

Dynamics of methane in amorphous and crystalline methane hydrate

Hiroshi Akiba, Menghan Zhang, Osamu Yamamuro
ISSP, Univ. of Tokyo

Methane hydrate (MH) has been studied extensively not only as a future energy resource but also from the interest in quantum and classical rotations of methane molecules. The crystalline methane hydrate (c-MH) is a compound with the host lattice composed of water molecules and methane guest molecules. c-MH forms a structure of type I with two dodecahedral (12-hedral) and six tetracahehedral (14-hedral) cages per unit cell (space group is Pm3n), and each cage contains one methane molecule [1]. The chemical formula of c-MH is $\text{CH}_4 \cdot 5.75\text{H}_2\text{O}$. The “amorphous” MH (a-MH) was first prepared with a vapor-deposition method by our group [2]. The radial distribution functions derived from the neutron diffraction data demonstrate that CH_4 molecules are still accommodated in the cage-like spaces even in amorphous structure. It is also known that the a-MH crystallizes into the c-MH around 175 K [3]. However, further details of the amorphous structure, crystallization process, and dynamics of amorphous clathrate hydrate have not been investigated so far.

In this study, the dynamics of methane molecules in a-MH was studied by quasielastic neutron scattering (QENS). The QENS experiment was conducted using AGNES (JRR-3). The a-MH was formed by vapor deposition, in which the sample vapor is deposited on the substrates kept at 5 K, using our custom-designed cryostats. The vapor-deposition was performed under 200 Pa of $\text{CH}_4 \cdot 5.75\text{D}_2\text{O}$ gas for 14 h to form a-MH sample. Then the sample was annealed at 170 K under 0.1 MPa of CH_4 gas to relax the sample to a stabler state. The quasi-elastic neutron scattering (QENS) and inelastic neutron scattering (INS) data were collected at several temperatures from 5 to 80 K for both as-deposited and annealed a-MH samples.

The QENS spectra of as-deposited and annealed a-MH showed QENS peak broadening

due to the rotational motion of accommodated CH_4 guest molecules. The clear inelastic peaks, which appeared in annealed sample due to the rotational excitations of CH_4 , were not observed in as-deposited sample. The data were fitted well using the combination of Delta and Lorentz functions as usual and additional Gauss functions to reproduce the INS peaks.

Fig.1 shows the Arrhenius plot of relaxation time τ corresponding to the inverse of the half width at half maximum (HWHM) of the Lorentz function. In the Arrhenius plot, there is a clear bending of the τ line around 20 K for both as-deposited and annealed a-MH, and the activation energy on the low-temperature side is very small. We guess that there is a crossover between the classical (high-T) and quantum (low-T) rotations around 20 K. The Arrhenius plot also shows that the as-deposited a-MH has longer τ than the annealed one, indicating that the cage space in as-deposited a-MH is narrower and more disordered than the annealed a-MH.

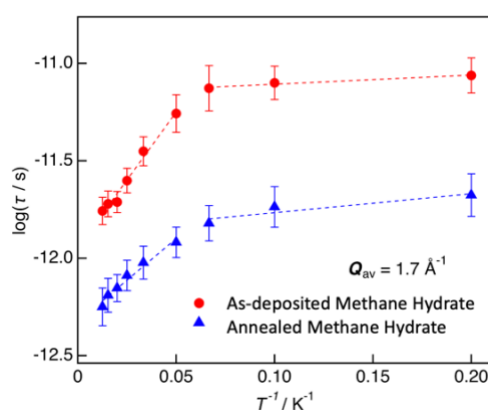


Fig. 1. Arrhenius plots of as-deposited and annealed a-MH.

[1] D. W. Davidson, et al., Nature, 311(5982), 142-143 (1984). [2] T. Kikuchi, et al., J. Phys. Soc. Jpn., 81(9), 094604 (2012). [3] M.Z. Faizullin, et al., Chem. Eng. Sci., 130, 135-143 (2015).