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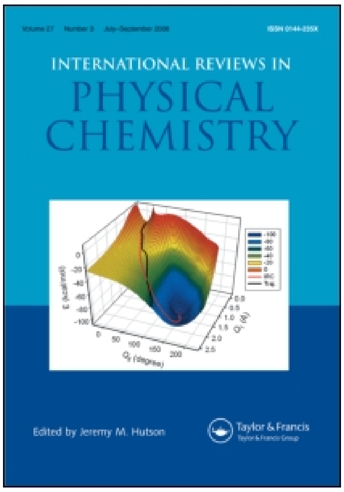

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# Dynamic EPR and ENDOR spectroscopies of organic radicals

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# Dynamic EPR and ENDOR spectroscopies of organic radicals

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Applications of density matrix theory to the analysis of dynamic EPR and ENDOR spectra of organic radicals in solution are reviewed. Using some significant examples it is shown that lineshape analysis often uniquely provides direct kinetic information on reorganizing chemical systems at thermodynamic equilibrium. Temperature-dependent hyperfine coupling constants are shown to be useful for extracting information on the dynamical processes. The potency and drawbacks of dynamic EPR and ENDOR techniques are compared and discussed.

## 1. Introduction

Magnetic resonance spectroscopy has been used as one of the most effective techniques for the investigation of chemical-dynamic processes. A wide variety of nuclear exchange processes in diamagnetic systems have been investigated by NMR techniques (Fraenkel 1986, Jackman and Cotton 1975, Kaplan and Fraenkel 1980), whereas EPR and ENDOR spectroscopies have been proved to be of unique value in the elucidation of both the structure and the dynamics of paramagnetic molecules over a wide range of temperatures.

A large body of results has accumulated and there are reviews of the many areas in which dynamic EPR (Hirota and Ohya-Nishiguchi 1986, Hudson and Luckhurst 1969, Sullivan and Bolton 1970) and ENDOR (Kurreck, Kirste and Lubitz 1984) spectroscopies have been applied. An exhaustive collection of data is available in the *Electron Spin Resonance, Specialist Periodical Reports* series (Norman 1973, 1974, 1976, Ayscough 1977, 1979, 1981, 1982, 1983, 1985, Symons 1986, 1987).

All manner of phenomena involving internal rotations, fast conformational flips, fluxionality, polytopal rearrangements, proton and cation transfers, etc., can be explored, provided that they occur on the time scale of the method, typically $10^{-9}$–$10^{-4}$ s for both EPR and ENDOR. The range of sensitivity begins when the rate $k$ of the process approaches the linewidth (slow motional limit) and continues until the rate exceeds the change $\Delta\omega$ in Larmor frequency caused by the process itself (fast motional limit):

$$\underset{\text{fast motional limit}}{0{\cdot}1} \quad \lesssim \quad \Delta\omega/k \quad \lesssim \quad \underset{\text{slow motional limit}}{10}$$

There are two distinct effects with respect to the temperature-dependent appearance of the spectra. Firstly, hyperfine coupling constants often show a marked temperature dependence due to internal motions. Secondly, lineshapes can be temperature-dependent because the molecule is involved in a rate process modulating isotropic hyperfine coupling, the rate being temperature-dependent. Furthermore, intermolecular exchange effects, i.e., chemical and Heisenberg exchange may cause line broadening.

Using the density matrix formalism, it is possible to calculate the EPR and ENDOR lineshape of any chemically reorganizing system or combination thereof under a variety of experimental conditions. Comparing calculated with experimental spectra, one can extricate the macroscopic first order (for an intramolecular process) or pseudo-first order (for an intermolecular process) rate constants $k_{\mathrm{MN}}$ (in $\mathrm{s}^{-1}$) for reorganization of species M into species N. The reciprocal mean lifetime of each species M is related to the rate constants for the different reorganization processes as

$$\tau_{\mathrm{M}}^{-1}=\sum_{\mathrm{N}\neq\mathrm{M}} k_{\mathrm{MN}} \tag{1}$$

In addition, a detailed balancing of the rate constants demands that

$$p_{\mathrm{M}}k_{\mathrm{MN}}=p_{\mathrm{N}}k_{\mathrm{NM}} \tag{2}$$

where $p_{\mathrm{M}}$ is the equilibrium population of species M. Thus, lineshape analysis often uniquely provides kinetic data on reorganizing chemical systems at thermodynamic equilibrium.

The general background of the density matrix formalism is set out in standard textbooks (Abragam 1961, Atherton 1973, Slichter 1978), and a very thorough analysis for ENDOR has been carried out by Freed (1965, 1967, 1972, 1979). The application of the density matrix theory to the analysis of dynamic EPR spectra has been discussed by, among others, Heinzer (1971), who has also described two computer programs for the synthesis (1972) and the iterative least-squares lineshape fitting (1974) of dynamic EPR spectra.

In the next section we present a brief outline of the density matrix theory of EPR and ENDOR spectra for reorganizing systems. The possibilities of simplifying the general formalism in view of practical applications of dynamic EPR and ENDOR spectroscopies are described and referenced. Since the complexity of the relevant material necessitates restrictions for an article of prescribed length, we will not consider intermolecular processes such as electron transfer and Heisenberg spin-exchange, or the relevant topic of relaxation phenomena due to modulation of anisotropic magnetic interactions by molecular tumbling. The subsequent section is a rather cursory treatment of the use of temperature-dependent hyperfine coupling constants for extracting quantitative information on the dynamics of reorganizing radicals. In the last sections we present a few examples of applications, with particular attention to dynamic ENDOR measurements, and compare the conditions which make EPR and ENDOR techniques suitable for studying dynamic phenomena in organic radicals.

## 2. Lineshape and mechanism

By the introduction of the effects of the exchange processes, the equation of motion for the density operator of the spin system can be given by the generalized Liouville equation

$$\dot{\chi}(t)=\mathrm{i}[\chi(t),\ \mathscr{H}_0+\varepsilon(t)]-\Gamma\chi(t)-E\chi(t)+(\mathrm{i}\hbar/\mathscr{A}k_{\mathrm{B}}T)[\varepsilon(t),\ \mathscr{H}_0] \tag{3}$$

where $\mathscr{H}_0$ is the static zero-order contribution to the spin hamiltonian

$$\mathscr{H}_0=(\bar{g}\beta_e/\hbar)B_0S_z-\sum_n(\gamma_nB_0J_{zn}+\gamma_e\bar{a}_nS_zJ_{zn}) \tag{4}$$

including isotropic electron Zeeman, nuclear Zeeman, and electron-nuclear hyperfine interactions; $\gamma_e$ and $\gamma_n$ are the electron and nuclear (for the $n$th nuclear species) gyromagnetic ratios, $B_0$ is the d.c. magnetic field, $\bar{a}_n$ is the isotropic hyperfine interaction for the $n$th species, and $\mathbf{J}$ is the coupled nuclear spin angular momentum operator of the $n$th group of completely equivalent nuclei, that is

$$\mathbf{J}_n=\sum_{i\in n}\mathbf{I}_i \tag{5}$$

$\varepsilon(t)$ describes the interaction of the spins with all electromagnetic radiation and Zeeman modulation fields and is given by (Dalton and Dalton 1979, Freed 1979)

$$\varepsilon(t)=\tfrac{1}{2}(\gamma_eS^+ +\Sigma_n\gamma_nJ_n^+\Sigma_jB_j\exp(-\mathrm{i}\omega_jt)+\tfrac{1}{2}(\gamma_eS^- +\Sigma_n\gamma_nJ_n^-)\Sigma_jB_j\exp(\mathrm{i}\omega_jt)$$
$$+\tfrac{1}{2}(\gamma_eS_z+\Sigma_n\gamma_nJ_{zn})B_m[\exp(\mathrm{i}\omega_nt)+\exp(-\mathrm{i}\omega_mt)] \tag{6}$$

In equation (6) $B_j$ are the magnitudes of the microwave and r.f. fields in the rotating frame with frequency $\omega_j$. $B_m$ and $\omega_m$ are the amplitude and the frequency of the Zeeman modulation field, respectively. $\Gamma$ is the stochastic relaxation superoperator, which yields the linewidths and the transition probabilities for relaxation from nonequilibrium population distributions. Since, in this report, the emphasis will be on chemical-dynamic processes, we shall not need to specify this superoperator more explicitly than to assume that it can be handled by Redfield theory (Redfield 1957, 1965), which holds in the motional narrowing regime, where molecular tumbling frequencies are much greater than the frequencies of anisotropic magnetic interactions (Freed and Fraenkel 1963, Freed 1979). However it should be realized that any distinction between relaxation and chemical-exchange phenomena is largely a matter of convenience. Relaxation and exchange processes may in fact be so closely interlinked that a separate treatment cannot be justified. $\chi(t)$ is the reduced density operator,

$$\chi(t)=\rho(t)-\rho_0 \tag{7}$$

which represents deviations of the spin density operator $\rho(t)$ from its value $\rho_0$ at thermal equilibrium. The last term in equation (3) is a part of a high-temperature approximation such that

$$\rho_0=\frac{\exp(-\hbar\mathscr{H}_0/k_BT)}{\mathrm{Tr}\exp(-\hbar\mathscr{H}_0/k_BT)}\simeq\frac{1}{\mathscr{A}}\left(1-\frac{\hbar\mathscr{H}_0}{k_BT}\right) \tag{8}$$

where $\mathscr{A}$ is the total number of spin eigenstates, $k_B$ is Boltzmann's constant, and $T$ the absolute temperature.

The term $E\chi(t)$ in equation (3) includes all reorganizing processes. In general, these processes can be described in terms of chemical exchange among different chemical species, so that $\chi(t)$ is a composite statistical operator

$$\chi(t)=|\chi^1(t),\ldots,\chi^M(t),\chi^N(t),\ldots| \tag{9}$$

which is a vector operator in the space of exchanging chemical species. The hamiltonian of the composite system is the direct sum of the constituent hamiltonians, and the same holds for the composite relaxation superoperator.

We need to distinguish between intramolecular and intermolecular exchange. When individual molecules undergo internal exchange processes, such as hindered rotation, certain atoms are moved to different positions and as a result the nuclear moments find themselves in different magnetic surroundings. A reasonable approach to the general intramolecular reaction is to number the atoms in a molecule and to consider all of the configurations that can be attained by these atoms as a result of interconversions and interchanges. For each configuration a hamiltonian can be written and a reaction can be represented by the random switching from one hamiltonian to another (Johnson 1964, 1965). All the hamiltonians have the same form and differ from each other only in that some magnetic quantities (hyperfine splitting constants, $g$-factors, etc.) have changed their values. Thus, for intramolecular processes, the exchange term in equation (3) can be given as

$$-E\chi^{M}(t)=\sum_{N\neq M} k_{NM}\chi^{N}(t)-\chi^{M}(t)/\tau_{M} \qquad (10)$$

leading to coupled equations, one for each site M, which are similar to the Kubo–Anderson–Sack–McConnel equations (KASM) (Anderson 1954, Kubo 1954, McConnell 1958, Sack 1958), and become identical to the KASM equations for $k_{NM}=k_{MN}$.

It appears from equation (10) that intramolecular processes change the species labels and the hamiltonian, but leave the spin product functions unchanged, i.e. the state of the spin system after an exchange is completely determined by its previous state.

In our laboratory we have extensively applied (Barzaghi *et al.* 1986) equation (10), both to the general non-degenerate rearrangement

$$\mathrm{A} \rightleftharpoons \mathrm{B} \qquad (11)$$

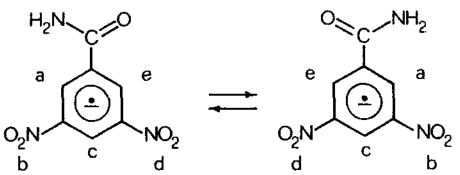
such as (Branca *et al.* 1982)

(12)

and to degenerate rearrangements

$$\mathrm{A} \rightleftharpoons \mathrm{A} \qquad (13)$$

such as (Barzaghi *et al.* 1980 a)



(14)

The latter case is an intramolecular mutual exchange where the hamiltonians of the nuclear configurations are identical except for the labelling of the particles. For this case equation (10) can be reformulated in the spin space of one particular nuclear reference configuration according to Kaplan (1958 a) and Alexander (1962 a)

$$-E\chi=k(P\chi P-\chi) \qquad (15)$$

Evaluation of the exchange operator $P$ in the eigenfunction representation is a cumbersome task. However, using product functions $P$ becomes a permutation matrix, each element of which is 1 or 0, and its effect on an element of $\chi$ is to invert the order of the spin functions. In the example of equation (14) we have

$$\langle \mathrm{abcde}|P\chi P|\mathrm{a'b'c'd'e'}\rangle = \langle \mathrm{edcba}|\chi|\mathrm{e'd'c'b'a'}\rangle \tag{16}$$

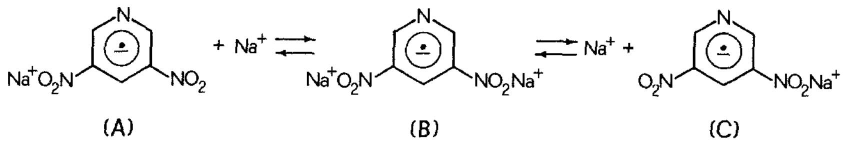
Thus, in the product representation changes in the nuclear spin wavefunction run exactly parallel to the chemistry.

In intermolecular exchange reactions, the nuclear spin state of the system of interest after the exchange is determined by the spin states of both colliding species as well as of the complex encounter. The matrix element of the exchange for the transition $\alpha\mathrm{a}\rightarrow\alpha'\mathrm{a}'$ of the species M will be given by (Kaplan 1958 b, Alexander 1962 b)

$$-(E\chi)^{\mathrm{M}}_{\alpha\mathrm{a},\alpha'\mathrm{a}'}=\left[\frac{1}{\mathscr{E}}\delta_{\alpha\alpha'}\Sigma_{\gamma}\chi^{\mathrm{M}}_{\gamma\mathrm{a},\gamma\mathrm{a}'}-\chi^{\mathrm{M}}_{\alpha\mathrm{a},\alpha'\mathrm{a}'}\right]\Big/\tau_{\mathrm{M}}+\delta_{\mathrm{aa}'}\sum_{\mathrm{N}\neq\mathrm{M}}\frac{k_{\mathrm{NM}}}{\mathscr{N}_{\mathrm{N}}}\Sigma_{\mathrm{b}}\chi^{\mathrm{N}}_{\alpha\mathrm{b},\alpha'\mathrm{b}} \tag{17}$$

where the Greek labels refer to spin product functions of the exchanging group and Roman labels refer to the product functions of the non-exchanging groups. $\mathscr{E}$ denotes the dimension of the exchanging group and $\mathscr{N}_{\mathrm{N}}$ denotes the dimension of the non-exchanging groups in radical N.

Equation (17) applies, for example, to intermolecular cation exchange reactions (Al-Baldawi and Gough 1970, 1071, Adams and Atherton 1968, Atherton *et al.* 1984, Barzaghi *et al.* 1978, 1980 a, b, 1981, Chen and Hirota 1971, Gough and Hindle 1969, 1970, 1971, Rutter and Warhurst 1968, 1970) which proceed by forming short-lived ion triplets



(18)

Now we return to equation (3) and seek its stationary solutions by expanding $\chi(t)$ in a generalized Fourier series

$$\chi(t)=\textstyle\sum_{\mathbf{k}}\sum_{r}Z(\mathbf{k},r)\exp\left[\mathrm{i}(\omega^{\dagger}\mathbf{k}+r\omega_{\mathrm{m}})t\right] \tag{19}$$

where $\omega^{\dagger}=|\omega_1,\omega_2,\ldots|$ contains the radiation frequencies and $\mathbf{k}^{\dagger}=|k_1,k_2\ldots|$ the corresponding harmonic identifiers.

In an ENDOR experiment we have a microwave 'observing' field $(B_1,\omega_1)$, which stimulates the electron spin response that is phase-detected and displayed, and a 'pump' r.f. field $(B_2,\omega_2)$ which stimulates nuclear transitions, in addition to the Zeeman modulation field $(B_{\mathrm{m}},\omega_{\mathrm{m}})$. As only the $\mathbf{k}=|1,0|$ harmonic of the radiation field is detected by the EPR spectrometer, only those harmonics that couple to $Z(1,0\mp r)$ need be considered.

The general solution can be achieved by the procedure outlined by Dalton and Dalton (1979) for an ELDOR experiment. However, for the purpose of our report, we shall neglect the effects of the Zeeman modulation field and seek steady-state solutions only for those particular elements which oscillate at a frequency close to resonance, $\chi_{\alpha\alpha'}(t)=Z_{\alpha\alpha'}\exp(\mathrm{i}\Omega_{\alpha\alpha'}t)\,\Omega_{\alpha\alpha'}$ is zero for diagonal elements, and equals $\omega_1$ and $\omega_2$ for allowed EPR and NMR transitions, respectively; finally, $\Omega_{\alpha\alpha'}$ is $\omega_1+\omega_2$ for a two-quantum transition.

One obtains after some algebraic manipulation the following supermatrix expression in the high-temperature limit,

$$\begin{vmatrix} \mathbf{A} & \mathbf{0} & -\mathbf{B} \\ \mathbf{0} & -\mathbf{A}^* & \mathbf{B} \\ -\mathbf{B}^{\dagger} & \mathbf{B}^{\dagger} & -\mathrm{i}\mathbf{C} \end{vmatrix} \begin{vmatrix} \mathbf{Z} \\ \mathbf{Z}^* \\ \mathbf{Y} \end{vmatrix} = \begin{vmatrix} \mathbf{Q} \\ -\mathbf{Q} \\ \mathbf{0} \end{vmatrix} \tag{20}$$

where **A**, **B** and **C** are supermatrices in the space of chemical configurations. Their elements, for an intramolecular process, are given by

$$\mathbf{A}_{\mathrm{MN}} = (\mathbf{K}_{\mathrm{M}} + \mathrm{i}\mathbf{R}_{\mathrm{M}} - \mathrm{i}\tau_{\mathrm{M}}^{-1}\mathbf{I})\delta_{\mathrm{MN}} + \mathrm{i}\mathbf{I}k_{\mathrm{NM}}(1-\delta_{\mathrm{MN}}) \tag{21}$$

$$\mathbf{B}_{\mathrm{MN}} = \mathbf{d}_{\mathrm{M}}\delta_{\mathrm{MN}} \tag{22}$$

$$\mathbf{C}_{\mathrm{MN}} = (\mathbf{W}_{\mathrm{M}} + \mathbf{I}\tau_{\mathrm{M}}^{-1})\delta_{\mathrm{MN}} - \mathbf{I}k_{\mathrm{NM}}(1-\delta_{\mathrm{MN}}) \tag{23}$$

The supervectors **Z**, **Y**, and **Q** are partitioned in a similar way, e.g.

$$\mathbf{Z} = \begin{vmatrix} \mathbf{Z}_1 \\ \mathbf{Z}_2 \\ \cdots \\ \mathbf{Z}_{\mathrm{N}} \\ \cdots \end{vmatrix} \tag{24}$$

Each vector $\mathbf{Z}_{\mathrm{N}}$ is defined in the $\mathscr{M}$-dimensional space of the induced transitions with elements $\mathbf{Z}^{\mathrm{M}}_{\lambda_j^-,\lambda_j^+} = \mathbf{Z}^{\mathrm{M}}_{\lambda_j}$, whereas $\mathbf{Y}_{\mathrm{M}}$ is a vector defined in the $\mathscr{A}$-dimensional space of all eigenstates with elements $\mathbf{Z}^{\mathrm{M}}_{\lambda_j^-,\lambda_j^-}$. In this notation $\lambda_j^-$ and $\lambda_j^+$ indicate two states which differ by at least the value of electron spin quantum number $M_S = \mp\frac{1}{2}$ and correspond to the $\lambda_j$th transition ($j$ serves as an index for the degenerate transitions). $\lambda_j^+$ and $\lambda_j^-$ have the same nuclear configuration if one has an allowed EPR transition, or they have different nuclear configurations if one has a forbidden EPR transition. $\mathbf{Z}^*$ is the complex conjugate of **Z**. It should be pointed out that the absorption signal of the $\lambda_j$th transition is proportional to the imaginary part of $\Sigma_{\mathrm{M}}\mathbf{Z}^{\mathrm{M}}_{\lambda_j}(1,0)$, whereas the dispersion signal is proportional to its real component. Owing to the conditions imposed to derive equation (20), these signals correspond to the zeroth Zeeman modulation harmonic (i.e. the absence of Zeeman modulation). However, signals at a given Zeeman modulation harmonic can be calculated as derivatives of the signal at the zeroth harmonic (Barzaghi and Simonetta 1983).

The width matrix $\mathbf{R}_{\mathrm{M}}$ is defined by the elements of the relaxation matrix $\Gamma_{\mathrm{M}}$ between transitions

$$R_{\lambda_j,\eta_k} = -\Gamma_{\lambda_j^-\lambda_j^+,\eta_k^-\eta_k^+} \tag{25}$$

and contains the (coupled) width of all the induced transitions.

The transition-moment matrix **d** is a $\mathscr{M} \times \mathscr{A}$ rectangular matrix, whose rows are labelled according to transition space, whereas its columns are labelled according to eigenstate space. Its elements represent the way pairs of eigenstates belonging to the $\lambda_j$th transition are coupled by the transitions induced by the radiation fields. The non-zero elements of **d** are of the type

$$d_{\lambda_j,\lambda_j^-} = -d_{\lambda_j,\lambda_j^+} = d_{\lambda_j} = \begin{cases} \frac{1}{2}\gamma_{\mathrm{e}}B_1(S^-)_{\lambda_j} & \text{(EPR)} \\ \frac{1}{2}B_2\Sigma_n\gamma_n(J_n^-)_{\lambda_j} & \text{(NMR)} \end{cases} \tag{26}$$

where $d_{\lambda_j}$ is either the EPR or the NMR transition moment. The coherence matrix $\mathbf{K}$ defined in transition space has as its $\lambda_j$th diagonal element the deviation of the Larmor frequency of the $\lambda_j$th transition from the applied radiation field,

$$\mathbf{K}_{\lambda_j, \lambda_j} = \omega^{\dagger}\mathbf{k} - \omega_{\lambda_j} \tag{27}$$

where $\omega_{\lambda_j}$ is the resonance frequency of the $\lambda_j$th transition. The off-diagonal matrix elements of $\mathbf{K}$ are proportional to the various moments given by equation (26). The matrix $\mathbf{W}$, defined in eigenstate space, is the transition probability matrix, whose $\alpha\beta$ element

$$\Gamma_{\alpha\alpha,\beta\beta} = \Gamma_{\beta\beta,\alpha\alpha} = -W_{\alpha\beta} = -W_{\beta\alpha} \tag{28}$$

for $\alpha \neq \beta$ is just minus the transition probability from state $\beta$ to state $\alpha$, and its diagonal elements are given by

$$\Gamma_{\alpha\alpha,\alpha\alpha} = W_{\alpha\alpha} = \sum_{\beta \neq \alpha} W_{\alpha\beta} = \tau_{\alpha}^{-1} \tag{29}$$

Since equations (25) through (29) hold for each chemical configuration M, we have left out label M without loss of generality. Detailed instructions for writing $\mathbf{R}$, $\mathbf{d}$, $\mathbf{K}$, and $\mathbf{W}$ matrices are given by Freed (1979).

Finally, the vector $\mathbf{Q}_{\mathrm{M}}$ has elements given by

$$Q^{\mathrm{M}}_{\lambda_j} = (\hbar/\mathscr{A}k_{\mathrm{B}}T)\omega_{\lambda_j} d_{\lambda_j} p_{\mathrm{M}} \tag{30}$$

where $p_{\mathrm{M}}$ is the equilibrium population of the Mth chemical configuration, and $\omega_{\lambda_j}$ and $d_{\lambda_j}$ are the resonance frequency and transition moment for the $\lambda_j$th transition; thus $Q^{\mathrm{M}}_{\lambda_j}$ is not zero only for allowed transitions. It should be understood that the null matrix $\mathbf{0}$ in equation (20) and the identity matrix $\mathbf{I}$ in equations (20)–(23) vary in dimensionality in order to be consistent with the matrices in these equations.

In solving equation (20) for the signal vector $\mathbf{Z}$, the normalization condition

$$\operatorname{Tr} \mathbf{Y} = \mathbf{0} \tag{31}$$

is needed because the transition probability matrix $\mathbf{W}$ and the $\mathbf{C}$ matrix are always singular (Freed 1979). The formal solution is given by

$$\mathbf{Z}'' = [\mathbf{I} + (\mathbf{L}^{-1}\mathbf{K})^2 + 4\mathbf{L}^{-1}\mathbf{B}(2\mathbf{C}^{j})^{-1}\mathbf{B}^{j}]^{-1}\mathbf{L}^{-1}\mathbf{Q} \tag{32$a$}$$

$$\mathbf{Z}' = \mathbf{L}^{-1}\mathbf{K}\mathbf{Z}'' \tag{32$b$}$$

$$\mathbf{Y} = -4(2\mathbf{C}^{j})^{-1}\mathbf{B}^{j}\mathbf{Z}'' \tag{32$c$}$$

where $\mathbf{C}^{j}$ is the matrix $\mathbf{C}$ with the $j$th row replaced by ones, and $\mathbf{B}^{j}$ is the $\mathbf{B}$ matrix with the $j$th row replaced by zero. $\mathbf{Z}'$ and $\mathbf{Z}''$ are the real and imaginary parts of $\mathbf{Z}$, respectively.

The supermatrix $\mathbf{L}$ is defined by matrix elements

$$\mathbf{L}_{\mathrm{MN}} = (\tau_{\mathrm{M}}^{-1}\mathbf{I} - \mathbf{R}_{\mathrm{M}})\delta_{\mathrm{MN}} - ik_{\mathrm{NM}}(1 - \delta_{\mathrm{MN}})\mathbf{I} \tag{33}$$

Equations (32) are nothing more than a generalized form of the well-known Bloch equations, where $\mathbf{L}^{-1}$ and $(2\mathbf{C}^{j})^{-1}$ play the role of $T_2$ and $T_1$, respectively.

The approach which has led to equations (32) is quite general and can be used without modifications for the description of electron nuclear triple resonance (TRIPLE) experiments (Möbius and Biehl 1979), as well as ELDOR and saturation experiments (Freed 1979). A general computer program for simulating magnetic multiresonance experiments, and including relaxation effects and Heisenberg spin exchange, has been described by Plato, Lubitz and Möbius (1981). Since the number of coupled equations (20) increases rapidly with the number of nuclei, solution of equation (20) for large molecules of low symmetry presents a rather forbidding computational problem, even in the absence of reorganization processes. Thus, only a few applications of an eight-level model system to the intramolecular cation migration in ion pairs have been discussed (Atherton and Kennedy 1978, Okazaki and Kuwata 1978).

When equation (20) is applied to an EPR experiment ($B_2=0$) in the limit of low microwave power ($\mathbf{d}\simeq\mathbf{0}$), it reduces to one matrix equation for each allowed EPR transition $\lambda$ (Heinzer 1971, 1972, 1974)

$$\mathbf{A}_\lambda\mathbf{Z}_\lambda=\mathbf{0}_\lambda \tag{34}$$

For a system undergoing intramolecular rearrangements as those in equations (12) and (14), one has

$$A_\lambda^{\mathrm{MN}}=[\omega_1-\omega_\lambda^{\mathrm{M}}-\mathrm{i}(T_{2,\lambda}^{\mathrm{M}})^{-1}-\mathrm{i}\tau_{\mathrm{M}}^{-1}]\delta_{\mathrm{MN}}+\mathrm{i}k_{\mathrm{NM}}(1-\delta_{\mathrm{MN}}) \tag{35}$$

and

$$Q_\lambda^{\mathrm{M}}=(\hbar/\mathscr{A}k_{\mathrm{B}}T)d\omega_1 p_{\mathrm{M}} \tag{36}$$

For the intermolecular cation exchange (18) equation (34) becomes

$$\begin{vmatrix} (\Sigma_q F_{\lambda q}^{\mathrm{A}})^{-1} & \mathrm{i}k_{\mathrm{BA}}/\mathcal{N}_{\mathrm{Na}}^2 & 0 \\ \mathrm{i}k_{\mathrm{AB}}/\mathcal{N}_{\mathrm{Na}} & (\Sigma_q F_{\lambda q}^{\mathrm{B}})^{-1} & \mathrm{i}k_{\mathrm{CB}}/\mathcal{N}_{\mathrm{Na}} \\ 0 & \mathrm{i}k_{\mathrm{BC}}/\mathcal{N}_{\mathrm{Na}}^2 & (\Sigma_q F_{\lambda q}^{\mathrm{C}})^{-1} \end{vmatrix} \begin{vmatrix} \Sigma_q Z_{\lambda_q}^{\mathrm{A}} \\ \Sigma_q Z_{\lambda_q}^{\mathrm{B}} \\ \Sigma_q Z_{\lambda_q}^{\mathrm{C}} \end{vmatrix} = -(\hbar/k_{\mathrm{B}}T)\omega_1 d \begin{vmatrix} p_{\mathrm{A}}/\mathscr{A}_{\mathrm{A}} \\ p_{\mathrm{B}}/\mathscr{A}_{\mathrm{B}} \\ p_{\mathrm{C}}/\mathscr{A}_{\mathrm{C}} \end{vmatrix} \tag{37}$$

where

$$(F_{\lambda q}^{\mathrm{M}})^{-1}=\omega_1-\omega_{\lambda_q}^{\mathrm{M}}+\mathrm{i}\tau_{\mathrm{M}}^{-1}+\mathrm{i}(T_{2,\lambda_q}^{\mathrm{M}})^{-1} \tag{38}$$

and $\lambda$ runs over all the allowed EPR transitions of the aromatic fragment, whereas $q$ runs over the nuclear spin product functions of the cation(s).

It is also common practice to apply equation (34) to the lineshape analysis of ENDOR spectra (Iwaizumi *et al.* 1980), thereby eliminating all saturation effects.

The theory described so far allows a complete lineshape analysis of dynamic EPR and ENDOR spectra, with no limitations about the rate of the motions and with the only assumption that the reorganizing phenomena can be described by jump models. Also, Heisenberg exchange and electron transfer effects can easily be included (Freed 1967, 1979, Eastman *et al.* 1969).

In the fast motional region, equations (32) and (34) are greatly simplified, as we are now dealing with one averaged spectrum, and dynamic effects can be treated by Redfield's relaxation matrix theory (Freed and Fraenkel 1963, Fraenkel 1967). In this region EPR spectra can be synthesized as a sum of lorentzian lineshapes of linewidth

$$T_{2,\lambda}^{-1}=(T_{2,\lambda}^{-1})_{\mathrm{aniso}}+(T_{2,\lambda}^{-1})_{\mathrm{iso}} \tag{39}$$

where $(T_{2,\lambda}^{-1})_{\mathrm{aniso}}$ gives the contribution to line broadening by anisotropic dipolar modulation through the well-known relationship

$$(2/\sqrt{3}|\gamma_{\mathrm{e}}|)(T_{2,\lambda}^{-1})_{\mathrm{aniso}}=A+\sum_\alpha B_\alpha M_{\lambda\alpha}+\sum_\alpha C_\alpha\eta(M_{\lambda\alpha})+\sum_{\alpha<\beta}E_{\alpha\beta}M_{\lambda\alpha}M_{\lambda\beta} \tag{40}$$

where the summations are over all the groups of equivalent nuclei (Freed and Fraenkel 1963, Fraenkel 1967), and $M_{\lambda\alpha}$ is the spin quantum number of the $\alpha$th group of equivalent nuclei in the $\lambda$th nuclear spin configuration.

The linewidth contribution $(T_{2,\lambda}^{-1})_{\text{iso}}$ produced by modulation of the isotropic hyperfine coupling constants can be expressed by a linear combination of proper functions of the spin-projection quantum numbers of the nuclei belonging to any set of 'equivalent but not completely equivalent' nuclei (Freed and Fraenkel 1963, Fraenkel 1967)

$$(2/\sqrt{3}|\gamma_e|)(T_{2,\lambda}^{-1})_{\text{iso}} = \sum_{\alpha \lesseqqgtr \beta} F'_{\alpha\beta} M_{\lambda\alpha} M_{\lambda\beta} + \Sigma_\alpha F''_\alpha \zeta_\alpha(m_1, m_2, \ldots)_\alpha$$
$$+ \sum_{\alpha<\beta} F''_{\alpha\beta} \zeta_{\alpha\beta}(m_{1\alpha} m_{2\alpha} \ldots; m_{1\beta} m_{2\beta} \ldots) \qquad (41)$$

where $F'$ and $F''$ are positive quantities which represent, respectively, the in-phase contribution and the out-of-phase contribution to the modulation process involved. They are related to the spectral density $j(0)$ through the equation

$$F = (2/\sqrt{3}|\gamma_e|) j(0) \qquad (42)$$

The explicit form of the $\zeta$ values depends on both the molecular system and the modulation process involved. A few examples are given by Barzaghi and Simonetta (1983), who also described a very efficient computer program for the least-squares fitting analysis of complex dynamic EPR bandshapes in the fast motional region.

In the case of ENDOR, Freed (1972, 1979) has shown that, under a few simplifying approximations, the signals have a simple saturated Block lineshape

$$Z''_n = \frac{(\hbar/\mathscr{A} k_B T)\omega_1 d_\lambda d_n^2 T_{2,n}(\Omega_{\lambda,n}^2/\Omega_\lambda^2)}{1 + [(\omega_2 - \omega_n) T_{2,n}]^2 + d_n^2 T_{2,n}[1 - (\Omega_{\lambda,n}^2/\Omega_\lambda \Omega_n)]\Omega_n} \qquad (43)$$

with a relaxation-dependent intensity factor.

The exchange contribution to the nuclear linewidth is given by (Freed 1965, Das *et al.* 1970)

$$(T_{2,n}^{-1})_{\text{iso}} = \tfrac{1}{4}\, j(0) = (\sqrt{3}|\gamma_e|/8) F \qquad (44)$$

In the very slow motional region, where the individual spectra of each chemical configuration are well resolved, the exchange contribution to the ENDOR linewidth is often estimated by the relationship

$$(T_{2,n}^{-1})_{\text{iso}} = k \qquad (45)$$

In this region, the rate constant for a two-jump process can also be derived by the separation $\Delta\omega$ of the two correlated ENDOR lines (Borczyskowski *et al.* 1975)

$$\Delta\omega = (\Delta\omega_{\max}^2 - 8k^2)^{1/2} \qquad (46)$$

with $\Delta\omega_{\max} = \tfrac{1}{2}|\gamma_e(a_{\text{I}} - a_{\text{II}})|$. At the coalescence point $\Delta\omega_{\max}/k = 2\sqrt{2}$.

## 3. Temperature dependence of hyperfine coupling constants

In the fast motional region, where averaged spectra of reorganizing systems are observed, the hyperfine patterns can be analysed in terms of averaged hyperfine coupling constants

$$\bar{a} = \sum_{\text{M}} a_{\text{M}} p_{\text{M}} \qquad (47)$$

where $a_{\text{M}}$ is the hyperfine coupling constant of a given nucleus (or group of completely equivlent nuclei) in the Mth chemical configuration, with population $p_{\text{M}}$.

By rearranging equation (47), the equilibrium constant for the corresponding reorganizing process can be obtained. For a two-jump process one has

$$K=(a_{\mathrm{I}}-\bar{a})/(\bar{a}-a_{\mathrm{II}}) \tag{48}$$

Equation (48) has been applied, for example, to the cis-to-trans isomerization of 3-nitrobenzaldehyde anion radical (12) (Branca *et al.* 1982) and to a large number of association–dissociation phenomena in ion pairs (Barzaghi *et al.* 1978, 1980, 1981, Echegoyen *et al.* 1984, Hirota 1968, Stevenson *et al.* 1984, Sullivan and Menger 1977, Szwarc 1972).

In general, if one hyperfine coupling constant shows a pronounced dependence on some structural parameters, such as a torsional angle $\vartheta$, it can be fitted to a Fourier series

$$a(\vartheta)=a_0+\sum_i(a_{\mathrm{c},i}\cos \mathrm{i}\vartheta+a_{\mathrm{s},i}\sin \mathrm{i}\vartheta) \tag{49}$$

This orientation dependence usually gives rise to a strong temperature dependence, since the observed coupling is the average of the expectation values of $a(\vartheta)$ for all torsional states weighted by their populations according to Boltzmann statistics, provided that transitions between the torsional levels are rapid on the time scale of the EPR experiment (Barzaghi *et al.* 1980, Kirste *et al.* 1979, Krusic *et al.* 1971 a, b, Shimoda *et al.* 1979).

Also the torsional potential is usually expanded in a Fourier series of the form

$$V(\vartheta)=V_0+\sum_i(V_{\mathrm{c},i}\cos \mathrm{i}\vartheta+V_{\mathrm{s},i}\sin \mathrm{i}\vartheta) \tag{50}$$

Potentials of this type should be viewed as effective potentials in which there are small adiabatic displacements in other modes of much higher frequency. The underlying assumption is that the torsional mode is approximately separable from all the higher-frequency modes of the radical. The Hamiltonian that corresponds to this model is

$$\mathscr{H}=\frac{-d}{\mathrm{d}\vartheta}B(\vartheta)\frac{\mathrm{d}}{\mathrm{d}\vartheta}+V(\vartheta) \tag{51}$$

where B($\vartheta$) is the internal rotation constant.

$B(\vartheta)$ is not truly a constant, but, rather it varies with the torsional angle $\vartheta$. Effectually, $B(\vartheta)$ is likewise expanded in a Fourier series of the form

$$B(\vartheta)=B_0+\sum_i(B_{\mathrm{c},i}\cos \mathrm{i}\vartheta+B_{\mathrm{s},i}\sin \mathrm{i}\vartheta) \tag{52}$$

Finally, the hamiltonian matrix $\langle i|\mathscr{H}|j\rangle$ is diagonalized by expanding the wavefunction in a Fourier series

$$\psi_j(\vartheta)=\sum_{i=0}(\psi_{\mathrm{c},ji}\cos \mathrm{i}\vartheta+\psi_{\mathrm{s},ji}\sin \mathrm{i}\vartheta) \tag{53}$$

and the dependence of the hyperfine coupling constant is estimated through the relationship

$$\bar{a}(T)=\sum_j\langle\psi_j(\vartheta)|a(\vartheta)|\psi_j(\vartheta)\rangle\exp(-E_j/k_{\mathrm{B}}T)/\sum_j\exp(-E_j/k_{\mathrm{B}}T) \tag{54}$$

where $\psi_j(\vartheta)$ and $E_j$ are the $j$th normalized eigenfunction and eigenvalue of the rotor. An alternative approach suggested by Krusic *et al.* (1971 a, b) is to consider the classical limit to which equation (54) tends as the reduced moment of inertia increases:

$$\bar{a}(T)=\frac{\int a(\vartheta)\exp[-V(\vartheta)/k_BT]\,d\vartheta}{\int \exp[-V(\vartheta)/k_BT]\,d\vartheta} \tag{55}$$

The potential barriers can be obtained by matching the calculated with the experimental hyperfine coupling constants over the explored range of temperatures. Equations (54) and (55) have been extensively applied to the analysis of temperature-dependent hyperfine coupling constants of $\beta$ protons, whose functional relation with the torsional angle had been established from single-crystal studies (Heller and McConnell 1960)

$$a_\beta^H(\vartheta)=B_0+B_2\cos^2\vartheta \tag{56}$$

## 4. Examples of applications

An exhaustive report on temperature-dependent splitting constants in the EPR spectra of organic radicals has been published by Sullivan and Menger (1977). Applications of equations (54) and (55) to ENDOR data are collected in table 1. Temperature dependence of $\beta$-proton splittings have been investigated to determine barriers to hindered internal rotation of alkyl groups in phenoxyl (Shimoda *et al.* 1979, Shimoda 1980) and galvinoxyl (Kirste *et al.* 1979) radicals, and in biphenyl (Nemoto *et al.* 1975 a, b) and naphthalene (Nemoto 1976) anion radicals. The restricted rotation of the ethyl and cyclopropyl groups is controlled by a two-fold potential, whereas a double-well potential is needed to fit the data for the isopropyl and cyclohexyl derivatives. In the case of anion radicals, the steric effect of the solvated counterion can alter the shape of the potential (Nemoto 1976). The estimated potential barriers range from 4·6 to 11 kJ mol$^{-1}$, depending on the system, and are attributed to both conjugative interaction and steric hindrance.

Applications of EPR linewidth and lineshape studies to kinetic problems have been explored extensively over the last thirty years and are covered by a number of authoritative reviews (Johnson 1965, Fraenkel 1967, Hudson and Luckhurst 1969, Sullivan and Bolton 1970, Hirota and Ohya-Nishiguchi 1986).

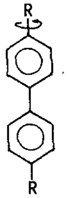
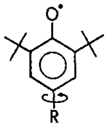
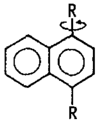
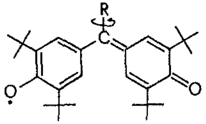
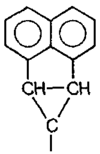
In this section we discuss some representative applications of the ENDOR technique in studying a variety of kinetic problems (Kurreck *et al.* 1984). The determination of rate constants from dynamic ENDOR experiments is largely analogous to the method used in dynamic NMR spectroscopy. As shown in a previous section, line-shape analyses as well as linewidths or peak separations can be used for the evaluation. The ENDOR linewidth is dependent upon the degree of saturation of the nuclear spin system by the r.f. field. Because of saturation broadening, it is necessary to extrapolate to zero r.f. power to obtain the true nuclear (ENDOR) linewidths to which equation (44) applies. However, the determination of the rate constant from line positions according to equation (46) was found to be uninfluenced by saturation broadening and by other ENDOR relaxation effects (Borczyskowsky *et al.* 1975). The activation energy $E_a$ of the dynamic process can be determined from the temperature dependence of the rate constant using the Arrhenius equation,

$$k=A\exp(-E_a/RT)$$

and the activation enthalpy $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ are obtained using Eyring's theory:

$$k=(k_BT/h)\exp(\Delta S^{\neq}/R)\exp(-\Delta H^{\neq}/RT)$$

Table 1. Rotational barriers of alkyl-groups from temperature dependences of $\beta$-proton hyperfine coupling constant.

| Compound and mechanism | | Method of analysis | Potential barrier (kJ/mol) | | References |
|---|---|---|---|---|---|
| | | | $V_0$ | $V_m$ | |
|  | | ENDOR, eqn (54) | | | |
| | R = ethyl | (*a*) | 4·2 | — | Nemoto *et al.* (1975) |
| | isopropyl | (*b*) | 5·0 | 2·1 | |
| | cyclohexyl, cyclopentyl | (*b*) | 5·0 | 2·5 | |
| | cyclopropyl | EPR | 1·9 | — | Hudson and Bauld (1972) |
|  | | ENDOR, eqn (54) | | | |
| | R = ethyl | (*a*) | 4·6 | — | Shimoda *et al.* (1979) |
| | isopropyl | (*b*) | 6·7 | 2·9 | |
| | cycloexyl | (*b*) | 6·7 | 2·9 | |
| | cyclopropyl | (*a*) | 11 | — | Shimoda (1980) |
|  | | ENDOR, eqn (54) | | | |
| | R = ethyl | (*c*) | 13 | 2·9 | Nemoto (1976) |
| | propyl | (*c*) | 25 | 5·0 | |
|  |  | ENDOR, eqn (55) | | | |
| R = cyclopropyl and | | (*a*) | 9·2 | | Kirste *et al.* (1979) |

(*a*) $V(\vartheta)=(V_0/2)(1-\cos 2\vartheta)$.

(*b*) $V(\vartheta)=\sum_{n=0}^{3} a_n \cos 2n\vartheta$ with $a_0=(1/18)(4V_0+9V_m)$, $a_1=2a_2=-(4/9)V_0$, $a_3=(1/18)(8V_0-9V_m)$.

(*c*) $V(\vartheta)=\sum_{n=0}^{3} a_n \cos n\vartheta$ with $a_0=a_2=(1/4)(V_0+V_m)$, $a_1=3a_3=(3/8)(V_0-V_m)$.

The rate parameters determined for representative examples are given in table 2.

A dynamic process observed in triphenylmethyl derivatives was interpreted as an interconversion of left- and right-handed propeller conformations (Hyde *et al.* 1966, Kispert *et al.* 1968). Restricted rotation of alkyl side chains in the radical anion of ubisemiquinone was studied by Das *et al.* (1970). Watanabe (1975) investigated the temperature dependence of the ENDOR spectra of tetraaryl and bis(biphenylylene)allyl radicals, and estimated the activation energy of the torsional vibration of the allyl skeleton to be about 10 kJ mol$^{-1}$ between 163 and 213 K. Above 398 K the torsional vibration becomes vigorous and the allyl skeleton begins to rotate internally with activation energy ranging between 54 and 92 kJ mol$^{-1}$.

Borczyskowski *et al.* (1975) analysed temperature-dependent linewidths and linepositions of H-ENDOR spectra of six silacyclo-pentadiene anion radicals and interpreted this dynamic behaviour as being due to hindered rotation of substituted phenyl rings. It was concluded that the main part of the barrier stems from $\pi$ conjugation effects.

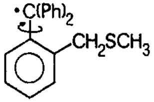
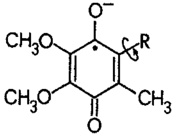
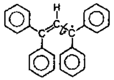
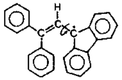
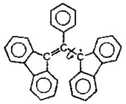
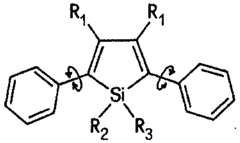
Internal rotation of phenyl groups has also been observed in the case of substituted naphthalenes (Borczyskowski and Mobius 1976) and in the case of terphenyl radical anions (Plato *et al.* 1976, Melzer *et al.* 1982), with an activation energy ranging between 18 and 38 kJ mol$^{-1}$. Relaxation effects due to torsional oscillations of phenyl rings turned out to be negligible, whilst molecular tumbling produces strong variations on linewidths at the lowest explored temperatures.

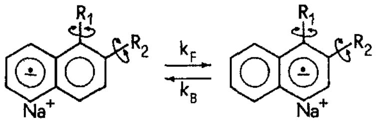
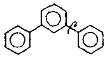
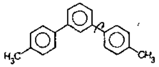
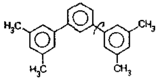
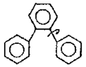
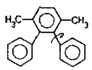
A study of N,N-diphenyl-N′-picrylhydrazyl (DPPH) by NMR, EPR, ENDOR, and TRIPLE techniques allowed four different dynamic processes to be distinguished on the NMR and ENDOR time scales. The kinetic data were determined by $^1$H-ENDOR and $^2$H-NMR spectroscopies after $^{15}$N-ENDOR and TRIPLE experiments, among others, enabled the complete determination of the hyperfine coupling constants and their signs (Biehl *et al.* 1979).

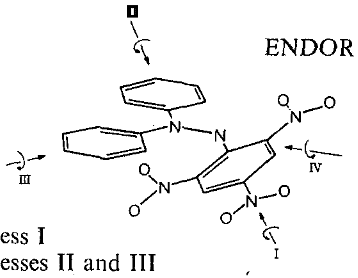
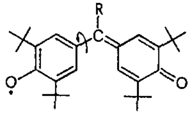
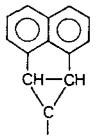
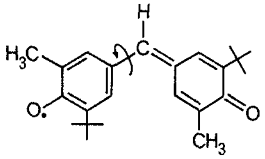
The hindered rotation of the aroxyl groups in galvinoxyls has been the subject of extensive investigations (Kirste *et al.* 1979, 1981, Steelink *et al.* 1968). The temperature dependence of linewidths and positions were analysed in terms of steric interference between bulky substituents at the methine carbon and aroxyl rings. In the case of significantly differently twisted aroxy rings, the properties of the galvinoxyl change from those of a delocalized system to a phenoxyl-type radical with really equilibrating quinoid/benzenoid rings. It was shown that one of the galvinoxyls exists in two stable conformations which can be discriminated by ENDOR-induced EPR (Kirste *et al.* 1981).

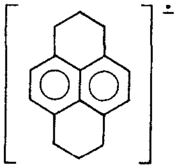
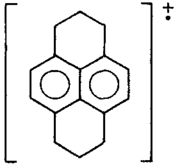
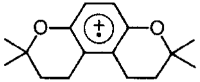
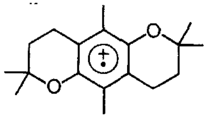
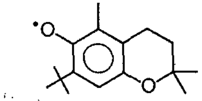
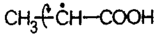
A number of radicals having flexible aliphatic systems show linewidths effects due to interconversion among conformational isomers. Iwaizumi *et al.* (1980) re-examined the conformational isomerization between a boat-like structure and a chair-like structure of the 1,2,3,6,7,8-hexahydropyrene anion radical by means of ENDOR spectroscopy, and the thermodynamic constants determined therefrom were in fair agreement with the values obtained by Claridge and Peake (1972) by EPR spectroscopy. Comparable values were obtained by Mäkelä and Vuolle (1985) for the 1,2,3,6,7,8-hexahydropyrene cation radical by using EPR, ENDOR and TRIPLE spectroscopies. It may be noted that the activation energy for both the anion and the cation radical (30–32 kJ mol$^{-1}$) is close to that for the ring inversion of tetralin-l-yl, namely 30 kJ mol$^{-1}$ (Conradi *et al.* 1979), and intermediate between that for the chair-chair interconversion of the neutral cyclohexane molecule, 42 kJ mol$^{-2}$ (Jensen *et al.* 1962), and the cyclohexyl radical, 21 kJ mol$^{-1}$ (Ogawa and Fessenden 1964). Mukai

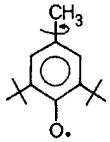
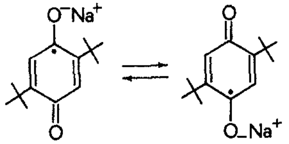
Table 2. Thermodynamic parameters from dynamic $^1$H-ENDOR spectra of representative compounds.

| Compound and mechanism | Method of analysis | Thermodynamic constants | | Reference |
|---|---|---|---|---|
| | | $E_a$ kJ/mol $^{(a)}$ | log $A$ $^{(b)}$ | |
|  | ENDOR (193–253 K) eqn (46) | 23 | 11 | Hyde *et al.* (1966),<br>Kispert *et al.* (1968) |
|  | EPR (253–313 K in DME) eqn (41) | 31·4 ± 5·36 | 13·6 ∓ 0·6 | |
| | ENDOR (223–253 K, in DME) eqn (44) | 34·1 ± 3·8 | 14·4 ∓ 0·8 | Das *et al.* (1970) |
| $R = (CH_2CH{=}C(CH_3)CH_2)_{10}H$ | | | | |
|  | EPR, eqn (34) | 56 | 14·36 | Watanabe (1975) |
|  | EPR, eqn (34) | 93 | 19·15 | Watanabe (1975) |
|  | ENDOR, eqn (46) | 10·5 | — | Watanabe (1975) |
|  | ENDOR | | | Borczyskowski *et al.* (1975) |
| (silole$^-$/MTHF + Dyglime/Na$^+$) | | | | |
| $R_1 = H$, $R_2 = R_3 = CH_3$ | Fast-jump, eqn (44) | $\Delta H^{\neq} = 27$ | $\Delta S^{\neq} = -22$ | |
| $R_1 = Ph$, $R_2 = R_3 = CH_3$ | Fast-jump, eqn (44) | $\Delta H^{\neq} = 19 \pm 3$ | $\Delta S^{\neq} = -28$ | |
| | Slow-jump eqn (46) | $\Delta H^{\neq} = 20 \pm 3$ | $\Delta S^{\neq} = -23$ | |

| | | | | |
|---|---|---|---|---|
| $R_1=Ph, R_2=H, R_3=CH_3$ | Fast-jump, eqn (44)<br>Slow-jump, eqn (46) | $\Delta H^{\neq}=23\pm5$<br>$\Delta H^{\neq}=24\pm5$ | $\Delta S^{\neq}=-4{\cdot}2$<br>$\Delta S^{\neq}=1{\cdot}7$ | |
| $R_1=R_3=Ph, R_2=H$ | Fast-jump, eqn (44)<br>Slow-jump, eqn (46) | $\Delta H^{\neq}=8{\cdot}8\pm2$<br>$\Delta H^{\neq}=9{\cdot}6\pm2$ | $\Delta S^{\neq}=-64$<br>$\Delta S^{\neq}=-65$ | |
| $R_1=R_3=Ph, R_2=CH_3$ | Fast-jump, eqn (44) | $\Delta H^{\neq}=12{\cdot}1\pm2$ | $\Delta S^{\neq}=-50$ | |
| $R_1=R_2=R_3=Ph$ | Fast-jump, eqn (44) | $\Delta H^{\neq}=6{\cdot}7\pm1$ | $\Delta S^{\neq}=-74$ | |
|  | ENDOR | | | Borczyskowski and Möbius (1976) |
| Hindered rotation<br>$R_1=Ph, R_2=H$ | Fast-jump, eqn (44)<br>Slow-jump, eqn (46) | $13{\cdot}4\pm0{\cdot}4$<br>$9{\cdot}6\pm0{\cdot}1$ | $10{\cdot}3$<br>$9{\cdot}0$ | |
| $R_1=H, R_2=Ph$ | Fast-jump, eqn (44)<br>Slow-jump, eqn (45) | $18{\cdot}8\pm6$<br>$22{\cdot}2\pm6$ | $12{\cdot}0$<br>$12{\cdot}0$ | |
| Cation exchange<br>$R_1=Ph, R_2=H$<br>$R_1=H, R_2=Ph$ | Eqn (48)<br>Eqn (48)<br>Eqn (44)<br>Eqn (44) | $\Delta H^{0}=-26\pm2{\cdot}5$<br>$\Delta H^{0}=-31\pm2$<br>$\Delta H^{\neq}_{F}=10{\cdot}5\pm2{\cdot}5$<br>$\Delta H^{\neq}_{B}=48\pm5$ | $\Delta S^{0}=-142\pm8$<br>$\Delta S^{0}=-163\pm8$<br>$\Delta S^{\neq}_{F}=-75\pm13$<br>$\Delta S^{\neq}_{B}=117\pm13$ | |
|  | ENDOR, eqn (34) | $18\pm0{\cdot}8$ | $12{\cdot}0\pm0{\cdot}5$ | Plato *et al.* (1976) |
|  | ENDOR, eqns (44) and (46) | $21\pm0{\cdot}8$<br>$\Delta H^{\neq}=19\pm0{\cdot}8$ | $13{\cdot}2$<br>$\Delta S^{\neq}=5{\cdot}4\pm10$ | Melzer *et al.* (1982) |
|  | ENDOR, eqns (44) and (46) | $19{\cdot}7\pm0{\cdot}8$<br>$\Delta H^{\neq}=18{\cdot}4\pm0{\cdot}8$ | $12{\cdot}7$<br>$\Delta S^{\neq}=-2{\cdot}0\pm10$ | Melzer *et al.* (1982) |
|  | ENDOR, eqn (34) | $27{\cdot}6\pm0{\cdot}8$ | $12{\cdot}8\pm0{\cdot}5$ | Plato *et al.* (1976) |
|  | ENDOR, eqn (34) | $38\pm1{\cdot}3$ | $14{\cdot}0\pm0{\cdot}5$ | |

| Compound and mechanism | Method of analysis | Thermodynamic constants | | Reference |
|---|---|---|---|---|
| | | $E_a$ kJ/mol [(a)] | log $A$ [(b)] | |
|  <br>DPPH | ENDOR (160–400 K), eqn (34) | | | Biehl *et al.* (1979) |
| Process I | | $22 \pm 0{\cdot}8$ | $12{\cdot}0 \pm 0{\cdot}5$ | |
| Processes II and III | | $31 \pm 1{\cdot}3$ | $14{\cdot}0 \pm 0{\cdot}5$ | |
| Process IV | | $E_a$ is too large to be determined at ENDOR frequencies (i.e., $10^4\,s^{-1} < k < 10^6\,s^{-1}$) | | |
|  | | | | Kirste *et al.* (1979, 1981) |
| (in toluene)<br>R = cyclopropyl | ENDOR, eqn (44) | $18 \pm 2$<br>$\Delta H^{\neq} = 16 \pm 2$ | $10{\cdot}6$<br>$\Delta S^{\neq} = -47 \pm 6$ | |
| R = isopropyl | ENDOR, eqn (45)<br>EPR, eqn (34) | $33 \pm 2$<br>$\Delta H^{\neq} = 31 \pm 2$ | $12{\cdot}9$<br>$\Delta S^{\neq} = -5{\cdot}9 \pm 6$ | |
| R =  | ENDOR, eqn (45)<br>EPR, eqn (34) | $31 \pm 2$<br>$\Delta H^{\neq} = 29 \pm 2$ | $12{\cdot}0$<br>$\Delta S^{\neq} = -21 \pm 6$ | |
|  | ENDOR, eqn (46) | $4{\cdot}2$ | | Steelink *et al.* (1968) |

| | | | | |
|---|---|---|---|---|
|  | ENDOR (178–213 K, in DME or diglyme with $Na^+$ or $K^+$) eqns (34), (45) and (46) | $30 \pm 2{\cdot}5$<br>$\Delta H^{\neq} = 28 \pm 2{\cdot}5$ | $13{\cdot}4 \pm 0{\cdot}8$<br>$\Delta S^{\neq} = 7{\cdot}5 \pm 3{\cdot}8$ | Iwaizumi *et al.* (1980) |
| | EPR (in DME with $Na^+$) eqn (34) | $27 \pm 2{\cdot}5$ | $13{\cdot}5 \pm 0{\cdot}8$ | Claridge and Peake (1972) |
| | EPR (in DME with $K^+$) | $48 \pm 1{\cdot}7$<br>$\Delta H^{\neq} = 40 \pm 1{\cdot}7$ | $14{\cdot}4$<br>$\Delta S^{\neq} = 22 \pm 0{\cdot}4$ | Pijpers *et al.* (1971) |
|  | ENDOR (143–263 K, in $FSO_3H/SO_2ClF$, $CF_3CF_2COOH$ and $CF_3SO_3H$) and EPR(143–369 K), eqn (34) | 32<br>$\Delta H^{\neq} = 31$ | $13{\cdot}7$<br>$\Delta S^{\neq} = 12$ | Mäkelä and Vuolle (1985) |
| | EPR (in $SO_2$ and $H_2SO_4$), eqn (34) | $15 \pm 1{\cdot}7$<br>$\Delta H^{\neq} = 12 \pm 1{\cdot}7$ | $9{\cdot}3$<br>$\Delta S^{\neq} = -75 \pm 1{\cdot}7$ | Pijpers *et al.* (1971) |
|  | ENDOR (168–233 K, in $AlCl_3/CH_2Cl_2$), eqn (46) | $18{\cdot}8 \pm 2{\cdot}5$ | | Mukai *et al.* (1985 a) |
|  | ENDOR (168–233 K, in $AlCl_3/CH_2Cl_2$), eqn (46) | $33 \pm 5$ | | Mukai *et al.* (1985 a) |
|  | ENDOR (173–243 K in toluene), eqn (46) | $26 \pm 1{\cdot}7$<br>$\Delta H^{\neq} = 24 \pm 1{\cdot}7$ | $12{\cdot}7 \pm 0{\cdot}4$<br>$\Delta S^{\neq} = -5{\cdot}4 \pm 3{\cdot}3$ | Mukai *et al.* (1985 b) |
|  | ENDOR (210–350 K) | | | |
| | crystal | 17 | $14{\cdot}3$ | Brustolon *et al.* (1986) |
| | powder | $17{\cdot}6$ | $14{\cdot}4$ | |
| | EPR (110–210 K) eqn (34) | $15 \pm 0{\cdot}8$ | $13 \pm 0{\cdot}6$ | Miyagawa and Itoh (1962) |

| Compound and mechanism | Method of analysis | Thermodynamic constants $E_a$ kJ/mol [(a)] | log $A$ [(b)] | Reference |
|---|---|---|---|---|
|  | ENDOR (210–350 K) | | | |
| | crystal | 3·3 | 12·5 | Brustolon *et al.* (1984) |
| | powder | 3·2 | 12·6 | |
| | ENDOR (tunnelling splitting at 4·2 K) | 2·7 | | Clough and Poldy (1969) |
|  | ENDOR (185–243 K, in DME) eqn (20) | 25 | 10·5 | Okazaki and Kuwata (1978) (see also Atherton and Kennedy (1978)) |
| | EPR (in DME with $K^+$) | 14 ± 4 | 9·5 ± 0·5 | Chippendale and Warhurst (1968) |
| | eqn 34 | 23 ± 1·7 | 10·1 ± 0·2 | Warhurst and Wilde (1971) |

(*a*) Activation energy, if not otherwise stated. Entry for activation enthalpy is $\Delta H^{\neq}$ (kJ mol$^{-1}$).
(*b*) Decimal logarithm of the preexponential factor (s$^{-1}$), if not otherwise stated. Entry for activation entropy is $\Delta S^{\neq}$ (J K$^{-1}$ mol$^{-1}$).

*et al.* (1985 a, b) measured EPR and ENDOR spectra of the cation radicals of benzodipyran compounds and of tocophenoxyl radicals as reliable models to elucidate the electronic structure, the conformation and the dynamical behaviour of vitamin E.

From detailed analysis of the temperature dependence of line positions and hyperfine couplings of $\beta$- and $\gamma$-methylene protons in the heterocyclic ring, the equilibrium conformation of the $\beta$-methylene group and activation energy for the ring inversion have been determined.

Recently, Bustolon *et al.* (1986) described an efficient method for the investigation of methyl group dynamics in free radicals in solids (both single crystals and powdered samples). The method, which is based on the temperature dependence of methyl proton ENDOR enhancement, allows the determination of the kinetic parameters for any rotation rate at relatively high temperatures and for hindering barriers of any height. The method was applied to the methyl H-ENDOR spectra of the free radicals produced by $\gamma$-irradiation of 1-alanine and 4-methyl-2,6-di-ter-butyl-phenol.

Ion pairs containing an anion radical and an alkali-metal cation can participate in a variety of exchange processes such as electron (or atom) transfer and cation exchange. Rates and mechanisms have been widely investigated through the temperature dependence of the hyperfine couplings and linewidths (Hirota 1968, Sullivan and Menger 1977, Szwarc 1972). Also $^1$H-ENDOR lineshapes of ion pairs can be affected by cation exchange. This mechanism can be discriminated from other possible dynamic processes, like hindered internal rotations, by a careful study of the temperature dependence of hyperfine couplings and linewidths (Borczyskowski and Möbius 1976).

The influence of intramolecular cation migration on both the linewidth and the intensity of the ENDOR spectra of the potassium-2,5-di-*ter*-butyl-*p*-benzoquinone ion-pairs were investigated by Atherton and Kennedy (1978) and Okazaki and Kuwata (1978). The results obtained were discussed theoretically using the Kaplan–Alexander formula and the full armoury of Freed's theory. It was demonstrated that intramolecular cation exchange processes as slow as $10^4\,\mathrm{s}^{-1}$ can show up in a reduced intensity of certain ENDOR lines even when the rate is too slow to contribute to the EPR spectra.

## 5. Concluding remarks

EPR spectroscopy is particularly well suited for studies of organic radicals in the condensed phase because of its relatively high resolving power. The natural linewidth of an EPR spectrum depends on a number of factors, such as the types of molecule, solvent, temperature, and concentration. However, it can be as narrow as 15 mG (Rataiczak and Jones 1972), and in many cases the linewidth of the spectrum may be determined by the resolution of the spectrometer.

Such a high resolution can only be achieved for homogeneously broadened lines. In the case of large and low-symmetry molecules, however, inhomogeneously broadened lines are normally observed since too many slightly shifted components contribute to the observed spectral response. Consequently, when trying to analyse the EPR spectra of large-low symmetry radicals, one is often hampered by problems of spectral resolution. These problems can, to a large extent, be overcome by means of ENDOR (Möbius *et al.* 1982, Plato *et al.* 1981), which during the last two decades has proved to be a powerful spectroscopic tool for the determination of isotropic hyperfine coupling constants, in particular for large asymmetric molecules in solution exhibiting unresolved EPR spectra (Atherton 1979, Kevan and Kispert 1976).

Though EPR spectroscopy is routinely used for studying a variety of kinetic problems, measuring the change in the linewidths of the EPR spectrum is difficult when the rate of the process is smaller than the apparent width of the inhomogenously broadened line. ENDOR is useful for the study of dynamic processes with such small rates (Okazaki and Kuwata 1978).

Moreover, the ENDOR linewidth does not depend on the secular terms of the $g$-anisotropy and of the hyperfine anisotropy of the nucleus, whose resonance frequencies are different from that of the pumping NMR transition (Freed 1979). The study by the ENDOR linewidth, however, has the difficulty that saturation broadening tends to hide the slight changes due to dynamic processes when the EPR and the NMR transitions are saturated to observe ENDOR (Okazaki and Kuwata 1978). Since saturation broadening is one of the main causes of the linewidth, special care has to be taken in the extrapolation of the ENDOR linewidths to vanishingly small NMR fields. Furthermore, the reference linewidth, which should not be perturbed by the dynamic effect, is less well defined because of the complicated relaxation mechanisms which determine the ENDOR linewidths. At temperatures lower than the coalescence point, the rate constant can be determined from line positions according to equation (46). This method is not influenced by saturation broadening and other ENDOR relaxation effects (Borczyskowski *et al.* 1975).

Besides linewidth effects, the ENDOR spectrum may respond to a dynamic process through variation in the strengths of the ENDOR signals for monitoring different hyperfine lines (Atherton and Kennedy 1978, Okazaki and Kuwata 1978). The investigation with the ENDOR intensity is more reliable in principle, and it could be extended to take advantage of the full lineshape information. However, to be quantitative it must be recognized that ENDOR response depends on more relaxation parameters than just those related to the dynamic process. Determination of all such parameters from the lineshape analysis of ENDOR spectra is made difficult in a sense by the relative 'simplicity' of the ENDOR signal itself. In contrast, the benefits to be derived from spectral 'complexity' when a least-squares iterative analysis of EPR bandshape is performed are well established (Barzaghi *et al.* 1986).

Though the ENDOR technique appeared to be sensitive to dynamic processes also in the rate range where the EPR spectrum is unaffected (Atherton and Kennedy 1978, Okazaki and Kuwata 1978), it should be mentioned that ENDOR spectra with a good signal-to-noise ratio are only observable in a much smaller temperature range. In addition, the ENDOR response to a dynamic process may be of the 'on-off' type (Atherton and Kennedy 1978), so that optimization of the experimental conditions such as solvent properties (temperature, viscosity) and microwave and r.f. field strengths become critical (Plato *et al.* 1981, Kurreck *et al.* 1984).

## References

ABRAGAM, A., 1961, *The Principles of Nuclear Magnetism* (Oxford University Press).

ADAMS, R. F., and ATHERTON, N. M., 1968, *Trans. Faraday Soc.*, **64**, 7.

AL-BALDAWI, S. A., and GOUGH, T. E., 1970, *Can. J. Chem.*, **48**, 2798.

AL-BALDAWI, S. A., and GOUGH, T. E., 1971, *Can. J. Chem.*, **49**, 2059.

ALEXANDER, S. A., 1962 a, *J. chem. Phys.*, **37**, 967. ALEXANDER, S. A., 1962 b, *J. chem. Phys.*, **37**, 974.

ANDERSON, P. W., 1954, *J. Phys. Soc. Japan*, **9**, 316.

ATHERTON, N. M., 1973, *Electron Spin Resonance. Theory and Applications* (Chichester: Ellis Horwood).

ATHERTON, N. M., 1979, *Multiple Electron Resonance Spectroscopy*, edited by M. M. Dorio and J. H. Freed (New York: Plenum).

ATHERTON, N. M., BLUSTIN, P. M., HUMPHREYS, C. A., and SHALABY, A. S., 1984, *Org. Magn. Reson.*, **22**, 456.

ATHERTON, N. M., and KENNEDY, P. A., 1978, *J.C.S. Faraday* II, **74**, 67.

AYSCOUGH, P. B., 1977–1985, *Electron Spin Resonance. A Specialist Periodical Report*, Vol. 4, 1977; Vol. 5, 1979; Vol. 6, 1981; Vol. 7, 1982; Vol. 8, 1983; Vol. 9, 1985 (London: Royal Society).

BARZAGHI, M., BRANCA, M., GAMBA, A., OLIVA, C., and SIMONETTA, M., 1986, *Advanced Magnetic Resonance Techniques in Systems of High Molecular Complexity*, edited by N. Niccolai and G. Valensin (Basel: Birkhäuser Verlag).

BARZAGHI, M., CREMASCHI, P., GAMBA, A., MOROSI, G., OLIVA, C., and SIMONETTA, M., 1978, *J. Am. Chem. Soc.*, **100**, 3132.

BARZAGHI, M., OLIVA, C., and SIMONETTA, M., 1980a, *J. Phys. Chem.*, **84**, 1959.

BARZAGHI, M., OLIVA, C., and SIMONETTA, M., 1980b, *J. Phys. Chem.*, **84**, 1717.

BARZAGHI, M., OLIVA, C., and SIMONETTA, M., 1981, *J. Phys. Chem.*, **85**, 1799.

BARZAGHI, M., and SIMONETTA, M., 1983, *J. Magn. Reson.*, **51**, 175.

BIEHL, R., MÖBIUS, K., O'CONNOR, S. E., WALTER, R. J., and ZIMMERMANN, H., 1979, *J. Phys. Chem.*, **83**, 3449.

BORCZYSKOWSKI, C., and MÖBIUS, K., 1976, *J. chem. Phys.*, **12**, 281.

BORCZYSKOWSKI, C., MÖBIUS, K., and PLATO, M., 1975, *J. Magn. Reson.*, **17**, 202.

BRANCA, M., GAMBA, A., BARZAGHI, M., and SIMONETTA, M., 1982, *J. Am. Chem. Soc.*, **104**, 6506.

BRUSTOLON, M., CASSOL, T., MICHELETTI, L., and SEGRE, U., 1986, *Molec. Phys.*, **57**, 1005.

CHEN, K. S., and HIROTA, N., 1971, *J. Am. Chem. Soc.*, **94**, 5550.

CHIPPENDALE, J. C., and WARHURST, E., 1968, *Trans. Faraday Soc.*, **64**, 2332.

CLARIDGE, R. F., and PEAKE, B. M., 1972, *J. Magn. Reson.*, **6**, 29.

CLOUGH, S., and POLDY, F., 1969, *J. chem. Phys.*, **51**, 2076.

CONRADI, M. S., ZELDES, H., and LIVINGSTON, R., 1979, *J. Phys. Chem.*, **83**, 633.

DALTON, L. A., and DALTON, L. R., 1979, *Multiple Electron Resonance Spectroscopy*, edited by M. M. Dorio and J. H. Freed (New York: Plenum), Chap. 5.

DAS, M. R., CONNOR, J. D., LENIART, D. S., and FREED, J. H., 1970, *J. Am. Chem. Soc.*, **92**, 2258.

EASTMAN, M. P., KOOSER, R. G., DAS, M. R., and FREED, J. H., 1969, *J. chem. Phys.*, **51**, 2690.

ECHEGOYEN, L., NIEVES, I., and STEVENSON, G. R., 1984, **88**, 4332.

FRAENKEL, G. K., 1967, *J. Phys. Chem.*, **71**, 139.

FRAENKEL, G., 1986, *Investigation of Rates and Mechanisms of Reactions*, edited by C. F. Bernasconi (New York: Wiley), Part II, Chap. X.

FREED, J. H., 1965, *J. chem. Phys.*, **43**, 2312.

FREED, J. H., 1967, *J. Phys. Chem.*, **71**, 38.

FREED, J. H., 1972, *Electron Spin Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (New York: Plenum), p. 503.

FREED, J. H., 1979, *Multiple Electron Resonance Spectroscopy*, edited by M. M. Dorio and J. H. Freed (New York: Plenum), Chap. 3.

FREED, J. H., and FRAENKEL, G. K., 1963, *J. chem. Phys.*, **39**, 326.

FREED, J. H., LENIART, D. S., and CONNOR, H. D., 1973, *J. chem. Phys.*, **58**, 3089.

FREED, J. H., LENIART, D. S., and HYDE, J. S., 1967, *J. chem. Phys.*, **47**, 2762.

GOUGH, T. E., and HINDLE, P. R., 1969, *Can. J. Chem.*, **47**, 1968, 3393.

GOUGH, T. E., and HINDLE, P. R., 1970, *Can. J. Chem.*, **48**, 3959.

GOUGH, T. E., and HINDLE, P. R., 1971, *Can. J. Chem.*, **49**, 1529.

GOUGH, T. E., and HINDLE, P. R., 1970, *Trans. Faraday Soc.*, **66**, 2420.

HEINZER, J., 1971, *Molec. Phys.*, **22**, 167.

HEINZER, J., 1972, *QCPE*, **11**, 209.

HEINZER, J., 1974, *J. Magn. Reson.*, **13**, 124.

HELLER, C., and MCCONNELL, H. M., 1960, **32**, 1535.

HIROTA, N., 1968, *Radical Ions*, edited by E. T. Kaiser and L. Kevan (New York: Wiley-Interscience).

HIROTA, N., and OHYA-NISHIGUCHI, H., 1986, *Investigation of Rates and Mechanisms of Reactions*, edited by C. F. Bernasconi (New York: Wiley), Part II, Chap. XI.

HUDSON, C. E., and BAULD, N. L., 1972, *J. Am. Chem. Soc.*, **94**, 1158.

HUDSON, A., and LUCKHURST, G. R., 1969, *Chem. Rev.*, **69**, 191.

HYDE, J. S., BRESLOW, R., and DE BOER, C., 1966, *J. Am. Chem. Soc.*, **88**, 4763.

IWAIZUMI, M., KITA, S., KOHNO, M., and ISOBE, T., 1980, *Bull. Chem. Soc. Jpn*, **53**, 1745.

JACKMAN, L. M., and COTTON, F. A., 1975, *Dynamic Nuclear Magnetic Resonance* (New York: Academic Press).

JENSEN, F. R., NOYCE, D. S., SEDERHOLM, C. H., and BERLIN, A. J., 1962, *J. Am. Chem. Soc.*, **84**, 386.

Johnson, C. S., Jr, 1964, *J. chem. Phys.*, **41,** 3277.

Johnson, C. S., Jr, 1965, *Adv. Magn. Reson.*, **1,** 33.

Kaplan, S., 1958 a, *J. chem. Phys.*, **28,** 278.

Kaplan, S., 1958 b, *J. chem. Phys.*, **29,** 462.

Kaplan, S., and Fraenkel, G., 1980, *NMR of Chemically Exchanging Systems* 'New York: Academic Press).

Kevan, L., and Kispert, L. D., 1976, *Electron Spin Double Resonance Spectroscooy* (New York: Wiley-Interscience).

Kirste, B., Harrer, W., Kurreck, H., Schubert, K., Bauer, H., and Gierke, W., 1981, *J. Am. Chem. Soc.*, **103,** 6280.

Kirste, B., Kurreck, H., Harrer, W., and Reusch, J., 1979, *J. Am. Chem. Soc.*, **101,** 1775.

Kispert, L. D., Hyde, J. S., De Boer C., La Follette, D., and Breslow, R., 1968, *J. Phys. Chem.*, **72,** 4276.

Krusic, P. J., and Kochi, J., 1971 a, *J. Am. Chem. Soc.*, **93,** 846.

Krusic, P. J., Meakin, P., and Jesson, J. P., 1971 b, *J. Phys. Chem.*, **75,** 3438.

Kubo, R., 1954, *J. Phys. Soc. Jpn*, **9,** 935.

Kurreck, H., Kirste, B., and Lubitz, W., 1984, *Angew. Chem. Int. Ed. Engl.*, **23,** 173.

Mäkelä, R., and Vuolle, M., 1985, *Magn. Reson. Chem.*, **23,** 666.

Melzer, P., Kurreck, H., and Kieslich, W., 1982, *Chem. Ber.*, **115,** 3597.

McConnell, H. M., 1958, *J. chem. Phys.*, **28,** 430.

Miyagawa, I., and Itoh, K., 1962, *J. chem. Phys.*, **36,** 2157.

Möbius, K., and Blehl, R., 1979, *Multiple Electron Resonance Spectroscopy*, edited by M. Dorio and J. H. Freed (New York: Plenum), Chap. 14.

Möbius, K., Fröhling, W., Lendzian, F., Lubitz, W., Plato, M., and Winscom, C. J., 1982, *J. Phys. Chem.*, **86,** 4491.

Mukai, K., Uemoto, Y., and Ishizu, K., 1985 a, *Bull. Chem. Soc. Jpn.*, **58,** 1928.

Mukai, K., Takamatsu, K., and Ishizu, K., 1985 b, *Bull. Chem. Soc. Jpn.*, **58,** 2515.

Nemoto, F., 1976, *Bull. Chem. Soc. Jpn.*, **49,** 1194.

Nemoto, F., and Ishizu, K., 1975 a, *J. Phys. Chem.*, **79,** 1730.

Nemoto, F., Shimoda, F., and Ishizu, K., 1975 b, *Bull. Chem. Soc. Jpn.*, **48,** 2627.

Norman, R. O. C., 1973, 1974, 1976, *Electron Spin Resonance. A Specialist Periodical Report* Vols I–III (London: Royal Society).

Ogawa, S., and Fessenden, R. W., 1964, *J. chem. Phys.*, **41,** 994.

Okazaki, M., and Kuwata, K., 1978, *Bull. Chem. Soc. Jpn.*, **51,** 385.

Pijpers, F. W., Arick, M. R., Hendricks, B. M. P., and De Boer, E., 1971, *Molec. Phys.*, **22,** 781.

Plato, M., Biehl, R., Möbius, K., and Dinse, K. P., 1976, *Z. Naturf.*, **31,** a, 169.

Plato, M., Lubitz, W., and Möbius, K., 1981, *J. Phys. Chem.*, **85,** 1202.

Rataiczak, R. D., and Jones, M. T., 1972, *J. chem. Phys.*, **56,** 3898.

Redfield, A. G., 1957, *IBM J. Res. Dev.*, **1,** 19.

Redfield, A. G., 1965, *Adv. Magn. Reson.*, **1,** 1.

Rutter, A. W., and Warhurst, E., 1968, *Trans. Faraday Soc.*, **64,** 2338.

Rutter, A. W., and Warhurst, E., 1970, *Trans. Faraday Soc.*, **66,** 1866.

Sack, R. A., 1958, *Molec. Phys.*, **1,** 163.

Shimoda, F., Hanafusa, T., Nemoto, F., Mukai, K., and Ishizu, K., 1979, *Bull. Chem. Soc. Jpn*, **52,** 3743.

Shimoda, F., 1980, *Bull. Chem. Soc. Jpn*, **53,** 1853.

Slichter, C. P., 1978, *Principles of Magnetic Resonance* (Berlin, Heidelberg, New York: Springer-Verlag).

Steelink, C., Fitzpatrick, J. D., Kispert, L. D., and Hyde, J. S., 1968, *J. Am. Chem. Soc.*, **90,** 4354.

Stevenson, G. R., Reiter, R. C., Ross, D. G., and Frye, D. G., 1984, *J. Phys. Chem.*, **88,** 1854.

Sullivan, P. D., and Bolton, J. R., 1970, *Adv. Magn. Reson.*, **4,** 39.

Sullivan, P. D., and Menger, E. M., 1977, *Adv. Magn. Reson.*, **9,** 1.

Symons, M. C. R., 1986, 1987, *Electron Spin Resonance. A Specialist Periodical Report*, Vols 10A, 10B (London: Royal Society of Chemistry).

Szwarc, M., 1972, 1974, *Ion and Ion Pairs in Organic Reactions*, Vols I, II (New York: Wiley-Interscience).

Warhurst, E., and Wilde, A. M., 1971, *Trans. Faraday Soc.*, **67,** 605.

Watanabe, K., 1975, *Bull. Chem. Soc. Jpn*, **48,** 1732.