Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Partitioning Photochemically Formed CO_2 into Clathrate Hydrate under Interstellar Conditions

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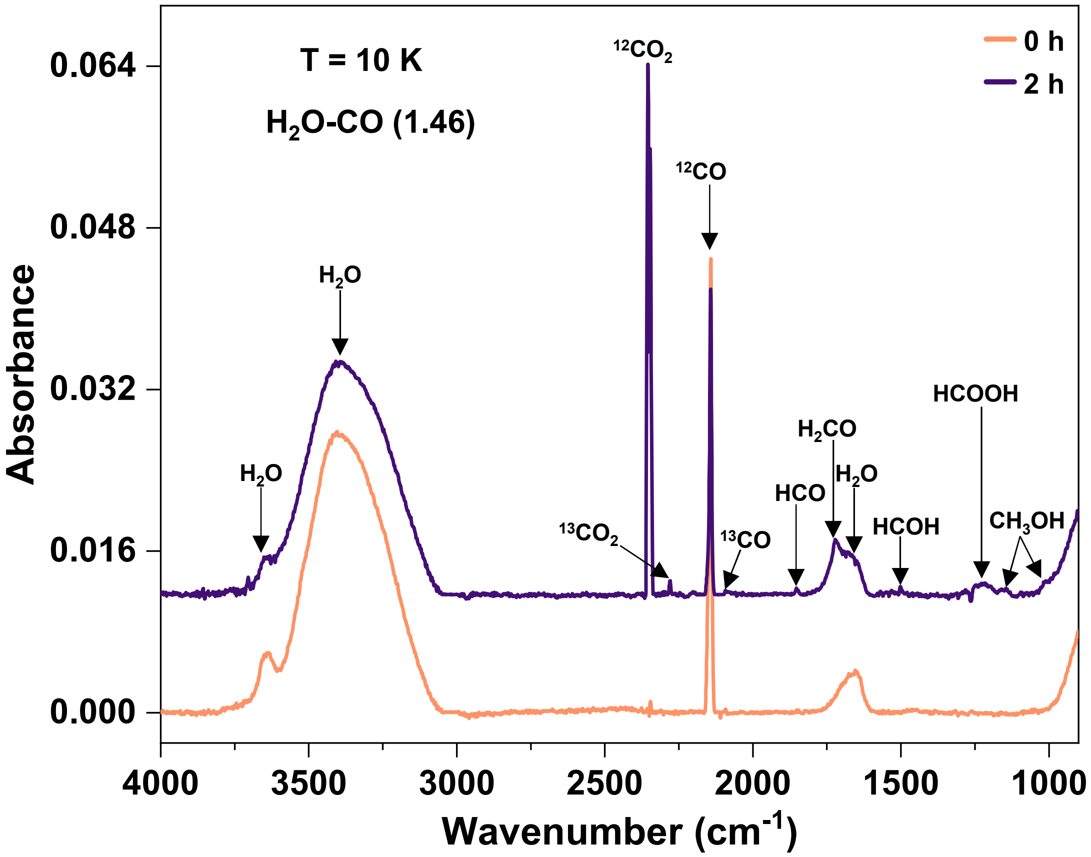

Fig. S1. Full range RAIR spectra of 100 ML H_2O-CO (1.46) mixture before and after VUV irradiation at 10 K. The ice mixture was co-deposited on Ru(0001) at 10 K, and the resulting sample was exposed to VUV irradiation for 2 h.

Table S1. Photochemical products obtained during 2 h of VUV irradiation of 100 ML H_2O-CO (1.46) mixture at 10 K

Position (cm^{-1})	**Vibrational Mode**	**Molecule**
~3704	Combination	CO_2
~3648	OH dangling	H_2O
~3400	OH stretch	H_2O
2353, 2346	^{12}CO stretch	CO_2
2282, 2278	^{13}CO stretch	$^{13}CO_2$
2149, 2141	^{12}CO stretch	CO
2092	^{13}CO stretch	^{13}CO
1850	CO stretch	HCO
1721	CO stretch	H_2CO
~1650	HOH bending	H_2O
1500	H_2 scissor	H_2CO
1219	C-O stretch	HCOOH
1140	CH_3 rocking	CH_3OH
1017	C-O stretch	CH_3OH

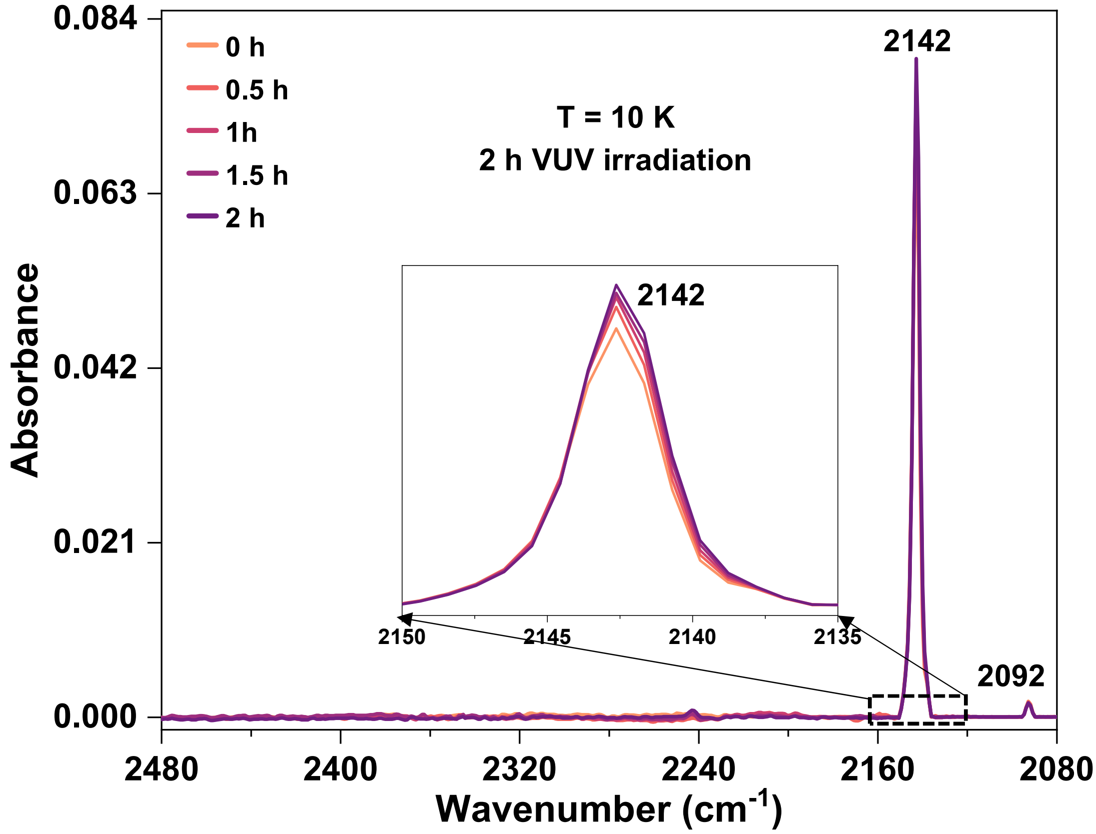

Fig. S2. Irradiation time-dependent RAIR spectra of 50 ML pure CO ice at 10 K in the 2480-2080 cm^{-1} region. Before VUV irradiation, a peak at 2142 cm^{-1} was observed for pure CO ice. During irradiation, we could not observe a decrease in the intensity of the peak at 2142 cm^{-1}; instead, a very small increase was observed, as presented in inset. This may be due to the background deposition of CO on the ice sample with time or physical changes induced by VUV photons.

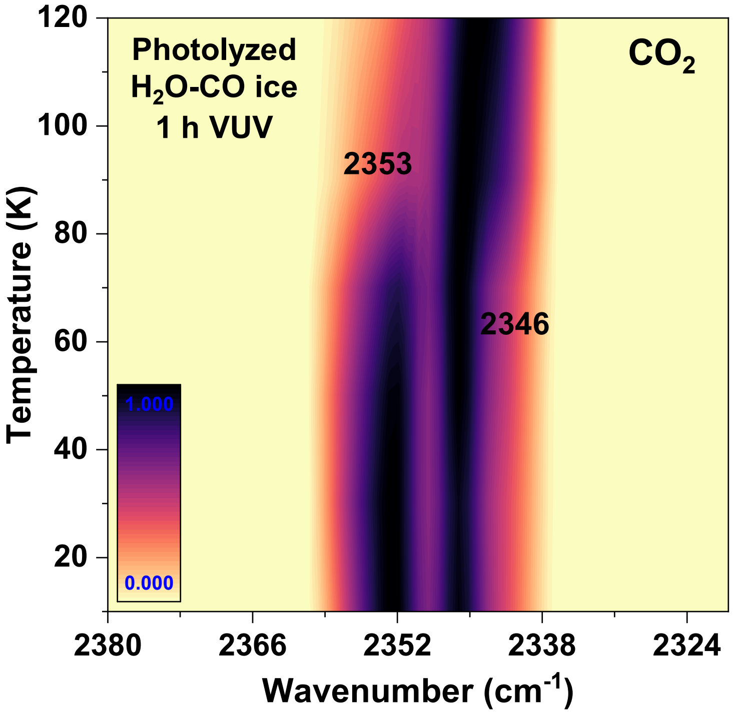

Fig. S3. Temperature-dependent normalized RAIR spectra of photolyzed 50 ML H_2O-CO (~4) ice in the 10−120 K window in the C=O antisymmetric stretching region of CO_2. The ice sample was prepared by co-depositing H_2O and CO vapors on Ru(0001) at 10 K. The as-prepared ice sample was photolyzed by VUV for 1 h. After photolysis at 10 K, the ice sample was heated at a rate of 5 K min^{-1} to 120 K, and RAIR spectra were collected at regular intervals. When the sample was heated beyond the desorption temperature of CO_2, around 90 K, the peak at 2353 cm^{-1} disappeared, while the peak at 2346 cm^{-1} persisted. This confirms our identification of the 2353 cm^{-1} peak as CO_2 trapped within the water matrix and the 2346 cm^{-1} peak as CO_2 confined inside the CH cage (5^{12} cage of sI).

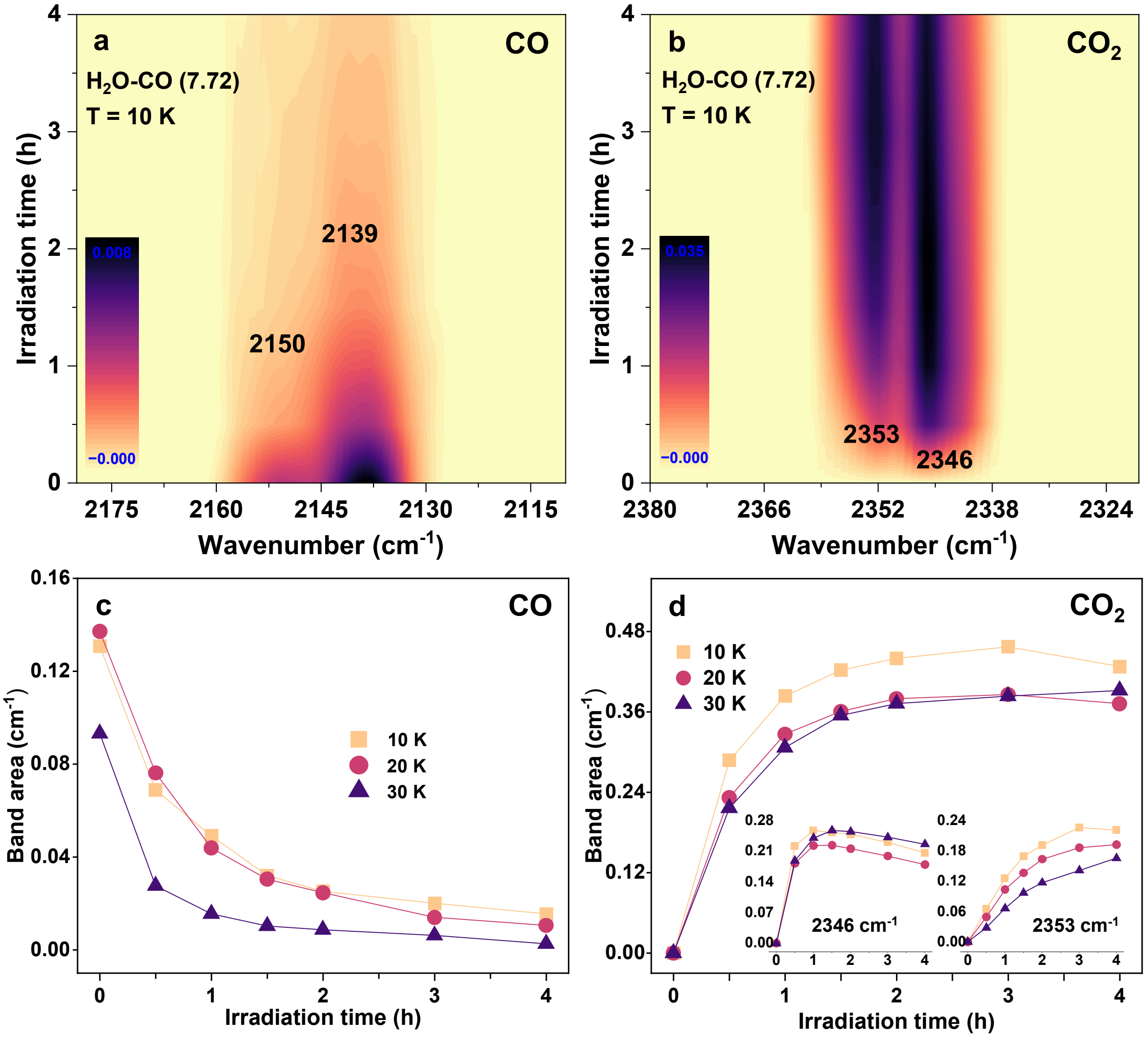

Fig. S4. Irradiation time-dependent RAIR spectra of 100 ML H_2O-CO (7.72) mixture at 10 K in the (**a**) C=O stretching region of CO and (**b**) C=O antisymmetric stretching region of CO_2. (**c**) Evolution of C=O stretching region of CO during VUV irradiation of H_2O-CO mixture. Integrated area of the 2180-2110 cm^{-1} band was plotted as a function of irradiation time for experiments carried out at 10 (yellow square), 20 (red circle), and 30 K (blue triangle). (**d**) Evolution of C=O antisymmetric stretching region of CO_2 during VUV irradiation of H_2O-CO mixture. Integrated area of the 2380-2320 cm^{-1} band was plotted as a function of irradiation time for experiments carried out at 10 (yellow square), 20 (red circle), and 30 K (blue triangle). Inset plots show the evolution of 2346 cm^{-1} (CO_2 in CH phase) and 2353 cm^{-1} (CO_2 in ASW phase) bands as a function of irradiation time, derived by deconvoluting the 2380-2320 cm^{-1} band. In Figs. (**c**) and (**d**), lines are only to guide the eye.

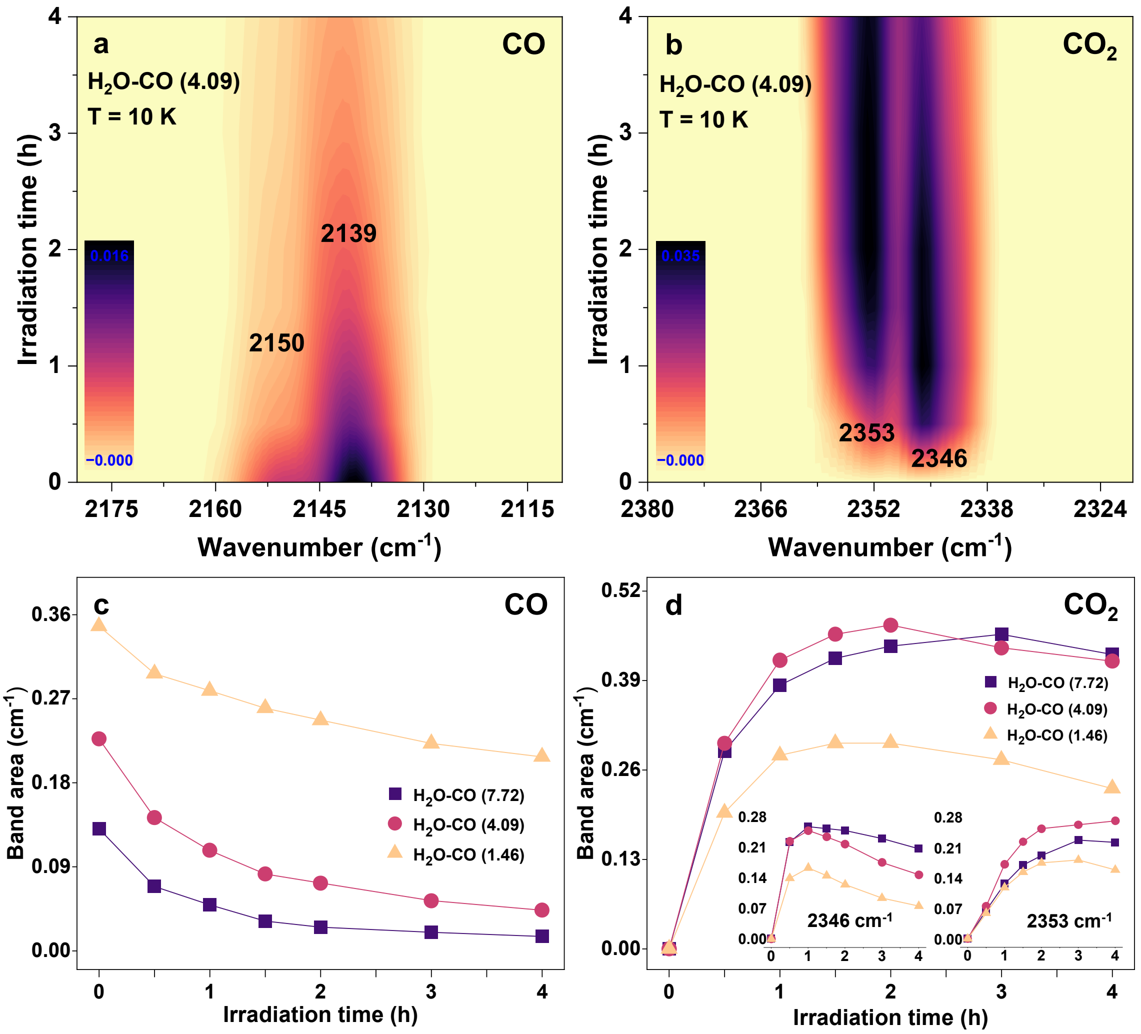

Fig. S5. Irradiation time-dependent RAIR spectra of 100 ML H_2O-CO (4.09) mixture at 10 K in the (**a**) C=O stretching region of CO and (**b**) C=O antisymmetric stretching region of CO_2. (**c**) Evolution of C=O stretching region of CO during VUV irradiation of H_2O-CO mixture. Integrated area of the 2180-2110 cm^{-1} band was plotted as a function of irradiation time for experiments carried out with ice mixtures having H_2O to CO ratios, 1.46 (yellow triangle), 4.09 (red circle), and 7.72 (blue square). (**d**) Evolution of C=O antisymmetric stretching region of CO_2 during VUV irradiation of H_2O-CO mixture. Integrated area of the 2380-2320 cm^{-1} band was plotted as a function of irradiation time for experiments carried out with ice mixtures having H_2O to CO ratios, 1.46 (yellow triangle), 4.09 (red circle), and 7.72 (blue square). Inset plots show the evolution of 2346 cm^{-1} (CO_2 in CH phase) and 2353 cm^{-1} (CO_2 in ASW phase) bands as a function of irradiation time, derived by deconvoluting the 2380-2320 cm^{-1} band. In Figs. (**c**) and (**d**), lines are only to guide the eye.

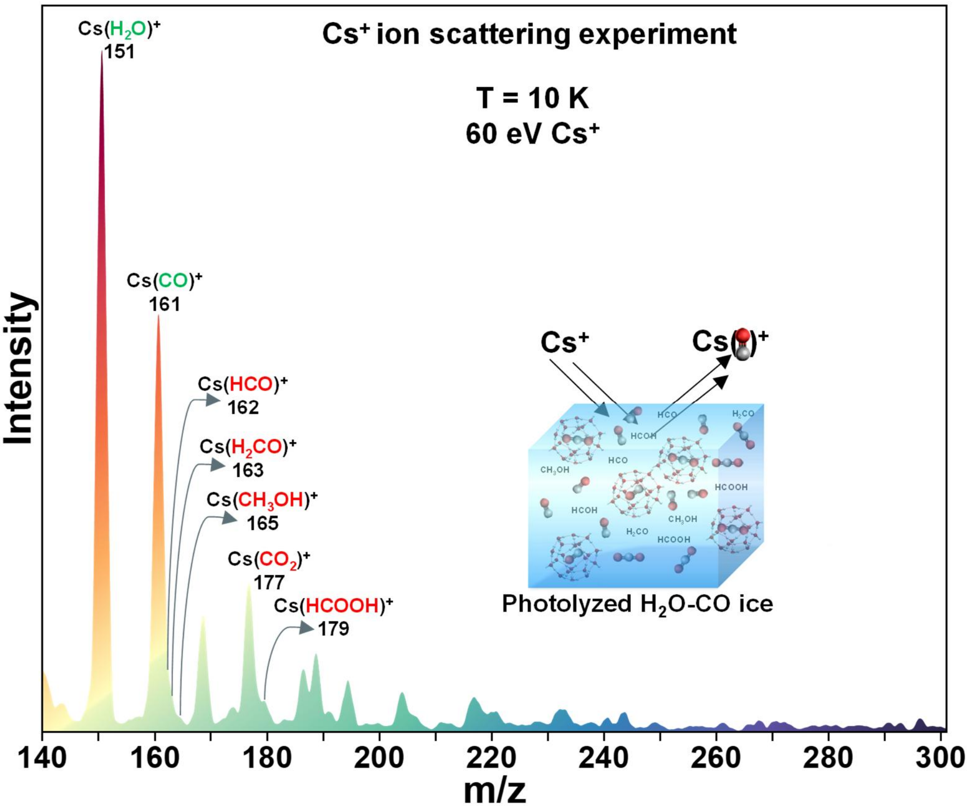

Fig. S6. Surface structure of photolyzed H_2O-CO mixture obtained from Cs^+ ion scattering experiment. The mass spectrum of the irradiated H_2O-CO mixture was obtained by colliding the sample with 60 eV Cs^+ ions at 10 K. The peaks marked in the mass spectrum correspond to the adducts of Cs^+ (m/z = 133) with H_2O (m/z = 151), CO (m/z = 161), HCO (m/z = 162), H_2CO (m/z = 163), CH_3OH (m/z = 165), HCOOH (m/z = 179). For clarity, the remaining peaks were not assigned. Inset illustrates a schematic representation of the Cs^+ ion scattering experiment.