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Molecular-tunneling spectroscopy in crystals with the use of a double-level-crossing technique

S. Clough and A. J. Horsewill
Department of Physics, Nottingham University, University Park, Nottingham, NG7 2RD, United Kingdom
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A method of measuring tunnel frequencies of molecular reorientation in crystals at low temperatures is demonstrated. Magnetic field variation brings the tunnel frequency to equality, first with the Larmor frequency of paramagnetic impurities and then with twice the Larmor frequency of protons whose magnetism has been saturated. In the first step paramagnetic ions cool the tunneling reservoir, and in the second the tunneling reservoir cools the proton Zeeman system, leading to enhanced proton relaxation.

The measurement of the frequencies of quantum-mechanical tunneling motions of molecules in crystals at low temperature has been aided by a number of level-crossing techniques in which anomalous nuclear-spin relaxation at certain magnetic fields is sought as evidence for the equality of two intrinsic frequencies. One of these is always a Larmor frequency ν_L (nuclear or electronic) and therefore field dependent and the other is a field-independent molecular tunnel frequency ν_t. Early examples involved magnetically tuning electronic Larmor frequencies to methane[1] and methyl[2] tunnel frequencies and the proton Larmor frequency to silane[3] tunnel frequencies.

With fields up to 6 T, the proton level-crossing technique enables molecular tunnel frequencies up to 500 MHz to be measured since anomalies are expected at ν_L and $2\nu_L = \nu_t$ in this case.[3] The most convenient method of measurement employs field cycling so that all measurements of recovered nuclear magnetization M can be made at a single value of magnetic field under identical conditions, while relaxation (i.e., recovery after saturation) occurs at a variable field B_r with rapid field switching between recovery and measurement fields. One then looks for peaks in $M(B_r)$. So far this simple technique has not been as productive as might have been expected though, since the anomalies turn out to be difficult to detect against a background of fluctuations which may have many origins, and peaks observed in one laboratory have not always proved easy to reproduce in others.

The basic problem is the very long relaxation times associated with the tunneling energy reservoir. The observation of a peak in $M(B_r)$ depends on the tunneling reservoir being cold so that it may rapidly cool the hot nuclear Zeeman reservoir when $\gamma B_r/2\pi = \nu_t$ or $\frac{1}{2}\nu_t$. If the tunneling reservoir is already hot then either no peak is observed or even a small trough is seen because of the nuclear Zeeman system cooling the tunneling reservoir. Since the temperature of the tunneling reservoir depends on previous experiments it is hard to reproduce results since well-defined initial conditions are not established.

Our solution to this problem is to combine features of the electronic and nuclear level crossing experiments. Although the basic experiment is to observe a resonance between a nuclear Larmor frequency and a molecular tunnel frequency, we introduce a small concentration of paramagnetic impurities. At a very low field the electronic Larmor frequency ν_e is equal to ν_t and energy can flow from the tunneling reservoir to the electronic Zeeman reservoir and thence to the lattice by virtue of the short electronic relaxation time. The paramagnetic ions produce local cooling of the tunnel system but this spreads through the crystal by means of spin symmetry diffusion.[4] Subsequently the cooled tunnel reservoir can be used to cool the nuclear Zeeman system.

To test the idea we have studied methyl tunneling

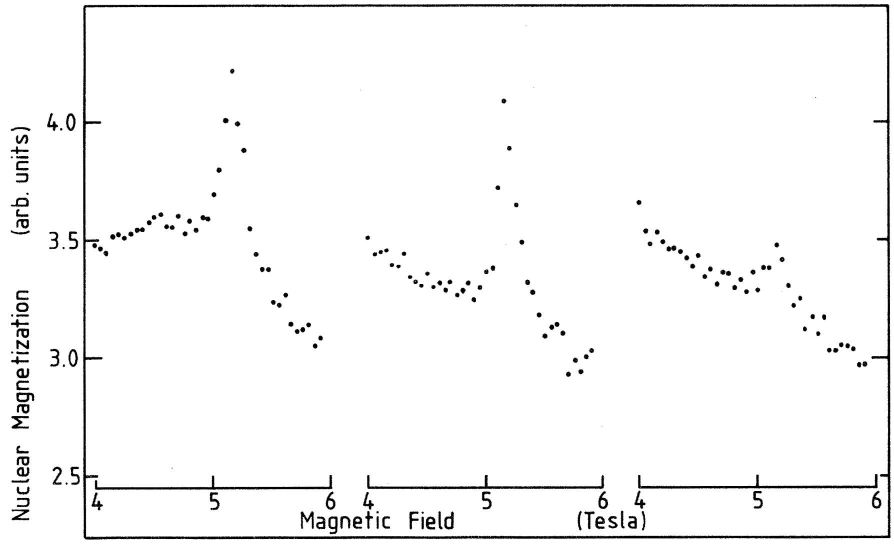

FIG. 1. Three scans through the tunnel resonance in magnesium acetate, preceded by 30 min at (a) zero field, (b) 0.015 T, and (c) 0.15 T showing the effect of precooling of the tunnel reservoir in (a) and (b) by paramagnetic impurities.

in magnesium acetate at 4.2 K. The tunnel frequency has already been measured by high-resolution inelastic neutron scattering[5] to be $\nu_t = 440 \pm 40$ MHz, so anomalies are expected at $B_r = 5.1$ and 10.2 T. We have studied the first of these. The analar grade material contained sufficient paramagnetic impurities for our purpose. Initial investigation revealed no peak at 5.1 T but an indication of a step. Then with a preliminary period at zero field the scan was repeated and a strong peak observed. Figure 1 shows three identical scans of $M(B_r)$. Before the scans the sample spent 30 min at zero field, 0.015 and 0.15 T, respectively. Precooling at fields between 0.2 and 4.5 T did not lead to an observable peak as shown in Fig. 2. All the measurements were made at a field of 0.61 T (proton NMR frequency is equal to 26 MHz) at which field the nuclear magnetization was destroyed. The magnetic field was then switched to B_r, spent 45 sec at that value and switched back. A time of 21 sec was allowed for switching.

An electron spin with $g = 2$ would be resonant with the CH_3 tunnel splitting at 0.015 T. The fairly large width of the electron-spin-resonance spectrum makes it easy to satisfy the low-field condition for resonance, and zero field is an adequate approximation.

Once the tunnel resonance at 5.1 T has been detected in this way, a second method of precooling the tunnel reservoir becomes available. This is to leave the sample at 5.1 T for a long period before commencing the field scan. The tunnel reservoir is then cooled via the nuclear Zeeman reservoir. The latter itself has a very long relaxation time but it still turns out to be rather more efficient than the paramagnetic ions whose concentration in our sample is low. Figure 2 shows the result of a field scan following precooling at 5.1 T.

The narrow peaks seen in Figs. 1 and 2 do not represent the true line shape of the tunnel spectrum since (1) the precooled tunnel reservoir is progressively warming up during the scan so that the peak becomes saturated as it is examined and (2) energy

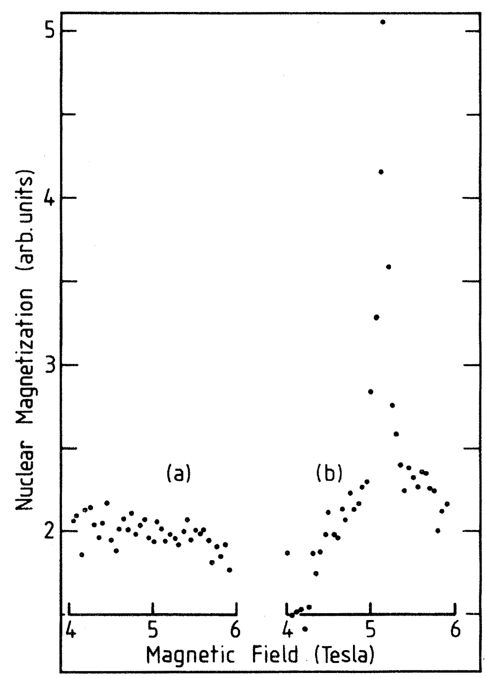

FIG. 2. That the tunnel reservoir may be precooled by the nuclear Zeeman reservoir is shown by spectrum (b) which was preceded by 30 min at a field of 5.1 T. Spectrum (a) was preceded by 30 min at 4.5 T.

transfer during the field switch cannot be neglected. Precooling before each measurement rather than before each spectrum solves the first problem, but not the second, though of course the line shape can be unfolded from the observations with the aid of a simple mathematical model for the system. The double-level-crossing technique enables one to detect the tunnel resonance condition initially and to achieve an adequate sensitivity for the unfolding process.

ACKNOWLEDGMENTS

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