

Glass–Liquid Transition of Carbon Dioxide and Its Effect on Water Segregation

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The interactions between CO₂ and D₂O molecules have been investigated by using time-of-flight secondary ion mass spectrometry in the temperature range 13–120 K. The monolayer of CO₂ tends to wet or intermix with the D₂O film below 40 K and dewets the surface above 60 K. The water nanoclusters deposited on the CO₂ multilayers also start to segregate at 50–60 K and are finally incorporated in the bulk at 85–90 K, where the morphology of the film changes abruptly together with the desorption rate of the CO₂ molecules. The break at 85 K should be caused by the occurrence of the fluidized film whereas the glass-transition temperature of CO₂, as determined from the onset of translational molecular diffusion, is assigned to 50 K. This behavior may be related to the ultraviscous nature of the supercooled liquid, arising from the decoupling between the translational molecular diffusion and viscosity. The He⁺ irradiation of the mixed CO₂–D₂O ice and the D₂⁺ irradiation of the CO₂ ice at 13 K do not yield any surface residues assignable to H₂CO₃ and its precursors above 100 K. This result may be related to the segregation between the CO₂ and D₂O molecules.

Introduction

The interaction of carbon dioxide with water is important in many biological, environmental, and astrophysical processes. In aqueous solutions, carbon dioxide is in equilibrium with carbonic acid: CO₂ + H₂O → H₂CO₃, though the majority of CO₂ is not converted into H₂CO₃ (the equilibrium constant at 25 °C is 1.70 × 10^{−3}). The mechanism of the hydrolysis of carbon dioxide is multimolecular:^{1–3} it proceeds through the attack of the CO₂ carbon by the water oxygen and a proton transfer to the CO₂ oxygen, which is assisted by a chain of hydrogen-bonded water molecules. The evidence for the presence of carbonic acid is indirect because it dissociates rapidly in water. On the other hand, the existence of stable carbonic acid has been claimed for many molecular-solid systems prepared by, for example, H⁺ and He⁺ ion irradiation of cryogenic CO₂/H₂O ice mixtures,^{4,5} proton irradiation of pure solid CO₂,⁶ and reaction between K₂CO₃ and HCl in vitreous methanol films,⁷ suggesting that low temperature would favor the creation and stabilization of carbonic acid. However, very little is known about the water–CO₂ interactions at cryogenic temperatures. The CO₂ molecules can be accommodated in a cage of water molecules linked by hydrogen bonds, as manifested by the formation of a clathrate hydrate at the liquid–liquid interface of CO₂ and H₂O⁸ and in thin films deposited by CO₂–H₂O mixtures at cryogenic temperatures.⁹ The higher solubility of CO₂ in liquid water than the typical hydrophobic species might suggest the presence of weak hydrogen bonds, but the infrared (IR) absorption study denies the presence of hydrogen bonds between water and the dissolved carbon dioxide.¹⁰ More insights into the water–CO₂ interactions may be gained from the adsorption/desorption experiments on the thin films of amorphous solid water (ASW). It is well-known that the ASW film formed at temperatures below 80 K is characterized by a microporous structure because the hydrophobic molecules can be incorporated in the bulk through

pores.¹¹ The trapped molecules should form some complexes in the bulk of ASW, and they are released abruptly at around 160–165 K.^{12,13} At this temperature, the desorption rate of water molecules themselves also decreases.¹² These phenomena have been explained in terms of the crystallization of water,¹² but it is recently claimed that the glass–liquid transition is responsible for this behavior.^{13,14}

The structure of CO₂ thin films on the NaCl(001) substrate has been studied extensively using IR absorption,^{15–17} low-energy electron diffraction (LEED),¹⁸ and helium atom scattering (HAS)¹⁹ techniques. The LEED and HAS studies concluded the formation of commensurate monolayer with a (2 × 1) superstructure, whereas the possibility of the 2D-lattice gas, equilibrating with the ordered 2D solid, is also suggested in the submonolayer-coverage regime.¹⁷ On the other hand, a thicker CO₂ film deposited at 10 K exhibits substantially broad IR spectra compared with the crystalline CO₂ at 77 K.¹⁵ Such a film has been assigned to amorphous solid CO₂. In general, glassy materials should melt into viscous liquid prior to crystallization, but very little is known about the properties of the supercooled liquid CO₂ and kinetics of the glass–liquid transition and crystallization of amorphous solid CO₂.

In the present paper, we study the wetting/dewetting and intermixing of the water and CO₂ molecules in the temperature range 13–120 K by using time-of-flight secondary ion mass spectrometry (TOF–SIMS). The usefulness of TOF–SIMS for investigating the intermolecular interactions has been demonstrated for various adsorption systems on the ASW film as a function of temperature.^{13,14} This was enabled because the sputtered ion species and their yields are sensitively dependent not only on the composition but also on the chemical environment of the parent atoms and molecules. Here, we present the experimental evidence for the occurrence of the segregation of the initially mixed water and CO₂ molecules as a consequence of the glass–liquid transition of the CO₂ film.

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2. Experiment

The experiments were conducted in an ultrahigh-vacuum (UHV) chamber (base pressure below 1×10^{-9} Pa) equipped with facilities for standard surface characterization. The He^+ ions, produced in an electron-impact-type ion source, were chopped by an electrostatic deflector into pulses with width of 50 ns and frequency of 40 kHz. The TOF–SIMS measurements were made in such a manner that the sample, floated with a bias voltage of +500 V, was irradiated with a primary He^+ beam of 2 keV through a grounded stainless steel mesh placed 4 mm above the sample surface (the ion impact energy was 1.5 keV), and the positive ions extracted through the mesh into the field-free TOF tube (65 cm in length) were detected with a channel electron multiplier. The incidence angle of the primary He^+ beam was 20° with respect to the surface normal, and the secondary ions emitted perpendicular to the surface were detected. A pulsed He^+ beam with a low incident flux (~ 10 pA/cm 2) was used to minimize charging and damage of a surface. The temperature-programmed and isothermal TOF–SIMS measurements were completed within the He^+ dosage of 2×10^{11} ions/cm 2 . The substrate was a Ni(111) surface which was mounted on a sample holder cooled to 15 K by means of a closed-cycle He refrigerator. The sample was heated for cleaning up to 1200 K by electron bombardment from behind. The water and CO_2 molecules, introduced through separate gas inlet valves, were deposited on the Ni(111) substrate by backfilling the UHV chamber. The one monolayer (1 ML) coverage of the adsorbed molecules was determined from the evolution curves of sputtered ion intensities as a function of exposure. The film thickness was estimated on the basis of this value. The temperature-programmed desorption (TPD) of the CO_2 molecule was measured by means of the differentially pumped quadrupole mass analyzer. The temperature was ramped at the constant speed (5.0 K/min) in both temperature-programmed TOF–SIMS and TPD.

3. Experimental Section Results

Figure 1 shows TOF–SIMS spectra from the 50-ML D_2O film before (upper) and after (lower) the adsorption of the 1-ML CO_2 molecules. The D_2O molecules were deposited on the Ni(111) surface at 100 K, so that the nonporous ASW film grows.¹¹ The CO_2 molecules were adsorbed on it at 13 K. The D^+ and D_3O^+ ions are the main ion species from the ASW film. From the adsorbed CO_2 molecules, a variety of fragment ions, such as C^+ , O^+ , and CO^+ , are sputtered, together with some deuterated species, such as DCO^+ and DCO_2^+ (indicated by asterisks). The deuterated ions should be created during collisions between the CO_2 and D_2O molecules or their fragments and, hence, their emission is indicative of the direct molecular contact or wetting of CO_2 on the ASW surface.

As regards the D^+ ion, its intensity decreases upon adsorption of CO_2 but a tail evolves in the shorter TOF side. Such a tail originates from the higher-energy D^+ ions. The energy distributions of the D^+ ion, as calculated from the flight time of the ion through the TOF tube, are shown in the inset (the ion extraction energy of 500 eV was subtracted). The D^+ ions emitted from the pure D_2O film exhibit a considerably narrow energy distribution (~ 10 – 20 eV), which corresponds to the energy resolution of the present experiment as estimated from the width of the primary beam. They are thought to form by breaking the partly ionic O–D bond (the bond-breaking mechanism²⁰) during the collision cascade. The kinetic energy of the D^+ ions ranges up to 200 eV when the CO_2 molecules cover the D_2O surface. Such D^+ ions, almost absent for the

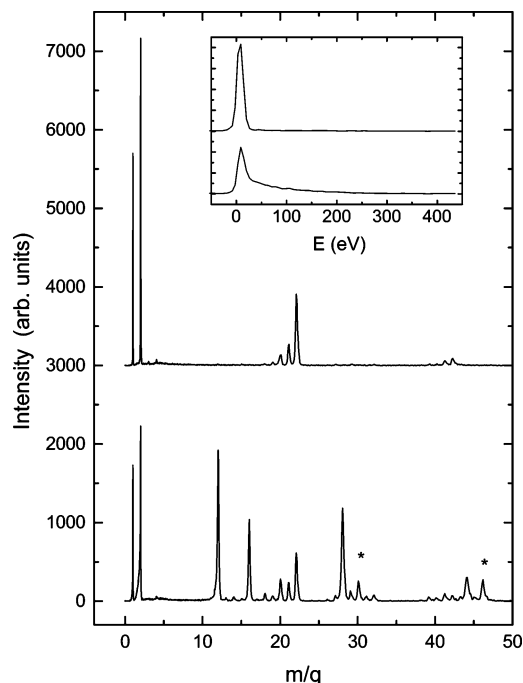


Figure 1. TOF–SIMS spectra of the 50-ML D_2O film (upper) and the 1-ML CO_2 molecules deposited on it (lower). The D_2O film was grown at 100 K, and the CO_2 molecules were deposited at 13 K. The asterisks indicate the secondary ion species indicative of wetting or mixing between the CO_2 and D_2O molecules (DCO^+ and DCO_2^+). Inset: the energy distribution of the D^+ ions from the D_2O film and CO_2 -adsorbed D_2O film obtained by conversion of the corresponding TOF spectra and subtraction of the ion acceleration energy of 500 eV.

pure D_2O surface, should be caused by ionization of energetic neutral species during collisions with the CO_2 molecules. The high-energy deuterium should be recoiled by the primary He^+ ions as will be discussed later. Thus, the origin of the high-energy tail is completely different from that of the low-energy peak. The ionization mechanism of the swift D^0 atoms can be inferred from the results of low-energy D^+ scattering experiments performed in the primary-energy range 10–200 eV;²¹ it was revealed that the D^+ ion that is once neutralized at the surface is reionized during collision with oxygen just before leaving the surface. The ionization probability increases with increasing the kinetic energy because (re)ionization is caused by the electron promotion mechanism. The ionization probability is high in collisions with physisorbed species but oxygen of water has much less efficiency (the ionization probability is about $1/60$ that of $\text{H}-\text{O}_2$ collisions) because the hydrogen bonds have some covalency through which the valence holes delocalize (the band effect).²¹ The mean free path of 100–200 eV deuterium is 5–10 nm as calculated by the TRIM code,²² so that it can be ionized provided that the CO_2 molecules exist within this reach. In the present study, the total intensity for both peak and tail (0–200 eV) is compared with the peak intensity (0–20 eV) as a measure of mixing between the D_2O and CO_2 molecules.

In Figure 2 is shown the intensity of typical secondary ions sputtered from the CO_2 -adsorbed D_2O film as a function of temperature. Above 60 K, the C^+ and CO^+ ion intensities decrease whereas the D_3O^+ and D^+ (peak) intensities increase. Since the glass-transition temperature of water is 136 K, the translational diffusion of the water molecules is frozen at such a low temperature as 60 K.²³ Therefore, this behavior can be ascribed to the increased mobility of the CO_2 molecules. The O_2^+ ion exhibits a rather different behavior from the other

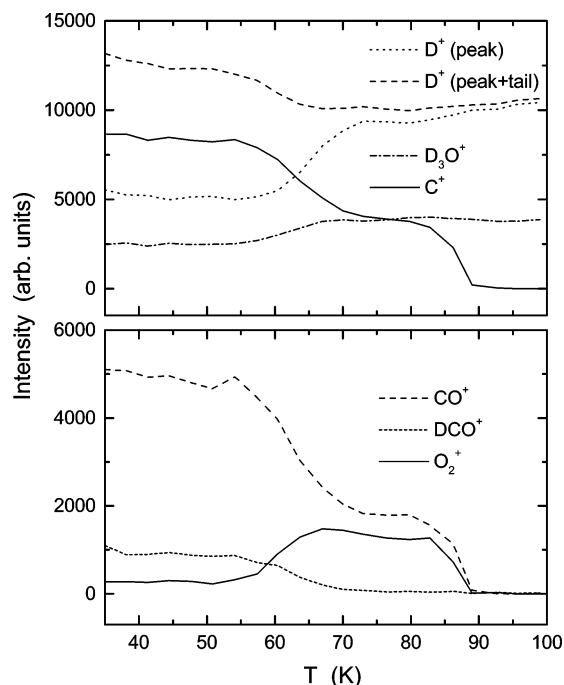


Figure 2. Temperature-programmed TOF-SIMS intensities of typical secondary ions from the CO_2 -deposited D_2O film. The nonporous D_2O film was grown at 100 K with a thickness of 50 ML, and then the 1 ML of CO_2 molecules was deposited on it at 13 K. The intensities were measured continuously at a ramping speed of 5 K/min.

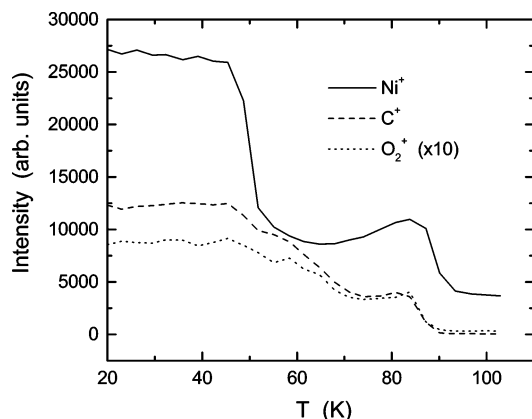


Figure 3. Temperature-programmed TOF-SIMS intensities of typical secondary ions from the CO_2 -adsorbed Ni(111) surface. The 1 ML of CO_2 molecules was deposited at 13 K and the temperature was ramped at a rate of 5 K/min.

fragment ions coming from the CO_2 molecules. This is because the O_2^+ ion forms during energetic collisions of the CO_2 molecules or its fragments and is never created via a simple fragmentation of the isolated CO_2 molecule. The O_2^+ intensity increases above 60 K simultaneously with the decrease of the DCO^+ intensity. Moreover, the D^+ intensity comes mainly from the high-energy tail below 60 K. All these experimental data clearly show that the CO_2 molecules wet the D_2O film initially and then almost pure CO_2 islands form above 60–70 K.

This behavior is further investigated for the other substrate. Figure 3 shows typical TOF-SIMS intensities from the 1 ML of CO_2 molecules adsorbed on the Ni(111) surface. In this case, the occurrence of wetting/dewetting can be identified not only from the fragment-ion intensities but also from the Ni^+ intensity. No Ni^+ ion is sputtered from the clean Ni(111) surface because of the efficient resonance neutralization. The presence of physisorbed and chemisorbed species on the surface is known

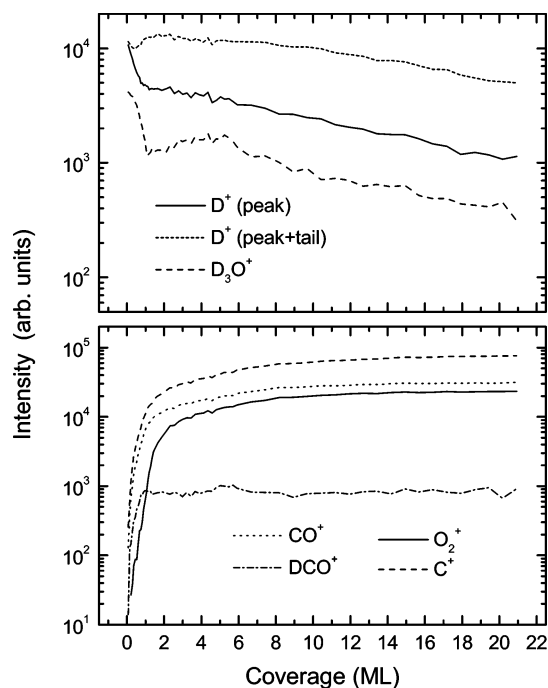


Figure 4. Evolutions of secondary ion intensities from the CO_2 -adsorbed D_2O film as a function of CO_2 coverage. The nonporous D_2O film was grown at 100 K, and then the CO_2 molecules were deposited after cooling to 40 K.

to increase the ionization probability of sputtered Ni^0 drastically:²⁴ the resulting Ni^+ intensity peaks at around 1 ML coverage and then decays exponentially with increasing coverage. The Ni^+ intensity drops steeply at around 50 K, which is followed by a rather gradual decrease in the fragment-ion intensities from CO_2 . The former may be caused by the surface diffusion of the CO_2 molecules to form islands whereas the latter, which is basically identical to that observed on the ASW surface, should be ascribed to dewetting of the CO_2 monolayer. At the ASW surface shown in Figure 2, the surface diffusion and dewetting take place simultaneously at slightly higher temperature (60 K). This result may suggest better wettability of CO_2 at the ASW surface. The initial intensity of O_2^+ is higher on the Ni(111) surface than that on the ASW surface because of the formation of 2D CO_2 islands. Thus, the interaction between CO_2 and the ASW surface is hardly characterized by the simple physisorption. The dewetting of the CO_2 molecules observed here has nothing to do with the desorption because it occurs above 70 K as will be shown later.

Figure 4 shows secondary ion intensities as a function of coverage of the CO_2 molecules adsorbed on the ASW film. The D_2O molecules (50 ML) were deposited at 100 K to form the nonporous ASW film, and then the CO_2 molecules were adsorbed on it at 40 K. The D_3O^+ and D^+ ions (the fragment ions from the CO_2 molecule) decrease (increase) steeply in intensity at the initial stage of CO_2 adsorption up to 1 ML coverage. The evolution of the O_2^+ ion delays relative to the other fragment ions because it comes from the multilayer of CO_2 . The secondary ion intensities from the D_2O molecules (upper panel) decrease rather gradually after the CO_2 multilayer grows. Moreover, the DCO^+ ion and the high-energy tail of the D^+ ion remain considerably even at higher CO_2 coverage. These results, together with those in Figure 2, may suggest the occurrence of intermixing between the D_2O and CO_2 molecules. Probably, a small amount of the D_2O molecule dissolves in the CO_2 film at low temperatures.

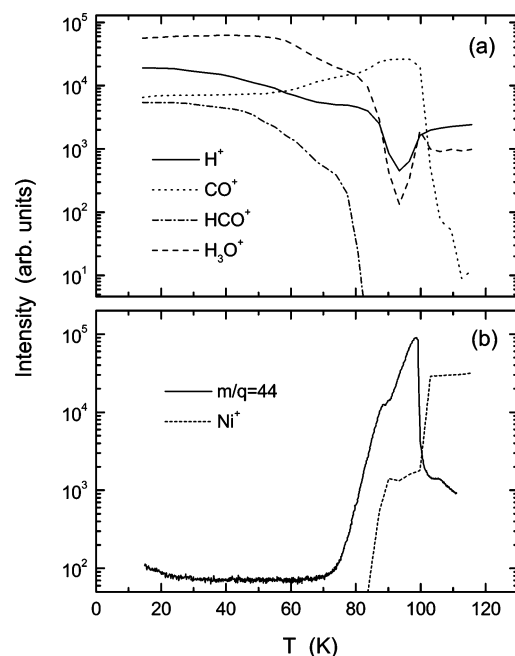


Figure 5. (a) Temperature-programmed TOF-SIMS intensities of typical secondary ions from the H_2O -deposited CO_2 film. The CO_2 film with a thickness of 25 ML was grown on the Ni(111) substrate at 13 K, and then the 0.1 ML of the H_2O molecules was adsorbed on it. In this procedure, physisorbed water nanoclusters can be formed. The temperature evolutions of the secondary ion intensities were measured continuously at a ramping speed of 5 K/min. (b) The thermal desorption spectrum of CO_2 ($m/q = 44$) is compared with the TOF-SIMS Ni^+ intensity from the CO_2 film (25 ML) adsorbed on the Ni(111) surface.

To gain more insights into the mechanism of segregation and mixing, the H_2O molecules are adsorbed on the surface of the CO_2 film. It is known that the cluster ions in the form, $\text{H}^+(\text{H}_2\text{O})_n$, are sputtered efficiently when the H_2O molecules are adsorbed on the CO_2 film at small coverage.²⁵ This is because the Coulombic fission of water nanoclusters takes place because of localization of valence holes. The experimental TOF-SIMS intensities from the H_2O (0.1 ML) adsorbed CO_2 film (25 ML) are shown in Figure 5a as a function of temperature. The H_3O^+ intensity from the water nanoclusters deposited at 13 K is enhanced by almost 2 orders of magnitude relative to that from the thick water film, whereas the H^+ intensity is basically independent of the coverage of water. The wetting or mixing of H_2O with the CO_2 film manifests itself in the emission of the HCO^+ ion at low temperatures. The H_3O^+ and HCO^+ intensities decrease considerably with increasing temperatures above 50–60 K. The dewetting is completed at 80 K where the HCO^+ ion disappears, and then the H_3O^+ intensity, together with the H^+ intensity, drops steeply above 85–90 K. The water nanoclusters do not undergo significant coalescence in the course of segregation (dewetting) as the H_3O^+ intensity is kept higher than the H^+ intensity, though the morphology of the cluster may be changed. Thus, this behavior can be explained by the penetration of the “almost suspended” H_2O nanoclusters in the bulk of the CO_2 film rather than the mixing at the well-defined interface. The TPD spectrum of the CO_2 molecule from the water (0.1 ML) deposited CO_2 film (25 ML) is shown in Figure 5b. There appears a shoulder at 87 K where the desorption rate of the CO_2 molecule decreases abruptly. It should be noticed that a small hump of the Ni^+ intensity occurs concomitantly with the shoulder in the TPD spectrum. This result can be interpreted by that the Ni(111) substrate is exposed because of dewetting of the CO_2 film.

The possibility of the carbonic acid formation is checked by the He^+ irradiation of the mixed CO_2 - D_2O film and the D_2^+ irradiation of the CO_2 film at 13 K (the experimental results are not shown explicitly). The films were irradiated by the 1.5-keV ion beam with a fluence of 2.5×10^{15} ions/ cm^2 . The H_2CO_3 molecules, if any, should be detectable in the present experiment because they can survive up to 200 K.⁷ However, no residues including the C atoms are observed for $T > 100$ K.

4. Discussion

The interactions between the H_2O (D_2O) and CO_2 molecules are investigated by analyzing the intensities of specific secondary ions as a function of temperature. The emission of the energetic H^+ (D^+) ion as well as the fragment/associate ions, such as HCO^+ and O_2^+ , is of particular importance because they provide information about the wetting/dewetting and intermixing of the initially layered films. However, there remains a question about the sputtering mechanism of these ions. The energetic H^+ ion (~ 200 eV) should not be sputtered via the collision cascade in which only a small amount of the momentum may be transferred. Apparently, it should be ejected during collision with the He^+ ion. The collision must happen to make the H^+ ion move toward the vacuum. This is likely to occur when the H atom is kicked out by the backscattered He atoms. To confirm this possibility, the yield of the backscattered He atoms from the water (7 nm corresponding to 50 ML of H_2O) adsorbed thick Ni substrate (100 nm) is calculated using the TRIM code.²² It is found that about 22% of the primary He is backscattered in this configuration though at most 3% of He comes out from the pure water film with the thickness of 100 nm. The cross section for the knock off of the hydrogen atoms might be small relative to that during collision cascade, but the recoiled hydrogen atoms with higher kinetic energies undergo ionization preferentially during collision with the CO_2 molecules, resulting in the considerable intensity of the high-energy tail of H^+ relative to the low-energy peak formed via the bond-breaking mechanism. The reaction pathways leading to the emission of the O_2^+ and HCO^+ ions are hardly identified, but they can be created during the collision cascade. In fact, mean energy of the sputtered O and H atoms, respectively, are 38 and 43 eV, as calculated using the TRIM code.²² They are sufficiently high to induce not only chemistry (~ 1 eV) but also ionization (> 10 eV). The presence of the backscattered He atoms would promote the formation of radical species and their chemistry.

As regards the carbonic acid formation, the experimental hydration energy is determined as 75 kJ mol^{-1} (0.78 eV)¹. The hydrolysis of CO_2 is not activated thermally at cryogenic temperatures, but the carbonic acid is expected to form in the collision cascade because a large number of energetic species including OH^- and H^+ are produced. Although no information about the fragment ions from H_2CO_3 is available, all secondary ions detected in the present experiment can be attributed to the parent H_2O and CO_2 molecules. This result seems reasonable because the multimolecular reaction that is necessary for the H_2CO_3 creation is not induced during the collision cascade that lasts for tens of femtoseconds. The H_2CO_3 molecules would rather form in the residues including neutral radical species after increasing temperature. However, the segregation of water and CO_2 molecules for $T > 60$ K is unfavorable not only in hydrolysis but also in radialysis of CO_2 . As a consequence, even if carbonic acid and its precursors are created after ion bombardment, they would not remain on the surface as residues. The confined geometry in thick water films would suppress the

molecular segregation, so that the stabilized carbonic acid species may be observed in the IR absorption experiments.^{4–7}

The dewetting of the initially uniform film can be interpreted by the occurrence of fluidity, which is associated with the glass–liquid transition. In fact, the instability of the fluidized film depends on the viscosity, interfacial tension, and thickness. The different dewetting behavior of the CO₂ monolayer between the Ni(111) and ASW surfaces can be attributed to the effect of interfacial tension. The 3D island is formed above 50–60 K as a consequence of the increased mobility of the CO₂ molecules. The IR absorption study claimed that the phase transition occurs at this temperature:¹⁵ the CO₂ films condensed below 30 K are amorphous as characterized by a broad IR spectrum, and they transform irreversibly to the sharp spectrum of crystalline CO₂ by warming above 50 K. This is apparently inconsistent with the present result because the morphology of the CO₂ film changes abruptly at 85–90 K. These behaviors are hardly expected from the already crystallized films with high rigidity. In general, the crystallization follows the glass–liquid transition since the latter defines the onset of the molecular diffusion. From our observations, T_g of CO₂ should be assigned to 50 K, and the homogeneous nucleation does not take place up to 85 K. In this temperature range, therefore, the CO₂ film can be regarded as supercooled liquid.

The supercooled liquid is known to exhibit some peculiar features in comparison with the normal liquid.²⁶ For example, the translational diffusion and viscosity are decoupled and, hence, the inverse proportionality between them (Stokes–Einstein relation) is broken near T_g : the viscosity of deeply supercooled liquid is higher by as much as 2 orders of magnitude than that expected from the molecular diffusion. Therefore, the supercooled liquid should be characterized by an ultraviscous nature at around T_g , so that the dewetting of the bulk CO₂ film is observed at higher temperature than T_g . On the other hand, the monolayer CO₂ film dewets the substrate at around T_g because it occurs as a consequence of the translational molecular diffusion. Probably, the thickness-dependent instability of the supercooled CO₂ film can be explained in this way on the basis of decoupling. Thus, dewetting of the CO₂ film and incorporation of water nanoclusters at 85 K should be attributed to the glass–liquid transition rather than to crystallization.

The TPD spectrum of CO₂ in Figure 5b exhibits a shoulder at 87 K, which occurs concomitantly with dewetting of the CO₂ film and incorporation of the physisorbed water nanoclusters. Essentially, the same TPD spectrum is obtained for the pure CO₂ film. This result reminds us of the well-known TPD spectrum of water multilayers, in which a quite similar shoulder occurs at around 160–165 K.^{12,13} This shoulder has been ascribed to crystallization,¹² but we interpret it as the morphological change of the supercooled liquid water¹³ because the water film dewets the Ni(111) substrate at 165 K following the onset of the translational diffusion of the water molecules at T_g = 136 K. These two characteristic temperatures arise from the decoupling as mentioned above. The crystallization is also a kinetic event that occurs above T_g , so that we cannot exclude the presence of crystallites in supercooled liquid. However, the homogeneous nucleation of CO₂ never occurs up to 85–90 K and probably does not occur until complete evaporation of the CO₂ film at 100 K. The present result is inconsistent with the conclusions of the IR absorption studies.¹⁰ We believe that the long-range order like crystallization cannot be discussed from the IR spectra though it provides useful information about the local molecular structures.

5. Conclusion

The monolayer and multilayers of carbon dioxide physisorbed on the surfaces of amorphous solid water and Ni(111) were studied by means of secondary ion mass spectrometry as a function of temperature. The CO₂ molecules wet the D₂O and Ni(111) surfaces when deposited below 40 K. The wetting or intermixing of CO₂ with the D₂O surface is evidenced by the emission of the DCO⁺, DCO₂⁺, and high-energy D⁺ ions, as well as by the delayed evolution of the O₂⁺ ions. The diffusion of the CO₂ molecules commences at 50 K, leading to dewetting of the monolayer CO₂ above 60 K. The infrared absorption studies revealed a drastic change in the spectra at around this temperature, and it was assigned to crystallization of CO₂. In the present study, however, the CO₂ multilayer exhibits fluidity even at 85–90 K, as evidenced by the abrupt change in the film morphology and the penetration of the physisorbed H₂O nanoclusters into the bulk. The glass-transition temperature of CO₂ should be assigned to 50 K as it defines the onset of the molecular diffusion. The occurrence of fluidity in the multilayers of CO₂ is delayed considerably relative to the onset of the glass–liquid transition because the translational diffusion and viscosity are decoupled in the supercooled liquid phase. No indications of the H₂CO₃ formation are obtained after He⁺ bombardment of the mixed CO₂–D₂O ice and the D₂⁺ irradiation of amorphous solid CO₂ at 13 K as far as the surface residues above 100 K are concerned. This behavior may be related to the segregation between the CO₂ and D₂O molecules above the glass-transition temperature.

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