

Study of Water on the Surface of Nano-Silica Material: An NMR Study

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Abstract—Water ^2H NMR signal on the surface of nano-silica material, MCM-41, consists of two overlapping resonances. The ^2H 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. Chemical exchange occurs between these two groups. Decomposition of the two signals is a crucial starting point for study the exchange process. In this article we have determined these spin component populations along with other important parameters for the ^2H water NMR signal over a temperature range between 223 K and 343 K.

Keywords—Nano-Silica, surface water, NMR

I. 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 consists 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 ^2H 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 ^2H , 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 ^2H 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 ^2H water NMR spectra into individual signals from different spin components in the system over a temperature range of 223 K to 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 ^1H data (comprised 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.

II. THEORY

The spin Hamiltonian of a deuterium nucleus is dominated by the quadruple interaction. The NMR spectrum of a deuteron in the O- ^2H bond, oriented at a unique angle θ , relative to the external magnetic field B_0 , 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 ^2H of $^2\text{H}_2\text{O}$ [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 $\cos\theta$ are equally probable and the superposition of the NMR lines arising from individual crystals gives a familiar NMR powder pattern line shape. The final ^2H powder spectrum is defined by the following expression [13, 15]:

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

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 smoothed. In order to reproduce the real powder spectrum, a convolution of Equation (2) with a shape function, $Sh(v)$, is often used and the final equation for the powder NMR line shape is given as [6]:

$$F(v) = \int_{-\infty}^{\infty} f(\bar{v} - v_o) Sh(v - \bar{v}) d\bar{v}. \quad (3)$$

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

$$Sh(v - \bar{v}) = (1/\Delta v_G \sqrt{2\pi}) \exp[-(v - \bar{v})^2 / 2(\Delta v_G)^2] \quad (4)$$

where Δv_G is the standard deviation of the line broadening. The powder pattern splitting in the rigid lattice for ^2H of $^2\text{H}_2\text{O}$ ($\Delta v_Q(RL)$) is about 160 kHz [16, 17], but this splitting is reduced due to the dynamics of the spin group. In the case of ^2H (of $^2\text{H}_2\text{O}$) bond in rotation with respect to an axis of rotation (see Figure 1) the splitting reduces according to the following equation [18]:

$$\Delta v_Q = \Delta v_Q(RL) S, \quad (5)$$

where S is an order parameter that characterizes the strength of quadrupolar interaction ($0 \leq S \leq 1$). This is defined as

$$S = \langle 3 \cos^2 \beta - 1 \rangle / 2 \quad (6)$$

where β is defined in Figure 1. The motion of the $\text{O}-^2\text{H}$ bond can be seen as a rotation around the C_2 symmetry axis. This motion may be anisotropic, thus an order parameter is introduced.

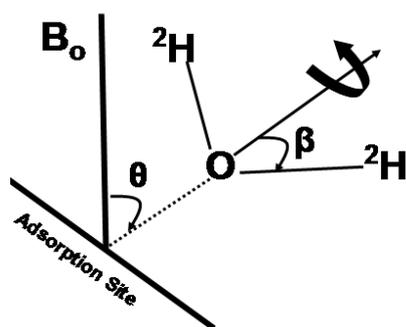


Fig. 1 A simple model of the water molecule at the adsorption site (silanol groups of MCM-41). The rotation frequency of the molecule around the axis of rotation ($\text{O}-^2\text{H}$ of silanol group $\text{Si}-\text{O}-^2\text{H}$) is assumed to be much faster than the rigid-lattice quadrupolar splitting

(~160 kHz). Here $\beta \approx 53.5^\circ$

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

$$L(v) = 2\Delta v_L / (\pi[4v^2 + (\Delta v_L)^2]), \quad (7)$$

where v is the frequency and Δv_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 Equation (7) to the middle part of Equation (2), and substitute this into Equation (3). Figure 2 is a simulated spectrum that includes both Lorentzian and a powder pattern line shape obtained using the equations described above.

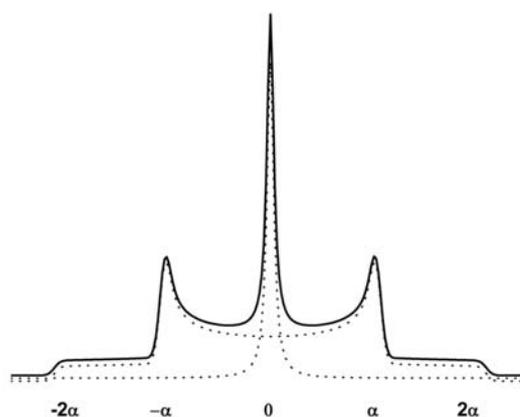


Fig. 2 Simulation of the powder pattern, Lorentzian line shape and the superposition of both into a single spectrum. ($\alpha = 5000\text{Hz}$,

$$\Delta v_G = 220\text{Hz}, \omega_o = 0, \Delta v_L = 365\text{Hz}$$

III. ANALYSIS OF THE DATA

MCM-41 dry powder is hydroxylated and hydrated using deuterated water ($^2\text{H}_2\text{O}$) to study the water on the surface of this material. A low hydration level sample (0.2 monolayer¹) is used because different surface-water spin components are more distinguishable. Details about the sample preparation can be found in reference [9]. The experimental data is taken using a Bruker DMX 500 spectrometer magnetic field of 11.7T. Figure 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).

¹ To hydrated one gram of MCM-41 to the one monolayer level, 0.416 gram of $^2\text{H}_2\text{O}$ is needed.

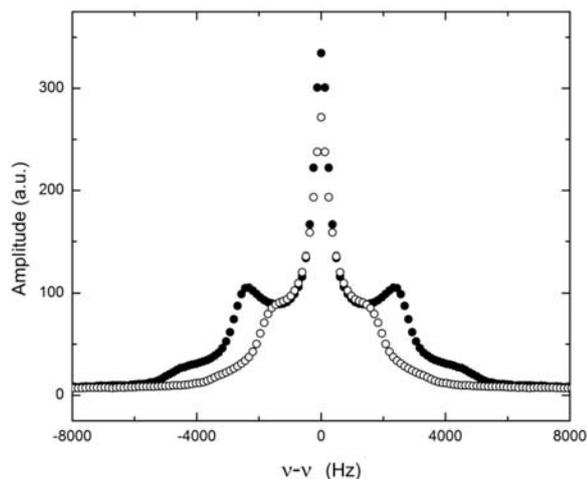


Fig. 3 Experimental ^2H water spectra in MCM-41 for the low hydration sample (0.2 monolayer of $^2\text{H}_2\text{O}$ in dry MCM-41) at two temperatures; 223 K (solid circles) and 343 K (open circles)

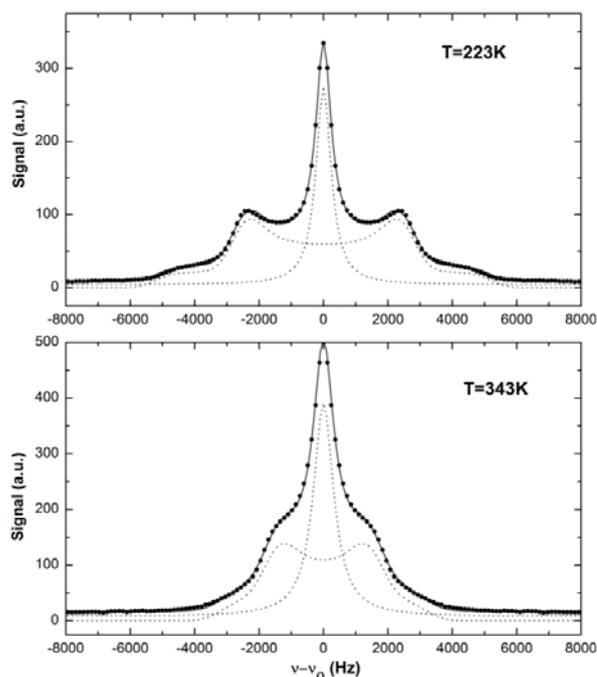


Fig. 4 The raw spectrum (Solid circle, see Figure. 3) and calculated spectrum (Solid line) resulting from the two spin components (Lorentzian line and powder pattern shapes dotted lines).

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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, while the Lorentzian line gets slightly broader. This is an indication that exchange occurs between these water deuterons and that such exchange is thermally activated. In analogy to the two site exchange (for spin $1/2$), in different exchange regimes (slow, intermediate and fast), the line shapes are dramatically changed. The line shapes change little in the slow limit, greatly in the intermediate range that can cause the two individual lines to merge while undergo no change in the fast exchange. In the present data, no broadening is observed in the powder pattern line. This is an indication that the exchange rate is much smaller than the powder splitting. On the other hand, slight changes are observed in the isotropic line shape but, in general, the overall shape of the two signals is retained even at the higher temperature (Figure 3). Based on the assumption of slow exchange regime, the exchange rates parameters are not incorporated within the equations described in the theory part. We have applied the theory described in section 2 to decompose the two water signals. Mathcad 14.0 software was used and the fitting relied on the minimization of the sum of the squares of the deviations between the experimental and the simulated line shapes (reduced Chi-square statistics) to obtain the optimum fitting. The best result of the signal decomposition of the experimental spectra which appeared in Figure 3 is shown in Figure 4.

As seen from Figure 4, an excellent agreement is obtained between the calculated and the experimental data except in regions close to the powder line shape shoulders. In the calculated spectrum, the reduced splitting is used for the powder pattern. This corresponds to an order parameter of $S=0.028$. This value is consistent with that reported in the literature [19] for water deuteron in MCM-41 hydrated to a similar level as the low hydration sample used in this study. A reduction in S of this order of magnitude is expected for water molecules forming hydrogen bonds ($\text{Si-O}^2\text{H}\cdots\text{O}^2\text{H}$) to the surface and undergoing rapid rotation about the hydrogen bond axis (Figure 1). Different parameters are optimized and the time of the optimization depends on the speed of the PC, number of experimental data points, and the initial parameters chosen. The experimental data provides some information regarding some of the initial parameters. Table 1 shows the optimized parameters obtained from the simulation of the data over the temperature range from 223 K to 343 K. The spin populations for both spin components are calculated from the area under the simulated curves and corrected by Curie's law [15]. The two spin percent populations are shown in Figure 5. The trend of the change in populations suggests the exchange between both groups enhanced by temperature. At first glance, this resembles the two-site exchange scenario treated

TABLE I

PARAMETERS OBTAINED FROM DE-CONVOLUTION OF THE DATA. PA AND LA ARE THE SITE POPULATIONS (GIVEN IN PERCENT), CORRECTED BY CURIE'S LAW, AND CALCULATED FROM THE AREAS UNDER THE SIMULATED CURVES OF THE POWDER PATTERN AND LORENTZIAN LINE SHAPES, RESPECTIVELY. THE LABELS L AND Q REFER TO LORENTZIAN AND POWDER PATTERN, RESPECTIVELY

T(K)	PA (%)	LA (%)	Δv_Q (Hz)	Δv_L (Hz)	Δv_G (Hz)
223	61	38	5390	498	421
228	62	38	5320	309	406
233	61	38	5190	284	358
238	61	38	5110	263	352
243	62	37	5040	256	341
248	62	37	4970	248	347
253	63	36	4910	253	347
257	62	37	4840	257	355
263	62	37	4750	273	355
273	62	37	4570	283	373
283	62	37	4410	322	395
293	61	38	4340	388	411
303	60	39	4090	441	426
313	59	40	3880	526	429
323	58	41	3690	613	441
333	56	43	3500	695	439
343	54	45	3360	775	446

extensively in NMR literature [20-22] (shown as the solid lines within the same graph). two-site exchange scenario, at higher exchange rates the two percent populations overlap and when the exchange speeds up more toward the fast exchange, the larger spin component gets much smaller than the smaller component. Of course, one should not use such a model to extract quantitative dynamical information from the present data. Such a model treats the magnetization exchange between two spin components each with its Lorentzian line shape. The dotted line in Figure 5 is obtained by using such a model [23] only to guide the eye, but no quantitative information is extracted from.

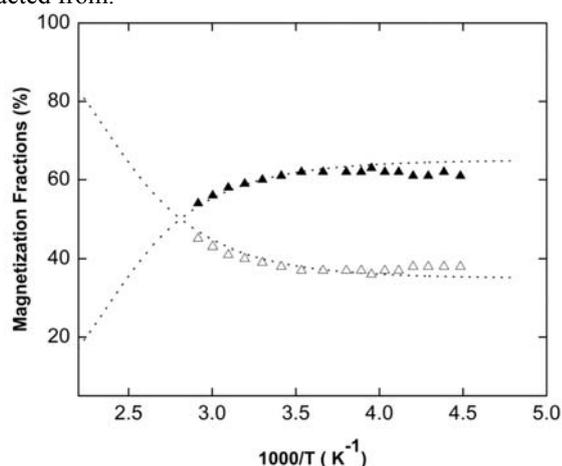


Fig. 5 The two spin populations (given in percent) obtained from the decomposition of the ^2H water experimental data at different temperatures and corrected by Curie's law. The typical exchange between the two spin groups is shown, enhanced by thermal energy. The dotted line is drawn using two-site exchange model

IV. DISCUSSION AND CONCLUSION

We have successfully decomposed the NMR signal from two spin groups of water on the surface of MCM-41. This is an important step toward extracting information regarding spin dynamics. The analysis used here is valid in the low exchange limit, where the line shapes are not significantly affected by the exchange. Thus the decomposition of the signals can be done using the equations described in section 2 without incorporating the exchange rate constant parameters. We assumed exchange is in the low regime between the two spin groups because; i) although some changes in the narrow and broad water deuteron signals are visible (Figure 3), the general shape of the spectrum is retained, ii) the chemical exchange between the two water groups has no effect on the powder splitting, as the rate is much smaller than the splitting, iii) for the isotropic site, the chemical exchange starts to affect the isotropic line only by broadening it slightly between 253 K to 313 K and to a higher effect from 313 K to 343 K, but no coalescence of the two line shapes occurs.

It is evident from both the experimental data and the obtained parameters from simulation that the spin-spin relaxation time $T_2 (= 1/(\pi\Delta v_L))$ for the water deuteron in the quasi-mobile state, which produces Lorentzian line shape, is changing with temperature. At 223 K, T_2 has a small value ($=0.64$ ms), which then increases with increasing temperature and reaches its maximum value at 248 K ($T_2=1.28$ ms). It then gradually decreases again ($T_2 = 0.41$ ms at 343 K). Such behavior is an indication of the magnetization exchange between the two water sites. This kind of exchange is not trivial to treat as it occurs between a site with a Lorentzian line shape and a site with a powder pattern line shape. Although the literature contains many investigations of exchange between groups with Lorentzian resonance lines, the present exchange scenario does not appear to be given much attention in the literature. A simplified method for exchange between two water spin groups (similar to our data, for proton data at a single temperature) in clay is given in reference [12]. It is important to mention that the assumption of *low exchange* between the two water groups is assumed because the powder pattern is considered as one entity. The shape of the powder pattern and its splitting are retained even at the highest temperature of the presented data. This discussion is considered without going into the fine details within the powder pattern. Such fine detail of the line shape gives us another description for the lineshape-exchange rate *limits* as follows: The powder pattern is a superposition of multiple individual lines with different absorption frequencies (depending on the angle of orientation) including zero. By analogy to the two-site exchange in spin $1/2$, the exchange rate between the water mobile Lorentzian line, located at the center of the powder pattern, and the individual lines at the center of the powder pattern is in the fast exchange regime. At higher exchange rate (at higher temperature), a broader region in the middle of the powder pattern will be in fast exchange with the Lorentzian line shape. Thus, a more detailed analysis is needed to fully explain this and to obtain quantitative

information regarding the two line shapes and exchange rate limits. A more detailed exchange study, reported upon separately deals with the composite signal as a whole incorporates exchange rate constants within the theoretical treatment. In the study the powder pattern is simulated using multiple Lorentzian lines. Each of these lines is in exchange with the main Lorentzian line. The exchange rates, between the powder pattern as one group and the Lorentzian line as the other group, obtained are in the order of a few hundred ms^{-1} . Compared with the splitting of the powder pattern (~ 4 kHz) of the present data, such exchange can be assumed to be in the low exchange regime without going into the details of the powder pattern. Although, the mathematical procedure used in the present paper is applicable to good approximation, it is not a *complete solution* for the exchange-NMR line shape problem. It gives a simple, clear and qualitative way of extracting information from the individual spin groups. In addition to that, this method can be used for similar multi-component magnetizations in the slow exchange limit in other materials (similar data are observed for water confined in nano-carbon tubes in our lab, data not published yet).

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