Pake Patterns from Zero to High Field

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High-field NMR of a two-spin-$\frac{1}{2}$ or spin-1 system in a powder results in the well-known "Pake pattern," a superposition of "Pake doublets" for all crystal orientations (*1*). An example of such a powder pattern is shown in Fig. 1 for solid barium chlorate hydrate, $Ba(ClO_3)_2 \cdot H_2O$. The corresponding spectrum in zero field, which we term the zero-field Pake pattern, consists of three lines of equal intensity, at 0 and $\pm 3\omega_d/2$, where $\omega_d = \gamma^2 \hbar / r^3$, the dipolar coupling constant (*2*). In this communication, we demonstrate how the spectrum changes from its zero-field form to the high-field pattern as the magnetic field is increased. This experiment constitutes a time-domain analog of low-field frequency-domain NMR using field cycling (*3, 4*). It should prove useful in cases where the high-field spectra are extremely broad (*5*) or where tunneling and other lattice resonances are being investigated (*6*).

The field cycle used for these experiments is shown schematically in Fig. 2. It is similar to the zero-field experiment, with the minor modification that the *z* magnetic field, instead of being reduced suddenly to zero, is changed suddenly to a variable low value B_1 along a direction perpendicular to *z*, say *x*. The spin system begins with a high-field density operator proportional to I_z which evolves for a period t_1 in the low
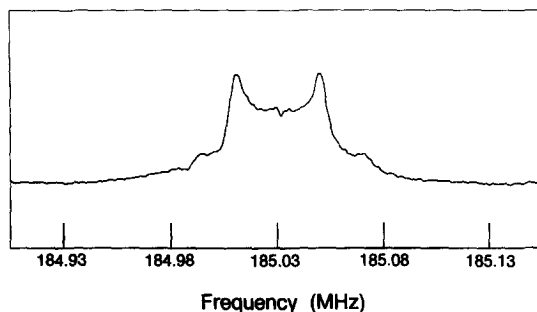

FIG. 1. High-field proton NMR spectrum of polycrystalline $Ba(ClO_3)_2 \cdot H_2O$. The proton pairs in the water molecules, well isolated from each other, yield a familiar Pake powder pattern.

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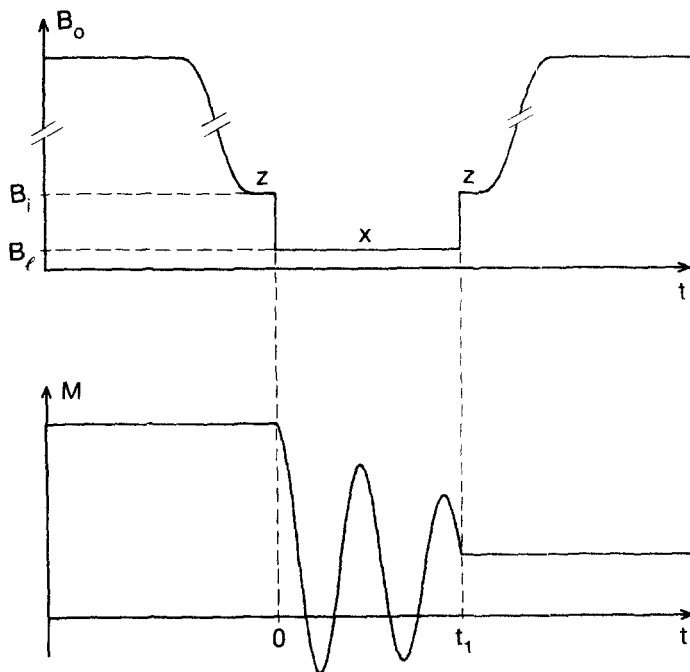
FIG. 2. Field cycle for the low-field NMR experiment. The sample is removed from the high-field magnet B_0 to an intermediate field B_i which is suddenly replaced by a low field B_l along the x axis. The evolved magnetization is stored by reapplication of the intermediate field followed by return of the sample to high field and NMR detection of the magnetization.
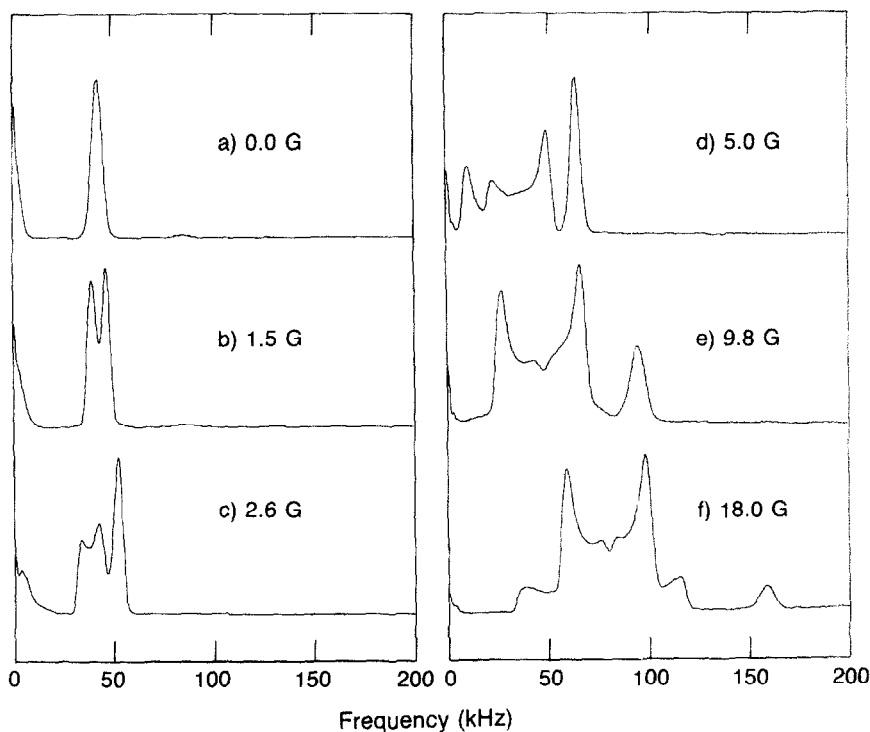

Frequency (kHz)

FIG. 3. Pake powder patterns for $Ba(ClO_3)_2 \cdot H_2O$ at different magnetic fields, obtained using the sequence shown in Fig. 2. In zero field, lines at zero frequency and $\pm 3\hbar\gamma^2/2r^3$ are observed. As the field is increased, the powder pattern of Fig. 1 emerges together with the $\Delta m = 2$ overtone transition.
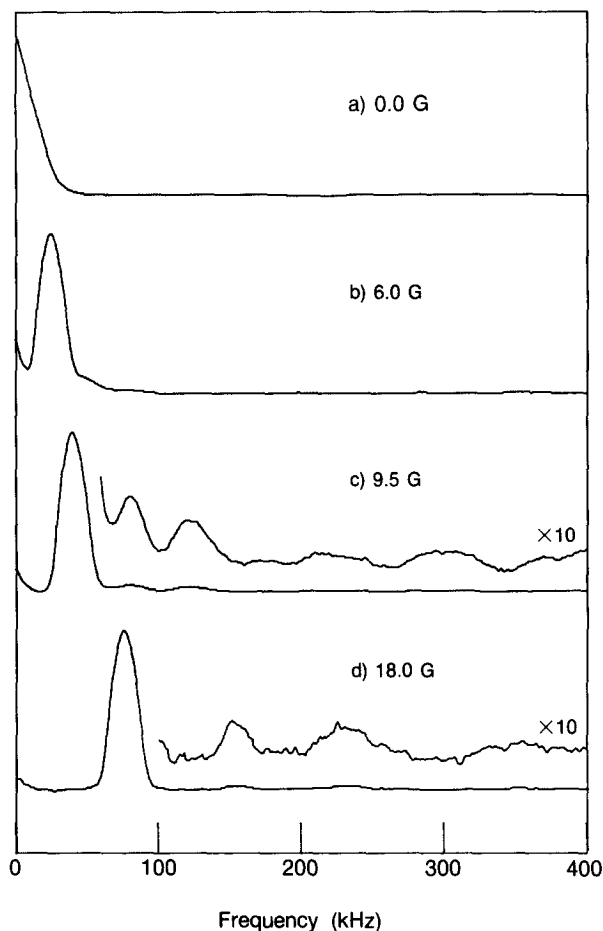
FIG. 4. Proton spectra of $(NH_4)_2SO_4$ in zero and low fields. The spectrum here is broad and unresolved at any field, owing to the complexity of the dipolar interactions in the multispin system. Lines at the second and third harmonics of the Larmor frequency are observable at low fields.

x field. The z magnetization is then stored by reapplication of the z field and is detected by normal high-field NMR. Fourier transformation with respect to the time t_1 yields the low-field NMR spectrum. A quadrature extension of this experiment is possible by separately detecting the low-field y component of magnetization. The experiment was performed for various values of B_1 from 0.0 to 18.0 G, and the results for barium chlorate hydrate are shown in Fig. 3. It is interesting to observe the emergence of the high-field powder pattern as the field is increased. The situation is analogous for a spin-1 nucleus such as deuterium or nitrogen-14, going from zero-field NQR to high-field quadrupole-perturbed NMR. The higher frequency line in Figs. 3e and 3f corresponds to the $\Delta m = 2$ transition, free (to first order) of dipolar or quadrupolar broadening. Such transitions are observed in overtone NMR spectroscopy (7) and double-quantum NMR spectroscopy (8) of deuterium and nitrogen-14.
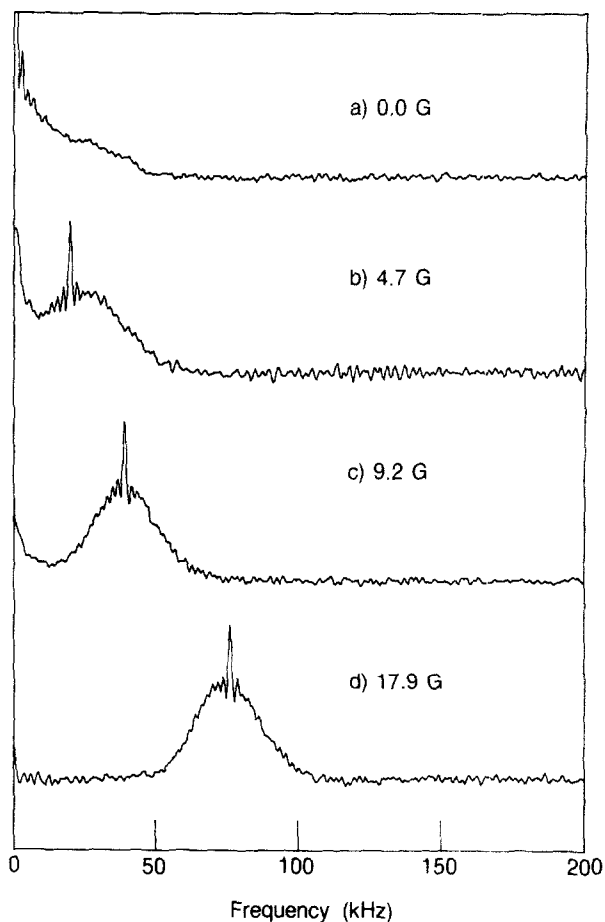
FIG. 5. Proton spectra of silver acetate in zero and low fields. For the methyl group, some of the transitions are not split or shifted by intramolecular couplings, so the spectrum includes a narrow component at all applied fields.

Solid ammonium sulfate, $(NH_4)_2SO_4$, is an example of a "crowded" multispin system, where the dipolar couplings result in a broadening of the proton NMR line, but no resolvable splittings in zero or high field. Figure 4 shows proton spectra of polycrystalline ammonium sulfate in fields from 0.0 to 18.0 G. The prominent peak, at the Larmor frequency ω_0, appears to change little in shape as a function of field strength. In the high-field limit, the intensities of the peaks at $2\omega_0$ and $3\omega_0$ are expected to fall off as B_1^{-2} and B_1^{-4}, respectively (3). Figure 5 displays low-field proton spectra of polycrystalline silver acetate, where all the protons occur in methyl groups. For well-isolated methyl groups, the high-field powder pattern consists of a Pake pattern superposed on a sharp line that is unaffected by couplings within the methyl group (9). The dipolar broadening is substantial, owing to relatively close intermolecular spacings, so the Pake pattern appears as a smooth, broad line. The central line, however, is relatively sharp and remains so at all fields. The low-field experiment described

above can be modified so that the field B_1 is along z instead of x. In that case, we observe oscillations of the z magnetization in low field. There is an analogous longitudinal experiment in overtone NMR spectroscopy (7), and this is also related to the field-cycling experiment of Strombotne and Hahn (10).

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