

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

A. Yabushita,<sup>1</sup> T. Kinugawa,<sup>1</sup> M. Kawasaki,<sup>2</sup> T. Hama,<sup>3</sup> N. Watanabe<sup>3</sup>

<sup>1</sup>*Department of Molecular Engineering, Kyoto University, Japan*

<sup>2</sup>*Research Institute for Humanity and Nature, Japan*

<sup>3</sup>*Institute of Low Temperature Science, Hokkaido University, Japan*

The importance of energetic processes caused by vacuum ultraviolet (VUV) photoirradiation is known in the cosmic regions, which can directly induce chemical reactions of the ice mantles. 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. Therefore, how the surface composition changes after VUV photoirradiation needs to be investigated 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 spectra and rotationally resolved resonance-enhanced multiphoton ionization (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 ( $v=0,1$ ,  $T_{\text{trans}}=1600$  K and  $T_{\text{rot}}=800$  K) and cold CO ( $v=0$ ,  $T_{\text{trans}}=90$  K and  $T_{\text{rot}}=150$  K) were observed as photodesorbed products, suggesting that the hot CO comes from CO<sub>2</sub> adsorbed atop the water ice surface, while CO<sub>2</sub> trapped in 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. Actually, 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.

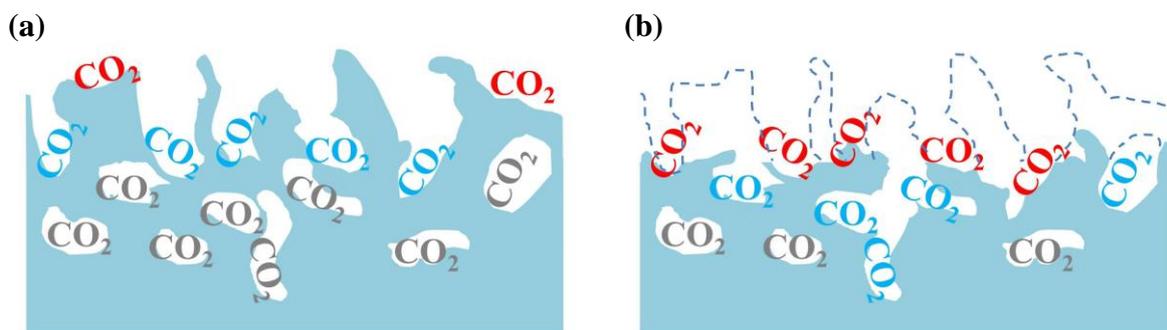


Figure 1: Schematic illustration of the distribution of CO<sub>2</sub> in CO<sub>2</sub>/H<sub>2</sub>O mixture ice, (a) as deposited before irradiation and (b) after prolonged 157 nm irradiation. CO<sub>2</sub> (red) stands for physisorbed CO<sub>2</sub> on the surface, CO<sub>2</sub> (blue) are trapped in the pores and CO<sub>2</sub> (gray) are buried in the bulk phase.

## References

- [1] T. Kinugawa, A. Yabushita, M. Kawasaki, T. Hama & N. Watanabe, 2011, *Phys. Chem. Chem. Phys.* 13, 15785