Dissociation and Reformation of CO₂ Clathrate Hydrate cages in Amorphous Ice Thin Film under Ultrahigh Vacuum

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This PDF file includes:

Experimental section (pages S2-S4)

Figure S1 to S6 (pages S5-S10)

Reference (pages S11)

Experimental Section

In this study, all experiments were carried out in an ultrahigh vacuum (UHV) instrument (with a base pressure of ~ 5×10^{-10} mbar), discussed in detail in our previous literature.^{1,2} The apparatus comprises three ultra-high vacuum (UHV) chambers: ionization, octupole, and scattering. It is equipped with various analytical techniques, including reflection absorption infrared spectroscopy (RAIRs), low energy ion scattering (LEIS), temperature-programmed desorption (TPD) mass spectrometry, and Cs⁺ ion-based secondary ion mass spectrometry (SIMS). A vacuum ultraviolet (VUV) lamp is also integrated into the setup. Six turbomolecular pumps are employed to create UHV, complemented by multiple oil-free diaphragm pumps. The chamber pressure is monitored through a Bayard-Alpert gauge, regulated by a MaxiGauge vacuum gauge controller (Pfeiffer, Model TPG 256 A). A highly polished Ru(0001) single crystal was used as the substrate to create thin ice films that was mounted on a copper holder. This assembly was connected to a helium cryostat (Cold Edge technology) capable of maintaining temperatures as low as 8 K. To heat the substrate to 1000 K, a resistive heater (25 Ω) under the control of a temperature controller (Lakeshore 336) was utilized. The temperature of the substrate was measured using a K-type thermocouple sensor with an accuracy of ± 0.5 K. Repeated heating to 400 K before each vapor deposition ensured a clean surface suitable for the current study. It is worth noting that the surface has a negligible role in the current study, as our experiments were on multilayer ice films.

RAIRS and TPD-MS Setup

The RAIRS data was collected in the 4000–550 cm⁻¹ range with a spectral resolution of 2 cm⁻¹, using a Bruker FT-IR spectrometer called Vertex 70. The ice sample was exposed to an incident angle of $80^0 \pm 7^0$ by focusing the IR beam through a ZnSe viewport. The reflected IR beam from the sample was detected by using a liquid N₂-cooled mercury cadmium telluride (MCT) detector. The IR beam outside the vacuum chamber was purged with dry N₂ to prevent absorption by atmospheric moisture. Each RAIR spectrum was obtained by averaging over 512 scans to improve the signal-to-noise ratio. An Extrel quadrupole mass spectrometer was used for TPD-MS in an out-of-sight configuration.

Materials and reagents

CO₂ gas (99.99%) was purchased from Indogas and used without further purification. Tetrahydrofuran (THF) (99.8%) was purchased from Thermo Fisher Scientific India Pvt. Ltd., and Millipore water (H₂O of 18.2 M Ω resistivity) was kept in a vacuum-sealed test tube and was further purified by several freeze-pump-thaw cycles. DME (99.9%, Sigma-Aldrich) was used without further purification.

Sample preparations

Thin ice films were prepared by vapor deposition of different molecules at 10 K on a Ru(0001) substrate. Two sample inlet lines were attached to the UHV chamber through high-precision all-metal leak valves. Out of two sample lines, one was used for CO₂/THF, and the other was used for H₂O/DME. These lines can be interchanged between each other. All the lines are connected to one rotary pump for cleaning purposes. When two molecules were used through a single line, we made sure that before filling each gas, sample lines were evacuated to a maximum pressure of 1×10^{-2} mbar. Further purity of each molecule was confirmed by the presence of their distinctive molecular ion peaks in the mass spectrum using a residual gas analyzer. The vapor deposition coverage was expressed in monolayers (ML), assuming that 1.33×10^{-6} mbar s = 1 ML, estimated to contain $\sim 1.1 \times 10^{15}$ molecules cm⁻², as followed in our earlier studies.^{3,4}

CO₂+H₂O (300 ML) (1:10)

To prepare CO_2 +water ice mixture thin film, the UHV chamber was backfilled to a total pressure of 5×10^{-7} mbar of CO_2 and water vapors for 10 min, with CO_2 pressure reaching 0.5×10^{-7} mbar and water pressure also maintained at 4.5×10^{-7} mbar approximately.

DME (150 ML) @ CO₂+H₂O (150 ML) (1:10)

To form DME (150 ML) @ CO_2 +H₂O (150 ML) (1:10) layered ice, at first, 150 ML of DME was deposited on the substrate by backfilling DME vapors at a pressure of 5×10⁻⁷ mbar for 5 min. Subsequently, a waiting period ensued to allow the UHV chamber pressure to return to base pressure. Then, on the top of DME ice-thin film, 150 ML of CO₂ and H₂O vapors were codeposited at a ratio of 1:10. For this, UHV chamber was backfilled to a total pressure of 5 × 10⁻⁷ mbar for 5

min, with CO₂ reaching 0.5×10^{-7} mbar and water pressure also maintained at 4.5×10^{-7} mbar approximately.

THF (50 ML) @ CO₂+H₂O (250 ML) (1:10)

To form THF (50 ML) @ CO_2 +H₂O (250 ML) (1:10) layered ice, 50 ML of THF was deposited on the substrate by backfilling THF vapors at a pressure of 5×10⁻⁷ mbar for 1 min 40 sec. Subsequently, a waiting period ensued to allow the UHV chamber pressure to return to 5×10⁻¹⁰ mbar. Then, on the top of the THF ice-thin film, 250 ML of CO₂ and H₂O were co-deposited at a ratio of 1:10. For this, again, we backfilled the UHV chamber to a total pressure of 5 × 10⁻⁷ mbar for 8 min 20 sec, with CO₂ reaching 0.5 × 10⁻⁷ mbar and water pressure also maintained at 4.5 × 10⁻⁷ mbar approximately.

THF (50 ML) @ DME (50 ML)@CO₂+H₂O (200 ML) (1:10)

For the formation of THF (50 ML) @ DME (50 ML)@ CO_2+H_2O (200 ML) (1:10) layered ice, 50 ML of THF was deposited on the substrate by backfilling THF vapors at a pressure of 5×10^{-7} mbar for 1 min 40 sec. Subsequently, 50 ML of DME was deposited atop the THF layer by backfilling DME vapors at a pressure of 5×10^{-7} mbar for 1 min 40 sec. Then, on the top of DME, 200 ML of CO₂ and H₂O codeposited at a ratio of 1:10. For this, again we backfilled the UHV chamber to a total pressure of 5×10^{-7} mbar for 6 min 40 sec, with CO₂ reaching 0.5×10^{-7} mbar and water pressure also maintained at 4.5×10^{-7} mbar approximately.

Supporting Information 1:



Figure S1. Temperature and time-dependent RAIR spectra of 300 ML of CO_2+H_2O (1:10) ice mixture. The ice sample was prepared by vapor deposition on Ru(0001) substrate at 10 K, then annealed to 130 K, and subsequently held at the same condition for 6 h.



Supporting Information 2:

Figure S2. Temperature-dependent RAIR spectra of DME (150 ML)@(CO_2+H_2O) (1:10) (150 ML) mixed ice in (a) C=O antisymmetric stretching region for CO₂, (b) C-O antisymmetric stretching region for DME. Time-dependent RAIR spectra of DME (150 ML)@(CO_2+H_2O) (1:10) (150 ML) mixed ice at 130 K in (a) C=O antisymmetric stretching region for CO₂, (b) C-O antisymmetric stretching region for CO₂, (b) C-O antisymmetric stretching region for CO₂, (b) C-O antisymmetric stretching region for CO₂, (c) C-O antisymmetric stretching region for CO₂, (b) C-O antisymmetric stretching region for CO₂, (c) C-O antisymmetric stretching region for DME.

Supporting Information 3:



Figure S3. Time and temperature dependent RAIR spectra of DME (150 ML)@(CO_2+H_2O) (1:10) (150 ML) mixed ice in O-H stretching region.

Supporting Information 4:



Figure S4. Temperature-dependent RAIR spectra of THF (50 ML)@(CO_2+H_2O) (1:10) (250 ML) mixed ice in (a) C=O antisymmetric stretching region for CO₂, (b) C-O antisymmetric stretching region for THF. Time-dependent RAIR spectra of THF (50 ML)@(CO_2+H_2O) (1:10) (250 ML) mixed ice at 130 K in (a) C=O antisymmetric stretching region for CO₂, (b) C-O antisymmetric stretching region for THF.

Supporting Information 5:



Figure S5: Time-dependent RAIR spectra of DME (150 ML)@(CO_2+H_2O) (1:10) (150 ML) mixed ice at 115 K in (a) C=O antisymmetric stretching region for CO₂, (b) C-O antisymmetric stretching region for DME.

Supporting Information 6:



Figure S6. Time-dependent RAIR spectra of THF (50 ML)@DME (50 ML)@(CO_2+H_2O) (1:10) (100 ML) mixed ice in (a) C=O antisymmetric stretching region for CO₂, (b) C-O antisymmetric stretching region for THF and DME at 130 K.

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