Formation of Methanol Clathrate Hydrate in Simulated Interstellar Ices

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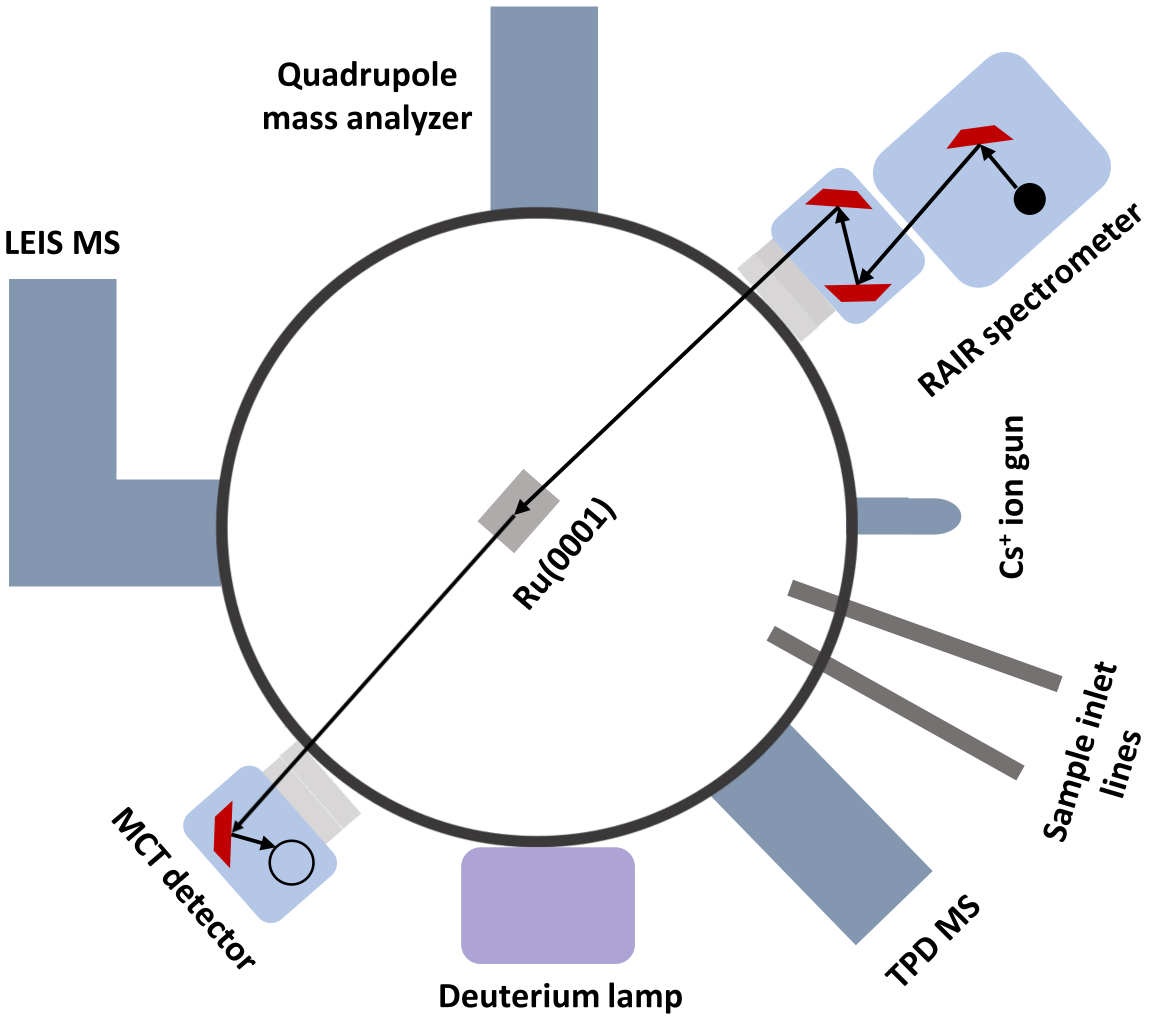
Experimental Section

Experimental Setup

The preparation of ice samples, experiments, and data acquisition were carried out using a custom-built ultrahigh vacuum (UHV) setup, detailed in previous reports.[1,2] This setup included a stainless steel UHV chamber with a base pressure of ~10^{-10} mbar, a metal substrate mounted to a helium cryocooler, and a gas inlet system. The UHV chamber was equipped with reflection absorption infrared spectroscopy (RAIRS), temperature-programmed desorption (TPD) mass spectrometry, Cs^+-based secondary ion mass spectrometry (SIMS), low-energy ion scattering (LEIS) mass spectrometry, and a vacuum ultraviolet (VUV) lamp, as shown in Scheme S1. UHV was maintained by multiple turbomolecular pumps, which were backed by oil-free diaphragm pumps (Pfeiffer Vacuum). The metal substrate, a highly polished single-crystal Ru(0001), was mounted on the cold end of the helium cryostat (Coldedge Technologies) and was integrated with a precision x-y-z-θ sample manipulator. Temperature control and monitoring were through a Lakeshore Model 336 temperature controller, which utilized a 25 Ω resistive heater, covering a temperature range of 8-1000 K. Temperature measurements were performed using a K-type thermocouple and a platinum sensor, providing an accuracy of ±0.5 K. The gas inlet system was equipped with two high-precision all-metal leak valves for precise control of vapor deposition.



Scheme S1. Schematic diagram of the experimental setup showing the Ru(0001) substrate orientation for RAIR measurements.

Materials

Methanol (anhydrous, ≥99.9%, Sigma-Aldrich), dimethyl ether (99.9%, Sigma-Aldrich), ethylene oxide (49.5%, 50 % N_2 gas, Vinayaka gas), and ultrapure water (18.2 MΩ cm) were used in all experiments. Liquid samples were transferred into vacuum-sealed glass tubes and purified by repeated freeze–pump–thaw cycles prior to deposition.

Sample Preparation

Prior to each sample preparation, the Ru(0001) substrate was cleaned by heating it to 400 K multiple times. Thin ice films were then prepared by vapor deposition on the pre-cooled Ru(0001) substrate. Two separate gas inlets, one exclusively for water and the other for dimethyl ether, ethylene oxide, or methanol, were utilized to introduce vapors into the UHV chamber for backfilling. The purity and ratio of dimethyl ether, methanol, ethylene oxide and water were confirmed using a residual gas analyzer during vapor deposition. In the current work, deposition coverage was measured in monolayers (ML) with an assumption that 1.33×10^{-6} mbar s equals 1 ML, which is estimated to contain $\sim 1.1 \times 10^{15}$ molecules cm^{-2}. The ice thickness (in ML) was determined from the deposition time, background pressure, and ionization gauge sensitivity factor.

RAIRS Setup

RAIR spectra were collected by Bruker Vertex 70 FT-IR spectrometer in the range of 4000-550 cm^{-1} with a spectral resolution of 2 cm^{-1}. Each RAIR spectrum was averaged over 512 scans to ensure a better signal-to-noise ratio. The RAIRS setup, connected to the UHV chamber via an IR-transparent ZnSe viewport, consists of an FT-IR spectrometer and a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. For experiments, the IR beam was focused on the ice sample at an incident angle of 80° ± 7°, and the reflected beam was recorded using the MCT detector. The IR beam outside the UHV chamber was purged with dry N_2 to avoid interference with atmospheric gases.

Supporting information 1:

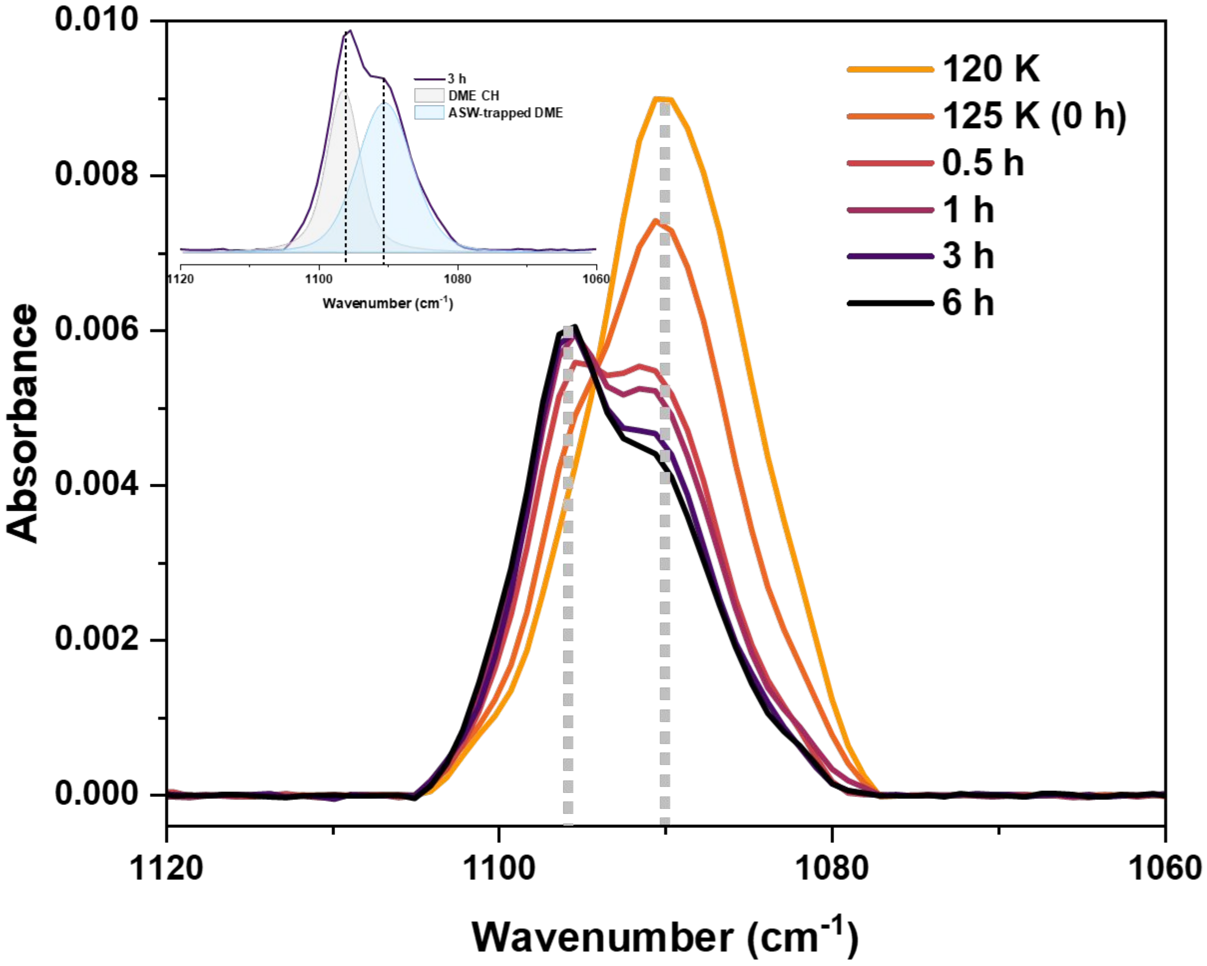


Figure S1. RAIR spectra of sequentially deposited DME, and H_2O in 150 and 150 ML. The deconvoluted spectrum of 3 h is shown in the inset.

Supporting information 2:

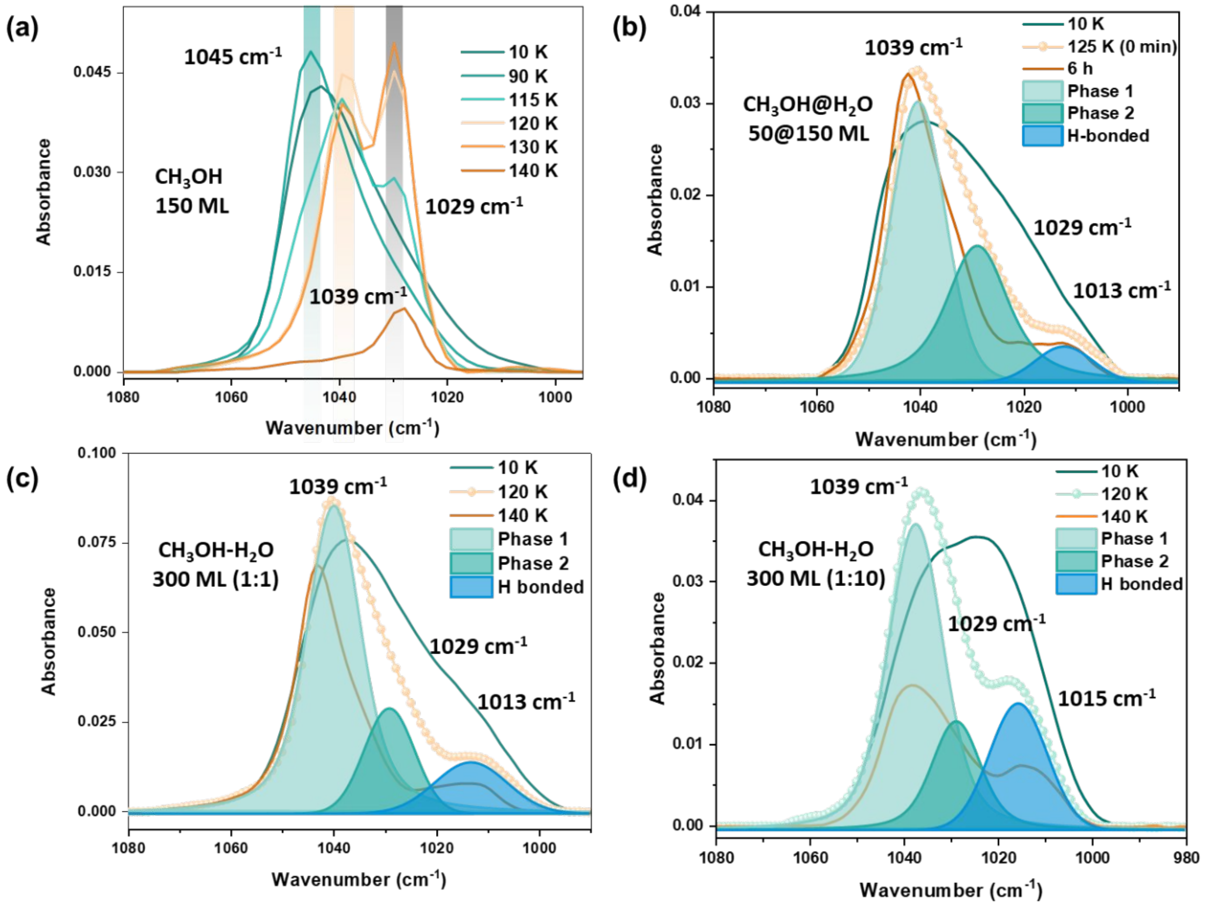


Figure S2. RAIR spectra of (a) 150 ML CH_3OH, (b) sequentially deposited CH_3OH, and H_2O in 50 and 150 ML (c), (d) co-deposited CH_3OH-H_2O in 1:1 and 1:10 ratio, respectively.

Supporting information 3:

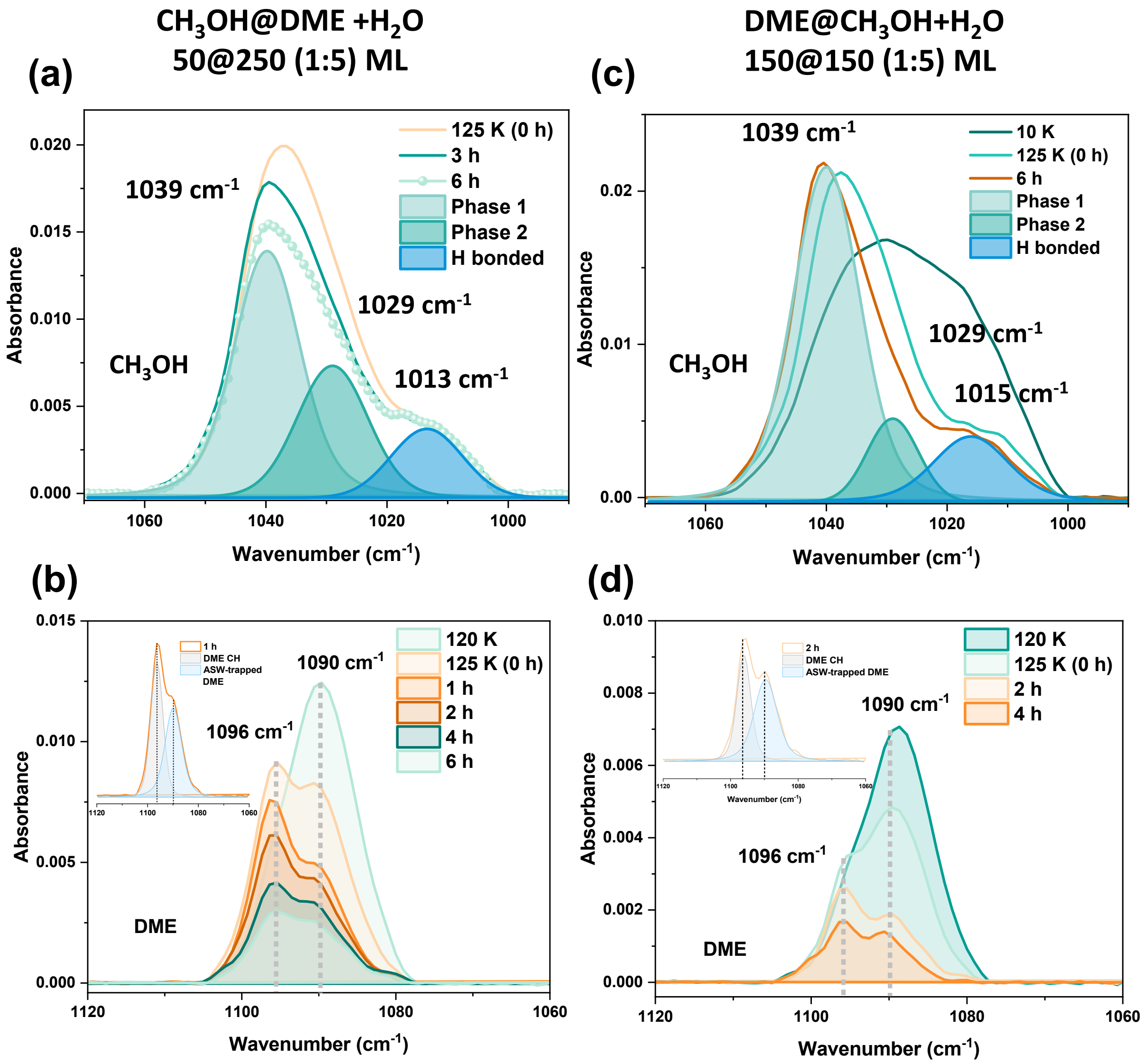


Figure S3. RAIR spectra of the mixed ices consisting of (a,b) 50 ML CH_3OH at the bottom, and a codeposited DME and H_2O layer at the top of 250 ML in 1:5 ratio (c,d) 150 ML DME at the bottom, and a co-deposited CH_3OH and H_2O layer at the top of 150 ML in 1:5 ratio. In the inset of (b, d) the deconvoluted spectra are shown.

Supporting information 4:

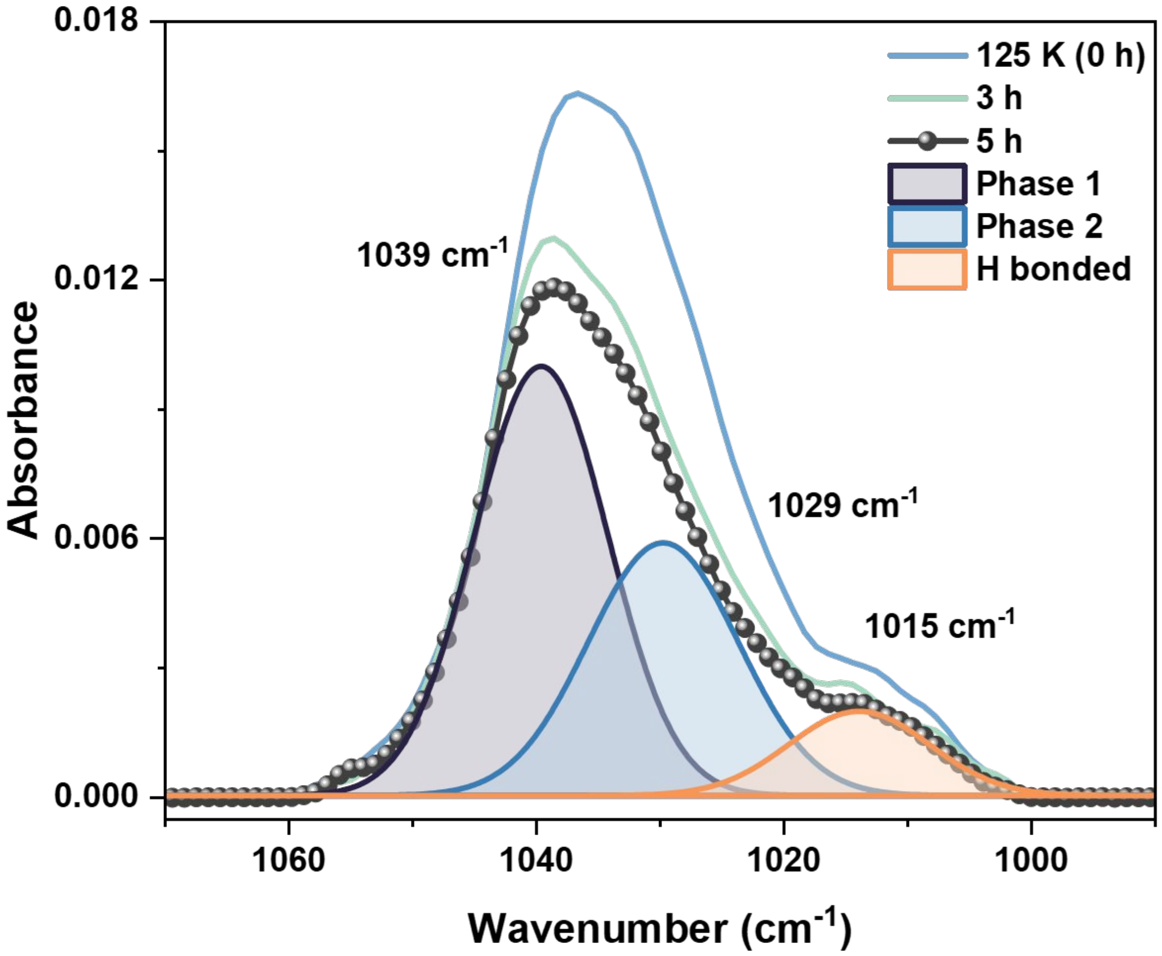


Figure S4. RAIR spectra of the mixed ices consisting of co-deposited DME and CH_3OH of 150 ML in a 1:2 ratio at the bottom, and a H_2O layer at the top of 150 ML.

Supporting information 5:

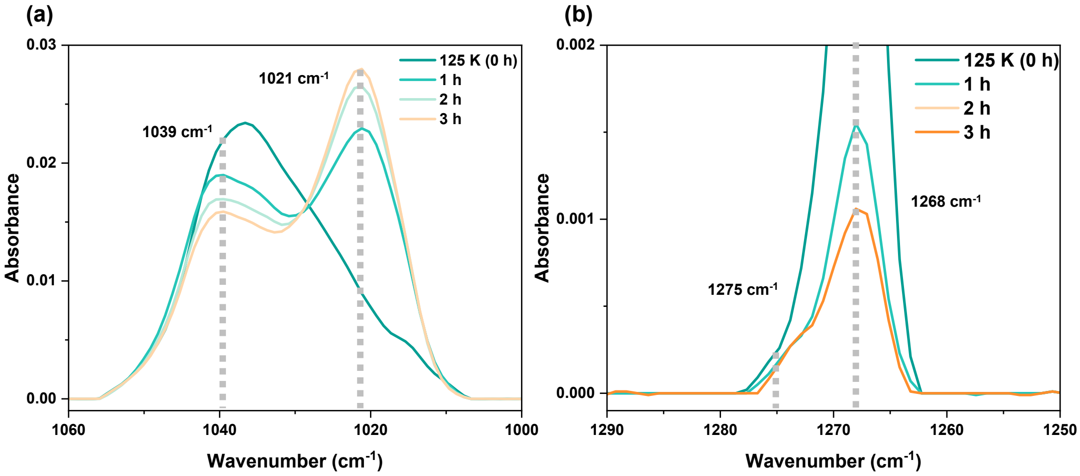


Figure S5. RAIR spectra of the mixed ices consisting of sequentially deposited ETO, CH_3OH, and H_2O of 150, 50, 150 ML, respectively. (a) CH_3OH C-O stretching region showing crystalline and CH of CH_3OH, and (b) ETO ring breathing region showing ETO CH.

Supporting information 6:

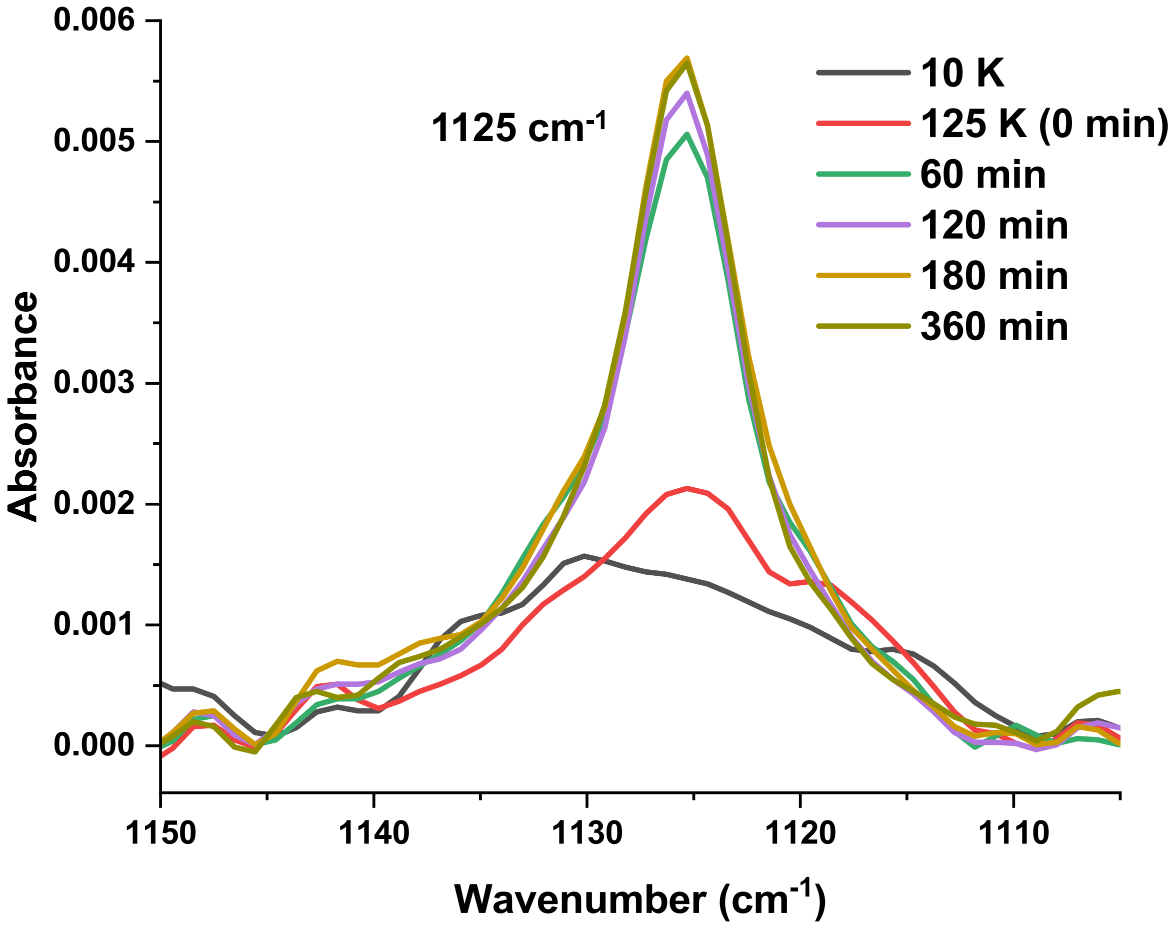


Figure S6. RAIR spectra of the layered ices consisting of sequentially deposited DME, CH_3OH, and H_2O of 150, 50, 150 ML, respectively, in the CH_3 rocking vibrational mode of CH_3OH.

Supporting information 7:

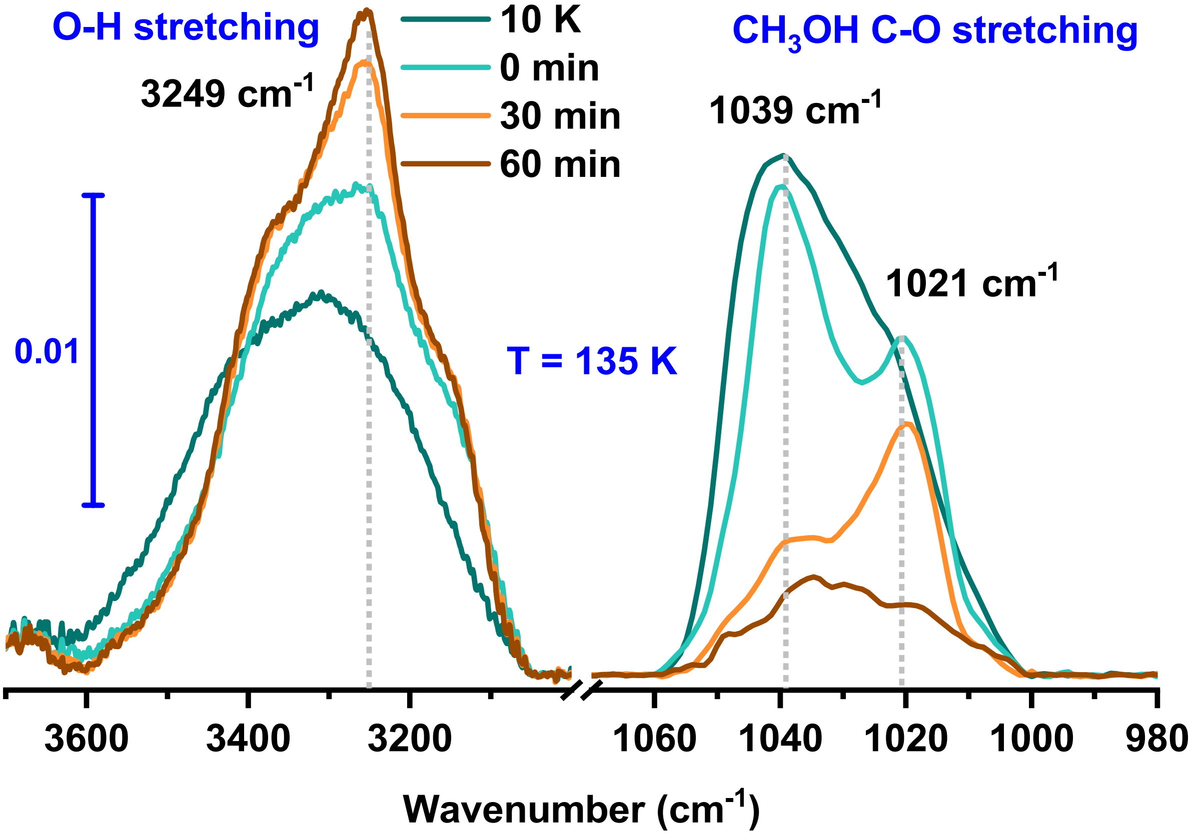


Figure S7. Time-dependent RAIR spectra of the layered ices at 135 K consisting of sequentially deposited DME, CH_3OH, and H_2O of 150, 50, 150 ML, in the O-H stretching, and CH3OH C-O stretching region.

Supporting information 8:

Table S1. Comparison of stabilization energies (kcal/mol) for methanol encapsulation in different clathrate cages

Clathrate Cage	Stabilization energy (in kcal/mol)
5^{12} CH_3OH	-5.89
$5^{12}6^{2}$ CH_3OH	-25.10
$5^{12}6^{4}$ CH_3OH	-11.21

References

(1) Bag, S.; Bhuin, R. G.; Methikkalam, R. R. J.; Pradeep, T.; Kephart, L.; Walker, J.; Kuchta, K.; Martin, D.; Wei, J. Development of Ultralow Energy (1-10 EV) Ion Scattering Spectrometry Coupled with Reflection Absorption Infrared Spectroscopy and Temperature Programmed Desorption for the Investigation of Molecular Solids. *Review of Scientific Instruments* **2014**, *85* (1), 14103. https://doi.org/10.1063/1.4848895.

(2) Chowdhury, S.; Malla, B. K.; Vishwakarma, G.; Nyayban, A.; Pradeep, T. Composition-Dependent Formation and Dissociation of Structure I and Structure II Clathrate Hydrates of Trimethylene Oxide in Ultrahigh Vacuum. *Journal of Physical Chemistry C* **2025**, *129* (19), 8937–8945. https://doi.org/10.1021/ACS.JPCC.5C01603.