Terahertz spectroscopy on ionic clathrate hydrates

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Clathrate hydrates are one of the inclusion compounds, which are stabilized by the interaction between water and guest species in the cavity of cages. Ionic clathrate hydrates are formed by the enclathration of either the cations or anions in cages and the incorporation of the counter-ions into the water framework. Because rather strong ionic interactions exist within ionic hydrates, they have some distinctive features such as their high thermal stability and complex structure. Tetra-n-butyl ammonium bromide (TBAB) hydrate, one kind of ionic clathrate hydrates, forms semi-clathrate hydrate in that part of some cages have a dangling bond for encaging the large tetra-n-butyl ammonium molecule. At atmospheric pressure, the melting point of TBAB hydrate is above the freezing point of water. In this study, the guest dynamics and thermal behavior of quaternary ammonium salt hydrates are studied by application of terahertz spectroscopy. The terahertz region ranging from 0.1 to 10 THz contains a lot of information on low-frequency vibration motion and enables to explore both intramolecular and intermolecular interactions. The THz spectra of quaternary ammonium salt hydrates with various anions (OH-, F-, Br-) are obtained and some physical constants of each hydrates are determined.