

Incoherent Inelastic Neutron Scattering of Clathrate Hydrates

Tomoko IKEDA-FUKAZAWA, Takeo HONDOH, Hiroshi FUKAZAWA¹ and Susumu IKEDA¹

*Institute of Low Temperature Science, Hokkaido University,
Sapporo 060-0819, Japan*

¹ *Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK)
Oho 1-1, Tsukuba, Ibaraki 305-0801, Japan*

We measured incoherent inelastic neutron scattering of clathrate hydrates of carbon dioxide, xenon and tetrahydrofuran in order to investigate the effect of the motion of guest molecule on the surrounding hydrogen-bonded network. The results showed that the peak of the transverse acoustic mode of the host water in the clathrate hydrates is stronger than that in the ice Ih. Furthermore, the intensity of the peak depends on the type of the guest molecule. The enhancement of the peak is attributed to the coupling of the translational vibration of the guest molecule and the lattice vibration of the host water, since these vibration modes are in the same energy region. It is concluded that the interaction between the guest molecules and the host waters is so strong that the coupling of the vibrations of the guest molecules and the host lattice depends on the type of guest molecule.

KEYWORDS: clathrate hydrate, vibrational spectra, neutron scattering

§1. Introduction

Clathrate hydrates¹⁾ are nonstoichiometric inclusion compounds consisting of water molecules and a variety of guest molecules. The water molecules are linked together by hydrogen bonds in the closest packing of polyhedral cage-like structures (host lattice), which can accommodate a guest molecule. Most clathrate hydrates form one of two distinct crystallographic structures, Stackelberg's type-I and -II,²⁾ depending on the sizes and shapes of the guest molecules inside the cages.

The cubic unit cell of the type-I (space group: $Pm3n$) contains 46 water molecules in a framework of 2 dodecahedral and 6 tetrakaidecahedral cages.³⁾ There are three crystallographically distinguishable oxygen atoms in sets of 6, 16 and 24 designated as types c , i and k (k is further classified to k_1 and k_2 by the distance from the center of the tetrakaidecahedral cage). The dodecahedral cage consists of 20 oxygen atoms from the 8-fold i and 12-fold k . The tetrakaidecahedral cage consists of 24 oxygen atoms from the 4-fold c , 8-fold i , 4-fold k_1 and 8-fold k_2 . The hydrogen atoms are equally distributed among the two possible sites on each O-O bond according to the ice rules.⁴⁾

For the type-II (space group: $Fd3m$), the cubic unit cell contains 136 water molecules in a framework of 16 dodecahedral and 8 hexakaidecahedral cages.⁵⁾ There are three crystallographically distinguishable oxygen atoms in sets of 8, 32 and 96 designated as types a , e and g (g is further classified to g_1 and g_2 by the distance from the center of the hexakaidecahedral cage). The dodecahedral cage consists of 20 water molecules from the 2-fold a , 6-fold e and 12-fold g . The hexakaidecahedral cage consists of 28 water molecules from the 4-fold e , 12-fold g_1 and 12-fold g_2 .

The thermodynamic stability and the phase equilibrium of the clathrate hydrate have been predicted by

the theory of van der Waals and Platteeuw.⁶⁾ This theory is based on a thermodynamic model in which the guest molecules are dissolved or absorbed in the host lattice. However, there is a slight but not a negligible discrepancy between the theoretically predicted and experimentally obtained dissociation pressures for most of the guest species.¹⁾ Molecular dynamics simulations showed that the guest-host interaction is the primary factor for the discrepancy.⁷⁾ Thus, the guest-host interaction has been studied as the most basic subject for the inclusion mechanism of the clathrate hydrate.

The type-I CO₂ clathrate hydrate is suitable for investigation of the guest-host interaction, since the CO₂ molecule is simple in its shape. Ratcliffe and Ripmeester⁸⁾ showed that the CO₂ molecules in the CO₂ clathrate hydrate rotate about the symmetry axis of the tetrakaidecahedral cage using NMR spectra. Ikeda *et al.*⁹⁾ measured crystal orientation dependence of Raman spectra of a single crystal of the type-I CO₂ clathrate hydrate. They found that the scattering intensities of the peaks, which are caused by Fermi resonance of the symmetric stretching mode and the overtone of the bending mode of the CO₂ molecules and the O-H symmetric stretching vibrational mode, vary with variation of the input polarization. Since the results were consistent with the results obtained from the measurements of Raman spectra of a single crystal of the type-II natural air clathrate hydrate in polar ice sheet,¹⁰⁾ they concluded that the uniaxial molecules in the cages rotate anisotropically and that the surrounding water molecules are affected by the motion of the uniaxial guest molecules.

In order to investigate the influence of the rotational motion of the guest molecule on the surrounding hydrogen bonded network, Ikeda *et al.*^{11,12)} measured neutron powder diffraction of deuterated clathrate hydrates of CO₂ and Xe. They found that the magnitudes of the thermal parameters of the host atoms of the

CO₂ clathrate hydrate depend strongly on the crystallographic site, while those of the Xe clathrate hydrate do not depend on the site. The site dependencies of the thermal parameters of the host atoms in the CO₂ clathrate hydrate are attributed to the rotational motion of the CO₂ molecules in the cages. It was concluded that rotational motion of guest molecules has a strong influence on the surrounding hydrogen bonded network. The motion of the guest molecules can be decomposed into two contributions: the localized translational motion of the center of the mass, and the rotational motion about this center.¹³⁾ Thus, It is expected that the translational motion of guest molecule also have influence on the surrounding hydrogen bonded network.

We measured incoherent inelastic neutron scattering (IINS) spectra of the type-I clathrate hydrates of Xe and CO₂, and the type-II clathrate hydrate of tetrahydrofuran (THF) in order to investigate the influence of the translational motion of the guest molecule on the host lattice. The IINS is useful to investigate the coupling between the translational vibration of the guest molecule and the lattice vibration of the host water, since these vibration modes are in the same energy region.¹³⁾

§2. Experimental

Powdered samples of the clathrate hydrates of CO₂ and Xe were prepared in the following manner. To provide a large reaction sureface, typically 13 g of H₂O ice Ih is finely powdered. The powder inserted in a stainless steel pressure cell and pressurized for about two months under the CO₂ (or Xe) gas pressures at 272.7 K. The pressure in the cell was 2.4 MPa for CO₂ and 0.3 MPa for Xe, almost twice as high as the dissociation pressure at 272.7 K.^{14,15)} A large excess of CO₂ (or Xe) was used to ensure complete enclathration. At the end of the reaction, the cell was cooled to 200 K. The THF clathrate hydrate was prepared from the solution of C₄D₈O·H₂O. The samples were packed between two sheets of thin aluminum and cooled to 21 K. The thickness of the sample is 0.4 mm and the sample area exposed to the neutron beam is about 30 cm².

The IINS spectra were measured at 21 K using a CAT spectrometer installed in a neutron scattering facility (KENS) along with the pulsed neutron source at KEK, Japan. CAT is a time-of-flight neutron spectrometer with an inverted geometry that realizes an energy resolution of $\Delta E/E = 2\text{--}3\%$ over a wide energy range of 1–1000 meV.¹⁶⁾

§3. Results and Discussion

Figs. 1(a)–(c) show the IINS spectra of the clathrate hydrates of CO₂, Xe and THF. The intensities are normalized by the peak height of the optic mode of the translational lattice vibration at 34 meV, which the intensity is independent of the guest molecules. The peaks observed at 6, 27 and 34 meV are the transverse acoustic mode and the optic modes of the translational lattice vibration, respectively.¹⁷⁾ The broad peaks observed around 69 meV are the librational modes. We found no difference in the energy between the clathrate hydrates of CO₂, Xe and THF within the experimental resolution.

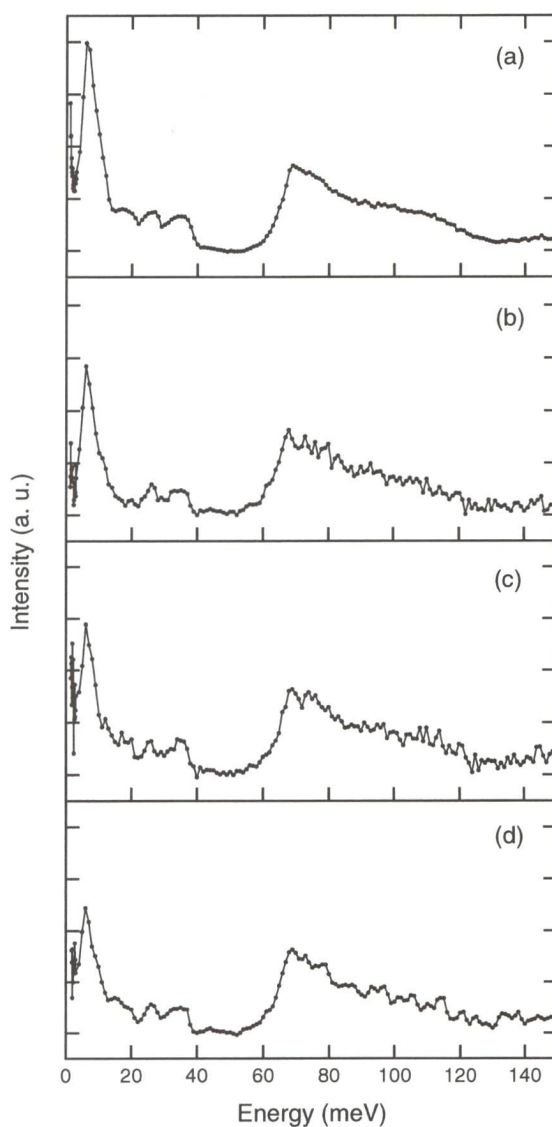


Fig. 1. Incoherent inelastic neutron scattering spectra of (a) type-I CO₂ clathrate hydrate, (b) type-I Xe clathrate hydrate, (c) type-II THF clathrate hydrate and (d) ice Ih.

These peaks correspond to the peaks at 6, 27, 34 and 69 meV for the hexagonal ice Ih (See Fig. 1(d)).¹⁸⁾ Tse *et al.*¹⁹⁾ reported that the transverse acoustic modes of the type-I Xe clathrate hydrate and the type-II krypton clathrate hydrate are shifted to high energies in comparison with that of the ice Ih. However, we found no energy shift within the experimental resolution.

From Fig. 1, it can be seen that the scattering intensities of the peak at 6 meV of the clathrate hydrates are higher than that of the ice Ih, although the general features of the spectra are similar. Since the cross section of the incoherent scattering for the proton is very much large in comparison with those of any other nuclides in the present system of clathrate hydrates, the scattering from the system is almost entirely attributed to the scattering by the proton in the host waters. However, the vibration energies of the translational motions of the encaged guest molecules are close to the energy region around 6 meV.¹³⁾ Thus, the enhancement of the

peak at 6 meV is thought to be caused by the coupling between the translational vibration mode of the guest molecule and the transverse acoustic modes of the host lattice.

The scattering intensity of the peak at 6 meV of the CO₂ clathrate hydrate is high in comparison with those in the clathrate hydrates of Xe and THF. The intensity of peak caused by coupling between two vibrations is determined by the scattering intensities and energy difference of the two vibrations.

The symmetry of the tetrakaidecahedral cage in the type-I clathrate hydrate corresponds to an oblate ellipsoid, while the dodecahedral cage is almost spherical in shape. Thus, the translational vibrations of the guest molecule in the type-I clathrate hydrate are decomposed into three contributions: translational motion in the dodecahedral cage, and two types of translational motion in the hexakaidecahedral cage. The energies of the translational vibrations of Xe in the dodecahedral and hexakaidecahedral cages of the type-I clathrate hydrate are 5.8, 4.3 and 2.1 meV, respectively.²¹⁾ The energy of the translational vibration of the guest molecules is proportional to $\mu^{-0.5}$, where μ is the reduced mass. The values of μ of the guest in a unit cell for Xe in the type-I clathrate hydrate, CO₂ in the type-I clathrate hydrate, and THF in the type-II clathrate hydrate are 463, 247 and 1077 g mol⁻¹, respectively. Using these values, the energies of the translational vibrations of CO₂ in the dodecahedral and hexakaidecahedral cages of the type-I clathrate hydrate can be estimated to be 7.7, 5.9 and 2.9 meV, respectively. The vibrational energy of CO₂ in the hexakaidecahedral cage is close to the energy of the transverse acoustic modes of the host lattice. In addition, the amplitude of the translational motion of CO₂ in the tetrakaidecahedral cage is large in comparison with that in the dodecahedral cage.¹²⁾ Therefore, we conclude that the enhancement of the peak at 6 meV of the CO₂ clathrate hydrate is attributed to the translational vibration of the CO₂ molecule in the hexakaidecahedral cage.

For the Xe clathrate hydrate, the amplitude of the translational motion of Xe in the dodecahedral cage is small at low temperature,¹²⁾ although the vibration energy of Xe in the dodecahedral cage (i.e., 5.8 meV) is close to the energy of the transverse acoustic modes of the host lattice. For the THF clathrate hydrate, the THF molecule is accommodated only in the hexakaidecahedral cage in the type-II clathrate hydrate.²⁰⁾ From the reduced masses of Xe and THF, the energy of the translational vibration of THF in the hexakaidecahedral cage can be estimated to be less than 3.7 meV. In addition, the amplitude of the translational motion of THF in the hexakaidecahedral cage is supposed to be small at low temperature, since the size of the THF molecule is large for the cavity. Thus, the intensities of the peak at 6

meV of the clathrate hydrates of Xe and THF are small in comparison with that of the CO₂ clathrate hydrate.

We conclude that the results show the effect of the motion of the guest molecule on the surrounding hydrogen-bonded network. The coupling between the translational vibration of guest molecule and the lattice vibration of host water is so strong that the scattering intensity of the coupling peak depends on the type of guest molecules. This effect is attributed to the strong guest-host interactions which are dominant factor governing the stability of the clathrate hydrate.

Acknowledgements

This work was supported by a Grant-in-aid for Scientific Research from the Ministry of Science, Education and Sports, Japan. T. I. F. and H. F. have been supported by a Research Fellowship of the Japan Society for the Promotion of Science.

- 1) D. W. Davidson: *Water-A Comprehensive Treatise*, ed F. Franks (Plenum Press, New York, 1972) chap. 3.
- 2) M. von Stackelberg and H. R. Muller: *Z. Elektrochem.* **58** (1954) 25.
- 3) R. K. McMullen and G. A. Jeffrey: *J. Chem. Phys.* **42** (1965) 2725.
- 4) L. Pauling: *J. Am. Chem. Soc.* **57** (1935) 2680.
- 5) T. C. Mak and R. K. McMullen: *J. Chem. Phys.* **42** (1965) 2732.
- 6) J. H. van der Waals and J. C. Platteeuw: *Adv. Chem. Phys.* **2** (1959) 1.
- 7) H. Tanaka and K. Kiyohara: *J. Chem. Phys.* **98** (1993) 4098.
- 8) C. I. Ratcliffe and J. A. Ripmeester: *J. Phys. Chem.* **90** (1986) 1259.
- 9) T. Ikeda, S. Mae and T. Uchida: *J. Chem. Phys.* **108** (1998) 1352.
- 10) T. Ikeda, H. Fukazawa, S. Mae, T. Hondoh and C. C. Langway, Jr.: *J. Phys. Chem.* **101** (1997) 6180.
- 11) T. Ikeda, O. Yamamuro, T. Matsuo, K. Mori, S. Torii, T. Kamiyama, F. Izumi, S. Ikeda and S. Mae: *J. Phys. Chem. Solids* **60** (1999) 1527.
- 12) T. Ikeda, S. Mae, O. Yamamuro, T. Matsuo, S. Ikeda and R. M. Ibberson: *J. Phys. Chem.* (in press).
- 13) J. S. Tse, M. L. Klein and I. R. McDonald: *J. Chem. Phys.* **81** (1984) 6146.
- 14) S. L. Miller: *Ices in the Solar System*, ed J. Klinger, D. Benest, A. Dollfus and R. Smoluchowski (D. Reidel, Dordrecht, 1985) p. 59.
- 15) M. von Stackelberg: *Naturewiss.* **36** (1949) 327.
- 16) S. Ikeda and N. Watanabe: *Nucl. Instr. Meth.* **221** (1984) 571.
- 17) J. S. Tse, M. L. Klein and I. R. McDonald: *J. Phys. Chem.* **87** (1983) 4198.
- 18) H. Fukazawa, S. Ikeda and S. Mae: *Chem. Phys. Lett.* **282** (1998) 215.
- 19) J. S. Tse, B. M. Powell, V. F. Sears and Y. P. Handa: *Chem. Phys. Lett.* **215** (1993) 383.
- 20) O. Yamamuro, T. Matsuo, H. Suga, W. I. F. David, R. M. Ibberson and A. J. Leadbetter: *Physica B* **213&214** (1995) 405.
- 21) J. S. Tse, M. L. Klein and I. R. McDonald: *J. Chem. Phys.* **78** (1983) 2096.