LOW FREQUENCY RAMAN SCATTERING OF CLATHRATE HYDRATE: *AB INITIO* CALCULATIONS AND NEW ANALYSIS

Y. Takasu[1], I. Nishio[2] and H. Yoshida[1,3]

[1]Center for Quantum Life Sciences, Hiroshima University, Higashi-Hiroshima, 739-8530, Japan; E-Mail: ytakasu@hiroshima-u.ac.jp
[2]Department of Physics, College of Science and Engineering, Aoyama-Gakuin University, Sagamihara, 229-8558, Japan; E-Mail: izumi@piggy.phys.aoyama.ac.jp
[3]Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan; E-Mail: yoshida@sci.hiroshima-u.ac.jp

Keywords: *clathrate hydrate, THF, low-frequency Raman spectroscopy, ab initio calculation, DFT*

Abstract: Low frequency Raman profiles of type II clathrate hydrate of various guest molecules, especially tetrahydrofuran, have been studied and their common feature, the sharp peak at 60 cm^{-1} which was confirmed by *ab initio* DFT calculation, identified as the most dominant low frequency Raman characteristic of those system. Using these profiles, we also demonstrated that the phase boundary of the coexisting phase of clathrate hydrate and tetrahydrofuran aqueous solution could be reconstructed.

Clathrate hydrate has attracted wide range of interest from the standing point of the new energy resource of the future, to the relation of network structure of water molecules in liquid state. In this investigation, we studied type II clathrate hydrate of various guest molecules including tetrahydrofuran (THF), acetone, 1,3-dioxolane and propylene oxide, and type I clathrate hydrate of guest molecules, trimethylene oxide, using low frequency Raman spectroscopy [1]. The structure of type II clathrate hydrate is cubic (diamond) which consists of 16 small 5^{12} and eight $5^{12}6^4$ cages form the unit cell with 136 H_2O molecules while the structure of type I clathrate hydrate is cubic (bcc) consisted of two small 5^{12} and six large $5^{12}6^2$ cages with 46 H_2O, where for example $5^{12}6^4$ cage is formed by 12 pentagons and four hexagons.

Among guest molecules which form type II clathrate hydrate, THF clathrate hydrate is one of the most well studied system. The THF/water system with the stoichiometric molar ratio of 1:17 is well known to form ideal type II clathrate hydrate below 4.4 ^{o}C under atmospheric pressure [2-5]. THF/water system can be separated into several phases. The most important phase boundary is the stoichiometric concentration and the temperature of the formation of clathrate hydrate has the highest temperature at this concentration. Below this concentration, the system has excess H_2O to form ideal clathrate hydrate, so this phase was consisted two species, one is the ideal clathrate hydrate and another is THF aqueous solution of proper concentration.

Low frequency Raman spectra of 0.1 molar fraction aqueous solutions in clathrate hydrate state of typical guest molecules of type II clathrate hydrate, THF, acetone, 1,3-dioxolane and propylene oxide were measured (see Fig. 1). The most characteristic feature of those profiles was the existence of the sharp peak at 60 cm^{-1}. From the result of isotope effect on this peak studied using D_2O and $H_2{}^{18}O$ as the solvent, it could safely concluded that the sharp peak at 60 cm^{-1} was assigned to the vibration of water molecules characteristic to the cage structure of clathrate hydrate. Moreover, the result of *ab initio* density fluctuation theory (DFT) calculations performed to 16-hedron and 12-hedron which were components of type II clathrate hydrate with 6-311G** level revealed that the mode around 60 cm^{-1} derived from the whole motions of cage structure of clathrate hydrate.

In the liquid state, observed reduced Raman spectra of the low frequency below 300 cm^{-1} cannot be reproduced by the linear combination of the low frequency Raman spectra of the pure water and of the neat THF. This is because the existence of significant interaction between water molecules

and THF molecules. Due to this interaction, it was found that the additional vibration mode around 60 cm^{-1} was reproduce observed low frequency Raman spectra of the low concentration THF aqueous solution. The most interesting result of this analysis was that the frequency of the additional vibration mode almost coincides with that of the sharp peak in clathrate hydrate phase. We believed this coincidence was the evidence of precursor of clathrate hydrate structure in low concentration THF aqueous solution. In contrast, low frequency Raman spectra of the solid phase of low concentration THF aqueous solution was found to be reconstructible by the linear combination of the low frequency Raman spectra of clathrate hydrate and that of ice I_h.

Here, using spectra of clathrate hydrate, pure water, 0.1 molar fraction THF aqueous solution and ice I_h, we would demonstrate that the coexisting phase can be not only qualitatively but also quantitatively identifiable by low frequency Raman spectra with the linear combination analysis. From the reconstruction, we can get the concentration of the coexisting liquid phase and, as the result, we can also get the coexisting curve obtained from only one concentration dependence measurement as shown in Fig. 2.

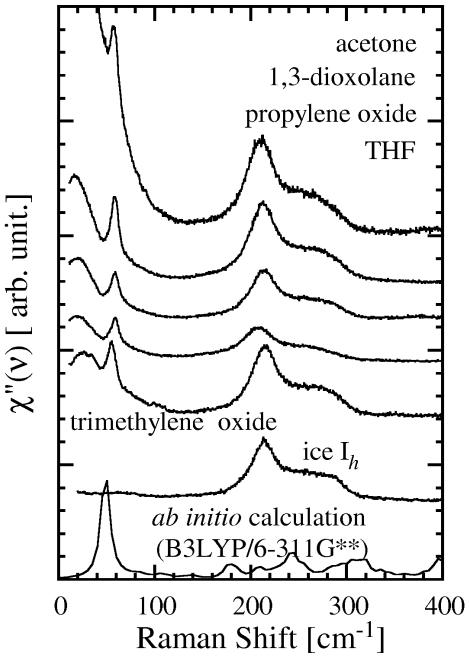

Fig. 1. Reduced observed Raman spectra of various aqueous solutions in clathrate hydrate phase and calculated Raman spectra of 16-hedron.

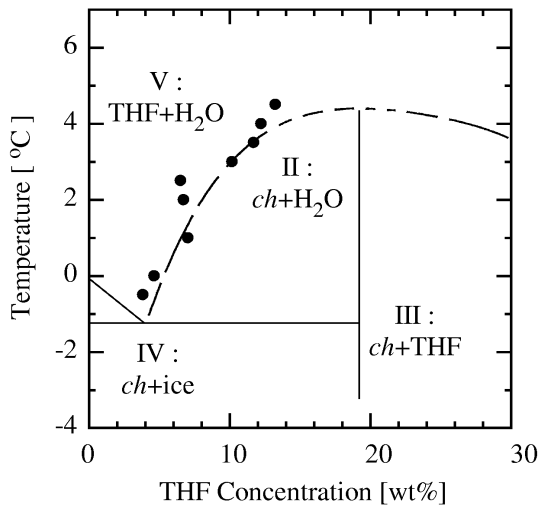

Fig. 2. Obtained phase boundaries as the result of the linear combination analysis are plotted with the phase diagram of THF/water system [6]. *ch* means clathrate hydrate.

Acknowledgements:
We express our gratitude to Prof. Y. Tominaga of Ochanomizu University for helpful discussion.

References:

1. Y. Takasu, K. Iwai and I. Nishio, J. Phys. Soc. Jpn. **72**, 1287 (2003); Y. Takasu and I. Nishio, J. Phys. Soc. Jpn. **72**, 2106 (2003).
2. B. Cadioli, E. Gallinella, C. Coulombeau, H. Jobic and G. Berthier, J. Phys. Chem. **97**, 7844 (1993).
3. G. P. Johari and H. A. M. Chew, Philos. Mag. B **49**, 281 (1984).
4. C. A. Tulk, Y. Ba, D. D. Klug, G. McLaurin and J. A. Ripmeester, J. Chem. Phys. **110**, 6475 (1999).
5. O. Yamamuro, T. Matsuo, H. Suga. W. I. F. David, R. M. Ibberson and A. J. Leadbetter, Physica B **213&214**, 405 (1995).
6. K. Otake *et al.*, Fluid Phase Equilibrium **171**, 175 (2000).