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## Resolved Dipolar Coupling Spectra of Dilute Nuclear Spins in Solids\*

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An elaboration of solid-state NMR double resonance yields detailed molecular structural information residing in the dipole-dipole interactions between a rare spin and its nearest abundant-spin neighbors. The experiment depends upon (1) suppression of dipolar interactions among the abundant spins, and (2) observation of oscillatory interchange of magnetization between individual rare spins and their neighbors. Structural and dynamical information can be had even from powdered or amorphous samples.

The earliest applications of NMR spectroscopy to chemical and solid state physics employed splittings produced by the nuclear magnetic dipole-dipole interaction to deduce atomic positions in solids.<sup>1</sup> This interaction has special appeal for the determination of structural parameters because, unlike any of the other perturbations experienced by nuclear spins, its strength is specified by interatomic distances and orientations directly without involvement of molecular theory. However, this experimental method has enjoyed relatively little popularity because the spectra characteristically have too few resolvable features to determine the large number of structural parameters needed. To see why this is true, consider the effect of neighboring dipoles on a particular reference spin having a particular structural environment:

(1) If  $N$  neighbors need to be considered in characterizing the spectrum of the reference spin to a given accuracy, a total of  $N(N+1)/2$  interactions enter, only  $N$  of which involve the reference spin itself.

(2) Reference spins of a particular species having structurally different environments, or en-

vironments that are structurally equivalent but differ in orientation with respect to the external field  $\vec{H}_0$ , generally give strongly overlapping resonance spectra, disguising the interesting spectroscopic detail that might exist in the spectrum of a single reference spin.

In this Letter we point out that extensions of "modern" NMR techniques are capable of ameliorating this situation considerably: Consider a rotating-frame double-resonance manipulation of the kind first employed by Hartmann and Hahn<sup>2</sup> for the detection of rare spins  $S$  surrounded by abundant spins  $I$  in a solid. Strong rotating fields of amplitudes  $H_{1S} = \omega_{1S}/\gamma_S$  and  $H_{1I} = \omega_{1I}/\gamma_I$  are applied at frequencies  $\omega_S$  and  $\omega_I$  which are near the resonance frequencies  $\omega_{0S} = \gamma_S H_0$  and  $\omega_{0I} = \gamma_I H_0$ , respectively. The secular behavior of the spins is calculated, as usual, in a frame of reference that suppresses the nutation of the spin species due to their respective applied static and rotating magnetic fields.<sup>3</sup> In this frame of reference the effective Hamiltonian is<sup>4</sup>

$$\mathcal{H} = \mathcal{H}_I^0 P_2(\cos \xi_I) + \mathcal{H}_{IS}^0 \cos \xi_I \cos \xi_S + \mathcal{H}_{ff}(t), \quad (1)$$

where  $\mathcal{H}_I^0$  and  $\mathcal{H}_{IS}^0$  are the secular parts of the

dipole interactions, and  $\xi_I$  and  $\xi_S$  are the angles that the  $I$  and  $S$  quantization axes make with the Zeeman field  $H_0$ . The  $S$ - $S$  interactions are negligibly small because of the large distances between rare  $S$  spins. The term  $\mathcal{H}_{ff}(t)$  is responsible for the exchange of Zeeman energy between the two species. If we consider a single  $S$  spin this term may be written

$$\mathcal{H}_{ff}(t) = T \sum_i K_i (I_{i+} S_- + I_{i-} S_+) T^{-1}, \quad (2)$$

with

$$T = \exp[-\frac{1}{2} it (\omega_{eI} - \omega_{eS})(I_z - S_z)], \quad (3)$$

where  $I_z = \sum_i I_{zi}$  and the effective coupling constant for the dipolar interaction is

$$K_i = -\frac{1}{2} \frac{\gamma_I \gamma_S \hbar}{r_i^3} P_2(\cos\theta) \sin\xi_I \sin\xi_S. \quad (4)$$

(If the interactions are scalar in nature,  $K_i = \frac{1}{4} J_i \sin\xi_I \sin\xi_S$ .)

A typical experiment begins with the  $S$  spins "hot," i.e., unpolarized,  $\langle S_z(0) \rangle = 0$ , and  $I$  spins "cold." Eventually, under the influence of (2) the two species come to a common temperature, and the polarization  $\langle S_z(\infty) \rangle$  may be detected either directly<sup>5</sup> or through measurements of  $\langle I_z(\infty) \rangle$ ,<sup>2</sup> since  $I_z + S_z$  is a constant of the motion. The approach to equilibrium, characterized by a first-order rate constant  $T_{IS}^{-1}$ , has been discussed for various cases by MacArthur, Hahn, and Walstedt<sup>6</sup> and Demco, Tegenfeldt, and Waugh.<sup>7</sup> However, during the early stages of  $I$ - $S$  communication an oscillatory behavior of  $\langle S_z(t) \rangle$  is expected<sup>2,4</sup> and has been strikingly demonstrated by Müller *et al.*<sup>8</sup> These oscillations, when  $\omega_{eI} = \omega_{eS}$  in (3), reflect dipole-dipole interactions of  $S$  with its immediate neighbors, so that a suitable analysis can yield local structural parameters.<sup>8</sup> Moreover, it is in the nature of the detection scheme used<sup>5</sup> that spectra of inequivalent  $S$  spins can be segregated on the basis of chemical shifts (*vide infra*), thus attacking problem (2) mentioned earlier in this Letter.

Resolution of the dipolar interactions is impeded by spin diffusion caused by  $\mathcal{H}_{II}^0$ . In fact, if the  $I$  spin diffusion rate were sufficiently rapid no oscillating exchange of energy would occur. In the presently reported experiments we suppress this effect by the application of coherent averaging schemes developed for other purposes.<sup>9,10</sup> We thus obtain prolonged oscillations and simplified spectra reflecting only direct  $I$ - $S$  interactions of the reference spin  $S$ , thus solving problem (1) mentioned earlier.

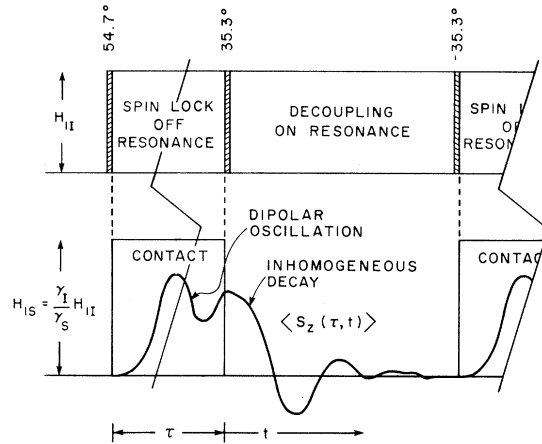


FIG. 1. Schematic diagram of experimental procedure.

A relatively simple version of the experiment goes as follows (see Fig. 1): (1) The  $S$ -spin system is saturated with several  $90^\circ$  pulses spaced in time by several times  $T_2$  for the rare spins. (2) The  $I$  spins, initially in thermal equilibrium with the lattice, are spin-locked *off resonance* by applying a  $\theta_M = 54.7^\circ$  pulse followed by a shift of carrier phase by  $90^\circ$  and carrier frequency by  $\Delta\omega_I = \omega_{0I} = \omega_I = \omega_{1I} \cos\theta_M$ . (3) A strong resonant rf field  $H_{IS}$  satisfying the Hartmann-Hahn condition  $\omega_{IS} = \omega_{eI}$  is applied to the  $S$  spins for a time  $\tau$ . (4) At the end of this mixing,  $H_{IS}$  is switched off,  $\Delta\omega_I$  is switched back to zero, and the  $I$  spin magnetization is pulsed an additional  $35.3^\circ$ , followed by a  $90^\circ$  carrier phase shift to spin-lock the  $I$  spins on resonance. This provides  $I$ - $S$  decoupling during the recording of the Bloch decay of  $\langle S_z(t, \tau) \rangle$ , where  $t=0$  corresponds to the end of the  $S$  excitation. (5) The  $I$  spins are restored to magic-angle spin-lock conditions by a  $-35.3^\circ$  pulse followed by appropriate shifts in phase and frequency. Steps (3)–(5) are now repeated cyclically with accumulation of the  $S$ -spin signal. (6) Finally, the accumulated result is stored and the whole experiment is repeated for varying values of  $\tau$ .

The accumulated data, in the form  $g(t; \tau) = \langle S_z(0; \infty) \rangle - \langle S_z(t; \tau) \rangle$ , are most easily manipulated through a two-dimensional Fourier analysis: A first Fourier transform as a function of  $t$  for fixed  $\tau$  gives a "high-resolution"  $S$ -spin spectrum,  $f(\omega; \tau)$ . This operation separates information corresponding to slightly different Larmor frequencies of the various spins present in the sample. For each of these spin packets,  $f(\omega; \tau)$

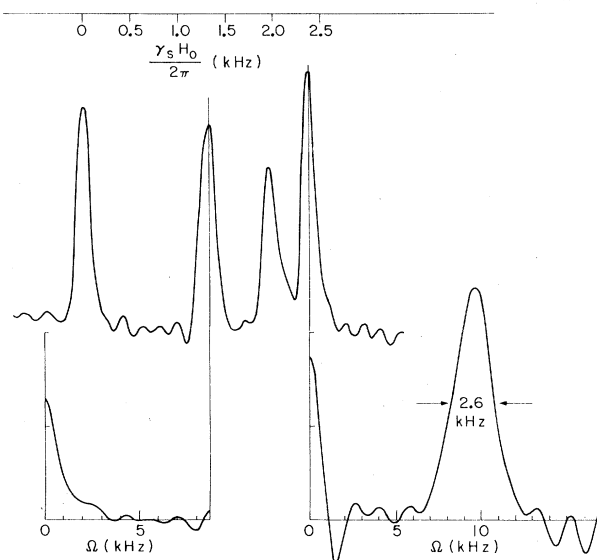


FIG. 2. Spectra of a single crystal of ammonium tartrate. The crystal orientation is such that there are only four lines. The dipolar oscillation spectra are shown for the two indicated lines. The zero-frequency peak arises from the asymptotic approach to equilibrium and its width is related to the rate constant  $T_{IS}^{-1}$ . The peak at 9.7 kHz for the CHO<sub>H</sub> line arises from the C-H coupling with the directly bonded proton. The linewidth is related to the proton spin diffusion rate.

exhibits the oscillatory exchange of magnetization between that spin and its *I*-spin neighbors. A second Fourier transformation over  $\tau$  gives the function  $F(\omega; \Omega)$  which reflects the eigenfrequencies  $\Omega$  of  $\mathcal{H}_{ff}$  for the chosen spin, and hence the related structural parameters.

Figure 2 shows results of this analysis for a single crystal of ammonium tartrate,  $(\text{NH}_4)_2\text{-(CHOH-COO)}_2$ , kindly provided by Dr. R. G. Griffin. Natural-abundance  $^{13}\text{C}$  comprises the *S*-spin system while *I* spins are protons. In this substance the most general crystal orientation exhibits four lines from  $\text{H}^{13}\text{COH}$  groups and four<sup>11</sup> from  $^{13}\text{COO}^-$  groups. The orientation chosen for Fig. 2 is such that these show pairwise structural equivalences in both chemical shift and C-H nearest-neighbor dipolar interactions. Accordingly each CHO<sub>H</sub> line is dominated by a single dipolar oscillation. The dipolar oscillation frequency for  $\text{COO}^-$  is too low to be resolved because of the large C-H distances.

Figure 3 compares the dipolar oscillation spectra of the higher frequency  $^{13}\text{CHOH}$  line for two values of  $\xi_I$ . It is evident that the spectrum is

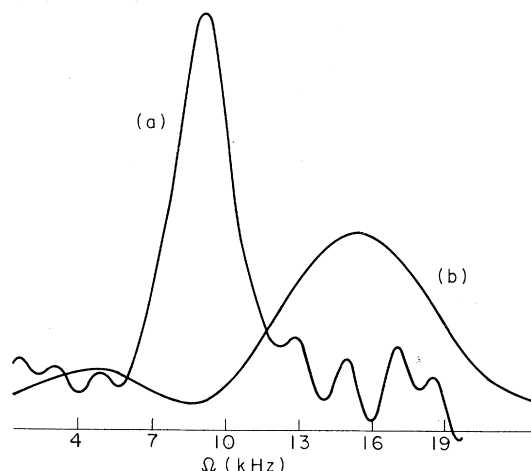


FIG. 3. Dipolar oscillation spectra of the lower frequency  $^{13}\text{CHOH}$  line for (curve *a*) off-resonance and (curve *b*) resonant spin-locking of the protons.

both broader and at higher frequency for the case of curve *b*,  $\xi_I = \pi/2$ . If one assumes that the directly bonded proton of this  $^{13}\text{CHOH}$  occupies a tetrahedral position in the direction determined by the known positions of the other tetrahedrally bonded atoms, then the measured dipolar oscillation frequency of 15.62 kHz, for the case  $\xi_I = \pi/2$ , corresponds to a C-H bond length of 1.09 Å. The residual width of curve *a* and its low frequency indicate that the value of  $\xi_I$  was actually  $\sim 45^\circ$  and not  $54.7^\circ$  as desired.

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