

Quantum Effects of Methyl-Group Rotations in Magnetic Resonance: ESR Splittings and Linewidths*

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The effects of internal rotations of methyl groups on ESR hyperfine lines are analyzed in terms of a quantum-mechanical description of the motion. The classical description of rotational averaging is replaced by (1) spin-rotational coupling from a hyperfine operator, and (2) rotational relaxation by thermal collisions. In the absence of collisions, the effects of (1) lead to a static set of splittings whose values depend upon the relative magnitudes of the hyperfine-versus-tunneling frequencies. In the presence of frequent collisions, represented by a strong-collision model, the effects of (1) lead to line broadening, the detailed nature of which also depends on the hyperfine-versus-tunneling frequencies. In general, results predicted from a classical treatment of the motion are obtained when the hyperfine frequency is significantly greater, while quantum effects become important for relatively larger tunneling frequencies. The results are illustrated by application to relevant experimental observations. In the Appendix, the strong-collision relaxation theory is generalized to apply to the present case where the spin-rotational coupling connects states of different nuclear spin symmetry.

I. INTRODUCTION

IN the pioneering work of Bloembergen, Purcell, and Pound¹ on nuclear magnetic relaxation, the effect of rotational relaxation of magnetic spins was treated "semiclassically" using a classical Brownian diffusion model for the rotational motion, while the spins were treated quantum mechanically. This semiclassical approach has predominated in most of the work on both NMR and ESR relaxation of molecular systems with considerable success. The use of a classical treatment of rotational diffusion implies a continuous, albeit weighted, spectrum of energies available to the spin system, so only the characteristic frequencies of the spin system need be considered. When, however, the splitting of rotational levels is no longer small compared to these spin-system frequencies, then the quantization of the rotational motion should have a significant effect on the magnetic resonance relaxation. Once the necessity of quantum effects is admitted, it also becomes necessary to consider the effects of the exclusion principle in determining allowed states and transitions.

In this paper, a formulation is developed to analyze the effects that quantized internal rotations of methyl groups can have on magnetic resonance. There have been a number of studies of classical models for rotational relaxation in methyl groups both in NMR²⁻⁵ and ESR.⁶ In NMR, one must consider the coupling between

spins and rotational motions due primarily to the anisotropic magnetic dipolar couplings between the protons.²⁻⁵ In ESR, the dominant coupling term is the methyl-proton isotropic hyperfine splitting,⁶ with considerably smaller contributions from their anisotropic dipolar interactions with the unpaired electron. We concern ourselves only with the ESR hyperfine splitting problem, although the same general approach should be applicable to the other.

Stejskal and Gutowsky,⁷ in a study of the NMR problem, recognized the necessity of quantum considerations for methyl protons. Their approach was to calculate the torsional splittings or "tunneling" frequencies for a particular barrier height and to obtain a Boltzmann average of "tunneling" frequencies. This average was used instead of a classical "reorientation" frequency, in a calculation otherwise equivalent to the BPP theory¹ (as modified by Solomon⁸). There are a number of conceptual difficulties with this model that are pointed out by these authors. Thus (1) if an average "tunneling" frequency is to be calculated, it implies that transitions between torsional levels are taking place at a frequency greater than the "tunneling" frequency, so that the broadening of levels is greater than the torsional splittings and thus the latter are no longer important. Also (2) if tunneling implies transitions between the split states of a particular torsional level, then such a transition is spin forbidden. And (3) no consistent method of introducing collisions or thermal motions of the lattice is used. The point of view adopted in the present work, while still highly approximate, represents a more consistent approach which

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¹ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

² J. G. Powles and H. S. Gutowsky, *J. Chem. Phys.* **23**, 1692 (1955).

³ P. S. Hubbard, *Phys. Rev.* **109**, 1153 (1958); **111**, 1746 (1958).

⁴ R. L. Hilt and P. S. Hubbard, *Phys. Rev.* **134**, A392 (1964).

⁵ L. K. Runnels, *Phys. Rev.* **134**, A28 (1964).

⁶ J. H. Freed and G. K. Fraenkel, *J. Am. Chem. Soc.* **86**, 3477 (1964).

⁷ E. O. Stejskal and H. S. Gutowsky, *J. Chem. Phys.* **28**, 338 (1958).

⁸ I. Solomon, *Phys. Rev.* **99**, 559 (1955).

circumvents these difficulties. It also gives an entirely different significance to the effects of tunneling.

II. GENERAL CONSIDERATIONS; MATRIX ELEMENTS

We treat an isolated methyl group bonded to a carbon atom (fixed in some heavy molecule or lattice) containing an unpaired electron in a $2p-\pi$ orbital. It is assumed that the wavefunction for this system is approximated by

$$\Psi = \psi_E \psi_V \psi_R \psi_S \psi_I, \quad (2.1)$$

where ψ_E , ψ_V , ψ_R , ψ_S , and ψ_I are, respectively, electronic, vibrational, rotational, electron spin, and nuclear spin wavefunctions. These component functions may be analyzed in terms of the permutation group of the three methyl protons, but only the subgroup, consisting of "feasible transformations," corresponding to cyclic permutations of the three protons, will be important.⁹ This subgroup is isomorphous with the point group C_3 so that there is an invariant irreducible representation Species A and a doubly degenerate one E . According to the Pauli principle Ψ must belong to Species A . It is assumed that ψ_E and ψ_V are always ground-state functions and of A symmetry. Thus, the product $\psi_R \psi_I$ must also be of this symmetry.

An ESR spectrum results from transitions induced between different $\psi_S \psi_I$ and one may define that part of the Hamiltonian appropriate to the spin system as:

$$\begin{aligned} \hbar \mathcal{H}_{SI} = & \hbar \gamma_e \mathbf{B} \cdot \mathbf{S} + \hbar \gamma_P \sum_{i=1}^3 \mathbf{B} \cdot \mathbf{I}_i \\ & + \frac{8}{3} \pi \hbar^2 \gamma_e \gamma_P \sum_{i=1}^3 \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{S} \cdot \mathbf{I}_i. \end{aligned} \quad (2.2)$$

The first two terms in Eq. (2.2) give the Zeeman interaction of the unpaired electron and of the three methyl-proton spins with the magnetic field B , while the last term is the isotropic hyperfine interaction of the electron spin with the nuclear spins; γ_e and γ_P are the magnetogyric ratios of an electron and a proton, respectively. Because the first two terms in Eq. (2.2) are dominant in the high-field approximation, simple products of $\psi_S \psi_I$ are the correct functions to first order in the isotropic interaction. This interaction serves as a probe of both the electronic and nuclear motions by its delta-function dependence on the locations of the unpaired electron r and of the protons r_i . Thus, it must first be evaluated over $\psi_E \psi_V \psi_R$. In the Born-Oppenheimer approximation upon which the separation Eq. (2.1) is based, we first evaluate ψ_E as a function of electronic and nuclear coordinates, and then determine ψ_V and ψ_R . Since we shall only be concerned with the (hindered) rotational motion of the methyl group, it

is only necessary in a first approximation to express ψ_E as a function of orientation of the methyl group. The usual calculation of ψ_E , so as to give a finite spin density at the methyl protons, involves the hyperconjugative mixing of hydrogenic $1s$ orbitals and the methyl carbon orbitals with the unpaired electron in the carbon $2p_z$ orbital.¹⁰ We are presently primarily concerned with the symmetries of these orbitals. Appropriate linear combinations of the hydrogenic orbitals for arbitrary orientation of the methyl group, are given by Bershon¹⁰ and may be rewritten as:

$$\chi_1 = N_1^{1/2} (\Phi_{H_1} + \Phi_{H_2} + \Phi_{H_3}), \quad (2.3)$$

$$\chi_2 = N_2^{1/2} [\cos \phi \Phi_{H_1} + \cos(\phi + \frac{2}{3}\pi) \Phi_{H_2} + \cos(\phi - \frac{2}{3}\pi) \Phi_{H_3}], \quad (2.4)$$

$$\chi_3 = N_3^{1/2} [\sin \phi \Phi_{H_1} + \sin(\phi + \frac{2}{3}\pi) \Phi_{H_2} + \sin(\phi - \frac{2}{3}\pi) \Phi_{H_3}]. \quad (2.5)$$

The angle ϕ is defined as the angle between the z axis, along which the partially filled $2p-\pi$ carbon orbital lies, and the bond between the methyl carbon and H_1 nucleus. These functions are all of Species A as required for the ground-state wavefunction. However, only χ_2 is of the proper π symmetry to interact with the carbon $2p-\pi$ orbital. Thus the odd electron will be in a molecular orbital approximated by:

$$\psi_E^0 \cong [\lambda_a \Phi_{2p_z}^{C_1} + \lambda_b \Phi_{2p_z}^{C_2} + \lambda_c \chi_2], \quad (2.6)$$

where the λ_i are an appropriate set of coefficients, and the expectation value of $\delta(\mathbf{r} - \mathbf{r}_i)$ may be taken over this orbital. Bershon's results¹⁰ indicate that the dominant terms are the ones which are diagonal in the Φ_{H_k} . This leads to:

$$\begin{aligned} & \frac{8}{3} \pi \hbar \gamma_e \gamma_P \langle \psi_E^0 | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{I}_i \cdot \mathbf{S} | \psi_E^0 \rangle \\ & \cong 2a [\cos^2 \phi \mathbf{I}_1 + \cos^2(\phi + \frac{2}{3}\pi) \mathbf{I}_2 + \cos^2(\phi + \frac{4}{3}\pi) \mathbf{I}_3] \cdot \mathbf{S}, \end{aligned} \quad (2.7)$$

where a depends on λ_c^2 and $[\Phi_{H_i}(0)]^2$. The usual calculations introduce, at some convenient point, a "rotational averaging" to achieve equality of the hyperfine splittings of the three protons. Thus, if Eq. (2.7) is "averaged" isotropically over all values of ϕ we obtain

$$a(\mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3) = a\mathbf{I} \quad (2.8)$$

and a/γ_e is the observed splitting constant which usually ranges from about 20–25 G. We are presently concerned with a quantum-mechanical treatment of the rotational motion. Thus, it is necessary to retain Eq. (2.7) which is still a rotational as well as spin operator. It is easily seen that this operator is of

⁹ H. C. Longuet-Higgins, *Mol. Phys.* **7**, 445 (1963).

¹⁰ R. Bershon, *J. Chem. Phys.* **24**, 1066 (1956).

TABLE I. Spin functions.

$\psi^A_{I,3} = \alpha\alpha\alpha\rangle$
$\psi^A_{I,1} = 1/\sqrt{3} [\alpha\alpha\beta\rangle + \alpha\beta\alpha\rangle + \beta\alpha\alpha\rangle]$
$\psi^A_{I,-1} = 1/\sqrt{3} [\beta\beta\alpha\rangle + \beta\alpha\beta\rangle + \alpha\beta\beta\rangle]$
$\psi^A_{I,-3} = \beta\beta\beta\rangle$
$\psi^{E_a}_{I,3} = 1/\sqrt{3} [\alpha\alpha\beta\rangle + \epsilon \alpha\beta\alpha\rangle + \epsilon^* \beta\alpha\alpha\rangle]$
$\psi^{E_b}_{I,1} = 1/\sqrt{3} [\alpha\alpha\beta\rangle + \epsilon^* \alpha\beta\alpha\rangle + \epsilon \beta\alpha\alpha\rangle]$
$\psi^{E_a}_{I,-1} = 1/\sqrt{3} [\beta\beta\alpha\rangle + \epsilon \beta\alpha\beta\rangle + \epsilon^* \alpha\beta\beta\rangle]$
$\psi^{E_b}_{I,-3} = 1/\sqrt{3} [\beta\beta\alpha\rangle + \epsilon^* \beta\alpha\beta\rangle + \epsilon \alpha\beta\beta\rangle]$

symmetry A . However, Eq. (2.7) may be rewritten as¹¹

$$[a\mathbf{I} + \frac{1}{2}a' \exp(2i\phi) (\mathbf{I}_1 + \epsilon^* \mathbf{I}_2 + \epsilon \mathbf{I}_3) + \frac{1}{2}a' \exp(-2i\phi) (\mathbf{I}_1 + \epsilon \mathbf{I}_2 + \epsilon^* \mathbf{I}_3)], \quad (2.9)$$

where $\epsilon = \exp(2\pi i/3)$ and the asterisk indicates complex conjugate. The first term corresponds to the "observable splitting," while the second and third terms may be seen to be the two A components of the cross product of the E type $\exp(\pm 2i\phi)$ rotational operator with the two-component nuclear spin operator of E symmetry. (For greater generality we have replaced a by a' in these terms.) It is useful to write all partner E functions as orthogonal pairs which are complex conjugates. These are distinguished as E_a and E_b ($E_a^* = E_b$) where the cyclic permutation (123) transforms the former into ϵ times itself and the latter into ϵ^* times itself. Thus, the second term of Eq. (2.9) is made up from an E_b rotational operator and an E_a spin operator (which is abbreviated as \mathbf{I}^{E_a}). The reverse is true for the third term. The multiplication rule, necessary for selection rules, etc., is $E_b E_a = E_a^* E_a = A$. Thus $E_a^3 = E_b^3 = A$. It should be clear that an operator of E_a or E_b symmetry can only have nondiagonal matrix elements, and these will connect states of the different species E_a , E_b , and A .

A. Nuclear Spin Functions

The different nuclear spin functions are listed in Table I where, for example, $\psi^A_{I,3}$ stands for the spin function of A symmetry and $M_I = \frac{3}{2}$.

¹¹ On the basis of simple symmetry considerations, the more general expression

$$\sum_{n=0}^{\infty} b_n [\cos 2n\phi \mathbf{I}_1 + \cos 2n(\phi + \frac{2}{3}\pi) \mathbf{I}_2 + \cos 2n(\phi + \frac{4}{3}\pi) \mathbf{I}_3] \cdot \mathbf{S}$$

may be obtained instead of Eq. (2.7) (see Ref. 6). The results given above merely imply $b_0 = b_1$ and b_n for $n > 1$ are negligible. The discussion presented here could be carried out for this more general expression without significant changes. Note, however, that terms for n equal to multiples of 3, the spin and rotation operators both have A symmetry, so they may have diagonal matrix elements.

B. Internal Rotor Functions

The Schrödinger equation for the internal rotation of the methyl group is given by¹²

$$\hbar^2 \mathcal{C}_R = [- (\hbar^2/2I) (d^2/d\phi^2) + V(\phi)] \psi_R(\phi) = \hbar E \psi_R(\phi) \quad (2.10)$$

which is closely related to the Mathieu equation.¹² The potential energy $V(\phi)$ must have at least threefold symmetry in ϕ due to the indistinguishability of the three methyl protons. We set¹²

$$V(\phi) = \frac{1}{2} V_3 (1 - \cos 3\theta), \quad (2.11)$$

where

$$\theta = \phi - \alpha \quad (2.11a)$$

and α represents one of the three potential minima. For the sake of simplicity, only the two limiting cases: (1) an unhindered rotor and (2) a highly hindered rotor are considered.

1. Plane Rotor

In Table II are found the wavefunctions of the plane rotor in the absence of a hindering barrier, V_3 . The plane rotor solution for the methyl-group rotation is a good approximation when $\frac{1}{4} V_3 \ll \hbar^2/2I$.¹²

TABLE II. Rotational functions.

Plane rotor functions	
$\psi_{R,m} = 1/(2\pi)^{1/2} \exp(im\phi)$	
$m = 3n$	Species A
$m = 3n + 1$	Species E_a
$-m = 3n + 2$	
$m = 3n + 2$	Species E_b
$-m = 3n + 1$	
$n = 0, 1, 2, 3, \dots$	
$\hbar E_{R,m} = m^2 \hbar^2/2I$	
Torsional (harmonic)-oscillator functions	
$\psi^A_{T,\nu} = 1/\sqrt{3} [H_\nu^{(1)} + H_\nu^{(2)} + H_\nu^{(3)}]$	
$\psi^{E_b}_{T,\nu} = 1/\sqrt{3} [H_\nu^{(1)} + \epsilon H_\nu^{(2)} + \epsilon^* H_\nu^{(3)}]$	
$\psi^{E_a}_{T,\nu} = 1/\sqrt{3} [H_\nu^{(1)} + \epsilon^* H_\nu^{(2)} + \epsilon H_\nu^{(3)}]$	
$H_\nu^{(k)} = H_\nu(\theta - [k-1]\frac{2}{3}\pi)$	$k = 1, 2, \text{ or } 3$
$\hbar E_{T,\nu} = 3\hbar(V_3/2I)^{1/2}(\nu + \frac{1}{2})$	
$\nu = 0, 1, 2, 3, \dots$	

¹² C. C. Lin and J. D. Swalen, Rev. Mod. Phys. **31**, 841 (1959).

2. Torsional Oscillator

In the limit of very high barriers to internal rotation, the potential energy $\frac{1}{2}V_3(1-\cos 3\theta)$ may be expanded about each of the minima at $\phi = \alpha, \alpha + \frac{2}{3}\pi$, and $\alpha + \frac{4}{3}\pi$ to give $\frac{3}{4}V_3[\theta - (k-1)\frac{2}{3}\pi]^2$ where $k=1, 2, 3$, respectively. Each wavefunction $H_{\nu}^{(k)}$ in Table II is an harmonic-oscillator function for the torsional motion about each of the three minima. Linear combinations of these functions having the proper symmetries are given, and they are degenerate to zero order. Let

$$\langle H_{\nu}^{(k)} | \mathcal{H}_R | H_{\nu}^{(k)} \rangle = E_{T,\nu} \quad (2.12)$$

and a first-order approximation of the torsional splitting given by

$$\langle H_{\nu}^{(k)} | \mathcal{H}_R | H_{\nu}^{(k')} \rangle = \Delta_{\nu} \quad \text{for } k \neq k', \quad (2.13)$$

so

$$E_{T,\nu}^A = E_{T,\nu} + 2\Delta_{\nu} \quad (2.14a)$$

and

$$E_{T,\nu}^B = E_{T,\nu} - \Delta_{\nu}. \quad (2.14b)$$

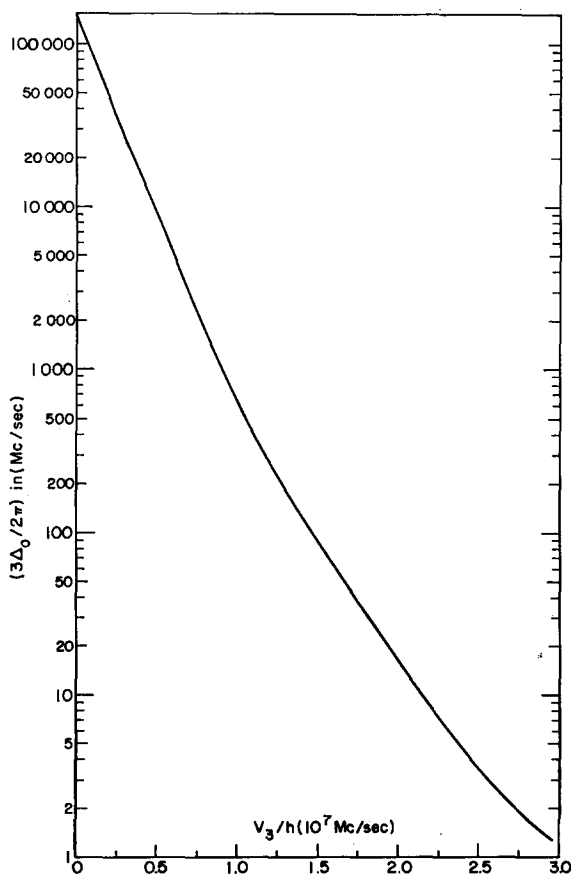


FIG. 1. Torsional-splitting frequency as a function of barrier height (V_3) for the lowest torsional level of a methyl rotor. The curve is extrapolated to the separation of lowest rotational levels for $V_3=0$.

The torsional splittings $3\Delta_0$ in the zeroth level are plotted as a function of V_3 in Fig. 1 where both are expressed in units of megacycles per second. This figure is based on a semiempirical relation given by Hecht and Dennison¹³ for large barriers, but is extrapolated to the separation of the ground pair of rotational levels when $V_3=0$.

C. Matrix Elements of the Spin-Rotational Coupling

The term aI_z has only diagonal matrix elements with value aM_I in the representation of Tables I and II. The nonvanishing matrix elements of the spin functions $I_z^{E_a}$ and $I_z^{E_b}$ are given by:

$$\begin{aligned} \langle \psi_{I,\pm\frac{1}{2}}^{s'} | I_z^{E_a} | \psi_{I,\pm\frac{1}{2}}^{s'} \rangle &= \langle \psi_{I,\pm\frac{1}{2}}^{s'} | I_z^{E_b} | \psi_{I,\pm\frac{1}{2}}^{s'} \rangle^* \\ &= \pm \epsilon \Gamma(s | E_a | s'), \end{aligned} \quad (2.15)$$

where

$$\Gamma(s | E_a | s') = \delta_{s,E_a} \delta_{s',A} + \delta_{s,A} \delta_{s',E_b} + \delta_{s,E_b} \delta_{s',E_a}. \quad (2.15')$$

Terms involving $a'I_{\pm}S_{\mp}$ are being neglected in the present formulation (see Sec. VI). For the plane rotor functions we get:

$$\langle \psi_{R,m} | \exp(\pm 2i\phi) | \psi_{R,m'} \rangle = \delta_{m,m' \pm 2}. \quad (2.16)$$

In order to evaluate the matrix elements of $\exp(\pm 2i\phi)$ in the torsional-oscillator representation, it is useful to expand this function around each of the three barrier minima, because the overwhelming probability is for ϕ to lie very close to one of these values. Thus

$$\begin{aligned} \exp(\pm 2i\phi) \\ \cong \exp(\pm 2i\alpha) (\epsilon)^{\pm(k-1)} [1 \pm 2i(\theta_k) - 2(\theta_k)^2 \dots], \end{aligned} \quad (2.17)$$

where

$$\theta_k = [\theta - (k-1)\frac{2}{3}\pi] \quad \text{and } k=1, 2, 3. \quad (2.17')$$

We assume in the evaluation of this term a "zero-differential overlap" approximation:

$$\langle H_{\nu}^{(k')} | \theta_k^n | H_{\nu}^{(k'')} \rangle \cong \langle H_{\nu}^{(k)} | \theta_k^n | H_{\nu}^{(k)} \rangle \delta_{kk'} \delta_{kk''}. \quad (2.18)$$

The matrix elements of interest may be found in standard references.¹⁴ The high-frequency terms for which $\nu' \neq \nu''$ turn out to be unimportant. Neglecting these terms we obtain

$$\begin{aligned} \langle \psi_{T,\nu}^{s'} | \exp(-2i\phi) | \psi_{T,\nu}^{s'} \rangle \\ = \langle \psi_{T,\nu}^{s'} | \exp(+2i\phi) | \psi_{T,\nu}^{s'} \rangle^* \\ = \exp(-2i\alpha) [1 - 2\bar{\theta}_{\nu}^2] \Gamma(s | E_a | s'), \end{aligned} \quad (2.19)$$

¹³ K. T. Hecht and D. M. Dennison, *J. Chem. Phys.* **26**, 13 (1957).

¹⁴ H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry*, (John Wiley & Sons, Inc., New York, 1944), p. 79.

where

$$\bar{\theta}_\nu^2 = (\nu + \frac{1}{2})/\beta \quad (2.20a)$$

and

$$\beta = 3\hbar^{-1}(\frac{1}{2}V_3I)^{\frac{1}{2}}. \quad (2.20b)$$

III. ISOLATED ROTOR—SPLITTINGS

It is assumed in this section that, while an ensemble of methyl-group rotors is thermally distributed, the thermal contact of the rotational and spin degrees with the rest of the degrees of freedom is much weaker than the spin-rotational coupling. Then the energy levels between which ESR transitions occur are obtained from the combined eigenfunctions of $\mathcal{H}_{SI} + \mathcal{H}_R$.

A. Free Rotation

For free rotation:

$$\langle \psi_{R,m} \psi_I \psi_S | \mathcal{H}_{SI} + \mathcal{H}_R | \psi_{R,m} \psi_I \psi_S \rangle = E_{R,m} + \gamma_e B_z M_S + \gamma_p B_z M_I + a M_S M_I \equiv E_{R,m} + E_{SI}. \quad (3.1)$$

Recognizing that $E_{R,m} \gg a'$ the only important non-diagonal terms are [from Eqs. (2.15) and (2.16)]

$$\langle \psi_{R,+1} \psi^{E_{b_I}} \psi_S | \mathcal{H}_R + \mathcal{H}_{SI} | \psi_{R,-1} \psi^{E_{a_I}} \psi_S \rangle = \mp \frac{1}{2} a' \epsilon M_S \quad (3.2)$$

and their Hermitian conjugates. Thus, in the high-temperature region, when few methyl groups are in the $m = \pm 1$ levels (see Sec. IV.B), the ESR spectrum consists primarily of four lines separated by $a/2\gamma_e$ G of equal width and intensity ratio nearly 1:3:3:1. However, for low temperatures corresponding to an appreciable population in the $m = \pm 1$ levels, the effect of Eq. (3.2) on the splittings must be considered. A diagonalization of the matrix

$$\begin{pmatrix} E_{R,+1} + E_{S,\pm\frac{1}{2}} & \mp \frac{1}{2} a' \epsilon M_S \\ \mp \frac{1}{2} a' \epsilon^* M_S & E_{R,-1} + E_{S,\pm\frac{1}{2}} \end{pmatrix}$$

yields the two eigenvalues

$$\begin{aligned} \lambda_{\pm} &= E_{R,\pm 1} + E_{S,\pm\frac{1}{2}} + \frac{1}{2} (a') M_S \\ \text{and} \\ \lambda_{\pm} &= E_{R,\pm 1} + E_{S,\pm\frac{1}{2}} - \frac{1}{2} (a') M_S, \end{aligned} \quad (3.3)$$

corresponding to splittings at $\pm \frac{1}{2} [(a \pm a')/\gamma_e]$ and $\pm \frac{1}{2} [(a \mp a')/\gamma_e]$ G, respectively.

B. Hindered Rotation

The diagonal matrix elements are again given by Eq. (3.1) with $E_{T,\nu}$ replacing $E_{R,m}$. But now there are important off-diagonal terms coupling states of the

same ν and M_I but different s , so that the 3×3 matrix:

$$\begin{pmatrix} E_{\nu,\pm} + 2\Delta_\nu & \mp t_\nu & \mp t_\nu^* \\ \mp t_\nu^* & E_{\nu,\pm} - \Delta_\nu & \mp t_\nu \\ \mp t_\nu & \mp t_\nu^* & E_{\nu,\pm} - \Delta_\nu \end{pmatrix} \quad (3.4)$$

must in general be diagonalized for each value of ν , where [from Eqs. (2.15) and (2.19)]

$$t_\nu = \frac{1}{2} (a') \epsilon \exp(2i\alpha) u_\nu M_S,$$

$$u_\nu = [1 - 2\bar{\theta}_\nu^2],$$

and

$$E_{\nu,\pm} = E_{T,\nu} + E_{S,\pm\frac{1}{2}}. \quad (3.5)$$

If

$$v_\nu \equiv a' u_\nu / 6\Delta_\nu \ll 1,$$

then the eigenvalues to second order are:

$$E_{\nu,\pm} + 2\Delta_\nu + 6\Delta_\nu v_\nu^2 M_S^2, \quad (3.6a)$$

$$E_{\nu,\pm} - \Delta_\nu + \frac{1}{2} (a') u_\nu M_S [(v_\nu \pm 1)^2 \mp 4v_\nu \sin^2 3\alpha]^{\frac{1}{2}}, \quad (3.6b)$$

$$E_{\nu,\pm} - \Delta_\nu - \frac{1}{2} (a') u_\nu M_S [(v_\nu \pm 1)^2 \mp 4v_\nu \sin^2 3\alpha]^{\frac{1}{2}}. \quad (3.6c)$$

For $v_\nu = 0$, these results are independent of the angle α and very similar to those of Eqs. (3.3). Note that the ESR transition corresponding to Eq. (3.6a) is unshifted in the second-order approximation while those from Eqs. (3.6b) and (3.6c) are shifted. If, however, $v_\nu \gg 1$, i.e., vanishingly small torsional splitting, then it is found that the correct zero-order wavefunctions are (for $M_I = +\frac{1}{2}$) given by

$$\frac{1}{\sqrt{3}} \sum_{k=1}^3 H_\nu^{(k)} | \alpha_i \alpha_j \beta_k \rangle \psi_S. \quad (3.7)$$

$k \neq i, j$ and $i < j$ and the two other functions obtained by cyclic interchange of the $H_\nu^{(k)}$ with the $| \alpha_i \alpha_j \beta_k \rangle$. The zero-order energies are given by:

$$E_{\nu,\pm} \mp a' u_\nu \cos(2\alpha + \frac{2}{3}\pi[k-1]) \quad k = 1, 2, 3, \quad (3.8)$$

yielding the splittings:

$$\pm \{ \frac{1}{2} a - a' u_\nu \cos(2\alpha + \frac{2}{3}\pi[k-1]) \}$$

which is just the classical result for a static methyl group except for the factor u_ν . All of the off-diagonal elements in the representation Eqs. (3.7) are equal to Δ_ν , and may be treated by simple perturbation theory except when $\alpha \approx \frac{1}{3}(n\pi)$, $n = 0, 1, 2, \dots$, for which the $k = 1$ and 2 energies in Eq. (3.8) are degenerate.

The hyperfine lines resulting from the $M_I = \pm \frac{3}{2}$ nuclear spin states are unaffected by the above considerations.

IV. RAPIDLY RELAXING ROTOR

A. Basic Model

It is now assumed that the rotational motion is in strong enough thermal contact, via interaction with the random, intermolecular motions of a liquid or the thermal lattice vibrations of the solid, that it is rapidly returned to thermal equilibrium despite its coupling to the spin system. This situation may be treated with a rigorous, albeit simplified model whereby the thermal contact of the rotational levels is introduced in the form of collisions occurring at a mean frequency, τ^{-1} . A theory based on a "strong collision" approximation has already been developed.¹⁵ However, it is necessary to generalize the treatment to include the case where the spin-rotational coupling is able to couple states of different nuclear spin symmetry in order to handle the present problem. The general considerations and results are given in the Appendix. The use of a single τ is certainly a great simplification over the actual situation, but after the formal results are obtained, it should still be possible to modify this assumption, but in an admittedly *ad hoc* fashion (see Sec. VI). Note that this theory is still developed on the assumption that thermal "collisions" are essentially nuclear spin independent in their effects.

In the present application we consider the E_a and E_b as well as the A spin symmetries as being distinct. Our arbitrariness in selecting the particular sets of degenerate E_a and E_b functions does not affect the final results, since all macroscopic observables are obtained by taking a trace over all states, and the trace is invariant to a choice of basis functions. The particular choices that are being made, however, permit a consistent account to be taken of the exclusion principle. We therefore have three spin density matrices:

$$\begin{aligned}\sigma^A &= \text{Tr}_R(\rho^A), \\ \sigma^{E_a} &= \text{Tr}_R(\rho^{E_a}), \\ \sigma^{E_b} &= \text{Tr}_R(\rho^{E_b}),\end{aligned}\quad (4.1)$$

which are defined according to Appendix A. The terms in the Hamiltonian (A4) are \mathcal{H}_R given by Eq. (2.10), $\hbar\mathcal{H}_{SI}$ given by the first two terms of Eq. (2.2) plus the first term of Eq. (2.9), and $\hbar\mathcal{U}_2$ given by the last two terms of Eq. (2.9). We are not considering any spin-rotational coupling effects which give rise to $\hbar\mathcal{U}_1$, so Eqs. (A17) through (A19) for the spin density matrices may be simplified accordingly. The further identifications:

$$\begin{aligned}F^{(E_a,2)} &= \exp(-2i\phi), \\ F^{(E_b,2)} &= \exp(+2i\phi), \\ K^{(E_a,2)} &= \frac{1}{2}(a')I_{T_i}^{E_a}S_z,\end{aligned}$$

¹⁵ J. H. Freed, J. Chem. Phys. **41**, 7 (1964).

and

$$K^{(E_b,2)} = \frac{1}{2}(a')I_{T_i}^{E_b}S_z \quad (4.2)$$

are made. This interaction has no effect on the outer components of the four-line ESR hyperfine pattern typical of a methyl group, since they involve only the $M_I = \pm\frac{3}{2}$ nuclear spin states.

B. Linewidths

The absorption spectrum of the two center lines is determined by the off-diagonal density matrix elements,¹⁶ which have steady-state values given by

$$\langle \psi_{S,+\frac{1}{2}}\psi_{I,\pm\frac{1}{2}}^j | \sigma^j | \psi_{S,-\frac{1}{2}}\psi_{I,\pm\frac{1}{2}}^j \rangle \equiv z_{j,\pm} \exp(i\omega t), \quad (4.3)$$

where $j = A, E_a, E_b$, when a rotating microwave field with angular frequency ω , and strength B_1 is applied. The power absorbed is given by

$$P_{\pm} \propto \sum_j S_{j,\pm}^- \text{Im}(z_{j,\pm}), \quad (4.4)$$

where S_j^- is the j th matrix element of the electron spin lowering operator. In the present case, in the absence of saturation, the z_j obey the equation¹⁶

$$\Delta\omega z_j - i \sum_k R_{j,k} z_k = q\omega f_j d, \quad (4.5)$$

where

$$d = \frac{1}{2}\gamma_e B_1 S_j^-,$$

$$\Delta\omega = \omega_e - \omega,$$

$$\omega_e = \gamma_e B_z + aM_I,$$

and

$$q = \hbar/kT.$$

Equation (4.5) is written separately for the $M_I = +\frac{1}{2}$ and $-\frac{1}{2}$ lines, and the results are identical for each. Now $R_{j,k}$ is the linewidth matrix which may be obtained from Eqs. (4.2), (A18), (A19), and (2.15)–(2.19), and is given by

$$\begin{pmatrix} 2rD & rD & rD \\ rD & D(1+r) & D \\ rD & D & D(1+r) \end{pmatrix}, \quad (4.6)$$

where

$$D = j^I(\alpha_{E_a} - \alpha_{E_b})(M_S M_I)^2 a'^2 \quad (4.6a)$$

and

$$r = j^I(\alpha_{E_a} - \alpha_A) / j^I(\alpha_{E_a} - \alpha_{E_b}). \quad (4.6b)$$

Equations (4.6) may be shown to follow because, by symmetry as well as the evenness of the spectral densities,

$$j^I(\alpha_{E_a} - \alpha_{E_b}) = j^I(\alpha_{E_b} - \alpha_{E_a}) \quad (4.7a)$$

¹⁶ J. H. Freed, "Theory of Saturation and Double-Resonance Effects in ESR Spectra," J. Chem. Phys. (to be published).

and

$$j^I(\alpha_{E_a} - \alpha_A) = j^I(\alpha_{E_b} - \alpha_A) = j^I(\alpha_A - \alpha_{E_a}). \quad (4.7b)$$

The particular forms of the spectral densities in Eqs. (4.6a) and (4.6b) depend upon the choice of rotational functions as well as the temperature. The coupled Eqs. (4.5) and (4.6) may be solved by first diagonalizing the R matrix. [This procedure may be simplified by first transforming to equations in $z_E = (z_{E_a} + z_{E_b})$ and $z_{E'} = (z_{E_a} - z_{E_b})$.] The solution may be written as

$$z_A + z_E = [g_+ G_- / (\Delta\omega - i/T_-) - g_- G_+ / (\Delta\omega - i/T_+)], \quad (4.8)$$

where

$$T_{\pm}^{-1} = D(1 + \frac{3}{2}r \pm \frac{1}{2}p), \quad (4.9a)$$

$$g_{\pm} = (pr)^{-1}(1 - \frac{5}{2}r \pm \frac{1}{2}p), \quad (4.9b)$$

$$G_{\pm} = q\omega_e d [f_A + \frac{1}{2}(2 - r \pm p)f_{E_a}], \quad (4.9c)$$

$$p = (9r^2 - 4r + 4)^{\frac{1}{2}}. \quad (4.9d)$$

Simple limiting cases exist for $r=1$ and $r=0$. For $r=1$, z_A and z_E are coupled, but

$$z_A + z_E = q\omega_e d / [\Delta\omega - (4D + \delta)i] \quad (4.10)$$

and for $r=0$

$$z_A = q\omega_e d f_A / (\Delta\omega - \delta i), \quad (4.11a)$$

$$z_E = q\omega_e d 2f_{E_a} / [\Delta\omega - (2D + \delta)i], \quad (4.11b)$$

where δ , which represents all other line-broadening effects (assumed independent of nuclear spin), has been inserted. Equation (4.10) is formally equivalent to the semiclassical result⁶ which shows that the $\pm\frac{1}{2}$ lines are broadened by the rotational mechanism. Equations (4.11) represent a quantum effect indicating that only the fraction of systems containing E spins are broadened, while the A spins are not. The situation expressed by Eq. (4.8) is intermediate between these two limits when $0 < r < 1$. The physical significance of these results may be seen by examining the following cases.

1. Highly Hindered Oscillations at Low Temperatures

We assume only the first torsional level is significantly populated. Then

$$D = \frac{1}{18}(a'^2 u_0^2 \tau) \quad (4.12a)$$

and

$$r = [1 + (3\Delta_0)^2 \tau^2]^{-1}, \quad (4.12b)$$

$$f_A = \frac{\exp(2\Delta_0/kT)}{2 \exp(-\Delta_0/kT) + \exp(2\Delta_0/kT)}, \quad (4.12c)$$

for $\Delta_0/kT \ll 1$, $f_A \cong \frac{1}{3}(1 + 2\Delta_0)$. Thus when $(3\Delta_0\tau)^2 \ll 1$, i.e., when the thermal broadening of the hindered rotational levels is greater than the splitting $3\Delta_0$, the formally classical line-broadening result (except for u_0^2 which approaches unity as $V_3 \rightarrow \infty$) Eq. (4.10) is obtained, but when $(3\Delta_0)^2 \gg 1$ the A level is well enough

separated that it will not be broadened. Note that for free rotations at low enough temperatures, where only the $m=0, \pm 1$ levels are significantly populated, the same discussion applies where now Eqs. (4.12a) and (4.12b) are replaced by $r = [1 + (\hbar\tau/I)^2]^{-1}$, and $D = \frac{1}{18}(a'^2 \tau)$.

2. Free Rotation at High Temperatures

The high-temperature condition means that

$$C \equiv \hbar^2/2IkT = 7.6^\circ/T \ll 1. \quad (4.13)$$

It then follows that

$$Z(R_A) = Z(R_{E_a}) = Z(R_{E_b}) = (C/\pi)^{\frac{1}{2}}$$

and

$$f_A = f_{E_a} = f_{E_b} = \frac{1}{3}.$$

The spectral densities in Eqs. (A18) and (A19) involve the frequencies given by

$$\omega_{rr'} = \hbar^{-1} C 4(1 \pm m_{r'}) = 4.0 \times 10^{12} (1 \pm m_{r'}) \text{ sec}^{-1} \quad (4.14)$$

since $m_r = m_{r'} \pm 2$ for nonvanishing terms. Now the Debye-type function $\tau/(1 + \omega_{rr'}^2 \tau^2)$ has its maximum value of $\tau_{\max}/2$ for $\tau_{\max}^{-1} \equiv |\omega_{rr'}|$. Thus, except for the $m_{r'} = \pm 1$ levels, this function can be no greater than 1.25×10^{-13} sec. Then $j^I(\alpha_i - \beta_j) < \frac{1}{2} \tau_M$ neglecting the $m_{r'} = \pm 1$ levels, or

$$D' \leq \frac{1}{2} a'^2 \tau_{\max} \sim (2\pi) 240 \text{ sec}^{-1},$$

assuming $a' \sim (2\pi) 70 \times 10^6 \text{ sec}^{-1}$, and is negligible compared to other sources of line broadening. The contribution from the $m_{r'} = \pm 1$ levels with fractional populations $e^{-C}(C/\pi)^{\frac{1}{2}} \cong (C/\pi)^{\frac{1}{2}}$ gives

$$D \cong \frac{1}{18}(a'^2 \tau) (C/\pi)^{\frac{1}{2}}$$

which should be small, if not negligible, while $r \sim 0$. This result is thus substantially different from the classical result for a free rotor,⁶ since the latter does not include the factor $(C/\pi)^{\frac{1}{2}}$, nor does it distinguish between A and E nuclear spins.

V. COMPARISON WITH EXPERIMENT

A. Solids

Horsfield *et al.*¹⁷ and Miyagawa and Itoh¹⁸ have found that the radical $\text{CH}_3\dot{\text{C}}\text{HCOOH}$ trapped in 1- α -alanine exhibits a methyl splitting whose $M_I = \pm\frac{1}{2}$ lines broaden and then split out upon cooling from room temperature to 77°K. This suggests that at higher temperatures the condition $\tau^{-1} \gg a'$, Δ is fulfilled while at lower temperatures $\tau^{-1} \ll a'$, Δ . They give a classical interpretation consistent with $\Delta \ll a'$, but the possibility of $\Delta \sim a'$ may not be excluded by their results, so that the observed low-temperature splittings could depend on Δ . Their linewidth analysis at 184°K sets $\tau = 5.4 \times 10^{-10}$ sec, where now τ is given the meaning used in the present paper.

¹⁷ A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.* **4**, 425 (1961); **5**, 115 (1962).

¹⁸ I. Miyagawa and K. Itoh, *J. Chem. Phys.* **36**, 2157 (1962).

Heller¹⁹ obtained the radicals $\text{CH}_3\dot{\text{C}}(\text{COOH})_2$ (I) and $\text{CH}_3\dot{\text{C}}\text{H}(\text{COOH})$ (II) trapped in methyl malonic acid and both contributed to a single spectrum. For a particular orientation of the crystal, the room-temperature spectrum was consistent with

$$a_{\text{Me(I)}} \cong a_{\text{Me(II)}} \cong a_{\text{H(II)}} \cong (2\pi)70 \times 10^6 \text{ sec}^{-1} \quad (5.1)$$

(only the σ proton in II exhibited markedly anisotropic character) yielding a nine-line spectrum, and the relative intensities of the lines indicate that the radicals are present in nearly equal concentrations. At 4°K, the ratios of those lines which were ascribed at high temperatures to (I) are no longer 1:3:3:1 but instead closer to 1:1:1:1. Heller explains this result as being due to nearly free rotation in (I) so that the $m = \pm 1$ levels are only weakly populated. In the present formulation rapid averaging would require that $\tau_{\text{I}}^{-1} \gg a'$. The further condition that $\Delta_{\text{I}} \gg a'$ could lead to a broadening of the two components of *E* symmetry, without the *A* component being affected, so that the intensity of the $M_{\text{I}} = \pm \frac{1}{2}$ lines could be considerably reduced without requiring that the rotation be essentially unhindered. However, the lines ascribed to II have the normal room-temperature intensity ratio of 1:4:6:4:1 at 4.2°K, implying that $\tau_{\text{II}}^{-1} \gg a'$, and also that τ_{II}^{-1} is so great that there is no broadening. Thus $\tau_{\text{II}}^{-1} \gg \tau_{\text{I}}^{-1}$, which is surprising, since they both measure the thermal motions in the same substance, although admittedly at different sites.²⁰ A related prediction is that $\tau^{-1} \gg a'$ at 4°K in a methyl malonic acid host, while $\tau^{-1} \ll a'$ at 77°K in an α -alanine host.²⁰ In view of such predictions, it may be worth considering an alternative explanation of Heller's 4°K spectrum. Let us assume that Eq. (5.1) holds, and furthermore that:

$$a'_{\text{Me(I)}} \cong a'_{\text{Me(II)}} \cong a \cong (2\pi)70 \times 10^6 \text{ sec}^{-1},$$

$$\Delta \gg a \gg \tau_{\text{I}}^{-1} \sim \tau_{\text{II}}^{-2},$$

and

$$\Delta_{\text{I}}, \Delta_{\text{II}} \ll (\hbar T)^{-1}.$$

Then from Eqs. (3.6) the predicted spectrum of I is given by Fig. 2(a), while that for II is given by Fig. 2(b). The superposition of I and II, assuming equal concentrations, leads to Fig. 2(c), i.e., nine equally spaced lines in the ratio of 1:3:4:5:6:5:4:3:1, which is not far from the observed spectrum.²¹ The composite room-temperature spectrum comes at the same frequencies as the 4°K spectrum, but one expects the

¹⁹ C. Heller, J. Chem. Phys. **36**, 175 (1962).

²⁰ If the τ are sensitive to large barrier heights, then one might expect that a longer τ be associated with a greater barrier height, although the detailed form of the thermal interaction should be considered. See Sec. VI.

²¹ The actual derivative spectrum obtained by Heller has ratio of derivative heights given by 1:3:4:3:6:3.5:4:3:1. However, graphical integration¹⁹ showed that the two lines coming at $\pm a/2$ are actually more intense (but presumably broadened), and ranging in relative intensity somewhere from 3.9 to 4.8. One should also consider the possibility of slight inequality of splitting constants, residual broadening effects, and overlap of lines in interpreting the results.

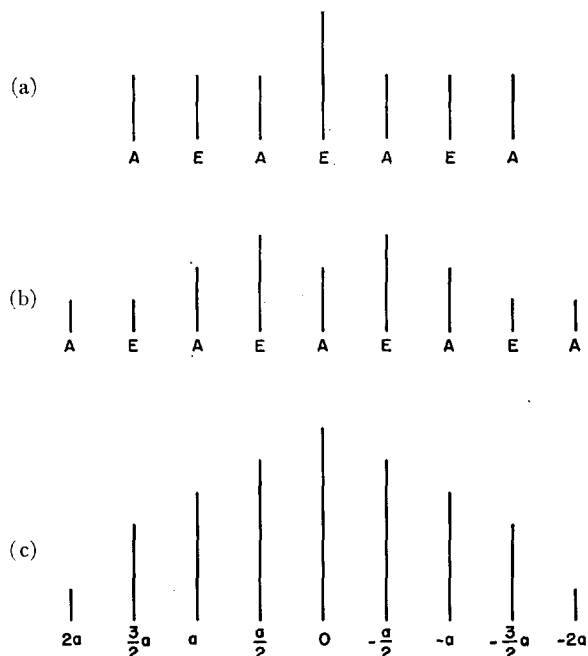


Fig. 2. Stick diagram of spectrum for: (a) methyl group weakly affected by thermal motions, but with large torsional splitting and $a' = a$; (b) same as (a) but including a single proton of hyperfine splitting a ; (c) superposition of (a) and (b) assuming equal concentrations. The lines in (a) and (b) are characterized according to the associated nuclear spin symmetries, and those in (c) according to their hyperfine frequencies.

ratio: 1:2:4:6:6:6:4:2:1 (which agrees with experiment). As the temperature is raised above 4°K, those components resulting from *E* nuclear spin symmetries should broaden, eventually shift to their room temperature locations, and then sharpen up to be comparable in width to the *A* symmetry components. [Figures 2(a) and 2(b) are labeled according to their spin symmetries.] Further experimental work should be able to distinguish between the various possibilities. They suffice, however, to illustrate the kinds of predictions obtained from the theory.

B. Liquids

Various liquid-state experiments have not indicated any relevant linewidth effects on methyl-proton splittings. This is consistent with $\tau^{-1} \gg a'$, but it places no condition on Δ for these experiments. The possibility of coupled motions of several methyl groups is of interest,^{6,22} but would require solving the related quantum-mechanical problem in order to analyze such situations.

VI. DISCUSSION—LIMITATIONS OF THE THEORY

As already noted, the introduction of a single mean collision time as a method of describing the undoubtedly detailed and complex processes by which rotational re-

²² J. H. Freed and G. K. Fraenkel, J. Chem. Phys. **41**, 699 (1964).

laxation occurs must certainly represent a great oversimplification of the actual situations, and further work would be necessary to elucidate such processes. There are a few comments, based on simple considerations, which may be made. In the present model, the collision frequency τ^{-1} functions as a measure of the strength of the thermal interaction with the lattice vs the spin-rotational coupling, and also represents the magnitude of nonsecular broadening of the rotational levels. This latter effect is important in the spectral densities as given by Eq. (A19). When detailed thermal mechanisms are considered it should be entirely possible that several different τ 's will be obtained.²³ In fact, we may expect the broadening of the rotational levels to be of the secular type, involving simple fluctuations of eigenenergies, as well as nonsecular, involving induced transitions.²³ Thus the τ appearing in $j^I(\alpha_{E_a} - \alpha_A)$ should, in general, result from both secular and nonsecular processes. However, the τ in $j^I(\alpha_{E_b} - \alpha_{E_a})$ should only involve nonsecular processes, since nuclear spin independent "collisions" must have identical effects on the degenerate pairs of E_a and E_b rotational levels, thus leading to a cancellation of secular effects. {This argument is based on the reasonable assumption that the terms in the spectral densities involving matrix elements of the operator F [cf. Eq. (4.2)] between states of the *same* torsional level are the most significant.} Now nonsecular, nuclear spin independent processes can only be effective by leading to high-frequency transitions between different torsional levels, and this requires strong or sudden collisional mechanisms. Thus, to the extent that secular processes become important, the results of Sec. IV must be modified to allow $\tau(\alpha_{E_a}, \alpha_A) \leq \tau(\alpha_{E_a}, \alpha_{E_b})$.

Another question exists about the detailed evaluation of the barrier height V . The usual simplifying assumption of a threefold barrier was introduced. But for a methyl group in a complex matrix it may be necessary to use the more general Fourier series

$$\sum_{n=-\infty}^{+\infty} V_{3n} \exp(i3n\phi)$$

to properly express the barrier height. Furthermore, the coefficients V_{3n} in such an expansion are themselves time dependent as a direct result of the collisional processes. This time dependence is a direct source of the secular and nonsecular broadening of the rotational levels, and is thus formally included in the collision frequency τ^{-1} . Then the strong-collision approximation is essentially equivalent to asserting that the relaxation be dominated by strong and sudden short-lived changes in the V_{3n} . If collisions continue to persist for times long compared to a'^{-1} , then the ESR experiment will sample a collection of methyl rotors experiencing a static distribution of barriers, but this is just equivalent to there being a distribution of types of lattice sites for the methyl rotor. True,

²³ J. H. Freed (to be published).

short-lived collisions become unimportant when their occurrence frequency τ^{-1} becomes small compared to a'^{-1} . Note also that as collisions become "weaker," their effectiveness in inducing transitions should begin to depend on the magnitude of the barrier height.

Another problem centers around the temperature dependence of τ . The experimental studies^{17,2} suggest that an exponential law of form $\tau = \tau_0 \exp(A/T)$ may be appropriate, but no theoretical justification is offered. Further refinements of the theory would involve the use of better approximations of the isotropic splittings, consideration of the effects of the off-diagonal $a'I_{\pm}S_{\mp}$ terms (which could become important when separations of rotational levels are comparable to ESR transition energies), and inclusion of the effects of the dipolar terms.

APPENDIX: STRONG-COLLISION RELAXATION WHERE STATES OF DIFFERENT NUCLEAR SPIN SYMMETRY ARE COUPLED

Let $\rho(t)$, the density matrix for the combined spin-rotational system,¹⁵ be factorable into the product $\lambda(t) \times \sigma(t)$ where $\lambda(t)$ and $\sigma(t)$ are reduced density matrices depending only on the rotational and spin degrees of freedom, respectively.¹⁵ Let $\rho^i(t) = \lambda^i(t) \sigma^i(t)$ be that portion of the density matrix which only includes all states corresponding to the i th nuclear spin symmetry. Then we may write ρ as the partitioned matrix:

$$\rho = \begin{pmatrix} \lambda^i \sigma^i & \lambda^{ij} \sigma^{ij} & \dots \\ \lambda^{ji} \sigma^{ji} & \lambda^j \sigma^j & \dots \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix} \quad i \neq j, \quad (\text{A1})$$

where submatrices $\lambda^{ij} \sigma^{ij}$ include all off-diagonal elements between states belonging to the i th and j th symmetry classes. Terms such as $\lambda^{ji} \sigma^{ij}$ or $\lambda^{ij} \sigma^i$ for $i \neq j$ are not allowed, since they violate the exclusion principle. Note that the mixed superscripts may not be simply permuted. However, the Hermitian property of the density matrix and the separability of the two reduced matrices leads to

$$(\sigma^{ji} \lambda^{ji})^\dagger = \sigma^{ij} \lambda^{ij}, \quad (\text{A2})$$

where \dagger indicates the Hermitian conjugate. The normalization of the density matrices is taken to be

$$\text{Tr}_S(\sigma) = 1 \quad (\text{A2a})$$

and

$$\text{Tr}_{R_i}(\lambda^i) = \text{Tr}_{R_j}(\lambda^j) = 1 \quad (\text{A2b})$$

so that any differences in population of states of different nuclear spin symmetries are contained in σ .²⁴ The subscripts S and R_i limit the trace operations to spin

²⁴ The significance of this normalization is most easily seen by considering the equilibrium density matrix $\rho_0^i = \lambda_0^i \sigma_0^i = Z(R)Z(S) \exp[-\hbar(\mathcal{H}_S^i + \mathcal{H}_R)/kT]$. Then $\lambda_0^i = B^i(R)$ defined by Eq. (A 12) and σ_0^i is given by Eq. (A 20).

states and to rotational states of i th symmetry, respectively.

The equation of motion for ρ [cf Eq. (2.2) of Ref. 15] may be written in terms of each submatrix. Thus for example

$$(d/dt)(\sigma^j \lambda^j) = -i[\mathcal{H}\mathcal{C}, \rho(t)]^{jj}. \quad (\text{A3})$$

Note that, while the matrix elements of the commutator itself are restricted to states of symmetry j , both $\mathcal{H}\mathcal{C}$ and $\rho(t)$ within the commutator could have matrix elements involving states of other symmetry. The Hamiltonian with which we are concerned is

$$\hbar\mathcal{H}\mathcal{C} = \hbar\mathcal{H}\mathcal{C}_R + \hbar\mathcal{H}\mathcal{C}_S' + \hbar\mathcal{U}'. \quad (\text{A4})$$

Now let

$$\mathcal{U}' = \mathcal{U}_1' + \mathcal{U}_2, \quad (\text{A5})$$

where \mathcal{U}_1' includes all spin-rotational coupling terms which do *not* connect states of different symmetry, while \mathcal{U}_2 includes *only* such terms. Define

$$\mathcal{H}\mathcal{C}_{S,j} = \mathcal{H}\mathcal{C}_S' + \langle \mathcal{U}_1' \rangle_j, \quad (\text{A6a})$$

$$\mathcal{U}_{1,j} = \mathcal{U}_1' - \langle \mathcal{U}_1' \rangle_j, \quad (\text{A6b})$$

where

$$\langle \mathcal{U}_1' \rangle_j = \text{Tr}_{R_i} \{ B^j(R) \mathcal{U}_1' \}. \quad (\text{A7})$$

The interaction representation is introduced as

$$\rho_j^*(t) = \exp[i(\mathcal{H}\mathcal{C}_R + \mathcal{H}\mathcal{C}_{S,j})t] \rho(t) \exp[-i(\mathcal{H}\mathcal{C}_R + \mathcal{H}\mathcal{C}_{S,j})t], \quad (\text{A8})$$

$$\mathcal{U}_{l,j}^*(t) = \exp[i(\mathcal{H}\mathcal{C}_R + \mathcal{H}\mathcal{C}_{S,j})t] \mathcal{U}_{l,j} \exp[-i(\mathcal{H}\mathcal{C}_R + \mathcal{H}\mathcal{C}_{S,j})t], \quad (\text{A9})$$

where the subscript j is used to indicate that these terms are expressed in terms of the $\mathcal{H}\mathcal{C}_{S,j}$ Hamiltonian, and l is either 1 or 2. Equation (A3) may then be transformed to this interaction representation. It is assumed that a strong collision occurred at time t_0 , and Eq. (A3) is expanded about t_0 to second order. It is also assumed that after a strong collision:

$$\begin{aligned} \text{Tr}_R \{ \rho_i^*(t_0) \} &= \text{Tr}_R \{ B(R) \times \sigma_i^*(t_0) \} \\ &= \begin{pmatrix} \sigma_i^{i*}(t_0) & 0 & \cdots \\ 0 & \sigma_i^{j*}(t_0) & \cdots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \end{pmatrix}, \quad (\text{A10}) \end{aligned}$$

where $B(R)$ is the matrix which may be partitioned so that

$$B^i(R) = Z^i(R) [\exp(-\hbar\mathcal{H}\mathcal{C}_R/kT)]^i \quad (\text{A11})$$

and

$$[Z^i(R)]^{-1} = \text{Tr}_{R_i} [\exp(-\hbar\mathcal{H}\mathcal{C}_R/kT)]. \quad (\text{A12})$$

$[Z^i(R)]^{-1}$ is the rotational partition function normalized for the i th symmetry states. Thus the strong collision is assumed to restore each set of rotational states belonging to a particular spin symmetry to its respective Boltzmann distribution, while also having

no effect on $\sigma^*(t_0)$, which includes the relative populations of states of different spin symmetry. The disappearance of off-diagonal submatrices $\lambda^{ij*}(t_0)$ in Eq. (A6) after a strong collision does not necessarily require that important nuclear spin dependent intermolecular forces exist. These submatrices contain only off-diagonal elements between rotational eigenstates, so they are relaxed by secular mechanisms which broaden each of the coupled rotational states differently and by all nonsecular processes (i.e., induced transitions) involving these levels, since they lead to uncertainty in lifetime broadening of each of the levels.²³ Under the above conditions, Eq. (A3) leads to

$$\begin{aligned} (\partial/\partial t) \sigma_i^{i*}(t, t_0) &= -i \text{Tr}_R \{ [\mathcal{U}_{1,i}^* + \mathcal{U}_{2,i}^*, B(R) \sigma_i^*(t_0)]^{ii} \} \\ &\quad - \text{Tr}_R \left(\int_{t_0}^t dt' [\mathcal{U}_{1,i}^*(t') + \mathcal{U}_{2,i}^*(t'), \right. \\ &\quad \left. [\mathcal{U}_{1,i}^*(t') + \mathcal{U}_{2,i}^*(t'), B(R) \sigma_i^*(t_0)]^{ii} \right) + \cdots \quad (\text{A13}) \end{aligned}$$

Now usually

$$\mathcal{U}_l' = \sum_q K^{(q,l)} F^{(q,l)}, \quad (\text{A14})$$

where $l=1$ or 2 , $K^{(q,l)}$ and $F^{(q,l)}$ are spin and rotational operators, respectively. So

$$\mathcal{U}_{1,j}^*(t) = \sum_q [F_1^{(q)*}(t) - \langle F_1^{(q)} \rangle_j] K_{1,j}^{(q)*}(t), \quad (\text{A15})$$

with a similar expression for $\mathcal{U}_{2,j}^*(t)$. Equation (A13) can be greatly simplified by noting that all terms first order in $\mathcal{U}_{2,j}^*$ must vanish, because by definition they can have no diagonal matrix elements between rotational states. Furthermore, the first-order term in $\mathcal{U}_{1,j}^*(t)$ vanishes as a result of Eqs. (A7) and (A15). This leaves one second-order term in $\mathcal{U}_{1,j}^*$ and another in $\mathcal{U}_{2,j}^*$. The arguments given with respect to Eqs. (2.10)–(2.12) of Ref. 15 may be applied here to show that

$$\frac{\partial}{\partial t} \sigma_j^{j*}(t) = \int_0^\infty \left[\frac{\partial}{\partial t} \sigma_j^{j*}(t, t_0) \right]_{t_0=t-\theta} \tau^{-1} \exp(-\theta/\tau) d\theta. \quad (\text{A16})$$

Thus Eqs. (A13) and (A16) yield an equation of motion for $\sigma_j^{j*}(t)$. The resulting equation is simplified by setting $\sigma^*(t_0)$ equal to $\sigma^*(t)$ and neglecting higher-order terms in the expansion, an approximation which is valid when $\mathcal{U}_1^2, \mathcal{U}_2^2 \ll \tau^{-2}$. The second-order term in $\mathcal{U}_{1,j}^*$ leads to results essentially equivalent to Eqs. (2.13) to (2.15) of Ref. 15 while the term in $\mathcal{U}_{2,j}^*$ gives the coupling between states of different spin symmetry. Thus

$$\frac{\partial}{\partial t} \sigma_i^{i*}(t)_{\alpha_i \alpha_i'} = \sum_{\beta_j \beta_j'} R_{\alpha_i \alpha_i', \beta_j \beta_j'} \sigma_i^{i*}(t)_{\beta_j \beta_j'}, \quad (\text{A17})$$

where

$$R_{\alpha_i \alpha_i' \beta_j \beta_j'} = \sum_{q, q', l} [K_{\alpha_i \beta_j}^{(q, l)} K_{\beta_j' \alpha_i'}^{(q', l)} 2j_{qq'}^l (\alpha_i - \beta_j) - \sum_{\gamma_k} \delta_{\alpha_i \beta_j} K_{\beta_j' \gamma_k}^{(q', l)} K_{\gamma_k \alpha_i}^{(q, l)} j_{qq'}^l (\gamma_k - \beta_j) - \sum_{\gamma_k} \delta_{\alpha_i \beta_j} K_{\alpha_i \gamma_k}^{(q', l)} K_{\gamma_k \beta_j}^{(q, l)} j_{qq'}^l (\gamma_k - \beta_j)] \quad (\text{A18})$$

and

$$j_{qq'}^l (\alpha_i - \beta_j) = Z^j(R) \sum_{r_i, r_j'} \left[\exp\left(\frac{-E_{r_j'}}{kT}\right) F_{r_i r_i'}^{(q, l)} F_{r_j' r_j}^{(q', l)} \times \frac{\tau}{1 + (\omega_{r_i r_i'} + \omega_{\alpha_i \beta_j})^2 \tau^2} - \langle F^{(q, l)} \rangle_i \langle F^{(q', l)} \rangle_j \times \frac{\tau}{1 + \omega_{\alpha_i \beta_j}^2 \tau^2} \delta_{ij} \delta_{l,1} \right]. \quad (\text{A19})$$

Here the α_i and β_j are eigenstates of $\mathcal{H}_{S,i}$ while the r_i and r_j are eigenstates of \mathcal{H}_{R} . The prime on the summation in Eq. (A17) indicates a restriction on the energies of the eigenstates given by

$$E_{\alpha_i} - E_{\beta_j} = E_{\alpha_i'} - E_{\beta_j'}.$$

We now introduce the *ad hoc* assumption²⁵ that $\sigma_i^{*j}(t)$ relaxes to a Boltzmann distribution given by

$$\sigma_{i,0^j} = f_j Z_i(S) \exp(-\hbar \mathcal{H}_{S,i} / kT), \quad (\text{A20})$$

where

$$[Z_i(S)]^{-1} = \text{Tr}_S \{ \exp(-\hbar \mathcal{H}_{S,i} / kT) \} \quad (\text{A20}')$$

and

$$f_j = \sum_i Z(R_i) / Z(R_j) \quad (\text{A21})$$

which measures the fractional population of rotational levels of j th symmetry at thermal equilibrium, is introduced to account for the normalization of $B^i(R)$, $\sigma^i(t)$ and $\lambda^i(t)$ given, respectively, by Eqs. (A12), (A2a), and (A2b). Whenever $l=1$ then $i=j$, and when $l=2$, $i \neq j$ for nonvanishing terms in Eqs. (A18) and (A19). Note that $\delta_{\alpha_i \beta_j}$ also implies δ_{ij} . Since the interaction representation in Eq. (A17) is dependent on i via Eqs. (A6) and (A9) it may be necessary to transform Eqs. (A17) back to the Schroedinger representation and then re-express them in a consistent set of spin basis functions, by means of appropriate unitary transformations.

²⁵ A rigorous demonstration should involve an argument based upon the exact conservation of energy for transitions induced by \mathcal{U}_1 and \mathcal{U}_2 , so that detailed balance is satisfied at equilibrium. The present treatment involving the broadening of rotational levels by collisions obscures this point.

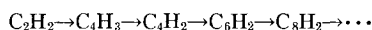
Thermal Decomposition of Acetylene in Shock Waves

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Using a shock tube and an improved T.O.F. mass spectrometer displaying spectra every 20 μ sec, the pyrolysis of acetylene was shown to proceed through the sequence



in the temperature range 1600°–2400°K. All these intermediates reach steady-state concentrations, that of the radical C_4H_3 being as large as that of diacetylene under favorable conditions. The primary bimolecular reaction of acetylene in which the radical C_4H_3 is formed must also yield hydrogen atoms. These catalyze an isotopic exchange in mixtures of $\text{C}_2\text{H}_2 + \text{C}_2\text{D}_2$ that is about three orders of magnitude faster than the formation of C_4H_2 . The initial yield of acetylene- d_1 is given by the expression

$$[\text{C}_2\text{HD}]_t = k[\text{C}_2\text{H}_2 + \text{C}_2\text{D}_2]_0^2 \tau^2,$$

which is consistent with the proposed partial reaction mechanism. The mechanism of conversion of C_4H_3 into C_4H_2 , etc., is uncertain but undoubtedly involves free radicals.

INTRODUCTION

THE pyrolysis of acetylene has been studied extensively. At lower temperatures conventional static methods have been used.^{1–3} Flow reactor techniques were employed to explore the intermediate temperature

range,^{4–10} while shock waves served to observe the re-

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