Formation of clathrate hydrate from amorphous ice during warming

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Water molecules are condensed on dust grains in interstellar molecular clouds and protester nebulae. The water exists as amorphous ice in the cold clouds and is transformed into various structures depending on thermal conditions and compositions with various deposited molecules. Blake *et al*. [1] proposed the presence of CO_2 clathrate hydrate in cometary ice. From the results using the transmission electron microscopy (TEM) and fourier transformed infrared spectroscopy (FT-IR), they showed the phase transition of vapor deposited amorphous ice including CO_2 and CH_3OH into type-II clathrate hydrate at around 120 K.

Clathrate hydrates are inclusion compounds consisting of water molecules and a variety of guests molecules. Most clathrate hydrates form one of two distinct crystallographic structures, type-I and –II, depending on the sizes and shapes of the guest molecules. The cubic unit cell of type-I clathrate hydrate contains 46 water molecules in a framework of two dodecahedral and six tetrakaidecahedral cages, and that of type-II clathrate hydrate contains 136 water molecules in a framework of 16 dodecahedral and eight hexakaidecahedral cages. The structure of CO_2 clathrate hydrate formed under a high pressure condition is type-I [2]. For the hydrate from the vapor deposited amorphous ice [1], the structure is type-II due to the help-gasses effect of CH_3OH. For the CO_2 clathrate hydrate grown epitaxially on a hydrate in low pressure conditions, the structure depends on the structure of the hydrate as the substrate [3]. In order to investigate the formation mechanisms of pure CO_2 clathrate hydrate in low pressure conditions, we analyzed infrared spectra of vapor deposited amorphous ice including CO_2 during the warming.

The gas mixtures of H_2O and CO_2 with 1:1 in H_2O:CO_2 were deposited with 10±8 μm/min onto a substrate of oxygen-free copper at 43 K. After the deposition, the substrate was warmed from 43 to 160 K with a rate of 1-4 K/min. During the warming, the infrared spectra were measured at intervals of 2 K using Shimadzu IRPrestige-21.

The results show that the spectral features change during the warming. From the analysis of the wave numbers of the O–H stretching modes of H_2O and the C–O asymmetric stretching modes of CO_2, significant changes were found at around 100 K. The wave numbers of the O–H stretching modes increase as the temperature increases at temperatures above 100 K, whereas those decrease in lower temperatures. The wave numbers of the C–O asymmetric stretching modes change significantly at around the temperature, and become almost constants at temperatures above 100 K. Furthermore, a remarkable gas release and exothermic temperature rise were also observed. The results suggest the crystallization of amorphous ice at around 100 K. The spectral feature of the C–O asymmetric stretching modes (i.e., the wave numbers, widths, and intensity ratio of two peaks) indicates that the crystal is the type-I clathrate hydrate. From the extrapolating the equilibrium line of the phase diagram of the H_2O-CO_2 system to our thermal condition, we propose the formation of CO_2 clathrate hydrate from the vapor deposited amorphous ice in vacuo.

References

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