conventional nuclear magnetic resonance are in progress. These include stimulated echoes, rotary echoes, spin locking, and multiple-pulse trains and their applications to molecular solids.

Finally, although the experiments were performed in triplet states by monitoring phosphorescence, in principle the optical absorption or fluorescence from a multiple-level system, in gases for example, could be monitored and the same pulse sequence adopted in the above experiments could be applied to many other radiative and nonradiative molecular states.

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Tunneling Resonances in Proton Spin-Lattice Relaxation

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Two sharp peaks have been observed in the magnetic field dependence of the proton spin-lattice relaxation rate of γ-irradiated 4-methyl 2, 6-ditertiarybutylphenol at liquid-helium temperatures. The peaks are attributed to resonances between the frequencies of tunneling rotation of the 4-methyl groups and the Larmor frequency of the unpaired electron spins associated with free radicals. One peak is assigned to the tunneling resonance of the methyl groups of the free radicals and the other to undamaged molecules.

At low temperatures proton spin-lattice relaxation is commonly dominated by the effects of rapidly relaxing paramagnetic impurities assisted by the process of proton spin diffusion which permits protons far from any impurity to relax via the protons located near paramagnetic centers. For solids which contain methyl groups undergoing tunneling rotation, an interesting possibility arises of a resonance between the frequency of tunneling rotation and the Larmor frequency of the paramagnetic center. In this case, energy-conserving processes become possible which involve simultaneous flips of electron and nuclear spins combined with a change in the rotational motion of the methyl group. They are expected to give rise to resonant features in the field dependence of proton relaxation rate, especially at low temperatures where there is little competition from other processes. Recently, Glättli, Sentz, and Eisenkremer have observed similar resonances in the conversion rate of spin isomers of irradiated methane.[1] Combined proton

spin and tunneling state transitions have also been observed[2] driven by an external microwave field of the electrons as in the present case.

We consider a single unpaired electron spin S and the proton spins I_j of a single fairly remote methyl group. The dominant part of the spin Hamiltonian consists of the Zeeman terms and the tunneling term representing the energy associated with methyl-group rotation. We use the irreducible tensor components, S_p and I_p, $p = 0$, ± 1, which transform like the spherical harmonics $Y_l^p(\theta, \varphi)$; and we combine terms involving the three proton spins to form a basis for the irreducible representations of the group of cyclic permutations of three particles, according to the

prescription $X^\lambda = X_1 + \lambda X_2 + \lambda^* X_3$, where $\lambda = 1, \epsilon, \epsilon^*$, with $\epsilon = \exp(2\pi i/3)$:

$$H_0 = H_Z + H_T, \tag{1}$$

$$H_Z = +\hbar\omega_s S_0 - \hbar\omega_n I_0^1, \tag{2}$$

$$H_T = \hbar J(P + P^{-1}). \tag{3}$$

The operator P has the effect of cyclically permuting the three spin coordinates so that $P I_p^\lambda = \lambda I_p^\lambda P$. H_T gives rise to a tunneling splitting of the molecular ground state of magnitude $3J\hbar$.

The interaction between electron and proton spins has the general form $\vec{S} \cdot \vec{U} \cdot \vec{I}$, where U is a symmetric second-rank tensor. For all three protons the interaction is

$$H_i = \sum_{\lambda = 1, \epsilon, \epsilon^*} \sum_{p = 0, 1} \sum_{p \geq q \geq -1} (U_{pq}^{\lambda^*} S_p I_q^\lambda + U_{-p-q}^\lambda S_{-p} I_{-q}^{\lambda^*}).$$

In the interaction representation, $H_i' = \exp(iH_0 t/\hbar) H_i \exp(-iH_0 t/\hbar)$; hence

$$H_i' = \sum_{\lambda = 1, \epsilon, \epsilon^*} \sum_{p = 0, 1} \sum_{p \geq q \geq -1} [U_{pq}^{\lambda^*} S_p I_q^\lambda \exp(iRt) + U_{-p-q}^\lambda S_{-p} I_{-q}^{\lambda^*} \exp(-iRt)], \tag{4}$$

$$R = p\omega_s - q\omega_n + J[(\lambda - 1)P + (\lambda^* - 1)P^{-1}]. \tag{5}$$

In deriving (4) and (5), it is useful to note that the four terms contributing to H_0 commute, so that the operator $\exp(iH_0 t/\hbar)$ may be written as a product of exponential operators and also $\exp(iA)B\exp(-iA) = B\exp(i\alpha A)$ if the commutation rule

$$[A, [A, [\cdots (n \text{ times}), B]] \cdots] = B(\alpha A)^n$$

applies as it does for $A = P$, $B = I_q^\lambda$ when $\alpha = \lambda - 1$.

The density matrix ρ evolves according to standard time-dependent perturbation theory,

$$d\rho/dt = -\int_0^\infty [H_i'(0), [H_i'(t), (\rho - \rho_{eq})]] dt, \tag{6}$$

where ρ_{eq} is the equilibrium density matrix. The rate of decay of macroscopic magnetization towards its equilibrium value M_0 is given by

$$-\frac{1}{M - M_0} \frac{dM}{dt} = -\frac{\text{Tr}(I_0^1 d\rho/dt)}{\text{Tr}[I_0^1(\rho - \rho_{eq})]} = \frac{1}{T_1}.$$

In evaluating the above traces, the only nonzero contributions come from the dependence of ρ on I_0^1, and in the high-temperature approximation this is linear:

$$1/T_1 = \int_0^\infty \text{Tr}\{I_0^1[H_i'(0), [H_i'(t), I_0^1]]\} dt / \text{Tr}(I_0^1 I_0^1). \tag{7}$$

Inserting (4) into (7), nonzero traces are easily identified because the corresponding operators are invariant to rotation and cyclic permutation,

$$\frac{1}{T_1} = \sum_{\lambda = 1, \epsilon, \epsilon^*} \sum_{p = 0, 1} \sum_{p \geq q \geq -1} \frac{2q^2}{9} |U_{pq}^{\lambda^*}|^2 \frac{\int_0^\infty \text{Tr}[S_p S_{-p} I_q^\lambda I_{-q}^{\lambda^*} \cos(itR)] dt}{\text{Tr}(I_0^1 I_0^1)}. \tag{8}$$

Now we assume that the components of S fluctuate with correlation time τ so that

$$2\text{Tr}_s S_0 S_0 = \text{Tr}_s S_1 S_{-1} = \exp(-t/\tau),$$

where Tr_s denotes trace evaluation over electron spin coordinates only.

The important parts of (8) are the low-frequency terms, namely (a) with $p = 0$, $q = -1$, $\lambda = 1$ for which $R = \omega_n$, and (b) with $p = 1$, $q = \pm 1$, $\lambda = \epsilon, \epsilon^*$ for which half the contributions have eigenvalues of R equal to $\omega_s - q\omega_n + 3J$ and half have $\omega_s - q\omega_n - 3J$. We retain only the latter half which are important when

$\omega_s \sim 3J$. The traces are then easily evaluated to obtain

$$\frac{1}{T_1} = \frac{\tau}{9}\left[\frac{|U_{0-1}{}^1|^2}{1 + \omega_n{}^2\tau^2} + \frac{2|U_{11}{}^\epsilon|^2}{1 + (\omega_s - \omega_n - 3J)^2\tau^2} + \frac{2|U_{1-1}{}^\epsilon|^2}{1 + (\omega_s + \omega_n - 3J)^2\tau^2}\right].$$ (9)

The first term on the right-hand side of (9) depends on the average interaction of the electron with the three protons, while the resonant terms depend on differences between the interactions with the protons and, therefore, for distant methyl groups on the gradient of the electron's dipolar field.

The details of relaxation are complicated by the existence of a diffusion barrier.[3] From (9), though, one may expect that at low temperatures $(\omega_n\tau \gg 1)$ one has $T_1 \propto \omega_n{}^2 \propto H^2$, where H is the applied field, except near those values of H for which $\omega_s \sim 3J$. The growth from zero of magnetization after a time t follows the field dependence

$$M(t) = aH[1 - \exp(-bt/H^2)]$$ (10)
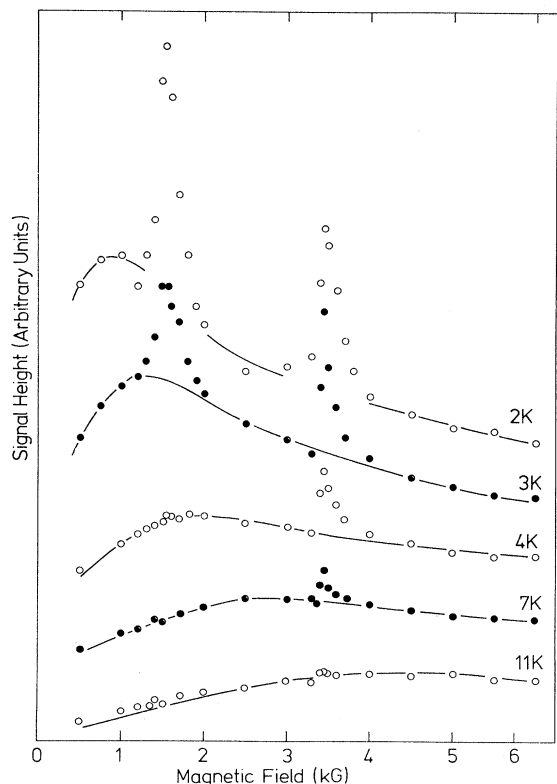
with anomalies near $\omega_s \sim 3J$.

FIG. 1. Magnetic field dependence of proton magnetization recovery showing tunneling resonances. The curves are calculated from Eq. (10) and are shifted vertically with the data for clarity.

Figure 1 shows measurements made at several temperatures on γ-irradiated polycrystalline 4-methyl 2, 6-ditertiarybutylphenol. Previous measurements by electron-nuclear double resonance[4] and by the temperature dependence of proton spin-lattice relaxation[5] have indicated a value of $3J/2\pi$ of about 4 GHz for the methyl group of the free radical and rather more for the undamaged molecule.

The experiments involved a field-cycling technique. First H was brought to resonance (25 MHz, for most measurements) and the magnetization destroyed by a series of rf pulses. Then the field was switched to a new value H (switching time 2.5 sec/kG), where it stayed for a time t (1 or 2 min). The field was then switched back to resonance and the magnetization M inspected by observing the free-induction decay following a rf pulse. Measurements at different frequencies confirmed that the results did not depend significantly on this parameter.

Of the two tunneling resonances observed, the lower frequency 4.35 GHz is probably the tunneling frequency of methyl groups in the free radicals.[4] In this case the interaction U is very large and at resonance it may cause electron spin flips at a rate which perturbs the noise spectrum of the electron's field at more distant protons beyond the diffusion barrier. The resonance at 9.7 GHz we assign to the effect of distant methyl groups in undamaged molecules due to the resonant term of (9). A parallel experiment on tritertiarybutylphenol showed no resonant features.

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