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## **UV-ray irradiation never causes amorphization of crystalline CO<sub>2</sub>: A transmission electron microscopy study**

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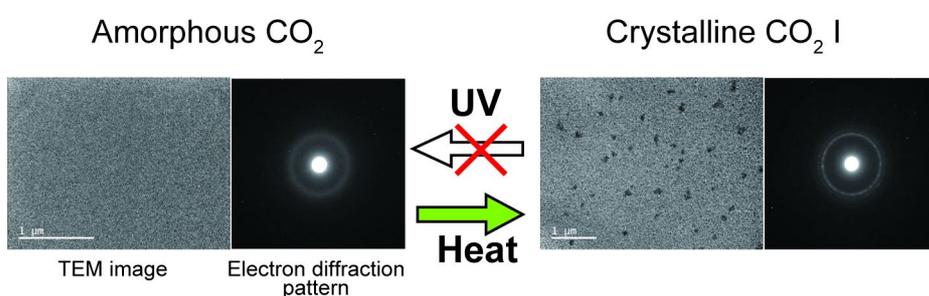
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## HIGHLIGHTS

- Crystallinity of CO<sub>2</sub> under UV-ray irradiation was directly observed by TEM
- Amorphization of crystalline CO<sub>2</sub> upon UV-ray irradiation was not observed
- Stronger UV-ray irradiation in IR experiments did not cause amorphization either
- UV-fluence expected in molecular clouds will not cause amorphization of CO<sub>2</sub> ice

## GRAPHICAL ABSTRACT



## ABSTRACT

The Crystallinity of ices, amorphous and crystalline, can be altered not only by heat but also by irradiation of UV-rays or charged particles. In this work, the effect of UV-irradiation on the crystallinity of CO<sub>2</sub> ice was investigated by using a transmission electron microscope. A crystalline CO<sub>2</sub> ice was produced by annealing amorphous CO<sub>2</sub> ice. We found that UV-ray irradiation of CO<sub>2</sub> crystals at approximately 10 K does not cause amorphization in contrast to the reported amorphization of crystalline water ice below 70 K. We discuss the difference based on the expected UV photochemistry of CO<sub>2</sub> ice.

## 1. Introduction

The crystallinity of ices, amorphous or crystalline, in icy grains and the surface of icy bodies that exist in space are important because it provides information on their thermal history. It had been widely accepted that amorphous H<sub>2</sub>O ice is formed at low temperatures and crystalline H<sub>2</sub>O ice at higher temperatures [1]. However, the crystallinity of ices formed by the condensation of H<sub>2</sub>O vapor could be determined by the temperature and deposition rate [2,3]. Furthermore, the time scale of crystallization of amorphous H<sub>2</sub>O ice depends on the observation temperature [2,4,5].

It had been implicitly assumed until 1980s that the phase transition from amorphous H<sub>2</sub>O ice to crystalline H<sub>2</sub>O ice (ice I) was irreversible, and that from ice I to amorphous H<sub>2</sub>O ice never occurred. However, the irradiation with UV-rays [6,7], electron beam [8,9] and other high-energy particle [10,11] causes the amorphization of ice I crystal at temperatures below ~70 K. These processes should be considered to evaluate the thermal history of ices because UV-rays and other particle irradiation hide the high-temperature history of ices. Although the amorphization of H<sub>2</sub>O ice has been extensively investigated [5,12], the detailed mechanism of amorphization, which should involve the dissociation of H<sub>2</sub>O molecules, has not been clarified.

Because CO<sub>2</sub> and CO are abundant ice components following H<sub>2</sub>O, the crystallinity of CO<sub>2</sub> and CO is essential to discuss the thermal history of ices at lower temperatures in space. However, there have been few reliable works on the crystallinity of these ices, especially the formation of amorphous CO<sub>2</sub>. Gerakines and Hudson noted that CO<sub>2</sub> solid used in past studies were not pure amorphous CO<sub>2</sub> but crystalline or mixture of amorphous and crystalline CO<sub>2</sub> [13]. Only Escribano et al. [14] and Gerakines and Hudson [13] succeeded in making pure amorphous CO<sub>2</sub>. On the other hand, Baratta and Palumbo [15] and He and Vidali [16] claimed that the band shape that had been attributed to amorphous CO<sub>2</sub> is induced by a small amount of water incorporated into the CO<sub>2</sub> ice. Nevertheless, we note that the discussion on crystallinity has been done mostly without direct evidence. Among these studies, Escribano et al. [14] developed theoretical models to reproduce observed spectra. Mangan et al. used the X-ray diffraction method to show that vapor-deposited solid CO<sub>2</sub> at temperatures of 80–130 K was crystalline CO<sub>2</sub>, CO<sub>2</sub> I [17]. It is noted here that crystalline polymorphs are usually distinguished using Roman numerals (e.g., CO<sub>2</sub> I, ice IX) or Greek letters (e.g.,  $\alpha$ -CO,  $\beta$ -quartz). Kouchi et al. experimentally demonstrated using transmission electron

microscopy that amorphous CO and CO<sub>2</sub> could be formed by vapor-deposition on amorphous H<sub>2</sub>O ice at temperatures below 18 and 50 K, respectively [18]. They also showed that crystalline forms,  $\alpha$ -CO and CO<sub>2</sub> I, were formed at temperatures higher than those temperatures. Kouchi showed by reflection electron diffraction method that amorphous CO crystallized at approximately 20 K to form  $\alpha$ -CO [19].

For CO<sub>2</sub> and CO, there has been no investigation on the amorphization of their crystals by the irradiation with UV-rays or high-energy charged particles. It is highly desirable to verify the possibility whether amorphization will occur because of the irradiation. Because CO is hardly dissociated at wavelengths of UV-rays generated in molecular clouds, we focus on CO<sub>2</sub> in this study. Using transmission electron microscopy and infrared spectroscopy, we have performed in situ observation of CO<sub>2</sub> crystals and amorphous CO<sub>2</sub> upon UV-ray irradiation.

## 2. Experimental

### 2.1. Transmission electron microscopy

We used an ultrahigh vacuum transmission electron microscope (UHV-TEM) (JEOL, JEM-2100VL) for the in situ observation of the irradiation process [18,20,21]. The UHV-TEM was evacuated by ion pumps and Ti-sublimation pumps. The pressure measured in the region between the TEM column and the ion pump was  $1 \times 10^{-6}$  Pa. Since the specimen is surrounded by a liquid-N<sub>2</sub> shroud, the pressure near the specimen may be lower than  $1 \times 10^{-6}$  Pa because of the deposition of residual water vapor to the shroud. For sample cooling, we used a liquid He cooling holder (Gatan, ULTST). We used a 5-nm thick nonporous amorphous Si film (SiMPore Inc., US100-A05Q33) for a substrate of sample deposition. The UHV-TEM has three ports directed at the sample surface with an incident angle of 55°. One of the ports is used for CO<sub>2</sub> deposition through a Ti tube (0.4 mm inner diameter) and another for UV-irradiation. A 30-W D<sub>2</sub> lamp (Hamamatsu, L7293), which is equipped with an MgF<sub>2</sub> window and emits photons in the range of 115–400 nm, was used as a UV source. The lamp was directly connected to the vacuum port. The UV photon flux was measured using another vacuum chamber with Si-photodiode (IRD, AXUV-100G) to be  $\sim 2 \times 10^{13}$  photons cm<sup>-2</sup> s<sup>-1</sup> before setting the lamp to TEM. UV-rays from the lamp equipped to TEM were collimated using a mirror-finished pure Al-collimator, which affects the actual UV flux at the sample position in TEM.

First, ~20-nm-thick amorphous CO<sub>2</sub> was deposited at 10 K with a deposition rate of ~1 nm min<sup>-1</sup>, since Gerakines and Hudson report that amorphous CO<sub>2</sub> can be formed at the deposition rate below 1.7 nm min<sup>-1</sup> [13]. The thickness of the CO<sub>2</sub> layer was measured following the method described by Kouchi et al. [18]. Then, amorphous CO<sub>2</sub> was crystallized by annealing at 60 K for 10 min. Crystalline CO<sub>2</sub> was subsequently cooled to 10 K and irradiated with UV-rays. We observed the entire process using TEM. To avoid electron beam damage, a low-dose technique has been applied following Tachibana et al. [21]: low magnification (×25000–50000), 80 kV accelerating voltage, and an electron beam density of 2–6 × 10<sup>-3</sup> electrons Å<sup>-2</sup>. Thus, we observed TEM images and electron diffraction patterns using a CCD camera (Gatan, ES500W). All electron diffraction patterns were taken in the 700-nm-diameter circular region of the central part of TEM images.

## 2.2. Infrared spectroscopy

We performed the following experiments for a longer duration using a stronger UV source. The experimental apparatus comprised a main ultrahigh vacuum chamber (base pressure < 2 × 10<sup>-7</sup> Pa), a Si(111) substrate (40 mm × 40 mm × 1 mm) mounted on the cold head of a closed-cycle He refrigerator (Sumitomo Heavy Industries, RDK-101D), and a Fourier transform infrared spectrometer (FT-IR) (Thermo Fisher Scientific, Nicolet iS50). CO<sub>2</sub> gas (Air Water, 99.999%) was introduced onto the Si substrate at 8 K by background deposition, typically for 90 min at 8.9 × 10<sup>-6</sup> Pa. The pressure was measured using a crystal ion gauge (Canon Anelva, M-336MX) and calculated using the gas correction factor for CO<sub>2</sub> (1.35) [22]. This corresponds to the flux of 2.0 × 10<sup>13</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>, and the deposited amount of CO<sub>2</sub> was estimated as 1.1 × 10<sup>17</sup> molecules cm<sup>-2</sup>.

Because we used a relatively slower deposition rate of CO<sub>2</sub>, co-adsorption of background H<sub>2</sub>O cannot be avoided. The partial pressures of background gasses were not determined in these experiments, but the dominant residual gas at such an ultrahigh vacuum condition should normally be hydrogen. Even we admit that the background pressure was dominated by water, the number of water molecules landing on the surface is less than 1 × 10<sup>15</sup> molecules cm<sup>-2</sup>. Therefore, the upper limit of H<sub>2</sub>O/CO<sub>2</sub> ratio will be 1/100. At such dilution, almost all the CO<sub>2</sub> molecules in ice sample interact with other CO<sub>2</sub> molecules but not with H<sub>2</sub>O, and one does not expect the change in the spectral

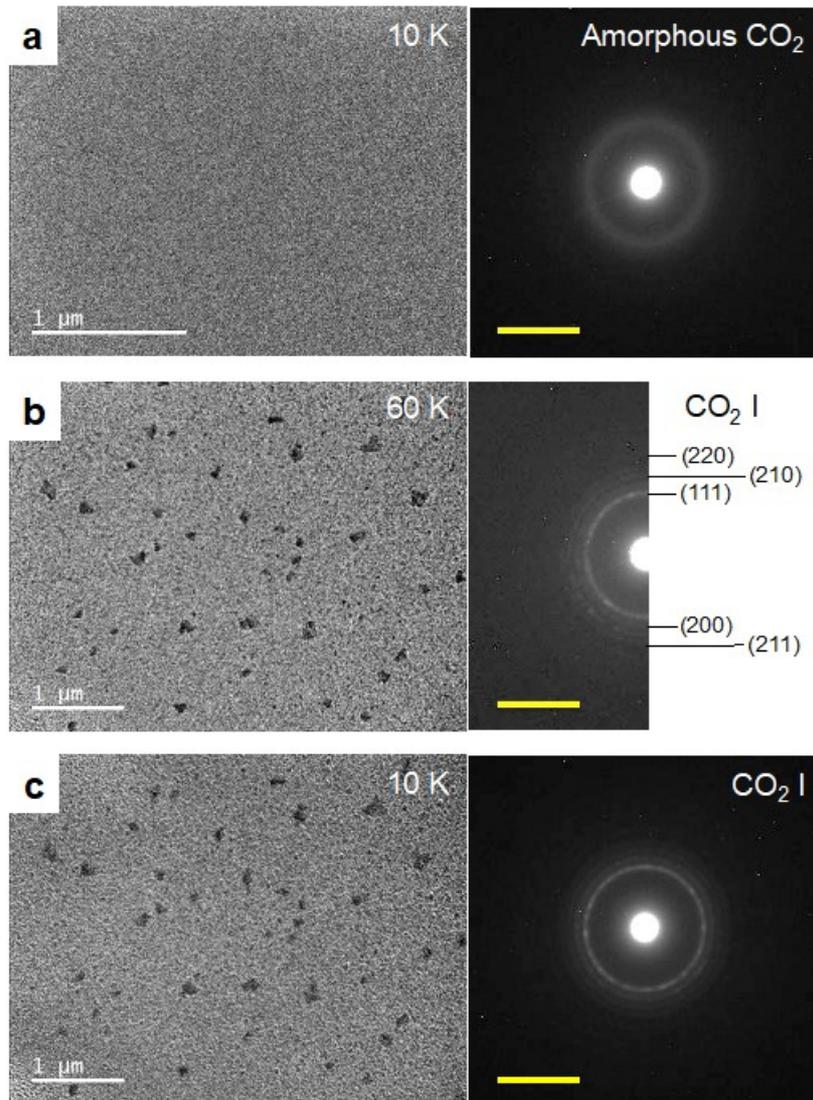
shape of CO<sub>2</sub> band. Moreover, such a small amount of H<sub>2</sub>O should not affect the UV-induced processes investigated in this paper. He and Vidali demonstrated that the deposition of H<sub>2</sub>O/CO<sub>2</sub> = 1/10 induces the spectral change of CO<sub>2</sub> band [16], but the H<sub>2</sub>O/CO<sub>2</sub> is so high, as compared to present experimental conditions, that most of CO<sub>2</sub> might interact with H<sub>2</sub>O molecule.

The prepared solid CO<sub>2</sub> sample was warmed to 60 K at a rate of 4 K min<sup>-1</sup> for crystallization, and the crystalline CO<sub>2</sub> was cooled to 8 K for UV-irradiation using a 150-W D<sub>2</sub> lamp (Hamamatsu, L11798). The UV photon flux measured by the Si-photodiode was  $\sim 3 \times 10^{14}$  photons cm<sup>-2</sup> s<sup>-1</sup>. The CO<sub>2</sub> samples were monitored in situ by the FT-IR in transmission geometry. The angles of incidence were 45° for UV-radiation from the D<sub>2</sub> lamp and IR light from the FT-IR due to the orthogonal configuration of the two vacuum ports in the chamber. For IR spectral measurements, the s-polarized IR light was employed to retrieve the pure transverse optic energy loss function from a sample without a contribution of longitudinal optic energy loss function [14]. Hence, the s-polarized transmission spectra can be directly compared to the normal incidence transmission spectrum of solid CO<sub>2</sub> previously reported in the literature [13,23]. Spectra were accumulated 100 times with a resolution of 4 cm<sup>-1</sup>.

### 3. Results

#### 3.1. TEM observation

Figure 1 shows the TEM images and electron diffraction patterns observed during UV irradiation experiments. CO<sub>2</sub> deposited at 10 K was amorphous (Figure 1a). After 10-min heating at 60 K, amorphous CO<sub>2</sub> completely crystallized to form CO<sub>2</sub> I crystals (Figure 1b). This is the first direct identification of crystalline structure of CO<sub>2</sub> formed by the crystallization of amorphous CO<sub>2</sub>. The grain size distribution is bimodal with large crystals of 100–200 nm in diameter (black images in Figure 1b) and smaller crystals (gray images). After 35 min of UV-irradiation (UV fluence  $\sim 4 \times 10^{16}$  photons cm<sup>-2</sup>), we did not observe any textural and crystalline structure change (Figure 1c), which shows that CO<sub>2</sub> I crystals are not amorphized by UV-rays. As demonstrated for crystalline H<sub>2</sub>O ice [7], the occurrence of UV-ray-induced amorphization process should be clearly seen as a change in electron-diffraction patterns.

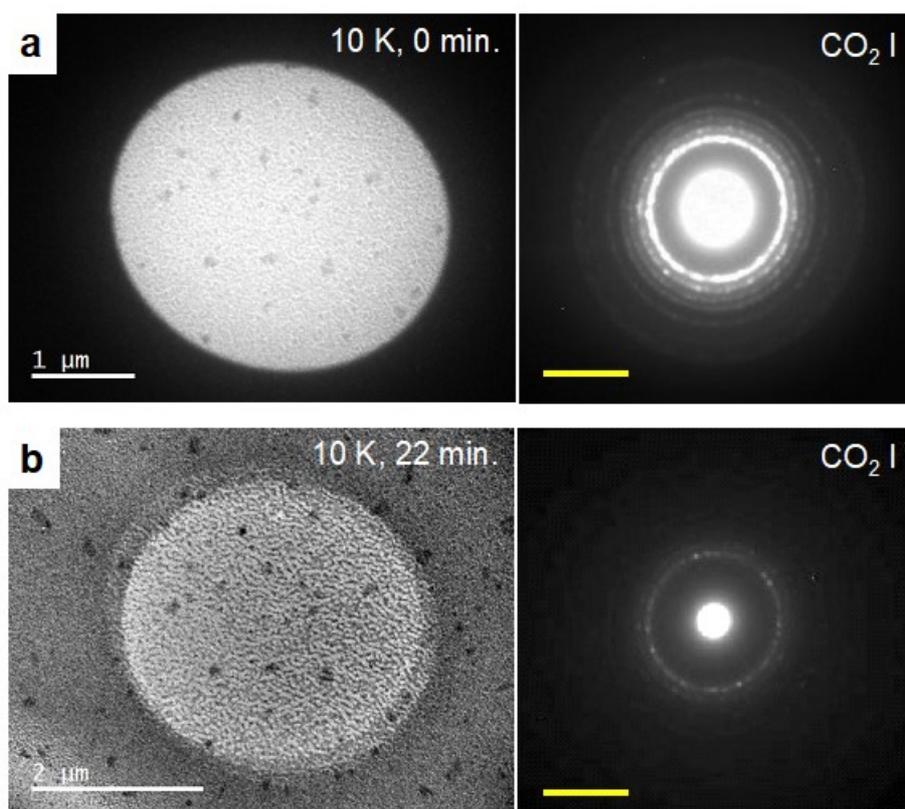


**Figure 1.** TEM observation of the UV irradiation experiment: (a) Amorphous CO<sub>2</sub> deposited on amorphous Si film at 10 K, (b) Crystallized CO<sub>2</sub> by 10 min of annealing at 60 K, and (c) 35-min UV-irradiated CO<sub>2</sub> at 10 K. The corresponding electron diffraction patterns are attached to the respective TEM images. The scale bars in electron diffraction patterns are 5 nm<sup>-1</sup>.

**(color on the WEB)**

We also evaluated the effect of the electron beam of TEM. The stronger electron beam of  $\sim 10$  electrons  $\text{\AA}^{-2}$  was applied for TEM measurement. Figure 2a shows the

TEM image and electron diffraction pattern immediately after starting the focused beam irradiation. After 22-min irradiation, most CO<sub>2</sub> I crystals have been sputtered as shown in Figure 2b. The roughly estimated sputtering rate of CO<sub>2</sub> I was  $\sim < 1 \text{ nm min}^{-1}$ , which corresponded to the sputtering yield of  $10^{-3} \text{ molecules electron}^{-1}$ . However, the electron diffraction pattern clearly shows that remnant CO<sub>2</sub> was crystalline. Thus, CO<sub>2</sub> I crystal shows strong resistance against both UV-rays and electron beam.



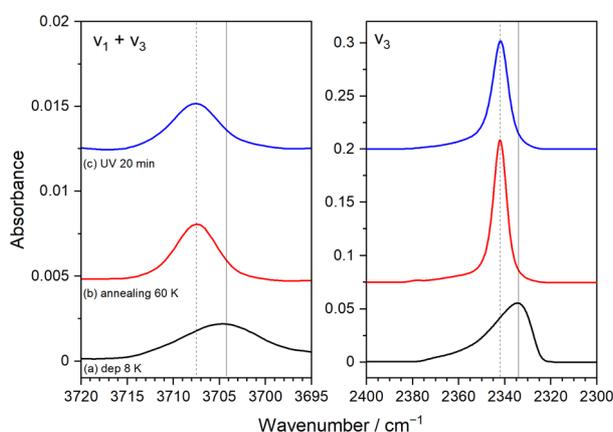
**Figure 2.** TEM images and corresponding electron diffraction patterns upon 80-kV electron beam irradiation: (a) immediately after starting irradiation and (b) after 22 min of irradiation. The electron beam was focused to 3- $\mu\text{m}$  diameter (bright circle in a). The TEM image and electron diffraction pattern in (a) and (b) were taken using a strong electron beam of  $\sim 10 \text{ electrons } \text{\AA}^{-2}$  and a weak electron beam of  $\sim 2 \times 10^{-3} \text{ electrons } \text{\AA}^{-2}$ , respectively. The scale bars in electron diffraction patterns are  $5 \text{ nm}^{-1}$ .

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### 3.2 IR spectroscopy

To complement the relatively small UV flux used in TEM experiments, we performed additional experiments using IR spectroscopy with the higher UV fluence which is equivalent to that for  $>10^7$  years in molecular clouds. We note that the interpretation of spectral shape of  $\text{CO}_2$ , which has been extensively debated in literature, is out of the scope of this paper. Figure 3 shows the IR spectra of a solid  $\text{CO}_2$  sample in the  $\nu_3$  (antisymmetric stretching) region and in the  $\nu_1 + \nu_3$  region. In the  $\nu_3$  region, the spectrum after deposition (trace a) shows an asymmetric band peaking near  $2333 \text{ cm}^{-1}$ , which is consistent with the spectral shape reported for amorphous  $\text{CO}_2$  [13]. Based on the TEM observation that slow  $\text{CO}_2$  deposition yields amorphous  $\text{CO}_2$  ice (Figure 1(a)), we attribute the observed band to amorphous  $\text{CO}_2$  ice. The  $\nu_1 + \nu_3$  band of amorphous  $\text{CO}_2$  ice was observed near  $3704 \text{ cm}^{-1}$ , consistent with the position reported by He and Vidali [16]. The amorphous  $\text{CO}_2$  sample was annealed at 60 K to obtain crystalline  $\text{CO}_2$  (trace b), which shows a more symmetric bands centering at  $2342 \text{ cm}^{-1}$  in the  $\nu_3$  region and at  $3708 \text{ cm}^{-1}$  in the  $\nu_1 + \nu_3$  region; the latter band has been assigned to crystalline  $\text{CO}_2$  [16]. During warm-up, an obvious shift in peak positions from  $2333$  to  $2342 \text{ cm}^{-1}$  was observed at temperatures above 35 K. Correlated changes in the  $\nu_3$  and  $\nu_1 + \nu_3$  regions upon annealing will be presented later. Integrated absorbance did not change upon crystallization, indicating that band strengths are more or less the same for amorphous and crystalline  $\text{CO}_2$ . The crystalline  $\text{CO}_2$  was irradiated at 8 K with the 150-W  $\text{D}_2$  lamp for 20 min (UV fluence  $3\text{--}4 \times 10^{17} \text{ photons cm}^{-2}$ ), and the spectrum measured after irradiation was shown as trace c. After this process, the peak position was unchanged, which confirms that UV-induced amorphization did not occur even when crystalline  $\text{CO}_2$  were irradiated with stronger UV-rays for longer duration. The decrease in integrated absorbance from  $1.251$  to  $1.153 \text{ cm}^{-1}$  ( $\sim 10\%$  decrease) guarantees that the applied UV fluence was sufficiently large for photoinduced processes of  $\text{CO}_2$  to occur. Longer UV irradiation induced a slight decrease of  $\text{CO}_2$  ( $\sim 15\%$  decrease after 90-min irradiation). The peaks of photoproduct were observed at  $2140$ ,  $2044$ , and  $1044 \text{ cm}^{-1}$ , which are thought to originate from  $\text{CO}$ ,  $\text{CO}_3$ , and  $\text{O}_3$ , respectively [24]. Although a precise quantitative analysis on photodissociation reactions is not possible due to the lack of information on the absorption coefficients of these species in solid  $\text{CO}_2$ , the

estimated column densities of products comparable to the decrease of CO<sub>2</sub> indicate that the photodissociation instead of photodesorption contributes to the decrease of CO<sub>2</sub>. The absence of UV-ray-induced amorphization can also be recognized in the IR spectra reported by Martín-Doménech et al. [25]. Although these authors did not mention the crystallinity of their solid CO<sub>2</sub> sample, their IR spectra indicate that mixture of amorphous and crystalline CO<sub>2</sub> sample became crystalline CO<sub>2</sub> upon UV-ray irradiation.

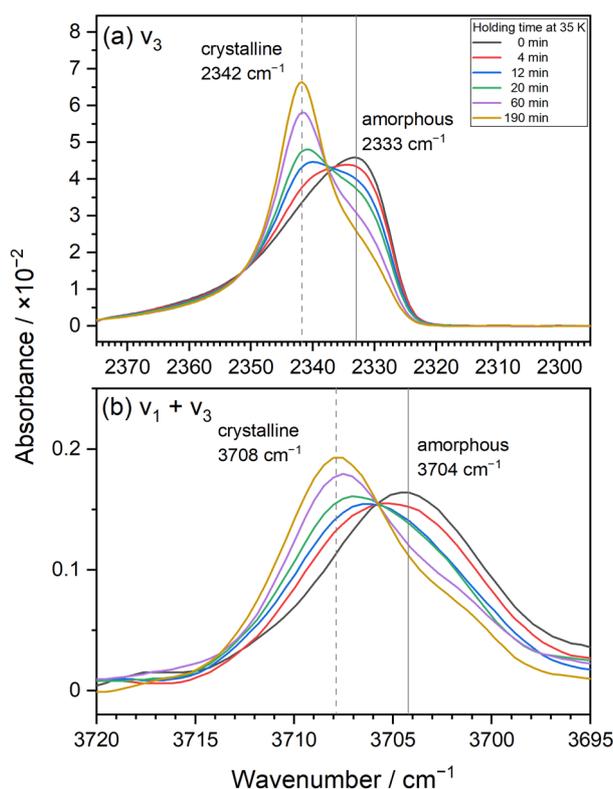


**Figure 3.** Infrared spectra of solid CO<sub>2</sub> in the  $\nu_1 + \nu_3$  region 3720–3695 cm<sup>-1</sup> and in the  $\nu_3$  region 2400–2300 cm<sup>-1</sup>. (a) After deposition at 8 K. (b) After annealing at 60 K for 10 min. The warming-up and cooling-down rate was 4 K min<sup>-1</sup>. (c) After irradiation by the D<sub>2</sub> lamp for 20 min. All spectra were measured at 8 K. Peak positions for amorphous CO<sub>2</sub> at 3704 and 2333 cm<sup>-1</sup> are indicated with solid lines and those for crystalline CO<sub>2</sub> at 3708 and 2342 cm<sup>-1</sup> are indicated with dashed lines.

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He and Vidali presented a method to investigate a degree of crystallinity in CO<sub>2</sub> sample by using the  $\nu_1 + \nu_3$  combination band since determining the degree of crystallinity from the spectral shape of the  $\nu_3$  band in IR spectra acquired with the reflection absorption configuration is difficult [16]. We found that, in the IR spectra measured with transmission configuration, the peak position of  $\nu_3$  band gradually shifts

from 2333 to 2342  $\text{cm}^{-1}$  as crystallization proceeds and the alternation correlates with the shape change of the  $\nu_1 + \nu_3$  combination band (see Figure 4), for which 3704 and 3708  $\text{cm}^{-1}$  peaks have been attributed to amorphous and crystalline  $\text{CO}_2$ , respectively. Therefore, when using IR spectra measured with transmission configuration, we deduce that the IR band of  $\nu_3$  mode is also representative of crystallinity.



**Figure 4.** Infrared spectra of solid  $\text{CO}_2$  in regions (A) 2375–2950 and (B) 3720–3695  $\text{cm}^{-1}$ . The sample was deposited at 8 K and annealed to 35 K. Just after reaching 35 K, IR measurements were started. The spectra measured after 0, 4, 12, 20, 60, and 190 min are presented in different colors. Peak positions for amorphous and crystalline  $\text{CO}_2$  are indicated with solid and dashed lines, respectively.

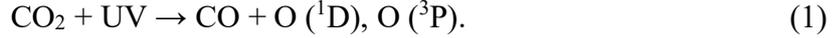
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#### 4. Discussion

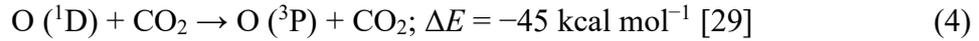
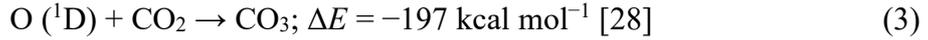
#### 4.1. Why does CO<sub>2</sub> I crystal not amorphize?

As mentioned earlier, the amorphization of crystalline H<sub>2</sub>O ice by UV-irradiation has been demonstrated [6,7]. In contrast, we found that UV-ray irradiation does not induce the amorphization of crystalline CO<sub>2</sub>. Below, we discuss possible UV-induced processes in CO<sub>2</sub> solid.

CO<sub>2</sub> molecule is decomposed by UV-rays [26]:



The formation of O (<sup>1</sup>D) is a major spin-allowed path. Although the dissociation to O (<sup>3</sup>P) is spin-forbidden, this channel was clearly observed in the gas phase [26]. The produced energetic O would not escape from the CO<sub>2</sub> I lattice because CO<sub>2</sub> I is compact face-centered cubic crystal. When an O (<sup>1</sup>D) atom is produced in reaction (1), several reactions are expected.



In the UV-ray irradiation experiments, the CO<sub>2</sub> depletion saturated after long irradiation (90 min, UV fluence  $\sim 1.5 \times 10^{18}$  photons cm<sup>-2</sup>), which suggests that CO<sub>2</sub> destruction (e.g., reaction (1)) and formation (reaction (2)) are well balanced at this moment. The occurrence of reactions (1) and (3) is inferred from the IR spectra of UV-ray-irradiated solid CO<sub>2</sub>, where products CO and CO<sub>3</sub> were observed. Even if an O (<sup>1</sup>D) atom is quenched to O (<sup>3</sup>P) in reaction (4), the resultant O (<sup>3</sup>P) atom can react with CO:



Because of the energy barrier, which is  $\sim 4$  kcal mol<sup>-1</sup> in the gas phase, this reaction requires energetic O (<sup>3</sup>P) atom and/or CO molecule. Nevertheless, the occurrence of reaction (5) in irradiated solid CO<sub>2</sub> has been reported in the literature [31] and is consistent with theoretical predictions [30].

Reactions (1)-(5) are exothermic reactions, which can heat the region where they occur. In other words, the occurrence of these reactions converts the energy of UV-rays into thermal energy. Because the crystalline structure is energetically more stable than the amorphous structure, these thermal energies should induce crystallization. The photolysis of CO<sub>2</sub>, which is reaction (1), is considered an amorphization process, since it creates a defect in the CO<sub>2</sub> lattice. Thus, a competition between this UV-induced amorphization and the crystallization induced by heat produced in reactions (1)-(5) is

important to determine the fate of UV-ray-irradiated CO<sub>2</sub> solid. The experimental results strongly suggest that the latter processes are significant in the CO<sub>2</sub> case.

Since the cosmic-ray-induced UV flux in molecular clouds is  $\sim 10^3$  photons cm<sup>-2</sup> s<sup>-1</sup>, one second of UV irradiation in the TEM and IR experiments corresponds to  $\sim 10^3$  and  $10^4$  years of UV irradiation in molecular clouds, respectively. We did not observe any amorphization even after 90 min of irradiation in the IR experiment, which corresponds to  $5 \times 10^7$  years in molecular clouds. Therefore, our results indicate that the UV-induced amorphization of CO<sub>2</sub> crystal is unlikely to occur in molecular clouds.

Similarly, UV-ray-induced chemical reactions are expected in crystalline H<sub>2</sub>O ice; i.e., exothermic reactions such as  $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$  and  $\text{H} + \text{H} \rightarrow \text{H}_2$  would occur following the decomposition by UV-ray,  $\text{H}_2\text{O} + \text{UV} \rightarrow \text{H} + \text{OH}$  or other products. However, it has been reported that UV-ray-induced amorphization of crystalline H<sub>2</sub>O ice occurs at temperature below 70 K [7]. In addition, preliminary experiments reveal that the UV-ray-induced crystallization of amorphous H<sub>2</sub>O occurs in the temperature range of 70–100 K (Kouchi et al. unpublished work). These different behaviors of CO<sub>2</sub> solid and H<sub>2</sub>O ice to UV-ray irradiation might be related to the dissipation rate of reaction heats. Famá et al. [12] discussed the ion-bombardment-induced amorphization of crystalline H<sub>2</sub>O based on a thermal spike model, which was modified based on Szenes's model [32], and they suggested that the very fast cooling of a transient liquid track produced by each ion led to amorphization. Analogously, we deduce that the cooling of locally heated CO<sub>2</sub> molecules is slower than the H<sub>2</sub>O case, so that CO<sub>2</sub> molecules in this region have sufficient time to return to the original positions. This local thermal dissipation process might not be scaled by bulk property of solids, e.g., thermal conductivity. To gain further insight into the difference between H<sub>2</sub>O ice and CO<sub>2</sub> solid, simulations including molecular level dynamics will be required, and they are out of the scope of this paper.

#### **4.2. The absence of amorphous CO<sub>2</sub> in molecular clouds**

Escribano et al. suggested the absence of amorphous CO<sub>2</sub> in space based on the comparison of 2343 cm<sup>-1</sup> band towards Elias 16 with the laboratory spectrum [14]. They simply assumed that the crystallization temperature of amorphous CO<sub>2</sub> in molecular clouds was identical to that observed in the laboratory, which is approximately 25 K. However, the crystallization temperature greatly depends on the

time scale of experimental observation as demonstrated for amorphous H<sub>2</sub>O [4]. Therefore, it is reasonable to assume that crystallization temperature of amorphous CO<sub>2</sub> in molecular clouds is much lower than 25 K. Recently, from the fitting of the 15- $\mu$ m band of Q21-1 using bands of crystalline CO<sub>2</sub> and amorphous CO<sub>2</sub>, Gerakines and Hudson suggested that up to ~9% of CO<sub>2</sub> might be amorphous [13]. However, the validity of their fitting requires further assessment.

Here, we will discuss some factors that control the crystallinity of CO<sub>2</sub>. First, we assume that CO<sub>2</sub> molecules formed by the following grain surface reaction [33,34] result in an amorphous form regardless of the reaction heat:



where asterisks indicate reaction intermediates. Crystalline CO<sub>2</sub> can be amorphized by the irradiation of high-energy particles, although we have no experimental evidence. Another possible crystallization mechanism of amorphous CO<sub>2</sub> is that crystallization might be promoted even at low temperature in molecular clouds. Because crystallization temperatures in the molecular cloud time scale are lower than those in the laboratory; crystallization temperatures in the time scale of 10<sup>6</sup> years might be lower than 20 K. Actually, Kouchi et al. (in prep.) estimated the time scale of crystallization at 15 K to be 10<sup>6</sup> years. Although the above discussion is still preliminary due to the lack of quantitative data, we suggest that the crystallization of amorphous CO<sub>2</sub> might proceed even in low-temperature molecular clouds, if amorphous CO<sub>2</sub> is formed at first.

Finally, we consider the direct formation of crystalline CO<sub>2</sub>. a) Chemical desorption is proposed as one of the nonthermal desorption mechanisms of molecules in low-temperature molecular clouds [35,36], and some experiments support this idea [37-39]. Thus, CO<sub>2</sub> formed by reaction (6) has sufficient energy to diffuse and cause crystallization, since the activation energy of surface diffusion is 0.3-0.5 of the desorption energy. b) Local heating by reaction (6) could induce the crystallization.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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