Communication

^{2}H Solid-State NMR of Mobile Protons: It Is Not Always the Simple Way

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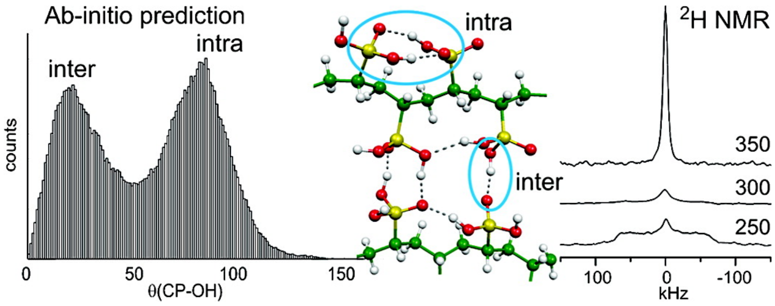

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^{2}H Solid-State NMR of Mobile Protons: It Is Not Always the Simple Way

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Knowledge concerning dynamic processes at microscopic scales is crucial to understanding long-range transport phenomena in condensed matter, especially for proton conductors.[1] Various techniques can be used to characterize both time scale and geometry of molecular dynamics. In particular, ^{2}H NMR spectroscopy has been successfully applied to various crystalline and amorphous materials.[2] In the absence of motion, a well-defined Pake pattern with a quadrupolar splitting is obtained, while in presence of motion, both the line shape and the amplitude of a solid-echo signal are influenced by the geometry and the rates of the dynamics. When the rate of molecular motion becomes comparable to the strength of the quadrupolar interaction, the signal intensity is significantly reduced because of destructive interferences during refocusing. A complete loss of the signal, for example, has been observed in ice when reorientation of water molecules occurs with a jump rate of 10^5 Hz.[3] In the fast motional regime, the spins experience an averaged interaction, giving rise to powder patterns which depend on the geometry of the motions.

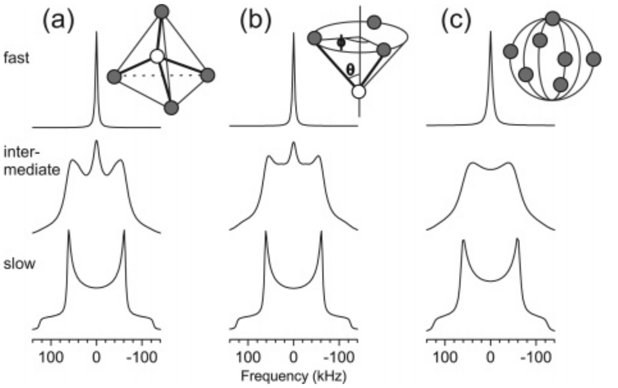

Figure 1. Simulated line shapes for motionally averaged ^{2}H NMR spectra by various motions, which lead to characteristic isotropization: (a) tetrahedral jump, (b) multisite angular jump ($n \geq 3$) on a cone at the magic angle ($\theta = 54.74°$), where θ and ϕ are cone angle and flip angle, respectively, and (c) jumps with random orientation.

However, it is not always trivial to derive from static ^{2}H NMR experiments the underlying elementary types of motion, especially for complex processes involving a distribution of jump angles or several mechanisms happening simultaneously.[2d,4] Moreover, a collapse of the anisotropic tensorial pattern may be observed for systems where the geometry of the motion is not well-defined. Simple dynamic models for the isotropization of second-rank tensorial interaction are (1) jumps of cubic symmetry (tetrahedral, octahedral), (2) multisite angular jump ($n \geq 3$) on a cone at the magic angle, and (3) jumps with random orientation.[2] Their effect on the ^{2}H NMR signal, as shown in Figure 1, are readily calculated from standard procedures available on the Web.[5] In the fast motional regime, these three motional models yield isotropic NMR line shapes, where the information associated with the anisotropic characteristics vanishes, rendering the line shape insensitive to the geometry of the motion. These three dynamic models give rise to different spectral patterns only in the intermediate motional regime. However, the difference is too small to distinguish these models by line-shape analysis alone. In such cases, an additional method such as two-dimensional exchange NMR spectroscopy can help identifying the motional process and the time scale of motion, independently.[6]

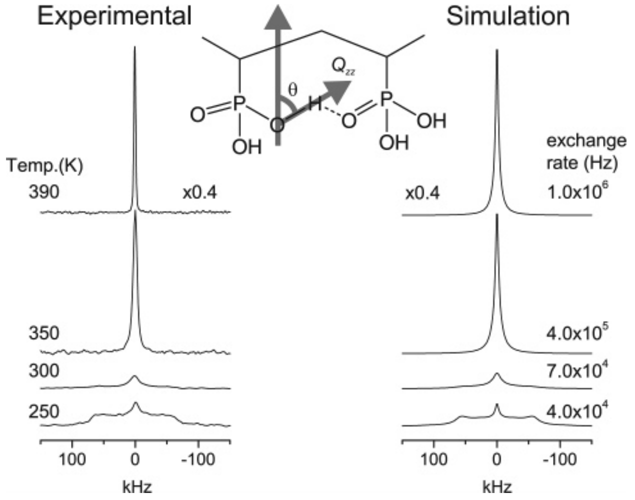

Figure 2. Experimental and simulated ^{2}H static NMR spectra of PVPA and geometry of O−H bonds for the NMR calculation. All experimental spectra were acquired using solid-echo pulse sequence with an echo-delay of 20 μs at various temperatures. Calculated line shape and the corresponding exchange rate were obtained with a motional model of 3-site jump on a cone at the magic angle.

While simple geometric models of motion may be adequate to describe rotation of molecules, dynamics of light ions such as H^+ might be more complex.[7] With the current advances in computer simulations, however, spectroscopic observables such as NMR relaxation rates and line shapes can now be calculated directly without the need of assuming simplified motional models.[8] Along these lines, a combined study of ^{2}H line-shape analysis and ab initio molecular dynamics simulations was carried out on poly[vinyl phosphonic acid] (PVPA, a water-free proton conducting material), to explore the complex proton motion in this class of systems.[1] Since it is presently not possible to achieve both high accuracy for the calculation of local forces and long simulation times in molecular dynamics simulations, we have designed a model system representing the main structural and dynamical features of the real material, in particular the characteristic intra- and interchain hydrogen-bonding network with a high proton mobility.[9]

Experimentally, we have investigated the proton motion in PVPA by ^{2}H NMR spectroscopy (Figure 2). At 250 K, a broad static line shape with a width of approximately 140 kHz is observed. The ill-defined powder pattern with obscured singularities indicates slow molecular motion, which suggests that the deuterons of phosphonic acid group undergo a motional process even at this low temperature. It is noteworthy that the ^{2}H signal is barely detectable at room

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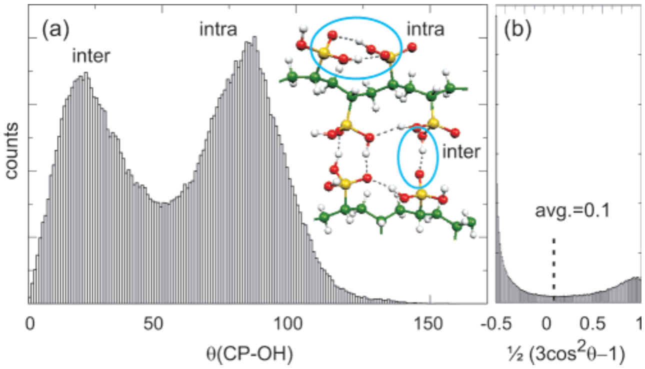

Figure 3. (a) Angular distribution of O−H bonds with respect to C−P bonds; (b) distribution of second-order Legendre polynomial.

temperature, indicating that the deuteron motion occurs with a uniform exchange rate of about 100 kHz. As the temperature increases, a single resonance with a Lorentzian line shape appears, which increases in intensity and decreases in line width. Most remarkable is the fact that the powder pattern becomes fully isotropic above room temperature. An activation energy of 38 kJ/mol is found from ^{2}H MAS NMR, described in the Supporting Information.

Assuming that the tensor orientation describing the quadrupolar interaction of deuterium aligns, to a first approximation, parallel to the O−D bond and that the quadrupolar interaction tensor is axially symmetric, we tried to fit the spectral pattern using various motional models with constrained geometries. The dynamic model involving random angular jumps was ruled out since it does not reproduce the experimental ^{2}H line shape below room temperature.[10] In contrast to this, the simulated spectra for tetrahedral and magic angle jumps are in remarkable agreement with the experimental data over the whole temperature range (Figure 2).

To distinguish the possible mechanisms of a proton motion, the fast local rearrangement of the hydrogen-bonding network was investigated by means of first-principles Car−Parrinello molecular dynamics simulations (15 ps at $T = 300$ K; for details see ref 9) under periodic boundary conditions.[9,11] Assuming that the eigenvector corresponding to the largest eigenvalue of the quadrupolar interaction tensor aligns along the O−H bond and the tensor is axially symmetric, the instantaneous CP−OH angle represents the angle between a potential rotation axis and the main component of the local electric-field-gradient tensor. During the MD simulation, as in experiment,[9] the orientation of the C−P bond with respect to the PVPA backbone was found to be essentially constant. In Figure 3, we show the computed histograms of the distribution of the angle θ(CP−OH) within a given phosphonic acid group, and the second Legendre polynomial, $P_2(\cos\theta) = {}^1/_2(3\cos^2\theta - 1)$, which describes the angular dependence of the quadrupole interaction. A simple rotation of the phosphonic acid groups around the C−P axis (retaining the geometry of O−H bonds) can be ruled out. This would lead to a distribution centered around the magic angle, which is not the case. Instead, Figure 3a reveals two Gaussian-like maxima, representing interchain (at 21°) and intrachain (at 84°) H-bonding. The averaged value of the CP−OH angle (57°) is remarkably close to the magic angle (54.74°). The corresponding $P_2(\cos\theta)$ (Figure 3b) reveals a broad distribution of quadrupole couplings due to interchain H-bonding and a narrow maximum at $\theta \cong 90°$ for intrachain protons. The average of 0.1 corresponds to a reduction of the coupling by 90%, in agreement with the significant narrowing of the experimental signal above room temperature. We then conclude that the latter does not result from a simple jump motion, but from a complex proton exchange path along and between polymer chains.

A quantitative simulation of the ^{2}H line shape from the trajectory of the CPMD calculations is not possible due to the limitations of present-day ab initio methods (especially simulation time and system size); our approach can only achieve a partial statistical phase-space sampling. Thus, it is expected that the reduction of the quadrupole interaction will be even stronger, eventually leading to a complete isotropization of the powder pattern.

Our study shows that for complex systems such as polymeric proton conductors with constant H-bond breaking and re-formation, only limited dynamical information can be obtained from ^{2}H NMR spectroscopy using simple dynamic models, which have been successful in describing reorientational motion of molecules. However, in combination with predictions from ab initio MD simulations, we can elucidate the geometry and even time scale of the motions for such complex systems. The relative occurrence of different hydrogen bonding conformations determines the experimental line shape due to averaging of the anisotropic quadrupole interaction. Our combined ^{2}H line shape analysis and ab initio MD calculations characterize the dynamical proton motion via the rearrangement of H-bonding network, which involves both intra- and interchain transfers. Our results shed light on cooperative microscopic transport processes whose understanding is crucial to designing novel proton conductors with improved properties for fuel cell applications.

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Supporting Information Available: ^{2}H MAS NMR spectra of PVPA and activation energy for proton motion. This material is available free of charge via the Internet at http://pubs.acs.org.

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