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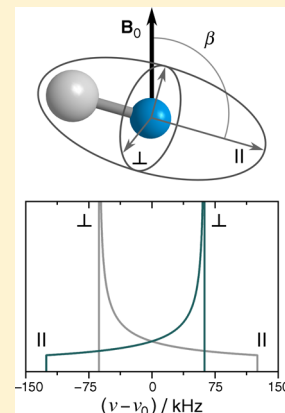
## Solid-State NMR Spectroscopy for the Physical Chemistry Laboratory

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## S Supporting Information

**ABSTRACT:** Solid-state nuclear magnetic resonance (NMR) spectroscopy finds growing application to inorganic and organic materials, biological samples, polymers, proteins, and cellular membranes. However, this technique is often neither included in laboratory curricula nor typically covered in undergraduate courses. On the other hand, spectroscopy and molecular structure taught in second-semester undergraduate physical chemistry courses meet the minimal background prerequisites for interpreting data obtained in many solid-state NMR experiments. A solid-state  $^2\text{H}$  NMR experiment is described in which the student obtains and interprets the spectrum of a powder sample of hexamethylbenzene- $d_{18}$  using a solution NMR spectrometer as found in many undergraduate institutions. A quadrupolar-echo pulse sequence is applied to the sample to obtain the  $^2\text{H}$  NMR spectrum. The spectrum of a randomly oriented powder sample consists of two spectral branches with broad shoulders. The quadrupolar frequencies corresponding to the nuclear spin transitions are interpreted in terms of molecular mobility in the solid state, that is, 3-fold rotation of the methyl groups and 6-fold rotation of the hexamethylbenzene ring. In this way, students discover that solid substances may have significant molecular motions. This undergraduate investigation employing solid-state  $^2\text{H}$  NMR provides an informative exposure to state-of-the-art research techniques by using facilities that are already in place at many undergraduate institutions. Furthermore, it demonstrates a real-life manifestation of quantum mechanics as explained in physical chemistry courses, as well as fundamentals of molecular motions such as rotation of aromatic ring compounds and methyl groups in the solid state.

**KEYWORDS:** Upper-Division Undergraduate, Analytical Chemistry, Physical Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Inquiry-Based/Discovery Learning, NMR Spectroscopy, Solids, Molecular Mechanics/Dynamics, Spectroscopy



Solid-state nuclear magnetic resonance (NMR) has found widespread application in many scientific fields such as biochemistry and biophysics, inorganic chemistry, material science, and biomedical engineering.<sup>1</sup> These applications often require specialized instrumentation that has limited the availability to students.<sup>2</sup> As a result, it is increasingly important to have a meaningful undergraduate exposure to solid-state NMR spectroscopy on commercially available systems.

Many programs in four-year colleges routinely train students in the analysis of organic compounds with solution NMR techniques. In addition, recent developments allow some two-year colleges access to NMR technology.<sup>3</sup> Yet, there have been few published studies that are feasible on theoretical and experimental levels regarding NMR with solid-like samples. Notable exceptions are a  $^{31}\text{P}$  NMR experiment<sup>4</sup> concerning organic synthesis and a  $^{129}\text{Xe}$  NMR experiment.<sup>5</sup> However, these experiments involve more specialized experimental procedures and are relatively limited in their range of applications.

The experiment uses a highly symmetric molecule, which simplifies the instrumental requirements, given practical laboratory time constraints, as well as the theoretical interpretation. Hexamethylbenzene (HMB) is a small molecule that is commercially available and used as a calibration standard in solid-state NMR spectroscopy (Figure 1). Although this

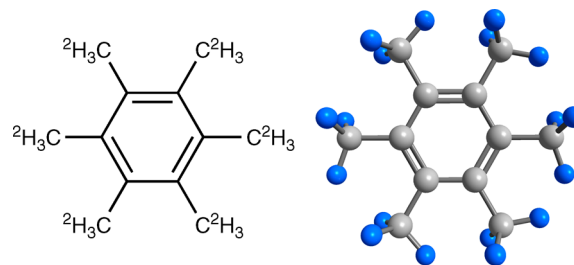


Figure 1. Structure of symmetric hexamethylbenzene- $d_{18}$ .

molecule is in powder form, it undergoes striking molecular motions about its rotational symmetry axes. In the solid-state NMR experiment, the methyl group hydrogens are replaced by deuterium (thus HMB- $d_{18}$ ), and this isotopic enrichment provides a strong signal that can be recorded in a short time (as little as 10 min). The resulting spectrum is known as a Pake doublet,<sup>6</sup> and the shape differs significantly from typical NMR spectra.

The basic principles of solid-state NMR spectroscopy are outlined as it relates to the interpretation of solid HMB- $d_{18}$  in powder form. This application to a real-life experimental

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**Table 1. Solid-State NMR and Solution NMR Techniques Observe Nuclear Properties and Typically Require Different Instrumentation**

Property	Liquids	Solid-State
Observables	<ul style="list-style-type: none"> <li>• Chemical Shift</li> <li>• Indirect Dipolar Coupling (Spin–Spin)</li> <li>• Direct Dipolar Coupling (NOE)</li> </ul>	<ul style="list-style-type: none"> <li>• Chemical Shift Anisotropy</li> <li>• Direct Dipolar Coupling</li> <li>• Quadrupolar Coupling</li> </ul>
Spectral Width	Narrow (Hz)	Broad (kHz)
Pulse Length	Long	Short
Amplifier	Low-Power	High-Power

investigation enhances the understanding of molecular structure and symmetry. The solid-state spectrum of HMB- $d_{18}$  contains information about simple molecular motions within the molecule. Amazingly, these are explained by the methyl group rotation as well as rotation about the benzene ring axis for HMB. The theoretical treatment of the HMB molecule described here is applicable to complex and relevant systems.<sup>6</sup> The spectrum may be obtained on typical liquids NMR spectrometers and provides an illustration of molecular motions in the solid state. Thus, undergraduate students in physical chemistry courses can easily conduct this experiment in their laboratory sessions. A student handout and instructions for the instructor are available in the Supporting Information.

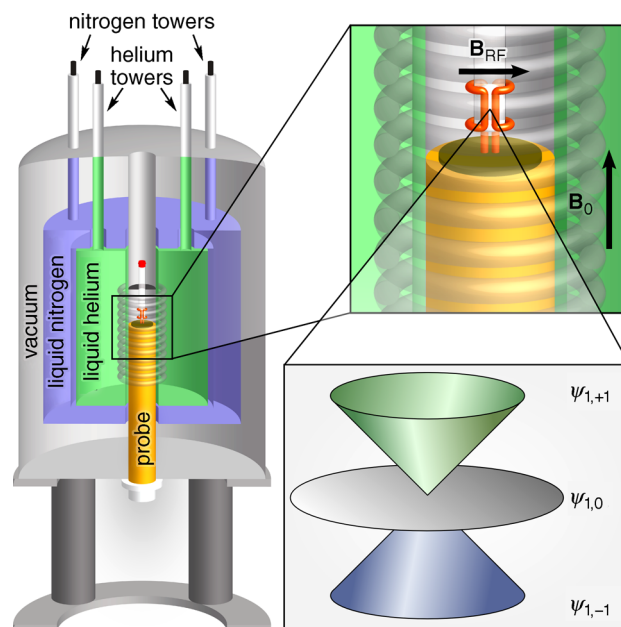
## ■ EXPERIMENT

### Background

Solid-state NMR uses expensive high-power amplifiers for wide-line spectra, whereas commercially available solution NMR spectrometers are geared toward high resolution over a narrow band of frequencies. Therefore, both techniques tend to observe different interactions within the sample (Table 1). Solution NMR assigns positions of atoms to bonds through chemical shifts and indirect dipolar couplings (through bond). Moreover, using the nuclear Overhauser enhancement (NOE), solution NMR can be employed to determine three-dimensional structures. By contrast, solid-state NMR obtains both structure and dynamics through chemical shift anisotropy, direct dipolar coupling (through space) between nuclei, and electric quadrupole coupling (discussed here). The importance of the proposed experiment is that it is feasible using ordinary solution spectrometers, which have weaker amplifiers and liquids NMR probes.

NMR spectroscopy entails the study of molecules whose atomic nuclei contain subatomic particles (protons and neutrons) with intrinsic angular momentum called spin.<sup>7,8</sup> The hydrogen nucleus, with only one proton, has a spin quantum number of  $1/2$ . For deuterium, which has one proton and one neutron, the total spin quantum number is  $I = 1/2 + 1/2 = 1$ . Here, the NMR notation is used for the angular momentum ( $\hat{J}$ ) operators, which correspond to the common angular momentum operators in this sense: the projection angular momentum operator is denoted by  $\hat{I}_z = \hat{J}_z/\hbar$  and the total angular momentum operator is  $\hat{I}^2 = \hat{J}^2/\hbar^2$ , where  $\hbar = h/(2\pi)$  and  $h$  is Planck's constant.

Each of these angular momentum states has a degeneracy that is removed by a magnetic field and is described by the magnetic quantum number  $m$ . The values of the projection index  $m$  range from  $-I$  to  $I$  in integer steps.<sup>7</sup> Nuclei with spin  $I = 1/2$  have  $m = -1/2$  and  $1/2$  and nuclei with  $I = 1$  have three values of  $m = -1, 0$ , and  $1$  (Figure 2). When a static magnetic field ( $B_0$  in Figure 2) is applied, the spin system has  $2I + 1$



**Figure 2.** A sample is placed in a strong magnetic field ( $B_0$ ) oriented in the vertical direction to produce the Zeeman effect. When a magnetic field is present, the degeneracy of the spin angular momentum states of a spin-1 nucleus ( $I = 1$  nucleus) is removed. A transverse radio frequency pulse ( $B_{RF}$ ) causes transitions between the Zeeman energy levels. The NMR signal is observed using the coil of the probe as the detector.

nondegenerate states. This interaction is called the Zeeman effect. In NMR, the static magnetic field is provided by a large superconducting magnet with the sample inserted into the center bore, as shown in Figure 2.

### Sample Preparation

A sample of HMB- $d_{18}$  is employed in its powder form (Sigma-Aldrich, St. Louis, MO; approximately \$30 per gram). A 20 mg sample of powdered HMB- $d_{18}$  is often enough to acquire an acceptable spectrum; otherwise, more sample may be used. The sample is added to a standard 5 mm o.d. glass solution NMR tube to about 1.5 cm from the bottom, which is the typical coil length for liquids NMR probes. Note that solution NMR normally requires the sample to be spun to increase resolution. However, spinning is unnecessary in this experiment, as the spectral improvements are negligible in the broad solid-state spectra.

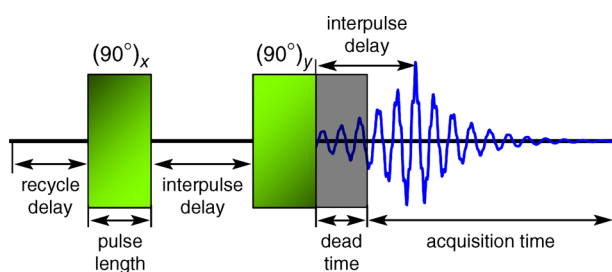
At very low temperatures (around  $-100\text{ }^{\circ}\text{C}$ ), crystals of HMB- $d_{18}$  have been observed aligning in the magnetic field of the NMR magnet (as seen by increased spectral shoulders). This may cause distortion in the shape of the NMR spectrum. Normally, at room temperatures, this will not be a problem unless an exceptionally strong magnet is used. If this is the case,

it can be remedied by tightly packing the HMB- $d_{18}$  powder before placing the sample within the magnet.

### Pulse Sequence

The NMR probe delivers a radiofrequency (RF) pulse to the nuclei, which is produced by the transmitter. This rotates the net magnetization due to the nuclear spins about an axis transverse to the main magnetic field in a classical picture. Initially, the spins precess coherently. As the spins relax back to equilibrium, they become out of phase, which generates a decaying signal in the coil of the probe called a free induction decay (FID). A second function of the probe is to act as a receiver for the FID signal. A fast Fourier transform (FFT) of the FID is performed computationally to yield the NMR spectrum.

In this experiment, a quadrupolar echo pulse sequence is applied as illustrated in Figure 3. The first pulse rotates the spin



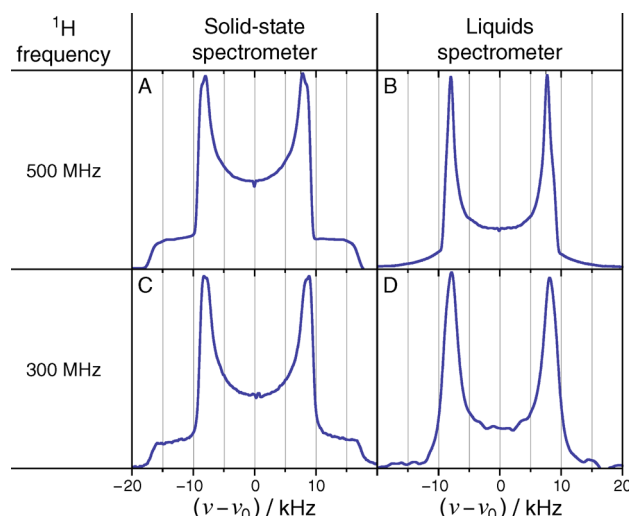
**Figure 3.** The general timing diagram illustrates the components of the quadrupolar-echo pulse sequence. Time delays are adjusted prior to execution of the experiment. The RF pulses are shown as boxes above the pulse length and must be calibrated to excite as much of the frequency bandwidth as possible. The echo is acquired and a FFT is begun at the maximum of the echo.

magnetization by  $90^\circ$  (about an  $x$  axis) and transverse relaxation occurs due to reversible and irreversible processes. Then, after some time (the interpulse delay), another  $90^\circ$  pulse is applied but now about the  $y$  axis (phase shift). The second pulse reverses the original free precession rates, so the spins are now converging instead of diverging. As a result, the signal builds up into what is called a spin echo.<sup>1</sup> Note that the echo cannot reverse all of the decay, because irreversible processes are also involved.

Creating the echo has several advantages over using a single pulse. Because the probe functions as both a transmitter of the pulse and a receiver of the signal, it has to rapidly switch from pulsing mode to signal acquisition mode within the dead time. With an echo, additional time for refocusing is built into the experiment, so the echo peak is shifted away from the RF pulses. In this way, the entirety of the echo is observable, without any distortion from frequency-dependent phase shifts.

### Spectral Acquisition for Solution Spectrometers

To demonstrate the applicability of this experiment, the results between solution and solid-state NMR spectrometers are compared. Spectra for two deuterium Larmor frequencies of 76.77 MHz ( $^1\text{H}$  frequency of 500 MHz) and 46.04 MHz ( $^1\text{H}$  frequency of 300 MHz) are shown in Figure 4. Note that the experiment can also be performed on NMR spectrometers with weaker magnetic field strengths (e.g., 200 MHz). A broad-band (variable frequency) probe (as used in Figure 4B) is recommended; however, the deuterium lock channel of a liquids NMR probe (Figure 4D) can also be used. For this experiment, the deuterium lock and the shimming are not



**Figure 4.** Comparison of  $^2\text{H}$  NMR spectra of HMB- $d_{18}$  obtained on solids (left) and liquids (right) NMR spectrometers. Spectra were acquired with NMR spectrometers operating at a hydrogen frequency of (A and B) 500 MHz and (C and D) 300 MHz. These spectra were recorded on (A) Bruker AMX-500, (B) Bruker DRX-500, (C) Bruker AMX-300, and (D) Varian Unity-300 consoles. This experiment is also feasible using weaker NMR magnets (e.g., 200 MHz). Spectra are plotted as a function of relative frequency  $\nu - \nu_0$ , where  $\nu_0$  is the Larmor frequency. Note that absolute frequency increases to the left, and hence, wavelength increases to the right.

needed because of the large spectral width. The spectra are typically plotted as a function of relative frequency  $\Omega/2\pi = \nu - \nu_{\text{ref}}$  where  $\nu_{\text{ref}}$  is the spectrometer reference (carrier) frequency. For  $^2\text{H}$  NMR, the reference frequency is  $\nu_0$ , the Larmor frequency. The transition frequencies  $\nu$  are negative (see below). The transition energies and, hence, the absolute frequencies (neglecting the sign) increase to the left, with wavelengths increasing to the right in accord with spectroscopic convention. Specifics on the instrumental parameters and precautions can be found in the Supporting Information.

### HAZARDS

HMB- $d_{18}$  has no known occupational safety and health administration (OSHA) hazards. It is not a dangerous substance according to the globally harmonized system of classification and labeling of chemicals (GHS). However, it is important to observe all safety precautions and avoid direct contact with the substance. NMR magnets may interfere with electronic and metallic implants; so those who have them should not come near the NMR magnet at any time.

### INTERPRETATION OF NMR SPECTRA

#### Nuclear Magnetic Resonance and the Zeeman Effect

NMR spectroscopy measures the transitions of nuclear spins between different energy states. Basic quantum mechanics—as described in undergraduate texts<sup>7,8</sup>—says the energies of each of the eigenstates in the perturbing magnetic field must be determined. The NMR spectrum directly provides information about both structure and dynamics.

To do this, Schrödinger's equation needs to be solved, which gives the energy eigenvalues directly:

$$\hat{H}_Z \psi_{I,m} = E_m \psi_{I,m} \quad (1)$$



The Zeeman Hamiltonian ( $\hat{H}_Z$ ) expresses the energies ( $E_m$ ) of the spin eigenstates:

$$\hat{H}_Z = -\gamma\hbar B_0 \hat{I}_Z = \hbar\omega_0 \hat{I}_Z \quad (2)$$

Here  $\omega_0$  is the Larmor frequency equal to  $-\gamma B_0$ , and  $B_0$  is the magnetic field strength in units of tesla (T). In eq 2,  $\gamma$  is the magnetogyric ratio ( $41.066 \times 10^6 \text{ rad s}^{-1} \text{ T}^{-1}$  for  $^2\text{H}$ ), which is the ratio of the magnetic moment to the spin angular momentum of the nucleus. The precession frequency of the  $^2\text{H}$  nucleus is negative (since  $\gamma$  is positive) and it occurs in the clockwise direction.

The Zeeman Hamiltonian is used to solve for the energies of each of the nuclear spin states. To do so, the angular momentum eigenvalue relations, as provided in eqs 3 and 4, are needed.

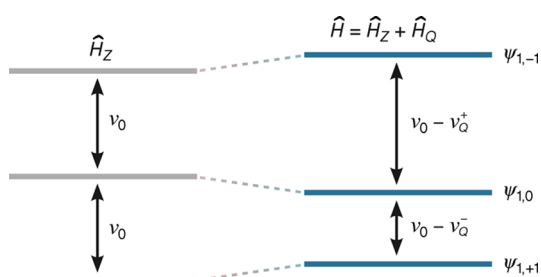
$$\hat{I}_Z \psi_{I,m} = m \psi_{I,m} \quad (3)$$

$$\hat{I}^2 \psi_{I,m} = I(I+1) \psi_{I,m} \quad (4)$$

The eigenvalue problem in eq 1 can be solved with use of eqs 2–4, to yield the Zeeman energies,  $E_m$ :

$$E_m = -\gamma\hbar B_0 m = m\hbar\omega_0 \quad (5)$$

Transitions between spin energy states (see Figure 5) are observed in NMR spectroscopy, and for this the radiofrequency



**Figure 5.** The Zeeman energy splitting removes the degeneracy of the nuclear spin energy states, and the quadrupolar perturbation causes an inequality of the two energy-level transitions.

of the electromagnetic radiation that is absorbed must be known. The Bohr frequency condition is used to equate the frequency of the transition to the energy gap between adjacent levels (single quantum transitions):

$$h\nu = \Delta E = E_{m+1} - E_m \quad (6)$$

By using eq 6 and only single-quantum transitions, the frequency for the transitions corresponding to the Zeeman effect,  $\nu_0$  (as depicted in the left half of Figure 5), can be found:

$$\nu_0 = \omega_0/(2\pi) = -\gamma B_0/(2\pi) \quad (7)$$

Here  $\nu_0$  is the Larmor frequency, which is observed in NMR spectroscopy. However, deviations from the nuclear Larmor frequency give more information about the molecular system. The quadrupolar interaction causes deviations from the main Larmor frequency and is discussed below.

### The Quadrupolar Interaction

The magnetic Zeeman effect is not the entire picture as deuterium is involved, which is a quadrupolar nucleus (and its shape is likened to an American football). If you imagine a dipole caused by a positive and negative charge separation, it has two lobes in its field lines (whether electric or magnetic).

For a quadrupole, there are four lobes in its field lines. This electric quadrupole moment of the nucleus can interact with electric field gradients that may surround it.

How can this contribution be evaluated? Again the Schrödinger's eigenvalue equation must be solved, but with a quadrupolar perturbation added:

$$\hat{H} = \hat{H}_Z + \hat{H}_Q \quad (8)$$

The quadrupolar Hamiltonian ( $\hat{H}_Q$ ) is a first-order perturbation of the Zeeman effect in the high static magnetic field limit, due to the electronic distribution of the carbon–deuterium bond.<sup>9</sup> The strength of the main magnetic field can be utilized to yield the secular part (the part that commutes with the Zeeman Hamiltonian) of the quadrupolar interaction:

$$\hat{H}_Q = \frac{1}{4}\chi_Q h(3\hat{I}_Z^2 - \hat{I}^2)P_2(\cos\beta) \quad (9)$$

where

$$P_2(\cos\beta) = \frac{1}{2}(3\cos^2\beta - 1) \quad (10)$$

In the preceding formulas,  $\chi_Q$  is the quadrupolar coupling constant (for carbon–deuterium bonds  $\chi_Q = 167 \text{ kHz}$ ), which contains information about the electric field gradient at the deuterium nucleus. The second-rank Legendre polynomial,  $P_2(x)$  where  $x = \cos\beta$ , depends on the electric field gradient orientation with respect to the nucleus (which is aligned relative to the main magnetic field). Thus, the Hamiltonian is dependent on the orientation of the molecule ( $\beta$ ) in the main magnetic field ( $B_0$ ). Note that Legendre functions also occur in the spherical harmonics as found in atomic wave functions in undergraduate courses.<sup>7,8</sup>

Next, the eigenvalue relations in eqs 1, 3, and 4 can be readily applied to obtain the solution for the energy-level shift due to the quadrupolar perturbation:

$$E_m = \frac{1}{4}\chi_Q h(3m^2 - 2)P_2(\cos\beta) \quad (11)$$

Because deuterium is a spin-1 nucleus ( $I = 1$ ) it is necessary to find the frequency shift for the transitions between eigenstates with projection indices  $m = -1, 0$ , and  $1$ . The transitions are shown in Figure 5 in terms of only the Zeeman effect ( $\hat{H}_Z$  on the left), and also with the quadrupolar perturbation included ( $\hat{H}_Z + \hat{H}_Q$  on the right). Applying the Bohr frequency condition, the differences between the energy states give rise to the frequencies of the transitions:

$$\nu_0 - \nu_Q^+ = (E_0 - E_{-1})/h \quad (12)$$

$$\nu_0 - \nu_Q^- = (E_{+1} - E_0)/h \quad (13)$$

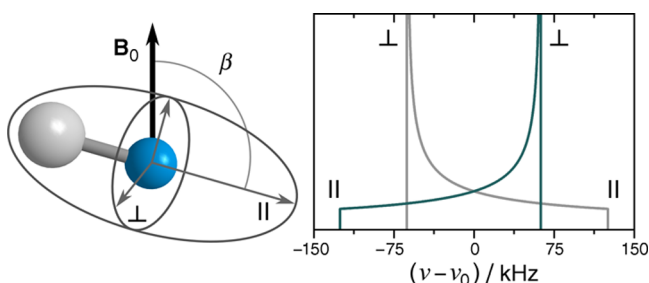
The resulting transition frequencies are as follows:

$$\nu_Q^\pm = \pm \frac{3}{4}\chi_Q P_2(\cos\beta) \quad (14)$$

Here, the  $\pm$  notation corresponds to the two transitions.

### Powder Spectrum and Motional Averaging

The quadrupolar splitting frequencies are modulated by static coupling and molecular motions of HMB- $d_{18}$  in powder form due to the dependence on the Euler angle  $\beta$ . This angle is between the principal axis of the interaction, defined by the carbon–deuterium bond shown in dark gray in Figure 6, and the laboratory frame, defined by the main magnetic field



**Figure 6.** Schematic illustration of instantaneous orientation of the carbon–deuterium bond within the main magnetic field (left) and its resulting powder-pattern line shape (right): the theoretical Pake doublet is a result of all of the orientations of the powder sample. Note that the intensity distribution is determined by the density of states that exist in each orientation.

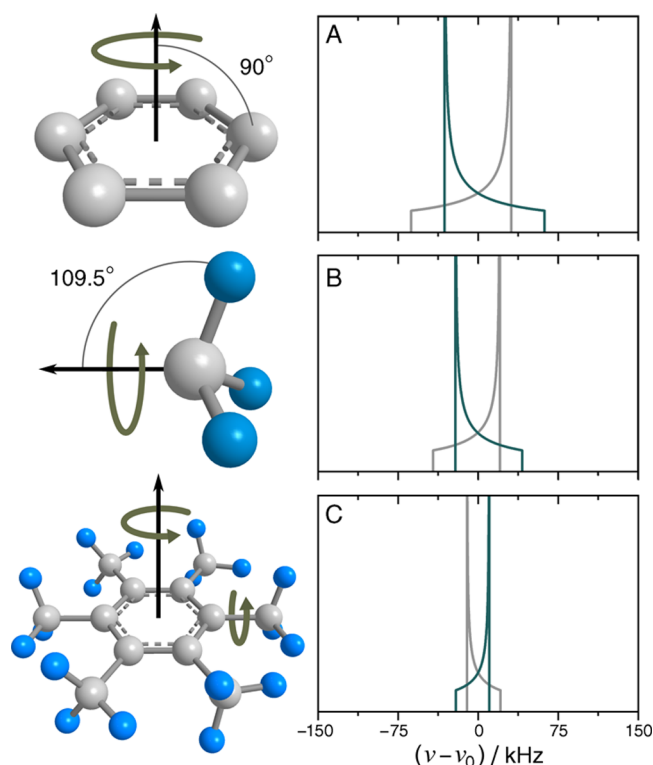
(labeled as  $B_0$  in Figure 6). Furthermore, this angle can be decomposed into multiple angles, each representing an interaction with the main magnetic field (static interaction) or molecular motion (motional averaging) as discussed below.

Because a powdered form of HMB- $d_{18}$  is used, as opposed to crystalline, it is necessary to sum over all of the nuclear spin orientations. Recall that there are two transitions that differ in sign; thus there will be two branches in the spectrum shown in different shades in Figure 6. The quadrupolar interaction is dependent on the orientation of the carbon–deuterium bond in the main magnetic field, as given by the angle  $\beta$  in Figure 6. By inserting this angle into eq 14, it becomes apparent which part of the spectrum corresponds to the orientation of the bond. The contributions due to parallel and perpendicular orientations of the bond (static interaction), relative to the main magnetic field, are illustrated in Figure 6. Intuitively, the shape of the spectrum can be understood by looking at how many states occupy each orientation. When  $\beta = 0$  ( $\parallel$  in Figure 6), only one state exists, just as there is only one north pole. The splitting is at a maximum, so this corresponds to the lowest and highest frequency components of the spectrum. Further, when  $\beta = 90^\circ$  ( $\perp$  in Figure 6), the splitting is reduced by  $-1/2$ , but now there is a maximum in the number of states, just as there are many points occurring on the earth's equator. Hence, the probability is at a maximum (which becomes finite due to line broadening). With this in mind, the spectrum will span negative frequencies to positive. Because there are two transitions, but with opposing signs, there are two branches of the spectrum—thus, the Pake doublet!

It is important to ascertain whether the experimental spectrum is as wide as the theoretically predicted powder spectrum (see Table 2 for specific values). The answer is clearly no, which means that there are molecular motions. If there are significant molecular dynamics within the system, the nucleus experiences an averaged electric field gradient that narrows the spectrum; this is also called motional averaging. Notably, this allows insight into the molecular motions of solid samples, as illustrated in Figure 7. When dynamics are present, an average over eq 14, as defined by the angular brackets  $\langle \rangle$  is needed:

$$\nu_Q^\pm = \pm \frac{3}{4} \chi_Q \langle P_2(\cos \beta) \rangle \quad (15)$$

In the above formula the average or expectation value of the Legendre polynomial is formally given by



**Figure 7.** Molecular motions result in a reduction of the spectral width according to the value of the second-order Legendre polynomial given in eq 10. Motional averaged spectra are shown for two simple types of motion: (A) rotation of the benzene ring and (B) methyl group rotation. If both motions are present (C), then the reduction of the spectral width is given by the product of their Legendre polynomials.

**Table 2. A Summary of Static Coupling and Types of Molecular Motions with Corresponding Spectral Narrowing**

Type	Angle ( $\beta$ )	$\langle P_2(\cos \beta) \rangle$	$\nu_Q^\pm$ /kHz
Static	$90^\circ$	$-1/2$	$\mp 62.6$
Methyl Rotation	$109.5^\circ$	$(-1/2)(-1/3)$	$\pm 20.9$
Ring Rotation	$90^\circ$	$(-1/2)(-1/2)$	$\pm 31.3$
Combined Rotation	$90^\circ, 109.5^\circ$	$(-1/2)(1/6)$	$\mp 10.4$

$$\langle P_2(\cos \beta) \rangle = \frac{\int_0^\pi \frac{1}{2} (\cos^2 \beta - 1) \sin \beta \, d\beta}{\int_0^\pi \sin \beta \, d\beta} \quad (16)$$

As an illustration of averaging, consider various types of rotational motion. First imagine a 6-fold rotation of the benzene ring. This is another way of saying the axis of rotation (which extends through the middle of the benzene ring) is perpendicular to the methyl groups, and thus,  $\beta = 90^\circ$  (Figure 7A). From the second-rank Legendre polynomial, this angle generates a coefficient of  $-1/2$ . Thus, the spectrum is reduced by one-half and the spectral branches are reversed! Does this reduction of the spectral width match the experimental results? It does not, so other types of motions need to be considered. For example, chemists may know that free rotation of methyl groups occurs where the angle of rotation is the tetrahedral angle such that  $\beta = 109.5^\circ$  (Figure 7B). From the second-rank Legendre polynomial, a coefficient of  $-1/3$  is found. Although the reduction of the splitting by one-third is an improvement, it is still not sufficient.

Now a combination of both motions is considered: methyl group rotation and rotation of the HMB- $d_{18}$  ring. A composite motional averaging results in a total averaging of  $(-1/3)(-1/2) = 1/6$ . The corresponding frequencies for the weak singularities are shown in Table 2. A theoretical calculation of this motionally averaged spectrum is shown in Figure 7C. Notably, this prediction of combined motions nearly fits the experimental spectra. An amazing correspondence of the theoretically predicted value to the observed spectrum is evident.

In this way, students are able to analyze a spectrum and discover the molecular motions in a seemingly immobile system. Optional MATLAB (MathWorks, Natick, MA) scripts that simulate the spectra are included in the Supporting Information. These may aid the student in predicting the motions present in the sample and are included in an optional section in the student portion of the Supporting Information.

## DISCUSSION

With use of hexamethylbenzene- $d_{18}$  a feasible and meaningful solid-state NMR experiment for undergraduate students can be readily performed. It relies on introductory knowledge of basic quantum mechanics (and molecular structure). The experiment can be a short one, neglecting time for setting it up, taking about a quarter of an hour or can be extended for a few hours for better signal-to-noise. It is shown that even for a solid there is a surprising amount of molecular mobility. This molecular motion is dramatically seen in the solid-state  $^2\text{H}$  NMR experiment and enables significant discovery-based learning.

Particular attention has been paid to making this experiment flexible to meet differing needs for institutions with varying capabilities. It can be done in as little as 10 min (the only sacrifice is a noisier spectrum). Moreover, the experiment can be accomplished using a broadband solution probe or the deuterium lock channel of a high-resolution probe. Thus, meaningful results can be obtained on any typical solution NMR spectrometer and with a variety of probes. In all cases, the line shape is symmetric about the Larmor frequency (designated as zero) and the predicted maxima due to the perpendicular orientations of the electric field gradient are clearly present. It may have been noticed that in the high-resolution experiments there is a lack of "shoulders" or parallel components of the quadrupolar interaction in the NMR spectra. In general, the more powerful the pulse the shorter is its pulse length, and the wider the range of frequencies that can be excited. However, to rotate the nuclear magnetization by a full  $90^\circ$  with a high-resolution probe at low power, small pulse lengths cannot be achieved, and the higher frequency Fourier components are lost. Nonetheless, the defining perpendicular components for the interaction remain—it is those transitions that explain the spectra in terms of molecular motions.

An undergraduate investigation employing solid-state  $^2\text{H}$  NMR provides an informative exposure to state-of-the-art research techniques that would otherwise neither be covered nor mentioned in an undergraduate experience. The experiment uses facilities that are generally already in place in many institutions. As colleges and universities continue to acquire solid-state NMR instrumentation in the future, such as magic-angle spinning, this exposure will become increasingly significant for students in physical, biological, and analytical chemistry.

## ASSOCIATED CONTENT

### Supporting Information

Instructions for the student; notes for the instructor; MATLAB program files that aid in theoretical prediction of spectra produced in this experiment; raw data (in both Bruker and ASCII formats), which students may analyze if they do not have access to a NMR spectrometer. This material is available via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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