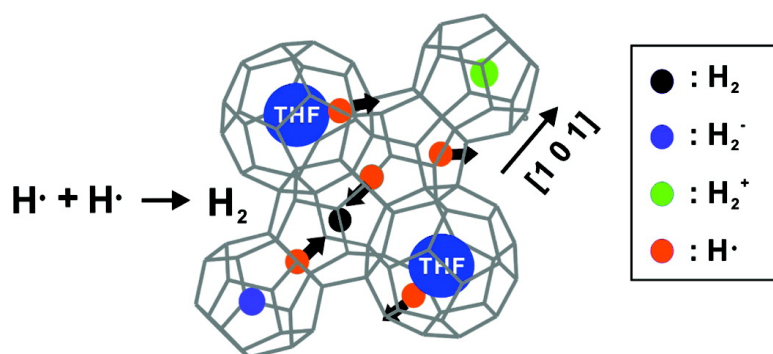Communication

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Spectroscopic Observation of Atomic Hydrogen Radicals Entrapped in Icy Hydrogen Hydrate

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At sufficiently low temperatures, a single hydrogen atom (H atom) that becomes an atomic free radical by irradiation is known to be a relatively stable paramagnetic species in a wide variety of substances.[1–3] Solid hydrogen in particular is a well-known quantum medium that has attracted much attention for its potential incorporation in novel materials having high-temperature superconductivity, because of its structural, magnetic, and electronic properties.[4,5] These molecular properties of H atoms at ultralow temperature have been explored through the identification of unpaired electrons in H atoms observed by electron spin resonance (ESR) spectroscopy. Pure solid para-hydrogen has been used only as a valuable matrix material and enables high-resolution measurements via ESR spectroscopy due to its paired nuclear spins.[6] Unlike pure liquid or solid hydrogen matrix, the successful imprisonment of a single hydrogen molecule in a cage could readily provide key clues for attaining a comprehensive understanding of the unique spectroscopic and dynamic patterns of the γ-irradiated hydrogen.

To explore the guest occupancy pattern of irradiated ionic hydrogen radicals we attempted to synthesize icy crystalline solids of the binary H_2 + THF (sII) hydrates and identify their radicals by ESR and MAS ^{1}H NMR spectra. Hydrogen molecules solely existing in confined icy hydrate cages often expose abnormal quantum behavior that is quite different from hydrogen molecules in a pure liquid or solid state. In an earlier study the direct neutron diffraction pattern of the binary hydrogen hydrate was successfully determined despite that the incoherent scattering exhibited by hydrogen unlike deuterium molecules generates a background signal that makes it difficult to detect coherent Bragg scattering from the sample.[7] For an icy water framework to act as a new reactive site the confined space must be created through a restructuring process of host–guest networks and the entrapped hydrogen molecules are subsequently irradiated, forming free hydrogen radicals. First, we examined the ESR spectra of binary 5.56 mol % THF-$d8$ (D_2O) + H_2 hydrate under varied doses of γ-ray irradiation at 123 K as shown in Figure 1a, where three signals of I, II, and III are clearly detected: (I) a doublet signal at $g = 2.0021 \pm 0.002$ with a hyperfine constant of $a(H) = 50.44$ mT, which is identified as a spectrum of the hydrogen atom radical (H·)[8] induced by γ-irradiation of a hydrogen molecule entrapped in a deuterated water framework of a 5^{12} cage; (II) a triplet signal at $g = 2.002 \pm 0.002$ with a hyperfine constant of $a(D) = 7.7$ mT of deuterium atom[8] resulting from interaction of an unpaired electron with the spin of the deuterium nucleus ($I = 1$). The signal corresponds to a detached D atom from a γ-irradiated THF-$d8$ molecule in an sII large cage; and (III) 15 hyperfine split signals of a THF-$d8$ radical, similar to patterns observed in various alkyl and cycloalkyl radicals.[9] A detailed description of signal III is presented in Figure 1b.
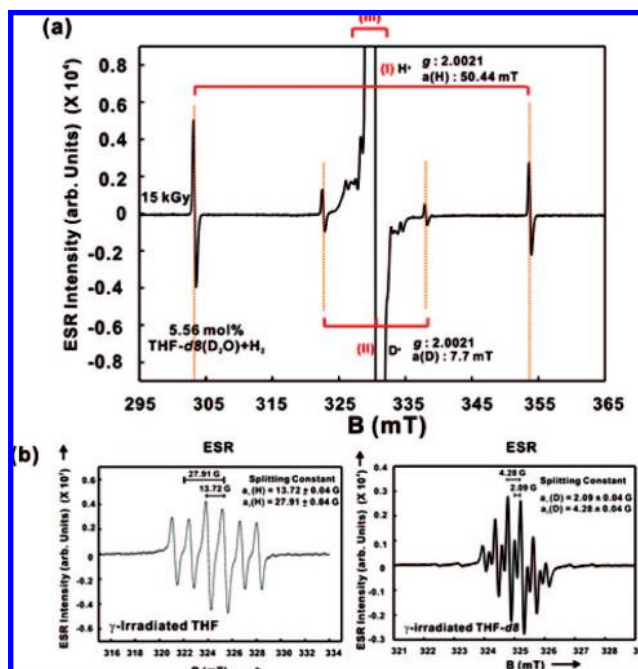

Figure 1. ESR spectra of 15kGy γ-irradiated (a) THF-$d8$ (D2O) + H2 hydrate and (b) THF (left) an THF-$d8$ (right).

To obtain the X-band ESR spectra both tetrahydrofuran and deuterated tetrahydrofuran were irradiated at 123 K and 15 kGy dose. The most plausible configuration for the appearance of the tetrahydrofuran radical is described with two forms. One form is a radical separated from one hydrogen atom of C1 in the vicinity of the oxygen atom, and the other is a radical derived from the loss of the hydrogen atom of C2. The spectrum of Figure 1b is dominated by six prominent lines separated by roughly 13.7 G with peak intensities of 1:1:1.5:1.5:1:1, arising from the hyperfine interaction of the unpaired electron wave function with the carbon nucleus, $I = {}^1/_2$. The intensities and spacing of six lines in Figure 1b result from a tetrahydrofuran radical with one group of one proton (α) and a second group of two equivalent protons (β). From these ESR spectra, the two equivalent protons are found to be equivalent to hyperfine coupling constants of $a_\alpha(H) = 13.7$ G and $a_\beta(H) = 27.9$ G. For the irradiated deuterated tetrahydrofuran samples, the 15 lines are observed with a hyperfine splitting constant of 2.09 G. This value agrees well with an equivalent proton splitting of 13.7 G, which is obtained from 2.09 G multiplied by twice the ratio of the magnetic moments of the proton and the deuteron ($2 \times 3.257 = 6.514$).[8] For the deuterated tetrahydrofuran radical the observed hyperfine splitting coupling constants are $a_\alpha(D) = 2.09$ G and $a_\beta(D) = 4.28$ G which are equivalent to proton hyperfine

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splitting constants of 13.7 and 27.9 G. Accordingly, it becomes clear that most of the tetrahydrofuran radicals are formed by the loss of hydrogen linked to C1. Another notable feature is that the trapped radicals in the icy hydrate cages suppress the spin exchange interaction between radicals and radicals which results in broad ESR signals. Thus the narrow ESR line shape appears for the trapped radicals in the cages of an icy hydrate matrix, while the free radicals evolve a broad peak pattern.

When solid pure hydrogen was exposed to ionizing radiation at 4.2 K, the two dihydrogen radicals of H_2^+ and H_2^- are likely to be derived[10] in addition to the hydrogen radical (H·) as clearly seen in Figure 1. However, in the normal hydrogen consisting of 25% para- plus 75% ortho-hydrogen used in this study, neither H_2^+ nor H_2^- were detected directly from ESR spectroscopy. This is because the nuclear spins of ortho-hydrogen are unpaired, and thus the ESR line is considerably broadened by the influence of the neighboring magnetic nuclei of ortho-hydrogen.[11] Through a solid-state MAS NMR technique, we attempted to identify three radicals of H_2^+, H_2^-, and H· that are provisionally expected to appear in the icy binary THF-H_2 hydrate. First, we checked the NMR spectra of unirradiated 5.56 mol % THF-d8 (D_2O) hydrate and 15kGy γ-irradiated 5.56 mol % THF-d8 (D_2O) + H_2 hydrate at 173 K. As anticipated, the irradiated sample of the binary THF-d8 (D_2O) + H_2 at a 15 kGy dose evolves three distinctive peaks, at 5.27, 4.17, and 3.07 ppm at 173 K (red), but no identifiable peak is observed for irradiated pure THF-d8 (D_2O) hydrate (black). It might be concluded that these three peaks represent the γ-irradiated H_2 derivatives entrapped in sII-S, because all other host and guest molecules except for hydrogen were deuterated and showed a distinct hydrogen signal through NMR. The H· encaged in the sII small cage of the γ-irradiated hydrogen hydrate could be assigned by confirming the identical chemical shift (3.07 ppm) of H· coming from the 15kGy irradiated CH_4 (D_2O) hydrate. On the other hand, even though two peaks at 4.17 and 5.27 ppm represent two dihydrogen radicals of H_2^+ and H_2^-, we failed at the present level to assign their one-to-one positions because of the absence of the corresponding reference spectra. The temperature of the same γ-irradiated sample was raised to 183 K to see the thermal behavior of hydrogen radicals and the resulting spectrum is shown in Figure 2 (blue). The stable position of hydrogen radicals in the icy hydrate matrix might be better rationalized by examination of two possible ways that these radicals can be incorporated: One is that they exist in the sII-S cage-like channels, migrating and reacting with hydrogen molecules via a thermal-induced diffusion pathway. The other possibility is that the radicals are strongly bound to the icy cage framework or react with host water molecules to yield the ionized species. The latter pathway for making ionized species appears to be extremely unlikely. In the case of γ-irradiated 5.56 mol % THF-d8 (D_2O) + H_2, three sharp resonance lines of H_2^+, H_2^-, and H· were distinctively observed at 173 K. However, with a little thermal variation to 183 K, they tend to merge into a single broadened peak, confirming that the substantial amount of hydrogen radicals are recovered to hydrogen molecules entrapped in sII-S (sII-S H_2 peak at the chemical shift of 4.3 ppm). The enclathrated hydrogen molecules can migrate and diffuse through pentagonal and hexagonal faces above 100K.[12] Moreover, the hydrogen transfer from guest propane molecule to n-propyl radical in adjacent hydrate-cages was described on the basis of ESR measurements.[13] Such a simple transformation from hydrogen radicals to hydrogen molecules will be very improbable if the radicals are changed to ionized species by reacting with icy cage framework. Based on the spectroscopic observation, it was also found that in the case of the γ-irradiated sII THF-d8 (D_2O) + H_2 hydrate, the H_2 peak grows weakly with temperature.
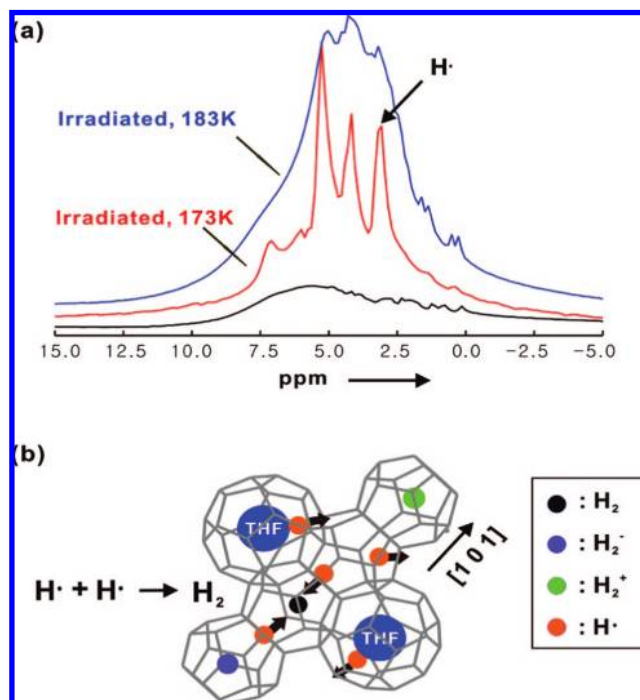

Figure 2. (a) MAS ^{1}H NMR spectra of unirradiated 5.56 mol % THF-d8 (D_2O) hydrate (black) and 15kGy γa-irradiated 5.56 mol % THF-d8 (D_2O) + H_2 binary hydrate at 173 K (red) and 183 K (blue); (b) recovery of atomic hydrogen radicals to hydrogen molecules in the sII-S channels.

In conclusion, through combined ESR and NMR approaches, we attempted to identify the existence of ionized hydrogen derivatives entrapped in the cages of icy hydrate materials. Such stable existence of single hydrogen molecule/radical in icy crystalline matrices may offer significant advantages in exploring hydrogen as a quantum medium because icy hydrogen hydrates can be formed at milder conditions when compared with pure solid hydrogen, which requires an ultralow temperature of 4.2 K. The novel design and synthesis of ionic and radicalized hydrates are expected to contribute to inclusion chemistry. Furthermore, the stable existence of guest-derived radicals in the hydrate cages might lead to suggesting the preliminary concept of the hydrate-based nanoreactor because of their high reactivity.

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