Enclathration of NF_3 and c-C_4F_8 molecules in gas hydrates and their thermodynamic and cage filling characteristics

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F-gases are man-made gases which are utilized in semiconductor industry and refrigeration systems. Since F-gases have a high potential of global warming effect, various methods to separate F-gases have been widely studied, including gas hydrate-based F-gas separation. However, gas hydrate formation of c-C_4F_8 and NF_3 has not been well-studied, even though they have high global warming potential (c-C_4F_8: 8,700, NF_3: 8,000) and long atmospheric lifetime (c-C_4F_8: 3,200 years, NF_3: 740 years). Therefore, in this study, the fundamental research focusing on the thermodynamic and spectroscopic characteristics of NF_3 and c-C_4F_8 gas hydrates was performed. The three-phase (H - L_W - V) equilibria of the pure NF_3 and mixed c-C_4F_8 + CH_4 hydrates were measured, and the crystal structures of NF_3 and c-C_4F_8 + CH_4 hydrates were identified through PXRD, while the cage-filling characteristics of NF_3 and c-C_4F_8 molecules in each hydrate were analyzed through ^{13}C & ^{19}F NMR, and in-situ Raman spectroscopy. The results obtained in this study are expected to be helpful in future studies about various F-gas hydrates.