

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

*Rentaro Netsu¹, Tomoko Ikeda-Fukazawa²

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 CH₃OH and CO₂ 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 CO₂ 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 CH₃OH. For the CO₂ 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 CO₂ hydrate including help-gases under vacuum conditions, we analyzed infrared spectra of vapor deposited amorphous ice including CO₂ and C₃H₆O during warming.

The CO₂/H₂O 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, CO₂ and C₃H₆O mixed hydrates were prepared from gas mixtures of H₂O, CO₂, and C₃H₆O with various compositions, and were measured spectra with the same procedures.

From the variation in spectral features of H₂O-CO₂ ice with warming, remarkable changes were found at 82 K. The wave numbers of the O-H stretching modes of H₂O and the C-O asymmetric stretching modes of CO₂ 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 CO₂ hydrate, we propose the phase diagram of the H₂O-CO₂ system under vacuum conditions. In addition, the formation processes of mixed hydrate including CO₂ and C₃H₆O 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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