Zero-Field Nuclear Magnetic Resonance

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In polycrystalline samples, NMR "powder spectra" are broad and much structural information is lost as a result of the orientational disorder. In this Letter Fourier-transform NMR in zero magnetic field is described. With no preferred direction in space, all crystallites contribute equivalently and resolved dipolar splittings can be interpreted directly in terms of internuclear distances. This opens the possiblity of molecular structure determination without the need for single crystals or oriented samples.

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Techniques for studying molecular structure, such as x-ray diffraction and nuclear magnetic resonance (NMR), often require the use of single crystals[1] or oriented samples.[2] NMR, for example, is sensitive to interatomic distances and angles through spectral splittings caused by internuclear dipole-dipole couplings in high magnetic field. Where only polycrystalline powders or amorphous materials are available, the distribution of molecular orientations (and thus internuclear vectors) with respect to the direction defined by the x-ray beam or by the magnetic field gives rise to a "powder pattern" in which most structural information is lost.[3]

Consider the notion of NMR with zero magnetic field, i.e., spectroscopy of pure dipole-dipole interactions. Without an externally imposed direction in space, all orientations are equivalent and the spectrum of a powder should be "crystal-like" with all equivalent molecules yielding identical splittings. We present in this Letter a novel experiment, Fourier-transform zero-field NMR, which provides just such spectra, opening the way for crystallography and molecular structure determination in polycrystalline or disordered materials.

Figure 1 illustrates the idea for the simple case of two coupled proton spins [$Ba(ClO_3)_2 \cdot H_2O$], showing increased resolution due to the removal of orientational broadening in zero field. Figure 1(a) is the normal high-field powder spectrum. Figure 1(b) is a normal high-field single-crystal spectrum where the doublet splitting depends on crystal orientation with respect to the field. Figure 1(c) is the zero-field powder spectrum in which the splittings assume only the largest values of the powder pattern in 1(a), resulting from the untruncated dipolar Hamiltonian $\mathcal{H}^D$.

While zero-field spectroscopy is known and

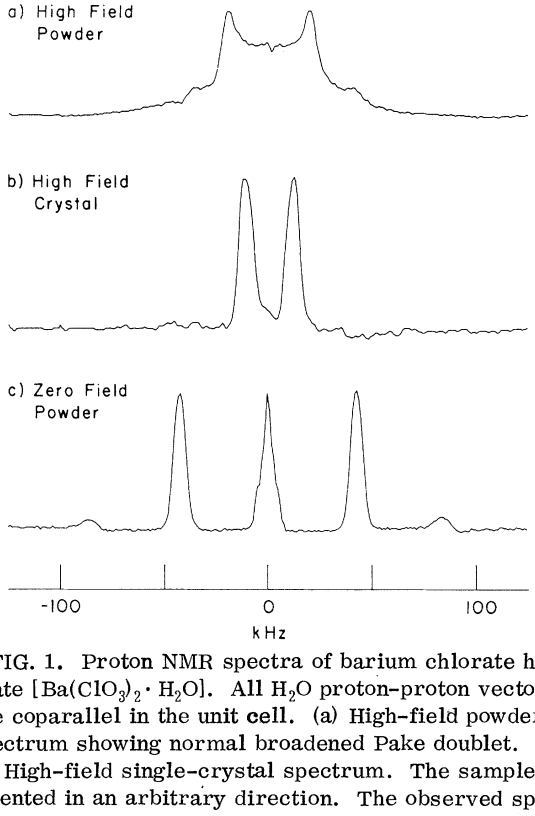

FIG. 1. Proton NMR spectra of barium chlorate hydrate [$Ba(ClO_3)_2 \cdot H_2O$]. All H_2O proton-proton vectors are coparallel in the unit cell. (a) High-field powder spectrum showing normal broadened Pake doublet. (b) High-field single-crystal spectrum. The sample is oriented in an arbitrary direction. The observed splitting depends on both internuclear distance and orientation. (c) Zero-field powder spectrum. The major features are those predicted by the simple treatment given in the text for a pair of coupled spins of $\frac{1}{2}$. The observed splitting is a direct, orientation-independent measure of the internuclear distance. The central peak arises from spins in crystallite orientations which did not evolve in zero field.

widely used for EPR and nuclear quadrupole resonance,[4] it is primarily done in the frequency domain (the analog of continuous-wave NMR) and the signals are prohibitively small except for large quadrupole frequencies. Aside from unique circumstances,[5] it is inapplicable to NMR. For low-sensitivity quadrupolar nuclei, field cycling with double resonance has been used.[6,7] Our method employs field cycling in a novel fashion and is illustrated in Fig. 2. The sample is polarized in a large magnetic field B_0, which is removed in two steps. The first step brings the sample adiabatically to an intermediate field which is still large compared to the local field of $\mathcal{H}^D$. The second step is sudden and initiates the coherent evolution period subject to $\mathcal{H}^D$. At time t_1, the field is switched back and the sample returned to B_0 for detection of a high-field signal $S(t_1)$. Fourier transformation of $S(t_1)$ results in a zero-field spectrum with the full sensitivity of high-field detection.

To understand the type of spectrum expected for a powder in zero field, consider an orientation-dependent transformation T which transforms between the laboratory frame (with z along B_0) and a crystallite frame which is fixed relative to the molecules and independent of crystallite orientation in the laboratory. If the initial density operator in zero field is $\rho(0)$, then at t_1 (ignoring spin-lattice relaxation)

$$\rho(t_1) = \langle T^{-1}\exp(-i\mathcal{H}^D t_1)\, T\rho(0)T^{-1}\exp(i\mathcal{H}^D t_1)\, T\rangle, \tag{1}$$

where angular brackets designate an average over the distribution of crystallite orientations in the laboratory. While all frequencies are orientation independent, line intensities are an average over T. For the case of normal high-field Zeeman polarization $[\rho(0)=I_z]$ and the simplest case of two coupled spins (i and j), evaluation of (1) yields, for the zero-field free-induction decay,

$$S(t_1) = \frac{\mathrm{Tr}\{I_z\rho(t_1)\}}{\mathrm{Tr}\{I_z^2\}} = \frac{1}{3} + \frac{2}{3}\cos\omega_{ij}{}^D t_1, \tag{2}$$

where

$$\omega_{ij}{}^D = 3\gamma^2\hbar/2\pi r_{ij}{}^3$$

and r_{ij} is the distance between i and j. Thus we expect the Fourier-transform spectrum to contain one line at zero frequency and one each at $\pm\omega_{ij}{}^D$, all of equal intensity, which is the main observation of Fig. 1(c). The additional features of the latter spectrum[8] arise from couplings between water molecules and are an indirect measure of these distances as well. The calculated proton-proton distance (assuming no motion) is 1.60 Å which is identical to the results of single-crystal NMR studies.[9] The small discrepancy from neutron-diffraction data[10] is a measure of librational motion which partially averages the observed coupling.

In larger spin systems, the spectrum will rapidly become more complex. An appealing idea is then to improve resolution by isotopic dilution of the protons in a deuterated host. ^{1}H-^{1}H couplings could be measured without the need for ^{2}D decoupling[11] since ^{1}H-^{2}D dipolar couplings are effectively quenched in zero field by the nonzero asymmetry parameter of the ^{2}D electric field gradient,[12] as has been seen in the pure nuclear quadrupole resonance spectra of deuterium.[7] As a preliminary example of this, Fig. 3 shows spectra of powdered dimethylterephthalate diluted to 16% in its perdeuterated analog. Whereas the normal high-field spectrum is essentially featureless, the zero-field spectrum yields resolved splittings which arise from couplings within the methyl group and between ortho aromatic protons. Resolution in these measurements will ultimately be limited by spin-lattice relaxation times, which can be controlled by variable temperature experiments.

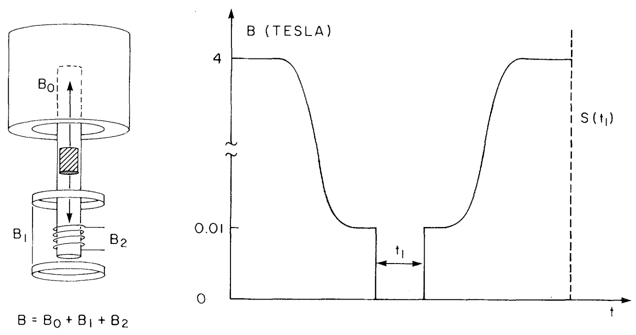

FIG. 2. Schematic diagram of the field cycling apparatus and the time-dependent effective field at the sample. The sample is moved adiabatically (~ 100 ms) from the bore of the superconducting magnet ($B_0 \sim 4.2$ T) to a position ~ 75 cm below where the fringe field due to B_0 is precisely canceled by B_1. At time $t_1 = 0$ coil B_2 (0.01 T) is switched off (~1 μs; residual field less than 10^{-5} T), and evolution under the zero-field Hamiltonian is initiated. Coherent evolution is terminated by reapplying B_2, followed by transit back to the bore of B_0 where the magnetization is sampled. The entire procedure is repeated for regularly incremented values of t_1. Fourier transformation of the resulting free-induction decay results in the zero-field spectrum.

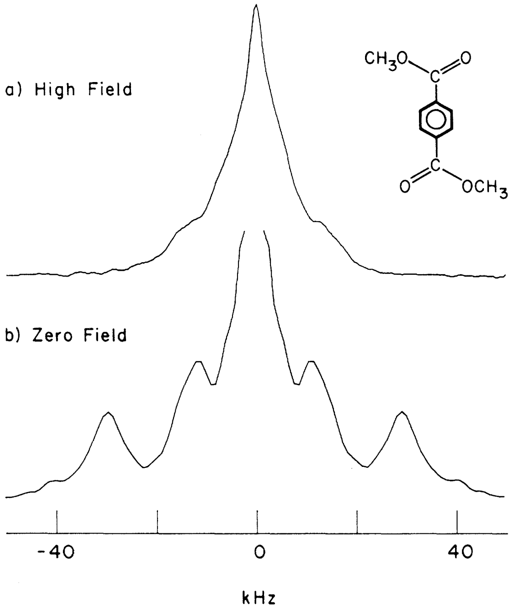

FIG. 3. NMR spectra of dimethylterephthalate powder. The sample is 16% dimethylterephthalate-h_{10} in dimethylterephthalate-d_{10}. (a) High-field powder spectrum. (b) Zero-field powder spectrum. The outside pair of lines are those expected from a rapidly spinning methyl group where the interproton distances are 1.83 Å. The interior pair of lines arise from the aromatic ring pairs of protons separated by 2.49 Å.

We conclude with some comments on possible applications and extensions of zero-field NMR. (a) The experiments described in this Letter began with an initial Zeeman state $\rho(0)=I_z$. States of multiple spin or n-quantum correlation[13,14] would yield different zero-field spectra, with additional information on dipolar couplings and structure. (b) The best resolved and most easily interpreted zero-field spectra arise from small sets of coupled spins. One approach is to work with randomly protonated materials in a perdeuterated host or dilute spin species such as ^{13}C-^{13}C (yielding backbone structures in organic molecules), ^{29}Si-^{29}Si or ^{1}H-^{29}Si (in silicates or semiconductors), or ^{1}H-^{31}P (in biological systems). Combining this with magic-angle spinning[15] (and replacing the zero field with a field matched to the spinning frequency) in a full two-dimensional experiment[16] would yield correlations between dipolar couplings and chemical shifts. (c) In cases where small quadrupolar coupling constants make direct low-frequency detection difficult, this technique could also be used to obtain the Fourier-transform pure quadrupole resonance spectrum. This would be particularly valuable when no abundant high-γ nuclei are available for double resonance[6,7]—for example, ^{23}Na and ^{27}Al in aluminosilicates.

In summary, we have introduced a novel zero-field NMR experiment which yields dipolar couplings in powders with high resolution and sensitivity. The spectra are devoid of orientational broadening and open the possibility of structure determination in a wide range of materials without the need for single crystals or oriented samples.

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[8] Note the structure on the central line and the small peaks at $\pm 2\omega_{ij}{}^{D}$: Interpair proton couplings introduce the possibility of four spin transitions at these additional frequencies.

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