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Superexchange-Like Interaction of Encaged Molecular Oxygen in Nitrogen-Doped Water Cages of Clathrate Hydrates

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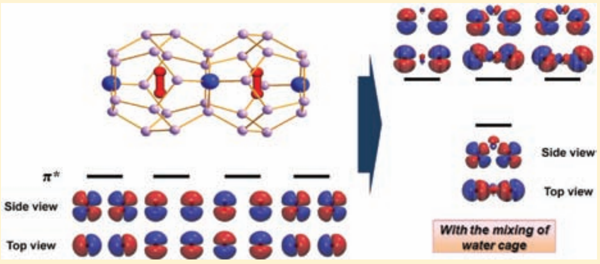
Supporting Information



ABSTRACT: Clathrate hydrates are a highly prospective material in energy and environmental fields, but the inherent nature of inclusion phenomena occurring in the stacked water cages has not been completely resolved yet. Investigating the magnetism of guest molecules is a new experimental approach in clathrate hydrate research to open the possibility of icy magnetic applications as a novel material as well as to understand the unrevealed host−guest interactions in icy inclusion compounds. In this study, we observed an indirect spin coupling between encaged dioxygen molecules via a nonmagnetic water framework through the measurement of guest magnetization. This spin coupling is reminiscent of superexchange coupling between magnetic ions through intervening oxygens in antiferromagnetic oxides, such as MnO and CoO. Theoretical calculations revealed that OH^- incorporated in the framework induced the mixing of perpendicular π^* orbitals of two distant dioxygens and that ammonia doping into the hydrate cage leads to a longer lifetime of that orientation.

1. INTRODUCTION

Clathrate hydrates have been among highlighted materials in the energy and environmental fields due to their impressive potential as energy storage media and application devices for shifting the paradigm of human society.[1−6] Numerous studies have been performed in order to explore the inherent nature of inclusion phenomena occurring in the cage-stacked framework of clathrate hydrates.[1−4] Notably, the magnetism of guest molecules encaged in water framework was investigated for the first time in a few recent studies.[7,8] The field-induced magnetization of guest molecules under a strong magnetic field can provide information that has previously been limited mainly to the results of theoretical studies in hydrate fields,[9] such as the spin state of guest molecules and charge interaction between host water and guest molecules. Thus, additional in-depth investigations are needed to understand the unique inclusion phenomena and unrevealed host−guest interactions occurring in icy materials.

In this study, we report the superexchange-like long-range coupling of molecular oxygen encaged in a nitrogen-doped water framework. Molecular oxygen is the simplest magnetic guest captured into a clathrate hydrate with a $^3\Sigma_g^-$ ground state. Several studies reported the magnetism of confined O_2 molecules absorbed in one-dimensional channel or two-dimensional layer structures, but they dealt with this as an extension of the inherent antiferromagnetism of solid oxygen.[10−14] Recently, Park et al.[8] focused on the magnetism of isolated O_2 molecules in hydrate cages and demonstrated that selective guest injection into water cages can modify the inherent magnetic property of the O_2 molecules. Additionally, Kaye et al.[15] reported on magnetic interaction between absorbed O_2 and a framework composed of microporous magnetic materials. However, these studies are related to the coupling between magnetic molecules only, and long-range indirect interaction between isolated O_2 molecules via nonmagnetic framework has not yet been reported. Here, we demonstrate the superexchange-like interaction between encaged O_2 molecules via a nitrogen-doped framework including OH^- anions. The magnetization of O_2 was measured by a magnetic property measurement system (MPMS), and molecular calculations were performed in order to support the superexchange-like coupling of $O_2-OH^--O_2$.

2. EXPERIMENTAL SECTION

Sample Preparation. Two well-mixed solutions (tetramethylammnonium hydroxide (Me_4NOH) + $16H_2O/Me_4NOH$ + NH_3 + $15H_2O$) were frozen at 210 K for 1 day and were then ground to a fine powder (∼200 μm) under liquid nitrogen temperature. The grounded

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powders were put into a high-pressure cell and exposed to O_2 (120 bar) at 210 K for 1 week. The synthesized hydrate samples were stored in liquid nitrogen, and some samples were irradiated at 30 kGy (15 kGy per 1 h) by a ^{60}Co γ-ray source at KAERI in Jeongeup, Korea.

Experimental Measurements. The high-resolution powder diffraction (HRPD) patterns of the samples were recorded at 80 K using the Pohang Synchrotron of the Pohang accelerator laboratory (λ = 1.54940 Å). The experiments were carried out in step mode with a fixed time of 2 s and at a step size of 0.01° for each sample. The obtained patterns were indexed using the Check Cell program.[16] A MPMS XL 5 (Quantum Design) was used for the field-dependent magnetization [M(H)] and magnetic susceptibilities [$\chi(T)$] plots (the M−H curve of γ-irradiated $Me_4NOH + O_2$ hydrate was obtained from MPMS XL 7). The weighed hydrate powder was placed in a quartz tube cooled by liquid nitrogen, and the tube was loaded into a magnetometer at 150 K. After loading the sample, the magnetization value of the sample was obtained at 1.9 K with variation of the magnetic field (from −5 to 5 T) for the [M(H)] pattern or at 0.01 T with changing temperature (from 1.9 to 82 K). Raman spectra were obtained using a high resolution dispersive Raman microscope (Horiba Jobin Yvon, France). The focused 514.5 nm line of an Ar ion laser was used for excitation, and the laser intensity was typically 25 mW. The scattered light was dispersed using a single-grating spectrometer and detected with an electrically cooled (−70 °C) CCD detector.

Computation. To investigate the magnetism between two guest dioxygen molecules, we calculated the relative energetics between different spin states. Two different spin configurations, $S = 5$ and 1 (open-shell singlet), were considered, which represent the cases when two triplet spins of dioxygen molecules are aligned along the same (ferromagnetic coupling) and opposite (antiferromagnetic coupling) directions, respectively. The magnetic coupling constant, J is then defined as $J = E_{S=1} - E_{S=5}$, where $J > 0$ indicates ferromagnetic coupling and $J < 0$ antiferromagnetic coupling. Due to a near degeneracy and the multireference character of this system, we employed complete active space self-consistent field (CASSCF) (4,4) calculations and refined the energetics using the second-order multireference perturbation (MRMP) theory implemented in the General Atomic and Molecular Electronic Structure System (GAMESS) program. Dunning's augmented correlation-consistent triple-ζ basis set (aug-cc-pVTZ) was used for the calculations, and the SCF convergence limit was set by 10^{-8} hartree. Since the multireference character is mainly caused by the interaction of four electrons occupied in four π^* orbitals of two dioxygen molecules, here, the MCSCF active space includes four electrons and four orbitals.

3. RESULTS AND DISCUSSION

We first synthesized a nitrogen-doped water framework. In a previous study,[17] we reported on structural transformation due to NH_3 inclusion as a cohost in Me_4NOH hydrate. In this case, the NH_3 acts as a hydrogen donor, and the ionic framework incorporating OH^- acts as a hydrogen acceptor due to its proton deficiency. As shown in Figure 1a, HRPD patterns exhibit that the added NH_3 induced a structural change from orthorhombic *Pnma* of Me_4NOH decahydrate to cubic *Fd*3*m*, known as structure-II (sII) hydrate having 8 $5^{12}6^4$ and 16 5^{12} cages in a unit cell. With exposure of the sample to O_2 gas at 210 K, we synthesized the sII hydrate, wherein the $5^{12}6^4$ and the 5^{12} cages are occupied by Me_4N^+ and O_2, respectively. Contained O_2 gas of the synthesized sample measured by direct gas release was 106.1 mL/g-sample (at 25 °C, 1 atm), corresponding with the value of undoped $Me_4NOH + O_2$ hydrate (105.9 mL/g sample). The included NH_3 replaces a water molecule as a part of the framework, and thus nitrogen-doped $Me_4NOH + O_2$ hydrate, as represented in Figure 1b, was synthesized.

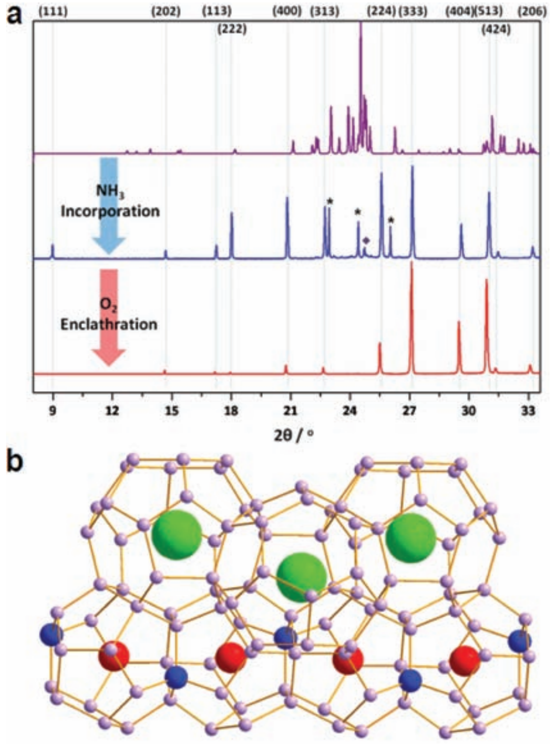

Figure 1. (a) HRPD patterns of Me_4NOH decahydrate (top, calculated pattern from orthorhombic *Pnma*; a = 16.031, b = 8.453, and c = 12.360 Å),[18] NH_3 incorporated Me_4NOH hydrate (middle, cubic *Fd*3*m*; a = 17.143(2) Å), and O_2 enclathrated $Me_4NOH + NH_3$ hydrate (bottom, cubic *Fd*3*m*; a = 17.200(4) Å). The diffraction peaks of hexagonal ice and Me_4NOH decahydrate impurities were marked by asterisks (*) and diamonds (♦), respectively. (b) NH_3-doped $Me_4NOH + O_2$ hydrate (green: Me_4N^+, red: O_2, cyan: O in water, and blue: N of NH_3; hydrogen is omitted).

In previous studies,[7,19,20] we reported that the molecular electron affinity of nonionic guest molecules can strongly affect the host−guest interactions, including the charge distribution of the system. In particular, the affinity of O_2 is superior to that of other homomolecular diatomic molecules, such as H_2 or N_2. In γ-irradiated ionic Me_4NOH hydrates, it was thus observed that O_2 molecules draw and trap the ejected electrons from the framework into O_2 itself, while N_2 or H_2 molecules in contrast disturb electron trapping into the $5^{12}6^4$ cage of Me_4N^+.[19] In order to investigate the interaction between O_2 and the host framework more deeply, the isothermal M−H curves of binary O_2 hydrates with a *Fd*3*m* crystal structure were measured at 1.9 K and compared to each other (Figure 2). As reported in a previous study,[8] the hydrate framework provides enough intermolecular distance between encaged O_2 molecules (Figure 1b) for each guest to feel the isolation from the spin of neighboring O_2. Notably, the magnetization value of O_2 molecule in THF + O_2 hydrate was measured as 1.95 μ_B/O_2 at 1.9 K and 7 T (Figure 2), which is much close to the theoretical value of 2 μ_B/O_2 due to two unpaired electrons of O_2. In contrast to nonionic THF + O_2 hydrate, the moment of O_2 entrapped in $Me_4NOH + O_2$ hydrate decreases to 1.53 μ_B/O_2 at 7 T, which is ∼75% of the theoretical value. Considering the high electron affinity of O_2, charge transfer from the anionic host to O_2 molecules may be one of the factors that can explain this discrepancy, as reported in a previous work.[20] Here, we also checked the magnetization of O_2

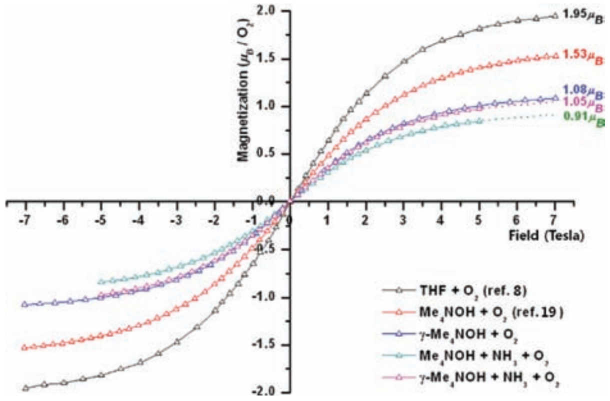

Figure 2. Isothermal M−H curves of binary O_2 hydrates at 1.9 K.

in nitrogen-doped water cages. Surprisingly, the moment of O_2 in this system dramatically decreases to 0.91 μ_B/O_2 at 7 T (predicted from the magnetization value of 0.84 μ_B/O_2 at 5 T), which is less than ∼50% of the theoretical value (Figure 2). Although nitrogen has slightly lower electronegativity than oxygen, this drastic decrease of the magnetization cannot be attributed entirely to the former, which accounts for 5.9% of the framework.

In order to identify cause of the unexpected decrease of O_2 magnetization, magnetic susceptibilities [$\chi(T)$] of undoped and nitrogen-doped $Me_4NOH + O_2$ hydrates were also measured under a 0.01 T magnetic field. The $1/\chi$ versus T curve for each hydrate is presented in Figure 3a, and the estimated Weiss constants [θ] are −1.42 and −0.54 K (20−82 K), respectively. It is remarkable that the nigrogen-doped $Me_4NOH + O_2$ hydrate has a smaller magnetization value than the undoped hydrate, but the former has a larger negative Weiss constant than the latter. Although the Weiss constants of both hydrates are considerably small, the negative values indicate a weak antiferromagnetic-like interaction among encaged O_2 guests. Thus, with the decrease of O_2 magnetization shown in Figure 2, these negative Weiss constants of anionic hydrate systems appear to indicate that nonmagnetic OH^- plays a role in bridging an antiferromagnetic spin interaction between O_2 molecules isolated in each cage. In addition, the larger Weiss constant (absolute value) and the smaller O_2 magnetization of nitrogen-doped $Me_4NOH + O_2$ hydrate relative to the undoped hydrate imply that NH_3 included in the ionic host framework promotes an indirect coupling between the magnetic guests via the nonmagnetic framework. Interestingly, this indirect coupling between O_2 molecules via nonmagnetic framework is reminiscent of superexchange coupling between magnetic ions through intervening oxygens in antiferromagnetic oxides, such as MnO and CoO.

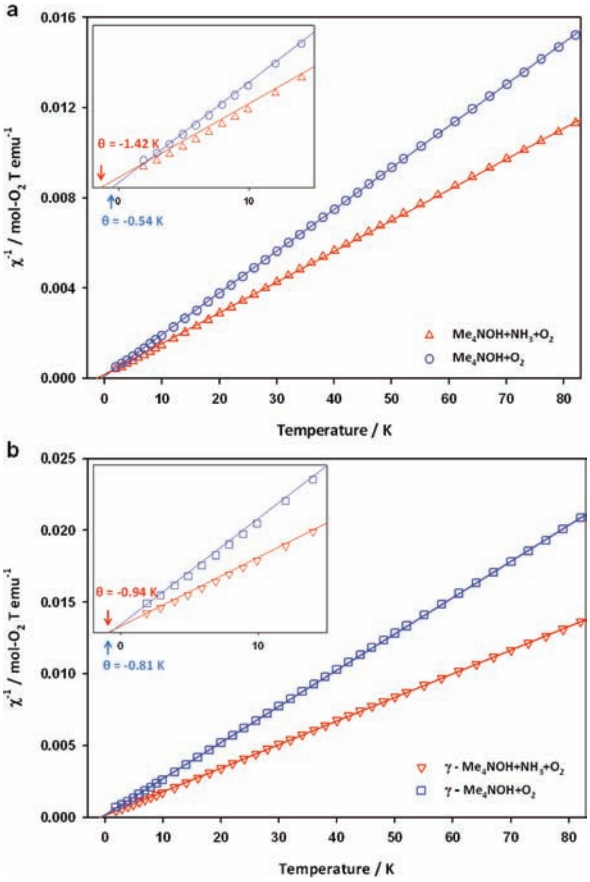

Figure 3. Magnetic susceptibilities [$\chi(T)$] (a) undoped and nitrogen-doped $Me_4NOH + O_2$ hydrates and (b) γ-irradiated, undoped, and nitrogen-doped $Me_4NOH + O_2$ hydrates.

At this stage, a key question arises: How can the OH^- and NH_3 incorporated host cause the superexchange-like interaction between isolated O_2 molecules? We attempted to answer this question using electronic structure calculations involving the spin state of O_2 molecules. MRMP calculations were performed using four electrons in four active orbitals to allow the interaction of two π^* orbitals of distant O_2 molecules. We considered quintet and singlet spin states to represent ferromagnetic and antiferromagnetic coupling schemes, respectively, for the model system shown in Figure 4a. Superexchange-like interactions are known to be very sensitive to the relative orientations, since the orbital overlaps among atoms govern the interactions between spins.[21] Thus, we systematically investigated the effects of the relative orientations on the magnetic coupling constant, J. In the water hydrate cage, possible orientations of OH anions are reduced into two distinct cases by symmetry (denoted as OH1 for the in-plane and OH2 for the out-of-plane position in Figure 4). For the relative orientation of two dioxygen molecules, we only consider the case where they are located in parallel, since this maximizes the overlaps between π^* orbitals, leading to a significant value of J. The relative orientation of the dioxygen molecule with respect to the OH anion is examined by varying the angle φ, which is defined in Figure 4a. The calculated J values as a function of different orientations are shown in Figure 4b. We found that the OH anion significantly enhances the interaction between two triplet spins (cf. calculated J value without the OH anion is −0.01 K). This tendency is maximized when the OH anion has the OH1 orientation and when φ is nearly 0 (the oxygen atom of the OH anion lies on the same plane as the oxygen atoms of dioxygen molecules). The calculated J values are mostly negative, which infers that the system prefers to have an "antiferromagnetic" coupling, and the value is as high as −1.32 K. Recalling the Ising model with mean-field approximation, the Weiss constant θ is given by $-zJ/k_B$, where z is the coordination number. If we take a $z = 6$ case by considering the small cage is neighbored by six other small cages in the cubic $Fd3m$ structure, θ is roughly estimated as 1.98 K. However, the anticipated real value might be lower because OH^- does not always retain the OH1 orientation due to the high proton conductivity of the ionic framework. Thus, the calculated result

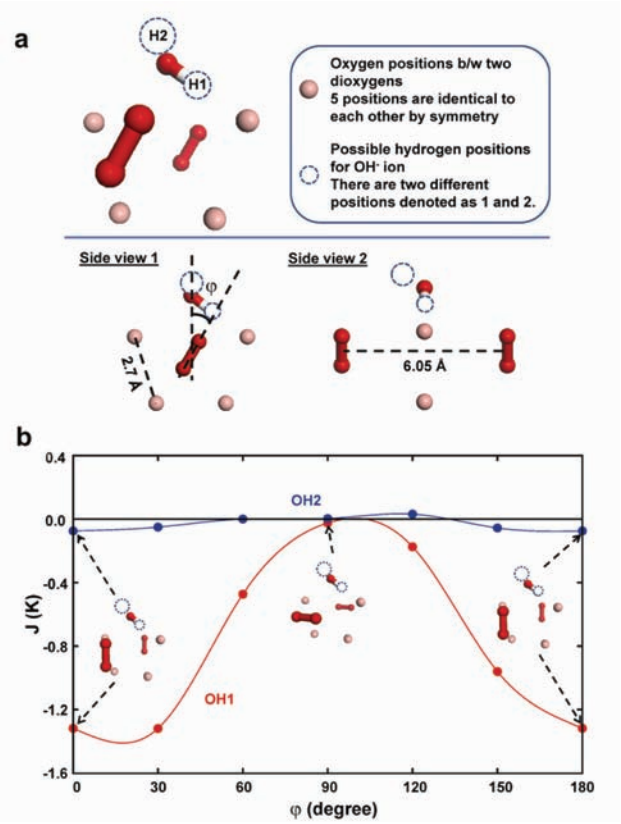

Figure 4. (a) Model system for MRMP calculations. (b) Calculated coupling constant (J) as a function of OH^- orientations. The J values are of the same order with the x-intercept of $1/\chi$ vs T curve from experiment.

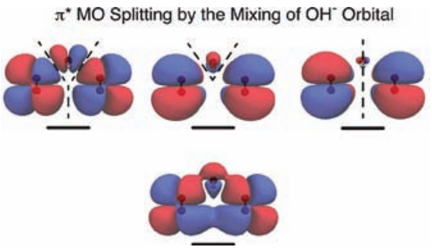

Figure 5. CASSCF orbitals of active space. OH^- induces the mixing of perpendicular π^* orbitals of two dioxygens, leading a split of energy eigenvalues: four π^* orbitals originally degenerated at -0.2108 hartree without OH^- ion are split into one at -0.0747 hartree and three at -0.0737 hartree when OH^- ion is located in OH1 position with $\varphi = 0$. Isodensity value of 0.001 was used to plot the orbitals.

is comparable to the experimental Weiss constant of 0.54 K determined from the $1/\chi$ vs T curve (Figure 3a).

In order to understand the origin of enhanced J by introducing OH^-, we visualized the CASSCF orbitals in Figure 5 when OH^- is located in the OH1 position with $\varphi = 0$, the orientation that maximizes J. For the bare $O_2{-}O_2$ interaction (without intercage OH^-), the four states are nearly degenerated, since the long distance between two dioxygen molecules (6.05 Å) results in almost zero orbital overlap. When OH^- is introduced between dioxygen molecules, the two π^* orbitals of distant dioxygen molecules start interacting indirectly via the p-orbital of OH^-. This mixing then induces antibonding characters to the higher occupied orbital and splits the energy eigenvalues, as shown in Figure 5.

Decomposition of MRMP energetics into CASSCF (that favors the quintet state by 0.06 K) and perturbative correction (that favors the singlet state by 1.38 K) indicates that the dynamic correlations play an important role in the stabilization of the singlet state. Thus, we can suggest that the antibonding character induced by the mixing of OH^- orbitals mediates the dynamic electron correlations between two dioxygen molecules. This significantly encourages the antiferromagnetic coupling between caged dioxygen molecules, which are 6 Å apart.

When ammonia is doped in the hydrate cage, the reorientation of host molecules is disturbed, because the proton-deficient sites (i.e., OH^-) are filled by the 'third' proton of ammonia, that is, the proton conductivity of the hydrate phase decreases.[22] Although we cannot determine the exact position of the nitrogen atom in the host framework here, the most likely position in the host framework is expected to be the (8a) symmetry position, as represented in Figure 1, when the multiplicity of atom positions is considered. With this possibility, NH_3 can increase the lifetime of the OH1 orientation, leading to higher antiferromagnetic coupling between encaged O_2 molecules. This results in a decreased magnetization of O_2 molecules at 1.9 K and an increased Weiss constant of 1.42 K (determined from the $1/\chi$ vs T curve) for the NH_3 incorporated hydrate cage.

For clearer identification of superexchange-like magnetic coupling occurring in the nitrogen-doped water framework, we also checked the magnetization of γ-irradiated $Me_4NOH + O_2$ hydrates. As we mentioned above, γ-irradiation extremely affects the electron distribution of both the host and the guest in an ionic system, and thus this approach can provide a better understanding of the effects of included NH_3 on $O_2{-}O_2$ spin coupling. Both undoped and ammonia-doped samples were γ-irradiated, and the amounts of contained O_2 were checked again. Contained O_2 volumes measured by direct gas release method were 96.3 mL/g sample for $Me_4NOH + O_2$ hydrate and 100.2 mL/g sample for ammonia-doped $Me_4NOH + O_2$ hydrate, respectively (25 °C and 1 atm). Samples were considered to be slightly damaged by γ-irradiation. In earlier studies,[19,20] it was reported that a part of O_2 molecules changes superoxide ions, O_2^-, accompanied with yellow coloration when $Me_4NOH + O_2$ hydrate is irradiated by γ-rays. Although O_2^- is still paramagnetic, the total spin angular momentum decreases from $S = 1$ for O_2 to $S = 1/2$ for O_2^-. Accordingly, the magnetization of γ-irradiated $Me_4NOH + O_2$ hydrate also decreases (1.08 μ_B/O_2 at 7 T), as shown in Figure 2. At this stage, we can expect that γ-irradiation of the nitrogen-doped system might reduce the magnetization of O_2 to much less than 0.91 μ_B, the value of an unirradiated system, due to the formation of O_2^- (the existence of O_2^- in the nitrogen-doped system was confirmed by ESR spectroscopy; see the Supporting Information). However, unexpectedly, the magnetization of γ-irradiated $Me_4NOH + O_2$ hydrate including NH_3 was obtained as 1.05 μ_B/O_2 at 7 T (predicted from the magnetization value of 0.97 μ_B/O_2 at 5 T), showing little difference from the undoped system with γ-irradiation (Figure 2). In addition, the Weiss constants of these γ-irradiated systems were estimated to be -0.81 and -0.94 K (20−82 K), respectively, from fitting of the magnetic susceptibilities to the Curie−Weiss law (Figure 3b). Insignificant differences of the magnetization and the Weiss constants between undoped and nitrogen-doped hydrates imply that the included NH_3 cannot continue to promote the superexchange-like interaction after γ-irradiation.

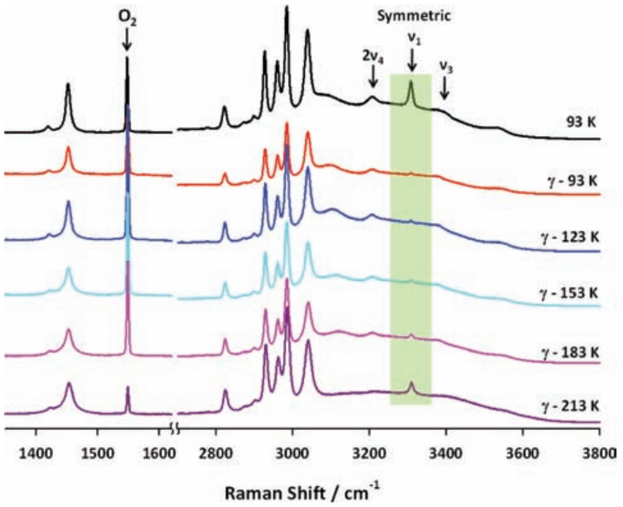

Figure 6. Raman spectra of nitrogen-doped Me_4NOH + O_2 hydrates before γ-irradiation at 93 K (black) and after γ-irradiation at 93 (red), 123 (blue), 153 (cyan), 183 (pink), and 213 K (purple).

We further explored the change of incorporated NH_3 after irradiation by examining Raman spectra, as shown in Figure 6. Before γ-irradiation, three bands due to incorporated NH_3 were observed at the Raman spectrum of nitrogen-doped Me_4NOH + O_2 hydrate; a sharp peak of the symmetric stretch (ν_1) at 3308 cm^{-1}, two weak peaks of the overtone of the asymmetric bend ($2\nu_4$) at 3208 cm^{-1}, and the asymmetric stretch (ν_3) at 3379 cm^{-1}.[23] One interesting feature, observed after irradiation, is that the symmetric stretching mode of NH_3 totally disappeared and recovered very slowly as the temperature was increased. In comparison to the Raman spectra of the nitrogen-doped hydrates without an O_2 guest, having the same structure as cubic *Fd*3*m* (Figure S2, Supporting Information), the disappearance of the ν_1 band is thought to be caused by the presence of O_2 molecules. Moreover, the recovery of the ν_1 band in Figure 6 clearly occurs simultaneously with the release of O_2 guest by temperature increasing. We note again that the superior electron affinity of O_2 draws the ejected electrons by the γ-ray into O_2 itself in the Me_4NOH + O_2 hydrate system, and thus O_2^- ions are formed and captured stably in the water cages, as reported in our previous studies.[19,20] Here, the difference between the simple anionic and nitrogen-doped anionic hosts should be considered. In contrast with the simple anionic host, i.e., only an OH^- incorporated water framework, the nitrogen-doped host contains fewer electronegative nitrogen sites in its framework. Thus, O_2^- formed in the cage, a good proton acceptor, can draw the protons of NH_3 more easily than those of more electronegative oxygen, while breaking the symmetric vibration motion of NH_3. Loss of the symmetric motion implies that one of three protons of ammonia does not belong to the framework and that the reorientation of host water is no longer disturbed by filling the proton deficiency. Therefore, the NH_3 cannot increase the lifetime of the OH1 orientation, which promotes superexchange-like spin coupling between dioxygen molecules, in the γ-irradiated system.

4. CONCLUSIONS

In this report, we demonstrate superexchange-like long-range spin coupling between encaged dioxygen molecules via nonmagnetic incorporated OH^- anions and also suggest the enhancement of this coupling by ammonia doping into the framework, through guest magnetization measurement, theoretical calculations, and Raman spectroscopy of unirradiated and γ-irradiated Me_4NOH + O_2 hydrate system. Because clathrate hydrates as energy storage media and application devices are highly prospective materials to change the lives of humankind, a comprehensive understanding of the nature of their inclusion chemistry is strongly required. Although the present work reveals a small part of the peculiar phenomena occurring in ice cages, this preliminary work is expected to provide meaningful information on both host−guest and guest−guest interactions, possibly opening up potential applications.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Electron spinning resonance and Raman spectra details. This material is available free of charge via the Internet at http://pubs.acs.org.

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