Supporting Information

Direct Observation of Atomic Hydrogen Generated from Water Framework of Clathrate Hydrates

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Reference in Experimental Methods

[a] LMGP-Suite Suite of Programs for the interpretation of X-ray Experiments, by Jean laugier and Bernard Bochu, ENSP/Laboratoire des Mate´riaux et du Ge´nie Physique, BP 46. 38042 Saint Martin d'He`res, France. www: http://www.inpg.fr/LMGP and http://www.ccp14.ac.uk/tutorial/lmgp/

[b] Y. Shao, L. F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. ONeill, R. A. DiStasio Jr., R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M. Herbert, C. Y. Lin, T. Van Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C. –P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Z. Liang, T. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer III, J. Kong, A. I. Krylov, P. M. W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.* 2006, **8**, 3172-3191.

Experimental Methods

Water of ultrahigh purity was obtained from a Millipore purification unit, and the THF, Me_4NOH, and D_2O were supplied by SIGMA-ALDRICH Inc. H_2, N_2, O_2, and D_2 were purchased from the Special Gas Company (Daejeon, Korea), with a stated minimum purity of 99.995 mol%. The well-mixed solution according to the mole-composition of THF, Me_4NOH, and H_2O (or D_2O) were frozen at 210 K for at least 1 day and were then ground to a fine powder (~ 200 μm). The grounded powders were put into a high pressure cell and exposed to H_2, N_2, O_2, or D_2 (120 bar) at 210 K for at least 1 week. The formed hydrate samples were stored in liquid nitrogen and irradiated as 30 kGy (15 kGy per 1hr) by a ^{60}Co γ-ray source at KAERI in Jeongeup, Korea.

The HRPD patterns of non-irradiated samples were recorded at 80 K using the Pohang Synchrotron of the Pohang accelerator laboratory (λ = 1.54950 Å). The experiments were carried out in step mode with a fixed time of 2 s and at a step size of 0.01 ^{o} for each hydrate sample. The obtained patterns were indexed using the Check Cell program.[a] The ESR spectra of the γ-irradiated samples were obtained using a JEOL PX2300 equipment. The samples were kept under liquid nitrogen during the experiments.

Electron affinity (EA) and proton affinity (PA) of each NIGM (i.e., N_2, H_2, and O_2) were evaluated through quantum mechanical calculations using Q-Chem 3.1 quantum chemistry software.[b] To obtain self-consistent energies with optimized geometries of neutral (n), anion (a), and protonated (p) species, the second-order Møller-Plesset perturbation theory (MP2) with 6-311++G** basis sets were employed. The electron and proton affinities were calculated as follows:

$EA=E_{NIGM(a)}-E_{NIGM(n)}$,

$PA= E_{NIGM(p)}-E_{NIGM(n)}$.

Fig. S1

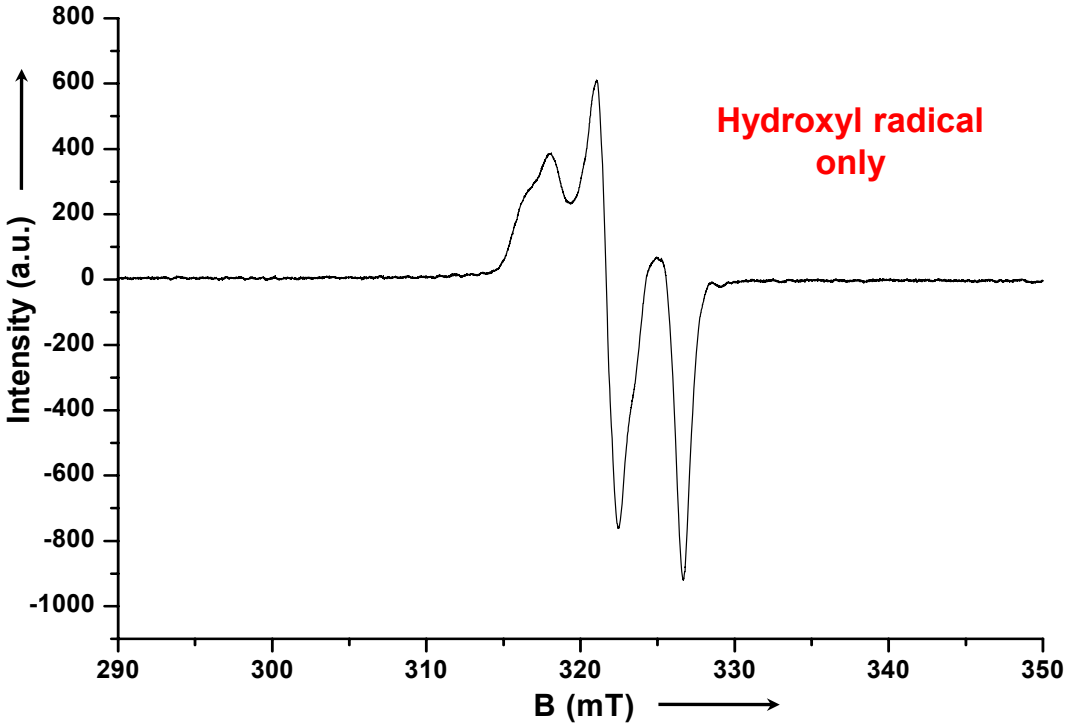
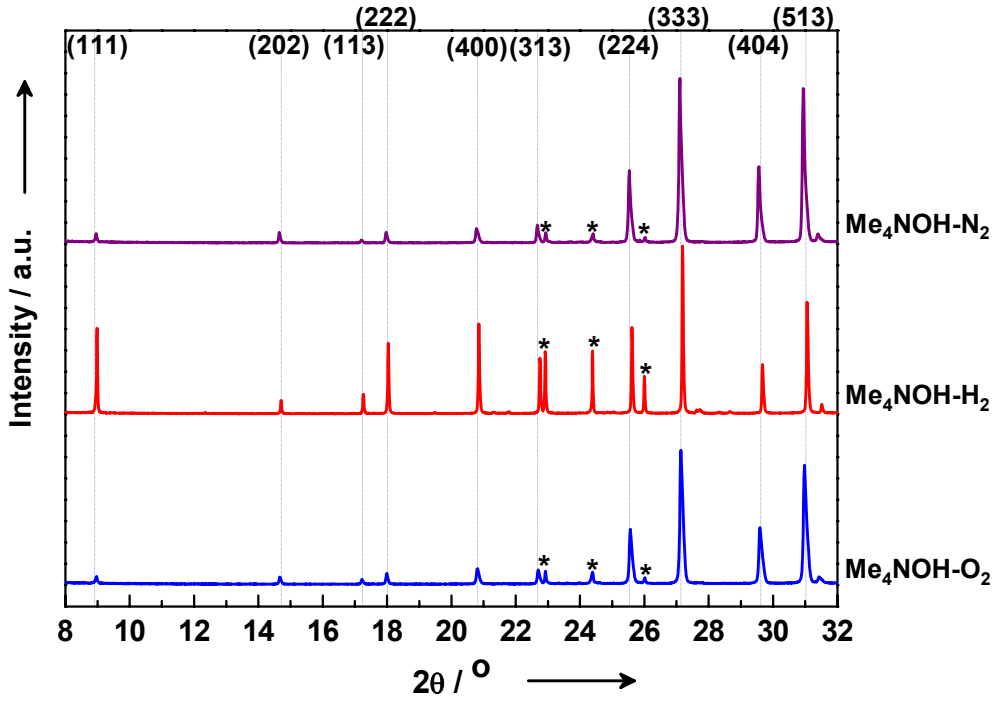

Hydroxyl radical only
Intensity (a.u.)
800
600
400
200
0
-200
-400
-600
-800
-1000
290
300
310
320
330
340
350
B (mT)

Fig. S2



All patterns are identified as cubic *Fd3m* structure (lattice parameter *a* = 17.1847(14) Å for N_2; *a* = 17.1239(11) Å for H_2; *a* = 17.1574(11) Å for O_2). The diffraction peaks of hexagonal ice were marked by asterisks (*).

Fig. S3

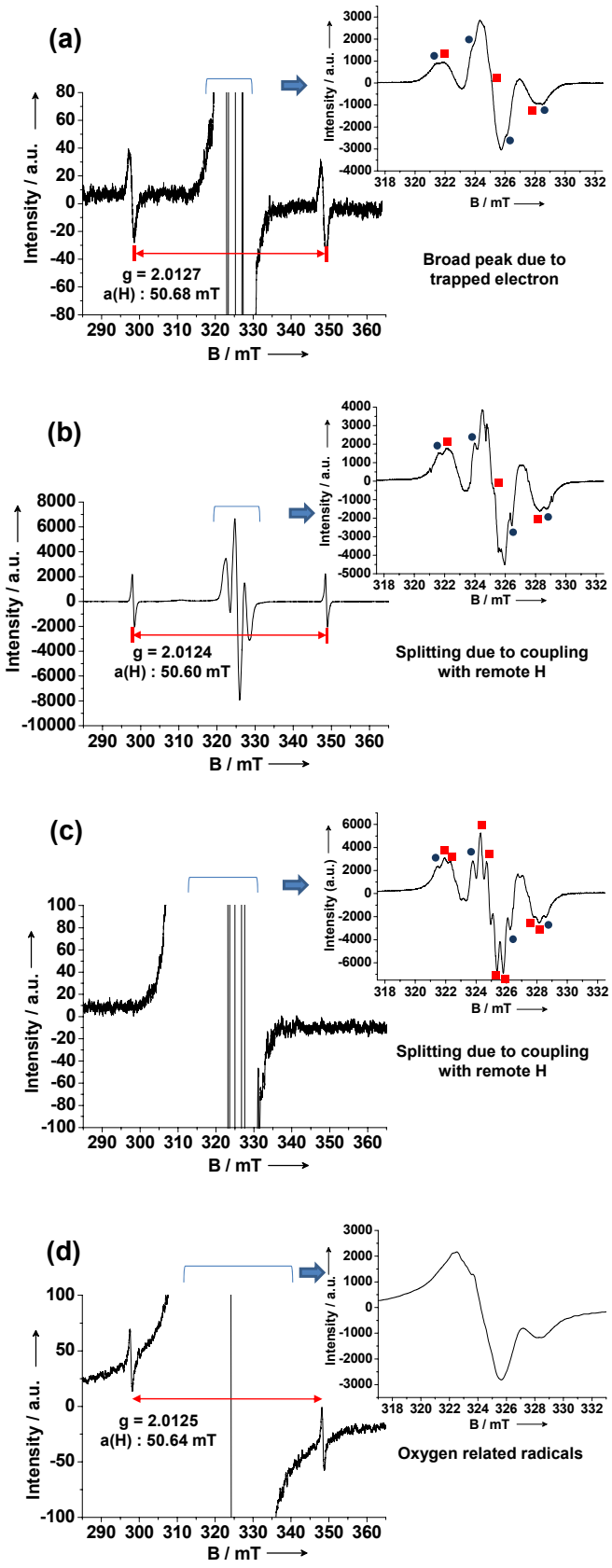
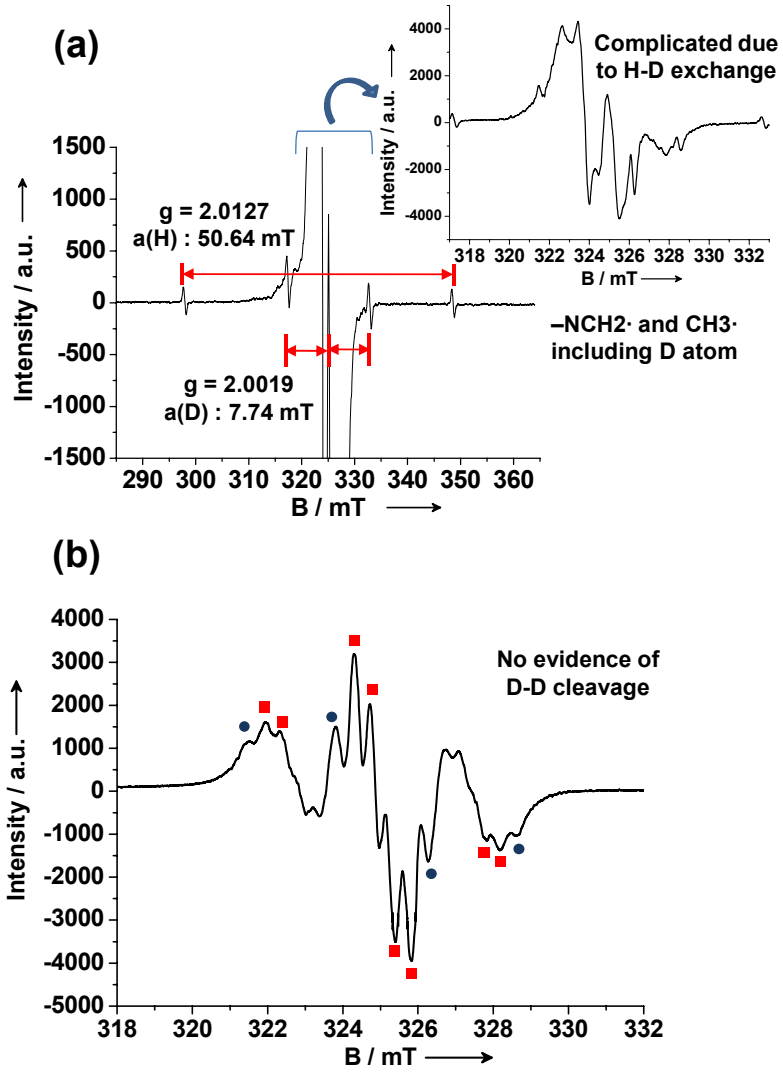

(a)
Intensity / a.u.
B / mT
g = 2.0127
a(H) : 50.68 mT
Broad peak due to
trapped electron
(b)
Intensity / a.u.
B / mT
g = 2.0124
a(H) : 50.60 mT
Splitting due to coupling
with remote H
(c)
Intensity / a.u.
Intensity (a.u.)
B / mT
Splitting due to coupling
with remote H
(d)
Intensity / a.u.
B / mT
g = 2.0125
a(H) : 50.64 mT
Oxygen related radicals

Fig. S4


(a)
Intensity / a.u.
B / mT
g = 2.0127
a(H) : 50.64 mT
g = 2.0019
a(D) : 7.74 mT
Complicated due
to H-D exchange
–NCH2· and CH3·
including D atom
(b)
No evidence of
D-D cleavage