

SQUID-NMR study of methyl quantum tunneling in a series of carboxylic acids

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Quantum tunneling frequencies of methyl groups at low temperature can be measured directly by low-field nuclear magnetic resonance (NMR) using our dc-SQUID (superconducting quantum interference device) spectrometer. From NMR spectra recorded in magnetic fields below 20 mT, tunneling frequencies between 140 and 250 kHz were measured for a homologous series of carboxylic acids at 4.2 K. For solids with equivalent crystal structures, we observe an exponential correlation between the tunneling frequency and the enthalpy of fusion; from this correlation we obtain information about the contribution of intermolecular interactions to the energy barrier for methyl rotation.

A methyl (CH_3) group is a particularly simple example of a hindered rotor that exhibits quantum tunneling at low temperatures, where classical internal rotation is essentially frozen [1]. The tunneling involves cyclic permutations of the three (indistinguishable) protons of the methyl group, under which the wavefunction is symmetric. The tunneling frequencies are of interest because they depend upon the energy barrier to rotation of the methyl group, and they can thereby provide information about the molecular interactions that affect the barrier. Previous studies of rotational tunneling have been carried out primarily by means of inelastic neutron scattering (INS) [2] and nuclear magnetic resonance (NMR) [3]. As shown in fig. 1, the proton spin eigenstates of the tunneling methyl group can be classified according to A and E representations (corresponding to the threefold symmetry of the hindering potential). In low magnetic fields, radio frequency-induced transitions between A and E states (normally forbidden in high field) are possible because of magnetic dipole-dipole interactions between the proton spins. In order to study such low-field A \leftrightarrow E transitions, which contain information

about the tunneling frequency, Clough and co-workers [4-7] have used magnetic field cycling, in which the low-field NMR spectrum (normally undetectable due to poor sensitivity) is observed by switching the magnet to high field during detection. It is possible, and often advantageous, however, to observe NMR transitions directly in low field by using a dc-SQUID (superconducting quantum interference device) as a sensitive detector of magnetic flux at zero frequency [8-12]. In this Letter, we report the measurement of tunneling frequencies in a series of carboxylic acids by direct low-field NMR with a dc-SQUID at 4.2 K. The tunneling frequencies show an interesting trend that can be related to the effects of intermolecular interactions on the tunneling barrier.

The samples in our spectrometer are at 4.2 K in a low magnetic field, typically between 3 and 20 mT, arising from trapped flux in a lead tube. The SQUID, coupled to the sample by means of a superconducting flux transformer, directly detects the change in sample magnetization while a small rf field is swept through resonance [10]. A low-field NMR spectrum of solid heptanoic acid, obtained in this way, is shown in fig. 2. In this case, the magnetic field was 12.0 mT, corresponding to a proton Larmor frequency, ω_0 , of 510 kHz. As the rf field is swept from 150 to 1150 kHz in 1000 s, five transitions are observed. The

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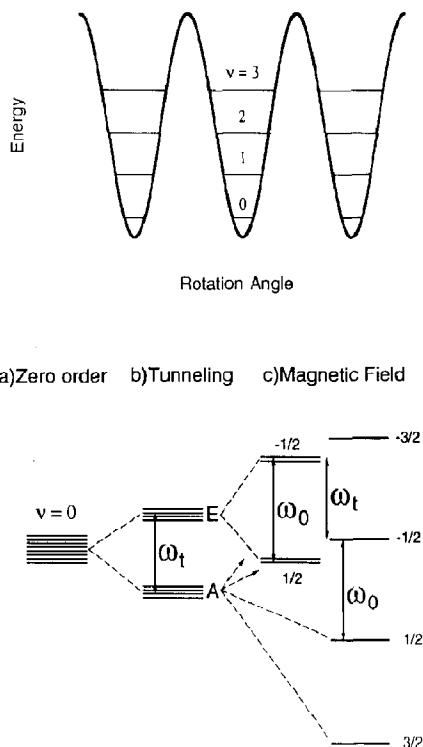


Fig. 1. Rotational energy levels of a methyl group in a triple well potential. (a) Without tunneling. (b) With tunneling: The eight spin states of the $v=0$ rotational state, degenerate in zero order, are split by the tunneling frequency, ω_t , into two manifolds, A and E, consisting of four degenerate states each. (c) When a magnetic field is applied, the A states split according to a spin- $3/2$ manifold and the E states split according to a doubly degenerate spin- $1/2$ manifold. This final energy level diagram corresponds to the experimental situation.

peaks with the highest amplitudes occur at the Larmor frequency, ω_0 (originating from transitions between states of the same symmetry with $\Delta m=1$) and at twice the Larmor frequency, $2\omega_0$ (resulting from $\Delta m=2$ transitions). These two peaks are off scale in fig. 2, in order to display the smaller peaks at 317, 703 and 827 kHz which correspond to tunneling transitions between states of different symmetry at frequencies $\omega_0 - \omega_t$, $\omega_0 + \omega_t$ and $2\omega_0 - \omega_t$, respectively. The tunneling frequency, ω_t , of the methyl group can be directly extracted from these transitions, and for heptanoic acid at 4.2 K, ω_t is measured to be 193 ± 4 kHz.

In order to determine the tunneling frequencies more accurately for each sample, two or more easily

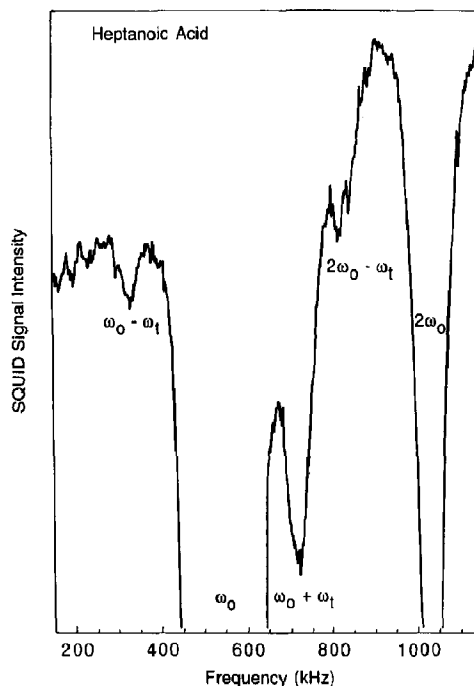


Fig. 2. The proton SQUID-NMR spectrum of solid heptanoic acid, in a single 1000 s sweep from 150 to 1150 kHz. The sample was at a temperature of 4.2 K in a magnetic field of 12.0 mT. The peaks at the Larmor frequency, $\omega_0=510$ kHz, and twice the Larmor frequency, $2\omega_0=1020$ kHz, are off scale in order to display the three smaller peaks arising from methyl group tunneling. These transitions occur at $\omega_0 - \omega_t=317$ kHz, $\omega_0 + \omega_t=703$ kHz, and at $2\omega_0 - \omega_t=827$ kHz, where ω_t is the tunneling frequency.

accessible transitions between states of different symmetry were studied independently. The sweep time to cover a typical frequency range of 100 to 200 kHz for a single transition is usually 100 to 250 s. Because the proton spin relaxation time, T_1 , for the carboxylic acids is of the same order of magnitude as the sweep time, decay of the sample magnetization due to relaxation is often observed in the spectrum. Therefore, to avoid a false shift of the observed transition frequency due to relaxation, forward and reverse sweeps (i.e. scans from low to high frequency followed by scans from high to low frequency) were combined in the final spectrum [12]. In each case, the experimental uncertainty in determining the transition frequency did not exceed ± 4 kHz.

The tunneling frequencies measured for powdered carboxylic acids are presented in table 1. The value

Table 1

Methyl group tunneling frequencies (± 4 kHz), ω_t , obtained from SQUID-NMR measurements, and the corresponding barrier potential heights, V_3 . The crystal phases are taken from refs. [13–16]. m denotes a monoclinic crystal structure. The other symbols refer to a notation from ref. [13]. The phases, A and A', are triclinic crystals and the B, C, and C' phases are monoclinic structures. Those phases with asterisks are inferred from the known crystal structures of the other acids. A value for butanoic acid was not obtained due to the existence of a low temperature phase change

Sample (No. of carbons)	Phase	ω_t (kHz)	V_3 (meV)	Sample (No. of carbons)	Phase	ω_t (kHz)	V_3 (meV)
propanoic acid (3)	m	215	140.0	butanoic acid (4)		phase transition	
pentanoic acid (5)	m	250	137.7	hexanoic acid (6)	m*	168	143.8
heptanoic acid (7)	m*	193	141.6	octanoic acid (8)	m*	170	143.6
nonanoic acid (9)	m*	156	144.9	decanoic acid (10)	A	189	141.9
undecanoic acid (11)	C'	140	146.8	dodecanoic acid (12)	C	177	142.9
undecanoic acid (11)	A'	193	141.6	dodecanoic acid (12)	A	168	143.8
tridecanoic acid (13)	A'	191	141.8	tetradecanoic acid (14)	A	162	144.3
pentadecanoic acid (15)	A'	190	141.9	hexadecanoic acid (16)	A	179	142.8

for propanoic acid has been determined previously by field cycling NMR [4] and is in agreement with the frequency measured in our work. Because the tunneling splitting depends on the structure of the material, crystal types from the literature [13–16] are also reported in table 1. This dependence on crystal structure is demonstrated for undecanoic and dodecanoic acids, where tunneling frequencies for two separate phases of each acid are reported. The two measurements for undecanoic acid are a particularly good example of significant change in the hindering potential due to a change in crystal structure. The absence of a value for butanoic acid reflects a low temperature transition [15,17–19] to a phase that may have a tunneling frequency outside the range of our SQUID spectrometer or the formation of a glass with undetectably broad lines due to rapid quenching of the sample from room temperature to 4.2 K.

The measured tunneling frequencies all fall within a range of 140 to 250 kHz. Such relatively low values correspond to high hindering potential barriers, as expected for methyl groups which are connected to sp^3 hybridized carbon atoms [5,6]. The simplest form of the hindering potential has the threefold symmetry of the methyl group rotation angle, ϕ , and is given by

$$V_{\text{barrier}} = \frac{1}{2} V_3 [1 + \cos(3\phi)] . \quad (1)$$

The values for V_3 also appear in table 1 and have been calculated from the tunneling frequencies and published eigenvalues [20].

In order to interpret these data for the homologous series, we assume that the potential barrier to methyl rotation consists of an intramolecular (gas phase) and an intermolecular contribution:

$$V_{\text{barrier}} = V_{\text{intra}} + V_{\text{inter}} . \quad (2)$$

In the case of the carboxylic acids, the barrier is dominated by the intramolecular contribution, and the addition of methylene groups in the homologous series should have little effect on the intramolecular contribution to the hindering potential, as demonstrated by the straight-chained alkanes [5] and ketones [6]. Thus, the changes in V_{barrier} between different samples should arise mainly from the intermolecular contribution, V_{inter} , which depends on the crystal structure of the sample and is dominated by the interactions of atoms close to the methyl group.

In order to study the effects of molecular packing on V_{inter} , we compare the tunneling splittings of acids having equivalent crystal structures, where we may expect to observe correlations with thermodynamic properties. Indeed, as shown in fig. 3, we observe an exponential dependence of ω_t on the enthalpy of fusion, ΔH_{fus} ,

$$\omega_t = a \exp(\Delta H_{\text{fus}}/b) , \quad (3)$$

where a and b are fitting parameters. Correlations for four crystalline phases of the carboxylic acids are presented in fig. 3 using enthalpy of fusion values from the literature [17–19,21]. A similar correlation exists between the tunneling frequency and the melting point temperature of the sample. To a good

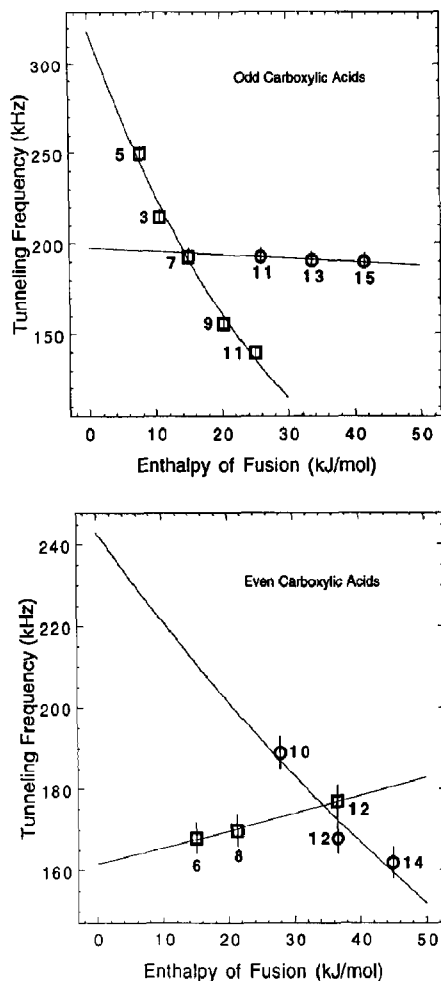


Fig. 3. Experimentally determined tunneling frequencies as a function of the enthalpies of fusion for homologous series of carboxylic acids. Each data point ((\square) monoclinic; (\circ) triclinic) represents one carboxylic acid identified by the number of carbon atoms for that acid. Correlations are presented for each set of carboxylic acids having equivalent crystal structures. The enthalpies of fusion are from refs. [17–19, 21]. For pentanoic acid there is considerable disagreement about the enthalpy of fusion.

approximation, small variations in the barrier height due to the intermolecular interactions cause an exponential change in the tunneling frequency [22], which implies a linear correlation between ΔH_{fus} and V_{inter} .

Both the intermolecular contribution to the hindering potential of the methyl group and the enthalpy of fusion represent a measure of the interaction between adjacent molecules. In the case of the carbox-

ylic acids, both of these values are determined by the interaction of the acid group with other parts of the molecule. As is well known, the high enthalpy of fusion and high melting point temperature of the carboxylic acids are due to the strong interactions between the acid groups. Likewise, the intermolecular contribution to the hindering potential seems to be dominated by the interaction between the methyl group and the surrounding acid groups. A further indication of the dominance of the carboxylic acid interactions is seen when the tunneling splittings of the carboxylic acids are compared with those for the alkanes. As the chain length increases, the tunneling frequency tends toward a limiting value. For the alkanes and ketones studied by Clough and co-workers [5,6], this limit is around 300 kHz. However, for the carboxylic acids, the value is less than 200 kHz, again indicating that interactions between the carboxylic acid groups provide a much higher barrier to rotation by significantly perturbing the methyl groups.

In summary, we have directly measured methyl quantum tunneling frequencies in a homologous series of solid carboxylic acids by means of a SQUID-NMR spectrometer. The tunneling frequencies depend on crystal structure. In the same crystal structure class, the tunneling frequency, ω_t , decreases exponentially with increasing enthalpy of fusion, ΔH_{fus} , implying a linear correlation between ΔH_{fus} and V_{barrier} . Because ω_t is sensitive to environmental and intermolecular interactions, such measurements should be useful in the study of molecules on surfaces [23] and in constrained environments.

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