H-D substitution in interstellar solid methanol: a key route for D enrichment

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ABSTRACT

Deuterium enrichment of interstellar methanol is reproduced experimentally for the first time via grain-surface H-D substitution in solid methanol at an atomic D/H ratio of 0.1. Although previous gas-grain models successfully reproduce the deuterium enrichments observed in interstellar methanol molecules (D/H of up to 0.4, compared to the cosmic ratio of $\sim 10^{-5}$), the models exclusively focus on deuterium fractionation resulting from the successive addition of atomic hydrogen/deuterium on CO. The mechanism proposed here represents a key route for deuterium enrichment that reproduces the high observed abundances of deuterated methanol, including multiple deuterations.

Subject headings: Astrochemistry — Molecular processes — ISM: molecules — dust, extinction

1. Introduction

Recent astronomical observations (Turner 1990; van Dishoeck et al. 1995; Loinard et al. 2000; Parise et al. 2002; Parise et al. 2004; Crovisier et al. 2004) have revealed that the abundances of some deuterated interstellar molecules are up to 4 orders of magnitude higher than the cosmic D/H ratio of $1.5 \times 10^{-5}$ (Linsky 1998). In the case of methanol
molecules in particular, even doubly and triply deuterated isotopologues have been detected in the vicinity of low-mass protostars (Parise et al. 2002; 2004). Deuterium fractionation in interstellar molecules has long been a topic of interest in interstellar chemistry, and the fractionation processes in molecular clouds have attracted attention from both astronomers and earth and planetary scientists as a potential explanation for the high D fractionations observed in our solar system (for a review, see Robert, Gautier, & Dubrulle 2000). Although many theoretical models of interstellar D fractionation have been proposed, pure gas-phase models have difficulties reproducing the high observed D enrichments, particularly multiple deuterations such as D$_2$CO and CD$_3$OH. It has thus been recognized that grain-surface chemistry is a necessary process for the production of multiply deuterated species. This is a readily understandable result for formaldehyde and methanol, which are likely to be produced efficiently on grains by tunneling reactions under the conditions of molecular clouds (Watanabe, Shiraki, & Kouchi 2003; Watanabe et al. 2004; Hidaka et al. 2004). Some of the proposed gas-grain models therefore provide reasonable estimates of the high D enrichment observed in interstellar formaldehyde and methanol (Tielens 1983; Charnley, Tielens, & Rodgers 1997; Caselli et al. 2002; Aikawa, Ohashi, & Herbst 2003). Recently, a model using direct master equations has also been successful in reproducing the D enrichment of methanol, including triple deuteration, on the assumption of a high atomic D/H ratio of ~0.3 in the accreting gas (Stantcheva & Herbst 2003). In such models, the high atomic D/H ratio is produced by ion–molecule reactions in the gas phase followed by hydrogenation and deuteration of CO on grain surfaces, leading to D enrichment of methanol. For instance, the atomic D/H ratio of up to 0.1 was achieved in the gas-phase model by Roberts, Herbst & Millar (2002). However, the results of these models are somewhat ambiguous due to the requirement of the very high atomic D/H ratio (0.3–1) and the lack of information regarding grain-surface reactions, including information such as reaction channels, activation energies, and the rates of hydrogenation (deuteration). It is therefore highly desirable to clarify experimentally the role of surface reactions in D fractionation.

Here we report the experimental results on the exposure of solid CO to cold H and D atoms. The observed D fractionation in methanol is experimentally reproduced by grain-surface reactions at an atomic D/H ratio of 0.1, revealing that the key reaction for D fractionation is the H-D substitution in solid CH$_3$OH with atomic D rather than successive addition of H and D on CO. As the interaction of D atoms with methanol has not been treated in previous models, this may offer an explanation for the observed abundance of deuterated methanol isotopologues in molecular clouds.
2. Experimental

Experiments were performed using the apparatus for surface reactions in astrophysics (ASURA) system described previously (Watanabe et al. 2004). The sample solid was produced by vapor deposition on an aluminum substrate at 10 K in an ultra high vacuum chamber (typically $1 \times 10^{-10}$ torr). Atomic H and D were produced by a microwave-induced plasma in a Pyrex tube and transferred via a series of polytetrafluorethylene (PTFE) tubes to the target. A deflector was mounted at the end of the PTFE tube to eliminate charged particles and metastable atoms that may escape from the plasma. Atomic beam were cooled in the PTFE tube, which was tightly sheathed with a copper tube connected to an He refrigerator. The kinetic temperature of atoms was set at 30 K. For the simultaneous exposure of solid CO to H and D atoms, $H_2$ and $D_2$ gases were mixed in a stainless steel bottle at a certain ratio and introduced into the Pyrex tube. The flux of atoms was measured using a quadrupole mass spectrometer installed close to the substrate and was maintained constant through the measurements. The infrared absorption spectra of the sample solid were measured during exposure to atoms by Fourier transform infrared spectroscopy (FTIR) with a resolution of 4 cm$^{-1}$.

3. Results and Discussion

A pure solid CO sample of approximately 10 monolayers was exposed to cold H and D atoms simultaneously at a D/H ratio of 0.1. This atomic ratio was adopted as a representative value that can be achieved in the gas-phase model (Roberts et al. 2002). Fig. 1 shows the infrared absorption spectrum of the initial solid and the variation in the spectrum upon exposure to H and D atoms. Formaldehyde ($H_2CO$), methanol ($CH_3OH$), HDCO, $D_2CO$, and Me-$d_n$-OH clearly appear, with the consumption of CO. Here, Me-$d_n$- represents $CH_2D$-, $CHD_2$-, and $CD_3$- for $n = 1-3$, respectively. It should be noted that $CH_3OD$ and Me-$d_n$-OD were not detected. The band for OD stretch of $CH_3OD$ locates at around 2430 cm$^{-1}$ with the band strength being 1.4 times larger than that of the CO-stretch of $CH_3OH$ at 1043 cm$^{-1}$. We did not observe the peak there. Taking account of the detection limit of the FTIR, the $CH_3OD$ yield should be 1 order of magnitude less than those of Me-$d_n$-OH at the maximum. This is consistent with the much lower abundances of Me-OD compared to Me-$d_n$-OH in molecular clouds (Parise et al. 2004). Using pure solid samples of deuterated methanol, the band strengths relative to that of pure $CH_3OH$ at 1043 cm$^{-1}$ and 10 K were determined to be 0.10, 0.18, 0.47, and 0.35 for $CH_2DOH$ (1330 cm$^{-1}$), $CHD_2OH$ (950 cm$^{-1}$), $CD_3OH$ (988 cm$^{-1}$), and $CD_3OD$ (982 cm$^{-1}$), respectively. The variation in column densities for CO, $CH_3OH$ and Me-$d_n$-OH and the sum of deuterated methanol are plotted in Fig. 2. Although
H$_2$CO, D$_2$CO and HDCO were also observed, these are not plotted because of the unknown band strengths of HDCO and D$_2$CO molecules. Assuming an H number density of 1 cm$^{-3}$ and an accreting atomic D/H ratio of 0.1, the D (H) atom fluences in a 10 K molecular cloud will be $1.3 \times 10^{16}$ ($1.3 \times 10^{17}$), $6.5 \times 10^{16}$ ($6.5 \times 10^{17}$), and $1.3 \times 10^{17}$ ($1.3 \times 10^{18}$) cm$^{-2}$ over $10^5$, $5 \times 10^{15}$ and $10^6$ yr, respectively. In the present experiments, these fluences approximately correspond to exposure times of 10, 35, and 70 minutes, respectively. The ratios of deuterated methanol to the amount of remaining CH$_3$OH, denoted in the form (CH$_2$DOH/CH$_3$OH, CHD$_2$OH/CH$_3$OH, CD$_2$OH/CH$_3$OH), after exposure times of 10, 35, and 70 min are (0.16, 0, 0), (0.09, 0.05, 0.01) and (0.11, 0.13, 0.03), respectively. These values are closely consistent with the observations of (0.3±0.05, 0.06±0.01, 0.014±0.006) (Parise et al. 2004; Aikawa et al. 2005) and clearly show that the D fractionation in methanol can be achieved via grain-surface reactions at the accreting atomic D/H ratio of 0.1. It should also be noted that this estimate is quite general and depends heavily on the conditions in the molecular cloud. Nevertheless, grain-surface D fractionation of CH$_3$OH in molecular clouds has been demonstrated to proceed more efficiently than predicted by previous models.

There are two possible routes to produce deuterated methanol in the present experiment: successive hydrogenation/deuteration of CO and the H-D substitution in CH$_3$OH. The profile of the variation curves of Me-$d_n$-OH in Fig.2 (a) is apparently dominated by the latter process rather than the former one. As the exposure time increases, the deuterated isotopologues appear in the following sequence, consuming the lower deuterated methanol from $d_0$ to $d_3$: CH$_3$OH → CH$_2$DOH → CHD$_2$OH → CD$_3$OH. Additionally, the curves of the CH$_3$OH and CH$_2$DOH yields have maxima. These features clearly differ from those expected for successive addition of atoms, indicating the H-D substitution in CH$_3$OH. If the deuterated isotopologues are mainly produced by successive hydrogenation/deuteration and no exchange occurs in methanol, the curves of CH$_3$OH and Me-$d_n$-OH should not have maxima. Furthermore, the ratios of Me-$d_2$-$d_3$-OH/CH$_2$DOH obtained are much larger than those in models, including only the former process, with the accreting D/H ratio of 0.1 (Stantcheva & Herbst 2003; Caselli et al. 2002).

The process of H–D substitution in CH$_3$OH was further examined by exposing pure solid methanol (CH$_3$OH) to a single D atom beam and to an H + D atomic beam (D/H ratio of 1) at 10 K. Fig. 3 shows the infrared absorption spectrum of the initial pure solid CH$_3$OH and the variation in the spectrum upon exposure to D atoms. When D$_2$ and HD molecules were deposited on the sample, no changes in the spectrum were found, indicating that CH$_3$OH is consumed upon exposure to cold D atoms. Fig. 4 shows the variation in column densities of CH$_3$OH and deuterated isotopologues for the D-exposure as a function of exposure time. For the exposure to H + D atoms, only the decrease in CH$_3$OH is plotted, because the variations of isotopologues are very similar to those for the single D-exposure. The
Deuterated isotopologues are clearly formed with exposure time in the following sequence: CH$_3$OH $\rightarrow$ CH$_2$DOH $\rightarrow$ CHD$_2$OH $\rightarrow$ CD$_3$OH. The production of Me-OD (OD stretching) was not observed again. These features are consistent with the measurements described above. The deuteration of CD$_3$OH was also investigated, but again no change in the spectrum was observed. This may be due in part to the larger dissociation energy of CH$_3$OH to CH$_3$O + H than that of CH$_3$OH to CH$_2$OH + H (Bauschlicher, Langhoff, & Walch 1991), as the O-H bond is more stable than the C-H bond. This is the first clear evidence that solid CH$_3$OH is deuterated through CH$_2$DOH and CHD$_2$OH to CD$_3$OH by exposure to D atoms at 10 K. Most of the grain models focus on the successive hydrogenation/deuteration of CO to produce the deuterium fractionation in methanol, and they partly succeed in reproducing the observations. However, the present results suggest that the H-D substitution is more efficient than the hydrogenation/deuteration process and thus should be included in the reaction network. In the previous models, the deuteration rates may have been overestimated because of the use of a simple potential for the tunneling reactions.

Exposure of solid CH$_3$OD, CD$_3$OH, CH$_2$DOH, CHD$_2$OH, and CD$_3$OD to H atoms at 10 K similarly did not induce any change in the infrared absorption spectrum, suggesting that deuterated methanol is very stable and that the hydrogenation of deuterated methanol is inhibited. Therefore, the present data show that the exposure of CH$_3$OH to D atoms represents a previously unknown mechanism for the efficient formation of deuterated methanol.

As shown in Fig. 3(b), exposure to D atoms results in the formation of methyl-deuterated methanol isotopologues, CH$_2$DOH, CHD$_2$OH, and CD$_3$OH, but no other isotopologues (e.g., CH$_3$OD, CH$_2$DOD, and CHD$_2$OD). Therefore, H–D substitution proceeds by either or both of the following reactions:

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\begin{align*}
\text{CH}_3\text{OH} & \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CHD}_2\text{OH} \rightarrow \text{CHDOH} \rightarrow \text{CHD}_2\text{OH} \rightarrow \text{CD}_2\text{OH} \rightarrow \text{CD}_3\text{OH} \\
\text{CH}_3\text{OH} & \rightarrow \text{CH}_2\text{DOH} \rightarrow \text{CHD}_2\text{OH} \rightarrow \text{CD}_2\text{OH} \rightarrow \text{CD}_3\text{OH}
\end{align*}
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Reaction (1) is a repetition of the formation of a hydroxymethyl radical by H abstraction from methanol and subsequent D addition to the hydroxymethyl radical to form deuterated methanol, e.g., CH$_3$OH + D $\rightarrow$ CH$_2$OH + HD and CH$_2$OH + D $\rightarrow$ CH$_2$DOH. For formaldehyde, the importance of this process was predicted by Tielen (1983). Reaction (2) represents direct H–D exchange, such as CH$_3$OH + D $\rightarrow$ CH$_2$DOH + H. Although it is unclear which process is dominant, deuteration rate depends mainly on the D atoms’ flux because the rate of deuteration for the single D beam is very similar to that for the H + D beam at the D/H ratio of 1, as shown in Fig. 4. The nondetection of Me-OD in the present experiments can be explained by the H-abstraction/D- addition (scheme of reaction (1)). The H-abstraction on the methyl-side by either H or D has a lower barrier than that in -OH (Kerkeni & Clary...
In conclusion, D enrichment in methanol at levels comparable to observations was demonstrated to be possible through surface reactions between cold D atoms and methanol at 10 K with an accreting atomic D/H ratio of 0.1. Since we have not tried another D/H ratio, it is not clear whether or not the present ratio of 0.1 is the minimum value for reproducing the observed enrichments. However, the fractionation levels for the different ratios can be roughly estimated from Fig. 2 (b) if we neglect the effect of hydrogen atoms. That is, the fluence of D atoms for the ratio of 0.05 corresponds to half of that for 0.1 at a certain exposure time. In this estimation, the ratio of 0.05 also seems to reproduce the observations fairly well. The deuteration proceeds mainly via the H–D substitution in solid methanol rather than successive hydrogenation and deuteration of CO. Although the fractionation level must decrease with the decrease of the atomic D/H ratio, the contribution of H–D substitution to D-enrichment would become more significant than successive hydrogenation/deuteration of CO because initially more CH$_3$OH is rapidly produced. On the other hand, at higher accreting D/H ratios, successive hydrogenation/deuteration of CO will be enhanced because the chance of D addition on CO relatively increases. Unfortunately, in the present work, it is difficult to compare the substitution with the H and D additions more quantitatively.

Other deuterated molecules, such as ammonia, formaldehyde, and water, are also present in molecular clouds and/or comets, and the degree of deuteration among the different molecules has been observed to differ substantially. Although we investigated NH$_3$ + D system, no reactions occurred in the exposure of solid NH$_3$ to cold D atoms at below 15 K. H. Hidaka, N. Watanabe, & A. Kouchi, (2005, in preparation) also found experimentally that no deuteration of H$_2$O occurs under D exposure at 10–20 K, even under fluences of up to $5 \times 10^{18}$ cm$^{-2}$. This is consistent with the findings of Parise et al. (2003), who did not detect HDO along the line of sight of low-mass protostars. However, the deuteration of formaldehyde is likely to proceed under D exposure, and significant amounts of HDCO and D$_2$CO were observed in the present experiments. Further experiments on formaldehyde should therefore prove helpful for developing a comprehensive understanding of the deuteration mechanism of interstellar molecules.

REFERENCES


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Fig. 1.— (a) Infrared absorption spectrum of initial solid CO deposited at 10 K. (b) Spectral change after simultaneous exposure to H and D atoms for 20, 80, and 210 min. Spectra were obtained by subtracting the initial (non-exposure) absorption spectrum from the irradiated spectra. Peaks below and above the baseline represent decreases and increases in absorbance, respectively. The newly formed molecules are denoted by arrows. Spikes at around 2685 cm$^{-1}$ are noise caused by vibration of the He refrigerator. The band above the baseline at 1040 cm$^{-1}$ represents the superposition of CH$_3$OH, CH$_2$DOH, and CHD$_2$OH in the CO stretching mode.
Fig. 2.— (a) Variation in column densities for CO, CH$_3$OH, CH$_2$DOH, CHD$_2$OH, and CD$_3$OH with H–D exposure time. Column densities are normalized to that of initial CO. Intensities of error bars represent statistical error. The CH$_3$OH yield was derived from the band area at 1040 cm$^{-1}$ after subtracting the increase in CH$_2$DOH and CHD$_2$OH in the same band. Column densities for CH$_2$DOH, CHD$_2$OH, and CD$_3$OH are magnified to 3 times, and column density for CO is divided by 3. Solid lines are guides. (b) Ratio of column density for the sum of deuterated methanol to that for the remaining CH$_3$OH.
Fig. 3.— (a) Infrared absorption spectrum of initial solid CH$_3$OH deposited at 10 K. (b) Spectral change after D exposure for 2, 20, 60 min. Spectra were obtained by subtracting the initial (non-exposure) absorption spectrum from the D-exposed spectra. Peaks below and above the baseline represent decreases and increases in absorbance, respectively. Spikes at 1905 and 1723 cm$^{-1}$ are noise caused by vibration of the He refrigerator. The band below the baseline at 1049 cm$^{-1}$ represents the superposition of a decrease (CH$_3$OH) and increase (CH$_2$DOH and CHD$_2$OH) in the CO stretching mode.
Fig. 4.— Variation in column densities for CH$_3$OH and isotopologues normalized to initial CH$_3$OH with D-exposure. For exposure to H + D atoms, only the decrease of CH$_3$OH is plotted: the red open circles represent H and D fluxes of $1 \times 10^{14}$ cm$^{-2}$ s$^{-1}$. The decrease in CH$_3$OH was derived from the band area at 1049 cm$^{-1}$ after subtracting the increase in CH$_2$DOH and CHD$_2$OH in the same band.