tables for Coulomb functions, but are very much simpler and more transparent than direct methods for the corresponding problems. More important, however, are the many avenues for generalization which are opened up by it, as well as the fact that for the first time a wave function accurate in all regions of space, and especially in regions exterior to the bonded atoms, is available with little effort for a molecular valence bond.

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[1] These are the common features of the orthogonalized plane-wave method and its descendants (including the augmented plane wave), the Korringa-Kohn-Rostoker method, and the quantum defect method and its ancestor, the cellular method. The two former use plane waves fitted to match realistic wave functions in the atom cores, the two latter Coulomb functions. A good review of the older literature on these methods is given by John R. Reitz, Solid State Phys. 1, 2 (1955), and of later work by W. A. Harrison, Pseudopotentials (W. A. Benjamin, Inc., New York, 1966).

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SOME EFFECTS OF QUANTIZATION OF INTERNAL ROTATION ON SPIN-LATTICE RELAXATION AND HYPERFINE STRUCTURE*

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The temperature dependence of the spin-lattice relaxation time of the oriented $\mathrm{H_3C}$-$\dot{\mathrm{C}}R_1R_2$ radical in x-irradiated single crystals of acetyl-(d,l)-alanine has been observed to be dominated by "spin-flip" transitions between the rotational states of the methyl group. The energy separation of these levels has been confirmed by an analysis of the ESR spectra of the radical. The low-temperature ESR spectra show quantum effects also not previously observed.

Several papers have appeared recently both on the effects of rotations on spin-lattice relaxation and on hyperfine structure.[1-6] In most cases, rotations in magnetic resonance have been treated "semiclassically" using a classical Brownian diffusion model for the rotational motion while treating the spins quantum mechanically as in the pioneering work of Bloembergen, Purcell, and Pound.[7] This Letter is to report what we believe to be the first observed case in which the effects of quantization of the rotational motion dominate the electron spin-lattice relaxation, as well as the first observation of some effects of the quantization of the rotational motion of the ESR spectra.

Both the spin-lattice relaxation time (T_1) and the ESR spectra of the $\mathrm{H_3C}$-$\dot{\mathrm{C}}R_1R_2$ radical[8] in x-irradiated single crystals of acetyl-(d,l)-alanine as well as the T_1 of the $\mathrm{H_3C}$-$\dot{\mathrm{C}}\mathrm{H}R$ radical[6] in x-irradiated single crystals of l-alanine were observed at 9 kMc/sec as a function of T from 1.2 to 300°K. R, R_1, and R_2 denote the remaining groups of the molecules. They make no significant contribution to the hyperfine structure. The T_1's were measured by observation of recovery from pulsed saturation.

In Fig. 1, second-derivative traces of the ESR spectrum of $\mathrm{H_3C}$-$\dot{\mathrm{C}}R_1R_2$ are shown for several values of the temperature (T). As can be seen, the spectrum consists of four lines of intensity ratio 1:3:3:1 at high temperatures and of seven equally spaced lines at low temperatures. One can account for this by assuming either of the following: (1) that the magnitudes of the three proton coupling constants have the ratios 1:2:3, and are tunneling or rotating sufficiently slowly at low temperatures so as to be distinguishable, or (2) that the ro-

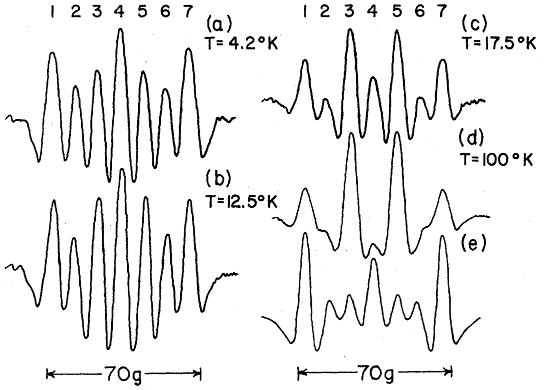

FIG. 1. (a)-(d) Second-derivative traces of the ESR spectrum at 9 kMc/sec of the H_3C-$\dot{C}R_1R_2$ radical in x-irradiated single crystals of acetyl-(*d,l*)-alanine at the indicated temperatures. The magnetic field is parallel to the [*c*] axis. (e) Plot of the second derivative of the absorption curve derived from the modified Bloch equation which should account for the spectra if the methyl protons were jumping between chemically inequivalent positions according to a classical Brownian diffusion model.

tation rate is sufficiently rapid even at 1.2°K to average the coupling constants and that quantum effects account for the appearance of lines 2, 3, and 4 at low temperatures. The first assumption is unacceptable for two reasons. First, the coupling due to hyperconjugative overlap[3] is of the form $2a[\vec{I}_1\cos^2(\varphi)+\vec{I}_2\cos^2(\varphi+\frac{2}{3}\pi)+\vec{I}_3\cos^2(\varphi+\frac{4}{3}\pi)]\cdot S$ and no value of φ exists such that these terms are in the above ratios. The second and far more persuasive reason is as follows: Extreme broadening of the internal lines should occur when the tunneling or rotation rate is of the order of the differences between the coupling constants, as observed by Miyagawa and Itoh[7] for the H_3C-$\dot{C}HR$ radical in *l*-alanine. In that case, the coupling constants for the methyl protons were quite different, and that part of the hyperfine structure due to the methyl protons consisted of four lines above, and seven lines below 160°K. At 160°K the internal lines were so broad that they were not observed. Their results were quantitatively accounted for at all temperatures by a modified Bloch equation[6,9,10] which should hold if the protons were jumping between chemically inequivalent positions according to a classical Brownian diffusion model. Figure 1(e) is a plot of the second derivative of the absorption curve derived from the modified Bloch equation and is an example of the kind of spectrum one would expect for the present case in the temperature region where the spectrum is changing from four to seven lines if assumption (1) held. As can be seen in Fig. 1, no such broadening occurred in acetyl-(*d, l*)-alanine. In fact, lines 3 and 5 increase monotonically with increasing temperature relative to the outside lines.

One is therefore left with the conclusion that the methyl group is rotating sufficiently rapidly even at 1.2°K to render the protons indistinguishable and that the lack of any broadening of lines 3 and 5, as well as the appearance of lines 2, 4, and 6 at low temperatures, must be due to the effects of quantization of the methyl-group rotations.

Freed[3] recently pointed out that under certain conditions spectra qualitatively identical to those herein reported should be observed. The Hamiltonian treated by Freed can be written as

$$\mathcal{H}=\mathcal{H}_R+\mathcal{H}_I+\mathcal{H}_{RI}, \tag{1}$$

where $\mathcal{H}_R=-(\hbar^2/2I)(d^2/d\varphi^2)+V(\varphi)$ is the rotational Hamiltonian, $\mathcal{H}_I=-\gamma_e\hbar S_zH_0-\gamma_p\hbar I_zH_0+\vec{a}\vec{I}\cdot\vec{S}$ is the spin Hamiltonian, $H_{RI}=\frac{1}{2}a[e^{2i\varphi}(\vec{I}_1+\epsilon^*\vec{I}_2+\epsilon\vec{I}_3)+e^{-2i\varphi}(\vec{I}_1+\epsilon\vec{I}_2+\epsilon^*\vec{I}_3)]\cdot\vec{S}$ is the spin rotational coupling, and $\vec{I}=\vec{I}_1+\vec{I}_2+\vec{I}_3$. For a fairly high barrier of the form $V=\frac{1}{2}V_0(1-\cos3\varphi)$ the first four energy levels of $\mathcal{H}_R$ are known[11] to have a spacing roughly as shown in Fig. 2(a). The levels marked *A* are nondegenerate and totally symmetric in φ. The levels marked *E* are doubly degenerate and transform like an irreducible two-dimensional representation of the

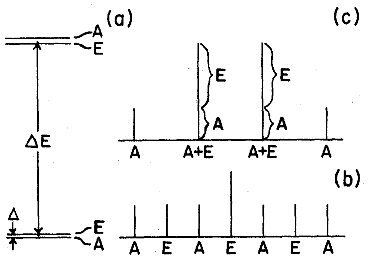

FIG. 2. (a) The horizontal lines show roughly the relative spacing of the first four rotational energy levels of a rigid rotor of C_{3v} symmetry tunneling through a fairly high potential barrier of the form $V=\frac{1}{2}V_0(1-\cos3\varphi)$. The letters show the symmetry of the levels. (b) The bars indicate the relative spacing and intensity of the ESR spectrum of $H_3C-\dot{C}R_1R_2$ radical as calculated by Freed (Ref. 3). The bars marked *A* are due to methyl groups in states of symmetry type *A*, while those marked *E* are due to the lowest rotational state of *E* symmetry. (c) Same as in (b) except that here the portions marked *E* are due to the excited states of *E* symmetry.

symmetry group C_{3v}. The average spacing between the two pairs of levels is denoted by ΔE, while the spacing between the lowest two is denoted by Δ. If the radical is assumed to be in its electronic and vibrational ground state, spin functions must be chosen so that the product of the spin and orbital wave functions are invariant with respect to a 120° rotation, since this operation is equivalent to a simultaneous exchange of two pairs of protons. It is further assumed that the coupling of the spin rotational system to the lattice is sufficiently strong to keep the system in thermal equilibrium with the lattice, but much smaller than the spin rotational coupling. Under these conditions the ESR transitions will be between the eigenstates of (1). Freed further demonstrated that either for free states with $V_0 = 0$ or V_0 large but of such a shape that $\Delta \gg a$, the following is true: All states of symmetry A have an ESR spectrum as indicated by the bars marked A in Fig. 2(b). Methyl groups in the lowest state of E symmetry have the spectrum indicated by the bars marked E in Fig. 2(b). The higher states of E symmetry have an ESR spectrum consisting of the two lines indicated in Fig. 2(c). Hence, Fig. 2(b) is the spectrum one would expect if only the lowest pair of levels were populated, and Fig. 2(c) is the spectrum one would get if only the upper pair were populated.

The temperature dependence of the ESR spectra is qualitatively as discussed below. Lines 1 and 7 are independent of the methyl-group motion, whether classical[6] or quantized,[3] so that the behavior of lines 2-6 will be discussed relative to them. The intensities of lines 3 and 5 increase together monotonically with increasing temperature, but the change up to 12°K is negligible. Lines 2, 4, and 6 decrease together monotonically with increasing temperature, but again the decrease up to 12°K is negligible. An analysis of this temperature dependence over the range from 1.2 to 30°K entirely in terms of a Boltzmann distribution of the spectra shown in Figs. 2(b) and 2(c), since they should be the only states significantly populated in this temperature range, yields a value $\Delta E = 25 \pm 4$°K. The fact that lines 2, 4, and 6 did not decrease at 1.2°K shows that $\Delta < 0.2$°K. The splitting between the upper pair of levels was found to be no greater than the experimental error. This value of ΔE will be seen to agree with the value obtained for this splitting from the temperature dependence of the spin-lattice relaxation.

The temperature dependence of the spin-lattice relaxation time for the $H_3C\text{-}\dot{C}R_1R_2$ radical in acetyl-(d,l)-alanine is shown in Fig. 3. Note that T_1^{-1} depends linearly on T for high temperatures and is hence similar to that for an Orbach process.[12] However, the existence of a low-lying excited electronic state is exceedingly unlikely in such a molecule, so that another explanation is given below.

Murphy[13] has recently shown that if spin-lattice relaxation were dominated by "spin-flip" transitions of an ion between two states in a bistable harmonic-oscillator potential, where the g value of the electron was essentially the same in each state, the spin-lattice relaxation time should vary with the temperature according to

$$T_1^{-1} = 2W[\operatorname{csch}(\Delta E/T)]. \tag{2}$$

Here ΔE is a measure of the separation of the levels between which the ion makes spin-flip transitions. Murphy also demonstrated that the temperature dependence due to spin-flip transitions between all levels of a square well should be quite similar to Eq. (2) except for a higher slope at high temperatures. As can

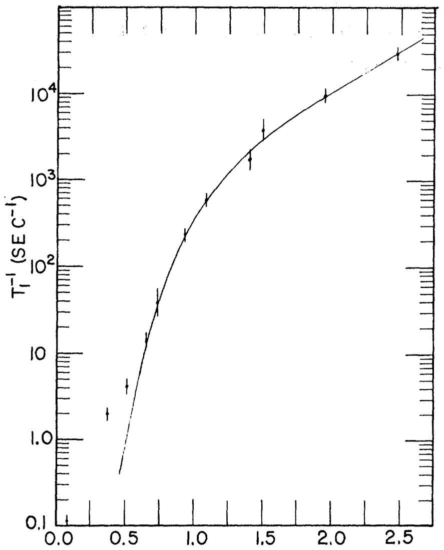

FIG. 3. Plot of the inverse of the electron spin-lattice relaxation time versus the logarithm$_{10}$ of the temperature for the $H_3C\text{-}\dot{C}R_1R_2$ radical in x-irradiated single crystals of acetyl-(d,l)-alanine. Each dot represents the average of several experimental values and the bars indicate the experimental error due mostly to spectrometer noise. The solid curve is a plot of $T_1^{-1} = 2W[\operatorname{csch}(\Delta E/T)]$, with $\Delta E = 26$°K and $W = 1.50 \times 10^3$ sec^{-1}.

be seen in Fig. 3, the agreement between Eq. (2) and the experimental data could hardly be better above 5°K. In this plot $\Delta E = 26 \pm 3$°K and $W = 1.5 \pm 0.2 \times 10^3$ sec^{-1}.

This value of ΔE agrees with the value for the splitting between the ground and first excited rotational states of the methyl group as obtained from the temperature dependence of the ESR spectra. An obvious conclusion is that transitions between the ground and first excited rotational states with a simultaneous spin flip are sufficiently frequent to dominate all other spin-lattice relaxation mechanisms. Significant contributions due to transitions between higher levels would appear to be ruled out by the linearity of the data at high temperatures. The temperature dependence of the spin-lattice relaxation time of the $H_3\dot{C}$-CHR radical in l-alanine in which case the classical theory holds was also observed,[14] and T_1 was found to have the temperature dependence of an ordinary Raman process above 4°K.

The crystals used in this experiment were grown by slow evaporation from aqueous solutions and were irradiated for about 3 h, at room temperature, about 8 cm from a tungsten x-ray tube operated at 45 kV and 35 mA. The acetyl-(d, l)-alanine crystals were then heated for about 5 h at 55°C in order to remove unstable centers.

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