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Foreword

The series of Specialist Periodical Reports continues to evolve in response to changes in emphasis in chemical research and to economic pressures. The volumes concerned with e.s.r. are not exempt from these pressures and most of the changes in Volume 9 reflect decisions based on financial constraints rather than academic judgement.

The overall size of the volume has been slightly reduced and some chapters have been omitted on this occasion in order to achieve this. In particular, to my considerable regret, it has not been possible to include a special review chapter of the kind which has appeared in the last five volumes. Despite these losses I believe that the quality of the contributions to Volume 9 will ensure that it provides a unique and comprehensive account of recent developments in e.s.r. I am once again most grateful to all Reporters for their splendid contributions.

October 1984

P. B. Ayscough

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Theoretical Aspects of E.S.R.

BY A. HUDSON

1 Introduction

The theory of E.S.R. is well understood and this chapter will be largely concerned with applications rather than new developments. There has been a significant increase in the number of papers dealing with spin-polarized (CIDEP) spectra. Moreover, such experiments are now being performed on chemically interesting systems. There was a time when CIDEP seemed to be largely confined to the photolysis of duroquinone.

The development of experimental techniques for the production of radical cations from saturated compounds has provided experimental data on a large number of interesting new radicals. The interpretation of the spectral parameters in terms of molecular geometries has led to a number of controversies and both *ab initio* and semi-empirical molecular orbital calculations have been used in an attempt to resolve some of the problems involved.

2 Numerical Methods and Spectral Analysis.

A new journal devoted to the use of computers in spectroscopy contains descriptions of microprocessor based data accumulation and reduction systems^{1,2}. Other recently described data systems include one based on an Apple II Plus (48 K)³ and another based on S-100 bus components⁴.

Morton and Preston⁵ have given a detailed account of the use of a computer-assisted two-circle goniometer to assemble the hyperfine-interaction and g^2 tensors in the crystallographic axis system. An explanation is given for each of the seven crystal classes. A general method has been described for extraction of the g -tensor from single crystal data⁶. A simplified method has

been developed for dealing with spectra showing strong quadrupole interactions and applied to the case of Ir^{2+} in MgO ⁷. Stevenson⁸ has published an extensive theoretical discussion of triplet state spectra.

The computer simulation of powder spectra is virtually essential if several hyperfine interactions are involved. A good recent example involves the spectrum of NP_3^+ trapped in a rigid matrix at 25 K. The program described is accurate to second order in all hyperfine terms and copes with up to four nuclei⁹. Rieger¹⁰ has written a program which performs a least squares analysis of powder patterns with noncoincident principal axes of the g and hyperfine tensors. Graphs have been published which may be used for the interpretation of powder spectra from axial sites with effective spins ranging from $S=1$ to $S=5/2$. The resonance fields are presented as functions of the zero-field splitting¹¹. A powder pattern analysis has also been described for cubic sites of Fe^{3+} in MgO ¹². In disordered solids it is necessary to include the distribution of spin Hamiltonian parameters. Bals and Kliava¹³ have simulated spectra for d^1 ions including Mo^{5+} in a phosphate glass.

A detailed study of the powder spectrum of an ^{15}N enriched nitroxide has led to the conclusion that such probes are significantly better than ^{14}N nitroxides in polycrystalline or amorphous systems¹⁴ since the hyperfine features are well resolved at X-band. An alternative solution is to work at Q-band and simulations have been presented of first and second derivative spectra for a variety of spin labels in frozen solutions¹⁵. A key factor in the successful simulation of field swept spectra is the Aasa and Vanngard $1/g$ factor. Pilbrow has considered this point in some detail in a discussion of lineshapes for frequency-swept and field-swept spectra¹⁶. Phillips and Herring have investigated¹⁷ the use of dispersion versus absorption plots for detecting lineshape distortions attributable to either the spectrometer or the sample. An interactive method allows for the elimination of baseline drift. A fast deconvolution procedure has been described for inhomogeneous resonance lines¹⁸. The deconvolution of hyperfine splittings is necessary in the investigation of

paramagnetic spin distributions by E.S.R. imaging¹⁹.

There have been further developments in the simulation of isotropic solution spectra using fast Fourier transform methods^{20,21}. A general iterative least-squares procedure has been described for fitting complex dynamic lineshapes in the fast motional region²². Two papers have been concerned with the problem of superhyperfine structure when simulating the E.S.R. spectra of nitroxide spin probes in solution^{23,24}. This is relevant to the measurement of spin exchange rates and the use of spin probes for monitoring the concentration of dissolved oxygen in biological samples. Bales has experimentally verified a previously published procedure for extracting spin exchange rates from inhomogeneously broadened lines²⁵.

A procedure based on correlation methods has been applied to the analysis of weak spectra. It is particularly useful for locating satellites due to ^{13}C or ^{29}Si in natural abundance²⁶. A product function produced by correlation of the digitized experimental spectrum with a test spectrum is used as a criterion of the goodness of fit. The test spectrum is initially a single line but becomes increasingly complex as the analysis proceeds and additional coupling constants are located.

3 Spin-relaxation and Line-broadening Effects

An interesting review article by Kurreck and his coworkers includes a good account of the various relaxation processes involved in ENDOR and its extension to triple resonance experiments²⁷.

There have been few developments in the theory of spin relaxation and lineshapes. Baram has discussed nonsecular lineshapes in the slow motion region²⁸. Exact solutions have been obtained for the modified Bloch equations with n -site chemical exchange²⁹ and a new formalism has been applied to the two-site problem in the intermediate exchange region³⁰. Kooser and Resing have investigated the effects of two-dimensional reorientation in partially ordered systems³¹. A generalised treatment for slow diffusional reorientation of axially

symmetric hyperfine centres³² has been applied to the spectra of nitroxide probes in amorphous polymers³³. Formulae have been derived for averaged tensor components when a dynamic process occurs between two symmetry related sites in a single crystal³⁴. Relaxation processes have been considered in trimeric clusters including both isotropic and anisotropic exchange interactions³⁵. Zaspel has studied the effect of antisymmetric exchange on E.S.R. linewidths and has shown that the angular dependence can have a period of 360° instead of 180° ³⁶. The lineshapes of alkali metal biphenyl salts have provided evidence for spin diffusion³⁷ in these quasi-two-dimensional magnetic systems.

Spin exchange in solution has been investigated for nitroxides in nematic liquid crystals³⁸ and in hydrocarbon solvents³⁹. In the latter case particular emphasis was given to the intermediate exchange region. A useful insight into the effects of spin exchange and rotational diffusion has been obtained by comparing the E.S.R. linewidths for the different magnetic isotopes in a molybdenum complex⁴⁰. A wide range of rotational correlation times has been found for vanadyls isolated from oil shale⁴¹. Linewidth variations in the solution spectra of dithiazolyl and related radicals have been analysed to calculate hydrodynamic radii⁴². A pronounced temperature dependence in the E.S.R. spectrum of the pentafluorocyclopentadienyl radical originates from averaging of the ^{19}F anisotropic hyperfine tensor⁴³.

We shall not deal in this chapter with the numerous applications of spin probes in biological systems. However, their use is not restricted to investigating the dynamical properties of biomolecules. Both neutral and positively charged nitroxides have been employed in a study of micelles formed from sulphate surfactants⁴⁴. Large and nearly cylindrical probes are highly ordered within the channels of thiourea-cyclohexane inclusion compounds, whereas smaller and nearly spherical probes reorient isotropically⁴⁵. An investigation of spin-labeled rodlike poly(benzylglutamate) suggests that the macromolecule behaves hydrodynamically as a very porous cylinder with an impenetrable core⁴⁶. Meirovitch⁴⁷ reports on stretching-induced molecular mobility and the

partitioning of spin probes among different sites in semicrystalline low-density polyethylene films. Another contribution deals with the intrinsic flexibility gradient found in hydrocarbon chains in lipid bilayers⁴⁸. Studies of liquid crystals include an investigation of molecular dynamics at the nematic to smectic A transition⁴⁹ and an analysis, using parallel-edge lines, of the orientational distribution of a spin probe in rigid MBBA⁵⁰. The E.S.R. spectra of nitroxides in some magnetically aligned liquid crystals formed from surfactants have been interpreted in terms of cylindrical micelle and disc-shaped micelle structures⁵¹. A combination of ELDOR, saturation and E.S.R. linewidth measurements has been used to study deviations from the Brownian motion model. Additional relaxation terms have been formulated in terms of a slowly relaxing local structure mechanism⁵². The motion of midchain peroxy radicals in poly(tetrafluoroethylene) is consistent with a model involving helical twisting of the polymer axis⁵³.

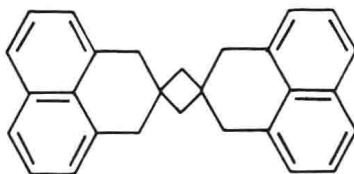
Two simple methods of determining the microwave field strength in E.S.R. should be useful in saturation transfer experiments⁵⁴. Recent applications of the latter technique include a study of multiple motions of the spectrin-actin complex⁵⁵ and an investigation of maleimide spin-labeled cowpea chlorotic mottle virus⁵⁶. [¹⁵N]nitroxides have been employed to determine the effects of non-coincident magnetic and diffusion tensor axes when there is anisotropic rotational diffusion⁵⁷. Fajer and Marsh⁵⁸ have analysed the sensitivity of X-band ST spectra to anisotropic rotation. The influence of experimental parameters has been considered by Delmelle⁵⁹; the effects of overmodulation are difficult to include in simulations because of very long computation times and Robinson has suggested various approximations to overcome this problem⁶⁰. The results of varying the modulation frequency have also been the subject of recent attention⁶¹. Improvements in cavity design have led to renewed interest in the dispersion mode method of recording ST E.S.R. spectra^{62,63}. A technique has been described for dealing with multicomponent spectra and applied to membrane systems⁶⁴. Saturation transfer has also been studied in pulse experiments using

an electron spin-echo spectrometer⁶⁵. The motion of nitroxide radicals in dibutyl phthalate is best accounted for by a large-angle jump model. Very slow motion can also be detected by a method involving double modulation of the E.S.R. spectrum⁶⁶. Another possibility is to use an ELDOR technique based upon spin echoes and rapid stepping of the magnetic field⁶⁷.

Baram has developed a theory of spin echoes in the slow motion regime⁶⁸. Pulse techniques feature increasingly in the literature and this trend will continue as the necessary equipment becomes commercially available. The diffusion of spins in the radical cation salt (fluoranthenyl)₂⁺AsF₆⁻ has been measured by observing electron spin echo decays in a magnetic field gradient⁶⁹. Irradiation of methanol absorbed on zeolites generates hydroxymethyl radicals. Electron spin echo spectra of these radicals have then been used to elucidate the geometrical arrangement of surrounding methanol molecules⁷⁰. A treatment of nuclear quadrupole effects on electron spin echo modulation by Shubin and Dikanov⁷¹ has been extended to three pulse sequences by Kevan and coworkers⁷² who point out a number of limitations in the expressions obtained by perturbation theory. Quadrupole splitting parameters have been estimated for ¹⁴N nuclei in a nitroxide biradical⁷³.

The determination of kinetic parameters from linewidth variations is long standing and well established. Stevenson and his coworkers⁷⁴ have investigated the hydrogen bonding of ethanol to the radical anion of *p*-cyanonitrobenzene in hexamethylphosphoramide and report for the first time activation parameters controlling hydrogen bond formation to an anionic species. Further work has been reported on intermolecular exchange of sodium ions in dinitrobenzene ion pairs⁷⁵. A detailed study of restricted rotation of the acetyl group in *m*- and *p*-nitroacetophenone anion radicals has been used to establish an optimum procedure for obtaining thermodynamic parameters from dynamic E.S.R. spectra⁷⁶. Ion pair formation has a significant influence on the hindered rotation of the phenyl rings in nitrobenzophenone radical anions⁷⁷. The dynamic behaviour of the 5-hydro-6-methyl-6-yl-uracil radical has been studied in single crystals,

polycrystalline powders and aqueous glasses⁷⁸. The detected variations can be accounted for by different molecular packings in the respective matrices. Barriers to rotation determined by E.S.R. have been used to estimate stabilisation energies in aminoallyl, aminopropynyl, and aminocyanomethyl radicals⁷⁹. Unusually large barriers to methyl group rotation have been found in cation radicals formed from methyl and ethyl esters⁸⁰. Barriers to rotation can also be estimated from the temperature dependence of β -hyperfine coupling constants. A recent unusual example involves muonic-substituted ethyl radicals⁸¹.



(1)

Electron spin transfer between naphthalene π -systems, which was first studied in 1961 by Atherton and Weissman, is still the subject of interesting research. A recent study involved a careful analysis, using E.S.R. and ENDOR, of intramolecular transfer between naphthalene rings separated by a variable number of spirobonded cyclobutane rings. With 3 or 5 of the latter, the intramolecular spin transfer was slow on the hyperfine time scale, but fast exchange was observed for (1) in media of high solvating power. The E.S.R. and ENDOR spectra actually consisted of a superposition of fast and slow exchange spectra and these have been assigned to the *syn*- and *anti*-conformations of (1) since the distance between the naphthalene units is significantly shorter in the former⁸².

4 CIDEP

The problem of developing a consistent mathematical theory for a spin 1/2 system undergoing first-order spin-selective reactions, has been considered by Pottinger and Lendi⁸³, who derive generalised Bloch equations employing the

theory of quantum Markovian master equations. The results of a theory of CIDEP and Heisenberg spin exchange have also been presented in terms of Bloch-type equations⁸⁴. An unusual pattern of oscillations in the time-resolved CIDEP signal has been observed in a study of photoelectrons in Rb/THF solutions⁸⁵. Baer and Paul have observed stationary nutations in the spectra of benzyl radicals produced by photolysis of methyl benzyl ketone with modulated UV light⁸⁶. This experiment yields both the relaxation times and the CIDEP of the spin system. Another novel experiment involves using the extra sensitivity offered by chemically induced polarization effects to detect the ENDOR of short lived radicals⁸⁷. If radicals are generated by a laser pulse in the absence of a microwave field which is later applied in a continuous wave fashion, the evolution and observation of the magnetization can be separated in a two-dimensional experiment⁸⁸, which yields the spin-lattice relaxation time and the polarization ratio. Basu and McLauchlan⁸⁹ have shown how a non-uniform concentration of free radicals produced by a light pulse can affect the subsequent kinetic behaviour of the system. It has been pointed out that overlapping spectra can often be separated in a time-resolved experiment by utilizing the different temporal variations of the two signals⁹⁰. A theory based on the Bloch equations has been used to account for the influence of electron transfer reactions on CIDEP spectra⁹¹. The Bloch equation approach has also been used to analyse a time-integration method which removes spurious sidebands in the E.S.R. spectra of spin-polarized radicals produced by laser flash photolysis⁹². The same paper also contains a useful discussion of numerical resolution-enhancement methods.

The time integration method has been used to study the spectra of α -aminoalkyl radicals produced by flash photolysis of benzene-1,2:3,4-tetracarboxylic dianhydride in the presence of tertiary amines⁹³. The Oxford group have also reported on the photophysics and photochemistry of diazanaphthalenes⁹⁴ and methylpyrazines⁹⁵. Interesting results have been found for radicals derived from aliphatic ketones⁹⁶. It has been shown