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Hydrogen–deuterium substitution in solid ethanol by surface reactions at low temperatures

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ABSTRACT

Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is one of the most abundant complex organic molecules in star-forming regions. Despite its detection in the gas phase only, ethanol is believed to be formed by low-temperature grain-surface reactions. Methanol, the simplest alcohol, has been a target for observational, experimental, and theoretical studies in view of its deuterium enrichment in the interstellar medium; however, the deuterium chemistry of ethanol has not yet been an area of focus. Recently, deuterated dimethyl ether, a structural isomer of ethanol, was found in star-forming regions, indicating that deuterated ethanol can also be present in those environments. In this study, we performed laboratory experiments on the deuterium fractionation of solid ethanol at low temperatures through a reaction with deuterium (D) atoms at 10 K. Hydrogen (H)–D substitution, which increases the deuteration level, was found to occur on the ethyl group but not on the hydroxyl group. In addition, when deuterated ethanol (e.g. $\text{CD}_3\text{CD}_2\text{OD}$) solid was exposed to H atoms at 10 K, D–H substitution that reduced the deuteration level occurred on the ethyl group. Based on the results, it is likely that deuterated ethanol is present even under H-atom-dominant conditions in the interstellar medium.

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

1 INTRODUCTION

Various types of deuterated molecules have been observed in the interstellar medium, such as cold dense cores and star-forming regions (Roueff & Gerin 2003; Caselli & Ceccarelli 2012). The relative abundances of these molecules compared to normal (i.e. fully hydrogenated) molecules can reach at most an order of 10^{-1} (Caselli & Ceccarelli 2012), which is several orders of magnitude higher than the Galactic D/H ratio ($\sim 10^{-5}$; Linsky 2003). Such D enrichment is linked to either ion–molecule reactions in the gas phase, grain-surface reactions, or a combination of both processes at temperatures as low as 10 K. Of deuterated interstellar molecules, methanol (CH_3OH) has attracted much attention in view of its chemical evolution in space because it is significantly enriched in D (Parise, Castets & Herbst 2004) and plays an important role as a precursor for various complex organic molecules (COMs; Öberg et al. 2009). Experiments and models have shown that ion–molecule reactions can yield various deuterated molecules (e.g. Gerlich & Schlemmer 2002; Aikawa et al. 2005), while multiply D-substituted molecules such as CD_3OH and CHD_2OH favour formation on grain surfaces (Roberts, Herbst & Millar 2004; Taquet, Ceccarelli & Kahane 2012). Laboratory experiments demonstrated that a series of deuterated methanol molecules were produced by the addition of D

atoms to relatively simpler molecules such as CO, H_2CO (Hidaka, Kouchi & Watanabe 2007; Hidaka et al. 2009), and H–D substitution of methanol (Nagaoka, Watanabe & Kouchi 2005, 2007). The H–D substitution reaction is of particular importance for D enrichment in interstellar molecules such as methanol and formaldehyde (Watanabe & Kouchi 2008). After deuterium fractionation on interstellar grains, methanol is desorbed and deuterated isotopologues are detected in the gas phase (e.g. $[\text{CH}_2\text{DOH}]/[\text{CH}_3\text{OH}] = 30$ per cent, $[\text{CD}_3\text{OH}]/[\text{CH}_3\text{OH}] = 1.4$ per cent in IRAS 16293; Parise et al. 2004).

In contrast to extensive studies related to methanol, the next simplest alcohol, ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), has attracted less attention in terms of D enrichment in the interstellar medium, although $\text{CH}_3\text{CH}_2\text{OH}$ itself is one of the dominant COMs (10^{-9} – 10^{-8} versus H_2 ; Nummelin et al. 2000; Ikeda et al. 2001). More recently, relatively abundant ethanol (0.12 per cent versus H_2O) was detected in comet C/2014 Q2 (Lovejoy) (Biver et al. 2015), suggesting its formation in low-temperature environments. Since the observed abundance cannot be reproduced in gas-phase chemistry models (Charnley et al. 1995), it is predicted that interstellar and cometary $\text{CH}_3\text{CH}_2\text{OH}$ is mainly formed by grain-surface reactions such as hydrogenation of CCO (Hall & Miller 2010) and reactions of CH_3 with CH_2OH (Garrod, Wicaksa Weaver & Herbst 2008). Laboratory experiments showed that photolysis of solid CH_3OH yielded $\text{CH}_3\text{CH}_2\text{OH}$, as well as other various COMs (Öberg et al. 2009). Therefore, ethanol may have a chance to become enriched in D

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during or after its formation on grains, similar to methanol. Given that interstellar ethanol is considered a precursor for larger COMs like ethylformate ($\text{C}_2\text{H}_5\text{OCHO}$; Belloche et al. 2009), it is necessary to comprehensively elucidate its deuterium fractionation pathway for better understanding of chemical evolution in space.

Astronomical observations showed two kinds of ^{13}C -substituted ethanol molecules ($^{13}\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3^{13}\text{CH}_2\text{OH}$) that were tentatively detected in Sgr B2(N) (Belloche et al. 2013), while D-substituted ethanol molecules have never been detected in the interstellar medium. Although spectroscopic data for deuterated ethanol has been scarce, laboratory millimetre-wave spectra (35–500 GHz) of deuterated ethanol ($\text{CH}_3\text{CH}_2\text{OD}$, CH_3CHDOH , and $\text{CH}_2\text{DCH}_2\text{OH}$) were very recently reported (Walters et al. 2015). Since the spectral range is consistent with that of Atacama Large Millimeter/submillimeter Array, future detection of deuterated ethanol is expected if it is present in the interstellar medium. In this study, we performed laboratory experiments on the deuterium fractionation of various kinds of solid ethanol isotopologues by surface reactions with D atoms at 10 K to examine a possible pathway for D enrichment of ethanol in the interstellar medium.

2 EXPERIMENTAL PROCEDURE

Experiments were performed using the Apparatus for Surface Reaction in Astrophysics (ASURA) system. The ASURA mainly consists of a reaction chamber and an atomic source, with multiple turbo-molecular pumps. Details of ASURA have been reported elsewhere (Watanabe et al. 2006; Nagaoka et al. 2007). Normal ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) (Kanto Kagaku, 99.5 per cent) and deuterated ethanol isotopologues, $\text{CD}_3\text{CH}_2\text{OH}$ (CDN Isotopes, 99.5 per cent), $\text{CH}_3\text{CD}_2\text{OH}$ (CDN Isotopes, 98.8 per cent), and $\text{CD}_3\text{CD}_2\text{OD}$ (Acros Organics, 99 per cent) were used without further purification for the experiments described below. About 15 monolayers (ML: 1 ML = 10^{15} molecules cm^{-2}) of solid ethanol were produced by vapour deposition of gaseous ethanol on to an aluminium (Al) substrate at 10 K through a capillary plate. The solid ethanol layer was exposed to D atoms which were produced by the dissociation of D_2 molecules in microwave-induced D_2 plasma. Experiments on D–H substitution were performed using the solids of deuterated ethanol isotopologues, which were exposed at 10 K to H atoms produced in the same manner as the D atoms. The fluxes of D and H atoms were estimated as 3.9×10^{14} and 4.6×10^{14} atoms $\text{cm}^{-2} \text{ s}^{-1}$, respectively, by the procedure described in Oba et al. (2014a). Atoms were cooled to 100 K through interactions with the inner wall of a cold Al pipe and sprayed onto the solid ethanol layer for up to 180 min. Reaction products were monitored in situ by a reflection-absorption-type Fourier-transform infrared spectrometer with a resolution of 4 cm^{-1} . Incident angle of the infrared (IR) beam was 83° to normal.

The band strength of $\text{CH}_3\text{CH}_2\text{OH}$ solid was reported in a previous study (2.0×10^{-18} cm molecules $^{-1}$ for the C–C stretching band at 879 cm^{-1} , determined by a transmittance method; Boudin, Schutte & Greenberg 1998); however, the band strengths of deuterated ethanol have not been reported. We estimated the band strengths of four kinds of deuterated ethanol samples by the method of Nagaoka et al. (2007). Briefly, each deuterated ethanol isotopologue was deposited onto the substrate under the same conditions as those for $\text{CH}_3\text{CH}_2\text{OH}$ (e.g. gas pressure in the gas mixing chamber and the deposition duration). In this way, equivalent amounts of each ethanol isotopologue were obtained as confirmed by their temperature programmed desorption spectra. The unknown band strengths were then derived from comparison to the previ-

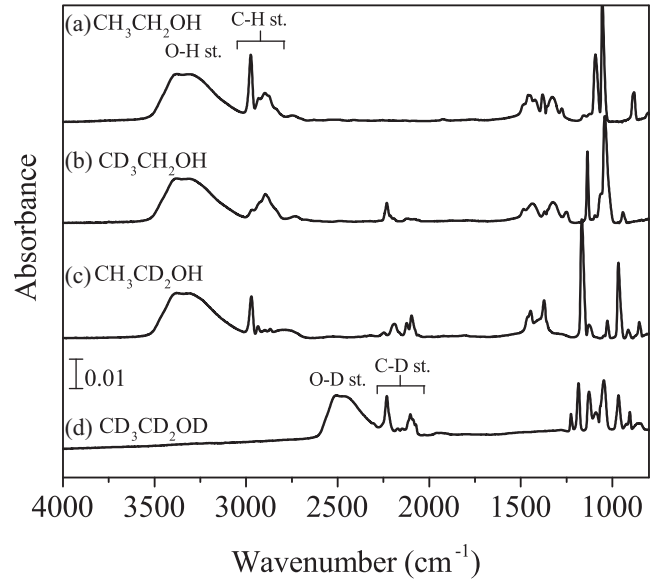


Figure 1. Infrared spectra of solid ethanol isotopologues: (a) $\text{CH}_3\text{CH}_2\text{OH}$, (b) $\text{CD}_3\text{CH}_2\text{OH}$, (c) $\text{CH}_3\text{CD}_2\text{OH}$, and (d) $\text{CD}_3\text{CD}_2\text{OD}$, deposited at 10 K. Peak assignments are derived from Perchard & Josien (1968).

ously reported strengths for $\text{CH}_3\text{CH}_2\text{OH}$. The IR spectra of ethanol isotopologues with a thickness of ~ 15 ML are shown in Fig. 1. The band strengths of $\text{CD}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CD}_2\text{OH}$, and $\text{CD}_3\text{CD}_2\text{OD}$ used for the calculation of the column densities were derived to be 1.8×10^{-18} cm molecules $^{-1}$ for the CD_3 stretching band at 2231 cm^{-1} , 2.7×10^{-18} cm molecules $^{-1}$ for the CH_3 stretching band at 2971 cm^{-1} , and 2.8×10^{-18} cm molecules $^{-1}$ for the CD_3 stretching band at 2231 cm^{-1} , respectively. Peak assignments for the deuterated ethanol were obtained from Perchard & Josien (1968). The column density of ethanol was calculated from the peak area and the derived band strength, as described in Hidaka et al. (2007).

3 RESULTS AND DISCUSSION

In this section, we first show the changes in the IR spectra for ethanol isotopologues after exposure to D or H atoms, and then propose possible reactions that occurred at 10 K. After that, kinetic parameters for the reactions are estimated. Finally, a possible D/H ratio of solid ethanol in molecular clouds is proposed from a simple rate-equation model under specific conditions.

3.1 Reaction of solid ethanol with D atoms at 10 K

3.1.1 $\text{CH}_3\text{CH}_2\text{OH} + \text{D}$

Fig. 2 shows an IR spectrum of $\text{CH}_3\text{CH}_2\text{OH}$ at 10 K before exposure to D atoms, the difference spectra after D-exposure for up to 30 min, and an IR spectrum of $\text{CD}_3\text{CD}_2\text{OD}$. With increasing D-exposure times, several new peaks appeared at $\sim 2200 \text{ cm}^{-1}$ concurrent with the consumption of $\text{CH}_3\text{CH}_2\text{OH}$. By comparing the difference spectrum with the IR spectrum of $\text{CD}_3\text{CD}_2\text{OD}$, the new peaks are assigned to the C–D stretching bands of deuterated ethanol. This result strongly suggests that H–D substitution occurred on a carbon-bound hydrogen in $\text{CH}_3\text{CH}_2\text{OH}$. Additionally, no evidence was observed for H–D substitution of the oxygen-bound hydrogen because of the absence of OD-stretching band at $\sim 2500 \text{ cm}^{-1}$. Drastic changes in the spectral shapes were also observed at 800–1500 cm^{-1} and some peaks clearly indicate the formation of deuterated ethanol; a

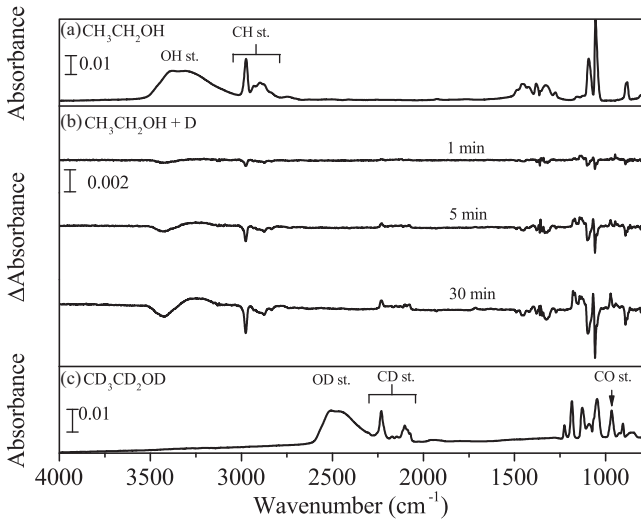
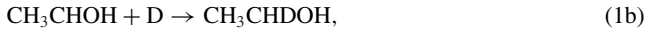
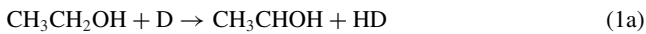


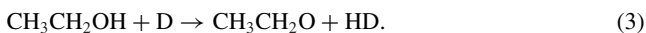
Figure 2. (a) Infrared spectrum of solid $\text{CH}_3\text{CH}_2\text{OH}$, (b) difference spectra of $\text{CH}_3\text{CH}_2\text{OH}$ after exposure to D atoms for up to 30 min, and (c) infrared spectrum of solid $\text{CD}_3\text{CD}_2\text{OD}$. No peaks were observed at $\sim 2500\text{ cm}^{-1}$ after exposure to D atoms, indicating that H–D substitution does not occur for the oxygen-bound hydrogen in $\text{CH}_3\text{CH}_2\text{OH}$.

new peak at 970 cm^{-1} is indicative of the C–O stretching band of ethanol with deuterium bound to the methylene carbon (Perchard & Josien 1968).

We propose the H–D substitution of ethanol is initiated by successive H-abstraction and D-addition reactions on either the methylene ($-\text{CH}_2-$; equations 1a and 1b) or methyl (CH_3- ; equations 2a and 2b) groups as follows

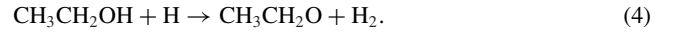


Since hydrogen abstraction from both the methylene and methyl carbon atoms of ethanol by D atoms would have large activation barriers, similar to abstraction by H atoms in the gas phase (~ 3600 and $\sim 6700\text{ K}$, respectively; Park, Xu & Lin 2003), these reactions hardly occur thermally without external energy input (e.g. UV or energetic ions) at temperatures as low as 10 K and thus require quantum tunnelling (Watanabe & Kouchi 2008; Hama & Watanabe 2013). Previous studies showed that H abstraction by D atoms from other molecules, such as CH_3OH (Nagaoka et al. 2007), H_2CO (Hidaka et al. 2009), CH_3NH_2 (Oba et al. 2014b), cyclohexane (C_6H_{12} ; Hama et al. 2015), glycine ($\text{C}_2\text{H}_5\text{NO}_2$; Oba et al. 2015), and dimethyl ether (Oba, Watanabe & Kouchi 2016), also requires quantum tunnelling to proceed on a surface at $\sim 10\text{ K}$; however, the oxygen-bound hydrogen of ethanol was not replaced with D atoms, suggesting that the H-abstraction reaction (equation 3) does not proceed at 10 K.



Although reaction (3) has not been studied, the following reaction, where an H atom is a reactant instead of a D atom (equation 4), was

reported to be slightly endothermic by $\sim 1100\text{ K}$ or less (Park et al. 2003; Carvalho et al. 2008; Sivaramakrishnan et al. 2010).



If reaction (3) is also endothermic, it does not proceed even by quantum tunnelling. In addition, these theoretical studies reached the consensus that hydrogen abstraction from the hydroxyl group has a higher barrier compared to that from the methylene and methyl groups. The absolute values of the activation barrier for those reactions in the gas phase are generally different from those on the surface. However, the difference should be negligible in the physisorption system when physisorption energy is much lower than the activation energy of reaction. Therefore, it is reasonable to consider that the activation barrier for the hydrogen abstraction from the hydroxyl group is also largest even on the surface and that H–D substitution on a hydroxyl group is not favoured under the present experimental conditions. In contrast, hydrogen abstraction from the hydroxyl group of CH_3CHOH formed in reaction (1a) could be energetically possible, which leads to the formation of CH_3CHO (Xu, Xu & Lin 2012) (see Supporting Information for further details). The change in the peak shape of the O–H stretching band could be caused in part by a peak shift due to changes in the interaction between molecules.

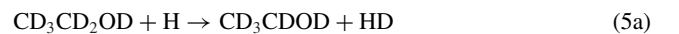
To study the H–D substitution of ethanol at the functional group level in more detail, similar experiments were performed by using partly deuterated isotopologues ($\text{CD}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CD}_2\text{OH}$) as described in the following sections.

3.1.2 $\text{CD}_3\text{CH}_2\text{OH}$ or $\text{CH}_3\text{CD}_2\text{OH} + \text{D}$

When solid layers of partly deuterated isotopologues ($\text{CD}_3\text{CH}_2\text{OH}$ or $\text{CH}_3\text{CD}_2\text{OH}$) were exposed to D atoms, we confirmed H–D substitution on the methylene or methyl group, likely a result of successive H abstraction–D addition reactions (see Supporting Information). In contrast, the hydroxyl group did not exchange its H atom with a D atom. Deuterium atoms on the methyl or methylene group may also be abstracted by D atoms; however, the formed radical may recombine with another D atom to yield the same molecule as the initial reactant, which does not change the total abundance of that reactant.

3.2 Reaction of deuterated ethanol isotopologues with H atoms

When solid layers of $\text{CD}_3\text{CD}_2\text{OD}$ were exposed to H atoms at 10 K, D–H substitution occurred on the ethyl group (CD_3CD_2-) (Fig. 3, equations 5 and 6). This behaviour is different from methanol where D–H substitution was not observed under similar experimental conditions (Nagaoka et al. 2007). We propose that D–H substitution is initiated by the following reactions.



In contrast to D–H substitution at the ethyl group, the O–D group did not exchange its D atom with an H atom (Fig. 3), suggesting that

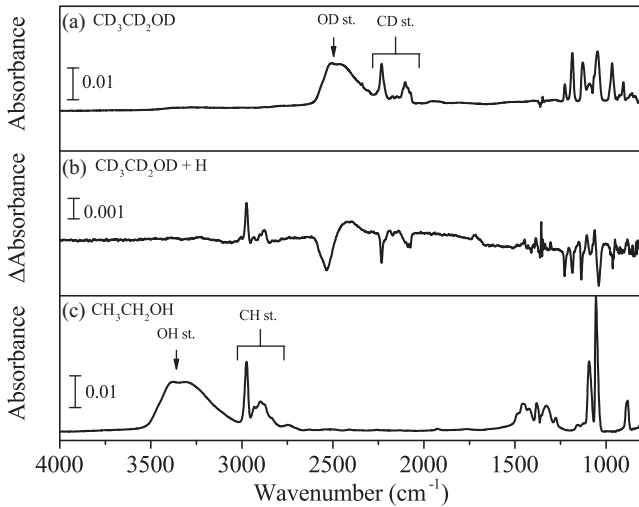
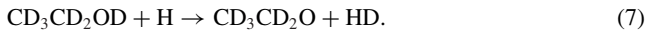


Figure 3. (a) Infrared spectrum of solid $\text{CD}_3\text{CD}_2\text{OD}$, (b) difference spectrum of $\text{CD}_3\text{CD}_2\text{OD}$ after exposure to H atoms for 120 min, and (c) infrared spectrum of solid $\text{CH}_3\text{CH}_2\text{OH}$. No peaks were observed at $\sim 3300\text{ cm}^{-1}$ after exposure to H atoms, indicating that D–H substitution does not occur for the oxygen-bound deuterium in $\text{CD}_3\text{CD}_2\text{OD}$.

deuterium abstraction from the O–D group by H atoms (equation 7) does not occur under the present experimental conditions.



This is consistent with the case of the H–D substitution of O–H group, which is likely due to the same reasons discussed earlier. Therefore, we conclude that H–D and D–H substitution reactions occur only with the carbon-bound hydrogen/deuterium atoms of ethanol.

When solid layers of $\text{CH}_3\text{CD}_2\text{OH}$ or $\text{CD}_3\text{CH}_2\text{OH}$ were exposed to H atoms at 10 K, we confirmed that D–H substitution occurred on the partly deuterated ethanol to yield $\text{CH}_3\text{CH}_2\text{OH}$ (see Supporting Information for the reaction pathways). Since D abstraction would have a large activation barrier of several thousands of kelvins, as the case for reactions (1a) and (2a), they require quantum tunnelling to proceed at low temperatures. Although carbon-bound H in $\text{CH}_3\text{CD}_2\text{OH}$ and $\text{CD}_3\text{CH}_2\text{OH}$ would also be abstracted by H atoms, the formed radical (e.g. $\text{CH}_2\text{CD}_2\text{OH}$ and CD_3CHOH , respectively) should recombine with another H atom to yield molecules that are the same as the reactants ($\text{CH}_3\text{CD}_2\text{OH}$ and $\text{CD}_3\text{CH}_2\text{OH}$).

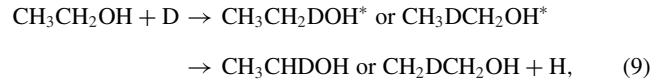
3.3 Other mechanisms for H–D and D–H substitution

H–D and D–H substitution reactions may also occur via another process; direct atom-exchange reactions via formation of unstable intermediates. In the case of methanol, for example, the following reaction (equation 8) was proposed for H–D substitution:

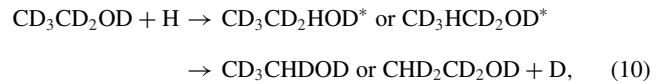


where CH_3DOH^* represents an excited intermediate species. Osamura, Roberts & Herbst (2004) calculated the activation barrier of a direct H–H exchange reaction between CH_3OH and an H atom to be $>35\text{ kcal mol}^{-1}$. Based on the barrier height of a similar reaction, Nagaoka et al. (2007) concluded that this process does not have a significant contribution to H–D exchange in methanol. In the case of ethanol, there have been no reports on the following direct H–D

exchange reaction (equation 9):



where $\text{CH}_3\text{CH}_2\text{DOH}^*$ and $\text{CH}_3\text{DCH}_2\text{OH}^*$ represent possible excited intermediate species. Since these reactions are exothermic, they would proceed if the activation barrier is low enough for the reactants to overcome or tunnel at low temperatures. In contrast, the following direct D–H exchange reactions do not occur at 10 K since these reactions (equation 10) are endothermic:



where $\text{CD}_3\text{CD}_2\text{HOD}^*$ and $\text{CD}_3\text{HCD}_2\text{OD}$ represent possible excited intermediate species. Since D–H substitution actually occurred when deuterated isotopologues reacted with H atoms (Fig. 3), we conclude that D–H substitution proceeded through successive D abstraction–H addition as previously proposed. Similarly, we deduce that the observed H–D substitution predominantly occurs via successive H abstraction–D addition, although H–D direct exchange cannot be excluded.

3.4 Rates for H–D and D–H substitution reactions

Fig. 4 shows variations in the column densities of partly deuterated ethanol isotopologues after exposure to D or H atoms. The column densities of isotopologues decreased with time. After an exposure of 180 min, the decrease in the reactants was up to ~ 15 per cent of the initial amount. Given that H–D or D–H substitution reactions proceed through successive atom abstraction and addition, the first atom-abstraction reaction, which has a large activation barrier of several thousands of kelvins (Park et al. 2003; Carvalho et al. 2008; Sivaramakrishnan et al. 2010), should be the rate-determining step. Under those conditions, the net rate of H–D or D–H substitution reactions can be expressed by the following pseudo-first-order single exponential decay function (equation 11):

$$N_t/N_0 = e^{-k't}, \quad (11)$$

where N_t and N_0 represent the column density of ethanol isotopologues at times t and 0, respectively, and k' represents the effective rate constant of a reaction ($k' = k \times N_X$, where k and N_X represent the rate constant and the number density of X atoms ($X = \text{H}$ or D) on the surface, respectively). Since it is difficult to measure the absolute value of N_X in this study, we cannot separate k and N_X from k' ; instead, we can obtain the value of k' for each reaction by fitting the plots in Fig. 4 into equation (11).

Unfortunately, fitting the entire data range up to 180 min was not successful. This may be a result of the multilayer properties of the solid samples. Ethanol molecules embedded in deeper layers may be much less reactive compared to those on the outermost surface, although the reaction itself may proceed in the deeper layers to some extent (Oba et al. 2016). Since the plots in Fig. 4 are considered to be reflective of reactions at the outermost surface and in the deeper layers, entire plots up to 180 min may not fit to a one-term single exponential function (11) in which we assume a sole value of k . Instead, we fitted the plots for shorter exposures time to function (equation 11) based on the assumption that H and D atoms preferentially react with the outermost ethanol molecules at such duration; hence, we expect to get a more reliable value for the kinetic parameters without taking the effect of multilayers into

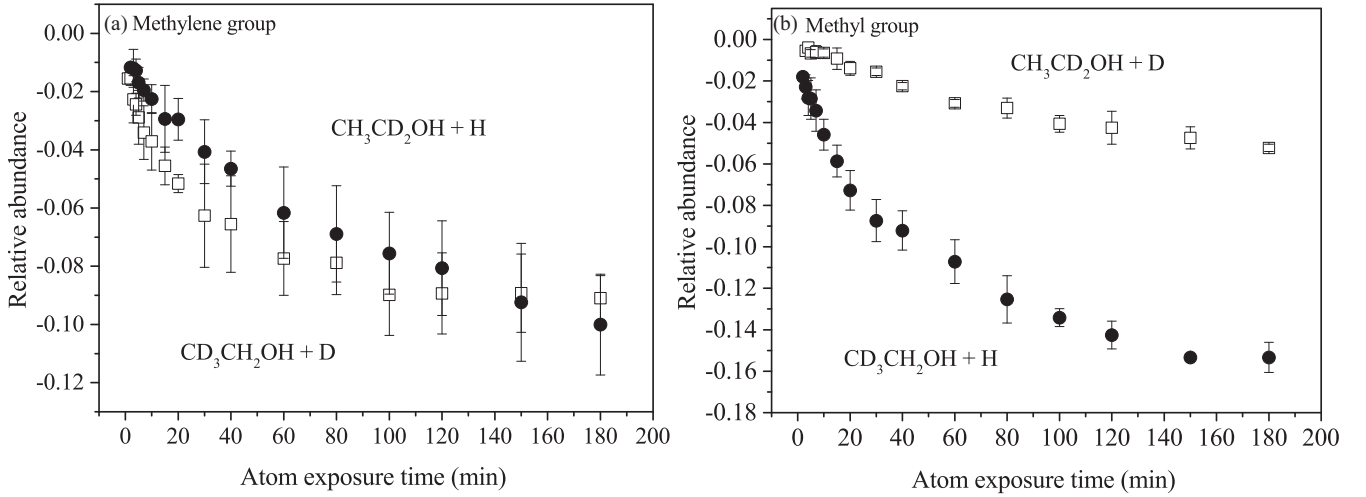


Figure 4. Variations in the column densities of ethanol isotopologues normalized to the initial molecule for reaction with D (open square) and H (filled circle) atoms on the (a) methylene and (b) methyl group. Symbols include statistical errors.

Table 1. Summary of the effective rate constant k' for H–D and D–H substitution reactions.

Reaction	Functional group	k' (min^{-1})
H–D substitution		
$\text{CD}_3\text{CH}_2\text{OH} + \text{D} \rightarrow \text{CD}_3\text{CHOH} + \text{HD}$	Methylene	$k_{\text{CH}_2\text{-D}'}$
$\text{CD}_3\text{CHOH} + \text{D} \rightarrow \text{CD}_3\text{CHDOH}$		
$\text{CH}_3\text{CD}_2\text{OH} + \text{D} \rightarrow \text{CH}_2\text{CD}_2\text{OH} + \text{HD}$	Methyl	$k_{\text{CH}_3\text{-D}'}$
$\text{CH}_2\text{CD}_2\text{OH} + \text{D} \rightarrow \text{CH}_2\text{DCD}_2\text{OH}$		
D–H substitution		
$\text{CH}_3\text{CD}_2\text{OH} + \text{H} \rightarrow \text{CH}_3\text{CDOH} + \text{HD}$	Methylene	$k_{\text{CD}_2\text{-H}'}$
$\text{CH}_3\text{CDOH} + \text{H} \rightarrow \text{CH}_3\text{CHDOH}$		
$\text{CD}_3\text{CH}_2\text{OH} + \text{H} \rightarrow \text{CD}_2\text{CH}_2\text{OH} + \text{HD}$	Methyl	$k_{\text{CD}_3\text{-H}'}$
$\text{CD}_3\text{CH}_2\text{OH} + \text{H} \rightarrow \text{CD}_2\text{CH}_3\text{OH} + \text{HD}$		

account. The plots of the initial 30 min were fitted to the function (equation 11) and the values of k' for the H–D and D–H substitution reactions of $\text{CD}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CD}_2\text{OH}$ were obtained. Given that only a methylene-H is substituted with a D atom when $\text{CD}_3\text{CH}_2\text{OH}$ reacted with D atoms, we assume that the value of k' obtained in this experiment represents the effective rate constant of H–D substitution for the methylene group of ethanol isotopologues (hereafter denoted as $k_{\text{CH}_2\text{-D}'} = k_{\text{CH}_2\text{-D}} \times N_{\text{D}}$). Likewise, the effective rate constants of H–D substitution on the methyl group ($k_{\text{CH}_3\text{-D}'}$) and that of D–H substitution in the methylene ($k_{\text{CD}_2\text{-H}'}$) and methyl ($k_{\text{CD}_3\text{-H}'}$) groups of the isotopologues were estimated as shown in Table 1. The value of $k_{\text{CH}_2\text{-D}'}$ is the largest, and $k_{\text{CD}_2\text{-H}'}$ is about 65 per cent of $k_{\text{CH}_2\text{-D}'}$. The values of $k_{\text{CH}_3\text{-D}'}$ and $k_{\text{CD}_3\text{-H}'}$ are comparable to each other, but are factor of ~ 2 smaller than $k_{\text{CH}_2\text{-D}'}$ and $k_{\text{CD}_2\text{-H}'}$.

In this study, the flux of H atoms (F_{H}) is slightly larger than that of D atoms (F_{D}) by a factor of 1.2. Assuming that correlation between atomic flux and the surface number density of atoms is independent from the atomic species, H or D, the obtained $k_{\text{CH}_2\text{-D}'}/k_{\text{CD}_2\text{-H}'}$ ratio (~ 1.6) leads to a $k_{\text{CH}_2\text{-D}}/k_{\text{CD}_2\text{-H}}$ ratio of ~ 1.9 . The small observed isotope effects are consistent with other reactions, such as H–D and D–H substitution reactions for H_2CO and CH_3NH_2 (Hidaka et al. 2009; Oba et al. 2014b), in contrast to those for methanol and glycine where significant isotope effects are observed (Nagaoka et al. 2005, 2007; Oba et al. 2015).

The rate of the quantum tunnelling reaction generally depends on various parameters such as the potential barrier shape of a reaction and the tunnelling mass (Hama & Watanabe 2013; Meisner

& Kästner 2016). The barrier shapes differ little between H- and D-atom abstraction reactions, except at zero point energy. In the case of D-atom abstraction reactions, the tunnelling mass is often ~ 1 regardless of the types of molecules, while the tunnelling mass is ~ 0.5 for H-atom abstraction. Therefore, the H-atom abstraction reaction, having a smaller tunnelling mass, is generally expected to be faster as is observed in the methanol and glycine systems. Therefore, another factor should be considered to explain the small isotope effect observed in H–D and D–H substitution of ethanol. Recently, tunnelling addition reactions of H or D atoms to solid benzene were found to have little isotope dependence on the reaction rates at 15–25 K (Hama et al. 2015). It was proposed that the isotope effect on the surface tunnelling reaction can weaken when the tunnelling rate is significantly large compared to the surface diffusion rate of H and D atoms. This is one of the scenarios used to explain the results from ethanol. In fact, the activation barrier for H-atom abstraction from ethanol is much smaller than that from methanol (Pardo, Banfeller & Osman 1992) and thus a faster tunnelling rate can be expected for ethanol. In addition, Kuwahata et al. (2015) demonstrated that even when $F_{\text{D}} = F_{\text{H}}$, the surface number density of D atoms ($= N_{\text{D}}$) is 4 or 10 times larger than that of H atoms ($= N_{\text{H}}$) on amorphous solid water and polycrystalline ice, respectively, because the recombination rate of H atoms is faster than that of D atoms due to the faster diffusion of the lighter particle. Since the direct measurement of N_{H} and N_{D} was difficult in this study, it remains unknown whether this is the case. Further theoretical studies are necessary to better understand the reaction mechanism and

the reason for the experimentally observed small isotope effect in the case of ethanol.

3.5 Estimation of the possible relative abundance of ethanol isotopologues

By using the obtained kinetic parameters (Table 1), we roughly estimated the possible relative abundances of ethanol isotopologues produced by H–D and D–H substitution reactions on grain surfaces within the lifetime of a typical molecular cloud (10^6 yr) under the following assumptions: only $\text{CH}_3\text{CH}_2\text{OH}$ is present at time $t = 0$, the total abundance of ethanol is constant throughout the time, the number density of H atoms (n_{H}) is 1 cm^{-3} , the atomic D/H ratio is 0.01, and no other reactions occur except for H–D and D–H substitution of ethanol. Note that we obtained kinetic parameters using pure solids of ethanol isotopologues, which are different from the actual conditions where H_2O is the predominant component in icy grain mantles. Under those water-dominant conditions, some kinds of molecules may form a hydrogen-bond (H-bond) with water on grains. It has been theoretically and experimentally demonstrated that the formation of H-bond could result in a suppression or enhancement of reactivity (Woon 2002; Oba et al. 2016). On the other hand, since the effect of H-bond is very small for alcohol molecules (Karpfen 2011), we expect that the reactivity of pure solid ethanol isotopologues may not significantly differ from that in water-dominant environments.

Since the OH/OD of ethanol does not show exchange with H or D atoms, we only need to consider the reactions of the methylene and methyl groups (See Supporting Information for the possible pathways of the H–D and D–H substitution reactions). Then, for example, in the case of $\text{CH}_3\text{CH}_2\text{OH}$, we set the rate equation as follows (equation 12):

$$\begin{aligned} dN_{\text{CH}_3\text{CH}_2\text{OH}}/dt = & -k_{\text{CH}_2-\text{D}}N_{\text{D}}N_{\text{CH}_3\text{CH}_2\text{OH}} + k_{\text{CD}_2-\text{H}}N_{\text{H}}N_{\text{CH}_3\text{CHDOH}} \\ & - k_{\text{CH}_3-\text{D}}N_{\text{D}}N_{\text{CH}_3\text{CH}_2\text{OH}} \\ & + k_{\text{CD}_3-\text{H}}N_{\text{H}}N_{\text{CH}_2\text{DCH}_2\text{OH}}, \end{aligned} \quad (12)$$

where $N_{\text{CH}_3\text{CH}_2\text{OH}}$, $N_{\text{CH}_3\text{CHDOH}}$, and $N_{\text{CH}_2\text{DCH}_2\text{OH}}$ represent the column densities of $\text{CH}_3\text{CH}_2\text{OH}$, CH_3CHDOH , and $\text{CH}_2\text{DCH}_2\text{OH}$, respectively. By setting similar equations for other isotopologues (see Supporting Information) and solving them under the specific conditions noted above, we estimated the relative abundance of ethanol isotopologues.

$\text{CH}_3\text{CH}_2\text{OH}$ was found to be dominant over other isotopologues, followed by CH_3CHDOH and $\text{CH}_2\text{DCH}_2\text{OH}$, whose relative abundances ($\text{CH}_3\text{CHDOH}/\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_2\text{DCH}_2\text{OH}/\text{CH}_3\text{CH}_2\text{OH}$, respectively) are 1.2×10^{-2} and 6.1×10^{-3} , respectively, after 10^6 yr in dense molecular clouds. Note that these values are only valid under the present assumptions. In the following paragraphs, we discuss a possible presence of ethanol deuterated isotopologues in molecular clouds given that the obtained values are applicable to the actual environment.

Although the calculated relative abundances are smaller than those of deuterated methylamine CH_2DNH_2 ($\text{CH}_2\text{DNH}_2/\text{CH}_3\text{NH}_2 \sim 7.5 \times 10^{-2}$; Oba et al. 2014a) estimated under the same assumptions (e.g. atomic D/H = 0.01, $t = 10^6$ yr, $n_{\text{H}} = 1 \text{ cm}^{-3}$), the relative abundance of CH_3CHDOH was slightly larger than atomic D/H. Other isotopologues having more than two D atoms are found to be much less abundant ($< \sim 10^{-4}$ versus $\text{CH}_3\text{CH}_2\text{OH}$) under the applied conditions.

In spite of the possible low abundances of deuterated ethanol isotopologues, we expect the detection of singly deuterated ethanol

because the abundance of $\text{CH}_3\text{CH}_2\text{OH}$ is relatively high (in the range 10^{-9} – 10^{-8} ; Nummelin et al. 2000; Ikeda et al. 2001) in various astronomical sources. We suggest that IRAS 16293-2422 is surely a good target for detection of deuterated ethanol because $\text{CH}_3\text{CH}_2\text{OH}$ has been clearly detected (Bisschop et al. 2008) and deuterium chemistry is very active in that region, as inferred from the detection of a number of deuterated species such as CD_3OH and DCOOCH_3 (Parise et al. 2004; Demyk et al. 2010). Moreover, mono-deuterated dimethyl ether ($\text{CH}_3\text{OCH}_2\text{D}$) was recently detected in IRAS 16293-2422 whose abundance is ~ 15 per cent of the non-deuterated molecule (Richard et al. 2013). Since dimethyl ether, which is a structural isomer of ethanol, is proposed to form on cold grains (Garrod et al. 2008), the detection of $\text{CH}_3\text{OCH}_2\text{D}$ promises the existence of deuterated ethanol because ethanol is also expected to form on grains. We confirmed the deuterium fractionation of dimethyl ether by the reaction of deuterium atoms with CH_3OCH_3 under similar conditions used in this study (Oba et al. 2016). Therefore, we strongly expect that H–D substitution of both ethanol and dimethyl ether occurs on interstellar grains and that deuterated ethanol will be found in future astronomical observations, as was the case for dimethyl ether.

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SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article.

Figure A1. (a) Infrared spectrum of solid $\text{CD}_3\text{CH}_2\text{OH}$, (b) difference spectra of $\text{CD}_3\text{CH}_2\text{OH}$ after exposure to D atoms for up to 180 min, and (c) infrared spectrum of solid $\text{CD}_3\text{CD}_2\text{OH}$.

Figure A2. (a) Infrared spectrum of solid $\text{CH}_3\text{CD}_2\text{OH}$, (b) difference spectra of $\text{CH}_3\text{CD}_2\text{OH}$ after exposure to D atoms for up to 180 min, and (c) infrared spectrum of solid $\text{CD}_3\text{CD}_2\text{OH}$.

Figure A3. (a) Infrared spectrum of solid $\text{CH}_3\text{CD}_2\text{OH}$, (b) difference spectra of $\text{CH}_3\text{CD}_2\text{OH}$ after exposure to H atoms for up to 60 min, and (c) infrared spectrum of solid $\text{CH}_3\text{CH}_2\text{OH}$.

Figure A4. (a) Infrared spectrum of solid $\text{CD}_3\text{CH}_2\text{OH}$, (b) difference spectra of $\text{CD}_3\text{CH}_2\text{OH}$ after exposure to H atoms for up to 30 min, and (c) infrared spectrum of solid $\text{CH}_3\text{CH}_2\text{OH}$.

Figure A5. Possible reaction pathways for H–D (solid line) and D–H (dashed line) substitution reactions in solid ethanol on grain surfaces at low temperatures. As the reaction proceeds, the deuteration level of ethanol increases. The number of D atoms in isotopologues is shown on the left side. (<http://www.mnras.oxfordjournals.org/lookup/suppl/doi:10.1093/mnras/stw1714/-/DC1>).

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