

## Novel Discoveries on sH hydrate forming F-gases

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This study made an important discovery on two F-gases ( $c\text{-C}_4\text{F}_8$  and  $\text{C}_3\text{F}_8$ ) which form sH hydrate in presence of suitable help gas molecules. Since  $\text{C}_3\text{F}_8$  and  $c\text{-C}_4\text{F}_8$  molecules have large molecular sizes (7.66 Å and 7.68 Å, respectively), those molecules have not been expected to be enclathrated in sI or sII hydrate cages. However, this study discovered that  $c\text{-C}_4\text{F}_8$  molecules can be enclathrated in sH large ( $5^{12}6^8$ ) cages in presence of  $\text{CH}_4$  as help gas, which was demonstrated through PXRD and  $^{13}\text{C}$  NMR spectroscopy. In addition,  $\text{C}_3\text{F}_8$  was found to act as a dual hydrate former between sH and sII hydrates according to help gas molecules. Via  $^{13}\text{C}$  NMR and Raman spectroscopy,  $\text{C}_3\text{F}_8$  was confirmed to form sH hydrate with  $\text{CH}_4$ , while forming sII hydrate in presence of  $\text{SF}_6$ . The discovery of  $c\text{-C}_4\text{F}_8$  and  $\text{C}_3\text{F}_8$  as sH hydrate former is very meaningful, since there have been no gas-phase sH hydrate former investigated until present. The overall results obtained in this study provide invaluable information of various properties of F-gas hydrates, and they are expected to be useful sources for gas hydrate application fields in the future.