J|A|C|S COMMUNICATIONS

Raman Spectroscopy and Cage Occupancy of Hydrogen Clathrate Hydrate from First-Principle Calculations

Jianwei Wang,*,† Hailong Lu,‡ and John A. Ripmeester‡

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, 48109, and Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario K1A 0R6, Canada

Received May 21, 2009; E-mail: jwwang@umich.edu

A major driving force for research on hydrogen clathrate hydrate is its potential use as a hydrogen storage medium for clean energy technology.[1−6] Hydrogen clathrate hydrate has a comparatively high storage capacity (~5 wt %) and an environmentally friendly character because upon combustion it simply releases water and hydrogen.[1] However, the storage capacity largely relies on hydrogen cage occupancy. The crystal structure has been determined to be type II clathrate (sII) with two kinds of cages. The high storage capacity can only be realized if the large cage holds four H_2 and the small cavity two.[1] Single occupancy in the small cage leads to a storage capacity of ~3.4 wt % for the pure H_2 hydrate and ~1 wt % for a binary hydrate, H_2•THF•$17H_2O$.[3]

Both experimental and theoretical studies support an occupancy of up to four H_2 molecules in the large cage.[1,2,4,7] However, conflicting explanations of experimental results have been reported regarding H_2 occupancy in the small cages, double[1] or single.[4] Although, theoretically, both single and double hydrogen occupancies are possible,[2,8−10] it is not clear how to identify different hydrogen occupancies experimentally using a spectroscopic method, especially for the small cages. Key to addressing these questions is a better understanding of the vibrational spectroscopy of hydrogen molecules in the clathrate cages.

Here, we try to tackle these questions by applying *ab initio* calculations and molecular dynamics simulations to compute averaged Raman spectra of the encaged H_2 with different cage occupancies. The results obtained provide an important prediction on spectroscopic features of the hydrogen occupancy. Molecular and electronic structural analyses offer additional insights into H_2-H_2 intermolecular interactions and vibrational coupling of H_2 molecules in the clathrate. The details of the method and results are described in a full article.[11]

Hydrogen clathrate structure (Figure 1a) has two types of cages: the large one (L) is a hexakaidecahedron ($5^{12}6^4$) with 28 H_2O (Figure 1b) and the small one (S) is a pentagonal dodecahedron (5^{12}) with 20 H_2O (Figure 1c). The unit cell has 136 H_2O, with 16 S and 8 L cages. The initial structure of the H_2O framework for the molecular modeling is based on a refined sII structure from X-ray single crystal diffraction methods.[12] Classical energy minimization and molecular dynamics simulations are performed on a supercell with 2 × 2 × 2 unit cells of sII structure, using the GROMACS package,[13] SPC/E model for H_2O,[14] and a rigid model for H_2.[7,15] After an equilibration run at 150 K and 200 MPa, the system is quenched, and the cages are isolated from the supercell. The density functional theory (DFT) calculations are performed on these MD generated cages with a two-level ONIOM model,[16] using the GAUSSIAN 03 package.[17] The high level includes only the H_2, and the low level the H_2O. Closed-shell spin-restricted DFT calculations are performed with the B3LYP hybrid density functional,[18] with the 6-31++G(2d,2p) basis set for the high level and 3-21+G(d,p) for the low level. 11 L cages with 4 H_2 (L^4), 11 L cages with 3 H_2 (L^3), 11 L cages with 2 H_2 (L^2), 11 L cages with 1 H_2 (L^1), 19 S cages with 2 H_2 (S^2), and 29 S cages with 1 H_2 (S^1) are successfully optimized with all atoms moveable. These cages are used as collections of configurations of the L and S cages with different H_2 occupancies.

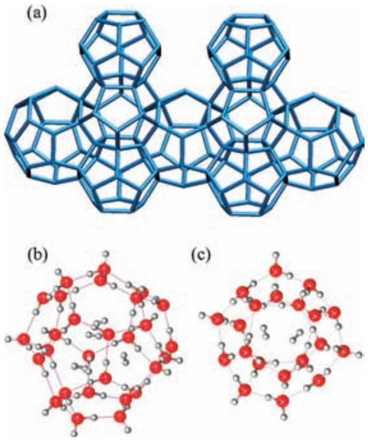

Figure 1. Structure of clathrate sII. (a) Polyhedral representation of the large and small cages, (b) a larger cage with four encaged hydrogen molecules; and (c) a small cage with two encaged hydrogen molecules. Red balls are oxygen atoms, and light gray balls are hydrogen atoms.

Raman spectra of H_2 stretching mode are computed as a moving average of the calculated Raman frequencies, weighted with calculated Raman activity and normalized with the numbers of the cages in the compound. The calculated frequencies are scaled by a factor of 0.9367, the ratio between 4155 cm^{-1} of free H_2 gas and 4436 cm^{-1} of the calculated H−H stretching frequency of free isolated single H_2. The results are plotted as fitted curves with a Gaussian function (original data are available from supporting materials) in Figure 2a, along with two experimental data from the literature (Figure 2b,c).[1,19] Although the numbers of the structural configurations are relatively small, statistically meaningful Raman spectra are obtained.

The peak assignment from a recent Raman spectroscopic study of hydrogen clathrate is adopted here.[5] For the calculated spectra, from low to high frequencies are the peaks from S^1, L^1, L^2, L^3, L^4, and S^2. The calculated Raman frequencies are in general consistent with the two experiments in terms of relative peak positions. The absolute peak frequencies, however, are underestimated by ~20 cm^{-1} for S^1 and 5−15 cm^{-1} for L^{4-1} cages. The discrepancies may arise from isolation of the cages from the crystal, which cause the cage sizes to decrease because of neglecting intercage hydrogen bonding.[11] The other possible reasons include the limitation of the

---

[†] University of Michigan.
[‡] National Research Council Canada.

10.1021/ja904140y CCC: $40.75

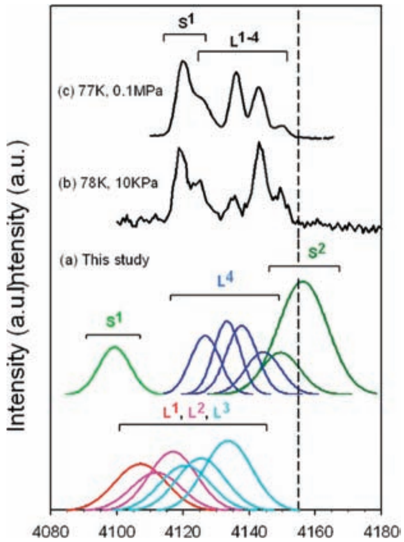

Figure 2. Raman spectra of hydrogen molecule in hydrogen clathrate hydrate. (a) Calculated spectra. Experiments by (b) Mao et al. (2002) and (c) Strobel et al. (2007). S1, singly occupied small cage; S2, doubly occupied small cage; L1, L2, L3, and L4, singly, doubly, triply, and quadruply occupied large cages. The vertical dashed line indicates 4155 cm^{-1} for free H_2 gas.

DFT method employed here because of the inaccuracy on describing weak dispersive intermolecular interactions and the statics of the calculations. Note also that multiple peaks due to a mixture of H_2 molecules in different rotational states (e.g., para-H_2 and ortho-H_2) at finite temperature contribute to variations in the observed Raman spectra.[5,6] Nevertheless, the calculated spectra are sufficient for use here as a qualitative guide for interpreting the trend of the observed Raman spectra.

Based on the calculations, the Raman frequencies of H_2 in S^2 cages are $\sim$10−30 cm^{-1} higher than the L^4 frequencies. Taking into account the underestimations on the calculated frequencies of the encaged H_2, the Raman vibrons from the doubly occupied small cage (S^2) are expected to be around or above 4155 cm^{-1}, blue-shifted with respect to the gas phase. This result suggests that the characteristic peaks of S^2 are not present in the two experiments[1,19] and in some recent experiments.[5,6] This conclusion, however, does not exclude the possibility of having double occupancy in the small cage. In general, a blue shift of the Raman frequency of an encaged molecule in gas clathrate is not uncommon. For example, the Raman stretching frequency of propane (C_3H_8) in the large cage of sII hydrate is blue-shifted by 7 cm^{-1},[20] and CO_2 in the large cage of sI is blue-shifted by 96 cm^{-1}.[20] The relative shift of Raman frequency of an encaged molecule in clathrates with respect to its gas phase is sensitive to the local molecular environment inside the cage. The red shift of the Raman frequencies of S^1 and L^{1-4} in the hydrogen hydrate suggests the H_2 molecules are loosely encaged in attractive potential field, while the blue shift indicates those in S^2 are tightly confined in repulsive potential field. This is formalized in the so-called loose-cage tight-cage model,[21,22] which is also consistent with the molecular structure and electronic structure of the encaged H_2 in the hydrogen clathrate.[11] The H_2 intramolecular bonds are stretched by $\sim$0.1−0.4% in L^{4-1} and 0.4% in S^1 cages and compressed by $\sim$0.1% in S^2 cages, relative to the calculated gas phase equilibrium. Total electron density analysis shows that electron sharing between the H_2 molecules in S^2 is more significant than in L^4, arising from a shorter intermolecular distance and stronger electronic interaction. Electrostatic potential analysis shows the negative electrostatic potential arising from the O of H_2O contributing more to the attractive interaction of H_2 molecules in L^4 than in S^2.[11]

One fundamental difference between the loose-caged S^1 and L^{1-4} and the tight-caged S^2 is intermolecular vibrational coupling. Based on normal-mode analysis, there is limited coupling for H_2 molecules in L^{2-4}, and each H_2 vibration is independent from the other H_2 molecules. In contrast, for two H_2 in S^2, a strong vibrational coupling is observed, with the $\sim$4150 cm^{-1} mode from an out-of-phase vibration and 4157 cm^{-1} from an in-phase vibration. Strong intermolecular coupling is suggested by a frequency difference of −7 cm^{-1} (out-of-phase minus in-phase frequencies) with respect to +3 cm^{-1} for solid hydrogen at zero pressure.[23] The difference between the confinement effect and pressure effect is also evidenced by the fact that encapsulating hydrogen in the clathrate can result in a stretching mode red shift while pressurizing solid hydrogen in ice always causes a blue shift.[23−25]

In conclusion, Raman spectra of hydrogen molecules encaged in hydrogen clathrate are computed using *ab initio* calculations and molecular dynamics simulations. The results obtained predict Raman peaks of the doubly occupied small cages to be around or above 4155 cm^{-1} of free H_2 gas frequency. This prediction could inspire new experiments for synthesizing hydrogen clathrate with higher hydrogen occupancy.

Acknowledgment. This research was supported in part by the National Science Foundation through TeraGrid resources provided by NCSA and NICS.

Supporting Information Available: The calculated Raman frequencies and activities for the H_2 stretching mode of encaged hydrogen with different occupancies. Complete ref 17. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Mao, W. L.; Mao, H.-K.; Goncharov, A. F.; Struzhkin, V. V.; Guo, Q. *Science* **2002**, *297*, 2247–2249.
(2) Patchkovskii, S.; Tse, J. S. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 14645–14650.
(3) Florusse, L. J.; Peters, C. J.; Schoonman, J.; Hester, K. C.; Koh, C. A. *Science* **2004**, *306*, 469–471.
(4) Lokshin, K. A.; Zhao, Y. S.; He, D. W.; Mao, W. L.; Mao, H. K. *Phys. Rev. Lett.* **2004**, *93*, 125503.
(5) Giannasi, A.; Celli, M.; Ulivi, L.; Zoppi, M. *J. Chem. Phys.* **2008**, *129*, 084705−084710.
(6) Strobel, T. A.; Sloan, E. D.; Koh, C. A. *J. Chem. Phys.* **2009**, *130*, 014506−014510.
(7) Alavi, S.; Ripmeester, J. A.; Klug, D. D. *J. Chem. Phys.* **2005**, *123*, 024507.
(8) Inerbaev, T. M.; Belosludov, V. R.; Belosludov, R. V.; Sluiter, M.; Kawazoe, Y. *Comput. Mater. Sci.* **2006**, *36*, 229–233.
(9) Sebastianelli, F.; Xu, M. Z.; Elmatad, Y. S.; Moskowitz, J. W.; Bačić, Z. *J. Phys. Chem. C* **2007**, *111*, 2497–2504. Sebastianelli, F.; Xu, M.; BaCic, Z. *J. Chem. Phys.* **2008**, *129*, 244706–244709.
(10) Alavi, S.; Klug, D. D.; Ripmeester, J. A. *J. Chem. Phys.* **2008**, *128*, 064506.
(11) Wang, J.; Lu, H.; Ripmeester, J. A. Manuscript in preparation.
(12) Kirchner, M. T.; Boese, R.; Billups, W. E.; Norman, L. R. *J. Am. Chem. Soc.* **2004**, *126*, 9407–9412.
(13) van der Spoel, D.; Lindahl, E.; Hess, B.; van Buuren, A. R.; Apol, E. *Gromacs user manual version*; University of Groningen, 2005.
(14) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269–6271.
(15) Silvera, I. F.; Goldman, V. V. *J. Chem. Phys.* **1978**, *69*, 4209–4213.
(16) Vreven, T.; Morokuma, K. *J. Comput. Chem.* **2000**, *21*, 1419–1432.
(17) Frisch, M. J. et al. *Gaussian 03 online manual*; Gaussian, Inc.: Pittsburgh, PA, 2003.
(18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
(19) Strobel, T. A.; Koh, C. A.; Sloan, E. D. *Fluid Phase Equilib.* **2007**, *261*, 382–389.
(20) Sum, A. K.; Burruss, R. C.; Sloan, E. D. *J. Phys. Chem. B* **1997**, *101*, 7371–7377.
(21) Buckingham, A. D. *Proc. R. Soc. London, Ser. A* **1958**, *248*, 169.
(22) Subramanian, S.; Sloan, E. D. *J. Phys. Chem. B* **2002**, *106*, 4348–4355.
(23) Mao, H.-K.; Hemley, R. J. *Rev. Mod. Phy.* **1994**, *66*, 671.
(24) Hirai, H.; Ohno, S.; Kawamura, T.; Yamamoto, Y.; Yagi, T. *J. Phys. Chem. C* **2007**, *111*, 312–315.
(25) Machida, S.-i.; Hirai, H.; Kawamura, T.; Yamamoto, Y.; Yagi, T. *J. Chem. Phys.* **2008**, *129*, 224505–224505.

JA904140Y