D exchange by Reaction (5), we compared the timescale of the forward reaction that was calculated by Lamberts et al. (2015) and the duration time of the warm-up timescale in our collapse model, and found that the forward reaction is much shorter than the latter at ≥80 K. Then D2O in ice would largely be lost prior to the sublimation of water ice, if Reaction (5) is as efficient in the ISM as in the laboratory. This challenges the D2O observations by Coutens et al. (2014), who showed that the D2O emission peak is located at the peak of the continuum emission as well as the H18O and the HDO emissions. A possible explanation for the discrepancy is the layered ice structure in the ISM. Ratajczak et al. (2009) experimentally demonstrated that the thermally activated H–D exchange between CD18O and H2O occurs efficiently in mixed ice at T > 120 K, while the exchange does not occur in the case of segregated ice, even at higher temperatures on a laboratory timescale. As noted in Ratajczak et al. (2009), this implies that the H/D exchange occurs only between closely interacting molecules in ice. In the experiments of Lamberts et al. (2015), mixed ices with the mixing ratio of (H2O:D2O) ~ (1:1) were used, which ensures that each D2O has at least one neighbour of H2O. In our scenario, however, D2O is mainly present in the CO/CH3OH-rich outer-layers, i.e., significant fraction of D2O would not be neighbored by H2O molecules, and it may be the limiting factor of the H/D exchange by Reaction (5) in the ISM.

### 5. Conclusion

Recent interferometer observations have found that the D2O/HDO ratio is higher than the HDO/H2O ratio in the warm gas surrounding the low-mass protostar NGC 1333–IRAS 2A, where water ice has sublimated (Coutens et al. 2014). In this study, we have proposed that the observed feature is a natural consequence of chemical evolution in the early cold stages of low-mass star formation as follows: 1) majority of oxygen is locked up in water ice and other molecules in molecular clouds, where water deuteration is not efficient; and 2) water ice formation continues with much reduced efficiency in cold prestellar/protostellar cores, where deuteration processes
are highly enhanced. Using a simple analytical model and gas-ice astrochemical simulations on the formation of molecular clouds (Paper I) and the gravitational collapse of dense cores, we have shown that the scenario can quantitatively explain the HDO/H$_2$O ratio and the D$_2$O/HDO ratio measured in IRAS 2A. Our model predictions are consistent with the low abundance of O$_2$, the low OPR(H$_2$), and the CH$_3$OH/CH$_4$OH ratio measured in low-mass protostellar sources, which further supports the scenario. We also found that the majority of HDO and D$_2$O ices are likely formed in cold prestellar/protostellar cores rather than in molecular clouds, where the majority of H$_2$O ice is formed. Taking the layered ice mantles into consideration, this implies that HDO and D$_2$O are predominantly present in the CO/CH$_3$OH-rich outer layers of ice mantles rather than in the H$_2$O-dominated inner layers. The layered ice structure indicates that the gaseous HDO/H$_2$O ratio that is produced by photodesorption does not reflect that of the bulk ice (see also Taquet et al. 2014).

The present study demonstrates the power of the combination of the HDO/H$_2$O and D$_2$O/HDO ratios as a tool to reveal the past history of water ice formation in the early cold stages of star formation and when the enrichment of deuterium in the bulk of water occurred. Further observations are desirable to investigate if the relation, D$_2$O/HDO > HDO/H$_2$O, is common in low-mass protostellar sources.

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