Furthermore, "light shifts" of the dispersion type[7] which depend on the displacement of structure in the lamp spectrum from the center of the absorber line cannot be caused by the broad spectrum of a white-light source. This freedom from light shifts may recommend white-light sources for high precision optical pumping at lower pressures.

We wish to thank P. Bender and V. W. Cohen for information on their unpublished work on Rb hyperfine linewidths and temperature gradients, and for enlightening comments on the theory of alkali–inert-gas collisions. We also wish to acknowledge the support and encouragement of V. W. Hughes in this work. Mr. R. J. Blume helped solve the frequency multiplication problems.

[1]S. Y. Ch'en, Phys. Rev. 58, 1051 (1940).

[2]F. A. Franz and J. R. Franz, Phys. Rev. 148, 82 (1966).

[3]L. Krause, Appl. Opt. 5, 1375 (1966).

[4]G. S. Hayne and H. G. Robinson, private communication; R. M. Herman, Phys. Rev. 175, 10 (1968).

[5]P. Bender, E. C. Beaty, and A. R. Chi, Phys. Rev. Letters 1, 311 (1958).

[6]P. A. Thompson, J. J. Amato, P. Crane, V. W. Hughes, R. M. Mobley, G. zu Putlitz, and J. E. Rothberg, Phys. Rev. Letters 22, 163 (1969).

[7]J. P. Barrat and C. Cohen-Tannoudji, Compt. Rend. 252, 93, 255 (1961), and J. Phys. (Paris) 22, 329, 443 (1961).

TUNNELING-ASSISTED NUCLEAR SPIN-LATTICE RELAXATION

P. S. Allen and S. Clough
Department of Physics, University of Nottingham, England
(Received 1 April 1969)

The tunneling splitting of the torsional-oscillator ground state of a hindered methyl group is taken into account in calculating the temperature dependence of the proton spin-lattice relaxation time. Thermal vibrations cause spin-independent transitions leading to a fluctuation in the sign of the splitting parameter. It is predicted that a second maximum in T_1^{-1} may occur at low temperature due to a tunneling-assisted process. This effect is detected in some methyl-substituted benzenes in good agreement with the theory.

Recent electron-spin resonance[1,2] and electron-nuclear double-resonance (ENDOR)[3] experiments have demonstrated important consequences of the splitting of the torsional-oscillator ground state of a hindered methyl group due to tunneling rotation. In one case the splitting has been measured by ENDOR,[3] but it may also be estimated roughly from the hindering barrier height using a relation due to Hecht and Dennison.[4] The splitting is also necessary to explain the narrow NMR lines observed at low temperatures,[5-7] but no satisfactory expression exists for calculating its effect on the temperature dependence of T_1, the spin-lattice relaxation time.

Numerous experimental studies of T_1 have been interpreted in terms of the classical Bloembergen-Purcell-Pound theory[8] which usually fits the data at high temperatures, though low-temperature anomalies have been observed.[9-12] The problem was discussed semiquantitatively by Stejskal and Gutowsky[13] who recognized the possibility of tunneling resonances when the splitting coincides with the Larmor frequency and the fact that lattice vibrations broaden the splitting spec-trum. In this Letter we give a theoretical model which describes both high- and low-temperature phenomena. It leads to detailed predictions concerning a low-temperature relaxation process related to the tunneling frequency and provides an explanation for the experimental data from methyl-substituted benzenes in the range 20-200 °K.

We consider first a methyl group constrained by some static hindering potential to small oscillations about its symmetry axis. The orientation of the group is characterized by an angle φ which may be regarded as the position coordinate of a particle in a three-well potential. The wave functions are therefore linear combinations of three harmonic-oscillator functions. Two types of combinations are possible, having regard for the threefold symmetry of the potential, corresponding to the A and E representations of the group C_3. The energy splitting between these states depends on the overlap of the harmonic-oscillator functions and is closely related to the frequency for tunneling between the wells. Particle indistinguishability requires that the pro-

duct of spatial wave function and spin function shall have A-type symmetry; so the eigenfunctions are of the form $A \times A$ or $E \times E$. The spin states are therefore separated and this fact can be introduced into the spin Hamiltonian by means of an exchange operator. The energy levels including the nuclear Zeeman energy in the external field H_0 are given relative to the zero-point energy of the harmonic oscillator by

$$E_{F,m} = -\gamma \hbar H_0 m - \hbar J[F(F+1) - 7/4]. \quad (1)$$

F is $\frac{3}{2}$ for the A states and $\frac{1}{2}$ for the E states, while m takes values from F to $-F$. The E states are doubly degenerate. The tunneling splitting is $3J\hbar$.

The agent of spin-lattice relaxation is that part of the interproton dipole-dipole interactions which has matrix elements D_{ab} between different Zeeman levels and is of E-type symmetry (since this is modulated by rotation). Because of the thermally activated rotation of the methyl group the matrix elements are random functions of time:

$$\langle D_{ab}(t')D_{ab}(t'+t)\rangle = \langle D_{ab}{}^2\rangle \exp(-t/\tau_c) \quad (2)$$

with τ_c the correlation time for the rotation. It obeys the Arrhenius equation

$$\tau_c = \tau_0 \exp(E/kT). \quad (3)$$

The activation energy E is assumed to be approximately equal to the height of the hindering barrier above the ground state. The transition probabilities for spin-lattice relaxation are obtained from time-dependent perturbation theory:

$$W_{ab} = 2\langle D_{ab}{}^2\rangle \int_0^\infty \exp(-t'/\tau_c)$$
$$\times \exp[it'(E_a - E_b)/\hbar]dt'. \quad (4)$$

Now E_a is given by (1) for a methyl group moving in a static potential when the nuclear spin and space coordinates are completely correlated. However, as the temperature rises the thermal vibrations of the lattice cause transitions between the methyl-group torsional-oscillator states. Since these transitions are spin independent the spatial part of the wave function must be regarded as fluctuating between A and E types without fluctuation of the spin part. The resulting effect on (4) is that the sign of J in the exponent fluctuates randomly. We therefore define

the frequency spectrum $f(\omega)$:

$$\exp[i\int_0^t 3J(t')dt'] = \int_{-\infty}^{\infty} f(\omega)\exp(-i\omega t)d\omega. \quad (5)$$

Now we replace $\exp(i3Jt)$ in (4) by (5) and integrate over time to obtain

$$^nW_{ab} = 2\langle {}^nD_{ab}{}^2\rangle$$
$$\times \int_{-\infty}^{\infty} f(\omega) \frac{\tau_c}{1+(\omega - n\omega_0)^2\tau_c{}^2} d\omega. \quad (6)$$

The superscript n takes the values 1 and 2 indicating a $\Delta m = n$ transition, and $\omega_0 = \gamma H_0$. The left-hand side of (5) will be recognized as the free-induction decay for a spin of $\frac{1}{2}$ jumping randomly between two sites with well-defined resonance frequencies $\pm 3J$. The spectrum is well known[14]:

$$f(\omega) = \frac{8y}{6\pi J[x^4 + 2x^2(2y^2-1) + 1]} \quad (7)$$

with $x = \omega/3J$ and $y = \frac{1}{3}J\tau_t$. We have introduced a second correlation time τ_t to describe the random fluctuation of the sign of J. Assuming that the transitions responsible for this fluctuation occur via the excited torsional-oscillator levels, we expect τ_t to obey (3) with an activation energy E_t corresponding to the height of the first excited state. Thus τ_t refers to transitions to levels within the potential well and τ_c to transitions to levels near the top of the barrier.

We make the usual spin temperature assumption[15] that the populations of the levels during relaxation are linearly dependent on m so that relaxation within the eight levels is described by a single relaxation time. This just involves sums over the transition probabilities:

$$\frac{1}{T_1} = \frac{1}{12}\left(\sum_{a,b} {}^1W_{ab} + 4\sum_{a',b'} {}^2W_{a'b'}\right). \quad (8)$$

Since we may expect that the two correlation times are very different, it will usually happen that (6) is small except in two temperature regions where the integral is solved trivially. At high temperatures $f(\omega)$ is a δ function at $\omega = 0$, while at low temperatures $\tau_c/\pi[1+(\omega - n\omega_0)^2\tau_c{}^2]$ is a δ function at $\omega = n\omega_0$. Then evaluating (8) one finds

$$\frac{1}{T_1} = C\left\{ \frac{\tau_c}{1+\omega_0{}^2\tau_c{}^2} + \frac{4\tau_c}{1+4\omega_0{}^2\tau_c{}^2} \right.$$
$$\left. + \pi f(\omega_0) + 4\pi f(2\omega_0)\right\}. \quad (9)$$

The first two terms in the bracket in (9) constitute the usual Bloembergen-Purcell-Pound formula. The other two terms represent the tunneling-assisted relaxation expected to be important at low temperatures.

The model introduces the parameters E_t and $3J$ which roughly fix the width and height of the low-temperature maximum in T_1^{-1}. For a simple cosine barrier these parameters have a known relationship with the barrier height E. Consequently, E determines the general form of the temperature dependence of T_1^{-1}. Of course, the barrier shape probably departs substantially from a simple cosine function but the latter provides some guidance for the parameters. Figure 1 shows measurements for pentamethylbenzene obtained by standard pulse methods using a resonance frequency of 25 MHz. The curve is calculated from (9) with $\omega_0/3J = 1.7$, $\tau_c = 1.22 \times 10^{-13}$ $\times \exp(1160/T)$, and $\tau_t = 7.8 \times 10^{-13} \exp(380/T)$, the parameters being chosen to fit the data at the turning points. The value $1160°K$ corresponds to a height of the barrier above the ground state of

2.3 kcal mole^{-1}. For a cosine barrier this would give $3J = 4$ MHz and $E_t/k = 300°K$ instead of the values 14 MHz and $380°K$ used above.

Secondary maxima in T_1^{-1} have also been observed in 1, 2, 3, 4- and 1, 2, 3, 5-tetramethylbenzenes.[9] If the latter is cooled rapidly the results are very similar to those in Fig. 1. Low-temperature maxima in T_1^{-1} can also be recognized in 1, 2, 3- and 1, 2, 4-trimethylbenzenes,[12] dimethylbutanes[11] and trimethylpentane.[10] Although other reasons have been given for these effects,[9] recent studies on deuterated isomers[16] have shown this former interpretation to be incorrect. The present theory provides a more satisfactory explanation for what is evidently a fairly general phenomenon.

In summary, the theory finds support from the available data and it brings the T_1 temperature dependence into line with the NMR linewidth, the ESR, and ENDOR measurements, all being interpreted in a consistent way from the same basic model.
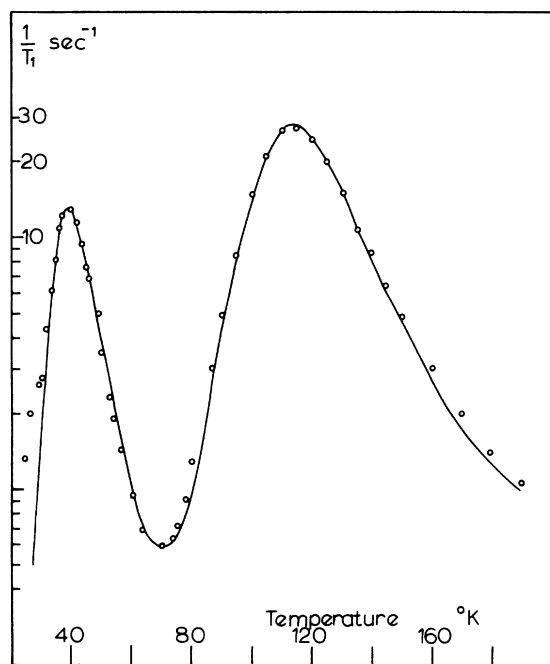

FIG. 1. The temperature dependence of the proton spin-lattice relaxation rate T_1^{-1} for pentamethylbenzene measured with a resonance frequency of 25 MHz. The curve is calculated from (9) with parameters given in the text. The peak around 45°K is attributed to tunneling-assisted relaxation.

[1]S. Clough and F. Poldy, Phys. Letters 24A, 545 (1967).

[2]W. L. Gamble, I. Miyagawa, and R. L. Hartman, Phys. Rev. Letters 20, 415 (1968).

[3]S. Clough and F. Poldy, Phys. Letters 25A, 186 (1967).

[4]K. T. Hecht and D. M. Dennison, J. Chem. Phys. 26, 31 (1957).

[5]J. G. Powles and H. S. Gutowsky, J. Chem. Phys. 21, 1695 (1953).

[6]P. S. Allen, J. Chem. Phys. 48, 3031 (1968).

[7]F. Apaydin and S. Clough, J. Phys. C: Phys. Soc. (London) Proc. 1, 932 (1968).

[8]N. Bloembergen, E. N. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

[9]P. S. Allen and A. Cowking, J. Chem. Phys. 49, 789 (1968).

[10]R. G. Eades, T. A. Jones, and J. P. Llewellyn, Proc. Phys. Soc. (London) 91, 632 (1967).

[11]R. G. Eades, G. P. Jones, J. P. Llewellyn, and K. W. Terry, Proc. Phys. Soc. (London) 91, 124 (1967).

[12]G. P. Jones, R. G. Eades, K. W. Terry, and J. P. Llewellyn, J. Phys. C: Phys. Soc. (London) Proc. 1, 415 (1968).

[13]E. O. Stejskal and H. S. Gutowsky, J. Chem. Phys. 28, 388 (1958).

[14]P. W. Anderson, J. Phys. Soc. Japan 9, 316 (1954).

[15]C. P. Slichter, Principles of Magnetic Resonance (Harper and Row Publisher, Inc., New York, 1963), p. 116.

[16]P. S. Allen and C. J. Howard, to be published.