

# Surface abundance change in vacuum ultraviolet photodissociation of CO<sub>2</sub> and H<sub>2</sub>O mixture ices

Takashi Kinugawa,<sup>a</sup> Akihiro Yabushita,<sup>a</sup> Masahiro Kawasaki,\*<sup>a</sup> Tetsuya Hama<sup>b</sup> and Naoki Watanabe<sup>b</sup>

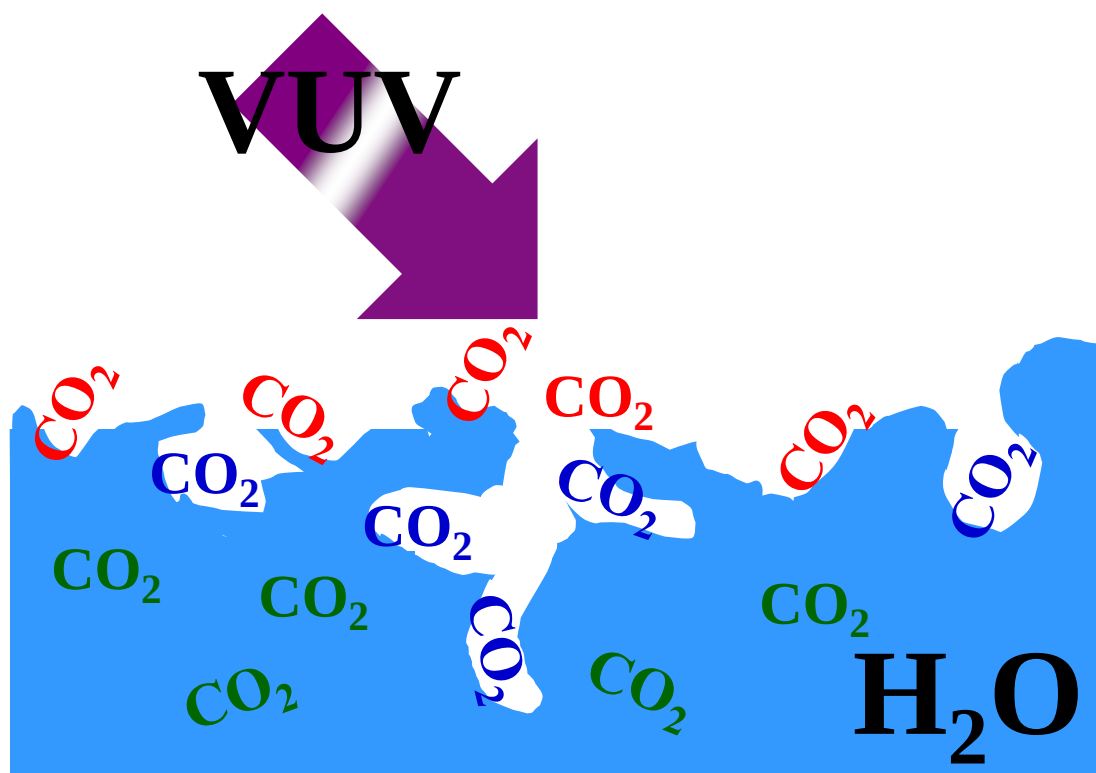
<sup>a</sup> Department of Molecular Engineering, Kyoto University, Kyoto 615-8510, Japan

<sup>b</sup> Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan

Photodissociation of amorphous ice films of carbon dioxide and water co-adsorbed at 90 K was carried out at 157 nm using oxygen-16 and -18 isotopomers with a time-of-flight photofragment mass spectrometer. O(<sup>3</sup>P<sub>J</sub>) atom, OH( $v=0$ ) radical, and CO( $v=0,1$ ) molecules were detected as photofragments. CO is produced directly from the photodissociation of CO<sub>2</sub>. Two different adsorption states of CO<sub>2</sub>, *i.e.*, physisorbed CO<sub>2</sub> on the surface of amorphous solid water and trapped CO<sub>2</sub> in the pores of the film, are clearly distinguished by the translational and internal energy distributions of the CO molecules. The O atom and OH radical are produced from the photodissociation of H<sub>2</sub>O. Since the absorption cross section of CO<sub>2</sub> is smaller than that of H<sub>2</sub>O at 157 nm, the CO<sub>2</sub> surface abundance is relatively increased after prolonged photoirradiation of mixed ice film, resulting in the formation of a heterogeneously layered structure in the mixed ice at low temperatures. Astrophysical implications are discussed.

To whom correspondence should be addressed.

Kawasaki@moleng.kyoto-u.ac.jp Phone +81-707-2460 Fax +81-707-2513



Surface abundance of CO<sub>2</sub> on the surface of CO<sub>2</sub>/H<sub>2</sub>O mixture ice increases during vacuum ultraviolet photoirradiation at 90 K.

# GRAPHICAL CONTENTS ENTRY

## 1. Introduction

Interactions of gas-phase species with water ice have been of importance in the fields of atmospheric and interstellar chemistry. Following the collision of gaseous species with the surface of water ice, physicochemical processes on the surface proceed, *e.g.*, adsorption on the surface, thermal desorption into the gas phase, diffusion from the surface into the bulk ice, and reaction with other species. Interactions of CO<sub>2</sub> with water ice at low temperature have been studied extensively due to the facts that 1) CO<sub>2</sub> is present in relatively large amounts at low temperatures in a variety of places: the terrestrial mesosphere, the poles of Mars, interstellar clouds and small solar system bodies such as comets or Triton;<sup>1</sup> and 2) CO<sub>2</sub> can be used as a tracer for investigating ice morphology and for studying the trapping and releasing of volatile molecules by water ice. For instance, temperature programmed desorption (TPD) studies showed that two different adsorption states of CO<sub>2</sub> exist in amorphous solid water (ASW). One consists of CO<sub>2</sub> adsorbing atop ASW to make a CO<sub>2</sub> adlayer similar to pure CO<sub>2</sub> ice.<sup>2</sup> The other consists of CO<sub>2</sub> trapped in the cavities of ASW.<sup>3</sup> The latter state has a larger activation energy for desorption than the former state.

The importance of energetic processes caused by vacuum ultraviolet (VUV) photoirradiation is known in the above-mentioned cosmic regions, which can directly induce chemical reactions of the ice mantles. According to Mason et al.,<sup>4</sup> solid CO<sub>2</sub> has smaller absorption cross sections in the VUV region compared with those of solid H<sub>2</sub>O. At Lyman- $\alpha$  photons ( $\lambda=121.6$  nm), for example, cross sections of  $\sim 4.0 \times 10^{-18}$  cm<sup>2</sup> and  $\sim 7.0 \times 10^{-19}$  cm<sup>2</sup> were reported for solid H<sub>2</sub>O and CO<sub>2</sub> respectively. This implies that H<sub>2</sub>O is efficiently photodissociated compared with CO<sub>2</sub> following VUV photoirradiation of H<sub>2</sub>O/CO<sub>2</sub> mixed ice. If such preferential H<sub>2</sub>O photodissociation proceeds, and the surface abundance of CO<sub>2</sub> in the mixed ice becomes higher, a layered structure of CO<sub>2</sub> on H<sub>2</sub>O may be formed after prolonged irradiation. Photoirradiation on pure or mixed ices triggers desorption of atoms, radicals, or molecules; and the desorption dynamics of photofragments are known to be sensitive to the adsorption states of the photoirradiated molecules. For example, when H<sub>2</sub>O molecules are dissociated at  $\lambda=157$  and 193 nm, the translational energy distributions of the photodesorbed H atoms strongly depend on the morphologies of the ice films as well as the secondary surface reactions.<sup>5,6</sup> Therefore, how the surface composition changes after VUV photoirradiation needs to be known in order to develop detailed modeling of gas-ice interactions including the reactivity of surface reactions.

In the present work, we have measured time-of-flight (TOF) spectra and rotationally resolved resonance-enhanced multiphoton ionization (REMPI) spectra of photodesorbed CO species from 157 nm photoirradiation of mixed CO<sub>2</sub>/H<sub>2</sub>O ice films at 90 K. Photodesorption processes of OH and O(<sup>3</sup>P<sub>J</sub>) were also investigated and are further discussed. Two different deposition gas mixtures were used for the mixed ice preparation to investigate the correlation between the CO<sub>2</sub> adsorption structures in the mixed CO<sub>2</sub>/H<sub>2</sub>O and the photodesorption dynamics.

## 2. Experimental

### 2.1. Apparatus and preparation of ice

Our experimental setup consisted of an ultrahigh vacuum chamber, two pulsed molecular flow sources, an excimer laser, and a dye laser. The experiment is concisely described here, but a more detailed explanation of the

experimental apparatus is described elsewhere.<sup>7</sup> The vacuum chamber was evacuated to a base pressure of  $10^{-8}$  Torr by turbo molecular pumps in tandem (Shimadzu, 800 and 50 L s<sup>-1</sup>). An optically flat sapphire disk substrate (12 mm dia., 2 mm thick), sputter coated with a thin polycrystalline film of Au(111), was supported in the center of the chamber by a liquid-nitrogen-cooled manipulator.

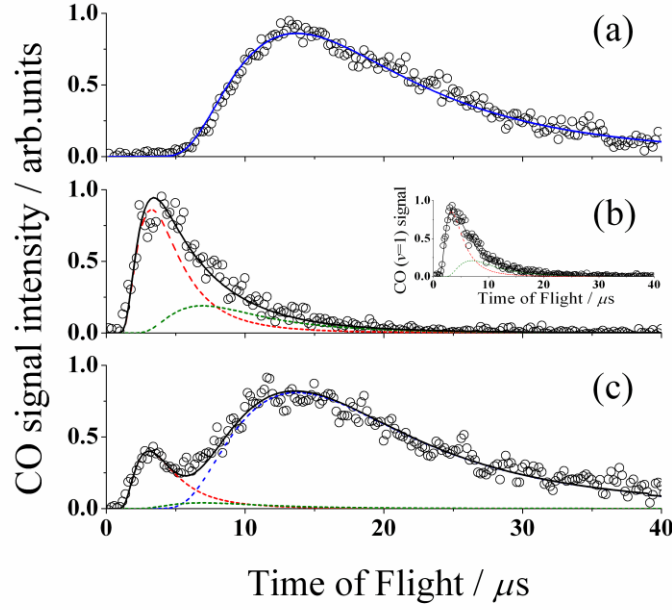
Two types of ASW mixture samples were prepared at 90 K: C<sup>16</sup>O<sub>2</sub>/H<sub>2</sub><sup>16</sup>O and C<sup>18</sup>O<sub>2</sub>/H<sub>2</sub><sup>16</sup>O. Co-adsorbed mixture ices were prepared by backfilling deposition of H<sub>2</sub>O vapor and CO<sub>2</sub> gas onto the substrate at 90 K by two pulse valves (General Valve). Pulsed molecular flows were introduced simultaneously into the chamber at the rate of 10 Hz. In order to spread vapors all over the chamber, a flat plate was attached in front of each pulse valve. The exposure was typically 900 L (1 L =  $1 \times 10^{-6}$  Torr s) and the mixing ratios of H<sub>2</sub>O and C<sup>16</sup>O<sub>2</sub> or C<sup>18</sup>O<sub>2</sub> ranged from 1:4 to 4:1 (typical ratio). Hereafter unless otherwise stated, O atom stands for <sup>16</sup>O atom.

In our experimental conditions, CO<sub>2</sub> can exist in two different forms on surface: 1) CO<sub>2</sub> adlayer adsorbed atop the mixture ice film<sup>2,3</sup> and 2) CO<sub>2</sub> trapped in the porous sites.<sup>8,9</sup> To investigate the photodynamics of the CO<sub>2</sub> adlayer on the surface, a prepared CO<sub>2</sub>/H<sub>2</sub>O mixture ice film was continually exposed to CO<sub>2</sub> gas during pulsed photoirradiation. In these intermittent sequential deposition experiments, the pulse valve for CO<sub>2</sub> was opened after each laser shot so as to deposit fresh CO<sub>2</sub> layers on the CO<sub>2</sub>/H<sub>2</sub>O mixture ice film. Hereafter, experiments using thus prepared ice samples are called “CO<sub>2</sub> adlayer” experiments. The term adlayer refers to the layers of CO<sub>2</sub> atop the ASW surface. For investigation of the photodynamics of CO<sub>2</sub> trapped in the CO<sub>2</sub>/H<sub>2</sub>O mixture ice film, fresh layers of the CO<sub>2</sub>/H<sub>2</sub>O mixture ice film were adsorbed by intermittent refreshment with the CO<sub>2</sub> and H<sub>2</sub>O gases. In the present experiment, the two pulse valves for CO<sub>2</sub> and H<sub>2</sub>O gases were opened after each laser shot to prepare a fresh layer of the CO<sub>2</sub>/H<sub>2</sub>O mixture ice. Hereafter, experiments using thus prepared ice samples are called “fresh CO<sub>2</sub>/H<sub>2</sub>O” experiments. The intermittent refreshments of the ice films exclude a potential influence of photoproducts such as H<sub>2</sub>CO<sub>3</sub> accumulated on the mixed ice surface by 157 nm photoirradiation on the energy distributions of measured photoproducts.<sup>10</sup> All of the present experiments were performed at a sample temperature of 90 K, and a typical chamber pressure for intermittent experiments was  $5 \times 10^{-7}$  Torr. The pressure without fresh deposition was  $5 \times 10^{-8}$  Torr.

Unfocused 157 nm laser radiation was incident at an angle of about 80° to the surface normal the ice surface at a fluence  $< 0.1 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ . CO photoproducts were subsequently ionized at a vertical distance of 3 mm normal to the substrate surface by 2 + 1 REMPI via the  $B \ ^1\Sigma^+ (v' = 0,1) \leftarrow X \ ^1\Sigma^+ (v'' = 0,1)$  sequential vibrational transitions at 229.90 - 230.35 nm, and collected with a small mass spectrometer aligned perpendicular to the ice surface.<sup>11,12</sup> OH and O(<sup>3</sup>P<sub>J</sub>) were detected by 2 + 1 REMPI via the  $\text{OH}(D \ ^2\Sigma^- \leftarrow X \ ^2\Pi)$  transition at 244.0 - 244.5 nm,<sup>13</sup> and the  $\text{O}(3p \ ^3P_J - 2p \ ^3P_J)$  transition at 225.6 - 226.4 nm.<sup>14</sup> PGOPHER, a program for simulating rotational structure, was used to estimate the rotational temperatures of the photoproducts.<sup>15</sup> Spectroscopic parameters were taken from Greenslade et al.<sup>16</sup> and Huber and Herzberg for OH,<sup>17</sup> and Huber and Herzberg,<sup>17</sup> Morton et al.,<sup>18</sup> and Chen and Yeung for CO.<sup>19</sup>

## 2.2. Simulation of time-of-flight spectra of CO photoproducts

The TOF spectra of photoproducts were taken as a function of delay time between the photolysis and REMPI laser



**Fig. 1** TOF spectra of CO [ $B^1\Sigma^+(v' = 0) \leftarrow X^1\Sigma^+(v'' = 0)$ ] following 157 nm photoirradiation of (a) fresh  $\text{CO}_2/\text{H}_2\text{O}$  mixture ice at 90 K for which  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are co-adsorbed with keeping the surface fresh. (b)  $\text{CO}_2$  adlayer for which  $\text{CO}_2$  are sequentially adsorbed on the surface of the  $\text{CO}_2/\text{H}_2\text{O}$  mixture ice, the inset shows the TOF spectrum of  $\text{CO}(v=1)$ . (c)  $\text{CO}_2/\text{H}_2\text{O}$  mixture after 1 hr photoirradiation. The solid curves are fits to the data derived with  $T_{\text{trans}} = 1600$  (red), 350 (green), and 90 K (blue). Probe laser wavelengths are 230.101 nm for (a) and 230.092 nm for (b, c).

pulses using a delay generator to investigate the translational energies of desorbing photoproducts. Details regarding the simulation of such TOF spectra have been reported previously.<sup>7</sup> The measured TOF spectra  $S(a_i, t, T_{\text{trans}})$  of the photoproducts were fit to a sum of one or more flux-weighted Maxwell - Boltzmann (MB) distributions  $S_{\text{MB}}$ , each defined by a translational temperature  $T_{\text{trans}}$ . The coefficients,  $a_i$ , are used for the relative population of each MB distribution,

$$S(a_i, t, T_{\text{trans}}) = \sum a_i S_{\text{MB}}(t, T_{\text{trans}}), \quad (1)$$

$$S_{\text{MB}}(t, T_{\text{trans}}) = r^3 t^{-4} \exp[-mr^2/2k_B T_{\text{trans}} t^2], \quad (2)$$

$$P_{\text{MB}}(E_{\text{trans}}) = (k_B T_{\text{trans}})^{-2} E_{\text{trans}} \exp[-E_{\text{trans}}/k_B T_{\text{trans}}], \quad (3)$$

where  $r$  is a flight length of photoproducts. The MB distribution  $P_{\text{MB}}(E_{\text{trans}})$  as a function of translational energy  $E_{\text{trans}}$  is characterized by the averaged translational energy  $\langle E_{\text{trans}} \rangle = 2k_B T_{\text{trans}}$ , where  $k_B$  is the Boltzmann constant. The Jacobian given by Zimmerman and Ho was used to obtain the translational energy distribution from the TOF distribution.<sup>20</sup> A small contribution of very slow TOF component ( $T_{\text{trans}} = 20 \pm 5$  K) appeared after  $t = 20 \mu\text{s}$ . This component is considered to be an artifact caused by the CO photofragments that were scattered once and bounced back to the REMPI detection region. This slowest component was subtracted from the TOF spectrum simulating MB distributions.

**Table 1** Translational and rotational temperatures of CO( $v=0$ ) photofragments.

|                                                          | Temperatures / K                                   |                                                      |
|----------------------------------------------------------|----------------------------------------------------|------------------------------------------------------|
|                                                          | Translation                                        | Rotation                                             |
| fresh CO <sub>2</sub> /H <sub>2</sub> O                  | 90 ± 10 (100%)                                     | 150 ± 50 <sup>b</sup>                                |
| CO <sub>2</sub> adlayer                                  | 1600 ± 400 (70%)<br>350 ± 50 (30%)                 | 800 ± 200 <sup>a</sup><br>—                          |
| CO <sub>2</sub> /H <sub>2</sub> O after photoirradiation | 1600 ± 400 (11%)<br>350 ± 50 (2%)<br>90 ± 10 (87%) | 800 ± 200 <sup>a</sup><br>—<br>150 ± 50 <sup>b</sup> |

Numbers in parentheses are contributions of each temperature component in TOF spectra.

—: not measured

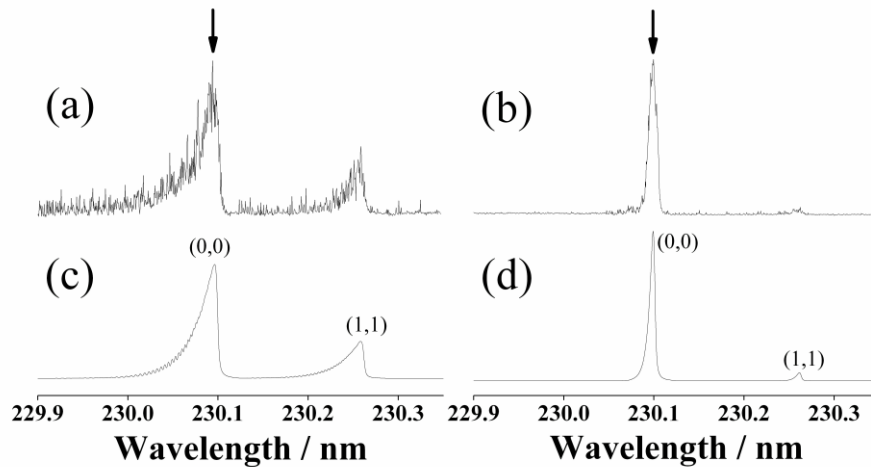
<sup>a</sup> TOF=3.0  $\mu$ s.

<sup>b</sup> TOF=12.0  $\mu$ s.

### 3. Results

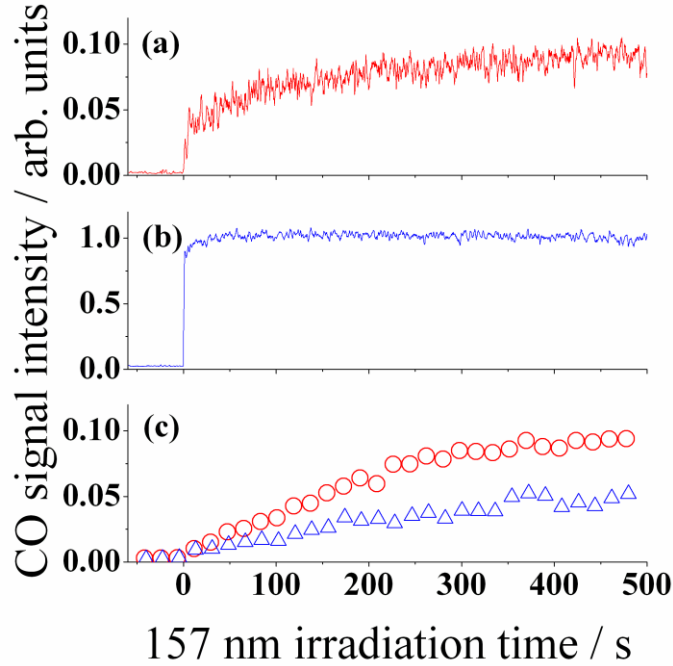
#### 3.1. CO photoproducts

Figure 1 shows typical TOF spectra of CO( $v=0$ ) following 157 nm irradiation on (a) fresh CO<sub>2</sub>/H<sub>2</sub>O mixture, (b) CO<sub>2</sub> adlayer and (c) CO<sub>2</sub>/H<sub>2</sub>O mixture after 1 hour 157 nm photoirradiation without refreshment, which were measured at a REMPI wavelength of the Q-head. The spectrum (a) is well reproduced by a single MB distribution with  $T_{\text{trans}}=90\pm10$  K. The spectrum (b) is reproduced with  $T_{\text{trans}}=1600\pm400$  K (70%) and  $350\pm50$  K (30%), while the  $T_{\text{trans}}=90$  K component is not observed. The spectrum (c) consists of three MB distributions with  $T_{\text{trans}}=1600\pm400$  (11%),  $350\pm50$  (2%) and  $90\pm10$  K (87%). Table 1 summarizes the results.

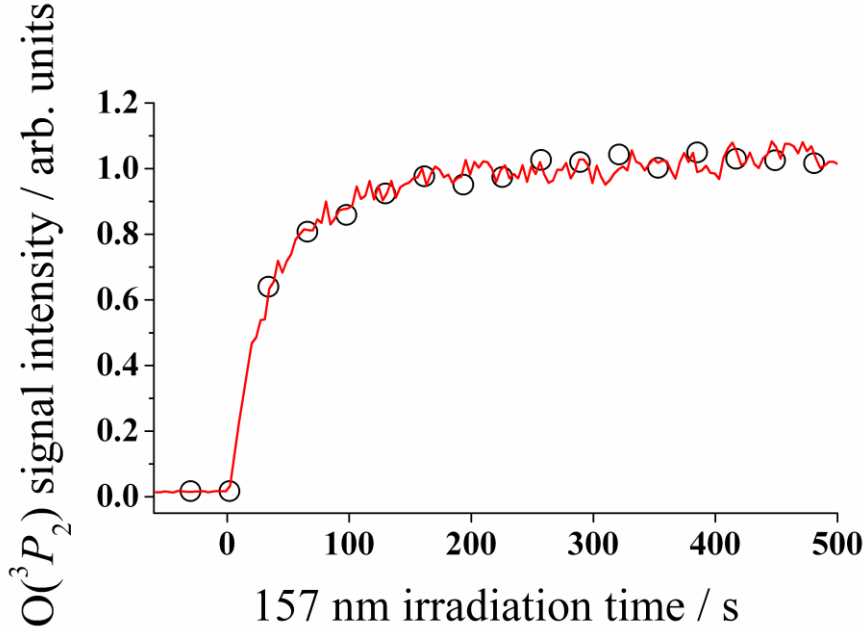


**Fig. 2** REMPI excitation spectra of the CO  $B^1\Sigma^+ \leftarrow X^1\Sigma^+$  transition from CO<sub>2</sub>/H<sub>2</sub>O mixture ice at 90 K, (a) at time-of-flight  $t=3.0$   $\mu$ s and (b)  $t=12.0$   $\mu$ s. The arrows indicate the Q-heads used for time-of-flight measurements in Fig. 1(c) and (d): Spectral simulation assuming Boltzmann rotational state population distributions with (c)  $T_{\text{rot}}=800$  K and (d) 150 K.

Figures 2(a) and (b) show REMPI excitation spectra of CO from CO<sub>2</sub>/H<sub>2</sub>O mixture after 1 hr irradiation at 157 nm at (a)  $t=3.0 \mu\text{s}$  and (b)  $12.0 \mu\text{s}$ , respectively. The rotational temperatures  $T_{\text{rot}}$  of CO( $v=0$ ) are estimated to be  $800\pm 200$  and  $150\pm 50$  K for  $t=3.0$  and  $12.0 \mu\text{s}$ , respectively, by spectral simulations as shown in Figs. 2(c) and (d). Figures 3(a) and (b) show time evolutions of CO( $v=0$ ) from a CO<sub>2</sub>/H<sub>2</sub>O mixture left under vacuum at 90 K for 1 minute after preparation of the ice at (a)  $t=3.0 \mu\text{s}$  for CO( $T_{\text{trans}}=1600$  K) and (b)  $t=12.0 \mu\text{s}$  for CO( $T_{\text{trans}}=90$  K) as a function of 157 nm irradiation time. These two signals immediately appeared after 157 nm irradiation. After initial rise of the signals, the CO( $T_{\text{trans}}=1600$  K) intensity increased with 157 nm irradiation time, while the CO( $T_{\text{trans}}=90$  K) intensity stayed constant. Figure 3(c) shows time evolution of CO( $v=0$ ) from CO<sub>2</sub>/H<sub>2</sub>O mixture when the ice sample was left under vacuum without photoirradiation at 90 K for 10 minute after ice preparation. Even for 20 min waiting time, the qualitatively same signal evolution was observed. In contrast to the above mentioned results, both the fast and slow signals do not promptly appear and their intensities increase gradually with irradiation time at 157 nm. CO<sub>2</sub> desorption from pure CO<sub>2</sub> ice at 90 K was studied experimentally and



**Fig. 3** Time evolutions of CO [ $B^1\Sigma^+ (v'=0) \leftarrow X^1\Sigma^+ (v''=0)$ ] from CO<sub>2</sub>/H<sub>2</sub>O mixture ice left under vacuum at 90 K for one-minute after ice preparation as a function of 157 nm irradiation time (a) at  $t = 3.0 \mu\text{s}$  at 230.092 nm, (b) at  $t=12.0 \mu\text{s}$  at 230.101 nm. (c) the mixture ice sample was left under vacuum without photoirradiation for ten min at 90 K after ice preparation, and it should be noted that relative intensities of the fast and slow components cannot be quantitatively compared to each other.



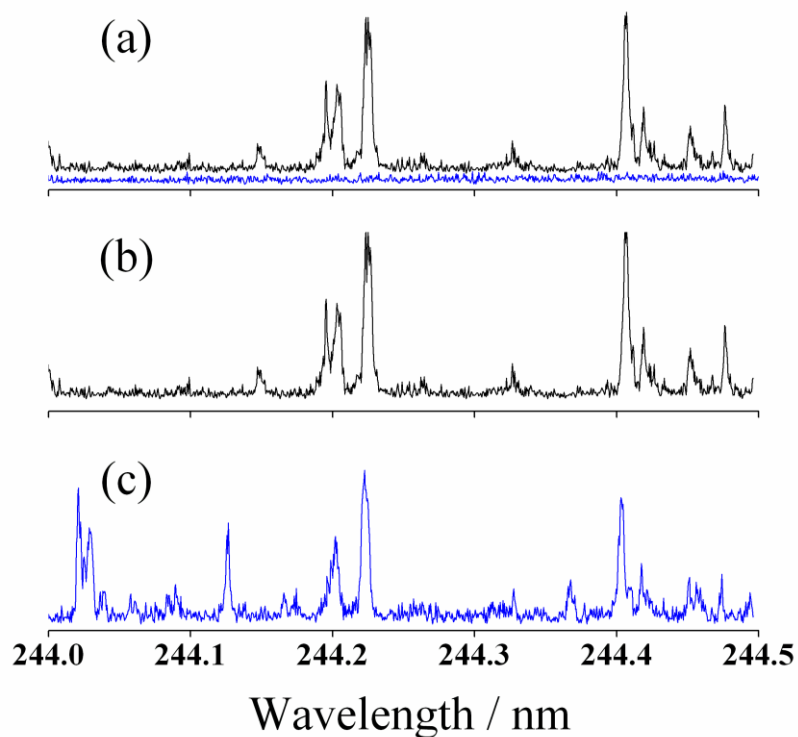
**Fig. 4** Time evolutions of  $O(^3P_2)$  from  $CO_2/H_2O$  mixture ice (red line) and from neat ASW( $H_2O$ ) (open circle) as a function of 157 nm irradiation time at TOF=1.5  $\mu s$ .

theoretically by Mate et al.<sup>2</sup> A film of pure  $CO_2$  ice of approximately 180 nm was deposited on the Al substrate at 90 K. Once the  $CO_2$  deposition was stopped,  $CO_2$  began to desorb. However,  $CO_2$  still remained on the substrate at least 30 minute after the deposition. Our previous experimental results suggest that the effect of further deposition of  $H_2O$  from residual gas to suppress an initial photolysis of  $CO_2$  on the ice surface was negligible.<sup>21</sup>

### 3.2. $O(^3P_J)$ atom from $CO_2/H_2O$ mixture and $CO_2$ adlayer

Figure 4 shows the time evolution of  $O(^3P_2)$  from a  $CO_2/H_2O$  mixture one-minute after preparation of the ice as a function of 157 nm irradiation time at 225.655 nm at  $t=1.5 \mu s$  corresponding to the maximum in its TOF spectrum. For comparison purpose, Fig. 4 includes the time evolution data of  $O(^3P_2)$  from ASW( $H_2O$ ) at  $t=1.5 \mu s$ , which corresponding to the maximum in its TOF spectrum from 157 nm photodissociation of neat ASW( $H_2O$ ), from which  $O(^3P_J)$  are produced.<sup>22</sup>

The evolution behaviors of  $O(^3P_2)$  from  $CO_2/H_2O$  mixture and ASW( $H_2O$ ) are in good accordance to each other. The branching ratio of angular momentum states of  $O(^3P_J)$  from  $CO_2/H_2O$  mixture after 1 hr irradiation at 157 nm was 2.4 : 1.8 : 1 for  $J=2, 1, 0$ , which is in accordance with that from ASW( $H_2O$ ). To further confirm the  $O(^3P_2)$  source, photoirradiation of the  $C^{18}O_2/H_2^{16}O$  mixture was made, in which detection of  $^{18}O(^3P_J)$  was not successful because strong  $^{16}O(^3P_J)$  signal disturbed weak  $^{18}O(^3P_J)$  signal, while  $C^{18}O$  was successfully detected at  $t=3.0 \mu s$ . These results suggest that the main  $O(^3P_2)$  source from the  $CO_2$  doped  $H_2O$  ice film is not  $CO_2$  but  $H_2O$ . Note that a weak signal of  $^{18}O(^3P_J)$  was successfully detected from neat  $C^{18}O_2$  adlayer experiment. This result suggests that  $CO_2$  dissociates mainly to  $CO + O(^1D)$  and to only a small extent  $CO + O(^3P_J)$ . Also that electronic quenching of  $O(^1D)$  to  $O(^3P_J)$  on the ASW surface plays only a minor role in the present photodesorption study. Zhu and Gordon



**Fig. 5** REMPI excitation ( $D^2\Sigma^- \leftarrow X^2\Pi$ ) spectra of  $^{16}\text{OH}$  and  $^{18}\text{OH}$  from ice samples after 1 hour 157 nm photoirradiation at  $t = 1.0 \mu\text{s}$ . (a)  $m/z = 17$  (black) for  $^{16}\text{OH}$  and  $m/z = 19$  (blue) for  $^{18}\text{OH}$  from  $\text{C}^{18}\text{O}_2/\text{H}_2^{16}\text{O}$  mixture ice. (b)  $^{16}\text{OH}$  and (c)  $^{18}\text{OH}$  from  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ .

reported that the yield of the  $\text{O}(^3P)$  production is 0.05 at 157 nm in the gas phase by a chemical scavenging technique,<sup>23</sup> which is confirmed by a molecular beam photofragment spectroscopy study by Stolow and Lee.<sup>24</sup>  $\text{O}(^1D)$  is known to react easily with parent  $\text{H}_2\text{O}$  molecules by collisions with ASW to produce OH or  $\text{H}_2\text{O}_2$ .<sup>25,26</sup>  $\text{CO}_3$  could be transiently formed through reaction of  $\text{O}(^1D)$  with  $\text{CO}_2$ , but it is reported to be stable only at lower than 50 K.<sup>27</sup>

**Table 2** O(<sup>3</sup>P<sub>2</sub>) and OH from amorphous solid water and CO<sub>2</sub>/H<sub>2</sub>O isotopomer mixture ice

|                                                                                                          | Photofragments                                              |                                                             |                               |                               |
|----------------------------------------------------------------------------------------------------------|-------------------------------------------------------------|-------------------------------------------------------------|-------------------------------|-------------------------------|
|                                                                                                          | <sup>16</sup> O( <sup>3</sup> P <sub>2</sub> ) <sup>a</sup> | <sup>18</sup> O( <sup>3</sup> P <sub>2</sub> ) <sup>a</sup> | <sup>16</sup> OH <sup>b</sup> | <sup>18</sup> OH <sup>b</sup> |
| C <sup>16</sup> O <sub>2</sub> /H <sub>2</sub> <sup>16</sup> O after photoirradiation                    | ○                                                           | —                                                           | ○                             | —                             |
| C <sup>18</sup> O <sub>2</sub> adlayer on C <sup>18</sup> O <sub>2</sub> /H <sub>2</sub> <sup>16</sup> O | ○                                                           | ○                                                           | —                             | —                             |
| C <sup>18</sup> O <sub>2</sub> /H <sub>2</sub> <sup>16</sup> O after photoirradiation                    | ○                                                           | ○                                                           | ○                             | ×                             |
| H <sub>2</sub> <sup>18</sup> O/H <sub>2</sub> <sup>16</sup> O after photoirradiation                     | ○                                                           | ○                                                           | ○                             | ○                             |

○ : observed, ×: not observed, —: not measured

<sup>a</sup> TOF=1.5 μs.

<sup>b</sup> TOF=1.0 μs.

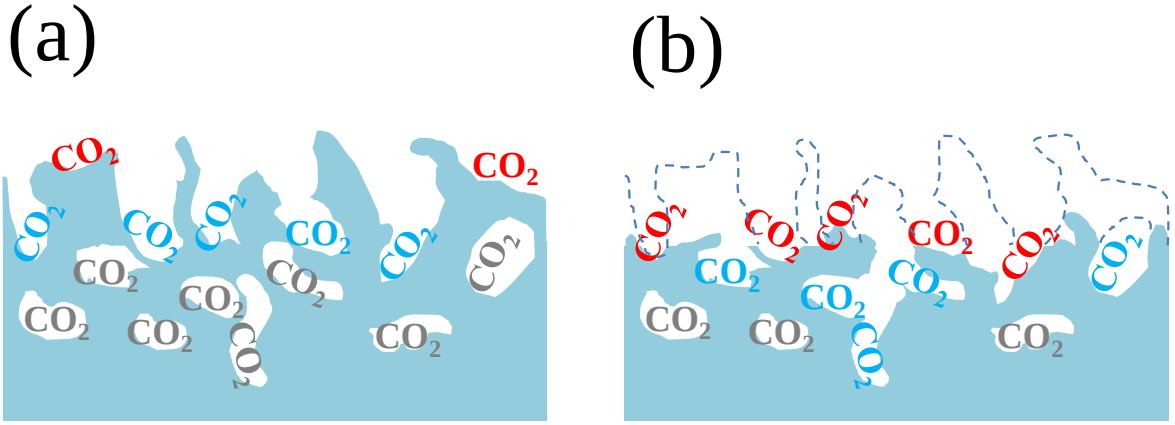
### 3.3. OH desorption from photoirradiation of C<sup>18</sup>O<sub>2</sub>/H<sub>2</sub><sup>16</sup>O mixture, neat ASW(H<sub>2</sub><sup>18</sup>O) and neat ASW(H<sub>2</sub><sup>16</sup>O)

Figure 5(a) shows REMPI excitation spectra of <sup>16</sup>OH from C<sup>18</sup>O<sub>2</sub>/H<sub>2</sub><sup>16</sup>O mixture after 1 hr 157 nm irradiation without intermittent deposition, while <sup>18</sup>OH was not detected. It is well known that H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>CO<sub>3</sub> were formed following energetic particle irradiations of pure H<sub>2</sub>O and CO<sub>2</sub>/H<sub>2</sub>O mixed ice, respectively.<sup>10,21,28-30</sup> Recognizing that these photoproducts would accumulate on the ice surface after prolonged irradiation by 157 nm photolysis pulses, we have also confirmed that weak <sup>16</sup>OH was also successfully detected from fresh C<sup>18</sup>O<sub>2</sub>/H<sub>2</sub><sup>16</sup>O mixture. These results suggest that H + C<sup>18</sup>O<sub>2</sub> → <sup>18</sup>OH + CO reaction does not occur efficiently. To confirm that our REMPI system could detect OH isotopomers, REMPI excitation spectra of <sup>16</sup>OH from ASW(H<sub>2</sub><sup>16</sup>O) and <sup>18</sup>OH from ASW(H<sub>2</sub><sup>18</sup>O) were measured as shown in Figs. 5(b) and (c). These spectra were taken at  $t = 1.0 \mu\text{s}$  corresponding to the TOF maximum of the OH formed via 157 nm irradiation of ASW (H<sub>2</sub>O) which both nascent H<sub>2</sub>O and photoproduct H<sub>2</sub>O<sub>2</sub> contribute to OH photodesorption.<sup>10</sup> Table 2 summarizes the results of the isotope experiments.

## 4. Discussion

### 4.1. Adsorption states of CO<sub>2</sub> and relevant photodissociation dynamics

In the present study, CO<sub>2</sub>/H<sub>2</sub>O mixture ice films were continually refreshed by intermittent exposure to CO<sub>2</sub> gas (CO<sub>2</sub> adlayer experiment) and CO<sub>2</sub>/H<sub>2</sub>O mixture gas (fresh CO<sub>2</sub>/H<sub>2</sub>O experiment) during pulsed photoirradiation to investigate CO<sub>2</sub> adsorption structures on ASW and their effects to the CO<sub>2</sub> photodynamics. Our experimental results showed that the translationally and internally hot CO ( $T_{\text{trans}}=1600 \text{ K}$ ,  $T_{\text{rot}}=800 \text{ K}$ ) components were observed in the CO<sub>2</sub> adlayer experiment, while cold ( $T_{\text{trans}}=90 \text{ K}$ ,  $T_{\text{rot}}=150 \text{ K}$ ) components appeared in the fresh CO<sub>2</sub>/H<sub>2</sub>O experiment. Adsorption and inclusion states of CO<sub>2</sub> on or in water ice at low temperature have been reported extensively. For crystalline water ice, the Arrhenius activation energy for CO<sub>2</sub> desorption at around 90 K is 0.20 - 0.24 eV with a pre-exponential factor of about  $10^{13} \text{ s}^{-1}$ , which gives an average residence time = 50 ms at 90 K.<sup>2,31-33</sup> However, the residence time for CO<sub>2</sub> trapped in the pores of ASW was estimated to be on the order of a few minutes, corresponding to a desorption activation energy of about 0.3 eV.<sup>33</sup> Maylk et al. found two different



**Fig. 6** Schematic illustration of the distribution of  $\text{CO}_2$  in  $\text{CO}_2/\text{H}_2\text{O}$  mixture ice, (a) as deposited before irradiation and (b) after prolonged 157 nm irradiation.  $\text{CO}_2$  (red) stand for physisorbed  $\text{CO}_2$  on surface,  $\text{CO}_2$  (blue) are trapped in the pore and  $\text{CO}_2$  (gray) are buried in the bulk phase. Due to the smaller absorption cross section of  $\text{CO}_2$  than that of  $\text{H}_2\text{O}$ , the surface abundance of  $\text{CO}_2$  increases after prolonged 157 nm photoirradiation. The fast time-of-flight component comes from  $\text{CO}_2$  (red), while the slow one from  $\text{CO}_2$  (blue).

$\text{CO}_2$  structures on the surface of the mixture ice in their TPD experiments: 1) adsorbed atop water ice surface, which evaporates at sublimation temperature of pure  $\text{CO}_2$ , and 2) trapped in the cavities desorbing during the amorphous-to-cubic ice phase transition.<sup>3</sup> Figure 6(a) schematically shows these two different structures. Sandford and Allamandola investigated the condensation and vaporization properties of  $\text{CO}_2$  in  $\text{H}_2\text{O}/\text{CO}_2$  mixed ice for various mixing ratios using infrared spectroscopic technique.<sup>32</sup> For ices with  $\text{H}_2\text{O}/\text{CO}_2 > 20$ , the  $\text{CO}_2$  is trapped in the strong hydrogen-bonded amorphous  $\text{H}_2\text{O}$  lattice with interconnecting molecular pores. Little  $\text{CO}_2$  is lost until the sublimation temperature of the  $\text{H}_2\text{O}$  matrix is reached. In contrast, in ice having  $\text{H}_2\text{O}/\text{CO}_2 < 5$ , the  $\text{CO}_2$  remains only to the temperature of about 90 K.<sup>32</sup> These reported results indicate that 1) in the present  $\text{CO}_2$  adlayer experiments, the ice surface is covered with a mono- or multilayered  $\text{CO}_2$  during the intermittent injection of neat  $\text{CO}_2$  gas into the vacuum chamber, which has a short residence time, and 2) for the fresh  $\text{CO}_2/\text{H}_2\text{O}$  mixture experiment, on the contrary,  $\text{CO}_2$  is physically trapped in the strong hydrogen-bonded amorphous  $\text{H}_2\text{O}$  lattice with interconnecting molecular pores, which has a long residence time. We propose that the translationally fast ( $T_{\text{trans}}=1600$  K) and internally hot ( $T_{\text{rot}}=800$  K) CO component observed in the  $\text{CO}_2$  adlayer experiments comes from  $\text{CO}_2$  adsorbed atop water ice surface. The translationally slow ( $T_{\text{trans}}=90$  K) and internally cold ( $T_{\text{rot}}=150$  K) CO component observed in the fresh  $\text{CO}_2/\text{H}_2\text{O}$  mixture experiment is due to energy relaxation process by collisions within the inner surface of the mixed ice *en route* to the vacuum, since it is trapped on the porous sites.

Once 157 nm irradiation started, both  $\text{CO}(T_{\text{trans}}=1600$  and 90 K) components appeared immediately from the  $\text{CO}_2/\text{H}_2\text{O}$  mixture film that was left for 1 min after the preparation, as shown in Figs. 3(a) and (b), suggesting that both  $\text{CO}_2$  adsorbed atop water ice surface and  $\text{CO}_2$  trapped in pores could survive for at least 1 min on the ice surface. Based on the facts that 1)  $\text{CO}(T_{\text{trans}}=1600$  K) intensity increased with 157 nm irradiation time as shown in Fig. 3(a), and 2) both the fast and slow CO signals do not promptly appear when the  $\text{CO}_2/\text{H}_2\text{O}$  mixture was left under vacuum at 90 K for 10 minute before 157 nm photoirradiation, we infer that a) the effective residence time of

CO<sub>2</sub> adsorbed on the top surface, which generates CO( $T_{\text{trans}}=1600$  K), is  $> 0.1$  s (corresponding to a 157 nm laser pulse rate of 10 Hz) at 90 K, and b) CO<sub>2</sub> on the ice surface were desorbed into vacuum during 10 minute. These numbers are in fair agreement with the reported residence times,  $\sim 50$  ms for CO<sub>2</sub> on crystalline ice surface and a few min for CO<sub>2</sub> in the pores at 90 K.<sup>33</sup> Possibility of thermal segregation of CO<sub>2</sub> molecules during waiting time will be discussed below.

#### 4.2. Formation of inhomogeneous layer structures by photoabsorption at 157 nm

An UV absorption cross section of ASW is  $\sim 5 \times 10^{-19}$  cm<sup>2</sup> at 157 nm.<sup>4</sup> Mason et al. also reported the absorption cross section of solid CO<sub>2</sub>,  $\sim 5 \times 10^{-20}$  cm<sup>2</sup> at 157 nm, which is about one order of magnitude smaller than that of ASW.<sup>4</sup> Since CO<sub>2</sub> has the smaller absorption cross section than H<sub>2</sub>O, the surface abundance of CO<sub>2</sub> in the mixed ice film is expected to become higher after prolonged 157 nm photoirradiation. This induces surface state change after photoirradiation. Actually, as shown in Figs. 3(a) and (b), the CO( $T_{\text{trans}}=1600$  K) intensity increased with 157 nm irradiation time, while CO( $T_{\text{trans}}=90$  K) intensity has no appreciable temporal change. These results indicate an increase of the surface abundance of the CO<sub>2</sub> adlayer adsorbed atop the CO<sub>2</sub>/H<sub>2</sub>O mixture ice at 90 K presumably by the preferential H<sub>2</sub>O photodissociation. This surface state change of CO<sub>2</sub> after photoirradiation is schematically illustrated in Fig. 6.

One might consider that CO<sub>2</sub> molecules could be thermally segregated at 90 K from the bulk ice to the surface, which result in increase of the surface abundance of CO<sub>2</sub>.<sup>34</sup> However, Fig. 3(c) shows both the fast and slow CO signals do not promptly appear when the CO<sub>2</sub>/H<sub>2</sub>O mixture was left under vacuum at 90 K for 10 minute before photoirradiation started, and also their intensities increase gradually with 157 nm photoirradiation time. These results indicate desorption of CO<sub>2</sub> into vacuum occurs more efficiently than the thermal surface-segregation during the 10 minute waiting time, and also the 157 nm photoirradiation induced the increase of the surface abundance of the CO<sub>2</sub> on the ice samples. The same results were obtained for 20 min waiting time.

Another possible reason for the increase of CO<sub>2</sub> abundance on the CO<sub>2</sub>/H<sub>2</sub>O mixture ice surface would be that CO<sub>2</sub> may be transferred from the bulk ice to the top surface by photo-induced local heating by pulsed 157 nm photoirradiation. The thermal consequence of pulsed laser irradiation was discussed by Yardley<sup>35</sup> and Osmundsen et al.<sup>36</sup> The optical depth for a 157 nm photon in an H<sub>2</sub>O ice, or the depth to which the UV transmission drops to  $1/e = 37\%$ , is  $\sim 100$  nm, and the reflectivity  $R = 0.06$ .<sup>37</sup> Assuming a square incident laser pulse with a pulse width of  $\tau$  (second), then the maximum temperature (K) rise of the surface is

$$\Delta T = 2I (1 - R) (1 - 1/e) (\beta\tau/\pi)^{1/2} / \kappa, \quad (4)$$

where  $R$  is the surface reflectivity at the laser wavelength, and  $I (1 - R) (1 - 1/e)$  is the energy absorbed in the optical depth ( $\sim 100$  nm). For the ASW ice, density  $\rho = 9.4 \times 10^{-1}$  g cm<sup>-3</sup>,<sup>38</sup> thermal conductivity  $\kappa = 7.2 \times 10^{-2}$  J s<sup>-1</sup> cm<sup>-1</sup> K<sup>-1</sup>,<sup>38</sup> heat capacity  $c = 7.9 \times 10^{-1}$  J g<sup>-1</sup> K<sup>-1</sup>,<sup>39</sup> and  $\beta = \kappa/\rho c = 9.7 \times 10^{-2}$  s<sup>-1</sup> cm<sup>2</sup>. Assuming 157 nm laser intensity  $I = 1 \times 10^4$  J s<sup>-1</sup> cm<sup>-2</sup>, and pulse width  $\tau = 10^{-8}$  s, then the maximum temperature rise is 2.9 K in 100 nm of ASW layer. This temperature rise would not enhance thermal processes at the surface. In fact, we have previously checked the possible influence of photoirradiation on an ASW surface if the partial annealing or modifications of the ice surface might occur by 157 nm laser irradiation.<sup>21</sup> As a result, the ASW surfaces maintained its distinct surface porosity during the 157 nm irradiation experiments at least for 1 hr. Therefore, the local heating by 157 nm photoirradiation

(and deposition of the photon energy of the photoproducts into the ice sample) play only a minor role in the present study.

### 4.3. Astrophysical implications

The reactivity of surface reactions is strongly affected by the surface composition. For example, Watanabe et al. studied surface reactions of non-energetic H atoms on solid O<sub>2</sub> or CO to understand the formation of water and organic compounds on interstellar grain surfaces, revealing that reactivity of CO hydrogenation is enhanced on ASW at temperatures above ~15 K when compared to pure solid CO.<sup>4</sup> They also report that the hydrogenation reactions become saturated at some stage although some O<sub>2</sub> or CO still remain unreacted. The hydrogenation reaction dominantly occurs at the surface of the solid O<sub>2</sub> or CO, and the formation of an onion-like layered structure by reaction products suppresses the further reactions because hydrogenation hardly proceeds with O<sub>2</sub> and CO buried by the products like H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>CO.<sup>40,41</sup> In the case of O<sub>2</sub> hydrogenation, during the H exposure, the reactions construct the layered structure on the sample solid with H<sub>2</sub>O on the top, H<sub>2</sub>O<sub>2</sub> in the middle, and O<sub>2</sub> at the bottom. However, in the interstellar environments where deposition rates of incoming atoms and molecules are quite low, the reaction-induced formation of layered structure on ice mantles would be inefficient. Our results indicate that the preferential photodissociation of H<sub>2</sub>O also can make the layered structure. Since VUV absorption cross sections of CO<sub>2</sub> are smaller than those of H<sub>2</sub>O in the entire wavelength region, CO<sub>2</sub> is less efficiently dissociated than H<sub>2</sub>O, and CO<sub>2</sub> may be condensed on the surface below the evaporation temperatures of H<sub>2</sub>O. The VUV source in interstellar molecular clouds is cosmic-ray pumped hydrogen, and thus, the dominant photoexcitation wavelengths available are H Lyman- $\alpha$  and photons within the Lyman band of H<sub>2</sub>. The predicted VUV flux is  $1.4 \times 10^3 \text{ cm}^{-2} \text{ s}^{-1}$ .<sup>42</sup> The estimated photon flux at the edge of the solar system is reported to be  $9.6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ .<sup>43</sup> The 157 nm laser used in the present study delivers a fluence of  $< 10^{14} \text{ cm}^{-2} \text{ pulse}^{-1}$ , which roughly corresponds to those in interstellar molecular clouds and Oort cloud  $10^4$  years and one month, respectively. Considering the residence times of ices in regions  $10^7$  years for interstellar ice mantles and  $10^9$  years for cometary ices in Oort cloud,<sup>43</sup> CO<sub>2</sub> is expected to be relatively concentrated on the top surface of such extraterrestrial ices due to the preferential H<sub>2</sub>O photodissociation.

## 5. Summary

We have measured time-of-flight spectra and rotationally resolved REMPI spectra of photodesorbed CO species following 157 nm photodissociation of mixed CO<sub>2</sub>/H<sub>2</sub>O (1:4) ice films at 90 K. Two different deposition gas mixtures were used for the mixed ice preparation to investigate CO<sub>2</sub> adsorption structures on H<sub>2</sub>O ice. Hot CO ( $v=0,1, T_{\text{trans}}=1600 \text{ K}$  and  $T_{\text{rot}}=800 \text{ K}$ ) and cold CO ( $v=0, T_{\text{trans}}=90 \text{ K}$  and  $T_{\text{rot}}=150 \text{ K}$ ) were observed as photodesorbed products, suggesting that the hot CO comes from CO<sub>2</sub> adsorbed atop water ice surface, while CO<sub>2</sub> trapped on the porous sites produces the cold CO component due to an energy relaxation process by collisions within the mixed ice *en route* to the vacuum. Photodesorption of OH and O(<sup>3</sup>P<sub>J</sub>) was also observed, which is predominantly produced from the photodissociation of H<sub>2</sub>O in the mixture ice. Formation of the heterogeneous structures from mixed ice films should depend on photoabsorption cross sections, ice temperatures and photon flux. Since the VUV absorption cross section of CO<sub>2</sub> is smaller than that of H<sub>2</sub>O in the entire VUV wavelength region,

CO<sub>2</sub> is less efficiently dissociated than H<sub>2</sub>O. After photoirradiation on the CO<sub>2</sub>/H<sub>2</sub>O mixture ices, CO<sub>2</sub> are relatively condensed on the ice surface at low temperatures.

## Acknowledgement

This work was supported by Grants-in-Aid (20245005 and 23684045) from Japan Society for the Promotion of Science

## References

- <sup>1</sup> M. H. Moore, R. L. Hudson and R. F. Ferrante, *Earth, Moon and Planets*, 2003, **92**, 291.
- <sup>2</sup> B. Mate, O. Galvez, B. M. Llorente, M. A. Moreno, V. J. Herrero, R. Escribano and E. Artacho, *J. Phys. Chem. A*, 2008, **112**, 457.
- <sup>3</sup> S. Malyk, G. Kumi, H. Reisler and C. Wittig, *J. Phys. Chem. A*, 2007, **111**, 13365.
- <sup>4</sup> N. J. Mason, A. Dawes, P. D. Holtom, R. J. Mukerji, M. P. Davis, B. Sivaraman, R. I. Kaiser, S. V. Hoffmann and D. A. Shaw, *Faraday Discuss.*, 2006, **133**, 311.
- <sup>5</sup> A. Yabushita, D. Kanda, N. Kawanaka, M. Kawasaki and M. N. R. Ashfold, *J. Chem. Phys.*, 2006, **125**, 133406.
- <sup>6</sup> A. Yabushita, T. Hama, D. Iida, N. Kawanaka, M. Kawasaki, N. Watanabe, M. N. R. Ashfold and H. P. Looock, *J. Chem. Phys.*, 2008, **129**, 044501.
- <sup>7</sup> A. Yabushita, Y. Inoue, T. Senga, M. Kawasaki and S. Sato, *J. Phys. Chem. B*, 2002, **106**, 3151.
- <sup>8</sup> A. Bar-Nun, G. Herman, D. Laufer and M. L. Rappaport, *Icarus*, 1985, **63**, 317.
- <sup>9</sup> M. P. Collings, M. A. Anderson, R. Chen, J. W. Dever, S. Viti, D. A. Williams and M. R. S. McCoustra, *Mon. Not. R. Astron. Soc.*, 2004, **354**, 1133.
- <sup>10</sup> T. Hama, A. Yabushita, M. Yokoyama, M. Kawasaki and S. Andersson, *J. Chem. Phys.*, 2009, **131**, 054508.
- <sup>11</sup> P. J. H. Tjossem and K. C. Smyth, *J. Chem. Phys.*, 1989, **91**, 2041.
- <sup>12</sup> S. Wurm, P. Feulner and D. Menzel, *J. Chem. Phys.*, 1996, **105**, 6673.
- <sup>13</sup> E. de Beer, M. P. Koopmans, C. A. de Lange, Y. Wang and W. A. Chupka, *J. Chem. Phys.*, 1991, **94**, 7634.
- <sup>14</sup> J. E. M. Goldsmith, *J. Chem. Phys.*, 1983, **78**, 1610.
- <sup>15</sup> C. M. Western, PGOPHER, a program for simulating rotational structure, University of Bristol, available at <http://pgopher.chm.bris.ac.uk>.
- <sup>16</sup> M. E. Greenslade, M. I. Lester, D. C. Radenovic, A. J. A. van Rooij and D. H. Parker, *J. Chem. Phys.*, 2005, **123**, 074309.
- <sup>17</sup> K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979)
- <sup>18</sup> D. C. Morton and L. Noreau, *Astrophys. J. Suppl.*, 1994, **95**, 301.
- <sup>19</sup> K. M. Chen and E. S. Yeung, *J. Chem. Phys.*, 1978, **69**, 43.
- <sup>20</sup> F. M. Zimmermann and W. Ho, *Surf. Sci. Rep.*, 1995, **22**, 127.
- <sup>21</sup> A. Yabushita, T. Hama, D. Iida and M. Kawasaki, *J. Chem. Phys.*, 2008, **129**, 014709.

- <sup>22</sup> T. Hama, A. Yabushita, M. Yokoyama, M. Kawasaki and N. Watanabe, *J. Chem. Phys.*, 2009, **131**, 114511.
- <sup>23</sup> Y. F. Zhu and R. J. Gordon, *J. Chem. Phys.*, 1990, **92**, 2897.
- <sup>24</sup> A. Stolow and Y. T. Lee, *J. Chem. Phys.*, 1993, **98**, 2066.
- <sup>25</sup> E. J. Dunlea and A. R. Ravishankara, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3333.
- <sup>26</sup> W. Zheng, D. Jewitt and R. I. Kaiser, *Phys. Chem. Chem. Phys.*, 2007, **9**, 2556.
- <sup>27</sup> C. J. Bennett, C. S. Jamieson and R. I. Kaiser *Phys. Chem. Chem. Phys.*, 2010, **12**, 4032.
- <sup>28</sup> Z. Peeters, R.L. Hudson, M.H. Moore, and Ariel Lewis, *Icarus*, 2010, **210**, 480.
- <sup>29</sup> Y. Oba, N. Watanabe, A. Kouchi, T. Hama, and V. Pirronello, *ApJ*, 2010, **722**, 1598.
- <sup>30</sup> Q. Zheng, and R. I. Kaiser, *Chem. Phys. Lett.*, 2007, **450**, 55.
- <sup>31</sup> C. E. Bryson and L. L. Levenson, *Surf. Sci.*, 1974, **43**, 29.
- <sup>32</sup> S. A. Sandford and L. J. Allamandola, *Icarus*, 1990, **87**, 188.
- <sup>33</sup> P. U. Andersson, M. B. Nagard, G. Witt and J. B. C. Pettersson, *J. Phys. Chem. A*, 2004, **108**, 4627-4631.
- <sup>34</sup> K. I. Öberg, E. C. Fayolle, H. M. Cuppen, E. F. van Dishoeck, and H. Linnartz, *A&A*, 2009, **505**, 183.
- <sup>35</sup> J. T. Yardley, Laser chemistry: processing at the micro level. In: M. Bass and M.L. Stitch, Editors, *Laser Handbook*, Elsevier, Amsterdam, 1985, 405.
- <sup>36</sup> J. F. Osmundsen, C.C. Abele and J.G. Eden, *J. Appl. Phys.*, 1985, **57**, 2921.
- <sup>37</sup> M. Seki, K. Kobayashi, and J. Nakahara, *J. Phys. Soc. Jpn.*, 1981, **50**, 2643
- <sup>38</sup> V. F. Petrenko, and R. W. Whitworth, *Physics of Ice*, Oxford Univ. Press, New York, 1999.
- <sup>39</sup> O. Haida, T. Matsuo, H. Suga and S. Seki, *J. Chem. Thermodynamics*, 1974, **6**, 815.
- <sup>40</sup> N. Watanabe, A. Nagaoka, T. Shiraki and A. Kouchi, *Astrophys. J.*, 2004, **616**, 638.
- <sup>41</sup> Y. Oba, N. Miyauchi, H. Hidaka, T. Chigai, N. Watanabe and A. Kouchi, *Astrophys. J.*, 2009, **701**, 464.
- <sup>42</sup> S. S. Prasad and S. P. Tarafdar, *Astrophys. J.*, 1983, **267**, 603.
- <sup>43</sup> M. H. Moore, R.L. Hudson and P.A. Gerakines, *Spectrochim. Acta, Part A*, 2001, **57**, 843.