Molecular Friction and Nuclear Magnetism

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Experiments are reported in which a controllable torque is exerted via nuclear dipole-dipole interactions on hindered methyl groups in crystals at low temperatures, resulting in coherent rotation resisted by molecular friction. The spectroscopic method reveals the lifting of a degeneracy through the breaking of time-reversal symmetry as a result of the friction. It is connected with the Berry quantum mechanical phase law.

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In this Letter we show that a methyl group in a crystal at low temperatures can be regarded as a microscopic viscometer, to which a torque can be applied to generate coherent rotation resisted by molecular friction. Our handle on the methyl group is through the nuclear magnetism of its protons and their mutual dipole-dipole interactions. We employ a spectroscopic technique[1] which separates the different parts of the dipole-dipole interactions. Low temperatures are necessary so that the applied torque is not swamped by thermal fluctuations. The discussion of the experiments bears on the question of whether the rotational wave function is single valued $[\psi(\phi)=\psi(\phi+2\pi)]$ or multivalued.[2] A minor purpose of this Letter is to point out that this controversy has effectively been settled by the abundant recent work on Berry's phase.[3-5] For a rotor embedded in a crystal lattice, the difference in the quantum phase for rotational angles ϕ and $\phi+2\pi$ represents the rotational response to the fluctuating lattice torque. The decomposition into system and environment will be shown to be important in retaining observable phenomena in the form of the phase factors, while discarding what is experimentally irrelevant. The second and main aim of this Letter is to show that it is also possible to apply a steady torque to a molecular group at low temperatures and to detect spectroscopically the consequent breaking of time-reversal symmetry, and the associated quantum phase shifts.

To introduce the topic we consider a hindered methyl group in a magnetic field at low temperatures, for which the energy levels of the ground state are sketched in Fig. 1(a). The system of methyl group plus lattice is invariant to the cyclic permutation of the space and spin coordinates of the three protons. The eigenfunctions are three kinds of products of space and spin fluctuations, $A\times A$, E^aE^b, and E^bE^a where the labels refer to the irreducible representations of C_3 and indicate the symmetry under cyclic permutations. The different rotational energies of the A and E spatial functions give rise to the tunnel splitting $h\nu_t$ and to these are added in Fig. 1(a) the nuclear Zeeman splittings, the A and E spin states having total nuclear spins $\frac{3}{2}$ and $\frac{1}{2}$, respectively. The methyl group is regarded as a rigid rotor with a single rotational coordinate ϕ. At low temperatures the interaction between rotor and lattice can be described in terms of a static hindering potential $V\cos(3\phi)$. Wave functions $\psi(\phi)$ for the methyl group only can be expanded in the functions $\exp(im\phi)$ where m must be integral (ϕ and $\phi+2\pi$ being indistinguishable because of the absence of lattice fluctuations), and restricted to the sets $3n$, $3n+1$, $3n-1$ (n any integer) for functions of type A, E^a, E^b, respectively. The rotational problem is analogous to the familiar translation of a particle in a periodic potential, for which the eigenfunctions are Bloch waves with wave number between π and $-\pi$ [indicated by the circle in Fig. 1(a)]. The rotational boundary condition

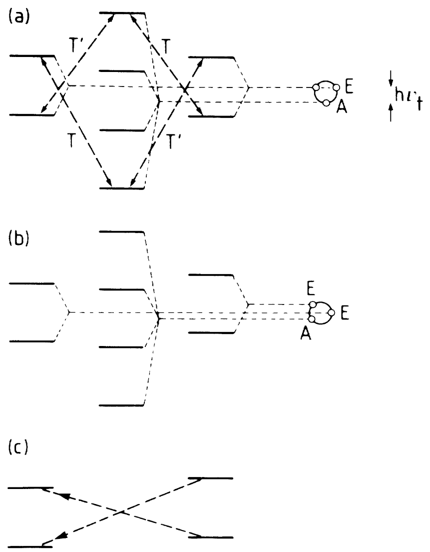

FIG. 1. (a) Energy-level diagram of a tunneling methyl group in a magnetic field at low temperatures. The tunnel splitting h_t splits the A and degenerate E species. Relaxation rates T and T' are not equal and magnetic relaxation generates a population difference between E^a and E^b species. (b) The effect of a frictional torque is to lift the E degeneracy. (c) Transitions between E species occur on either side of the main NMR frequency and generate magnetization of opposite signs as found in Fig. 2.

$\psi(\phi)=\psi(\phi+2\pi)$, though, only allows wave numbers 0 and $\pm 2\pi/3$ (i.e., A and E).

The key question was how to take account of the dynamic nature of the interactions at finite temperature. It was conventional[6-9] to start by retaining the cyclic boundary condition in the form $\psi(\phi,t)=\psi(\phi+2\pi,t)$. The evolution in time of $\psi(\phi,t)$ can be illustrated[10] by the modeling of the dynamic interaction as an additional fluctuating component of the hindering potential $V(\phi,t)=V(\phi+2\pi,t)$. The ground-state wave functions of symmetry types $E^a\times E^b$ and $E^b\times E^a$ evolve in different ways with respect to transition to excited vibration-rotation states, and their angular momenta, initially equal and opposite, become unbalanced. $V(\phi,t)$ thus breaks the time-reversal symmetry of the static problems, and results in the transfer of angular momentum between methyl group and lattice. The effect is a fluctuation torque driving a fluctuating rotational motion. The Hamiltonian for the whole system exhibits time-reversal symmetry, but that only means that there is another possible state in which $V(\phi,t)$ is reversed in time and the torque and rotation are also reversed.

The rotational energy resulting from the torque is off diagonal in the ϕ representation. We may consider a transformation in the total coordinate space to make it diagonal. In the new representation, the coordinate ϕ' which most nearly corresponds to ϕ is not a pure angle, but includes admixtures of lattice displacements. The rules of the ϕ representation therefore no longer apply: $\phi'\neq\phi'+2\pi$; $V(\phi',t)\neq V(\phi'+2\pi,t)$; and $\psi(\phi',t)\neq\psi(\phi'+2\pi,t)$. However, $V(\phi',t)$ is now random and uncorrelated with $\psi(\phi',t)$ so that the ϕ' representation is the one in which time-dependent perturbation theory may be used. The torque is now connected with the difference between $V(\phi',t)$ and $V(\phi'+2\pi,t)$ and with an associated vector potential term[11] and the resulting motion is connected with the difference between $\psi(\phi',t)$ and $\psi(\phi'+2\pi,t)$ which can be associated with Berry's phase, the rotor being driven (though not necessarily adiabatically) around a trajectory in its coordinate space. The spatial function $\psi(\phi',t)$ cannot be classified A, E^a, or E^b though the wave function of the whole system can be so classified. This is because the information on permutation symmetry is not to be found on the ϕ' axis, but on the inclined ϕ axis which now has a component in the heat bath.

The choice of representation, followed by a projection to obtain a one-coordinate Hamiltonian, determines which features are retained as relevant to experiments and which are discarded as concealed in the heat bath. In the ϕ' projection, the cyclic boundary condition is partly concealed by the heat bath but the torque and resulting rotation are retained. It is in this representation that the Berry's phase factors and their cause occur. In the ϕ projection, the cyclic boundary condition is retained and the torque and rotation resulting from the local breaking of time-reversal symmetry are lost. The common pattern has been to start with the cyclic boundary condition and accept the ϕ representation that goes with it. The characteristic feature of such treatments is that they only allow the calculation of one rate process instead of two, namely torsional vibration excitation and rotation, the latter having been lost. The lifetime broadening, though, has been wrongly attributed to rotation, thereby transferring to the rotation rate the property of dependence on the host-lattice phonon spectrum, a property really belonging to the vibrational excitation rate. Experimentally[12] the rotation rate depends only on the barrier height V and the temperature. This also explains the existence of a second very different type of theory[13,14] of the rotation rate, which, because of assumptions which implicitly discard the cyclic boundary condition, successfully obtains the true rotation rate in good agreement with experiments.[14] These are effectively using the ϕ' projection in which the two rate processes are clearly separated and both calculable. The experiments described here are additional confirmation that it is ϕ' which is measured rather than ϕ, and that the correct decomposition is the one leading to the most random heat bath.

The most general Hamiltonian in the ϕ' projection is

$$\mathcal{H}=(1/2I)[i\hbar\,\partial/\partial\phi'+I\omega(t)]^2 + V\cos(3\phi')+V(\phi',t), \qquad (1)$$

where $\omega(t)$ and $V(\phi',t)$ are the vector and scalar potentials dependent respectively on the velocities and displacements of the environment. Figure 1(b) shows energy levels for a finite value of ω. The labels A, E^a, and E^b refer to the nuclear spin function, the spatial part being characterized by wave numbers k which are shifted as a result of the vector potential from the values 0 and $\pm 2\pi/3$ by amounts which depend on the state of the heat bath as represented by $V(\phi',t)$ and $\omega(t)$. The splitting of the E levels is a measure of the heat-bath–driven rotation rate and fluctuates in sign in thermal equilibrium, appearing only as a broadening. Low temperatures and some external way of applying a torque are needed to generate an observable steady splitting.

A torque is applied by a change in the nuclear magnetization. The internuclear dipole-dipole interactions have a helicity illustrated by the examples of transition-matrix elements T and T' in Fig. 1(a). Generally $T\neq T'$ so that a dipolar-driven change in the nuclear magnetization is accompanied by a change in the difference of the populations of the E^a and E^b species and hence a change in the mean angular velocity.[15] In this way when spin angular momentum changes, it is partly converted into methyl rotational angular momentum. We suppose that rotation is not dissipationless and that the environment responds with a resistive torque whose effect is to split the E levels.

The experimental technique employed is low-field dipole-dipole–driven nuclear magnetic resonance.[1] At low field (10 mT) and low temperature, the NMR selection rules are very different from those at high field. Instead of transitions being driven directly by the applied rf field, they are instead driven by the dipole-dipole interactions which are modulated by the rf field. Since the dipole-dipole interaction is very rich in matrix elements, transitions which are forbidden at high field become allowed at low field. Of particular importance for our present purpose is that we are able to drive transitions between the two E species, because of dipole-dipole interactions between the methyl group and neighbor protons. As shown in Fig. 1(c) these occur at frequencies $\omega_0 \pm \delta$ where ω_0 is the ordinary $\Delta m = 1$ NMR frequency and $\hbar\delta$ the E splitting. In order to achieve good sensitivity, a rapid field-cycling technique is used so that preparation of an initial magnetic-rotational state is carried out at high field, as is the measurement of the nuclear magnetization at the end of a cycle. A typical sequence is as follows. At 0.6 T the nuclear magnetization is destroyed by a series of rf pulses. The field is then switched to a value B_p for a preparation period t_p during which the magnetization partially recovers and a rotational velocity is generated. The field is then switched to a low value B_m and a radio-frequency field of frequency ω_m is applied for a period t_m, after which the field is switched back to 0.6 T and the magnetization measured by means of a single 90° inspection pulse of 26 MHz. The sequence is repeated many times, incrementing B_m, and the data are presented as a plot of residual magnetization M_z as a function of B_m. Transitions generally show up as negative peaks on a horizontal background since they correspond to destruction of the recovered magnetization. Transitions within a single spin-symmetry species occur at $B_m = \omega_m/\gamma$ and $\omega_m/2\gamma$ ($\Delta m = 1,2$ transitions) where γ is the magnetogyric ratio. These are labeled A and B in Figs. 2 and 3. Transitions between A and E species occur at $(\omega_m \pm \omega_t \pm \frac{1}{2}\delta)/\gamma$ and $(\omega_m \pm \omega_t \pm \frac{1}{2}\delta)/2\gamma$ giving rise to satellites of the $\Delta m = 1$ and $\Delta m = 2$ peaks, labeled a and b, respectively, in Fig. 2. Transitions between the two E species occur at $(\omega_m \pm \delta)/\gamma$.

In Figs. 2 and 3 are shown the results of two experiments. The first aims to observe the magnetic rotation state set up during the preparation period t_p, and so the measurement period t_m is kept short. The second observes the effect of the rf field during the measurement period which is therefore relatively long. In Fig. 2 are shown results for tetradecane obtained at 4.2 K. The crystal structure of the even-numbered n-alkanes ($n > 6$) is very simple with the molecules having their axes parallel and the terminal methyl groups forming interfaces perpendicular to the molecular axes. All methyl groups are equivalent, and the tunnel frequency $\omega_t/2$ is 305 kHz as can easily be seen from the positions of the satellites a and b in the lower trace of Fig. 2. The upper trace is obtained in a fairly rapid experiment with the field-switching time 3 s and $t_m = 5$ s. The preparation was carried out at 0.6 T for $t_p = 60$ s. The important features are (a) the large antisymmetric component in the line shape and (b) the fact that the signal rises above the background. This demonstrates that the prepared state contains a form of order other than nuclear magnetization and that the rf field is able to convert this order into magnetization. This order we attribute to a population difference between the E^a and E^b species generated as a result of A-E transitions during the magnetization recovery at 0.6 T. It can only be converted into magnetization by E-E transitions if the E levels are split. This separates the $E^a_{1/2} \to E^b_{-1/2}$ from $E^a_{-1/2} \to E^b_{1/2}$ since they occur at fields $B_m = (\omega_m \pm \Delta)/\gamma$. The effect is that opposite polarizations are generated for B_m greater or less than ω_m/γ, with the consequence that the response has the antisymmetric component evident in the upper trace of Fig. 2. The measurement technique is only sensitive to M_z, the nuclear magnetization parallel to the field, and allows plenty of time for the establishment of a

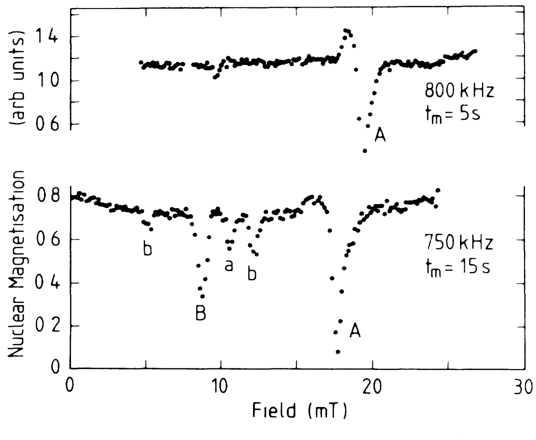

FIG. 2. Dipolar-driven NMR spectra of tetradecane at 4.2 K. The antisymmetric component, best seen in the upper trace, shows the existence of a difference of population of the E species (rotational velocity) and a splitting of the E degeneracy due to the frictional reaction, as in Fig. 1(b).

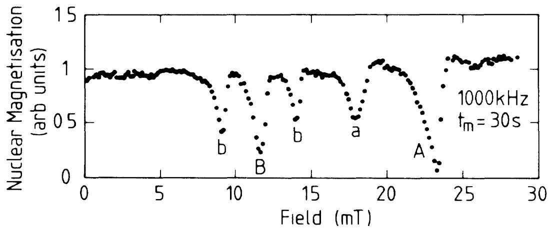

FIG. 3. Dipolar-driven NMR spectra of propionic acid. The tail on the low-field side of peak A occurs as the 1000-kHz radiation excites rotation which lifts the E degeneracy shifting the E-E transition away from the center of the peak. The shift on the high-field side is towards the centers and so there is no tail.

Zeeman spin temperature. The antisymmetric line shape is therefore strong evidence for an E splitting.

It is also interesting to consider the effect on the energy levels of irradiating strongly slightly off resonance, starting with a state of very small angular velocity and small Δ. For $B_m < \omega_m/\gamma$, the E-E transitions which are driven have the effect of increasing the angular velocity which already exists, so increasing Δ. The driven transition frequency is thus pulled to become more nearly resonant with the rf frequency, and the methyl rotation speed (i.e., Δ) increases. If $B_m > \omega_m/\gamma$, on the other hand, transitions can only reduce the rotation rate and the rf frequency moves further from resonance. The reason for this can be simply explained. If $B_m > \omega_m/\gamma$ then the quantum energy $\hbar\omega_m$ is too small to cause nuclear Zeeman transitions, which therefore only occur by absorption of rotational energy associated with δ. The effect is to stop coherent directional rotation. If $B_m < \omega_m/\gamma$ then $\hbar\omega_m$ is too large for the Zeeman splitting but the surplus energy can be adsorbed by an increase in the rotational speed. It follows that very asymmetric line shapes may be expected.

Figure 3 shows data obtained at 4.2 K with use of propionic acid and showing the expected effect. The tunnel frequency is 210 kHz and the positions of the $\Delta m = 1$ and $\Delta m = 2$ peaks and their A-E satellites are shown. The low-field tail on peak A shows that it is possible to destroy nuclear magnetism by irradiation with a frequency slightly in excess of the nuclear Larmor frequency. The radiation is absorbed with the onset of coherent directional rotation (clockwise or anticlockwise), thereby lifting the E degeneracy and breaking the time-reversal symmetry. The observed phenomena are thus explicable in terms of (1) with the vector potential $\omega(t)$ coupled to the populations to describe molecular friction. They are not explained by the ϕ projection when the cyclic boundary condition requires $\omega(t)$ to be zero and the E levels to be degenerate.

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