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1. Introduction

Ice photochemistry, driven by ultraviolet (UV) irradiation of interstellar and cometary ice analogues, is crucial for understanding the synthesis of complex organic molecules in space.¹ Water (H₂O) and carbon dioxide (CO₂) ices are among the most prevalent in various astrophysical environments, including comets, molecular clouds, icy satellites, and protostellar regions.² Consequently, the photolysis of H₂O–CO₂ mixtures has been considerably studied under laboratory conditions, typically at ~10–18 K and vacuum of the order of ~10⁻⁸ mbar.^{3–5} These studies, however, face significant challenges in identifying photoproducts due to the strong

Ultraviolet photolysis of CO_2 clathrate hydrate and H_2O-CO_2 mixed ice under ultrahigh vacuum⁺

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Photolysis of mixed ices, such as H_2O-CO_2 , is a key driver of chemical evolution in planetary, cometary, and interstellar environments. Despite their ubiquitous presence, the photolysis of H_2O-CO_2 ices remains underexplored experimentally, largely due to the significant attenuation of vacuum ultraviolet light caused by the intermixing of H_2O and CO_2 , which restricts the formation of new species. Here, we demonstrate two previously unknown photolysis pathways for H_2O-CO_2 ices at 10 K under ultrahigh vacuum ($\sim 10^{-10}$ mbar), revealing differences between bulk and surface photochemistry. In bulk, first, we trapped CO_2 within clathrate hydrate (CH) cages to prevent intermixing with H_2O , then subjected it to photolysis and analyzed it *via* reflection absorption infrared spectroscopy. Our results demonstrate that photon-induced destruction of the clathrate cages prompts the free CO_2 to migrate into the ice matrix without producing any new photoproducts. In contrast, a mixed solid formed by the simultaneous deposition of residual H_2O on CO_2 ice produces a variety of photoproducts such as CO, H_2CO_3 , and CH_3OH , along with elusive intermediates such as HCO, H_2CO , and HCO₃ were seen on the surface but were not observed in the bulk. These results present a better understanding of the synthesis and chemical evolution of H_2O-CO_2 -rich astrophysical environments.

attenuation of vacuum ultraviolet (VUV) light in H₂O-CO₂ mixtures, which limits UV penetration and the extent of photochemical reactions.⁶ For instance, using infrared spectroscopy, Gerakines et al.3 reported the formation of carbonic acid (H_2CO_3) , carbon monoxide (CO), and carbon trioxide (CO₃) through VUV (10.20 eV) photolysis of H₂O-CO₂ (1:1) mixed ices at 18 K. In contrast, Wu et al.⁴ observed only H₂CO₃ and CO when using extreme ultraviolet (40.78 eV and 21.23 eV) photolysis on H₂O-CO₂ (4:1) mixed ices at 10 K. Extending these findings, Radhakrishnan et al.⁵ demonstrated that pure CO₂ ice produces molecular and radical species such as CO, CO₃, and ozone (O_3) , while their formation is significantly suppressed in an $H_2O-CO_2(1:1)$ mixture, likely due to the trapping of oxygen (O) atoms within the H₂O matrix. They also demonstrated that CO_3 and O_3 form exclusively in pure CO_2 ice, and this finding could be used to infer the coexistence of H2O-CO2 ice, with CO3 indicating pure CO₂ domains and its absence suggesting H₂O-CO₂ mixing. However, the detection of intermediate species like HCO, H₂CO, and HCO₃ has been proven elusive in these studies. Another often overlooked study by Berger et al.7 demonstrated that UV photolysis of CO₂ embedded in amorphous solid water (ASW) on Ru(001) (where CO2 molecules were initially adsorbed onto the Ru(001) surface prior to water exposure), resulted in the formation of CO, atomic oxygen (O), and H₂CO, tentatively identified as formaldehyde.

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Previously, to avoid VUV attenuation in solid H₂O-CO₂ ices and identify photoproducts through IR analysis, simultaneous condensation and UV photolysis of the H₂O + CO₂ gas mixture was employed.^{3,6} In this current study, we report two novel photolysis pathways. In the first pathway, we trapped CO₂ within clathrate hydrate (CH) cages (via previously known methods)⁸⁻¹¹ in the bulk of H_2O-CO_2 ice, which prevents CO_2 from mixing with H₂O. We then photolyzed the water ice containing CO₂ CHs. We studied the photolysis of CH of CO₂ also in view of our earlier studies (see below). In the second pathway, rather than co-depositing the H₂O and CO₂ gas mixture, we first created a CO₂ ice film, followed by simultaneous residual water deposition and photolysis. The resulting ices were analyzed using reflection absorption infrared spectroscopy (RAIRS) for bulk composition and Cs⁺-based secondary ion mass spectrometry (SIMS) for surface composition.

CHs are inclusion compounds formed by water molecules encasing small guests such as CH4, CO2, N2, and H2 within Hbonded cages.^{12,13} While experimental evidence for CHs in a high vacuum was noted since the 1980s,^{8,14-18} our group had recently reported their existence under ultrahigh vacuum (UHV) and cryogenic conditions.9 This study9 had generated reactions19 and they were answered.²⁰ Subsequently, several other molecules were reported to form CHs under UHV and cryogenic conditions.^{11,21-26} The formation of CHs under UHV, observed through RAIRS was subsequently proved by reflection high energy electron diffraction (RHEED).27 Notably, RHEED has been widely used to study ice nucleation and growth during water vapor deposition as well as the heating of ASW films on substrates like HOPG, Pt(111), Ru(0001), Ni(111), and Si(100)/(111).22,28-33 However, no reports have yet explored the photolysis of CHs under these conditions. In this study, we report the photolysis of CO₂ CH for the first time. Some studies reported gamma-ray irradiation of CHs, formed under high pressures.³⁴⁻³⁶ During irradiation, CHs enabled distinctive hydrogen transfer reactions with radicals. Also, clathrate cages were found to stabilize free radicals within the cages.³⁷

Thus, the current study aims to advance our understanding of how H₂O-CO₂ thin ice film changes chemically under VUV light exposure, simulating astrophysical conditions. In the current study, we have carried out VUV photolysis experiments with H₂O-CO₂ model interstellar ice by slicing the thin film to two segments—bulk ice and surface layers—under UHV and cryogenic conditions (10 K and ~10⁻¹⁰ mbar) using a custombuilt UHV setup.^{11,38,39} Our findings are expected to contribute to a better understanding of the chemical evolution within H₂O-CO₂-rich astrophysical environments.

2. Experimental

2.1. Experimental setup

Photolysis of H₂O–CO₂ model interstellar ice has been performed under ultrahigh vacuum (UHV) using a custom-built apparatus described elsewhere.^{9,11,38} The apparatus mainly comprises a stainless steel UHV chamber with a base pressure of ~5 × 10⁻¹⁰ mbar, a gas inlet system, and a metal substrate

connected to a closed-cycle He cryostat for sample preparation. The UHV chamber is equipped with several tools such as reflection absorption infrared spectroscopy (RAIRS), temperatureprogrammed desorption (TPD) mass spectrometry, Cs⁺-based secondary ion mass spectrometry (SIMS), low energy ion scattering (LEIS) mass spectrometry, and a vacuum ultraviolet (VUV) lamp.¹¹ Several turbomolecular pumps backed by oil-free diaphragm pumps were used to maintain the vacuum inside the chamber. The gas inlet system is equipped with two highprecision all-metal leak valves to control the vapor deposition. Whereas the metal substrate is a highly polished single-crystal Ru(0001). The substrate is mounted at the cold end of the He cryostat and fitted with a precision $x-y-z-\theta$ sample manipulator. The substrate temperature was monitored and controlled by a temperature controller, Lakeshore, Model 336, and adjusted by using a resistive heater (25 Ω) in the range of 8–1000 K. A K-type thermocouple and a platinum sensor were used to measure the temperature with an accuracy/uncertainty of 0.5 K.

2.2. Materials and reagents

We have used Millipore water (H_2O of 18.2 M Ω resistivity) and CO_2 gas (99.99%) for all the experiments. Millipore water was taken in a vacuum-sealed test tube and further purified *via* several freeze-pump-thaw cycles. Moreover, CO_2 gas was purchased from Indogas and used without further purification.

2.3. Sample preparation

Prior to each sample preparation, the Ru(0001) substrate was heated to 400 K multiple times to ensure that the surface was sufficiently clean. Thin ice films were created on the pre-cooled Ru(0001) substrate by vapor deposition. For this, two gas inlets, one for H₂O and the other for CO₂ exclusively, were used to introduce the vapors to backfill the chamber. The purity of H₂O and CO₂ gas was confirmed during vapor deposition using a residual gas analyzer quadrupole mass spectrometer. The deposition coverage or the thickness of ice samples was expressed in monolayers (ML) with an assumption of 1.33×10^{-6} mbar *s* = 1 ML, which was estimated to contain ~1.1 × 10^{15} molecules cm⁻², as implemented in previous studies.^{9,11,40,41} All coverages were >50 ML, and therefore, no substrate effect is expected.

2.4. Experimental protocol

2.4.1. Bulk photochemistry. In the first photolysis pathway, CO₂ was trapped within clathrate hydrate (CH) cages to avoid mixing with H₂O. To form CH of CO₂, the H₂O-CO₂ thin film was prepared by co-depositing H₂O and CO₂ vapors on Ru(0001) at 10 K in a 5:1 ratio, as adopted in our previous study.⁹ ~ 100 ML of H₂O-CO₂ (5:1) ice was created at a total pressure of ~5 × 10⁻⁷ mbar for 3 minutes 20 seconds where the inlet pressure of H₂O vapor was ~4 × 10⁻⁷ mbar and that of CO₂ gas was ~1 × 10⁻⁷ mbar.

To comprehend the bulk photochemistry of H_2O-CO_2 thin film, two sets of experiments were carried out. In the first (control) set, the as-deposited ~50 ML of pure CO₂ and ~100 ML H₂O-CO₂ (5:1) thin films at 10 K were exposed to VUV for 4 h, and

RAIR spectra were collected at regular intervals. In the second set, to form CO₂ CH, the as-prepared ~100 ML H₂O-CO₂ (5:1) thin film and ~30 ML O₂@100 ML H₂O-CO₂ (5:1) composite ice at 10 K were annealed to 120 K to create CO₂ CH and to get rid of free CO₂ from the ice matrix, as adopted previously.^{8,9} It should be noted that heating the H₂O-CO₂ ice sample above the desorption temperature (90 K) of pure CO₂ ice to ~120 K will result in CH formation and desorption of free CO₂.^{9-11,42} After preparing CO₂ CH at 120 K, the samples were cooled back to 10 K and exposed to VUV for 2 h, followed by RAIR spectral collection at regular intervals. Further, the photolyzed samples (at 10 K) were heated to 120 K. The ~30 ML O₂@100 ML H₂O-CO₂ (5:1) composite ice was prepared by first depositing ~30 ML of pure O₂ on the clean Ru(0001) substrate, followed by a co-deposition of ~100 ML of H₂O-CO₂ thin film in a 5:1 ratio over it.

2.4.2. Surface photochemistry. For the second photolysis pathway, we first created a CO₂ ice film, followed by simultaneous residual water deposition and photolysis. Control SIMS experiments were performed on the surface of (i) ~ 50 ML pure H_2O_2 , (ii) ~ 50 ML pure CO_2 , and (iii) ~ 50 ML H_2O-CO_2 ice at 10 K before VUV exposure. For ~ 50 ML H₂O-CO₂ ice, we first prepared ~ 50 ML pure CO₂ ice on clean substrate and then waited for the adsorption of residual water vapor from the UHV chamber at 10 K. This was done for the fact that in the codeposition experiments, due to excess H₂O (accumulating on the ice surface through background deposition), detection of other extremely low-abundant species by Cs⁺ was challenging. After sample preparation at 10 K, SIMS spectra were collected by colliding Cs⁺ at a particular kinetic energy (details are given in the SIMS setup section). For time-dependent experiments, the first SIMS spectrum collected after the deposition of the sample was noted as a time zero spectrum. Then, after 15, 30, and 60 min, spectra were collected subsequently. For temperature-dependent experiments, samples were heated to the set temperatures, 10, 20, 30, 40, and 50 K, at a rate of 5 K min⁻¹, and SIMS spectra were collected at the corresponding temperatures. To minimize the time-dependent effects on the ice sample, the experiment was completed within 20 min. For photolysis and identification of photoproducts on the surface of the H2O-CO2 system, H2O condensation (on CO_2 film) and photolysis were carried out simultaneously for 4 h at 10 K. After photolysis, the resulting ice collided with 80 eV Cs^+ to detect the photoproducts at 10 K.

2.5. VUV lamp

To carry out the photolysis of molecular ices, we have added a VUV lamp to our existing UHV chamber.¹¹ The UV light source was a deuterium lamp (McPherson, Model 634, with MgF₂ window, 30 W) of VUV range, 115–400 nm. The VUV lamp was attached to the UHV chamber through the MgF₂ window (with a cut-off at ~114 nm (10.87 eV)) and differentially pumped with a turbomolecular pump. The UV lamp flux was determined by applying the widely used ozone method $(O_2 \rightarrow O_3 \text{ conversion})$.^{43,44} The average photon flux reaching the ice sample was estimated to be ~6 × 10¹² photons cm⁻² s⁻¹.

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2.6. RAIRS setup

RAIR setup was attached to our UHV chamber externally through an IR transparent ZnSe viewport. The setup comprised of a Bruker Vertex 70 FT-IR spectrometer and a liquid nitrogencooled mercury cadmium telluride (MCT) detector. RAIR spectra were collected in the 4000–550 cm⁻¹ range with a spectral resolution of 2 cm⁻¹. For a better signal-to-noise ratio, each RAIR spectrum was averaged over 512 scans which took 7 min for acquisition. During experiments, the IR beam was focused on the ice sample at an incident angle of 80° ± 7° through ZnSe viewport. The reflected beam from the ice sample was recorded with the MCT detector. The IR beam outside the vacuum chamber was purged with dry nitrogen to avoid absorption from atmospheric gases.

2.7. SIMS setup

 Cs^+ with a mass-to-charge ratio (m/z) of 133 is a widely recognized choice as the primary ions in SIMS studies. This technique is highly sensitive only to the topmost layer of the sample. Through a low-energy collision, Cs⁺ transforms neutral adsorbate species (X) into gas-phase ions (CsX⁺) via an association reaction, a phenomenon commonly referred to as reactive ion scattering (RIS). We have conducted ion collision experiments on the H2O/CO2/H2O- CO_2 ice using Cs^+ of 60/80 eV kinetic energy produced from a lowenergy alkali ion gun (Kimball Physics Inc.). The resulting scattered ions from the ice sample were analyzed using a quadrupole mass analyzer. We have used the RIS signal intensities corresponding to the complex of Cs^+ with H_2O {such as, m/z = 151, $Cs(H_2O)^+$, m/z = 169, $Cs(H_2O)_2^+$, m/z = 187, $Cs(H_2O)_3^+$, etc.}, with CO_2 {such as, m/z = 177, $Cs(CO_2)^+$, m/z = 221, $Cs(CO_2)_2^+$, etc.}, and with H₂O-CO₂ complexes {such as, m/z = 195, Cs((H₂O-CO₂)⁺), m/z = 213, Cs((H₂O)₂-CO₂)⁺, m/z = 239, Cs(H₂O-(CO₂)₂)⁺, etc.} to identify the species present on the topmost surface of ice sample. Here, the signal intensities are directly proportional to the surface population of the molecule (or complex) on the ice surface.

Results and discussion

The photochemistry of H₂O-CO₂ ices in bulk was investigated *via* RAIRS. To begin with, we photolyzed ~ 50 ML of pure CO₂ and ~100 ML of a 5:1 mixture of H_2O-CO_2 ices at 10 K for 4 h and collected RAIR spectra at regular intervals, as shown in Fig. 1a and b. After 4 h of VUV exposure, pure CO_2 ice was depleted by ~19.5%, forming CO, CO₃, and O₃ (Fig. 1a and Fig. S1, ESI[†]).⁵ In contrast, no photodissociation products were detected in the 5:1 H₂O-CO₂ mixed ice (Fig. 1b and Fig. S2, ESI[†]). Nonetheless, VUV photons did penetrate the ice matrix, albeit with attenuation, as evidenced by changes in the O-H stretching region (Fig. S3a, ESI†). Fig. 1b presents the RAIR spectra of the H₂O-CO₂ (5:1) mixed ice in the C=O antisymmetric stretching region of CO2. Prior to VUV exposure, two peaks at 2346 and 2353 cm⁻¹ and two shoulders at 2340 and 2360 cm⁻¹ are evident (see deconvoluted peaks in Fig. 1c). After 4 h of VUV exposure (Fig. 1b), no significant depletion was observed in the 2340, 2346, or 2353 cm⁻¹ peaks, while the



Fig. 1 (a) RAIR spectra of ~50 ML pure CO₂ ice before and after 4 h of VUV photolysis in the C=O antisymmetric stretching region at 10 K. The shift and reduction in the peak intensity of 2380 cm⁻¹ is attributed to the decrease in the fraction of pure CO₂ ice, as observed previously.^{11,45} (b) RAIR spectra of ~100 ML H₂O-CO₂ (5:1) ice before and after 4 h of VUV photolysis in the C=O antisymmetric stretching region of CO₂. No photon-induced products were detected by RAIRS, see Fig. S2. A slight depletion in the 2360 cm⁻¹ shoulder may be attributed to the photodesorption of CO₂ molecules with prolonged exposure to VUV. At the right bottom of (a) and (b), the insets show the composition of the initial ice used for the study. Normalized RAIR spectra of ~100 ML H₂O-CO₂ (5:1) ice in the C=O antisymmetric stretching region at (c) 10 K and (d) 120 K before VUV photolysis. The ice sample was heated from 10 K to 120 K at a rate of 5 K min⁻¹.

2360 cm⁻¹ shoulder showed slight depletion, suggesting photodesorption of adsorbed CO₂. The absence of photodissociation products in the H₂O-CO₂ (5:1) mixed ice (Fig. S2, ESI[†]), in contrast to pure CO₂ ice (Fig. S1, ESI[†]), is likely due to limited UV transmission in the bulk ice matrix, as previously reported in the literature.^{3,4,6}

At 10 K, the absorption band at 2353 cm⁻¹ and its accompanying shoulder at 2360 cm⁻¹ are attributed to CO₂ present as either bulk ice or isolated molecules in the pores of amorphous solid water (ASW).^{9,13} In contrast, the peak at 2346 cm⁻¹ and the shoulder at 2340 cm⁻¹ are tentatively assigned to CO₂ molecules interacting with H₂O *via* weak van der Waals forces.^{9,10,46} Notably, the 2346 cm⁻¹ peak has also been associated with CO₂ trapped within the 5¹² cages of sI CH in previous studies.^{8-11,14} To minimize molecular intermixing and enhance VUV penetration, it is essential to remove free CO₂ (present in ASW pores, 2353 and 2360 cm⁻¹) and encapsulate the remaining CO₂ within CH cages. This was achieved by heating the H_2O-CO_2 (5:1) ice sample to 120 K (Fig. 1d), beyond the desorption temperature of pure CO₂. This approach aligns with established literature methods.^{10,11,14,16} The corresponding changes in water (O-H stretching band) are shown in Fig. S4 (ESI^{\dagger}). Upon heating to 120 K, the 2353 and 2360 cm⁻¹ peaks disappeared (Fig. 1d), confirming their assignment to bulk CO₂ or CO₂ in ASW pores, while the 2346 and 2340 cm⁻¹ peaks varied in intensity, correlating with changes in the O-H stretching region (shown in Fig. S4, ESI†). The 2346 and 2340 cm^{-1} features have previously been assigned to CO₂ enclosed in the 512 and 51262 cages of sI CH above 90 K, provided that concurrent changes occur in the O-H stretching region.^{10,14,16} It should be noted that above the desorption temperature of CO₂, CO₂ does not exists in an amorphous or crystalline phase within ASW; rather, it may exist as trapped gas or be confined within CH cages. Thus, heating the ice sample to 120 K will result in the desorption of CO₂ present in ASW pores and the persistence of CO₂ trapped in CH cages. After isolating



Fig. 2 Normalized RAIRS spectra for ~100 ML H_2O-CO_2 (5:1) ice before and after VUV photolysis (a) without O_2 and (b) with 30 ML O_2 film in the C=O antisymmetric stretching region of CO₂. In both systems, the ice samples were prepared at 10 K and then heated to 120 K. Further, the samples were cooled to 10 K and irradiated with VUV for 2 h. Finally, the photolyzed sample was further heated to 120 K. At the top corner of (a) and (b), the insets show the composition of the initial ice used for the study. For simplicity, CO₂ is categorized into two phases: CO₂ in ASW (light grey shade) and CO₂ in CH cages (light orange shade). This is because VUV radiation photodissociates the H_2O molecules in 5^{12} and $5^{12}6^2$ cages without preference.

 $\rm CO_2$ in CH cages at 120 K, the ice sample was cooled to 10 K for photolysis.

Trapping of CO₂ inside cages can effectively prevent the mixing of CO₂ with bulk water ice, which may allow the transmission of photons in the bulk. After creating CO₂ CH in the water matrix at 120 K and cooling it back to 10 K, the ice sample was photolyzed by VUV exposure for a duration of 2 h, as presented in Fig. 2a. For simplicity, we have categorized the CO2 into two phases: CO2 in ASW and CO2 in CHs, as indicated by light grey and orange shades, respectively (a detailed deconvoluted spectra are presented in Fig. 1c and d). This is because, VUV photodissociates the H_2O molecules of 5^{12} and $5^{12}6^2$ cages without preference. A full range (4000–1000 cm⁻¹) RAIR spectrum of the photolyzed sample is shown in Fig. S5a (ESI⁺), revealing no new photoproducts. However, Fig. 2a shows the reappearance of the 2353 cm⁻¹ peak following 1 h of VUV exposure, indicating potential CO₂ migration from clathrate cages to the ice matrix. This phenomenon likely stems from the photon-induced decomposition of the CH structures. Further confirmation of this was sought by examining the O-H stretching band of the same system presented in Fig. S3b and S5a (ESI⁺). The RAIR traces in Fig. S3b (ESI⁺) display a notable change in the O-H stretching band. The decrease in the intensity of the O-H stretching band after VUV exposure indicates the decomposition of CH structures and the rearrangement/disordering of ordered H₂O molecules. Notably, upon annealing to 120 K, the H₂O matrix undergoes a process of ordering its molecules.^{40,41,47} Furthermore, exposure to UV radiation has been reported to induce disordering (amorphization) in the ordered/crystalline water structures.²⁹ Thus, the IR study of the VUV photolysis of CO_2 CH at 10 K suggests the decomposition of clathrate cages and subsequent migration of CO_2 to the water matrix without yielding new photoproducts in the bulk of the ice matrix.^{11,48} Obviously, VUV does penetrate the clathrate matrix, although with attenuation.

In the current study, we propose that annealing the H₂O- CO_2 (5:1) mixed ice to 120 K made the ice sample transparent to VUV transmission. This may primarily be due to the desorption of free CO₂ from the water matrix and confinement of the remaining CO₂ within clathrate cages. This allowed us to study the photolysis of CH of CO_2 for the first time. Fig. 2a reveals that following 1 h of VUV irradiation, even a minute amount of free CO₂ within the water matrix made the system opaque to VUV transmission, limiting further decomposition of CO₂ CH. This can be comprehended by comparing the RAIRS traces of VUV exposed samples of 1 and 2 h in Fig. 2a. This indicates that increased CO2 migration from clathrate cages to the water matrix or, in other words, an increased fraction of free CO_2 in the water matrix would make the system opaque to VUV, inhibiting further CH decomposition. Finally, the resulting ice after 2 h of VUV irradiation was heated to 120 K (top trace in Fig. 2a) to validate the assignment of the 2353 cm^{-1} peak to free CO_2 within the water matrix and that at 2346 and 2340 cm⁻¹ to CO_2 within the CH cages. The vanishing of the 2353 cm⁻¹ peak and the persistence of the 2346 and 2340 cm⁻¹ peaks served as a confirmation for our assignments.^{9,11}

To induce photochemistry or investigate the impact of a third molecule on the decomposition of CO₂ CH during VUV exposure, we incorporated O_2 in the H_2O-CO_2 (5:1) mixed ice. In the solid state, O_2 is known to readily dissociate by UV ($\lambda <$ 240 nm) to produce highly reactive atomic O.49 We created a composite ice film of ~30 ML O_2 (alo ML H_2O -CO₂ (5:1) at 10 K (see the Experimental section for details of sample preparation). The composite ice underwent treatment using a method similar to that used for Fig. 2a, and the outcomes are displayed in Fig. 2b (a full range RAIR spectra are presented in Fig. S5b, ESI[†]). The findings illustrated in Fig. 2b suggest that in the presence of O₂, a slightly larger fraction of CO₂ migrated from the clathrate cages, while the overall outcome closely resembles the pattern seen in Fig. 2a. Thus, the presence of foreign molecules can impact the photolysis of CO₂ CH. Faster decomposition of CO₂ CH in the presence of O₂ and CH₃OH is also observed at ambient conditions.12

Next, we examined the surface photochemistry of the H_2O-CO_2 ice under VUV exposure. To do this, we employed Cs⁺based SIMS due to its exceptional sensitivity for the first few monolayers of the ice surface. The higher sensitivity of the technique allows species of low abundance on the ice surfaces to be detected.^{40,50,51} In the current study, SIMS was used in reactive ion scattering (RIS) mode.^{40,51,52} To detect photoproducts on the ice surface by SIMS, we have prepared the samples by the 'condensation and simultaneous photolysis' method. Before performing the photolysis experiment, we analyzed the

surface of pure H₂O, pure CO₂, and H₂O-CO₂ ices at 10 K by SIMS, as presented in Fig. 3a, b, and c, respectively. Fig. 3a shows a series of mass peaks for the pickup of $n H_2O(m/z = 18)$ by Cs^+ (m/z = 133), such as, $Cs(H_2O)_n^+$ at m/z = 151 (n = 1), 169 (n = 2), 187 (n = 3), etc. Similarly, Fig. 3b shows the pickup of n CO_2 , such as, $Cs(CO_2)_n^+$ at m/z = 177 (n = 1), 221 (n = 2), etc., and Fig. 3c shows the pickup of $n H_2O$, $m CO_2$ and H_2O-CO_2 complexes from H₂O-CO₂ surface. Notably, three H₂O-CO₂ complexes were detected at m/z = 195, $Cs(H_2O-CO_2)^+$, 213, $Cs((H_2O)_2-CO_2)^+$, and 239, $Cs(H_2O-(CO_2)_2)^+$ at 10 K. Kim et al., in a similar study by SIMS, reported that CO₂ adsorption on a H₂O ice film does not form H₂O-CO₂ complexes at 80 K.⁵³ However, in the present study, when residual H₂O vapor was allowed to adsorb on CO₂ ice film at 10 K, three H₂O-CO₂ complexes were detected by SIMS. For this, we first prepared ~ 50 ML CO₂ ice at 10 K and waited for the adsorption of residual water vapor from the UHV chamber. Such weakly bound complexes of CO2 and H2O are important in atmospheric systems, planetary bodies, and in the context of cometary and interstellar ices. Consequently, they have attracted considerable theoretical and experimental interest.54-57 We have further examined the H2O-CO2 system by SIMS to monitor the residual deposition of H2O vapor and the stability of H2O-CO₂ complexes. Two sets of experiments were performed. The first experiment was a time-dependent SIMS at 10 K for 60 min, as presented in Fig. 4a. We observed that, with time, the fraction of H₂O on the CO₂ ice film was increasing. This can be realized by observing the intensity of m/z 169, 187, and 205. Simultaneously, with time, the fraction of CO_2 at the surface



Fig. 3 RIS mass spectra taken from the surface of (a) \sim 50 ML pure H₂O, (b) \sim 50 ML pure CO₂, and (c) \sim 50 ML H₂O-CO₂ ice in the mass range of 135–245 amu. The mass spectrum was obtained by colliding the sample with 60 eV Cs⁺ ions at 10 K. The \sim 50 ML H₂O-CO₂ ice was prepared by creating \sim 50 ML pure CO₂ ice on clean Ru(0001) and letting the residual water vapor from the UHV chamber adsorb on it over time.

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Fig. 4 RIS mass spectra for \sim 50 ML H₂O-CO₂ ice. (a) Time-dependent mass spectra were taken for H₂O-CO₂ ice at 10 K for 60 min. After sample preparation, the first spectrum collected was noted as the time zero spectrum. (b) Temperature-dependent mass spectra were taken at 10–50 K. The mass spectrum in the range of 135–245 amu was obtained by colliding the sample with 60 eV Cs⁺ ions. The table on the right shows the assignment of mass peaks. In (a) and (b), peaks of H₂O-CO₂ complexes were highlighted by red, blue, and green shades.

decreases (see the peaks at m/z 177 and 221) so, as do the fractions of H₂O–CO₂ complexes (m/z 195, 213, and 239). In the second set, temperature-dependent SIMS experiments were carried out in the range of 10–50 K, and the results are presented in Fig. 4b.

This experiment was done to examine the stability of H_2O-CO_2 complexes. At 50 K, all three mass peaks corresponding to the H_2O-CO_2 complexes disappeared, aligning with the finding of Kim *et al.* of no H_2O-CO_2 complexes at 80 K.⁵³



Fig. 5 RIS mass spectra for the photolyzed H_2O-CO_2 ice taken at 10 K in the mass range of 135–245 amu. The mass spectrum was obtained by colliding the sample with 80 eV Cs^+ ions at 10 K. Inset figure presents the ice sample and RIS process schematically. The table on the right shows the assignments of mass peaks for both reactants and photoproducts.

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For the photolysis experiment, we created a $\sim 50 \text{ ML CO}_2$ ice film on Ru(0001) at 10 K. Then, after waiting for 5 minutes, we switched on the VUV lamp, assuming continuous condensation of residual H₂O vapor onto the CO₂ film, as can be inferred from Fig. 4a. In other words, H₂O condensation (on CO₂ film) and photolysis were carried out simultaneously for 4 h. Importantly, our study does not involve a pre-deposited CO2@ASW mixed film. After photolysis, RAIR detected only CO, CO₃, and O_3 in the bulk ice sample. However, when the resulting ice collided by 80 eV Cs⁺, several photoproducts were detected on the sample surface. Fig. 5 presents the mass spectrum of picked-up photoproducts and a table containing the list of detected reactants and photoproducts. Fig. 5 confirms the detection of CO, HCO, H2CO, CH3OH, HCO3, and H2CO3 by SIMS, which were previously unidentified using RAIRS. The hydrogen (H) in the detected photoproducts on the H_2O-CO_2 surface comes from the breakdown of residual H₂O through photolysis in both the gas phase and on the CO₂ ice surface. Photolysis of H₂O is known to produce primary and secondary photoproducts such as $H_2O + h\nu \rightarrow H$, OH, H_2 , O, HO_2 , HO_3 , H_2O_2 , O_2 , O_3 .⁵⁸ A few small peaks at (marked by *) m/z 145, 157, and 169, are tentatively assigned to C1, C2, and C3 carbons. However, additional isotope labelling experiments are required to validate this. The earlier H₂O-CO₂ photolysis studies have only reported the identification of CO, CO₃, O₃, and H₂CO₃ by IR analysis.^{3,4} They could not positively identify the HCO, H₂CO, HCO₃, and CH₃OH in their study. Thus, this study shows the formation of not only CO, CO₃, O₃, H₂CO₃, and CH₃OH but also the intermediates, HCO, H₂CO, and HCO₃, which have not been detected earlier.

The contrasting photochemistry of H_2O-CO_2 ice was not only observed due to the different experimental approaches but also because of the experimental tool used to detect the photoproducts. When CO₂ was mixed with H₂O ice in bulk, it does not photodissociate likely due to limited VUV photon penetration. However, when CO₂ was confined within clathrate cages in a water matrix, allowing VUV penetration, it underwent decomposition upon photon exposure. This led to the diffusion of CO₂ from CH cages to the water matrix, possibly triggered by VUV photons causing the photodissociation of H₂O molecules within the CH structure (5^{12} and $5^{12}6^2$ cages). However, RAIRS did not observe any photoproducts or chemical changes. In contrast, simultaneous deposition of residual H₂O on CO₂ ice and VUV exposure resulted in the photodissociation of both CO₂ (C, O, CO) and H₂O (H, O, OH) at the ice-vacuum interface, inducing chemical changes with several detectable photoproducts by mass spectrometry.

Our study provides critical insights into the photochemistry of H_2O-CO_2 ices across a broad range of astrophysical and planetary environments, from interstellar ice mantles to cometary nuclei and planetary surfaces. By distinguishing the photochemical behavior of bulk and surface ice, we demonstrate that CO_2 CH act as molecular reservoirs, regulating the release and reactivity of volatiles, whereas surface photolysis leads to the formation of key photoproducts, including CO, H_2CO_3 , CH₃OH, and intermediates such as HCO, H_2CO_3 and HCO₃. These findings have direct implications for planetary processes, including the seasonal evolution of CO_2 -H₂O ice deposits on Mars and radiolytic ice chemistry on Europa and Ganymede. Furthermore, our results contribute to a growing understanding of how UV-driven processes in H₂O-CO₂-rich environments facilitate the synthesis of complex organics, which may be relevant to prebiotic chemistry and the organic inventory of planetary atmospheres. This study advances the discussion on the role of CHs in trapping and releasing volatile species, influencing atmospheric compositions and surface chemistry on planetary bodies. By bridging laboratory astrochemistry and planetary science, our work refines perspectives on the molecular evolution of ices in extraterrestrial settings and their potential contributions to the chemical complexity of habitable environments.

4. Conclusions

This study provides experimental insights into the photolysis pathways of H₂O-CO₂ ices under UHV and cryogenic conditions, revealing a distinction between bulk and surface photochemistry. In the bulk, CO2 molecules trapped within CH cages remain photochemically inert, as photon-induced decomposition of the hydrate structure results solely in CO₂ migration into the surrounding ice matrix without forming new photoproducts. In contrast, photolysis at the surface of the H₂O-CO₂ mixed film leads to the formation of various reaction products, including CO, CH₃OH, H₂CO₃, and crucial intermediates such as HCO, H₂CO, and HCO₃, which were identified using Cs⁺based SIMS. These findings highlight the critical role of ice morphology and molecular confinement in governing photochemical reactivity and provide valuable implications for understanding the synthesis and evolution of H2O-CO2-rich astrophysical environments.

Author contributions

T. P. and G. V. designed the research. G. V. and B. K. M. have performed the experiments. T. P. supervised its progress. G. V., B. K. M., S. C., J. G., R. R. J. M., R. K. and T. P. analyzed the results. The first draft of the manuscript was written by G. V. The final version of manuscript was prepared including the contributions of all authors.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare no competing financial interests.

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