Supplementary Information

Ultraviolet Photolysis of CO_2 Clathrate Hydrate and H_2O-CO_2 Mixed Ice under Ultrahigh Vacuum

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Supplementary Information 1

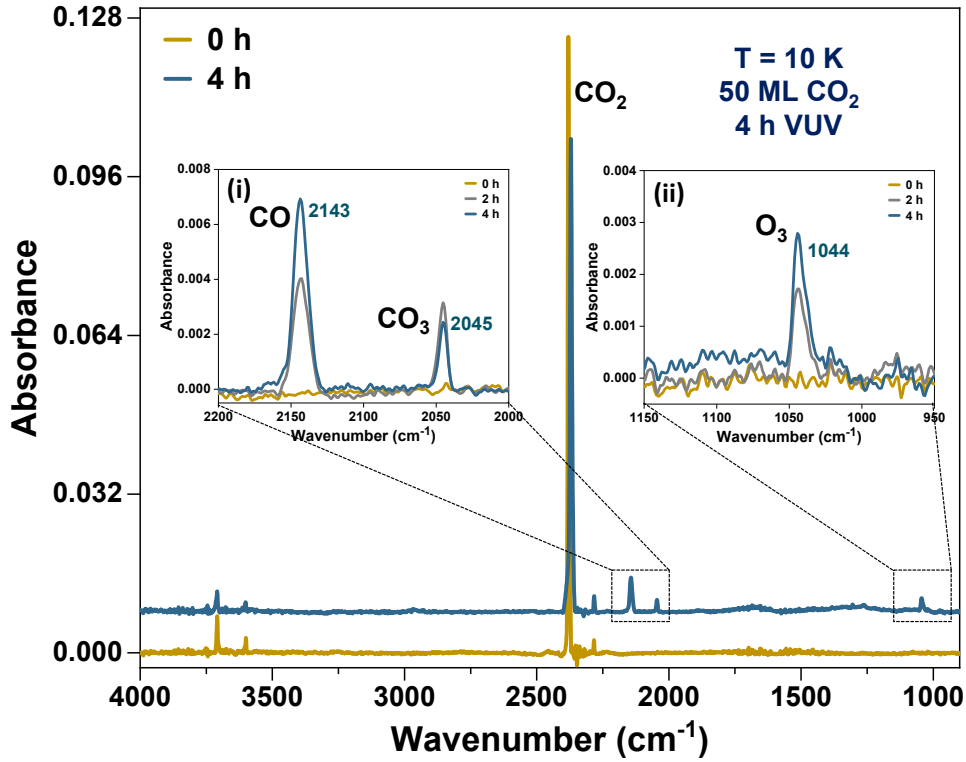

Fig. S1. RAIR spectra recorded before (golden trace) and after 4 h of photolysis (blue trace) of ~50 ML pure CO_2 ice at 10 K. For this, ~50 ML of pure CO_2 ice was prepared by vapor deposition at 10 K and photolyzed by VUV for 4 h. The photon-induced products detected by RAIR were CO (2143 cm^{-1}), CO_3 (2045 cm^{-1}), and O_3 (1044 cm^{-1}). The peak assignments are consistent with previous studies.[1,2] The inset (i) illustrates the evolution of CO and CO_3. CO production steadily increases over time, while CO_3 initially rises before declining. Similarly, inset (ii) shows the production of O_3 which increases with prolonged exposure to VUV. By estimating the area under the curve of 3708 cm^{-1} peak, we calculated the column density of CO_2 (band strength of 3708 cm^{-1} = 1.4 × 10^{-18} cm $molecule^{-1}$)[3] and found that after subjecting the pure CO_2 ice to VUV exposure for 4 h, approximately 19.51% of the total CO_2 was depleted.

Supplementary Information 2

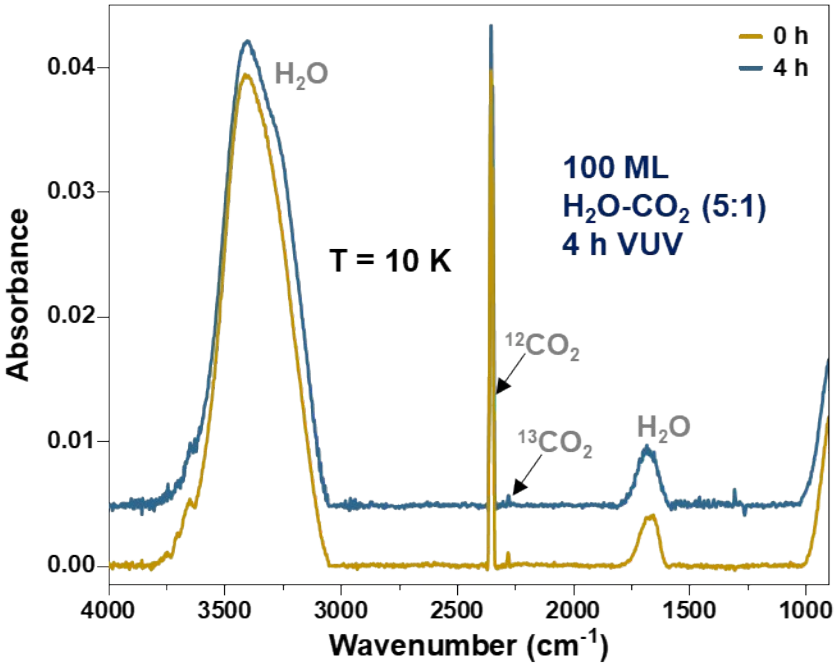

Fig. S2. RAIR spectra of ~100 ML H_2O-CO_2 (5:1) ice before and after VUV exposure in the full range, 4000-1000 cm^{-1}. Ice sample was prepared by vapor deposition at 10 K and photolyzed for 4 h. RAIR spectra were collected at regular intervals. No photon-induced products were detected by RAIRS.

Supplementary Information 3

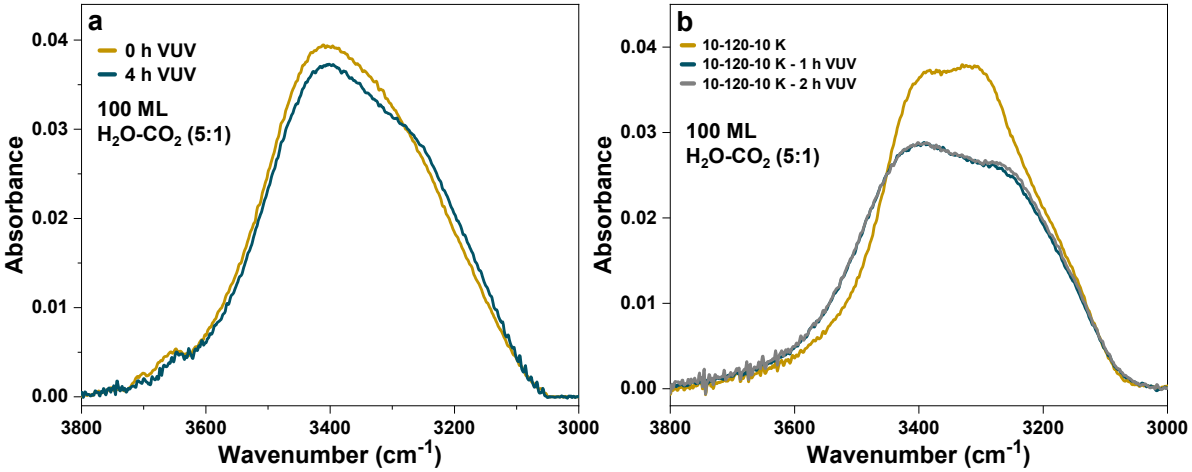

Fig. S3. RAIR spectra of ~100 ML H_2O-CO_2 (5:1) mixed ice in the O-H stretching region: (a) before and after VUV exposure at 10 K, and (b) after annealing to 120 K, cooling back to 10 K, and subsequent 2 h of VUV photolysis at 10 K. The greater intensity decrease in (b) compared to (a) occurs because annealing to 120 K orders H_2O molecules, which then undergo disordering during VUV photolysis.

Supplementary Information 4

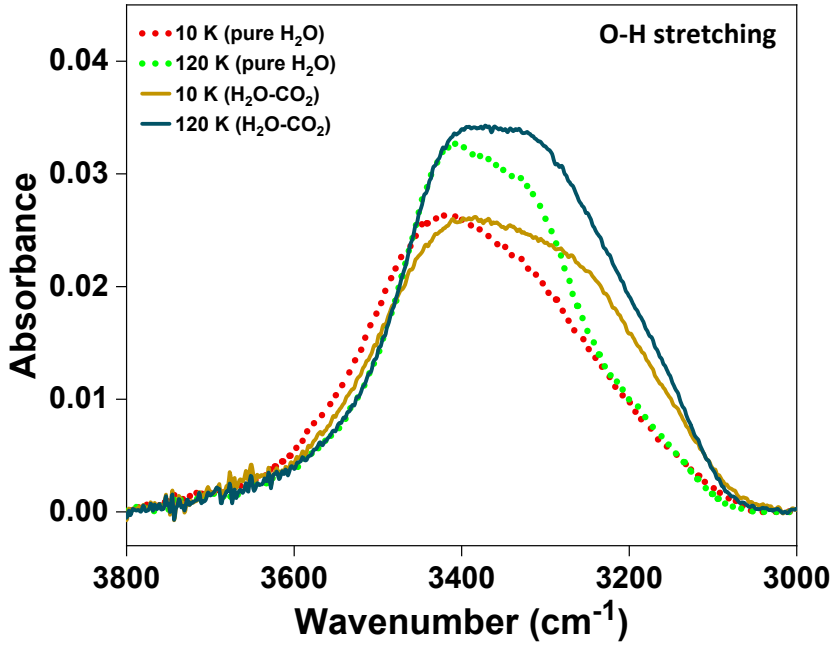

Fig. S4. Comparison of RAIR spectra in the O-H stretching bands of pure water (dotted lines) and H_2O-CO_2 (5:1) mixture (solid lines) at 10 and 120 K. The change in shape and intensity of the O-H stretching band in the presence of CO_2 at 10 and 120 K suggests the formation of CO_2 sI CH.[4]

Supplementary Information 5

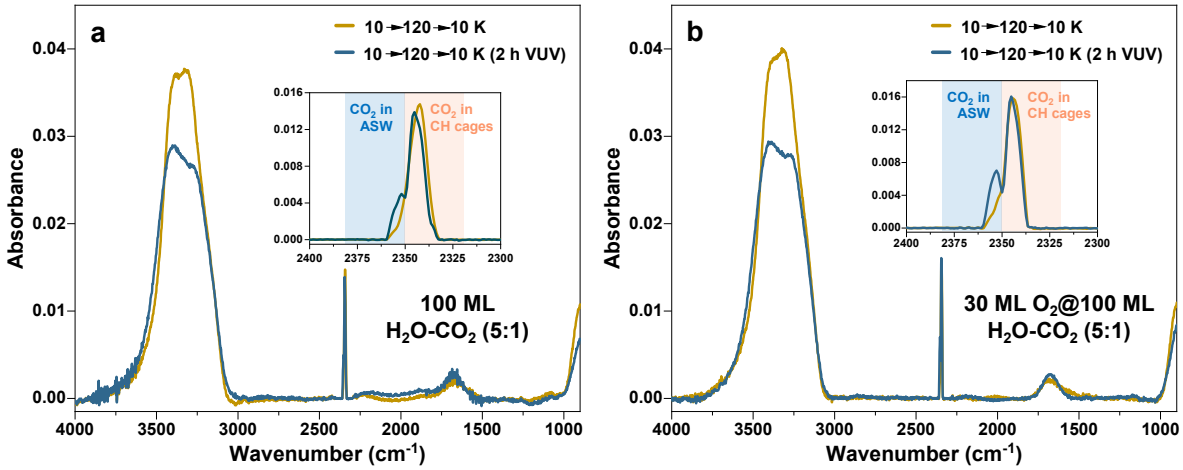

Fig. S5. Full range RAIR spectra of (a) ~100 ML H_2O-CO_2 (5:1) ice, and (b) ~30 ML O_2@100 ML H_2O-CO_2 (5:1) composite film at 10 K before and after VUV exposure. In both cases, sample was prepared by vapor deposition at 10 K. The resulting ice was heated at rate of 5 K min^{-1} to 120 K, and cooled down to 10 K. Then, the ice sample was exposed to VUV for 2 h and RAIR spectra were collected at regular intervals. Insets in both (a) and (b) show the reduction in the area under the curve for CH peaks while increase for CO_2 in ASW, which depicts CH decomposition and migration of CO_2 to the water matrix. For the H_2O-CO_2 (5:1) ice containing a small fraction of O_2, the decomposition of CH was slightly higher, as presented in the inset of (b). For ~100 ML H_2O-CO_2 (5:1) ice, the ice was prepared on Ru(0001) by codeposition of CO_2 gas and H_2O vapor at 10 K. The ~30 ML O_2@100 ML H_2O-CO_2 (5:1) composite film was prepared by first creating 30 ML of O_2 ice on Ru(0001) followed by codeposition of ~100 ML H_2O-CO_2 (5:1) mixture on top of it.

References

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