Supporting Information

Growth of Clathrate Hydrates in Nanoscale Ice Films Observed Using Electron Diffraction and Infrared Spectroscopy

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Experimental Section

RHEED Setup

Details of the home-built UHV chamber system and the procedures for thin-film deposition and RHEED experiments have been described previously.[1–3] In this study, anhydrous THF (≥99.9%, inhibitor-free) and anhydrous DIOX (99.8%) were purchased from Sigma Aldrich and used without further purification. The pure compounds were loaded separately into a stainless-steel reservoir and then quickly connected to the effusion-type doser assembly, followed by several freeze-pump-thaw cycles to ensure the purity of the molecular sources. The UHV chamber for molecular depositions, annealing, and RHEED measurements had a base pressure of $<3\times10^{-10}$ mbar. The sample holder was coupled to a cryostat with an integrated heater. Using liquid nitrogen as the cryogen, the substrate reached ~100 K, whose temperature was directly measured by a K-type thermocouple at the surface. The deposition rate of immobilized molecules was a few nm/min at this low temperature. The deposited thin films then underwent thermal annealing with a typical ramp rate of ~1.3 K/min. The co-deposition method used premixed THF/DIOX and water vapors with a deposition time of 10 minutes. During the deposition, it was observed that a total of 134 seconds was required for the complete disappearance of the HOPG pattern. Considering the probe depth of RHEED (1-2 nm), it can be inferred that after 134 seconds, a homogeneous thin film of approximately 5 nm was formed. Given that the total deposition time was 600 seconds, this resulted in an estimated thin ice film thickness of approximately 25 nm. The substrate surfaces used for deposition and RHEED include highly oriented pyrolytic graphite (HOPG, ZYA grade), single-crystalline Au(111) (Princeton Scientific), and a hydrophobic self-assembled monolayer (SAM) of 1-octadecanethiol on Au(111). Methods of preparation of the substrate surfaces can be found in earlier reports.[3] The use of different substrates helped examine the possible effects of surface structures and affinities on the formation of CHs.

For RHEED, the kinetic energy of electron source was 30 keV, corresponding to a de Broglie wavelength of 0.07 Å. The electron diffraction patterns were recorded by an imaging assembly consisting of a phosphor screen fiber-coupled to an image intensifier and then a CMOS camera (Andor Zyla HF). The average flux of probe electrons was maintained at an extremely low level of <1 pA/mm^2 and confirmed to have no induced changes caused by electron impact or radiation damage within the measurement time. The typical image acquisition time was 1 second per frame

during thermal annealing of the deposited thin films. Given the large electron–matter scattering cross-section, the probe depth of RHEED was only up to a few nm at the typical angle of grazing incidence of ~1°. The surface sensitivity of RHEED signifies the formation of CHs at the top of a film, not within the bulk.

RAIRS Setup

All the RAIRS experiments were carried out in a custom-built ultrahigh vacuum (UHV) instrument with a base pressure of ~5×10^{-10} mbar, discussed in detail in our previous reports.[4,5] Millipore water (H_2O of 18.2 MΩ resistivity) and THF/DIOX (purity ≥ 99.9/99.8 %, anhydrous, Sigma Aldrich) were taken in two separate vacuum-sealed test tubes (with a glass-to-metal seal) and were further purified by several freeze-pump-thaw cycles. Water and THF/DIOX are connected to the vacuum chamber through separate sample inlet lines. The deposition of two samples is controlled through all metal leak valves. A highly polished Ru(0001) single crystal was used as the substrate for creating thin ice films. The substrate was connected to a helium cryostat (ColdEdge Technologies), providing temperature cool down to 8 K. Temperatures ranging from 8 K to 400 K were achieved using a resistive heater (25 Ω), which was regulated by a temperature controller (Lakeshore 336). The vapor deposition coverage in the case of N_2 (ion gauge sensitivity factor - 1) was expressed in ML, assuming 1.33×10^{-6} mbar s = 1 ML, which was estimated to contain ~1.1×10^{15} molecules cm^{-2}, as outlined in other reports.[1,2] A mixed ice was prepared on Ru(0001) substrate at 105 K by backfilling THF/DIOX-water vapor for 10 min at a total pressure of 5×10^{-7} mbar where THF/DIOX and water contributed equally.[3] Taking into account the ion gauge sensitivity factors for water (0.97), THF (3.29), and DIOX (3.5), 150 ML of water and 45 ML of THF/DIOX were co-deposited with a THF/DIOX-to-water ratio of 1:3.[2] Based on the molecular diameters, this corresponds to approximately 37 nm of water and 23 nm of THF/DIOX, resulting in a total thin ice film thickness of about 60 nm. Considering potential inaccuracies in pressure readings and variations in the sticking coefficient at different temperatures, there may be an error of few nm in the calculated thickness values.

. During vapor deposition, mass spectra were recorded simultaneously to check the purity and the ratio of the deposited molecules. RAIR spectra were collected in the 4000−550 cm^{-1} range with a spectral resolution of 2 cm^{-1} using a Bruker Vertex 70 FT-IR spectrometer with a liquid-nitrogen-

cooled mercury cadmium telluride (MCT) detector. The IR beam path outside the UHV chamber was purged with dry nitrogen gas.

Supporting Information 1

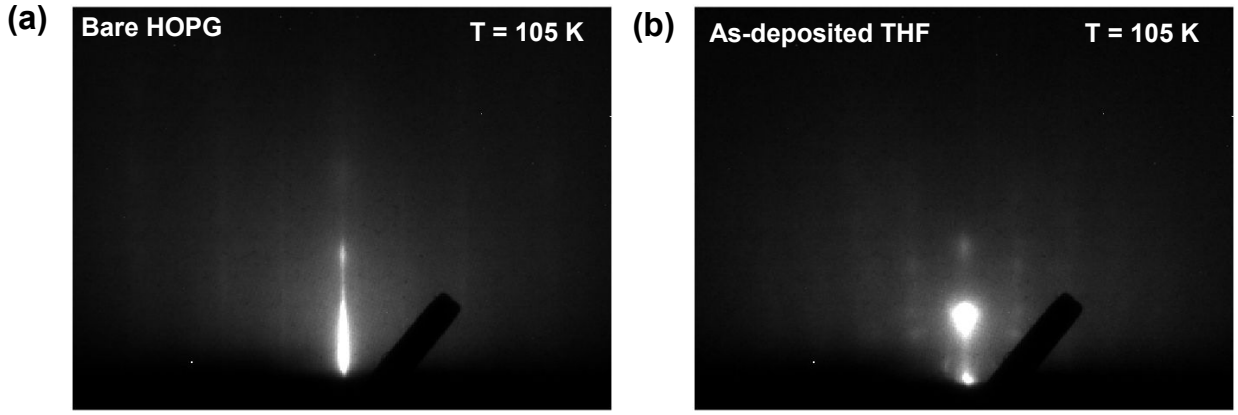

Figure S1. (a) RHEED image of bare HOPG substrate at 105 K. (b) RHEED image of as-deposited pure THF on HOPG substrate at 105 K.

Supporting Information 2

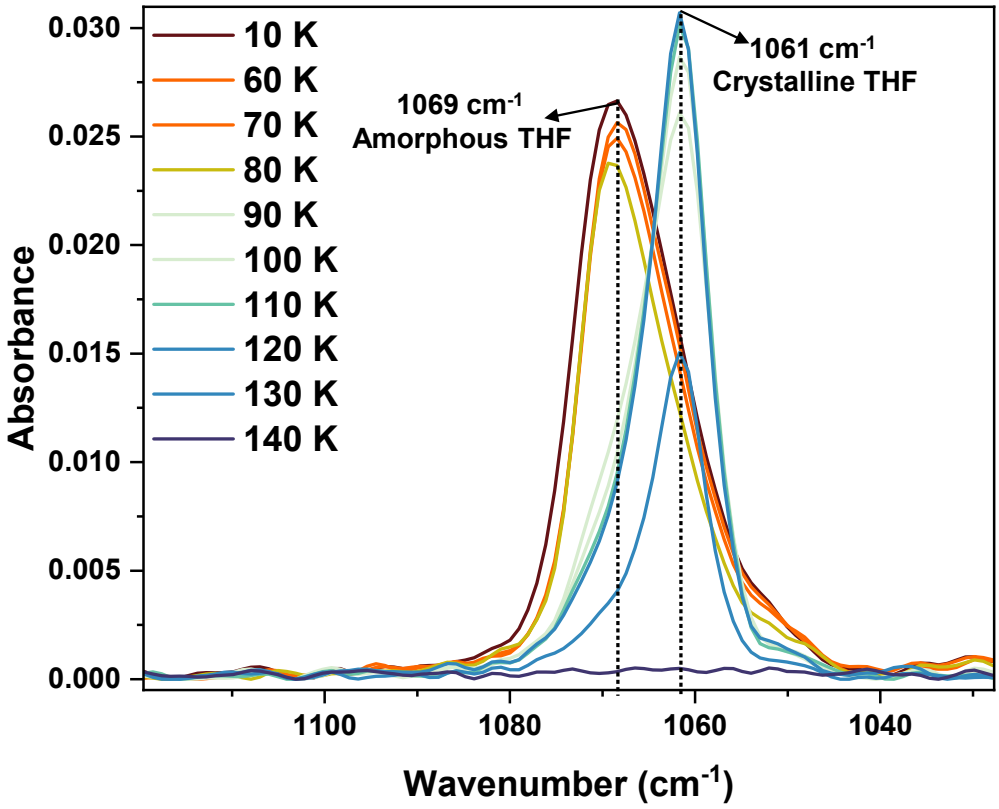

Figure S2. Temperature-dependent RAIR spectra of 150 ML of pure THF ice in C-O antisymmetric stretching region. Pure THF ice was prepared by vapor deposition on a Ru(0001) substrate at 10 K. The sample was then annealed to 140 K at a rate of 2 K/min.

Supporting Information 3

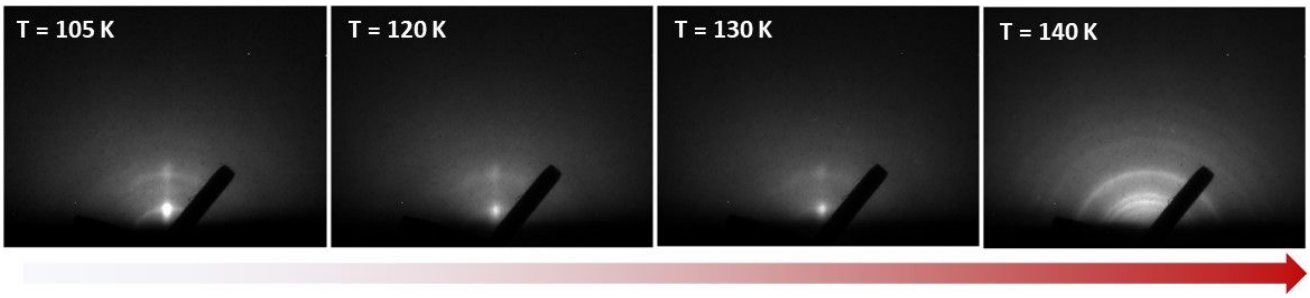

Figure S3. Temperature-dependent RHEED images of THF-water mixed vapor deposited on HOPG at 105 K, followed by thermal annealing.

Supporting Information 4

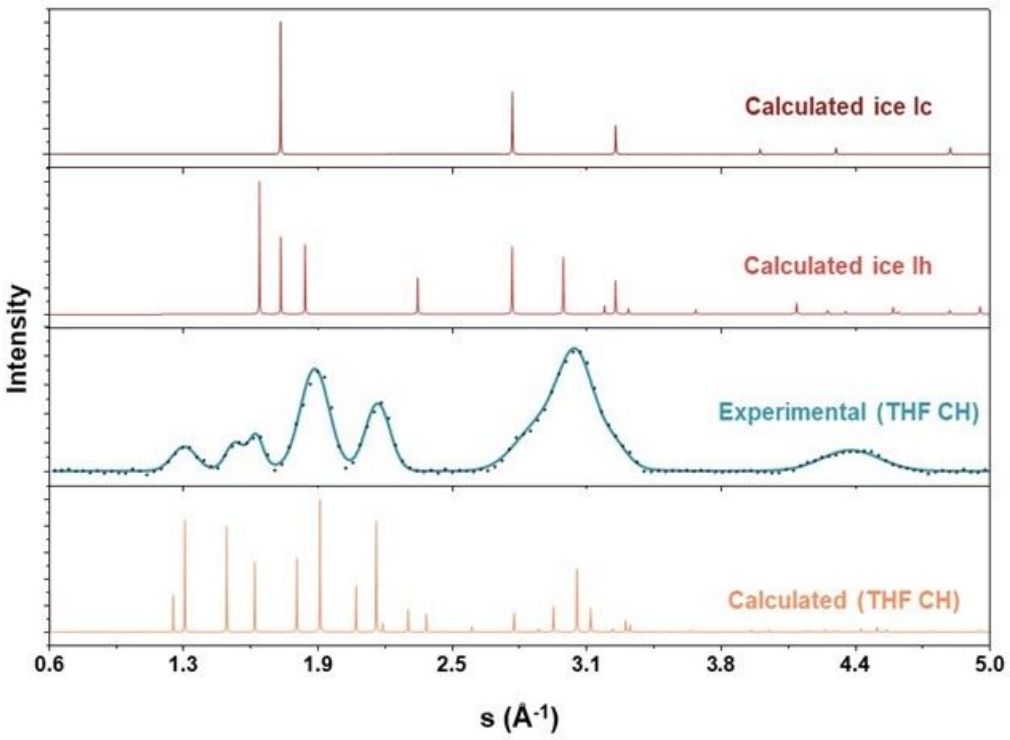

Figure S4. Comparison of the experimental radially-averaged electron diffractions of annealed THF-water ice at 140 K with the calculated diffraction peaks of sII THF CH, ice Ic, and ice Ih.

Supporting Information 5

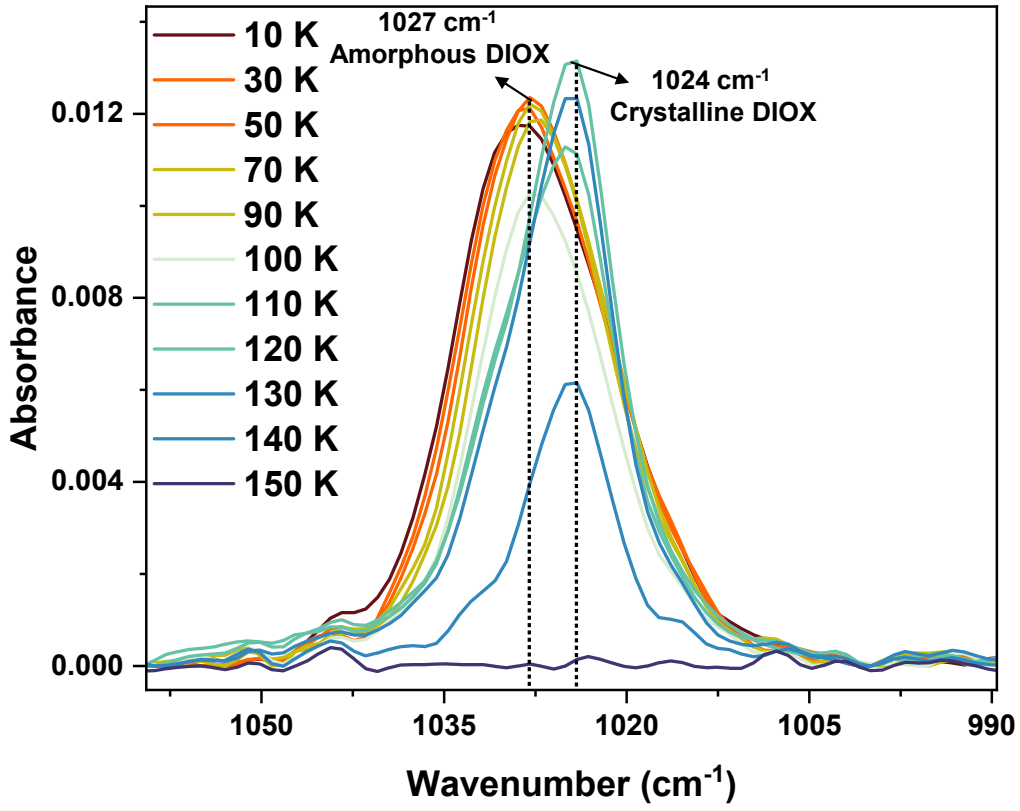

Figure S5. Temperature-dependent RAIR spectra of 150 ML of pure DIOX ice in C-O antisymmetric stretching region. Pure DIOX ice was prepared by vapor deposition on a Ru(0001) substrate at 10 K. The sample was then annealed to 140 K at a rate of 2 K/min.

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