

## Molecular Tunneling Measured by Dipole-Dipole—Driven Nuclear Magnetic Resonance

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In low-field nuclear magnetic resonance in solids, transitions are not driven directly by the oscillating field, but by the dipole-dipole interactions modulated by the applied oscillating field. This results in strong  $\Delta m = 2$  transitions due to oscillating internal field gradients. Tunnel sidebands, symmetry forbidden in ordinary NMR, become strongly allowed. Tunnel frequencies of rotating molecular groups are measured in a previously inaccessible frequency range.

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Nuclear magnetic resonance spectroscopy is normally carried out at high field and the transitions are subject to the selection rule  $\Delta m = 1$  (single nuclear spin flips) where  $m$  is the magnetic quantum number of the nuclei. This rule arises from the magnetic dipole matrix elements for linearly or circularly polarized radiation in the plane perpendicular to the strong magnetic field. Weak spectra corresponding to  $\Delta m = 2, 3$  transitions are also predicted at high field, because the internuclear dipole-dipole interactions slightly mix the  $|m\rangle$  states. Since the dipole-dipole interaction, a second-rank tensor interaction, has matrix elements corresponding to  $\Delta m = \pm 1$  and  $\Delta m = \pm 2$ , the intensities of the  $\Delta m = \pm 2$  and  $\pm 3$  spectra are similar, and weaker than the main  $\Delta m = \pm 1$  spectrum by the factor  $H_{\text{loc}}^2/H_0^2$  where  $H_0$  is the external field and  $H_{\text{loc}}$  is a measure of the dipole-dipole fields. This factor is small in most NMR experiments. At low fields the factor becomes quite large and  $\Delta m = \pm 2$  and  $\pm 3$  spectra are observable, but then it becomes apparent for low-field measurements using magnetic field cycling that the simple perturbation description outlined above is inappropriate. For example, Jones and Daycock<sup>1</sup> found that the intensities of  $\Delta m = \pm 2$  and  $\pm 3$  spectra at low field depend quite differently on the amplitude of the rf field, while the discussion above points to similar behavior. We shall also present low-field data in strong contradiction with the above conventional analysis.

We shall describe low-field spectra in which  $\Delta m = \pm 1$  and  $\Delta m = \pm 2$  transitions have similar intensities. Another unexpected result is that transitions which are symmetry forbidden at high field are found to be strongly allowed at low field. We propose the following analytical approach to account for these features. The central idea is that the observed transitions are driven by the modulated dipole-dipole interaction rather than by the oscillating applied field. The applied rf field  $H_1 \sin(\omega t)$ , polarized along the  $x$  axis, has the effect of tilting the resultant field  $[H_0^2 + H_1^2 \sin^2(\omega t)]^{1/2}$  through an angle  $\tan^{-1}[H_1 \sin(\omega t)/H_0]$ . The  $z$  direction may be chosen to lie along the instantaneous resultant field, thereby incorporating the rf field into the unperturbed Zeeman Hamiltonian and rendering it time independent (apart from a small oscillating component parallel to the field).

This transformation<sup>2</sup> has the effect of making part of the dipole-dipole interaction time dependent, and this part can now be used with time-dependent perturbation theory to calculate transition probabilities. Since the transitions are now regarded as driven by the dipole-dipole interaction, the  $\Delta m = \pm 1$  and  $\Delta m = \pm 2$  spectra are expected to be of comparable magnitude, and the  $\Delta m = \pm 3$  to be much weaker. This is what is observed. The treatment is quite similar to the transformation into the rotating frame<sup>3</sup> which is conventional in NMR. The low-field dipole-dipole—driven spectra form a bridge between the ordinary rf-field—driven NMR at high field and the pure dipolar spectra observable at zero field.<sup>4</sup>

The chief feature of interest in dipole-dipole—driven spectra is the occurrence of  $\Delta m = \pm 2$  transitions in which pairs of nuclear spins are flipped. The selection rules are quite different from those that apply to ordinary NMR. This is very clearly illustrated in the case of rotating groups of protons such as methyl groups. The spin states of such systems belong to different symmetry species corresponding to the irreducible representations of the permutation group. The rf field cannot drive transitions between different symmetry species, but because of its greater complexity, the dipole-dipole interaction can. Transitions which are forbidden in ordinary NMR become allowed in the low-field spectra. Besides being a particularly convincing demonstration of the dipolar character of low-field transitions, this application is of considerable utility since it opens for study a range of molecular tunnel frequencies which has been inaccessible.

In solids at low temperatures molecular groups like  $\text{CH}_3$  and  $\text{NH}_4$  undergo hindered tunnel motion with frequencies  $f_t$  dependent on the size of the hindering barrier. Several magnetic resonance methods have been used to measure these frequencies.<sup>5-9</sup> The smallest tunnel frequencies which have been measured fall in a narrow window near 100 kHz. They give rise in high-field NMR to weak, almost forbidden sidebands<sup>10</sup> at  $f_0 \pm f_t$ , flanking the strong central  $\Delta m = \pm 1$  spectrum at  $f_0$ . The intensity of the sidebands falls off like  $f_t^{-2}$  so that only relatively small values of  $f_t$  can be measured. If  $f_t$  is too small, the sidebands merge with the central peak and are again unobservable.

The reason that the sidebands are almost forbidden in high-field NMR is that they correspond to transitions in which there is a change in the symmetry of the state function (both spin and spatial parts). For a methyl group, the functions belong to the irreducible representations  $A$  or  $E$  of the group  $C_{3v}$ . The interaction of the nuclei with the rf field has  $A$  symmetry and cannot cause transitions between  $A$  and  $E$  states. A weak intensity is transferred to the sideband transitions, though, as a result of mixing of the symmetry states by the dipole-dipole interactions which have both  $A$  and  $E$  parts. This mixing depends on  $f_t^{-1}$ , which accounts for the reduction of the sideband intensity for large  $f_t$ .

At low field, when transitions are driven by the dipole-dipole interactions, that part of these interactions which is of  $E$  symmetry generates allowed sidebands of both  $\Delta m = \pm 1$  and  $\Delta m = \pm 2$  spectra. Their intensity is not dependent on  $f_t$ , so that much larger values of  $f_t$  become accessible to measurement. We shall illustrate this for the case of three tunnel frequencies, two of the order of 100 kHz which have been measured previously and one of 750 kHz which falls in a frequency range from 200 kHz to 5 MHz which until now has been inaccessible.

The experimental method employs rapid magnetic field cycling which enables the preparation of an initial magnetic state and the measurement of a final magnetic state to be carried out at high field while the resonant absorption occurs at low field. This provides the sensitivity associated with high field. The measurements were made at 4.2 K with a 26-MHz pulsed NMR spectrometer for which the resonant field ( $\Delta m = \pm 1$ ) is 0.6 T. The sequence was as follows: (a) The nuclear magnetization was destroyed by a comb of 26-MHz pulses at 0.6 T to establish reproducible starting conditions. (b) The field was set to a high value (2–3 T) for a preparation time  $t_p$  (typically 5 min) to allow an initial magnetization to grow. (c) The field was switched rapidly (in a few seconds) to a low value  $H_L$  for a time  $t_L$  (10–30 s) during which the rf field at frequency  $f$  was switched on. (d) The field returned to 0.6 T and the final magnetization  $M_f$  was measured by means of a single  $90^\circ$  pulse. A plot of  $M_f$  vs  $H_L$  provides the spectra, examples of which are shown in Figs. 1 and 2.

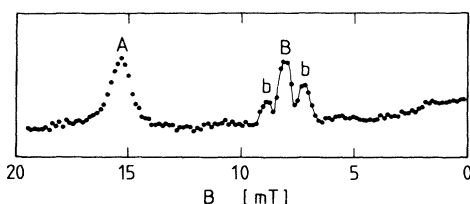


FIG. 1. Dipole-dipole-driven NMR spectrum of methyl malonic acid,  $\text{CH}_3\text{CH}(\text{COOH})_2$ , observed with  $f=600$  kHz.  $\Delta m = \pm 1$  and  $\pm 2$  spectra are labeled A and B with the allowed tunnel sideband transitions labeled b. The figure has been inverted so that these show as peaks.

Figure 1 shows a spectrum of methyl malonic acid for which the tunnel sidebands have been previously observed.<sup>11</sup> The results have been inverted so that the resonances appear as peaks instead of troughs. The notable features are the rough equality of the intensities of the  $\Delta m = \pm 1$  and  $\Delta m = \pm 2$  spectra labeled A and B, respectively, and the very prominent sidebands (labeled b) on the latter which enable the tunnel frequency to be measured with ease. Transitions are expected at  $H = (2\pi/\gamma)f$  and  $(\pi/\gamma)f$  for the central  $\Delta m = \pm 1$  and  $\pm 2$  spectra with the sidebands at  $(2\pi/\gamma)(f \pm f_t)$  and  $(\pi/\gamma)(f \pm f_t)$ . Here  $\gamma$  is the nuclear magnetogyric ratio. The  $\Delta m = \pm 1$  spectrum is probably best regarded as a superposition of rf-field-driven and dipole-dipole-driven spectra, but the  $\Delta m = \pm 2$  spectrum is almost purely of dipole-dipole character. This accounts for its more prominent sidebands. The low-field sideband is also stronger than the other one because the depth of modulation of the dipole-dipole interaction is greater at the lower field. The value of tunnel frequency ( $72 \pm 5$  kHz) obtained from this spectrum is in excellent agreement with previous results.

Figure 2 shows spectra for dimethylsulfide. Here there are two methyl groups, probably coupled together mechanically. A single tunnel splitting of 93.8 kHz had been observed previously.<sup>10</sup> This is again confirmed by the clear sidebands of the  $\Delta m = 2$  spectrum. In addition, though, a prominent pair of satellite peaks at very low field is observed. The dependence of the position of these on  $f$  confirms that they are sidebands. One (labeled a) is a sideband of the  $\Delta m = \pm 1$  spectrum, being displaced

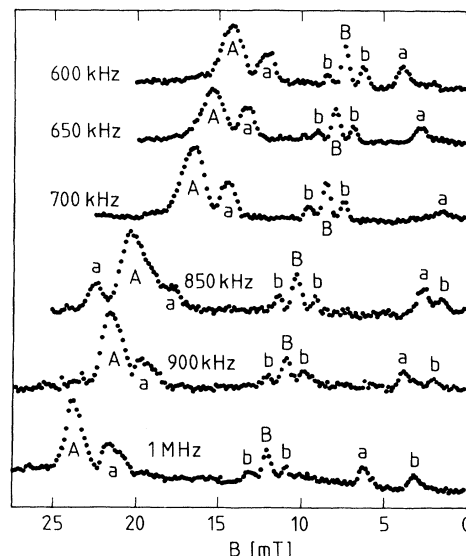


FIG. 2. Spectra of dimethylsulfide,  $(\text{CH}_3)_2\text{S}$ , for several values of  $f$ . The most important feature is the pair of peaks marked a and b on the right-hand side of the diagram. These are satellites of the  $\Delta m = \pm 1$  and  $\Delta m = \pm 2$  peaks, labeled A and B. Such relatively distant satellites are strongly forbidden in high-field NMR.

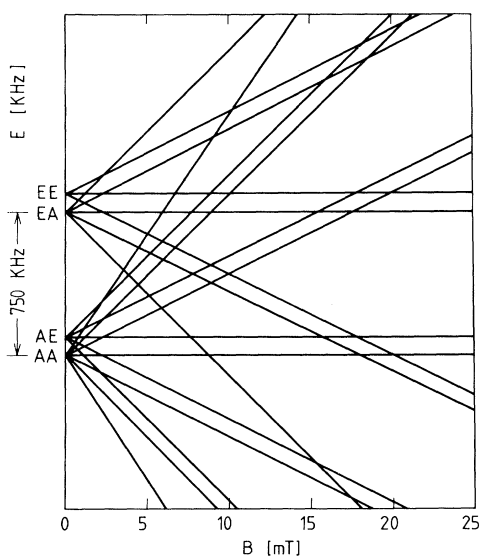


FIG. 3. An energy-level diagram which accounts for the spectra of Fig. 2. Two zero-field splittings of 83 and 750 kHz are observed. The nuclear-spin symmetry species for a pair of methyl groups are labeled AA, AE, EA, and EE and have total nuclear spins 3, 2, 2, and 1. The remarkable intensity variation of the close satellites of peak A in Fig. 2 is connected with the level crossings near 18 mT.

from the central peak A by 0.018 T or by  $2(\omega/\gamma) - 0.018$  T, whichever is smaller, while the other (labeled b) is a sideband of the  $\Delta m = \pm 2$  spectrum, with a displacement from that spectrum of 0.009 T. Both correspond to a tunnel splitting of 750 kHz. These transitions, forbidden at high field, have become allowed by being brought close to zero field. The molecule exhibits two tunneling modes with frequencies 94 and 750 kHz. A simple energy-level diagram for two methyl groups is shown in Fig. 3. The spectra of Fig. 2 are easily obtained from this diagram. This molecule is of special interest because of the mechanical coupling and the very detailed information on the coupled tunnel states which the two-dimensional spectrum  $M_f(H_L, f)$  contains. This is illustrated in Fig. 2 by the remarkable dependence on  $f$  of the  $\Delta m = \pm 1$  sideband intensities. This is connected with crossings of the energy levels. Full details will be published elsewhere.

Our description of the low-field NMR as dipolar

driven provokes the question of whether this is consistent with conventional NMR analysis. It is important to note two aspects of our measurements. First, we do not, as in conventional NMR, measure transverse magnetization, but changes in longitudinal magnetization (i.e., parallel to the field). Second, the magnetization changes during the measurement towards its equilibrium value (near zero in low field). Thus an alternative description of our data would be to regard it as displaying the field dependence of the photon-assisted spin-lattice relaxation rate. This is particularly rapid at the two fields corresponding to  $\Delta m = \pm 1$  and  $\Delta m = \pm 2$  transitions, because this is effectively relaxation in the rotating frame. This approach suggests that analysis of the line shapes of Figs. 1 and 2 could be informative on the dynamics of the nuclei.

The present results demonstrate that the low-field dipolar-driven spectroscopy is clearly the most powerful and general method yet developed for measuring fairly small tunnel frequencies. It also has application to other normally forbidden transitions, to zero-field pure dipole-dipole spectra measured in the frequency domain, and to the study of dipole-dipole interactions between different nuclear species and the structural and dynamic information to which this gives access.

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