# ELECTRON SPIN RESONANCE

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## INTRODUCTION

Symons, in the last review of ESR in the *Annual Review of Physical Chemistry* (1), has already noted that the vast applications of ESR in the fields of chemistry, physics, and biology render it virtually impossible to attempt anything like a full coverage of the literature. I have, therefore, also adopted the approach of selecting topics that are primarily of interest to me, but have found that space and time limitations have made it necessary to reduce even these.

The main coverage given may be roughly described as the broad overlap region between the ESR of liquids and spin-relaxation phenomena. However, other topics directly or indirectly related (sometimes perhaps only by the author's imagination) are also included. I have emphasized more recent developments and some recent theoretical developments, including the new theoretical and experimental results on ESR spectra for slow tumbling radicals, rotational reorientation in liquids and solids, spin relaxation theory and line-width studies, ion pairs, the new phenomenon of chemically induced electron polarization (CIDEP), and the (probably) related old one of Heisenberg spin exchange, saturation and double resonance studies, liquid crystals, and finally gas phase ESR. The most recent detailed review of ESR relaxation in liquids has been given by Hudson & Luckhurst, who covered the literature through 1967 (2). The literature surveyed here covers primarily the period 1969 through 1971. Virtually no coverage has been given to the important applications in structural studies and hyperfine interactions, triplet states and triplet dynamics, radicals in (and adsorbed on) solids, and biological studies.

Part of the problem of dealing with the vast and growing literature in magnetic resonance may be alleviated by the appearance of a new quarterly journal *Magnetic Resonance Review* (3), which will survey this literature. In particular, Bolton has already covered the literature of 1970 for ESR in solution (4) and it will continue to be done.

Recent international activities in ESR include the second symposium on ESR spectroscopy at the University of Georgia, December 7–9, 1970 (5). NATO Summer School Lectures on ESR Relaxation in Liquids held in Norway in 1971 are to appear in book form (6) and are frequently referred to in this review.

A most important publication has been the book by Abragam & Bleaney (7), which provides very extensive coverage of ESR of transition ions and

discussions of many general aspects of ESR (7). Poole & Farach have written a book which reviews relaxation in magnetic resonance (8), and electron-spin relaxation in solids has been discussed by Standley & Vaughan (9). Recent introductory texts on ESR include the ample coverage by Bolton & Wertz (10) and a briefer one by Gerson (11). Discussions and reviews of the biological applications of ESR are given in several places (12–17). A review covering, in part, dynamical aspects of triplet state spectroscopy has appeared in last year's *Annual Review of Physical Chemistry* (18). A review of halogen hyperfine interactions has been given by Hudson & Root (19). Other reviews are referred to in the discussions of the relevant topics below

## LINESHAPES AND RELAXATION

*Theory of slow tumbling.*—An important recent development has been the successful theoretical analysis of ESR lineshapes in the slow or intermediate rotational regions. In these regions, the radical is tumbling too slowly for the earlier relaxation theories to apply, yet it is not slow enough for the spectrum to have approached its rigid limit. If we define $\mathscr{H}_1(t)$ as the rotational-dependent perturbation in the spin Hamiltonian and $\tau_R$ the rotational correlation time, then slow tumbling in magnetic resonance means the inequality $|\mathscr{H}_1(t)\tau_R| \ll 1$ is no longer fulfilled. As a result of the new developments, it is now possible to describe ESR lineshapes over the whole range of $\tau_R$ from the motional narrowing region ($|\mathscr{H}_1(t)\tau_R| \ll 1$) through the rigid limit.

The basic approach is, in principle, a simple generalization to the continuous-site problem of well-known techniques for handling spin-relaxation resulting from jump phenomena occurring between a finite number of sites (20). The solution to this whole class of problems is obtained by what may be called the stochastic Liouville method (21, 22) since it parallels the well-known classical generalization of Liouville's theorem to include Markoff processes (e.g. Brownian motion). That is, the density matrix equation of motion due to the random Hamiltonian $\mathscr{H}(t)$ obeys

$$\frac{\partial\rho}{\partial t} = -i[\mathscr{H}(t), \rho] \equiv -i\mathscr{H}(t)^{\times}\rho \qquad\qquad 1.$$

with $\mathscr{H}(t)^{\times}$ a Liouville operator. Now let the time dependence of $\mathscr{H}(t)$ be governed by a stationary Markoff process which modulates $\Omega$ the "orientations," so that

$$\frac{\partial}{\partial t} P(\Omega, t) = -\Gamma_\Omega P(\Omega, t) \qquad\qquad 2.$$

where $P(\Omega, t)$ is the probability of finding $\Omega$ at the particular state at time $t$ and $\Gamma_\Omega$ is a time-independent Markoff operator with equilibrium distribution $P_0(\Omega)$ obeying $\Gamma_\Omega P_0(\Omega) = 0$. One can then combine Eqs. 1 and 2 into an equation for $\rho(\Omega, t)$, i.e. the spin density matrix which includes the orientational dependence of the spin states. It may be written in the form

$$\frac{\partial}{\partial t} \rho(\Omega, t) = -i\mathscr{H}(\Omega)^{\times}\rho(\Omega, t) - P_0(\Omega)^{-1}\Gamma_\Omega[P_0(\Omega)\rho(\Omega, t)] \qquad\qquad 3.$$

One must then solve for appropriately averaged values, e.g.

$$\bar{\rho}(t) = \int P_0(\Omega)\rho(\Omega, t)\mathrm{d}\Omega$$

Note that for equal a priori probabilities, $P_0(\Omega)$ is a constant, so

$$P_0(\Omega)^{-1}\Gamma P_0(\Omega) = \Gamma$$

and this is the case for tumbling in isotropic liquids.[1]

Equation 3 or somewhat related forms have received either detailed justification or discussion by several authors (21–35). If there are a finite number of jump sites, then $\Gamma_\Omega$ is simply a transition probability matrix. Equation 3 then becomes the coupled set of equations

$$\frac{\partial\rho^i}{\partial t} = -i\mathcal{H}(\Omega_i)^\times \rho^i + \sum_j W_{ji}\rho^j P_{0j}/P_0 \qquad 4.$$

in terms of the transition probabilities $W_{ji}$ and we have written $\rho^i$ for the density matrix of the $i$th jump site. Equation 4 is a well-known expression in magnetic resonance, and it is the quantum mechanical generalization of the modified Bloch equations (20).[2] Usually one can write $\mathcal{H}(\Omega) = \mathcal{H}_0 + \mathcal{H}_1(\Omega_i)$, where $\mathcal{H}_0$ is independent of $\Omega_i$. Then if $[\mathcal{H}_0, \mathcal{H}_1(\Omega_i)] = 0$, so that Eq. 3 can be immediately analyzed in terms of the spin eigenfunctions of $\mathcal{H}_0$ (this condition specifies what is known as the secular case), then there is an *exact* equivalence between Eq. 4 and writing modified Bloch equations for each distinct resonance line [cf Eq. 40 or 48 of (20)].

Now, if we suppose

$$-\Gamma_\Omega = R\nabla_\Omega^2 \qquad 5.$$

where $\nabla_\Omega^2$ is the rotational diffusion operator and $R$ is the rotational diffusion coefficient, then there is a continuous range of values of the Euler angles denoted by $\Omega$. Clearly, one method of solution would be to approximate the continuous range of $\Omega$ by a discrete number of grid points in $\Omega$ exactly in the manner used for calculating polycrystalline spectra. This finite difference method could then be represented by Eq. 4 and then solved as one would any finite jump problem. That is

$$R\nabla_\Omega^2 \to W(\Omega_m, \Omega_n) \qquad 6.$$

where $W(\Omega_m, \Omega_n)$ is now a transition-probability matrix whose elements $W_{mn}$ give the transition probability between the $m$th and $n$th discrete values of $\Omega$.

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[1] Note, however, that one can always write the last term in Eq. 3 simply as $\Gamma_\Omega\rho(\Omega, t)$ provided one adopts the averaging convention of postmultiplying by $P_0(\Omega)$ and then integrating so that, e.g. $\bar{\rho}(t) = \int \{\rho(\Omega, t)P_0(\Omega)\}\mathrm{d}\Omega$. In this convention, all integrations over $\Omega$ must also involve this averaging (21–24).

[2] Note that the matrix of $W_{ji}$ can generate spin-dependent transitions if $\rho^j$ is evaluated in a basis set of spin eigenfunctions dependent on the parameter $j$. This gives rise to nonadiabatic effects (see below and 25).

Brownian rotational diffusion is, in this case, equivalent to jumps between grid points of $\Omega_m$ and $\Omega_n$ adjacent on the unit sphere. One must take a sufficiently large number of orientational grid points to make this method converge to an accurate solution (see 26, 27, 33, 35).

Another powerful method for solving Eq. 3 is to expand the steady state solution

$$Z(\Omega) \equiv \rho(\Omega, t)e^{-i\omega t} \qquad 7.$$

(i.e. the steady state density matrix in the rotating frame) in a complete set of orthogonal functions in $\Omega$, ideally (but not necessarily) the eigenfunctions of the operator $\Gamma_\Omega$. For rotational diffusion, the eigenfunctions of $\nabla_\Omega^2$ are given by the Wigner rotation matrices (or generalized spherical harmonics) $\mathscr{D}_{K,M}{}^{(L)}(\Omega)$.[3]

That is, the operation $\Gamma_\Omega \mathscr{D}_{K,M}{}^L(\Omega) = L(L+1)R\mathscr{D}_{K,M}{}^L(\Omega)$. In general, if we let $G_n(\Omega)$ represent a complete orthogonal set for which $\Gamma G_m = E_m G_m$ with $E_0 = 0$, then the expansion is

$$Z(\Omega) = \sum_n C_n(\omega)G_n(\omega) \qquad 8.$$

and one obtains in the absence of saturation and for isotropic liquids (by premultiplying Eq. 3 by $G_m{}^*(\Omega)$ and integrating over $\Omega$ after substituting in Eqs. 7 and 8) the result:

$$[(\omega + \mathscr{H}_0{}^\times) - iE_m][C_m] + N_m{}^{-1}\sum_n \int d\Omega G_m{}^*(\Omega)G_n(\Omega)\mathscr{H}_1(\Omega)^\times[C_n]$$
$$= \tfrac{1}{2}\omega_1[S_-, \rho_0]\delta_{m,0} \qquad 9.$$

Here $C_m$ is still an operator in spin space and $\rho_0$ is the equilibrium spin-density matrix which is assumed to be essentially dependent only on $\mathscr{H}_0$ [i.e. $|\mathscr{H}_0| \gg \mathscr{H}_1(\Omega)$].[4] The steady state spectrum is simply the average

$$\bar{Z} \equiv \int d\Omega P_0(\Omega)Z(\Omega, \omega) = C_0(\omega) \qquad 10.$$

In the secular case ($[\mathscr{H}_0, \mathscr{H}_1(\Omega)] = 0$) Eqs. 3 and 9 may be rewritten as a modified Bloch equation for a particular line by making the replacements

$$Z \to \tilde{M}_+ = \tilde{M}_x + i\tilde{M}_y \qquad 11.$$

and

$$[S_-, \rho_0] \to 2M_0 \qquad 11a.$$

where $\tilde{M}_x$ and $\tilde{M}_y$ are the rotating magnetization components and $M_0$ is the equilibrium magnetization. The expansion coefficients $C_m$ are now simply

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[3] For simpler problems (e.g. axially symmetric magnetic parameters) it is sufficient to use the spherical harmonics $Y_M{}^L(\theta, \varphi)$. It is often useful to use the normalized functions $\sqrt{[(2L+1)/8\pi^2]}\mathscr{D}_{K,M}{}^L(\Omega)$.

[4] Note that $\omega_1 \equiv \gamma_e H_1$, $S_-$ is the electron-spin lowering operator, and $N_m = \int d\Omega G_m{}^*(\Omega)G_m(\Omega)$ is a normalizing factor.

functions and not spin operators, and $\mathscr{H}_1(\Omega)^\times$ becomes simply a function of $\Omega$ (i.e. just the orientation-dependent contribution to the resonance frequency). Suppose one has a simple line with average $g$ value, and axially symmetric $g$ tensor with components $g_\parallel$ and $g_\perp$. If we let

$$\mathscr{F} = \tfrac{2}{3}\hbar^{-1}\beta_e B_0(g_\parallel - g_\perp)$$

then Eq. 9 becomes

$$[(\omega - \omega_0) - iRL(L + 1)]C_{0,0}{}^L(\omega) - (2L + 1)\mathscr{F} \sum_{L'} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 C_{0,0}{}^{L'}(\omega)$$
$$= \omega_1 M_0 \delta_{L,0} \quad 12.$$

where the $C_{0,0}{}^L$ are the coefficients in an expansion in $\mathscr{D}_{KM}{}^L(\Omega)$ and the $3j$ symbols (closely related to the Clebsh-Gordan coefficients) have been used (29). Equation 12 shows how the perturbation $\mathscr{H}_1(\Omega)$ couples $C_{0,0}{}^0(\omega)$ to the other coefficients generating an infinite set of coupled algebraic equations. One must terminate after a finite number of terms to make the method tractable. One finds that this depends largely on the magnitude of the ratio $r = |\mathscr{H}_1(\Omega)/R|$. Thus for Brownian rotational diffusion and $r \lesssim 100$ only about 3 or 4 terms are sufficient and for larger values of $r$ the number of terms goes as $r^{1/2}$ (29, 30, 33, 34). We note that the results of ordinary spin relaxation theory are readily obtained from just the first two terms.

When, however, $[\mathscr{H}_1(\Omega), \mathscr{H}_0] \neq 0$, Eqs. 3, 4, or 9 cannot generally be reduced to modified Bloch equations. The quantum mechanical coupling of different (motional narrowing) resonance lines becomes important. (These coupling terms in $\mathscr{H}_1(\Omega)$ are known as pseudosecular.) These effects and the appropriate analysis needed have been discussed in detail (29, 30) for the eigenfunction expansion method, dealing particularly with nitroxide radical-type spectra, and giving results valid over the whole tumbling region. Recent analysis of nitroxide spectra from an equivalent point of view has yielded very similar results (33).

A treatment of nitroxides (36–38) uses an interesting approximation: the "adiabatic" approximation, in conjunction with eigenfunction expansions. They first diagonalize $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1(\Omega)$ as a function of orientation $\Omega$, which yields orientation-dependent energies (or transition frequencies) and eigenvectors. The nuclear spin $I$ is assumed to be quantized by its interaction with the electron spin $S$, since the nuclear Zeeman energy is small. Then a separate resonance line is assumed to arise for each of the three values of $I_z = 0, \pm 1$, i.e. the rotational motion does not change the value of $I_z$ even though the quantization axis is orientation dependent. This is the "adiabatic" approximation, which reduces the problem to that of the secular case analogous to Eq. 12, although the integral in Eq. 11 is now over a complicated function of $\theta$ (37, 38 use axially symmetric parameters) whose integrated values with the $\mathscr{D}_{KM}{}^L$ are no longer simple. They therefore approximate it by a simpler function. (Their theoretical analysis is different from the discussion based on Eq. 3 but appears to be equivalent in the secular case.) However, as the motion becomes more

rapid, we would expect that it can induce transitions between different values of $I_z$, since the axis of quantization is not a constant of this motion. Formally, we note that if spin matrix elements of Eq. 3 are taken which diagonalize $\mathcal{H}(\Omega)$, then $\Gamma_\Omega$ now becomes an operator on these spin functions by virtue of their orientation dependence, and these spin functions are not diagonal in $\Gamma_\Omega$. The condition $\tau_R \gg (A_z - A_\perp)/A_\perp^2$ has been given for the validity of the adiabatic approximation for Brownian motion, but this condition has not been tested. Very recently McConnell and co-workers (39) have used this "adiabatic" approximation for nitroxides, but they use the finite difference method, as well as the Bloch equation analogue of Eq. 4, since the problem has been reduced to a secular one as already noted. While they need not approximate any orientation-dependent frequency terms by using the finite difference method their approach is again limited by the neglect of "nonadiabatic" effects.

Freed et al (29) have also used Eq. 3 [for $P_0(\Omega)$ a constant] to analyze saturation effects in the case of a simple line with $g$ tensor line broadening. They find that significant lineshape changes resulting from saturation are dependent on the rotational diffusion rates and the nature of the $T_1$ mechanism. To guarantee relaxation of the spins to thermal equilibrium, these authors found it necessary to introduce an ad hoc assumption somewhat like that used in semiclassical relaxation theory. This assumption is equivalent to replacing $\Gamma_\Omega\rho(\Omega, t)$ in Eq. 3 written for isotropic liquids ($P_0(\Omega)$ a constant) by $\Gamma_\Omega[\rho(\Omega, t) - \rho_0(\Omega)]$ where

$$\rho_0(\Omega) \equiv e^{-\hbar\mathcal{H}(\Omega)/kT}/Tre^{-\hbar\mathcal{H}(\Omega)/kT} \qquad 13.$$

is then written for high temperatures, i.e. $\hbar\mathcal{H}(\Omega)/kT \ll 1$.

While Eq. 3 is very useful in many cases, the situation when $\mathcal{H}_1(\Omega)$ is not small compared to $\mathcal{H}_0$ cannot simply be treated in this manner. This is the case e.g. for triplets with zero field splittings (zfs) of the order of the Zeeman energy. High field approximations are no longer valid, and one encounters the quantum mechanical analog of the problem of modifying the Bloch equations for low fields (40). However, by means of a linear response approach, sound descriptions of the lineshapes can be obtained without such difficulties. Equation 3 is replaced by the equivalent expression for the time-dependent spin operator $S_x(t)$

$$\frac{\partial}{\partial t} S_x(\Omega, t) = i\mathcal{H}(\Omega)^\times S_x(\Omega, t) - P_0(\Omega)^{-1}\Gamma_\Omega P_0(\Omega)S_x(\Omega, t) \qquad 14.$$

subject to the initial condition

$$S_x(\Omega, 0) = S_x(0) \qquad 15.$$

The Fourier-Laplace transform of Eqs. 14 and 15 then yields

$$[\pm i\omega - i\mathcal{H}^\times + P_0(\Omega)^{-1}\Gamma_\Omega P_0(\Omega)]S_x(\Omega, \pm i\omega) = S_x(0) \qquad 16.$$

where

$$S_x(\Omega, \pm i\omega) = \int_0^\infty e^{\mp i\omega t}S_x(\Omega, t)dt$$

Then the absorption due to a weak *linearly polarized* rf field is given in the high temperature approximation by

$$I(\omega) \propto ReTr[\{\bar{S}_x(i\omega) + \bar{S}_x(-i\omega)\}S_x(0)] \qquad 17.$$

with

$$\bar{S}_x(\pm i\omega) = \int d\Omega P_0(\Omega)S_x(\Omega, \pm i\omega) \qquad 18.$$

The method of solution of Eq. 16 is virtually the same as that for the steady state solutions to Eq. 3. One has the choice of finite difference or eigenfunction expansion methods. The latter method has been used by Freed et al (30) to analyze triplet lineshapes and slow tumbling in isotropic liquids for high, low, and zero Zeeman fields. The linear response approach has also been used to analyze doublet lineshapes (26, 27, 33).

Roberts & Lynden-Bell (31), who report preliminary calculations on tumbling triplets for a strong collision model (see below), chose to deal with the problems with Eq. 3 by introducing the ad hoc assumption $\Gamma_\Omega \rho(\Omega, t) \rightarrow \Gamma_\Omega[\rho(\Omega, t) - \rho_0(\Omega)]$ already noted. However, to get complete correspondence with linear response theory in the absence of saturation, it would be necessary to redefine $\rho_0(\Omega)$ of Eq. 13 in terms of an $\mathcal{H}(\Omega) = \mathcal{H}_0 + \mathcal{H}_1(\Omega) + \epsilon(t)$, where $\epsilon(t)$ is the interaction of the spin with the rf field. This is equivalent to the assumption of relaxation to equilibrium at the instantaneous value of the applied field. Note, however, in high fields, where $|\mathcal{H}_0| \gg |\mathcal{H}_1(\Omega)|, |\epsilon(t)|$, such considerations are not important except for saturation effects, where they have not yet been rigorously proven for slow motion.

Symmetry considerations for the combined Liouville space of spins and orientations (32) have proved very useful in particular for zero-field spectra of triplets.

Pietrzak & Wood (41) have used Itzkowitz's earlier Monte Carlo method (42) to study hindered motions of radicals adsorbed in synthetic zeolites. Itzkowitz's method is based on the adiabatic approximation, but it suffers for not having a means to *explicitly* include the dynamics of the motion. Saunders & Johnson (43) have, however, explicitly included the dynamics in the purely secular case using a Monte Carlo approach. They encounter difficulties with the numerical solutions, but Pedersen (44) has recently resolved these difficulties and has treated the case of a slowly tumbling nitroxide in the adiabatic approximation, although the method can be extended to include nonsecular terms.

Thus, much of the basic theoretical formulation for slow motional effects has been developed. The remaining problems tend to be that of obtaining viable mathematical and numerical solutions in more complex cases. A very rapid computer method has been developed (33) for diagonalizing complex symmetric matrices which should have wide applicability.

*Experiments on slow tumbling and on rotational reorientation.*—Norris & Weissman (35) studied the $\Delta m = 1$ slow motional spectra of several triplets,

including monoanion pairs chelated to metal ions and dianions of symmetrical
aromatic hydrocarbons dissolved in glasses of 2-methyltetrahydrofuran. Since
$D$, the zfs was small enough, they could use the secular approximation. They
found good agreement between calculated and observed results once the large
superimposed monoradical peak is subtracted out of the observed results.
From diffusional rate constants varying over two orders of magnitude, they
could obtain activation energies which were typically ca 3 kcal/mole, or of the
order of those expected for normal viscosity activation energies. Their results
are given for Brownian reorientation, since they report that other mechanisms,
e.g. strong collisions, do not yield predictions consistent with their observed
spectra.

Goldman et al (45) report a detailed study of the "nitroxide radical"
peroxylamine disulfonate (PADS) dissolved in 85% glycerol and also in a
presumed clathrate cage in frozen water. In both cases it was possible to
explore the whole range of tumbling from motional narrowing, where relaxa-
tion theory applies, through to the rigid limit spectra without any phase
changes. The magnetic parameters obtained from the rigid limit spectra could
then be utilized for the motional results. Careful analysis of the motional
narrowing results leads to the conclusions that 1. rotational motion is aniso-
tropic with faster rotation about the molecular axis perpendicular to both the
N–O bond axis and the axis of the N–O $2p$-$\pi$ orbital; diffusion about this axis
is 2.9 ± 1 and 4.7 ± 1 times faster for frozen water and glycerol respectively.
2. activation energies of 14.7 ± 0.1 and 11.3 ± 0.1 kcal/mole respectively
were obtained in the two solvents; the value for frozen water is very close to
that of other transport processes in ice such as dielectric relaxation and isotope
diffusion, although the latter have preexponential factors about $10^6$ times
smaller than the rate of reorientation of PADS. Analysis of the slow motional
spectra showed rather poor agreement between calculated and observed
spectra in certain regions of the spectrum, although good agreement was
obtained in other portions. Analysis of these results in terms of different
reorientational models showed very markedly improved agreement by using
models of reorientation including either inertial effects in an approximate
manner or jumps with moderate (not small) average jump angle. General
models of these types can be incorporated by minor modifications of the
Brownian motional equations, when the eigenfunction expansion method (Eqs.
8 and 9) is employed by simply introducing a "model parameter" $B_L$ such that

$$R\Gamma_\Omega \mathscr{D}_{KM}{}^L(\Omega) = B_L L(L + 1) R \mathscr{D}_{KM}{}^L(\Omega) \qquad 19.$$

where $B_L = 1$ for Brownian diffusion, but becomes a function of $L$ for the
other models, in general reducing the overall $L$ dependence of the eigenvalues
of Eq. 19. Note that $\tau_R$ is defined for $L = 2$ and for Brownian diffusion is
$\tau_R^{-1} = 6R$. A simple expression including anisotropic reorientation based on
Eq. 19 for different models was used to show that introduction of anisotropic
reorientation into the simulated spectra also leads to improved agreement with
the observed spectra. [Sillescu (26, 27) has discussed some non-Brownian

models from the point of view of the finite difference method, e.g. Eq. 4, and strong collision models have been employed in a relatively simple approach for triplets (31) and for an $N^{15}$ labelled nitroxide (46).]

Another demonstration of the existence of significant deviations from Brownian reorientation in (45) was the fact that the correlation times extrapolated from motional narrowing results in frozen water were in agreement with those obtained for the best non-Brownian models and not for a Brownian model. An interesting comparison to these results is obtained from recent work (39) on aqueous solutions of spin-labeled oxyhemoglobin which is known to undergo isotropic Brownian diffusion by virtue of its macromolecular size and isotropic overall shape. The spectral features found to be model sensitive (45) are, in the case of oxyhemoglobin, clearly characteristic of Brownian motion and distinctly different from those for the non-Brownian models. McConnell et al (39) discuss some general aspects for easily obtaining values of $\tau_R$ for slow tumbling spin-labeled macromolecules. Goldman et al (47) discuss similar aspects including model dependence and anisotropic motion as well. Kuznetsov et al (48) give a preliminary report of results on two nitroxide radicals in glycerol solvent over the fast through slow motional region. Note, however, that Poggi & Johnson (49) in their analysis of factors involved in the determination of rotational correlation times in the motional narrowing region for spin labels show that consistent values for $\tau_R$ and its activation energy can be obtained only if 1. the nitroxide magnetic parameters are determined separately for *each* radical-solvent system and 2. proper linewidth corrections are made to account for inhomogeneous broadening due to unresolved proton hyperfine structure. They do not, however, consider possible effects of anisotropic diffusion nor do they actually measure any of the $g$-tensor parameters. Wasserman et al (50) have analyzed linewidth studies on several nitroxides in different solvents in terms of anisotropic diffusion, obtaining intriguing results, but they do not appear to make the corrections which Poggi and Johnson found to be important.

Other work (51) has described the microwave power saturation characteristics of flavin radical spectra in the slow tumbling region. Hubbell & McConnell (52) have used an analysis based on Itzkowitz's method for the spectra obtained from spin-labeled phospholipids and membranes.

It should be evident from this discussion that studies of slow motional ESR spectra have considerable potential for yielding detailed information on the microscopic features of molecular reorientational processes in liquids.

As a postscript to this discussion of slow motional and anisotropic rotational effects, we note that Goldman et al also report preliminary results in the rapid narrowing region where $|\omega_0\tau_R| \sim 1$. In this region, proper analysis of the linewidths yields spectral densities of the correlation function for reorientation: i.e.

$$j(\omega) = \tfrac{1}{2}\int_{-\infty}^{\infty} e^{-i\omega\tau}\langle\mathscr{D}_{KM}^{(2)*}(t)\mathscr{D}_{KM}^{2}(t-\tau)\rangle/N_{\mathscr{Z}}d\tau \qquad 20.$$

While secular and pseudosecular terms involve $j(0) \equiv \tau_R$ or the integral of the correlation function, $j(\omega_0)$ is sensitive to the shorter time behavior ($t \sim \omega_0^{-1} = 1.7 \times 10^{-11}$ sec at $X$ band). Significant deviations from the Debye spectral density $j(\omega_0) = \tau_R/(1 + \omega_0^2\tau_R^2)$ were observed by Goldman et al, which suggests that perhaps short time, nondiffusive aspects of the reorientation might be manifested. Such short time features could include, for example, inertial effects to which the slow tumbling spectra would be sensitive.

*Rotational motion in solids and quantum effects.*—The (hindered) rotational reorientation of radical impurities in solids is a fairly common observation, and the slow tumbling analysis should be applicable to many such cases. Recent reports of such motions include CN (53), $CH_3$ (54), $NO_2$ (55–58), $NH_2$ (59), $CO_2^-$ (60), $CO_3^-$ (61), $ClO_2$ (62), $NH_3^+$ (63), $HNO_2^-$ (64), $HBO^-$ (65), $BO_3^-$ (65), $CH_2CO_2^-$ (66, 67), and for the metallic species $VO^{2+}$ (68–70), and $GeCl_3$ (71). Relatively free rotation is also observed in radicals trapped in an adamantane matrix (72–74). Studies on these types of systems, e.g. $NO_2$ and $CO_2^-$, tend to point up the importance of preferred orientations (and axes of orientation) between which random jumps are occurring, a feature which is less evident, though probably not unimportant, in spectra obtained in liquids.

As one considers the motion of smaller units, and as the temperatures are reduced, then quantum effects become important in the rotational motion. This has already been established for the case of internal rotation of methyl groups in radicals of type $CH_3-\dot{C}R_2$; more recent reports have been published (75–78). The basic model (79) in the static limit (at liquid helium temperatures) is 1. that the Pauli exclusion principle applied to the methyl protons places limitations on the symmetry of the product of nuclear spin functions and the internal rotational (or torsional) functions; and 2. the hyperfine interaction in the Hamiltonian for the three protons, which is an operator both in spin and internal rotational space, is nondiagonal in such a representation, so that the hyperfine pattern is distinctly different from the classical case. While the original analysis (79) included only the isotropic hyperfine terms (for simplicity), which was successful in several cases (80–83), Davidson & Miyagawa (77) found that for the radical $CH_3\dot{C}HR$ from L-alanine, the anisotropic hyperfine term was important and had to be included in the analysis, although the basic model (79) is the same.

Another matter of interest is how the quantum-type of hyperfine pattern changes into the typical $1:3:3:1$ pattern as the sample is warmed. A description based on a simple Boltzmann average over all torsional states (83) has been criticized (75) in terms of inconsistencies in the required barrier heights and torsional splittings and in the dramatic spectral changes they observe in the intermediate region. Clough & Poldy first introduced a classical "excitation over the barrier" model (75) to give a classical two-jump averaging of the spins in the lowest doubly degenerate torsional level. To account for some of their observations they later introduce (76) a "tunneling frequency modulation" mechanism by the ad hoc assumptions that, even at low temperatures, vibra-

tional modes affecting the methyl group permutation symmetry are not necessarily in the ground states and transitions between such states are important, thus allowing mixing of states of different spin symmetry. The basic dynamic model given earlier (79) is capable of explaining the observations in a simple and consistent manner without recourse to any of the unrealistic requirements of the Clough models. The Freed model (79, 84, 85) merely assumes that the torsional levels are increasingly broadened by thermal interactions as the temperature is raised. The nature of the spectrum then changes between its static and averaged appearance when the widths associated with torsional levels are comparable to hyperfine interactions. It is even possible to get mixing of hyperfine lines of different nuclear spin symmetry when, for example, 1. the torsional splitting is small or 2. the thermal broadening of the torsional levels is largely secular (i.e. fluctuations in energy) as opposed to nonsecular (i.e. uncertainty in lifetime) (79, 84, 85). General theoretical techniques for dealing with spin relaxation via quantum molecular levels have been reviewed (85).

Recent work on $NO_2$ at 2°K (58) has demonstrated that it is involved in uniaxial hindered rotation, which must be treated quantum mechanically, and the tunneling splitting is estimated to be about 3 cm$^{-1}$. In this work in a solid matrix, it was nevertheless necessary to introduce a spin-rotational interaction referred to the axis of rotation to explain the results. Because the two equivalent oxygen atoms are spinless, there are no Pauli principle constraints on thermal excitations amongst the different torsional levels. In the case of $N_2^-$, however, recent work demonstrates the important role of the exclusion principle (86).

An interesting example of motional effects in solids is provided by recent studies on the $CH_2$ radical (87–92). This radical is of particular interest because it is the smallest polyatomic triplet state. For this bent molecule, motion about an axis parallel to the H–H line is largely free (87, 88), and at 4°K only the lowest rotational state is populated. Deuterium substitution (88, 90), which increases the moment of inertia, reduces the partial quantum mechanical averaging of the zfs terms.

*Hindered internal rotations in liquids.*—The study of hindered internal rotations in liquids by means of alternating linewidth effects is now utilized extensively. Sullivan & Bolton (93) have reviewed the alternating linewidth phenomenon and its applications. Kochi & Krusic (94) have in part reviewed hindered internal rotation in alkyl radicals determined either by line broadening or by the temperature dependence of the hyperfine interactions. We include a number of recent references to the applications of the linewidth and hyperfine-interaction procedures to hindered internal rotations (95–113).

*Linewidths and G values.*—Segal et al (114) describe a comprehensive study of linewidths of the ESR spectra of dilute solutions of the naphthalene, anthracene, and tetracene radical anions and tetracene cation to test the Freed-Fraenkel theory (114a). While they were able to achieve qualitative

agreement between the experimental linewidth parameters and those calculated based on anisotropic $g$-tensor and electron-nuclear dipolar (END) interactions, the quantitative agreement is not satisfactory. They show that these discrepancies are not accounted for by uncertainties in the exact spin-density distributions nor of the detailed form of the atomic orbital function used for the unpaired electron. In fact they find that the calculated ratios of linewidth parameters are relatively insensitive to changes in spin density. The calculations indicate that both anisotropic rotational motion and isotropic hyperfine fluctuations may make significant contributions to the linewidths, though neither factor alone is sufficient to explain the observed values.

Ahn & Johnson (115) have performed a detailed linewidth study of the N,N'-dimethylpyrazine cation over a range of temperatures. They analyze their results using estimated values of the anisotropic dipolar interactions (including those for the methyl groups), and they also consider isotropic hfs modulation through ion-pair association-dissociation reactions. They found that the observed linewidth variations are mainly due to the anisotropic interactions.

Fassaert & De Boer (116) have performed careful linewidth studies on the positive and negative ions of anthracene, tetracene, and perylene to test the prediction from Stone's theory that the difference between the in-plane $g$-tensors components for positive and negative ions of even-alternant molecules (made up of six-membered rings) is equal in magnitude but opposite in sign for both ions. The theoretical analysis of the results, similar to (114), does indeed show the expected change in sign in all three cases, even though quantitative discrepancies exist. Further progress in this area seems to require the development of experimental techniques for measuring magnetic parameters of hydrocarbon radicals. In this connection Owen & Vincow (117) have extended the computer simulation of polycrystalline spectra to handle the cases of cations of naphthalene, anthracene, and perylene, but their primary objective was to extract out the isotropic hyperfine terms by using approximations to the $g$ and dipolar tensors.

In work on $g$ values Goldberg & Bard (118) report an anomalously low value for the $g$ factor of the diphenyl diacetylene anion and offer as a tentative explanation that the phenyl groups exert a perturbation to alter the degeneracy of the acetylene and the $g$ values have contributions from the orthogonal (to the $\pi$ system) carbon $p$ orbitals. Solvent effects on the $g$ factors of semiquinones have been analyzed (119) by relating the solvent effect theory (120) to solvation of the O atoms and then utilizing Stone's equation for $g$ factors. Allendoerfer (121) has pointed out a correction to the method of determining absolute $g$ values (122), which amounts to lowering these $g$ values by $14 \times 10^{-6}$. De Montgolfier & Harriman (123) have made a theoretical study of the $g$ tensor in one-electron systems. They find that 1. LCAO results are not very good, 2. neglect of multicenter terms is very dangerous, and 3. one cannot use a single value for the spin-orbit coupling parameter for different orbitals on the same atom.

Luckhurst & Pedulli (124) have considered in some detail the analysis of line broadening in the spectra of biradicals. While at high temperatures the dominant relaxation process is modulation of the exchange interaction $J$, at reduced temperatures the rotational modulation of the anisotropic magnetic parameters is dominant. In their treatment of the latter, they show that the results are very sensitive to the ratio $J/a$, the sign of $J$, and the dependence of the zfs on the interelectron separations and the relative orientations of the interacting monomers. The analysis is applied to a stable nitroxide biradical. In an earlier analysis of the higher temperature spectra of this radical, these authors attribute the increasing widths with increasing temperature to the existence of different configurations with different Boltzmann factors and $J$ values (125). The possible importance of linewidth effects from modulation of $J$ is noted by these authors (126) in a criticism of the report by Ferruti et al (127) which discusses the effects on $J$ of ionizing or neutralizing polar groups contained in flexible biradicals. The analysis of spectra for a proposed vanadyl tartrate dimer in terms of rotational averagings of the zfs was shown to be consistent with the dimer having the same structure in both liquid and solid phases (128, 129).

*Spin rotation.*—Spin rotational relaxation is of considerable interest because it directly reflects the angular momentum correlation function of the free radical. Burlamacchi (130) has shown that the linewidth of $SO_2^-$ is linear in $T/\eta$ for water solution and for different aqueous and glycerol solutions. Here $\eta$ is the viscosity. This is given as strong evidence for the spin-rotational mechanism being dominant. However, an unexplained $T/\eta$-independent width of 0.5 G is also observed. Similar observations on aqueous solutions of PADS have been made (131), viz a linear fit of the linewidths to the form $AT/\eta + B$, with $B = 97$ mG, and a comparison with the results from rotational reorientation is given. Burlamacchi & Romanelli (132) report a study which extends the earlier work of McClung & Kivelson (133) on spin relaxation in the $ClO_2$ radical. It is shown in the latter that, while spin rotation is dominant in nonviscous liquids, it is necessary to consider the effects of precessions (i.e. the contributions from free, nondiffusive motions as well as reorientations of the diffusive axis) to account for the nonlinearities of the linewidth in $T/\eta$. They introduce the adjustable parameter $\kappa$ ($0 < \kappa \leq 1$ and $\kappa = r^3/r_0^3$) where $r_0$ is the diffusional hydrodynamic radius obtained from diffusion measurements and $r$ is the rotational hydrodynamic radius from the ESR results assuming a Stokes-Einstein relation for $\tau_R$, which is a measure of the anisotropy of the intermolecular potentials in their analysis. Burlamacchi & Romanelli (132) obtained results on $ClO_2$ in a solvent whose high temperature linewidths are dominated by spin rotation, but at low temperatures by anisotropic interactions modulated by rotational tumbling. They obtain $\kappa = 0.07$ and $0.126$ instead of expected equal values from the analysis of the high and low temperature results respectively. However, they neither consider nor rule out nuclear quadrupole contributions, their low temperature spectral fit might be

improved, and there may be another high temperature mechanism present. A study on $ClO_2$ and $SO_2^-$ yielded results similar to the others; but on the basis of the greater sensitivity of $SO_2^-$ to the addition of $t$-butyl alcohol, it was postulated that $SO_2^-$ participates directly into the structural network of the water molecules, while $ClO_2$ tends to be enclathrated by water. Gilbert et al (135) find that the phenoselenazine cation has an appreciable spin-rotational contribution to the linewidth at room temperature.

The theoretical implications of the parameter $\kappa$ have been explored in detail (136). McClung (137) has applied an extended diffusion model, which embodies as opposite limiting cases Brownian diffusion and the free rotor, to spherical-top molecules and their spin-rotational relaxation. Freed (138) has recently shown that in a one-dimensional Brownian diffusion model, the zero-frequency spectral density $J(0)$ from the combined angular momentum-orientational correlation functions, which appear in the theory of spin-rotational relaxation, is identically zero, in marked contrast to the assumptions of the Hubbard (139) theory for three dimensions. The topic of spin-rotational relaxation in ESR has been recently reviewed by Atkins (140).

*Linewidths of metallic ions in solution.*—Hudson & Luckhurst (141) have discussed in detail the factors determining ESR linewidths of $^6S$ state ions in solution in terms of an analysis of the relaxation matrix for rotational modulation of the zfs and discuss the importance of solvent-induced fluctuations in zero-field splitting for relaxation especially for $Mn^{2+}$ ions. This is important because the zfs is zero for an undistorted octahedral environment. This topic of $^6S$ state ions has recently been reviewed (142). For $Mn^{2+}$ ion spectra at low temperatures, only the $|\tfrac{1}{2}\rangle \rightarrow |-\tfrac{1}{2}\rangle$ transition may be observed (143), and this plus the linewidth variations was explained (144) in terms of (141) by noting that this transition is usually broadened mainly by nonsecular spectral density terms $J_n(\omega_0) = \tau/(1 + n^2\omega_0^2\tau^2)$, which are very small at reduced temperature, while the secular terms are only weakly mixed in by corrections to high field spin functions (of order $a^2/\omega_0^2$). At room temperatures all five ESR transitions are observed, and the full relaxation matrix must be diagonalized but explicitly including the differences in resonant field (due to second order corrections in $a/\omega_0$) for each transition (142, 145). That is, one must diagonalize the complex non-Hermitian matrix: $i\omega_{\alpha\alpha'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} + R_{\alpha\alpha'\beta\beta'}$. Luckhurst & Pedulli report good agreement of such an analysis with experiment (145), but Rubenstein & Luz (146) did not obtain fully satisfactory agreement with a similar analysis. Rubenstein et al (147) have analyzed the relaxation caused by modulation of the quadratic zfs in terms of a random collisional model which causes fluctuations in the zfs (from its average value of zero) that are fast ($\tau_t$) compared to rotational reorientation times $\tau_R$. They analyze the combined $X$- and $Q$-band results for hydrates of $Cr^{3+}$, $Fe^{3+}$, and $Mn^{2+}$ (at both $X$ and $Q$ band) (148, 149), which permit determination of both the zfs value for a given distortion and $\tau_t$ which ranged from $4$–$9 \times 10^{-12}$ sec at room temperature. Poupko & Luz (150) in a study of $Cu^{2+}$ solutions at both

$X$ and $Q$ band (including measurement of the magnetic parameters) could obtain $\tau_R$ from the spin-rotational contribution and $\tau_i$ for random modulation of the $g$ tensor. Nyberg (151) discusses results on $Cu^{2+}$ in $NH_3$ solution in terms of spin-rotational and anisotropic $g$ and $A$ tensor relaxation. Reed et al (152) in a study of $Mn^{2+}$ in various ligand environments point out that the transient zfs has no simple relation to the static zfs from the solid state spectrum. Burlamacchi (153–155) also reports results on $Mn^{2+}$ in various solvents, and finds in a study on mixed water-glycerol systems (154) that there is an extra unexplained contribution to the linewidths which is nearly independent of viscosity but is solvent dependent. Effects due to ionic association have also been studied (155–157) as have widths of $Mn^{2+}$ in aqueous surfactant solutions (158) and molten salts (159).

Hudson & Lewis (160) discuss the relaxation matrix for $^8S$ ions in solution, and calculate linewidths as a function of $\tau_t$; Reuben (161) reports on studies of $Gd^{3+}$ analyzed in terms of these results, finding essentially a transient zfs.

Angerman & Jordan (162) have studied the linewidths of vanadyl complexes in a variety of solvents to obtain $\tau_R$. The activation energies for $\tau_R$ were generally nearly the same as that for the corresponding solvent viscosity, and $\kappa = r^3/r_0^3$ (where $r_0 = 3.80$ Å from diffusion experiments) ranged from $\frac{1}{2} < \kappa \le 1$ for the different solvents. Also, at low temperatures some mechanism in addition to spin-rotational relaxation is contributing to the "residual" linewidth. Linewidth studies on a family of vanadyl-phosphine complexes could be explained with $r^3$ as the only adjustable parameter (163). Luckhurst & Ockwell (164) have studied vanadyl acac in liquid $o$-terphenyl. They find that replacement of an isotropic diffusion constant by that estimated for the perpendicular component of an axially symmetric diffusion tensor is preferred for this molecule. Their results favor the free volume model over the possibility of loose, short-lived clusters for this liquid. A variety of $Ti^{3+}$ chelates in aqueous solution have been studied, and the linewidths are interpreted by Watanabe & Fujiwara (165) in terms of an Orbach process on the basis of their magnetic field independence, their increase with temperature and correlation with $\Delta g^2$. But for a low lying excited state of 3000 to 7000 cm$^{-1}$ (or 15 to 35 times $kT$) the Orbach process should not be important (166). The authors do not appear to give adequate consideration to spin-rotational relaxation which appears to be consistent with their results. The Russian literature includes relaxation studies on $Mn^{2+}$ (167, 168), $Cr^{3+}$ (169), $Cu^{2+}$ (170), and $Fe^{3+}$ (171).

O'Reilly (172) has measured the low frequency (7 MHz) linewidths of alkali metal-$NH_3$ solutions. He analyzes these results in terms of the hyperfine and spin-orbit interactions being modulated by the diffusive motions of the solvent molecules and possibly metal ions. His analysis indicates the onset of exchange processes in the conductivity as the concentration of alkali metal is increased. Nicely & Dye (173) studied the linewidths of dilute solutions of Cs in ethylamine-ammonia mixtures. They analyze the Cs hyperfine linewidth variations in terms of a two-state model which modulates the $g$ factor and the hyperfine interaction, but could not distinguish between several possible models.

Acrivos & Azebu (174) describe unusual linewidth effects seen in Na-NH$_3$ solutions doped with Pb. They find that $T_1 \gg 10^{-2}$ sec $\gg T_2 \geq 10^{-5}$ sec. The long $T_1$ values lead to fast passage effects when $\nu_m$ (the field modulation frequency) is $\nu_m \geq 80$ Hz, since $2\pi\nu_m T_1 \gg 1$; while for $\nu_m = 100$ kHz such that $2\pi\nu_m T_2 \gtrsim 1$ sideband spectra are obtained. These authors give an analysis of the sideband technique in ESR and of the fast modulation effects. They conclude that a metal-nonmetal transition results from adding the Pb and by localizing the unpaired electrons; this almost eliminates the effectiveness of motional modulation of the hfs in causing electron-spin flips and in broadening the lines.

*Other theoretical developments.*—Atkins (175) gives a detailed analysis showing how the Kivelson-Kubo-Tomita (176) theory may be used to correctly predict alternating linewidths. One should label the contributions to the correlation function coming from spin systems with different nuclear configurations before exponentiating the first terms in the moment expansion. However, he notes this approach does not allow for pseudosecular or nonsecular effects in the presence of degeneracies. Kivelson (177) has recently reviewed such considerations in his review of ESR relaxation in liquids.

It should be noted, however, that by the generalized cumulant expansion method, whereby the moment expansion of the Kubo-Tomita approach is replaced by an already exponentiated cumulant operator, rigorous and general relaxation equations are obtained [equivalently for $\rho(t)$ or $S_x(t)$], which can apply to all orders in perturbation theory and is in principle valid even when correlation times are slow enough that relaxation theory no longer applies (23, 178). Freed has also shown the connection between these approaches and the stochastic Liouville approach when the assumption of a Markov process is introduced (23).

Deutch (179) has recently considered the theory of spin relaxation from the general point of view of the complete microscopic Liouville equation (i.e. the many-body dynamical equations) to which projection operator techniques are employed. When the general expression is developed to second order in the perturbation and the long time limit is taken, one obtains a Redfield-Langevin equation, i.e. the Redfield-type relaxation equation, which now includes a fluctuating (random) force that describes the effect of the rapid lattice motion on the spins. When averaged over an equilibrium ensemble, the Redfield equation is obtained, since the average of the fluctuating force is zero. This general approach should be useful in providing insight into the connections between microscopic statistical mechanical descriptions and the macroscopic spin observables particularly when the assumption of a stochastic Markovian process is not immediately invoked.

## ION PAIRS

The analysis of ion-pair ESR spectra has now developed to the point where serious attempts are being made to determine the detailed structure of the ion

pairs from spectral observables. Goldberg & Bolton (180) have analyzed the alkali metal hfs in terms of MO theory incorporating the electrostatic effect of the alkali metal ion acting on a $\pi$-electron system. They utilize McClelland's (181) method and a modified form of the Atherton-Weissman (182) model involving weak mixing of metal $s$ orbitals with hydrocarbon $\pi$ orbitals. They also assume 1. negligible contributions from the $\sigma$ system of the aromatic hydrocarbon; 2. the alkali metal is located above the nuclear plane of the hydrocarbon taken as $\sim 0.3$ nm thick; and 3. they otherwise neglect the finite size of cation and the solvation of the system. They give maps of their estimates of the unpaired-electron density on the alkali metal ion as a function of the position of the ion. They also give contour maps for the energy of ion association and obtain a shallow double minimum potential well for $Na^+$ naphthalenide$^-$ ($NL^-$), but a single central minimum for $Na^+$ antracenide with less certainty regarding the biphenylenide. The shallow double minimum would imply a rapid electron hopping. These mappings allow for an interpretation of the experimental alkali metal hfs in terms of the most likely positions, as well as for their variations with alkali metal size. They point out that negative hfs can be accounted for by allowing for different orbitals for different spins of the $\pi$-electrons in the hydrocarbon radical and then including the interaction of all these orbitals with the metal $s$ orbital. Pedersen & Griffin (183) performed an INDO calculation for $Li^+NL^-$ and could obtain negative spin densities for short distances.

Canters et al (184) have performed detailed calculations on alkali NL systems to account for negative spin densities, but they employ a configuration-interaction approach to first order. They find that this first-order correction is often of the same order of magnitude as the zero order spin density and usually has a different sign. As a result, the metal hfs may have different signs in different regions of space, with negative spin density expected around the nodal plane of the first antibonding orbital. They find that the larger the ion, the greater will be the first order, negative spin density.

Hirota and co-workers have discussed the effects of cross-excitations from the nonbonding orbitals of oxygen or nitrogen in free radical ions containing these atoms to the empty metallic orbitals. They suggest that this may be responsible for the observed negative alkali hfs in alkali 2,2'-dipyridyl (185) as well as in lithium fluorenone (186), if the cation is located in the nodal plane of the $\pi$ MO containing the unpaired electron. They have recently (187) given a detailed analysis of the effects of ion-pair formation on proton, $^{13}C$, $^{14}N$ hfs and $g$ factors for prototype aromatics, ketyls, semiquinones, and nitrogen heterocyclics. They also use McClelland's method as well as McLachlan's MO method but (unlike other studies) they give serious consideration to the effects of solvation of the cation, by introducing as a perturbation $-Ze^2/\epsilon(r)r$ where $\epsilon(r)$ is a screening factor dependent on the location of the cation relative to the $\pi$ molecular orbital. They find that, in general, the size of the perturbation required to reproduce the observed spin-density changes, upon ion-pair formation, is not very large. Thus relatively large screening factors have to be

used, which are closer to macroscopic dielectric constants than to a value of unity, despite the fact they are discussing tight ion pairs. They also suggest from their calculations that the distances between ions could be significantly larger than those expected from ionic and van der Waals radii. This all suggests strong solvation of the cation even for tight ion pairs. They also found the analysis of the $g$ values useful, in particular, for determining oxygen spin densities. Williams et al (188) have made careful studies of the effect of ion pairing on the $g$ value of the naphthalene anion radical. From temperature-dependent studies of both the alkali metal hfs and the $g$ values they show that the model of equilibrium changes between two types of ion pairs (Hirota model) adequately accounts for the data for $Na^+NL^-$ in THF, but not for $Cs^+NL^-$ in DME. They argue that the latter is probably a fixed ion pair, with the populations of the vibrational energy levels of the cation being temperature dependent (Atherton-Weissman model). Hirota and co-workers (189) report detailed studies on the structures of ion pairs of ketyls in ethereal solvents. In particular they find the ketyls never exist as solvent-separated ion pairs but are contact ion pairs at all temperatures under their experimental conditions. They found that DMF solvates the cations forming only DMF-solvated ion pairs. They analyze the observed linewidth variations of the Cs hfs in terms of the Hirota model, but the absence of any such linewidth effects for the Na ion pairs prevented them from coming to any definite conclusions.

An interesting experimental accomplishment has been the direct demonstration by ESR of the existence of triple ions of type: $(Na_2\text{-semiquinone})^+$ for several semiquinones by obtaining hfs from two equivalent Na nuclei. Gough & Hindle (190, 191) were able to form the triple ions by reduction in THF solvent in the presence of Na tetraphenylboride (NaTPB). They attribute the spectrum to the triple ion rather than an ionic quadruple, because 1. the addition of $Na^+$ in excess of those introduced by the reduction process is necessary for the formation of the species; 2. there is a marked increase in solubility ($>10^3$) of semiquinone in the presence of added NaTPB; 3. there is an upfield $g$ shift compared to the ion pair. The fact that the overall symmetry of the semiquinones is preserved (as determined from proton hfs) indicates the two sodiums are equivalently placed relative to the O—O axis (e.g. for durosemiquinone along this axis or in the plane perpendicular to the ring and containing this axis). There is significant asymmetric broadening within the $^{23}Na$ hyperfine multiplets, and a preliminary interpretation is given to show that the Na ions lie in the plane of the semiquinone anion with each Na ion associating with an O.

Triple ions of pyrazine and tetramethylpyrazine have also been observed and analyzed in an analogous manner (192, 193). Al-Baldawi & Gough (193) point out that from linewidth studies, one can get some idea of the anisotropic dipolar interactions of metal nuclei with the unpaired electron and this is an indication of the metal-nitrogen distance. They find the linewidth term quadratic in metal quantum number is inversely proportional to the dielectric constant of the solvent. In general, the triple ion is stable (190–195), but the

ion pair can engage in intramolecular exchange (195–200) between equivalent sites or intermolecular exchange of the cation (190, 194, 196, 201, 202). The intramolecular exchange often gives rise to distinctive alternating linewidth effects on the proton hyperfine patterns, from which the exchange rates may be measured (195–200). Warhurst & Wilde (200) discuss the mechanism in terms of a transition state more solvated than the initial state, but conclude that a general correlation of results is complex. The mechanism of inter-molecular exchange has been studied and evidence given that it proceeds via a symmetric triple ion (196, 201). Simultaneous linewidth effects from both intra- and intermolecular mechanisms have been analyzed in detail (196). Adams et al (203) have shown that in the exchange between durosemiquinone triple ions and the parent quinone in THF, both $Na^+$ are transferred in the process. Evidence for the formation of species $[DQ, Na^+, DQ^{\cdot-}]$ and $[DQ, 2Na^+, DQ^{\cdot-}]$ is given.

The question of the ion-pairing model and alternating linewidth effect for the pyracene anion appears to have been resolved by Reddoch (204) by using partial deuteration. He shows that the average position of the $K^+$ ion is above or below the center of the plane containing the C atoms of the anion, and it may jump between these two positions. A similar model has been found for the 5,12-dihydrotetracene anion (205), while for the 9,10-dihydroanthracene (206) anion the primary effect is migration from one benzene ring to another, with a slower effect involving jumps above and below the plane. Similar models should also apply to the benzocyclobutene anion (207).

The ketyls of the alkali earths are solvent-shared ion pairs of form $R^{\cdot-}SM^{2+}SR^{\cdot-}$, and the alternating linewidth for barium acenaphthene semi-quinone has been analyzed in terms of movement of the $Ba^{2+}$ between equivalent sites unsymmetrically located with respect to the two anions (208). Alter-nating linewidths resulting from $K^+$ jumping between the two rings of the heptafulvene anion have also been observed (209). Ion pairing effects in nitro-benzene (initially prepared as a stable solid salt) (210, 211) are also reported. Unless proper precautions are taken, $K^+$ salts present as impurities in the glass or the sodium may exchange with $Na^+$ ion pairs to give appreciable $K^+$ ion pairs (212, 213).

Interesting ion-pairing effects also show up in the study of triplet dianions of aromatic systems (214–218). In many cases it is possible to form triple ions, i.e. the dianion with two metal counter-ions. From an analysis of the zfs parameters of such triple ions, de Boer and co-workers suggest that for tri-phenylene dianion, the two counter-ions are above and below the center of the same noncentral ring, while for the triphenylbenzene dianion, they are on the threefold axis (214–217). Results on triphenyl-sym-triazine dianion (218) indicate the multiplicity of the ground state is dependent on counter-ion and solvent.

Ion pairs and ESR have recently been discussed in two detailed review articles (219, 220).

## CIDEP AND HEISENBERG SPIN EXCHANGE

*CIDEP.*—Anomalous ESR spectra arising from nonequilibrium populations of the spin levels have been observed for some short-lived free radicals generated in liquids by irradiation or chemical reaction (221–227). Initially mixed emission-absorption spectra were observed (221–223), but more recently completely emissive spectra have been observed (224, 225). Completely emissive spectra have also been seen for ethereal electrons from alkali metals (228). This phenomenon has been called chemically induced electron polarization (CIDEP) by analogy with chemically induced nuclear polarization (CIDNP).

The analyses given for CIDEP bear a similar, but not identical, relation to those for CIDNP, but are probably less certain than the latter (229–236). We attempt to summarize them in the following. It is conceivable that when a radical pair is formed from a dissociating molecule some (residual) singlet or triplet character of the molecule is preserved. The question then arises as to the time development of these spin states. They may be affected by several interactions: 1. the Zeeman terms, $g_1 S_{z_1} H_0 + g_2 S_{z_2} H_0$; 2. hyperfine terms, $A_1 M_1 S_{1z} + A_2 M_2 S_{2z}$; 3. exchange interaction, $2J S_1 \cdot S_2$; 4. spin-rotational and orientation-dependent terms. While the radicals are close, $2J S_1 \cdot S_2$ is very large and the dominant term. Since it commutes with $S = S_1 + S_2$, it preserves the singlet-triplet character of the radical pair. If $g_1 \neq g_2$, then the Zeeman terms do not commute with $S$, so they would be capable of mixing the singlet and triplet levels. Type 2 and 4 terms could also provide such mixing. However, when any of these terms are so much smaller than $J$, the singlet-triplet energy separation, they cannot be very effective. We first analyze the importance of this mixing considering just the $M_s = 0$ triplet $|T_0\rangle = 1/\sqrt{2}|\alpha\beta + \beta\alpha\rangle$ and the singlet $|S\rangle = 1/\sqrt{2}|\alpha\beta - \beta\alpha\rangle$ spin states. Thus $M_s = 0$ at all times, or $M_{s_1} = -M_{s_2}$, one can then define the unpaired electron spin density on radical 1 as (233)

$$\rho_1(t) = M_{s_1}(t) - M_{s_2}(t) = -\rho_2(t) \qquad 21.$$

where we define $M_{s_i}(t) = \langle \psi(t)|S_{z_i}|\psi(t)\rangle$ and $\psi(t)$ is the time-dependent spin eigenfunction. Note that $\rho_1 > 0$ corresponds to a potentially emissive situation while $\rho_1 < 0$ to absorption. If we write

$$|\psi(t)\rangle = C_S(t)|S\rangle + C_T(t)|T_0\rangle \qquad 22.$$

it then follows

$$\rho_1(t) = C_T(t)C_S^*(t) + C_T^*(t)C_S(t) \qquad 23.$$

so that a mixture of singlet and triplet character in $|\psi(t)\rangle$ can lead to a net excess of spins for radicals 1 in either upper (emissive) or low (absorptive) states. Several schemes have been proposed to allow the mixing by terms of types 1 or 2 to take place when the value of $J$ is significantly reduced from the presumed large radical-pair value (but still non-negligible). [Note that once the radicals have separated, and $J$ is zero, radical 1 can experience no further spin

polarization.] The important terms for polarization at the first encounter (assuming $J$ is time independent) is

$$\rho_1(t) = \frac{\Delta H_{1,2} J'}{\omega^2} \left[ |C_s(0)|^2 - |C_T(0)|^2 \right] \sin^2 \omega t \qquad 24.$$

where $\Delta H_{1,2}$ is half the difference in Larmor frequency between radicals 1 and 2, $J' = 2J$ and $\omega^2 = [\Delta H_{1,2}{}^2 + J^2]$. If $J$ is to have a certain value $J_0$ for mean duration $\tau_c$, then an ensemble average $\rho_1(t)$ is obtained as

$$\bar{\rho}_1 = \frac{\Delta H_{1,2} J_0'}{\omega^2} \left[ |C_s(0)|^2 - |C_T(0)|^2 \right] p \qquad 25.$$

where $p$ is the probability of exchange during the encounter

$$p = \frac{1}{2} \cdot \frac{(2\omega\tau_c)^2}{1 + (2\omega\tau_c)^2} \qquad 26.$$

For the radical pair with $\omega \sim J_0 \gg \tau_c{}^{-1}$ then $p = \frac{1}{2}$ and $\bar{\rho}_1 \sim \Delta H_{1,2}/J_0$, which is expected to be too small ($< 10^{-3}$) for appreciable effects. If, on the other hand, one can assume that as the radicals separate they remain in a region where $|\Delta H_{1,2}| \sim (J) \sim \omega/2$ for time $\tau_c$, then $\bar{\rho}_1 \sim p/2[|C_s(0)|^2 - |C_T(0)|^2]$. Now for $\omega^2 \tau_c{}^2 \ll 1$, then $p \simeq 2\omega^2\tau_c{}^2$ and typical values would place $\bar{\rho}_1 \lesssim 10^{-4}$. One must ask that $\tau_c \sim 10^{-9}$ sec when $\Delta H_{1,2} \sim 10^8$ sec to get significant polarizations. An alternative picture assumes that the wavefunction of the radical pair follows adiabatically the decrease in $J$ upon radical separation (228, 231), but the strong (essentially exponential) dependence of $J$ on $r$, the interradical separation, tends to argue against this point of view.

To circumvent such difficulties Adrian (233) chose to consider the situation where the radical pair may separate by diffusion but then suffer a new encounter. This has the particular advantage of allowing the polarization process to be broken up into two steps of differing time duration. During the relatively long interval between separation and return of the radicals, only $\Delta H_{1,2}$ is effective, while during the relatively short period of the second encounter the large $J' S_1 \cdot S_2$ is effective. Adrian (233) obtains as an expression for $\rho_1$ averaged over the former interval

$$\bar{\rho}_1(\tau_c) = 0.85 \frac{\Delta H_{1,2} J}{|\Delta H_{1,2} J|} (|\Delta H_{1,2}|\tau_D)^{1/2} [|C_s(0)|^2 - |C_T(0)|^2] \sin |J'|\tau_c \quad 27.$$

where $\tau_D$ is the average time between diffusive jumps of the radicals and $\tau_D \sim \tau_c$. The final result may be obtained by finding an average over the collision duration of $\langle \sin |J'|\tau_c \rangle = (J_0'\tau_c)/[1 + (J_0'\tau_c)^2]$ for the simple model analogous to that used for Eq. 25. Strong spin exchange ($|J_0'\tau_c| \gg 1$) implies $\langle \sin |J'|\tau_c \rangle \simeq (2J_0'\tau_c)^{-1} \ll 1$, while weak exchange implies $\langle \sin |J'|\tau_c \rangle \simeq (2J_0'\tau_c) \ll 1$. Adrian points out that there may be a range of strengths of spin exchange collisions depending on the range of possible radical-pair trajectories, and assumes $\langle \sin |J'|\tau_c \rangle \sim 0.1$ for order-of-magnitude estimates. Appreciable polarizations are then predicted for $|\Delta H_{1,2}| \sim 10^8$ sec$^{-1}$ and $\tau_D \sim 10^{-11}$ sec.

While Adrian has used a jump diffusion model, one may obtain virtually the same results from continuous diffusion [cf a discussion of CIDNP in (234)].

Note from Eq. 27 that the sign of the polarization depends on 1. the sign of $\Delta H_{1,2} J$ and 2. the sign of $(|C_S(0)|^2 - |C_T(0)|^2)$. Thus, for example, if $\Delta H_{1,2}$ is dominated by hyperfine terms between otherwise identical radicals, both emissive and absorptive lines will appear in the same spectrum, while if the differences in Zeeman terms between the two radicals dominate, the radical observed will be either pure emissive or absorptive. Polarizations can also result from collisions of independently produced radicals with uncorrelated spins, since the recombination reaction of the radicals will tend to deplete singlet character. It could be important for polarizations not involving radical-radical reactions (3, 5). This mechanism might also allow for the possible repolarization of radicals in new encounters until the radicals are depleted. Clearly all electron-spin polarizations which develop are subject to return to thermal equilibrium polarizations by electron-spin relaxation processes typically $\sim 10^{-6}$ sec in solution.

The above summary involves the $S_0 \leftrightarrow T_0$ intersystem crossing. The possibility that $S_0 \leftrightarrow T_{\pm 1}$ intersystem crossings may be effective in CIDEP does not appear to be the case for hyperfine interactions (the differences in isotropic Zeeman terms are not important here), since they are small compared to the Zeeman splittings in high magnetic fields. Atkins et al (235) have suggested the possibility of the (large) spin-rotational interactions yielding effective polarizations by $S_0 \leftrightarrow T_{\pm 1}$ crossings, but they do not consider any of the time-dependent aspects in their preliminary discussion. Adrian's time-dependent analysis can, however, be applied to their analysis (236). We note, however, that the spin-rotational interactions of radicals in liquids are themselves fluctuating in time and typically have extremely short relaxation times, $\tau_J < 10^{-12}$ sec, so that the duration of their effectiveness is typically much shorter than even $\tau_c$ or $\tau_D$. Another relevant consideration for the theory of CIDEP would be the inclusion of the electron electron-dipolar or zfs terms, which can mix the $T_0$ and $T_{\pm 1}$ levels in an orientation-dependent manner (228).

Clearly further work is required in developing the theory for these very interesting phenomena.

As we have already noted, the recent observations of the CIDEP effect are a direct result of the development of techniques for the production and observation of transient radicals. The most powerful new technique appears to be the coupling of flash photolysis with ESR detection (224, 237) using a pulsed uv laser (237) or a more conventional flashtube (238). Conventional steady state photolysis (226, 239, 240) can show the transient CIDEP effects provided radicals with short enough chemical lifetimes are observed so that $T_1$ processes have not yet completely brought the spins to thermal equilibrium or else very long $T_1$ values would be required. The pulse technique just requires observation in times short compared to $T_1$ and tends to show more pronounced effects. Similar comments apply to pulse radiolysis (222, 241) and steady state radiolysis techniques (221, 242, 243). An important development in ESR

radiolysis is the extension of this technique to the observation of radicals generated in aqueous solutions (222, 241–245). Neta et al (243) have developed an interesting approach to obtain rate constants for reaction of hydrogen atoms with organic compounds in aqueous solution. They use in a semi-empirical fashion the steady state competition between the $T_1$ relaxation of the initially polarized H atom spins and the chemical reaction. The effect of microwave power saturation on the competitive situation is in good agreement with their analysis. Optical pulsing techniques are also being used in obtaining kinetic behavior of photoexcited triplet states (246).

*Heisenberg spin exchange.*—Heisenberg spin exchange (HE) is a phenom-enon closely related to the above-described mechanisms for CIDEP, since it involves the spin-relaxation effects of colliding radical pairs. Eastman et al (247) have given a compact general theory which shows that as long as

$$|J'|, \tau_c^{-1} \gg \Delta H_{1,2}, \omega_1 \qquad 28.$$

then HE appears as a simple exchange process to which the Kaplan-Alexander chemical exchange methods (20) apply, provided the rate constant is taken as

$$k_{HE} = \omega_{HE}/[R] = ([R]\tau_2)^{-1}2p \qquad 29.$$

where for Eq. 28 we have (cf Eq. 26):

$$p = \tfrac{1}{2}(J'\tau_c)^2/(1 + J'^2\tau_c^2) \qquad 30.$$

Here $\tau_2$ is the mean time between successive new bimolecular encounters of radicals. Most ESR results are consistent with strong exchange for which $\omega_{HE} = \tau_2^{-1} \propto T/\eta$, a diffusion-controlled process. This was demonstrated in a careful study of $K^+$ tetracyanoethylene (TCNE) anion in dimethoxyethane (247), but anomalies were observed when tetrahydrofurane was solvent. (No such anomalies appeared when ditertiary butyl nitroxide (DTBN) radical was studied.) The effects of HE on saturation were also discussed and demon-strated experimentally to be significantly different from the linewidth effects (247). While the linewidths broaden with increase in concentration, the satura-tion parameters first decrease, but then rapidly approach asymptotic values, reflecting the fact that spin exchange is not a direct electron-spin relaxation mechanism, but rather induces "exchange" between all the hyperfine lines.

The effects of radical charge and ionic strength on HE are discussed in several works (247–250). A particularly interesting case of PADS in aqueous solution (248–251) shows apparent weak exchange, $|J'\tau_c| \sim 1$, with both $\tau_2^{-1}$ and $|J'\tau_c|$ increasing significantly with increase in electrolyte concentra-tion, which screens the repulsive charges of dianions (248). The behavior of $\tau_2^{-1}$ for cases of low ionic strength can be reasonably analyzed in terms of the Debye theory (248, 249), but simple Stokes-Einstein and Debye-type analyses do not appear to be fully adequate for dealing with the dependence of $\tau_c$ on

$\eta/T$ and ionic strength (248). The strong exchange for $K^+TCNE$ already noted implies that it exists as an ion pair. For DTBN in aqueous solution, $\omega_{HE}$ decreases with increasing ionic strength, presumably due to the formation of DTBN aggregates (248). [Other hydrophobic effects on the ESR spectra of a nitroxide radical have been studied in terms of the changes in rotational correlation times (252, 253). Values of $\tau_R$ were greater in the aqueous solutions than in organic solutions of the same viscosity, presumably due to local influence of hydrophobic groups on water.] The HE of DTBN has recently been used as a probe of diffusion in a binary liquid solution at its critical point (254). Although there is a critical anomaly in the macroscopic viscosity, none is observed in the HE-broadened linewidths, presumably because the diffusive motions of the radicals are determined by interactions much shorter ranged than critical fluctuations. Deviations from simple Stokes-Einstein-type behavior $\tau_2^{-1} \propto T/\eta$, which are observed, are to be expected for nonideal solutions. DTBN has also been used as a probe of a water-oil emulsion as a model lipid-water system (255). Marshall (256) has found that the spectrum of a carboxylic acid nitroxide shows weak lines characteristic of the biradical dimer. He finds both $J$ and the equilibrium constant are functions of both solvent and temperature. Such effects could be important in the study of weak HE relaxation.

The theoretical analysis of (247) has been extended by Zitserman (257) to spins $S > \frac{1}{2}$, and he gives results when one exchanging spin has $S_1 = \frac{1}{2}$ while $S_2 \geq \frac{1}{2}$. The general form of Eqs. 29 and 30 are again obtained, but with somewhat different numerical factors in Eq. 30 for $p$. Salikhov et al (258) have analyzed the same problem from $S$-matrix theory which gives equivalent results, for the approximations used, to the stochastic Liouville approach used by Freed (259) and Johnson (260). They also explicitly discuss effects of an intrinsic $T_1$ which become important in the expressions for HE when $T_1 \ll \tau_c$, for which the condition of weak exchange becomes $J'^2T_1\tau_c \lesssim 1$. They summarize a variety of experimental results of free radicals exchange-broadened by different metallic ions in support of their analysis. McCain (250) discusses similar types of experiments using PADS as the radical and focusing on the ionic repulsion effects and the relative importance of exchange vs dipolar contributions, while experiments between $Mn^{2+}$ and other paramagnetic ions have been analyzed in terms of dipolar contributions to yield $T_1$ values for those ions (261).

Spin exchange in concentrated solutions has also been studied (262–264). Strother et al (262) discuss the exchange narrowing region at high $Mn^{2+}$ concentrations. However, they analyze their results in terms of "exchange" transitions induced only between adjacent hyperfine levels instead of having all transitions equally likely, which is the case for $J \gg a$ (257–260).

## SATURATION AND DOUBLE RESONANCE

*Saturation and relaxation in orbitally degenerate ground state radicals.*— Recently serious attempts have been made to develop the continuous saturation

method to yield quantitative and reproducible $T_1$ measurements for realistic experimental conditions. These efforts have been motivated largely by the desire to study the anomalously short relaxation times exhibited by orbitally degenerate hydrocarbon free radicals in liquid solution. Kooser et al (131) describe such measurements on the benzene anion, tropenyl, and PADS. They introduce procedures to correct for 1. distortions of the cavity microwave modal patterns due to the presence of large Dewars etc, 2. nonuniform microwave and modulating fields over the sample, and 3. variation of cavity $Q$ with temperature. They show that good agreement may be achieved with $T_1$ results obtained when such complicating features are not present (265). This technique was then used to study other orbitally degenerate free radicals (266), as well as to elucidate Heisenberg exchange effects on saturation parameters (247). These methods have been reexamined and elaborated by Rataiczak & Jones (267), who obtain very good agreement with the correction procedures of Kooser et al, and whose $T_1$ measurements on benzene ion are typically within the anticipated 20% accuracy of the method. These results encourage one to believe in the reproducibility of the method provided all the necessary precautions (131, 267) are taken.

The $T_1$ measurements were performed initially in the belief that the $T_1/T_2$ ratio can shed light on the nature of the anomalous mechanism(s) for these degenerate ground state radicals (131, 268), but a careful analysis of the various proposed mechanisms (including spin-orbit pulse, Orbach-type processes, and spin-orbit tunneling processes) indicated that $T_1$ should equal $T_2$ for all of them (268). In general, it was found experimentally that $T_1 \sim T_2$ for the degenerate ground state hydrocarbon anions while $T_1 > T_2$ for the non-degenerate ones (131, 266). More interesting is the observation that the anomalous $T_1$ and $T_2$ values tend to be independent of temperature, solvent, and counter-ion over the range of cases studied (131, 266). This was most clearly evidenced for the coronene and triphenylene anions (and tropenyl) which exist as free ions. The results for the smaller benzene and cyclo-octatetraene anions (alkali-metal prepared) are complicated by counter-ion and solvent-dependent ion-pairing effects; this is also the case for the smaller nondegenerate hydrocarbon anions. The intrinsic temperature-independent $T_2$ values for these five orbitally degenerate radicals correlated well with the small but anomalous deviations of their $g$ values from those typical for the non-degenerate hydrocarbons (cf 122). This was taken as positive evidence (266) for the role of anomalous spin-orbit interactions (268) in the relaxation times, while the milieu independence suggests that the anomalous relaxation mechanism is largely intramolecular, although for the case of benzene the counter-ion effects interfere with the interpretation.

The possible existence of ion pairing in the benzene anion was first suggested (269) on the basis of the slow rate constant for the electron transfer reaction (269, 270). Das et al (266) pointed out that the observed deviations from Lorentzian lineshape and its temperature dependence could be the result of inhomogeneous broadening due to the $K^+$. Jones et al (271) have recently

carefully analyzed the lineshapes to extract out the unresolved metal splitting on the assumption that exchange of the metal ion is slow, and this assumption is supported by the proposed electron transfer mechanism: $B^- M^+ + B \rightleftharpoons B + B^- M^+$ with the metal transferred intact (270). An ESR spectrum originally ascribed to a nondegenerate state of the benzene anion has been shown to be a reaction product with the solvent (272). Smentowski & Stevenson have examined the effects and implications of ion pairing and solvent on cyclooctatetraene anion in their study of its electron transfer mechanisms (273, 274). The predominant electron transfer is between the anion and dianion.

Studies on trinaphthylene (TN) (215, 275) have shown that $TN^-$ and $TN^{2-}$ are orbitally nondegenerate contrary to most other aromatic molecules with trigonal symmetry. However, $TN^{3-}$ has anomalously short relaxation characteristics and a large $g$ shift, both typical of a degenerate ground state radical, which is expected both for Hückel and self-consistent field molecular orbitals (SCF MO) energy level schemes. Although MO calculations predict that the 1,3,5-triphenylbenzene anion is orbitally degenerate, the ESR spectrum in liquid ammonia is characterized by $g$ value, $T_1$ and $T_2$ typical of orbitally nondegenerate radicals (214, 276). It is conjectured that twisting of the phenyl rings out of the molecular plane may lift the orbital degeneracy. Graf & Günthard have obtained the spectra of the pentachloro- (277) and pentabromocyclopentadienyl (278) radicals, finding $g$ values of 2.008 and 2.020 respectively. Although a major component of the $g$ shift is due simply to the larger spin-orbit parameters, they wish to attribute some portion to the effects of orbital degeneracy, but this is inconclusive.

Volland & Vincow (279) have measured the hyperfine and $g$ tensors for tropenyl in polycrystalline perdeuterionaphthalene aided by the presumed rapid rotation of the radical about its sevenfold axis. They find $g_\parallel$ is close to the value expected for nondegenerate radicals. Sadlej & Witkowski (280, 281) have given an analysis of the tropylium radical in crystalline matrices in terms of intramolecular vibronic coupling and the influence of intermolecular vibrations, and do not assume any free rotation about the symmetry axis. But they do not consider averaging of the anisotropic dipolar terms, which would need such motions.

Noack et al (282) find that in aqueous solution the tris(2,2′-dipyridine)-copper(II) complex shows an apparent $\tau_R$ with a small temperature coefficient, and it is quite insensitive to solvent viscosity unlike the behavior of partially substituted complexes. They take this to be evidence of a dynamic Jahn-Teller effect, i.e. fast reorientations of the axis of distortion. Studies are reported for $Cr(C_6H_6)_2^+$ (283) indicating fast rotation around its symmetry axis even in the solid, and for $Fe(C_5H_5)_2^+$ (284) which shows significant relaxation due to its predicted orbitally degenerate ground state. Shih & Dessau (285) have found that in the mesitylene dimer cation the orbital degeneracy has been removed, as evidenced by the nonequivalence of the ring proton and of the methyl proton splittings (285). This is probably due to an intermolecular shift of the relative position of the two rings away from threefold symmetry. A detailed theoretical

analysis of the lifting of orbital degeneracy by small perturbations is given by Purins & Karplus (286) for toluene ions.

*Pulse experiments.*—In principle, pulse-type techniques are the most accurate methods of performing $T_1$ measurements. However, they typically have not been useful for short $T_1$ values, and the minimum sensitivity is such as to preclude most studies on dilute systems. But recently there have been encouraging reports of spin-echo experiments in liquids. Braendle et al (287) describe a pulse spectrometer which delivers 90° pulses of 20 nsec duration which they claim may be used to determine relaxation times of 30 nsec and longer. (Their results on crystalline DPPH are $T_1 \sim T_2 \sim 50$ nsec.) They report results of $T_1$ and $T_2$ measurements for several free radicals in solutions of various organic liquids and ammonia (with estimated 10 and 20% errors respectively), where the radical concentrations range from ca $10^{-2}$ to ca $10^{-1}M$. This is the concentration region where the ESR spectrum is just a single exchange-narrowed line. The concentration-dependent parts of both $T_1$ and $T_2$ are ascribed to modulation of the intermolecular electron-electron dipolar interaction by translational diffusion, and the data are analyzed in terms of expressions developed by Krüger (288) from Torrey's general theory (289). Typical values for the appropriate correlation time: $\tau_c = (\frac{1}{5}d^2 + \frac{1}{12}\langle r^2 \rangle)/D$ (where $d$ is the distance of closest approach of spins, $\langle r^2 \rangle$ the mean square flight path, and $D$ the diffusion coefficient) are $3-10 \times 10^{-11}$ sec at room temperature or $\omega\tau_c > 1$. Thus the concentration-dependent part of $T_1$ has essentially an $(\omega^2\tau_c)^{-1}$ dependence, which is an advantage over NMR experiments for which $T_1$ does not usually depend on $\omega$ in normal liquids. Analysis of the $T_1$ and $T_2$ data then can yield $\tau_c$ and $\alpha = \langle r^2 \rangle/(12d^2)$. $\tau_c$ has activation energies typical of that for the solvent diffusion coefficient, which is independently measured, while typically $0 \leq \alpha \leq \frac{1}{12}$, although no error estimates are given. Any exchange effects in the concentration range studied are not considered, presumably because $\omega_{HE} \ll \tau_c^{-1}$, so exchange modulation of the dipolar terms should not be important compared to translational diffusion. Milov et al (290) describe a similar experiment. They also report $T_2$ (but not $T_1$ measurements) as low as ca $3 \times 10^{-4}M$, which are interpreted in terms of spin exchange. We note that equivalent experiments measuring $T_1$ and $T_2$ could also be performed by the continuous wave (cw) saturation techniques for these ranges of concentration.

Results pertinent to the degenerate ground state relaxation problem have been obtained by Brown (291, 292) using a spin-echo technique (293) to study a variety of radical cations, anions, and neutral radicals randomly oriented in rigid glass matrices (292). The spin-lattice relaxation times of radical ions with orbitally degenerate ground states are much shorter than those for the orbitally nondegenerate radicals in the solid state. For coronene and triphenylene cations at room temperature, they are so short that no echo could be observed. The relaxation times for 1,3,5-triphenylbenzene cation is not quite so short. Brown also describes how to perform spectroscopy by electron spin echoes. The echo height yields an absorption (as opposed to a derivative) pattern. This technique

has also been applied to show that the spin of a triplet dimer is not mobile (294).

*ENDOR.*—Leniart (295) has made a detailed study of electron nuclear double resonance (ENDOR) of semiquinones in solution. The main objective was to obtain a detailed quantitative test of Freed's theory for ENDOR in liquids (296, 297). This approach was first to use linewidth and saturation analyses to obtain basic information on the details of the various spin-relaxation processes. The experimental electron spin-flip ($W_e$) rates, nuclear spin-flip rates ($W_n$), Heisenberg exchange frequencies ($\omega_{HE}$), cross-relaxation, and secular line-broadening estimated from the ESR studies could then be utilized to predict the detailed features of the ENDOR lineshape, including the observed ENDOR signal heights and the ENDOR widths as a function of temperature, solvent, and rf power. The results for *p*-benzosemiquinone are analyzed in greatest detail and show reasonable agreement between the experimentally measured ENDOR spectra and those predicted from the ESR data over a wide variety of conditions. The theoretical analysis involved a consideration of the details of ENDOR from degenerate hyperfine lines such as arise from several equivalent protons, as well as the effects of coupled relaxation of multilevel spin systems. The average $T_{2,n}$ values are typically about four times longer than the $T_{2,e}$ values. This shows that the dominant ESR line-broadening mechanism is a secular nuclear-spin independent process such as a secular *g*-tensor contribution. In general, the narrowness of the ENDOR line makes it a more sensitive measure of spin-relaxation contributions that only have a marginal effect on the ESR linewidth. Another relevant observation is that $W_e$ is more than an order of magnitude greater than estimates based on spin-rotational and *g*-tensor relaxation mechanisms analyzed in terms of Brownian motion theory. It is quite possible that the Hubbard-type (139) Brownian motion theory for spin-rotational relaxation may not be as appropriate as another dynamical model such as the Brown et al model for these cases (298).

Allendoerfer & Maki (299) have used a phenomenological approach to analyze their ENDOR results for the tri-*t*-butyl phenoxyl radical under various conditions. They do not measure any of the basic relaxation parameters, but find they can predict the proper functional dependence of the ENDOR signal upon microwave and rf power if they simply assume (following Bloch's equation) the basic ESR line is that of a saturated Lorentzian, and the ENDOR effect is to replace $T_1$ by $T_1 - \Delta T_1$, where $\Delta T_1$ is essentially a saturated Lorentzian involving the nuclear rf field. Precisely this type of dependence was rigorously predicted by Freed (296) for the case when rf and microwave power levels are not sufficiently strong to cause coherence effects. In this case Freed found that the absorption (recall $Z''$ is equivalent to the Bloch equation $M_y$) for one of the simple ESR transitions resulting from an electron spin interacting with a nuclear spin is

$$Z'' = \frac{\hbar\omega_e}{NkT} \gamma_e H_1 T_{2,e} / [1 + (\Delta\omega_e^2) T_{2,e}^2 + \tfrac{1}{4}(\Omega_e - \xi_e) T_{2,e}\gamma_e^2 H_1^2] \quad 31.$$

where

$$\xi_e = \tfrac{1}{4}\gamma_n{}^2 H_2{}^2 \Omega_{e,n}{}^2 T_{2,n}/[1 + (\varDelta\omega_n{}^2)T_{2,n}{}^2 + \tfrac{1}{4}\Omega_n T_{2,n}\gamma_n{}^2 H_2{}^2] \qquad 32.$$

where $\varDelta\omega_e$ and $\varDelta\omega_n$ are the deviations of the microwave and rf applied frequencies from the resonant values. Phenomenologically one can let $\tfrac{1}{4}\Omega_e \rightarrow T_{1,e}$ and $\tfrac{1}{4}\Omega_n \rightarrow T_{1,n}$.[5] The saturation parameters $\Omega_e$ and $\Omega_n$ and cross-saturation parameter $\Omega_{e,n}$ are readily calculated from the matrix of spin-transition probabilities. These considerations have recently been reviewed (297), and the saturation parameters given in terms of the relevant transition probabilities for a variety of cases. When there are multiple or degenerate hyperfine lines and/or nuclear transitions then Eqs. 31 and 32 generally become more complex. However, Leniart (295) finds it is useful to define an "average" ENDOR signal having the general form of Eqs. 31 and 32 but with "average" $T_2$ and $\Omega$ values, which then describe the observations, although the average parameters were ultimately computed by first simulating ENDOR spectra using the correct general expressions. Leniart discusses some conditions for the validity of the average ENDOR line concept. They include having ESR and NMR linewidths that are nearly nuclear-spin independent and only mildly saturating the nuclear (NMR) transitions.

Atherton et al (300) have reported an unusual observation (apparently not observed by other workers) of an *inversion* in the ENDOR signal as the duty cycle of the rf pulses is increased. They venture the possibility that they are seeing a coherence effect in which the strong rf fields are perturbing the ESR lineshape tending to split the ESR line, a mechanism discussed by Freed et al (301). However, this effect should appear as the superposition of a broad negative line on the sharper positive and normal ENDOR line, and also the role of the duty cycle is not clear. The predicted coherence effect has been seen in well-characterized form in these laboratories (302).

Freed (303) has predicted that, in those cases where $W_n \ll W_e$, it might be useful to perform a triple resonance experiment where both NMR resonance frequencies $\omega_n = |\gamma_n H_o \pm a_n|$ are simultaneously irradiated, but in those cases large enough rf powers such that $\gamma_n{}^2 H_2{}^2 T_{2,n}T_{1,e} \gtrsim 1$ are required (instead of the weaker condition $\gamma_n{}^2 H_2{}^2 T_{2,n}T_{1,n} \gtrsim 1$ for regular ENDOR). Such an experiment has been performed (304) using Coppinger's radical. The result, while positive, showed only a very small increment on the signal expected from a simple sum of two ENDOR signals. This is believed to be due to the failure to adequately satisfy the condition $\gamma_n{}^2 H_2{}^2 T_{2,n}T_{1,e} \sim 1$ in liquids. Successful triple resonance signals have, however, been observed in solids (305, 306). Leniart et al (307) report the first solution ENDOR signals from nitrogen nuclei of several nitroxide radicals in *n*-heptane solution. In their

[5] [The distinction between $\Omega$ values or saturation parameter and $T_1$ values, however, is that the former are not simple $T_1$ values nor decay times. In fact there are as many as $(N - 1)$ different, nonzero decay constants in the transient solution (which come from diagonalizing the transition probability matrix).]

preliminary analysis, they point out that 1. the $^{14}N$ transition moment ($d_N$) arises primarily from the large size of $\bar{a}_N = 14.3$ G, that is (296)

$$d_N = \frac{1}{\sqrt{2}} \gamma_N H_2 [1 \pm (\gamma_e/\gamma_N)\bar{a}_N/2H_0] \qquad 33.$$

and 2. both nonsecular dipolar (yielding $W_x$) as well as pseudosecular terms (yielding $W_n$) contribute to the ENDOR enhancements.

Over the past three years a variety of types of free radicals in liquids have been studied by the ENDOR technique. These include substituted triphenyl-methyl radicals (308), substituted phenoxy radicals (299, 309–311), semi-quinones (312, 313), nitroxides (307, 314), a ketyl (315), hydrocarbon radical anions (316, 317) including also the hexahelicene anion (318), and an analysis of lifting of orbital degeneracy by methyl substitution in pentaphenylcyclo-pentadienyl radicals (319), cyclopropylaryl radicals (320), a conjectured biradical shown to be a monoradical (321), and flavin radicals (322). In many cases the methyl proton ENDOR lines persist upon freezing, presumably due to relatively unhindered methyl group motions, while the ring proton signals disappear. Successful ENDOR has recently been performed on radicals in a viscous liquid crystal permitting accurate hyperfine structure (hfs) measure-ments (323). In (312) the alternating linewidth in ESR for hindered rotation is compared with the linewidth effect seen in ENDOR, viz a standard two-site jump case where the two lines first broaden and then merge. Kwiram (324) has recently given a detailed review of ENDOR with a thorough coverage of solid state ENDOR.

*ELDOR.*—Eastman et al (325) report on a quantitative test of the ELDOR theory given (326) for free radicals in liquids. The reduction factors, due to HE, extrapolated to infinite pump power for aqueous PADS were shown to be in very good agreement with the theory which predicts the ELDOR effect of HE is just to transmit the saturation of the line being pumped to *all* the other hyperfine lines. Das et al (266) report on an ELDOR experiment on the benzene anion. It was possible to demonstrate that its anomalously large width has no significant contribution from any chemical or Heisenberg exchange processes. It is expected that the ELDOR technique will play an increasingly useful role in elucidating spin-relaxation mechanisms.

Hyde et al (327) give a detailed discussion of the frequency-swept ELDOR technique, which they applied to liquid and frozen solutions of DPPH in toluene. They show, as an example of the potential value of ELDOR as an analytical technique, how the large nitrogen hfs can be determined with a precision greater by more than an order of magnitude than has been possible by conventional ESR means. They also show how the frequency-swept display can be suitable for observing a component line within an inhomogeneously broadened envelope. A pulsed ELDOR experiment on an irradiated single crystal of malonic acid is described (328). The method is used to determine relaxation times, and it is found that a display of the transient signal intensity

at a constant delay as a function of pump frequency yielded very narrow ESR lines. The ELDOR technique has also been used in the study of triplet excitons (329–332). An ELDOR technique employing a cavity and a helix arranged orthogonally has been used successfully on a free radical in solution (333).

## LIQUID CRYSTALS

The application of ESR to the study of liquid-crystal properties has seen considerable activity. The work focuses on probing the structure and properties of the liquid crystal and/or of the paramagnetic probe. The most popular probe appears to be vanadylacetylacetonate (VA). Chen & Luckhurst (334) have studied the degree of alignment of this probe in liquid crystal mixtures containing varying amounts of nonmesomorphic solutes. Although the isotropic-nematic transition point is depressed, the alignment of the probe at the same reduced temperature is independent of either the solute or its concentration, which suggests that the ordered structure of the mesophase is not affected by the solute.

Schwerdtfeger & Diehl (335) studied VA in a room temperature liquid crystal, which is viscous enough to produce a glassy-type spectrum. They observe a very large intensity ratio ($\sim 20/1$) of the $\perp$ to $\parallel$ components of the glassy VA spectrum due to the preferred orientation of VA such that $\beta = \pi/2$ is most probable (where $\beta$ is the angle between the molecular $z$ axis, which is $\perp$ to the VA plane, and the magnetic field). They could dramatically change the ESR spectrum by reorienting the axis of the liquid crystal (and thereby the preferred VA axis) by applying 2 kV/cm electric field $\perp$ to the magnetic field. They (336) also varied the angle between the two fields to study the ESR spectrum as a function of this angle. (The liquid crystal axis is taken to be along the electric field.) The angular-dependent intensities may then be used to determine the a priori probability distribution $P_0(\Omega)$ for the probe.

Fryburg & Gelerinter (337) found a similar viscous effect with a long temperature range liquid crystal when near its melting point; but it had more typical nematic behavior near its transition point. James & Luckhurst (338) studied VA in a binary mixture of nematogens supercooled sufficiently below their melting points to give the glassy-type ordered spectra. The molecular motion was so slow that they could obtain the angular dependence of the spectra simply by rotating the sample tube. They analyze more rigorously than Schwerdtfeger & Diehl (335) the spectral intensities by computing the spectral lineshapes in a manner analogous to that for glassy spectra, but weighting each orientation with the distribution function $P_0(\Omega) = (8\pi^2)^{-1}P_0(\beta) = C \exp (a \sin^2 \beta + b \sin^4 \beta)$. Their mixed solvent results required both quadratic and quartic terms for a good fit, although their reanalysis of the data given in (335) for a pure nematogen required only the quadratic term. Later (339) it was noted that $P_0(\Omega)$ is more rigorously represented by an expansion of even Legendre functions in the exponent. Schwerdtfeger et al (340) more recently point out that in viscous nematics the effective order parameter must be corrected for slow motional effects on the spectral separations (cf 45) to obtain

true order parameters. Other workers (341, 342) have also discussed ESR spectra in nematic glasses.

Application of the stochastic Liouville method to an analysis of the ESR spectra for viscous ordered liquids would be helpful in understanding such spectral observations rigorously. Kaplan (343) briefly outlines how the finite difference approach (cf Eq. 4) may be applied when only secular terms are kept.

Brooks et al (344) have recently suggested an explanation for the asymmetric deviations from Lorentzian shape of VA lines near their transition point in terms of a random distribution of director, which is expected to reorient slowly ($\gtrsim 10^6$ Hz) on ESR time scales. They take this distribution to be of form $f(\theta) = C \exp (\alpha \cos^2 \theta)$, and obtain $\langle \sin^2 \theta \rangle$ of 0.05 to 0.08 from their analysis of the experimental lineshapes, compared to 0.04 using De Gennes' theory (345). They offer argument against the lineshape asymmetry being due to a slow rate of molecular reorientation.

There have been other experiments on ordering of liquid crystals in combined electric and magnetic fields (346–348). These results demonstrate a consistent discrepancy with the prediction of alignment of the director along the electric field, and it requires assuming that the director must be tilted relative to the electric field (angle $\varphi$) to get good agreement with experiment (347, 348). Luckhurst (349) has recently reexamined the experiment of (347) utilizing a more accurate expression of observed hyperfine splitting as a function of director magnetic angle $\theta$ and assuming that $\theta = \varphi - \delta$ where $\delta$ is the angle between electric and magnetic fields.

Other studies in nematic liquid crystals have used a variety of paramagnetic probes. Nitroxide radicals have been popular because of their stability, knowledge of their magnetic parameters, and great range of synthetic possibilities. Ferruti et al (350) studied the ordering of a spin-labeled rodlike probe, similar to the host nematic molecules, in a variety of solvents and find it is substantially ordered. They later show (351) with other spin labels that there can be nonunique ordering, due either to more than one allowed conformation of the piperidine ring containing the N–O relative to the long axis of the spin label, and/or for L-shaped molecules there may be two stable patterns in which either one of the arms of the L substitutes for a nematogen molecule. Corvaja et al (352) studied a series of nitroxide radicals and biradicals, finding that the degree of orientation increases with molecular length, as expected. Nordio (353) points out that their observed linewidth variation for an elongated nitroxide biradical is qualitatively consistent with more rapid rotational diffusion about the long axis of the molecule than about the other axes.

The ordering of other free radicals and the relationship between their theoretically predicted $A$ and $g$ tensors and the $A$ and $g$ values observed in nematics is discussed by several authors (354–358) with a particularly detailed summary by Falle & Luckhurst (358). Haustein et al (354) also studied the effect of counter-ion on the ordering of TCNE$^-$. Hudson & Kennedy (359) have observed a slowly rotating Cu$^{2+}$ dimer in a nematic solvent, and Cu$^{2+}$ stearate

has been observed in a nematic phase (360). Studies of charge transfer complexes oriented in liquid crystal glasses have also been reported (361, 362).

An interesting experiment bearing a close resemblance to ESR in nematics is reported by Trapp et al (363). They find that a magnetic field tends to align magnetically anisotropic paramagnetic colloidal suspensions yielding partially oriented spectra. They are able to determine a mass average mass of the particle from a comparison of theoretical and experimental spectra.

Nordio & Busolin (364) solve the rotational diffusion equation with an orienting force tending to align the molecules along the direction of the magnetic field. (They use expansions in Wigner rotation matrices related to methods used in the slow tumbling work already discussed.) The force is such that $P(\Omega_0) = C \exp (\lambda^2 \cos^2 \beta)$ where $\lambda^2$ measures its strength. This would be a reasonable first approximation for molecules having the same elongated shape as the solvent molecules. General expressions for the spectral densities are given for secular and pseudosecular terms (i.e. zero-frequency Fourier transforms of correlation functions), and isotropic diffusion coefficient, although they indicate how to include axially symmetric diffusion. Each irreducible component of the dipolar and $g$ tensors relaxes with its own set of "characteristic times" which are functions of $\lambda^2$. Their work represents the basis for a more rigorous analysis of electron-spin relaxation in nematics than the earlier treatment by Glarum & Marshall (365), who used only a single correlation time for the motional effects. Kuznetsov (366) has considered the problem from the viewpoint of an anisotropic viscosity where the principle axes of the diffusion tensor are fixed in a laboratory (as opposed to a molecular) frame. He obtains results for an arbitrary orientation of the diffusion symmetry axis (e.g. the director) relative to the magnetic field, but does not consider any molecular ordering effects which would yield a nonisotropic $P_0(\Omega)$, since he assumes a spherical radical. The major difference with asymmetric rotational diffusion in isotropic liquids is that now the relaxation times are $\tau_{L,K,M}^{-1} = L(L + 1)R_1 + (R_3 - R_1)M^2$, where $M$ is the projection "quantum number" along the lab symmetry axis. The case of uniaxial rotation of a nitroxide in an anisotropic medium has also been considered (367).

While most liquid crystal experiments have been performed on the nematic phase, there have been some studies involving the smectic mesophase. Francis & Luckhurst (368) found the direction of the ordering potential of VA to be fixed with respect to the sample tube. Sentjurc & Schara (348) report that a dc electric field aligns the molecules with their long axes perpendicular to the field. Gelerinter & Fryburg (369, 370) discuss how to determine the tilt angle characteristic of the smectic $C$ liquid crystal (i.e. the angle between the director and the optic axis) by rotation of the sample, and have recently studied smectic $A$ liquid crystals. Luckhurst & Sundholm (371) give a more complete analysis of the tilt angle determination. Seelig (372) has studied several spin labels which dissolve in smectic liquid crystals with a bilayer structure. This is a model system for bilayer membranes. The bilayer structure is homogeneously oriented

between two parallel glass surfaces. Thus the ESR spectrum depends on the orientation of the sample with respect to the applied magnetic field. This permits a determination of the ordering of the N–O principle axis system relative to the optical axis (i.e. the normal to the glass plates). The long-chain spin labels are in an almost extended configuration, although there is considerable flexibility of amphiphilic spin labels. In later work (373) Seelig extends his measurements to determine the temperature dependence of the flexibility and analyzes the results in terms of the rotational isomeric model for polymers.

Luckhurst has written several reviews on liquid crystals and ESR (374–376).

## GASES

ESR of gaseous free radicals appears to be a blossoming field. The observed radicals to date are atomic, diatomic, and triatomic. Westenberg & De Haas (383) continue to develop their techniques for measuring rates of atom-molecule reactions. In an improved system they can now measure rate coefficients nearly $10^3$ cm$^3$/mole$^{-1}$ sec$^{-1}$, and they report results on reactions of O atoms with OCS, CS$_2$, and NO$_2$ and H with C$_2$H$_4$ (377). In their improved system they obtained better results on the O atom reactions with H$_2$ and CH$_4$ (378). Rate measurements have been made on the reactions of N and H atoms with O$_2$ in its excited $^1\Delta$ states (379). They have employed a homogeneous reactor entirely contained within the detection cavity to study the O + OH $\rightarrow$ O$_2$ + H reaction (380). Kurylo & Timmons have studied the reactions of H and CH$_4$ (381), and that of O and H$_2$S (382).

Westenberg & De Haas (383) have reviewed the factors which affect linewidths of gas phase atoms and diatomics such as O$_2$. These considerations are important in determining relative concentrations of atoms from the ESR signal peak heights. They give experimental results showing that the widths of non-$S$ state atoms Cl, O (and O$_2$) in dilute concentration, are simply determined by the total pressure of the inert gas mixtures, since collisions with any atoms of molecules serve to perturb the $M_L$ or $M_J$ levels. However, for $S$-state atoms (e.g. H and N) the linewidths are dependent on the paramagnetic atom concentration via spin-exchange collisions. The measured spin exchange cross sections are reported. Ultee (384) reports cross sections for F and I (both $^3P_{3/2}$) broadening with He, Ar, and F$_2$ or I$_2$. The ESR of H atoms in a free-burning flame are broadened primarily by interaction with molecular oxygen (385). Brennen & Brown (386) have used ESR to determine N-atom concentrations in a study on the visible nitrogen afterglow spectrum.

Zijlstra et al (387) report the ESR spectra of $^{31}$P, $^{75}$As, $^{121}$Sb, and $^{123}$Sb in their $^4S_{3/2}$ ground states, which are produced by the reaction of atomic H with vapors of PX$_3$. Atoms were also produced by a heterogeneous wall reaction. Tiedemann et al (388) have observed atomic Se and Te. Atherton & Cook (389) have observed the lineshapes of the spectra of $^3P_2$ atomic O, in particular those due to multiple quantum transitions, and obtain collision cross sections in agreement with those determined by other workers.

Multiple quantum transitions have also been observed (390) for O and Cl (391). Forbidden transitions parallel to the external magnetic field have been observed for halogen atoms (392).

Carrington et al (393–395) have reviewed the electron resonance of gaseous diatomic molecules and discuss the magnetic and electric interactions in $^2\pi$ states and give a detailed discussion of the theory of diatomic molecules (395). The analysis of these spectra in terms of the effective Hamiltonian, which operates in the rotational subspace of the ground vibronic state, can yield the bond length (from the Zeeman effect) and the electric dipole moment (from the Stark effect). The spectra and analysis of SF and SeF are given in these terms (396). Uehara & Morino discuss the analysis of the NS ($^2\pi_{3/2}, J = \frac{3}{2}$) spectrum (397) and the $K$-band transitions of $^3\Sigma^-$ SO (398). The Zeeman effect of the latter yields the bond length. Carrington & Lucas (399) analyze the gas phase spectra of $^{17}$OH and $^{17}$OD to obtain the $^{17}$O magnetic hyperfine and electric quadrupole parameters. Carrington et al (400) have studied SeO in its $^3\Sigma$ and $^1\Delta$ states, and have obtained the triplet spin-spin splitting and rotational constant (yielding the bond length). Miller (401) has recently shown that the anomalously large $g$ factor observed in $^1\Delta$ SeO might be explained by corrections related to the transformations for obtaining an effective rotational Hamiltonian, which become non-negligible for molecules with heavy atoms. The rotational constant, $\Lambda$-doubling, hyperfine structure, and dipole moments of SeH and SeD have been obtained by Carrington et al (402). Uehara & Morino (403) observed the $^2\pi_{3/2}, J = \frac{5}{2}$ rotationally excited states of SH and ClO at $C$ band (4.47 GHz). Carrington et al (404) have analyzed the spectra of BrO and IO in their $^2\pi_{3/2}, J = \frac{3}{2}$ levels and have confirmed that both radicals have $^2\pi_{3/2}$ ground electronic states. The CF radical in its ground $^2\pi_{3/2}$ state has been obtained and analyzed (405).

Cupitt & Glass (406) have calculated transition probabilities for several lines of SH and SO to estimate their absolute concentrations. The relative rate constants for the reactions (a) $NO_2 + O \rightarrow NO + O_2$ and (b) $NO_2 + SO \rightarrow NO + SO_2$ was then estimated from experimental measurements. The $^1\Delta$ state of $O_2$ has been studied by Miller (407) in both the $J = 2$ and 3 rotational levels, yielding rotational constant, rotational $g$ factor, electronic orbital $g$ factor, and anisotropy of the magnetic susceptibility. Arrington et al (408) also studied $^1\Delta$ $O_2$ obtaining the $^{17}$O hyperfine coupling, and they obtained only partial agreement (409) with Miller's work. Also $^1\Delta$ $O_2$ produced by a photosensitized process using naphthalene vapor has been detected by ESR. The $^1\Delta$ SO spectra have been studied by Uehara (410) at both $C$ and $X$ bands. To explain an anomaly in the molecular $g$ values for the $J = 2$ and 3 levels they utilized mixing with the $^1\Phi$ electronic states. Miller has observed the $^{33}$S hyperfine and quadrupole structure, and obtains these parameters (411). Curran et al have observed the $^3\Sigma^-$ ground state and $^1\Delta$ $J = 2$ level of NF which is isoelectronic with $O_2$ (412). Vibrationally excited spectra of OH have been observed by Clough et al (413, 414) and by Lee et al (415). They discuss the variation of $\Lambda$-doubling and hyperfine coupling constants with vibrational energy.

The spectra of triatomic radicals $^2\pi_{3/2}$ NCS and both the $^2\Delta_{5/2}$ ($n = 2$) vibronically excited and $^2\pi_{3/2}$ ($n = 1$) NCO were obtained by Carrington et al (416) who mixed the products of a microwave discharge in $CF_4$ with HNCO and HNCS respectively. In later work (417) they also observed the $^2\Phi_{7/2}$ ($n = 3$) state of NCO. They extend the theory of the Renner coupling of electronic and vibrational modes to account for anomalous contributions to the $g$ values. Guichon et al (418) derive an expression for the microwave susceptibility of NO below 300°K. It decreases slightly faster than predicted by the Curie law.

Hess & McCourt (419) have outlined a theory for electron-spin relaxation in the gas phase based on the generalized Boltzmann equation (420) for the density matrix $\rho$ of single molecules (here $\rho$ includes molecular as well as spin degrees of freedom): $d\rho/dt = -i\mathscr{H}^\times\rho - R(\rho)$ where $R(\rho)$ is a general collision superoperator given by Snider (420). The analysis of this equation is simplified by linearizing it assuming only small deviations from equilibrium. They illustrate the analysis with the simplest case of a $^2\Sigma$ molecule with spin-rotational interaction using a simple description of the collision dynamics. The basic features are of a spectrum which initially broadens with increasing pressure at low pressures, followed by only a dominant central line whose width then decreases with increasing pressure. Freed (85) recently reviewed the stochastic Liouville approach to gas phase spin relaxation. Here one has $\dot{\rho} = -i\mathscr{H}^\times\rho - \Gamma\rho$ where $\Gamma$ is a Markovian operator, which describes in a general way the relaxation of the molecular system as a result of its intermolecular (thermal) interactions; the simplest form of $\Gamma$ is the strong collision case. One can then obtain general expressions analogous to Redfield's equation for semiclassical spin relaxation (85), provided $|\Gamma| \gg |V|$ where $V$ is the term in $\mathscr{H}$ for the spin-molecular interactions. When $|V| \gtrsim |\Gamma|$ methods of solution analogous to that for the slow tumbling problem are required.

Schaafsma & Kivelson (421) have reported essentially the only study of gas phase electron-spin relaxation for a polyatomic molecule [$(CF_3)_2NO$]. At pressures below 0.1 atm a broad Gaussian line arising from unresolved structure is seen. As the pressure is increased the line narrows, and above 10 atm is Lorentzian with width inversely proportional to total pressure. This is explained by assuming the angular momentum is relaxed by the intermolecular collisions, thus modulating the spin-rotational interaction. Cross sections could be estimated both for angular momentum relaxation as well as for spin exchange between radicals (for relatively high radical partial pressures).

Iannuzzi (422) has speculated on the possibility of observing ESR in a fully ionized, low temperature gaseous plasma. Maguire & Bernheim (423) report that in observing cyclotron resonances from a gaseous discharge, fine structure begins to appear as the pressure of the gaseous discharge is decreased; they conjecture that this fine structure may be due to plasma oscillations. Janzen & Gerlock (424) describe how gas phase free radicals produced by photolysis of volatile organic compounds may be trapped in the ESR cavity by spin trapping techniques. Kotake et al (425) describe how the gas phase ESR data of the

group VIB hydride radicals may be used to interpret their amorphous ESR spectra.

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