Supporting Information

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

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Contents

1. Possible H-D and D-H substitution reactions of ethanol isotopologues.

We consider that H–D substitution of CD_3CH_2OH and CH_3CD_2OH proceeds through the successive H abstraction-D addition reactions as follows:

$$CD_3CH_2OH + D \rightarrow CD_3CHOH + HD, \quad \text{(A1a)}$$

$$CD_3CHOH + D \rightarrow CD_3CHDOH, \quad \text{(A1b)}$$

$$CD_3CHDOH + D \rightarrow CD_3CDOH + HD, \quad \text{(A2a)}$$

$$CD_3CDOH + D \rightarrow CD_3CD_2OH. \quad \text{(A2b)}$$

$$CH_3CD_2OH + D \rightarrow CH_2CD_2OH + HD, \quad \text{(A3a)}$$

$$CH_2CD_2OH + D \rightarrow CH_2DCD_2OH, \quad \text{(A3b)}$$

$$CH_2DCD_2OH + D \rightarrow CHDCD_2OH + HD, \quad \text{(A4a)}$$

$$CHDCD_2OH + D \rightarrow CHD_2CD_2OH, \quad \text{(A4b)}$$

$$CHD_2CD_2OH + D \rightarrow CD_2CD_2OH + HD, \quad \text{(A5a)}$$

$$CD_2CD_2OH + D \rightarrow CD_3CD_2OH. \quad \text{(A5b)}$$

The hydroxyl group of ethanol did not exchange its hydrogen with D atoms.

For the D–H substitution, the following reactions are considered to occur at low temperatures:

$$CH_3CD_2OH + H \rightarrow CH_3CDOH + HD, \quad \text{(A6a)}$$

$$CH_3CDOH + H \rightarrow CH_3CHDOH. \quad \text{(A6b)}$$

$CH_3CHDOH + H \rightarrow CH_3CHOH + HD,$ (A7a)

$CH_3CHOH + H \rightarrow CH_3CH_2OH.$ (A7b)

$CD_3CH_2OH + H \rightarrow CD_2CH_2OH + HD,$ (A8a)

$CD_2CH_2OH + H \rightarrow CHD_2CH_2OH.$ (A8b)

$CHD_2CH_2OH + H \rightarrow CHDCH_2OH + HD,$ (A9a)

$CHDCH_2OH + H \rightarrow CH_2DCH_2OH,$ (A9b)

$CH_2DCH_2OH + H \rightarrow CH_2CH_2OH + HD.$ (A10a)

$CH_2CH_2OH + H \rightarrow CH_3CH_2OH.$ (A10b)

2. Other chemical reactions

We found that a small peak was observed at ~1715 cm^{-1} when ethanol isotopologues were exposed to H or D atoms (e.g. Figures 2 & 3). Since ethanol isotopologues do not have absorption at this region (Figure 1), this peak could be derived from other species except for ethanol. One of the possible scenarios is that this peak is derived from the C=O stretching band of acetaldehyde (CH_3CHO) or its deuterated isotopologues. In the reaction of CH_3CH_2OH with D, for example, the formation of acetaldehyde might be possible through the following successive hydrogen abstraction reactions:

$$CH_3CH_2OH + D \rightarrow CH_3CHOH + HD, \quad (1a)$$

$$CH_3CHOH + D \rightarrow CH_3CHO + HD. \quad (A11)$$

Xu et al. (2012) showed that reaction (A11) is exothermic with an activation barrier in the gas phase (~13 kJ mol^{-1}). Although the main product of the reaction of CH_3CHOH with D should be CH_3CHDOH (reaction 1b), reaction (A11) could also proceed even at 10 K via quantum tunnelling.

Another candidate for the 1715 cm^{-1} band is the C=C stretching band of vinyl alcohol, CH_2=CHOH, which could be formed from CH_3CHOH by the following exothermic hydrogen abstraction reaction:

$$CH_3CHOH + D \rightarrow CH_2=CHOH + HD. \quad (A12)$$

Since the activation barrier of reaction (A12) is lower than reaction (A11) by ~10 kJ mol^{-1} (Xu et al. 2012), reaction (A12) may preferentially occur over reaction (A11). Nevertheless, both reactions (A11) and (A12) should be very minor compared to the competitive barrierless reaction (1b), which results in the conclusion that the contribution to the obtained kinetic parameter should be very small. This is consistent with the weak intensity of the observed 1715 cm^{-1} band for the possible reaction products.

3. Rate equations for all ethanol isotopologues.

N_X represents the number density of species X (H, D, or ethanol isotopologues).

$$dN_{CH3CH2OH}/dt = -k_{CH3\text{-}D}N_D N_{CH3CH2OH} + k_{CD3\text{-}H}N_H N_{CH2DCH2OH} - k_{CH2\text{-}D}N_D N_{CH3CH2OH} + k_{CD2\text{-}H}N_H N_{CH3CHDOH}, \quad (12)$$

$$dN_{CH2DCH2OH}/dt = k_{CH3\text{-}D}N_D N_{CH3CH2OH} - k_{CD3\text{-}H}N_H N_{CH2DCH2OH} - k_{CH3\text{-}D}N_D N_{CH2DCH2OH} + k_{CD3\text{-}H}N_H N_{CHD2CH2OH} - k_{CH2\text{-}D}N_D N_{CH2DCH2OH} + k_{CD2\text{-}H}N_H N_{CH2DCHDOH},$$

(A12)

$$dN_{CH3CHDOH}/dt = k_{CH2\text{-}D}N_D N_{CH3CH2OH} - k_{CD2\text{-}H}N_H N_{CH3CHDOH} - k_{CH3\text{-}D}N_D N_{CH3CHDOH} + k_{CD3\text{-}H}N_H N_{CH2DCHDOH} - k_{CH2\text{-}D}N_D N_{CH3CHDOH} + k_{CD2\text{-}H}N_H N_{CH3CD2OH},$$

(A13)

$$dN_{CHD2CH2OH}/dt = k_{CH3\text{-}D}N_D N_{CH2DCH2OH} - k_{CD3\text{-}H}N_H N_{CHD2CH2OH} - k_{CH3\text{-}D}N_D N_{CHD2CH2OH} + k_{CD3\text{-}H}N_H N_{CD3CH2OH} - k_{CH2\text{-}D}N_D N_{CHD2CH2OH} + k_{CD2\text{-}H}N_H N_{CHD2CHDOH},$$

(A14)

$$dN_{CH2DCHDOH}/dt = k_{CH2\text{-}D}N_D N_{CH2DCH2OH} - k_{CD2\text{-}H}N_H N_{CH2DCHDOH} + k_{CH3\text{-}D}N_D N_{CH3CHDOH} - k_{CD3\text{-}H}N_H N_{CH2DCHDOH} - k_{CH3\text{-}D}N_D N_{CH2DCHDOH} + k_{CD3\text{-}H}N_H N_{CHD2CHDOH} - k_{CH2\text{-}D}N_D N_{CH2DCHDOH} + k_{CD2\text{-}H}N_H N_{CH2DCD2OH}, \quad (A15)$$

$$dN_{CH3CD2OH}/dt = k_{CH2\text{-}D}N_D N_{CH3CHDOH} - k_{CD2\text{-}H}N_H N_{CH3CD2OH} - k_{CH3\text{-}D}N_D N_{CH3CD2OH} + k_{CD3\text{-}H}N_H N_{CH2DCD2OH}, \quad (A16)$$

$$dN_{CD3CH2OH}/dt = k_{CH3\text{-}D}N_D N_{CHD2CH2OH} - k_{CD3\text{-}H}N_H N_{CD3CH2OH} - k_{CH2\text{-}D}N_D N_{CD3CH2OH} + k_{CD2\text{-}H}N_H N_{CD3CHDOH}, \quad (A17)$$

$$dN_{CHD2CHDOH}/dt = k_{CH2\text{-}D}N_D N_{CHD2CH2OH} - k_{CD2\text{-}H}N_H N_{CHD2CHDOH} + k_{CH3\text{-}D}N_D N_{CH2DCHDOH} - k_{CD3\text{-}H}N_H N_{CHD2CHDOH} - k_{CH3\text{-}D}N_D N_{CHD2CHDOH} + k_{CD3\text{-}H}N_H N_{CD3CHDOH} -$$

$k_{CH2\text{-}D}N_D N_{CHD2CHDOH} + k_{CD2\text{-}H}N_H N_{CHD2CD2OH}$, (A18)

$dN_{CH2DCD2OH}/dt = k_{CH2\text{-}D}N_D N_{CH2DCHDOH} - k_{CD2\text{-}H}N_H N_{CH2DCD2OH} + k_{CH3\text{-}D}N_D N_{CH3CD2OH} - k_{CD3\text{-}H}N_H N_{CH2DCD2OH} - k_{CH3\text{-}D}N_D N_{CH2DCD2OH} + k_{CD3\text{-}H}N_H N_{CHD2CD2OH}$,

(A19)

$dN_{CD3CHDOH}/dt = k_{CH2\text{-}D}N_D N_{CD3CH2OH} - k_{CD2\text{-}H}N_H N_{CD3CHDOH} + k_{CH3\text{-}D}N_D N_{CHD2CHDOH} - k_{CD3\text{-}H}N_H N_{CD3CHDOH} - k_{CH2\text{-}D}N_D N_{CD3CHDOH} + k_{CD2\text{-}H}N_H N_{CD3CD2OH}$,

(A20)

$dN_{CHD2CD2OH}/dt = k_{CH2\text{-}D}N_D N_{CHD2CHDOH} - k_{CD2\text{-}H}N_H N_{CHD2CD2OH} + k_{CH3\text{-}D}N_D N_{CH2DCD2OH} - k_{CD3\text{-}H}N_H N_{CHD2CD2OH} - k_{CH3\text{-}D}N_D N_{CHD2CD2OH} + k_{CD3\text{-}H}N_H N_{CD3CD2OH}$,

(A21)

$dN_{CD3CD2OH}/dt = k_{CH2\text{-}D}N_D N_{CD3CHDOH} - k_{CD2\text{-}H}N_H N_{CD3CD2OH} + k_{CH3\text{-}D}N_D N_{CHD2CD2OH} - k_{CD3\text{-}H}N_H N_{CD3CD2OH}$, (A22)

4. Additional Figures

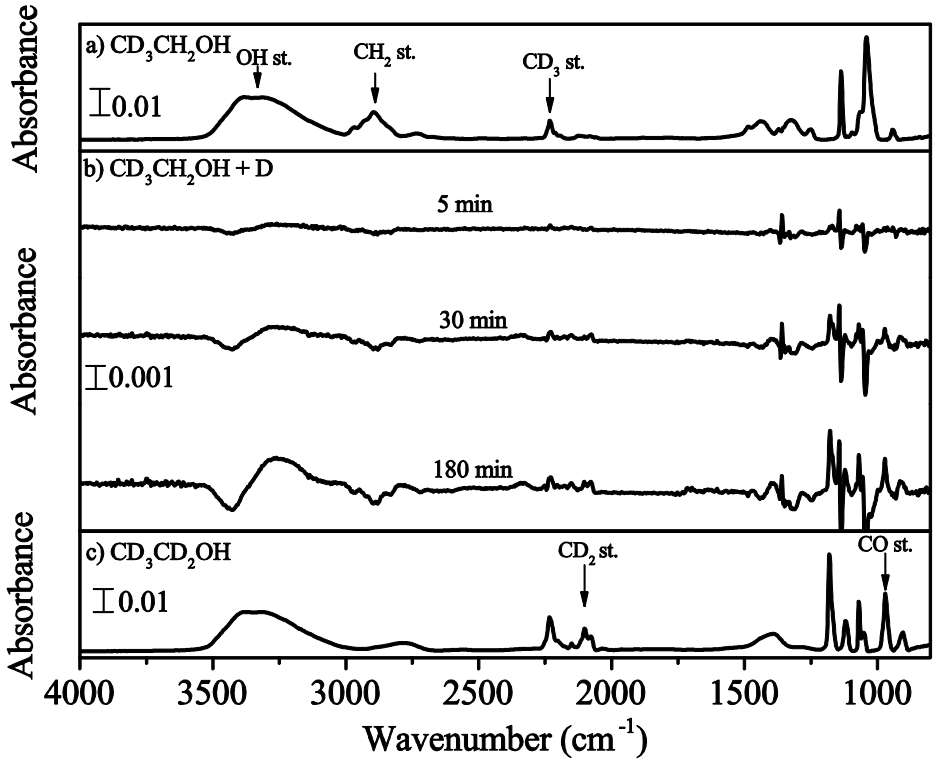

FIG. A1

(a) Infrared spectrum of solid CD_3CH_2OH, (b) difference spectra of CD_3CH_2OH after exposure to D atoms for up to 180 min, and (c) infrared spectrum of solid CD_3CD_2OH.

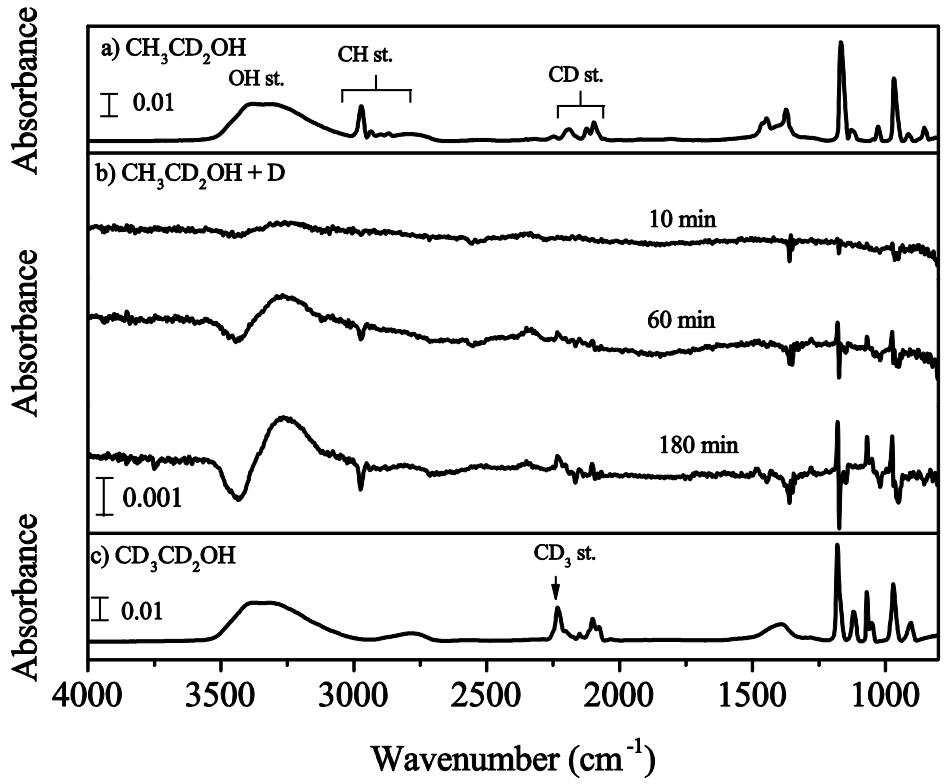

FIG. A2

(a) Infrared spectrum of solid CH_3CD_2OH, (b) difference spectra of CH_3CD_2OH after exposure to D atoms for up to 180 min, and (c) infrared spectrum of solid CD_3CD_2OH.

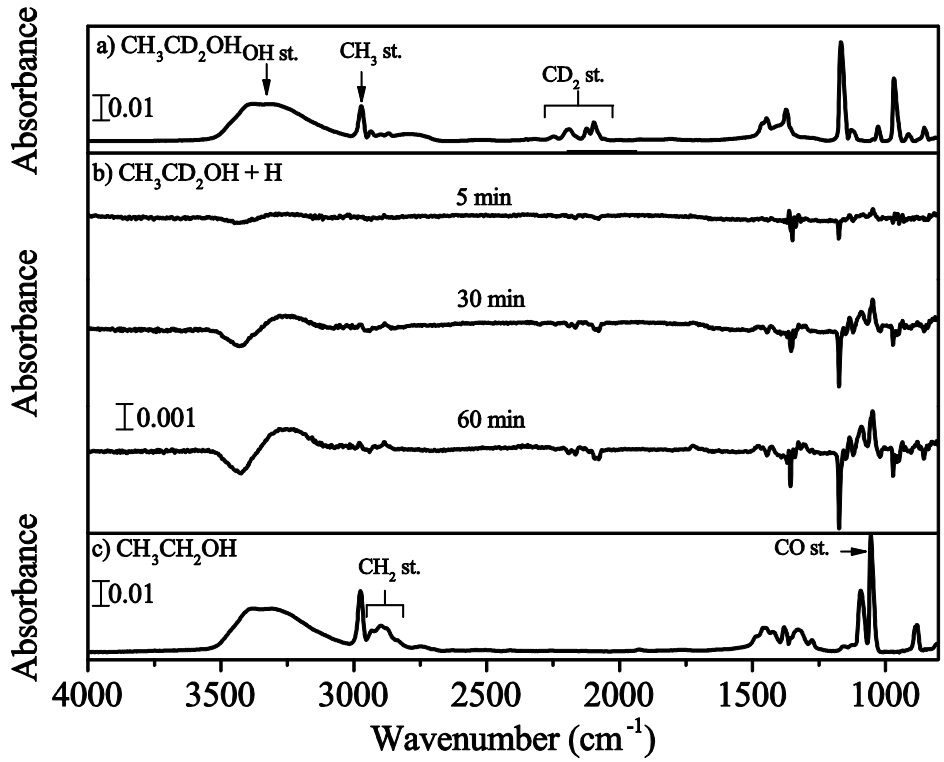

FIG. A3

(a) Infrared spectrum of solid CH_3CD_2OH, (b) difference spectra of CH_3CD_2OH after exposure to H atoms for up to 60 min, and (c) infrared spectrum of solid CH_3CH_2OH.

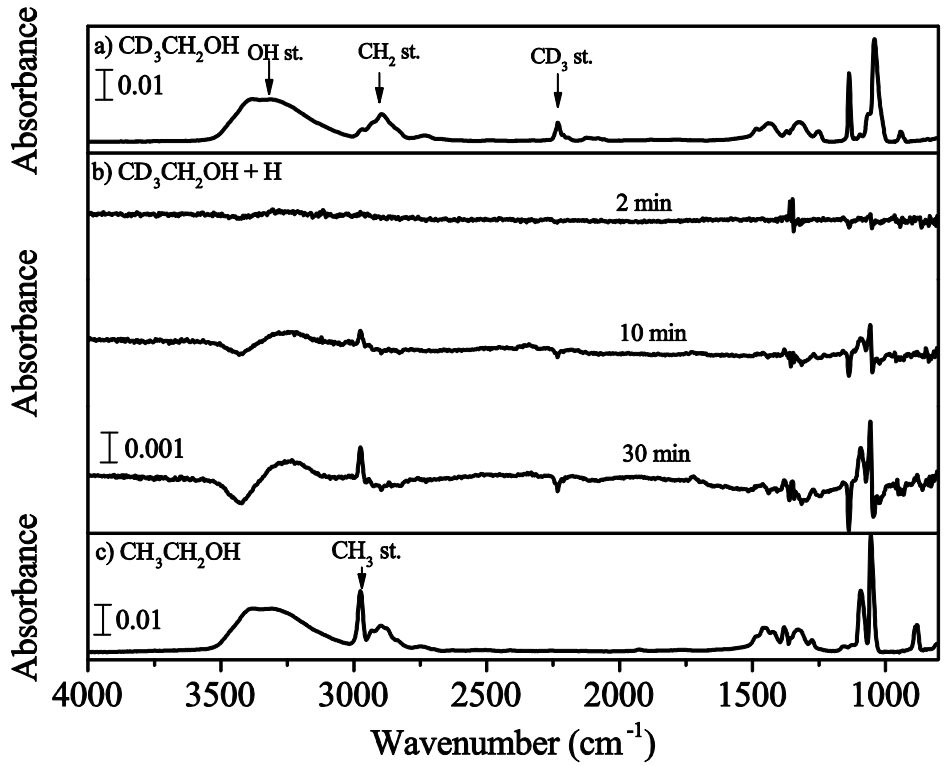

FIG. A4

(a) Infrared spectrum of solid CD_3CH_2OH, (b) difference spectra of CD_3CH_2OH after exposure to H atoms for up to 30 min, and (c) infrared spectrum of solid CH_3CH_2OH.

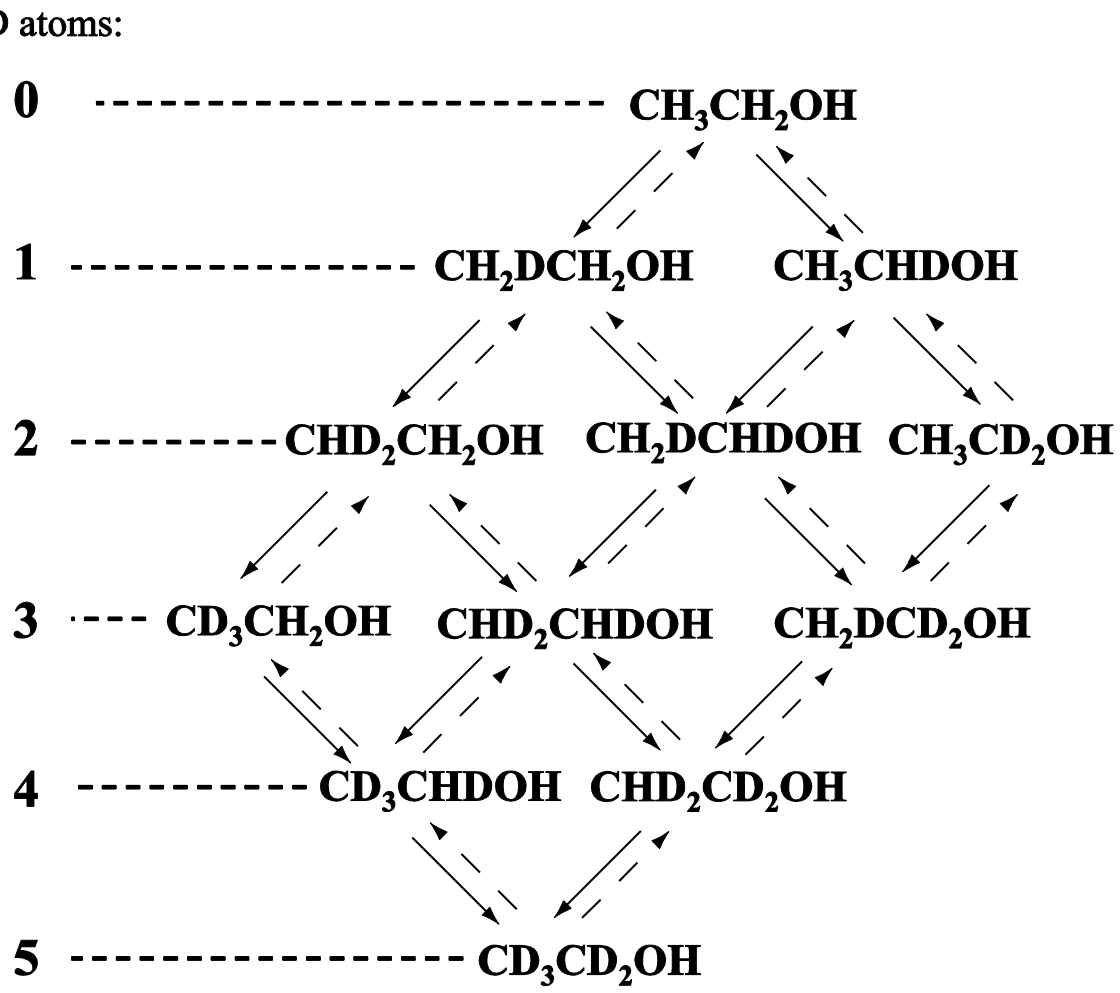

FIG. A5

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.