Deuterium Fractionation upon the Formation of Hexamethylenetetramines through Photochemical Reactions of Interstellar Ice Analogs Containing Deuterated Methanol Isotopologues

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Abstract

Hexamethylenetetramine (HMT) is a representative product after the photolysis of interstellar ice analogs containing methanol followed by warming-up to room temperature. Since interstellar methanol is often significantly enriched in deuterium (D), the HMT photoprodut is expected to inherit D atoms from deuterated methanol. However, D fractionation upon the formation of HMT is not well understood, especially when it is produced from partly deuterated methanol isotopologues such as CH2DOH and CH3OD. Here, we experimentally studied the composition of deuterated HMT (dn-HMT, where n is the number of D atoms) at the isotopologue level formed by the photolysis of ice mixtures containing deuterated methanol, CH2DOH or CH3OD, at 10 or 77 K. The analyses were performed using a state-of-the-art high-resolution mass spectrometer coupled with a compound-specific separation technique. The formation of dn-HMT (n = 0–8) was confirmed under all experimental conditions. In addition, methyl- and hydroxyl-substituted HMT and their deuterated isotopologues were also obtained in the products. The deuterium enrichment was outstanding when CH2DOH was used rather than CH3OD, and when photolysis was performed at 77 K rather than 10 K. We found that the deuteration level of the formed HMT far exceeded that of the reactants under the present experimental conditions. These results obtained during stable isotope probing of deuterium strongly suggest that HMT can play a role as an organic pool of interstellar D atoms. These may be distributed into other chemical species through molecular evolution in space.

Key words: astrochemistry – ISM: clouds – solid state: volatile – ultraviolet: ISM

1. Introduction

Deuterium (D) enrichment is a well-known property of interstellar molecules (Ceccarelli et al. 2014). Since the degree of their D-enrichment often overwhelmingly exceeds the cosmic abundance of D atoms (D/H ~ 10^-5; Linsky 2003), there must be specific mechanisms for the D-enrichment of interstellar molecules. Methanol (CH3OH), one of the simplest complex organic molecules (COMs) observed in a variety of astronomical environments, such as pre-stellar molecular cores, protostellar envelopes, protoplanetary disks, and comets (Caselli & Ceccarelli 2012; Walsh et al. 2016), is a representative organic molecule enriched in D: even doubly deuterated methanol (CD2OH) and triply deuterated methanol (CD3OH) isotopologues have been observed toward low-mass protostars (Parise et al. 2002, 2004). Since the formation of CH3OH and its deuterated isotopologues through gas-phase reactions is ineffective in explaining these abundances in the interstellar medium (Parise et al. 2004; Geppert et al. 2006), it is generally accepted that they are formed on interstellar icy grains. Laboratory experiments have demonstrated the formation of solid CH3OH and its deuterated isotopologues through the successive hydrogen (H) addition to carbon monoxide (CO; Watanabe & Kouchi 2002; Watanabe et al. 2003) and H–D substitution of CH3OH, respectively (Nagaoka et al. 2005, 2007).

Solid methanol that forms on icy grains, as well as other solid components in the ice, such as water (H2O), CO, and ammonia (NH3), will be further processed through external energy inputs such as ultraviolet (UV) photons and cosmic rays at low temperatures, and may further experience heating events that are expected to take place through the period of star formation. These processes may result in the formation of more COMs, including amino acids (AAs) and sugars through radical chemistry on/in the ice (e.g., Bernstein et al. 2002; Muñoz Caro et al. 2002; Kaiser et al. 2015; Meinert et al. 2016; Öberg 2016). Given the fact that interstellar methanol is highly enriched in D, to some extent, the COMs may also inherit the deuterium enrichment from interstellar methanol. Recently, we reported on deuterium fractionation upon the formation of AAs through the photolysis of interstellar ice analogs containing singly deuterated methanol (CH3DOH) using an orbitrap-type high-resolution mass spectrometer coupled with a high-performance liquid chromatograph and an electrospray ionization interface (HPLC/ESI-MS; Oba et al. 2016). Five types of AAs and their deuterated isotopologues were identified in the product of organic films and the degree of deuteration was slightly higher than that expected if a statistical distribution of D atoms in AAs is assumed. These results indicate that the deuteration enrichment of interstellar methanol is inherited by more complex molecules (Oba et al. 2016).

Although AAs are one of the representative COMs formed by photochemical reactions in the interstellar ice analogs and are regarded as astrobiologically important molecules (e.g., Bernstein et al. 2002; Nuevo et al. 2008; Modica et al. 2014), they are not a major constituent in terms of abundance in
the products. Hexamethylenetetramine (C₆H₁₂N₄; hereafter, denoted as HMT; Figure 1) is the most abundant organic molecule (>60%) present in organic residues, especially when methanol is present in the ice analogs (Bernstein et al. 1995; Cottin et al. 2001; Muñoz Caro et al. 2002; Muñoz Caro & Schutte 2003; Muñoz Caro et al. 2004). However, it has not yet been detected in any astronomical object nor extraterrestrial samples such as meteorites, interplanetary dust particles, and cometary return samples. Nevertheless, the abundance and D/H ratio of photochemically produced HMT in the interstellar medium may have an impact on chemical evolution in regions, such as protoplanetary disks and planetary systems, where photon- and heat-driven chemical reactions may be more common than in dense clouds (Ciesla & Sandford 2012). In such regions, the photoysis and pyrolysis of HMT yields simple molecules, such as NH₃ and HCN, in/on dust (Iwaki et al. 1968; Wolman et al. 1971; Bernstein et al. 1995; Cottin et al. 2002; which are the building blocks of biologically important molecules such as AAs) via Strecker synthesis (Islam & Powner 2017). Although such volatile molecules are abundant in the interstellar medium (Tielens 2013), depending on the distance from their central star, they will escape from dust or planetary bodies due to thermal heating. Therefore, HMT, which is much less volatile and can stay in dust or planetary bodies at higher temperatures, may be an important source of gases such as NH₃ and HCN.

To date, there have been no studies that systematically investigate the deuterium fractionation of HMT upon its formation through photochemical reactions. Based on their D-labeled experiments, where the photolysis of a solid mixture of D₂O, CH₃OD, CO, and ND₃ yielded nondeuterated HMT, Bernstein et al. (1995) reported in their pioneering study on HMT formation that H atoms in HMT are derived from the methyl group of methanol. However, the deuterium fractionation pathway of HMT is entirely unknown when partially deuterated methanol isotopologues, such as CH₂DOH and CHD₂OH, which are two of the most abundant deuterated methanol isotopologues in the low-mass protostar IRAS 16293-2422 (Parise et al. 2004; see Census of COMs in IRAS 16293-2422, Jaber et al. 2014), are used in the formation of HMT. Depending on the parent deuterated species, the degree of deuterium enrichment of the produced HMT can vary significantly. Therefore, based on the fact that HMT is the most abundant product of photochemical reactions in interstellar ice analogs, further systematic studies are necessary to better understand the entire picture of deuterium fractionation through molecular evolution in space. In the present study, using a high-resolution mass spectrometer, we quantitatively analyzed the deuterium distribution of HMT in organic residues produced by the photolysis of interstellar ice analogs containing deuterated methanol at the isotopologue level.

2. Experiments

2.1. Laboratory-based Photochemistry of Interstellar Ice Analogs

The photolysis of interstellar ice analogs was performed using the Setup for Analysis of Molecular and Radical reactions of Astrochemical Interest (SAMRAI; Figure 1). The importance of stable isotope probing of deuterium and related experimental procedures have been reported in our previous paper (Oba et al. 2016). The SAMRAI mainly consists of an ultra-high-vacuum reaction chamber, a Fourier transform infrared spectrometer (FTIR), a quadrupole mass spectrometer, and an aluminum (Al) substrate that can be cooled to 10 K by a helium (He) refrigerator. The base pressure is on the order of 10⁻⁷ Pa. Two D₂ discharge lamps (L12098, Hamamatsu Photonics), whose photon fluxes are in the range of 10¹³–10¹⁴ photons cm⁻² s⁻¹, are attached to the reaction chamber. Photon fluxes are estimated from an electric current measured using a photodiode (AXUV199G, Opto Diode Corp.) placed in front of the substrate. Gaseous samples comprised of H₂O, CO, NH₃, and deuterated methanol with a mixing ratio of 5:2:2:2 were supplied by continuous vapor deposition (gas-deposition rate ~10⁻³ molecules cm⁻² s⁻¹) with photoirradiation onto the Al substrate at 10 K. The photon to gas flux ratio is therefore in the range of 1–10. The methanol isotopologues were varied with experiments as follows. CH₃DOH in experiment (exp.) 1 and CH₃OD in exp. 2. CH₃OD was introduced from a separate gas line to avoid a hydrogen isotopic exchange of the OD group with other polar molecules (i.e., H₂O and NH₃) before vapor deposition. Photolysis of the CH₃OH-containing ice was also performed at 77 K to study the effect of temperatures on the composition of the produced HMT (exp. 3). We also performed another experiment similar to exp. 1 except for the absence of CO (exp. 4). In exp. 5, we used a mixture of CH₃OH:CH₃DOH:CHD₃OH:CD₃OH:CH₃OD (100:30:6:1:2), which simulates the observed composition of deuterated methanol isotopologues in IRAS 16293-2422 (Parise et al. 2004). In addition, nondeuterated methanol, CH₃OH, was used in a control experiment (exp. 6). The experimental conditions of the present study are summarized in Table 1. The samples were exposed to UV photons throughout the deposition period of ~200 hr.
2.2. Analytical Procedure for the Experimental Products

After simultaneous gas-deposition and photon irradiation, the substrate was warmed to room temperature to remove volatile species, and the formation of solid organic residues was confirmed using FTIR (Oba et al. 2016). These organic residues were extracted from the substrate by dissolving them in several tens of microliters of a water/methanol mixture (1/1 by vol./vol.). Half of the sample solution was analyzed using a high-resolution mass spectrometer without further chemical treatment. The other half was hydrolyzed in 6 M HCl at 110°C for 12 hours, followed by acid removal for further analysis using the mass spectrometer. After hydrolysis, the sample was dried once and dissolved in distilled and deionized water. The hydrolyzed samples are hereafter denoted as “free” and “bound” fractions, respectively. The isolated fractions were stored in the dark at −20°C before HPLC/MS analysis.

Five microliters of each fraction were injected into an orbitrap mass spectrometer (Q Exactive Plus, Thermo Fischer Scientific) with a mass resolution m/Δm ~ 140,000 at a mass-to-charge ratio (m/z) = 200 through an HPLC system (UltiMate 3000, Thermo Fischer Scientific) equipped with a Hypercarb separation column (4.6 mm × 150 mm, particle size 5 μm, Thermo Fischer Scientific). Detailed analytical conditions of the HPLC system have been previously described (Takano et al. 2015; Oba et al. 2016). The mass spectra were recorded in the positive ESI mode with an m/z range of 50–400 and a spray voltage of 3.5 kV. The injected samples were vaporized at 300°C. The capillary temperature of the ion transfer was 300°C. The same volume of distilled water was used to check the contamination level of the mass spectrometer; however, no HMT was detected during the analytical blank measurement. For further confirmation of procedural blank control, we also concluded that no HMT was formed when no gases were deposited (i.e., UV photons only) on the substrate and the sample was processed with the same procedure as described above. An authentic standard reagent of HMT (purity >99.0%; from Tokyo Chemical Industry Co., Ltd) was dissolved in distilled H2O, then the HMT-solution (1 μg/μl) was analyzed using the abovementioned procedure to firmly identify HMT in the organic residues based on the retention time in the mass chromatogram.

3. Results

HMT and its deuterated isotopologues (hereafter denoted as \(d_n\)-HMT, where \(n\) is the number of D atoms in the structure) were identified in the free fraction of all samples, as shown in Figure 2. On the other hand, they were not identified in the bound fraction of all samples for the reason that HMT is chemically very weak against acid hydrolysis (Wolman et al. 1971; Blažević et al. 1979). Therefore, the present study, hereafter, focuses on HMT and its related molecules in the free fraction. The concentrations of \(d_n\)-HMT were estimated from the peak areas from the mass chromatogram results at the m/z values of the corresponding protonated ions (e.g., \(C_6H_5N_2H^+\) for \(d_0\)-HMT with \(m/z = 141.1135\) based on the assumption that the ionization efficiency is unity among all \(d_n\)-HMTs. The concentrations of the total HMT were almost constant (\(7.3 ± 1.1 × 10^{-3} \mu mol/5 \mu l\)) among samples processed at 10 K. The small deviation (~15% of the mean value) suggests that the formation and extraction of HMT in the experiments at 10 K were highly reproducible. The concentration of HMT was one order of magnitude lower in the sample processed at 77 K (\(7.0 × 10^{-4} \mu mol/5 \mu l\); Table 1). In a separate experiment performed under the same conditions as with exp. 3, we confirmed that the experimental results at 77 K were also highly reproducible.

3.1. Relative Abundance of \(d_n\)-HMT

Figure 2 shows a mass chromatogram (m/z = 141.1135 for \(C_6H_5N_2H^+\)) for the organic residue of the free fraction after the photolysis of a mixture of H2O, CO, CH3DOH, and NH3 at 10 K (exp. 1) followed by warming-up to room temperature. The extracted mass chromatogram of the aqueous solution of a standard HMT reagent is also shown for comparison. Based on the consistency of the peak retention time with the standard, a strong peak at ~29 minutes on the sample chromatogram was derived from \(d_0\)-HMT. Figure 2 also shows the mass spectra of the peak at ~29 minutes at m/z values of 141–149. Several peaks are distributed at almost the same intervals as for the free sample (~1.0062), which is consistent with the mass difference between hydrogen and deuterium atoms. As seen in the results for the standard reagent (Figure 2(d)), \(^{13}\)C-HMT was clearly discriminated from \(d_1\)-HMT and was much less abundant relative to \(d_1\)-HMT in this experiment. These mass distributions, therefore, indicate the presence of a series of \(d_n\)-HMT whose number of D atoms ranges from 0 to 8. Since all of the H atoms in HMT are bound to carbon atoms and it has six carbon atoms in its molecular structure, at least two methylene groups (–CH2–) are fully deuterated (–CD2–) in \(d_0\)-HMT. Among the \(d_n\)-HMT species, \(d_2\)-HMT was the most abundant (~30% of the total \(d_n\)-HMTs), followed by \(d_3\), \(d_1\), \(d_4\), and \(d_0\)-HMT.

### Table 1

| Exp. No. | Gas Composition (H2O:CO:methanol:NH3) | Methanol Composition | Deposition Temperature (K) | \(d_n\)-HMT abundance (µmol/5 µl) | \(F_D\) (%) |
|----------|--------------------------------------|----------------------|----------------------------|---------------------------------|-------------|
| 1        | 5:2:2:2                              | CH3DOH               | 10                         | \(7.2 × 10^{-3}\)              | 249         |
| 2        | 5:2:2:2                              | CH2OD                | 10                         | \(9.0 × 10^{-3}\)              | 45          |
| 3        | 5:2:2:2                              | CH3DOH               | 77                         | \(7.0 × 10^{-4}\)              | 351         |
| 4        | 5:0:2:2                              | CH2DOH               | 10                         | \(7.2 × 10^{-3}\)              | 279         |
| 5        | 5:2:2:2                              | CH2DOH, CH3DOH, CD2OH, CD4OH, CH4OD* | 10                          | \(7.0 × 10^{-3}\)              | 293         |
| 6        | 5:2:2:2                              | CH2OH                | 10                         | \(5.9 × 10^{-3}\)              | ND*         |

Notes.

*CH3OH:CH2DOH:CH2DOH:CD2OH:CD4OH:CH4OD = 100:30:6:1:2.

* Not calculated.
These five isotopologues comprise more than 95% of the $d_n$-HMTs. When CH$_3$OD was used instead of CH$_3$DOH (exp. 2), multiple types of $d_n$-HMTs were also observed in the mass spectrum (Figure 3). However, unlike exp. 1, the dominant $d_n$-HMT species was $d_0$-HMT (∼63% of the total $d_n$-HMT), and the $d_n$-HMT concentration decreased with an increasing number of D atoms.

The presence of HMT in organic residues photoprocessed at 77 K was suggested in previous studies (Danger et al. 2013; de Marcellus et al. 2017), while the present study is the first to quantify its abundance precisely (exp. 3). We observed multiple $d_n$-HMT species whose number of D atoms reached up to 7. The most abundant isotopologue was $d_3$-HMT, whose abundance is seven times larger than $d_0$-HMT, followed by $d_2$- and $d_4$-HMT species. In addition, even $d_5$-HMT was more abundant than $d_0$-HMT ($d_5$-HMT/$d_0$-HMT = 2.8).

When CH$_3$OH was used as a solid component (exp. 6), the predominant $d_7$-HMT species was $d_0$-HMT, followed by a small amount of $d_1$-HMT. The $d_1$-HMT probably originated from the incorporation of D atoms originally present in the CH$_3$OH reagent with the D/H ratio being identical to the natural abundance (D/H $\sim$ 10$^{-5}$). These two HMT isotopologues comprised more than 99.9% of the total $d_n$-HMTs. The relative abundances of $d_n$-HMT ($d_n$-HMT/$d_0$-HMT) for experiments 1–6 are summarized in Figure 4. The $d_n$-HMT distribution for exp. 4 and exp. 5 will be discussed in detail in Sections 4 and 5, respectively.

### 3.2. Detection of HMT-related Species

Muñoz Caro et al. (2004) first suggested the presence of HMT-derivatives, such as methyl-HMT (HMT-CH$_3$: $m/z$ = 154.1218) and hydroxy-HMT (HMT-OH: $m/z$ = 156.1011), in the $^{13}$C- and $^{15}$N-labeled organic residues produced under similar experimental conditions (e.g., photolysis temperature and gas composition), where these assignments were based on the mass spectra obtained using gas chromatography/mass spectrometry. In the present study, we detected several mass peaks corresponding to these derivatives as well as their deuterated isotopologues whose number of D atoms reached up to 8 (Figure 5). Due to the lack of standard reagents for HMT-CH$_3$ and HMT-OH, we were not able to firmly identify both derivatives based on a comparison of their retention times on the HPLC column. Nevertheless, by comparing the retention times of the observed peaks with those reported by Muñoz Caro et al. (2004), we can consider that these mass peaks are derived from HMT-CH$_3$ and HMT-OH. These derivatives were detected in all the samples prepared in the present study. Given that their ionization efficiencies through ESI are the same as that for HMT, for the same sample, their abundances are

![Figure 2](image-url) Extracted mass chromatograms ($m/z = 141.1135$) of (a) the free fraction in exp. 1 (b) HMT standard reagent at 20–40 minutes and the mass spectra ($m/z$: 141–149) of the observed peak at ~29 minute (c) for the free fraction in exp. 1, and (d) for the HMT standard reagent. The inset in Figure 2(c) shows an enlarged spectrum for $m/z = 148–150$. $^{13}$C-HMT represents an HMT that possesses one $^{13}$C but no D in its structure. The inset in Figure 2(d) shows an enlarged spectrum for $m/z = 142.113–142.121$ to show that $^{13}$C-HMT is clearly distinguishable from $d_1$-HMT. The molecular structure of $d_0$-HMT is shown in Figure 1(b).

![Figure 3](image-url) Mass spectrum of HMT formed in exp. 2 for $m/z = 141–149$. The inset shows an enlarged spectrum for $m/z = 146–149$. 

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**Figure 2.** Extracted mass chromatograms ($m/z = 141.1135$) of (a) the free fraction in exp. 1 (b) HMT standard reagent at 20–40 minutes and the mass spectra ($m/z$: 141–149) of the observed peak at ~29 minute (c) for the free fraction in exp. 1, and (d) for the HMT standard reagent. The inset in Figure 2(c) shows an enlarged spectrum for $m/z = 148–150$. $^{13}$C-HMT represents an HMT that possesses one $^{13}$C but no D in its structure. The inset in Figure 2(d) shows an enlarged spectrum for $m/z = 142.113–142.121$ to show that $^{13}$C-HMT is clearly distinguishable from $d_1$-HMT. The molecular structure of $d_0$-HMT is shown in Figure 1(b).

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**Figure 3.** Mass spectrum of HMT formed in exp. 2 for $m/z = 141–149$. The inset shows an enlarged spectrum for $m/z = 146–149$.
estimated to be one to two orders of magnitude smaller than for HMT. The much smaller abundances of these HMT-related species compared with HMT are intrinsically consistent with previous studies (HMT-CH$_3$/HMT < 0.004 and HMT-OH/HMT < 0.12; Muñoz Caro et al. 2004). Variations in the relative abundances of $d_n$-HMT-CH$_3$ and $d_n$-HMT-OH show the same trend as those for HMT in the same sample (Figure 6).

In addition to HMT-CH$_3$ and HMT-OH shown above, the present data imply the presence of other HMT-derivatives in the organic residues; e.g., dimethyl- (HMT-2CH$_3$; m/z = 168.1375) and methanyl-HMT (HMT-CH$_2$OH; m/z = 170.1168). Moreover, we confirmed the presence of other types of HMT isotopologues as well as their deuterated species, which possess $^{13}$C or $^{15}$N with their natural abundances ($^{13}$C/$^{12}$C = $\sim$ 1.1 $\times$ 10$^{-2}$, $^{15}$N/$^{14}$N = $\sim$ 3.7 $\times$ 10$^{-3}$; Belglund & Wieser 2011). Due to the very high mass resolution of the orbitrap mass spectrometer, the $^{13}$C- or $^{15}$N-containing isotopologues can be definitely separated from HMT species that do not have those isotopes, as in the case for the analysis of glycine (Oba et al. 2015). Although they are presumably deuterated as well, due to their very small expected abundances compared to HMT (e.g., HMT-2CH$_3$/HMT < 10$^{-4}$ in terms of their peak area), HMT-CH$_3$, and HMT-OH, further identification and quantification were not performed for those HMT-derivatives and isotopologues.

3.3. Deuterium Fractionation upon the Formation of HMT

The degree of deuterium fractionation ($F_D$) from the reactants to HMT can be estimated using the following equation:

$$F_D(\%) = \left[ \frac{N_{D-HMT}/N_{H-HMT}}{N_{D-reactant}/N_{H-reactant}} \right] \times 100,$$

where [N$_X$-HMT] and [N$_X$-reactant] represent the total number of X atoms (X = D or H) in HMT and in the all reactants, respectively. The value of $F_D$ exceeds 100% for experiments 1, 3, 4, and 5, where the highest value was obtained in exp. 3 (351%), which means the enrichment of D atoms in HMT compared to the reactants. While it was lower than 100% for exp. 2 (45%), which means the depletion of D atoms in HMT compared to the reactants (Table 1). The value of $F_D$ was not determined in exp. 6 since the methanol was not D-labeled.

4. Constraints on the Formation and Deuteration Mechanisms of HMT

4.1. Effect of Methanol Composition

Experiments 1 and 2 were performed under very similar conditions except for the composition of the methanol isotopologues: CH$_3$DOH for exp. 1 and CH$_3$OD for exp. 2. Although the total number of D atoms deposited on the substrate was the same in the two experiments, the value of $F_D$ (249 for exp. 1 and 45 for exp. 2) and the distribution of the $d_n$-HMT/$d_0$-HMT ratio with respect to the number of D atoms.
formation of HMT through photochemical reactions of interstellar ice analogs containing methanol (Bernstein et al. 1995; Donati et al. 2007; Vinogradoff et al. 2013). Most studies have assumed the formation of formaldehyde (H$_2$CO) through the photolysis of CH$_3$OH as the first step toward HMT formation:

$$\text{CH}_3\text{OH} + h\nu \rightarrow \text{H}_2\text{CO} + \text{H}_2.$$ (2)

This type of reaction is known as unimolecular molecular hydrogen elimination (UMHE) and has been experimentally demonstrated to occur even at low temperatures (Gerakines et al. 1996; Hama et al. 2009). In the case of CH$_3$DOH, the following pathways are possible:

- **(3a)** $\text{CH}_3\text{DOH} + h\nu \rightarrow \text{H}_2\text{CO} + \text{HD}$,
- **(3b)** $\text{CH}_3\text{DOH} + h\nu \rightarrow \text{HDCO} + \text{H}_2$.

The formed H$_2$CO or HDCO may further react with NH$_3$ to yield methyleneimine (CH$_2$=NH or CHD=NH). If reaction 3 (b) proceeds, the formed HMT will possess at least one D atom in its structure.

In the case of CH$_3$OD, the UMHE process yields only H$_2$CO as follows:

$$\text{CH}_3\text{OD} + h\nu \rightarrow \text{H}_2\text{CO} + \text{HD}.$$ (4)

If reaction (4) is a unique process for the photolysis of CH$_3$OD, the formed HMT should not have any D atoms. However, this is not true, as shown in Figure 3, where the formation of deuterated HMT was actually confirmed. Hence, $d_x$-HMT in exp. 2 should be formed via other pathways. Then, the following successive elimination of H atoms may contribute to the formation of formaldehyde as follows:

- **(5)** $\text{CH}_3\text{OD} + h\nu \rightarrow \text{CH}_2\text{OD} + \text{H}$,
- **(6)** $\text{CH}_2\text{OD} + h\nu \rightarrow \text{H}_2\text{CO} + \text{D}$.

Note that even in this pathway, the formed formaldehyde does not have D atoms. However, unless the D atom desorbed from the substrate, the formed D atom may have a chance to further react with molecules or radicals in the ice to yield some deuterated species. Note that HMT itself is proposed to form at temperatures higher than 280 K (Vinogradoff et al. 2011). If this is the case, hydrogen–deuterium substitution reactions are unlikely to occur on HMT after its formation because D atoms cannot remain on the substrate at such high temperatures. Instead, the formed D atoms would be incorporated into some intermediate species for HMT formation (hereafter denoted as HMT-intermediates). For example, CH$_2$OD radical formed in reaction (5) may recombine with a D atom, resulting in the formation of deuterated methanol, which has a C–D bond:

$$\text{CH}_2\text{OD} + \text{D} \rightarrow \text{CH}_2\text{DOD}.$$ (7)

D atoms should be derived from the photodissociation of the O–D bond in CH$_3$OD. This reaction may partly explain the formation of $d_x$-HMT in exp. 2. Since the formation of D atoms is expected to be a minor process in exp. 2 based on the CH$_3$OD photodissociation channel (Öberg et al. 2009), the formation of CH$_3$DOD would not occur frequently, which does not contradict with the observed low levels of D-enrichment in HMT (Table 1). This result successfully updates the previous understanding about the origin of hydrogen in HMTs where all H atoms in HMTs are derived from the methyl group in methanol (Bernstein et al. 1995).

The relative abundance of $d_x$-HMT-CH$_3$ ($d_x$-HMT-CH$_3$/ $d_0$-HMT-CH$_3$) was about twice as large as that of $d_x$-HMT and $d_x$-HMT-OH at the same number of D atoms in exp. 1, while it was not in exp. 2 (Figures 4 and 6). This result implies that the methyl group of HMT-CH$_3$ is more D-enriched compared to other methylene groups. Unlike HMT, a formation pathway for HMT-CH$_3$ has not yet been proposed. We expect that the formation of HMT-CH$_3$ can be initiated by the formation of ethanimine (CH$_3$CH-={NH}), which has been observed toward Sgr B2 (N) (Loomis et al. 2013). A possible pathway is as
follows.

\[
\begin{align*}
\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_3 + \text{OH}, \\
\text{CH}_3 + \text{HCO} \rightarrow \text{CH}_3\text{CHO}, \\
\text{CH}_3\text{CHO} + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}=\text{NH} + \text{H}_2\text{O}.
\end{align*}
\]

The HCO radical can be formed via multiple reaction pathways such as the hydrogenation of CO (Watanabe & Kouchi 2008) and the photolysis of CH$_3$OH (Öberg 2016) under the present experimental conditions. Reaction (10) is proposed to occur with the aid of formic acid (HCOOH) at temperatures higher than 70 K (Vinogradoff et al. 2012). When CH$_3$DOH is used, the methyl group of the ethanamine is expected to have a D atom, which may result in the formation of HMT-CH$_3$ whose methyl group has a D atom. In the case of HMT-OH, its formation pathways have also not been considered thus far. Considering that HMT is formed at temperatures around 280 K or higher, the incorporation of an OH group may not occur after the formation of a HMT structure. Further theoretical and experimental studies are necessary to elucidate the formation pathways of HMT-CH$_3$ and other HMT-derivatives.

4.2. Effect of Temperature

Experiments 1 and 3 were intrinsically performed under the same conditions except for the gas-deposition/photolysis temperatures (10 K and 77 K, respectively). We found that the difference in temperature strikingly affects the abundance of the total $\text{d}_p$-HMT: the concentration of the total $\text{d}_p$-HMT in exp. 1 was about one order of magnitude larger than that in exp. 3 (Table 1). This means that HMT formation was more favored when gas-deposition and photolysis were performed at lower temperatures. Since CO cannot stick to the substrate at 77 K, it should not be related to any reactions for HMT formation, which can result in a large difference in the abundance of the formed HMT and $F_D$. However, in exp. 4, whose experimental conditions were the same as with exp. 1 except for the absence of CO, the $\text{d}_p$-HMT abundance and the $F_D$ value did not differ from those in exp. 1 (Table 1). This result strongly suggests that the presence of CO does not have a significant effect on the abundance of HMT and $F_D$.

If some HMT intermediaries cannot remain on the surface at 77 K, it would have resulted in the lower abundance of HMT. Since the desorption temperatures of possible HMT-intermediates, such as H$_2$CO and CH$_3$=NH, are higher than 77 K (Theule et al. 2011; Butscher et al. 2016), they should remain on the substrate if they are produced. On the other hand, smaller radicals, such as OH and CH$_3$, are more likely to desorb from the surface at higher temperatures. If these small radicals play a role in the formation of HMT-intermediates, the yield of HMT may become smaller at 77 K; however, the desorption temperatures of small radicals are not yet well understood.

In contrast to the lower absolute abundance of $\text{d}_p$-HMT in exp. 3, the “relative” abundances of deuterated HMT and its derivatives were clearly higher than in the other experiments when compared for the same number of D atoms (Figures 4 and 6). In addition, the value of $F_D$ (351%) apparently exceeds other experiments performed at 10 K (<300%, Table 1). We can consider that this difference may be related to the deuteration levels of radicals formed by the photolysis of methanol in the ice. When molecules are exposed to UV photons, they are dissociated into smaller reactive radicals (e.g., reactions 5 and 8). We expect that the efficiency and branching ratios of photolysis are independent of the substrate temperatures. Once they encounter reaction partners, they can immediately yield new species even at 10 K. However, even though the formed radicals (e.g., CH$_3$D and CHDOH) possess excess energy during the photolysis of the parent molecules, those radicals hardly diffuse in the ice at 10 K (Andersson & van Dishoeck 2008). On the other hand, some fractions of atomic H and D in the photo-fragments can be retrapped and remain on the ice at 10 K. These atoms can diffuse on the surface (Hama & Watanabe 2013) and have more chances to encounter the other radicals and molecules even at 10 K and also during warming-up. Since D atoms in methanol that are more favorable for incorporation into HMT (i.e., D in the methyl group) can be exchanged with H atoms at colder temperatures, the deuteration levels in the produced HMT might have been lowered. For example, when an H or D atom is photofragmented from the methyl group of methanol (reaction 11) at 10 K, which is proposed to be the dominant pathway for the photolysis of solid methanol (Öberg et al. 2009), the formed radicals (CHDOH or CH$_2$OH) may recombine preferentially with an H atom because there are abundant sources of H atoms in the ice (e.g., H$_2$O and NH$_3$). This results in the formation of CH$_2$DOH or CH$_3$OH (reaction 12).

\[
\begin{align*}
\text{CH}_2\text{DOH} + h\nu \rightarrow \text{CHDOH} + \text{H}, \\
\text{CH}_2\text{DOH} + h\nu \rightarrow \text{CH}_2\text{OH} + \text{D}, \\
\text{CHDOH} + \text{H} \rightarrow \text{CH}_2\text{DOH}, \\
\text{CH}_2\text{OH} + \text{H} \rightarrow \text{CH}_3\text{OH}.
\end{align*}
\]

The repetition of a cycle of photolysis (reaction 11) and recombination (reaction 12) may eventually lead to the accumulation of CH$_3$OH in the ice. Since the photodissociation of CH$_3$OH yields CH$_3$OH only through this channel, the abundance ratio of CHDOH/CH$_3$OH should become lower than the statistically expected value at the initial state (CHDOH/CH$_3$OH = 2). In contrast, in exp. 3, the formed H and D atoms would desorb immediately from the substrate at 77 K. Under those situations, the aforementioned radicals (CHDOH and CH$_2$OH) may have little chance to react with H atoms, which prevents recombination to yield methanol. In that case, the abundance ratio of the formed radicals remains constant (CHDOH/CH$_3$OH = 2) after their formation in/on the ice. This is highly suitable for the formation of HMT and its derivatives enriched in D at 77 K, although the absolute abundances become lower than for photolysis at 10 K as explained earlier.

5. Astrochemical Implications

The present study shows that HMT has a significant potential to accumulate deuterium from interstellar deuterated methanol in its structure. Although methanol was used as a sole deuterium carrier in the present study, there are a number of other deuterated species found in the actual interstellar medium (Caselli & Ceccarelli 2012). Among those species, formaldehyde is also outstanding in terms of deuterium enrichment; the relative abundances of its singly and doubly deuterated isotopologues often exceed 10% of H$_2$CO (e.g., HDO/H$_2$CO $\leq$ 0.25 and D$_2$CO/H$_2$CO = 0.13 in IRAS
reported the formation of several types of AAs after acid hydrolysis of HMT at 110°C. In addition, more recently, HMT has been reported to decompose in an aqueous solution under basic pH conditions at 150°C, resulting in the formation of nitrogen-heterocyclic compounds (Vinogradoff et al. 2017). Since it is likely that some planetary bodies experienced such a mild heating mainly due to the decay of 26Al after their formation (Grimm & McSween 1989), it may be acceptable that there has been no detection, thus far, of HMT in any extraterrestrial materials. Upon the decomposition of $d_n$-HMT, D atoms in $d_n$-HMT can be distributed into products, although the fraction of D transfer remains to be understood. Then, we can expect that D-enriched decomposition products may be a source of similarly D-enriched meteoritic organic species, such as AAs and insoluble organic matter, through molecular synthesis on planetary bodies.

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16293-2422; Ceccarelli et al. 1998). Since the absolute abundance of formaldehyde is comparable to that of CH3OH in the interstellar medium (e.g., van Dishoeck et al. 1995) and H2CO is expected to play a role as an intermediate in HMT formation (Bernstein et al. 1995); the deuterated formaldehyde may also have a contribution to the formation of $d_n$-HMT. As for possible contributions from other deuterated interstellar molecules, which especially possess polar functional groups, such as −OD and −ND (e.g., HDO and NH2D, respectively), the formation of $d_n$-HMT is likely to occur if the conditions are sufficient for HMT formation. However, the degree of deuterium enrichment would not be significant, as can be inferred from the results of exp. 2, where a D atom is present in the polar functional group (−OD) of methanol. Based on the present experimental results, we can infer that possible contributions from such polar molecules to $d_n$-HMT formation are about one order of magnitude lower than those from deuterated methanol and formaldehyde if the number of D atoms is the same as that for a source molecule.

In exp. 5, we reproduced the composition of deuterated methanol isotopologues observed from IRAS 16293-2422 (Parise et al. 2004) to figure out a possible composition of $d_n$-HMT in the source. We realize that the ice composition used in the present study does not exactly represent the actual ice composition in IRAS 16293-2422. Moreover, the ice composition may be significantly different from the observed gas composition in IRAS 16293-2422. Nevertheless, it would be reasonable to consider that the present result is a clue to infer the possible composition of $d_n$-HMT in IRAS 16293-2422. This is because the relative composition of these four species in the ice observed in typical low-mass protostars (H2O:CO:NH3:CH3OH = 10:1:4:<1:1:3; Tielens 2013) does not significantly differ from that in the present study (10:4:4:4) and the relative composition of $d_n$-HMT strongly depends on the composition of the methanol isotopologues. The predominant isotopologue was $d_8$-HMT and the relative abundances of deuterated isotopologues decreased with an increasing number of D atoms, which is similar to exp. 2. However, deuterated isotopologues are clearly more abundant than in exp. 2; even $d_3$-HMT is relatively abundant (∼15% of $d_0$-HMT; Figure 4). Among those $d_n$-HMTs, $d_1$-HMT is of special interest as a target for future astronomical observations because it is the most abundant (∼84% of $d_0$-HMT) deuterated HMT. In addition, most importantly, it would be detectable because of a nontetrahedral ($T_d$) symmetry, unlike $d_0$-HMT, which cannot be detected using microwave spectroscopy (Pirali & Boudon 2015). As far as we have surveyed, there has been no report on the microwave spectrum of $d_1$-HMT; however, we expect that deuterated HMTs will be detected toward astronomical objects, where there is active deuterium chemistry as observed in the IRAS 16293-2422.

After the accumulation of deuterium in its structure, the formed $d_n$-HMT may be incorporated into some planetary bodies, such as planetesimals and asteroids, through planetary evolution. Since HMT has never been detected in extraterrestrial materials, such as meteorites and cometary return samples, it is straightforward to consider that it would have decomposed in/on planetary bodies even if it was initially present. Its thermal decomposition was experimentally studied about 50 years ago, where it was decomposed at temperatures above 270°C, leading to ammonia, methane, and some nitrile and amine compounds (Iwakami et al. 1968). Wolman et al. (1971)
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