# Water Dynamics on the Surface of MCM-41 via ${ }^{2} \mathrm{H}$ Double Quantum Filtered NMR and Relaxation Measurements 

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#### Abstract

Dynamics of water adsorbed on MCM-41 has been investigated by line shape analyses of ${ }^{2} \mathrm{H}$ double quantum filtered (DQF) NMR and $T_{1}$ measurements. From temperature-dependent studies with various water loadings on MCM-41, it is found that there are three sites for water adsorption on MCM-41, namely, a "slow site", a "fast site I", and a "fast site II". The signal of water molecules in the slow site dominates in the observed DQF NMR. Fast site I is adjacent to the slow site, and the water molecules are exchangeable in these two sites. The fast site II is next to the fast site I, and water in the fast site II is only exchangeable with that in the fast site I. The influence of silanol groups on the MCM-41 surface strongly affects the motion of water molecules in the slow site, resulting in a residual quadrupolar interaction. As the signal of water in the fast site I dominates that observed in single quantum spectra, it also appears in DQF spectra through an exchange process. We found that when the fast site I is saturated, it has no influence on the internal rotation, but the wobbling motion of adsorbed $\mathrm{D}_{2} \mathrm{O}$ in the slow site becomes faster, i.e., the translational diffusion of $\mathrm{D}_{2} \mathrm{O}$ in the fast site I may increase the wobbling motion of adsorbed $\mathrm{D}_{2} \mathrm{O}$ through collision.


## Introduction

The properties of simple liquids in the vicinity of solid surfaces, both for bulk liquids and particularly when they are confined in some specific regions, have received much attention. For example, a single smooth solid surface may induce layering in liquids in contact with it. ${ }^{1-6}$ To understand more complete processes such as adsorption and catalysis, detailed knowledge of the dynamics and diffusion of adsorbates in porous systems is essential.

Recent advances in theory and experimental techniques have substantially increased the information obtainable by NMR characterization of porous materials. ${ }^{7-14}$ The use of double quantum filtered (DQF) NMR spectroscopy as a diagnostic tool for the detection of anisotropy in porous systems has recently been demonstrated, ${ }^{14}$ for example, as a sensitive method for the determination of the residual quadrupolar interaction in adsorbed layers. For a spin- 1 system, the double quantum coherence vanishes in an isotropic medium. Hence, observation of the DQF spectra indicates the presence of residual quadrupolar coupling, and so the order parameter for the adsorbed spinbearing molecules must be nonzero. ${ }^{15-19}$

We report ${ }^{2} \mathrm{H}$ NMR relaxation studies to investigate temper-ature-dependent water dynamics and exchange processes in $\mathrm{D}_{2} \mathrm{O}$ loaded to various extents in MCM-41. In addition, we report line shape analysis and DQF NMR spectra to address dynamics. The water-saturated mesoporous materials have been commonly studied by conventional NMR spectroscopy. ${ }^{1,8,20}$ The spectra have been interpreted in terms of a water molecule interacting with the specific adsorption sites on the pore surface. Examination of the double quantum coherence of quadrupolar spins may be helpful in selective excitation of adsorption-related spin species in the presence of isotropic species. ${ }^{15}$ The signal

[^0]sensitivity of DQF spectra essentially depends on the number of quadrupolar nuclei with nonvanishing residual interaction. ${ }^{16-19}$ The resulting spectra depend on the residual interaction. To interpret the adsorbate dynamics and to calculate the spectral density functions for restricted motion of adsorbed water molecules we employ a three-site exchange model.

## Theory

Three-Site Exchange Model Incorporating a Residual Quadrupolar Interaction. We decide a density matrix approach including exchange and coherence transfer. The problem may be simplified by expressing the rate equation in an irreducible tensorial basis ${ }^{22,23}$ where the individual elements of the density matrix transform as components of the full rotation group. The $q$ th component of a rank $K$ irreducible tensorial component, $T_{K q}$, can be related to the elements of the usual density matrix. The basic relaxation theory including three-site exchange is similar to that used by Price et al. ${ }^{24}$ In the present study, we assume that the residual quadrupolar interaction, given as the motionally averaged Hamiltonian, is axially symmetric with respect to the principal axis of motion, ${ }^{14-18}$ e.g.,

$$
\begin{align*}
H & =\omega_{q, \theta}\left(I_{z}^{2}-\frac{1}{3} I(I+1)\right) \\
& \equiv \omega_{q}\left(\frac{1}{2}\right)\left(3 \cos ^{2} \theta-1\right)\left(I_{z}^{2}-\frac{1}{3} I(I+1)\right) \tag{1}
\end{align*}
$$

with $\theta$ being the angle between the $z$-axis of the molecular frame and the Zeeman field, e.g., the angle between the hexagonal cylindrical axis of the MCM-41 and the Zeeman field. Here, the hexagonal pore of MCM-41 has been approximated to possess cylindrical symmetry. $\omega_{q, \theta}$ and $\omega_{q}$ are the residual quadrupolar interactions, defined in the laboratory and the molecular frame, respectively, after averaging over all the


Figure 1. Schematic representation of three-site model for $D_{2} O$ adsorption in MCM-41. The water molecules exchange between the site $s$ and site $f_{1}$ independently of the exchange between site $f_{1}$ and site $f_{2}$. The population of water in site $s$, site $f_{1}$, and site $f_{2}$, is denoted by $P_{f 1}, P_{f 2}$, and $P_{s}$, respectively. $k_{x y}$ is the microscopic rate constant for transfer from site $x$ to site $y$.
coordinates of molecular motions and orientational distribution of adsorbate. For the relaxation studies presented in this work, a two-site model cannot satisfactorily explain the experimental results. Therefore, in the present case we use a model with three sites: a "slow site", a "fast site I", and a "fast site II", denoted by $s, f_{1}$, and $f_{2}$, respectively. We have made the following assumptions in the present model: (i) Site $s$ is on the surface wherein $\mathrm{D}_{2} \mathrm{O}$ adsorption occurs, site $f_{1}$ is above site $s$ which is under the influence of $s$; (ii) site $f_{2}$ is independent of $s$; and (iii) there are only two allowed $\mathrm{D}_{2} \mathrm{O}$ exchange processes. One is exchange between site $s$ and site $f_{1}$, and the other is between site $f_{1}$ and site $f_{2}$. A schematic diagram of the model is presented in Figure 1. An isotropic distribution of $\theta$ is applied to approximate the location of adsorption sites under the random orientational distribution of MCM-41 crystals in our powder sample. In the rotating frame, the equation of motion for the related irreducible tensor components under the influence of the residual quadrupolar interaction, in the absence of spin relaxation processes, is given by refs $14-18$

$$
\frac{d}{d t}\left[\begin{array}{l}
T_{11}  \tag{2}\\
T_{21}
\end{array}\right]=\left[\begin{array}{ll}
0 & -i \omega_{q, \theta} \\
-i \omega_{\mathrm{q}, \theta} & 0
\end{array}\right]\left[\begin{array}{l}
T_{11} \\
T_{21}
\end{array}\right]
$$

where the tensorial components are related to the usual spin operators by $T_{11} \equiv I_{+} / 2$ and $T_{21} \equiv I_{Z} I_{+}+I_{+} I_{z}$.

DQF spectra are conventionally measured using the pulse sequence ${ }^{14-18} \pi / 2-\tau-\pi / 2-\delta-\pi / 2-$ (Acq.). Since we have restricted the problem to the case of a spin-1 system, the only coherence-transfer pathways (Figure 3) to be considered are between rank one and rank two, as described in eq 2 . The first $90^{\circ}$ pulse transforms Zeeman order $T_{10}\left(T_{10} \equiv I_{z} / \sqrt{2}\right)$ into single-quantum coherence $T_{11}$, which then generates $T_{21}$ in the evolution period via the residual quadrupolar interaction given in eq 2. The second $90^{\circ}$ pulse, with DQF phase cycling, transforms $T_{21}$ into double-quantum coherence, $T_{22}\left(T_{22} \equiv I_{+} I_{+} /\right.$ 2 ) and $T_{2-2}\left(T_{2-2} \equiv I_{-} I_{-} / 2\right)$. The last $90^{\circ}$ pulse transforms the double-quantum coherence into an observable signal. In the present relaxation study, the molecular dynamics characterized by the modulation with a residual quadrupolar interaction by a prescribed exchange process is given. Hence, the evolution of the related transverse components $T_{11}$ and $T_{21}$ at sites $f_{1}, f_{2}$, and $s$, expressed by the superscripts, may be described by the following rate equation of density matrix operators. ${ }^{14,15}$

$$
\begin{align*}
& \frac{d}{d t}\left[\begin{array}{l}
\sigma_{f_{2}} \\
\sigma_{f_{1}} \\
\sigma_{s}
\end{array}\right]= \\
& {\left[\begin{array}{lll}
-R_{f_{2}}-K_{f_{2} f_{1}} & K_{f f_{2}} & 0 \\
K_{f_{2} f_{1}} & -R_{f_{1}}-K_{f, f_{2}}-K_{f_{1} s} & K_{s f_{1}} \\
0 & K_{f_{1} s} & -R_{s}-K_{s f_{1}}-\Omega_{q, \theta}
\end{array}\right]\left[\begin{array}{l}
\sigma_{f_{2}} \\
\sigma_{f_{1}} \\
\sigma_{s}
\end{array}\right]} \tag{3a}
\end{align*}
$$

where

$$
\begin{align*}
\sigma_{\alpha} \equiv\left[\begin{array}{l}
T_{11}^{\alpha} \\
T_{21}^{\alpha}
\end{array}\right]  \tag{3b}\\
K_{\alpha \beta} \equiv k_{\alpha \beta}\left[\begin{array}{ll}
1 & 0 \\
0 & 1
\end{array}\right]  \tag{3c}\\
R \equiv\left[\begin{array}{ll}
R_{11}^{\alpha} & 0 \\
0 & R_{21}^{\alpha}
\end{array}\right] \tag{3d}
\end{align*}
$$

and

$$
\Omega_{q, \theta} \equiv\left[\begin{array}{ll}
0 & i \omega_{q, \theta}  \tag{3e}\\
i \omega_{q, \theta} & 0
\end{array}\right]
$$

for $\alpha$ and $\beta=f_{1}, f_{2}$, and $s$. $k_{f_{1} s}$ is the microscopic rate constant for transfer from site $f_{1}$ to site $s$, and $k_{s f_{1}}$ is the microscopic rate constant for transfer from site $s$ to site $f_{1}, k_{f f_{2} f_{2}}$ is the microscopic rate constant for transfer from site $f_{1}$ to site $f_{2}$, and $k_{f_{2} f_{1}}$ is the microscopic rate constant for transfer from site $f_{2}$ to site $f_{1}$. In addition, the detailed balance applied to the exchange process requires that

$$
\begin{gather*}
P_{f_{1}} k_{f_{1} s}=P_{s} k_{s f_{1}}  \tag{4a}\\
P_{f_{1}} k_{f_{1} f_{2}}=P_{f_{2}} k_{f_{2} f_{1}} \tag{4b}
\end{gather*}
$$

where we define $P_{f 1}, P_{f 2}$, and $P_{s}$ as the populations in site $f_{1}$, site $f_{2}$, and site $s$, respectively. In eq 3 , the spin relaxation rate constants for single and double quantum coherence (expressed by the first subscript of $R$ ) with different sites (expressed by the superscript) are given in ref 15 .

$$
\begin{align*}
R_{11}^{\alpha} & \equiv C^{\alpha}\left(3 J_{0}^{\alpha}+5 J_{1}^{\alpha}+2 J_{2}^{\alpha}\right)  \tag{5}\\
R_{21}^{\alpha} & =C^{\alpha}\left(3 J_{0}^{\alpha}+J_{1}^{\alpha}+2 J_{2}^{\alpha}\right)
\end{align*}
$$

where $C^{\alpha} \equiv 3 \chi_{\alpha}^{2} / 160$, for $\alpha=f_{1}, f_{2}$, and s and where the quadrupolar coupling constants $\chi_{f_{1}} \equiv e^{2} Q q_{f_{1}} / \eta, \chi_{f_{2}} \equiv e^{2} Q q_{f_{2}} / \eta$, and $\chi_{s} \equiv e^{2} Q q_{s} / \eta$ are for sites $f_{1}, f_{2}$, and $s$, respectively, and the corresponding spectral density functions defined below for motional relaxation of $\mathrm{D}_{2} \mathrm{O}$ molecules are $J_{n}^{f_{1}}, J_{n}^{f_{2}}$, and $J_{n}^{s}$. Since the $\mathrm{O}-\mathrm{D}$ bond of the water molecule is considered to be cylindrical, the contribution of the asymmetry parameter of the electric field gradient to relaxation is negligible. It is worth noting that all the parameters used for the slow site have the characteristics of adsorption interactions. To guarantee the validity of this equation, the condition $\tau_{\mathrm{ex}} \gg \tau_{\mathrm{c}}$ must hold, where $\tau_{\mathrm{c}}$ represents the microscopic motional correlation times defined below, and $\tau_{\mathrm{ex}}$ is defined as $\tau_{\mathrm{ex}}^{f_{1} s} \equiv P_{f_{1}} / k_{s f_{1}}=P_{s} / k_{f_{1} s}$ and $\tau_{\mathrm{ex}}^{f_{\mathrm{i}} f_{2}} \equiv$ $P_{f_{1}} / k_{f_{2} f_{1}}=P_{f_{2}} / k_{f_{1} f_{2}}$.

The DQF spectra are simulated using a complete formulation of the relaxation processes occurring throughout the DQF and the subsequent acquisition period. Starting from thermal equilibrium, eq 3 is used to follow the creation of $T_{21}^{f_{1}}, T_{21}^{f_{2}}$, and $T_{21}^{s}$ components during the period $\tau$. The resulting double-quantum terms, $T_{21}^{f_{1}}, T_{21}^{f_{2}}$, and $T_{21}^{s}$, form an initial condition for calculating the transverse evolution during the acquisition period. This equation is also used for simulation of the single quantum spectrum. For the calculation of $T_{1}$ the time evolution of the longitudinal components follows the rate equation ${ }^{14,15}$

$$
\begin{align*}
& \frac{d}{d t}\left(\begin{array}{l}
T_{10}^{f_{1}} \\
T_{10}^{f_{2}} \\
T_{10}^{s}
\end{array}\right)= \\
& \left(\begin{array}{lll}
-R_{10}^{f_{1}}-k_{f_{1} s}-k_{f_{1} f_{2}} & k_{f_{2} f_{1}} & k_{s f_{1}} \\
k_{f_{1} f_{2}} & -R_{10}^{f_{2}}-k_{f_{2} f_{1}} & 0 \\
k_{f_{1} s} & 0 & -R_{10}^{s}-k_{s f_{1}}
\end{array}\right)\left(\begin{array}{l}
T_{10}^{f_{1}} \\
T_{10}^{f_{2}} \\
T_{10}^{s}
\end{array}\right) \tag{6}
\end{align*}
$$

where $R_{10}^{f_{1}}, R_{10}^{f_{2}}$, and $R_{10}^{s}$ are the longitudinal relaxation rates for site $f_{1}, f_{2}$, and site $s$, as defined in ref 15 .

$$
\begin{align*}
& R_{10}^{f_{1}}=2 C^{f_{1}}\left(J_{1}^{f_{1}}+4 J_{2}^{f_{1}}\right) \\
& R_{10}^{f_{2}}=2 C^{f_{2}}\left(J_{1}^{f_{2}}+4 J_{2}^{f_{2}}\right)  \tag{7}\\
& R_{10}^{s}=2 C^{s}\left(J_{1}^{s}+4 J_{2}^{s}\right)
\end{align*}
$$

The calculations of $T_{1}$ and the single-quantum line shape were also employed in the determination of simulation parameters.

Spectral Density for Fast Motion Site. For the fast motion sites, $f_{1}$ and $f_{2}$, the reorientational Brownian motion of water molecules averages the anisotropic quadrupole interaction experienced by the ${ }^{2} \mathrm{H}$ nucleus to zero. The spectral-density function expressed in eq 7 for the fast sites is given by the spectral-density functions related to the reorientational motion of water molecules, i.e.,

$$
\begin{equation*}
J_{n}^{\alpha}=\frac{2 \tau_{c}^{\alpha}}{1+\left(n \omega_{0} \tau_{c}^{\alpha}\right)^{2}} \tag{8}
\end{equation*}
$$

where $\alpha=f_{1}$ and $f_{2} . \tau_{c}^{\alpha}$ is the effective reorientational correlation time of water molecules and $\omega_{0}$ is the Larmor precesion frequency of the deuteron.

Spectral Density for Slow Motion Sites. The spectral-density functions for site $s$ including the residual quadrupolar interaction are given by the following expressions. ${ }^{15}$

$$
\begin{gather*}
J_{0}^{s} \equiv j_{0}^{s}\left(1+\frac{10}{7}\left\langle D_{00}^{(2)}\right\rangle+\frac{18}{7}\left\langle D_{00}^{(4)}\right\rangle-5\left\langle D_{00}^{(2)}\right\rangle^{2}\right) \\
J_{1}^{s} \equiv j_{1}^{s}\left(1+\frac{5}{7}\left\langle D_{00}^{(2)}\right\rangle-\frac{12}{7}\left\langle D_{00}^{(4)}\right\rangle\right)  \tag{9}\\
J_{2}^{s} \equiv j_{2}^{s}\left(1-\frac{10}{7}\left\langle D_{00}^{(2)}\right\rangle+\frac{3}{7}\left\langle D_{00}^{(4)}\right\rangle\right)
\end{gather*}
$$

where $j_{n}^{s}$ is the spectral density for the dynamic part of the motion at site $s, D_{00}^{(n)}$ is the Wigner rotation matrix element, with the orientation specified by principal axis of deuteron quadrupolar interaction tensor relative to the laboratory frame. $\rangle$ means taking the average over the space of motion not restricted by the adsorptive interaction, and also the orientation distribution of adsorbate on MCM-41 surface.

To describe the motion of the adsorbate in the slow motion sites, we use a modification of the cone model of Brainard and Szabo. ${ }^{21}$ This facilitates the calculation of the time-correlation function and the spectral-density functions of the adsorbed water molecule. The modified cone model is depicted schematically in Figure 2. In the present work, for the dynamics of the adsorbed water molecule we have ignored the overall reorientation of the adsorbate molecule from their model because of the restricted motion caused by adsorption. Then the spectral density function is modified after omitting the overall reorientation ${ }^{25}$ as follows


Figure 2. The modified cone model for $\mathrm{D}_{2} \mathrm{O}$ molecule adsorption in site $s$ used in the present studies. $\tau_{w}$ is correlation time of restricted wobbling motion, and $\tau_{i}^{s}$ is correlation time of internal rotation motion.

$$
\begin{gather*}
j_{n}^{s}=4 S^{2}\left(d_{10}^{2}(\beta)\right)^{2} \frac{D_{i}}{D_{i}^{2}+\left(n \omega_{o}\right)^{2}}+ \\
4 S^{2}\left(d_{20}^{2}(\beta)\right)^{2} \frac{4 D_{i}}{\left(4 D_{i}\right)^{2}+\left(n \omega_{\mathrm{o}}\right)^{2}}+ \\
2\left(d_{00}^{2}(\beta)\right)^{2} \frac{\left(1-S^{2}\right)\left[6 D_{w} /\left(1-S^{2}\right)\right]}{\left[6 D_{w} /\left(1-S^{2}\right)\right]^{2}+\left(n \omega_{\mathrm{o}}\right)^{2}}+ \\
4\left(d_{10}^{2}(\beta)\right)^{2} \frac{\left(1-S^{2}\right)\left[D_{i}+5 D_{w} /\left(1-S^{2}\right)\right]}{\left[D_{i}+5 D_{w} /\left(1-S^{2}\right)\right]^{2}+\left(n \omega_{o}\right)^{2}}+ \\
4\left(d_{20}^{2}(\beta)\right)^{2} \frac{\left(1-S^{2}\right)\left[4 D_{i}+2 D_{w} /\left(1-S^{2}\right)\right]}{\left[4 D_{i}+2 D_{w} /\left(1-S^{2}\right)\right]^{2}+\left(n \omega_{\mathrm{o}}\right)^{2}} \tag{10}
\end{gather*}
$$

where the internal rotation of $\mathrm{D}_{2} \mathrm{O}$ has a correlation time $\tau_{i}^{s} \equiv$ $1 /\left(4 D_{i}\right)$, and the wobbling motion of the $\mathrm{D}_{2} \mathrm{O}$ molecule along its $C_{2}$ axis has a correlation time $\tau_{w} \equiv 1 /\left(6 D_{w}\right), d^{2}{ }_{m n}(\beta)$ are elements of the reduced Wigner rotation matrix and $\beta$ is the fixed angle between the $\mathrm{C}_{2}$ axis of $\mathrm{D}_{2} \mathrm{O}$ molecule and principal axis of the residual quadrupolar interaction, i.e., the $O-D$ direction. In the present study, we consider the interaction of the bound water molecule with the silanol group only along the $C_{2}$ axis of water and $\beta=54^{\circ}$. The wobbling motion of $\mathrm{D}_{2} \mathrm{O}$ about the $\mathrm{C}_{2}$ axis is assumed to be within a cone, having a correlation time $\tau_{w}$ (cf. Figure 2). The orientational distribution of the cone in the molecular frame may be expressed by an order parameter $S \equiv\left\langle D_{00}^{(2)}\right\rangle_{m}$ where the average is over the orientational distribution due to the wobbling motion and also due to the available site arrangement for water to interact with the silanol groups on the pore surface of MCM-41. When $S=$ 0 the bound water molecules have a completely randomized orientational distribution and for $S=1$ all the bound water molecules are inclined at an angle along the $C_{2}$ axis with respect to the adsorption site. With this assumption, the second terms in eq 9 can be readily evaluated as $\left\langle D_{00}^{(2)}\right\rangle=S D_{00}^{(2)}(\theta)$, where axial symmetry of the adsorption interaction and site distribution are assumed and the third term in eq 9 can be deduced from the term $\left\langle D_{00}^{(4)}\right\rangle=\left\langle D_{00}^{(4)}\right\rangle_{m} D_{00}^{(4)}(\theta)$. To evaluate $\left\langle D_{00}^{(4)}\right\rangle$ in terms of $S$, a specific distribution for the cone model is needed. For an isotropic distribution with a cone angle of $b$, Brainard and Szabo ${ }^{21}$ obtained $S=1 / 2 \cos b(1+\cos b)$. Using this, we then obtain $\left\langle D_{00}^{(4)}\right\rangle_{m}=S\left(7 S / 2-7(1+8 S)^{1 / 2}+1\right)$. Hence, with this particular model one may evaluate the spectral density functions for site $s$.

Order Parameter and Residual Quadrupolar Interaction. It is noted that $\omega_{q m}$ is the maximum residual quadrapolar interaction for a $\mathrm{D}_{2} \mathrm{O}$ molecule adsorbed on the adsorption site with maximum strength of interaction. For $\mathrm{D}_{2} \mathrm{O}$ quadrapolar interaction, $\omega_{q m}=3 / 4 \chi_{s}$, where $\chi_{s}$ is the quadrapolar coupling constant.

In the formulation, both the $S$ and $\omega_{q}$ represent the same essential quantity of the system, i.e., their respective quantities are averaged over the same coordinates of molecular motion and the orientational distribution of adsorbate. Therefore, the residual quadrupolar anisotropy, $\omega_{q}$, is proportional to the order parameter, $S$, with the relation

$$
\begin{equation*}
S \equiv \omega_{q} / \omega_{q m} \tag{11}
\end{equation*}
$$

where $S$ characterizes the strength of residual interaction for adsorbed water molecules ranging in the limits $0 \leq S \leq 1$.

Calculation of Line Shape in $\mathbf{T}_{\mathbf{1}}$ Process. The above theory may be used in simulating the signal of the free induction decay after the inversion recovery pulse sequence (i.e., $\pi-\tau^{\prime}-\pi / 2-$ Acq.). The equilibrium multipoles can be calculated from the corresponding density matrix elements as $T_{10, \text { eq }} \equiv\left(\gamma \eta \mathrm{B}_{0} I(I+\right.$ $1) / 3 \sqrt{2} k T$ ), where $\gamma$ is the gyromagnetic ratio, $k$ is the Boltzmann constant, and $B_{0}$ is the Zeeman field.

Since we have exchanging species, the individual multipoles must be population-weighed. The effects of the $\pi$ pulse are then calculated, and thus immediately after the $\pi$ pulse and including population-weighted multipoles as the initial conditions before evolution of $\tau^{\prime}$ we have $T_{10}^{f_{1}}(0)=-P_{f_{1}} T_{10, \mathrm{eq}}, T_{10}^{f_{2}}(0)=$ $-P_{f_{2}} T_{10, \text { eq }}$, and $T_{10}^{s}(0)=-P_{s} T_{10, \text { eq }}$.

For the calculation of $T_{1}$, eq 6 is used to follow the evolution of the longitudinal magnetization during the delay time $\tau^{\prime}$. In eq $6, R_{10}^{s}$ is calculated from eq 7 with the help of eqs 9 and 10 for the slow motion site. $R_{10}^{f_{1}}$ and $R_{10}^{f_{2}}$ is calculated from eq 7 with the help of eq 8 for the fast motion site. An isotropic distribution of $\theta$ is applied to simulate the situation of the random orientational distribution of pore systems relative to the field direction in the powder sample. Then the longitudinal magnetization after the delay time $\tau^{\prime}$ can be evaluated as

$$
\begin{equation*}
M_{\mathrm{z}}\left(\tau^{\prime}\right) \propto \int_{0}^{\pi}\left(T_{10}^{f_{1}}\left(\tau^{\prime}\right)+T_{10}^{f_{2}}\left(\tau^{\prime}\right)+T_{10}^{s}\left(\tau^{\prime}\right)\right) \sin \theta d \theta \tag{12}
\end{equation*}
$$

The calculation is performed by numerical integration, with the inversion-recovery spectra evaluated from $M_{\mathrm{z}}$ at various $\tau^{\prime}$ described previously. ${ }^{24}$

Simulation of Double Quantum Spectra. The first $\pi / 2$ pulse of the DQF sequence transforms the Zeeman order $T_{10, \text { eq }}$ into single-quantum coherence $T_{11}$, which then generates $T_{21}$ in the evolution time $\tau$ via the residual quadrupolar interaction given in eq 2 . Equation 3 is used to calculate $T_{11}^{f_{1}}, T_{21}^{f_{1}}, T_{11}^{f_{2}}, T_{21}^{f_{2}}, T_{11}^{s}$, and $T_{21}^{s}$ during the evolution time $\tau$ with the initial conditions $T_{11}^{f_{1}}(0)=(1 / \sqrt{2}) P_{f_{1}} T_{10, \mathrm{eq}}, T_{11}^{f_{2}}(0)=(1 / \sqrt{2}) P_{f_{2}} T_{10, \mathrm{eq}}, T_{11}^{s}(0)=(1 /$ $\sqrt{2}) P_{s} T_{10, \mathrm{eq}}$, and $T_{21}^{f_{1}}(0)=T_{21}^{f_{2}}(0)=T_{21}^{s}(0)=0$. In eq $3, R_{11}^{s}$ and $R_{21}^{s}$ are calculated from eq 5 with the help of eqs 9 and 10 according to the distribution of $\theta$ for the slow motion site, and $R_{11}^{f_{1}}, R_{21}^{f_{1}}, R_{11}^{f_{2}}$, and $R_{21}^{f_{2}}$ are calculated from eq 5 with the help of eq 8 for the fast-motion site. The relaxation rate associated with $T_{22}^{s}$, denoted $R_{22}^{s}$, is found to be much slower than $R_{21}^{s} \cdot{ }^{15} \mathrm{We}$ have also made a similar observation in our present study where $R_{22}^{s} \approx 10^{2} \mathrm{~s}^{-1} \ll R_{21}^{s} \approx 3 \times 10^{3} \mathrm{~s}^{-1}$. Thus, in a period of $\delta=$ $10 \mu \mathrm{~s}, T_{22}^{s}$ coherence is maintained. Immediately after the third $\pi / 2$ pulse with DQF phase cycling, the signal is proportional to the double-quantum coherence $T_{21}^{f_{1}}(\tau), T_{21}^{f_{2}}(\tau)$, and $T_{21}^{s}(\tau)$. Thus
with the initial condition $T_{21}^{f_{1}}=T_{21}^{f_{1}}(\tau), T_{21}^{f_{2}}=T_{21}^{f_{2}}(\tau), T_{21}^{s}=$ $T_{21}^{s}(\tau)$, and $T_{11}^{f_{1}}=T_{11}^{f_{2}}=T_{11}^{s}$, eq 3 is used again to calculate the free induction decay (FID) during the acquisition time $t$. In analogy to eq 12, the FID signal and the DQF spectra are obtained as described in the previous section. The DQF spectra may also be obtained by using a Fourier transform procedure. ${ }^{24}$

## Experimental Section

Sample Preparation. Cetyltrimethylammonium bromide (CTAB) (Acros, 99\%) was dissolved in distilled water at 35 ${ }^{\circ} \mathrm{C}$ under stirring. To it a solution of sodium silicate (Aldrich, $14 \% \mathrm{NaOH}$ and $27 \% \mathrm{SiO}_{2}$ ) was added and stirred for 20 min . The pH of the solution was adjusted to 10 by dropwise addition of 1.2 M sulfuric acid (Acros). The molar composition of the gel mixture was $1.00 \mathrm{SiO}_{2} / 0.35 \mathrm{CTAB} / 0.28 \mathrm{H}_{2} \mathrm{SO}_{4} / 100 \mathrm{H}_{2} \mathrm{O}$. The gel mixture was further stirred for 1 h . The resulting mixture was transferred to a Teflon ${ }^{\mathrm{q}}$-lined autoclave and then heated at $100^{\circ} \mathrm{C}$ for 48 h . The final solid product obtained after filtration, was washed with distilled water, dried in air at room temperature, and calcined at $560^{\circ} \mathrm{C}$ for 6 h .

X-ray powder diffraction data of the MCM-41 was collected on a Scientag XI diffractometer using $\mathrm{CuK}_{\propto}$ radiation. The average pore diameter was estimated from the $\mathrm{d}_{100}$-spacing of the X-ray diffractograms. The surface-area and pore-size measurements were performed on a homemade high vacuum system. Assuming the thickness of the walls to be 1 nm , the estimated average pore diameter is $3.38 \pm 0.17 \mathrm{~nm}$. The sample was degassed at 590 K and 1 mPa for 16 h . The sample has BET surface areas of $900 \pm 45 \mathrm{~m}^{2} \mathrm{~g}^{-1}$, which is a characteristic of mesoporous material.

The MCM-41 was initially dried under a vacuum of $10^{-5}$ Torr at 650 K for at least 16 h . Then it was transferred into a 8 mm i.d. tube approximately $40-\mathrm{mm}$ long. An appropriate amount of $\mathrm{D}_{2} \mathrm{O}$ was introduced to get $\mathrm{D}_{2} \mathrm{O} / \mathrm{MCM}-41$ weight ratios of 11,7 , and $4 \mathrm{D}_{2} \mathrm{O}$. These are denoted as samples $\mathrm{A}, \mathrm{B}$, and C , respectively. Then the sample tubes were sealed and kept at 373 K for at least 24 h to ensure a homogeneous distribution of adsorbate in the sample before the NMR measurement. In case of the structure changing of MCM-41, all NMR measurement had were within one month of making the sample.

NMR Measurement. The ${ }^{2} \mathrm{H}$ NMR measurements were performed on Bruker MSL-500 and MSL-300 spectrometers operating at $76.78 \mathrm{MHz}(11.75 \mathrm{~T})$ and $46.07 \mathrm{MHz}(7.05 \mathrm{~T})$ with a $90^{\circ}$ pulse of 30 and $20 \mu \mathrm{~s}$, respectively. The receiver recovery time is less than $10 \mu \mathrm{~s}$, and probe dead time is $10 \mu \mathrm{~s}$. For the quadrupolar echo measurement, a $90^{\circ}$ pulse of $9 \mu \mathrm{~s}$ and a delay of $5 \mu$ s were used with the high power unit. The line shape in single pulse experiment is not significantly different from that in a quadrupolar-echo measurement for the $\mathrm{D}_{2} \mathrm{O}$ samples at 210 K . Thus, single pulse experiments were used to obtain the spectra for analyses.

The pulse sequence for DQF NMR is shown in Figure 3. We used the following ${ }^{2} \mathrm{H}$ NMR acquisition parameters 125 kHz spectral width, 16 K data points, and $\mathrm{NS}=20000$ scans per spectrum. A delay of at least $5 \mathrm{~T}_{1}$ was allowed between scans for the $T_{1}$ and DQF spectra. Phase cycling was used. The temperature was controlled to a precision of $\pm 0.1^{\circ} \mathrm{C}$ and was calibrated using methanol. The magnetic inhomogeneity was estimated by comparing Hahn spin-echo and line width measurements. The magnetic inhomogeneity was found to account for less than 5 Hz of the observed line width at halfheight in the spectra. The longitudinal relaxation measurements were obtained using the inversion-recovery pulse sequence.


Figure 3. Pulse sequence and coherence-transfer pathway used in DQF experiment. $T_{l q}$ represents the irreducible tensorial component with rank $l$ and coherence $q . \tau$ is the DQ evolution time for double quantum coherence and $\delta$ was set at $10 \mu$ s.
(a)

(b)


Figure 4. Experimental (top) and simulated (bottom) ${ }^{2} \mathrm{H}$ double quantum filtered spectra at various evolution times cited for (a) sample $B$ and (b) sample $C$ at 260 K . The DQ evolution times are cited underneath the spectra. The spectra were acquired at 76.78 MHz .

Reproducibility of relaxation data has been checked to examine whether equilibrium is reached in the pore systems over a period of two months.

## Results

The comparison of simulation with experimental spectra is presented in Figure 4 and Figure 5. Knowledge of the value of quadrupolar coupling constant $(\mathrm{QCC})$ for $\mathrm{D}_{2} \mathrm{O}$ is important when analyzing ${ }^{2} \mathrm{H}$ NMR spectra. Several NMR measurements ${ }^{26-31}$ and theoretical calculations ${ }^{34}$ have reported the values of $\mathrm{D}_{2} \mathrm{O}$ quadrupolar coupling constant for different structures. Molecular dynamics simulation of liquid water indicates that the values usually vary with the geometry of $\mathrm{D}_{2} \mathrm{O}$, in particular it strongly


Figure 5. Experimental (top) and simulated (bottom) ${ }^{2} \mathrm{H}$ spectra of inversion recovery experiments at 260 K cited for (a) sample B and (b) sample C at 76.78 MHz .
depends both on intra- and intermolecular $\mathrm{O}-\mathrm{D}$ bond distance. ${ }^{32}$ The range of quadrupolar coupling constant is from 180 to 373 $\mathrm{kHz} .{ }^{32}$ From NMR studies, it is observed that the quadrupolar coupling constant of ice is between 213 and $226 \mathrm{kHz} .{ }^{26-34}$ For liquid-phase water at 300 K , the values of the quadrupolar coupling constant is between 208 and $259 \mathrm{kHz} .{ }^{26-34}$ In MCM41 , some fraction of water molecules are adsorbed on the surface and the rest are condensed by capillary action. QCC values and internal rotation correlation time would affect both the null point of the inversion-recovery spectra and the line width of SQ spectra. As described below, we find out that 213 kHz is the best QCC value of determination for water molecules in site $s$. Water molecules present in sites $f_{1}$ and $f_{2}$ as similar to bulk water due to its isotropic motion, and thus we take $\chi / 2 \mathrm{p}=256$ kHz for sites $f_{1}$ and $f_{2}$ in accordance with the ab initio calculation ${ }^{32}$ and NMR measurements. ${ }^{33}$

Evaluation of the Order Parameter. As shown in Figure 6a for sample A at a temperature below 240 K , the spectra demonstrate an edge splitting $\sim 4 \mathrm{kHz}$, which represents the anisotropically moving adsorbed $\mathrm{D}_{2} \mathrm{O}$ molecules. The invariance of the line shape with temperature indicates the existence of a single water component, the "bound water". It possesses a residual quadrupolar interaction $\omega_{q} / 2 \pi \equiv 3 / 4 \chi_{s} S / 2 \pi \sim 4 \mathrm{kHz}$. Accordingly, the magnitude of $S$ may thus be evaluated with the choice of a $\chi_{s}$ value between 180 and 373 kHz . The relative intensity of the wiggling peaks in DQF spectra at DQ evolution time, $500 \mu \mathrm{~s}$, is only sensitive to $S$, e.g., Figure 4a, sample B at 260 K. Furthermore, the magnitude can be reconfirmed by the change in the negative peak intensity at different DQ evolution time. Besides, the obtained values of $\chi_{s}$ and $S$ can be justified


Figure 6. Experimental ${ }^{2} \mathrm{H} \mathrm{SQ}$ spectra at 76.78 MHz from temperature range of 200 K to 273 K for (a) sample A, (b) sample B, and (c) sample C.


Figure 7. Experimental ${ }^{2} \mathrm{H}$ DQF spectra at 76.78 MHz from temperature range of 200 to 273 K for (a) sample A, (b) sample B, and (c) sample C with different DQ evolution times. For a given temperature, the six DQF spectra from left to right are obtained with DQ evolution time, $\tau$, given by $80,160,220,280,400$, and $500 \mu$ s, respectively.
also from the edge splitting in the SQ spectra. It yields $S=$ $0.022 \pm 0.001$ and then $\chi_{s}=213 \pm 10 \mathrm{kHz}$. It is believed that $\chi_{s}$ has negligible temperature dependency, and we take this quantity as a constant throughout the calculation in this work.

Determination of $\boldsymbol{\tau}_{w}$ from DQF Spectra. In Figure $7{ }^{2} \mathrm{H}$ DQF NMR spectra for samples A, B, and C at temperatures $240,259,260$, and 273 K are presented at frequency of 76.78 MHz . Field-independent DQF spectra were found for all samples studied. The intensity profile of the central peaks with increasing DQ evolution times may be utilized to determine $\tau_{w}$.

Determination of $\boldsymbol{P}_{f_{1}}, \boldsymbol{P}_{f_{2}}, \boldsymbol{\tau}_{\mathrm{ex}}{ }^{f_{1} s}$, and $\boldsymbol{\tau}_{\mathrm{ex}}{ }^{f_{1} f_{2}}$. Figure 4 represents the two characteristics of DQF spectra which are very useful in
determining $P_{f_{1}}$ and $P_{s}$ : (i) at shorter DQ evolution times, $\tau=$ 80 to $220 \mu \mathrm{~s}$, the sharp embedded tip of the central peak can be used to determine $P_{f_{1}}$. (ii) at longer DQ evolution times, $\tau=$ 220 to $500 \mu \mathrm{~s}, P_{f_{1}}$ could affect the intensity of central peak through an exchange process. For instance, in the DQF spectra of sample C in Figure 4b, the tips embedded in the central peaks demonstrate narrower line widths than those in low loading samples at higher temperatures. Thus, the contribution of the $\mathrm{D}_{2} \mathrm{O}$ in site $f_{1}$ through exchange with the $\mathrm{D}_{2} \mathrm{O}$ in site $s$ gives rise to the appearance of sharp tips in peaks. One may utilize this feature to determine the exchange rate $\tau_{\mathrm{ex}}^{f_{1} s}$ and the population ratio between site $f_{1}$ and $s$. Utilizing the parameters given above, one may obtain the population of site $f_{2}$ and also the value $\tau_{\mathrm{ex}}^{f_{\mathrm{f}} f_{2}}$ by fitting the central peak in the SQ spectra. Furthermore, we can check $P_{f_{1}}, P_{s}$, and $\tau_{\mathrm{ex}}^{f_{1} s}$, predetermined from DQF spectra, may be contributed by simulation of the SQ line shape. In particular, $\tau_{\mathrm{ex}}^{f_{1} s}$ is sensitive to the line shape in the shoulder region. With mutual successive trials of $P_{f_{1}}, P_{f_{2}}$, $P_{s}, \tau_{\mathrm{ex}}^{f_{1} s}$, and $\tau_{\mathrm{ex}}^{f_{\mathrm{f}} f_{2}}$, a distinct set of parameters may be determined unambiguously. The values of $P_{s}$ determined for the system are given in Tables $1-3$ in terms of $P_{f_{1}} / P_{s}$ and $P_{f_{2}} / P_{s}$ ratios.

Determination of $\boldsymbol{\tau}_{c} f_{1}, \boldsymbol{\tau}_{c}{ }^{f_{2}}$, and $\boldsymbol{\tau}_{i}^{s}$ from $\mathbf{T}_{1}$ Spectra. In the inversion-recovery experiment, the line shapes of inversionrecovery spectra depend on temperature. By analysis of $\mathrm{T}_{1}$ data, $\tau_{c}^{f_{1}}, \tau_{c}^{f_{2}}$, and $\tau_{i}^{s}$ may be determined. The relative population of $\mathrm{D}_{2} \mathrm{O}$ in each site may be found by line shape analysis, as described previously. The comparisons of simulated line shapes in $T_{1}$ measurements are given in Figure 4.

Sample A. Figure 6a shows the SQ spectra of sample A from 200 to 273 K . The central peak has contributions from sites $f_{1}$ and $f_{2}$, and the solidlike band is from molecules at site $s$. It is observed that the central peak decreases with decreasing temperature from 270 to 250 K and totally disappears at 240 K , with only the solidlike band at lower temperatures. The peak broadening in the shoulder region with decreasing temperature indicates slower molecular motions of water molecules, a result corroborated by the $T_{1}$ measurement. Accordingly, we obtained order parameter $S=0.020 \sim 0.026$ depending on temperatures for sample A. Figure 7a shows the DQF spectra from 200 to 273 K . The $\tau_{w}$ in sample A is unaffected by the temperature variation from 220 to 273 K . The DQF spectral profiles at 200 and 210 K differ from those at elevated temperatures. The drastic drop in DQF spectral intensity with DQ evolution time represents a slower $\tau_{w}$. The results listed in Table 1 shows the magnitude of $\tau_{w}$ is approximately $10^{-5} \mathrm{~s}$. The motion is too slow to apply a second-order perturbation treatment within the validity of the Redfield relaxation scheme. However, the difference in magnitudes still shows the relative slowness of the motion.

Sample B. The water loading in sample B is higher than in sample A. From Figure 6b, it is obvious that the central peak of the SQ spectra of sample B is larger than sample A. In Figure 7b from 240 to 273 K , DQF spectra of sample B also present a larger central peak at $\tau=220$ to $500 \mu$ s than those of sample A at the same $\tau$ values. As mentioned above, the central peak of DQF spectra result from a contribution of water in site $f_{1}$ through an exchange process. Although the intensity of the central peak in DQF spectra is different, in Table 2, $\tau_{w}$ remains around $10^{-5} \mathrm{~s}$ from 220 to 273 K . The water in site $f_{1}$ shows up at a temperature higher than 230 K . There is a significant increase of 1 order of magnitude in the internal rotation of water molecules at site $f_{1}$ in the range from 240 to 250 K . Internal rotation of water molecules at site $s$ also changes significantly from 230 to 240 K . Even at temperatures higher than 250 K ,

TABLE 1: Parameters Used in Simulation for Sample A

| temp | $P_{f_{1}} / P_{s}$ | $P_{f_{2}} / P_{\mathrm{s}}$ | $\tau_{c}^{f_{1}}$ | $\tau_{c}^{f_{2}}$ | $\tau_{w}$ | $\tau_{i}^{\text {s }}$ | $\tau_{\text {ex }}^{f_{1} \mathrm{~s}}$ | $\tau_{\mathrm{ex}}^{\mathrm{f}_{1} f_{2}}$ | $S$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 200 K | * ${ }^{\text {a }}$ | * | * | * | $>10^{-4}$ | $1.5 \pm 0.1 \times 10^{-10}$ | * | * | $0.026 \pm 0.001$ |
| 210 K | * | * | * | * | $>10^{-4}$ | $1.2 \pm 0.1 \times 10^{-10}$ | * | * | $0.026 \pm 0.001$ |
| 220 K | * | * | * | * | $2.5 \pm 0.5 \times 10^{-5}$ | $9.5 \pm 0.5 \times 10^{-11}$ | * | * | $0.026 \pm 0.001$ |
| 230 K | * | * | * | * | $2.5 \pm 0.6 \times 10^{-5}$ | $8.5 \pm 0.4 \times 10^{-11}$ | * | * | $0.025 \pm 0.001$ |
| 240 K | * | * | * | * | $2.3 \pm 0.3 \times 10^{-5}$ | $7.5 \pm 0.3 \times 10^{-11}$ | * | * | $0.025 \pm 0.001$ |
| 250 K | $<0.01$ | * | * | * | $3.2 \pm 0.8 \times 10^{-5}$ | $3.8 \pm 0.2 \times 10^{-11}$ | * | * | $0.022 \pm 0.001$ |
| 260 K | 0.01 | * | * | * | $2.5 \pm 0.5 \times 10^{-5}$ | $3.8 \pm 0.2 \times 10^{-11}$ | $>10^{-3}$ | * | $0.020 \pm 0.001$ |
| 273 K | 0.18 | * | $4.0 \pm 0.2 \times 10^{-10}$ | * | $4.0 \pm 0.4 \times 10^{-5}$ | $2.0 \pm 0.1 \times 10^{-11}$ | $1.5 \pm 0.1 \times 10^{-4}$ | * | $0.018 \pm 0.001$ |

${ }^{a}$ Asterisks (*) indicate the physical phenomenon of the represented parameter was not observed.
TABLE 2: Parameters Used in Simulation for Sample B

| temp | $P_{f_{1}} / P_{\mathrm{s}}$ | $P_{f_{2}} / P_{\mathrm{s}}$ | $\tau_{c}^{f_{1}}$ | $\tau_{c}^{f_{2}}$ | $\tau_{\text {w }}\left(\times 10^{-5}\right)$ | $\tau_{i}^{\text {s }}$ | $\tau_{\text {ex }}^{f_{1} \mathrm{~s}}$ | $\tau_{\mathrm{ex}}^{f_{\text {f }}}\left(\times 10^{-3}\right)$ | $S$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 K | *a | * | * | * | $6.0 \pm 0.2$ | $1.4 \pm 0.1 \times 10^{-10}$ | * | * | $0.027 \pm 0.001$ |
| 220 K | * | * | * | * | $3.0 \pm 0.2$ | $1.2 \pm 0.1 \times 10^{-10}$ | * | * | $0.026 \pm 0.001$ |
| 230 K | 0.15 | * | $4.0 \pm 0.2 \times 10^{-9}$ | * | $2.8 \pm 0.3$ | $1.0 \pm 0.1 \times 10^{-10}$ | $3.0 \pm 0.2 \times 10^{-3}$ | * | $0.025 \pm 0.001$ |
| 240 K | 0.41 | * | $1.2 \pm 0.1 \times 10^{-9}$ | * | $1.5 \pm 0.1$ | $5.2 \pm 0.3 \times 10^{-11}$ | $6.3 \pm 0.3 \times 10^{-4}$ | * | $0.024 \pm 0.001$ |
| 245 K | 0.43 | 0.01 | $4.3 \pm 0.2 \times 10^{-10}$ | * | $1.2 \pm 0.1$ | $4.0 \pm 0.2 \times 10^{-11}$ | $5.0 \pm 0.3 \times 10^{-4}$ | * | $0.023 \pm 0.001$ |
| 250 K | 0.46 | 0.08 | $2.0 \pm 0.1 \times 10^{-10}$ | $2.0 \pm 0.1 \times 10^{-10}$ | $1.2 \pm 0.1$ | $5.2 \pm 0.3 \times 10^{-11}$ | $3.5 \pm 0.2 \times 10^{-4}$ | $1.0 \pm 0.1$ | $0.023 \pm 0.001$ |
| 260 K | 0.47 | 0.09 | $4.0 \pm 0.2 \times 10^{-11}$ | $7.0 \pm 0.4 \times 10^{-11}$ | $1.5 \pm 0.1$ | $5.2 \pm 0.3 \times 10^{-11}$ | $3.0 \pm 0.2 \times 10^{-4}$ | $1.0 \pm 0.1$ | $0.022 \pm 0.001$ |
| 273 K | 0.47 | 0.20 | $9.0 \pm 0.5 \times 10^{-12}$ | $2.0 \pm 0.1 \times 10^{-11}$ | $2.5 \pm 0.1$ | $4.3 \pm 0.2 \times 10^{-11}$ | $1.5 \pm 0.1 \times 10^{-4}$ | $1.0 \pm 0.1$ | $0.020 \pm 0.001$ |

${ }^{a}$ Asterisk (*) indicates the physical phenomenon of the represented parameter was not observed.
TABLE 3: Parameters Used in Simulation for Sample C

| temp | $\begin{gathered} P_{f_{1} /} / \\ P_{\mathrm{s}} \end{gathered}$ | $\begin{gathered} P_{f_{2}} / \\ P_{s} \end{gathered}$ | $\tau_{c}^{f_{1}}$ | $\tau_{c}^{f_{2}}$ | $\tau_{\text {w }}$ | $\tau_{i}^{s}$ | $\tau_{\text {ex }}^{f_{1} s}$ | $\tau_{\mathrm{ex}}^{\mathrm{f}_{1} \mathrm{f}_{2}}$ | $S$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 K | *a | * | * | * | $5.0 \pm 0.2 \times 10^{-5}$ | $1.2 \pm 0.1 \times 10^{-10}$ | * | * | $0.025 \pm 0.001$ |
| 220 K | 0.06 | * | $7.0 \pm 0.4 \times 10^{-9}$ | * | $3.5 \pm 0.2 \times 10^{-5}$ | $1.2 \pm 0.1 \times 10^{-10}$ | $6.0 \pm 0.3 \times 10^{-3}$ | * | $0.025 \pm 0.001$ |
| 230 K | 0.56 | 0.05 | $5.0 \pm 0.3 \times 10^{-9}$ | $5.0 \pm 0.3 \times 10^{-9}$ | $3.0 \pm 0.2 \times 10^{-5}$ | $8.0 \pm 0.4 \times 10^{-11}$ | $6.0 \pm 0.3 \times 10^{-3}$ | > 1.0 | $0.024 \pm 0.001$ |
| 235 K | 0.64 | 0.18 | $3.8 \pm 0.2 \times 10^{-9}$ | $3.8 \pm 0.2 \times 10^{-9}$ | $2.0 \pm 0.1 \times 10^{-5}$ | $6.0 \pm 0.3 \times 10^{-11}$ | $9.0 \pm 0.5 \times 10^{-4}$ | $1.0 \pm 0.1 \times 10^{-3}$ | $0.024 \pm 0.001$ |
| 240 K | 0.71 | 0.38 | $4.0 \pm 0.2 \times 10^{-10}$ | $4.0 \pm 0.2 \times 10^{-10}$ | $6.0 \pm 0.5 \times 10^{-6}$ | $6.0 \pm 0.3 \times 10^{-11}$ | $3.5 \pm 0.2 \times 10^{-4}$ | $1.0 \pm 0.1 \times 10^{-3}$ | $0.020 \pm 0.001$ |
| 250 K | 0.86 | 0.52 | $1.3 \pm 0.1 \times 10^{-10}$ | $1.3 \pm 0.1 \times 10^{-10}$ | $2.0 \pm 0.3 \times 10^{-8}$ | $6.0 \pm 0.3 \times 10^{-11}$ | $2.5 \pm 0.1 \times 10^{-4}$ | $1.0 \pm 0.1 \times 10^{-3}$ | $0.020 \pm 0.001$ |
| 260 K | 1.05 | 0.58 | $4.8 \pm 0.3 \times 10^{-11}$ | $4.8 \pm 0.2 \times 10^{-11}$ | $2.0 \pm 0.3 \times 10^{-8}$ | $6.0 \pm 0.3 \times 10^{-11}$ | $2.5 \pm 0.1 \times 10^{-4}$ | $1.0 \pm 0.1 \times 10^{-3}$ | $0.020 \pm 0.001$ |
| 273 K | 1.11 | 0.67 | $5.0 \pm 0.3 \times 10^{-12}$ | $6.0 \pm 0.3 \times 10^{-12}$ | $2.0 \pm 0.3 \times 10^{-8}$ | $6.0 \pm 0.3 \times 10^{-11}$ | $1.5 \pm 0.1 \times 10^{-4}$ | $1.0 \pm 0.1 \times 10^{-3}$ | $0.020 \pm 0.001$ |

${ }^{a}$ Asterisks (*) indicate the physical phenomenon of the represented parameter was not observed.
water at site $f_{2}$ appears only with very low population. This implies that the site $f_{2}$ is distant from site $s$.

Sample C. In Figure 7c, at a temperature higher than 240 K, the central peak of the DQ spectra of sample C at longer DQ evolution times is more intense than those in the same temperature range for samples A and B. As listed in Table 3, $\tau_{w}$ valves at 250 to 273 K are around $10^{-8} \mathrm{~s}, 3$ orders of magnitude faster than $\tau_{w}$ observed in the temperature range from 235 to 273 K . Larger populations of water in site $f_{1}$ and $f_{2}$ are found for sample $C$ than those in samples A and B. Figure 6c illustrates that the central peak of the SQ spectra of sample C disappears at 210 K , lower than for samples A and B. This indicates that the water loading in MCM-41 affects the temperature-dependent behavior of the SQ spectra. In accordance with the simulation results given in Table 3, one finds an abrupt slow-down of $\tau_{\mathrm{c}}^{f_{1}}$ at temperatures below 235 K . The same phenomenon also happens in sample B in the temperature range from 240 to 245 K .

## Discussion

DQF NMR and Water Adsorption of MCM-41. In practice, when referring to real surfaces the formation of adsorption layers involves various complicated surface interactions. For systems containing quadrupolar nuclei the effective adsorption interactions for $\mathrm{D}_{2} \mathrm{O}$ are expressed in terms of residual quadrupolar interactions of deuterium nuclei. Therefore, the study of quadrupolar relaxation may reflect the main feature of adsorption interaction, short-range adsorption interaction. With DQF NMR selective excitation of the spin species possessing residual
quadrupolar interaction address the investigation of these species. However, the long $90^{\circ}$ pulse indeed affects the DQF experiment at the shortest evolution time. For evolution times of $80 \mu \mathrm{~s}$, the effect results in a relatively larger disagreement between the experimental ${ }^{2} \mathrm{H}$ DQF spectra and the simulation in comparison with other DQF spectra with larger evolution times.

From Tables 1 to 3, the total number of water molecules per gram of MCM-41 in each site for samples A, B, and C can be calculated. Figure 8 depicts the plot of the number of water molecules in site $s$ vs temperature. The water signal from site $s$ increases abruptly at temperatures below 240 K for both samples B and C, and it may result from the freezing of water molecules at sites $f_{1}$ and $f_{2}$. Although the number of water molecules in these three samples is too small to form a threedimensional hydrogen-bonding network and to show the bulk properties of ice, the drastic slow of $\tau_{c}^{f_{1}}$ and $\tau_{c}^{f_{2}}$ also implies the freezing process of water in site $f_{1}$ and $f_{2}$, (cf. Tables 2 and 3 ), and the freezing temperature for samples B and C is between 235 and 245 K . Previous studies of the freezing of water in MCM-41 also indicate that the freezing temperature is around 235 to 245 K , depending on the pore size of samples. ${ }^{3,6}$ From Figure 8, we can also conclude that there are about $3 \times 10^{21} \sim$ $4 \times 10^{21}$ water molecules/g of MCM-41 in site $s$. Moreover, the results of fast internal rotations of water molecules in those three sites indicate that sites $f_{1}$ and $f_{2}$ are more isolated than site $s$. It also indicates that the water molecules in sites $f_{1}$ and $f_{2}$ are not directly restricted by the surface. This implies that the only site in contact with the surface is site $s$. It has been


Figure 8. The plot of numbers of water molecules in site $s$ per gram of MCM-41 vs temperature. In samples A, B, and C, the total water molecules per gram of MCM-41 are $3.03 \times 10^{21}, 4.76 \times 10^{21}$, and $8.33 \times 10^{21}$, respectively. For sample A, ( $\square$ ) indicates the numbers of water molecules in site $s$. For sample B, ( ) indicates the numbers of water molecules in site $s$. For sample C, ( $\mathbf{\Delta}$ ) indicates the numbers of water molecules in site $s$.
previously shown that silylated MCM-41 surfaces are very hydrophobic without significant adsorptions of water molecules. ${ }^{35-37}$ The probable adsorption centers on the MCM-41 surface for water adsorption are silanol groups. The total silanol groups on the MCM-41 surface have been investigated by ${ }^{29} \mathrm{Si}$ CPMAS. ${ }^{13}$ The number of silanol groups on MCM-41 surface is around $7.2 \times 10^{20} / \mathrm{g}$ of MCM-41, and in our observation, there are $3 \times 10^{21} \sim 4 \times 10^{21}$ water molecules/g of MCM-41 in site $s$. Thus, the ratio of water molecules to each silanol group is around 4 to 5 at 273 K . Lee et al. indicated that the water molecules in the vicinity of the surfaces participate in three hydrogen bonds with the surface silanol groups. ${ }^{38}$ In our study, some of the water molecules may not interact with silanol groups directly. Recently, Smirnov et al. investigated the monolayer water structure on MCM-41 surface by X-ray diffraction. ${ }^{39}$ Although they have used a higher-surface-area MCM-41 than ours, they found around six water molecules in the vicinity of one silanol group which is in close agreement with our observation.

Order Parameter. As described in our three-site cone model, the order parameter $S$ is the average over the orientational distribution due to the wobbling motion and also due to the available site arrangement for water to interact with the silanol groups on the pore surface of MCM-41. One may estimate the cone angle to be $b=88^{\circ}$. Obviously, it is not feasible for water molecules, adjacent to the surface, to wobble with such a large angle. Hence, one can conclude that the small order parameter is due to the randomized site arrangement for water on the surface of MCM-41. According to molecular dynamics simulations by Lee et al., the orientation of water molecules on the silica surface is almost random, ${ }^{38}$ which implies that the small magnitude of order parameter may mainly result from the orientational distribution of water molecules in site $s$.

The Wobbling Motion of $\mathbf{D}_{2} \mathbf{O}$ in the Slow Site. Most of the values of $\tau_{w}$ listed in Tables 1 to 3 are around $10^{-5} \mathrm{~s}$. Although these values may violate the validity of spin relaxation theory, as we mentioned above, one still can judge the relative slowness of the $\tau_{w}$ process by comparing the intensity profiles of DQF spectra. The differences in $\tau_{w}$ for samples A and B are negligible for all temperatures tested. However, the magnitude of $\tau_{w}$ in sample C varies significantly between 235 and 250 K . This is related to the population differences among sites $f_{1}, f_{2}$, and $s$. Comparing sample B with sample C (cf. Tables 2 and 3 ), the site $f_{2}$ in sample C is more populated with water than that in sample B. Thus, it is reasonable to assert that water in site $f_{1}$ in the former sample might be fully laden. Through collision, the translational diffusion of water in site $f_{1}$ would result in momentum transfer to the bound water molecules, and therefore a fast $\tau_{w}$ process in site $s$. This is consistent with the observation of Takahara et al. that shows that part of the monolayer water has the same dynamic property as capillarycondensed water. ${ }^{3}$

## Conclusion

The dynamics of $\mathrm{D}_{2} \mathrm{O}$ molecules on the MCM-41 surface have been investigated by DQF NMR and $T_{1}$ measurements. The solid-like pattern with 4 kHz edge splitting may reflect the presence of anisotropic interactions on the adsorption of pore sites. Moreover, the DQF spectral analysis provides detailed dynamic information on water mobility and related exchange processes. Thus, the division of water adsorbed on pore surface into slow motion and two fast motion components is consistent with the experimental observations. The amount of water distributed in each site depends on temperature and total water loading. The saturated water loading in site $f_{1}$ increases the wobbling motion of water molecules in site $s$. Thus, translational diffusion of water in site $f_{1}$ results in the influence of a wobbling motion of water molecules in site $s$ through collision.

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## References and Notes

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