INELASTIC NEUTRON SCATTERING STUDY OF HOST AND GUEST MOLECULAR MOTIONS IN METHANE HYDRATE

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ABSTRACT

Methane hydrate has a unique structure that the host water framework forms two kinds of cages, which contain one methane molecule each. Therefore, it has been expected that there may exist three kinds of translational modes of a methane molecule and also the distortion of translational mode of host water molecules compared with normal ice. We need information of the host and guest molecular dynamics over the wide momentum and energy transfer region for studying such dynamics. In this study inelastic neutron measurements were carried under 40 K with MARI spectrometer at ISIS in UK, TAS at JRR-3 and CAT at KENS in Japan. For the methane molecular motion we could confirm its freelike rotation by complementary use of MARI and TAS spectra. After the subtraction of the scattering intensity of the rotation evaluated by the free rotation model from the experimental data, three kinds of translation modes were identified at first experimentally. On the experimental spectra there still remains the excess intensity which could not explain the single mode excitation. The libration mode of the water framework shows the different momentum and energy transfer dependence with those of normal ice. The feature of the libration mode is resemble to ice-IX, that could be considered as a proton ordering of the cage structure appeared in ice-II, VIII and IX.

Keywords: methane hydrates, neutron inelastic scattering, molecular motion

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NOMENCLATURE

$B_T(J)$: Boltzman factor at T

d: Bond length of C-H

E: energy transfer

E_{JJ}': Energy transfer from J to J'

J, J': Quantum number of rotational state

$j_1(Qd)$: spherical Bessel function

k, k_0: wave vectors for final and incident neutrons

Q: momentum transfer

σ: neutron cross section

T: temperature [K]

Ω: solid angle

INTRODUCTION

Methane hydrate (MH) is a kind of non-stoichiometric inclusion compound with the host framework composed of water molecules. It consists of two kinds of water cages, two pentagonal dodecahedra and six tetrakaidecahedra, which can contain one methane molecule each. Intensive studies of MH by neutron scattering have been undertaken and have made clear the structure [1] and spectral features [2,3,4] and given the structural formation [5]. In addition to these their unique structure gives interesting physical properties such as thermal conductivity [6]. The properties can be affected its isolated guest and host structures and interactions between them.

As a first approximation MH can be regarded as a discrete system of guest molecular motions, because the guest molecules, methane, are separated each other by water cages. In our previous report [7], we revealed the neutron cross sectional features on the $Q = 1 - 13$ Å^{-1} and $E = -20 - 90$ meV region. There was an impressive Q^2 dependent peak in the region, which was caused by the methane rotational motion. The result implied the prospect of interactions between the methane molecule and the water cage was weak, and the interactions between the methane molecules were much weaker. It was said that in the cage the methane molecular rotational motion was practically free, and we had made clear its quantum rotation in detail from the lower Q-E space measurement of dynamical structure factors [8,9].

On the other hand, there are still considered the translational motions of the methane molecule, which is strongly restricted with the water cage, and the host framework motions. In this study we reveal such modes of MH based on the wide Q region measurement.

EXPERIMENTAL

CH_4-D_2O (MH-D_2O) and CH_4-H_2O (MH-H_2O) were made at the Hokkaido National Industrial Research Institute (HNIRI) for neutron scattering samples. These were prepared by grinding crushed ice at around 268 K into contact with methane gas at 5 MPa for 72 h. The methane inclusion densities were 80% for MH-D_2O and 87% for MH-H_2O, respectively. Crushed ice Ih samples of H_2O and D_2O were prepared for comparison. Samples were
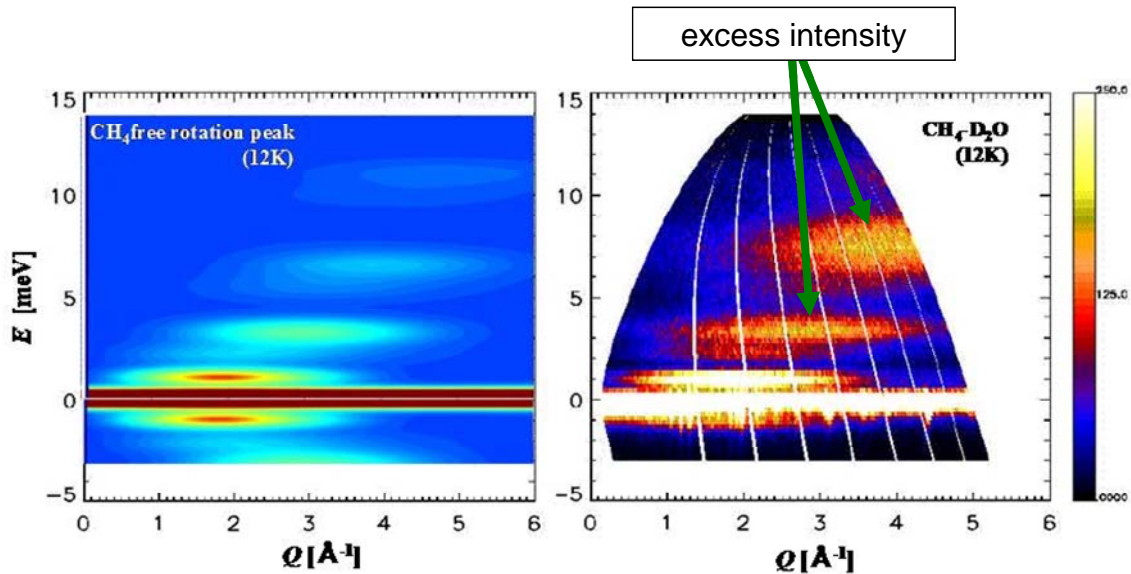

Figure 1. Dynamical structure factor $S(Q,E)$ of CH_4-D_2O at 12 K measured by MARI (right). Calculated $S(Q,E)$ for free rotational component of methane molecule at 12 K (left).

handled under a liquid nitrogen temperature and stored in aluminum containers. An annular geometry was used for the container to minimize self-shielding effects. A double walled can with a diameter of 42 mm was used, with the thicknesses of the MH-H_2O and MH-D_2O samples being 0.5 and 1.5 mm, respectively.

The neutron scattering experiments were performed on the MARI spectrometer at the pulsed neutron source of the ISIS at Rutherford Appleton Laboratory in UK, the triple-axis spectrometer TAS-1 at Japan Atomic Energy Research Agency in Japan and the inverted geometry spectrometer CAT at the pulsed neutron source of the KENS at High Energy Accelerator Research Organization in Japan. The sample was attached to a cryogenic system keeping the temperature under 150 K during the sample change. The neutron scattering measurements were carried around 12 K with incident energies of 15 meV, 100 meV and 500 meV on MARI and 30 meV on TAS-1.

RESULTS AND DISCUSSION
CH₄ free rotation model
On the low energy region around meV, there appear the inelastic peaks corresponding to the methane rotation and it is suggested that there exist translational modes of methane in a small and large cages. We calculated the intensity of CH_4 rotational mode by assuming the free rotation (FRM). The formula of the free rotation of a spherical top molecule is

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\sigma_b}{4\pi}\left|\frac{k}{k_0}\right|\sum_{JJ'}\frac{2J'+1}{2J+1}B_T(J)\sum_{l=|J-J'|}^{J+J'}j_l^2(Qd)\delta(E-E_{JJ'}) \qquad (1).$$

Figure 1 shows the obtained spectrum by MARI (right) and the calculated one using the FRM (left). The measured dynamical structure factor $S(Q,E)$ of MH and the methane FRM shows well agreement with their characteristic peaks, but there still remains the excess intensity of the cross-section around 4 meV toward over 8 meV. Figure 2 shows the comparison between the experimental $S(Q,E)$ and the methane FRM on the some Q axes. The experimental features are agreed with the CH_4 FRM very well. On the other hand, at the energy region over 4 meV the experimental $S(Q,E)$ and CH_4 FRM has a great difference as shown in figure 3. Such difference could not be explained by CH_4 FRM, then we done the detailed analysis of the E and Q dependence of the excess mode.

CH₄ translation mode
The subtraction of the calculated CH_4 FRM from the experimental $S(Q,E)$ leaves the excess intensity (figure 4). In the molecular dynamics (MD) calculation by Tse et. al. [2] there appears three peaks due to the translational motion of $CH4$ molecule in the two kinds of water cages. Fig. 4 shows an example of three Gaussian functions fitting to the subtracted intensity. The fitting
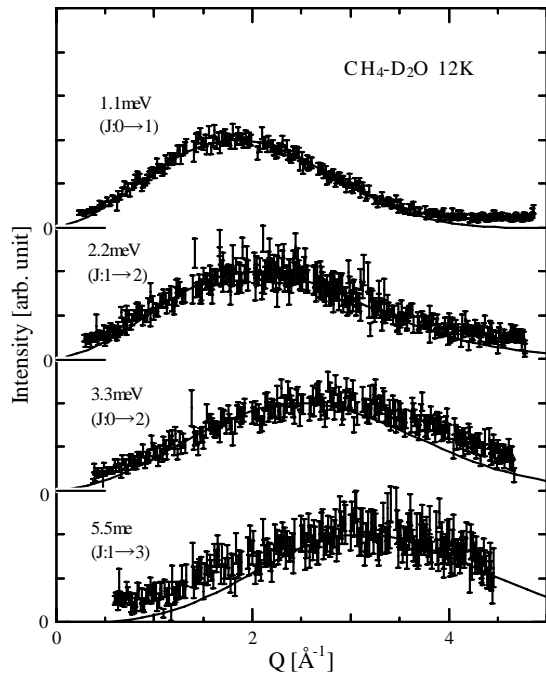

Figure 2. An example of the momentum dependent scattering intensity comparison between the measured $S(Q,E)$ and the calculated $S(Q,E)$ for the methane free rotation model at constant Q.
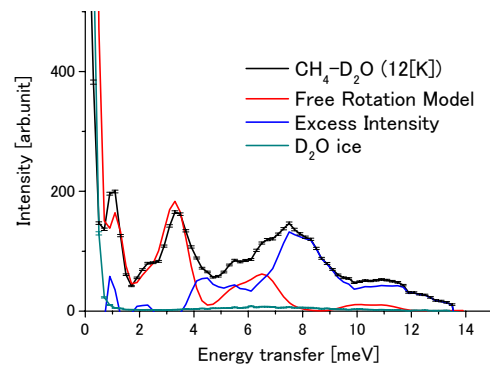

Figure 3. An example of the energy dependent scattering intensity comparison between the measured $S(Q,E)$ and the calculated $S(Q,E)$ for the methane free rotation model at constant $Q = 6$ Å⁻¹.

procedure worked well, and the fitting results show good agreements with the subtracted spectrum.

Figure 5 shows the Q dependence of the peak positions of the fitting results for MARI spectrum. The decomposed peak positions appear on the nearly constant energy around E = 3.9, 4.8 and 7.8 meV. These peaks seem to correspond to the positions of methane translational peaks in the water cages calculated by MD as 3.4 and 6 meV in large cage or 8.6 meV in small cage [2]. We think that we could assign the origin of the excess peaks at the lower energy region as such hindered translational motions of the methane molecules in the water cages.

Excess intensity over 40 meV region

Figure 6 shows the $S(Q,E)$ intensity map obtained by MARI with 100 meV incident neutrons. We can recognize that there are some unknown modes between 40 to water libration regions in MH-D_2O and MH-H_2O compared to the D_2O and H_2O ice spectra. The modes are originated by CH_4 existence, because they appear just on the MH spectra. Decomposition of such unknown modes is shown in figure 7. The experimental data were taken by MARI and TAS-1, and their trends were corresponded. In the figure we placed the one of decomposed peak candidate. The assumed peaks have their tops at around 38 and 46 meV. In the region the CH_4 FRM makes some very weak transition modes, then the excess modes are not by
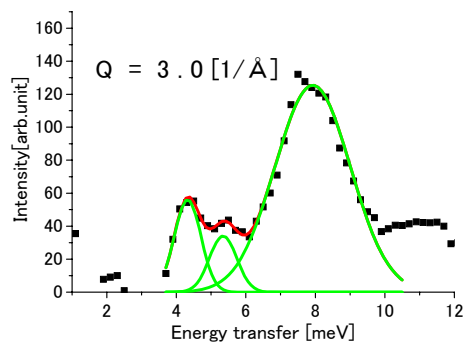

Figure 4. An example of three Gaussian fitting to the excess intensity, which appears after subtracting the methane free rotation model from the measured $S(Q,E)$. This spectra ($Q = 3$ Å^{-1}) was obtained by MARI at 12 K.
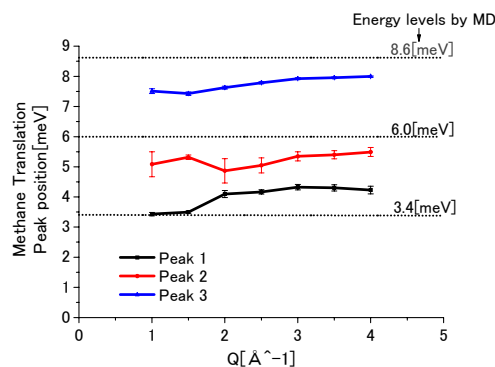

Figure 5. Q dependence of the Gaussian fitted peaks. Energy constant dotted lines correspond to the methane translational modes calculated by MD [2].
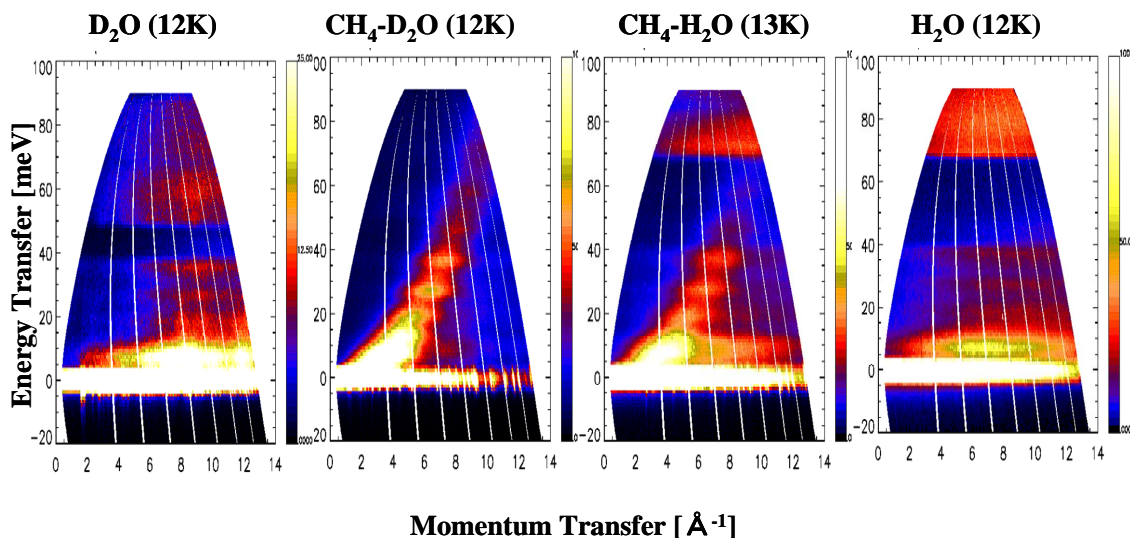

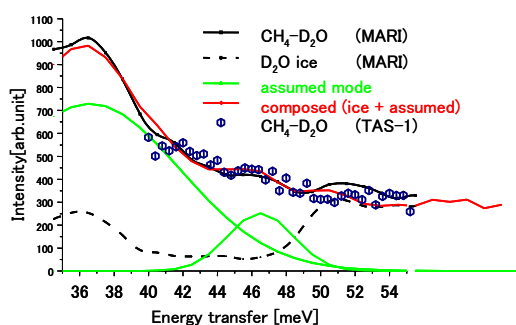Figure 6. $S(Q,E)$ intensity map obtained by MARI with 100 meV incident neutrons

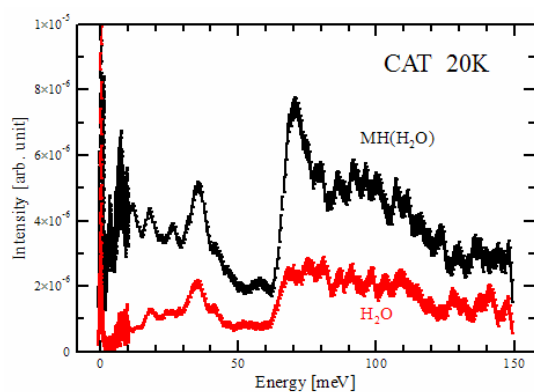Figure 7. Assumed excess modes at higher energy region. Assumed modes were made by Gaussian functions.

Figure 8. Inelastic neutron scattering spectra of CH_4-H_2O and H_2O ice.

the CH_4 free rotation. One of possibilities can be said as the coupled mode between CH4 molecular modes and water lattice modes, because the region is just above the ice lattice modes between 7 and 40 meV. Unfortunately, the experimental spectra have poor resolution for detailed analysis, because the Q-E region is difficult to reach by the present spectrometers. For the confirmation of such assumption, we have to carry the more precise experiment at the new neutron facility.

Water lattice mode
In fig. 6 we can show the difference between the intensity distributions of librational mode of water lattice. Over 70 meV for H_2O and over 50 meV for D_2O the scattering intensities are almost uniform. On the other hands, MH-H_2O shows the characteristic intensity distribution. Figure 8 shows the neutron spectra over wide energy region for MH-H_2O and normal H_2O ice. The libration mode region from 60 to 120 meV shows the large

difference between them. H_2O ice has flat structure, but MH-H_2O has sharp peak at 70 meV. Such peak feature of the libration mode is resemble to ice-IX, then the reason would be considered as a proton ordering of the cage structure appeared in ice-II, VIII and IX.

SUMMARY
We have carried on the inelastic neutron scattering measurements of methane hydrate in the wide energy and momentum range. We analyzed the obtained $S(Q,E)$ on the assumption of methane free rotation, which shows very good consistency with the $S(Q,E)$ under 3 meV. After subtracting the rotational component from the $S(Q,E)$, there remained excess three peaks around 4 to 8 meV. Because these peak positions are close to the methane translational modes in the water cages, we could assign the peaks as such modes. In the higher energy region around 40 to 50 meV there were exsess modes for MH-D_2O. The origin of the modes were still unknown, but one possibility was coupled mode between methane molecular modes and water lattice modes. For the host lattice mode, the libration region showed the large difference between H_2O ice and MH-H_2O. The libration region feature of MH is resemble to ice-IX, which could be considered as a proton ordering of the cage structure.

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