THE ELECTRON RESONANCE LINE SHAPES OF RADICALS IN SOLUTION

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Contents

- I. Introduction 191
- II. Redfield Theory 191
- III. The Alternating Line-Width Effect 192
  - A. Theory 192
  - B. *cis–trans* Isomerism 195
  - C. Restricted Rotations 195
  - D. Ring Inversion 196
  - E. Proton Exchange 198
  - F. Ion Pairs 199
  - G. Polynitro Compounds 200
- IV. Dynamic Frequency Shifts 202
- V. Ligand Exchange 202
- VI. Electron Transfer 202
- VII. Asymmetric Line Broadening 204
  - A. Theory 204
  - B. Experimental Tests 206
  - C. The Structure of Liquids 208
  - D. Assignment of Coupling Constants 208
  - E. Sign Determinations 209
  - F. Relative Sign Determinations 210
  - G. Degenerate Transitions 211
  - H. Anisotropy of *g* Tensors 213
  - I. Quadrupole Relaxation 213
- VIII. Spin-Rotational Interactions 214
- IX. Higher Spin Multiplicities 215
- X. Anisotropic Motion 218
  - A. Anisotropic Diffusion 218
  - B. Partial Orientation 219
- XI. Spin Exchange 221
  - A. Intramolecular 221
  - B. Intermolecular 223
- XII. Special Effects. Radicals with Degenerate Ground States 224

I. Introduction

An understanding of the factors which can effect the widths of hyperfine lines in an electron resonance spectrum is important not only as an aid to analysis but because the line widths often contain useful chemical information. The basic concepts for an interpretation of relaxation in electron resonance were first set out in 1948 by Bloembergen, Purcell, and Pound[1] when they developed the theory for the widths of proton resonance lines. The subsequent application of their ideas,[2] and other more general theories,[3-7] to the investigation of the line shapes of electron resonance spectra in solution[8-11] has led to an understanding of a wide range of phenomena. An account of some of the most useful theoretical techniques has been given by Fraenkel[12] and some applications have been reviewed,[13,14] but no comprehensive survey has appeared. In this review we shall cover all relaxation processes which occur in fluid media with particular reference to the chemical information which can be obtained and the underlying physical concepts. The survey of the literature is intended to be complete to the end of 1967. We shall not consider saturation effects, mainly because such studies do not yield additional chemical information, although their understanding is of increasing importance in ENDOR experiments.[15]

Although experimentally one measures hyperfine coupling constants in magnetic field units, it should be pointed out that these have no precise meaning unless the *g* factor is also quoted. In line-shape studies where time-dependent processes are involved, it is natural to work in frequency units, and all coupling constants appearing in this review are in megahertz. It is also to be understood that line widths, usually denoted by T_2^{-1}, are measured in angular frequency units (radians second^{-1}).

II. Redfield Theory

The most commonly used form of relaxation theory in magnetic resonance is the matrix method developed by Redfield.[6,7] An equivalent formulation due to Bloch[5] which uses operator techniques has been applied to electron resonance,[16] but the matrix method provides greater physical insight and is often easier to handle.[11] The basic theory which aims at developing a master equation for the time development of the spin magnetization in the presence of fluctuating electromagnetic

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(1) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).
(2) H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).
(3) R. Kubo and K. Tomita, *J. Phys. Soc. Jap.*, **9**, 888 (1954).
(4) R. K. Wangsness and F. Bloch, *Phys. Rev.*, **89**, 728 (1953).
(5) F. Bloch, *ibid.*, **102**, 104 (1956); **105**, 1206 (1957).
(6) A. G. Redfield, *IBM J. Res. Develop.*, **1**, 19 (1957).
(7) A. G. Redfield, *Advan. Magnetic Resonance*, **1**, 1 (1965).
(8) D. Kivelson, *J. Chem. Phys.*, 27, 1087 (1957).
(9) D. Kivelson, *ibid.*, 33, 1094 (1960).
(10) M. J. Stephen and G. K. Fraenkel, *ibid.*, 32, 1435 (1960).
(11) J. H. Freed and G. K. Fraenkel, *ibid.*, 39, 326 (1963).
(12) G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967).
(13) C. S. Johnson, *Advan. Magnetic Resonance*, **1**, 33 (1965).
(14) D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125 (1967).
(15) J. H. Freed, *J. Phys. Chem.*, **71**, 38 (1967).
(16) A. D. McLachlan, *Proc. Roy. Soc.*, **A280**, 271 (1964).

interactions is described in a number of texts. We shall summarize in this section the results necessary for applying the method to electron resonance and refer to the texts for their derivation.[17,18]

The line shape is found from the imaginary part of the magnetic susceptibility of the spins, $\chi''(\omega)$. At high temperatures and low microwave power this is proportional to the Fourier transform[3]

$$\int_{-\infty}^{\infty} \langle M_x(0)M_x(t)\rangle e^{-i\omega t}\,\mathrm{d}t \qquad (2.1)$$

where $M_x(t)$ is the x magnetization in the Heisenberg representation

$$M_x(t) = e^{i\mathcal{H}t}M_xe^{-i\mathcal{H}t} \qquad (2.2)$$

and the angular brackets denote an average over the nuclear and electron spin states. Classically this corresponds to taking the Fourier transform of the autocorrelation function of the mean magnetic dipole moment.

The total Hamiltonian, $\mathcal{H}$, may be written

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}'(t) \qquad (2.3)$$

where $\mathcal{H}^0$ is time independent and determines the sharp line spectrum. $\mathcal{H}'(t)$ is time dependent with zero time average. It is the fluctuations in $\mathcal{H}'(t)$ which give rise to relaxation. Line broadening arises in two ways: the fluctuations induce transitions within the spin system and they modulate the transition frequencies. By a procedure equivalent to second-order, time-dependent perturbation theory, it may be shown that for rapid fluctuations the matrix elements of $M_x(t)$ obey a linear equation

$$\frac{\mathrm{d}M_{\kappa\kappa'}}{\mathrm{d}t} = \sum_{\lambda\lambda'} R_{\kappa\kappa'\lambda\lambda'}M_{\lambda\lambda'} \qquad (2.4)$$

where κ, λ, ... are eigenstates of $\mathcal{H}^0$. There is a separate relaxation matrix for each line in the spectrum. It has the important property that its eigenvalues multiplied by -1 are the widths of the components of the spectral lines.[17] These have a Lorentzian shape

$$L(\omega) = (T_2/\pi)[1 + (\omega - \omega_0)^2T_2^2]^{-1} \qquad (2.5)$$

and have width at half-height $2T_2^{-1}$. For the more usually measured first-derivative curve, the distance between the two extrema is $2T_2^{-1}/\sqrt{3}$. The terms in $\mathcal{H}'(t)$ consist of products of spin operators with spatial operators which reflect the lattice motions. The latter are usually treated classically, and the matrix elements in eq 2.4 are evaluated in a basis of pure spin functions. If we write

$$\mathcal{H}'(t) = \sum_q A_qS_q \qquad (2.6)$$

where the A_q's operate on lattice variables only, the elements of R are given by[6,7]

$$\begin{aligned} R_{\kappa\kappa,\lambda\lambda'} = {} & 2\sum_{qq'}\langle\kappa|S_q|\lambda\rangle\langle\kappa'|S_{q'}|\lambda'\rangle j_{qq'}(\omega_\kappa - \omega_\lambda) - \\ & \sum_{\gamma}\sum_{qq'}\{\delta_{\kappa'\lambda'}\langle\gamma|S_q|\kappa\rangle\langle\lambda|S_{q'}|\gamma\rangle j_{'}(\omega_{\gamma qq} - \omega_\kappa) + \\ & \delta_{\kappa\lambda}\langle\gamma|S_q|\kappa'\rangle\langle\lambda'|S_{q'}|\gamma\rangle j_{qq'}(\omega_\gamma - \omega_{\kappa'})\} \end{aligned} \qquad (2.7)$$

The $j_{qq'}$'s are correlation functions defined by

$$j_{qq'}(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} \langle A_q(t')A_{q'}^*(t' + t)\rangle \cos \omega t\,\mathrm{d}t \qquad (2.8)$$

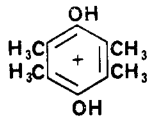
whose form depends on the model chosen for the molecular motions. The evaluation of eq 2.7 therefore falls into two parts. The calculation of the matrix elements of spin operators S_q within a set of basis functions κ, κ', ... and the solution of a dynamical problem to determine the correlation functions. Several examples of these procedures will be described in later sections.

It is convenient to distinguish between a number of different types of terms in $\mathcal{H}'(t)$. Firstly there are secular terms which commute with $\mathcal{H}^0$ and give only $j(0)$ contributions; secondly there are nonsecular terms like S_+I_- which cause electron spin transitions; and thirdly there are pseudosecular terms which contain I_+ and I_- but not $S_\pm$, and cause only nuclear spin transitions. It is often possible to neglect the nonsecular terms, but the secular and pseudosecular terms are of comparable importance.[11]

III. The Alternating Line-Width Effect

A. THEORY

The appearance of the electron resonance spectrum of the durosemiquinone cation (I) in concentrated sulfuric acid



I

is markedly temperature dependent.[19] The line positions may be analyzed in terms of a 13-line multiplet from the methyl protons and a 1:2:1 triplet from the hydroxyl protons, but their intensities are anomalous. In the spectra, shown in Figure 1, the lines of the methyl proton multiplet marked by * and • alternate in width. This effect becomes more apparent as the temperature is lowered when the spectrum also shows an asymmetric broadening of the type to be discussed in section VII. This behavior arises because the molecule is involved in rapid isomerization between *cis* and *trans* forms according to the scheme shown in Figure 2. The effect of this is to modulate the isotropic hyperfine coupling constants of the methyl protons in a correlated fashion.

The term alternating line-width effect has rapidly assumed an important place in the vocabulary of electron resonance; numerous examples have been reported and will be the subject of later discussion. Because the observation of alternating line widths implies that a radical is involved in a dynamic situation, the study of the phenomenon has had far-reaching effects in the applications of electron resonance to kinetic problems.

The line-broadening effects of modulating an isotropic hyperfine coupling constant may be investigated most rigorously using the relaxation matrix theory, provided that the observations are made in the fast-exchange region. The time-dependent Hamiltonian

$$\mathcal{H}'(t) = \sum_i(a_i(t) - \bar{a}_i)I^{(i)}\cdot S \qquad (3.1)$$

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(17) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961.

(18) C. P. Slichter, "Principles of Magnetic Resonance," Harper and Row Publishers, New York, N. Y., 1962.

(19) J. R. Bolton and A. Carrington, *Mol. Phys.*, 5, 161 (1962).

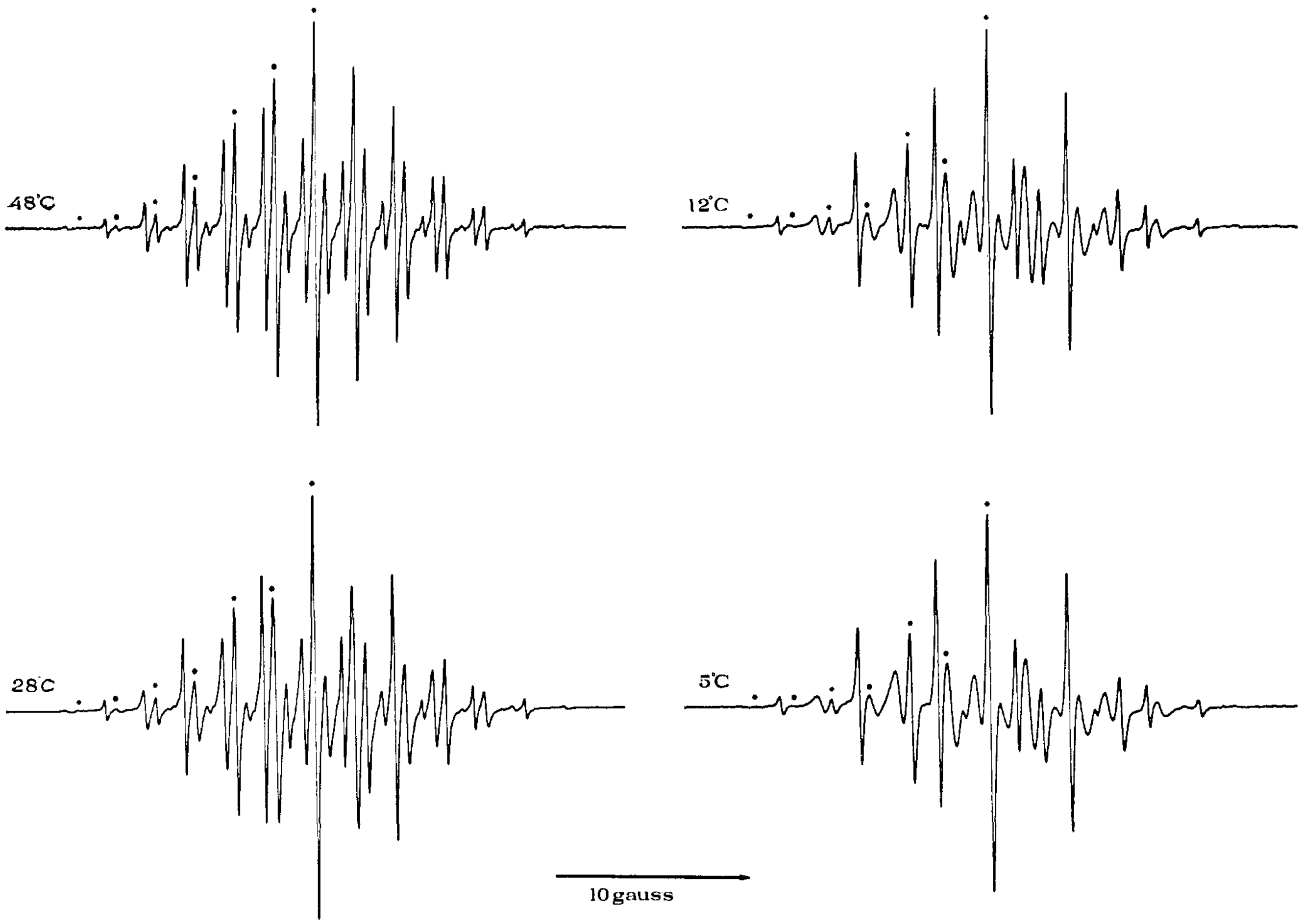

Figure 1. The electron resonance spectrum of the durosemiquinone cation in concentrated sulfuric acid.

has secular terms involving I_zS_z and nonsecular terms in $(I_+S_- + I_-S_+)$.

Although there is no inherent difficulty in including the latter, their effect is negligible in most cases of interest. The nonsecular contribution is smaller than the secular one by a factor of $[1 + \omega_0{}^2\tau^2]^{-1}$, where ω_0 is the angular Larmor frequency.

A common situation is one in which two nuclei, or groups of equivalent nuclei, interchange their coupling constants. This two-site problem occurs, for example, in ring inversions (section III.D), intramolecular cation exchange (section III.F), and proton-transfer equilibria (section III.E). In the fast-exchange region the observed coupling constant is the average of those for the two sites

$$\bar{a} = \frac{1}{2}(a_1 + a_2) \tag{3.2}$$

and for two nuclei of spin I there are $4I + 1$ lines. In the absence of the nonsecular terms, the relaxation matrix is diagonal, and for the hyperfine component with total nuclear spin quantum number $M = m_1 + m_2$

$$-R_{\kappa\kappa',\kappa\kappa'} = T_2^{-1} = \sum j_{ij}(0)m_im_j = j_{11}(0)M^2 + 2[j_{12}(0) - j_{11}(0)]m_1m_2 \tag{3.3}$$

The spectral densities $j_{ij}(\omega)$ are the Fourier cosine transforms of correlation functions $g_{ij}(t)$. We shall write j_{ij} for $j_{ij}(0)$.

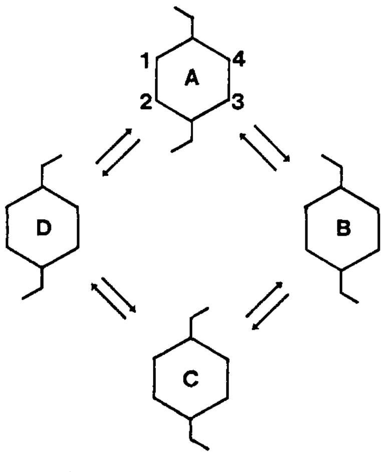

Figure 2. The equilibrium scheme for *cis–trans* isomerism of the durosemiquinone cation.

$$j_{ij}(\omega) = \int_0^\infty g_{ij}(t)\cos\omega t\, dt \tag{3.4}$$

where

$$g_{ij}(t) = 4\pi^2\langle(a_i(t') - \bar{a})(a_j(t' + t) - \bar{a})\rangle \tag{3.5}$$

Their explicit form depends on the dynamical model taken for the modulating process. The dependence on the nuclear

Table I

Line Widths from a Modulation of the Isotropic Splittings of Two Nuclei, or Two Completely Equivalent Subgroups of Nuclei

No. of nuclei	I	M	(M_1, M_2)	$D_k{}^a$	D^a	$T_2{}^{-1}$	$T_2{}^{-1}$ $(j_{11} = -j_{12})$
2	$^1/_2$	±1	$(\pm{}^1/_2, \pm{}^1/_2)$	1	1	$^1/_2(j_{11} + j_{12})$	0
		0	$(\pm{}^1/_2, \mp{}^1/_2)$	2	2	$^1/_2(j_{11} - j_{12})$	j_{11}
2	1	±2	$(\pm1, \pm1)$	1	1	$2(j_{11} + j_{12})$	0
		±1	$(\pm1, 0)$	2	2	j_{11}	j_{11}
		0	$(\pm1, \mp1)$	2	3	$2(j_{11} - j_{12})$	$4j_{11}$
			$(0, 0)$	1		0	0
2	$^3/_2$	±3	$(\pm{}^3/_2, \pm{}^3/_2)$	1	1	$^9/_2(j_{11} + j_{12})$	0
		±2	$(\pm{}^3/_2, \pm{}^1/_2)$	2	2	$^1/_2(5j_{11} + 3j_{12})$	j_{11}
		±1	$(\pm{}^3/_2, \mp{}^1/_2)$	2	3	$^1/_2(5j_{11} - 3j_{12})$	$4j_{11}$
			$(\pm{}^1/_2, \pm{}^1/_2)$	1		$^1/_2(j_{11} + j_{12})$	0
		0	$(\pm{}^3/_2, \mp{}^3/_2)$	2	4	$^9/_2(j_{11} - j_{12})$	$9j_{11}$
			$(\pm{}^1/_2, \mp{}^1/_2)$	2		$^1/_2(j_{11} - j_{12})$	j_{11}
4	$^1/_2$	±2	$(\pm2, \pm2)$	1	1	$2(j_{11} + j_{12})$	0
		±1	$(\pm1, 0)$	4	4	j_{11}	j_{11}
			$(\pm1, \mp1)$	2	6	$2(j_{11} - j_{12})$	$4j_{11}$
		0	$(0, 0)$	4		0	0
6	$^1/_2$	±3	$(\pm{}^3/_2, \pm{}^3/_2)$	1	1	$^9/_2(j_{11} + j_{12})$	0
		±2	$(\pm{}^3/_2, \pm{}^1/_2)$	6	6	$^1/_2(5j_{11} + 3j_{12})$	j_{11}
		±1	$(\pm{}^3/_2, \mp{}^1/_2)$	6	15	$^1/_2(5j_{11} - 3j_{12})$	$4j_{11}$
			$(\pm{}^1/_2, \pm{}^1/_2)$	9		$^1/_2(j_{11} + j_{12})$	0
		0	$(\pm{}^3/_2, \mp{}^3/_2)$	2	20	$^9/_2(j_{11} - j_{12})$	$9j_{11}$
			$(\pm{}^1/_2, \mp{}^1/_2)$	18		$^1/_2(j_{11} - j_{12})$	j_{11}

[a] D is the degeneracy, and D_k the degeneracy of the kth component, of a hyperfine line with nuclear spin quantum number M.

spin quantum number is easily determined. Thus for two ^{14}N nuclei the outer $M = \pm2$ lines of the hyperfine quintet are broadened by $2[j_{11} + j_{12}]$ and both components of the $M = \pm1$ lines by j_{11}. The component of the central line with $m_1 = m_2 = 0$ is unbroadened, but the other two components have width $2[j_{11} - j_{12}]$. In the simple example we have outlined, in which the radical can exist in two states differing only by an interchange of the ^{14}N coupling constants, there is said to be complete out-of-phase correlation[11] and

$$j_{11} = -j_{12} = 4\pi^2(a_1 - a_2)^2\tau/8 \tag{3.6}$$

The widths for this case and for a number of other situations are given in Table I. The treatment given here is equally applicable to groups of equivalent nuclei provided that m_1 and m_2 are replaced by M_1 and M_2, where the latter are eigenvalues of J_z, and $J = \Sigma I_i$ is the sum of the nuclear spin angular momenta in the group. The reason for the term "alternating line width" is seen most clearly from the results for complete out-of-phase correlation. In the case of four equivalent protons, the $M = \pm2$ lines and four components of the central line are unbroadened. The $M = \pm1$ lines and two components of the central line have widths j_{11} and $4j_{11}$, respectively. When j_{11} is large the quintet collapses to three sharp lines with a 1:4:1 intensity pattern. It should be emphasized that although the alternation is largest when there is complete out-of-phase correlation, it will be observed whenever $j_{11} > {}^1/_2(j_{11} + j_{12})$, provided of course that the line widths are not dominated by another mechanism. The advantage of the relaxation matrix method is that it facilitates the incorporation of a wide range of dynamical models.[20] The results for the jump models are easily derived from less sophisticated theories. In the two site case the fast-exchange broadening for a system jumping between two frequencies ω_1 and ω_2 with lifetime τ in each site is[21]

$$T_2{}^{-1} = (\omega_1 - \omega_2)^2\tau/8 \tag{3.7}$$

Putting

$$\omega_1 = \omega + 2\pi(a_1M_1 + a_2M_2) \tag{3.8}$$

and

$$\omega_2 = \omega_0 + 2\pi(a_1M_2 + a_2M_1) \tag{3.9}$$

$$T_2{}^{-1} = 4\pi^2(a_1 - a_2)^2(M_1 - M_2)^2\tau/8 \tag{3.10}$$

It is clear that hyperfine components with $M_1 = M_2$ are unbroadened. This result is identical with that obtained from the relaxation matrix. It is implicit in the secular approach that the nuclear spin state does not change during a jump and hence each hyperfine component may be treated individually.

It is often possible in systems exhibiting the alternating linewidth phenomenon to follow the changes in the appearance of the spectrum into the slow-exchange region. It then consists of a superposition of the individual spectra whose time average is seen in the fast-exchange region. The slow and intermediate rates of exchange are not covered by the relaxation matrix theory, and the modified Bloch equations[21–24] are commonly employed in interpreting the observed line shapes.

The philosophy behind these is well known and is treated

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(20) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 3623 (1964).

(21) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 222.

(22) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(23) H. M. McConnell, *ibid.*, **28**, 430 (1958).

(24) A. Carrington, *Mol. Phys.*, **5**, 425 (1962).

in a number of texts. A differential equation is written for the magnetization of the electron at each site and is modified by the addition of phenomenological exchange terms. The absorption line shape is then determined from the imaginary part of the net average electron magnetization $\langle G \rangle$. For two sites this takes the form

$$\langle G_k \rangle = -\frac{i\omega_1 M_0 D_k(4 + \eta_{1k}\tau + \eta_{2k}\tau)}{2(\eta_{1k}\eta_{2k}\tau + \eta_{1k}\eta_{2k})} \tag{3.11}$$

and for the four-site scheme[24] of Figure 2

$$\langle G_k \rangle = -i\omega_1 M_0 D_k \times \frac{(\gamma_1 + \gamma_2)(\gamma_3 + \gamma_4 + 2\gamma_3\gamma_4) + (\gamma_3 + \gamma_4)(\gamma_1 + \gamma_2 + 2\gamma_1\gamma_2)}{4\gamma_1\gamma_2\gamma_3\gamma_4 - (\gamma_1 + \gamma_2)(\gamma_3 + \gamma_4)} \tag{3.12}$$

M_0 and ω_1 are constants, D_k is the degeneracy of the nuclear spin states referred to by subscript k, and the numerical subscripts refer to individual sites

$$\gamma_1 = 1 + \eta_{1k}\tau \tag{3.13}$$

$$\eta_{1k} = T_2^{-1} - i(\omega_0 - \omega + \delta\omega_{1k}), \quad \text{etc.} \tag{3.14}$$

T_2^{-1} is the line width in the absence of exchange, ω_0 is the Larmor frequency of the electron in the absence of hyperfine interactions, and $\delta\omega_{1k}$ is the shift in resonance frequency in site 1 due to the nuclear spin state k.

Using these results it is possible to reconstruct spectra for various values of τ and by matching these with experimental results over a range of temperatures to determine the rate law and activation parameters for the dynamic process involved. If the slow-exchange region is unobservable, it is not possible to reconstruct line shapes in the fast-exchange region without guessing the values of the hyperfine splittings of the exchanging species. This is a difficult task and would appear to rule out a kinetic analysis of the situation. A partial answer to this problem is provided by considering the fast-exchange broadenings in Table I. It is apparent that in two-jump situations the outer lines remain sharp. The outer lines but one are broadened, but all components have the same width. These lines therefore retain an over-all Lorentzian shape. This is not true for the other lines in the spectrum which generally have components which broaden at different rates and are no longer Lorentzian. It is therefore possible to use the amplitudes of the two outer lines of the multiplet to determine the relative broadening due to exchange. For a 1:4:6:4:1 quintet the broadening of the $M = \pm 1$ lines is $T_2^{-1} = 2[A(2)/A(1)]^{1/2} - 1$ in relative units. $A(M)$ is the peak-to-peak amplitude of the first-derivative line with nuclear spin quantum number M. The assumption that

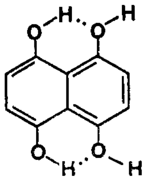
$$k = \tau^{-1} = \tau_0^{-1} \exp(-\Delta H^{\ddagger}/RT) \tag{3.15}$$

leads to the result that a plot of $\ln 2[A(2)/A(1)]^{1/2} - 1$ against $1/T$ should be linear with slope $-\Delta H^{\ddagger}/R$. It is thus possible to determine the activation energy without a knowledge of the hyperfine coupling constants of the various species involved. Similar results are obtained for a number of three-and four-site situations. This approach facilitates the measurement of activation parameters in systems where the slow exchange region is experimentally inaccessible.

B. *cis–trans* ISOMERISM

As we have described earlier, the durosemiquinone cation exhibits a temperature-dependent line-width alternation in the 13-line multiplets from the 12 methyl protons when prepared in concentrated sulfuric acid.[19] This was attributed to an isomerism between *cis* and *trans* isomers according to the scheme of Figure 2. It was not possible to reduce the temperature sufficiently to observe the individual isomers because of the high viscosity and freezing point of sulfuric acid. The existence of such isomers is, however, well established in radicals such as the terephthaldehyde anion[25] and various *para*-substituted benzaldehyde anions.[26,27] More recently the durosemiquinone cation has been prepared by the reaction of aluminum chloride with duroquinol in nitromethane. The spectra were measured from −90 to +10°, and at low temperatures the separate *cis* and *trans* forms were resolved.[28] By calculating theoretical spectra using a four-jump model and matching these with experiment, the potential barrier to rotation has been estimated to be 4.2 ± 0.6 kcal mole^{-1}. A similar investigation of the hydroquinone cation[29] gave a potential barrier of *ca.* 10 kcal mole^{-1}. The higher value in the latter case may be a result of decreased steric interactions in the planar conformation.

The four-jump model has also been successfully applied to the temperature-dependent changes found in the spectrum of the naphthazarin semiquinone cation in concentrated sulfuric acid.[30] The barrier for isomerism between the *cis* and *trans* isomers (II and III) is 4 ± 1 kcal mole^{-1} with a frequency factor of 10^{10} sec^{-1}. The mechanism almost certainly involves the breaking of an intramolecular hydrogen bond.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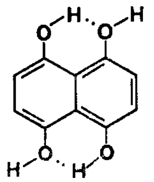
III

C. RESTRICTED ROTATIONS

The influence of intramolecular steric interactions on the observed values of hyperfine splitting constants is well documented and has recently been reviewed.[14] A clear example of the effect of restricted rotation is provided by the tetraisopropylnitrobenzene radical anion in acetonitrile.[31] It exists in two forms differing in the degree of twist of the nitro group out of the plane of the benzene ring. The two forms have nitrogen coupling constants of 66.1 and 61.6 MHz and differ in free energy by about 0.5 kcal mole^{-1}.

If transitions between conformations occur at a rate comparable with the difference in hyperfine splittings, one expects to see line-broadening effects. A simple example would be

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(25) A. H. Maki, *J. Chem. Phys.*, **35**, 761 (1961).

(26) A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, **83**, 1852 (1961).

(27) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

(28) P. D. Sullivan, *J. Amer. Chem. Soc.*, **89**, 4294 (1967).

(29) A. B. Barabas, W. F. Forbes, and P. D. Sullivan, *Can. J. Chem.*, **45**, 267 (1967).

(30) J. R. Bolton, A. Carrington, and P. F. Todd, *Mol. Phys.*, **6**, 169 (1963).

(31) T. M. McKinney and D. H. Geske, *J. Chem. Phys.*, **44**, 2277 (1966).

the restricted rotation of a methyl group attached to a π system. The proton coupling constants vary as $A + B\cos^2\theta$, θ being the angle between the C–H bond and the $2p\pi$ orbital containing the unpaired electron. For a freely rotating methyl group $\langle\cos^2\theta\rangle = {}^1/_2$ and an interaction of $A + (B/2)$ is observed with three equivalent protons. If the methyl group is locked in an arbitrary orientation, up to three different proton couplings may be apparent. This possibility is realized in the $CH_3\dot{C}HCOOH$ radical trapped in *l*-alanine.[32] On lowering the temperature from 200°K, when the methyl group is freely rotating, some of the lines broaden, and at 100°K the methyl group is effectively locked so the three different isotropic proton interactions are resolved. The application of a simple jump model gave an activation energy of 4.8 ± 1 kcal mole^{-1}.

The theory of the line widths in such situations has been investigated in terms of classical rotational diffusion and three-jump models for the motion of the methyl group.[33] The possibility of quantum mechanical tunneling has also been discussed.[34,34a] For a single methyl group the time-dependent Hamiltonian is

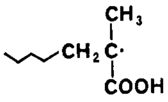
$$\mathcal{H}(t) = \sum_{i=1}^{3}(a_i(t) - a_i)I^{(i)}\cdot S \qquad (3.16)$$

and both the secular and nonsecular contributions to the line width have been evaluated. In the secular approximation the $M = \pm{}^3/_2$ lines are unaffected and the three components of the $M = \pm{}^1/_2$ lines have width $j_{11}(0)$. The nonsecular terms contribute ${}^3/_4 j_{11}(\omega_0)$ to the outer lines. The $M = \pm{}^1/_2$ lines have nondiagonal relaxation matrices, and the line shape consists of a superposition of two Lorentzian curves of different widths. The nonsecular contributions would be important if $\omega_0\tau < 1$; however, the predicted non-Lorentzian character of the $M = \pm{}^1/_2$ lines has not yet been observed. There are, in fact, very few reported examples of the restricted motion of a methyl group in solution.

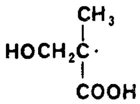
At −140° the propyl radical shows a 1:3:3:1 quartet splitting, but at −180° the pattern has changed and corresponds to a coupling with only two protons.[35] The barrier is about 3.7 kcal mole^{-1}. The claim that the rotation of the 1-methyl group in methylated anthrasemiquinones is restricted[36] has been challenged.[14]

Recently evidence of restricted rotation has been found in a number of compounds containing CF_3 groups. The radical anion of 2-trifluoromethylnitrobenzene gives a spectrum in which the $M_F = \pm{}^1/_2$ lines of the expected fluorine quartet are missing.[37,38] Similar results are found in the 4-NH_2 and 4-OMe derivatives, but the broadened $M_F = \pm{}^1/_2$ lines were observed in the 4-OH compound.[37] The $CF_3O\dot{O}$ radical has been prepared by photolysis of CF_3OOCF_3 and exhibits hyperfine coupling to two types of fluorine atoms in the range −196 to −170°.[39] The barrier for interconversion is 2–3 kcal mole^{-1}.

The nature of the radical formed by irradiating poly(methyl methacrylate) has been the subject of much discussion. The spectrum consists of nine lines of alternating intensities. It is suggested that the spectrum arose from the radical IV and



IV



V

that the line-width alternation is due to a modulation of the methylene proton coupling constants which interchange between preferred orientations.[40] This hypothesis is supported by an investigation of the radical V prepared from methacrylic acid and hydroxyl radicals using rapid mixing techniques.[41,42] The failure to recognize the existence of an alternating line-width effect had caused earlier workers to suggest that two radicals were present.

D. RING INVERSION

The study of the interconversion of conformational isomers of cyclic compounds by the measurement of line-width effects in nuclear magnetic resonance spectra is well established.[43] As might be expected, similar effects are found in the electron resonance spectra of nonrigid cyclic free radicals.

The cyclohexyl radical exemplifies the sort of information obtainable and has been more thoroughly investigated than other cyclic radicals in which line-width effects have been observed. Early observations on solids suggested that at 77°K only two of the four β protons had appreciable coupling constants.[44] A detailed temperature-dependent study of the radicals produced by continuous irradiation of cyclohexane with 2.8-MeV electrons confirmed this proposition.[35,45] At −80° the spectrum of a single form of the radical was observed, with splittings of 110.4 and 14.8 MHz from two equivalent pairs of β protons and a 59.6-MHz α-proton hyperfine coupling. On raising the temperature, ring inversion interchanges pairs of equivalent protons, and in the fast-exchange limit a 1:4:6:4:1 quintet splitting from the four β protons is predicted. At 10°, the highest temperature at which the radical was observed, a 1:4:1 pattern is apparent. The alternate lines of the quintet are still broadened and unobservable.[46] The line-width variations between −85 and 0° have been interpreted in terms of a two-jump model.[45] The Bloch equations used to calculate theoretical peak heights as a function of jumping rate were modified to give Gaussian line shapes because the measurements were made on solids rather than liquids. The activation energy of 4.9 ± 0.5 kcal mole^{-1} found for ring inversion in cyclohexyl is to be compared with a value of 10.3 kcal mole^{-1} for cyclohexane itself.[43] It seems probable the interconversion is between two chair forms of the radical. An

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(32) A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, **5**, 115 (1962).

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

(34) J. H. Freed, *J. Chem. Phys.*, **43**, 1710 (1965).

(34a) NOTE ADDED IN PROOF. Interesting quantum mechanical effects have recently been found in the low-temperature spectra of crystals containing radicals with rotating methyl groups: W. L. Gamble, I. Miyagawa, and R. L. Hartman, *Phys. Rev. Lett.*, **20** 415(1968); J. W. Wells, and H. C. Box, *J. Chem. Phys.*, **48**, 2542 (1968).

(35) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

(36) R. M. Elofson, K. F. Schulz, B. E. Galbraith, and R. Newton, *Can. J. Chem.*, **43**, 1553 (1965).

(37) E. G. Janzen and J. L. Gerlock, *J. Amer. Chem. Soc.*, **89**, 4902 (1967).

(38) J. W. Rogers and W. H. Watson, *J. Phys. Chem.*, **72**, 69 (1968).

(39) N. Vanderkooi and W. B. Fox, *J. Chem. Phys.*, **47**, 3634 (1967). The radical may be $CF_3OO\dot{O}$ according to R. W. Fessenden, *ibid.*, **48**, 3725 (1968).

(40) M. C. R. Symons, *J. Chem. Soc.*, 1186 (1963).

(41) H. Fischer, *Z. Naturforsch.*, **19a**, 866 (1964).

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(43) J. E. Anderson, *Quart. Rev.* (London), **19**, 426 (1965).

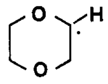
(44) N. Ya. Cherniak, N. N. Bubnov, L. S. Poliak, Yu. D. Tsvetkov and V. V. Voevodskii, *Opt. Spectrosk.*, **6**, 360 (1959).

(45) S. Ogawa and R. W. Fessenden, *J. Chem. Phys.*, **41**, 994 (1964).

(46) M. K. Leung and J. W. Hunt, *J. Phys. Chem.*, **71**, 3177 (1967).

approximate activation energy of 5–6 kcal mole^{-1} was obtained by Buben and coworkers who considered the broadening at a particular temperature and compared the rate constant thus obtained with that for cyclohexane itself.[47]

In investigations of the reactions of hydroxyl radicals with organic substrates, line-width alternation has been observed in radicals formed by hydrogen abstraction from alicyclic compounds like piperidine, dioxane, cyclohexanol, and cyclohexylamine, and attributed to the interconversion of chair conformations.[48,49] The radical VI from dioxane has also been seen during the photolysis of acetone containing 10% of the ether,[50] the central line of the 1:2:1 triplet from the β protons being broadened. Similar effects are found in the electron resonance spectra of nitroxide radicals from piperidine and morpholine.[51]



VI

The temperature dependence of the line broadening in morpholine-oxyl is illustrated in Figure 3. At 20° the four β protons give rise to a 1:4:1 splitting of the nitrogen triplet; at 60° broad lines are apparent midway between the sharp lines. By measuring the relative widths of the $M = \pm 2$ and $M = \pm 1$ β proton lines as a function of temperature, Hudson and Hussain have been able to estimate activation energies for ring inversion in morpholine-oxyl and piperidine-oxyl of 8.6 and 5.6 kcal mole^{-1}, respectively.[52]

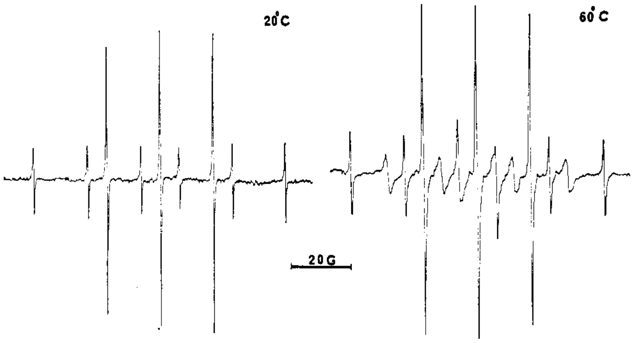
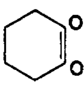


Figure 3. The electron resonance spectrum of morpholine-oxyl in aqueous solution.

Line broadening due to conformational changes has been reported in radicals generated by the action of potassium on degassed solutions in dimethoxyethane (DME) of alicyclic ketones containing 6 to 12 carbon atoms.[58] It was originally supposed that the species formed were the alicyclic ketyls. However, it seems probable that the radicals observed were semidiones[54] produced by the presence of traces of oxygen in the system.[55] Spectra were recorded over a wide temperature range, and it was possible to observe both the slow and fast exchange limits, but no kinetic parameters were determined.[58] More recently the temperature dependence of the electron resonance spectra of several cycloalkanesemidiones has been extensively investigated.[56] Cyclohexanesemidione (VII) interconverts between half-chair conformations with $\Delta H^{\ddagger} = 4.0$ kcal mole^{-1} and $\Delta S^{\ddagger} = 1.0$ cal deg^{-1} mole^{-1}. 3,3,5,5-Tetramethylcyclohexanesemidione has a $\Delta H^{\ddagger}$ of only 2.6 kcal mole^{-1} but $\Delta S^{\ddagger} = -8$ cal deg^{-1} mole^{-1}. Kinetic data were obtained from the line broadening above the coalescence temperature, the coalescence temperature, and peak separation below the coalescence temperature. The temperature at which a degenerate peak splits, because the lifetime of a conformational state is comparable with the reciprocal of the difference in coupling constants, has been widely used in nuclear resonance studies.[43] At the coalescence temperature the rate constant is given by



VII

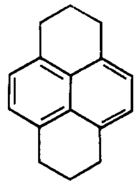
$$k = 4\pi\sqrt{2}|a_1 - a_2| \text{ sec}^{-1} \qquad (3.17)$$

where a_1 and a_2 are the limiting values of the coupling constants in the two forms.[57]

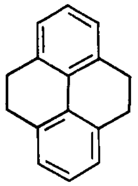
The conformational aspects of the extensive work of Russell's group on semidiones have been reviewed.[14,58]

There are, as yet, few studies of conformational interconversions in other than six-membered rings. In their investigation of the cyclopentyl radical, Fessenden and Schuler found that at −40° the four β protons are completely equivalent.[35] At lower temperatures some broadening of the $M = \pm 1$ lines was observed, suggesting that the molecule is oscillating between nonplanar isomers.

Interesting alternating line widths have been reported in the radical ions of 1,2,3,6,7,8-hexahydropyrene (VIII) and 4,5,9,10-tetrahydropyrene (IX). de Boer and Praat studied both the positive and negative radical ions of VIII. At low temperatures both boat and chair conformations are observed.[59] As the temperature is raised, the β proton coupling constants are averaged and the eight nuclei give rise to an alternating pattern with sharp components in the ratio 1:8:18:8:1. Iwaizumi and Isobe[60] have also studied the anion of VIII.



VIII



IX

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(58) G. A. Russell, E. T. Strom, E. R. Talaty, K. Y. Chang, R. D. Stephens, and M. C. Young, *Rec. Chem. Progr.*, **27**, 3 (1966); G. A. Russell in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N. Y., 1968, p 87.

(59) E. de Boer and A. P. Praat, *Mol. Phys.*, **8**, 291 (1964).

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In tetrahydrofuran (THF) at low temperatures an additional feature was observed with an alternation in the widths of the hyperfine components of the β axial protons.[60] This was attributed to the oscillation of an alkali metal counterion between two sites. No such effect was found in DME (*cf.* section III.F). The radical anion of IX also shows line-width alternation in the nonet from the methylene protons.[60] The inversion barrier has been estimated as 4–5 kcal mole^{-1}. The interconversion of methylene protons has also been investigated in the neutral radical, 1,2,3-trihydropyrenyl (1,9-trimethylenephenalenyl).[61]

E. PROTON EXCHANGE

The investigation of rapid processes involving proton transfer is of some importance in modern chemistry, and the use of electron resonance to study radicals involved in such equilibria is an attractive possibility. It is surprising therefore that only a few studies have been reported. The systems which have been analyzed have often been examined by more than one group of investigators. It is possible, by comparing the results of independent experiments, to assess the reliability of line-shape analysis as a method of obtaining kinetic data.

The simplest process one might envisage is an exchange of a labile proton analogous to the acid-catalyzed exchange of the hydroxyl proton in ethanol, the effects of which are well known in nuclear resonance. The theory for the effect of the exchange of a proton on its hyperfine coupling is a straightforward example of a spin jumping with equal probability between two sites with different resonance frequencies. An incoming proton enters the radical with either α or β spin with equal probability, thus changing the environment of the odd electron between the two states of the hyperfine doublet. There is an even chance of an exchanging proton altering the spin state which thus has a lifetime twice the lifetime of the radical between chemical exchanges. As the latter gets shorter, the two lines of the proton doublet broaden and draw together, eventually merging and finally sharpening.

Fischer has prepared the radical $\cdot CH_2OH$ by hydrogen abstraction from methanol in aqueous solutions using a rapid mixing technique.[62,62a] The observed pH dependence of the OH proton splitting was attributed to the reaction

$$\dot{R}OH + H_3O^+ = \dot{R}OH_2^+ + H_2O$$

The rate constant k is computed from the relation

$$\tau^{-1} = (1/[\dot{R}OH])(d[\dot{R}OH]/dt) = k[H_3O^+] \qquad (3.18)$$

where τ is the mean lifetime between chemical exchanges. The rate was independent of the concentrations of methanol and of the radical, and by measuring the peak separation in the slow-exchange region as a function of pH a value of $k = 1.76 \times 10^8$ l. mole^{-1} sec^{-1} was determined at 17°. The same reaction has also been studied in a rapid flow system in which an aqueous solution of acetone and methanol was photolyzed in the cavity of the electron resonance spectrometer.[59] The rate constant was determined by noting the pH at which the two peaks of the OH doublet coalesced. The values of k at 28° were found to be 3.6×10^7 and 7.2×10^7 l. mole^{-1} sec^{-1} for $\dot{C}H_2OH$ and $(CH_3)_2\dot{C}OH$, respectively. The result for $\dot{C}H_2OH$ is about a factor of 5 slower than the rate found by Fischer although he worked at a lower temperature. He observed coalescence at a pH of 1.11 from which we calculate $k = 1.54 \times 10^8$ l. mole^{-1} sec^{-1} which is close to his value from the peak separations. The solutions used in the photolysis experiments contained 10% acetone which may account for the difference in rates.

The electron resonance spectrum of the biacetylsemidione has been the subject of several investigations.[63–66] In strongly acidic or basic media a seven-line hyperfine pattern is observed from the six methyl protons. However, at pH 1–2 the hyperfine structure shows a strong alternation in line widths with sharp components in the ratio 1:9:9:1. This has been attributed to a tautomerism of the monoprotonated *trans*-semidione which interchanges the isotropic hyperfine coupling constants of the two groups of methyl protons. At pH 3 a spectrum is observed with a different coupling to the two methyl groups and a small coupling to the OH proton. By treating the tautomerism as a two-jump situation[67] and using the modified Bloch equations to calculate relative peak intensities, it has been demonstrated that the rate of the line-broadening process is first order in hydrogen ion concentration with a rate constant of 4.53×10^9 l. mole^{-1} sec^{-1}. The same radical has been observed during the photolysis of solutions of biacetyl in isopropyl alcohol.[68] The addition of varying amounts of concentrated HCl produced similar changes to those found in aqueous solutions.

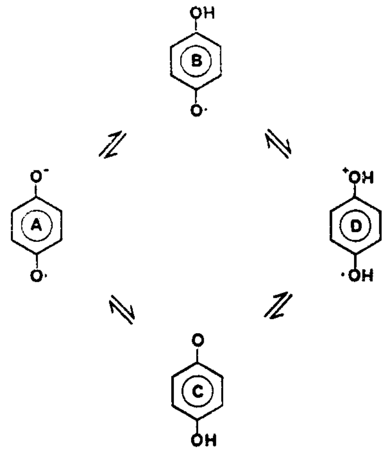

Figure 4. Proton exchange equilibria involving 1,4-benzosemiquinone radicals.

Similar phenomena have been observed during the oxidation of hydroquinones in rapid flow systems, the equilibria involved being summarized in Figure 4.

In basic solutions the semiquinone anion A is seen with a

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[61] F. Gerson, E. Heilbronner, H. A. Reddoch, D. H. Paskovich, and N. C. Das, *Helv. Chim. Acta*, **50**, 813 (1967).

[62] H. Fischer, *Mol. Phys.*, **9**, 149 (1965).

[62a] Note Added in Proof. K. Poupko and H. Lowenstein *J. Chem. Soc.*, *A*, 949 (1968), have reinvestigated these proton-exchange reactions. Their results are in agreement with those of ref 50, rather than ref 62.

(63) J. R. Steven and J. C. Ward, *Chem. Commun.*, 273 (1965); *Aust. J. Chem.*, **20**, 2005 (1967).

(64) G. A. Russell, E. R. Talaty, and M. C. Young, *J. Phys. Chem.*, **70**, 1321 (1966).

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1:4:6:4:1 hyperfine pattern (a = 6.7 MHz). However, as the pH is lowered the $M = \pm 1$ lines broaden and at pH 2.2 have almost disappeared, leaving a 1:4:1 pattern of sharp lines.[69,70] At a still lower pH the broadened lines reappear and the spectrum is attributed to the cation D. In concentrated acid a 1:2:1 triplet is seen from the OH protons. The spectra in the range pH 5.4–2.2 which show line-width alternation have been computed using the modified Bloch equations and the assumption that the intermediates B and C have a coupling of 13.4 MHz to the protons *ortho* to the unprotonated oxygen atom, and zero coupling to the *meta* protons. In this range it seems reasonable to neglect species D and one may write

$$\mathrm{d[A]}/\mathrm{d}t = -2k_{\mathrm{A}}[\mathrm{A}][\mathrm{H}^+] \tag{3.19}$$

$$\mathrm{d[B]}/\mathrm{d}t = \mathrm{d[C]}/\mathrm{d}t = -2k_{\mathrm{B}}[\mathrm{B}] \tag{3.20}$$

$$K = k_{\mathrm{B}}/k_{\mathrm{A}} \tag{3.21}$$

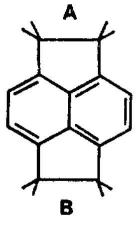
The spectra were computed for various values of the lifetimes of A and B and fitted to the experimental results,[70] giving $\mathrm{p}k_{\mathrm{A}} = -10.6 \pm 0.3$, $\mathrm{p}k_{\mathrm{B}} = -6.9 \pm 0.2$, and hence $\mathrm{p}K = 3.7 \pm 0.5$.

In an earlier study[69] over a more limited pH range, the values of $\mathrm{p}K_{\mathrm{a}} = -10.2$ and $\mathrm{p}K \sim 4.5$ were found in reasonable agreement with the more detailed investigation. Similar results have also been found in an investigation of the corresponding equilibria of the catechol semiquinone.

F. ION PAIRS

Since the discovery by Adam and Weissman of hyperfine coupling from sodium ions in ethereal solutions of the benzophenone ketyl,[71] electron resonance has been widely exploited in the investigation of ion-pairing phenomena. The structural implications of this work have been reviewed.[72,73]

Relaxation processes due to the movement of a cation between two positions in a negative ion were first reported[74,75] in studies on pyracene (X). When DME was the solvent, no ion association was observed and the splitting pattern arose from a set of eight equivalent aliphatic (α) protons and four equivalent aromatic (β) protons. In 2-MeTHF a quite different spectrum was obtained. Not only was a sodium splitting apparent, but at −80° two distinct aliphatic proton coupling constants of 19.4 and 17.8 MHz were resolved compared with the single α-proton coupling of 18.4 MHz in DME. The change in spin density distribution was attributed to the presence of a counterion at one of the positions marked A and B in X.



X

The potassium derivative at −30° in THF gave yet another type of spectrum. The nonet from the α protons had alternate sharp and broad components. This effect arises because migration of the cation between A and B modulates the isotropic coupling constants of the aliphatic protons. For alternation to be observed, the rate constant, k, for the hopping must occur within the range $10^5\ \mathrm{sec}^{-1} < k < 10^7\ \mathrm{sec}^{-1}$.

A subsequent study[76] of the behavior of the potassium and sodium systems in 2-MeTHF at low temperatures demonstrated the existence of another dynamic process. The cation at A or B oscillates in a potential well and modulates the isotropic splitting factors of the four neighboring protons. The spectrum then shows a further characteristic line-width alternation. Similar results have been reported for alkali-metal acenaphthene ion pairs where the two sites probably lie above and below the naphthalene ring.[77] Related phenomena have been found in the investigation of ion pairs of the pyrazine radical anion with alkali metals,[78–80] involving a modulation of the ring proton coupling constants. The kinetics of the intramolecular exchange reaction have been studied over a wide range of conditions. Activation energies were determined both by comparison of observed and calculated spectra, and from relative line-breadth measurements in the fast-exchange region.[80] Good agreement was obtained between the two methods. The rate constant for the sodium complex in a DME–THF mixture containing 0.72 mole fraction of THF is $10^{13.3} \exp(-7.4/RT)\ \mathrm{sec}^{-1}$. The activation energy is higher in mixed solvents and much higher for lithium (15 kcal mole^{-1}). No line-width alternation was observed with rubidium or cesium.[80]

Closely related systems in which ion pairing has been extensively investigated are those involving semiquinones. Line-width alternation has been observed in alkali metal complexes of *p*-benzosemiquinone in a variety of solvents.[81–83] In the limit of extreme broadening a 1:4:1 pattern is observed from the four ring protons.[81] Similar effects have been found in experiments using duroquinone[84] and estimates of the rates of cation exchange have been reported.[85] It is now agreed that a model in which the cation oscillates between two equivalent sites is the most probable mechanism.[86]

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(75) E. de Boer and E. L. Mackor, *J. Amer. Chem. Soc.*, **86**, 1513 (1964).

(76) E. de Boer, *Rec. Trav. Chim. Pays-Bas*, **84**, 609 (1965).

(77) M. Iwaizumi, M. Suzuki, T. Isobe, and H. Azumi, *Bull. Chem. Soc. Jap.*, **40**, 2754 (1967).

(78) N. M. Atherton and A. E. Goggins, *Mol. Phys.*, **8**, 99 (1964).

(79) J. dos Santos-Veiga and A. F. Neiva-Correia, *ibid.*, **9**, 395 (1965).

(80) N. M. Atherton and A. E. Goggins, *Trans. Faraday Soc.*, **61**, 1399 (1965); **62**, 1702 (1966).

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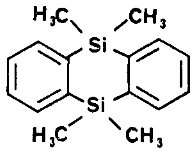
Alternating line widths are observed when 5,10-dihydrosilanthrene (XI) is reduced with potassium in THF, and it is suggested that the counterion oscillates between positions in which it is associated with silicon d orbitals.[87]



XI

The complex line broadening reported in lithium ion pairs of phthalonitrile[88] is consistent with a model in which the cation associates alternately with each nitrile group, and all three pairs of coupling constants are modulated.

Another sort of line broadening found in the investigation of ion pairs involves metal hyperfine structure. In an attempt to explain the temperature variation of the latter in some anion radicals, Hirota and Kreilick proposed a model in which two ion pairs with different alkali metal coupling constants are in rapid equilibria.[89,90] If the metal splittings in the two forms are a_A and a_B, and p_A and p_B are the fractions of A and B, then the observed splitting is

$$\bar{a} = p_A a_A + p_B a_B = (a_A + K a_B)/(1 + K) \qquad (3.22)$$

where $K = p_A/p_B$, and the broadening due to fast exchange is[21]

$$T_2^{-1} = (\omega_A - \omega_B)^2(1 + K)p_A{}^2 p_B{}^2 \tau_A \qquad (3.23)$$

ω_A and ω_B are the resonant frequencies of the two forms and τ_A the lifetime of A.

Tight ion pairs with large metal splittings are favored at high temperatures and loose ion pairs are favored at low temperatures. It follows from the line-width expression that the line broadening should depend on the nuclear quantum number of the cation. For Na or Li ($I = {}^3/_2$), peaks with $M = \pm{}^3/_2$ should broaden more rapidly than those with $M = \pm{}^1/_2$. The broadening is proportional to M^2 if the differences between the *g* factors and the other hyperfine couplings of the two species are small compared with the change in metal hyperfine coupling. The model has been applied to sodium anthracene and sodium 2,6-di-*t*-butylnaphthalene anion radicals in a variety of solvents[91] and to acenaphthene–sodium ion pairs in THF.[92]

An asymmetrical line-width variation is found in the metal ion quartets of lithium naphthalene in tetrahydropyran and 2-MeTHF and has been discussed[93] in terms of a modulation of both the lithium splitting and the α-proton coupling constant. This leads to a cross term in $M_\alpha M_{Li}$ in the expression for the line broadening. The lithium–naphthalene system has also been investigated by Atherton.[94]

The Li and Na ion pairs of 4-cyanopyridine in DME show an asymmetric line-width dependence on the alkali metal nuclear spin quantum number, suggesting an exchange between different species.[95] The potassium ion pair showed no resolvable metal structure, but the spectrum was temperature dependent and could be analyzed as a superposition of two species in equilibrium. The equilibrium constant is 4.3 at 25° with an enthalpy difference of 3.5 kcal mole^{-1} between the two forms.[95]

G. POLYNITRO COMPOUNDS

Because they readily form stable anions the aromatic nitro compounds have been extensively studied in solution. In this section we consider those aspects of the many investigations in the literature relevant to alternating line widths. Early work established that, with the exception of 1,2-dinitrobenzene, alkali metal reduction of di- and trinitrobenzenes in ether solvents gave spectra characterized by a single large nitrogen hyperfine interaction.[96–98] Thus the sodium salt of 1,3-dinitrobenzene had nitrogen coupling constants of 25.2 and 0.81 MHz at 0° in DME, whereas the anion of 1,2-dinitrobenzene appeared to have two equivalent ^{14}N interactions. The observations were interpreted by postulating tight ion pairing with one of the nitro groups in the radical anion. This behavior is to be contrasted with that in solvents such as acetonitrile when electrolytic reduction of the dinitro compound gives a radical with a symmetrical spin distribution. The effect of the solvent was clearly demonstrated by Blandamer, *et al.*,[99] who prepared the sodium salt of 1,3-dinitrobenzene in DME and observed a large coupling to one ^{14}N nucleus. On removing the DME and adding acetonitrile, a spectrum with two equivalent ^{14}N nuclei was obtained.

Ion pairing of the dinitrobenzene radical anions with all of the alkali metals has been extensively investigated.[100–107] The perturbing effect of the counterion increases in the series Cs → Li, and the spectra have been discussed in terms of intramolecular cation exchange. For 1,2-dinitrobenzene the exchange is fast, and at room temperature the spectrum may be analyzed in terms of splittings from two equivalent nitrogen nuclei, two pairs of equivalent protons, and an alkali metal cation. On lowering the temperature a complicated line-width alternation is observed. Rates of intramolecular cation exchange have been estimated by a comparison of experimental and computer-simulated spectra.[103] In contrast 1,3-dinitro-

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benzene generally gives spectra in the slow-exchange region with two different ^{14}N coupling constants.

The radical anion of 1,4-dinitrobenzene shows fast-exchange spectra when prepared in methanol but the addition of dioxane, or similar solvents, produces an alternating line-width effect.[100–102] This could be due to asymmetric solvation as no alkali metal structure is observed. However, no alternation is observed in solvent mixtures which are not expected to favor ion pairing, and it is suggested that solvent-separated ion pairs are involved.[102]

The *sym*-trinitrobenzene anion and several related compounds have been investigated in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetonitrile.[108] Interactions with various monovalent and divalent cations produced line-width alternation in the 1:3:6:7:6:3:1 septet expected for a coupling with three equivalent ^{14}N nuclei. The situation is similar to that in the trinitromethyl dianion which we discuss later. The two outer lines and one component of the central line remain sharp, giving a 1:1:1 pattern in the limit of extreme broadening.

Electrolytic reduction of 1,3-dinitrobenzene in DMF at −50° gives an electron resonance spectrum[109,110] in which the $M_N = \pm 1$ lines are considerably broader than those with $M_N = \pm 2$. This behavior is not found in the radical anions of 1,2- and 1,4-dinitrobenzene measured under the same conditions, although as we shall discuss in section VII.F a strong asymmetric effect is observed.[111] It is suggested that the modulation of the ^{14}N coupling constants is caused by the formation of fluctuating solvent complexes with the nitro groups. Detailed line-width measurements have been reported for this system.[112] A strong alternation is found when 1,3-dinitrobenzene is electrolytically reduced in DMF–ethanol mixtures at room temperature.[113] The $M_N = \pm 1$ lines broaden as the amount of alcohol is increased and disappear when it reaches a concentration of 50%. Only one ^{14}N coupling is observed when the same compound is reduced with sodium dithionite in 40% aqueous alkaline acetone.[113]

In the compounds we have dealt with up to now the nitro groups have been sterically unhindered. One of the earliest examples in which line-width alternation was reported was the dinitrodurene anion.[114,115] It was suggested that a modulation of the ^{14}N isotropic hyperfine coupling constants occurred through internal rotations of the nitro groups relative to the plane of the benzene ring.[114] Similar effects are found in several other sterically hindered polynitro compounds.[116,117] The dinitrodurenes and mesitylenes have recently been the subject of detailed investigations in which second-order frequency shifts have been used to clarify the mechanism involved.[118,119] We defer discussion of these until section IV.

Line-width alternation in the trinitromethyl dianion, $C(NO_2)_3^{2-}$, is one of the few examples of a three-site situation which have been reported.[120–122] At room temperature the hyperfine pattern shown in Figure 5 consists of the seven lines expected, but they are all of similar amplitude. On cooling the aqueous solution the line broadening becomes more pronounced and, as in the case of *sym*-trinitrobenzene, only three sharp components are observed. These observations are readily understood in terms of a simple jump model in which the molecule moves at random between three states, in each of which one ^{14}N coupling constant, a_1, is different from the other two, a_2.

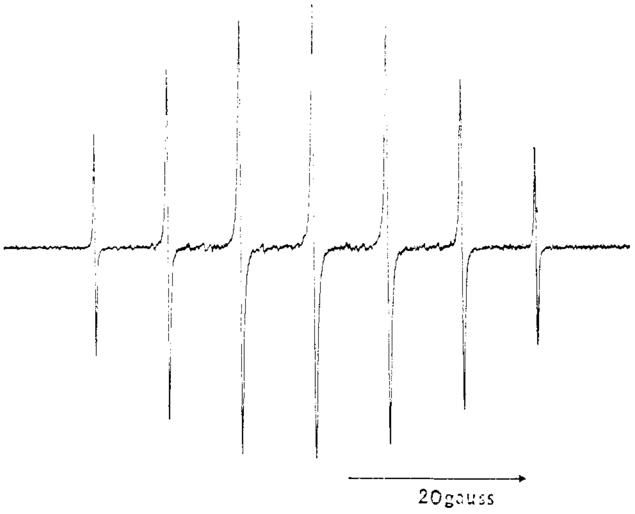

Figure 5. The electron resonance spectrum of the trinitromethyl radical dianion in aqueous solution.

As in the two-jump model of section III.A, the broadening may be derived by considering the frequencies seen by a particular nuclear spin state $|m_1m_2m_3\rangle$. These may be written

$$\begin{aligned}\omega_1 &= \omega_0 + 2\pi\{a_1m_1 + a_2(m_2 + m_3)\}\\ \omega_2 &= \omega_0 + 2\pi\{a_1m_2 + a_2(m_1 + m_3)\}\\ \omega_3 &= \omega_0 + 2\pi\{a_1m_3 + a_2(m_1 + m_2)\}\end{aligned} \qquad (3.24)$$

In the fast-exchange region the broadening due to exchange between three sites takes the form

$$T_2^{-1} = \frac{2\tau}{27}\{(\omega_1 - \omega_2)^2 + (\omega_2 - \omega_3)^2 + (\omega_3 - \omega_1)^2\} \qquad (3.25)$$

which for the model proposed becomes

$$T_2^{-1} = 8\pi^2(a_1 - a_2)^2 \times \{(m_1 - m_2)^2 + (m_2 - m_3)^2 + (m_3 - m_1)^2\}\tau/27 \qquad (3.26)$$

It is clear that only those hyperfine components with $m_1 = m_2 = m_3$ remain unaffected by the dynamic process. A consideration of the broadening for each of the 27 possible nuclear spin states involved shows that all components of the $M = \pm 2$ lines have the same width. These lines therefore retain an overall Lorentzian shape, and by measuring their amplitude rela-

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tive to the unbroadened $M = \pm 3$ lines as a function of temperature it is possible to study the kinetics of the jump process. An activation energy of 6.55 kcal mole^{-1} has been reported.[122] It would seem that restricted rotation of the nitro groups is the most likely cause of the observed phenomena. In a series of radicals $RC(NO_2)_2^{2-}$, alternation was observed[121] only when $R \equiv H_2NCOCH{=}CH$, most probably because of a hindered rotation of the nitro groups caused by intramolecular hydrogen bonding.

IV. Dynamic Frequency Shifts

As we have shown, the line broadening from the modulation of an isotropic coupling constant depends on the product of a correlation time and the mean-square deviation of the hyperfine interaction (*cf.* eq 3.6). If the slow-exchange region is inaccessible, the observation of line-width alternation gives no information about the relative magnitude of these two quantities, and it is often difficult to decide between a number of alternative mechanisms which might be operative. It has been shown[12,123] that in certain cases an accurate measurement of the second-order frequency shifts of hyperfine lines can resolve the dilemma.

In the derivation of eq 2.4 using second-order perturbation theory, a number of small imaginary terms are omitted. This is justifiable in nuclear resonance, to which theory was first applied, because the frequency shifts they produce are less than the line widths. Strictly speaking the relaxation matrix should be written

$$R_{\kappa\kappa'\lambda\lambda'} = R_{\kappa\kappa'\lambda\lambda'}^{(r)} + iR_{\kappa\kappa'\lambda\lambda'}^{(i)} \qquad (4.1)$$

where $R_{\kappa\kappa'\lambda\lambda'}^{(r)}$ is given by eq 2.7. Both $R^{(r)}$ and $R^{(i)}$ are Hermitian and are generally real. The terms in $R^{(i)}$ involve Fourier sine transforms, analogous to the cosine transfrom in eq 2.8. The complete matrix is therefore symmetric, but neither Hermitian nor real. The effect of the complex terms in eq 4.1 is most readily seen by considering a situation in which $\mathcal{H}^0$, $R^{(r)}$, and $R^{(i)}$ are simultaneously diagonal. The width of the transition between the states κ and κ' is then $-R_{\kappa\kappa'\kappa\kappa'}^{(r)}$, and the resonance is shifted to $(\omega_{\kappa'\kappa} - R_{\kappa\kappa'\kappa\kappa'}^{(i)})$. The frequency shifts are of most interest when there is a large alternating line-width effect because they are measurable for the sharp components, although they are still small compared with the widths of the broadened components.

The theory has been applied to the sterically hindered radical anions of dinitromesitylene and dinitrodurene,[119] and to 1,3-dinitrobenzene and several of its derivatives.[118] All the situations were adequately described by a two-jump model except that of the 3,5-dinitrobenzoate radical anion.[118]

For two equivalent ^{14}N nuclei the theory[12,123] predicts that the difference between the separations of the low-field and center lines and the high-field and center lines is $2\langle a^2\rangle/H_0$, where

$$\langle a^2\rangle = \langle a\rangle^2 + \langle(\delta a)^2\rangle \qquad (4.2)$$

and H_0 is the value of the external field at the central line. The line broadening depends on $\langle(\delta a)^2\rangle\tau$. Since $\langle a\rangle$ is measured from the spectrum, it is possible to determine $\langle(\delta a)^2\rangle = {}^1/_4(a_1 - a_2)^2$ and hence τ. For the dinitrodurene anion instantaneous values of a_1 and a_2 are close to $2\langle a\rangle$ and zero and $\tau = 0.6 \times 10^{-10}$ sec. This is strong evidence foı the restricted rotation model in which only one nitro group is coplanar with the ring at a given time.

The magnitude of the second-order frequency shifts is quite small (10–50 mG), and considerable care is necessary to measure them accurately. However, the stability of modern spectrometers is such that their determination is likely to become much more common in the future. Unfortunately, the shifts are not likely to be so useful for protons[123] or other nuclei of spin $^1/_2$ as for nuclei of spin 1.

V. Ligand Exchange

Five-coordinate vanadyl acetylacetonate is known to form adducts with heterocyclic bases, and the equilibrium

$$VO(acac)_2 + \text{pyridine} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} VO(acac)_2\cdot\text{pyridine}$$

has been investigated by electron resonance.[124] Both the g and hyperfine tensors are modulated, and from the line broadening the rate constants k_f and k_b were found to be 1.0×10^9 mole^{-1} sec^{-1} and 1.3×10^7 sec^{-1}, respectively. These results were obtained from the modified Bloch equations for a system jumping between two nonequivalent sites. It is clear that in any process in which an isotropic coupling is modulated, the components of the corresponding anisotropic tensor also fluctuate. In a transition metal ion these anisotropies coupled with the Brownian motion are a dominant line-broadening mechanism. Furthermore, the rotational correlation time will be different for the coordinated and uncoordinated species. It has been shown[125] that it is valid to use the fast-exchange limit of the modified Bloch equations only when the rotational correlation times are short compared with the lifetimes of the individual complexes.

VI. Electron Transfer

The kinetics of electron transfer between a neutral molecule and its radical anion were first investigated by electron resonance[126] as early as 1954, but subsequent developments were slow to emerge, and it is only recently that the field has begun to expand rapidly. The subject has been reviewed by Weissman[127] and by Johnson.[13]

The theory of electron transfer is a straightforward example of a jump process involving many sites. Consider an electron transferring between molecules which have n equivalent protons. Before transfer it is associated with one of 2^n possible nuclear spin states and jumps into one of 2^n sites on the other molecule. If it becomes associated with a nuclear spin state which belongs to a different hyperfine line, its resonance frequency is modulated. The problem is essentially an $(n + 1)$ site situation with the sites possessing a binomial distribution of relative populations. Only the secular parts of the isotropic hyperfine interaction are important, and the process is adequately described by Anderson's stochastic theory[128–132] or the modified Bloch equations.[22,23]

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In the former the line shape, $I(\omega)$, is determined by inverting a complex matrix and for n sites

$$I(\omega) \propto -Re\mathbf{W}\cdot[i(\boldsymbol{\Omega} - \boldsymbol{\omega}) + \boldsymbol{\pi}]^{-1}\cdot\mathbf{1} \tag{6.1}$$

where $\boldsymbol{\omega}$ is ω times the unit matrix, $\mathbf{W}$ is a vector with its n components proportional to the occupation probabilities of the sites in equilibrium, $\mathbf{1}$ is a unit vector, and $\boldsymbol{\Omega}$ is a diagonal matrix with elements ω_j. The elements of π are

$$\pi_{jk} = P_{jk} \qquad \pi_{jj} = \sum_{k \neq j} P_{jk} \tag{6.2}$$

and P_{jk} is the probability per unit time of a Markovian-type transition from the jth to the kth site. For example,[133] for a 1:2:1 triplet with spacing $2\pi a$ centered on $\omega = 0$

$$I(\omega) \propto Re[1,2,1] \times$$

$$\begin{bmatrix} i(\omega - 2\pi a) - \frac{3}{4\tau} & \frac{1}{2\tau} & \frac{1}{4\tau} \\ \frac{1}{4\tau} & i(\omega) - \frac{1}{2\tau} & \frac{1}{4\tau} \\ \frac{1}{4\tau} & \frac{1}{2\tau} & i(\omega + 2\pi a) - \frac{3}{4\tau} \end{bmatrix}^{-1} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \tag{6.3}$$

Because of the difficulties of inverting large matrices, almost all of the work so far reported has been concerned with the limits of fast or slow exchange when the theoretical line shapes are more readily determined.

For slow exchange rates the application of perturbation theory to (6.1) shows that each line retains a Lorentzian shape and is broadened by $(1 - P_i)/\tau$, P_i being the fraction of nuclear spin states associated with the ith line.[134] The outer lines of the hyperfine pattern broaden most rapidly, and in the case of the 1:2:1 triplet their width due to exchange is $^3/_4\tau$ compared with $^1/_2\tau$ for the central line, as may be seen by expanding (6.3) in powers of $1/\tau$. These predictions rest on the assumption that the rate is independent of nuclear spin state, a hypothesis which is supported by measurements on various lines of the naphthalene anion broadened by exchange with neutral naphthalene.[135]

The rate constants are easily determined from measurements of peak-to-peak intensities, $A(R)$, in the first-derivative spectrum as a function of the concentration of the diamagnetic form, R. The width, $\Delta\nu$, may be written as[18,127]

$$\Delta\nu = \Delta\nu_0 + \Delta\nu_R \tag{6.4}$$

where the subscript 0 refers to the situation when no diamagnetic form is present, and

$$\left(\frac{A(0)}{A(\mathrm{R})}\right)^{1/2} = 1 + \frac{\Delta\nu_R}{\Delta\nu_0} \tag{6.5}$$

The lifetime between exchanges, τ, found from $\Delta\nu_R$ is related to the rate constant by $\tau^{-1} = k[\mathrm{R}]$.

It is only recently that the fast-exchange limit has been used to measure rates of electron transfer. In this region the spectrum collapses to a single Lorentzian line whose width depends on the second moment ∇ (in MHz^2) of the electron resonance spectrum in the absence of exchange.[134,136] The second-order rate constant may be written

$$k = 5.71 \times 10^7\nabla/\Delta H_0[\mathrm{R}] \tag{6.6}$$

where ΔH_0 is the line width in MHz measured as the separation between extrema in the first-derivative spectrum.

The computational difficulties involved in the intermediate exchange region may be overcome by using high-speed computers. It has been suggested that the density matrix theories of Kaplan[137,138] and Alexander[139,140] are most suitable for use in these calculations.[141,142] The equation of motion of the density matrix is modified by the addition of terms allowing for exchange and by phenomenological terms to account for the line width in the absence of exchange

$$\dot{\rho} = i[\rho, \mathcal{H}] + \dot{\rho}(\text{exchange}) + \dot{\rho}(T_2^{-1}) \tag{6.7}$$

The line shape is found from the imaginary part of the sum of the off-diagonal elements of ρ, which for the n site problem takes the convenient form[141]

$$\sum \rho_{ij} = [-iC\sum_k F_k][1 + \tau^{-1}\sum_k F_k]^{-1} \tag{6.8}$$

where

$$F_k = n_k[i(\omega - \omega_k) - T_2^{-1} - \tau^{-1}]^{-1}$$

This formalism, which is mathematically equivalent to the stochastic theories, has been used to investigate the line shapes of the biphenyl–biphenylide exchange reaction and should facilitate experiments over a wider range of conditions than was formerly possible.

Typical electron-transfer rates determined by electron resonance lie in the range 10^7–10^9 l. mole^{-1} sec^{-1}. A selection of results are collected together in Table II.[143–155]

In the fast-exchange region the sodium ketyl of benzophenone gives a four-line spectrum, thus retaining the alkali metal hyperfine structure.[71] This requires that the nuclear spin state of the counterion be preserved and indicates that an atom transfer is taking place. Similar effects are found with other ketyls.[143]

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Table II

Typical Electron-Transfer Rates Determined by Electron Resonance

System	*Solvent*	*Temp, °C*^{c}	*k (l. mole^{-1} sec^{-1}) × 10^{-8}*	*$\Delta H^{\ddagger}$, kcal mole^{-1}*	*Ref*
Na^+ xanthone$^-$/xanthone	THF	25	4.48 ± 0.34	4.3 ± 0.2	143
Na^+ benzophenone$^-$/benzophenone	DME	25	1.10 ± 0.04	6.3 ± 0.2	143
Benzene$^-$/benzene	2:1 THF/DME	18	0.77 ± 0.08	2.8 ± 0.6	144
Benzonitrile$^-$/benzonitrile	DMF	RT	2.0	...	145
Fluoranil$^-$/fluoranil	9:1 THF/CH_3CN	−75	~1.0	...	146
$(C_6H_5)_3C\cdot/(C_6H_5)_3C^+$	3:7 TFA^a/HA^b	25	1.3	...	147
Benzoquinone$^-$/benzoquinone	DMF	RT	3.8	...	148
Nitrobenzene$^-$/nitrobenzene	DMF	RT	0.3	...	148
p-Dinitrobenzene$^-$/*p*-dinitrobenzene	DMF	RT	5.9 ± 0.4	...	149, 150
TCNE$^-$/TCNE	THF	RT	2.1	...	151
Tris-*p*-nitrophenylmethyl/methide	DME, K	25	5.99 ± 0.81	1.99 ± 0.07	152
Naphthalene$^-$/naphthalene	2-MeTHF	−23	0.028 ± 0.007	12.8 ± 3.2	153
Na^+ naphthalene$^-$/naphthalene	2-MeTHF	21	0.045 ± 0.001	12.4 ± 3.6	153
Naphthalene$^-$/naphthalene	THF	13	0.38	13.2 ± 1.5	154
Stilbene$^-$/*trans*-stilbene	DME, Na	16	0.21 ± 0.01	2.6 ± 0.3	155

^{a} TFA = trifluoroacetic acid. ^{b} HA = acetic acid. ^{c} RT = room temperature.

In a solution in which ion pairing is important the two processes

$$R^- + R \rightleftharpoons R + R^- \quad \text{(i)}$$

$$R^-M^+ + R \rightleftharpoons R + R^-M^+ \quad \text{(ii)}$$

may both occur simultaneously. Observations on the naphthalene–naphthalenide system in both the slow-[156] and fast-exchange[136] regions indicate that (i) is generally faster than (ii).

The measurement of electron exchange rates in the system

$$2COT^- \rightleftharpoons COT + COT^{2-}$$

(COT = cyclooctatetraene) demonstrates that transfer is more rapid between COT^- and COT^{2-} and supports the assumption of planar structures for the anion and dianion.[157–160] The influence of ion pairing on the activation parameters for electron transfer has been reported.[159]

The effects of optical activity upon rates of electron transfer have been investigated. Line-breadth measurements made in ethereal solutions of the neutral molecule 1-(α-naphthyl)-1-phenylethane and its radical anion, using both the pure *d* enantiomer and racemic mixtures, indicate statistically significant differences in rates and activation parameters.[161] In DME at 25°, $k_{dd} = (0.68 \pm 0.07) \times 10^8$ and $k_{dl} = (1.10 \pm 0.34) \times 10^8$ mole^{-1} sec^{-1}; $\Delta H_{dd}^{\ddagger} = 1.6 \pm 0.5$ and $\Delta H_{dl}^{\ddagger} = 0.6 \pm 0.5$ kcal mole^{-1}. Measurements on optically active hexahelicene in the fast-exchange region give similar differences in rates.[162] For the potassium salt in THF at 23°, $k_{dd} = (1.2 \pm 0.3) \times 10^{10}$ and $k_{dl} = (3.0 \pm 0.3) \times 10^{10}$ mole^{-1} sec^{-1}. It is possible that the difference in rates is directly related to the asymmetry in the π-electron distribution.

Intramolecular electron transfer has been studied in the radical anions of paracyclophanes[163] and in a series of bis(4-nitrophenyl) anions[164] $(O_2N\text{–}C_6H_4\text{–})_2X$ where X ≡ CH_2, S, O, CH_2CH_2. Interactions are seen with nuclei in one or both rings depending on the rate of exchange, and at intermediate rates alternating line widths are observed.

VII. Asymmetric Line Broadening

A. THEORY

Because of their stability transition metal ions were among the first paramagnetic species to be studied in solution by electron resonance. The vanadyl ion (VO^{2+}) contains a single d electron, and since the nuclear spin of vanadium is $^7/_2$, the electron resonance spectrum of an aqueous solution of VO^{2+} shown in Figure 6 contains just eight lines.[165,166] Although the integrated intensities of the lines are identical, it is immediately obvious that their widths vary considerably. Similar asymmetric line-width variations have been observed in spectra of other transition metal ions, including copper(II)[167] and niobium(IV)[168] complexes. The resulting asymmetry is particularly marked for planar copper complexes such as copper *n*-propylacetylacetonate whose spectrum is shown in Figure 7. It is now well established that these line-width variations are caused by the anisotropies in the *g* and hyperfine tensors coupled to the Brownian motion of the complex as was first suggested by McConnell.[2] Since his early treatment, there have been developments in the general theory of magnetic relaxation which make it possible to apply more rigorous methods to the problem.

In order to illustrate the techniques for handling modulation by molecular rotations, we shall consider the line widths resulting from the isotropic rotation of a radical possessing

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(156) P. J. Zandstra and S. I. Weissman, *J. Amer. Chem. Soc.*, **84,** 4408 (1962).

(157) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32,** 1873 (1960).

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(160) R. D. Allendoerfer and P. H. Rieger, *ibid.*, **87,** 2336 (1965).

(161) W. Bruning and S. I. Weissman, *ibid.*, **88,** 373 (1966).

(162) R. Chang and S. I. Weissman, *ibid.*, **89,** 5968 (1967).

(163) S. I. Weissman, *ibid.*, **80,** 6462 (1958).

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(165) N. S. Garif'ianov and B. M. Kozyrev, *Dokl. Akad. Nauk SSSR*, **98,** 929 (1954).

(166) G. E. Pake and R. H. Sands, *Phys. Rev.*, **98** (A), 226 (1955).

(167) B. R. McGarvey, *J. Phys. Chem.*, **60,** 71 (1956).

(168) M. Lardon and H. H. Günthard, *J. Chem. Phys.*, **44,** 2010 (1966).

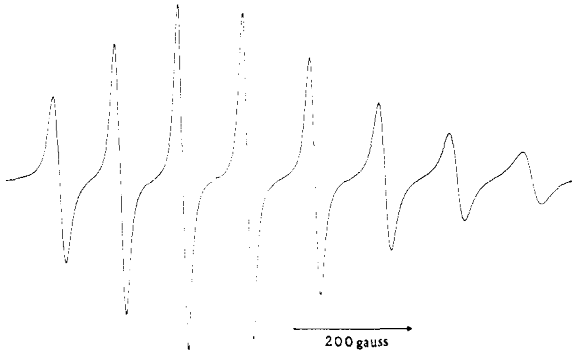

Figure 6. The electron resonance spectrum of an aqueous solution of vanadyl sulfate.

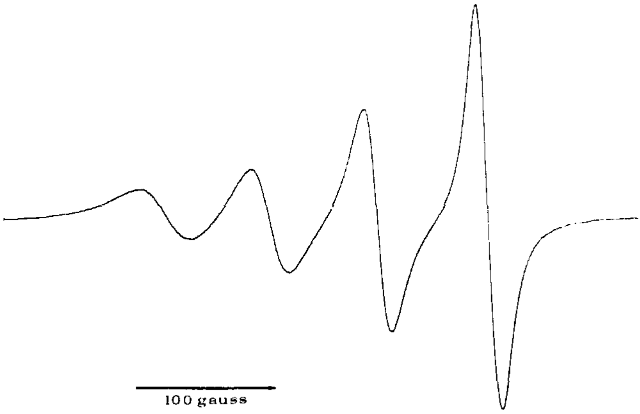

Figure 7. The electron resonance spectrum of copper *n*-propylacetylacetonate in chloroform.

an anisotropic g tensor and a single magnetic nucleus of spin I with an anisotropic hyperfine tensor. The static spin-Hamiltonian is

$$\mathcal{H}^0 = g\beta HS_z + aI\cdot S \tag{7.1}$$

while the dynamic perturbation is

$$\mathcal{H}'(t) = \beta H_\alpha g_{\alpha\beta}'(t)S_\beta + I_\alpha A_{\alpha\beta}'(t)S_\beta \tag{7.2}$$

where α, β, ... form a space fixed axis system and the tensor convention is assumed.[169] The anisotropic tensors $g_{\alpha\beta}'$ and $A_{\alpha\beta}'$, given by

$$g_{\alpha\beta}' = g_{\alpha\beta} - g\delta_{\alpha\beta} \tag{7.3}$$

and

$$A_{\alpha\beta}' = A_{\alpha\beta} - a\delta_{\alpha\beta} \tag{7.4}$$

fluctuate in time because of the molecular motion, but we can remove this by transforming to a molecule fixed axis system a, b, ..., using direction cosines to obtain

$$\mathcal{H}'(t) = \beta 1_{\alpha a}1_{\beta b}g_{ab}'H_\alpha S_\beta + 1_{\alpha a}1_{\beta b}A'_{ab}I_\alpha S_\beta \tag{7.5}$$

Indeed, one may care to think of a second-rank Cartesian tensor as being defined by this behavior.[170]

This particular form of the analysis is useful in that it employs familiar techniques, but it does contain several unsatisfactory features which are removed by writing $\mathcal{H}'(t)$, or indeed any spin-Hamiltonian, as[171]

$$\mathcal{H}'(t) = \sum_{m,\mu}(-1)^m F_\mu^{(2,m)}T_\mu^{(2,-m)} \tag{7.6}$$

The only real difference between eq 7.2 and 7.6 is that (7.2) employs Cartesian operators while (7.6) uses irreducible spherical tensor operators which we shall specify later. The operators $T_\mu^{(2,-m)}$ are for a space-fixed axis system, and so the coefficients $F_\mu^{(2,m)}$ are time dependent as are g' and $A_{\alpha\beta}'$. The rank of the irreducible tensor is 2 (the first number in the superscript) because we are only concerned with the anisotropic coupling of the spins by a second-rank tensor ($g_{\alpha\beta}$ and $A_{\alpha\beta}$). A particular component is denoted by the letter in the superscript and can take the values 0, ±1, and ±2. The different types of interaction, in our case the Zeeman and hyperfine couplings, are represented by the subscript μ.

As before, it is convenient to transform the coefficients from a space-fixed to a molecular axis system, but now we use Wigner rotation matrices $\mathcal{D}_{n,m}^{(2)}(\alpha\beta\gamma)$ since the irreducible tensors transform according to

$$F_\mu^{(2,m)} = \sum_n F_\mu'^{(2,n)}\mathcal{D}_{n,m}^{(2)} \tag{7.7}$$

where the prime denotes the new axis system related to the old by the Euler angles α, β, and γ (*cf.* ref 170, p 51, and ref 171, p 77). The dynamic perturbation can now be written as

$$\mathcal{H}'(t) = \sum_{m,n,\mu}(-1)^m F_\mu'^{(2,n)}\mathcal{D}_{n,m}^{(2)}(t)T_\mu^{(2,-m)} \tag{7.8}$$

The element of the relaxation matrix, R, depends on sums of Fourier transforms of the matrix elements $\langle[\mathcal{H}'(t)]_{\kappa\lambda}][\mathcal{H}'^*(t'+t)]_{\kappa'\lambda'}\rangle$, where $|\kappa\rangle$, $|\kappa\rangle$, $|\lambda\rangle$, and $|\lambda'\rangle$ are eigenfunctions of $\mathcal{H}^0$. Substitution of eq 7.8 for the dynamic perturbation gives

$$\langle[\mathcal{H}'(t')]_{\kappa\lambda}[\mathcal{H}'^*(t'+t)]_{\kappa'\lambda'}\rangle = \sum_{\substack{m,m',n,n'\\ \mu,\mu'}}(-1)^{m+m'}\langle\mathcal{D}_{n,m}^{(2)}(t')\mathcal{D}_{n',m'}^{(2)*}(t'+t)\rangle F_\mu'^{(2,n)}F_{\mu'}'^{(2,n')*} \times [T_\mu^{(2,-m)}]_{\kappa\lambda}[T_{\mu'}^{(2,-m')*}]_{\kappa'\lambda'} \tag{7.9}$$

Provided the motion of the system is restricted to molecular rotation, the time dependence is contained entirely in the Wigner rotation matrices and the correlation function is

$$g(t',t) = \langle\mathcal{D}_{n,m}^{(2)}(t')\mathcal{D}_{n',m'}^{(2)*}(t'+t)\rangle \tag{7.10}$$

The perturbation is said to be stationary if g depends on t' and $(t'+t)$ only through their difference t, and we further assume that g decays exponentially with time, that is

$$\langle\mathcal{D}_{n,m}^{(2)}(t')\mathcal{D}_{n',m'}^{(2)*}(t'+t)\rangle = \langle\mathcal{D}_{n,m}^{(2)}\mathcal{D}_{n',m'}^{(2)*}\rangle e^{-t/\tau_R} \tag{7.11}$$

where τ_R is the Debye correlation time for the rotation. The ensemble average denoted by angular brackets in eq 7.11 can be replaced by the spatial average $(^1/_{8}\pi^2)\int\mathcal{D}_{n,m}^{(2)}(\alpha\beta\gamma)\cdot\mathcal{D}_{n',m'}^{(2)*}(\alpha\beta\gamma)\sin\beta\, d\beta d\alpha d\gamma$, but this is simply the orthogonality relationship for the rotation matrices (*cf.* ref 170, p 122) which states

$$\int\mathcal{D}_{n,m}^{(2)}(\alpha\beta\gamma)\mathcal{D}_{n',m'}^{(2)*}(\alpha\beta\gamma)\sin\beta\, d\beta d\alpha d\gamma = (8\pi^2/5)\delta_{mm'}\delta_{nn'} \tag{7.12}$$

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(169) A. Carrington and H. C. Longuet-Higgins, *Mol. Phys.*, **5**, 447 (1962).

(170) D. M. Brink and G. R. Satchler, "Angular Momentum," Oxford University Press, London, 1962, Chapter IV.

(171) M. E. Rose, "Elementary Theory of Angular Momentum," John Wiley and Sons, Inc., New York, N. Y., 1957, p 80.

The appearance of the δ functions is extremely important, for it shows that cross-terms between different components (m) of the spherical tensors do not make any contribution to the relaxation matrix. The result reduces considerably the labor involved in calculating R, for the summation in eq 7.9 is now restricted to m, n, μ, and μ'.

To proceed further we must have explicit forms for the operators $T_\mu^{(2,m)}$, and these are given by

$$T^{(2,0)} = \left(\frac{2}{3}\right)^{1/2}\left\{T_0(1)T_0(2) - \frac{1}{4}[T_+(1)T_-(2) + T_-(1)T_+(2)]\right\}$$

$$T^{(2,\pm1)} = \mp\frac{1}{2}\{T_\pm(1)T_0(2) + T_0(1)T_\pm(2)\} \qquad (7.13)$$

$$T^{(2,\pm2)} = \frac{1}{2}T_\pm(1)T_\pm(2)$$

where

$$T^{(1,0)} = T_Z$$

$$T^{(1,\pm1)} = \mp\frac{1}{\sqrt{2}}(T_x \pm iT_y) = \mp\frac{1}{\sqrt{2}}T_\pm \qquad (7.14)$$

The numbers 1 and 2 in parentheses denote a particular spin operator, *e.g.*, S or I. The components of the second rank tensor as defined here differ by a constant factor of $^1/_2$ from those used by Freed and Fraenkel.[11]

The irreducible tensors $F_\mu{}'^{(2,m)}$ can be related to the components of the appropriate Cartesian tensor by a rather similar procedure. It would be preferable, however, to use the components of the Cartesian tensor itself, as opposed to their linear combinations, since they are the quantities determined experimentally. Examination of eq 7.9 shows that this is possible, for we can extract part of the summation which depends explicitly on n and hence $F_\mu{}^{(2,n)}$. The quantity which concerns us is $\sum_n\langle\mathfrak{D}_{n,m}{}^{(2)}\mathfrak{D}_{n,m}{}^{(2)*}\rangle e^{-t/\tau_R}F_\mu{}'^{(2,n)}F_{\mu'}{}'^{(2,n)*}$, and since the value of $\mathfrak{D}_{n,m}{}^{(2)}\mathfrak{D}_{n,m}{}^{(2)*}$ is independent of both m and n (*cf.* eq 7.12), we are left with $\sum_n F_\mu{}'^{(2,n)}F_{\mu'}{}'^{(2,n)*}$. But this is simply the scalar or inner product of two second-rank tensors μ and μ' and is equal to $F_{\alpha\beta}{}'^{(\mu)}F_{\alpha\beta}{}'^{(\mu')}$. We shall denote this inner product of two second-rank tensors by $(F'^{(\mu)}:F'^{(\mu')})$.

Now that we have arrived at a particularly useful form for writing the perturbation, we have virtually solved the problem. Strictly the functions $|\kappa\rangle$ should be eigenfunctions of $\mathcal{H}^0$ given in eq 7.1; however, it is convenient to take them to be simple product functions $|\pm{}^1/_2,m\rangle$ when calculating $R_{\kappa\kappa',\kappa\kappa'}$. The approximation implies that the Zeeman splitting is much greater than the hyperfine interaction and so will be valid for the majority of free radicals, but may not be valid for transition metal ions. After calculation for all the contributions to the single element of R, the line width is found to be

$$T_2^{-1}(m) = A + Bm + Cm^2 \qquad (7.15)$$

where m is the nuclear quantum number and

$$A = \left(\frac{2}{15}J_0 + \frac{J_1}{10}\right)\frac{\beta^2H^2}{\hbar^2}(g':g') + 4\pi^2\left(\frac{J_0}{20} + \frac{7J_1}{60}\right)I(I+1)(A':A')$$

$$B = 2\pi\left(\frac{4J_0}{15} + \frac{J_1}{5}\right)\frac{\beta H}{\hbar}(g':A') \qquad (7.16)$$

$$C = 4\pi^2\left(\frac{J_0}{12} - \frac{J_1}{60}\right)(A':A')$$

In eq 7.16 J_0 and J_1 stand for the spectral densities $J(0)$ and $J(\omega_e)$ defined as $\tau_R/(1+\omega_e^2\tau_R^2)$ where ω_e is the electron resonance frequency.

Equation 7.16 was obtained by making one further assumption, namely that the spectral density, $J(a)$, produced by the pseudosecular terms ($I_\pm S_z$) in $\mathcal{H}'(t)$ can be replaced by $J(0)$ because $a^2\tau_R^2$ is normally much less than one. Indeed, since eq 7.15 and 7.16 were derived using Redfield theory, they will only be valid if $\Delta\omega^2\tau_R^2 \ll 1$ where $\Delta\omega$ is a measure of the anisotropy.

An equation of the same form as (7.15) was first derived by McConnell using an approximate form of time-dependent perturbation theory; consequently his formulas for the constants A, B, and C are not precise.[2] Carrington and Longuet-Higgins[169] have also tackled the rotational problem, but the perturbation theory which they employed did not permit them to allow for the important nuclear relaxation. Therefore, only their result for coefficient B is correct. Kivelson[9] was the first to obtain 7.16 although unfortunately his notation differs considerably from ours.

B. EXPERIMENTAL TESTS

Because eq 7.15 predicts a linear and quadratic dependence on the nuclear quantum number, m, for the line widths, it is clearly in accord with the line-width variations shown in Figures 6 and 7. In the case of the vanadyl ion the spectrum is approximately symmetric showing the dominance of the Cm^2 term, whereas the spectrum of the copper complex shows a marked asymmetry implying that the cross term, Bm, is dominant. These observations suggest that $2\pi(A':A') > (\beta H/\hbar)(g':A')$ for the vanadyl ion while the reverse is true for the copper chelate and indeed measurement of the appropriate g and hyperfine tensors has shown this to be the case.[172,173]

Rogers and Pake made the first attempt to test eq 7.15 and 7.16 for the vanadyl ion in aqueous solutions.[174] Although the g and hyperfine tensors necessary to calculate the line widths are available for VO^{2+}, eq 7.16 still contains an arbitrary parameter, the rotational correlation time. They therefore tested the predicted dependence of the line widths on the static field H by measuring the line widths at both X- (9 GHz) and Q-band (35 GHz) frequencies. The line widths obtained at X-band were used to obtain the constants in the equation

$$T_2^{-1}(m) = Y + A'H^2 + B'Hm + Cm^2 \qquad (7.17)$$

where Y was intended to account for all other relaxation processes and was assumed to be independent of both the magnetic field and the nuclear quantum number. The $T_2^{-1}(m)$ at the Q band calculated from the coefficients Y, A', B', and C obtained at the X band were in remarkable agreement with the experimental results, thus providing good evidence for the proposed relaxation mechanism.

The most convincing quantitative text of the theory has been provided by Wilson and Kivelson,[175] who have made accurate measurements of the widths of the eight lines in the spectrum of vanadyl acetylacetonate dissolved in toluene as a function of temperature. Because the isotropic vanadium hyperfine splitting is 298 MHz, two of the earlier assumptions are no longer

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(172) D. Kivelson and S. K. Lee, *J. Chem. Phys.*, **41**, 1896 (1964).
(173) A. H. Maki and B. R. McGarvey, *ibid.*, **29**, 31 (1958).
(174) R. N. Rogers and G. E. Pake, *ibid.*, **33**, 1107 (1960).
(175) R. Wilson and D. Kivelson, *ibid.*, **44**, 154 (1966).

valid. The first is relatively easy to correct for and concerns the actual value of H in the formulas for A and B. When the hyperfine splitting is small, the value of H at any particular line is virtually the same as the value H_0 at the center of the spectrum, but when a is large we must replace H by $H_0[1 - (amh/g\beta H_0)]$. The correction produces additional contributions to B of order a/H_0 and to C of order a^2 which are readily calculated. Unfortunately, it is much more tedious to correct for the second assumption. Since a is no longer small compared with $g\beta H/h$, the nonsecular terms must be retained in $\mathcal{H}^0$, and the simple spin functions $|\pm {}^1/_2,m\rangle$ are no longer eigenfunctions of $\mathcal{H}^0$. It is necessary to take them to second order in $ah/g\beta H$ to obtain the improved functions

$$\begin{aligned} |``{}^1/_2,m"\rangle &= |{}^1/_2,m\rangle + \epsilon_1|-{}^1/_2,m+1\rangle \\ |``-{}^1/_2,m"\rangle &= |-{}^1/_2,m\rangle + \epsilon_2|{}^1/_2,m-1\rangle \end{aligned} \tag{7.18}$$

These functions are then used to calculate the single R matrix element for the nondegenerate transition $|``{}^1/_2,m"\rangle \leftrightarrow |``-{}^1/_2,m"\rangle$. The calculation shows that the line width also depends on m^3 and is now given by

$$T_2^{-1}(m) = A + Bm + Cm^2 + Dm^3 \tag{7.19}$$

Although the coefficients are rather complicated functions[175] of the inner products $(g':g')$, $(g':A')$, and $(A':A')$, they still contain a single unknown, namely the rotational correlation time τ_R. If the temperature dependence of τ_R was known, we could calculate the temperature dependence of the coefficients in (7.19) and compare them with experiment. According to Bloembergen, Purcell, and Pound,[1] the rotational correlation time is given by

$$\tau_R = 4\pi r^3\eta/3kT \tag{7.20}$$

where η is the bulk viscosity of the solvent at absolute temperature T and r is the molecular radius. This equation also contains an arbitrary parameter, r, but now this is temperature independent, and by using the line-width coefficients at one temperature to calculate a value of r, it is possible to calculate the values of the line-width coefficients at all other temperatures. Wilson and Kivelson[175] adopted this procedure when analyzing their results for vanadyl acetylacetonate in toluene and found good agreement with the theoretical values of B and C by taking the molecular radius as 3.28 Å. The sort of agreement which they obtained is demonstrated in Figure 8, which shows the experimental values of B and C for vanadyl acetylacetonate dissolved in o-terphenyl plotted as a function of temperature; the full curves were calculated using r = 3.04 Å.[176] Unfortunately, the magnitude of D is subject to a large experimental error, and it is not possible to make a meaningful comparison with theory.

Although the results for B, C, and D are in agreement with theory, the experimental value of A was always greater than the theoretical value. Further, the difference, known as the residual line width, was found to increase with *decreasing* η/T and to be independent of the microwave frequency. It is now known that the residual line width is caused by spin-rotational relaxation which we shall discuss in section VIII.

An alternative, though less usual, method of changing the solvent viscosity is to increase the pressure; the viscosity of methylcyclohexane[177] increases from 0.73×10^{-2} P (poise) at

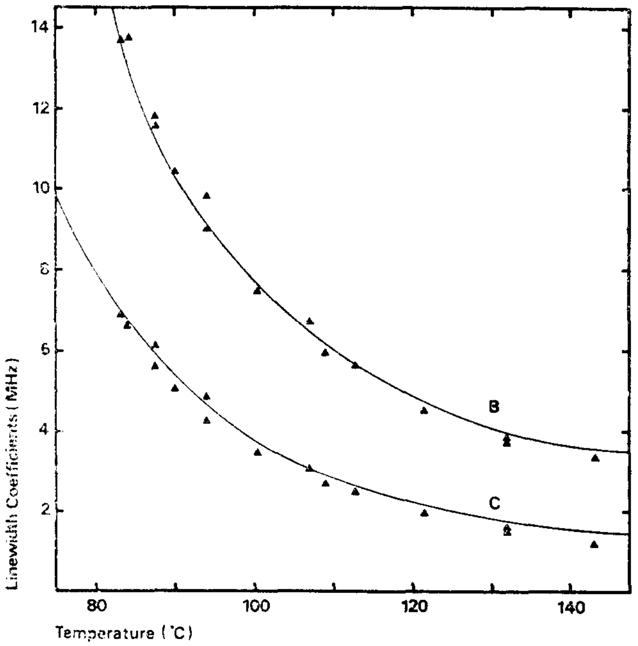

Figure 8. Temperature variation of the line-width coefficients B and C for vanadyl acetylacetonate in o-terphenyl.

atmospheric pressure to about 5.6 P at 10^4 kg cm^{-2}. The relaxation theory could therefore be tested by measuring line widths as a function of pressure, and experiments have been made with di-t-butyl nitroxide dissolved in methylcyclohexane.[178] The line-width coefficients B and C when plotted as a function of pressure are readily related through Bridgman's results[177] to viscosity. The anisotropic g and hyperfine tensors were obtained from the powder spectrum of the radical in a frozen glass of toluene and methylcyclohexane. Unfortunately, it was wrongly assumed that the g tensor had cylindrical symmetry in contrast to single crystal data for related nitroxide radicals[179] which have $g_x' = 0.0030$, $g_y' = 0.0002$, $g_z' = -0.0032$. Use of the wrong g tensor leads to good agreement for the pressure dependence of B, while that of C is good up to 2.5 P, but then the experimental coefficient increases more rapidly than predicted. The close correlation between theory and experiment is not too surprising, because the theory contains an adjustable parameter r.

Redfield's theory is equivalent to second-order time-dependent perturbation theory, and so should only be valid when the matrix elements of $\mathcal{H}'(t)$ are small compared with those of $\mathcal{H}^0$. It is not clear, however, just how large the perturbation may be before the theory breaks down. The greatest anisotropy for vanadyl acetylacetonate is in the hyperfine tensor, which is roughly 3% of the Zeeman splitting. On the other hand, the anisotropy in the g tensor is most pronounced for copper acetylacetonate, being roughly 9% of the isotropic g factor. Precise line-width measurements on this complex should then allow one to test the relaxation theory for a large perturbation.

Because natural copper consists of two isotopes, ^{63}Cu and ^{65}Cu, in the ratio 7:3 with the same nuclear spin but different

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(176) G. R. Luckhurst and J. N. Ockwell, *Mol. Phys.*, in press.

(177) P. W. Bridgman, "The Physics of High Pressures," G. Bell and Sons Ltd., London, 1952.

(178) N. Edelstein, A. Kwok, and A. H. Maki, *J. Chem. Phys.*, **41**, 179 (1964).

(179) O. H. Griffith, D. W. Cornell, and H. M. McConnell, *ibid.*, **43**, 2909 (1965).

magnetic moments, Wilson and Kivelson[180] were forced to use a sample enriched with ^{63}Cu for their line-width measurements. They analyzed the line-width coefficients, B and C, using the technique developed for vanadyl acetylacetonate and again found good agreement with the theoretical values. This result is important, for it not only confirms the earlier results for vanadyl acetylacetonate, but shows that the perturbation expansion, used by Redfield, must converge rather rapidly.

Prior to Wilson and Kivelson's results for copper (^{63}Cu) acetylacetonate, Gibson[181] had made similar measurements using copper dithiocarbamates. Unfortunately, his complexes were not isotopically enriched and so the line widths, which were obtained as a function of temperature, are difficult to analyze, although it is clear that the values calculated from the equations given by McConnell[2] and Kivelson[9] are too small.

We have been entirely concerned with nondegenerate transitions and have found that, where it is possible to make meaningful comparisons, the theoretical results are in quantitative agreement with experiment.

C. THE STRUCTURE OF LIQUIDS

One of the more obvious, although less exploited, use of line-width variations is the measurement of rotational correlation times which could provide an insight into the structure of liquids. Wilson and Kivelson[182] have measured the electron resonance spectrum of vanadyl acetylacetonate, a particularly convenient probe, in a number of solvents at various temperatures. Analysis of the line widths yields the parameters B and C which allow one to calculate τ_R. By using the viscosity of the solvent, the radius r of the complex can be calculated from τ_R; measurements at different temperatures provide a comforting check on the determination. According to the simple theory, which leads to eq 7.20, the value of r should be independent of the solvent, but examination of the results in Table III shows this is not so. Clearly if the complex is strongly solvated, its effective volume will be greater than if it were not. We might view chloroform as an extreme case; it is an excellent solvent for the complexes, presumably because of hydrogen bonding. The radius of the hydrogen-bonded species will be larger than the unsolvated complex, and this is reflected in the larger value of r found in this solvent. However, because of solvent exchange, r may be intermediate in size between that of the solvated and hydrogen-bonded complex.

A similar study[180] has been made for copper acetylacetonate, but for only two solvents. The values for the radius, also given in Table III, appear to be in accord with simple ideas concerning the similarity of the two complexes.

Comparable line-width measurements have been made[176] to help determine the structure of fluid *o*-terphenyl. The viscosity of this compound has been measured; a plot of ln η against $1/T$, which is linear for the majority of liquids, shows a marked departure from linearity.[183] The deviation from linearity has been attributed[184] to the formation of compact clusters of molecules which increase the measured viscosity η compared with the intrinsic viscosity η_S of the surrounding fluid. The two quantities are related by the equation

$$\eta = \eta_S(1 + 2.5\phi + 7\phi^2 \cdots) \tag{7.21}$$

where ϕ is the volume fraction of clusters. Unfortunately, the line-width coefficients do not provide any evidence for the existence of clusters, for the theoretical curves for the temperature dependence of B and C calculated from η and r = 3.04 Å are in excellent agreement with experiment (*cf.* Figure 8). The value of r is close to that found in diphenylmethane, a similar solvent. On the other hand, if clusters did exist, the paramagnetic probe would be expected to reside in the surrounding fluid. Calculations of B and C using η_S do not predict the correct temperature dependence for these line-width coefficients.

Table III

Solvent	*Radius, Å* *Vanadyl acetylacetonate*	 *Copper acetylacetonate*
Chloroform	3.55	3.65
Acetophenone	3.40	...
Carbon disulfide	3.34	...
Toluene	3.28	3.19
Nitrobenzene	3.26	...
Benzene	3.22	...
Diphenylmethane	2.98	...

D. ASSIGNMENT OF COUPLING CONSTANTS

One of the problems in interpreting solution electron resonance spectra is the assignment of coupling constants to particular nuclei in the radical. For example, the spectrum of the nitrobenzene anion in aqueous solution contains two 1:2:1 triplet splittings of 9.49 and 3.16 MHz, and it is not immediately apparent which should be associated with the *ortho* protons and which with the *meta*. A possible solution to the problem is to resort to molecular orbital theory and compute the π-spin density, $\rho^{(i)}$, at the two positions and use McConnell's relationship[185]

$$a^{(i)} = Q\rho^{(i)} \tag{7.22}$$

where Q is approximately constant and equal to about -70 MHz, to calculate the proton coupling constants $a^{(i)}$. Although both molecular orbital theory and eq 7.22 are approximate, they are sufficiently accurate to permit assignments when the coupling constants differ by several megahertz. There is also a chemical solution to the problem, and this involves specific deuteration of the radical. If a single proton is replaced by a deuteron (of spin 1), a doublet splitting will be replaced by a triplet, and further since the nuclear g factor of the proton is 6.514 times that of the deuteron, the triplet splitting is only 0.154 that of the replaced proton. The reduced coupling must therefore be associated with the proton replaced by the deuteron.

Similar techniques can also be applied to carbon-13, but now the hyperfine splittings depend not only on the spin density at the carbon atom, i, in question (referred to as the local spin density) but also on the spin density on the adjacent carbon atom, j. The coupling constant is therefore given by

$$a_c^{(i)} = Q'\rho^{(i)} + Q''\sum_j \rho^{(j)} \tag{7.23}$$

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(180) R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 4445 (1966).

(181) J. F. Gibson, *Trans. Faraday Soc.*, **60**, 2105 (1964).

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where Q'' is -39.0 MHz and Q' is 99.8 MHz if there are two adjacent carbon atoms, and 85.8 MHz if there are three.[186] Again the calculations may be used with confidence when the couplings constants are markedly different. If this is not so, then one may make the assignment by enriching a particular position with carbon-13 and observing which pairs of satellites increase in intensity.

Bolton and Fraenkel[187] have suggested an alternative solution to the problem based on the observation of line-width variations among the various carbon-13 satellites. The technique depends on the fact that the line width predicted by eq 7.15 and 7.16 will be greater the larger the value of the anisotropic hyperfine tensor. However, the magnitude of this tensor depends largely on the local spin density and not on the neighboring spin density. Thus, the broader carbon-13 lines can be assigned to the positions of high *local* spin density.

To examine the problem more rigorously, we require theoretical expressions for the components of the anisotropic hyperfine tensor produced by the dipolar interactions of a nucleus, *i*, with an electron in a 2p orbital on atom *j*. These have been provided by McConnell and Strathdee,[188] and the results for the principal components are

$$\begin{aligned} A_{zz}' &= P - Q \\ A_{xx}' &= -2P \\ A_{yy}' &= P + Q \end{aligned} \tag{7.24}$$

where the *z* axis is parallel to the symmetry axis of the 2p orbital, *x* is along the internuclear axis of nuclei *i* and *j*, and *y* is orthogonal to both *x* and *z*. *P* and *Q* are given by

$$P = \frac{\rho^{(i)}g|\beta|\gamma_i}{r_{ij}^3}\left\{1 - \frac{9}{a^2} + \left(a^3 + 4a^2 + 10a + 17 + \frac{18}{a} + \frac{9}{a^2}\right)e^{-2a}\right\}$$

$$Q = \frac{\rho^{(i)}g|\beta|\gamma_i}{r_{ij}^3}\left\{\frac{9}{2a^2} - \left(a^3 + 3a^2 + 6a + 9 + \frac{9}{a} + \frac{9}{2a^2}\right)e^{-2a}\right\} \tag{7.25}$$

where a is $Z_j r_{ij}/1.038$, Z_j being the effective nuclear charge, r_{ij} is the internuclear separation, and γ_i is the magnetogyric ratio for nucleus *i*.

The anisotropic hyperfine tensor for a nucleus in a particular radical is caused by the sum of many such contributions, one for every nucleus in the π system. It is convenient to divide the contributions into those coming from neighboring atoms and that from the local spin density. The local contribution may be found using the limiting forms of eq 7.25, *i.e.*

$$\begin{aligned} A_{zz}' &= \rho^{(i)}g|\beta|\gamma_i Z_i^3/4.441 \\ A_{xx}' &= A_{yy}' = -\rho^{(i)}g|\beta|\gamma_i Z_i^3/8.882 \end{aligned} \tag{7.26}$$

The numerical values calculated using these equations may be unrealistic since they depend on Slater orbitals which are poor in the vicinity of the nucleus, and the values calculated from Hartree–Fock self-consistent-field wave functions are to be preferred.[189] However, the important point is that because of the $1/r_{ij}^3$ dependence, the neighbor contribution to the anisotropic hyperfine tensor is relatively small even when the ratio of local to neighbor spin density is small.[187]

The technique has been successfully applied to the assignment of carbon-13 splittings in the anthracene anion[187,190] and to the ring carbon-13 splittings of the *p*-xylene anion where the 18.2 MHz splitting was assigned to the 2 position and the 14.6 MHz splitting to the 1 position.[187] The latter assignment is in agreement with an earlier analysis[191] based on the relative intensity of the lines, for the line from positions 2, 3, 5, and 6 should be twice as intense as that from positions 1 and 4. Similar problems arise in the assignment of fluorine hyperfine splittings for fluorine has spin $^1/_2$, and the splittings can often be confused with those from the same number of protons. For example, the spectrum of the anion of 3,5-difluoronitrobenzene contains two 1:2:1 triplet splittings of 7.67 and 9.15 MHz. Because the local spin density must be zero for aromatic protons, but not for fluorine nuclei, we expect the fluorine lines to be wider than the proton lines. On the basis of this analysis, the 7.67 MHz splitting was attributed to fluorine.[192]

E. SIGN DETERMINATIONS

The separations between the lines in an electron resonance spectrum yield only the magnitudes of the isotropic coupling constants and not their signs. Knowledge of the sign of the hyperfine interaction is important, both as an aid to the correct assignment of the splitting and for a test of theoretical ideas concerning the hyperfine interaction. Although determination of the total hyperfine tensor from a single-crystal study yields the sign, the instability of most radicals and spectral complexity precludes them from this technique. Fortunately observation of line-width variations can often lead to sign determination.

Rather than deal with the problem generally, we shall illustrate the principles by considering a specific example, namely the sign of the nitrogen hyperfine coupling in the nitrobenzene anion. The spectrum of the nitrobenzene anion, and indeed most of its derivatives,[193,194] exhibits a large triplet splitting with the high-field line broader than the central and low-field lines which have about the same width. In contrast proton lines with the same nitrogen quantum number do not show any marked variation in width, and for the purpose of this discussion we shall ignore the proton hyperfine structure. If second-order effects are small, the value of the field, $H(m)$, at which a hyperfine line with nitrogen quantum number m occurs, is given by

$$H(m) = H_0 - \frac{a^{\mathrm{N}}hm}{g\beta} \tag{7.27}$$

where H_0 is the value of the field at the center of the spectrum,

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(186) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

(187) J. R. Bolton and G. K. Fraenkel, *ibid.*, **41**, 944 (1964).

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(193) P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963).

(194) P. L. Nordio, M. V. Pavan, and C. Corvaja, *Trans. Faraday Soc.*, **60**, 1985 (1964).

$(\omega_0\hbar/g\beta)$. When a^{N} is positive, lines with a negative quantum number will occur at high field, while those with a positive value of m will be at low field; the situation is reversed when a^{N} is negative. Clearly we cannot label the lines correctly until we know the sign of a^{N}, and to eliminate this difficulty when referring to specific lines in a spectrum, Freed and Fraenkel[111] have defined spectral index numbers, $\tilde{m}$, denoted by a tilde over the quantum number such that $\tilde{m}$ is positive on the high field of the spectrum and negative on the low-field side. Thus, if the coupling constant is negative, $\tilde{m}$ is equal to m, but when a is positive, $\tilde{m}$ is minus m. In the spectrum of nitrobenzene anion the high-field line corresponds to $\tilde{m} = 1$ and the low-field line to $\tilde{m} = -1$.

Clearly, knowledge of the sign of the quantum number m for either the high- or low-field line would give us the sign of a^{N}. This information is contained in the line widths as a glance at the theoretical values for the nitrobenzene anion, given in Table IV, shows. Experimentally the high-field line ($\tilde{m} = 1$) is the widest, and so if B is positive a^{N} will be negative, whereas if B is negative a^{N} will be positive. Now the sign of B is given by the inner product $(g':A')$ in eq 7.16.

Table IV

$\tilde{m}$	$a^{\mathrm{N}} < 0$	$a^{\mathrm{N}} > 0$
1	$A + B + C$	$A - B + C$
0	A	A
-1	$A - B + C$	$A + B + C$

The main contribution to the nitrogen anisotropic hyperfine tensor comes from the local spin density, and so to a good approximation the tensor will be cylindrically symmetric about an axis (1) perpendicular to the molecular plane. The inner product can now be written as

$$(g':A') = \frac{3}{2}A_1'g_1' \qquad (7.28)$$

Equation 7.26 shows that provided the spin density at the nitrogen is positive, A_1' will also be positive, and it simply remains to find the sign of g_1'. Theoretical studies show that for hydrocarbon radicals the component of the g tensor perpendicular to the molecular plane is close to the free-spin value.[195,196] Since the isotropic g factor is usually greater than the free spin value, g_1' is negative and is predicted to be negative for oxygen-containing radicals such as the nitrobenzene anion. The coefficient B is also negative, and therefore the isotropic nitrogen coupling constant must be positive in agreement with theory. If we were not so confident about the sign of the spin density on the nitrogen, we could only use the line-width results to show that the product $\rho^{\mathrm{N}}a^{\mathrm{N}}$ was positive.

This technique was first used to determine the sign of the carbon-13 splitting of the α position in the naphthalene anion.[197] The coupling is positive in agreement with the value calculated from eq 7.23 and the Hückel spin densities. Similarly, the hyperfine splitting of the central carbon atom in triphenylmethyl is positive.[198] This result is in complete agreement with theory and corrects the anomalous sign obtained from a single-crystal determination of the carbon-13 hyperfine tensor.[199]

The spin density distribution obtained from hyperfine coupling constants is often compared with that calculated using various forms of molecular orbital theory. The agreement can usually be improved by varying certain Coulomb (α) and resonance (β) integrals, but this can only be done with any meaning when there are more spin densities than unknown integrals. An extreme example is provided by the 1,4-benzoquinone anion which shows the expected quintet hyperfine pattern with a proton coupling constant of 6.64 MHz. Since the spin density is known only for the 2, 3, 5, and 6 positions, it is not possible to obtain the best values for α_{O} and β_{CO}. However, the problem can be solved by measuring the two carbon-13 splittings which in aqueous solution are $a_1^{\mathrm{C}} = 1.12$ MHz and $a_2^{\mathrm{C}} = 1.67$ MHz.[200] The spin density at position 1 can then be calculated from eq 7.23, and since the total spin density must equal 1, the spin density on the oxygen can be calculated. To obtain an unambiguous result it is necessary to know the signs of the two carbon-13 splittings, and these were obtained from line-width variations among the carbon-13 satellites; in fact they are both negative.

An alternative solution would have involved measurement of the oxygen-17 coupling constant, but the low natural abundance of ^{17}O (0.037%) precludes the use of unenriched samples. The availability of ^{17}O is increasing, and two groups of workers have reported values of the oxygen-17 hyperfine splitting in the 1,4-benzoquinone anion.[201,202] The spin of ^{17}O is $^5/_2$ and the lines with $\tilde{m} = {}^5/_2$ are wider than those with $\tilde{m} = -{}^5/_2$. Because the magnetogyric ratio for oxygen-17 is negative, the theoretical value for the line-width coefficient B is positive and so the hyperfine splitting must be negative. The oxygen spin density is certainly positive and the sign of a^{O} simply reflects the negative sign of the magnetogyric ratio implying that the mechanism for the hyperfine interaction is analogous to that for carbon-13.

F. RELATIVE SIGN DETERMINATIONS

When a radical contains several magnetic nuclei with anisotropic hyperfine tensors, the perturbing Hamiltonian given in eq 7.2 must be modified. Provided the electron resonance transitions are nondegenerate, calculation of the line width presents few problems and for n nuclei

$$T_2^{-1}(m_1m_2\cdots m_n) = A + \sum_{i=1}^{n} B_i m_i + \sum_{i=1}^{n} C_i m_i^2 + \sum_{i\neq j=1}^{n} E_{ij} m_i m_j \qquad (7.29)$$

where the coefficients B_i and C_i are identical with those in eq 7.16. The coefficient E_{ij} is the result of the cross term between the different hyperfine tensors and is

$$E_{ij} = (A^{(i)\prime}:A^{(j)\prime})\left(\frac{4}{15}J_0 + \frac{J_1}{10}\right) \qquad (7.30)$$

In many cases it is possible to calculate the sign of the inner

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(201) W. M. Gulick and D. H. Geske, *J. Amer. Chem. Soc.*, **88**, 4119 (1966).

(202) B. L. Silver, Z. Luz, and C. Eden, *J. Chem. Phys.*, **44**, 4258 (1966).

product $(A^{(i)\prime}:A^{(j)\prime})$ and hence the sign of E_{ij}. Armed with this information we can proceed to determine the relative signs of $a^{(i)}$ and $a^{(j)}$ from the observed line widths.

It is helpful to illustrate this point by considering the electron resonance spectrum of the 4-fluoronitrobenzene anion in aqueous solution shown in Figure 9. The spectrum exhibits a large nitrogen triplet of 40.40 MHz and a doublet due to the fluorine of 22.51 MHz, together with two proton triplets. Fortunately the line-width variations are restricted to the nitrogen and fluorine lines, so permitting us to neglect the proton structure.[193,203] Because no pair of lines differ by just $E_{N,F}m_Nm_F$, we cannot use the simple device introduced in section VII.E. Instead we write eq 7.29 in terms of the spectral index numbers, $\tilde{m}_i$. The coefficients $\tilde{C}_i$ are unaffected by this change, but now

$$\tilde{B}_i = \epsilon_i B_i \tag{7.31}$$

$$\tilde{E}_{i,j} = \epsilon_i \epsilon_j E_{ij} \tag{7.32}$$

where ϵ_i is -1 if the hyperfine splitting is positive and $+1$ if $a^{(i)}$ is negative. Experimentally $\tilde{E}_{i,j}$, which is the only quantity one can calculate from the line widths, is found to be positive[203] and it simply remains to calculate the sign of $(A^{N\prime}:A^{F\prime})$. Because of the local spin density on both the nitrogen and fluorine, both anisotropic hyperfine tensors are expected to possess cylindrical symmetry about an axis (1) perpendicular to the molecular plane.[203] Thus the inner product is given by

$$(A^{N\prime}:A^{F\prime}) = \frac{3}{2}A_1^{N\prime}\cdot A_1^{F\prime} \tag{7.33}$$

and since molecular orbital calculations show that both the fluorine and nitrogen spin densities are positive, E_{ij} must also be positive. We conclude therefore that the nitrogen and fluorine coupling constants must be the same sign; in fact, the nitrogen splitting is positive and so a^F is also positive. Again when the signs of the spin densities are not so certain, such an analysis only yields the sign of $(a^N\rho^N)(a^F\rho^F)$.

Except in extremely viscous solvents the three nitrogen hyperfine lines obtained for the peroxylamine disulfonate radical dianion have equal widths.[204] However, when the radical is enriched with oxygen-17 and the spectrum is measured in aqueous solution, line-width variations are observed among the ^{17}O satellites.[205] Further, lines with the same oxygen quantum number but different nitrogen quantum numbers have different widths, implying that the cross term $E_{O,N}$ is not zero. Line-width measurements show that $\tilde{E}_{O,N}$ is positive. Both hyperfine tensors should be axially symmetric about the 2p orbitals containing the unpaired electron, and so the inner product $(A^{O\prime}:A^{N\prime})$ will be given by an equation analogous to (7.33). Since the oxygen magnetogyric ratio is negative, $E_{O,N}$ will also be negative, and so the oxygen and nitrogen coupling constants must have opposite signs. The nitrogen splitting is undoubtedly positive, and so that of oxygen must be negative in agreement with theoretical concepts. However, an attempt[205] was made to derive the sign of the nitrogen splitting from previous line-width variations[204] using the following unjustified argument. As with most nitroxides the $\tilde{m} = 1$ line is wider than the other two components,[178,206] and to use this information to determine the sign of a^N, we require g_1' where as before axis 1 is parallel to the 2p orbital. There are no theoretical estimates of g_1' available, and so it was correctly argued that the similar structures of peroxylamine disulfonate and organic nitroxides means they have the same sign for g_1'. Several organic nitroxides have now been studied in single crystals and glasses,[179] and g_1' is negative, and therefore a^N must be positive. However, the single-crystal studies also yield the nitrogen hyperfine tensor from which one can obtain directly the sign of the isotropic splitting thus making the use of line-width variations superfluous.[203]

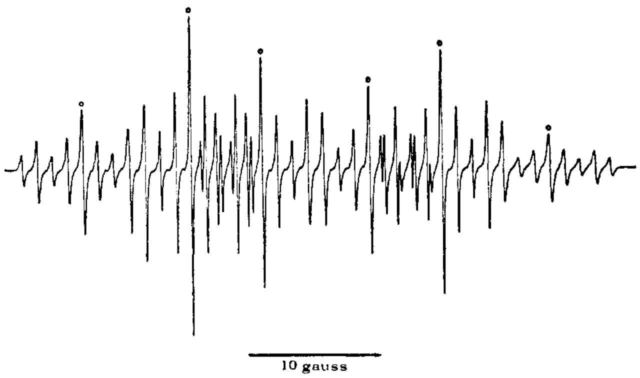

Figure 9. The electron resonance spectrum of the 4-fluoronitrobenzene radical anion in aqueous solution at room temperature.

Often a particular hyperfine line is the sum of several degenerate transitions. When the widths of the component Lorentzian lines differ markedly from one another, it is very difficult to extract useful information from the line shape. However, under certain conditions we can define an average line width, which will be given by equations analogous to eq 7.16, 7.29, and 7.30, as we shall see in section VII.G. When these conditions hold, it is possible to use the line-width variations to determine the signs and relative signs of coupling constants. Asymmetric line-width variations have now been studied in many radicals, and the signs of the coupling constants are given in Table V.[111,112,192,207–210]

G. DEGENERATE TRANSITIONS

According to Redfield the line shape of a nondegenerate transition is Lorentzian with the width given by the single element of the relaxation matrix $R_{\kappa\kappa'\kappa\kappa'}$ multiplied by -1. When the spectrum contains degenerate transitions, the line is a sum of Lorentzians with widths given by the eigenvalues of the relaxation matrix and with strengths which are related to the squares of the matrix elements $\langle\kappa|S_x|\kappa'\rangle$. In general, a sum of Lorentzians with different widths does not produce a Lorentzian line shape.[17] The application of Redfield's theory to electron resonance leads therefore to a result in marked contrast to that obtained by Kivelson[9] who, using Kubo and Tomita's theory,[3] showed that all lines should

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(210) A. Carrington, P. F. Todd, and J. dos Santos-Veiga, *Mol. Phys.*, **6**, 101 (1963).

Table V

Signs of Hyperfine Splittings

Radical	*Sign*	*Ref*
Pyracene cation	The aromatic and aliphatic protons have opposite signs	207
1,4-Dinitrobenzene anion	The nitrogen splitting has an opposite sign to that of the proton and is therefore positive	111
2,6-Dinitrophenolate dianion	Both a^{N} and $a_4{}^{H}$ are positive	112
3,5-Difluoronitrobenzene anion	$a^{N}\rho^{N}$ and $a^{F}\rho^{F}$ are both positive; a_F is probably negative	192
5-Nitropyrimidine anion	$a_5{}^{N}$ is positive as well as the product $a_1{}^{N}\rho_1{}^{N}$	208
Dihydropyrazine cation	The nitrogen splitting is positive whereas the NH proton splitting is negative	209
1,4-Dicyanotetrazine	The ring nitrogen has a positive coupling constant	210

be Lorentzian. The observation of alternating line widths discussed in section III demonstrates, quite clearly, that in general a resonance line is a sum of Lorentzians with different widths.

When the dominant relaxation mechanism is the coupling of the anisotropic g and hyperfine tensors to the molecular motion, the differences in the component line widths may be small and the subsequent departure from a Lorentzian can be quite subtle. For example, in Figure 10 the curve labeled "a" is the sum of two Lorentzians of equal intensity with one having a width twice that of the other, whereas curve b is a single Lorentzian computed with a line width taken directly from curve a. Clearly the difference between curves a and b is extremely small. When attempting to distinguish between such curves, it is helpful to define a shape factor, S_i, for line i by

$$S_i = (A_i/D_i)^{1/2}\delta_i \tag{7.34}$$

where A_i is the amplitude of the line, D_i is its degeneracy, and δ_i is the separation between the derivative extrema.[211] The line-shape factor is important because it is related to the shape function, g_i, which for a particular shape is

$$S_i = \frac{\delta_i}{\Delta_i}\left\{\frac{I_i}{D_i}[g_i'(x_i)_{\max} - g_i'(x_i)_{\min}]\right\}^{1/2} \tag{7.35}$$

where Δ_i is a parameter which measures the width of the line, I_i is the integrated intensity, and x_i is the reduced variable $(H - H_{0i})/\Delta_i$. In the spectrum of a free radical the ratios I_i/D_i and δ_i/Δ_i are constant for the various hyperfine lines, and the relative shape factors defined with respect to the central line depend only on the shapes of the lines. Clearly, if the hyperfine lines have the same form, the relative shape factors will all be unity. When all the lines do have the same shape, the line-width theory can be simplified by taking an average over the eigenvalues of the relaxation matrix to give the width. Such a procedure is particularly important if the line-width analysis is to be used to obtain quantitative information, for example, the components of the g tensor.

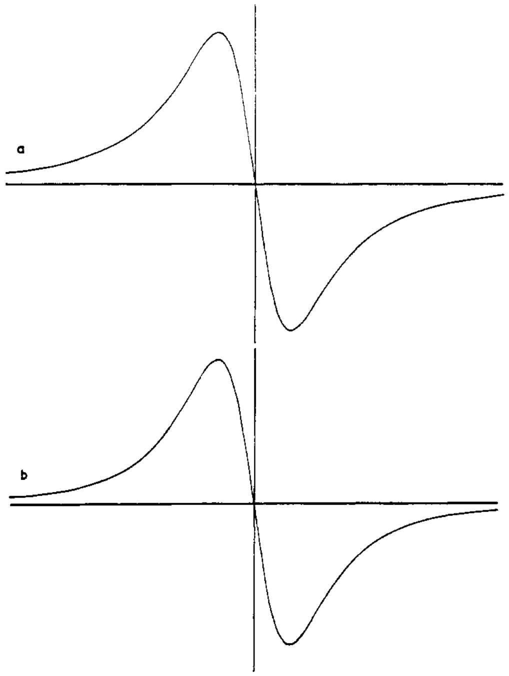

Figure 10. First derivative Lorentzian line shapes: (a) a superposition of two curves with widths in the ratio of 2:1; (b) a single Lorentzian with a width taken directly from (a).

The tetracyanoethylene anion provides an example of a spectrum whose line widths cannot be analyzed using the average line-width approximation. The spectrum in aqueous solution does not exhibit any line-width variations, but by using a mixture of absolute ethanol and glycerine the rotational correlation time was increased sufficiently to produce an asymmetric broadening. Because of the low intensity of the outside nitrogen lines and overlap with carbon-13 satellites, the relative shape factors could only be obtained for lines $M = \pm 2$, and $M = \pm 1$; the results are given in Table VI together with the relative line widths.[211] The different shapes of the various nitrogen hyperfine lines are immediately apparent from Table VI. The theoretical values of the relative widths and shape factors were calculated from sums of Lorentzians whose widths were obtained from the full relaxation matrix. The excellent agreement with the experimental results was obtained by treating the products of the tensor invariants and rotational correlation time as adjustable parameters when fitting the relative widths.[211]

Table VI

	Relative widths		*Relative shape factors*	
M	*Exptl*	*Theoret*	*Exptl*	*Theoret*
−2	1.895	1.942	1.140	1.100
−1	1.210	1.215	1.062	1.037
1	1.376	1.385	1.073	1.055
2	2.213	2.265	1.140	1.110

This procedure for analyzing the line shapes, although correct, is often tedious, but fortunately when the widths of the

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[211] J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, 41, 949 (1964).

component lines are similar, the over-all line shape is Lorentzian[212] with a width

$$\langle T_2^{-1}\rangle = \sum_i W_i T_{2i}^{-1} \Big/ \sum_i W_i \tag{7.36}$$

where W_i corresponds to the intensity of transition i and T_{2i}^{-1}'s are the eigenvalues of the relaxation matrix. Equation 7.36 may also be written as

$$\langle T_2^{-1}\rangle = \frac{1}{D} \sum_i T_{2i}^{-1} \tag{7.37}$$

where D is the degeneracy of the line, and the summation is over all components taken to have the same intensity.[11] Calculation of the widths of the individual degenerate transitions is a difficult task; fortunately, the relaxation matrix is often diagonal in a particular set of basis functions. This particular problem in relaxation theory has been discussed in great detail by Freed and Fraenkel.[11] Although the averaging technique has been used in the majority of line-width studies involving degenerate transitions, it should be emphasized that strictly it can only be applied quantitatively when the relative line-shape factors have been shown to be unity.

H. ANISOTROPY OF *g* TENSORS

The components of the g tensor for a paramagnetic species can be obtained by growing a magnetically dilute single crystal and studying the angular dependence of the electron resonance spectrum. For various reasons this technique is not often used for organic free radicals and attention has been focused on other methods. Clearly, if the solution electron resonance spectrum exhibits an asymmetric broadening effect, the line-width coefficients can yield the components of the anisotropic g tensor, $g_{\alpha\beta}'$. Examination of eq 7.16 shows that the cross term B depends on $g_{\alpha\beta}'$ together with $A_{\alpha\beta}'$ and τ_R. Provided eq 7.25 can be confidently used to calculate $A_{\alpha\beta}'$ we can obtain the rotational correlation time from the pure dipolar term C. Because there are other relaxation processes which are independent of the nuclear quantum numbers, the coefficient A in the line-width expressions cannot be used to obtain equations for $g_{\alpha\beta}'$. Even if the hyperfine and g tensors have the same principal axis system, there is still insufficient information to calculate all the components $g_{\alpha\beta}'$. Since the anisotropic g tensor is traceless, we require at least two B cross terms; when this information is available we can use the dipolar cross term, E_{ij}, and the two pure dipolar terms, C_i, to obtain the best value of τ_R with which to calculate $g_{\alpha\beta}'$.

Surprisingly this important technique has been used for a relatively small number of radicals with the results given in Table VII; axis 1 is perpendicular to the molecular plane, axis 2 passes through carbon atoms 1 and 4 in the radical, and axis 3 is orthogonal to 1 and 2. Inspection of the inner product $(g':A')$ for a hyperfine tensor possessing cylindrical symmetry about axis 1 shows that $(g':A')$ is just ${}^3/_2 g_1' A_1'$, and so the line-width variations yield just one component of the g tensor. This is why the line widths for the fluoronitrobenzene and 1,4-benzoquinone (^{17}O) anions gave only the component perpendicular to the molecular plane. These results are in good agreement with the theory of g factors which predicts that the component perpendicular to the molecular plane is close to the free-spin value. Indeed, Schreurs and Fraenkel's results[213] for the proton line widths of 1,4-benzoquinone anion were analyzed by assuming that $g_1 = 2.0023$.

Table VII

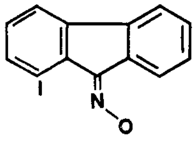
g Tensors Determined from Line-Width Measurements

Radical	g	$g_1' \times 10^3$	$g_2' \times 10^3$	$g_3' \times 10^3$	*Ref*
1,4-Benzoquinone anion	2.0046	−2.3	4.5	−2.3	211
1,4-Benzoquinone (O^{17}) anion	...	−1.9	...	...	202
1,4-Dinitrobenzene anion	2.0051	−2.1	2.6	−0.5	111
2-Fluoronitrobenzene anion	2.0047	−1.3	...	...	203
3-Fluoronitrobenzene anion	2.0046	−1.8	...	...	203
4-Fluoronitrobenzene anion	2.0047	−1.5	...	...	203

I. QUADRUPOLE RELAXATION

The widths of the nuclear magnetic resonance lines for nuclei with spins greater than ${}^1/_2$ are often extremely broad, and this has been attributed to nuclear relaxation by the quadrupole tensor coupled to the Brownian motion. The phenomenon is well understood (ref 17, p 346) and in many ways is similar to relaxation by the zero-field splitting tensor in molecules containing several unpaired electrons, a problem which we discuss in section IX. In electron resonance, quadrupole relaxation appears to be relatively unimportant, mainly because the quadrupole tensor of most covalently bonded nuclei is small in comparison to the anisotropic g and hyperfine tensors. For example, in the tetracyanoethylene anion the contribution of the quadrupole tensor to the line width is only 0.16 times that of the anisotropic hyperfine tensor.[211]

The only reported example, for which quadrupole relaxation is important, is the 1-iodofluorenone iminoxy radical,[214] XII, presumably because of the large iodine quadrupole moment. The spin of iodine is ${}^5/_2$ and the spectrum of XII consists of a sextet splitting of 38.0 MHz and a dominant nitrogen triplet of 98 MHz characteristic of iminoxy radicals.[215] The line widths in a variety of solvents are extremely broad, although the iodine lines with $m_I = \pm {}^5/_2$ are sharper than the remainder. In principle we can allow for the quadrupole relaxation by adding the term $I_\alpha Q_{\alpha\beta} I_\beta$, where $Q_{\alpha\beta}$ is the quadrupole tensor, to the perturbation given by eq 7.2. In practice, because of the structure of iminoxy radicals, the anisotropies in the nitrogen and iodine hyperfine tensors as well as the g tensor are expected to be small compared with the quadrupole tensor. The time-dependent perturbation can therefore be taken as



XII

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[212] D. Kivelson, *J. Chem. Phys.*, **41**, 1904 (1964).

[213] J. W. H. Schreurs and G. K. Fraenkel, *ibid.*, **34**, 756 (1961).

[214] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.*, *B*, 981 (1967); H. Sillescu, *Mol. Phys.*, **14**, 381 (1968).

[215] R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967).

$$\mathcal{H}'(t) = \sum_{m}(-1)^m Q^{(2,m)}(t)T^{(2,-m)} \tag{7.38}$$

where $T^{(2,-m)}$'s are the irreducible tensor operators for the nuclear spins. The line width resulting from such a modulation is readily found to be

$$T_2^{-1}(m) = \frac{(Q:Q)}{20}\{I(I + 1)[I(I + 1) - 1 + 2m^2] - 3m^4\}J_0 \tag{7.39}$$

where I is the nuclear spin and J_0 is the rotational correlation time describing the molecular motion.[318] Equation 7.39 is often written in terms of the nuclear quadrupole moment, Q, and the derivatives, $V_{\alpha\beta}$, of the electric potential

$$Q_{\alpha\beta} = \frac{eQV_{\alpha\beta}}{I(2I - 1)} \tag{7.40}$$

In the principal axis system x, y, z, it is customary to write

$$eq = V_{zz} \tag{7.41}$$

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \tag{7.42}$$

where q is the field gradient at the nucleus and η is called the asymmetry parameter. Kivelson[9] was the first to derive an expression for the quadrupole line width, although his equation differs by numerical factors from (7.39).

Since the spin of ^{127}I is $^5/_2$, the widths of the lines are

$$\begin{aligned} T_2^{-1}(\pm {}^5/_2) &= (Q:Q)J_0 \\ T_2^{-1}(\pm {}^3/_2) &= 1.53(Q:Q)J_0 \\ T_2^{-1}(\pm {}^1/_2) &= 1.20(Q:Q)J_0 \end{aligned} \tag{7.43}$$

According to the theory then the sharpest lines should be those with $m_I = \pm {}^5/_2$ in agreement with experiment. The line widths of XII have recently been the subject of a detailed investigation.[214b] Quadrupole relaxation is expected to be relatively unimportant for the other halogens, because typical values of e^2qQ are much smaller than that for iodine (*cf.* ref 18, p 175).

VIII. Spin-Rotational Interactions

As we have described, investigations of a number of radicals have demonstrated that the dependence of the width of a line on the nuclear quantum numbers of the states involved in the transition may generally be explained in terms of relaxation brought about by the anisotropies of the g tensor and the hyperfine interaction tensors. It was apparent, however, that there remained a residual broadening of each line which could not be accounted for by such mechanisms. In many cases the residual width can be accounted for in terms of spin-rotational interactions.

When a molecule rotates, its motion sets up magnetic fields, proportional to the rotational angular momentum J, which couple with the electron and nuclear spins. The interaction energy of an electron spin is represented by $S_\alpha C_{\alpha\beta} J_\beta$, where $C_{\alpha\beta}$ is the spin-rotational interaction tensor. Because of molecular collisions and intermolecular interactions, both C and J may be time dependent. The spin thus experiences a fluctuating magnetic field which can produce relaxation.

The theory of such effects was first developed for nuclear magnetic resonance, and Hubbard's classical theory[216] has been applied to electron resonance.[217] For molecules with axial symmetry, the contribution to the line width may be written

$$T_2^{-1} = (4\pi)^{-1}(\mathcal{I}^2/r^3\hbar^2)\frac{1}{3}[(2C_\perp{}^2 + C_\parallel{}^2)kT/\eta] \tag{8.1}$$

where r is the molecular radius, $\mathcal{I}$ is the moment of inertia, η is the viscosity, and $C_\parallel$ and $C_\perp$ are the components of C parallel and perpendicular to the molecular symmetry axis. The significant feature is that the broadening is proportional to (T/η), and therefore increases with increasing temperatures, and is independent of the applied field.

The spin-rotational tensor is not known in most cases of interest, but it may be related to the g tensor of the unpaired electron by the approximate expression[218,219]

$$\mathbf{C} = 2\mathbf{A}\cdot\Delta\mathbf{g} \tag{8.2}$$

where

$$\Delta g_{\alpha\beta} = g_{\alpha\beta} - 2.0023\delta_{\alpha\beta} \tag{8.3}$$

and A is the rotational constant tensor for the rigid molecule. The broadening is therefore greatest when there are large g shifts, but not necessarily anisotropies.

Spin-rotational broadening has also been discussed by Nyberg, who derives the line width using Bloch's equation[5] for the density matrix.[220] The problem is rather similar to that of an anisotropic g tensor discussed in section VII.A. The time-dependent Hamiltonian is written in the form

$$\mathcal{H}'(t) = \mathcal{C}J(t)S + J_\alpha(t)c_{\alpha\beta}(t)S_\beta \tag{8.4}$$

where $\mathcal{C} = {}^1/_3 Tr(C)$ and $c_{\alpha\beta}(t) = C_{\alpha\beta}(t) - \mathcal{C}\delta_{\alpha\beta}$. $J(t)$ varies randomly in time because of collisions and $c(t)$ fluctuates because of the molecular tumbling. In general two correlation times are required to describe the statistical properties of the molecular motion, but these are related in the Einstein–Debye theory of Brownian motion. The extension to a nonaxial spin-rotational interaction is straightforward and

$$T_2^{-1} = \frac{1}{9}\mathcal{I}^2/\hbar^2(C:C)\frac{1}{\tau_\mathrm{R}} \tag{8.5}$$

Nyberg includes the case of paramagnetic species with multiplicities greater than two and discusses a wide range of experimental results for transition metal ions and organic free radicals.[220] The theory has also been extended to include the effects of anisotropic rotational diffusion.[221]

In a series of papers on the line widths of vanadyl and copper acetylacetonates, Wilson and Kivelson have made extensive studies of the residual broadening as a function of temperature, viscosity, solvent, and applied field.[176,180,182] It is linear in (T/η) and field independent in agreement with the spin-rotational mechanism.

Spin-rotation relaxation also makes an important contribution to the line widths of copper(II) ions in aqueous solution. The spectrum of copper sulfate consists of a single line whose width increases with increasing temperature. This effect was

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(216) P. S. Hubbard, *Phys. Rev.*, **131**, 1155 (1963).
(217) P. W. Atkins and D. Kivelson, *J. Chem. Phys.*, **44**, 169 (1966).
(218) R. F. Curl, *J. Chem. Phys.*, **37**, 779 (1962).
(219) R. F. Curl, *Mol. Phys.*, **9**, 585 (1965).
(220) G. Nyberg, *ibid.*, **12**, 69 (1967).
(221) P. W. Atkins, *ibid.*, **12**, 133 (1967).

first attributed to fluctuations within the solvent sheath,[222] but it is now known to be due to spin-rotational relaxation.[223] Above 0° an aqueous solution of copper nitrate yields a single line, but at −10° copper hyperfine structure is apparent, and it is possible to obtain the hyperfine coupling constant. Using this value the line shape at higher temperatures can be fitted by spectrum simulation, and hence the widths of the component hyperfine lines can be determined. The anisotropic g and hyperfine tensors were measured from the spectrum of the complex in a glycerine–water glass, but were then scaled in order to obtain a correlation time of 6.4×10^{-11} sec from both the line-width coefficients B and C.[223] The residual line width was calculated in the normal way and was found to be given by

$$T_2^{-1}(\text{residual}) = 2.04 \times 10^4[(T/\eta) + 0.23T^2] \qquad (8.6)$$

where the term in T^2 was added to account for Van Vleck relaxation.[224] The coefficient of the spin-rotation term T/η corresponds to the reasonable value of 3.17 Å for the effective radius of the copper complex. It is suprising, perhaps, to find that the coefficient of T^2 is in good agreement with the coefficient obtained by extrapolation from 20°K.[225]

Copper(II) ions complexed with ethylenediamine have also been studied in aqueous solution[226] and dissolved in pure ethylenediamine.[227] In both cases the single electron resonance line was measured as a function of temperature, and the component line widths were obtained by computer simulation of the spectrum. For this complex the residual line width is found to be in good agreement with that predicted for spin-rotational relaxation, and there is no need to introduce the Van Vleck process.

The observation that the electron resonance line widths of chlorine dioxide in solution were anomalously broad, led to the conjecture that a spin-rotational mechanism was involved.[228] An investigation of the spectrum from 25 to −180° in the solvents CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, and CF_4 indicated that the line widths were linear in (T/η) as required.[229] The spin-rotation interaction is stronger in ClO_2 than in any other known polyatomic radical, stable in solution, and has the advantage that the interaction tensor is known from microwave spectroscopy. The viscosity dependence in aqueous glycerol solutions at 25° is in agreement with the rotational-diffusion model we have been considering.[230] However, in paraffin solutions, where there is a small solvent–solute interaction, it is found that the line widths are linearly proportional to temperature, but essentially independent of viscosity.[230] This result may be accounted for in terms of a random-jump model.[231] It is assumed that the molecule hops at random between uncorrelated orientations relative to a randomly rotating cage of solvent molecules. During the jump the molecule occupies a rotational eigenstate and the electron spin experiences a magnetic field. Adams estimates that this mechanism gives a line width contribution for ClO_2 of

$$T_2^{-1} = \frac{1}{6}(\gamma_e^2\langle\langle H_{sr}\rangle\rangle_{av})(\Delta^2/\tau) \qquad (8.7)$$

where $\langle\langle H_{sr}^2\rangle\rangle_{av}$ is the average magnetic field arising from the spin-rotational interaction, τ is the average time between jumps, and Δ is the average time spent in a rotational eigenstate. The temperature variation is essentially dependent on τ. The assumption that $\tau = \tau_0 \exp(E/RT)$, where E is the activation energy for escape into a rotational eigenstate, gives $E \simeq$ 900 cal/mole for n-pentane and $E \simeq 1100$ cal/mole for n-heptane. These values give a linear variation with temperature over the range in which measurements were made. To obtain accurate line widths second derivative spectra were employed and compared with computer simulations. The problem is complicated by the presence of two isotopes of chlorine.

The isoelectronic radical SO_2^- has line widths an order of magnitude less than ClO_2 in aqueous solution, presumably because the charge on the former causes a strong quenching of molecular rotation.[232]

IX. Higher Spin Multiplicities

Because of their stability, transition metal ions may be studied in magnetically dilute single crystals, although it may be necessary to lower the sample temperature in order to obtain sharp lines. Such experiments can provide a considerable amount of structural information, for example, the g, hyperfine, and quadrupole tensors, and in addition the zero-field splitting tensor when the ion possesses more than one unpaired electron. There would therefore seem to be little need to study the line positions of the solution spectra of transition metal complexes, since they are determined only by the isotropic g factor and hyperfine splittings. However, by measuring the widths of the lines one might hope to learn something about the dynamics of the solvent sphere surrounding the metal ion and the rate of ligand exchange. Whereas the line widths for complexes containing a single unpaired electron are determined by the anisotropies in the g and hyperfine tensors coupled to the Brownian motion, an entirely different relaxation process can occur for ions with higher multiplicities.

In these species the degeneracy of the spin multiplet is partially lifted, even in the absence of a magnetic field, by the combined effect of spin–orbit and spin–spin interactions. McGarvey[233,233a] was the first to realize that the resulting zero-field splitting tensor, when coupled to the Brownian motion, would provide a powerful relaxation process. Indeed, the fluctuating force is often so strong that the extreme line width makes it impossible to observe a resonance and is one of the reasons for the failure to detect a photoexcited triplet state in solution.[234] Certain transition metal ions do give measurable spectra, and the line widths of various chromium(III), iron(III), and manganese(II) complexes are in qualitative agreement with McGarvey's results,[233] which are an extension of McConnell's treatment of doublet states.[2] Subsequently more rigorous techniques have been employed.[16,235]

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(223) W. B. Lewis, M. Alei, Jr., and L. O. Morgan, *ibid.*, **44,** 2409 (1966).

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(230) J. Q. Adams, *J. Chem. Phys.*, **45,** 4167 (1966).

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(232) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier Publishing Co., Amsterdam, 1967, p 146.

(233) B. R. McGarvey, *J. Phys. Chem.*, **61,** 1232 (1957).

(233a) NOTE ADDED IN PROOF. W. B. Lewis and L. O. Morgan, *Transition Metal Chem.*, 4 33 (1968), discuss the electron resonance spectra of complex ions in solution.

(234) S. I. Weissman, *J. Chem. Phys.*, **29,** 1189 (1958).

(235) A. Carrington and G. R. Luckhurst, *Mol. Phys.*, **8,** 125 (1964).

If the coupling to the nuclear spins is ignored, the static Hamiltonian is

$$\mathcal{H}^0 = g\beta HS_z \tag{9.1}$$

and relaxation effects are provided by the dynamic perturbation

$$\mathcal{H}'(t) = \sum_{m,n}(-1)^m D'^{(2,n)}\mathfrak{D}_{n,m}{}^{(2)}T^{(2,-m)} \tag{9.2}$$

where $D^{(2,n)}$ is the zero-field splitting tensor in a molecule fixed axis system. $T^{(2,-m)}$, the irreducible tensor operator for the dipolar coupling, is given by eq 7.14 in which I is replaced by S, and $\mathfrak{D}_{n,m}{}^{(2)}$ is the Wigner rotation matrix. In general, the degeneracy of the resonance line is equal to the number of unpaired electrons in the complex, which in turn is equal to the order of the relaxation matrix. The basis set for constructing the relaxation matrix is formed from the eigenfunctions of $\mathcal{H}^0$, namely $|m_s\rangle$. The results will be given for the triplet, quartet, and sextet states.

Although no transition metal complex in a triplet state has been observed in solution, the theory is appropriate for certain stable biradicals such as bisgalvinoxyl[236] and the nitroxide biradicals discussed in section XI.A. Solution spectra have been observed from the thermally excited triplet state of the coronene dianion, and its zero-field splitting has been estimated from the width of the single broad line.[237] The triplet problem is isomathematical with quadrupole relaxation for a nucleus with spin 1 (ref 17, p 313) and also with dipolar relaxation for two nuclei of spin $^1/_2$ (ref 17, p 289). The result is that the resonance line is the sum of two Lorentzians corresponding to the $|0\rangle \longleftrightarrow |1\rangle$ and $|-1\rangle \longleftrightarrow |0\rangle$ transitions which have equal widths given by

$$T_2^{-1} = \frac{(D:D)}{10}\{3J_0 + 5J_1 + 2J_2\} \tag{9.3}$$

J_2 is just the spectral density $\tau_R/(1 + 4\omega_e^2\tau_R^2)$. The electron resonance line shape of a triplet in solution should remain Lorentzian irrespective of the rotational correlation time, provided the fluctuations are sufficiently fast that Redfield theory is valid.

This is not the case for the quartet state and here the spectrum is the sum of three transitions, namely $|^3/_2\rangle \longleftrightarrow |^1/_2\rangle$, $|^1/_2\rangle \longleftrightarrow |-^1/_2\rangle$, and $|-^1/_2\rangle \longleftrightarrow |-^3/_2\rangle$ with widths

$$(T_2^{-1})_{^1/_2,-^1/_2} = {}^6/_5(D:D)\{J_1 + J_2\} \tag{9.4}$$

$$(T_2^{-1})_{\pm^1/_2,\pm^3/_2} = {}^6/_5(D:D)\{J_0 + J_1\} \tag{9.5}$$

The relaxation matrix is not diagonal, and the results for the line widths are obtained from its eigenvalues. The relative strengths are $^2/_5$ for the $|^1/_2\rangle \longleftrightarrow |-^1/_2\rangle$ and $^3/_5$ for the $|\pm ^3/_2\rangle \longleftrightarrow |\pm ^1/_2\rangle$ transitions.

Examination of eq 9.4 and 9.5 shows that the transitions only have the same line width when $\omega_e\tau_R < 1$ and

$$J_0 = J_1 = J_2 \tag{9.6}$$

Otherwise the lines have different widths, and indeed whereas the widths $(T_2^{-1})_{\pm^1/_2,\pm^3/_2}$ always increase with increasing τ_R, $(T_2^{-1})_{^1/_2,-^1/_2}$ should increase, pass through a maximum, and then decrease.[235] Since the intensities of electron resonance lines are often used to determine the concentrations of transition metal complexes,[238] it is clearly of some importance to know whether all of the transitions contribute to the signal or not. Experiments in aqueous solution suggest that in this solvent all of the transitions do contribute to the resonance line for chromium(III) and manganese(II) complexes.[235]

The relaxation matrix for a sextet state tumbling in solution is[16]

$$\begin{array}{c|ccccc|}
 & |2\rangle & |1\rangle & |0\rangle & |-1\rangle & |-2\rangle \\
\langle 2| & A & D & E & 0 & 0 \\
\langle 1| & D & B & 0 & F & 0 \\
\langle 0| & E & 0 & C & 0 & E \\
\langle -1| & 0 & F & 0 & B & D \\
\langle -2| & 0 & 0 & E & D & A
\end{array} \tag{9.7}$$

where the symbols $|2\rangle$, $|1\rangle$, . . . represent the transitions $|^5/_2\rangle \longleftrightarrow |^3/_2\rangle$, $|^3/_2\rangle \longleftrightarrow |^1/_2\rangle$ etc., and

$$\begin{aligned}
A &= -\left(\frac{D:D}{5}\right)\{24J_0 + 48J_1 + 28J_2\} \\
B &= -\left(\frac{D:D}{5}\right)\{6J_0 + 36J_1 + 46J_2\} \\
C &= -\left(\frac{D:D}{5}\right)\{16J_1 + 56J_2\} \\
D &= (D:D)4\sqrt{\frac{2}{5}}J_1 \\
E &= (D:D)\frac{12}{\sqrt{5}}J_2 \\
F &= (D:D)\frac{36}{5}J_2
\end{aligned} \tag{9.8}$$

In general three different values of T_2^{-1} are obtained. However, when the molecular motion is so rapid that eq 9.6 holds, diagonalization shows that the resonance signal of a sextet state tumbling rapidly in solution is Lorentzian[16,239] with a single value of T_2^{-1} equal to $^{32}/_5(D:D)J_0$.

When the arrangement of the ligands about the transition metal ion possesses cubic symmetry, the zero-field splitting vanishes and the first nonzero spin–spin interaction contains quartic terms.[235,240] The perturbation is then

$$\mathcal{H}'(t) = \sum_{m,n}(-1)^m F^{(4,n)}\mathfrak{D}_{n,m}{}^{(4)}T^{(4,-m)} \tag{9.9}$$

where the irreducible operators $T^{(4,-m)}$ are constructed from $T^{(2,-m)}$ using Clebsch–Gordon coefficients. Bloembergen and Morgan[240] have used a technique described by Abragam and Pound,[241] in order to estimate the importance of relaxation by quartic terms. By comparison of their calculation with the frequency dependence of the proton relaxation times of aqueous manganese solutions, it was concluded that the hexadecapole interaction was not the most significant mechanism. The principal mode of relaxation was attributed to fluctuations in the arrangement of the six water molecules in the solvent sheath which destroy the cubic symmetry, so inducing a zero-field splitting and providing a time-dependent perturbation.

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(239) B. B. Garrett and L. O. Morgan, *J. Chem. Phys.*, **44**, 890 (1966).

(240) N. Bloembergen and L. O. Morgan, *ibid.*, **34**, 842 (1961).

(241) A. Abragam and R. V. Pound, *Phys. Rev.*, **92**, 943 (1953).

The spin operators in the perturbation take the same form as those in eq 9.2, but now the coefficients are time dependent because of solvent fluctuations. In calculating the matrix elements of R, the spectral densities J_0, J_1, and J_2 are replaced by Z_0, Z_1, and Z_2, where[239]

$$Z_n = \frac{(-1)^n C_2{}^2 \tau}{\hbar^2(1 + n^2\omega_e{}^2\tau^2)} \tag{9.10}$$

τ is the correlation time characteristic of the motion, and C_2 is the trace of the perturbing Hamiltonian. The problem of ligand fluctuations and exchange has also been studied by Al'tshuler and Valiev.[242]

The spectrum of manganese(II) in aqueous solution has been measured many times since its first observation.[243] It contains six hyperfine lines with different widths, although not because of a relaxation effect. The manganese hyperfine splitting is large, and the nonsecular parts of the hyperfine interaction mix states with different m_s values. As a result the five components of a particular hyperfine line do not occur at the same field. Examination of the eigenvalues of the spin Hamiltonian taken to fourth order[244a] shows that the spread of resonant field values produces asymmetric inhomogeneous broadening of the manganese hyperfine lines. The spectrum of hydrated manganese(II) has been measured as a function of temperature and microwave frequency[244b] in an attempt to test a theory developed earlier[240] for spin lattice relaxation. By assuming $T_2 \approx T_1$, a fit to experiment was obtained for an exponential temperature dependence of the correlation time.

A potentially more significant test was provided by the measurement of the spectrum of manganese(II) perchlorate dissolved in water, dimethylformamide, diethylformamide, and dimethyl sulfoxide as a function of temperature.[239] Line-width measurements were restricted to the fourth line ($m_I = +{}^1/_2$) in the spectrum since this is least dependent upon inhomogeneous broadening. Whereas for aqueous solutions the line width decreases with increasing temperature, in the organic solvents the width first decreases but then increases. Although the latter behavior may be a result of ligand exchange,[239] it is thought that spin-rotational relaxation is more important.[220] The relaxation theory for solvent fluctuations was developed in some detail. The line widths were not obtained by taking the eigenvalues of the relaxation matrix, but for the transition $|\kappa\rangle \longleftrightarrow |\kappa + 1\rangle$ were calculated from[244c]

$$(T_2{}^{-1})_{\kappa,\kappa+1} = \sum_{\lambda=-S}^{S-1} \frac{[(S - \lambda)(S + \lambda + 1)]^{1/2}}{[(S - \kappa)(S + \kappa + 1)]^{1/2}} R_{\lambda,\lambda+1,\kappa,\kappa+1} \tag{9.11}$$

a result which was derived using arguments developed for spin ${}^1/_2$ systems.[231] In the limit of fast exchange the derived component widths are

$$\begin{aligned}(T_2{}^{-1})_{\pm 5/2,\pm 3/2} &= 2.633Z_0\\ (T_2{}^{-1})_{\pm 3/2,\pm 1/2} &= 2.312Z_0\\ (T_2{}^{-1})_{\pm 1/2,-1/2} &= 1.971Z_0\end{aligned} \tag{9.12}$$

The prediction of unequal component line widths was tested by computer simulation of the first and fourth lines in the spectrum assuming a sum of five transitions with widths given by eq 9.12. The agreement between the theoretical and experimental line shapes was reasonable, but as section VII.G showed, subtle differences in shape are not easily determined. The temperature dependence of Z_0 was taken to be that of ΔH_0, the peak-to-peak line width, minus a correction (of 1.6 G) for the inhomogeneous broadening. To test the theory further, the temperature dependence of the correlation time, τ, in eq 9.10 was required, and this was equated with that of the structural correlation time[245] given by

$$\tau \propto \eta M/\rho T \tag{9.13}$$

where M is the molecular weight of the solvent of density ρ. At low temperatures the plots of τ against ΔH_s for organic solvents are linear, but at higher temperatures the line widths increase, whereas for water the plot is linear over the whole temperature range. The theory employed in this analysis attributes the time dependence entirely to solvent fluctuations, but in principle the rotation of the complex should also be important and could be allowed for using the theory developed for ligand exchange.[125] More recently measurements have been made on the species $Mn(CH_3CN)_6{}^{2+}$, $MnCl_4{}^{2-}$, and $MnBr_4{}^{2-}$ in acetonitrile solutions. Computed spectra using component widths in the ratios given by eq 9.12 gave better agreement with experiment than the assumption of an over-all Lorentzian shape.[246]

Although a complete analysis is still required for relaxation processes in the manganese system, it is interesting to observe the effects of adding anions on the line width. At temperatures below 100°, the line widths are independent of the chloride ion concentrations.[247,248] The line-width variations were originally ascribed to spin relaxation of a single manganese ion,[247] but later measurements show that ligand exchange is responsible.[248] In fact, three types of manganese ion can be distinguished: (a) a solvated ion (Mn^{2+}), (b) manganese with a chloride ion in the second coordination sphere (Mn^{2+}-H_2OCl^-), and (c) one with a chloride in the first coordination sphere ($Mn^{2+}Cl^-$).

$$Mn^{2+} + Cl^- \underset{k_{ba}}{\overset{k_{ab}}{\rightleftharpoons}} Mn^{2+}H_2OCl^- \tag{9.14}$$

$$Mn^{2+}H_2OCl^- \underset{k_{cb}}{\overset{k_{bc}}{\rightleftharpoons}} Mn^{2+}Cl^- \tag{9.15}$$

The relaxation times for the three ions differ because of the lower symmetry of the chloride complexes resulting in a zero-field splitting. The line shape for such a system can be derived using the modified Bloch equations.[22,23] and some of the aspects of the theory have been considered when both the cation

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(242) S. A. Al'tshuler and K. A. Valiev, *Sov. Phys. JETP*, **35**, 661 (1959).

(243) M. Tinkham, R. Weinstein, and A. F. Kip, *Phys. Rev.*, **84**, 848 (1951).

(244) (a) F. K. Hurd, M. Sachs, and W. D. Hershberger, *ibid.*, **93**, 373 (1954); (b) A. W. Nolle and L. O. Morgan, *J. Chem. Phys.*, **36**, 378 (1962).

(244c) NOTE ADDED IN PROOF. The derivation[239] of eq 9.11 assumes a 1:1 correspondence between the line widths and the degenerate transitions and can lead to erroneous results. This point, together with a reconsideration of the theory of the line widths of ^6S state ions, is discussed in a forthcoming publication by the authors: A. Hudson and G. R. Luckhurst, *Mol. Phys.*, in press.

(245) J. Frenkel, "Kinetic Theory of Liquids," Dover Publications Inc., New York, N. Y., 1955, p 188.

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(247) V. I. Avvakumov, N. S. Garif'yanov, B. M. Kozyrev, and P. G Tishkov, *Zh. Eksp. Teor. Fiz.*, **37**, 1564 (1959); *Sov. Phys. JETP*, **37**, 1110 (1960).

(248) R. G. Hayes and R. J. Myers, *J. Chem. Phys.*, **40**, 877 (1964).

and anion are paramagnetic, the results being in reasonable agreement with experiment.[249] The general solution using the Bloch equations is extremely complex for the manganese system, and we must be content with certain limiting forms. For example, if only equilibrium 9.14 is involved and the rate of exchange is fast, the well-known result for the average line width is

$$\langle T_2^{-1}\rangle = p_aT_{2a}^{-1} + p_bT_{2b}^{-1} \tag{9.16}$$

where p_a and p_b are the mole fractions of species a and b. Further if $p_a > p_b$ and $T_{2a} > T_{2b}$, as expected, then

$$\langle T_2^{-1}\rangle - T_{2a}^{-1} = p_a\frac{k_{ab}}{k_{ba}}[\mathrm{Cl}^-](T_{2b}^{-1} - T_{2a}^{-1}) \tag{9.17}$$

The excess line width, $\langle T_2^{-1}\rangle - T_{2a}^{-1}$, is obtained by subtracting the line width for a manganese perchlorate solution from that for a solution containing chloride ions. Experimentally the excess line width is proportional to the concentration of chloride ions. A plot of ln $\{(\langle T_2^{-1}\rangle - T_{2a}^{-1})/[\mathrm{Cl}^-]\}$ against $1/T$°K yields an activation energy of 9.4 kcal mole^{-1}. This value is felt to be rather high and is said to indicate participation of the first coordination sphere complex in the equilibrium scheme[248] when under certain conditions

$$\frac{\langle T_2^{-1}\rangle - T_{2a}^{-1}}{[\mathrm{Cl}^-]} = p_a\frac{k_{ab}}{k_{ba}}\left\{k_{bc} - \left(1 + \frac{k_{bc}}{k_{cb}}\right)T_{2a}^{-1}\right\} \tag{9.18}$$

Unfortunately, the presence of so many unknowns precludes an accurate evaluation of any of the rate constants, although k_{bc} is about 1.5×10^8 sec^{-1} at 25° with an activation energy of about 6 kcal mole^{-1}. Analogous effects are observed on addition of sulfate ions, but now the excess line width is not proportional to the sulfate concentration, and no rate information can be extracted.[248]

Ferric chloride is another sextet state, but the width of its single electron resonance line is so large that it cannot be seen in solution. However, in organic solvents, such as acetonitrile and acetone, iron trichloride is in equilibrium with the tetrachloroferrate anion.

$$\mathrm{FeCl_3} \rightleftharpoons \mathrm{FeCl_4^-} + \mathrm{FeCl_2^+}$$

Whereas the low symmetry of $\mathrm{FeCl_3}$ and $\mathrm{FeCl_2^+}$ implies a large zero-field splitting, and hence wide electron resonance lines, the tetrahedral environment[250] in $\mathrm{FeCl_4^-}$ produces a narrow line. Indeed, the intensity of the electron resonance signal is proportional to the concentration of $\mathrm{FeCl_4^-}$ determined optically.[251] As the temperature of the sample is increased, the line width decreases, a result which might be caused by the increase in the concentration of the tetrachloroferrate ion as well as by a decrease in the rotational correlation time.

X. Anisotropic Motion

A. ANISOTROPIC DIFFUSION

The assumption of isotropic rotational diffusion describable by a single correlation time τ_R is central to the evaluation of the spectral densities given in section VII. Clearly if the radical shows a marked departure from spherical symmetry, as for example vanadyl acetylacetonate, then reorientation about one axis may be easier than about the other two. The rotational correlation times will then be anisotropic, and this should be reflected in the line widths. The general theory of anisotropic diffusion has been developed by Perrin[252] in connection with dielectric relaxation and also by Favro.[253] The formulas contained in these papers have been applied to relaxation in nuclear resonance and used to analyze experimental relaxation times.[254] Freed[255] has removed the assumption of isotropic rotational diffusion from the earlier treatments of electron resonance line widths.

Essentially the problem is to calculate $\mathfrak{D}_{n',m'}^{(2)*}(\Omega)$ given in eq 7.10, where the time in the parentheses is replaced by the value of the Euler angles, Ω, at time $t' + t$. In fact

$$\mathfrak{D}_{n',m'}^{(2)*}(\Omega) = \int \mathrm{d}\Omega P(\Omega_0|\Omega;t)\mathfrak{D}_{n',m'}^{(2)*}(\Omega) \tag{10.1}$$

where $P(\Omega_0|\Omega;t)$ is the probability that the value of the rotation matrix at time t (t' being set equal to zero) is $\mathfrak{D}_{n',m'}^{(2)*}(\Omega)$ given an initial value of $\mathfrak{D}_{n',m'}^{(2)*}(\Omega_0)$. For anisotropic rotations the probability can be written as[253]

$$P(\Omega_0|\Omega;t) = \sum_i \phi_i^*(\Omega_0)\phi_i(\Omega)e^{-E_it} \tag{10.2}$$

where the functions ϕ_i correspond to a complete set of rigid rotor wave functions with eigenvalues E_i. Substitution of eq 10.2 into 10.1 gives the required value for $\mathfrak{D}_{n',m'}^{(2)*}(\Omega)$ and hence the correlation functions and spectral densities.

The results for the general problem are rather cumbersome, and it is helpful to consider the case of a symmetric top molecule when the rotor wave functions can be written in terms of Wigner rotation matrices (ref 171, p 55)

$$\phi_{K,M}^{(2)}(\Omega) = (-1)^{K-M}\left(\frac{5}{8\pi^2}\right)^{1/2}\mathfrak{D}_{K,M}^{(2)}(\Omega) \tag{10.3}$$

where K and M are the rotational quantum numbers. The eigenvalues are written in terms of the diffusion tensor $\mathcal{R}$ and are

$$E_{2,k} = 6\mathcal{R}_1 + (\mathcal{R}_3 - \mathcal{R}_1)K^2 \tag{10.4}$$

where 1, 2, 3 are the principal axes of $\mathcal{R}$. In order to appreciate the physical significance of the diffusion tensor, it may help to note that when the motion is isotropic $1/6\mathcal{R}$ is τ_R. Substitution of eq 10.3 and 10.2 into 10.1 together with the orthonormality relationship for the Wigner rotation matrices (*cf.* eq 7.12) gives

$$\mathfrak{D}_{n',m'}^{(2)*}(t) = \mathfrak{D}_{n',m'}^{(2)*}(\Omega) = \sum_{n'}\mathfrak{D}_{n',m'}^{(2)*}(\Omega_0)e^{-E_{2,n'}t} \tag{10.5}$$

The correlation function is therefore a sum of exponential terms, with each product of the irreducible tensors decaying with its own correlation time $E_{2,n}^{-1}$, thus emphasizing the advantage of writing the interaction tensors in terms of their irreducible components. The line-width coefficients are sums of products of the tensor components with certain correlation times, $\sum_n F_\mu'^{(2,n)}F_{\mu'}^{(2,n)*}E_{2,n}^{-1}$, and the summations can no longer be collapsed to give the tensor invariant.

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Under certain conditions the line widths will depend on a single correlation time. If the principal axis systems of the diffusion, g and hyperfine tensors, coincide and the interaction tensors are cylindrically symmetric, all but $F_\mu'^{(2,0)}$ vanish. For a symmetric top molecule the line-width coefficients given in eq 7.15 will still hold although τ_R is replaced by $1/6\mathcal{R}_1$ where axis 1 is perpendicular to the symmetry axis. The equations for the line-width coefficients are still valid even if the molecule undergoes asymmetric rotational diffusion although τ_R is now a complicated function of all three principal components of $\mathcal{R}$. Even though vanadyl acetylacetonate cannot rotate isotropically, the experimental line widths are in excellent agreement with the assumption of a single correlation time;[175] this is because the complex fulfills the conditions which we have just discussed.[176]

The line-width theory involving anisotropic diffusion has been applied[255] to line-width measurements for the 1,4-dinitrobenzene anion. The assumption of isotropic motion and theoretical values for the anisotropic hyperfine tensors had given three values for τ_R, from different line-width coefficients of 2.01×10^{-10}, $\lesssim 0.35 \times 10^{-10}$, and 1.36×10^{-10} sec. The discrepancy was tentatively attributed to fluctuations in the isotropic hyperfine splittings. If, however, the line widths are analyzed assuming anisotropic motion, then two elements of the diffusion tensor are found to be negative, a physically unacceptable result. It is not surprising that inclusion of fluctuations of the isotropic hyperfine splittings does produce realistic values of $\mathcal{R}$.[255]

Anisotropic diffusion is said to be important in understanding the widths of the hyperfine lines in the spectra of 4-substituted nitrobenzene anions.[256] However, examination of the line-width analysis shows this claim to be unjustified. Experimentally it is easier to measure line heights as opposed to line widths, and so the heights of the major nitrogen lines ($\tilde{m}_N = \pm 1$) relative to the central component $\tilde{m}_N = 0$ were measured as a function of temperature and found to decrease with decreasing temperature. Provided the widths of the component transitions for the degenerate transitions are not too different, the ratios of the heights are, it is argued,[256] proportional to the squares of the ratios of sums of certain line-width coefficients. (There would seem to be a misprint in eq 2 of ref 256, for this implies the height of a line is inversely proportional to the *square root* of its width.) In the limit of rapid motion all of these coefficients are proportional to τ_R, and so the ratio of the heights should be independent of temperature. There are two flaws in this argument: the first is that the spin-rotational contribution with its inverse dependence on τ_R is neglected, and secondly it is not obvious that the rotation is rapid and part of the temperature dependence could come from terms in J_1.

The same anions have also been studied by Allendoerfer and Rieger[257] who obtained the more meaningful line-width parameters at a single temperature. The dipolar cross term between the nitrogen and *meta* protons was found to be larger than that between the nitrogen and the *ortho* protons in contradiction to the theoretical values.

Although the calculated hyperfine tensors may be inaccurate, anisotropic diffusion could conceivably be responsible for the discrepancy.

B. PARTIAL ORIENTATION

Although electron resonance has provided little evidence for the existence of anisotropic diffusion, it is well known[258] that in the nematic mesophase of a liquid crystal[259] not all orientations are equally probable. Application of a magnetic field greater than 1000 G to a fluid nematic mesophase, for example, *p*-azoxyanisole, aligns the molecules with their long axes parallel to the magnetic field. Addition of a paramagnetic species to this solvent results in partial alignment of the solute and, because of the presence of anisotropic magnetic interactions, a drastic change in the isotropic electron resonance spectrum. To obtain the static spin-Hamiltonian which describes the partially oriented radical, we must take a time or ensemble average of the perturbation $\mathcal{H}'(t)$, which vanishes when the motion is isotropic, and add it to $\mathcal{H}^0$. The starting point is eq 7.8 for the second-rank anisotropic interactions. The Wigner rotation matrix can be written as

$$\mathfrak{D}_{n,m}^{(2)}(\alpha\beta\gamma) = e^{in\alpha}d_{n,m}^{(2)}(\beta)e^{im\gamma} \qquad (10.6)$$

but because of the axial symmetry about the magnetic field, all values of γ are equally probable and the average of $\mathfrak{D}$ will vanish unless m is zero. The average of $\mathcal{H}'$ can now be written as

$$\overline{\mathcal{H}}' = \sum_{\mu,n} F_\mu'^{(2,n)}\overline{\mathfrak{D}_{n,0}^{(2)}}T_\mu^{(2,0)} \qquad (10.7)$$

or by using the relationship between the spherical harmonics and $\mathfrak{D}_{n,0}^{(2)}$ as [260]

$$\overline{\mathcal{H}}' = \sqrt{\frac{4\pi}{5}}\sum_{\mu,n}(-1)^n F_\mu'^{(2,n)}\bar{Y}_{2n}^*(\beta\alpha)T_\mu^{(2,0)} \qquad (10.8)$$

If the nonsecular terms in $T_\mu^{(2,0)}$ are neglected, the effect of partial alignment is to change the g factor to

$$\bar{g} = g + \sqrt{\frac{8\pi}{15}}\sum_n(-1)^n g'^{(2,n)}\bar{Y}_{2n}^*(\beta\alpha) \qquad (10.9)$$

and a particular hyperfine splitting to

$$\bar{a} = a + \sqrt{\frac{8\pi}{15}}\sum_n(-1)^n A'^{(2,n)}\bar{Y}_{2n}^*(\beta\alpha) \qquad (10.10)$$

The alignment of a solute can also be described by an ordering matrix,[261] $\mathcal{O}_{ab}$, defined in terms of the direction cosines of a molecular axis system with respect to the magnetic field

$$\mathcal{O}_{ab} = (3l_{za}l_{zb} - \delta_{ab})/2 \qquad (10.11)$$

The symbol $\mathcal{O}$ is used to denote the ordering matrix in preference to S used in nuclear magnetic resonance to avoid confusion with the electron spin operator.[262] The summations in eq 10.9 and 10.10 are now replaced by $^2/_3(\mathcal{O}:g')$ and $^2/_3(\mathcal{O}:A')$, respectively.[263] The magnitude of the observed hyperfine splittings will depend as the relative signs of a and $(\mathcal{O}:A')$. For example, the isotropic vanadium splitting is negative whereas $(\mathcal{O}:A')$ is positive for vanadyl tetraphenylacetylacetonate

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dissolved in *p*-azoxyanisole. The hyperfine spacing below the nematic–isotropic transition point (135°) is therefore smaller than the isotropic spacing, as shown in Figure 11.

Closer examination of the spectra in Figure 11 reveals an unusual line-width variation,[264] for the lines at the end of the anisotropic spectra are sharper than those in the center, the reverse of the situation found for isotropic fluids. The dominant relaxation process is still the anisotropy in the *g* and hyperfine tensors coupled to the molecular motion, but this is no longer isotropic in the sense that the probabilities for various orientations are not identical. The time-dependent Hamiltonian for the problem is obtained by taking eq 10.7 from eq 7.8 and the single element of the R matrix calculated in the usual way. This procedure is rather complex and can be considerably simplified by neglecting those terms, $F_{\mu}'^{(2,\pm1)}$ and $F_{\mu}'^{(2,\pm2)}$, resulting from the small departure from axial symmetry of the *g* and hyperfine tensors.[175] In this way the orientation of the complex can be defined by a single parameter β, the angle between the magnetic field and the symmetry axis of the complex. After evaluating the appropriate matrix elements and correlation functions for the time dependence of β, the line widths are found to be given by eq 7.15 but with

$$\begin{aligned} A &= \frac{g'_{\parallel}{}^2 A'_{\parallel}{}^2 H^2}{4}\{4J_0(0) + 3J_1(\omega_e)\} + \\ &\qquad \frac{A'_{\parallel}{}^2 I(I+1)}{16}\{3J_1(0) + J_0(\omega_e) + 3J_2(\omega_e)\} \\ B &= \frac{g'_{\parallel}A'_{\parallel}H}{2}\{4J_0(0) + 3J_1(\omega_e)\} \qquad (10.12) \\ C &= \frac{A'_{\parallel}{}^2}{8}\{8J_0(0) + 3J_1(\omega_e) - 3J_1(0) - \\ &\qquad J_0(\omega_e) - 3J_2(\omega_e)\} \end{aligned}$$

The spectral densities should not be confused with those encountered for isotropic motion; they are[264]

$$\begin{aligned} J_0(\omega) &= \frac{9}{4}\langle\cos^4\beta - \langle\cos^2\beta\rangle^2\rangle J(\omega) \\ J_1(\omega) &= \frac{3}{2}\langle\cos^2\beta - \cos^4\beta\rangle J(\omega) \qquad (10.13) \\ J_2(\omega) &= \frac{3}{8}\langle(1 - \cos^2\beta)^2\rangle J(\omega) \end{aligned}$$

where the angular brackets denote an average over all orientations and $J(\omega) = \tau/(1 + \omega^2\tau^2)$. The motion is therefore assumed to be characterized by a single correlation time τ. The expressions in (10.12) can be simplified by noting that the viscosity of *p*-azoxyanisole[265] is very similar to that of toluene at −60° and suggests that the nonsecular contributions to the line width are negligible.[175] The sign of the C coefficient, which must be negative to explain the line-width variations, will be determined by the relative magnitudes of the secular term, J_0, and the pseudosecular, J_1. To evaluate the formulas for J_0 and J_1 given in eq 10.13, we require the probability distribution function, and this has been taken to be[266]

$$P(\beta) \propto \exp(-\lambda\cos^2\beta) \qquad (10.14)$$

Evaluation of the spectral densities using this distribution function shows that for high degrees of alignment C goes through zero and then becomes negative and finally becomes zero again on complete alignment.[264] The predicted value for the degree of alignment when C changes sign is in good agreement with the value calculated from the observed splitting and the anisotropic hyperfine tensor. When allowance is made for the nonsecular terms in $\mathcal{H}^0$, the formula for B is modified, as in the isotropic problem, and B is also predicted to change sign; again the value at which this change occurs is in good agreement with theory. Clearly, precise line-width studies in liquid-crystal solvents are capable of yielding valuable information concerning both the static and dynamic structure of the nematic mesophase.

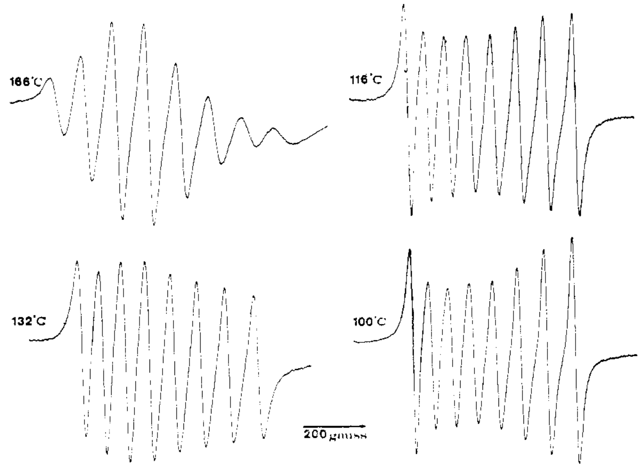

Figure 11. The electron resonance spectrum of vanadyl phenylacetylacetonate in the nematic mesophase of *p*-azoxyanisole.

Analogous line-width effects have been observed in the electron resonance spectrum of carbazole-oxyl in *p*-azoxyanisole.[267] Just below the nematic–isotropic transition point the spectrum exhibits pronounced asymmetric broadening which decreases as the temperature is decreased until, in the supercooled mesophase at 100°, the three nitrogen lines have the same width. The observation, of decreasing line width with increasing alignment, can be readily understood using the theory just developed, which is based implicitly on the distortion theory,[268] but they were interpreted[267] using the swarm theory.[269] This pictures the nematic mesophase as swarms or clusters in which the long axes of the molecules are parallel and the swarms are surrounded by an isotropic fluid. In a strong magnetic field the clusters are aligned parallel to the field, and any solute partitioned between the clusters and isotropic liquid will also be aligned. The system is in a state of flux, and exchange between the clusters and the surrounding fluid modulates the *g* and hyperfine interactions, thus leading to line broadening, which decreases with increasing alignment.[267] This model alone cannot account for the negative sign of the C coefficient for the vanadyl complex, and it is necessary to consider relaxation caused by librations of the complex within a cluster. The librations will modulate the pseudosecular terms and give a negative contribution to C.

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The spectra of biradicals dissolved in liquid crystals have also been observed,[270] and here the degeneracy of the $|1\rangle \longleftrightarrow |0\rangle$ and $|0\rangle \longleftrightarrow |-1\rangle$ transitions is split by the partially averaged zero-field splitting tensor. Application of the theory developed in section XI to partially aligned triplets would predict that each line should have the same width. Experimentally the spectrum of tetramethyl 2,2,6,6-piperidinol-1-oxyl-4-terephthalate consists of three doublets, and the lines of each doublet have different widths.[270] The motion in the liquid crystal modulates both the zero-field splitting and the anisotropic nitrogen tensor and the presence of a cross term between these interactions leads to the unequal widths for the components of the doublet.[262] Similar effects have been observed for the nitroxide triradical discussed in section XI.A when the components of the 1:2:1 triplets produced by the unaveraged zero-field splitting have different widths.[262]

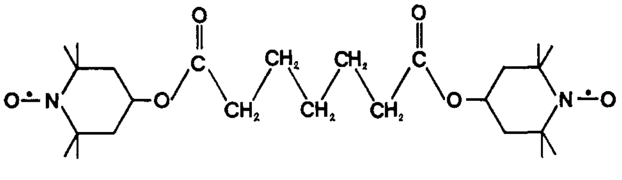
XI. Spin Exchange

A. INTRAMOLECULAR

One of the more interesting advances in electron resonance is provided by the chemist's ability to link together virtually any number of nitroxide radicals to form a stable polyradical.[271–274]

The electron resonance spectrum of the polyradical is determined not only by the interaction of the electrons with the nitrogen nuclei, but by the scalar interaction of the electrons with each other.[275] The spin-Hamiltonian[271,276] for a nitroxide biradical such as bis(2,2,6,6-tetramethyl-4-piperidinol-1-oxyl) succinate (XIII) is

$$\mathcal{H}^0 = g\beta H(S_z^{(1)} + S_z^{(2)}) + a(I_z^{(1)}S_z^{(1)} + I_z^{(2)}S_z^{(2)}) + JS^{(1)}\cdot S^{(2)} \quad (11.1)$$



XIII

where J is the exchange integral. Because the hyperfine interaction does not commute with the exchange term, the eigenvalues and eigenfunctions of $\mathcal{H}^0$ depend on the relative magnitudes of J and a. When $J \ll a$ the biradical behaves as two independent monoradicals, and the electron resonance spectrum consists of just three lines separated by a, the nitrogen hyperfine coupling constant. At the other extreme, if $J \gg a$ the singlet, $|0\rangle_E$, and the triplet, $|1\rangle_A$, $|0\rangle_A$, and $|-1\rangle_A$, electronic spin functions are eigenfunctions of $\mathcal{H}^0$ to zeroth order in J/a, while the eigenvalues to first order are

$$E|1\rangle_A|m_1,m_2\rangle = g\beta H + \frac{a}{2}(m_1 + m_2) + \frac{J}{4}$$

$$E|0\rangle_A|m_1,m_2\rangle = \frac{J}{4} \quad (11.2)$$

$$E|-1\rangle_A|m_1,m_2\rangle = -g\beta H - \frac{a}{2}(m_1 + m_2) + \frac{J}{4}$$

for the triplet functions and

$$E|0\rangle_E,|m_1,m_2\rangle = -\frac{3J}{4} \quad (11.3)$$

for the singlet, where we have used simple product functions for the nuclear spin basis. It is easily shown that the allowed electron resonance transitions occur at $g\beta H + aM/2$, where M is the total nuclear quantum number. For the case of two ^{14}N nuclei a five-line hyperfine pattern with intensities 1:2:3:2:1 and separation $a/2$ is predicted and indeed observed.[271,272]

Figure 12 shows the spectrum of the nitroxide biradical XIII dissolved in benzene, and although the spectrum does contain five lines implying $J \gg a$, the widths of the lines clearly alternate; similar effects have been observed in other biradicals.[278] This alternation is caused by modulation of the exchange energy,[277] and to calculate its effect we take the time-dependent perturbation to be

$$\mathcal{H}'(t) = (J(t) - \bar{J})S^{(1)}\cdot S^{(2)} \quad (11.4)$$

where the average value of J in $\mathcal{H}^0$ is now denoted by $\bar{J}$. If this perturbation is used to calculate the elements of the relaxation matrix, together with spin functions (11.2) and (11.3), then no broadening is predicted because the transition frequencies calculated with these functions are independent of J. In fact, the levels $|0\rangle_A$ and $|0\rangle_E$ are mixed by the hyperfine interaction, and the corrected first-order functions are

$$|\text{“0”}\rangle_A|m_1m_2\rangle = \{|0\rangle_A + \epsilon|0\rangle_E\}|m_1m_2\rangle \quad (11.5)$$

$$|\text{“0”}\rangle_E|m_1m_2\rangle = \{|0\rangle_E - \epsilon|0\rangle_A\}|m_1m_2\rangle \quad (11.6)$$

where ϵ is $a\Delta m/2\bar{J}$ with $\Delta m = m_1 - m_2$. Clearly levels with $m_1 = m_2$ should not be broadened; in fact, the line widths are given by

$$T_2^{-1} = \frac{a^2\Delta m^2}{4\bar{J}^2}j(\bar{J}) \quad (11.7)$$

where $j(\bar{J})$ is the spectral density $\frac{1}{2}\int_{-\infty}^{\infty}(J(0) - \bar{J})(J(t) - \bar{J})$ $\cos \bar{J}t\, dt$. The widths of the hyperfine components calculated from eq 11.7 are given in Table VIII. Modulation of J, presumably by conformational changes, thus results in line-width alternation independently of the form of the spectral density $j(\bar{J})$.[277]

It is tempting to consider whether line-width measurements could yield information concerning the various conformations accessible to these nonrigid biradicals. Since the biradical can adopt many conformations, it is reasonable to assume exponential decay which gives

$$j(\bar{J}) = \bar{J}^2\frac{\tau}{1 + \bar{J}^2\tau^2} \quad (11.8)$$

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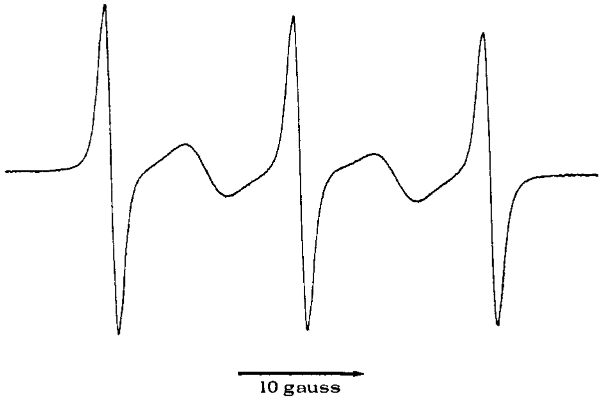


Figure 12. The electron resonance spectrum of bis(2,2,6,6-tetramethyl-4-piperidinol-1-oxyl) succinate in benzene.

for the spectral density. Since $\bar{J}$ is only of the order of 400 MHz, $\bar{J}^2\tau^2$ *might* be less than unity, in which case

$$T_2^{-1} = a^2(m_1 - m_2)^2(\overline{J^2}\tau/\bar{J}^2) \tag{11.9}$$

Even with these assumptions the line-width expression contains three unknown parameters, and attempts to measure the activation energy for the modulation process must fail because the temperature dependences of $\overline{J^2}$ and $\bar{J}^2$ are unknown.

Table VIII

M	m_1	m_2	T_2^{-1}
± 2	± 1	± 1	0
± 1	± 1	0	$a^2j(\bar{J})/4\bar{J}^2$
	0	± 1	$a^2j(\bar{J})/4\bar{J}^2$
0	0	0	0
	± 1	∓ 1	$a^2j(\bar{J})/\bar{J}^2$

The situation is not quite so intractable when the exchange interaction is of the same order as the hyperfine coupling, for under these conditions the magnitude of $\bar{J}$ may be determined from the spectrum. Indeed, the near-equality of $\bar{J}$ and a mixes the triplet and singlet levels, and it is convenient to take the eigenfunctions to be of the form

$$|0\rangle_{\varphi} = \cos\varphi|0\rangle_{\mathrm{A}} + \sin\varphi|0\rangle_{\mathrm{E}}$$
$$|0\rangle_{-\varphi} = \sin\varphi|0\rangle_{\mathrm{A}} - \cos\varphi|0\rangle_{\mathrm{E}} \tag{11.10}$$

where $\tan 2\varphi = a\Delta m/\bar{J}$. The transition frequencies are then

$$\omega = g\beta H + \frac{a}{2}(m_1 + m_2) + \bar{J}\begin{pmatrix}\sin^2\varphi \\ \cos^2\varphi\end{pmatrix} \mp \frac{a\Delta m}{4}\sin 2\varphi \tag{11.11}$$

and the widths are found to be

$$T_2^{-1} = \begin{pmatrix}\cos^4\varphi \\ \sin^4\varphi\end{pmatrix} j(0) + \frac{\sin^2 2\varphi}{4} j(\Delta\omega) \tag{11.12}$$

where $\Delta\omega$ is $\bar{J}\cos 2\varphi + a\Delta m \sin 2\varphi$, and the width predicted by the upper value in the bracket is for the line which occurs at the frequency obtained by taking the upper values in eq 11.11.[278] Measurement of a and $\bar{J}$ gives φ which could then be used in conjunction with the line widths to obtain the spectral densities $j(0)$ and $j(\Delta\omega)$. The temperature dependence of these could then yield information concerning the relative motion of the ends of the biradical. Although the line-width variations predicted by eq 11.12 have been observed, no detailed analysis has been published.[278]

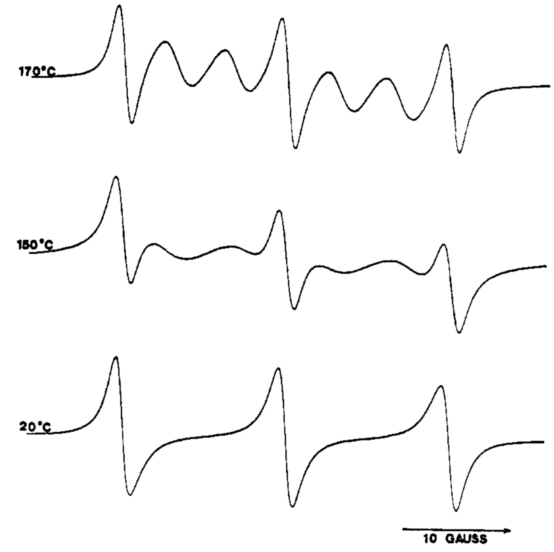
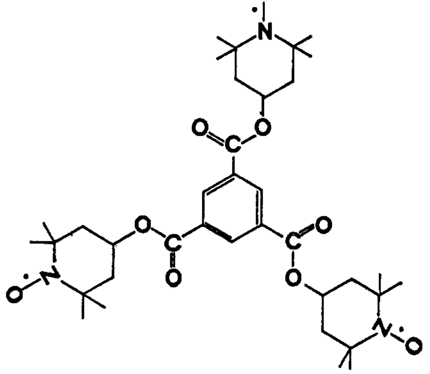


Figure 13. The electron resonance spectrum of the triradical XIV in mesitylene.

In view of the many biradicals which exhibit line-width variations caused by modulation of J, we expect this to be an important relaxation process for polyradicals. Indeed the line widths in the spectrum of the triradical XIV do alternate as can be seen from Figure 13, and furthermore the broadening decreases with increasing temperature.[274,279] The effect of modulation of the exchange interaction between the three unpaired electrons on the line width can be understood using exactly the same procedure as for the biradical problem. The static spin-Hamiltonian is now



XIV

$$\mathcal{H}^0 = g\beta H\sum_{i=1}^{3} S_z^{(i)} + a\sum_{i=1}^{3} I_z^{(i)}S_z^{(i)} + \bar{J}\sum_{i>j=1}^{3} S^{(i)}\cdot S^{(j)} \tag{11.13}$$

and the dynamic perturbation is

$$\mathcal{H}'(t) = \sum_{i>j=1}^{3}(J_{ij}(t) - \bar{J})S^{(i)}\cdot S^{(j)} \tag{11.14}$$

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[278] S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **47**, 1374 (1967).

[279] A. Hudson and G. R. Luckhurst, *Mol. Phys.*, **13**, 409 (1967).

The appropriate electron spin functions are a quartet (A) and two doublet (E) states. As before transitions with $m_1 = m_2 = m_3$ are not broadened by modulation of J, and these are the three lines observed at room temperature. All other doublet state transitions are broadened in zeroth order and are never seen. On the other hand, broadening of the quartet state transitions occurs through the first-order admixture by the hyperfine interaction of the E into the A state. The line widths are then a^2/J^2 less than for the doublets and are observed at high temperatures. The detailed line-width analysis[279] has confirmed the previous identification of the radical based largely on its mode of synthesis.[274]

B. INTERMOLECULAR

When measuring the spectrum of a radical in solution it is important, as every electron resonance spectroscopist knows, to work at low radical concentrations, and sometimes at low temperatures, in order to obtain sharp lines. If the radical concentration is progressively increased, the individual hyperfine lines begin to broaden until they collapse to a single line whose width decreases with further increase in concentration.[280] Similar effects are also produced by increasing the temperature of the sample. This phenomenon, known as concentration broadening, is consistent with relaxation by intermolecular spin exchange as first suggested by Pake and Tuttle.[281] Their model for the relaxation process is as follows. In dilute solutions radicals rarely collide, but as the concentration increases the probability of collisions also increases. During a collision the electrons experience a strong scalar coupling analogous to that discussed for biradicals in section XI.A. The effect of the perturbation $J(t)\, S_{\pm}^{(1)}S_{\mp}^{(2)}$ is to induce spin exchange during a collision and therefore limits the lifetime of a particular state leading to line broadening.

The line width resulting from spin exchange has been calculated using various techniques[3,9,128,282] including the Bloch equations.[283] The natural way of treating the problem would be to use the density matrix formalism discussed in section VI.[284,285] The rate equation for the elements of the density matrix for a single radical is

$$\dot{\rho}_1 = (Tr_2\rho_D - \rho_1)/\tau + i[\rho_1,\mathcal{H}_1] \qquad (11.15)$$

where τ is the time between collisions, $\mathcal{H}_1$ is the spin-Hamiltonian for the radical including the radiofrequency field, and Tr_2 indicates a trace over the states of radical 2 in the joint density matrix, ρ_D, for the two colliding radicals. The rate equation for ρ_D is

$$\dot{\rho}_D = (\rho_1 \times \rho_2 - \rho_D)/\tau_D + i[\rho_D,\mathcal{H}_D] \qquad (11.16)$$

where τ_D is the lifetime of the dimer and $\mathcal{H}_D$ is the sum of $\mathcal{H}_1$ and $\mathcal{H}_2$ together with the electron spin interaction $JS^{(1)}\cdot S^{(2)}$ but neglecting the radiofrequency field. We are therefore assuming that the exchange integral takes the value J during a collision, and is zero at all other times. This treatment of the problem is very similar to that used to explain relaxation effects resulting from triplet exciton collisions in crystals.[286]

In the absence of magnetic nuclei, spin exchange will only result in relaxation when the g factors for the colliding species are different. Under these conditions the exchange frequency is predicted to be field dependent,[287] although this dependence has yet to be observed. The next simplest problem involves exchange between radicals containing a single magnetic nucleus of spin $^1/_2$. Using simple product spin functions together together with eq 11.15 and 11.16, the widths of the two lines in the slow-exchange region ($a \gg W/2\tau$) are

$$T_2^{-1} = W/2\tau \qquad (11.17)$$

where W is $^1/_2\{(J\tau_D)^2/[1 + (J\tau_D)^2]\}$. This result was derived by assuming that the hyperfine interaction, a, is much less than J, and also that the product $a\tau_D$ is less than 1. This result differs by W from the line broadening caused by slow electron transfer (*cf.* section VI) and emphasizes that W is just the probability of spin exchange during a collision. In a strong collision when $J^2\tau^2_D \gg 1$ and spin exchange occurs many times throughout the lifetime of the dimer, W is just $^1/_2$. In the fast-exchange limit ($a \ll W/2\tau$), the width of the collapsed line is

$$T_2^{-1} = \pi^2a^2\tau/W \qquad (11.18)$$

Equation 11.18 is also analogous to that obtained for fast electron transfer in which the electron resonance frequency is modulated between $\omega_0 + a/2$ and $\omega_0 - a/2$. The line width resulting from this perturbation can be calculated using eq 3.7, but now the value of τ is the time between effective collisions, $2\tau/W$. The factor of 2 arises because the rate of collisions between radicals having different proton spin orientations is half the bimolecular collision frequency. These formulas are readily extended to radicals containing a single magnetic nucleus of spin I by calculating the fraction of effective collisions, and the extension to many magnetic nuclei is straightforward although tedious.[284]

To make any test or use of these results we require an expression for the time interval between radical collisions. For an ideal solution[245]

$$\tau = (N_S/zN_R)\tau_d \qquad (11.19)$$

where N_S and N_R are the number of moles of solvent and radical, respectively, per unit volume, z is the number of new neighbors encountered with each step, and τ_d^{-1} is the hopping frequency. According to the Stokes–Einstein equation

$$\tau_d = \frac{\pi r'\lambda^2}{k}\frac{\eta}{T} \qquad (11.20)$$

where r is the effective hydrodynamic radius for translation (not to be confused with r for rotation) and λ is the jump length for the random walk. At a given viscosity and temperature, the line broadening should be proportional to the radical concentration in the low-exchange region whereas the width of the collapsed line is inversely proportional to concentration. Several experimental studies have shown that this behavior is indeed observed.

Jones[283] has measured the line widths of peroxylamine disulfonate in aqueous solution and finds that they are proportional to the concentration up to 10^{-1} *M*. He implicitly

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assumes that every collision results in spin exchange ($J^2\tau_D^2 \gg 1$) and so eq 11.17 for a spin of 1 is

$$T_2^{-1} = 1/3\tau \qquad (11.21)$$

which is written as

$$T_2^{-1} = kN_R/N_S \qquad (11.22)$$

and he finds k to be 1.5×10^9 l. mole^{-1} sec^{-1}. Electron exchange also reduces the coupling constant,[288] and it is comforting to find that k calculated from the change in a is also about 10^9 l. mole^{-1} sec^{-1}. Because of the limited solubility of peroxylamine disulfonate, the measurements could not be extended to the fast-exchange region. This is also true for the naphthalenide radical dissolved in tetrahydrofuran.[154] The line width in the slow-exchange region is linear in concentration and yields rate constants of 2.8×10^9 l. mole^{-1} sec^{-1} at 20° and 1.1×10^9 l. mole^{-1} sec^{-1} at −60°. The effects of spin exchange have also been investigated for solutions of the biphenyl negative ion.[288]

The radical di-*t*-butyl nitroxide is extremely soluble in dimethylformamide, and the line widths have been measured over the complete range of exchange rates.[159] For slow exchange the widths of the three hyperfine components were linear in the radical concentration with k equal to 3.7×10^9 l. mole^{-1} sec^{-1}. The line shown in Figure 1 of ref 150 does in fact pass through the origin because a constant factor has been subtracted from the line width in an attempt to allow for unresolved hyperfine structure.[289] At about 0.06 *M* concentration of radical the three nitrogen hyperfine lines collapsed to a single line whose width decreased linearly with increasing concentration up to 0.3 *M*. The width of the single line can be found from eq 3.25 by assuming that the electron takes stochastically the values ω_0, $\omega_0 + a$, and $\omega_0 - a$ which gives

$$T_2^{-1} = {}^4/_3 a^2\tau \qquad (11.23)$$

The experimental slope gives a value of $k = 3.8 \times 10^9$ l. mole^{-1} sec^{-1} in excellent but possibly fortuitous agreement with the slow-exchange result. Further, the k calculated from the Smoluchowski equation for diffusion[290] is 4.1×10^9 l. mole^{-1} sec^{-1}, justifying the assumption that exchange does indeed occur at every effective collision.

At concentrations greater than 0.6 *M*, the line width begins to increase with increasing concentrations.[150] This increase is attributed to dipole–dipole relaxation caused by fluctuating local fields produced by neighboring radicals. Dipole–dipole broadening is said to be important in the spectra of manganese(II) ions both in aqueous solutions[291] and ionic melts.[292]

Miller and Adams[148] have extended their earlier measurements of bimolecular rate constants for electron exchange to the 1,4-benzoquinone anion, its tetramethyl derivative, and the nitrobenzene anion. The results for the charged species are about half that for neutral di-*t*-butyl nitroxide as expected. Whereas the rate constants for electron exchange are roughly constant, those for electron transfer vary markedly from one molecule to the next, presumably because of the geometrical requirements of electron transfer.

An alternative test of the theory is provided by the viscosity dependence of the line width, $T_2^{-1}(e)$, due to exchange, for according to eq 11.17, 11.19, and 11.20, $T_2^{-1}(e)$ is proportional to T/η in the slow-exchange region. The line widths of di-*t*-butyl nitroxide have been measured in propane and *n*-pentane as a function of temperature[293] and pressure[294] and attempts made to obtain $T_2^{-1}(e)$ from these. Whereas Plachy and Kivelson[293] corrected for (1) solvent vaporization, (2) spin-rotational relaxation, (3) unresolved hyperfine structure, and (4) the onset of strong spin exchange, Edelstein, *et al.*, only made the first correction.[294] However, the important point of both studies is that for low values of T/η the line width due to exchange is linear in T/η, but at higher values the width tends to a limiting value. This behavior is attributed by Edelstein, *et al.*, to a dependence of W on viscosity,[294] and they argue

$$W = \frac{1}{2}[1 - \exp(-J\tau_D)] \qquad (11.24)$$

Because τ_D also depends on T/η, they are able to fit their results, but the theoretical form of W does not agree with (11.24). On the other hand, Plachy and Kivelson[293] retain the theoretical form for W and suggest that the jump length λ will be density dependent. According to the hole theory of liquids, the dependence is

$$\lambda^3(T) = \lambda_0^3\rho_L(0)/\rho_L(T) \qquad (11.25)$$

where 0 refers to the solvent melting point. This function accounts for the experimental observations and would seem to be the more reasonable. According to the detailed analysis J is 10^4 MHz and Z is about 2.5, showing that a radical encounters two or three new neighbors per jump.

XII. Special Effects. Radicals with Degenerate Ground States

In dilute solutions where intermolecular effects are negligible, the line widths of most free radicals are almost entirely accounted for by the effects of anisotropic g and hyperfine tensors and by spin-rotational interactions. In certain highly symmetrical molecules, the line widths are not satisfactorily explained by these mechanisms. A well-known example is the spectrum of the benzene radical anion which has unusually broad lines.[295,296] A further characteristic property is that spin-lattice relaxation is enhanced compared with less symmetrical species, and the spectrum is not easily saturated. This type of behavior has been reported in a variety of highly symmetrical radicals including the coronene and triphenylene anions,[295] $C_6H_6^+$,[297] $C_6Me_6^+$,[298,299] $C_8H_8^-$,[158] $C_6(CF_3)_6^-$,[300] the coronene cation,[301] and C_7H_7.[302] The observed g factors are often anomalous.[303]

The fact that all these species have an orbitally degenerate

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ground state means that there is a possibility of a dynamic Jahn–Teller effect being operative. The vibronic problem in the benzene anion has been studied theoretically.[304] The vibronic ground state is doubly degenerate, and solvent interactions could lead to a time-dependent oscillation of the electron spin distribution relative to the molecular framework. However, a rapid exchange between distorted forms would lead to correlated fluctuations in the isotropic hyperfine interactions and an alternation in the line width from one hyperfine line to the next.[305] Experimentally it is found that all of the seven lines in the spectrum of $C_6H_6^-$ have the same width; this implies that for any switching process $\tau \leq 10^{-9}$ sec, and it cannot be the dominant mechanism.

The vibronic degeneracy also leads to an increased spin–orbit interaction, and when modulated by solvent collisions this could explain the enhanced spin–lattice relaxation.[306] A variety of similar "electric field fluctuation" mechanisms have been considered.[307] These are analogous to the mechanisms responsible for spin relaxation in crystals.[308] The crystal or molecular binding fields are modulated by molecular vibrations and collisions with solvent molecules and interact with the spin through spin–orbit coupling. These are all probably negligible at X band apart from the so-called Orbach process, which is relevant when the system has a low-lying excited state.[309] Solvent motion and spin–orbit coupling change both the spin and electronic states simultaneously.[309,310] This mechanism seems the most likely cause of the anomalous line broadening in the benzene and coronene anions, and in aqueous solutions of Cu^{2+}. The possibility that collisions in solution modulate the hyperfine coupling constants by changing the vibrational state has been considered.[311] Vibrational fluctuations in the isotropic hyperfine interaction in NO_2 probably give a contribution comparable to that from the g and hyperfine tensors.[312] However, the dominant mechanism is a spin-rotational interaction.[220,312]

A recent study of the 1,4-benzosemiquinone radical anion in the Zeeman region[313] has demonstrated the probable importance of Van Vleck second-order Raman processes in determining the line widths of low-field solution electron resonance spectra. Similar considerations apply to an early low-field investigation of the peroxylamine disulfonate ion[314] for which the field-independent contribution to the transition probabilities is[307] about 2×10^4 sec^{-1}. Further low-field studies are required to fully elucidate the importance of these mechanisms.

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