Induced Nuclear-Spin-Symmetry Species Conversion in Solid Hexamethylbenzene Using Level Crossing*

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We demonstrate the existence of nuclear spin states associated with the protons of the CH_3 groups in solid hexamethylbenzene, using a level-crossing experiment to observe conversion of the associated A and E nuclear spin species. The experiment also determines the torsional ground-state splitting of the CH_3 group to be 11.0 ± 2.5 MHz.

Just as in the well-known case of hydrogen, the permutation symmetry of identical nuclei in polyatomic molecules restricts the possible molecular states to those having well-defined "nuclear spin symmetry." In the case of polyatomic molecules in solids, the energy separations of different nuclear-spin-symmetry states are closely related to the tunneling frequencies of the molecules in the crystalline electric field of the solid.[1-3] Very little precise information is presently available on the energy levels of nuclear-spin-symmetry states of molecules in solids. In the case of CH_4 and its deuterated modifications, measurements of the heat capacity[4,5] and nuclear spin susceptibility[6-10] as a function of temperature in the liquid-helium range indicate tunneling splittings of the order of 10^{10} Hz. Similar results have been obtained for solids containing NH_3 groups.[11,12] For molecular solids containing CH_3 groups, analyses of the second moments and relaxation times of the proton magnetic resonance line[13-20] indicate tunneling frequencies $\omega_t/2\pi$ from a few kilohertz or less for CH_3 groups, whose reorientation is hindered by a high potential barrier, to frequencies as high as 100 MHz for systems having relatively low barriers.

Up to now, only two *direct* measurements of ω_t have been reported. One involved the observation of a splitting of the NMR line of a system in which $\hbar\omega_t$ is of the same order of magnitude as the intramolecular dipolar interaction energy $\hbar\omega_d$.[21] This type of measurement would be extremely difficult to make for $\omega_t \gg \omega_d$ and is thus of limited applicability.[22] The second measurement[23] involved the detection of resonant conversion of the nuclear-spin-symmetry species in solid CH_4 by tuning the Larmor frequency of trapped free radicals to ω_t. This clever experiment is very well suited to the large values of ω_t found in the methane system, but would probably be difficult to apply with precision to systems such as CH_3 groups which have values of ω_t well below the microwave region.

In this paper, we report the experimental observation of a level-crossing effect which has been predicted to occur[22,24] when the proton Larmor frequency ω_0 in a CH_3 group in a solid is varied from low values through the region $\omega_0 = \omega_t$ or $\omega_0 = \frac{1}{2}\omega_t$, where level crossing occurs. The experiment involves the observation of a nuclear magnetization induced by the process of adiabatic magnetization after the system has been allowed to relax for a long enough time in *zero* magnetic field for a population difference to be established between states of different nuclear spin symmetry because of the energy difference $\hbar\omega_t$. As we shall discuss below, the magnitude of the nuclear magnetization established by this procedure has enabled us to estimate the value of ω_t for $C_6(CH_3)_6$ to better accuracy than has been possible from previous measurements on this system. Furthermore, by using the effect which has now been established experimentally as a probe, it should be possible to measure the field at which level crossing occurs with precision for a wide range of tunneling frequencies.

The idea of the experiment is illustrated in Fig. 1 by the energy levels of a system of three identical spin-$\frac{1}{2}$ nuclei on an equilateral triangle in a potential having C_3 symmetry.[3] The eightfold degeneracy of the ground state of torsional oscillation is partially removed by the process of tunneling, the states of type A having total nuclear spin $I = \frac{3}{2}$ being lowest and the two E-type states, each having $I = \frac{1}{2}$, being at an energy $\hbar\omega_t$ above the A state. The application of an external mag-

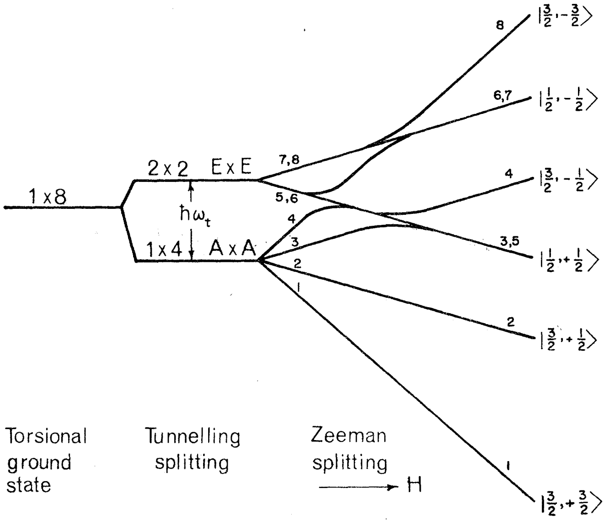

FIG. 1. Schematic energy-level diagram of the ground state of torsional oscillation of a three-spin system such as CH_3 in a potential having C_3 symmetry. The degeneracies and symmetry assignments are indicated. The high-field assignments of the angular-momentum quantum number $|I, M_I\rangle$ are also shown. The indices $n = 1, 2, \cdots, 8$ indicate the states in low and high magnetic fields, which are coupled to each other by the adiabatic process described in the text.

netic field removes the fourfold degeneracy of the A state and the twofold degeneracy of each of the E states. The A states and one set of E states, differing in their magnetic quantum numbers by $\Delta M = 0$, ± 1, and ± 2, are coupled by the intramolecular dipolar interactions. However, provided that $\omega_t \gg \omega_d$, the molecular states are well characterized by the A or E spin-symmetry indices, respectively, in the regions not near the level crossings. In the vicinity of the level crossings, $\omega_0 \simeq \omega_t$ or $2\omega_0 \simeq \omega_t$, an A state is mixed with one of the E states so that nuclear spin symmetry is not well defined in these regions. At the "crossing points," the mixed states are separated by an energy of order $\hbar\omega_d$ which, for CH_3 groups, is expected to be of the order of 10 kHz. Therefore, if the field $H_0 = \omega_0/\gamma$ is varied through the level-crossing region at a rate sufficiently slow to satisfy the inequality

$$d\omega_0/dt \ll \omega_d^2, \tag{1}$$

an adiabatic change of nuclear spin symmetry is expected to take place, as the probability that a molecule perform a transition between nondegenerate states is extremely small. States having the same index $n = 1, 2, \cdots, 8$ in low and high fields in Fig. 1 are coupled to each other by the adiabatic process described above. It should be noted that the inequality (1) was very well satisfied in the experiments to be described below.

It is easy to show that if a system initially is in equilibrium at a temperature T in zero field so that

$$n_i/n_j = \exp(-\hbar\omega_t/kT) \simeq 1 + \hbar\omega_t/kT, \tag{2}$$

where $i = 1$, 2, 3, or 4 and $j = 5$, 6, 7, or 8 and $\hbar\omega_t \ll kT$, then the magnetization M_a induced by adiabatic magnetization to high field is related to the equilibrium magnetization M_0 at high field by

$$M_a/M_0 = \omega_t/3\omega_0. \tag{3}$$

The sample of hexamethylbenzene used in this experiment was manufactured by Eastman Kodak Co. The experiment was carried out at 4.2 and 24 K at a frequency of $\omega_0/2\pi = 30$ MHz using a conventional pulsed NMR spectrometer. The nuclear magnetization was assumed to be proportional to the amplitude of the free induction decay following a 90° rf pulse.[6] In the adiabatic magnetization process, the magnetic field was turned on at various rates, a typical rate being 1000 G/sec. Usually, the nuclear magnetization was measured approximately 30 sec after we began to turn on the magnetic field. Since the proton spin-lattice relaxation time T_1 was of the order of hours at 4.2 K, M_0 was determined by extrapolation from higher temperatures, where T_1 is shorter, using the Curie law $M_0 \propto T^{-1}$. For the measurements at 24 K, M_0 was measured directly. Identification of the ratio of the measured signal, after adiabatic magnetization to that of a system in equilibrium with the lattice at the measuring field with M_a/M_0 in Eq. (3), gave the following result on the basis of two measurements at 4.2 K and six measurements at 24 K:

$$\omega_t/2\pi = 11.0 \pm 2.5 \text{ MHz},$$

for $C_6(CH_3)_6$. This result is in agreement with the value estimated by Allen and Cowking[14] on the basis of the barrier height given by measurements of T_1 versus T and a theoretical relationship between barrier height and ω_t given by Freed.[3] They obtain a splitting of about 1.5 $\times 10^{-6}$ kcal/mole which corresponds to a value of $\omega_t/2\pi \simeq 16$ MHz.

In using Eq. (3) to obtain a value of ω_t, we have assumed that the passage through the level-crossing fields at $\omega_0 = \omega_t$ and $\omega_0 = \frac{1}{2}\omega_t$ is adiabatic and reversible. Though the inequality (1) is well satisfied in these experiments, there is another effect which can give rise to irreversibility, namely, the intermolecular dipolar interactions. A local magnetic field parallel to H_0 and oscillating at an angular frequency close to ω_d can induce transitions between the mixed A and E states near the "level-crossing fields." If the transition probability during one passage is appreciable, it can be shown that the process of saturation of the NMR signal at high field corresponding to transitions $\Delta I = 0$ and $\Delta M_I = \pm 1$, followed by cycling of the external field through the level-crossing regions and back to high field, would give rise to a measureable magnetization *even in the absence of relaxation during the field cycle*. We observed no such magnetization induced by field cycling after saturation at high field, thus enabling us to use Eq. (3) with some confidence. However, at 4.2 K, we did observe a small signal, about 3% of M_0, measured about 1 min after the resonance was saturated at H_0 and the magnetic field either held constant or cycled adiabatically to zero and back to H_0. Several tests led us to believe this signal results either from protons in the sample, which have a short relaxation time (those near paramagnetic impurities for example), or perhaps from protons outside the sample. In the determination of ω_t, this signal was subtracted from M_a. A similar, larger signal observed at 24 K was undoubtedly due to the fact that T_1 processes are not altogether negligible during the time the measurements are made.

As a result of our experiment it should now be possible to develop a systematic technique for the precise determination of tunneling frequencies in a wide variety of solid compounds containing CH_3 groups, and probably other symmetric arrangements of protons such as NH_4^+ as well.[25] This could be accomplished by inducing transitions between the mixed A and E states near the level-crossing fields by means of an externally applied magnetic field parallel to H_0 and oscillating at an angular frequency close to ω_d. Under these conditions, passage through the level-crossing region would be signaled by a change in the nuclear magnetization at the measuring field. Systematic measurements of tunneling frequencies would give information on the height of the potential barrier inhibiting molecular jumps between equivalent orientations and hence make possible the independent determination of the parameters involved in thermally activated molecular reorientation at higher temperatures.

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