

Supplementary information for

Ethanol-ethylene conversion mechanism on hydrogen boride sheets probed by *in situ* infrared absorption spectroscopy

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Figure S2. Schematic image of the home-made experimental apparatus

Figure S3. IR spectra for the gaseous CH₃CH₂OH, CD₃CH₂OH, and CH₃CD₂OH

Figure S4. IR spectra for the HB sheets with heating after CH₃CH₂OH exposure

Figure S5. IR spectra for the HB sheets with heating after CD₃CH₂OH exposure

Figure S6. IR spectra for the HB sheets with heating after CH₃CD₂OH exposure

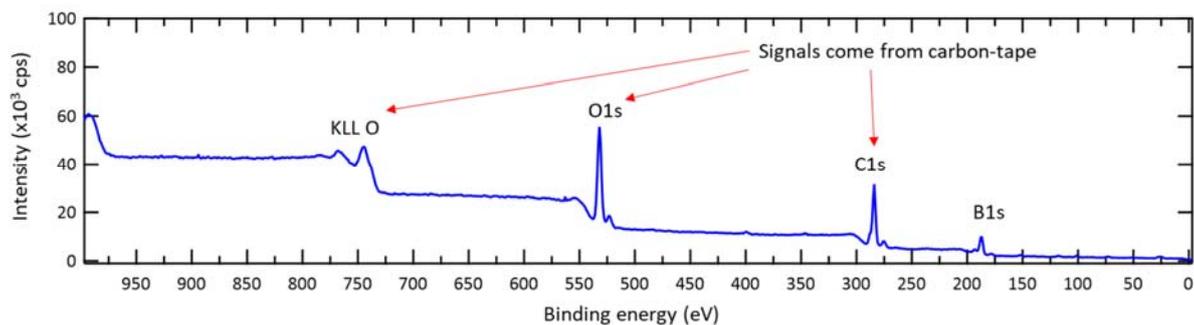


Figure S1 Survey X-ray photoelectron spectrum of the HB sheets. The powder sample was fixed on a piece of carbon tape, and so C1s, O1s, and KLL-O signals (from the carbon tape) were detected in addition to the B1s signal from the sample. We note that a very small N1s signal was also detected at 400 eV; this may originate from acetonitrile or its fragments remaining in the sample as impurities. The absence of oxygen, nitrogen, and carbon in the HB sheet was confirmed by electron energy loss spectroscopy, as reported previously.¹⁷ The absence of Mg and other species is clearly shown.

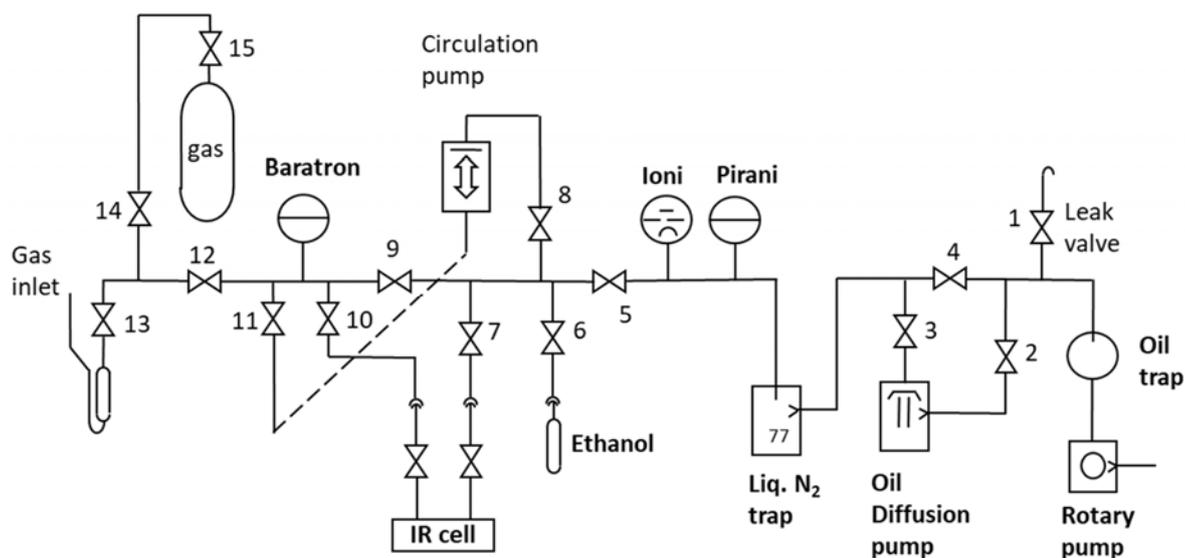


Figure S2 Schematic diagram of the homemade experimental apparatus employed for the purpose of this study. The “oil diffusion pump” is a Hickman type oil diffusion pump (Makuhari Rikagaku Glass Inc., Chiba, Japan). The “rotary pump” is a 2010SD rotary pump (Pfeiffer Adixen Alcatel). The “Baratron” is a pressure gauge (Baratron capacitance manometer, MKS Instruments Japan Co., Tokyo, Japan). The Baratron is connected to a digital panel meter (OMRON Corporation, Temperature Intelligent Signal Processor, Model K3TH) to display the pressure. The “Ioni” is an ionization vacuum gauge (VG-51, Wakaida Science Co., Tokyo, Japan). The “Pirani” is a Pirani vacuum gauge (No. 627F13TCC18, Wakaida Science Co., Tokyo, Japan). Both the Ioni and the Pirani are connected to a WVG-1T (Wakaida Science Co., Tokyo, Japan) to display the pressure. The apparatus is equipped with a “circulation pump” (Makuhari Rikagaku Glass Inc., Chiba, Japan), but this pump was not used for the purpose of this study. Each device is connected using Pyrex glass. Valve Nos. 1–13 are “high vacuum grease glass valve” (1005-8, Makuhari Rikagaku Glass Inc., Chiba, Japan).

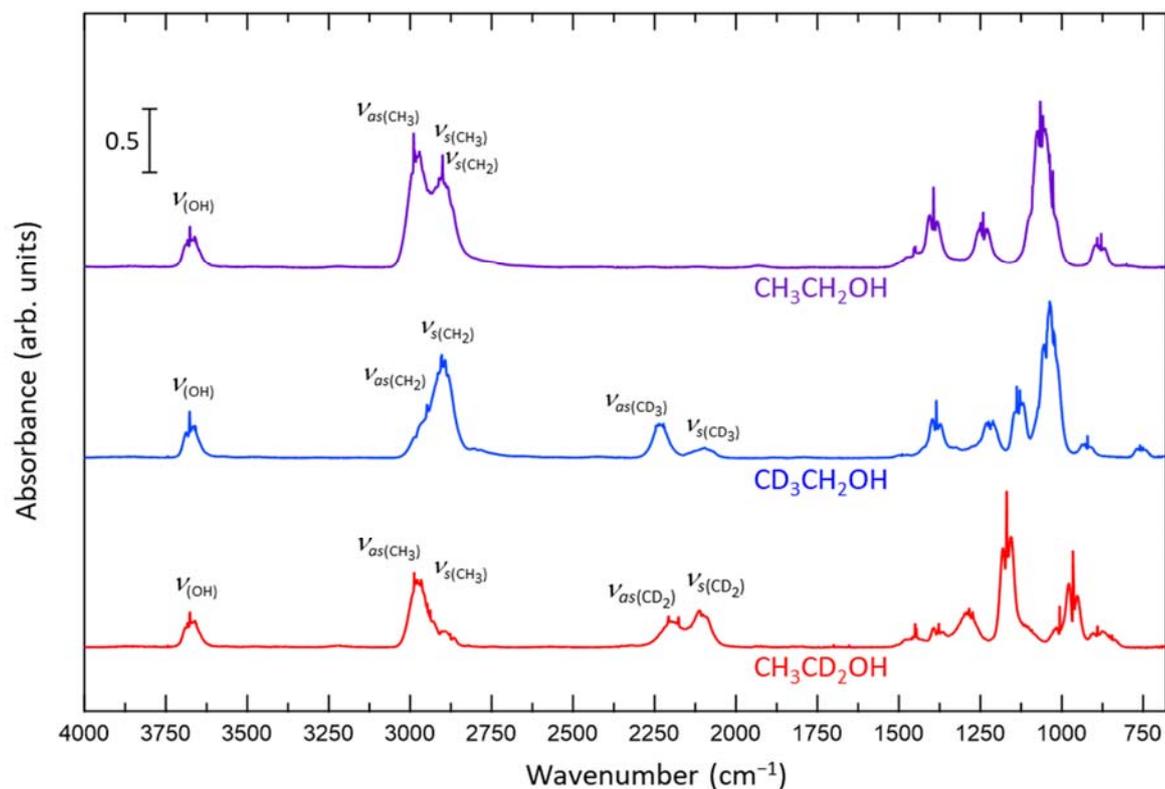


Figure S3 Experimentally obtained FT-IR spectra for ethanol gas and the isotope-labelled ethanol gas. Spectra were taken at 298 K and 3.0 kPa ethanol (or isotope-labelled ethanol) partial pressure using an FT/IR 4600 instrument (Jasco, Ltd., Tokyo, Japan) with a resolution of 1.0 cm^{-1} . The peaks were assigned based on comparisons with the DFT (B3-LYP) calculation results for a free ethanol molecule with trans-geometry, and literature results for ethanol under various conditions (Table 1).³¹⁻⁴⁰

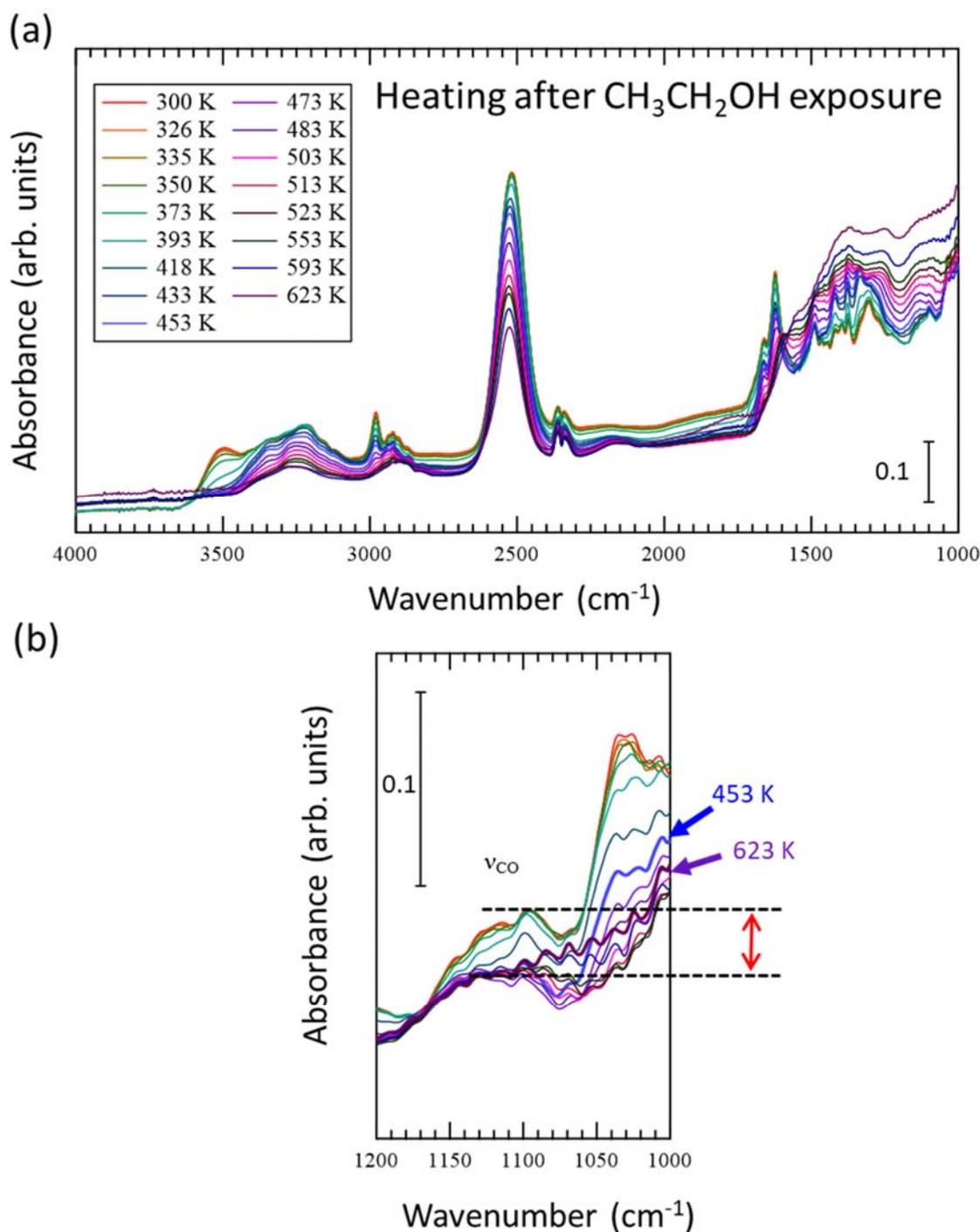


Figure S4 (a) IR spectra for the HB sheets with heating after CH₃CH₂OH exposure. (b) Magnified spectra in the region from 1000 to 1200 cm⁻¹, where the relative spectrum positions are adjusted to be the same at ~1165 cm⁻¹ for easy comparison. Here we assigned that the peak at ~1100 cm⁻¹ corresponds to the CO stretching vibrational mode (ν_{CO}) of ethanol, which shows clear decrease in intensity with heating up to 453 K as indicated by red arrow.^{S1-S7} The other intensity variations in the displayed wavenumber region with temperature may be caused by the change of the absorbance for the rocking mode of methyl group (ρ_{CH_3}) of ethanol.^{S1-S7} For the comparison, the spectra at 453 K and 623 K are shown with thick curve. Here we note that the broad background at 1070-1170 cm⁻¹ can be interpreted to be present even above 453 K (the intensity decrease is saturated between 453–623 K); the possible candidate for the remaining species are ethoxy species (C₂H₅O-) (see detail in the main text).

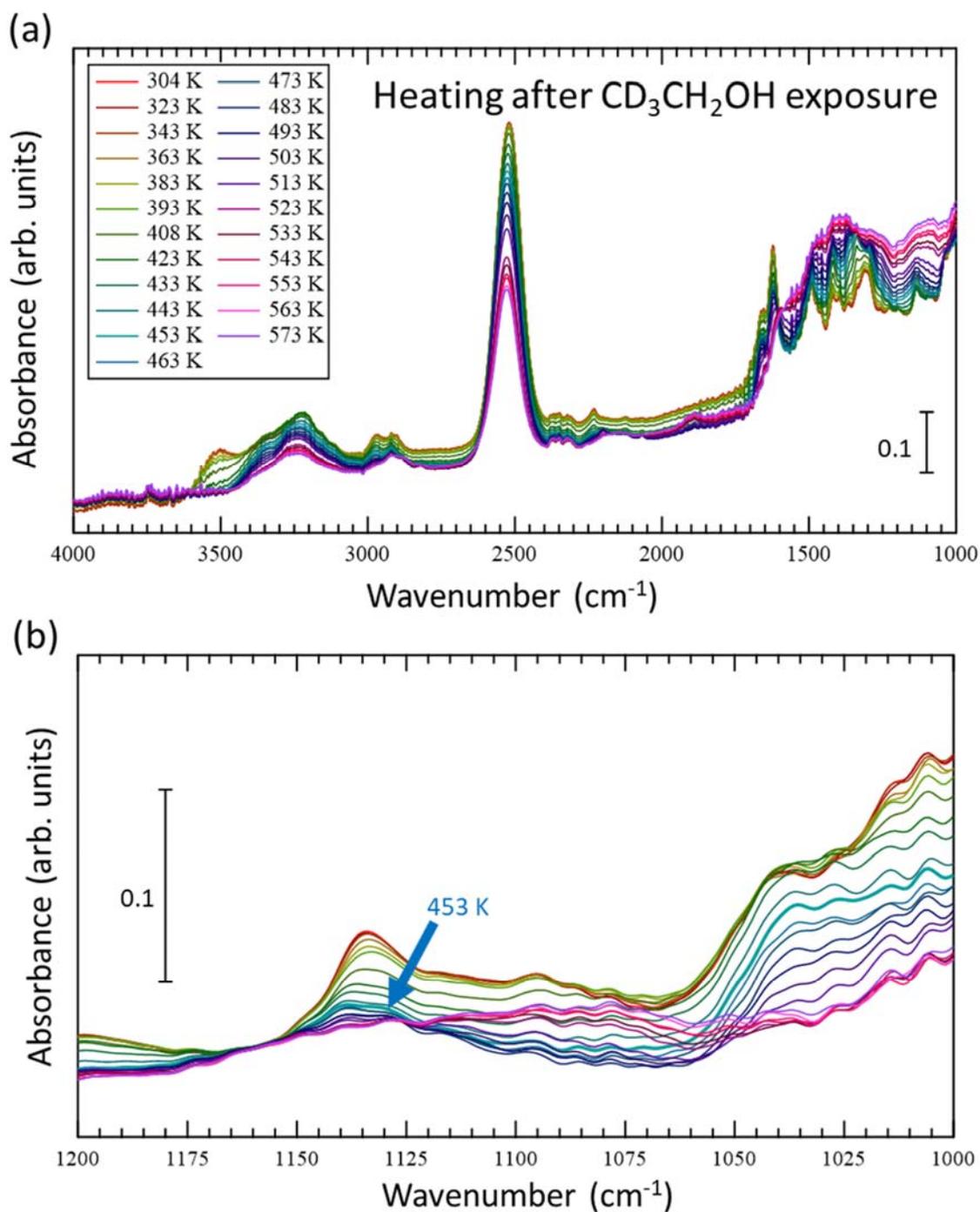


Figure S5 (a) IR spectra for the HB sheets with heating after $\text{CD}_3\text{CH}_2\text{OH}$ exposure. (b) Magnified spectra in the region from 1000 to 1200 cm^{-1} , where the relative spectrum positions are adjusted to be the same at $\sim 1160 \text{ cm}^{-1}$ for easy comparison. The peak components appeared in the displayed region can be assigned to the CO stretching vibrational mode (ν_{CO}) of ethanol and/or the bending mode of deuterated methyl group (δ_{CD_3}) of ethanol.^{S1-S7} For the comparison, the spectrum at 453 K is shown with thick curve.

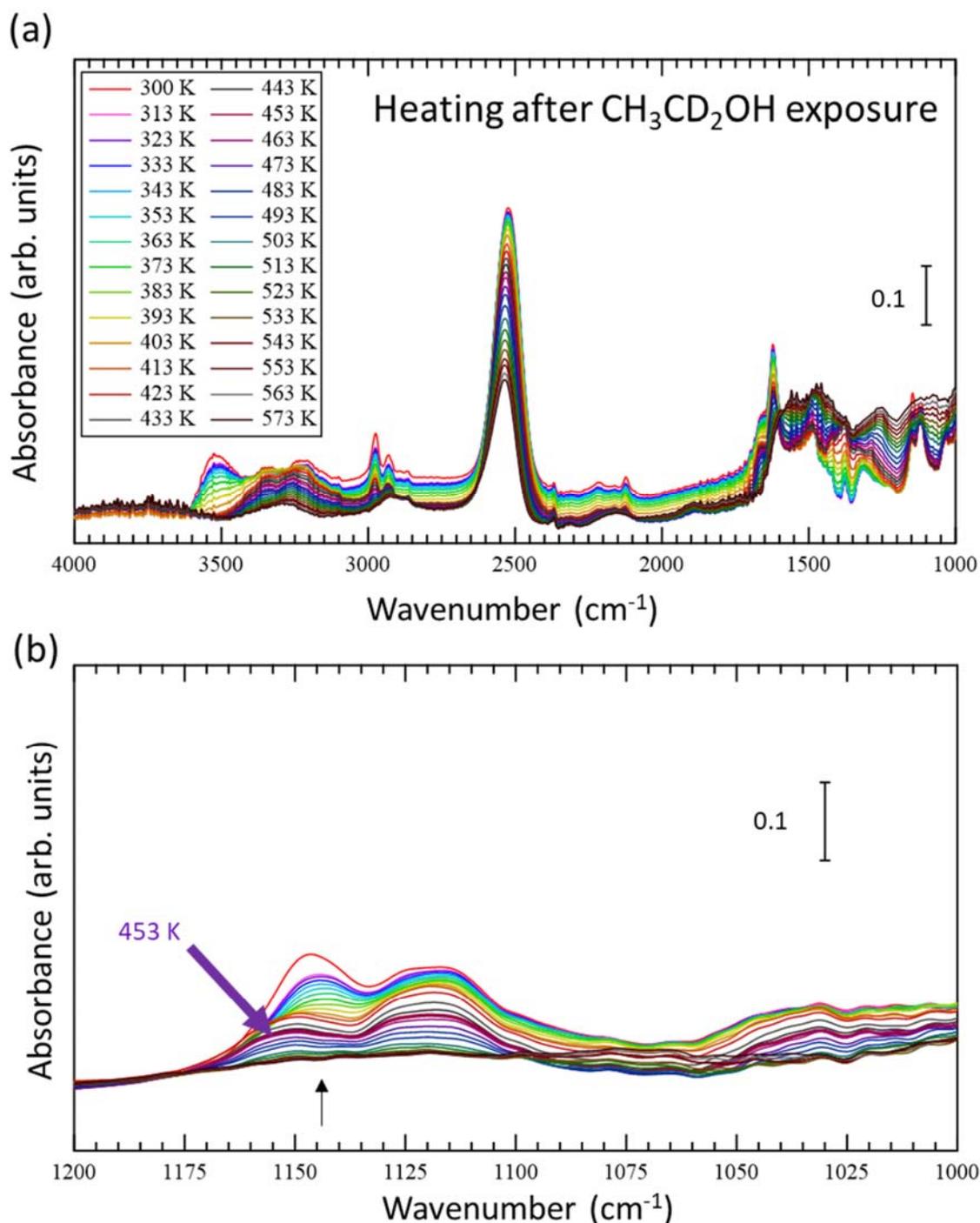


Figure S6 (a) IR spectra for the HB sheets with heating after $\text{CH}_3\text{CD}_2\text{OH}$ exposure. (b) Magnified spectra in the region from 1000 to 1200 cm^{-1} , where the relative spectrum positions are adjusted to be the same at ~ 1175 cm^{-1} for easy comparison. The peaks appeared in the displayed region can be assigned to the CO stretching vibrational mode (ν_{CO}) of $\text{CH}_3\text{CD}_2\text{OH}$, the rocking mode of methyl group (ρ_{CH_3}) of $\text{CH}_3\text{CD}_2\text{OH}$, and/or bending mode of deuterated methylene group (δ_{CD_2}) of $\text{CH}_3\text{CD}_2\text{OH}$.^{S1-S7} Black arrow indicates the absorbance peak component, in which the peak intensity rapidly decreases with temperature up to ~ 430 K, which can be assigned to ν_{CO} because CH_3 and CD_2 groups are still left on the sample above 430 K as indicated by Fig. 4. For the comparison, the spectrum at 453 K is shown with thick curve.

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