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Analysis of ^{2}H NMR spectra of water molecules on the surface of nano-silica material MCM-41: Deconvolution of the signal into a Lorentzian and a powder pattern line shapes

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ABSTRACT

Water ^{2}H NMR signal on the surface of nano-silica material MCM-41 consists of two overlapping resonances. The ^{2}H water spectrum shows a superposition of a Lorentzian line shape and the familiar NMR powder pattern line shape, indicating the existence of two spin components. Exchange occurs between these two groups. Decomposition of the two signals is a crucial starting point to study the exchange process. In this article we have determined these spin component populations along with other important parameters for the ^{2}H water NMR signal over a temperature range between 223 K and 343 K.

1. Introduction

Important information regarding dynamics, structure and exchange rates between different spin groups that might exist in a system can be extracted from their NMR signals. To accomplish this, one often needs to decompose different NMR signal components within the final spectrum. Often, this step is very straightforward as in the case of a spectrum consisting of multiple Lorentzian lines with different chemical shifts. In this case, one usually deals with NMR Free Induction Decay (FID) to decompose the two (or more) spin groups using an equation with bi-exponential or multi-exponential decay rates [1–5]. On the other hand, if the system contains two (or more) spin groups with restricted motions, each with an NMR powder pattern line shape [6], with different splittings [7,8], one usually deals with the frequency data to decompose individual signals. There are cases when the system is comprised of a spin group that is mobile and isotropic in motion in such a way that it exhibits a Lorentzian line shape along with another spin group that is more restricted and anisotropic in motion. The latter might produce an NMR powder pattern such that the final spectrum includes Lorentzian and powder pattern line shapes. Spin exchange can take place between the two groups. This exchange causes the individual NMR signal within the final spectrum to overlap more (with increasing thermal energy), so that the shape of the spectrum changes with temperature. This is the case for the ^{2}H water NMR signal on the surface of MCM-41. Recently, we have shown that water molecules on the surface of nano-silica material MCM-41 are attached to different distinct hydration sites (namely single and hydrogen-bonded silanol, Si–O^{2}H, groups) [9]. In addition to that, we have determined that deuterons of water bound to hydrogen-bonded silanol groups produce the powder pattern in the ^{2}H spectrum, while deuterons of water bound to single silanol groups produce the single Lorentzian line shape. Water molecules bound to single silanol groups are expected to be more mobile (rotation of the water molecule about hydroxyl group bond and motion of the silanol group itself). The mobility of surface silanols has been reported in the literature for the MCM-41 pore surface [10] and similar surfaces [11]. These motions combine to average the quadrupolar Hamiltonian to a considerable degree, which results in a Lorentzian line shape. In this article we decomposed the ^{2}H water NMR spectra into individual signals from different spin components in the system over a temperature range of 223 K–343 K. This is a first step toward the study of the exchange process and to obtain dynamic parameters of different spin species within the sample. A successful simplified method of extracting exchange rates for ^{1}H data (comprising of a Lorentzian and powder pattern line shapes) in clays was previously used [12] by focusing on FID data. In this article we focused on the NMR frequency-domain data.

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2. Theory

The spin Hamiltonian of a deuteron is dominated by the quadruple interaction. The NMR spectrum of a deuteron in the O–^{2}H bond, oriented at a unique angle, θ, relative to the external magnetic field B_o, produces two absorption lines at frequencies [13]:

$$\nu = \nu_o \pm (3/8)\chi(3\cos^2\theta - 1) \quad (1)$$

where ν_o is the Larmor frequency and χ is the quadrupolar coupling constant ($\chi = 213$ kHz for ^{2}H of ^2H_2O [14]). The quadrupolar line splitting ($\Delta\nu_Q$) is related to χ as ($\Delta\nu_Q = (3/4)\chi$). In the case of a sample having different orientations of nuclear interaction vectors (distribution of angles θ), each orientation will produce two absorption lines positioned symmetrically with respect to the Larmor frequency. The final spectrum will be a superposition of these lines. In a powder sample, crystallites are oriented randomly in all possible directions. Therefore different values of cos θ are equally probable and the superposition of the NMR lines arising from individual crystals gives a familiar NMR powder pattern line shape. The final ^{2}H powder spectrum is defined by the following expression [13,15]:

$$f(h) = \begin{Bmatrix} \left(\frac{-h}{\alpha}+1\right)^{-(1/2)}, & -2\alpha < h < -\alpha \\ \left(\frac{-h}{\alpha}+1\right)^{-(1/2)} + \left(\frac{h}{\alpha}+1\right)^{-(1/2)}, & -\alpha < h < \alpha \\ \left(\frac{h}{\alpha}+1\right)^{-(1/2)}, & \alpha < h < 2\alpha \end{Bmatrix} \quad (2)$$

where α is half of the quadrupolar splitting. In a real spectrum, each of these lines is broadened by the interaction of spins with neighboring spins in the sample. Thus, the spikes of the powder pattern will be broadened and smoothened. In order to reproduce the real powder spectrum, a convolution of Eq. (2) with a shape function, $Sh(\nu)$, is often used and the final equation for the powder NMR line shape is given as follows [6]

$$F(\nu) = \int_{-\infty}^{\infty} f(\overline{\nu}-\nu_o)Sh(\nu-\overline{\nu})d\overline{\nu} \quad (3)$$

For the shape function a Gaussian line shape is usually used:

$$Sh(\nu-\overline{\nu}) = (1/\Delta\nu_G\sqrt{2\pi})\exp[-(\nu-\overline{\nu})^2/2(\Delta\nu_G)^2] \quad (4)$$

where $\Delta\nu_G$ is the standard deviation of the line broadening. The powder pattern splitting in the rigid lattice for ^{2}H of ^2H_2O ($\Delta\nu_Q(RL)$) is about 160 kHz [16,17], but this splitting is reduced due to the dynamics of the spin group. In the case of ^{2}H–O (of ^2H_2O) bond rotation with respect to an axis of rotation (see Fig. 1) the splitting reduces according to the following equation [18]:

$$\Delta\nu_Q = \Delta\nu_Q(RL)\left(\frac{3\cos^2\beta - 1}{2}\right)S \quad (5)$$

where S is the order parameter pertaining to the C_2 axis of the water molecule:

$$S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle \quad \text{with} \quad -0.5 \le S \le 1 \quad (6)$$

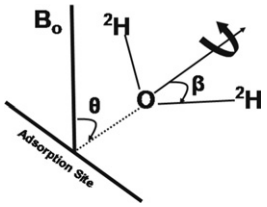

Fig. 1. Simple model of the water molecule at the adsorption site (silanol groups of MCM-41). The rotation frequency of the molecule around the axis of rotation (O–^{2}H of silanol group Si–O–^{2}H) is assumed to be much faster than the rigid-lattice quadrupolar splitting ($\sim$160 kHz). Here $\beta = \sim 53.5^\circ$.

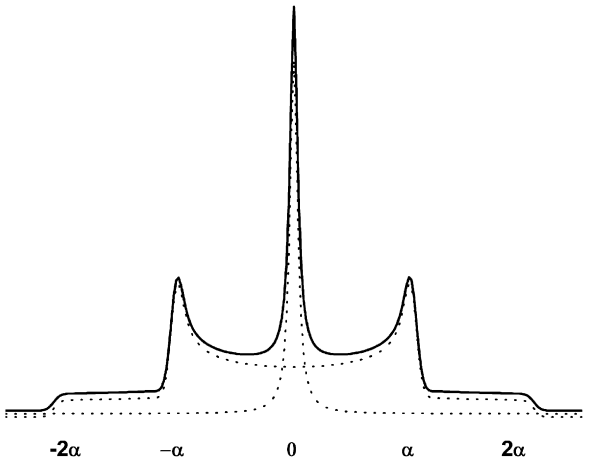

Fig. 2. Simulation of the powder pattern, Lorentzian line shape and the superposition of both into a single spectrum ($\alpha = 5000$ Hz, $\Delta\nu_G = 220$ Hz, $\omega_o = 0$ and $\Delta\nu_L = 365$ Hz).

where the angles are defined in Fig. 1. The motion of the O–^{2}H bond can be seen as a rotation around the C_2 symmetry axis. This motion may be anisotropic, thus an order parameter is introduced.

If the spins are in isotropic motion, the quadrupolar interaction will be averaged. In this case, NMR data in the frequency domain has a Lorentzian line shape spectrum $L(\nu)$, which is given by

$$L(\nu) = (\Delta\nu_L)^2/(4\nu^2 + (\Delta\nu_L)^2) \quad (7)$$

where ν is the frequency and $\Delta\nu_L$ is the standard Full Width at Half Maximum (FWHM) of the Lorentzian peak. In the experimental data used in this study, the Lorentzian line is superimposed at the center of the powder pattern line shape. For the slow exchange limit, where the line shapes are not significantly affected by the exchange, the spectrum can be simulated by adding Eq. (7) to the middle part of Eq. (2), and substituting this into Eq. (3). Fig. 2 shows a simulated spectrum that includes both Lorentzian and a powder pattern line shape obtained using the equations described above.

3. Analysis of experimental data

MCM-41 dry powder is hyroxylated and hydrated using deuterated water (^2H_2O) to study the water on the surface of this material. A low hydration level sample (0.2 monolayer[1]) is used because different surface-water spin components are more distinguishable. Details about the sample preparation can be found in Ref. [9]. The experimental data is taken using a Bruker DMX 500 spectrometer with magnetic field of 11.7 T. Fig. 3 shows the experimental data for only two temperatures, 223 K and 343 K (complete data sets are taken over the temperature range from 223 K to 343 K but are not shown here). According to the shape of the individual spectra in the figure, one can easily state that the spectrum is produced by two spin group contributions [9]. The spectra also show that the powder pattern has a much smaller splitting (around 4 kHz) than that for the rigid lattice case (around 160 kHz). This suggests that the anisotropic motion has a frequency component that is slightly larger than the rigid lattice line-width. Furthermore, it is obvious that as the temperature increases, the splitting of the powder pattern becomes smaller,

[1] To hydrated 1 g of MCM-41 to the one monolayer level, 0.416 g of ^2H_2O is needed.