Formation of Carbon-Dioxide Clathrate Hydrates including Help Gases under Vacuum Conditions

*Rentaro Netsu[1], Tomoko Ikeda-Fukazawa[2]

1.Graduate School of Science and Technology, Meiji University, 2.Department of Applied Chemistry, Meiji University

In interstellar molecular clouds, water molecules condense on dust grains. The condensed water exists as amorphous ice in the cold clouds and is transformed into various structures depending on thermal conditions and compositions of including molecules. Blake et al. [1] proposed the presence of clathrate hydrates in cometary ice. From the results using transmission electron microscopy and Fourier transformed infrared spectroscopy, they showed the phase transition of vapor deposited amorphous ice including CH_3OH and CO_2 into type-II hydrate at around 120 K.
Clathrate hydrates are inclusion compounds consisting of water molecules and a variety of guest molecules. Most hydrates form one of two distinct crystallographic structures, type-I and -II, depending on the sizes and shapes of the guest molecules. The structure of CO_2 hydrate formed under a high-pressure condition is type-I [2]. For the hydrate from the vapor deposited amorphous ice by Blake et al. [1], the structure was type-II due to the help-gases effect of CH_3OH. For the CO_2 hydrate grown epitaxially on a hydrate under vacuum condition, the structure depends on the structure of the hydrate as the substrate [3]. In order to investigate the formation mechanisms of CO_2 hydrate including help-gases under vacuum conditions, we analyzed infrared spectra of vapor deposited amorphous ice including CO_2 and C_3H_6O during warming.
The CO_2/H_2O ratios of the prepared gas mixtures were 0.13–16.8. The gas mixtures were deposited onto a substrate of oxygen-free copper at 43 K. After the deposition, the substrate was warmed from 43 to 160 K. Infrared spectra were measured at approximately 1 min intervals during deposition at 43 K and at 2 K intervals during warming. Furthermore, CO_2 and C_3H_6O mixed hydrates were prepared from gas mixtures of H_2O, CO_2, and C_3H_6O with various compositions, and were measured spectra with the same procedures.
From the variation in spectral features of H_2O–CO_2 ice with warming, remarkable changes were found at 82 K. The wave numbers of the O–H stretching modes of H_2O and the C–O asymmetric stretching modes of CO_2 change significantly at this temperature. Furthermore, significant gas release and exothermic temperature rise were observed. These results suggest that the crystallization of amorphous ice begins at 82 K. From the wave numbers of C–O asymmetric stretching modes, the formed crystal is determined to be type-I hydrate. From the formation conditions of CO_2 hydrate, we propose the phase diagram of the H_2O–CO_2 system under vacuum conditions. In addition, the formation processes of mixed hydrate including CO_2 and C_3H_6O were analyzed. The result shows that the transition temperature of the mixed hydrate depends on the guest composition. From the results, we discuss the formation mechanisms of clathrate hydrates under vacuum conditions.
References
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