Communication

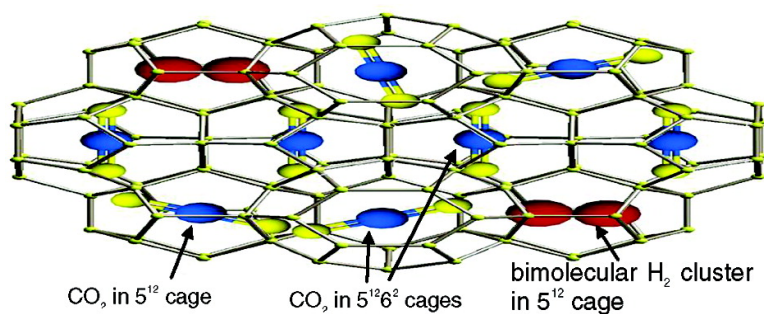# Spectroscopic Identification of the Mixed Hydrogen and Carbon Dioxide Clathrate Hydrate

Do-Youn Kim, and Huen Lee

CO$_2$ in 5^{12} cage   CO$_2$ in 5^{12}6^2 cages   bimolecular H$_2$ cluster in 5^{12} cage

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 7 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Spectroscopic Identification of the Mixed Hydrogen and Carbon Dioxide Clathrate Hydrate

Do-Youn Kim and Huen Lee*

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong Yuseong-gu, Deajeon 305-701, Korea

Received April 10, 2005; E-mail: h_lee@kaist.ac.kr

Clathrate hydrates, commonly named the *gas hydrates*, are a class of crystalline inclusion compounds formed by the physically stable interaction between a host lattice of water molecules connected by hydrogen bonding and relatively small guest molecules, such as CH_4, C_2H_6, CO_2, N_2, Xe, Ar, and Kr, under suitable temperature and pressure conditions.[1] These nonstoichiometric crystalline compounds are divided into three distinct structures, sI, sII, and sH.[2,3] One cubic sI clathrate hydrate has two 5^{12}(D) cages and six $5^{12}6^2$(T) cages, and the other cubic sII clathrate hydrate has sixteen 5^{12}(D) cages and eight $5^{12}6^4$(H) cages per unit cell.[1] The hexagonal sH clathrate hydrate consists of three 5^{12}(D) cages, two $4^35^66^3$(D′) cages, and one $5^{12}6^8$(I) cage per unit cell.

Recently, the stability and cage distribution of clathrate hydrates, including H_2 clusters, have been identified through spectroscopic methods and a statistical mechanical model.[4-9] Pure H_2 clathrate hydrates can be stable at extremely high pressures or low temperatures.[6] Mao et al.[6] reported that H_2 clusters stabilized both 5^{12} cages and $5^{12}6^4$ cages of sII clathrate hydrate with a unit cell parameter of 17.047 Å. More recent studies revealed that the inclusion of H_2 molecules can readily occur by introducing water-soluble hydrate promoters, such as tetrahydrofuran (THF), within a water lattice at relatively low pressure and moderate temperature conditions.[4,5] In particular, we reported that H_2 molecules stored in THF-containing binary clathrates can be increased by tuning their composition to allow the H_2 guests to enter both the larger and the smaller cages.[4]

However, instead of water-soluble liquid guests, we first attempted to examine the possibility of forming the mixed hydrogen hydrate with carbon dioxide acting as a gaseous guest. CO_2 is known to occupy both 5^{12} and $5^{12}6^2$ cages of sI clathrate hydrate with a unit cell parameter of 11.893 Å.[10] Therefore, when the mixed H_2 + CO_2 hydrate forms, two guest molecules compete with each other for better occupancy and stabilization in hydrate cages. The resulting structure, sI or sII, of the mixed H_2 + CO_2 hydrates is, of course, determined by relative distribution of guest molecules in hydrate cages. Here, with spectroscopic evidences, we identify the stable mixed hydrate containing H_2 molecules in the presence of CO_2. The X-ray powder diffraction that represents the long-range order and nuclear magnetic resonance (NMR) spectrum that is sensitive to short-range order provide molecular-detailed information of hydrate structure and guest distribution.[11] We also made direct gas chromatography (GC) analysis in order to determine hydrate phase compositions including H_2.

Figure 1 shows the X-ray powder diffraction pattern of the mixed H_2 + CO_2 hydrate. The X-ray diffraction data identify the mixed hydrate with an exemplary sI crystal structure. Also, it can be indexed with a regular cubic unit cell (space group *Pm3n*) with a unit cell parameter of 11.8602 ± 0.0010 Å. This result agrees with the reported values for the unit cell parameter of pure sI CO_2 clathrate hydrate.[9,12] Similarly, when the N_2 molecules were
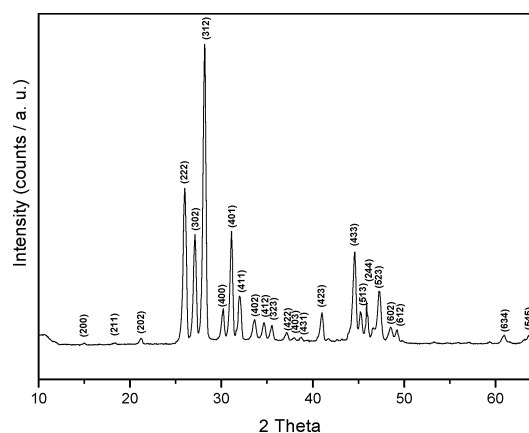
Figure 1. The X-ray diffraction pattern of the mixed H_2 + CO_2 hydrate formed from 20 mol % of CO_2 and balanced H_2. The structure of mixed hydrate was identified by a D/max-RB (Rigaku) diffractometer with a scintillation counter and graphite monochromated Cu Kα1 radiation (λ = 1.5406 Å). The X-ray powder diffraction data were collected by step mode with a fixed time of 5 s and a step size of 0.05° over 2 h (10−65° in 2θ) at 1 bar and 123.15 K.

introduced to form the mixed hydrate with CO_2 instead of H_2 molecules, the mixed N_2 + CO_2 hydrate formed from 20 mol % of CO_2 and balanced N_2 was confirmed to be a sI crystal structure.[13]

The knowledge of dynamics for CO_2 molecules in 5^{12} and $5^{12}6^2$ cages of sI could be obtained from the analysis of the solid-state ^{13}C NMR spectral shape of mixed hydrates. For CO_2 entrapped in hydrate cages, an anisotropic chemical shift is induced by asymmetry in the immediate environment of the molecules and is sensitively affected by the guest distribution in hydrate cages.[14] The ^{13}C cross-polarization (CP) NMR spectrum of the mixed H_2 + CO_2 hydrate is shown in Figure 2a. As the 5^{12} cages of sI hydrate produced the pseudospherical symmetry causing molecular motions to be isotropic, only a sharp peak at the isotropic chemical shift of 123.9 ppm was observed. However, for CO_2 molecules in the $5^{12}6^2$ cages of sI hydrate, the powder pattern was observed due to the asymmetric shape of the $5^{12}6^2$ cages and reflected the anisotropic motions of CO_2 molecules. The anisotropic chemical shift could be defined as $\Delta = \delta_{iso} - \delta_{zz}$,[14] where $\delta_{iso} = (2\delta_{xx} + \delta_{zz})/3$ is the isotropic chemical shift. The δ_{xx} = 101.1 ppm and δ_{zz} =182.7 ppm are the *xx* and *zz* components of the chemical shift tensor in Figure 2a, respectively. The powder pattern having an anisotropic chemical shift of −54.4 ppm was observed, which reflects the anisotropic motion of CO_2 molecules in asymmetric $5^{12}6^2$ cages.

The ^1H MAS NMR spectroscopy was used to monitor H_2 molecules in the product of the reaction of H_2 with deuterium oxide (D_2O), so that only the H_2 signal and residual protons in water would be observed and readily assigned from the comparison with the ^1H MAS NMR spectra of our previous work.[4] The spectrum in Figure 2b shows a broad peak at 6.4 ppm that comes from residual
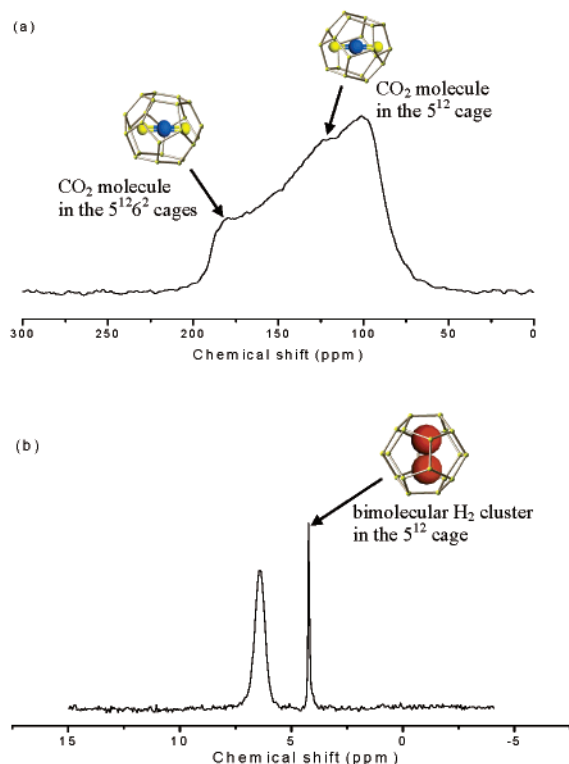
Figure 2. (a) ^{13}C CP NMR spectrum and (b) ^1H MAS NMR spectrum of the mixed $H_2 + CO_2$ hydrate formed from 20 mol % of CO_2 and balanced H_2. In the structural diagram, the hydrogen atoms were excluded to simplify the structure of hydrate.

HDO protons because D_2O includes a small amount of HDO impurity and a sharp peak at 4.2 ppm that can be attributed to H_2 molecules confined in cages of hydrate. The chemical shift of guest molecules entrapped in 5^{12} cages of sI is nearly identical to that of sII hydrate, as 5^{12} cages consist of 12 pentagonal faces of almost similar dimensions in both sI and sII hydrate; the chemical shifts of CH_4 entrapped in 5^{12} cages of sI and sII hydrate were assigned to -4.0 and -3.95 ppm, respectively.[15] Thus, we could suggest that the resonance peak with a chemical shift of 4.2 ppm in Figure 2b indicates the bimolecular H_2 cluster in a small 5^{12} cage of sI clathrate hydrate. We cross-checked the confinement of H_2 molecules in cages of hydrate by using Raman spectroscopy, and a broad band at around 4130 cm^{-1} also identified the existence of H_2 molecules captured in hydrate cages. However, it must be noted that the Raman spectroscopy does not generate two split peaks corresponding to H_2 occupancy in small and large cages, and only NMR provides two different chemical shifts with clear distinction.

These microscopic approaches for hydrate analysis enable one to provide more accurate descriptions of hydrate structure and guest distribution in hydrate cages. However, the compositions of CO_2 and H_2 occupying hydrate cages cannot be directly determined because molecular distributions of CO_2 and H_2 in the hydrate phase are very hard to simultaneously obtain the corresponding NMR spectra. Apparently, the macroscopic approach might be readily introduced to determine relative compositions showing the basic inclusion pattern of two guests in hydrate cages. The equilibrium composition of the hydrate sample was analyzed by GC, and the

entrapped amount of CO_2 and H_2 appeared to be 92.5 and 7.5 mol %, respectively. Both GC and spectroscopic results enable us to understand more clearly the inclusion/exclusion phenomena of binary guests, CO_2 and H_2, occurring in the nanosized cages and advance meaningful progress on highly complicated cage dynamics that are still very much unanswered.

Nevertheless, we found that H_2 molecules form the mixed hydrate with CO_2 even though H_2 molecules are partially entrapped in small 5^{12} cages filling two H_2 molecules for double occupancy. The synthesized crystal maintains sI, which might be expected because the excess CO_2 more strongly influences the determination of the hydrate structure. However, we need to note that CO_2 molecules occupy most of 5^{12} and $5^{12}6^2$ cages with significant interactions of host−guest molecules. The present work offers the firm spectroscopic evidence for forming the mixed hydrate of H_2 and CO_2, but a number of binary H_2 hydrates of sI, sII, and sH may possibly form with various gaseous guests. More importantly, the multiple occupancies of H_2 molecules must be carefully explored to accurately describe molecular details occurring in cages and also to determine the degree of absolute cage filling in both a qualitative and a quantitative manner. The favorable condition that two gaseous guests of H_2 and the other can form hydrates at ambient temperatures and moderate pressures provides a new means for studying technological applications, such as the separation of H_2 and CO_2, and purification in the H_2 production process and many other hydrate-based separation/recovery processes.

Supporting Information Available: Experimental procedure and X-ray diffraction, NMR spectroscopy, Raman spectroscopy, and gas chromatography measurement details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Sloan, E. D. *Clathrate Hydrates of Natural Gas*, 2nd ed.; Marcel Dekker Inc.: New York, 1998.
(2) Jeffrey, G. A. *Inclusion Compounds*; Academic Press: London, 1984; Vol. 1.
(3) Ripmeester, J. A.; Tse, J. S.; Ratcliffe, C. I.; Powell, B. M. *Nature* **1987**, *325*, 135.
(4) Lee, H.; Lee, J.-W.; Kim, D. Y.; Park, J.; Seo, Y. T.; Zeng, H.; Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A. *Nature* **2005**, *434*, 743.
(5) Florusse, L. J.; Peters, C. J.; Schoonman, J.; Hester, K. C.; Koh, C. A.; Dec, S. F.; Marsh, K. N.; Sloan, E. D. *Science* **2004**, *306*, 469.
(6) Mao, W. L.; Mao, H.; Goncharov, A. F.; Struzhkin, V. V.; Guo, Q.; Hu, J.; Shu, J.; Hemley, R. J.; Somayazulu, M.; Zhao, Y. *Science* **2002**, *297*, 2247.
(7) Lokshin, K. A.; Zhao, Y.; He, D.; Mao, W. L.; Mao, H.; Hemley, R. J.; Lobanov, M. V.; Greenblatt, M. *Phys. Rev. Lett.* **2004**, *93*, 125503.
(8) Patchkovskii, S.; Tse, J. S. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 14645.
(9) Mao, W. L.; Mao, H. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 708.
(10) Udachin, K. A.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Phys. Chem. B* **2001**, *105*, 4200.
(11) Ripmeester, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 289.
(12) Henning, R. W.; Schultz, A. J.; Thieu, V.; Halpern, Y. *J. Phys. Chem. A* **2000**, *104*, 5066.
(13) Seo, Y. T.; Lee, H. *J. Phys. Chem. B* **2004**, *108*, 530.
(14) Ripmeester, J. A.; Ratcliffe, C. I *Energy Fuels* **1988**, *2*, 197.
(15) Subramanian, S.; Kini, R. A.; Dec, S. F.; Sloan, E. D. *Chem. Eng. Sci.* **2000**, *55*, 1981.

JA0523183