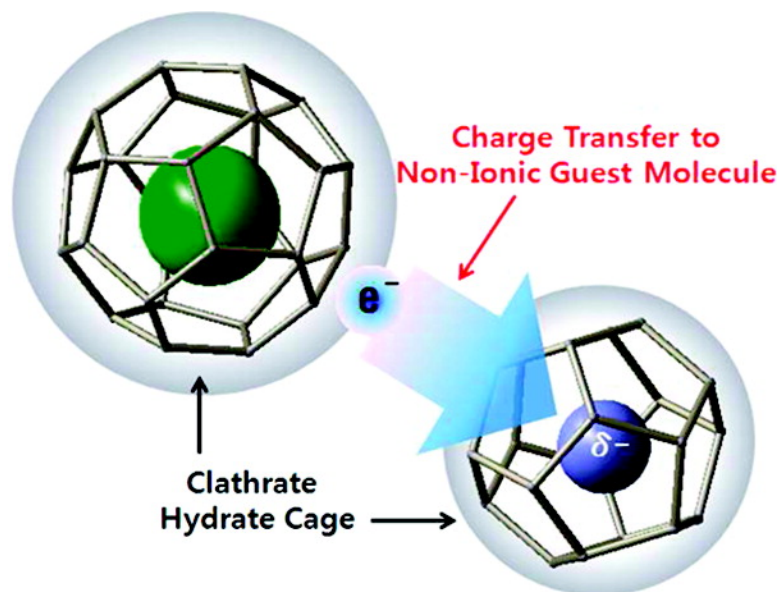


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## Discrete Magnetic Patterns of Nonionic and Ionic Clathrate Hydrates

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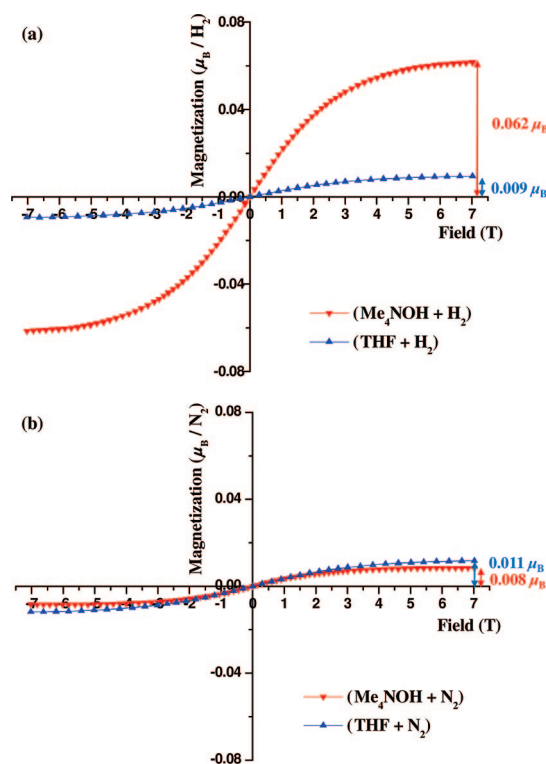
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Notable physicochemical characteristics of ionic clathrate hydrates have been introduced in several studies.<sup>1–6</sup> Unlike nonionic clathrate hydrates stabilized solely by van der Waals interaction, ionic clathrate hydrates are greatly affected by ionic interaction between a cationic or anionic guest and the surrounding host lattice balanced by counterions.<sup>7</sup> The ionic guest molecules tend to readily form the clathrate or “clathrate-like” structures with water depending on the existence of OH<sup>−</sup>, but their exposure to nonionic guest molecules (NIGM) occasionally induces structural transformation through their occupation in cages.<sup>3</sup> In particular, ionic clathrate hydrates tend to exhibit the extraordinary physicochemical behavior in cage-stacked channels.<sup>3,4</sup> In the icy matrix of the ionic clathrate hydrate, two unique features merit examination: one is the ionic conductivity enhancement appearing from the ionic behavior of the charged host, and the other is the new vacant cage creation by structural transformation.

Here, a key question arises as to the charge interaction between the NIGM and charged host matrix surrounding the NIGM. The charged diatomic molecules appear often as intermediates of a cleavage reaction,<sup>8–10</sup> and thus, their stable positioning might provide an active role in implementing a specific function in icy clathrate hydrate materials. We attempt to answer this question through a close comparison of the magnetic and spectroscopic patterns of (1) nonionic tetrahydrofuran (THF) + NIGM and (2) ionic tetramethylammonium hydroxide (Me<sub>4</sub>NOH) + NIGM clathrate hydrates. For potential NIGM, two homomolecular diatomic molecules of H<sub>2</sub> and N<sub>2</sub> with *D<sub>∞h</sub>* symmetry were used. These molecules are known to reveal the diamagnetic electron configuration because their total spin and orbital angular momentums are zero.<sup>11</sup>

First, the isothermal M–H curves of (THF + NIGM) clathrate hydrate (NIGM = H<sub>2</sub> and N<sub>2</sub>), which has a structure-II (sII) cubic *Fd3m* structure,<sup>7,12</sup> were measured at 1.9 K, and the results are shown in Figure 1a and 1b.<sup>13,14</sup> Here, the magnetization value of pure THF clathrate hydrate (Figure S1) was subtracted to determine the net magnetic behavior representing only the NIGM effects. Unexpectedly, the magnetic signals induced by the secondary guest of NIGM do not exhibit diamagnetics, but instead weak paramagnetics, leading to exhibiting the field-induced saturation behavior, which might be due to quite small charge transfers of about  $-0.01 e$  from water molecules in a neutral host lattice.<sup>15</sup>

Meanwhile, the (Me<sub>4</sub>NOH + NIGM) clathrate hydrate exhibits the dual feature of a proton-deficient anionic host lattice and structural transformation.<sup>3</sup> Because the proton-deficient site is disordered, the negative charge of OH<sup>−</sup> is delocalized to the whole host lattice.<sup>1</sup> For comparison, the electron state of NIGM is also examined through magnetization measurements of the (Me<sub>4</sub>NOH



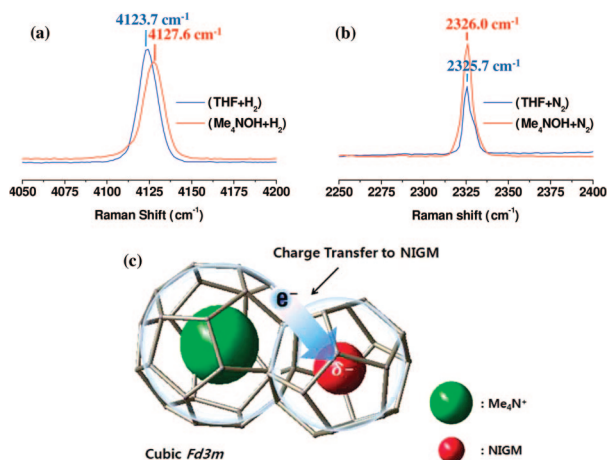
**Figure 1.** M–H curves of cubic *Fd3m* (Me<sub>4</sub>NOH + NIGM) clathrate hydrates (red lines) and (THF + NIGM) clathrate hydrates (blue lines) measured at 1.9 K. NIGM = (a) H<sub>2</sub> and (b) N<sub>2</sub>.

+ NIGM) clathrate hydrate under strong magnetic fields. Here, we might conjecture that the magnetic behavior of secondary guests in the ionic clathrate hydrates appears to be quite similar to that in the nonionic clathrate hydrates if both crystal structures are the same and the van der Waals interaction only prevails in a cage. We note that the (Me<sub>4</sub>NOH + NIGM) clathrate hydrate was found to have sII cubic *Fd3m* structure when the hydration number per one Me<sub>4</sub>NOH is 16 (see the Supporting Information for powder X-ray diffraction patterns).<sup>16</sup> The isothermal M–H curves of (Me<sub>4</sub>NOH + NIGM) clathrate hydrate measured at 1.9 K are shown in Figure 1a and 1b.<sup>13</sup> As treated in (THF + NIGM), the magnetization value of Me<sub>4</sub>NOH–16H<sub>2</sub>O (Figure S1) was subtracted from each curve to determine the net magnetic behavior of NIGM only. The magnetic moment of (Me<sub>4</sub>NOH + H<sub>2</sub>) clathrate hydrate significantly increases up to 0.062  $\mu_B$  per one H<sub>2</sub> at 7 T, which is about 7 times higher than that of (THF + H<sub>2</sub>) clathrate hydrate (Figure 1a). Obviously, this increase is not due to the proton-deficient anionic host or the Me<sub>4</sub>N<sup>+</sup> captured into a cage because the magnetization value of Me<sub>4</sub>NOH–16H<sub>2</sub>O, which does not contain NIGM of H<sub>2</sub>, is lower than that of THF–17H<sub>2</sub>O as

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shown in Figure S1. Therefore, this unexpectedly enhanced magnetic moment strongly suggests that some of the diamagnetic  $H_2$  molecules change to paramagnetic ones by either losing an electron for a cation or gaining an electron for an anion. One  $H_2$  guest molecule is surrounded by a hydrogen-bonded anionic host cage, and thus, some  $H_2$  tends to be changed into  $H_2^-$  by a charge transfer of  $-0.062 e$  per  $H_2$  from the host lattice. On the other hand, the magnetic moment of  $N_2$  does not significantly increase when compared to (THF +  $N_2$ ) clathrate hydrate (Figure 1b). This discrepancy is quite interesting because the charge transfer occurring in the anionic host structure is considered to be affected by the molecular characteristics of NIGM, even though the NIGM of  $H_2$  and  $N_2$  have similar diamagnetic electron configurations.



**Figure 2.** Raman spectra of (THF + NIGM) hydrate and ( $Me_4NOH$  + NIGM) hydrate for NIGM stretching region. NIGM = (a)  $H_2$  and (b)  $N_2$ . (c) Charge transfer from anionic host lattice to NIGM.

This charge transfer phenomenon occurring in ionic clathrate hydrate was checked using Raman spectroscopy. The charge transferred to diatomic NIGM tends to cause the bond-length elongation, exerting influence on the vibrational frequency of NIGM.<sup>11,17</sup> In Figure 2a, the Raman spectra of nonionic (THF +  $H_2$ ) and ionic ( $Me_4NOH$  +  $H_2$ ) hydrates are shown, where a single peak appearing in each spectrum represents the stretching frequency of enclathrated  $H_2$  in each hydrate. Although the previous well-defined Raman study for hydrogen hydrate confirms the double peaks of  $H_2$ ,<sup>18</sup> this peak pattern does not always appear because of its dependence on the measurement conditions such as temperature and pressure.<sup>19</sup> Close comparison of the two peaks represented in Figure 2a indicates the existence of a significant difference (about  $4\text{ cm}^{-1}$ ) of the enclathrated  $H_2$  vibrational mode between nonionic and ionic clathrate hydrates. To confirm whether or not this difference possibly comes from an instrumental measuring error, we attempted to examine the Raman spectrum of the mixture that contains an equal amount of both nonionic and ionic clathrate hydrates and observed two split peaks (Figure S4a). Accordingly, together with the discrete magnetic patterns (Figure 1a), the Raman shift difference implying the bond elongation of  $H_2$  strongly supports the electron behavior that the charge transfer arises in the crystalline structure of ionic clathrate hydrate (Figure 2c). Raman analysis for  $N_2$  was also attempted (Figure 2b and S4b), but a significant peak difference was not observed. Thus, the bond elongation directly caused by  $N_2$  is hardly expected because of the absence of charge transfer even in an ionic hydrate system, which matches well with the corresponding magnetic moment (Figure 1b).

Thus, both magnetic and spectroscopic patterns of  $H_2$  and  $N_2$  imply that the charge transfer phenomenon occurs in ionic clathrate hydrate, following the NIGM-specific magnetic behavior. This means that the charge transfer degree is substantially influenced by the unique properties of NIGM such as molecular electron affinity or electron-transfer kinetics in the complex host water framework.

The present findings on the magnetic and spectroscopic properties of NIGM in ionic clathrate hydrate might provide meaningful information on the unrevealed nature of host–guest interactions in solid ionic clathrate hydrate, possibly opening up potential application fields such as solid electrolytes by ion transport and proton conductivity promotion. However, this preliminary work, which primarily focuses on the charge transfer phenomenon, only provides a few fragments of physicochemical characteristics of ionic clathrate hydrates, and thus, more extensive research should be carried out for a better understanding at the atomic and molecular levels.

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**Supporting Information Available:** Experimental section, powder X-ray diffraction patterns, M–H curves of the (THF + 17  $H_2O$ ) and ( $Me_4NOH$  + 16  $H_2O$ ) system, Raman spectra and cage occupancy information of hydrates details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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