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Orientation-Dependent Proton Relaxation of Water Molecules Trapped in Solids: Crystallites with Long-Lived Magnetization

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Abstract

The longitudinal spin-lattice relaxation properties of water molecules trapped in a static powdered polycrystalline sample of barium chlorate monohydrate are investigated by means of solid-state ^1H NMR spectroscopy. Different portions of the inhomogeneous Pake pattern that are associated with crystallites at different orientations with respect to the external magnetic field show either a mono- or a bi-exponential recovery. At high field (9.4 T), the chemical shift anisotropy is the main interaction that is responsible for the inhomogeneity of the relaxation rates. A theoretical description of rapid two-site hopping about the H-O-H bisector in the framework of Liouville space agrees very well with the experimental evidence. Numerical simulations predict a distribution of mono-exponential time constants associated with individual single-crystal orientations. Overlapping signals give rise to bi-exponential recovery. This is confirmed experimentally by ^1H NMR spectra of static single crystals.

Introduction

Water is not only essential to all living organisms, but also found in mineral phases such as wadsleyite and ringwoodite that are constituents of the Earth's lower mantle.¹⁻³ The knowledge of the amount of water trapped in the Earth's interior is important to understand and analyze the propagation of seismic waves.^{4,5} The study of hydrates is crucial to understand polymorphism in pharmaceutical formulations.^{6,7} These affect drug solubility and stability and are therefore of vital importance for pharmaceutical industry. Water is also at the very core of technologies such as MRI, where local variations of relaxation rates of H₂O molecules are responsible for contrast in images used for diagnostic purposes.⁸ Despite its ubiquity and essential functions, some properties of water still remain unclear. Dynamic processes such as hopping about the two-fold axis of water molecules, tunneling,⁹⁻¹¹ and chemical exchange between neighboring water molecules make studies of some of the most basic properties of H₂O molecule remarkably challenging.

Longitudinal relaxation of nuclear magnetization in solid samples is known to be orientation dependent.¹² Understanding the orientation dependence of the relaxation time constants T_1 is crucial for the identification of *para* water in solid materials, both at room temperature and at spin temperatures in the mK range that can be achieved by dynamic nuclear polarization, where the NMR-invisible singlet state can be depleted with respect to the observable triplet state.¹³ As the overpopulation of the singlet state by means of *rf*-pulse schemes requires non-equivalent spin pairs, the chemical shift anisotropy (CSA)¹⁴ offers a means to lift the degeneracy between the two otherwise equivalent protons of a water molecule. This may provide access to the singlet-triplet manifolds¹⁵⁻¹⁷ in view of creating imbalances. Furthermore, dynamics in solid samples may result in modulations of the CSA interactions that affect the relaxation properties of water molecules trapped in solids.

We report a proton NMR relaxation study of water molecules in a static powdered sample of barium chlorate monohydrate (Ba(ClO₃)₂·H₂O) in a field $B_0 = 9.4$ T at room temperature $T = 298$ K. This system offers a unique opportunity to study water relaxation properties as H₂O molecules are located at a sufficient distance from one another in the unit cell

so as to result in a quasi-ideal Pake pattern¹⁸ in static solid-state NMR spectra at low fields. In addition to the predominant intramolecular ^1H - ^1H dipolar couplings of *ca.* 30 kHz, smaller interactions such as the CSA (*ca.* 15 ppm or 6 kHz at 9.4 T) that affect the Pake pattern can be investigated by means of NMR spectroscopy as they result in a clear asymmetry of the ‘shoulders’ of the powder pattern at high fields.^{19–22} Furthermore, peculiar cross-term splittings which stem from the orientational inequivalence of the two proton CSA tensors have been recently observed by ^1H MAS NMR spectroscopy at temperatures below 150 K.²³

In this study, the orientation dependence of T_1 across the static lineshape is determined experimentally and rationalized theoretically. In some parts of the Pake pattern, the relaxation behavior is bi-exponential, in other parts it is mono-exponential. The main interaction that is responsible for the orientation-dependence of T_1 is found to be the CSA. The distribution of T_1 time constants across the Pake pattern is interpreted by a theoretical treatment in Liouville space to describe rapid two-fold hopping about the H-O-H bisector that averages the CSA tensors. The wide spread of T_1 values observed near the ‘horns’ of the Pake pattern is shown to obey simple bi-exponential laws, whereas the narrower distribution of T_1 values near the ‘shoulders’ and in the center of the Pake pattern obeys a mono-exponential behavior. Weak long-range intermolecular couplings and minor librations give rise to a small *isotropic* contribution to the predominantly *orientation-dependent* relaxation rates. We show that at some orientations, the magnetization of *ortho* water can have life-times T_1 that are comparable to the time constant T_5 for *para-to-ortho* interconversion observed for water in fullerene cages at room temperature.

Experimental Section

All spectra were recorded on a wide-bore Bruker 400 spectrometer (9.4 T) with an Avance-III console, using non-spinning 4 mm ZrO_2 rotors in a double-resonance MAS probe. The *rf*-field amplitude for proton pulses was $\nu_1 = 100$ kHz, corresponding to a 90° pulse length of $\tau_p = 2.5$ μs . A recovery delay of 30 s was used in all cases, although this is not sufficient for $T_1^{(\text{max})} \approx 40$ s. The final 90° pulse of inversion recovery experiments was replaced by a 90° - τ - 90° - τ -solid echo with $p = 0 \rightarrow p = +1 \rightarrow p = -1$ coherence pathway selection using a four-step phase cycle²⁴ so as to i)

eliminate strong background signals and ii) refocus both shielding *and* dipolar interactions that would otherwise result in distorted lineshapes.²⁵ The sample of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ was purchased from Sigma-Aldrich and used without purification. The powder was kept in an oven overnight at 80°C to remove loosely bound water that would otherwise result in a sharp isotropic peak in the center of the Pake pattern. Single crystals were grown by allowing a saturated aqueous solution of barium chlorate monohydrate to dry out over a few days at room temperature. For the spectra of Fig. 5, a single crystal was roughly cut to a cube so as to be able to move freely in a 4 mm rotor. Ejection and insertion cycles of this rotor were used to generate ‘random’ orientations of the crystal with respect to the static field.

Results and discussion

Figure 1(a) shows experimental ^1H NMR spectra obtained by inversion-recovery experiments combined with dipolar echoes. The initial and final lineshapes correspond to almost perfectly inverted and nearly fully relaxed magnetization. The variation of the lineshapes as a function of the recovery delay indicates a dramatic orientation dependence of T_1 relaxation time constants across the Pake pattern. A spectrum acquired near the zero-crossing at $\tau_{\text{rel}} = 10$ s is highlighted in red. This spectrum clearly shows that some portions of the lineshape (positive signals near the ‘shoulders’ and ‘horns’) recover faster than others (negative signals between the ‘horns’). Moreover, the central part of the Pake pattern, associated with crystallites oriented so that the H-H vector lies near to the magic angle ($\beta = 54.74^\circ$) with respect to the static field, relaxes faster than neighboring orientations. In Figure 1(b), black data points indicate the integrals of the spectra of (a) as a function of $0 < \tau_{\text{rel}} < 350$ s. When attempting to fit this recovery to a mono-exponential function, the curve shown by the dashed black line was obtained ($T_1^{(\text{app})} = 16.3 \pm 0.5$ s). Clearly, such a model is not compatible with the experimental evidence. When fitting to a bi-exponential function of the form $I(\tau_{\text{rel}}) = A_0 - A_1 \exp\{-\tau_{\text{rel}}/T_1^{(1)}\} - A_2 \exp\{-\tau_{\text{rel}}/T_1^{(2)}\}$, a much better agreement is obtained, as shown by the continuous red line ($T_1^{(1)} = 10.3 \pm 0.3$ s and $T_1^{(2)} = 33.5 \pm 1.5$ s, with relative weights $A_1 = 0.62 \pm 0.03$ and $A_2 = 0.38 \pm 0.03$). A semi-logarithmic plot of the same data points of Fig. 1(b) is shown in the inset. It is worth mentioning that x-ray and neutron diffraction reveal only a single crystallographically

distinct water molecule in the unit cell.^{26,27} This latter fact is also in agreement with data reported in the literature about solid-state NMR studies of ^2H , ^1H and ^{17}O in barium chlorate monohydrate.²⁸⁻³¹ In order to interpret the experimental evidence of a bi-exponential relaxation for water magnetization, we consider the theoretical framework introduced by Torchia and Szabo¹² and Vold and Vold³² that describe the orientation dependence of T_1 in solid-state NMR. The main orientation-dependent interaction in our system is the intramolecular dipolar coupling between the two protons in each water molecule. These protons are ca. 1.6 Å apart, resulting in a dipolar coupling constant $b_{ij} \approx 29$ kHz. Relaxation requires that spin transitions be induced by fluctuating interactions. Twofold flips about the H–O–H bisector cannot contribute to relaxation, since the dipolar interaction is invariant to 180° rotations. Therefore, other interactions need to be invoked to explain the experimental evidence. We have characterized the proton CSA interaction in the same system by means of both static and MAS techniques.²² The experimental findings in our previous studies were in excellent agreement with DFT calculations based on planewave-pseudopotential methods and indicate a CSA tensor with $\Delta_{CS} = \delta_{zz} - \delta_{iso} = -15.4$ ppm and $\eta_{CS} = (\delta_{yy} - \delta_{xx})/\Delta_{CS} = 0.1$ in the absence of motions. At room temperature, the CSA tensors are partly averaged by rapid 180° rotations about the H–O–H bisector, leading to average values $\bar{\Delta}_{CS} = -7.6$ ppm and $\bar{\eta}_{CS} = 1.0$. As the intermolecular dipolar couplings with neighboring water molecules do not exceed ca. 1.6 kHz (more than an order of magnitude smaller than the intramolecular couplings), we conclude that the CSA must be the dominant relaxation mechanism that is responsible for the orientation dependence of relaxation shown in Fig. 1(a-b). Long-range intermolecular dipolar couplings and small librations about the H–O–H bisector give rise to small contributions to the relaxation rates that we shall assume to be isotropic.

According to this model, the relaxation time constants $T_1^{(1)}$ and $T_1^{(2)}$ must depend on two Euler angles that express the orientation of the averaged CSA tensors with respect to the external magnetic field. Obviously, as stated by Torchia, this implies that “it is not possible to ascribe a single T_1 value at a particular position within inhomogeneous lineshapes”. The relevant expression for the relaxation rates is:³³

$$R_1 = \frac{1}{T_1} = \frac{(\Delta_{CS}\omega_0)^2}{2} J_1(\omega_0), \quad (1)$$

assuming for simplicity that the rhombicity of the CSA tensors can be neglected ($\eta_{CS} = 0$) and expressing Δ_{CS} in ppm. For hopping about the H-O-H bisector through 180° , the orientation dependence of the spectral density $J_1(\omega_0)$ is given by:³²

$$J_1(\omega_0) = \frac{1}{2} \frac{3k_{ex}}{4k_{ex}^2 + \omega_0^2} \sin^2 \beta \cos^2 \beta \left[1 - 3\cos^2 \beta_{CR} + 4\cos^4 \beta_{CR} + (4\cos^4 \beta_{CR} - 5\cos^2 \beta_{CR} + 1) \cos 2\alpha_{CR} \right], \quad (2)$$

where k_{ex} is the exchange rate for the two-fold flip. The angle β describes the relative orientations of the main axes of the *non-averaged* CSA tensors with respect to the H-O-H bisector and amounts to 54.3° in our case, i.e., very close to the magic angle.²⁹ The angles β_{CR} and α_{CR} relate the crystal frame C to the rotor frame R and must be averaged over all orientations in the powder. The usual subsequent transformation to the lab frame L is irrelevant in static experiments. A more general expression, which includes the effects of the asymmetry η_{CS} on $J_1(\omega_0)$, may be found in the literature³² but for simplicity will not be used in this study.

Figure 2(a) shows a contour plot of the function $J_1(\omega_0)$ of Eq. 2 versus β_{CR} and α_{CR} , assuming a fast exchange rate of two-fold hopping $k_{ex} = 4.5 \times 10^9 \text{ s}^{-1}$ at 298 K ²³ and $\omega_0 = 400 \text{ MHz}$. Figure 2(b) shows a three-dimensional plot of the same function. Two regions in the $(\beta_{CR}, \alpha_{CR})$ space, in particular, near $(45^\circ, 0^\circ)$ and $(90^\circ, 90^\circ)$, show remarkably long T_1 values beyond 40 s. In contrast, subspaces where the magnetization is short lived, with T_1 values below 10 s, can be found near $(90^\circ, 0^\circ)$ and in a vertical band $([0^\circ-30^\circ], [0^\circ-90^\circ])$. A narrow saddle point or ‘sweet spot’ with $T_1 \approx 25 \text{ s}$ is found in the region $(62^\circ, [0^\circ-90^\circ])$. Importantly, the contour plot shows that, for different values of β_{CR} , i.e., for different positions within the Pake spectrum, the T_1 values vary in a range from 10 to 40 s.

In order to further investigate the consequences of these predictions, vertical cross sections were taken from Fig. 1(a) and analyzed to extract the relevant relaxation parameters across the Pake pattern. The corresponding data is shown in Figure 3(a). Interestingly, a bi-exponential function is clearly required to model the inversion-recovery data near the ‘horns’ of

the Pake pattern. In contrast, mono-exponential functions (green dots) suffice near the shoulders and near the center of the Pake pattern, where the latter correspond to crystals oriented near the magic angle $\beta_{CR} = \arctan(2^{1/2}) = 54.74^\circ$. This finding can be rationalized by considering how doublets associated with individual crystallites contribute to the Pake pattern: (i) between the horns, pairs of different crystallite orientations with different relaxation time constants result in identical splittings due to the homonuclear dipole-dipole coupling; (ii) this does not give rise to significantly different relaxation time constants around the magic angle; and (iii) only dipolar doublets with a single relaxation time constant contribute to the shoulders outside the horns.

Figure 3(b) shows how the weights A_1 and A_2 of the bi-exponential components obtained by fitting the data of Fig. 1(a), are scattered across the Pake pattern. The sum $A_1 + A_2$ of these weights, indicated by black points, closely resembles the Pake pattern and testifies for the overall quality of the individual fits. It is interesting to note that, near the ‘horns’ of the Pake pattern, $T_1^{(2)} \approx 40$ s is comparable if not longer than the singlet-state time constant T_S reported for *para-to-ortho* conversion of water confined in fullerene C_{60} cages.³⁴ In our case, each water molecule undergoes continuous disruption and reestablishment of two H-bonds with chlorate oxygen atoms as a result of rapid hopping about the H–O–H bisector at room temperature. The resulting fluctuations of the CSA interaction near the Larmor frequency lead to the observed relaxation. In contrast, the dominant relaxation mechanism for freely tumbling water molecules confined in fullerene cages is spin rotation, since the water molecules are only subject to vibrational motions with frequencies on the order of $10^{13} \text{ s}^{-1} \gg \omega_0$ that are not expected to make a significant contribution to longitudinal relaxation.^{29,34}

The presence of the CSA interaction renders the assignment of specific dipolar doublet splittings in the Pake pattern to particular sets of Euler angles more complicated than for the simple case where only dipolar interactions are present. In the latter case, varying a single angle β_{CR} suffices to accurately reconstruct the full Pake pattern by associating any position within the pattern to one or at most two β_{CR} values. In contrast, in the case at hand, the presence of the CSA interaction requires a second angle α_{CR} to fully describe the powder average. In order to

take this situation into account, we analyzed our experimentally observed profiles in a Liouville space framework where both rapid chemical exchange due to fast hopping and inhomogeneous longitudinal relaxation rates due to the CSA are taken into account. The evolution of populations and coherences can be evaluated by means of the master equation:^{35,36}

$$\rho(t) = \exp\{-iL_{coh} + L_{incoh}\}\Delta t\}\rho(0), \quad (3)$$

where L_{coh} is the commutation superoperator that describes coherent effects and L_{incoh} takes into account incoherent effects, namely, chemical exchange and orientation-dependent relaxation. The recovery of Zeeman order can be fully described in the basis $B' = \{I_z, S_z\}$ with the corresponding superoperator:

$$L'_{incoh} = \begin{pmatrix} R_{1,I} + k_{ex} & -k_{ex} \\ -k_{ex} & R_{1,S} + k_{ex} \end{pmatrix}, \quad (4)$$

with $R_{1,I} = R_{1,S} = R_1$ of Eq. (1). The simulation of the subsequent solid echo requires a single-quantum subspace spanned by the basis $B'' = \{I_x, I_y, S_x, S_y, 2I_xS_z, 2I_yS_z, 2I_zS_x, 2I_zS_y\}$ with the following superoperator:

$$L''_{incoh} = \begin{pmatrix} k_{ex} & 0 & -k_{ex} & 0 & 0 & 0 & 0 & 0 \\ 0 & k_{ex} & 0 & -k_{ex} & 0 & 0 & 0 & 0 \\ -k_{ex} & 0 & k_{ex} & 0 & 0 & 0 & 0 & 0 \\ 0 & -k_{ex} & 0 & k_{ex} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & k_{ex} & 0 & -k_{ex} & 0 \\ 0 & 0 & 0 & 0 & 0 & k_{ex} & 0 & -k_{ex} \\ 0 & 0 & 0 & 0 & -k_{ex} & 0 & k_{ex} & 0 \\ 0 & 0 & 0 & 0 & 0 & -k_{ex} & 0 & k_{ex} \end{pmatrix}, \quad (5)$$

where transverse relaxation is neglected. Longitudinal recovery of Zeeman order can be evaluated within the B' subspace, starting from the initial state $\rho'(0) = \{-1, -1\}$, to evolve according to Eq. (3) during the time interval τ_{rel} . Subsequently, transverse magnetization is allowed to evolve during the $90^\circ - \tau - 90^\circ - \tau$ - solid echo sequence within the B'' subspace after a change of the basis $\rho''(0) = \{\rho'(\tau_{rel})_1, 0, \rho'(\tau_{rel})_2, 0, 0, 0, 0, 0\}$ that mimics the effect of the first

(ideal) 90° pulse. A further change of basis $\rho'''(\tau) = \{\rho''(\tau)_1, -\rho''(\tau)_2, \rho''(\tau)_3, -\rho''(\tau)_4, -\rho''(\tau)_5, \rho''(\tau)_6, -\rho''(\tau)_7, \rho''(\tau)_8\}$ was utilized to simulate the $p = 1 \rightarrow p = -1$ coherence selection performed by the second (ideal) 90° pulse. Finally, a further change to the basis $\rho''''(0) = \{\rho'''(2\tau)_1, 0, \rho'''(2\tau)_3, 0, 0, 0, 0, 0\}$ was performed at the end of the echo, prior to detection.

Figure 3(c) shows the relaxation time constants $T_1^{(1)}$ and $T_1^{(2)}$ calculated across the Pake pattern by simulating an inversion-recovery experiment combined with a dipolar echo sequence by means of Eq. (3). The quantitative agreement with the experimental distribution of Fig. 3(a) is remarkable. More specifically, a mono-exponential relaxation behavior is found both near the ‘shoulders’ and near the center of the Pake pattern, while a bi-exponential behavior is found near the ‘horns’. Furthermore, the predicted coefficients A_i shown in Fig 3(d) agree very well with the experimental ones of Fig. 3 (b). These simulations clearly indicate that our theoretical description of the observed relaxation rates of protons in water molecules trapped in crystals of barium chlorate monohydrate is very accurate.

Since the fluctuations of the CSA interactions provide the driving force of relaxation, we have repeated our relaxation measurements at $B_0 = 18.8$ T (800 MHz for ^1H) and, surprisingly, found substantially identical results, with a bi-exponential behavior of the integral over the entire width of the Pake pattern described by $T_1^{(1)} = 9.9 \pm 0.6$ s and $T_1^{(2)} = 35.7 \pm 2.9$ s, bearing in mind that the orientation dependence is not affected by the static field. This can be rationalized by noting that the term $(\Delta_{CS}\omega_0)^2$ in Eq. (1) can be compensated by the term $3k_{ex}/(4k_{ex}^2 + \omega_0^2)$ in Eq (2). Indeed, simulations show that for $k_{ex} = 4.5 \times 10^8 \text{ s}^{-1}$ (i.e., 10 times slower than the value estimated at $T = 298$ K by extrapolation in our earlier study),²³ the relaxation rates are predicted to increase by no more than 10% between 400 and 800 MHz. This mismatch is reasonable if one considers that we did not observe changes in spectral features for temperatures above 200 K.

Equations 1 and 2 and the plots of Fig. 2 indicate that a given crystallite orientation within the powdered sample is characterized by one and only one relaxation rate, and therefore by mono-exponential relaxation. This agrees with both the experimental and calculated data of Fig. 3, which clearly show that either only one or at most two T_1 values are required to interpret

the relaxation behavior at any point in the Pake pattern. In order to get insight into this aspect, the numerical simulations of Fig. 3 (c-d) were carried out for some single crystallite orientations.

Figure 4(a) shows some typical T_1 values calculated in the ranges $0^\circ < \alpha_{CR} < 180^\circ$ and $0^\circ < \beta_{CR} < 90^\circ$, plotted along the horizontal axis according to their contributions to the Pake pattern. As previously stated, the T_1 values vary considerably at almost any position within the Pake pattern and seem to contradict our experimental evidence that it is sufficient to postulate a bi-exponential behavior to rationalize the decays of Fig. 3. Figure 4(b) shows six mono-exponential decays that reflect the T_1 values for the six equiprobable crystallites with $\beta_{CR} = 90^\circ$ located near the low-frequency ‘horn’, as indicated by arrows in Fig. 4(a). A semi-logarithmic plot is shown in the inset. The red points in Figure 4(c) show the normalized sum of these six decays. An attempt to fit these red points to a mono-exponential decay is represented by a dashed blue line. A more satisfactory bi-exponential fit is shown by a red dashed line. A semi-logarithmic plot is shown in the inset. Clearly, despite the great range of time constants involved in the overall relaxation process at a given position within the Pake pattern, a simple bi-exponential fit suffices to describe the system. This finding fully supports our experimental profiles of Fig. 3 and the continuous distribution of T_1 values predicted in Fig. 2.

The mono-exponential relaxation behavior of individual crystallites was confirmed by means of ^1H spectra of a static single crystal. Figure 5 shows a series of dipolar doublets obtained for a small single crystal of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ that was allowed to settle freely in a non-spinning 4 mm rotor as the latter was inserted into the probe. By repeatedly inserting and ejecting the rotor, we could obtain four ‘arbitrary’ orientations of the crystal with respect to the external field B_0 . These doublets all have clearly distinct T_1 values, as expected by inspection of Fig. 2. Moreover, and in agreement with the theory outlined above, the recovery was always mono-exponential for each orientation of the single crystal.

Conclusions

The orientation dependence of the longitudinal relaxation time constants T_1 of protons in water molecules confined in crystals of barium chlorate monohydrate has been investigated by

means of ^1H NMR spectroscopy in a static (non-spinning) polycrystalline powdered sample. By analyzing the role of modulation of the proton CSA interaction, this study offers new insights compared to the work by Long et al.²⁹ on relaxation of deuterium in similar powders where relaxation is induced by modulations of much larger quadrupolar couplings. Some portions of the spectra near the ‘horns’ of the Pake pattern reveal a clear bi-exponential relaxation profile. In contrast, a simple mono-exponential recovery is found near the center and near the ‘shoulders’ of the Pake pattern. A theoretical description in Liouville space that takes into account the orientation dependence of T_1 and fast chemical exchange agrees very well with the experimental evidence. Each individual crystal orientation is predicted to have a purely mono-exponential recovery behavior, which was confirmed by experiments on different orientations of a single crystal. The distribution of time constants and crystallite orientations found in a powder can be adequately interpreted with a simple bi-exponential model. We show that, in spite of fast hopping about the H-O-H bisector that requires the breaking of two hydrogen bonds, the magnetization of *ortho* water in crystallites of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ at some orientations may have lifetimes comparable to, if not longer than, those of *para-to-ortho* conversion of water in fullerene cages. This study shows that the relaxation time constants of water molecules can be controlled by adjusting their orientation with respect to the external magnetic field.

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Figures

Figure 1 (a) Proton NMR spectra of a static powdered sample of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ at $B_0 = 9.4$ T (400 MHz for ^1H) and $T = 298$ K, observed with an inversion-recovery dipolar echo sequence $180^\circ - \tau_{\text{rel}} - 90^\circ - \tau_e - 90^\circ_\phi - \tau_e - \text{acquisition}$, with $\tau_e = 30 \mu\text{s}$. The 180° and 90° pulse widths were 5 and $2.5 \mu\text{s}$, respectively. The phase of the last 90° pulse was cycled through $\phi = \{0^\circ, 90^\circ, 180^\circ, 270^\circ\}$ while the receiver phase was alternated $\phi_{\text{rec}} = \{0^\circ, 180^\circ, 0^\circ, 180^\circ\}$. Consecutive experiments were separated by a recovery interval of 30 s. (b) Normalized signal intensity resulting from integration over the entire width of the Pake patterns in (a) as a function of the relaxation interval τ_{rel} . Experimental integrals are shown as black circles. An attempt to fit a mono-exponential function is represented by a dashed black line, whereas the continuous red line shows a bi-exponential fit to the function $I(\tau_{\text{rel}}) = A_0 - A_1 \exp\{-\tau_{\text{rel}}/T_1^{(1)}\} - A_2 \exp\{-\tau_{\text{rel}}/T_1^{(2)}\}$. An analogous semi-logarithmic plot is shown in the inset.

Figure 2 (a) Contour plot of the spectral density $J_1(\omega_0)$ of Eq. (2) that determines the longitudinal relaxation constant $T_1 = 1/R_1$, obtained by Fourier transformation of the correlation function $C(\tau)$ of the fluctuations of the proton chemical shift anisotropy (^1H CSA) at the Larmor frequency $\omega_0/(2\pi) = 400$ MHz, as a function of the angles α_{CR} and β_{CR} that describe the orientation of a crystallite and must be integrated for powder averaging. The exchange rate assumed at 298 K was $k_{ex} = 4.5 \times 10^9$ Hz. (b) Three-dimensional plot of the function shown in (a).

Figure 3 (a) Distribution of longitudinal relaxation time constants T_1 across the Pake pattern extracted from the inversion-recovery spectra of Fig. 1(a). When mono-exponential fitting was satisfactory, the resulting short relaxation time constants $T_1^{(1)}$ are shown by green circles, whereas data resulting from bi-exponential fitting are represented by red and blue circles, for short and long relaxation time constants $T_1^{(1)} = T_1^{(short)}$ and $T_1^{(2)} = T_1^{(long)}$, respectively. (b) Coefficients A_1 and A_2 of the fitting function $I(\tau_{rel}) = A_0 - A_1 \exp\{-\tau_{rel}/T_1^{(1)}\} - A_2 \exp\{-\tau_{rel}/T_1^{(2)}\}$ shown using the same color code. The black circles indicate the sum $A_1 + A_2$ of the weights. All experimental intensities are sampled in steps of 2 kHz across the Pake pattern of Fig. 1a. (c) Calculated short and long relaxation time constants $T_1^{(1)} = T_1^{(short)}$ and $T_1^{(2)} = T_1^{(long)}$, with the same color codes as for the experimental values of (a), derived from the spectral density function of Eq. (2) shown in Fig. 2. (d) Calculated coefficients A_1 and A_2 with the same color codes. The data in (c, d) were calculated in steps of 3.125 kHz across the Pake pattern of Fig. 1a. In (c, d), the rate of two-fold hopping about the H-O-H bisector was assumed to be $k_{ex} = 4.5 \times 10^9$ Hz at 298 K. Most error bars are smaller than the size of the data points. An isotropic contribution to the relaxation rates $R_1^{(iso)} = 1/T_1^{(iso)} = 0.018$ Hz was included to take long-range intermolecular dipolar couplings and small librations into account.

Figure 4 (a) Distribution of calculated relaxation time constants T_1 across the Pake pattern for 66 single crystallite orientations associated with $0^\circ \leq \beta_{CR} \leq 90^\circ$ and $0^\circ \leq \alpha_{CR} \leq 180^\circ$, in 5 and 10 steps of 18° , respectively. (b) Six simulated mono-exponential decays corresponding to the calculated T_1 values indicated by blue arrows in (a) for equiprobable crystallite orientations with $\beta_{CR} = 90^\circ$. An analogous semi-logarithmic plot is shown in the inset. (c) The red points indicate the normalized sum of the six decays of (b). A bi-exponential fit to these red points is shown by a red dashed line, whereas an attempt to fit a mono-exponential decay is represented by a blue dashed line. The inset shows a semi-logarithmic plot of the same data points.

Figure 5 Experimental proton doublets of a single crystal of barium chlorate monohydrate $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ at $B_0 = 9.4$ T (400 MHz for ^1H) and $T = 298$ K, observed at four different random orientations with respect to the external magnetic field. The sharp isotropic peaks appearing in the center of the doublets are attributed to water molecules that are loosely bound on the surface of the crystals. These peaks provide a measure of the homogeneity of the static field B_0 . Inversion-recovery experiments show monoexponential relaxation with time constants between 10 and 20 s.

TOC Graphic