SULPHUR-COORDINATED IRON AND COPPER COMPLEXES RELEVANT TO FERREDOXINS AND BLUE-COPPER-PROTEINS

a thesis by

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ABSTRACT

SULPHUR-COORDINATED IRON AND COPPER COMPLEXES RELEVANT TO FERREDOXINS AND BLUE-COPPER-PROTEINS.

EPR, Mössbauer and vibrational studies are reported for some iron-sulphur protein model complexes of the type $[Fe(SR)_4]^-$, $[Fe_2S_2(SR)_4]^{2-/3-}$, $[Fe_4S_4(SR)_4]^{2-/3-}$, and for their selenium homologues.

The unstable trianion $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{3-}$ is identified by EPR and Mössbauer as the product from chemical reduction of the corresponding dianion and is found to have similar properties to some $[2Fe\text{-}2S]^{1+}$ ferredoxins. EPR spectra for other reduced $[Fe_2X_2(YR)_4]^{2-}$ (X,Y=S,Se) complexes having monodentate aryl-chalcogenide ligands show solvent-dependent behaviour which is analysed in terms of their varying g-tensors.

Broadening of the low field peaks in the EPR spectra of $[Fe_2X_2(S_2\text{-}$ $\text{o-xylyl})_2]^{3-}$ (X = S, Se) and $[Fe_2S_2(SC_6H_4Cl)_4]^{3-}$ is interpreted as originating from a dominant Orbach spin-lattice relaxation mechanism involving the first excited state of the antiferromagnetic exchange-interaction spin manifold at energies ranging 600-900 cm^{-1}.

X- and Q-band EPR spectra are described for frozen solutions of $[Fe(S_2\text{-o-xylyl})_2]^-$ and are interpreted in terms of a high D value ($\sim2cm^{-1}$) and a distribution in $\underline{D}$ symmetries centered at $\lambda\simeq0.13$ and ranging over $\lambda\simeq\pm0.05$ in half-width. Comparison is made with spectra for rubredoxins and desulforedoxin.

The three groups of complexes (1-Fe,2-Fe and 4-Fe) and their selenium homologues have been studied by resonance Raman and infra-red spectroscopy. Many of the observed bands have been assigned to normal vibrations and correlations have been made between the efficiency in resonance enhancement of some Raman totally symmetric modes and deconvoluted electronic absorption profiles. Some reassessment of previously reported iron-sulphur protein Raman spectra is made possible by comparison with the model complexes.

An extensive series of $Cu(II)N_2S_2$ substituted-βaminothione complexes with systematically variable stereochemistry have been prepared at low temperatures as models for the type 1 centre in blue-copper-proteins. Spectroscopic and redox measurements on these complexes are consistent with pseudo-tetrahedral coordination geometry in which the degree of tetrahedral distortion is dependent upon the steric bulk of the amino substituent. Small parallel copper-hyperfine splitting in the EPR and intense "blue" S→Cu charge transfer bands in the electronic spectra of the model complexes correlate with similar features in the type 1 protein spectra and further confirm the general pseudo-tetrahedral CuN_2S_2 coordination of the latter.

ACKNOWLEDGEMENTS

Against the 'lone and level sands' of these pages, and in praise of Him from whom nothing is hidden.

"Let not the wise man glory in his wisdom, let not the mighty man glory in his might, let not the rich man glory in his riches; but let him who glories glory in this, that he understands and knows me, that I am the LORD who practise steadfast love, justice, and righteousness in the earth; for in these things I delight, says the LORD."

Jeremiah 9

*To my parents
with much affection*

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at the end of each section under Experimental.

Abbreviations, Nomenclature and Symbols

ACN^-	Acenaphthylenide radical anion
Ar	Aryl substituent
Bz	Benzyl substituent
CT	Charge transfer
D	Axial component of $\underline{D}$ tensor
DMF	N,N-dimethylformamide
DMSO	Dimethylsulphoxide
$E_{\frac{1}{2}}$	Half-wave potential
EDTA	Ethylene diamine tetraacetic acid
en	1,2-diaminoethane
ENDOR	Electron nuclear double resonance
EPR	Electron paramagnetic resonance
EXAFS	Extended X-ray absorption fine structure
$Fd_{ox/red}$	Ferredoxin (oxidised/reduced)
H	Magnetic field
HMDE	Hanging mercury drop electrode
IR	Infrared absorption spectroscopy
LMCT	Ligand to metal charge transfer
J	Antiferromagnetic exchange constant
NMP	N-Methyl pyrrolidinone
NMR	Nuclear magnetic resonance
Ph	Phenyl substituent
PTFE	Polytetrafluoroethylene
R	Organic substituent
Rd	Rubredoxin
RDME	Rapid dropping mercury electrode

RR	Resonance Raman spectroscopy
S_2-o-xylyl	α,α'-dithio-o-xylene (also S_2-o-xyl)
T_1	Electron spin-lattice relaxation time
THF	Tetrahydrofuran
Tol	Tolyl substituent

As per context:-

δ —	isomer shift
	deformation vibration
	NMR shift
λ —	Wavelength (visible)
	Rhombic component of $\underline{D}$ tensor
	Spin orbit coupling constant
ν —	Stretching vibration
	microwave frequency

In describing spectral bands:-

w	weak	pr	poorly resolved
m	medium	dl	double
s	strong	mlt	multiplet
v	very	ρ	depolarisation ratio
sh	shoulder	p	polarised
br	broad	dp	depolarised
n	narrow		

$[2Fe-2S]^{(2+,1+)}$	——	$[Fe_2S_2(SR)_4]^{2-/3-}$ in complexes and ferredoxins
$[4Fe-4S]^{(2+,1+)}$	——	$[Fe_4S_4(SR)_4]^{2-/3-}$ in complexes and ferredoxins
$(RN-R_2R_1S)$	——	

$$R_1 \diagdown \diagup \diagdown \diagup R_2$$
$$S \qquad HNR$$
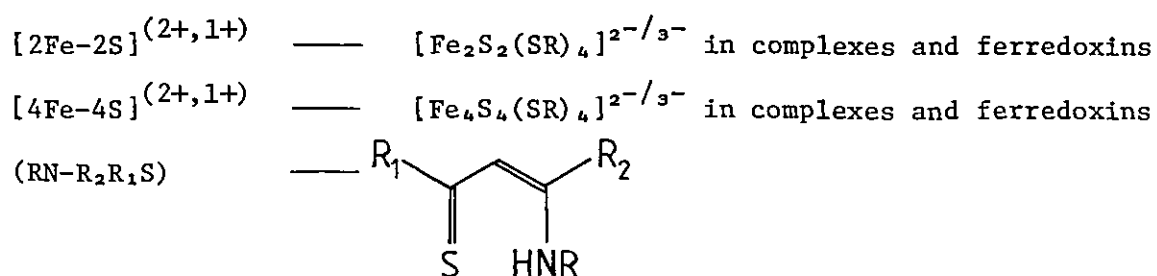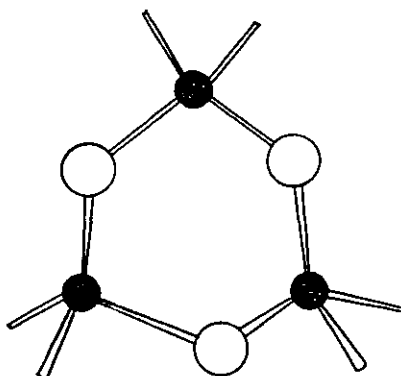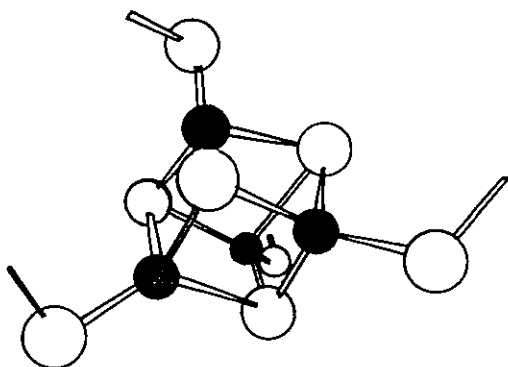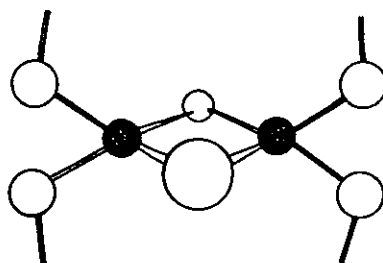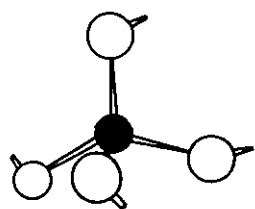
INTRODUCTION

0. INTRODUCTION.

Many metal-containing biomolecules have been discovered in the last few decades. The most prominent metals involved are Mg, Mn, Fe, Co, Cu, Zn and Mo. In order to achieve some particular function the metal ions are often coordinated in an unusual manner and lead to physico-chemical properties not previously encountered in synthetic chemistry. Study of the similarities and differences between metallobiomolecules and model metal complexes has proven to be of considerable use in understanding their structure and function. The bulk of such investigation has centred around iron-heme complexes, iron-sulphur complexes and model-complexes for the blue copper proteins.[1] A brief description of progress in mimicking the coordination and properties of Type 1 blue copper proteins may be found in Section 5.1. Development of model complexes for iron-sulphur proteins has been dominated by R.H. Holm and co-workers.

Three types of iron-sulphur centres in proteins are well established, involving 1Fe, [2Fe-2S] and [4Fe-4S], coordinated, in general, to four cysteinyl sulphurs, Figures 0.1.1 to 0.1.3. In the rhombic FeS_4 coordination characteristic of rubredoxins (Rd) the iron may be ferric or ferrous. The two-iron ferredoxins (Fd) contain a [2Fe-2S] cluster in which the two irons are bridged by two sulphides and may take up oxidation states Fe(III)Fe(III) = $[2Fe-2S]^{2+}$ and Fe(III)Fe(II) = $[2Fe-2S]^{1+}$. A cubane [4Fe-4S] unit, consisting of interpenetrating 4Fe and 4S approximate tetrahedra, is found in the four-iron ferredoxins. In nature, nearly all [4Fe-4S] proteins divide into two groups of two oxidation levels,

1. [Rd]

2. [2Fe-2S]

●Fe

○S

3. [4Fe-4S]

4. [3Fe-3S]
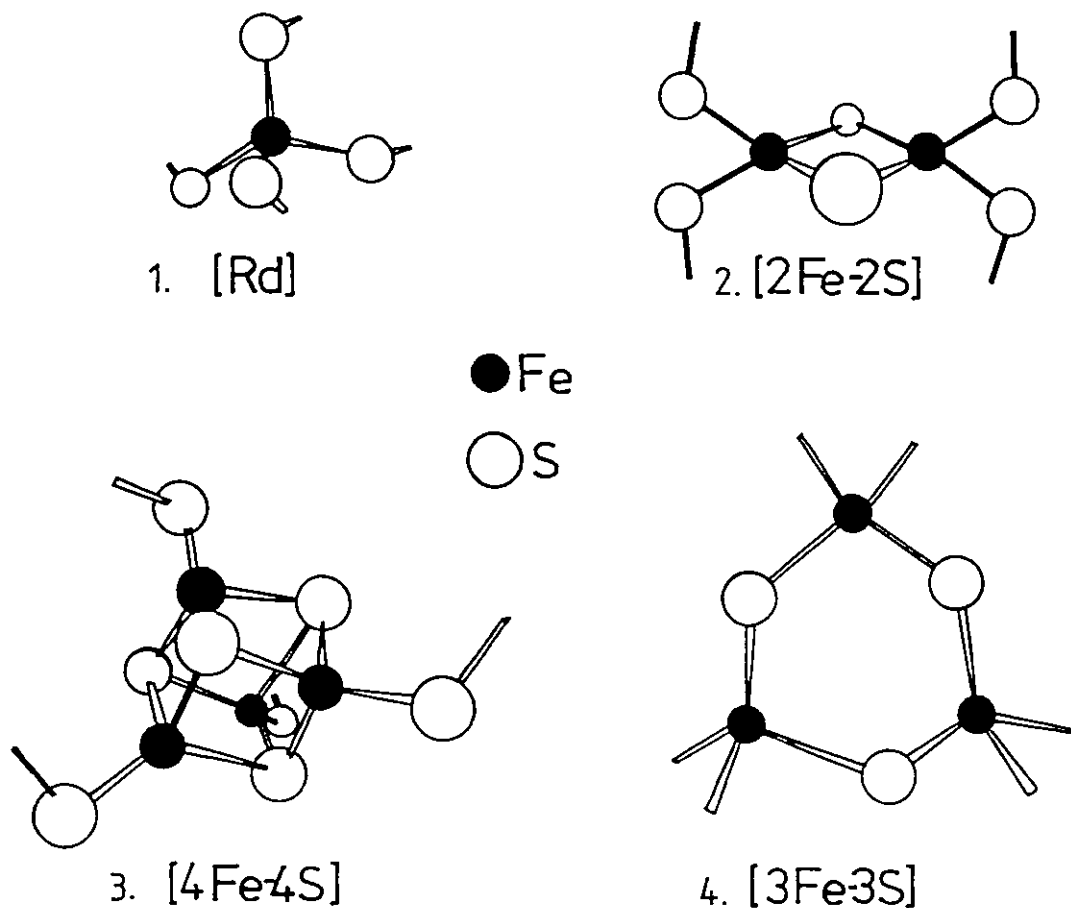
Figure 0.1. Iron-sulphur bonding arrangements in (1) 1-Fe(rubredoxin, Rd),

(2) 2-Fe and (3) 4-Fe (ferredoxin, Fd) protein centres and

(4) in the proposed 3-Fe centre.

firstly, $[4Fe-4S]^{(2+, 1+)}$ [i.e., 2Fe(III)2Fe(II) and Fe(III)3Fe(II)] and

secondly, $[4Fe-4S]^{(3+, 2+)}$ [i.e., 3Fe(III)Fe(II) and 2Fe(III)2Fe(II)]. A

fourth type of centre involving [3Fe-3S] has recently been recognised,

Figure 0.1.4, but this cluster together with its structure and properties

are not yet well established.[2]

Some of the terms and symbols used here are taken from the

nomenclature recommendations of the NC-IUB.[3] These will not always be

strictly adhered to in this thesis as the nomenclature recommended may

have confusing connotations in the context of inorganic chemistry. Iron-

FIG. 0.2 SYNTHESIS OF SOME 1—Fe, 2—Fe AND 4—Fe SULPHUR COMPLEXES & THEIR CHEMICAL—ELECTROCHEMICAL INTER-RELATIONSHIPS

$[FeCl_4]^{2-} \xrightarrow[EtO^-]{\overset{exs}{(HS)_2-o-xyl}} [Fe(S_2-o-xyl)_2]^{2-}$ [Rd]$^{2+}$

$[Fe(SPH)_4]^{2-}$ [Rd]$^{2+}$

$O_2 \updownarrow$ −1.02V

$[Fe(S_2-o-xyl)_2]^{1-}$ [Rd]$^{3+}$

S_8 or $(PhCH_2S)_2S$

HS^-
MeO^-

PhCOX

$FeCl_3 \xrightarrow[HS^- or S_8^*, MeO^-]{(HS)_2-o-xyl} [Fe_2S_2(S_2-o-xyl)_2]^{2-}$ [2Fe—2S]$^{2+}$ $\xrightarrow[PhSH]{} [Fe_2S_2(SPh)_4]^{2-}$ [2Fe—2S]$^{2+}$ $\underset{PhS^-}{\rightleftharpoons} [Fe_2S_2X_4]^{2-}$ (X=Cl,Br)

$\updownarrow$ −1.49V

$\updownarrow$ −1.09V

$\updownarrow$ e$^-$

$\dagger[Fe_2S_2(S_2-o-xyl)_2]^{3-}$ [2Fe—2S]$^{1+}$

DMSO or HMPA,H$_2$O
spont.

$\dagger[Fe_2S_2(SPh)_4]^{3-}$ [2Fe—2S]$^{1+}$

$Fe(C_5H_5)_2^+$

$\dagger[Fe_2S_2X_4]^{3-}$

$\updownarrow$ −1.73V

$\updownarrow$ −1.37V

$\dagger[Fe_2S_2(S_2-o-xyl)_2]^{4-}$

$\dagger[Fe_2S_2(SPh)_4]^{4-}$

$\dagger[Fe_4S_4(StBu)_4]^{1-}$ [4Fe—4S]$^{3+}$

$\uparrow$ R=tBu 0.01V

$FeCl_3 \xrightarrow[HS^- *, MeO^-]{PhSH} [Fe_4S_4(SPh)_4]^{2-}$ [4Fe—4S]$^{2+}$ $\underset{PhSH}{\leftarrow} [Fe_4S_4(SR)_4]^{2-}$ [4Fe—4S]$^{2+}$ $\underset{SR^-}{\overset{PhCOX}{\rightleftharpoons}} [Fe_4S_4X_4]^{2-}$ (X=Cl,Br)

spont.

$C_{12}H_8^- \updownarrow$ −1.04V

$\updownarrow$ e$^-$

$[Fe_4S_4(SPh)_4]^{3-}$ [4Fe—4S]$^{1+}$

$\dagger[Fe_4S_4X_4]^{3-}$

$\updownarrow$ −1.75V

$\dagger[Fe_4S_4(SPh)_4]^{4-}$

$\updownarrow$ $E_{1/2}/V$ vs. SCE FOR e$^-$ REACTION

* ALSO WITH μSe IN PLACE OF S

$\dagger$ SOLIDS NOT YET ISOLATED

sulphur proteins and their properties have been very widely reviewed.[3-10]
$[Fe(SR)_4]^{1-,2-}$, $[Fe_2S_2(SR)_4]^{2-,3-,4-}$ and $[Fe_4S_4(SR)_4]^{1-,2-,3-,4-}$ synthetic species have been prepared and characterised or detected spectroscopically or electrochemically by Holm and others.[1,11-13] These complexes have been demonstrated to be excellent analogues for the three major iron-sulphur centres found in proteins. The scheme in Figure 0.2 shows some of the reaction chemistry for the interrelated 1Fe, 2Fe and 4Fe compounds and the correspondence with the oxidation levels found for rubredoxins and ferredoxins.

In this present work some further, mainly spectroscopic, investigation is undertaken into the properties of several of the iron-sulphur complexes in Figure 0.2. EPR and Raman are used as the main means of study and the results are compared with corresponding protein characteristics. Some new 2Fe-complexes involving ligation by selenium are examined also. Lastly, a number of 2N2S coordinated cupric complexes with non-planar geometry are described as model complexes for blue copper proteins.

SECTION 1

EPR IN $[Fe_2S_2(SR)_4]^{3-}$

1. EPR in $[Fe_2S_2(SR)_4]^{3-}$.

ABSTRACT

$[Et_4N]_2[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]$ may be reduced in DMF using sodium

acenaphthylenide to give paramagnetic solutions containing 60-80% of

the trianion $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{3-}$. The EPR spectrum is characteristic

of reduced ferredoxins, having g-values of 2.007, 1.940 and 1.922. An

^{57}Fe enriched sample shows splittings from two iron atoms, with mean

hyperfine interactions of <u>ca</u>. 14 G.

Mössbauer spectra for $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ in solution are found

to be more compatible with $[2Fe\text{-}2S]^{2+}$ ferredoxin spectra than are

similar spectra obtained for solid samples, and a slight inequivalence

between the two irons is observed. Mössbauer spectra of the reduced

dimer give clear evidence of antiferromagnetically coupled components

of a paramagnetic species, closely resembling those found in $[2Fe\text{-}2S]^{1+}$

ferredoxins.

Other sulphur-bridged diferric complexes with monodentate aryl-

thiolate ligands, $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$ (Y = Cℓ, H, Me), may also be reduced

to yield 20-60% of the corresponding paramagnetic trianion, as evidenced

by EPR. The signals observed are found to be highly solvent-dependent

and also to be affected by the presence of excess thiol. Some preliminary

interpretation of these effects is attempted by analysis of the <u>g</u>-tensor.

EPR spectra of the reduction products of related selenium-bridged and

selenium terminally-ligated diferric complexes are also reported.

1. **EPR IN** [Fe$_2$S$_2$(SR)$_4$]$^{3-}$.

1.1. **EPR in 2Fe2S Ferredoxins.**

EPR has proven to be of considerable use in the characterisation of iron-sulphur proteins and in elucidation of their metal-site structures.[6,14-16] Figure 1.1.1 shows spectra typical of 2Fe ferredoxins (Fd) isolated from three different natural sources. In each case the lineshape can be attributed to a ground-state doublet having two principal g-values below 2.0. The signals saturate easily at low temperatures and broaden rapidly at higher temperatures. This unusual form and behaviour of the spectra is now well understood in terms of the classic interpretation of Gibson and Thornley et al.,[17,18] involving antiferromagnetic coupling between ferric and ferrous irons via two bridging sulphide ligands,

Figure 1.1.1. Typical EPR spectra for 2Fe-Fd$_{red}$,

Figure 1.1.2. Model for the 2Fe-Fd centre.
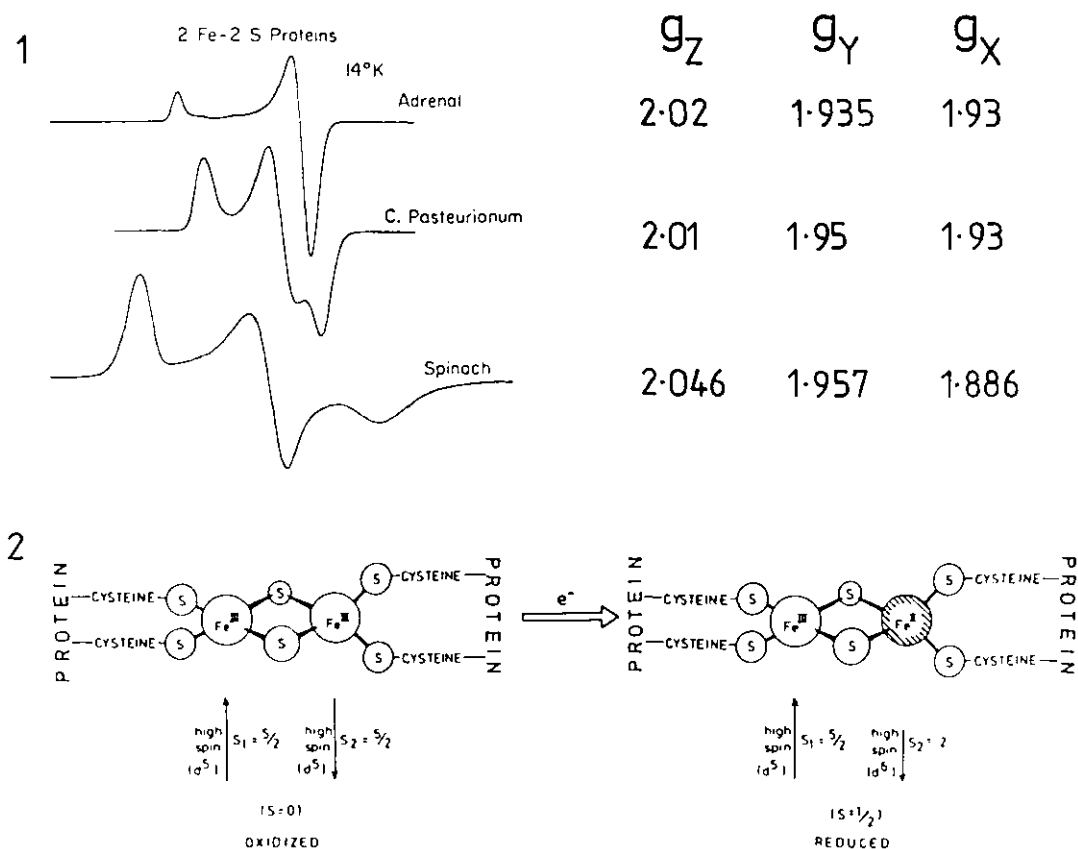
(Figure 1.1.2.). The appropriate spin Hamiltonian for such coupling of two different spins, S_1 and S_2, is given in equation E1.1; J is the exchange constant and takes by convention negative values for an

$$\hat{\mathcal{H}}_S = \beta H. (\underline{g}_1.\hat{S}_1 + \underline{g}_2.\hat{S}_2) - 2J\hat{S}_1.\hat{S}_2 \qquad (E1.1)$$

antiferromagnetic interaction. Defining $\hat{S} = \hat{S}_1 + \hat{S}_2$, $\underline{g}\hat{S} = \underline{g}_1\hat{S}_1 + \underline{g}_2\hat{S}_2$ and rearranging gives equation E1.2, and for ferric ($S_1 = 5/2$,

$$\underline{g} = (\frac{\hat{S}^2 + \hat{S}_1{}^2 - \hat{S}_2{}^2}{2\hat{S}^2})g_1 + (\frac{\hat{S}^2 - \hat{S}_1{}^2 + \hat{S}_2{}^2}{2\hat{S}^2})g_2 \qquad (E1.2)$$

$\hat{S}_1{}^2 = 35/4$) and ferrous ($S_2 = 2$, $\hat{S}_2{}^2 = 24/4$) equation E1.3.

$$\underline{g} = \frac{7}{3} \underline{g}_1 - \frac{4}{3} \underline{g}_2 \qquad (E1.3)$$

Assuming tetrahedral sulphur coordination, a reasonable value for g_1 is 2.02, whilst for the ferrous ion admixture of two excited orbital states (d_{xz} and d_{yz}) into the ground state (d_{z^2}) can lead to its g_2 being considerably greater than 2.0 in the x and y directions. Thus, for the coupled pair, two g-values are expected to be below the free spin value (g_e).

The $J\hat{S}_1.\hat{S}_2$ Hamiltonian term results in spin states characterised by S ranging from (S_1-S_2) to (S_1+S_2) (1/2, 3/2, 5/2, 7/2, 9/2) at energies 0, -3J, -8J, -15J and -24J. A two-phonon resonant relaxation process involving the higher spin states was postulated to explain the

anomalous temperature dependence of the EPR signal from the ground state.[17] This interpretation was later demonstrated to be correct.[19] The different temperature ranges over which broadening occurs for the various ferredoxins, can be understood in terms of variation in the strength of exchange coupling.

When both irons are ferric the anti-ferromagnetic coupling results in a singlet ground-state and hence the oxidised ferredoxin is found experimentally to be devoid of EPR.

The electronic model proposed by Gibson et al. has subsequently been amply borne out by experiments of many kinds. ENDOR and Mössbauer techniques demonstrate that the ferric and ferrous ions are indeed distinct, being non-equivalent.[20-23] Coordination of the irons is considered to be tetrahedral, with the 2Fe2S unit ligated in general by four cysteinyl residues (Figure 1.1), as originally proposed by Brintzinger[24] et al. X-ray diffraction data for Spirulina platensis at 2.8 $\overset{o}{A}$ resolution confirms such a chelate structure.[25,26]

1.2. 2Fe2S Ferredoxin Model Complexes: $[Fe_2S_2(SR)_4]^{2-}$.

The first well-defined synthetic analogue of the oxidised form of 2Fe2S proteins was reported in 1973 by Holm and coworkers.[27] This involved coordination of a coupled 2Fe2S unit by two terminal o-xylyl-$\alpha-\alpha'$-dithiolate (S_2-o-xylyl) ligands.

Whilst the synthesis of other alkyl-mercaptide coordinated 2Fe2S species has not yet been achieved, $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$, (Y = H, Me, C$\ell$) complexes have been prepared by ligand substitution[28] or more recently by direct synthesis.[29] Two further species involving the same type of

2Fe6S metal centre have been isolated: $[(PhS)_2FeS_2FeS_2MoS_2]^{3-}$ [30] and the

novel $[S_5FeS_2FeS_5]^{2-}$.[31] Iron-sulphur complexes with cysteine-containing

synthetic peptides have been reported to show visible solution spectra

comparable with 2Fe-Fd$_{ox}$ but could not be isolated.[32] Other potential

2Fe-Fd analogues have either been prepared only in solution and are

consequently of indeterminate structure [33,34] and refs.therein or involve

decidedly non-physiological ligands.[35-37]

The $[Fe_2S_2(SR)_4]^{2-}$ complexes, and in particular that involving the

chelating o-xylyl ligand, have been extensively studied by Holm and his

associates[27,28,38] using X-ray crystallography, electronic spectroscopy,

Mössbauer , magnetic susceptibility, NMR and voltammetry. Additionally,

Teo and Shulman et al.[39] have made an EXAFS investigation comparing

$[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ with 2Fe-Fd, and a vibrational study for several

of the complexes is reported in Section 4 of this thesis.

$[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ is considered to be a suitable minimal

structural and electronic representation of 2Fe-Fd$_{ox}$ sites confirming

the μ_2-sulphido structure $[Fe_2S_2(S-Cys)_4]$ proposed for the proteins.

From their discovery the ferredoxins have been characterised,

when reduced, by the unusual EPR signal described in the previous section.

Several model iron-complexes have been proposed on the grounds that they

reproduce some feature of the Fd$_{red}$ spectra.[40-42,37,34,33] None of these

are known to possess tetramercapto coordination of a coupled μ_2-sulphido-

diiron unit. Reduction of $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ to a stable trianion

species has on the other hand proven elusive,[43,44] and thiol-extrusion

of the metal centre of reduced spinach Fd yields mainly only the dianion.

This instability is in keeping with the quasi-reversibility of the reduction process as observed by cyclic voltammetry.[28] $[Fe_2S_2(SR)_4]^{2-}$ itself is found to convert spontaneously in protic media to $[Fe_4S_4(SR)_4]^{2-}$, and the non-redox process $[Fe_2S_2(SR)_4]^{3-} \longrightarrow [Fe_4S_4(SR)_4]^{2-}$ involving reactant $(2[Fe_2S_2]^{1+})$ and product $([Fe_4S_4]^{2+})$ cores in the same oxidation level is facile even in aprotic solvents. Thus, prolonged electrolysis of dimer dianion solutions at a potential above that for the first one-electron reduction yields $[Fe_4S_4(SR)_4]^{3-}$ from further reduction of the initially formed tetramer dianion[45]:-

$$2[Fe_2S_2(SPh)_4]^{2-} \xrightarrow{\;+2e^-\;} 2[Fe_2S_2(SPh)_4]^{3-}$$

$$[Fe_4S_4(SPh)_4]^{3-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Fe_4S_4(SPh)_4]^{2-} + 4PhS^-$$
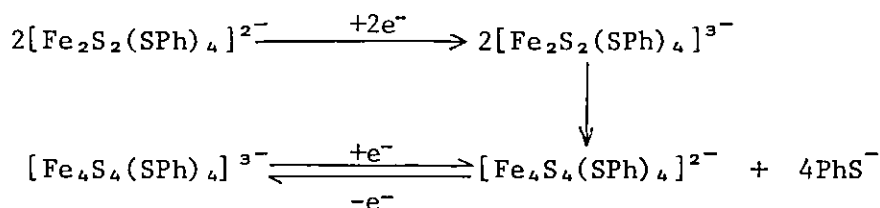
In this present work it has been found that chemical reduction of $[Fe_2S_2(SR)_4]^{2-}$, followed by the rapid quenching of further reactions with low temperature solvent glassification, enables EPR signals of the dimer trianion to be observed.

1.3. $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$.

1.3.1. EPR.

Figure 1.2 shows the first (1.2.1) and second (1.2.4) derivative EPR signals for a sample resulting from the reduction of a DMF solution of $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ with just over one equivalent of acenaphthylenide radical anion (ACN^-). n-Bu_4NClO_4 (0.1 M) has been added to the solution to increase the solubility of the iron complex and to ensure

Fig. 1. 2 EPR of $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ in DMF(0.1M nBu_4NClO_4) at 100 K
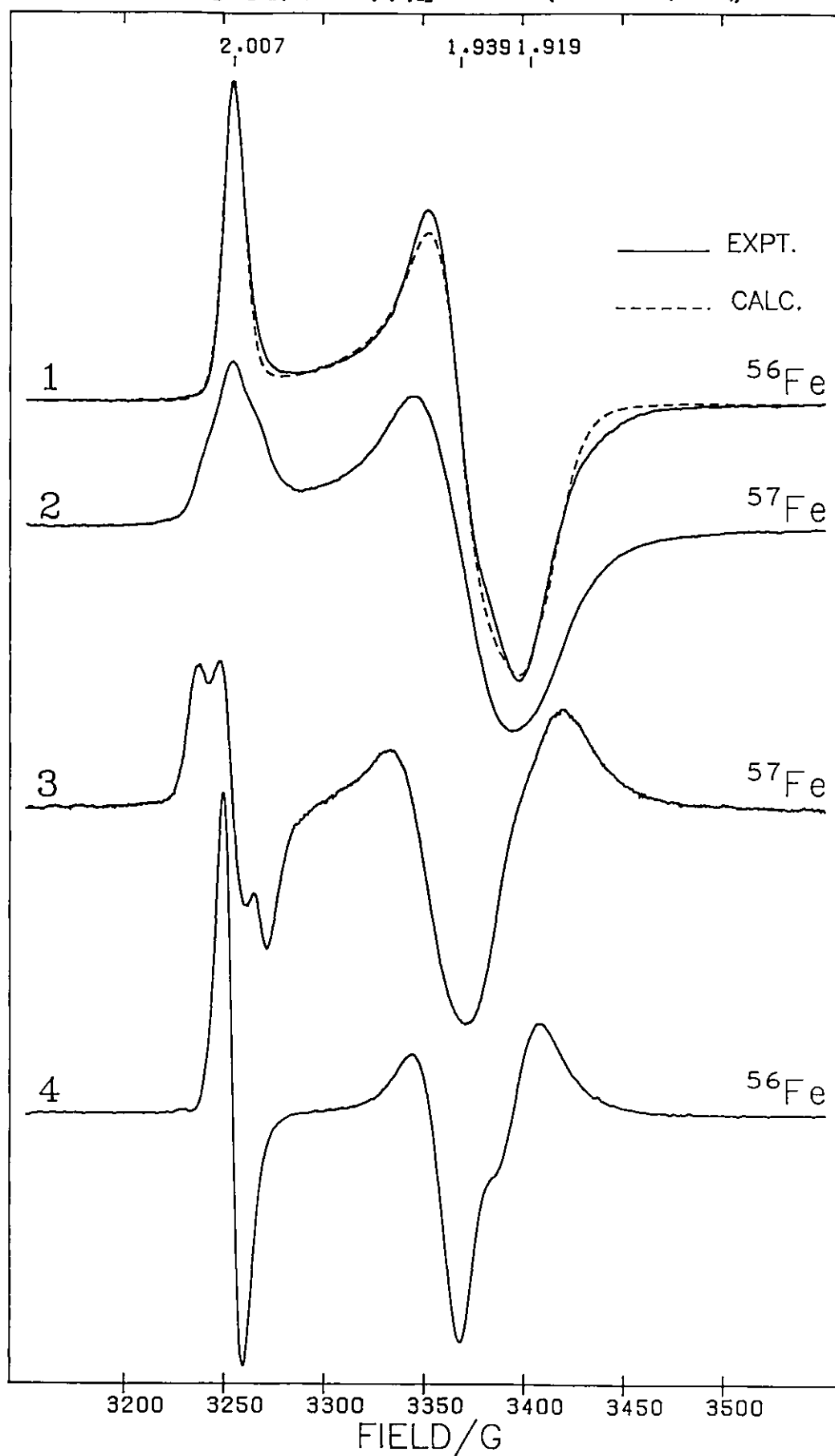
glassification on freezing. Similar spectra are obtained when, for example, CH_2Cl_2 ($\sim$ 2M), H_2O ($\sim$ 2M) or DMSO (50/50) is added in order to obtain a vitreous sample. A non-glassy sample results from the use of pure DMF, and the EPR spectrum then has a larger linewidth. Comparable lineshapes are found when pure DMSO is used as solvent (Figure 1.3.1). These non-vitreous samples demonstrate a reversible broadening of the signal in the temperature range 100 — 200 K (Figure 1.3.1-2).

At liquid nitrogen temperatures the signals are only slightly power saturated at 200 mW, on the instrument used, as can be seen from Figure 1.4. Spectra measured at $\sim$ 12 K show very similar lineshapes to those observed at 100 K but could easily be extensively saturated at powers above 0.2 mW.

The g-values measured from these spectra at maximum, crossover and minimum are 2.007, 1.940 and 1.922. These are invariant to $\pm$ 0.001 for the various solvent systems used. Simulation of the lineshape does not lead to significantly different values; neither can this technique be considered more accurate in view of the difficulty in fitting the high field part of the spectrum. On the whole, low temperature spectra are better simulated with a Gaussian rather than Lorentzian lineshape; however, neither is entirely adequate, and it has been found necessary to use a convolution of these two functions to get acceptable results.

The least-squares fitted calculated lines in Figures 1.2.1 and 1.3.1 result from the use of such a mixed Gaussian-Lorentzian convolution product. Despite giving, as might be anticipated, a closer match to the experimental

Fig. 1. 3 EPR of $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ in DMSO
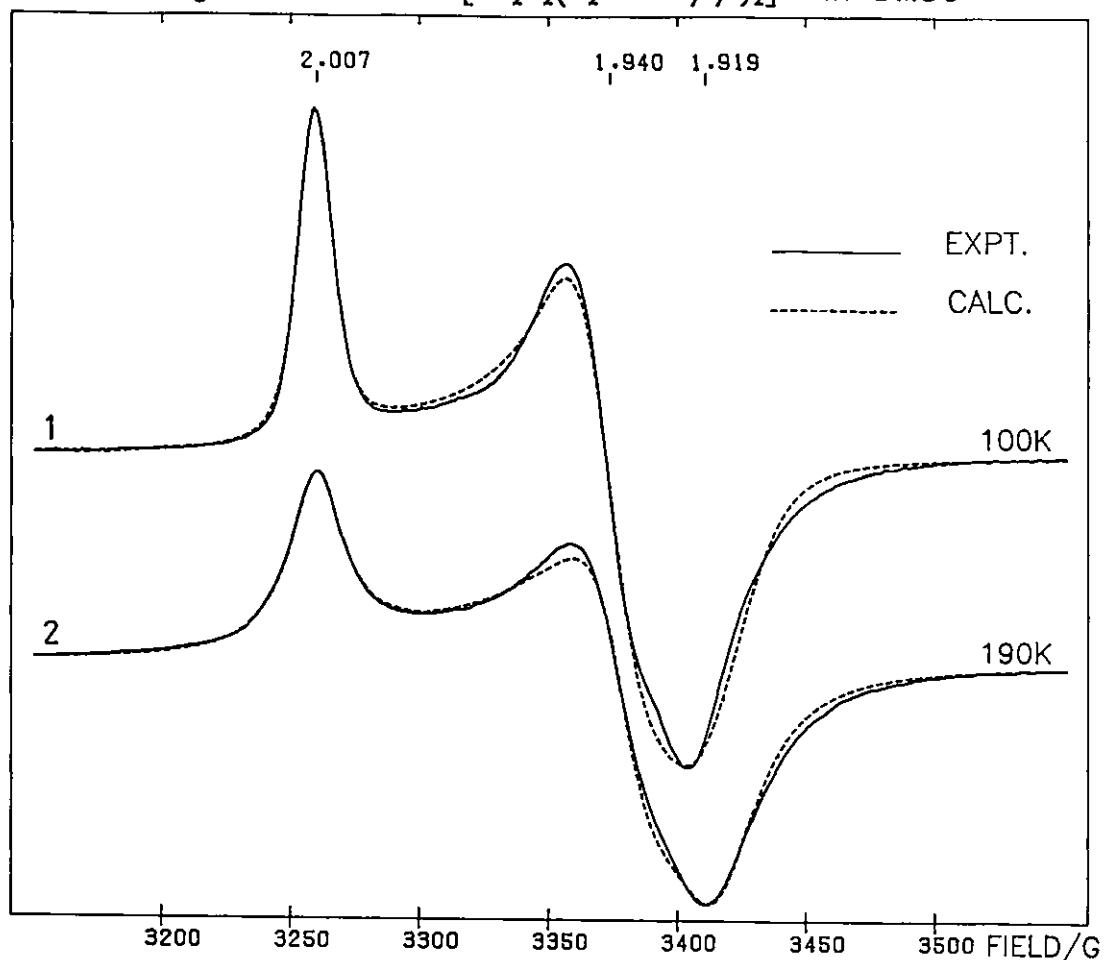
Fig. 1. 4 Power saturation in EPR of $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$
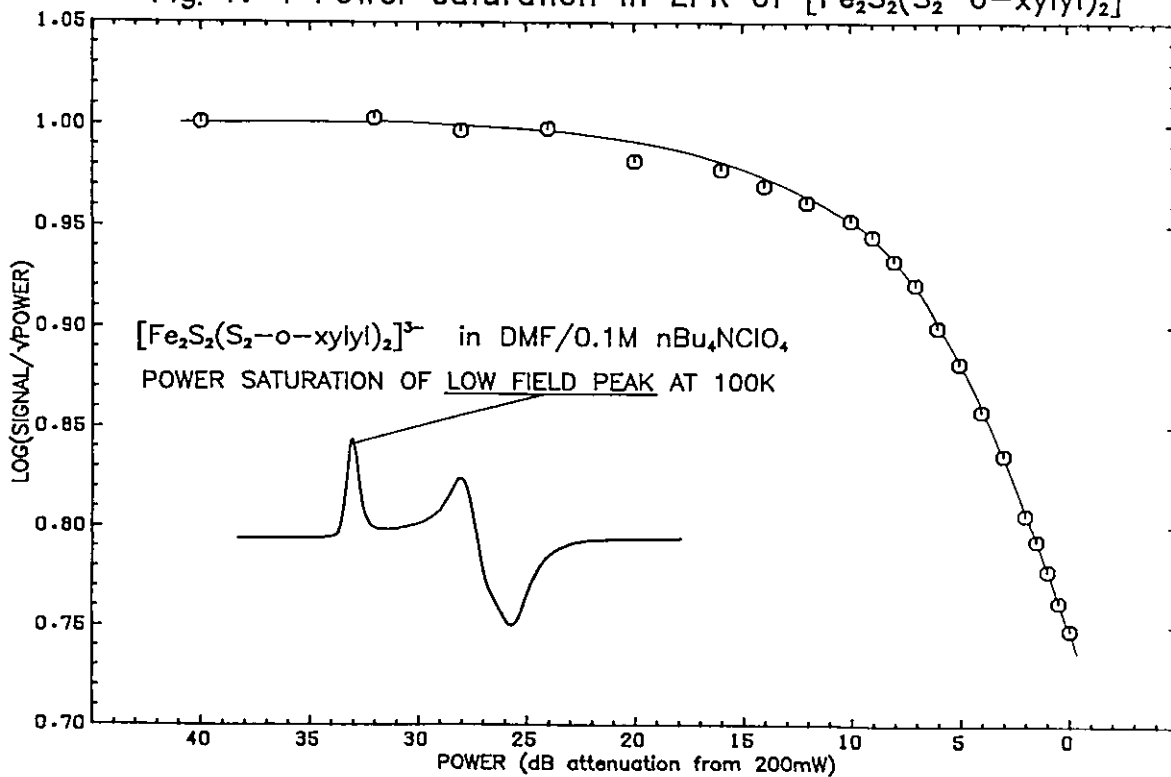
TABLE 1.1. EPR Parameters for $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{3-}$.

DMF, 0.1 M n-Bu$_4$NClO$_4$ (Figure 1.2.1).

Measured	2.007	1.940	1.922
Pure Gaussian (F = 1.9)	2.0064	1.939	1.919
Gaussian widths (G)	6.7	14.1	16.7
Pure Lorentzian (F = 2.5)	2.0065	1.939	1.920
Lorentzian widths (G)	6.2	11.5	14.0
Lorentz-Gaussian (F = 1.4)	2.0065	1.939	1.919
Lorentzian widths (G)	1.5	3.2	4.2
Gaussian widths (G)	5.5	12.4	14.2

DMSO (Figure 1.3)

100 K

Measured	2.008	1.940	1.923
Lorentz-Gaussian	2.0077	1.940	1.919
Lorentzian widths (G)	4.0	9.1	9.8
Gaussian widths (G)	5.8	10.2	14.2

190 K

Pure Lorentzian	2.008	1.937	1.916
Lorentzian widths (G)	12.4	18.1	20.5

F = least squares fitting parameter.

spectrum, even this simulation method also proves inadequate at high field. Details of measured and fitted parameters are given in Table 1.1.

For EPR signals obtained by chemical reduction at low temperatures in DMF, comparison of doubly-integrated intensities with a Cu(II) EDTA standard indicates 60 to 80% yield of trianion in the majority of reductions. The signal intensities of such solutions, measured at 100 K, were observed to have decayed completely after 2 to 3 minutes at 20°C. At -50°C on the other hand, solutions $\underline{ca}$. 0.5 mM in $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{3-}$ have greatly increased stability such that the EPR signal intensity measured at 100 K decreases only slightly over a period of a few hours in the strict absence of molecular oxygen. For these reasons reactions effected in DMSO led to only $\underline{ca}$. 20% yield of trianion as they must be performed above the solvent freezing point of $+18^{\circ}$C.

1.3.2. ^{57}Fe EPR.

^{57}Fe enriched (83%) $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{2-}$ prepared on a small scale and reduced in DMF with ACN$^{\pm}$ gives the EPR signal shown in Figure 1.2.2. Whilst to high field only an overall broadening results from ^{57}Fe enrichment, for the low field peak side shoulders are apparent and a splitting is seen quite clearly in the second-derivative lineshape (Figure 1.2.3). With the level of isotopic enrichment employed the spectrum resulting from a spin-coupled ferric-ferrous dimer is expected to possess three component spectra. For parity of nuclear hyperfine interaction from the iron sites, the majority of the sample (69%),

Fig 1.5 ^{57}Fe hyperfine splitting at low field in the EPR of
$[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$
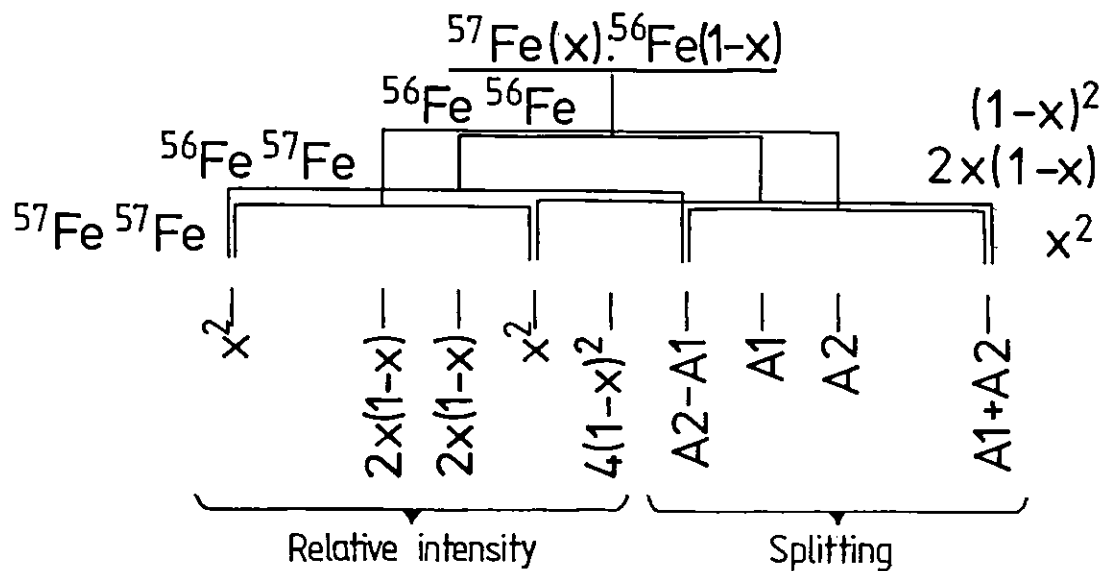
83% ^{57}Fe enriched $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ in DMF(0.1M nBu$_4$NClO$_4$)
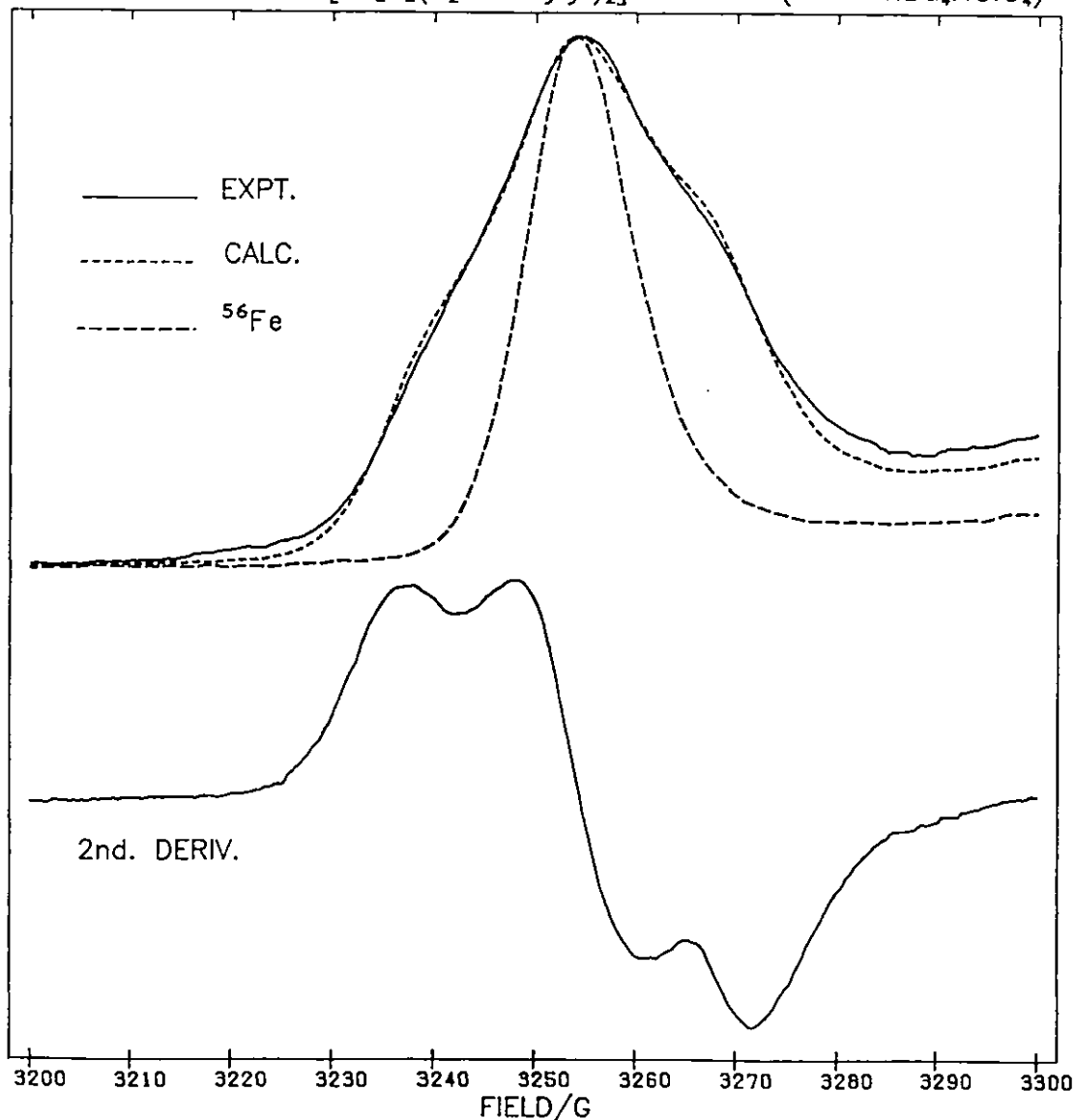
containing two ^{57}Fe ions, will give rise to a 1:2:1 triplet for the low field peak.[46] The substantial proportion of mixed ^{56}Fe $/^{57}$Fe dimers (28%) will result in a splitting to a doublet and the remaining small fraction will appear similar to the unenriched spectrum. By field-shifting the spectrum for the natural abundance ^{56}Fe sample with the ^{57}Fe hyperfine splitting, and adding component spectra according to the expected statistical distribution for the three isotopic mixtures it is possible to obtain a reasonable fit to the low field peak of the ^{57}Fe enriched spectral lineshape. A least squares fitting procedure leads to an estimated hyperfine splitting of 14 G. If the splittings produced by ferric and ferrous sites are allowed to be inequivalent, values of 15.2 G and 13.5 G achieve the best fit (Figure 1.5). The splitting, assuming equivalent hyperfine interactions, is quite compatible with the 14 G obtained for Putidaredoxin[47] and spinach ferrodoxin[48] by a similar method, or the 15 G found for parsley ferredoxin.[49] ENDOR measurements for several 2Fe2S proteins have indicated effective splittings of around 12-13 G and 14-15 G along the hyperfine tensor z-axis for ferrous and ferric sites respectively.[20,50]

1.3.3. Mössbauer of [Fe$_2$S$_2$(S$_2$-o-xylyl)$_2$]$^{2-,3-}$.*

The synthesis of a ^{57}Fe enriched sample of [Fe$_2$S$_2$(S$_2$-o-xylyl)$_2$]$^{2-}$ has enabled the measurement of solution Mössbauer spectra for this compound. Previously only the solid has been studied due to its limited solubility leading to very poor signal to noise ratio for solutions with natural abundance in ^{57}Fe.

1.3.3.1. Mössbauer for the Dianion.

Figure 1.6 shows low temperature spectra for a DMF solution in zero applied field and with fields of 3, 6 and 10 T applied perpendicular to the γ-ray beam. Temperature independence is demonstrated by the similarity of the zero-field spectrum obtained at 77 K to that at 4.2 K.

The Mössbauer spectra of the dianion may be characterised by 1:1 addition of two spectra having slightly different quadrupole splittings but which are otherwise identical. The absence of an observable hyperfine field is in keeping with the diamagnetism of the compound, resulting from the anti-ferromagnetic coupling between the two ferric ions. Table 1.2 lists the parameters used to obtain best least-squares fit of spin-Hamiltonian calculated spectra to the experimental results. The

TABLE 1.2. Parameters Used to Fit Mössbauer Spectra of $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ in DMF at 4.2 K.

Perpendicular Field	Site	Isomer shift (δ) mm/s rel. Fe metal	Full Linewidth (Γ) Lorentz (mm/s)	η
0T	1 2	0.27 0.27	0.31	–
3T	1 2	0.26 0.28	0.30	0.5 0.5
6T	1 2	0.27 0.31	0.29	0.48 0.75
10T	1 2	0.26 0.31	0.30	0.64 0.67
Generalised parameters	1 2	0.27 0.29	0.30	0.6

Quadrupole splitting ΔE_Q (mm/s)   site 1 = 0.4   site 2 = 0.57
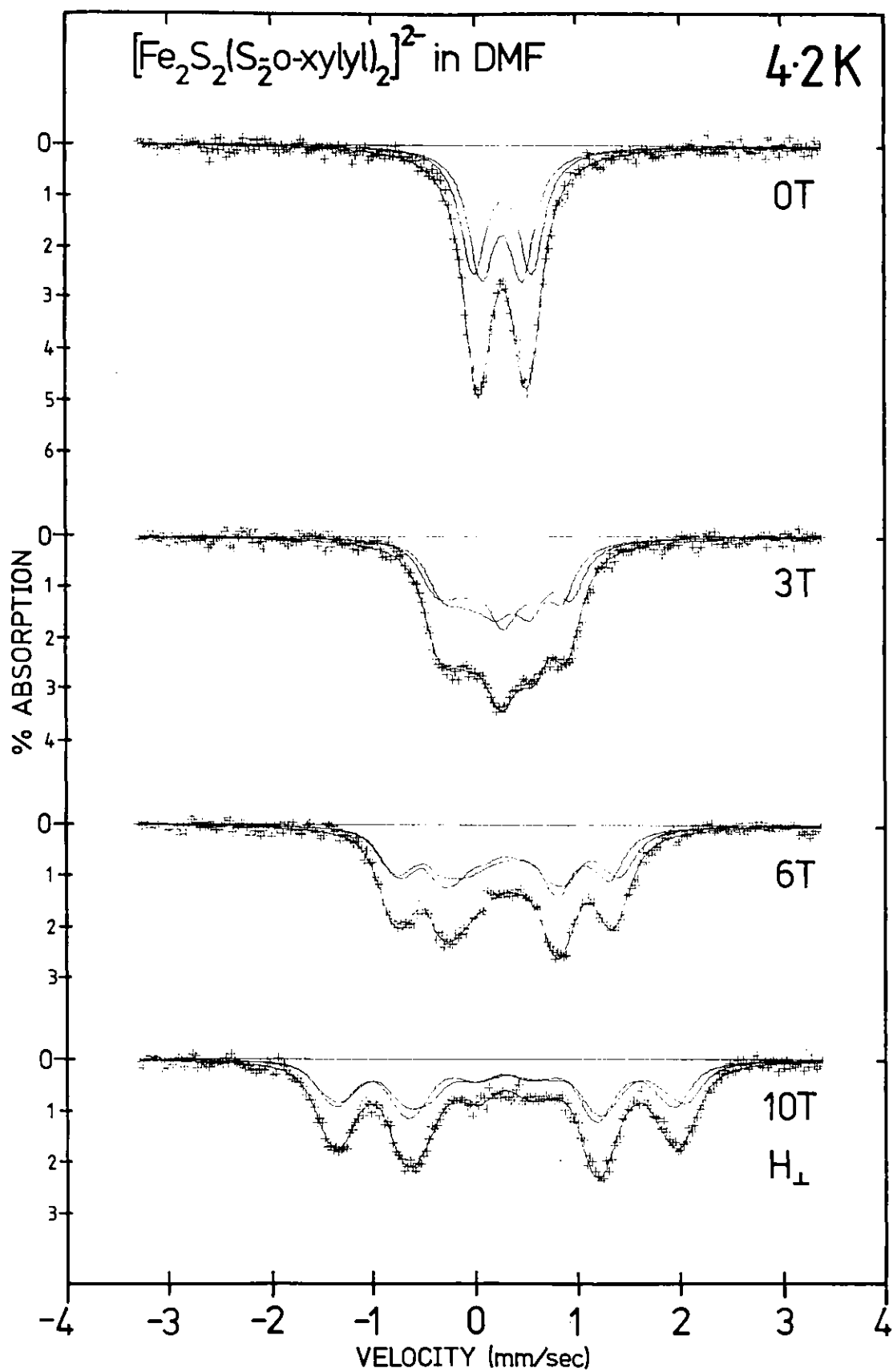
Fig 1.6 Mossbauer spectra of $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ in DMF

inequivalence in the quadrupole splittings for the two ferric sites is

revealed in the zero-field spectrum in that the linewidth is rather

larger than the instrumental linewidth. Oxidised-ferredoxin spectra

also show slight inequivalence for the two irons. Table 1.3 collects

some Mössbauer data obtained from simulation of spectra for several

$2Fe-Fd_{ox}$ and also for solid $[Fe_2S_2(SR)_4]^{2-}$ salts. The solution results

for the model complex compare quite favourably with those for the

proteins, although the quadrupole splitting is observed to be somewhat

lower than in the proteins.

TABLE 1.3. Mössbauer Spectral Parameters for $2Fe-Fd_{ox}$ and

$[Fe_2S_2(SR)_4]^{2-}$ Salts at 4.2 K.

	δ (mm/s)	ΔE_Q (mm/s)	γ
Adrenodoxin[51]	0.285	0.622	
Euglena[52]	0.22	0.65	
Scenedesmus[53]	0.20	0.60	
Putidaredoxin[54]	0.27	0.602	0.42
Spinach[22]	0.27	0.65	0.5
Parsley[22]	0.28	0.66	0.5
Clostridial[22]	0.28	0.62	0.5
Azotobacter I[22]	0.31	0.73	0.5
Azotobacter II[22]	0.29	0.71	0.5
Synechococus[50]	0.22	0.55 & 0.83	0.5
Halobacterium[55]	0.25 & 0.29	0.47 & 0.87	
$[Et_4N]_2[Fe_2S_2(S_2-o-xylyl)_2]$[38]	0.17	0.36	
$[Et_4N]_2[Fe_2S_2(SPh)_4]$[38]	0.17	0.32	
$Et_4N[Fe(S_2-o-xylyl)_2]$[56]	0.13	0.57	

It is interesting to note the difference between the parameters

for the frozen solution spectra and those for Et_4N^+ and Ph_4As^+ salts,

where there is rigorous equivalence between the two iron atoms.[27,38]

The increased quadrupole splitting may be interpreted as indicating a

lowering of symmetry in frozen DMF compared to the crystalline solid.

Solution Raman spectra for this anion show bands in close agreement

with solid state spectra, however, the reflectance spectrum for powdered

$[Et_4N]_2[Fe_2S_2(S_2-o-xylyl)_2]$ shows significant differences from visible

spectra recorded for solutions (Section 4). The isomer shift measured

for $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ in solution is more in keeping with values

obtained for $2Fe-Fd_{ox}$ than is the value obtained for the solid. Hoggins

and Steinfink[57] have given empirical equations relating Fe-S bond

distances and δ for tetrahedral sulphur coordination; $V = 178.2 \sum(R_i)^{-6.81}$,

$\delta = 1.4-0.4$ V (relative to Fe metal) where V is the valence and R_i bond

length in Å. Application of these equations to $[Et_4N]_2[Fe_4S_4(SCH_2Ph)_4]$[58]

leads to $<\delta> = 0.345$ mm/s in excellent agreement with the observed

0.34 mm/s.[59] Using the crystal structure bond-lengths for $[Et_4N]_2[Fe_2S_2(S_2-$

$o-xylyl)_2]$, V is calculated to be 2.83 and $\delta = 0.27$ mm/s. Thus,

according to the empirical bonding relationships the solid state stereo-

chemical data indicate an isomer shift corresponding to the values found

in frozen solution and in Fd_{ox} rather than in the solid.

1.3.3.2. Mössbauer for the Trianion.

Figure 1.7 compares the zero-field Mössbauer spectra for ^{57}Fe-enriched

$[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ in DMF with a chemically reduced sample measured

in a small magnetic field, sufficient to decouple electron and nuclear
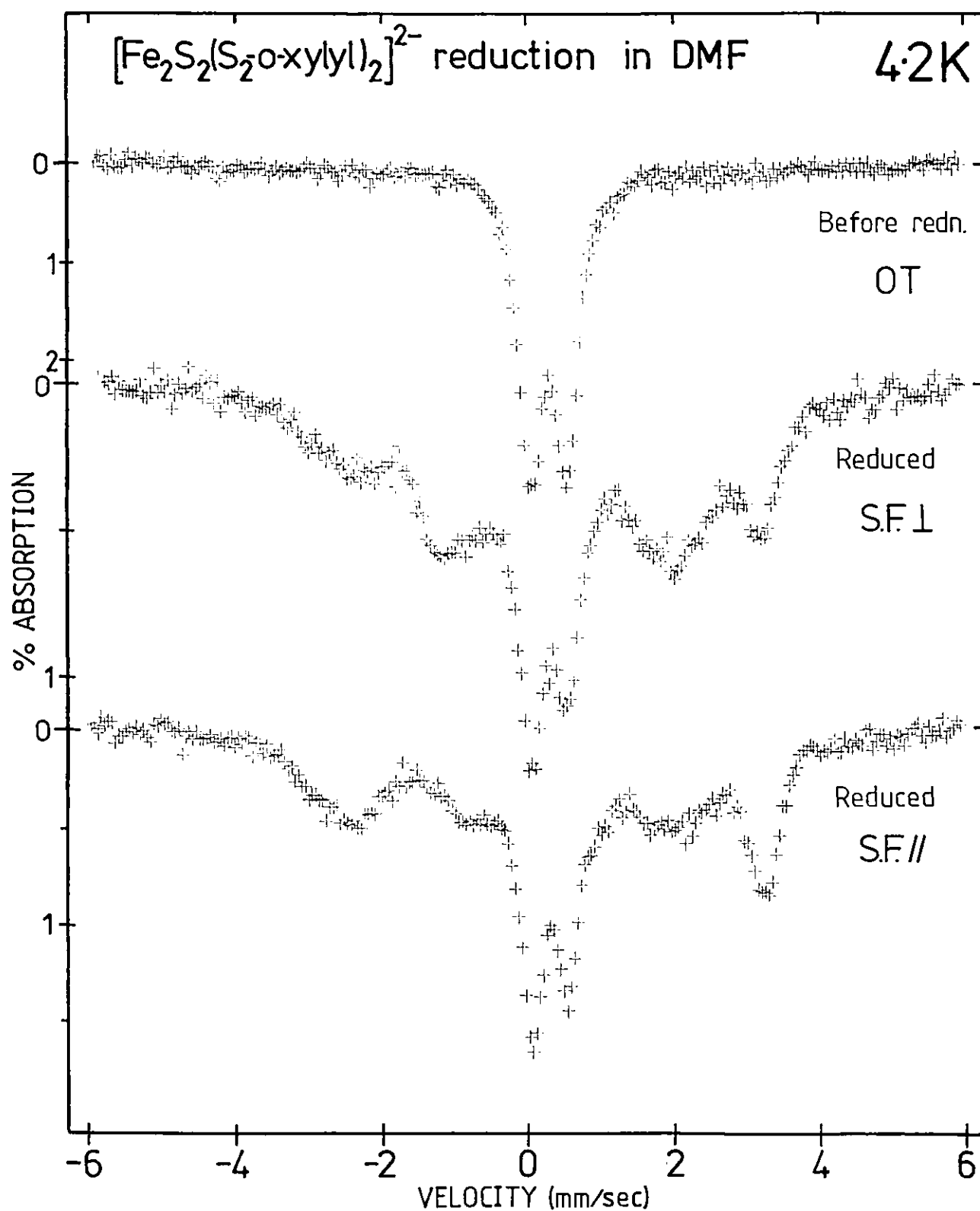
FIG. 1.7   Mössbauer spectra of $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ and its reduction product. (SF = Small Field).

spins, applied perpendicular and then parallel to the γ-ray beam. The latter spectra show clearly the presence of a paramagnetic species together with some dianion. The effect of applying a stronger perpendicular field of up to 10 T is shown in Figure 1.8. These spectra may be fitted quite well by a procedure involving addition of calculated spectra corresponding to an anti-ferromagnetically coupled ferric-ferrous pair, together with a proportion of the diferric species as simulated in the prereduced state. Parameters for the $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{3-}$ reduced ferredoxin analogue are given in Table 1.4.

TABLE 1.4. Parameters Used to Fit Mössbauer Spectra of $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{3-}$ in DMF at 4.2 K.

$H_\perp$	0.25 T		6 T		10 T		Generalised	
Site	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}
δ (mm/s)	0.33	0.76	0.33	0.71	0.29	0.60	0.33	0.7
ΔE_Q (mm/s)	−0.8	2.8	−0.67	2.93	−0.67	3.22	−0.7	3.0
Γ_{full} (mm/s)	0.31		0.32		0.31		0.31	
ϑ	0.7	0.35	0.6	0.3	0.65	0.35	0.65	0.35
A_x' (MHz)	−53.7	13.4	−58.8	12.4	−56.8	10.3	−55	11
A_y' (MHz)	−46.5	5.16	−42.3	8.26	−43.4	8.26	−45	8
A_z' (MHz)	−49.6	33.0	−49.6	39.2	−52.6	39.2	−50	39
A_x' (G)	−20.0	4.98	−21.9	4.61	−21.1	3.83	−20	4
A_y' (G)	−17.1	1.90	−15.6	3.04	−16.0	3.04	−16	3
A_z' (G)	−17.7	11.7	−17.7	14.0	−18.7	14.0	−18	14
% dianion	42%		40%		40%		40%	
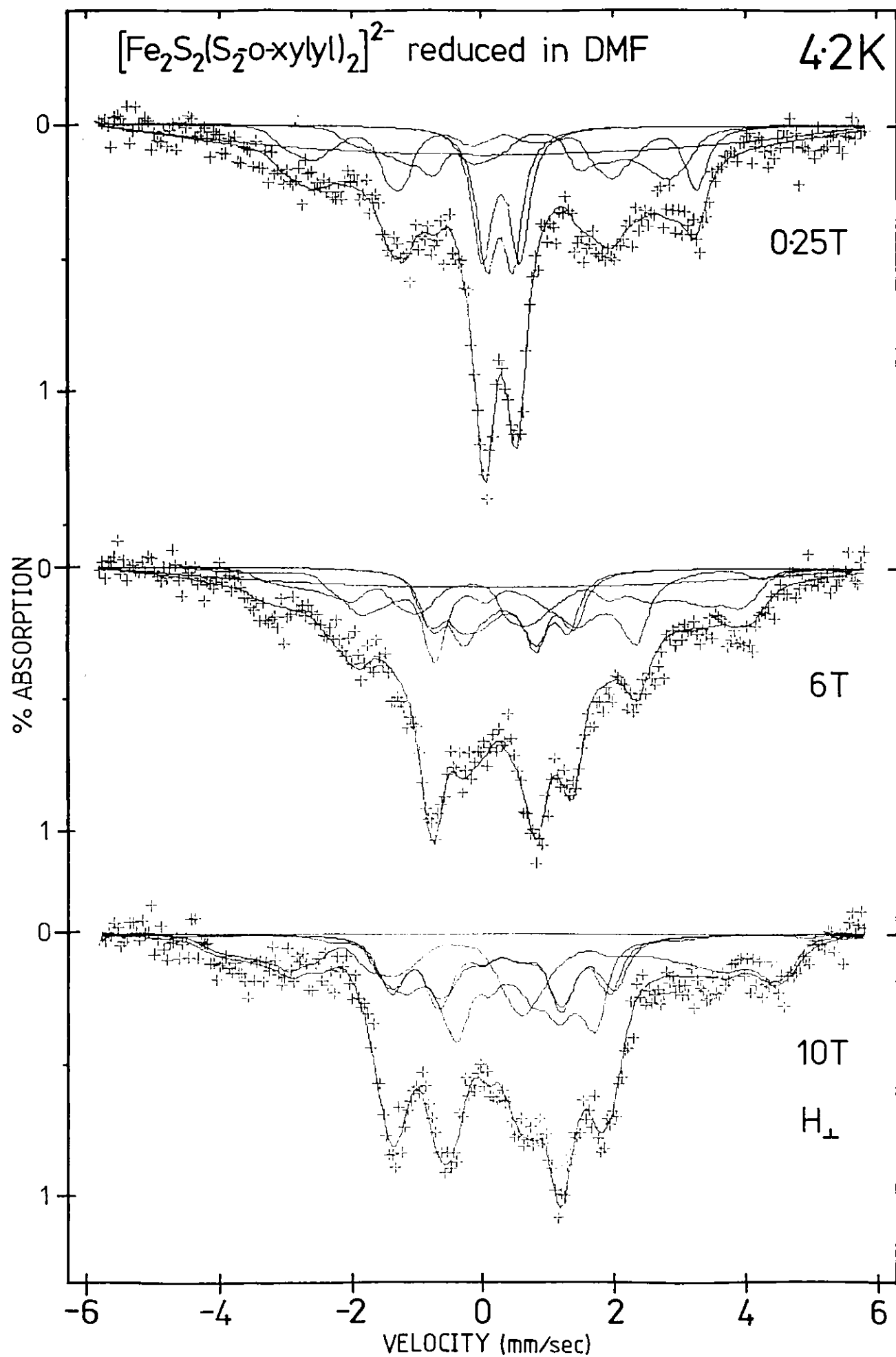
FIG. 1.8 Mössbauer spectra of reduced $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$.

The separation of the lines in the Mössbauer spectrum for a given

site is proportional to the effective hyperfine field. The sign of

the hyperfine field may be deduced by observing whether the splitting

in the spectrum increases or decreases with increased applied field.

Analysis of the Mössbauer spectra in Figure 1.8 in terms of the

calculated lineshapes shown, demonstrates that the paramagnetic species

has one site with a conventional negative hyperfine field and one with

a positive hyperfine field. Disregarding the two nearly superimposed

calculated lines from the dianionic species, of the remaining two

lines, one has peaks which split further apart at high applied field

whilst the other has somewhat sharper peaks which close together. These

latter two calculated spectra may be assigned to ferrous and ferric

ions respectively, antiferromagnetically coupled. Considering the case

in which the coupled electron spin (S_z = 1/2) is aligned with the

applied field, the ferric spin (S_z = 5/2) will also be aligned whilst

the ferrous spin (S_z = 2) will be directed anti-parallel to the external

field. Since for each ion the nuclear magnetic moment is in opposition

to the hyperfine field which it experiences from the atom's electron

spin, the hyperfine interaction for the ferric is observed negative,

and for the ferrous positive, with respect to the external field. For

the excited electronic spin-state the signs are of course reversed, but

at low temperatures and large applied fields the population of the

S_z = 1/2 state is small relative to that with S_z = -1/2.

Thus, the Mössbauer results for reduced $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{2-}$

confirm the EPR results by demonstrating the presence of an antiferro-

magnetically coupled ferric-ferrous dimer. The Mössbauer behaviour is

typical of 2Fe-Fd$_{red}$ proteins. Table 1.5 lists parameters derived for several proteins. Corresponding values for the reduced analogue dimer compare reasonably well with these.

TABLE 1.5. Mössbauer Spectral Parameters for 2Fe Fd$_{red}$ at 4.2 K.

2Fe Fd$_{red}$		δ (mm/s)	ΔE$_Q$ (mm/s)	η	A$_x$'	A$_y$'	A$_z$'(MHz)
Putidaredoxin[54]	Fe^{3+}		+0.6		-56	-50	-43
	Fe^{2+}		-2.7		14	21	35
Parsley[22]	Fe^{3+}	0.25	+0.68	-0.9	-51	-46.2	-42
	Fe^{2+}	0.54	-3.00	0	11.2	14	33.6
Spinach[22]	Fe^{3+}	0.25	+0.64	-0.6	-51	-49.1	-42
	Fe^{2+}	0.54	-3.00	0	11.1	16.8	35.3
Scenedesmus[53]	Fe^{3+}	0.22	0.59				
	Fe^{2+}	0.56	2.57				
Synechococcus[50]	Fe^{3+}	0.15	0.60	-0.3	-51.6	-50.0	-42.0
	Fe^{2+}	0.42	-3.20	0	13.0	15.0	36.5
Halobacterium[55] at 200 K	Fe^{3+}	0.30	0.60				
	Fe^{2+}	0.55	2.64				
Adrenodoxin[22] at 250 K	Fe^{3+}	0.28	0.81				
	Fe^{2+}	0.54	2.72				

The average values of the **A** tensors for the two sites in the analogue are, like those found for the proteins, considerably smaller than the value expected for an ionic iron compound. This implies a high degree of 3d electron delocalisation. Furthermore, the ferric site **A** tensor exhibits a far larger anisotropy than expected for an S-state ion under a crystal field approximation.

The effective hyperfine interaction along the z-axis for the ferrous site in $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{3-}$ is in good agreement with the estimated splitting of $\sim$ 14 G for the g_z EPR peak. The z-axis value for the ferric hyperfine at the electron is somewhat larger than the maximum of 15.2 G obtained from fitting the EPR assuming inequivalent sites, but is in reasonable agreement considering an estimated evaluation error of $\pm$ 1 G and the assumption necessary with regard to alignment of the $\underline{g}$ and $\underline{A}$ tensor axes. Bertrand and Gayda[60] have attempted to correlate principal axis A($=\frac{3}{4}$. A') tensor components for the ferrous sites of several 2Fe Fd_{red} with the extent of rhombic distortion at this ion as measured by $(g_y\text{-}g_x)$ (see Section 1.5.1 for a more detailed description of the distortion parameter). The z-axis value for $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{3-}$ agrees well with this analysis, but the x and y axis hyperfine components are found to be rather smaller than predicted.

For Mössbauer spectra measured with magnetic fields applied parallel to the γ-ray beam there is evidence for a small amount of absorption in addition to that from dianion and trianion dimers (around +2 and -1 mm/s in the lowest spectrum of Figure 1.7). The species causing this appears paramagnetic and presumably results from decomposition or further reaction of the $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{3-}$. A sample deliberately thawed and held at room temperature for several minutes showed a radically different low temperature Mössbauer spectrum, but this could not readily be interpreted in terms of any likely product, such as a tetrameric iron-sulphur cluster. Alternatively, the additional absorption in the parallel field spectra could genuinely arise from the trianion if for example, the effective field at the iron nuclei is not parallel to the applied field.

The estimate from the Mössbauer of a 6:4 ratio of trianion to
dianion dimer in the sample studied falls at the low end of the
percentage yield estimated from integration of EPR spectra (60 to 80%).
Only two Mössbauer samples of reduced dimer have been studied in this
work and the percentage yield result is in consequence less representative
than that from EPR. The other Mössbauer sample showed, by visual
inspection of the small-field spectra, a higher proportion of trianion
but also a somewhat larger amount of the signal described above as
impurity. In view of the stability of the trianion at low temperature
it seems likely that a more sophisticated preparation and sample
transfer technique might lead to purer trianion Mössbauer spectra.

1.3.4. Addendum.

Subsequent to the writing of this report Mascharak et al. [J. Amer. Chem. Soc., 103, 6110 (1981)] have described an EPR lineshape attributed to $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ in 7:3 v/v acetonitrile/hexamethylphosphoramide which is very similar to that presented in Figure 1.2.1, and which has comparable g-value extrema. Due to the improved solubility of the salt used by these authors the concentration of $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ attained prior to reduction was some twenty times that employed here. They have used reduction reaction times of the order 0.5 to 4.5 hrs. which are surprisingly long in view of the instability found in this work for the trianion in DMF or DMSO. Indeed, they report substantial impurities in their EPR spectra, in particular a strong feature at g $\sim$ 4.3 which was not observed in the measurements in this present work. A crude calculation allowing for the different spectrometer conditions used indicates that their 80 K EPR spectrum of $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ represents less than 1% of the total iron present in the solution being measured, compared with the 60 to 80% observed here.

The major difference between the measurements reported here and those of Mascharak et al. is, however, in the Mössbauer spectra. After a 4.5 hr reduction of $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$, the latter authors have assigned two quadrupole doublets having δ = 0.19 mm/s, ΔE_Q = 0.54 mm/s and δ = 0.60 mm/s, ΔE_Q = 3.06 mm/s to ferric and ferrous respectively in $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ at 4.2 K. The absence of magnetic hyperfine interaction in these spectral features implies that the electron spin on the trianion is relaxing extremely rapidly. EPR on the other hand, demonstrates that the electron spin of $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ is not

relaxing fast even at 100 K (see Section 2). Even the most rapidly relaxing reduced ferredoxins, for which the EPR spectra are substantially broadened and diminished at 100 K, show hyperfine interaction in their 4 K Mössbauer spectra. The Mössbauer spectra reported in this present work are, however, entirely compatible with the EPR measurements and compare favourably with the behaviour of reduced ferredoxins.

1.4. Reduced $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$, (Y = Cℓ, H, Me).

1.4.1. Effect of Solvent Vitrification.

Figure 1.9 shows spectra obtained for the three $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$ (Cℓ, H, Me) complexes after reduction in N-methylpyrrolidinone (NMP). The first spectrum in each group (1, 4 and 7) results from using pure dry solvent, the second (2, 5 and 8) from solutions 0.1 to 0.2 M in n-Bu₄NCℓO₄ frozen as transparent glasses, and the last spectrum in each group is derived from the one above following devitrification of the sample (see later). Corresponding sets of spectra for DMF solvent are given in Figure 1.10 and relevant g-values are collected in Table 1.6.

1.4.1.1. Spectral Types and Simulations.

The three basis spectral types responsible for the lineshapes in Figures 1.9 and 1.10 are exemplified in the larger scale diagram, Figure 1.11, which also shows attempted simulations. For purposes of simplifying description and discussion these three types will be referred to as (1) " N-type" (narrow), (2) " W-type" (wide) and (3) " VW-type" (very wide); the narrow-wide description referring to spectral anisotropy. Spectra for vitreous samples are best simulated assuming a Gaussian convolution lineshape. The non-vitreous samples on the other hand give spectra more closely approaching Lorentzian. This may be indicative of dipolar broadening in the latter samples due to increased magnetic concentration as a consequence of exclusion of the reduced dimer from the DMF crystal lattice. In all the spectra it proved difficult to obtain a good fit around g_x.

FIG. 1.9 EPR OF $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$ (Y=Cl,H,Me) REDUCED IN NMP
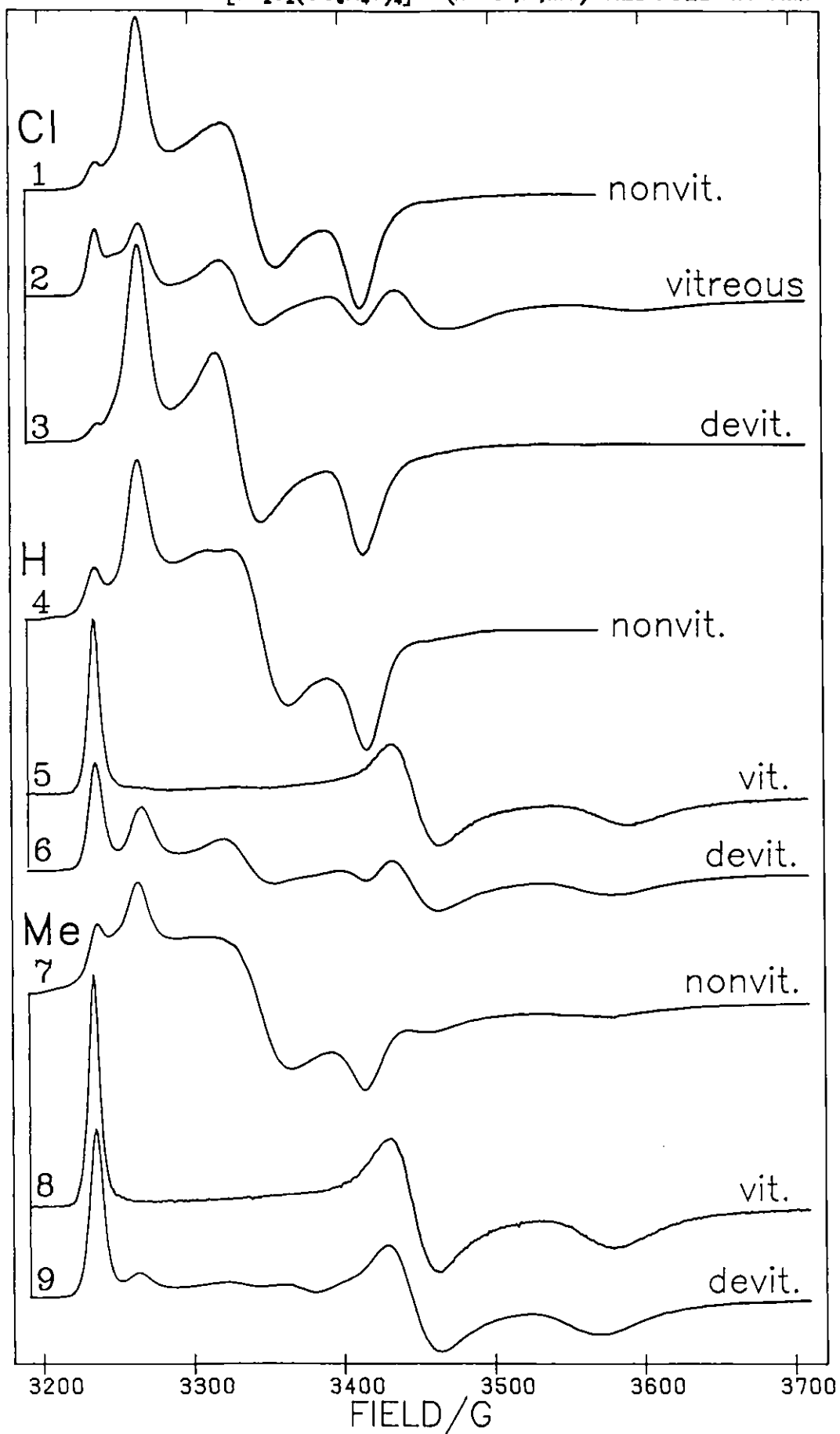
FIG. 1.10 EPR OF $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$ (Y=Cl,H,Me) REDUCED IN DMF
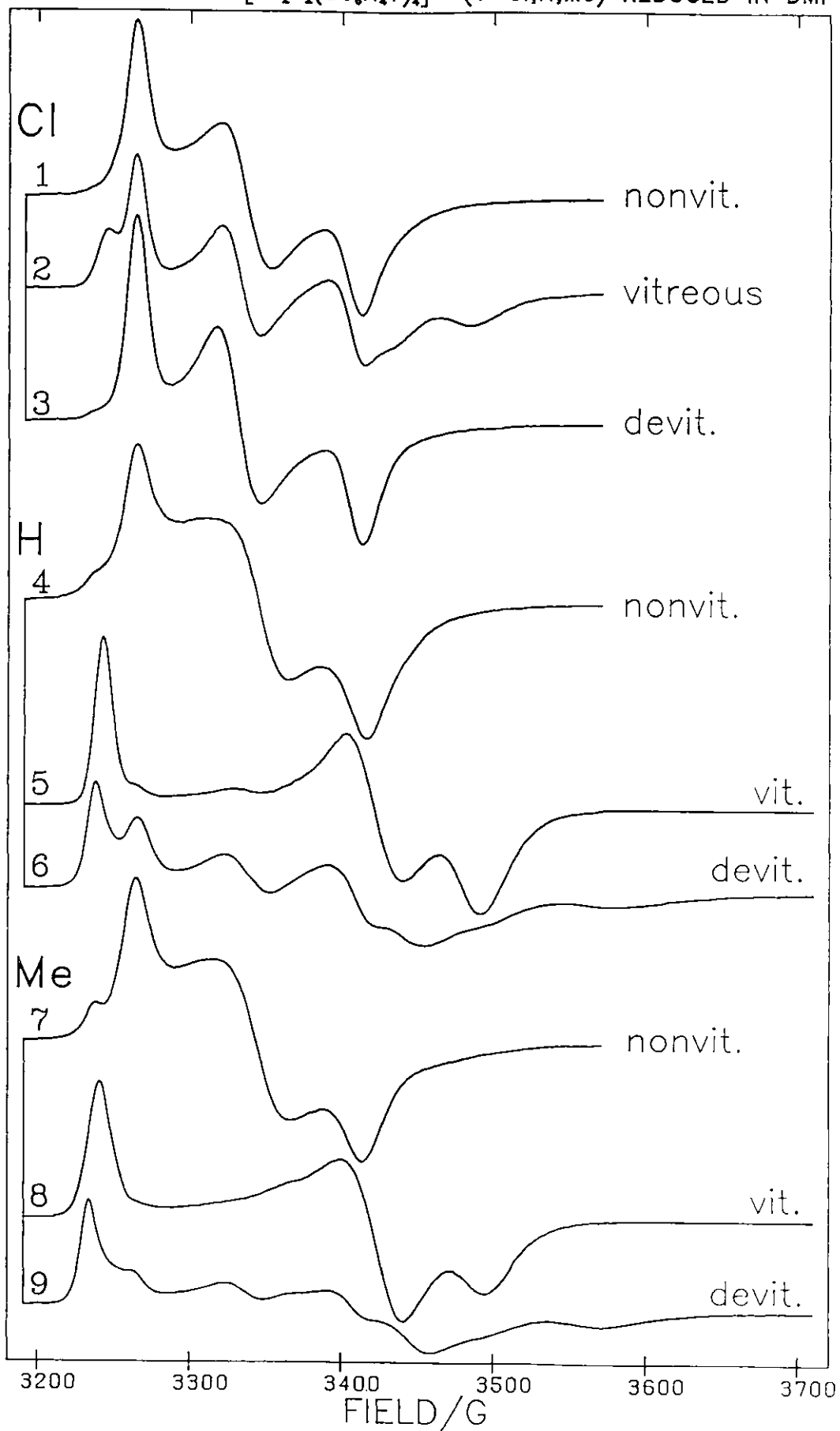
FIG. 1.11 EPR OF REDUCED $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$

EXPT. ----- CALC.

1.958

1   2.001   Y=Cl/DMF

2.014

1.914

1.910

2   1.870   Y=H/DMFv

1.895

3   2.019   Y=Me
NMPv

1.822

FIELD/G

3200   3300   3400   3500   3600   3700
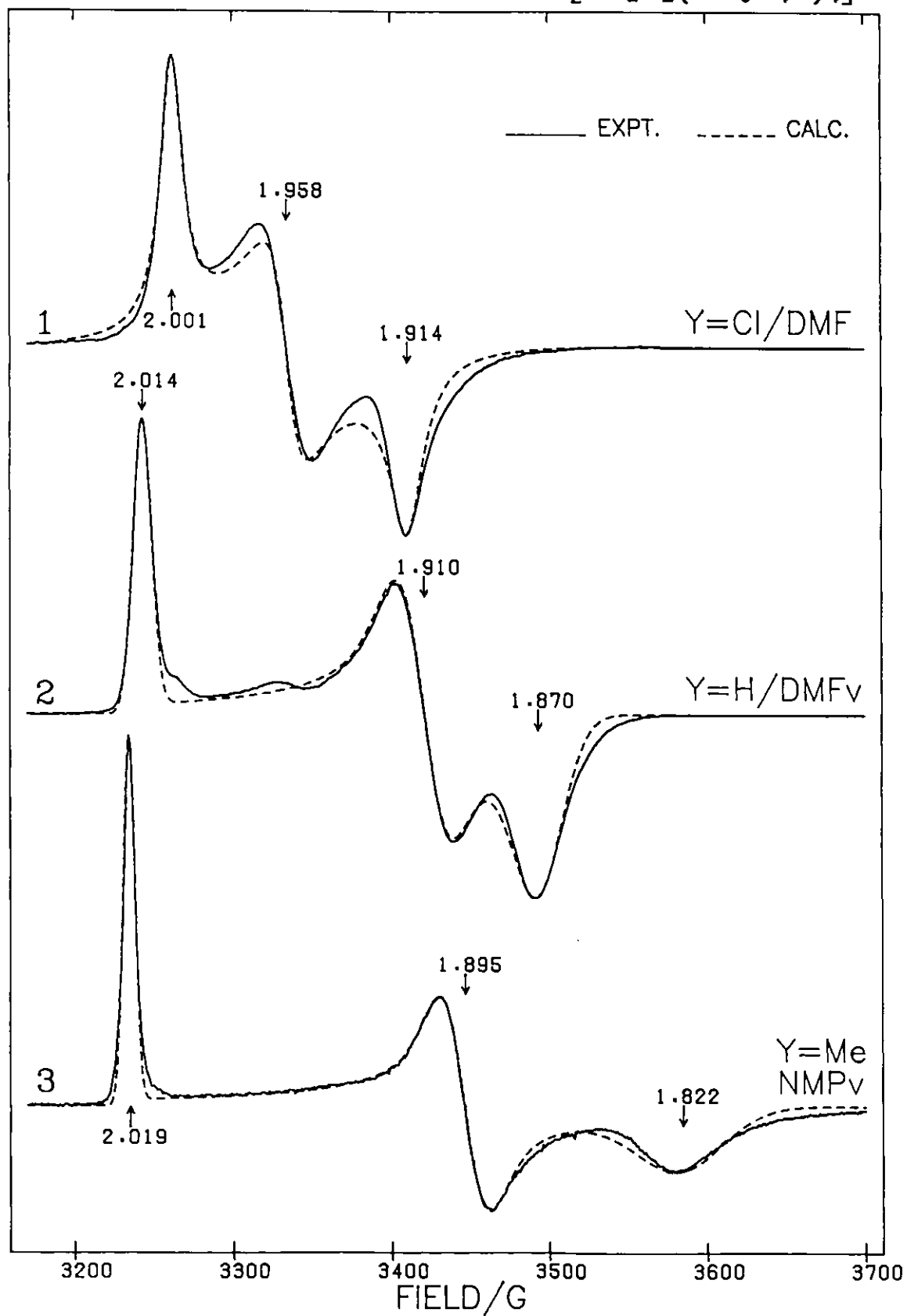
TABLE 1.6. EPR Data for Reduced $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$.

Y	Solvent	Sec. 1 Figure		$\sim$ composition		g_z	g_y	g_x	g_{av}
				%	rest				
Cℓ	DMFnv	10.1		100N		2.002	1.958	1.915	1.958
		11.1	g_{sim}			2.001	1.958	1.914	1.958
			LW			8.5G	13.5G	13G	
Cℓ	DMFdv	10.3	0.1 M n-Bu₄NCℓO₄ g_{sim}	100N		2.001	1.960	1.914	1.958
H	DMFnv	10.4		95N	W	2.001	1.954	1.913	1.956
			g_{sim}			2.001	1.954	1.913	1.956
H	DMFnv	12.3	10 exs. PhSH	100N		2.002	1.954	1.916	1.957
Me	DMFnv	10.7		90N	W	2.002	1.954	1.914	1.957
Me	DMFv	12.4	10 exs. TolSH, 0.1 M n-Bu₄NCℓO₄	100N		2.002	1.952	1.917	1.957
			g_{sim}			2.002	1.954	1.916	1.957
Cℓ	NMPnv	9.1		95N	VW	2.002	1.957	1.915	1.958
			g_{sim}			2.002	1.957	1.915	1.958
Cℓ	NMPdv	9.3	0.2 M n-Bu₄NCℓO₄ g_{sim}	95N	VW	2.002	1.962	1.915	1.960
H	NMPnv	9.4		80N	VW	2.002	1.953	1.913	1.956
Me	NMPnv	9.7		70N	VW	2.001	1.954	1.914	1.956
Cℓ	Ph CNnv	12.2		100N		2.001	1.957	1.914	1.957
H	Ph CNnv			100N		2.001	1.952	1.911	1.955
Me	Ph CNnv			80N	W	2.001	1.953	1.911	1.955
Cℓ	DMFv	10.2	0.1 M n-Bu₄NCℓO₄	30W	N	2.013	−	1.875	−

TABLE 1.6 (cont.)

Y	Solvent	Sec. 1 Figure		~ composition		g_z	g_y	g_x	g_{av}
				%	rest				
H	DMFv	10.5	0.1 M n-Bu₄NClO₄	95W	N	2.014	1.910	1.871	1.932
		11.2	g_{sim}			2.014	1.910	1.870	1.931
			GW			6.8G	16.5G	18.5G	
H	DMFdv	10.6	0.1 M n-Bu₄NClO₄	70VW	N	2.019	~1.90	1.825	—
Me	DMFv	10.8	0.1 M n-Bu₄NClO₄	100W		2.015	1.913	1.873	1.934
Me	DMFdv	10.9	0.1 M n-Bu₄NClO₄	90VW	N	2.019	~1.90	1.831	—
Cl	NMPv	9.2	0.2 M n-Bu₄NClO₄	50VW	N	2.019	~1.90	1.817	—
H	NMPv	9.5	0.2 M n-Bu₄NClO₄	100VW		2.019	1.895	1.820	1.911
			g_{sim}			2.019	1.894	1.818	1.910
Me	NMPv	9.8	0.2 M n-Bu₄NClO₄	100VW		2.020	1.895	1.824	1.913
		11.3	g_{sim}			2.019	1.895	1.822	1.912
			GW			4.8G	14.7G	29.0G	
H	PhCNv		0.4 M n-Bu₄NClO₄	60W	VW	2.011	~1.93	1.90	—
H	PhCNdv		0.4 M n-Bu₄NClO₄	70VW	N	2.019	—	1.83	—
Me	PhCNv		0.4 M n-Bu₄NClO₄	40W	VW	2.011	—	—	—
Me	PhCNdv		0.4 M n-Bu₄NClO₄	90VW	N+W	2.018	1.914	1.83	1.921
H	DMFv	13	17% CH₂Cl₂	100W		2.014	1.908	1.871	1.931
			g_{sim}			2.013	1.908	1.870	1.930
Me	DMFv		17% CH₂Cl₂	100W		2.014	1.909	1.872	1.932
Me	NMPv		17% CH₂Cl₂	95w	N	2.019	1.894	1.821	1.911

TABLE 1.6 (cont.)

Y	Solvent	Sec. 1 Figure		~ composition		g_z	g_y	g_x	g_{av}
				%	rest				
H	DMFv	12.1	5% H_2O	100W		2.013	1.911	1.872	1.932
Me	DMFv		2% H_2O	100W		2.015	1.913	1.874	1.934
			0.1-0.2 M n-Bu$_4$NCℓO$_4$ + 50 exs. thiol						
H	DMFv		t-BuSH	95VW	N	2.019	1.887	1.845	1.917
H	DMFv		EtSH	100VW		2.020	1.894	1.846	1.920
Me	DMFv		t-BuSH	95VW	N	2.020	1.891	1.843	1.918
Cℓ	NMPv		t-BuSH	100VW		2.021	1.889	1.843	1.918
Me	NMPv	15.1	t-BuSH	100VW		2.020	1.890	1.842	1.917
				g_{sim}		2.020	1.888	1.841	1.916
	DMFv		[Fe$_2$S$_2$(S$_2$-o-xylyl)$_2$]$^{3-}$ + t-BuSH	100VW		2.020	1.882	1.846	1.916
		15.2		g_{sim}		2.020	1.882	1.845	1.916
				GW		4.3G	15.5G	21G	
	DMFv		[Fe$_2$S$_2$(S$_2$-o-xylyl)$_2$]$^{3-}$+ EtSH	95VW	N	2.020	1.892	1.848	1.920

LW - Lorentzian widths, GW - Gaussian widths, N - Narrow, W - Wide, VW - Very-Wide, v - vitreous, nv - non-vitreous,

dv - devitrified.

In DMF some variability in the W-type spectra for vitreous samples with Y = H or Me has been observed. The two high field features shown in Figure 1.10.5 for Y = H sometimes look more like those in Figure 1.10.8 for Y = Me, and vice versa. The experimental origin of the difference has not been traced. Both types of spectra have very similar g-values but the shape shown in Figure 1.10.5 is most easily fitted in calculations (Figure 1.11.2). Possibly, this latter lineshape represents one species and distortions in the high field part arise due to an underlying signal from another species.

1.4.1.2. Vitreous Samples.

Vitreous samples showing increased or wholly W/ VW-type signals may be produced by addition of glassifying agents other than $n-Bu_4NClO_4$. Figure 1.12.1 shows a W-type spectrum obtained in low yield ($\sim$ 10% S = 1/2 per 2 Fe) following reduction of $[Fe_2S_2(SPh)_4]^{2-}$ in DMF containing $\sim$ 2M H_2O (20:1, DMF:H_2O). The same complex reduced in DMF containing concentrations of CH_2Cl_2 ranging from 0 to $\sim$ 2 M shows a steady change from an N-type to a W-type spectrum as the frozen solution becomes increasingly vitreous (Figure 1.13). Similar W-type signals have also been observed using DMF solvent containing toluene or methanol, though these have been less extensively studied.

No appreciable signals were observed when reductions were performed in DMSO, MeCN, dimethyl-acetamide, aniline or CH_2Cl_2. Visible spectral examination of DMSO and MeCN solutions subsequent to $ACN^{\pm}$ addition revealed 80 to 90% dimer to tetramer conversion. Reduction in PhCN (by $ACN^{\pm}$ in DMF) gives weak but well resolved N-type signals (Figure 1.12.2). PhCN

FIG. 1.12   EPR OF REDUCED $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$ (Y=Cl,H,Me)

1

1.911
2.013
1.872

FIELD/G
3200   3300   3400   3500

Y=H in DMF(5%H₂O)

2

1.957
2.001
1.914

FIELD/G
3200   3300   3400   3500

Y=Cl in PhCN

3

1.954
2.002
1.916

FIELD/G
3200   3300   3400   3500

Y=H+10 exs. PhSH in DMF

4

1.954
2.002
1.916

FIELD/G
3200   3300   3400   3500
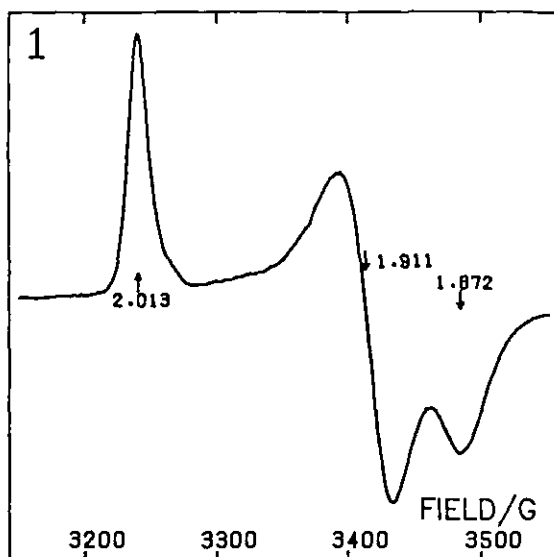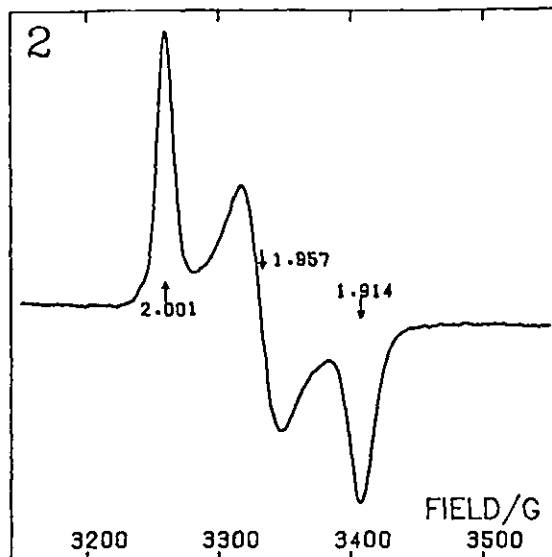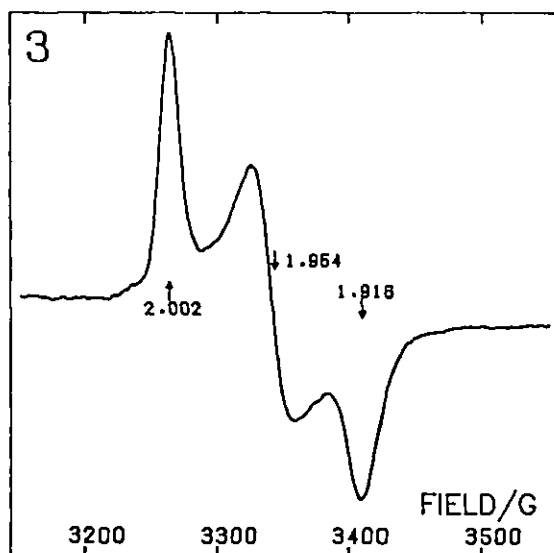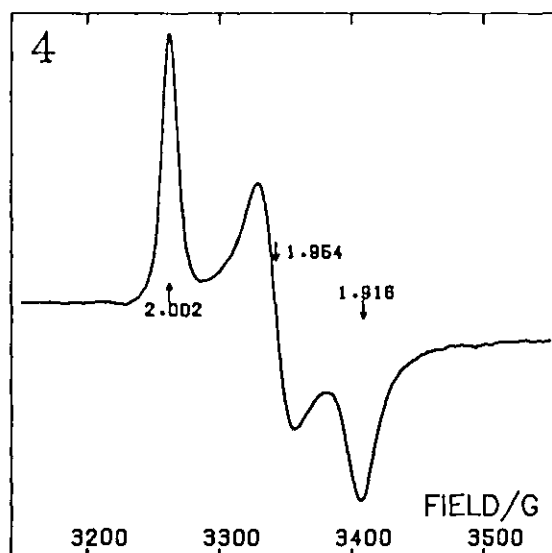
Y=Me+10 exs. TolSH
in 0.1M nBu₄NClO₄ DMF

will glassify at low temperature when a considerable concentration of

n-Bu₄ClO₄ is present (0.4 M) and resultant EPR signals are mixtures of

N-type, W-type and VW-type, but extensive investigations of reductions

in this solvent have not been undertaken. That the W-type and VW-type

signals were not due to the DMF solvent employed for the ACN⁻ was checked

by using ACN⁻ in Ph CN, though this is an inferior solvent for general use.

Fig. 1.13   EPR of $[Fe_2S_2(SPh)_4]^{2-}$ reduced in varying concentrations of CH_2Cl_2/DMF
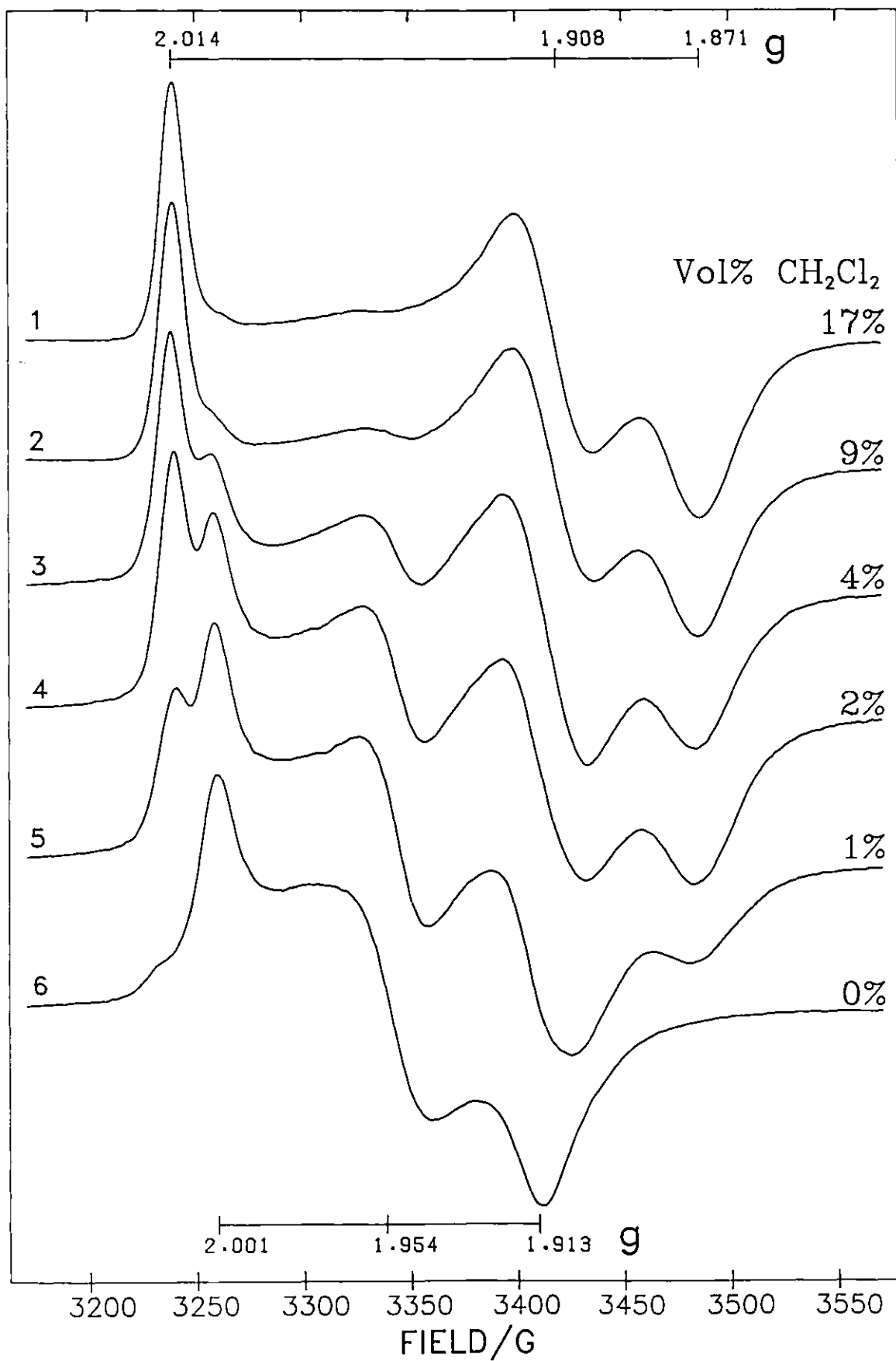
Returning to Figures 1.9 and 1.10 it can be seen that the propensity to produce a W or VW-type signal on reduction increases along the series Y = Cℓ, H, Me. This is further exemplified in Figure 1.14 which shows spectra for the three complexes after reduction in DMF containing a low CH_2Cl_2 concentration. In these terms $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ must be placed at the beginning of the series since no appreciable vitrification or solvent dependency is found for the g-values observed on its reduction.

Fig. 1.14 $[Fe_2S_2(SR)_4]^{2-}$ reduced in 2% v/v CH_2Cl_2/DMF
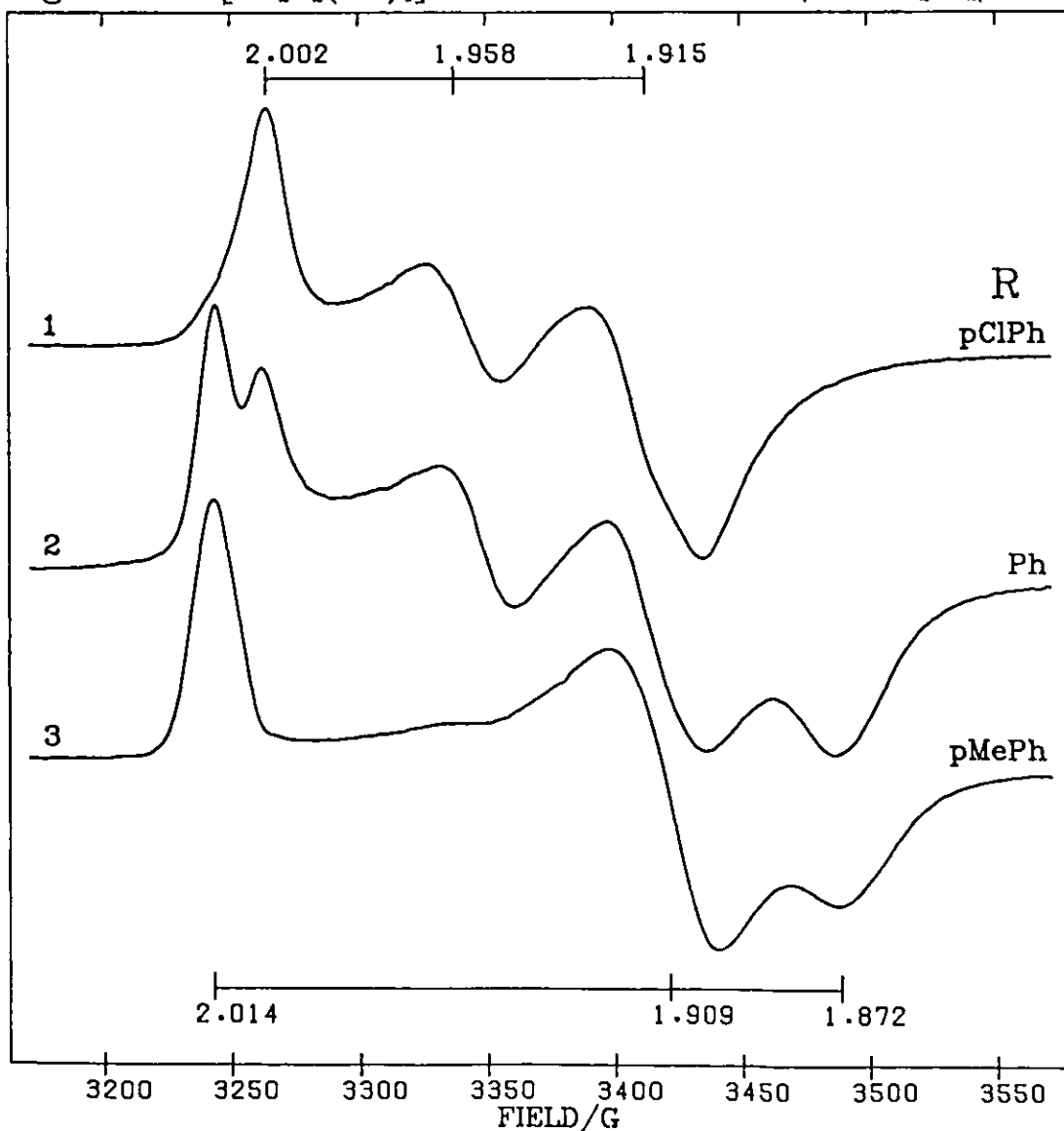
1.4.1.3. Devitrified Samples.

Low temperature glasses,formed as a result of adding n-Bu$_4$NCℓO$_4$

to the solvent,devitrify on warming to a few degrees below the solvent

melting point, and may be maintained in this state by recooling before

thawing onsets. Changes in the EPR are observed following this process,

and generally occur with retention of overall doubly-integrated intensity.

The simplest case is with NMP as solvent, for which a change from

VW-type to the N-type signal is observed as shown in Figure 1.9. The

extent of this change is dependent on the para-substitutent on the

thiolate ligand. For Y = Cℓ the process goes to completion, whilst

for Y = Me, very little change is found. Rapid thawing and refreezing

of a devitrified originally glassy sample enables return to a transparent

glassy state and restoration of the original lineshape, albeit with

decreased signal amplitude.

With DMF as solvent, there is an additional complication. Conversion

of W-type to N-type is again observed on devitrification, being total

for Y = Cℓ and only slight for Y = Me. For Y = H or Me the majority of

the rest of the signal is found, however, to be VW-type (Figure 1.10.6

and 1.10.9). The W-type signal is restored on thawing and rapidly

refreezing as a glass. Devitrified samples for the three complexes having

PhCN as solvent closely follow those obtained with DMF. In the case

of this solvent, however, the VW-type signal already forms a considerable

($\sim$ 1/2) proportion of the vitreous sample signal for Y = H , Me prior

to devitrification, and thus features more significantly in the

devitrified spectrum.

1.4.2. Stability.

In mobile solution, reduced monodentate aryl-thiol ligated dimers are less stable than $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{3-}$. Conversion to the corresponding tetramer, $[Fe_4S_4(SC_6H_4Y)_4]^{2-}$, is readily seen on comparing room temperature visible absorption spectra before and after reduction. These spectral results indicate 80 to 90% dimerisation. Yields of the trianion dimer from reductions are dependent on ligand, solvent and additives. The yield obtained also varies from one reduction to another by around $\pm$ 10% due to differences in the time taken to perform the reaction, transfer and freezing procedures. The highest yields were found for Y = H , Me in NMP (50-60%) whilst the overall range averaged $\sim$ 20-60%.

1.4.3. Effect of Added Thiols.

Addition of an excess of the appropriate ligand thiol to the $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$ (Y = $C\ell$, H, Me) solution prior to reduction has been observed to promote an increase in the proportion of N-type signal in the resulting EPR spectrum. Because the aryl thiols used readily donate their mercapto proton it was found necessary to add considerable excess of $\text{ACN}^{\pm}$ in order to achieve cluster reduction. Consequent inherent difficulty in accurate estimation of the amount of $\text{ACN}^{\pm}$ required for cluster reduction, together with decreased stability of the resulting reduced species, led to weaker signals. The use of an alkali mercaptide in place of thiol, whilst alleviating this difficulty, was not found to lead to the extent of the effects described below for the free thiol.

Figure 1.12.3 shows a signal resulting from reduction of

$[Fe_2S_2(SPh)_4]^{2-}$ in DMF containing a 10 fold excess of PhSH over the

cluster concentration. The g-values are identical to those observed

in the absence of thiol, however, the spectrum is better resolved,

having smaller linewidth. The reduced linewidth is concomitant

with the low signal intensity, indicative of increased magnetic

dilution compared to the corresponding spectrum (Figure 1.10.4) where

no excess thiol is present.

Rather more significantly, reduction in the presence of excess

thiol, together with a glassifying agent produces a similar N-type

spectrum (Figure 1.12.4). This should be compared with Figure 1.10.8

where reduction in the absence of thiol is seen to yield entirely a

W-type signal for Y = Me. When only a four-fold thiol excess is used

the resulting spectrum is still more than 90% N-type. Thiol promotion

of the production of the N-type signal over the W or VW-type is found

for both $n-Bu_4ClO_4$ and CH_2Cl_2 glassificants, for both DMF and NMP solvents

and for all three compounds (Y = Cl, H, Me). The effect is also

produced by benzyl mercaptan, but not by phenol. Comparable excesses

of sodium mercaptide in place of thiol led to increased N-type signal

for Y = Me or H on devitrifying a glassy sample, but to little or no

effect on the EPR observed in the vitreous state.

When the less protic thiols, t-butyl or ethyl mercaptan are added

in large excess prior to reduction, and a glassificant is also present,

a new signal results (Figure 1.15.1) similar to the VW-type signal of

Figure 1.11.3. This may be observed in both DMF and NMP. On
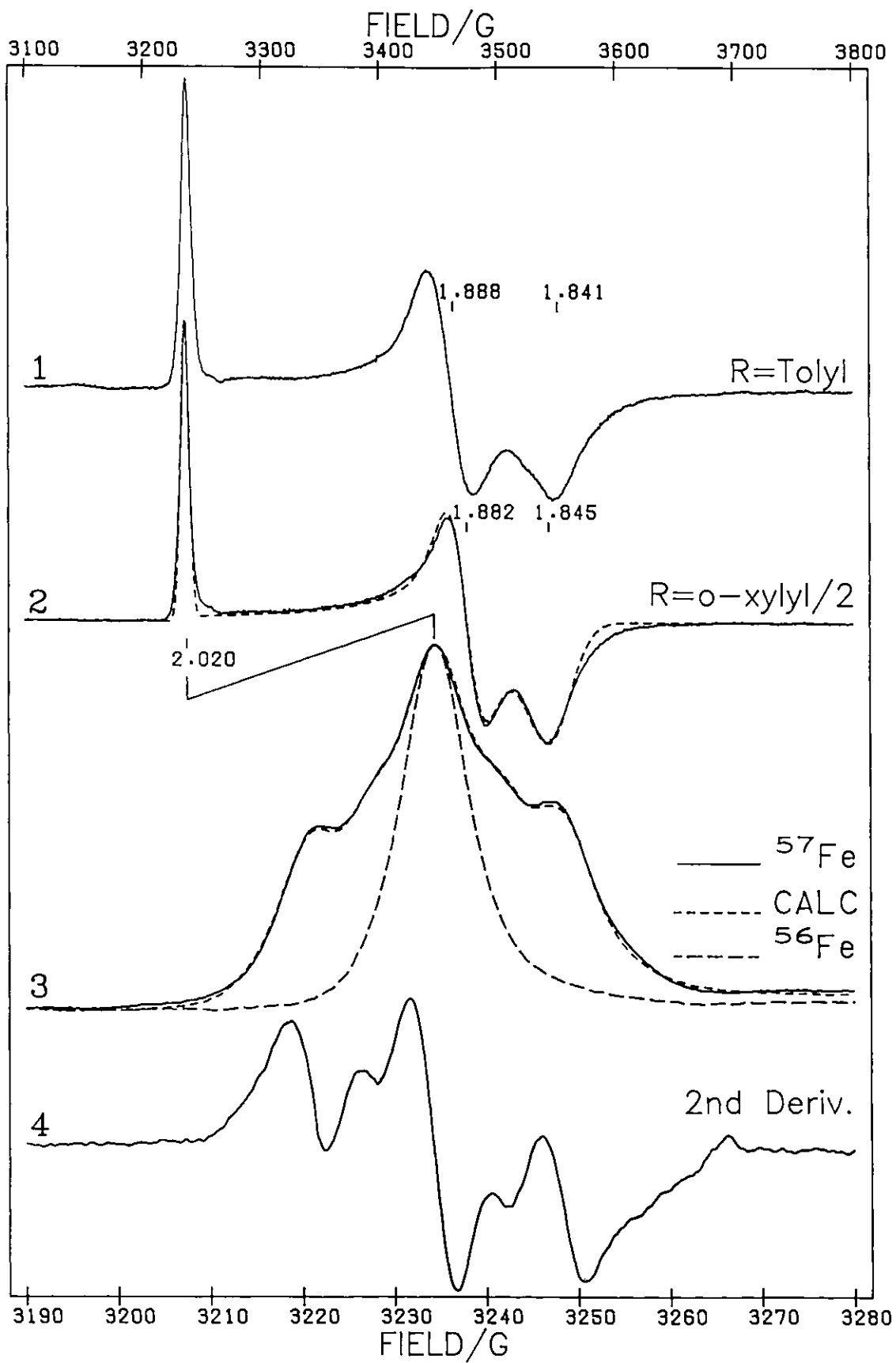
FIG. 1.15 EPR OF $[Fe_2S_2(SR)_4]^{2-}$ + tBuSH, AFTER REDUCTION

devitrification of such a sample,part conversion to N-type signal

occurs, the extent being dependent upon the original compound (Y = Cℓ,

H, Me). If no glassificant is present in the solvent the signal

observed is predominantly N-type with a proportion of the t-BuSH signal

similar in magnitude to that of the VW-type resonance in the non-

vitreous sample spectra of Figure 1.9.

Similar signals of large anisotropy result from the reduction of

$[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ in the presence of excess t-BuSH or EtSH (Figure

1.15.2 and 1.16). A reduction performed with excess t-BuSH and 83%

^{57}Fe enriched $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ gives an EPR spectrum which has

its low field peak split according to the expected statistical distribution

of ^{57}Fe $-^{56}Fe$ in a dimer. Because the linewidth is so narrow for the

lines composing this peak (half-height half width 4.3 G) the splittings

for $^{57}Fe^{56}Fe$ and $^{57}Fe^{57}Fe$ (Figure 1.5) may be clearly seen. A

simulation from field-shifting the natural abundance spectrum achieves

quite a good fit (Figure 1.15.3), with average splitting of 14 G.

Thus it seems reasonable to assume that the Fe_2S_2 core is retained

in the species giving the new signals and that the t-BuSH$/$EtSH act

as additional ligands or substitute for one or more of the original

coordinated mercaptides.

1.4.4. Summary.

1. All compounds (Y = Cℓ, H, Me) give spectra having very similar g-

values ($2.00\frac{1}{2}$, $1.95\frac{2}{8}$, $1.91\frac{1}{5}$, type N) on reduction in pure solvents

which freeze to a non-vitreous state.

1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55

LOG(SIGNAL/√POWER)

$[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ + 50 FOLD EXCESS tBuSH

REDUCED IN DMF/0.1M nBu$_4$NClO$_4$

POWER SATURATION OF LOW FIELD PEAK AT 100K

40   35   30   25   20   15   10   5   0

POWER (dB attenuation from 200mW)
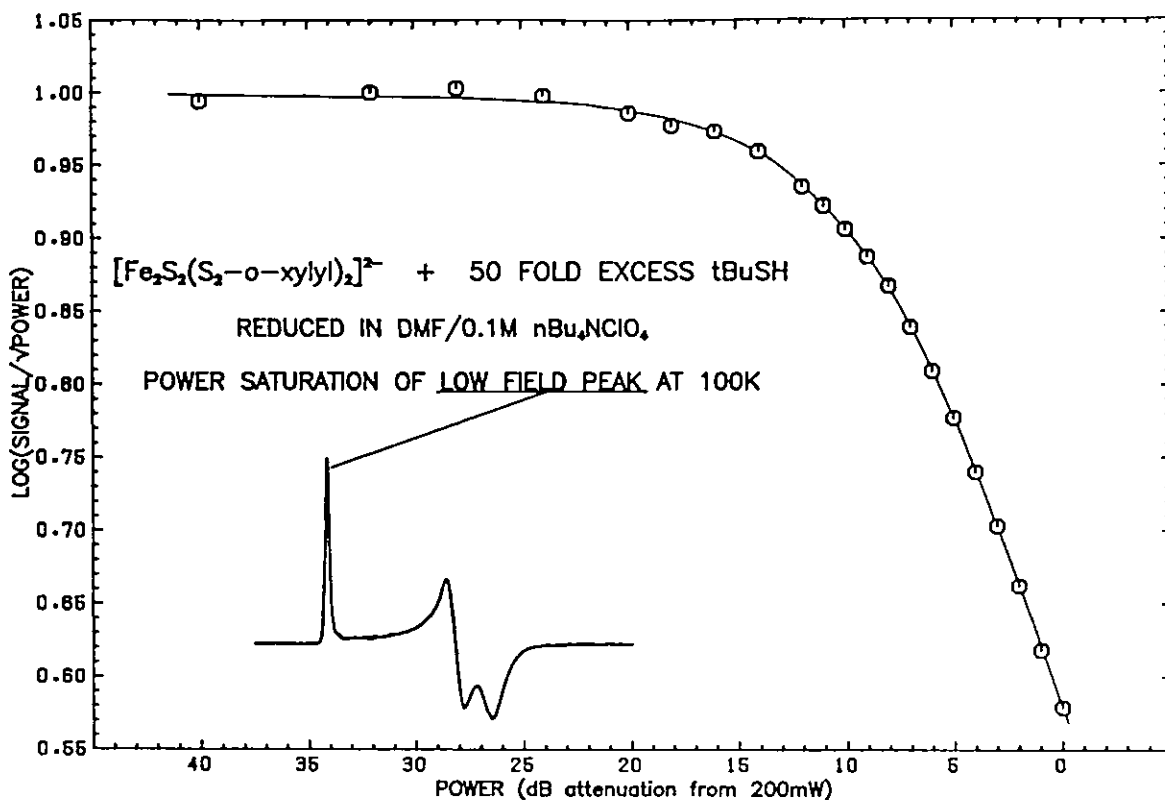
Figure 1.16. Power Saturation in the EPR signal from $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ reduced in the presence of excess t-BuSH.

2. Reduction in solvent mixtures which vitrify on freezing results in an increased proportion of a signal with solvent dependent g-values $(2.01^3_5$, 1.9^{08}_{14} , 1.87^1_5 in DMF, type W; 2.0^{19}_{20} , 1.89^4_5 , 1.8^{17}_{24} in NMP,type VW).

3. Devitrification of a glassy sample leads to conversion of some W/VW-type signal to N-type. The majority of any remaining signal then appears as a VW-type resonance.

4. Formation of the W/VW-type signals is promoted in the order Y = Cℓ < H < Me.

5. Reduction in the presence of excess ligand thiol promotes formation of the N-type signal.

6. t-BuSH and EtSH added to reductions in glass forming solvent mixtures produce new signals having large anisotropy (g = 2.0^{19}_{21} , 1.8^{82}_{94} , 1.8^{42}_{48}).

1.5. Discussion.

1.5.1. Analysis of g-Tensor Principal Values.

Bertrand and Gayda have given a theoretical interpretation of the g-tensor variations in $[2Fe-2S]^{1+}$ ferredoxins.[60,61] They consider a rhombic C_{2v} distortion in the environment of the Fe^{2+} ion, having the same geometrical character for each protein, but variable in intensity. The differences in g, and other physical parameters, amongst the reduced ferredoxins may then be correlated with the variable mixing of certain d-orbitals consequential upon the proposed distortional differences. Expressions can be derived for the three principal g-values in terms of a parameter θ which measures the C_{2v} symmetry-allowed mixing of the two A_1 ferrous states (E1.4-E1.6).

$$g_x(\theta) = \frac{7}{3} g_{1x} - \frac{4}{3} g_e + \frac{32\lambda_2}{3\Delta_{yz}} \sin^2 (\theta + \frac{\pi}{3}) \tag{E1.4}$$

$$g_y(\theta) = \frac{7}{3} g_{1y} - \frac{4}{3} g_e + \frac{32\lambda_2}{3\Delta_{xz}} \sin^2 (\theta - \frac{\pi}{3}) \tag{E1.5}$$

$$g_z(\theta, \Delta_{xy}) = \frac{7}{3} g_{1z} - \frac{4}{3} g_e + \frac{32\lambda_2}{3\Delta_{xy}} \sin^2 \theta \tag{E1.6}$$

g_{1x}, g_{1y}, g_{1z} are the main components of the $\underline{g}_1$-Fe(III) tensor; λ_2 is the spin-orbit coupling constant of the Fe(II) ion; and Δ_{xy}, Δ_{xz}, Δ_{yz} are the energies of the first three excited levels of Fe(II) above the groundstate. The different orbital states, in order of increasing energy are given in E1.7.

$$|\phi_0\rangle = \cos\theta \, d_{z^2} + \sin\theta \, d_{x^2-y^2}$$

$$|\phi_1\rangle = d_{xy}$$

$$|\phi_2\rangle, \quad |\phi_3\rangle = d_{xz}, \, d_{yz}$$

$$|\phi_4\rangle = \cos\theta \, d_{x^2-y^2} - \sin\theta \, d_{z^2} \tag{E1.7}$$

The parameters λ_2 and g_1 are most affected by covalency, but these effects are considered to vary little amongst the different Fd. Similarly, Δ_{yz} and Δ_{xz}, having values imposed mainly by the tetrahedral part of the ligand field, are considered as constants in the analysis given by Bertrand and Gayda. With these approximations, the expressions for the principal values of the g tensor reduce to functions of θ and Δ_{xy} only (E1.4-E1.6). For small values of θ first order expansion of these equations leads to $\theta \approx -\chi$ where $\chi = (g_y - g_x)$ and to the approximate expressions (E1.8 and E1.9).

$$g_x(\chi) \sim g_0 - \Delta_{xz}\chi/(\Delta_{xz} + \Delta_{yz}) \tag{E1.8}$$

$$g_y(\chi) \sim g_0 + \Delta_{yz}\chi/(\Delta_{xz} + \Delta_{yz}) \tag{E1.9}$$

where

$$g_0 = \frac{7(\Delta_{yz}g_{1x} + \Delta_{xz}g_{1y}) + 48\lambda_2}{3(\Delta_{yz} + \Delta_{xz})} - \frac{4}{3}g_e \tag{E1.10}$$

Experimental g-values, for several proteins, plotted against χ are shown in Figure 1.17, after Coffman and Stavens.[62] Considering reasonable values for the six constant parameters: λ_2 (-80 cm^{-1}, reduced from the free ion value of 105 cm^{-1} by covalency); Δ_{xz}, Δ_{yz} (6000 cm^{-1}, 4000 cm^{-1}, estimated from IR spectroscopy[63]); and g_{1x}, g_{1y}, g_{1z} (2.015, 2.034, 2.030), Bertrand and Gayda have obtained a fit to the experimental data using the functions E1.4-E1.6. Also plotted in Figure 1.17 are the g-values for the four complexes $[Fe_2S_2(SR)_4]^{2-}$ [$2R = o$-xylyl and $R = C_6H_4Y$ ($Y = C\ell$, H, Me)], reduced in the various solvent systems. A clear distinction is demonstrated between the g-values for the S_2-o-xylyl chelated complex and N-type signals in comparison with those for the W/VW-type spectra observed with vitreous

Fig. 1.17 Plot of g—values vs. (g_y-g_x) for reduced model complexes and 2Fe Fd.(see Tables 1.1,1.6,1.7)
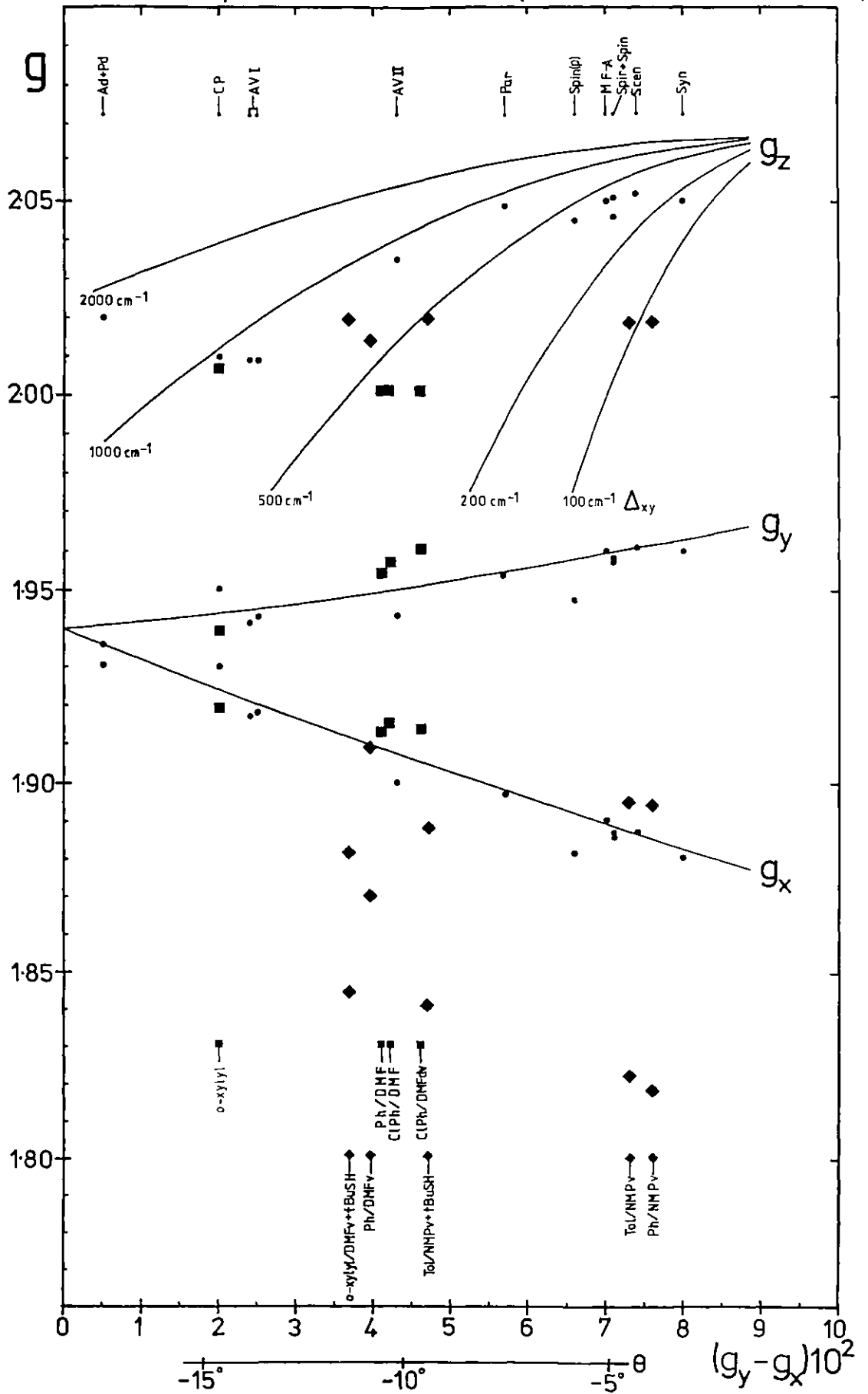
TABLE 1.7. EPR Data for Two-Iron Ferredoxins.

	Source	g_z	g_y	g_x
Ad	Adrenal glands[20]	2.02	1.935	1.93
Pd	P. Putida[20]	2.02	1.935	1.93
CP	Clostridium pasteurianum[15]	2.01	1.95	1.93
AV I	Azotobacter vinelandii[64] IA	2.009	1.941	1.917
AV I	IB	2.009	1.943	1.918
AVII	II	2.035	1.943	~1.90
Par	Parsley[49]	2.049	1.954	1.897
Spin (p)	Spinach-powder[65]	2.045	1.947	1.881
MF-A	Microcystis flos-acquae[66]	2.05	1.96	1.89
Spin	Spinach[49]	2.046	1.957	1.886
Spir	Spirulina maxima[60]	2.051	1.958	1.887
Scen	Scenedesmus[60]	2.052	1.961	1.887
Syn	Synechococcus lividus[50]	2.05	1.96	1.88

samples. The former fit well with the experimental protein values and with the analysis of Gayda and Bertrand. Large g_z/g_{xy} anisotropy in signals for glassy samples leads on the other hand to considerable departure of g_x and g_y below that expected for the $[2Fe-2S]^{1+}$ Fd centre.

Blumberg and Peisach[67] have formerly given a less rigorous qualitative analysis of $[2Fe-2S]^{1+}$ Fd g-value trends in terms of Fe^{2+} d-orbital energies in the absence of mixing. They consider the relationship between the parameters g_z, C (E1.11) and R (E1.12), taking g_z as a measure of the covalency of the Fe^{3+} ion, C as indicating

$$C = (4/3)[1/(g_z - g_x) + 1/(g_z - g_y)] \qquad \text{(E1.11)}$$

$$R = (g_y - g_x)/(2g_z - g_y - g_x) \qquad \text{(E1.12)}$$

the ligand field strength and the extent of covalency at the Fe^{2+} ion

and R as being sensitive to the ferrous geometrical environment. A

hyperbolic relationship between g_z and C has been interpreted in terms

of varying Fe_2S_6 longitudinal charge distribution. Plotting the

results for the reduced synthetic models on the graphs of g_z vs. C

and g_{av} vs. R in the Blumberg and Peisach paper (Figure 1 and 3, ref.

67), leads to a differentiation amongst the signal types comparable

to that revealed in Figure 1.17. The W and VW-type spectra are found

to lie at some considerable separation from the main $[2Fe-2S]^{1+}$ Fd

trends.

On the above grounds it is believed that the signals from reduced

$[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ and also the N-type signals from reduced

$[Fe_2S_2(SC_6H_4Y)_4]^{2-}$ (Y = Cl, H, Me) result from the corresponding

trianions and are genuine analogue spectra for those observed in

$[2Fe-2S]^{1+}$ ferredoxins. The temperature dependence and power saturation

behaviour of the signals further supports this assignment.

The range of (g_y-g_x) for these signals and their small resonance

field spread is consistent with changes in protein spectra produced by

solvents, chaotropic anions or denaturing agents.[68-70,62] These cause

a decrease of the large x-y anisotropy found for plant two-iron

ferredoxin signals. Of particular interest and relevance are the changes

in signal observed by Cammack[68,69] when employing DMSO or guanidine

hydrochloride as denaturants. Under these conditions, where the protein is presumed unfolded to give a coordination environment more closely resembling that in the analogous model compounds, a variety of proteins produce similar spectra with g extrema in the range 1.9 to 2.0.

Blumberg and Peisach have suggested that a significant departure from the main trend of their observed relationship between g_z and C represents a change of chemical composition in the binuclear iron-sulphur cluster. This is demonstrated in their analysis by disparity in the trends for sulphur and selenium-bridged reduced ferredoxins. A comparable disparity is found for the chalcogen homologues in the analysis of Bertrand and Gayda.[61] It seems likely then that the gross departure of the g-values found for the W and VW-type signals from those for the ferredoxins results from some chemical modification of the Fe_2S_6 core.

1.5.2. Further Discussion of Spectral Solvent Dependency.

The EPR data presented above for the reduced monodentate thiol-ligated dimers is insufficiently extensive to formulate a full under-standing of its physico-chemical origins, but an attempt is made here to rationalise the results.

Reversible chemical modification of the reduced dimer, suggested in the last section, might involve additional coordination by, for example, solvent, and/or loss of a labile thiol ligand.

$$[Fe_2S_2(SR)_4]^{3-} + L \rightleftharpoons [Fe_2S_2(SR)_3L]^{2-} + RS^-$$

or

$$[Fe_2S_2(SR)_4]^{3-} + LH \rightleftharpoons [Fe_2S_2(SR)_3L]^{3-} + RSH$$

$$[Fe_2S_2(SR)_4]^{3-} + L \rightleftharpoons [Fe_2S_2(SR)_4L]^{3-}$$

$$[Fe_2S_2(SR)_4]^{3-} \rightleftharpoons [Fe_2S_2(SR)_3]^{2-} + RS^-$$
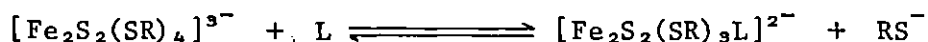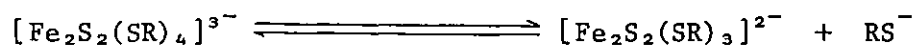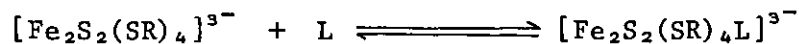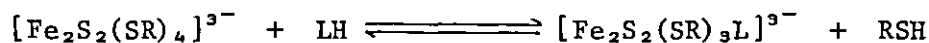
For reduced $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$ the ordering observed for the ease of formation of W or VW-type signals, as opposed to N-type, is $Y = C\ell < H < Me$. This is the order of expected increasing pK_a for $p\text{-}YC_6H_4SH$ on the basis of the Y-substituent Taft parameter[72] and of observed decreasing thiol acidity.[73] For $[Fe_4S_4(SR)_4]^{2-}$ the ease with which coordinated thiolate (RS^-) is replaced by another ligand is found to increase with increasing pK_a of the thiol (RSH).[74-76] This has been explained in terms of the affinity of RS^- for a proton or other electrophile. In the case of the reduced dimers, if the aprotic solvents DMF, NMP and PhCN are regarded as potential ligands then the origin of such a proton or other electrophile is not obvious. The efficacy of added excess thiol, as opposed to thiolate, in promoting N-type signal would seem to implicate the involvement of a proton in any considered ligand displacement process.

The S_2-o-xylyl ligand, being an aliphatic thiol, should have a higher pK_a than the aromatic thiols and facili-tated substitution would be expected in $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{3-}$. No solvent dependency of the EPR

signal has been observed with this ligand and the expected increased

lability must be considered offset by chelation-incurred stability

(it is noted, however, that the EPR signal is modified to one of large

anisotropy in the presence of excess t-BuSH).

On the assumption of a ligand displacement process for the

formation of the W/VW-type signal-producing species, the reversal of

the effect by introduction of excess ligand thiol would seem reasonable.

That this may be achieved with such a low thiol concentration relative

to that of the prospective solvent ligand is surprising. Additionally

exceptional is the necessity to accept that the reverse of the thiol

displacement reaction can occur in frozen solution at low temperature

during a devitrification procedure, when W/VW-type signals are observed

to transform wholly or partially to N-type. Whilst it is conceivable

that solvent crystallisation might cause loss of a weakly bound solvent

ligand it seems unlikely that thiolate replacement would then occur in

view of the solid state immobilisation. Partial transformation to N-type

signal has also been found following devitrification of samples

containing t-BuSH and which originally gave characteristic large aniso-

tropy spectra. It is difficult to understand why this should occur.

Visible spectra of the dimeric iron complexes, obtained prior to

reduction, show no changes indicative or interaction with either solvent

or added thiol.

The negative g_x & g_y shifts for the W and VW-type signals from those

characteristic of the majority of ferredoxins might be a result of

reduced g-values at the ferric ion. This could arise if there was

decreased Fe(III) covalency as might be expected following the replace-
ment of a thiolate ligand by one coordinating through a nitrogenous
or oxygenous donor. Thiol substitution involving t-BuSH or EtSH would
not, however, be expected to lead in this case to the observed decrease
in g_{av}. At first sight it also seems somewhat peculiar that DMF and
NMP, which both contain the fragment $-CH_2-NMe-CO-$, should coordinate
to produce such disparate g-values as those for the W-type and VW-type
signals. However, observation of transformation of W-type to VW-type
signal on devitrification of a glassy DMF sample would seem to indicate
that the signal difference does not originate from the nature of any
additional or replacement ligand so much as, for example, the number of
these ligands. Thus, the W-type signal might represent further additional
or replacement coordination to that present in the species giving rise
to the VW-type signal. Given that the production of different signals
by similar potential ligating solvents might be explained in this way
then it remains somewhat exceptional that signals closely resembling
these should arise in Ph CN, a rather different potential ligand.

It is noted that Salmeen and Palmer[77] have suggested from PMR data
that for reduced spinach ferredoxin there may be non-cysteine amino acids
coordinated at the ferric ion. No corresponding proton resonances have
been found in the oxidised protein.

Both the 4-methoxybenzoate O-demethylase monooxygenase from
P. Putida (Putidamonooxin)[78] and the oxidation factor of cytochrome b-c_1
in succinate- cyt c-reductase[79] are proteins containing [2Fe-2S] centres.
EPR signals have been recorded for these proteins which have quite
similar g-values to those for the VW-type signals observed for the analogue

complexes on reduction in NMP (Putidamonooxin 2.01, 1.91, 1.78 and

oxidation factor 2.02, 1.90, 1.78). This is of particular interest

in that both proteins form parts of enzyme complexes and may be directly

involved in chemical modification processes during which additional or

substitutional ligand coordination could take place.

1.6. Reduction of Selenium-Substituted Dimers.

Selenium bridged $[Fe_2Se_2(SR)_4]^{2-}$ complexes are easily synthesised in

a similar manner to their sulphur homologues. Additionally ligand

substitution on the complex $[Fe_2X_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ (X = S, Se) using

PhSeSePh leads to $[Fe_2X_2(SePh)_4]^{2-}$. It has proven possible to observe

EPR signals from all these dimer complexes subsequent to reduction with

$\overset{\text{\_}}{ACN}$ followed by rapid freezing.

Figure 1.18 compares spectra for $[Fe_2X_2(S_2\text{-}o\text{-}xylyl)_2]^{3-}$ (X = S, Se).

The selenium-bridged complex, like the sulphur, gives a signal with

g-values which are independent of the glassification state of the

frozen solvent.

Signals from reduction of complexes coordinated by monodentate

chalcogenide ligands display the same solvent and vitrification

dependence described in previous sections for $[Fe_2S_2(SR)_4]^{2-}$. Spectra

of the corresponding N-type, from non-vitreous or devitrified samples,

are shown in Figure 1.19 for the series reduced-$[Fe_2X_2(YPh)_4]^{2-}$ [X =

S, Se (Y = S, Se)], and g-values are collected in Table 1.8. Also given

in this table are g-values obtained for vitreous DMF and NMP solvents,

and Figure 1.20 shows some representative spectra.

FIG.1.18
$[Fe_2X_2(S_2-o-xylyl)_2]^{3-}$ (X=S,Se) in DMF
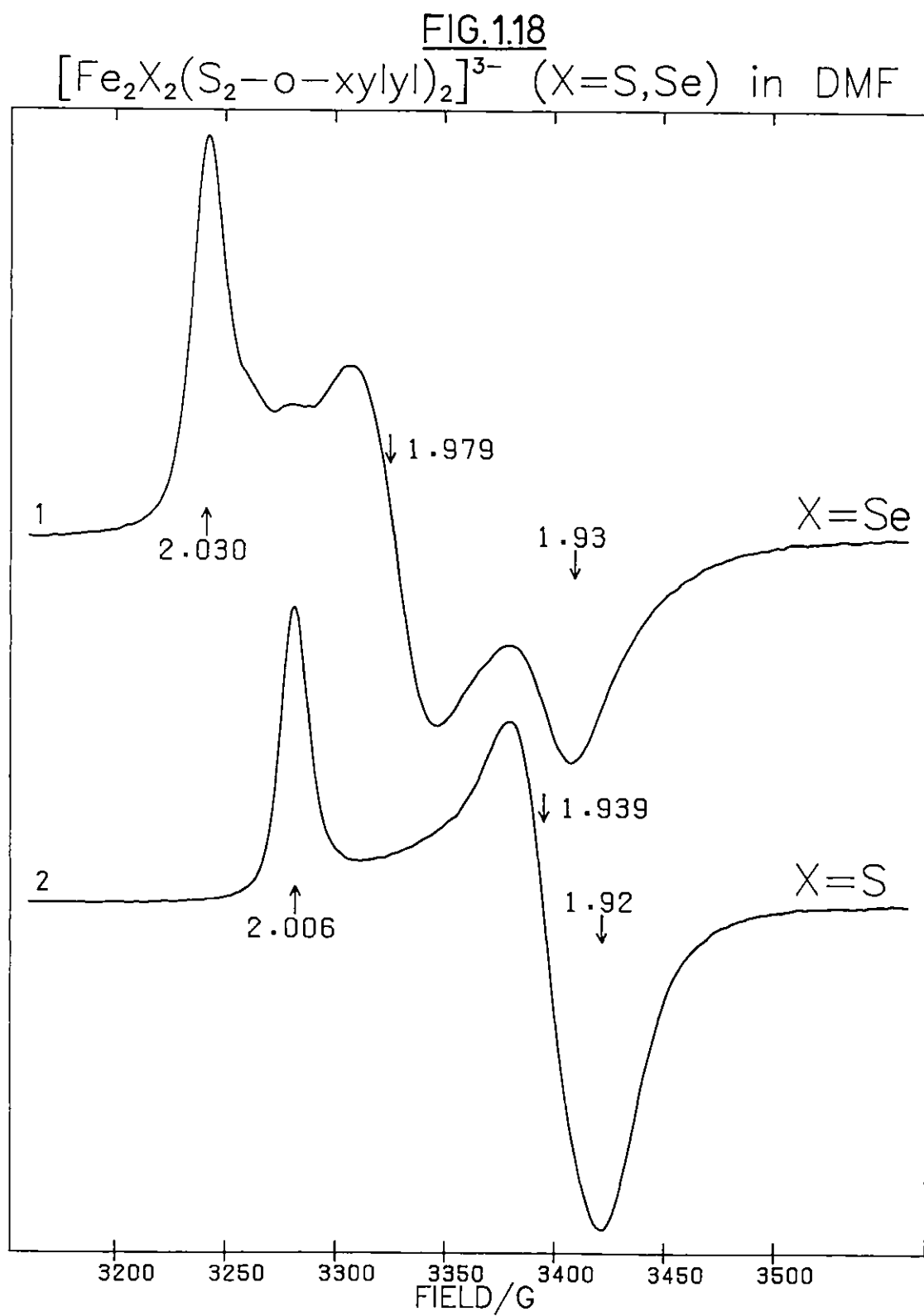
FIG. 1.19 $[Fe_2X_2(YPh)_4]^{2-}$ (X,Y=S,Se) REDUCED IN DMF
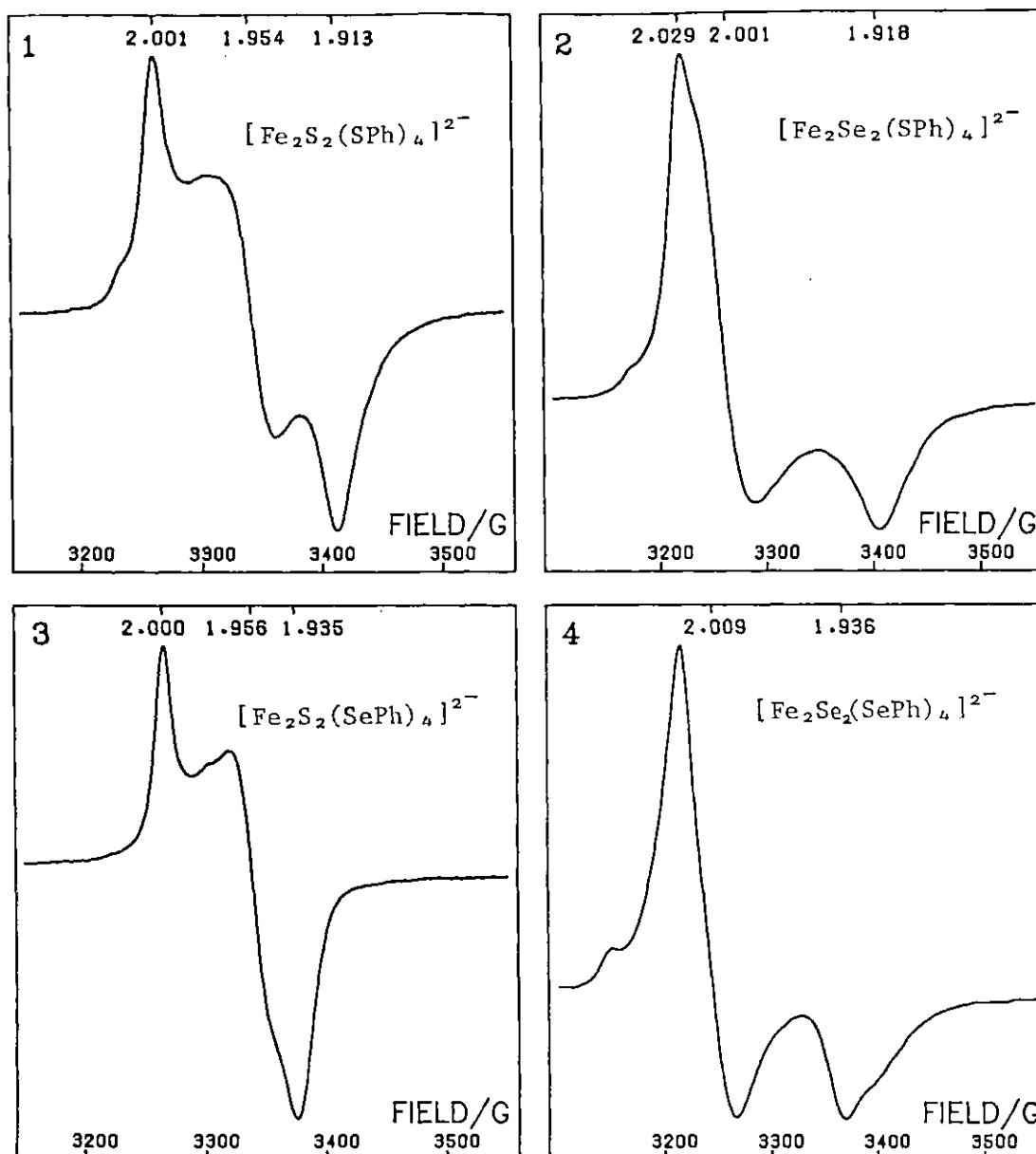
Figure 1.21 displays the g-values for many of these spectra plotted against (g_y-g_x). Also plotted are some measurements for proteins, together with theoretical curves from equations E1.4-E1.6, after Bertrand and Gayda[61]: g_{1x} = 2.020, g_{1y} = 2.049, g_{1z} = 2.054,[82] λ_2 =-80 cm^{-1}; Δ_{xz} = 5500 cm^{-1}, Δ_{yz} = 4450 cm^{-1}.[83] For reduced $[Fe_2Se_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ and $[Fe_2Se_2(SR)_4]^{2-}$ (non-vitreous solvent) the g-values agree well with the analysis of Bertrand and Gayda considering the experimental origin

FIG. 1.20 EPR OF REDUCED $[Fe_2X_2(YPh)_4]^{2-}$ (X,Y=S,Se)

1 ↑2.047 ↓1.928 1.879↓ PhS—Se/DMFv

2 ↑2.033 ↓1.882 1.837↓ PhS—Se/NMPv

3 ↑2.019 ↓1.908 1.824↓ PhSe—S/NMPv

FIELD/G
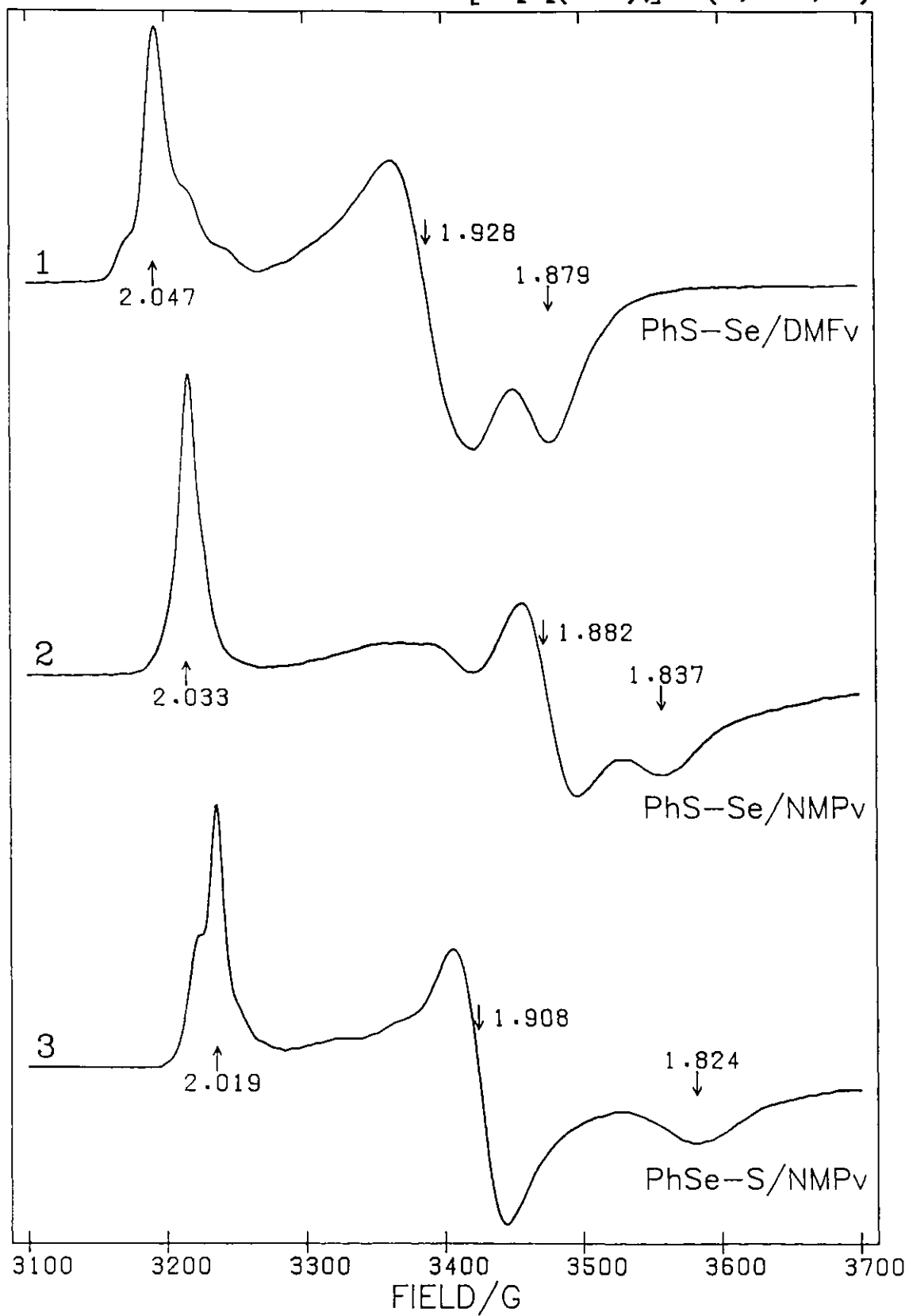
TABLE 1.8. EPR Data for Reduced $[Fe_2X_2(YR)_4]^{2-}$,

(X,Y = S, Se).

Compound			Solvent	Sec. 1 Figure	Additives	$\sim$ %	g_z	g_y	g_x	g_{av}
R	X	Y								
o-xylyl/2	Se	S	DMFnv	18.1		95	2.030	1.979	1.930	1.980
o-xylyl/2	Se	S	DMFv		0.1 M n-Bu₄NClO₄	95	2.032	1.981	1.928	1.980
Ph	Se	S	DMFnv	19.2		100	2.029	2.001	1.918	1.983
Ph	Se	S	DMFv	20.1	0.2 M n-Bu₄NClO₄	90	2.047	1.928	1.879	1.951
Ph	Se	S	DMFv		17% CH₂Cl₂	90	2.048	1.929	1.880	1.952
Ph	Se	S	NMPnv			95	2.030	2.004	1.917	1.984
Ph	Se	S	NMPv	20.2	0.2 M n-Bu₄NClO₄	90	2.033	1.882	1.837	1.917
Ph	S	Se	DMPnv	19.3		95	2.000	1.956	1.935	1.964
Ph	S	Se	DMFv		0.1 M n-Bu₄NClO₄		⌐2.025 ⌊2.017	1.917	—	—
Ph	S	Se	NMPv	20.3	0.2 M n-Bu₄NClO₄	90	2.019	1.908	1.824	1.917
Ph	Se	Se	DMFnv	19.4		90	2.009	2.009	1.936	1.985
Tolyl	Se	S	DMFnv			95	2.030	1.999	1.914	1.981
Tolyl	Se	S	DMFv		0.2 M n-Bu₄NClO₄		⌐2.046 ⌊2.059	1.927	—	—

Fig 1.21 Plot of g—values vs. (g_y-g_x) for reduced selenium derivatives of model complexes and 2Fe Fd.(Tables 1.8,1.9)
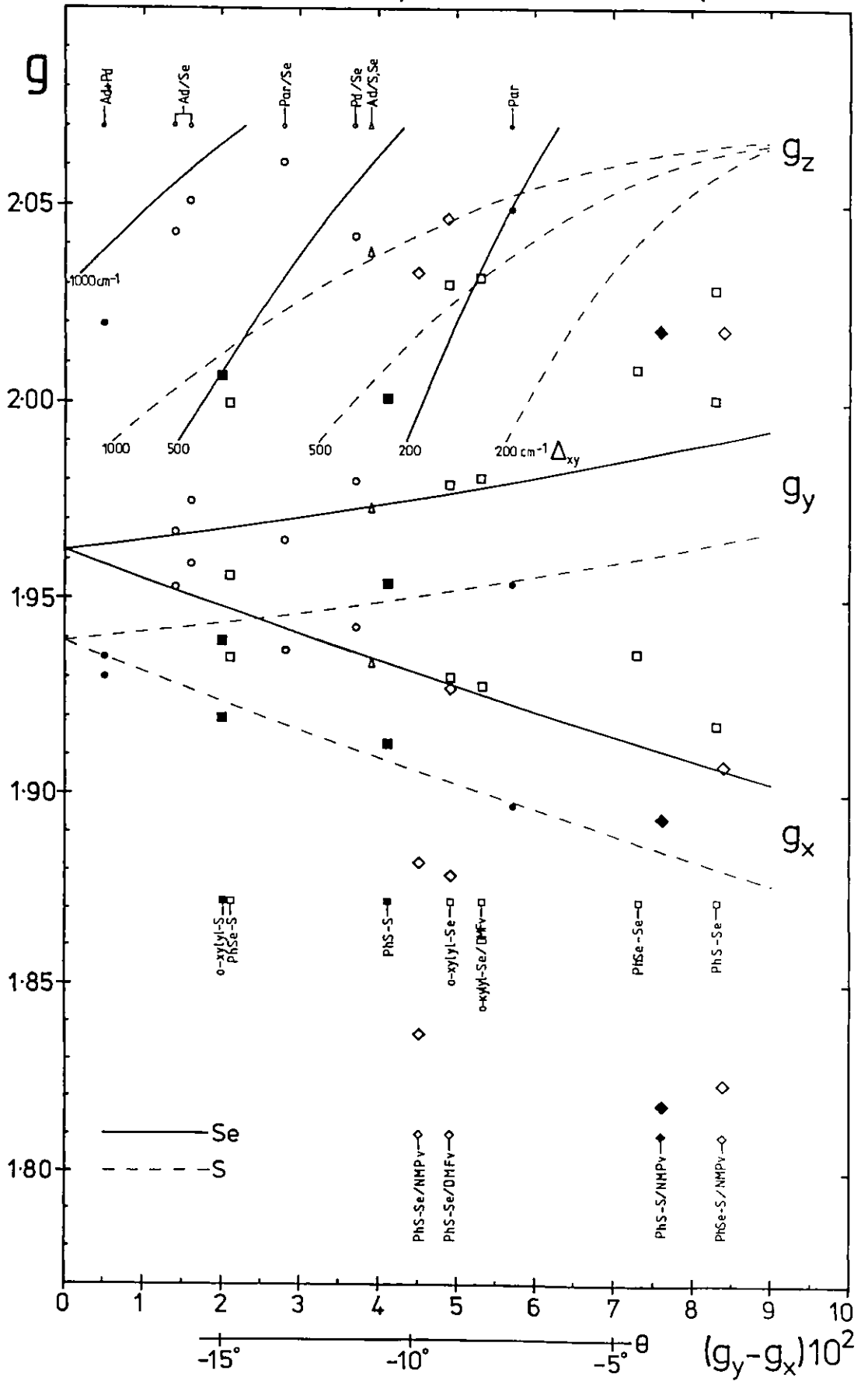
TABLE 1.9. EPR Data for Selenium-Bridged Fd_{red}.

		g_z	g_y	g_x
Ad	Adrenal glands pig[80]	2.043	1.967	1.953
	beef[81]	2.051	1.975	1.959
Par	Parsley[49]	2.061	1.965	1.937
Pd	P. Putida[80]	2.042	1.980	1.943
Ad	Adrenal glands - beef - mixed S, Se[81]	2.038	1.973	1.934

of the different parameters used in El.4-El.6. The g-values assumed for the ferric ion are consistent with increased covalency over that for $Fe(III)S_4$. $Fe(III)Se_4$ shows a further positive departure of g-value from 2.0023 compared to $Fe(III)S_2Se_2$[82] and consistent with this a non-vitreous sample of reduced $[Fe_2Se_2(SePh)_4]^{2-}$ has g_x closer to 2.0 than in the thiophenolate-ligated homologue. Reduced $[Fe_2S_2(SePh)_4]^{2-}$ on the other hand gives a signal in non-glassy frozen solvent with g_x & g_y intermediate between the values expected for sulphide and selenide bridged species. This could be indicative of intermediate ferric covalency such that the electron delocalisation is more to the bridging than to the terminal ligands.

Whilst the non-vitreous samples of reduced $[Fe_2S_2(YPh)_4]^{2-}$ (Y = S, Se) show substantially different signals, very similar g-values are observed with glassy frozen NMP as a solvent. Vitreous NMP solutions of reduced $[Fe_2Se_2(SPh)_4]^{2-}$ have on the other hand quite different

signals from these. Such results may be consistent with a large degree of ligand replacement in the vitreous samples. Results for glassy samples with DMF solvent are less clear.

As with the sulphur homologues, it seems reasonable to assign the signals for the S_2-o-xylyl-ligated dimer and non-vitreous samples containing aryl-chalcogenide ligated dimers, to trianion species resulting directly from reduction of the dianions. Such an assignment is made largely on the grounds of g-value compatibility to the Bertrand-Gayda model and because of their solvent-invariant lineshapes.

1.7. Concluding Remarks.

From the above spectroscopic evidence it is concluded that a substantial proportion of $[Fe_2S_2(SR)_4]^{3-}$ may be observed following chemical reduction of $[Fe_2S_2(SR)_4]^{2-}$ in solution using a fairly simple technique of reaction and product capture. As expected, these trianion species exhibit characteristics closely matching those of reduced 2Fe2S ferredoxins.

The peculiar solvent dependency of spectra for the monodentate thiol ligated complexes and the spectral changes in the presence of added thiols seem indicative of a considerably enhanced reactivity compared with the dianionic precursors. Trianionic tetramer species are also observed to have greatly increased reactivity compared with dianions.[76,84-87] $[Fe_4S_4(SPh)_4]^{3-}$ has been observed to form an adduct with carbon monoxide of undetermined structure,[85] but no differences were observed in EPR signals obtained in this present work following reductions of $[Fe_2S_2(S_2$-o-xylyl)$_2]^{2-}$ or $[Fe_2S_2(STol)_4]^{2-}$ under CO, H_2 or argon atmospheres.

With regard to reduction of $[Fe_2S_2(SR)_4]^{2-}$, it has not proved

possible, with the present extent of investigation, to formulate an

exact rationalisation for the origin of the various spectral differences

observed for a variety of solvents and additives. Certainly the

changes in the EPR spectra must result from some chemical modification

of the coordination at one or both irons, but the precise nature of

the interactions between the dimer and solvent or added thiol have not

been elucidated.

EPR proves to be a particularly useful technique in observing the

reduced dimers in view of its selectivity for these species at liquid

nitrogen temperatures, since precursor dianion and tetramer reaction

products give no interferring signals. No other readily available

spectroscopic method offers this advantage. Thus, in keeping with its

considerable contribution to the discovery, isolation and characterisation

of ferredoxin proteins, EPR has been found gratifyingly indispensible

in detection and study of the reduced 2Fe2S model complexes.

1.8. Experimental.

Synthetic details concerning the compounds used in this section

may be found in Section 6.

1.8.1. One Electron Reduction of $[Fe_2X_2(YR)_4]^{2-}$ (X, Y = S, Se).

Reductions of dianionic dimers were performed anaerobically in

DMF, DMSO, NMP or PhCN with sodium acenaphthylenide, generated in

solution (usually DMF or NMP) from acenaphthylene reduced over 0.1 to

0.2% Na/Hg amalgam.

In a typical reduction 5 ml of a filtered solution around 0.5 to
3 mM in iron-cluster was transferred to a septum-capped Schlenk tube
and further deoxygenated by several evacuation-freeze-thaw-N_2 flush
cycles. An EPR sample tube or Mössbauer cell, well flushed with
dinitrogen, was assembled on a stainless steel or PTFE transfer tube
inserted into the Schlenk-tube septum, ready for immediate transfer
of part of the cluster solution subsequent to reduction. In the cases
where the solvent had a low freezing point the cluster solution was
again frozen at this stage and thawed just prior to addition of reducing
agent. Around 1.5-fold excess (more in cases where some oxidising
additive was present) of sodium acenaphthylenide in about 100 µℓ of
solvent was then added to the dimer solution from a syringe, rapidly
mixed by swirling the solution in the Schlenk tube, and an aliquot
immediately transferred to the sample holder under pressure of N_2, where
it was quickly frozen in liquid nitrogen. With experience, the whole
process, from addition of reducing agent to completion of solvent
solidification, could be performed in 15 to 20 seconds. The reaction
is accompanied by a colour change caused by loss in intensity of low
energy spectral features.

In general EPR samples were collected in a normal 10 cm tube sealed
at the upper open end by a rubber septum and purged of oxygen by
evacuation and flushing; where prolonged quantitative measurements or
extensive thawing of a sample was to be undertaken a tube was employed
which could be filled and then sealed, via a stopcock joined to the EPR
tube with a graded quartz-pyrex connection. The Mössbauer cell sample

containers, of a cylindrical "pill-box" design, were loaded by

tight fit insertion of a steel transfer needle into a hole drilled

in the side, pre-flushed inert gas was allowed to escape through a

second smaller hole bored adjacent to the inlet.

1.8.2. ^{57}Fe Enriched $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$.

This was prepared from 82.94% ^{57}Fe via $[Fe(S_2-o-xylyl)_2]^-$.   20 mg

(0.35 mmol) of the enriched metal (AERE, Harwell) was dissolved in

0.15 ml AR cHCℓ and 0.3 ml MeOH at 70°C over 5 hrs in a 10 ml centrifuge

tube.   The solution was evacuated to dryness and 210 mg (1.2 mmol)

(HS)$_2$-o-xylyl thiol, 290 mg (1.8 mmol) Et$_4$NCℓ and 2.5 ml deoxygenated

EtOH added.   1.6 ml of a 1.5 M NaOEt solution (2.4 mmol) was added to

the above under N$_2$, via a septum seal, at 0°C over 15 mins.   N$_2$ was

bubbled gently to stir the solution a further 15 mins at 0°C.   Precipi-

tated NaCℓ was centrifuged down and the supernatant liquid drawn off

anaerobically into another centrifuge tube.   The NaCℓ was washed with

EtOH, again centrifuged down, and the washing added to the bulk

solution.   Oxidation of the combined product solution was accomplished

by controlled ingress of atmospheric oxygen, and the precipitated red/black

Et$_4$N[Fe(S$_2$-o-xylyl)$_2$] collected by centrifugation and washed well with

EtOH.   Conversion to [Et$_4$N]$_2$[Fe$_2$S$_2$(S$_2$-o-xylyl)$_2$] was accomplished in

warm MeCN with NaHS as described by Cambray, et al.[45]   Overall yield

based on Fe metal was 87%.

1.8.3. Experimental Details for Figures.

Figure   2. $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{3-}$ in 0.1 M n-Bu$_4$NCℓO$_4$/DMF.

2.1. 1.2 eq. ACN, P20, MA 1.6G, v 9.142 simulation " EPRPOW"
(Gaussian) then " CONV" (Lorentzian).

2.2. 83% ^{57}Fe enriched, 2 eq ACN, P20, MA 3.2G, v 9.142.

2.3. 83% ^{57}Fe, P10, MA 4G, v 9.144.

2.4. P10, MA 2.5G, v 9.141.

Figure   3. $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{3-}$ in DMSO.

3.1. 2 eq ACN, P6, MA 2.5, v 9.160;simulation - as 2.1

3.2. P6, MA 4, v 9.160;simulation - " EPRPOW" (Lorentzian).

Figure   4. The signal intensity was measured as the uncorrected height
at the low field peak.

Figures   6 — 8. 0.6 mM $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ in DMF, and product of
reduction with 2 eq ACN.

Figure   9. $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$ (Y = Cℓ, H, Me) reduced in NMP with 1.5 eq
ACN.

Spectra in each group are normalised by integrated intensity.

Y = Cℓ. 9.1. P10, MA 4, v 9.149; 9.2.0.2 M n-Bu$_4$NCℓO$_4$, P10, MA5, v 9.148;
9.3.0.2 M n-Bu$_4$NCℓO$_4$ devit., P16, MA4, v 9.149.

Y = H. 9.4. P10, MA 2.5, v 9.147; 9.5.0.2 M n-Bu$_4$NCℓO$_4$, P16, MA 2.5,
v 9.147; 9.6. 0.2 M n-Bu$_4$NCℓO$_4$ devit., P10,MA2, v 9.147.

Y = Me. 9.7. P10, MA 3.2, v 9.146; 9.8.0.2 M n-Bu$_4$NCℓO$_4$, P14, MA 2.5,
v 9.141; 9.9.0.2 M n-Bu$_4$NCℓO$_4$ devit., P10, MA 3.2, v 9.141.

Figure   10. $[Fe_2S_2(SC_6H_4Y)_4]^{2-}$ (Y = Cℓ, H, Me) reduced in DMF with
1.5 eq. ACN.

Spectra in each group are normalised by integrated intensity.

Y = Cℓ. 10.1. P10, MA4, v 9.145; 10.2. 0.1 M n-Bu₄NCℓO₄, P10, MA5, v 9.144;

10.3. 0.1 M n-Bu₄NCℓO₄ devit., P10, MA 3.2, v 9.145.

Y = H. 10.4. P10, MA5, v 9.143; 10.5. 0.1 M n-Bu₄NCℓO₄, P10, MA2, v 9.143;

10.6. 0.1 M n-Bu₄NCℓO₄ devit., P10, MA5, v 9.143.

Y = Me. 10.7. P10, MA5, v 9.142; 10.8. 0.1 M n-Bu₄NCℓO₄, P10, MA5, v 9.142;

10.9. 0.1 M n-Bu₄NCℓO₄ devit., P10, MA5, v 9.142.

Figure 11. 11.1 as Figure 10.1; 11.2 as Figure 10.5; 11.3 as Figure 9.8.
Simulations using " EPRPOW" .

Figure 12. Reduced [Fe₂S₂(SC₆H₄Y)₄]²⁻ (Y = Cℓ, H, Me).

12.1. Y = H, 1.5 eq ACN, 5% H₂O/DMF, P0, MA5, v 9.130; 12.2. Y = Cℓ,

1.4 eq ACN, PhCN, P10, MA5, v 9.129; 12.3. Y = H, 6 eq ACN, 10 excs PhSH,

P2, MA5, v 9.145; 12.4. Y = Me, 6 eq ACN, 10 excs TolSH, 0.1 M

n-Bu₄NCℓO₄, P8, MA4, v 9.140.

Figure 13. Spectra are height normalised.

1.5 eq ACN, P10, MA3.2, v 9.13 to 9.14.

Figure 14. Reduced [Fe₂S₂(SC₆H₄Y)₄]²⁻ (Y = Cℓ, H, Me) with 1.5 eq ACN.

14.1. Y = Cℓ, P10, MA3.2, v 9.146; 14.2. Y = H, P10, MA3.2, v 9.140;

·14.3. Y = Me, P10, MA4, v 9.141.

Figure 15. [Fe₂S₂(SR)₄]²⁻ + 50 exs t-BuSH.

15.1. R = Tolyl, 2.2 eq ACN, 0.2 M n-Bu₄NCℓO₄, P8, MA4, v 9.144.

15.2. R = o-xylyl/2, 1.6 eq ACN, 0.1 M n-Bu₄NCℓO₄, P12, MA2, v 9.149.

15.3. 83% ⁵⁷Fe enriched R = o-xylyl/2, 3 eq ACN, 0.1 M n-Bu₄NCℓO₄, P10,

MA3.2, v 9.149.

Figure 18. [Fe₂X₂(S₂-o-xylyl)₂]³⁻ (X = S, Se).

18.1 . X = Se, 1 eq ACN, P10, MA5, v 9.209; 18.2 X = S, 1.3 eq ACN, P10,

MA2, v 9.214.

Figure   19. $[Fe_2X_2(YPh)_4]^{2-}$ (X, Y = S, Se) reduced in DMF.

19.1 X = Y = S, as Figure 10.4; 19.2 X = Se, Y = S, 2 eq ACN, P10,

MA3.2, v 9.141; 19.3 X = S, Y = Se, 1.5 eq ACN,P10, MA5, v 9.140;

19.4 X = Y = Se, 1.5 eq ACN, P10, MA5, v 9.127.

Figure   20. $[Fe_2X_2(YPh)_4]^{2-}$ (X, Y = S, Se) reduced in 0.2 M n-Bu$_4$NCℓO$_4$

with 1.5 eq ACN.

20.1 X = Se, Y = S, DMF, P10, MA4, v 9.143; 20.2 X = Se, Y = S, NMP,

P10, MA5, v 9.146; 20.3 X = S, Y = Se, NMP, P8, MA5, v 9.144.

Notes. 1) unless otherwise stated, the sample temperature is ∿ 100 K

2) non-vitreous samples were often warmed after freezing to
induce further crystallisation.

3) P = Power/dB attenuation from 200 mw, MA = modulation
amplitude/G, v = microwave frequency/GHz, eq ACN = equivalents acenaph-
thylenide.

SECTION 2

SPIN-LATTICE RELAXATION IN $[Fe_2X_2(SR)_4]^{3-}$ $(X = S,Se)$
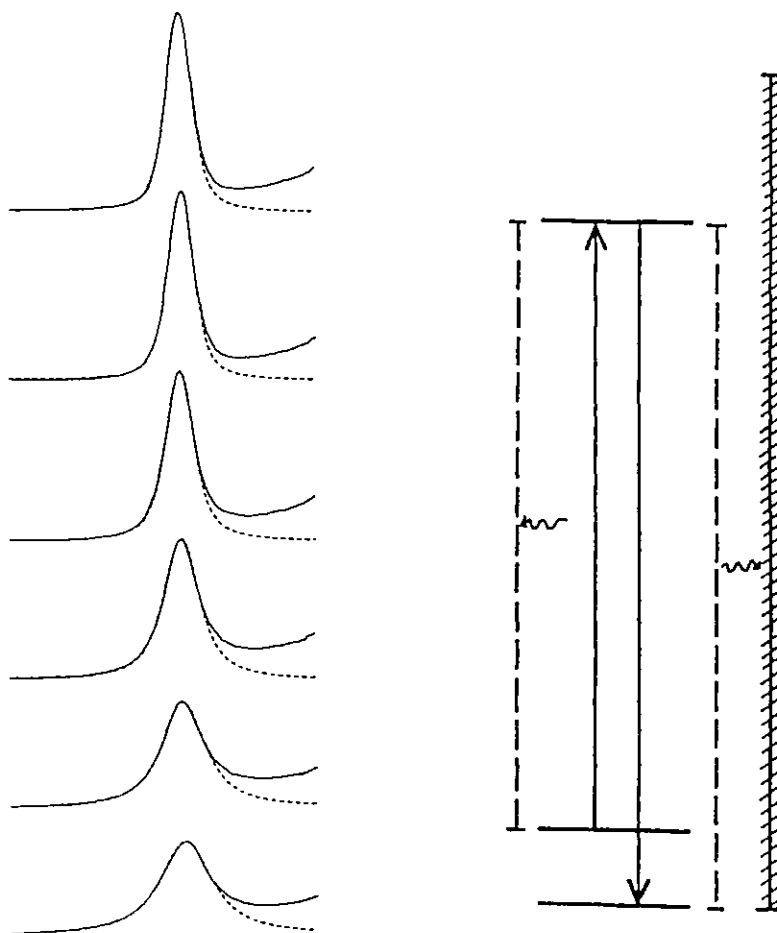
2. <u>SPIN-LATTICE RELAXATION IN $[Fe_2X_2(SR)_4]^{3-}$ (X = S, Se)</u>.

ABSTRACT

The low field peaks for the EPR spectra of $[Fe_2X_2(S_2\text{-}o\text{-}xylyl)_2]^{3-}$

(X = S, Se) and $[Fe_2S_2(SC_6H_4C\ell)_4]^{3-}$ in frozen DMF and/or DMSO are

analysed in terms of a convolution product between Gaussian and

Lorentzian functions, over the temperature range <u>ca</u>. 90–200 K. The

temperature-dependent component of the Lorentzian function responsible

for the broadening at the higher temperatures is related to the spin-

lattice relaxation time T_1. Variation of T_1 with temperature may be

fitted according to a relationship $(1/T_1) \propto T^n$ or according to a dominant

Orbach relaxation mechanism involving an excited state at ΔE such that

$(1/T_1) \propto \exp(\Delta E/kT)$. This last interpretation is considered more

appropriate and the excited state is related to the S = 3/2 spin level

for antiferromagnetic coupling of the irons involving exchange inter-

actions of 300 cm^{-1} for $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{3-}$, 200 cm^{-1} for

$[Fe_2Se_2(S_2\text{-}o\text{-}xylyl)_2]^{3-}$ and 240 cm^{-1} for $[Fe_2S_2(SC_6H_4C\ell)_4]^{3-}$.

2. Spin-Lattice Relaxation in [Fe$_2$X$_2$(SR)$_4$]$^{3-}$, (X = S, Se).

2.1. Introduction: Spin-Lattice Relaxation in Ferredoxins.

The proposal of Gibson, et al.,[17] than an anti-ferromagnetic

interaction exists between the iron atoms in two-iron ferredoxins

is well established and has been briefly described in Section 1.1

of this thesis. The manifolds of spin states resulting from this

coupling are shown in Figure 2.1. for the ferric-ferric and ferrous-

ferric oxidation levels. In the original description of the anti-

ferromagnetic coupling model, it was suggested that the anomalous

temperature dependence of the EPR observed from the ground state in

Fd$_{red}$ might be explained in terms of a resonant two-phonon relaxation

process involving low lying excited states of the spin manifold.

Figure 2.1. Spin-state manifolds for antiferromagnetic coupling of

two irons in ferric-ferric and ferrous-ferric oxidation

levels.
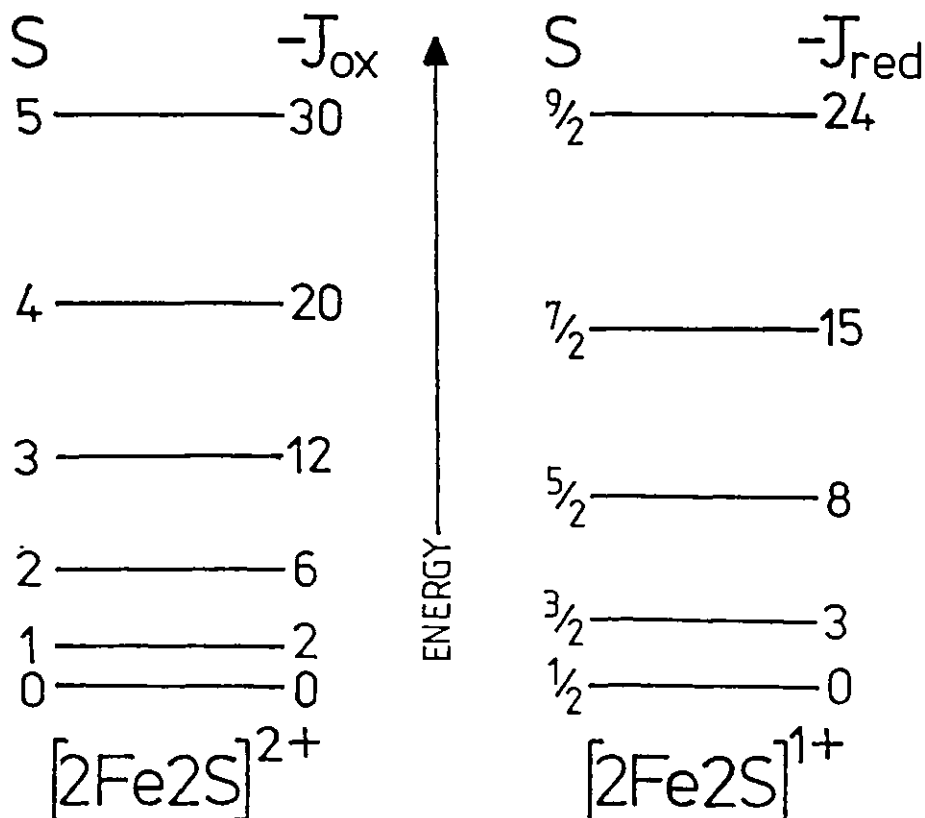
2.2. Relaxation Mechanism.

For processes other than emission or spin-diffusion an excited

spin must lose its energy to its surroundings (lattice) in the form

of interatomic vibration. It is considered that lattice vibrations

modulate the orbital moment via the ligand field, and through spin-

orbit coupling this leads to an oscillatory electromagnetic field

at the spin. The efficiencies of the various mechanisms by which

this process occurs are dependent on the distribution of phonon

energies in the sample, as determined by its temperature. The overall

rate of net transfer of spin energy to the lattice is characterised

by T_1, the spin-lattice relaxation time. The variation of this

parameter with temperature may be used to identify the dominant spin-

lattice relaxation mechanism, provided the sample maintains thermal

equilibrium with the cryostatic bath. Equation E2.1 contains terms

describing the temperature dependence of the relaxation rate $1/T_1$

for three important processes which are illustrated in Figure 2.2.

Detailed accounts of these may be found in references 88-90. The

direct process, involving only a narrow band of phonons with energies

very close to that for the spin-transitions, only makes an appreciable

contribution to $1/T_1$ at the lowest temperatures. Raman processes

involve pairs of phonons from anywhere in the lattice continuum,

provided their energy difference coincides with that for the EPR

spin system. These two-phonon relaxation mechanisms are strongly

temperature dependent with exponents (n) typically equal to 7, 9

or 5. Despite having lower transition probabilities, due to involving

two phonons, Raman processes dominate direct processes at higher

temperature since they make use of the entire phonon-spectrum. If an
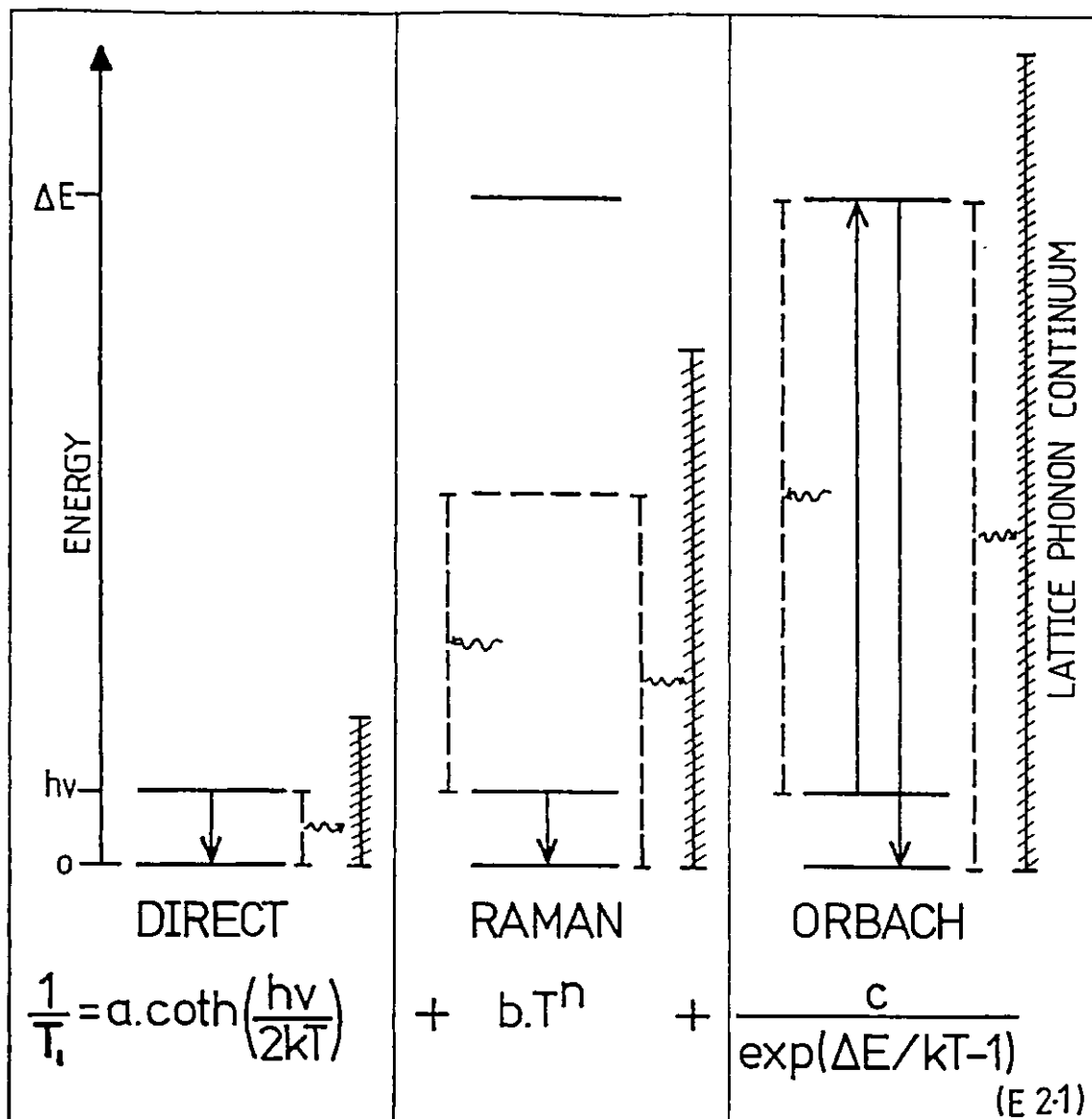
Figure 2.2. Three relaxation mechanisms of an EPR spin system and their temperature dependence.

excited state (at ΔE) lies within the phonon energy continuum it may take the place of the virtual level in the normal Raman process and the resulting resonant Orbach [90] relaxation mechanism, although involving only two narrow bands of phonon frequencies, has a greatly increased transition probability. For $\Delta E \gg kT$, the temperature dependence of the relaxation rate when an Orbach mechanism is dominant is given in equation E2.2.

$$1/T_1 = C.\exp(-\Delta E/kT) \qquad \text{E2.2}$$

For the 2Fe2S Fd_{red} from Spirulina maxima, Gayda et al. [19]

studied the temperature variation of T_1 as manifested in the changing

anisotropic homogeneous broadening of the EPR lineshape. They found

a good fit to E2.2 in the temperature interval 90 to 130 K with

$\Delta E \sim 250$ cm^{-1} (~ 350 K) and interpreted this in terms of a dominant

Orbach relaxation mechanism involving the first excited state from

anti-ferromagnetic ferric-ferrous coupling with exchange integral

$J = -83$ cm^{-1}.

2.3. Deduction of T_1 from Homogeneous Broadening.

Shortening of the lifetime of a spin state by some relaxation

process will lead to an increased uncertainty in its energy. For a

group of spins (spin-packets) having otherwise identical resonance

fields, this will lead to a broadening of Lorentzian shape with a

width δH_L (half-width at half-height) which is directly proportional

to the relaxation rate (E2.3).

$$\frac{1}{T_1} (\text{sec}^{-1}) = \frac{g\beta}{\hbar} \cdot \delta H_L (\text{Gauss}) \qquad \text{E2.3}$$

If other sources of homogeneous or inhomogeneous broadening are

present, or if there is resonance anisotropy, δH_L must be extracted

from the experimental lineshape by some deconvolution procedure. In

general then, the EPR lineshape is the convolution product of a

theoretical absorption spectrum, a Gaussian inhomogeneous broadening

function and the Lorentzian spin-packet lineshape as shown in Figure

2.3. The widths of the latter two broadening functions may exhibit

anisotropy.
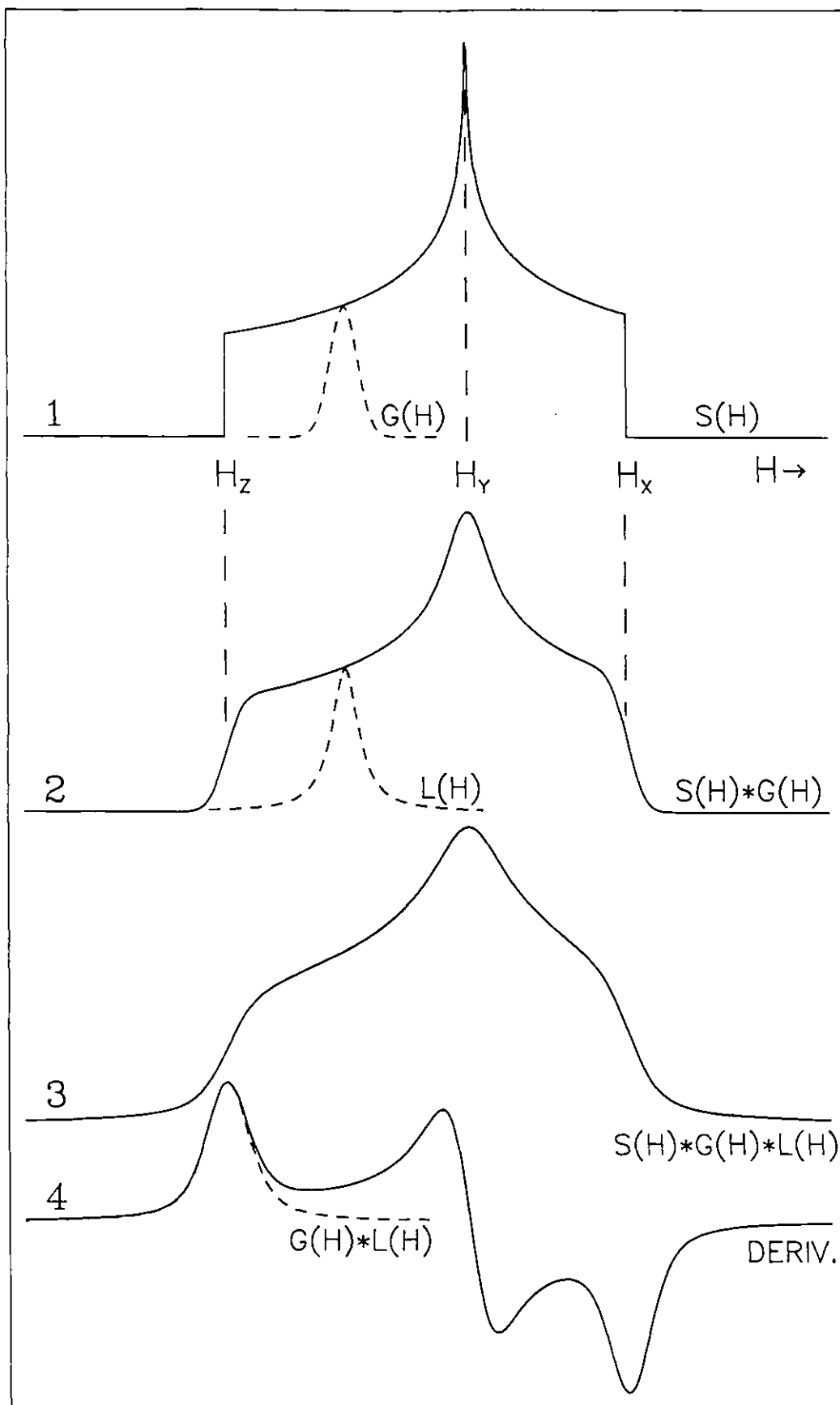
Fig. 2.3 Convolution product of theoretical EPR absorption spectrum S(H) with Gaussian G(H) and Lorentzian L(H) functions,together with deconvolution of H_z derivative peak by simulation with G(H)*L(H) product.

Analytical expressions are available for $S = 1/2$ theoretical absorption curves[91] or the curves may be derived numerically by spatial integration. Numerical convolution with Gaussian and Lorentzian functions leads to a synthesised EPR lineshape which may be fitted to that obtained experimentally. This simulation approach was the method used by Gayda, et al.[19] to determine T_1 at various temperatures from the lineshape of <u>Spirulina maxima</u> Fd_{red}. In the temperature interval studied, the Lorentzian contribution to the broadening was sufficiently greater than the Gaussian contribution to allow the use of a purely Lorentzian function. One of the main difficulties inherent in extracting δH_L by simulation, is the choice of an empirical law to describe the anisotropy of the relaxation time. If, however, one principal axis resonance lies well separated in the spectrum of interest, then the theoretical absorption curve appears like a step function at this point and this part of the broadened derivative spectrum has a shape closely approaching Gaussian-Lorentzian. Deconvolution of such a peak may then lead to an evaluation of T_1 along this axis-orientation. Bertrand et al.[92] have made a detailed analysis of the accuracy and applicability of this method by studying synthesised spectral lineshapes. Figure 2.4 is reproduced from their work as it represents a useful summary of the results.

$\delta_L = \delta H_L / |H_L - H_{\parallel}|$, $\delta_G = \delta H_G / |H_L - H_{\parallel}|$ are Lorentzian and Gaussian widths respectively, used in the synthesis of a derivative lineshape from which a half-width, δ', is measured for half-height at $H_{\parallel}$ and away from H_L. For small broadening this may be taken as a Gaussian-Lorentzian convolution product, with the width of the Gaussian function given by the width of the peak when $\delta_L = 0$. Bertrand et al. then extract the
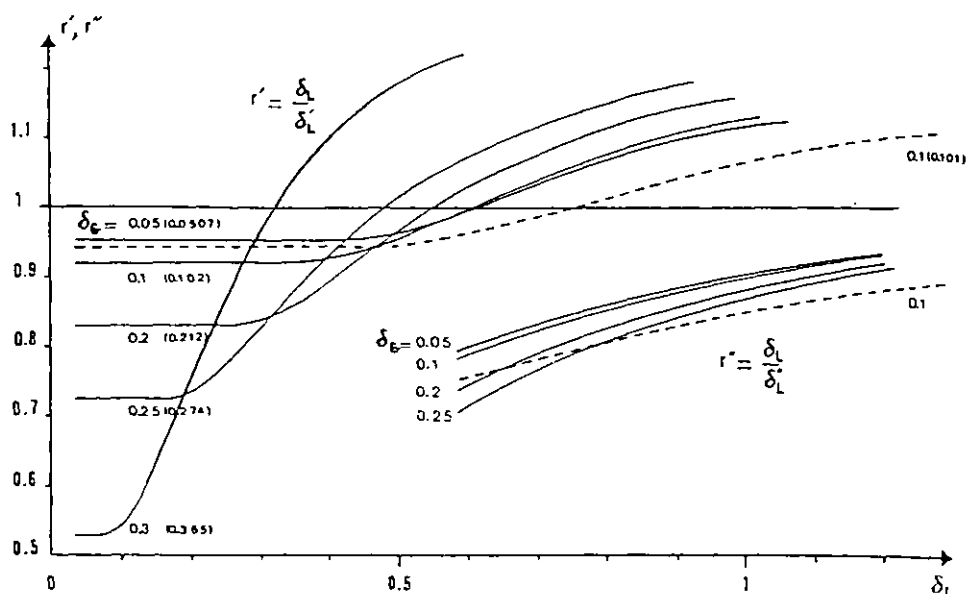
FIG. 2.4 Variations of the parameters r' and r'' upon δ_L for different values of δ_G. The values in parentheses are the half-widths of the peaks measured for $\delta_L = 0$.——, axial spectrum; – – –, symmetric rhombic spectrum with $\delta_G = 0.1$. The values of r' and r'' were calculated with a precision of about 1% [92]

half-width δ_L' of the Lorentzian packet from δ' using Gauss-Lorentz convolution product tables.[93] $r' = \delta_L/\delta_L'$ is an error function for which departure from unity indicates over-estimation of the Gaussian or Lorentzian width due to incursive contributions from outside the peak. For very large broadenings the lineshape at $H_{\parallel}$ and away from $H_{\perp}$, approximates a pure Lorentz derivative and the Lorentzian half-width δ_L'' is obtained as 1.236 δ_L'. The error function $r'' = \delta_L/\delta_L''$ tends to unity as δ_L increases. It is readily apparent from this analysis of Bertrand et al.[92] that provided there is a reasonably well resolved spectral extremum for which $\delta_G \overset{\sim}{<} 0.1$, the homogeneous packet width may be measured for a single direction to better than 10% using a combination of these methods. Analysis of EPR lineshapes for Spirulina maxima Fd$_{red}$ in this way has demonstrated dominance of the Orbach relaxation mechanism down to 50 K.[92]

Other methods which have been used to extract δH_L from $[2\text{Fe}2\text{S}]^{1+}$,

$[4\text{Fe}4\text{S}]^{1+}$ and $[4\text{Fe}4\text{S}]^{3+}$ ferredoxins have involved procedures of rather

dubious accuracy. The equation $\delta H^2 = \delta H_L^2 + \delta H_G^2$, where δH is the

width of some spectral feature, has been used to evaluate the extent

of homogeneous broadening,[94,95] but is strictly valid only as $\delta H_L \to 0$.

Another method involves simulation of broad high temperature spectra

by convolution of an unbroadened low-temperature spectrum with an

isotropic Lorentzian function. This ignores T_1-anisotropy or any

temperature dependency of the $\underline{g}$ tensor and has only been applied to

absorption EPR spectra, where inferior lineshape detail enables easier

fits to be obtained.[95-97]

An additional method of measuring the energy of the first excited-

state by observing the thermal depopulation of the ground-state is

sometimes applicable to ferredoxin EPR spectra.[94-99]

2.4. Spin-Lattice Relaxation in 2Fe Synthetic Complexes.

EPR spectra have been obtained for $[\text{Fe}_2\text{X}_2(\text{S}_2\text{-o-xylyl})_2]^{3-}$ (X = S,

Se) and $[\text{Fe}_2\text{S}_2(\text{SC}_6\text{H}_4\text{C}\ell)_4]^{3-}$ in DMSO and/or DMF solvents in the temperature

range ca. 90 K to 200 K. In each case the low field peak is well

resolved at ca. 100 K and broadens substantially as the temperature is

increased towards ca. 200 K. This Lorentzian broadening, δH_L, has been

evaluated by least-squares fitting the lowest field part of the peak

with a Gaussian-Lorentzian convolution function in a similar manner to

Figure 2.3.4. As the function is not expected to be a good fit to the

high-field side of the peak, accumulation of the squared difference

between the experimental and calculated lines was terminated a little

above H_z. H_z was often found to change slightly from spectrum to spectrum

and in order to attain the most accurate linewidth analysis the calculated line was in general evaluated at such a position that the crossover of its derivative superimposed the crossover of the derivative experimental lineshape.

The theoretical accuracy of the method of extraction of δH_L in the present applications is found to be better than -5% according to the analysis of Bertrand et al.[92] in Figure 2.4. Since no measurements were taken for which $\delta_L > 0.3$ the error is constant over all measurements and affects only the magnitude of T_1 and not the analysis according to E2.2.

2.4.1. $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ in DMSO and DMF.

The low field peak of the $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ EPR spectrum shows only slight broadening below ca. 140 K. Above this temperature the whole signal rapidly broadens, Figure 2.5. The contribution to T_1 of the additional spin-lattice relaxation process responsible for the broadening is shown for three samples in Figure 2.6. Two of the samples are from preparations in DMSO whilst the third is for DMF as solvent. For the purpose of clarity, the points for the sample DMSO2 have halved values whilst for the DMF sample the values have been divided by four.

At 100 K the H_z peaks of the EPR spectra for the three samples were best fitted with respective Gaussian and Lorentzian half-width at half-height contributions of 5.8 G and 4.0 G for DMSO1, 5.8 G and 2.0 G for DMSO2 and 6.2 G and 2.9 G for the DMF sample. The residual Gaussian broadening of ca. 6 Gauss ($\delta_G \simeq 0.05$) may result from hetero- geneity in the molecular environment of the cluster ions similar to

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FIG. 2.5 TEMPERATURE DEPENDENT BROADENING OF THE $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$/DMSO EPR LINESHAPE

FIG. 2.6 T_1-BROADENING WITH TEMPERATURE
AT H_z IN $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ EPR

$(1/T)/(K^{-1}\times10^{-3})\rightarrow$

DMSO1
$\Delta E=890cm^{-1}$

DMSO2÷2
$\Delta E=890cm^{-1}$

DMF÷4
$\Delta E=900cm^{-1}$

$(1/T_1)/(s^{-1}\times10^7)\rightarrow$

$\delta H_L/Gauss\rightarrow$

$\leftarrow T/K$
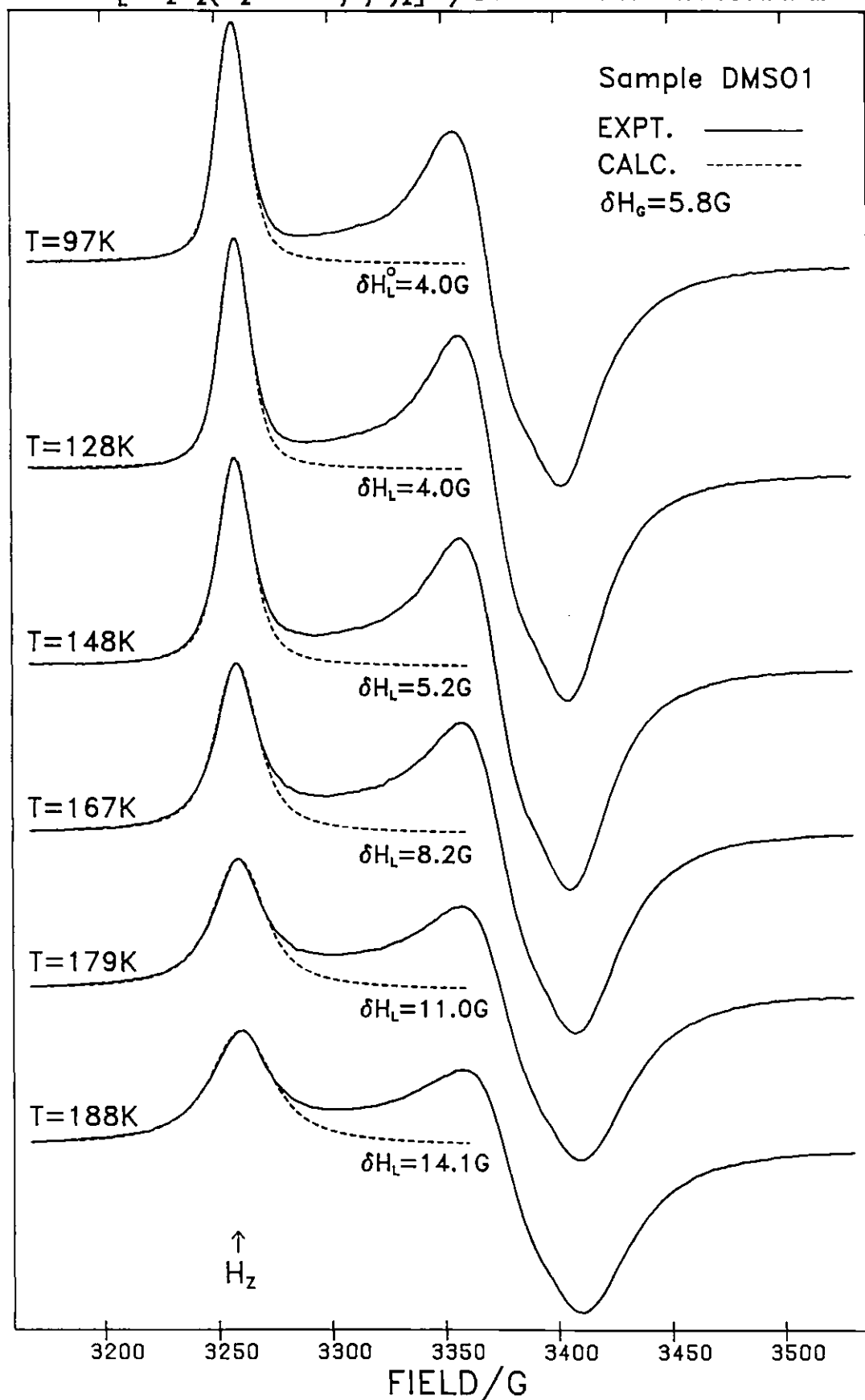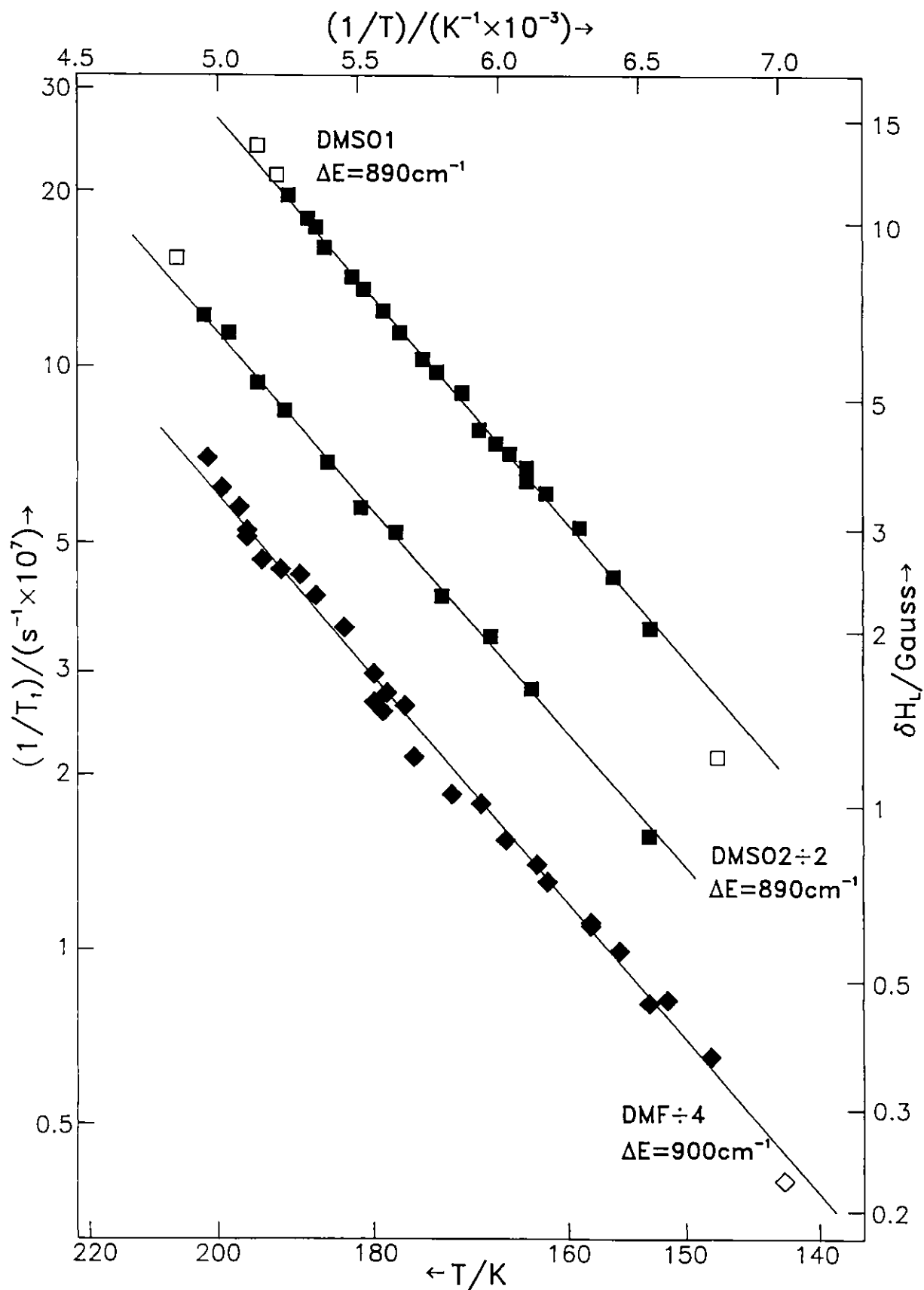
that suggested for the $[2Fe-2S]^{1+}$ centres in some ferredoxins.[6] At

36 GHz the half-height half-width of the low field peak for spectra

of samples in DMF or DMSO is 22 $\pm$ 2 Gauss and is quite compatible

with a Gaussian distribution in g-value of the magnitude found at

X-band (9.2 GHz).

The residual low-temperature Lorentzian broadening component

could originate from spin-spin relaxation enhancement. The extent of

this residual homogeneous broadening is found to be significantly

variable from one sample to another suggesting differences in the

expectation proximities of the $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ paramagnetic

ions. This latter could be caused by differences in the degree of

crystallinity adopted by the solvent on freezing. Thus, the residual

Lorentz width is smallest (1.5 G) when the complex is contained in a

vitreous matrix (0.1 M $nBu_4NC\ell O_4$/DMF, Table 1.1).

The residual low temperature Lorentzian width does not present

any problems to the analysis,[90, pg. 477] and may be subtracted from

the Lorentzian width determined at higher temperatures in order to

investigate the temperature-dependent broadening process.

Accurate evaluation of the additional homogeneous broadening

could be made only in the interval 150 K to 200 K. For temperatures

below this range the broadening was too weak to be measured with

sufficient accuracy. The upper limit is imposed by sensitivity

conditions; also in the case of DMF, solid-state solvent changes onset

above 200 K, resulting in irreversible changes in the EPR lineshape.

For the plots of $\log(1/T_1)$ against $1/T$ in Figure 2.6, linear

least-squares fits have been made to the full data points according

to equation E2.2. From the slopes of these linear fits the separation

ΔE of the upper level involved in the proposed resonant relaxation

process from the ground state is found to be 890 cm^{-1} for DMSO1,

890 cm^{-1} for DMSO2 and 900 cm^{-1} for DMF solvent (std. error of ΔE/cm^{-1},

coefficient C/s^{-1} in E2.2 together with its std. error, correlation

coefficient = $\pm$ 10, 1.6 $\pm$ 0.10 x 10^{11}, 0.9989 for DMSO1; $\pm$ 15,

1.4 $\pm$ 0.2 x 10^{11}, 0.9990 for DMSO2; $\pm$ 15, 1.5 $\pm$ 0.2 x 10^{11}, 0.9965

for DMF). Although the standard errors on these energies are only

1-2%, an error of $\pm$ 5% is probably more applicable as judged by

making alternative fits to the data.

Provided the temperature was not taken too high, which causes

irreversible broadening, the low temperature lineshape could be

reproduced on cooling together with subsequent compatible broadening

as the temperature was increased a second time.

2.4.2. $[Fe_2Se_2(S_2-o-xylyl)_2]^{3-}$ in DMF.

Only a single $[Fe_2Se_2(S_2-o-xylyl)_2]^{3-}$/DMF sample was studied in

the temperature range 85 K to 190 K. The low field peaks in the lowest

temperature spectra could be analysed in terms of a half-width at

half-height Gaussian contribution of 6.3 G and a Lorentzian contribution

of 3.9 G. Significant broadening onset at 110 K and could be

successfully extracted in the manner described in the previous section

up to ca. 170 K. Above this temperature the lineshapes were not so

well formed due to depletion in intensity. Also at the highest

temperatures some irreversible broadening occurred, probably due to

crystalline structural changes in the solvent matrix as suggested in the

previous section. Taking account of this additional Lorentzian broadening,

the relaxation-broadening depicted in Figure 2.7 could be successfully

reproduced in a second incrementing temperature cycle.

FIG. 2.7 T_1–BROADENING WITH TEMPERATURE AT H_z IN $[Fe_2Se_2(S_2-o-xylyl)_2]^{3-}$/DMF EPR

$\Delta E = 600 cm^{-1}$

EPR OF $[Fe_2Se_2(S_2-o-xylyl)_2]^{3-}$

EXPT.

CALC.

T=86K
δH_L=3.93G
δH_e=6.26G

T=161K
δH_L=11.4G
δH_e=6.26G

FIELD/G
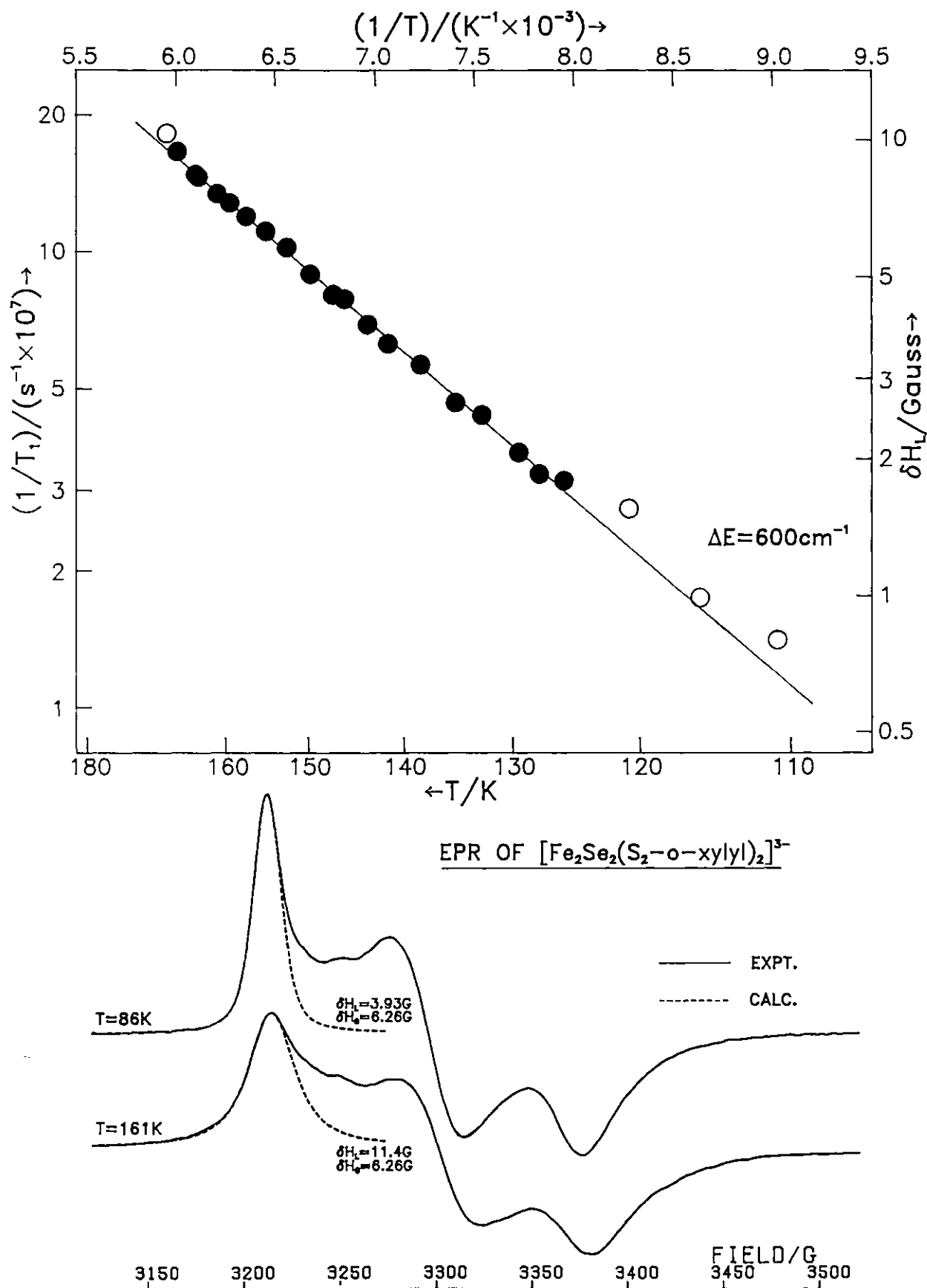
A linear least-squares fit is made to the full data points in Figure 2.7 according to equation E2.2 assuming an efficient resonant-relaxation mechanism involving an excited state at 600 $\pm$ 30 cm^{-1} above the doublet ground state. (Std. error of $\Delta E = \pm 5$ cm^{-1}, coefficient C in E2.2 = 2.9 $\pm$ 0.2 x 10^{10} s^{-1}, correlation coefficient = 0.9992).

2.4.3. [Fe$_2$S$_2$(SC$_6$H$_4$Cℓ)$_4$]$^{3-}$ in DMF.

Figure 2.8 presents data from an analysis, in the manner previously described, of the low field peak in EPR spectra from two incremental temperature cycles for [Fe$_2$S$_2$(SC$_6$H$_4$Cℓ)$_4$]$^{3-}$ in DMF. After reduction and transfer to the anaerobic EPR tube the sample was frozen in an isopentane-slush bath,rather than in liquid nitrogen,in order to produce a finely crystalline DMF matrix. In this way problems with lineshape changes at high temperature, due to solvent crystalline structural reorganisation, could be mitigated.

The sample was studied from 85 K to 200 K. At the lowest temperatures the H_z peak was found to be a product of a Gaussian function of half-height half-width 4.4 G and a Lorentzian function of half-width 6.3 G. Little broadening occurred below ca. 130 K. Extraction of the additional Lorentz broadening could be achievedbetween 150 K and 190 K with adequate accuracy, and the variation of these half-widths and corresponding T_1-values with 1/T shown in Figure 2.8 is reasonably well fitted with a straight line according to equation E2.2 using $\Delta E = 710 \pm 70$ cm^{-1} (Std. error of $\Delta E = 20$ cm^{-1}, coefficient C in E2.2 = 2.1 $\pm$ 0.4 x 10^{10} s^{-1}, correlation coefficient = 0.9858).

FIG. 2.8 T_1–BROADENING WITH TEMPERATURE AT H_z IN $[Fe_2S_2(SC_6H_4Cl)_4]^{3-}$/DMF EPR

$\Delta E = 710 cm^{-1}$

EPR OF $[Fe_2S_2(SC_6H_4Cl)_4]^{3-}$

EXPT.

CALC.

T=90K

δH_L=6.3G
δH_e=4.4G

T=181K

δH_L=10.8G
δH_e=4.4G
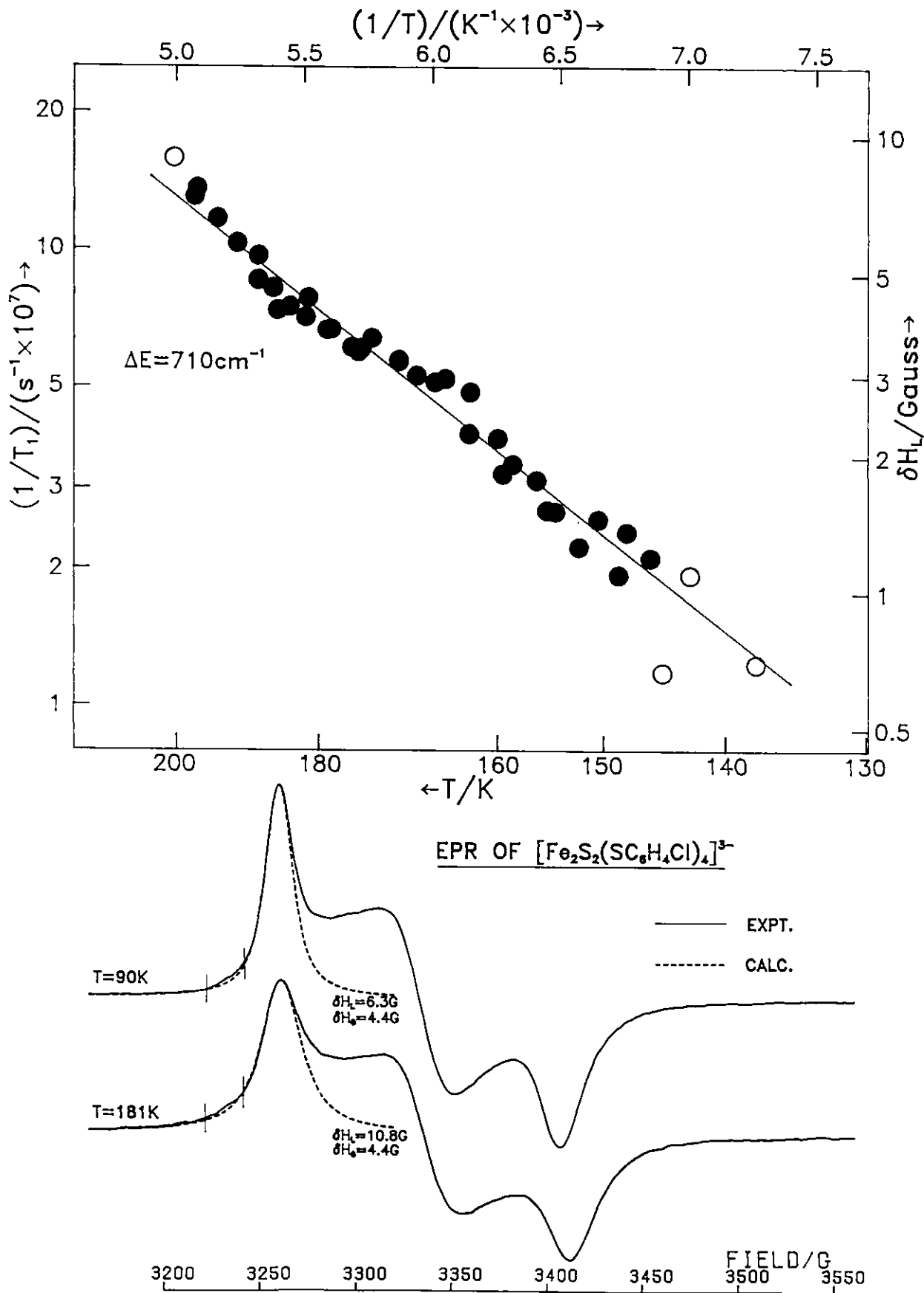
The appearance of a small impurity peak at g = 2.013, from the
W-type signal associated with the vitreous samples (see Section 1.4),
necessitated the use of a weighting function for the accumulation of
the squared-difference values in order to avoid distortion of the
fit to the g = 2.002 peak. This additional region over which squared-
differences were not accumulated is shown in the simulations at the
bottom of Figure 2.8.

2.5. Discussion.

The straight line fits to the five sets of data for $[Fe_2X_2(S_2$-o-
xylyl$)_2]^{3-}$ (X = S, Se) and $[Fe_2S_2(SC_6H_4C\ell)_4]^{3-}$, according to E2.2,
figures 2.6-2.8, are as good as is expected for the quality of data
obtained. If the same data are plotted bilogarithmically, equally
convincing fits can be obtained to the data sets according to a $1/T_1 \propto$
T^n (E2.3) process where n = 7.5 $\pm$ 0.3 (correlation coefficient ca.
0.998) for the three $[Fe_2S_2(S_2$-o-xylyl$)_2]^{3-}$ samples, n = 6.0 $\pm$ 0.2
(0.999) for $[Fe_2Se_2(S_2$-o-xylyl$)_2]^{3-}$ and n = 6.0 $\pm$ 0.4 (0.986) for
$[Fe_2S_2(SC_6H_4C\ell)_4]^{3-}$. The logarithmic and inverse temperature scales
show a relationship too close to linear in the 140-200 K interval to
permit a clear distinction between the processes E2.2 and E2.3 to be
based on the quality of fit to the data. The distinction can at
present only be based on the plausibility of the relaxation mechanisms
leading to the different temperature dependencies. Before discussing
the results in such a context, reference is made at this point to
measurements of T_1 obtained at lower temperatures.

Figure 2.9. T_1 variation with temperature for $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{3-}$ in (1:1) DMSO/DMF.
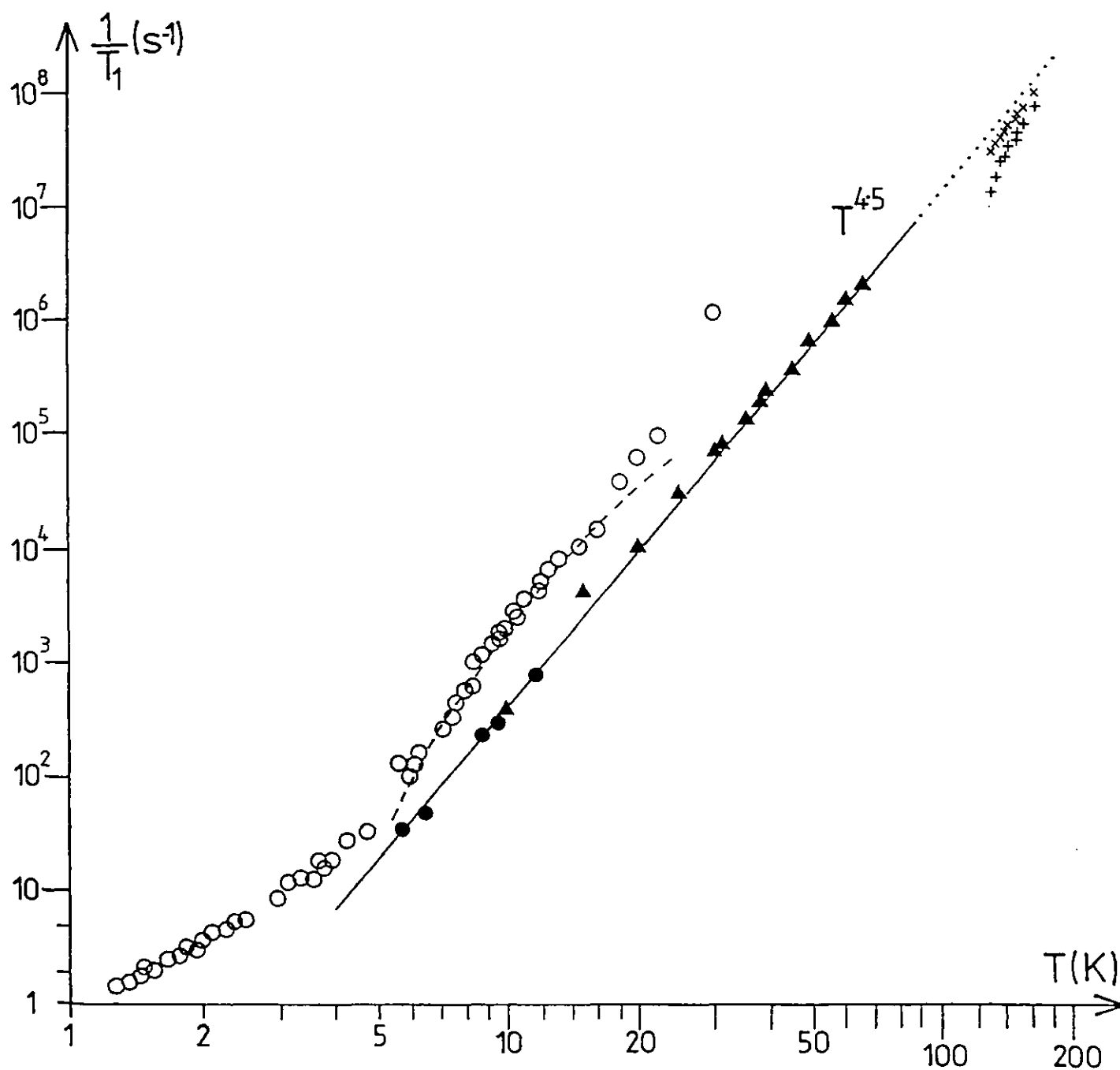
●   saturation pulse data

▲   continuous saturation data

×   uncorrected broadening data

+   broadening data corrected by subtracting the low temperature residual Lorentz component.

○   Data for _S. maxima_ Fd_{red} (ref. 101)

– – – – – 2nd order Raman process with θ_D = 60 K

――――― $(1/T_1) = 0.013T^{4.5}$

Figure 2.9 shows T_1 data for $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ in 1:1

DMSO/DMF obtained by J.P. Gayda and P. Bertrand (Département d'

Electronique, Université de Provence, Marseille)[100] using a continuous

saturation method[101] in the range 10-65 K and a saturating-pulse method

between 6 K and 11 K. The sample was prepared by the present author.

The temperature dependence of T_1 is well fitted in this overall range

by the relationship $1/T_1 \propto T^{4.5}$. Such a relationship cannot be

interpreted in terms of a simple Debye model. The data are, however,

not dissimilar to those for the reduced 2Fe2S ferredoxin from Spirulina

maxima[101] which are also plotted for comparison in Figure 2.9.

T_1 obtained by Gayda and Bertrand from relaxation broadening at

H_z in the same $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ sample for the range 130 to 165 K

is also given in this figure for comparison with the low temperature

data. One set of results is shown where the entire Lorentzian component

has been assumed to originate from T_1-broadening (the mixed solvent

freezes in the glassy state and so spin-spin broadening effects are

probably small). A second set of results where the low temperature

($\sim$ 100 K) component has been subtracted is also given and is compatible

with the results reported in this thesis, being reasonably fitted by

an Orbach process involving an excited state at 770 $\pm$ 50 cm^{-1} or by a

$1/T_1 \propto T^{7.5}$ law (the smaller value of ΔE for this solvent system

compared with the values for pure DMSO and DMF may be a consequence of

the differences in the way the solvents freeze).

One puzzling factor is that the width measurements yield T_1

relaxation times greater than the linear extrapolation of the saturation

results, Figure 2.9. It could be, however, that linear extension from

the points at low temperature is not strictly correct, and that the relaxation rate due to the process dominant in this region actually curves at high temperature to lower values of $1/T_1$ than those indicated by $1/T_1 \propto T^{4.5}$. Such a curvature does occur for all Raman temperature dependencies when T becomes of the order of the Debye temperature, θ_D.

On the other hand a plot of T_1 derived from the total Lorentz width closely parallels a linear extrapolation of the low-temperature results. Thus, it is possible that the $1/T_1 \propto T^{4.5}$ law is also being observed in the high temperature region. For the $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ sample, DMSO2, which amongst the three samples studied here has the smallest δH_L residual H_z lineshape component at 100 K, the data extend to higher temperature than for the sample of Figure 2.9, and a bilogarithmic plot of $1/T_1$, as obtained from the total uncorrected Lorentz width, against T, displays a poor linearity involving an approximate $1/T_1 \propto T^6$ relationship. The $1/T_1 \propto T^{4.5}$ parallelism of the extrapolated low temperature linewidth data for the DMSO/DMF sample studied by Gayda and Bertrand may then be adventitious.

Treating the results obtained in this present work in isolation from the low temperature data presented in Figure 2.9, a return is now made to the question of the plausibility of the T_1 temperature variation models represented by E2.2 and E2.3. The $(1/T_1) \propto T^n$ relationship of E2.3 is expected to hold for dominant Raman relaxation mechanisms with n = 7 and 9 respectively for first and second order processes when $T \ll \theta_D$ and with n = 2 when $T \gg \theta_D$. For $T \sim \theta_D$ a curvature between these two limits is anticipated. The direct process, for which n = 1 is predicted, and the first-order Raman process, are

in general only efficient at lower temperatures. The exponents found from bilogarithmic plots for the three 2Fe2S complexes are all too low to be associated with the value of n = 9 predicted for a second order Raman mechanism. Specific heat measurements in DMSO have been interpreted with two Debye temperatures, θ_{D1} = 130 K and θ_{D2} = 265 K,[102] thus, transient bilogarithmic $(1/T_1)/T$ derivatives lower than 9 could be expected, but linearity over the range of temperatures measured would not be anticipated.

On going from a structure in which the Debye phonon spectrum is equivalent in all three dimensions to a structure of lower dimensionality the exponent n is predicted to be lower.[103,104] Thus, a relaxation-temperature relationship of the type E2.3 with n = 6.3 has been considered on this basis in some hemo-proteins[103] and in a 4Fe4S ferredoxin.[105] This exponent is comparable with that of 6.0 found for $[Fe_2Se_2(S_2-o-xylyl)_2]^{3-}$ and $[Fe_2S_2(SC_6H_4C\ell)_4]^{3-}$. The lowering of dimensionality for the phonon propagation in the proteins is considered to be present because of their convoluted peptide-chain structure, wherein the efficiency of vibrational transmission along the chain is greater than across adjacent chain segments. But it is difficult to see how this could apply to the bare 2Fe2S complexes in intimate contact with organic solvent.

Thus, there is no readily apparent interpretation of the results in terms of a $1/T \propto T^n$ relationship with the experimentally determined exponent values. The fact that the exponents for $[Fe_2X_2(S_2-o-xylyl)_2]^{3-}$ range from 7.5 for X = S to 6 for X = Se is a further indication that this relationship is not applicable. If the relaxation process is more

dependent on the characteristics of the surrounding mileu (in particular θ_D) than of the iron-chalcogenide complex, as might be expected for any non-resonant Raman process, then little difference in the relaxation behaviour with temperature would be expected over the three complexes studied, and more dependence on the solvent. For an Orbach mechanism, variation in the slope for fits according to E2.2 is easily understood in terms of differences in the energies of the first excited states of the spin manifolds as determined by the coupling between the irons which may vary among the complexes.

The variation of T_1 with temperature in the region of broadening of several 2Fe2S and 4Fe4S ferredoxins has been interpreted in terms of a dominant Orbach mechanism.[19,92,94,105-107,95-97,108] The same mechanism is reasonably expected in the 2Fe2S model complexes studied here, and as demonstrated by Figures 2.6-2.8 the T_1 data for these complexes are well fitted assuming efficient resonant-relaxation processes involving excited states ranging from 900 cm^{-1} for $[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$ through 710 cm^{-1} for $[Fe_2S_2(SC_6H_4C\ell)_4]^{3-}$ to 600 cm^{-1} for $[Fe_2Se_2(S_2-o-xylyl)_2]^{3-}$. These energy gaps are not unreasonable for the $-3J$ splitting of the $S = 3/2$ level from the doublet ground-state in the coupled binuclear complexes, but are all well above the Debye temperatures of the organic solvents, such that the excited state cannot be in the phonon continuum. In this case efficient Orbach relaxation could not be expected. However, the vibrations of the required energy could originate from local vibrations of the ligands or of the solvent molecules. Such an origin has been suggested for an Orbach mechanism associated with some 4Fe4S ferredoxins where the excited state ranges 100-300 cm^{-1} and is thus above the Debye limit

of ca. 45 cm^{-1}.[105,107] For the dianionic forms of the complexes studied here only weak Raman or IR bands are observed in the required regions (section 4). DMF and DMSO show vibrational bands in the 600-900 cm^{-1} region which may have broad enough absorption tails to supply modes of the frequency required by the suggested Orbach process.[109-111]

A good test of the applicability of the proposed Orbach mechanism would be an independent confirmation of the excited-state to ground-state energy separations deduced. In some ferredoxins magnetic susceptibility measurements have been used to determine this energy gap.[112,50,16] For a gap of the order of magnitude suggested by the present relaxation measurements the population of the excited state would likely be too small to give any significant deviation of magnetic behaviour from $S = 1/2$. This was found to be the case for adrenodoxin,[113] for which a first excited state at ca. 800 cm^{-1} has been estimated from fitting T_1 vs. T data assuming dominant resonant relaxation.[94]

This same difficulty precludes the accurate determination of the energy gap by observing the deviation of EPR signal intensity from Curie-law behaviour at higher temperatures as the ground state depopulates. This method has been applied to some ferredoxins[94-98] and to $[Fe_4S_4(SPh)_4]^{3-}$.[99] For the three complexes studied here a very wide scatter is seen in the data on plotting $\log(T_o/IT-1)$ against $1/T$ (I = intensity of signal at temperature T relative to intensity at T_o - the lowest temperature employed), and only an order of magnitude indication is obtainable for the energy separation; $\Delta E = 300$ to 1500 cm^{-1} covers all compounds. The intensity in each case does in fact drop rather more appreciably below the Curie law than expected, and indicates the excited state to have a

multiplicity relative to the ground state well in excess of the expected

value of 2. This has no theoretical justification, but has been

observed for all applications of this method to iron-sulphur centres[94-98]

[note that the multiplicity value of 4.5 is incorrectly quoted in

reference 99 and should be 90 (= $e^{4.5}$)] .

A third method of measuring the energy ΔE in ferredoxins using

Raman has been suggested[114,115] but is not convincing and has not been

found to be applicable to the dianionic forms of the present complexes

(Section 4).

2.6. Conclusion.

Assuming the broadening of the EPR signals in the range 100-200 K

to result from a dominant Orbach relaxation mechanism involving the

$S = 3/2$ first excited state at energy $-3J$, the derived anti-ferromagnetic

coupling constants for $[Fe_2S_2(S_2\text{-}o\text{-xylyl})_2]^{3-}$ (X = S, Se) and

$[Fe_2S_2(SC_6H_4Cl)_4]^{3-}$ are collected in Table 2.1 and compared with corres-

ponding values for some iron-sulphur proteins. The J values for the

sulphur-bridged complexes are large and compare well with the value

estimated for adrenodoxin.[94] A relationship between J and $(g_y\text{-}g_x)$ has

been suggested whereby rhombic distortion at the ferrous ion leads to

large $(g_y\text{-}g_x)$ anisotropy, as in the theoretical model of Bertrand

and Gayda[60] (see also Section 1), and also to lower exchange coupling

due to decreased overlap for both direct and indirect (bridging) Fe-Fe

orbital interaction.[94] Thus maximal orbital overlap is expected in the

undistorted axial case and adrenodoxin has a large exchange interaction.

A high $|J|$ value is also expected of $[Fe_2S_2(S_2\text{-}o\text{-xylyl})_2]^{3-}$ from the

TABLE 2.1. Antiferromagnetic Coupling Parameter, J, for $[2Fe-2S]^{(1+,2+)}$

Centres in Ferredoxins and Synthetic Analogues.

$[2Fe-2S]^{1+}$	$-J/cm^{-1}$		Reference
$[Fe_2S_2(S_2-o-xylyl)_2]^{3-}$	300 ± 15		This
$[Fe_2Se_2(S_2-o-xylyl)_2]^{3-}$	200 ± 10		
$[Fe_2S_2(SC_6H_4Cl)_4]^{3-}$	240 ± 20		work
Spirulina maxima	83 ± 5		19,92
Spirulina maxima	98^{+5}_{-10}	M	112
Scenedesmus	83		92
Spinach	110	M	16
Synechococcus lividus	98-115	M	50
Succinate dehydrogenase (S-1)	90		94
Rieske's centre	65		94
NADH:UQ ubiquinone reductase	90		94
Adrenodoxin	270		94
$[2Fe-2S]^{2+}$			
$[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$	149 ± 8	M	38
Spirulina maxima	182 ± 20	M	112

The data were obtained from interpreting EPR-lineshape broadening in terms of an Orbach relaxation mechanism, except where marked with an " M " indicating magnetic measurement.

small $(g_y - g_x)$ splitting (0.020) and a somewhat weaker interaction for $[Fe_2S_2(SC_6H_4C\ell)_4]^{3-}$ which has increased $(g_y - g_x)$ separation (0.043). This is borne out in the results, Table 2.1. The $|J|$ values are both higher than would be anticipated from the empirical plot of $|J|$ vs. $(g_y - g_x)$ for 2Fe2S Fd_{red} presented by Salerno et al.[94]

Xα-VB calculations for $[Fe_2S_2(SH)_4]^{3-}$ predict $J \sim 80$ cm^{-1} using a symmetry based upon the crystal structure for $[Et_4N]_2[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]$,[116] but the dimensions of the reduced cluster could well be different.

A preliminary study on S. maxima Fd_{red} in 80% DMSO, where the peptide chain is unfolded and the 2Fe2S centre exposed to the solvent, does not show appreciable broadening up to 170 K, so that large exchange interactions are also expected in this case [J-P. Gayda, personal communication].

2.7. Experimental.

Solution samples of the trianionic dimers were obtained in the manner described in Section 1. Initial concentration of the dianion $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$, prior to reduction, ranged from a maximum 3 mM in DMSO to a minimum 0.6 mM in DMF, but as reduction of the latter could be carried out at lower temperature attaining yields in the range 60 to 80% as against yields of ca. 20% in DMSO, the final concentrations of $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{3-}$ were found by integrated intensity of the EPR signal to range from 0.3 to 0.6 mM. The initial concentrations of $[Fe_2Se_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ and $[Fe_2S_2(SC_6H_4C\ell)_4]^{2-}$ in DMF were 0.84 mM and 1.2 mM respectively and ca. 20% yield of trianion was obtained in each case as judged by the intensities of the EPR signals

Within the EPR cavity samples were cooled in a nitrogen gas stream, the temperature of which was regulated to within 1 degree by a Varian variable temperature controller. The sample temperature was measured by a copper-constantan thermocouple in contact with the sample-tube, but just above the resonant-cavity. In the case of the $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{3-}$ samples, this thermocouple was calibrated in the same position and using the same gas flow-rate against a platinum resistance of known calibration which had comparable dimensions to the solutions used and was in a similar quartz tube within the cavity dewar.

EPR spectra were collected digitally over 1000 points to a resolution of 10 bits.

SECTION 3

COMMENTS ON THE EPR SPECTRUM OF $[Fe(S_2\text{-o-xylyl})_2]^-$ IN FROZEN SOLUTION
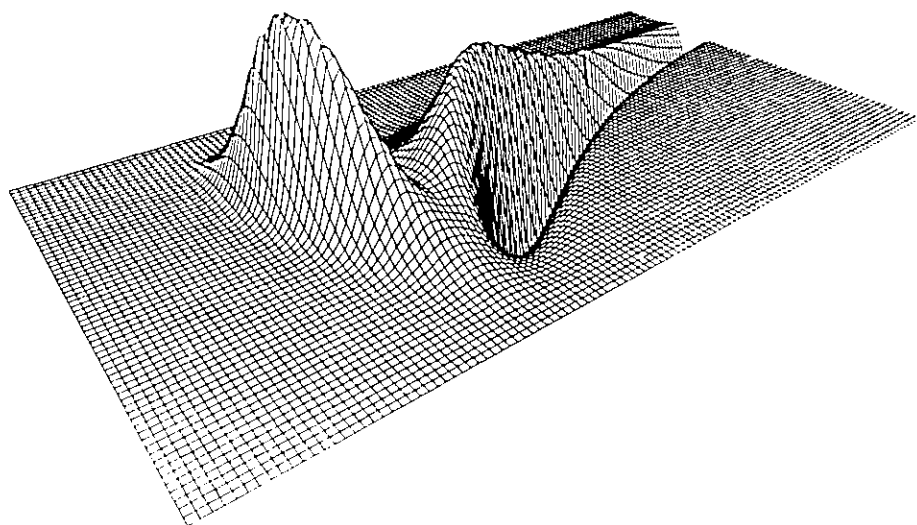
3. COMMMENTS ON THE EPR SPECTRUM OF $[Fe(S_2-o-xylyl)_2]^-$ IN FROZEN

   SOLUTION.

ABSTRACT

The X and Q band EPR spectra for frozen solutions of $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ are interpreted in terms of a high D value and a distribution of $\underline{D}$ symmetries centred at $\lambda \simeq 0.13$ and ranging over $\lambda \simeq \pm 0.05$ in half-width. D is estimated at $2.0^{+0.8}_{-0.5}$ cm^{-1} from an analysis of the temperature-dependent intensity variation of the feature at lowest field which has been assigned to resonance in the $S = 1/2$ Kramers doublet. Comparison of the EPR for $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ is made with spectra for rubredoxins and desulforedoxin. Several explanations are considered for the origin of a sharp feature at $g' = 4.28$ in the $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ spectra, but none is found to be entirely satisfactory.

3. Comments on the EPR Spectrum of $[Fe(S_2\text{-}o\text{-}xylyl)_2]^-$ in Frozen Solution.

3.1. Introduction: EPR in High Spin $Fe(III)S_4$.

S_2-o-xylyl ligated iron(III) has been demonstrated spectroscopically and crystallographically closely to approach the coordination found in oxidised rubredoxin, serving as a good, albeit symmetrised, synthetic analogue.[117,118,56] [See also Section 4.2.2.].

EPR spectra of Rd_{ox} show strong absorption centred around an effective g-value of 4.3 together with weaker derivative-maxima at $g' \simeq 9.4$.[119-124] Very weak broad features are also sometimes observed at high fields ($g' \sim 1$).[125] Signals of this sort can arise from high-spin Fe(III) in a low symmetry crystal field. Whilst the sextet ground-state in high spin ferric complexes is orbitally non-degenerate, a spin-orbit coupling interaction with excited non-spherical quartet and doublet states can result in a zero-field splitting of the six ^6S spin states into three Kramers doublets. These higher interacting orbital states are sensitive to the symmetry of the local crystalline-field environment, which consequently determines the nature of the zero-field splitting.

Without considering either the actual coordination symmetry of the ligand atoms producing the crystalline field at the iron, or the exact mechanism of the spin-orbit coupling producing the zero-field splitting, it is possible to understand their effects in terms of a phenomenological spin-Hamiltonian operator which acts on the spin-state wave functions, (E3.1).

$$\hat{\mathcal{H}}_s = \beta.\underline{H}.\underline{g}.\hat{\underline{S}} + \hat{\underline{S}}.\underline{D}.\hat{\underline{S}} \qquad (E3.1)$$

In this expression, the first part contains the magnetic interaction with the static field and the second the spins orientational preference.

The $\underline{D}$ tensor is normally expressed in terms of D and λ (or E = λD), coefficients representing the anisotropic part of the spin-orbit coupling contribution (E3.2).

$$\underline{\hat{S}}.\underline{D}.\underline{\hat{S}}. = D_{xx}\hat{S}_x^2 + D_{yy}\hat{S}_y^2 + D_{zz}\hat{S}_z^2$$

$$= D[\hat{S}_z^2 - \frac{1}{3}S(S+1) + \lambda(\hat{S}_x^2 - \hat{S}_y^2)] + \frac{1}{3}(D_{xx} + D_{yy} + D_{zz})S(S+1)$$

$$D = D_{zz} - (D_{xx} + D_{yy})/2, \quad \lambda = (D_{xx} - D_{yy})/2D \qquad (E3.2)$$

All components of the ground-state are shifted equally by the last term in this equation and it is not usually included in the spin-Hamiltonian.

An Hamiltonian of the same form as E3.1 results from the dipolar spin-spin interaction between unpaired electrons. Experimentally it is not possible to separate the spin-orbit and spin-spin contributions to $\underline{D}$, but the latter is expected to be small for S = 5/2 Fe(III).[126]

Additional spin-Hamiltonian terms quartic in $\underline{S}$ with coefficients a (or μ = a/D) and F are sometimes important in determining the energies of the spin states, but are not considered for the present as the quadratic terms are generally dominant.

The range of values taken by D and λ, and their significance, is dependent upon the choice of coordinate system. If the intuitive choice of D_{xx}, D_{yy} and D_{zz} axes is made such that $|D|$ is maximised and λ made positive, then λ is minimised and restricted to values from 0 to 1/3.[127,128] Such a system has been widely adopted and is used here. Transformation

formulae have been derived to convert D and λ to the other five reasonable definitions of axes.[129-131]

Under the chosen axis system, when expressed in terms of D and λ, the symmetry of the D tensor, but not necessarily that of the crystalline field, is such that D = 0 represents cubic; λ = 0, D $\neq$ 0 represents axial and $0 \leq \lambda \leq 1/3$ represents rhombic symmetry. When D is small relative to the Zeeman splitting five $\Delta M_s = \pm 1$ transitions produce an EPR signal centred around g' = 2. When the zero-field splitting is comparable to or in excess of hν, solution of the spin-Hamiltonian (E3.1) for S = 5/2 to obtain the relative energies of the six spin-states, over a range of magnetic fields, makes possible an evaluation of the resonance fields for spin-state transitions. Graphs of D or λ against resonance positions for fields orientated along the D tensor axes, or sometimes more usefully in the case of " powder spectra" for zero angular variation, provide a summary useful in the interpretation of spectra.[132,133,127,128] For large zero-field splitting the observed EPR spectrum is mainly dependent upon λ. Figure 3.1 shows the principal-axis g' values and the energy separations for the three Kramers doublets at the extremes λ = 0 (D axial) and λ = 1/3 (maximum D anisotropy).

A value of λ close to 1/3 provides an explanation for the observed resonances seen in Rd$_{ox}$. The strong signal around g' = 4.3 results from the middle Kramers doublet[134] and changes intensity with temperature in a way in keeping with an excited state. The lowest doublet gives rise to peaks at g' $\sim$ 9.4 and g' $\sim$ 1 which are weaker due to their greater anisotropy, the former being, however, more prominent at very low temperatures.[125] Resonances originating from
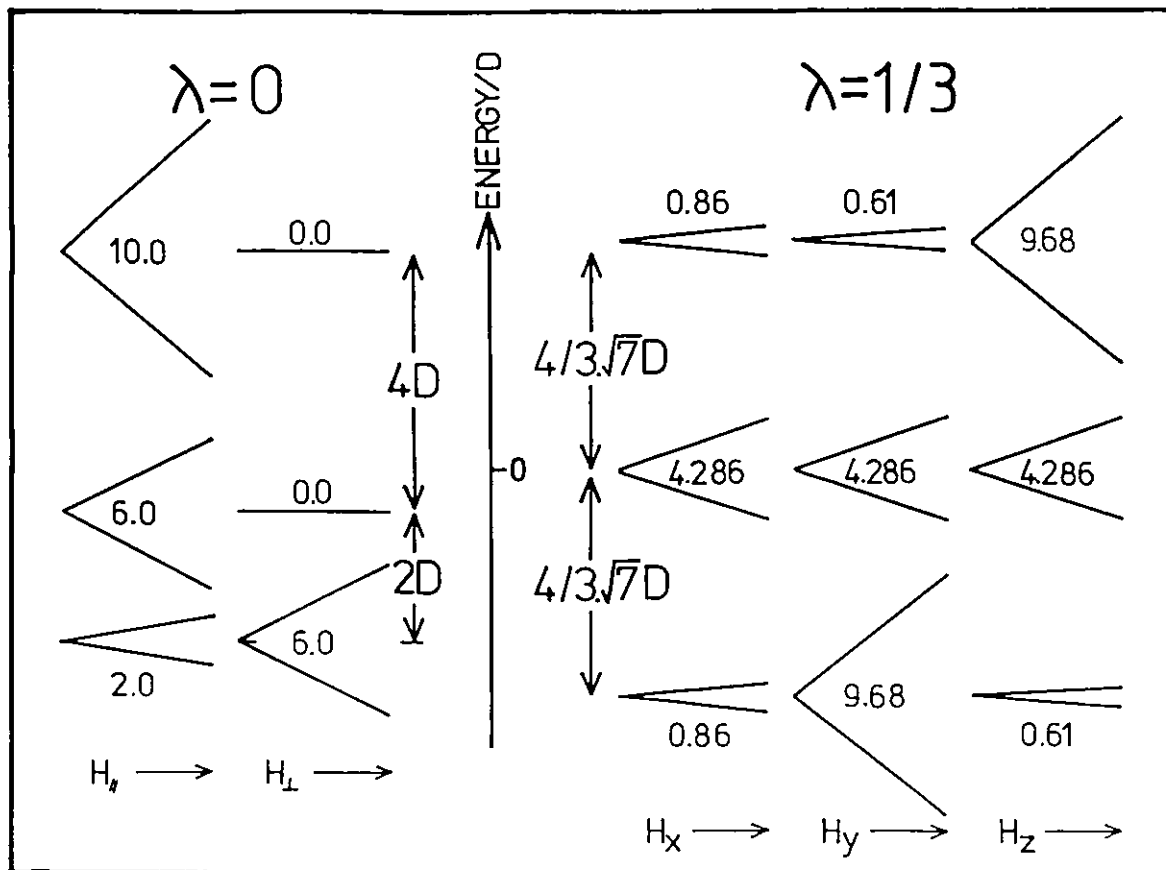
Figure 3.1. Splitting of the three Kramers doublets for S = 5/2 under

axial (λ = 0) and fully rhombic (λ = 1/3) symmetries.

The figure at each doublet represents the g value of a

signal from that doublet.

the highest doublet are not generally observed in Rd_{ox} as the transition

probability is low for such spin-state changes, the $\underline{g}'$ anisotropy is high

and the fractional population is smaller at low temperatures than for

the lower levels.

Since the resonance fields for Rd_{ox} are quite sensitive to λ, a

reasonably accurate evaluation of this parameter may be made by comparison

with fields predicted from solution of the spin-Hamiltonian. Peisach

et al.[125] have obtained a value of 0.28 for λ in P. oleovarans Rd_{ox}

whilst for C. acidi-urici Rd_{ox} an EPR spectrum was observed, characteristic

of $\lambda \sim 1/3$.[135] Other rubredoxins give similar or intermediate spectra

and must have comparable rhombic character.

The insensitivity of the Rd_{ox} EPR to D precludes the determination

of this parameter in the manner used for λ. If, however, λ is known,

then an evaluation of the magnitude of the zero-field splitting leads

to a direct estimation of D. The zero-field splitting may be obtained

from a variable temperature study of the changing fractional population

of a Kramers doublet as revealed by the varying relative intensity of

part of its resonance signal. Values of $D = 1.76 \text{ cm}^{-1}$ and $D = 1.89 \text{ cm}^{-1}$

have been determined for P. oleovarans and C. acidi-urici respectively.[125,135]

For iron coordination giving a high λ value, Blumberg and Peisach

have correlated the zero-field splitting with the nature of the ligand

atoms. An energy separation of $1-2 \text{ cm}^{-1}$ between lowest and middle

Kramers doublets is found for ligation primarily by oxygen, whilst

$5-6 \text{ cm}^{-1}$ is characteristic of a ligand system consisting mainly of

sulphur atoms. A cautionary note should be added, however, exemplified

in the case of the enzyme protocatechuate 3,4-dioxygenase. This shows

a strong $g' = 4.3$ resonance having $\lambda = 0.29$ and has been described as

primarily sulphur ligated on the grounds of its 5.39 cm^{-1} zero-field

splitting.[135] Mössbauer spectra of this protein are consistent with

such D and λ values, but do not support sulphur coordination.[136]

3.2. EPR of $[\text{Fe}(S_2\text{-o-xylyl})_2]^-$; Determination of λ.

Holm, Lane and co-workers report having measured the EPR spectra of

$[\text{Fe}(S_2\text{-o-xylyl})_2]^-$ in several solvent media over the temperature range

1.5 to 140 K.[56] They have described the spectra as being more complicated

than those for Rd_{ox} but have given no details beyond noting the presence

of a sharp $g' = 4.3$ signal thought to be indicative of fully rhombic

symmetry.

Figure 3.2 shows X-band EPR measurements on a frozen 3:1 DMF/CH$_2$Cℓ_2

solution of Et$_4$N[Fe(S$_2$-o-xylyl)$_2$] at 100 K and 5 K. Two intense low

field features are seen at g' = 8.40 and g' = 5.44, a broad trough is

centred around g' = 2.9 and a sharp isotropic line found at g' = 4.28.

It has been suggested that the complexity of the spectrum, in comparison

to those for Rd$_{ox}$, might result from exchange interactions within the

sample which are absent in the proteins due to greater separation of

the FeS$_4$ centres.[118] Whilst, as expected, it is true that for the pure

solid a radically different spectrum is obtained, no major changes

have been observed in the lineshape when concentrations ranging from

1 mM to 20 mM have been employed in the DMF/CH$_2$Cℓ_2 solvent system. An

integrated form of the high temperature derivative spectrum is shown in

the lower part of Figure 3.2 and demonstrates clearly that the sharp

g' = 4.3 resonance is weak compared with the remainder of the signal.

This isotropic line cannot then be connected with the g' = 8.4 peak

in the way that g' = 4.3 and 9.4 resonances are believed to arise. In

addition, on cooling from around 100 K toward around 10 K, the intensity

of the sharp line is observed to increase more rapidly than predicted

by a Curie-Law temperature dependence, an observation opposite to the

expected behaviour for a signal arising from a middle Kramers doublet.

The intensity of this line relative to the low field features is

also found to be rather solvent dependent and the signal is, for the

time being, excluded from the interpretation of the rest of the spectrum

on the grounds that it possibly arises from another species.

A fairly sharp change in intensity in the trough between the low

field lines indicates that they probably do not arise from different

orientations of the same resonance. If then the g' = 8.4 peak results

Fig. 3.2   X—band EPR spectra for $Et_4N[Fe(S_2-o-xylyl)_2]$
in frozen $DMF/CH_2Cl_2(3/1)$
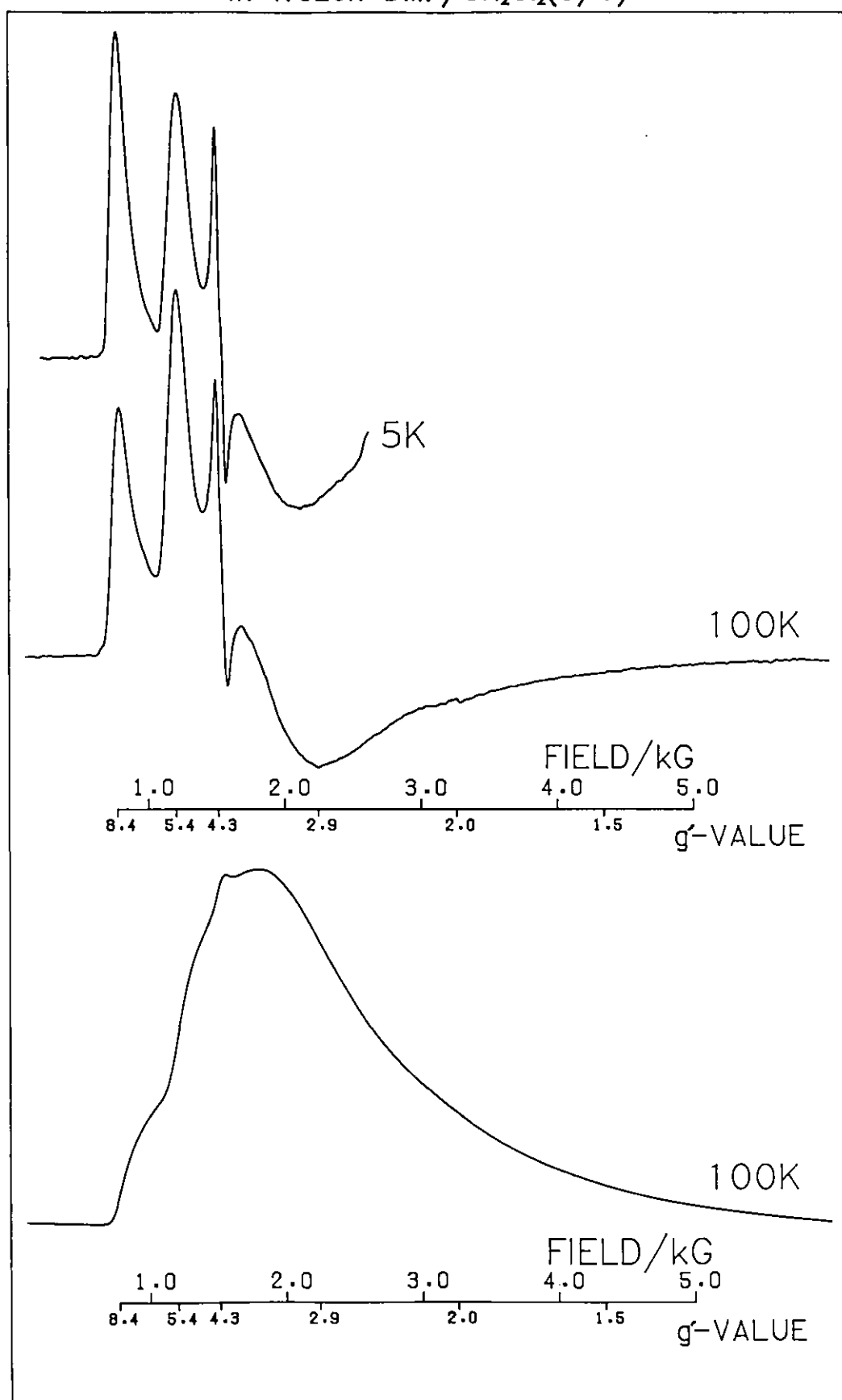
from the lowest Kramers doublet and the g' = 5.4 peak from the middle

doublet,the two resonances must have comparable anisotropy in order

to possess similar intensities. Such a situation can only arise when

λ is midway between values giving axial and values giving fully

rhombic $\underline{D}$ symmetry.

The upper part of Figure 3.3 shows a plot of principal-axis

resonance fields predicted from solution of the spin-Hamiltonian (E3.1)

for S = 5/2 with $0 \leq \lambda \leq 1/3$ (D = 2.0 cm^{-1}, ν = 9.117 GHz). Resonance

positions of the lines at low field indicate that λ lies between 0.12

and 0.16 for $[Fe(S_2-o-xylyl)_2]^-$. The broad trough around g' = 2.9 is

considered to arise from the middle doublet along x and y orientations

and from the x direction for the lowest doublet. Lines representing

these resonances in Figure 3.3 intersect in the region of λ given

above. The lineshape for a sample of randomly orientated molecules

is expected to have a derivative form along the directions specified,

however, the simulated spectrum in Figure 3.4 shows that with large

linewidths a shape may result quite comparable to that observed

experimentally. This calculated spectrum is the result of adding

together Boltzmann-population-weighted spectra simulated for lower and

middle doublets with a ficticious S = 1/2 spin and using $\underline{g}$'-values

from solution of the S = 5/2 spin-Hamiltonian (an isotropic g' = 4.28

line has been added in also). The resonance in the upper doublet is

highly anisotropic, and the only principal-axis field position (z) in

the region under consideration has very low transition probability.

Linewidths for the x,z resonance field orientations of the lowest

doublet and x,y orientations of the middle doublet have been varied
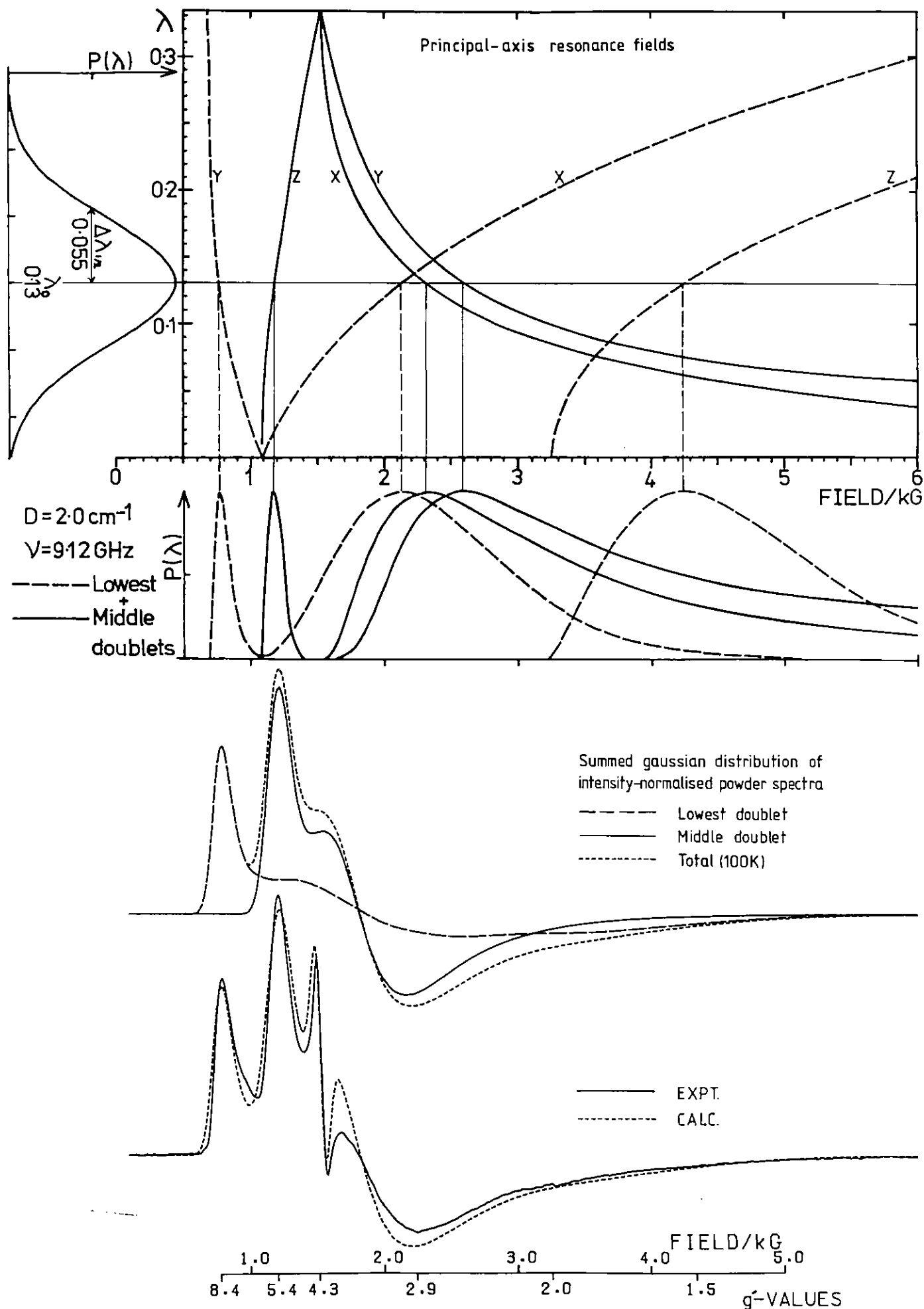
Fig 3.3 Predicted principal−axis fields for D=2cm⁻¹, ν=9.12GHz, λ=0 to 1/3. A simulation procedure involving a Gaussian distribution in λ is portrayed.

EXPT(100K)
CALC

CALC
Lowest dblt.
Middle dblt.

FIELD/G

500   1000   1500   2000   2500   3000   3500   4000

8.4   5.4   4.3   2.9   2.0   g-VALUE
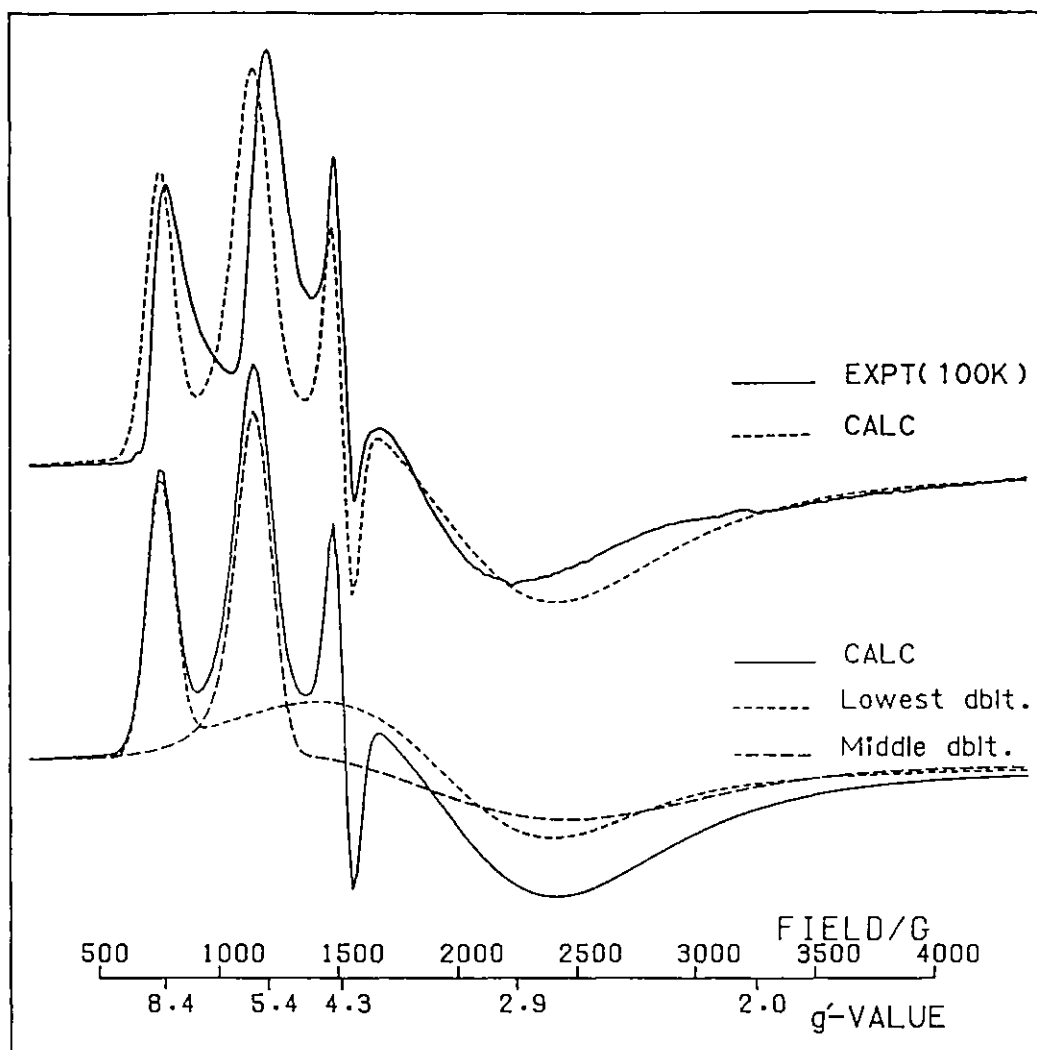
Figure 3.4. Additive powder spectra, for lowest and middle doublets

resulting from fields predicted at λ = 0.13.

to least squares fit the spectral lineshape above g' = 4. Best overall

fits result from g parameters generated with λ between 0.13 and 0.14.

Outside this best fit λ range, certain of the line widths are required

to be excessively large or the relative intensities of the two sharp

low field peaks deviates from those experimentally observed. For

close agreement to the experimental lineshape at λ = 0.13, Gaussian

half-height half-widths, in order of increasing on-axis resonance

field, were 65, 450, 2500 G and 74, 700, 2500 G for the lower and

middle doublets respectively. A linear linewidth-anisotropy between

principal axis values has been employed. The large linewidth in the z direction for the ground state resonance, prevents resolution of any feature between 4000 and 5000 Gauss, in keeping with the observed spectrum for which only a broad tailing-off is found in this field interval.

Very anisotropic linewidths are not unexpected for this sort of compound,[137,133] an example being NaCo[Fe(III)]ethylene-diamine-tetra-acetate.$4H_2O$, for which single crystal linewidths vary from twelve to several hundred Gauss depending on field orientation.[138] An important linewidth contribution may arise from random variations in spin-Hamiltonian parameters for molecules in different local environments of a glassy matrix. For small variations it may be sufficient to perform a convolution of a calculated spectrum with a Gaussian broadening function in order adequately to reproduce an experimental lineshape. This is the approach used in generating Figure 3.4 and whilst the result is a reasonable fit to the observed spectrum the method can only be considered approximate. When random structural distribution produces a large fluctuation in one or more parameters, as is often the case in glasses, it has frequently proven useful in lineshape simulation calculations to vary these parameters according to a Gaussian or skewed Gaussian distribution and sum the individual component spectra resulting from the resonance equation.[139 & eg. 140-143]

In the present case for $\lambda \sim 0.15$ most of the line positions are quite independent of D for values ranging from 1.0 to 3.0 cm^{-1}. However, as can be seen from Figure 3.3, when λ is centred on 0.13, but ranges by $\pm$ 0.05, the resonances contributing to the trough at

$g' \sim 2.9$ vary over some 1000 to 2000 Gauss, whilst the two low field lines change position relatively little.

If then this is the source of the line broadening to high field, a more physically reasonable simulation model for the $[Fe(S_2-o-xylyl)_2]^-$ spectrum would involve summation of calculated lineshapes resulting from a Gaussian-weighted distribution in λ. Returning to Figure 3.3, the results of performing such a calculation with 0.055 half-height half-width variation in λ centred at 0.13 can be seen in comparison to the experimental spectrum (once again an isotropic $g' = 4.3$ resonance has been added in as well). Individual component spectra for lower and middle doublets at any given value of λ were generated in a similar manner to that described above for the fixed-λ simulation of Figure 3.4. The lineshapes for the fictitious $S = 1/2$ resonances were generated by a conventional all angles (θ, ϕ) summation, the detailed equations for g and transition probability as functions of $\underline{g}$, θ and ϕ being given in Section 6.3 (routine EPRPOW). The program " EPR" [144] used to generate the $\underline{g}'$ values for lowest and middle doublets, which has a more rigorous approach to transition probability, is also capable of integrating θ and ϕ for an octant using an icosahedral subdivision approximation, but could not be employed here due to its use of some two orders of magnitude more computation time for comparable orientational resolution. However, the transition probabilities for principal-axis resonances given by the equation used in " EPRPOW" $(g_x^2 + g_y^2$ along z, etc.) are seen to compare quite favourably to those from the program " EPR" (Table 3.1).

TABLE 3.1. Transition Probabilities Derived from the Programs " EPR"

and " EPRPOW" Using the Parameters λ = 0.13, D = 2.0 cm^{-1}

ν = 9.12 GHz Normalised to 10 for the Largest Probability.

Transition	Field	$\underline{g}'$	Transition Probability	
			" EPR"	" EPRPOW"
1-2 x	2129.8	3.058	9.08	9.13
1-2 y	771.4	8.444	1.47	1.45
1-2 z	4238.2	1.537	10.0	10.0
3-4 x	2309.4	2.821	4.56	4.55
3-4 y	2581.3	2.534	4.70	4.75
3-4 z	1182.5	5.509	1.79	1.78
5-6 z	653.9	9.962	0.003	-

The true $\underline{g}$ tensor was set isotropically at 2.0 for generation of

the principal-axis resonance fields.[144] Use of values such as

g_x = 2.013, g_y = 2.034 and g_z = 2.030 found previously for FeS$_4$

coordination,[82] might be considered more appropriate, but cause a

deviation from the resonance positions used here which is less than

2% at any field.

Choice of a physically reasonable linewidth anisotropy equation

is difficult, as is often the case. It is still necessary to use

considerably larger linewidths at higher fields for the coarse λ

interval employed. If residual linewidth is considered to arise from

a g' distribution, $\Delta g'$, then the resonance equation $h\nu$ = $g'\beta H$ predicts

a field incrementing linewidth factor $\Delta H \propto \Delta g' H^2$.[138] Although it is

difficult to account for the origin of an additional uniform

variation in g', the relevant linewidth-dependency relationship,

$\Delta H = \Delta H_0 + \Delta H_1 . H^2$, is conveniently simple and leads to a complete

description of linewidth, for all component spectra, which involves

only two parameters.

Having generated a file of 66 lineshapes corresponding to lower

and middle doublet resonances for increments of 0.01 in the range

$0.01 \leq \lambda \leq 0.33$, it was possible fairly simply to add them in many

trial Gaussian-weighted λ distributions. Boltzmann distribution

weighting between lower and middle doublets was made, corresponding

to 100 K and a zero field splitting of 4.6 cm^{-1} (see later), and all

66 spectra were height-normalised to the inverse of their S = 1/2

g-corrected integrated intensities. The whole process was repeated

for several different values of the linewidth coefficients and thus

involved a total of four variable parameters; ΔH_0, ΔH_1 and the λ

distribution variables λ_0 and $\Delta \lambda_{\frac{1}{2}}$ (expectation and half-width

respectively).

An idea of the variation in component lineshape can be obtained

from Figures 3.5 and 3.6 which correspond to the parameters used for

the simulation in Figure 3.3.

Figure 3.7 shows resultant spectra simulated with $\Delta \lambda_{\frac{1}{2}} = 0.05$ for

λ_0 = 0.11, 0.12, 0.13, 0.14, and 0.15, with ΔH_0 and ΔH_1 constrained

to give a line-width of 60 Gauss at a field of 1000 Gauss such that

the low-field peaks have reasonable widths. It can be seen that the

general lineshape form is reproduced for a wide range of ΔH_0 , ΔH_1

coefficients, thus the choice of values for these parameters whilst
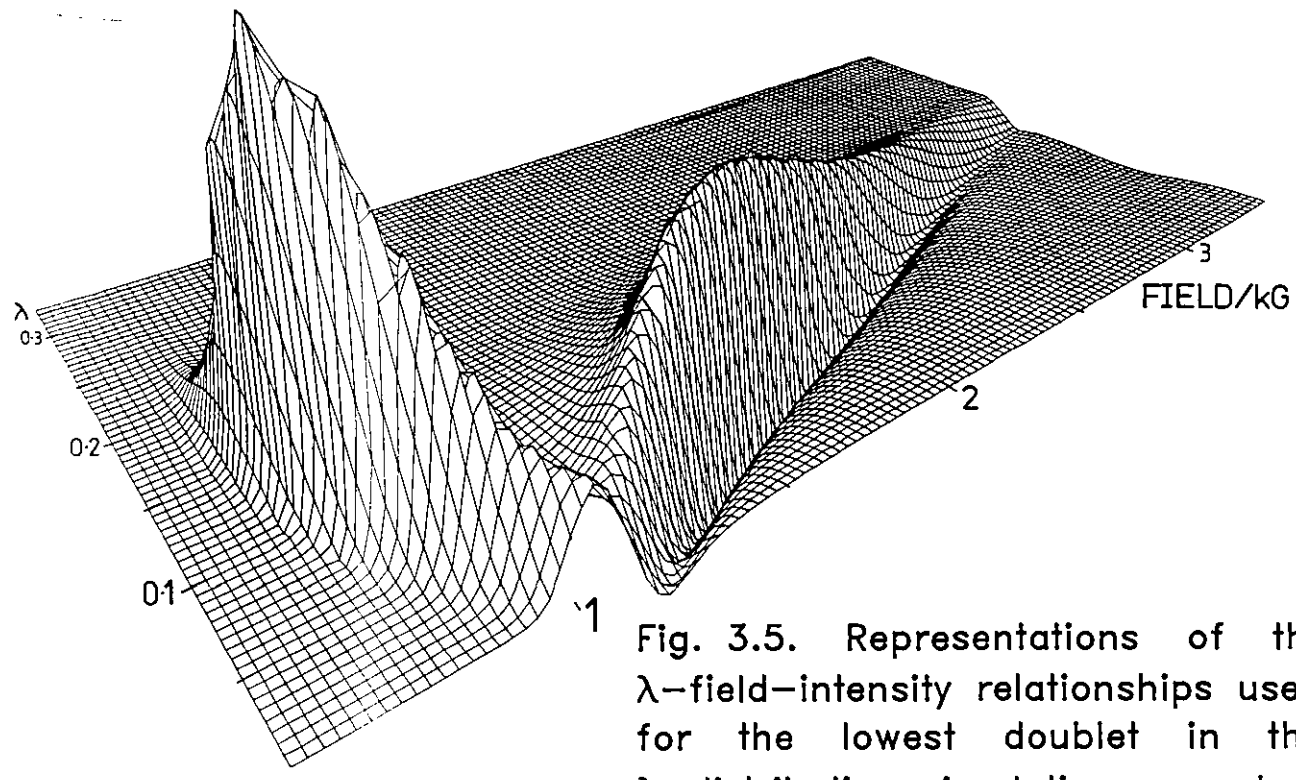
Fig. 3.5. Representations of the λ−field−intensity relationships used for the lowest doublet in the λ−distribution simulation procedure.

INTENSITY−NORMALISED

GAUSSIAN DISTRIBUTION

$\lambda_0 = 0.13 \quad \Delta\lambda_{1/2} = 0.055$

HEIGHT−NORMALISED
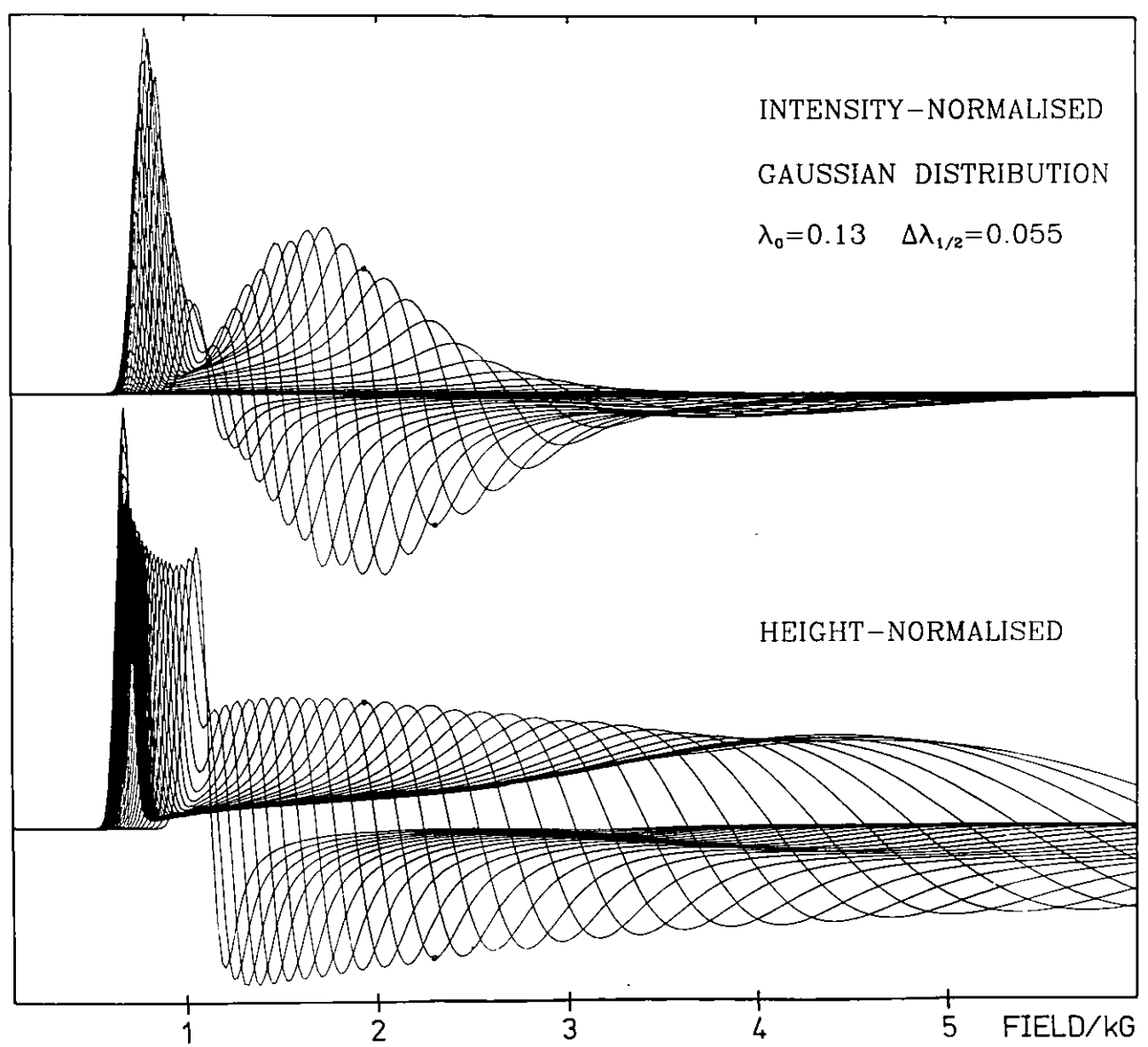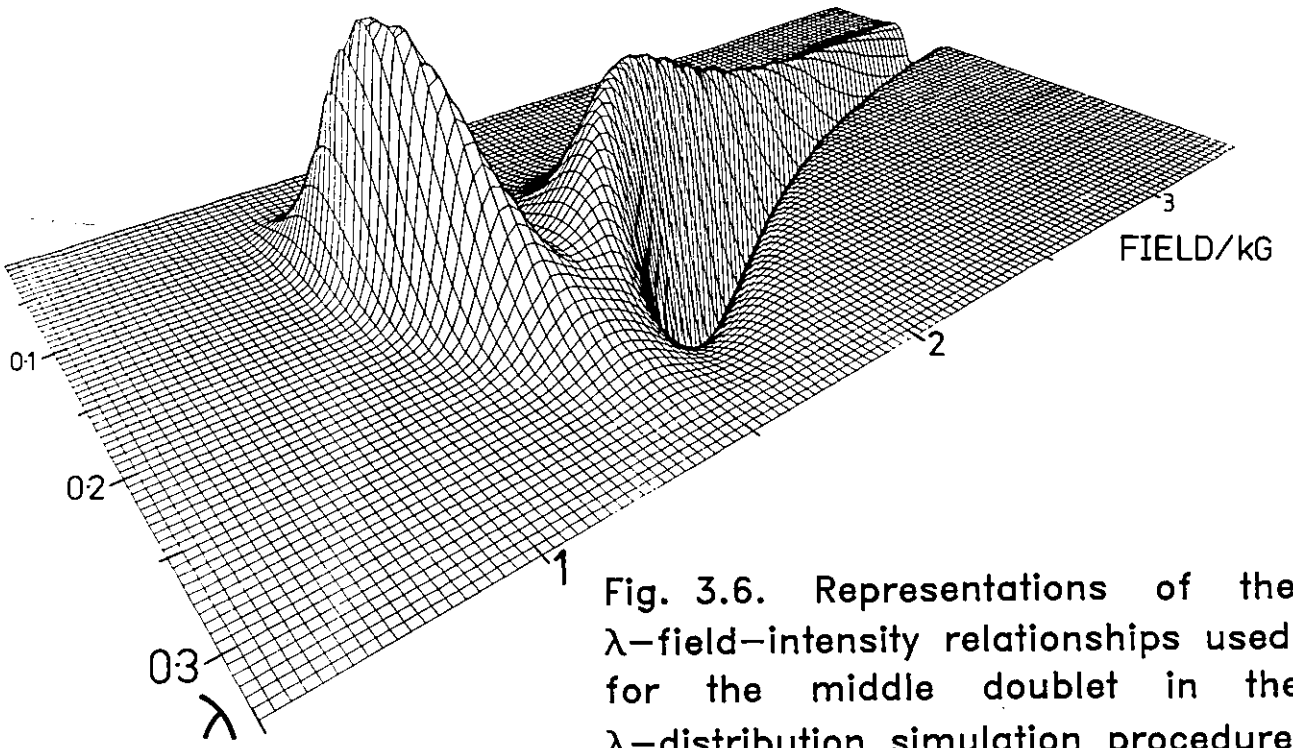
Fig. 3.6. Representations of the λ–field–intensity relationships used for the middle doublet in the λ–distribution simulation procedure.

FIELD/kG

INTENSITY–NORMALISED

GAUSSIAN DISTRIBUTION

$\lambda_0 = 0.13 \qquad \Delta\lambda_{1/2} = 0.055$

HEIGHT–NORMALISED

FIELD/kG

1 2 3

λ_0

0.11

4 5 6

0.12

7 8 EXPT CALC 9

0.13

$\dfrac{H}{kG}$

1.0   2.0   3.0

10 11 12

0.14

13 14 15

0.15

$\Delta H_{1/2}(\,G\,)=60H^2(\,kG\,)$ $\Delta H_{1/2}=30+30H^2$ $\Delta H_{1/2}=50+10H^2$
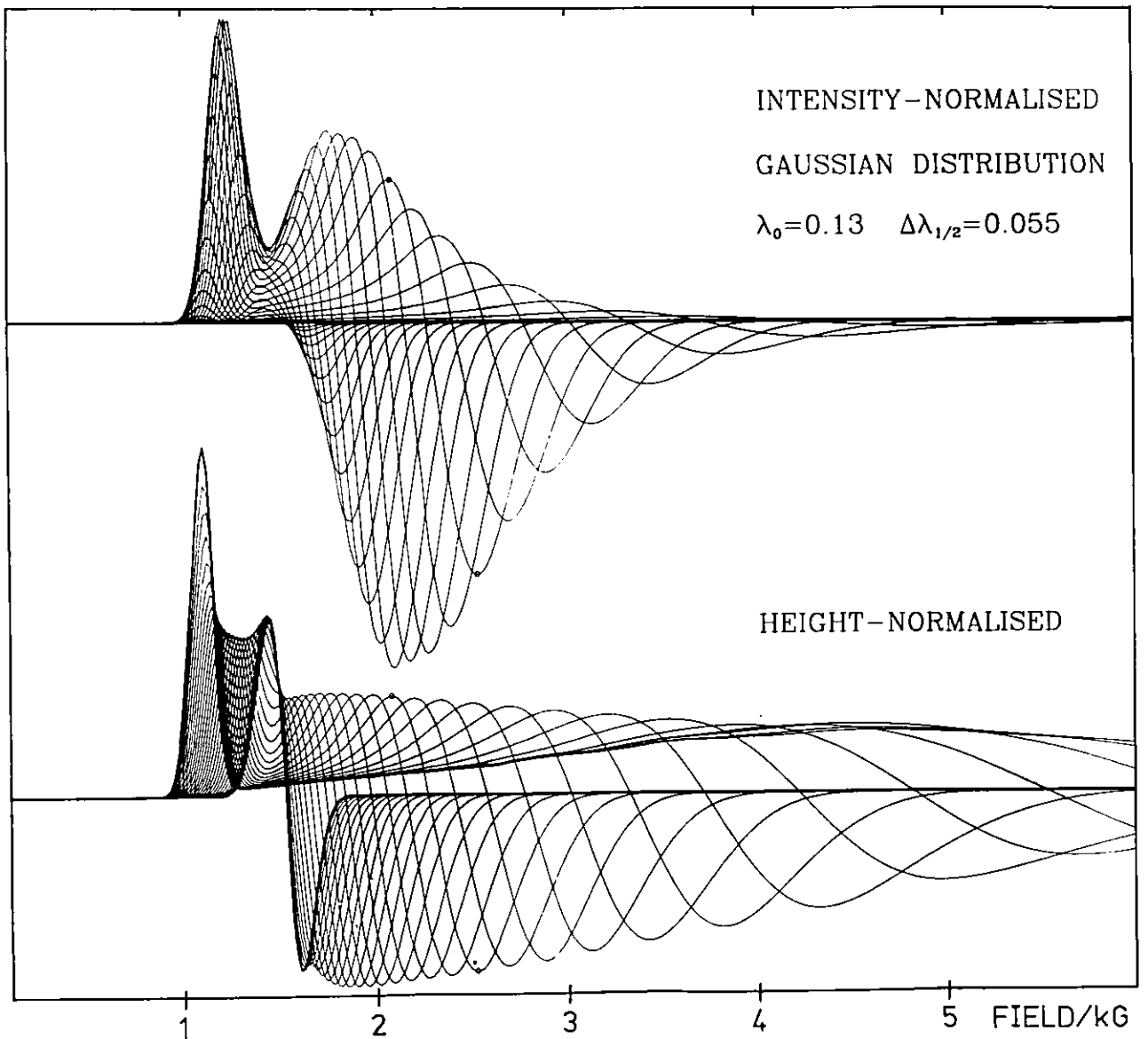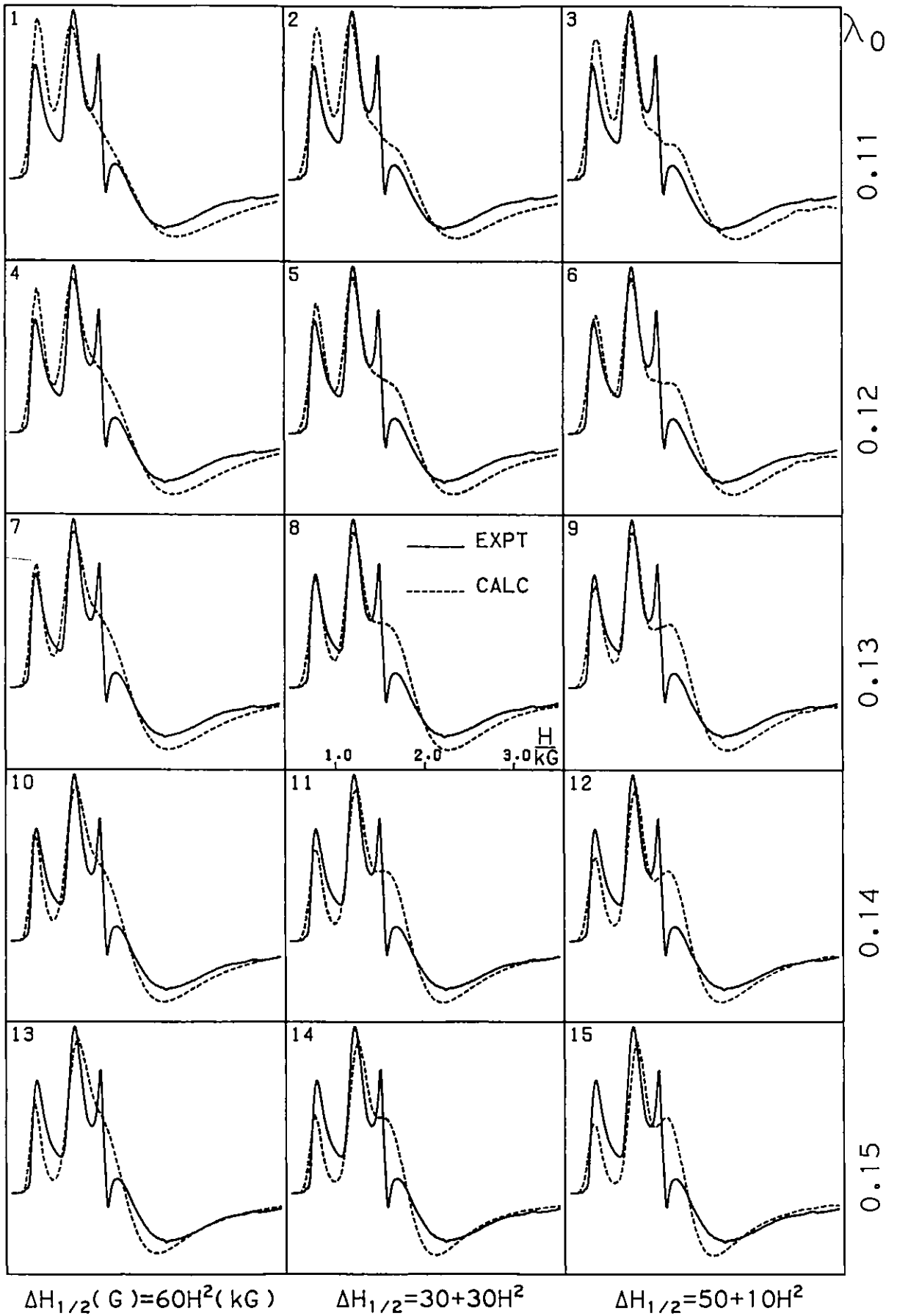
Fig 3.7 Trial simulations involving five different λ−distribution centerings ($\Delta\lambda_{1/2}=0.05$) and three linewidth formulae.

$$\Delta H_{1/2}(\text{G})=30+30H^2(\text{kG}) \qquad \lambda_0 = 0.13$$

$$\Delta\lambda_{1/2} \quad 0.040 \qquad\qquad 0.055 \qquad\qquad 0.070$$
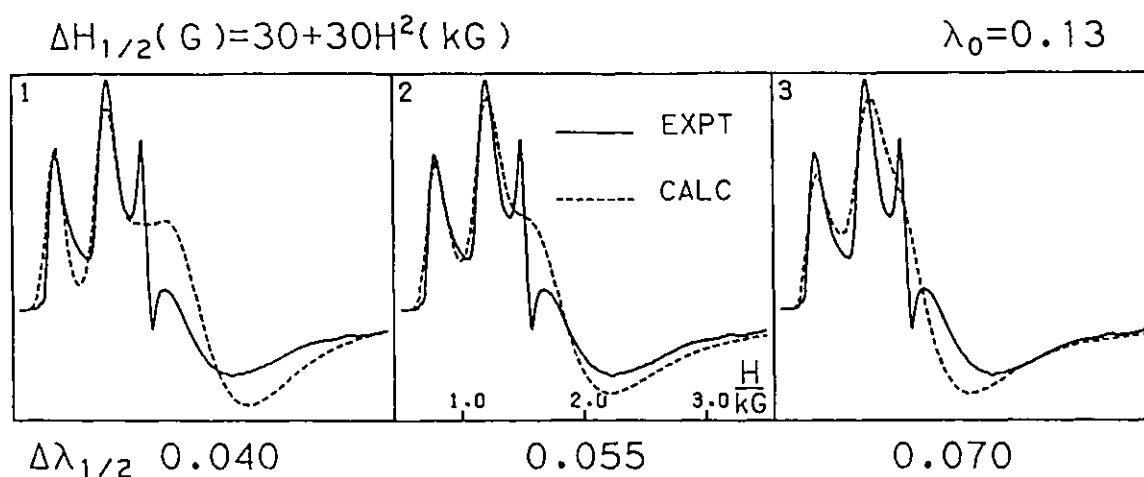
Figure 3.8. Trial simulations involving three different λ-distribution half-widths ($\lambda_0 = 0.13$).

being necessarily arbitrary is not too crucial. The fit of the calculated lines to the experimental on the other hand is seen to be a sensitive function of λ_0, best fits being obtained for $\lambda_0 = 0.13-$ 0.14. It was found necessary to restrict $\Delta\lambda_{\frac{1}{2}}$ to between 0.04 and 0.06 (see for example, Figure 3.8). Such a broad spread in E/D is not without precedent, a variation of $\pm$ 0.04[145] or distribution of width 0.05[146] having been proposed for example for Cr^{3+} in an alumino-phosphate glass.

The closest approach to the experimental spectrum is that in Figure 3.3 where the distribution of principal-axis resonance positions resulting from the Gaussian variation in λ is also shown.

The simulation method shows that the assumption of a λ distribution as the origin of the large high-field linewidths is probably correct in that the experimental lineshape is matched quite well using greatly reduced component spectral linewidths compared with the previous fixed-λ convolution method. An attempt has been made in formulating the

simulation procedure to minimise the number of variable parameters

involved and to this extent better reproduction of the experimental

spectrum might be achieved using more sophisticated linewidth aniso-

tropy or λ-distribution formulae.

Recently the EPR spectrum of desulforedoxin has been described.[147,122]

This protein, isolated from the sulphate-reducing bacterium

Desulfovibrio gigas, with one iron atom and four cysteines per monomer

unit has visible and Mössbauer general spectral features resembling

rubredoxin, but indicative of a higher coordination symmetry at the

iron. The X-band EPR spectrum shows an intense and relatively narrow

peak at $g' = 7.7$, a smaller feature of similar width at $g' = 5.7$, a

broad derivative line at $g' = 4.1$ and very broad minimum at $g' = 1.8$.

These results have been interpreted in terms of $\lambda = 0.08$ for which

resonances are predicted at $g' = 4.09$, 7.70, 1.80 and $g' = 1.87$, 1.74,

5.79, from lower and middle Kramers doublets respectively. Thus, this

protein has an EPR spectrum quite different to rubredoxin, and the

spectrum for $[Fe(S_2-o-xylyl)_2]^-$ is intermediate between the spectra

found for these two $Fe(III)S_4$ proteins. The distribution of line-

widths in desulforedoxin also takes a similar form to that observed

here for $[Fe(S_2-o-xylyl)_2]^-$.

3.3. EPR at Q-Band.

At low fields the solution Q-band (36 GHz) spectrum for

$[Fe(S_2-o-xylyl)_2]^-$ shows two maxima at $g' = 7.8$ and 5.3, and a broad

crossover at $g' \approx 3.0$ (Figure 3.9). No sharp isotropic resonance is

observed around 6 kG. Predicted fields at Q-band for $S = 5/2$ with

$D = 2.0$ cm^{-1} are given in Figure 3.9. Analysis of the experimental

spectrum follows as for the X-band lineshape using these curves.
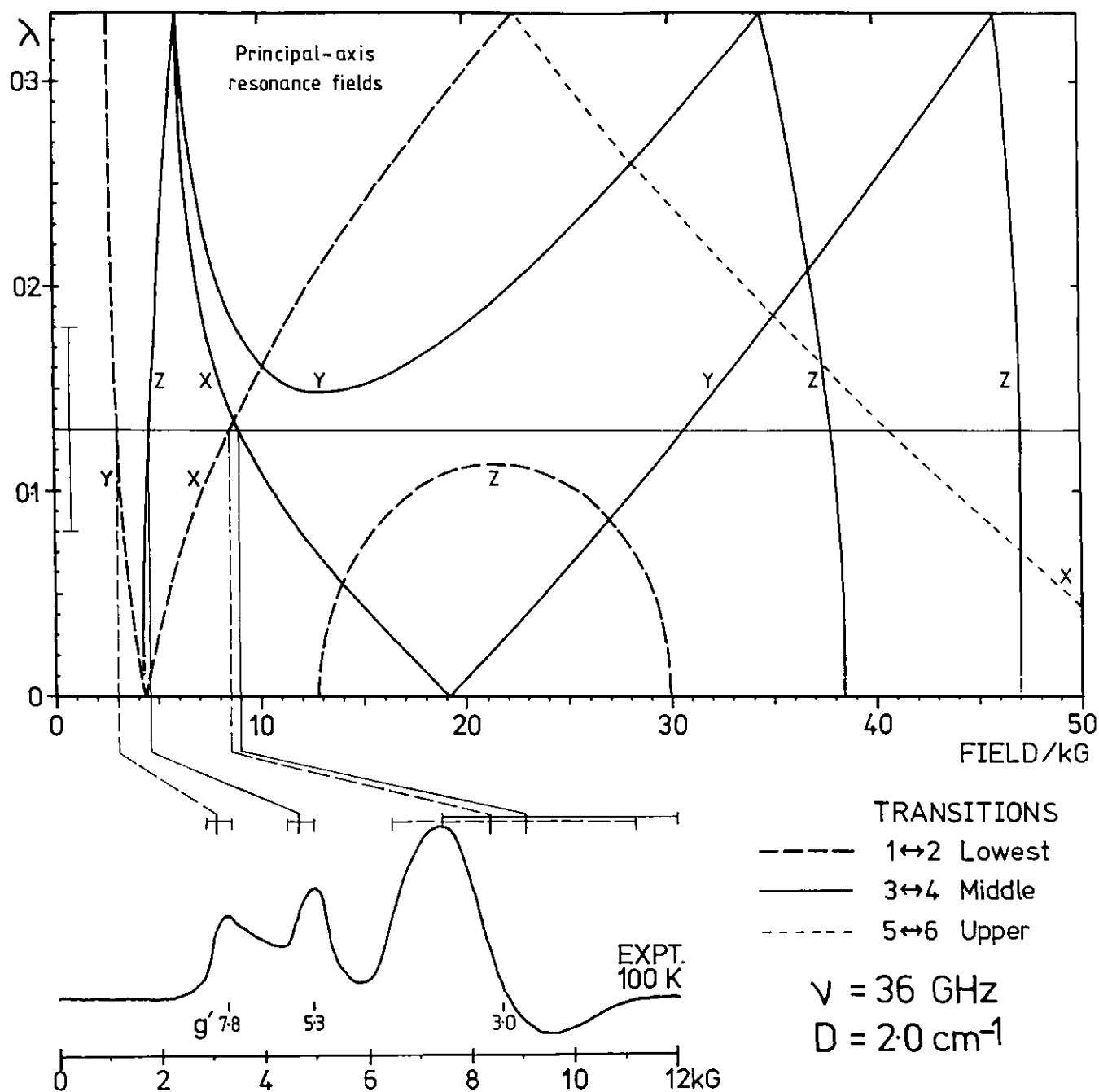
Fig. 3.9 Predicted principal—axis resonance fields for $D=2.0cm^{-1}$, $\nu=36GHz$, $\lambda=0$ to $1/3$ compared with the experimental Q—band spectrum for a frozen solution of $Et_4N[Fe(S_2-o-xylyl)_2]$ in $3/1$ DMF/CH_2Cl_2

The two lowest-field lines correspond to those in the X-band spectrum
and are due to respective y and z orientations for lowest and middle
doublets. Resonance-fields for these transitions are relatively
independent of D or λ, but the position and width of the peaks in
the experimental spectrum are quite consistent with a distribution
in λ centred around 0.13. The broad derivative shaped absorption
at about $g' = 3$ is considered to arise mainly from the x-orientations
for resonance involving the first and second pairs of energy levels.
As at X-band, H vs. λ curves for these resonances are seen to cross
close to $\lambda = 0.13$ (Figure 3.9). Considering the variation $\lambda = 0.13$
$\pm$ 0.05 their Q-band resonance fields span the interval 6 to 12 kG and
quite adequately account for the width of the $g' = 3$ spectral feature.
It is indeed a little surprising that this feature is so well resolved
compared with the X-band spectrum considering the large λ-distribution
width invoked there. λ-dependency of the remaining orientations,
z and y respectively, for resonance in the first and second energy
level pairs, is however more complicated at the higher frequency.
For a λ-distribution of the magnitude suggested in the previous
section, the differences evident in the λ-H plots of Figures 3.3 and
3.9 may well account for the disparity in spectral lineshape at
X and Q-band frequencies. This could only be demonstrated in detail
by performing a simulation procedure for Q-band similar to that employed
at X-band. In view of the complexity of the Q-band resonance positions
for $\lambda = 0.13 \pm 0.05$ this would be rather more difficult to undertake.
Due to local instrumentation difficulties it has not proven possible
to measure the Q-band spectrum above ca. 10 kG. However, taking into
account the factors of large anisotropy, appearance of a resonance
along one principal direction only, or wide field variation for small

changes in λ, it is unlikely that any further peaks would be observed
at fields greater than the maximum used in the present measurements.

3.4. Determination of D.

Measurement of the X-band EPR spectrum of $[Fe(S_2\text{-}o\text{-}xylyl)_2]^-$ over
the temperature range 5-100 K enables an estimation of the value of
D. It is important to know the temperature of the sample accurately
and in addition to the modified Au/Fe-Chromel thermocouple built into
the cryostat beneath the sample space, two additional sensors were
employed; a further similar thermocouple constructed from very fine
wire was spiralled some 50 times around the sample tube and terminated
in the sample just outside the EPR cavity, and a thin quartz tube
containing a 3 mM aqueous solution of Cu-EDTA was frozen into the
solution of $[Fe(S_2\text{-}o\text{-}xylyl)_2]^-$. The temperature available from the
intensity of the $g_\perp$ part of the Cu^{2+} spectrum via the Boltzmann
population relationship, $I \propto (1 - e^{-h\nu/kT})$, was standardised at 77.3 K
to that from the Au/Fe-chromel sample thermocouple by obtaining a
spectrum with the emf of the latter balanced to zero in reference to
a second junction in liquid nitrogen. Under the conditions used, the
Cu^{2+} lineshape is invariant and (I) was taken as the height of the
derivative shaped $g_\perp$ feature. Whilst over the range of application
both sensors gave temperatures generally agreeing within 5%, that for
the Cu^{2+} signal was considered better to represent the actual sample
temperature in that it originated from the entire region of the frozen
solution giving rise to the Fe(III) EPR spectra.

Denoting the zero field splitting between middle and lowest

doublets by Z_1 and highest and middle doublets by Z_2 the intensity

(I) of EPR spectral features relating to the lowest doublet is given

by E3.3, where C is a proportionality factor reflecting instrumental

conditions and the arbitrary choice of intensity measurement.

$$I = C.(1 - e^{-(h\nu/kT)})/(1 + e^{-Z_1/kT} + e^{-(Z_1 + Z_2)/kT}) \qquad (E3.3)$$

For a zero field splitting of the present magnitude there is negligible

deviation of fractional doublet populations given by the denominator

term in E 3.3 from the more exact expression involving Boltzmann

distribution between the six spin-state energy levels at each resonance

field.

In the purely axial ($\lambda = 0$) and fully rhombic ($\lambda = 1/3$) cases

simple expressions are available relating Z_1, Z_2 and D as shown in

Figure 3.1. More generally, substitution for the $\widehat{S}_x{}^2$, $\widehat{S}_y{}^2$, $\widehat{S}_z{}^2$ spin

matrices in E3.2 and subtraction of the energy term ω from the diagonal

elements leads to the secular determinant which is set equal to zero

and may be reduced to equation (E3.4) with doubly degenerate solutions.

$$\begin{array}{cc} & \begin{array}{ccc} |\pm 5/2\rangle & |\mp 3/2\rangle & |\pm 1/2\rangle \end{array} \\ \begin{array}{c} |\pm 5/2\rangle \\ |\mp 3/2\rangle \\ |\pm 1/2\rangle \end{array} & \left| \begin{array}{ccc} \dfrac{10}{3} - \dfrac{\omega}{D} & & \lambda\sqrt{10} \\[2mm] & -\dfrac{2}{3} - \dfrac{\omega}{D} & \lambda\sqrt{18} \\[2mm] \lambda\sqrt{10} & \lambda\sqrt{18} & -\dfrac{8}{3} - \dfrac{\omega}{D} \end{array} \right| = 0 \end{array}$$

$$(E3.4)$$
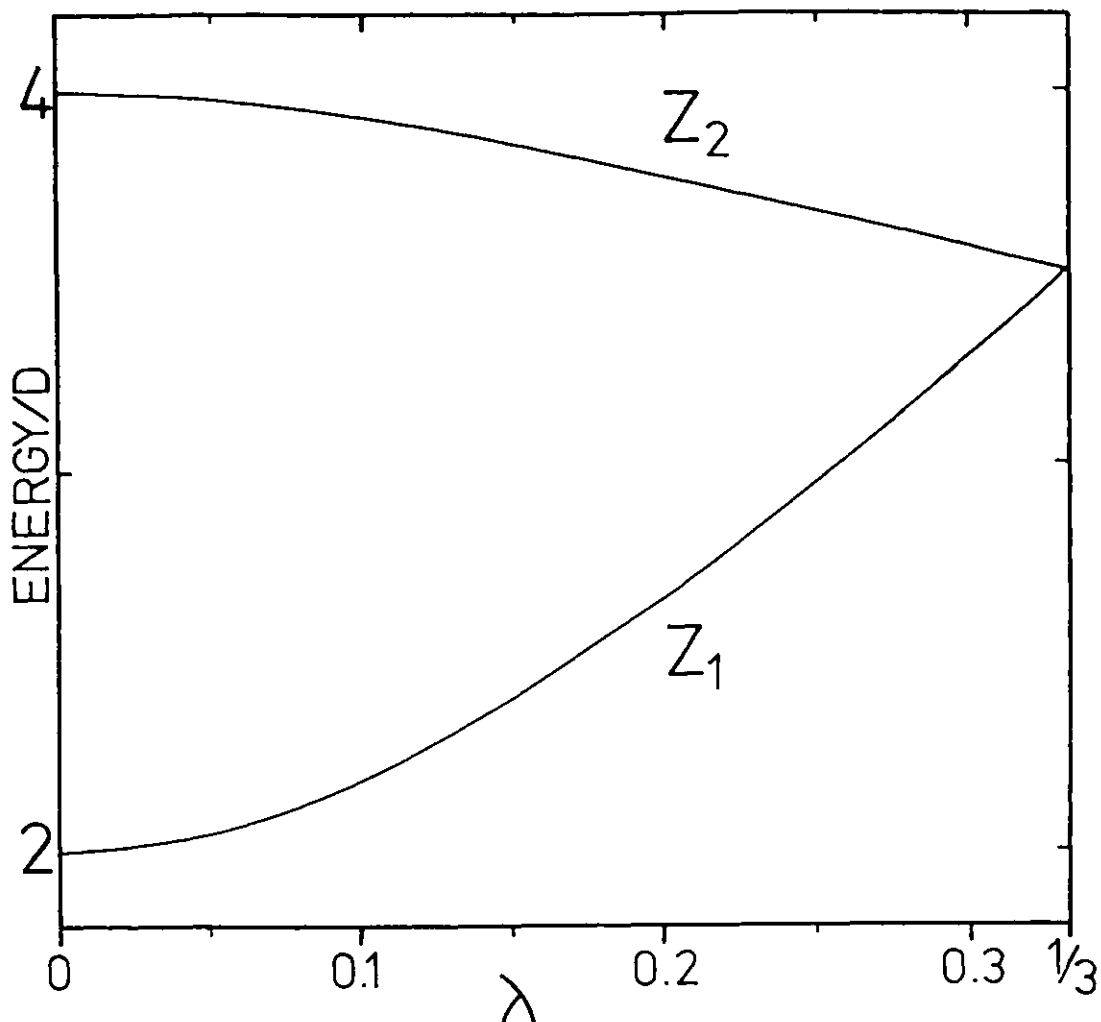
Figure 3.10. λ-Dependence of zero-field splitting between lowest

and middle and between middle and upper Kramers

doublets.

Expansion of this expression to a cubic in ω followed by numerical

trigonometric solution yields three real degenerate spin-state

relative energies, as multiples of D. The λ-dependence of the

energy separations Z_1 and Z_2 for the doublets is shown in Figure

3.10. In this way it becomes possible to evaluate E3.3 in terms

of the more directly useful parameters λ, D and C.

These three variables have been used in a least squares fit

of equation E3.3 to the experimental data for the g' = 8.4 peak

plotted as $I/(1 - e^{-(h\nu/kT)}).C$ against inverse temperature. The

g' = 8.4 line has temperature invariant linewidth to low field
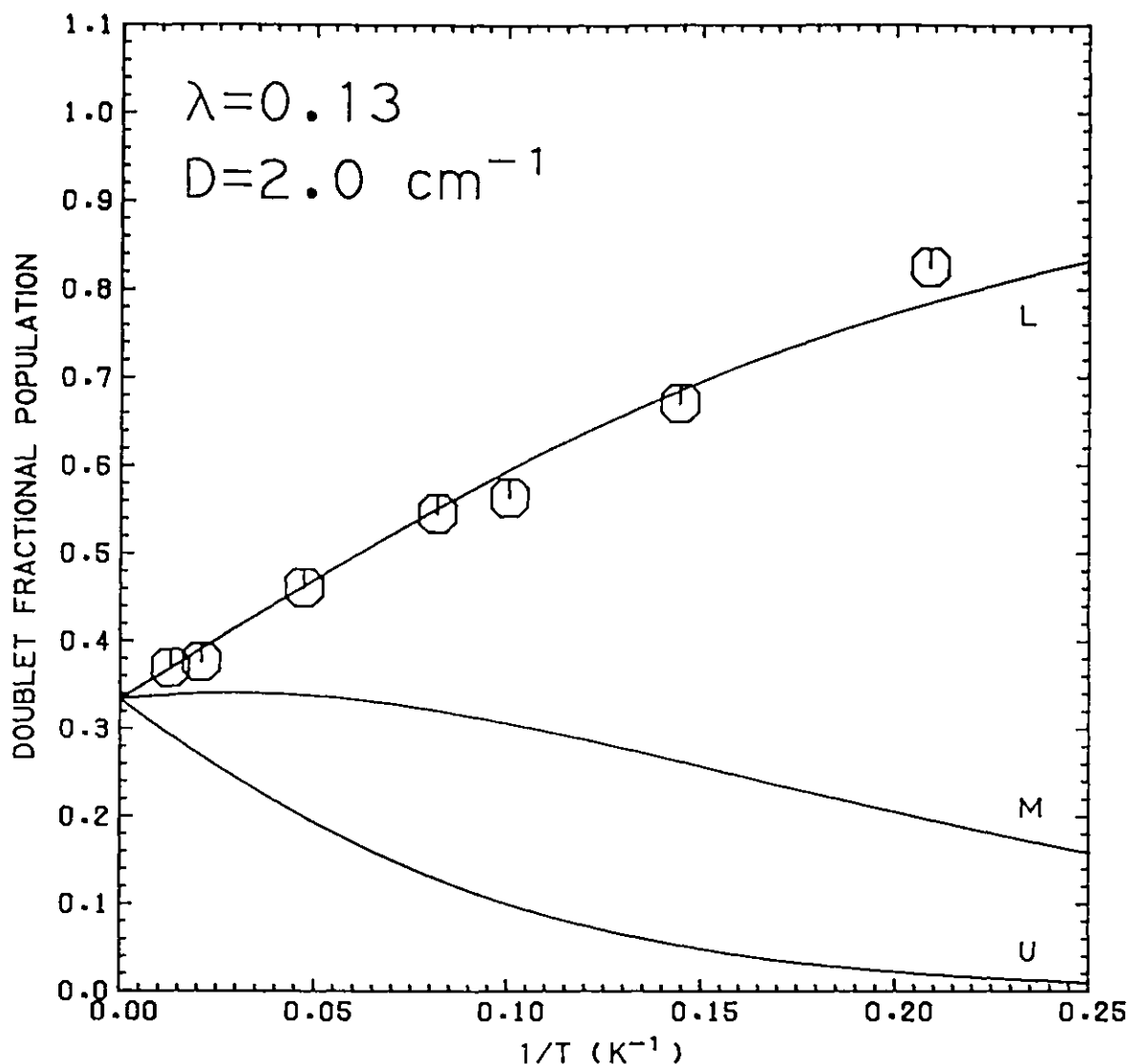
Figure 3.11. Temperature dependence of the fractional populations for
the three S = 5/2 doublets (L = lower, M = middle, U =
upper) with D = 2.0 cm^{-1} and λ = 0.13 compared with
experimental normalised intensities for the g' = 8.4
peak of [Fe(S$_2$-o-xylyl)$_2$]$^-$.

of its maximum and its height was taken directly for I. Standard

deviation of the data from E3.3 is insensitive to λ over the meaning-

ful range 0 $\leq$ λ $\leq$ 1/3 and this parameter was removed as a variable

being assigned the value 0.13 consistent with the interpretation of the

resonance field positions and simulation procedures given above. The

best fit with D = 2.0 cm^{-1} is shown in Figure 3.11. C has been chosen

in such a way that the ordinate is the fractional population given by

the denominator of E3.3. Fitting the data for fixed values of D

while still varying C shows that an accuracy of around -0.4, +0.7

is appropriate to D, compared with a 5% standard deviation for the

best fit. In view of the λ distribution implicit in the lineshape

analysis given in the previous section, the peak-intensity temperature

dependence must be somewhat more complicated than the analysis under-

taken. Taking into account the possible range $\lambda = 0.13 \pm 0.05$ by

refitting the data for $\lambda = 0.08$ and 0.18 whilst varying D and C,

leads to an increase in the estimated error such that $D = 2.0 \begin{smallmatrix} +0.8 \\ -0.5 \end{smallmatrix}$.

For the g' = 5.4 line the intensity temperature product

appears roughly constant over the range of the present measurements,

although it is more difficult accurately to assess a baseline for this

peak, particularly at higher temperatures. Figure 3.11 shows that for

the λ and D values quoted the fractional population of the middle

Kramers doublet is expected to be fairly constant above 10 K but

should drop off at lower temperatures.

From a theoretical fit of magnetisation data for $Et_4N[Fe(S_2-o-$

xylyl)$_2$], Frankel et al.[118] have obtained a value of $D = 1.5 \ cm^{-1}$

when assuming $\lambda = 1/3$. For $\lambda = 0.13$, D becomes $2.3 \ cm^{-1}$, though this

would probably be slightly lowered if Z_1 were to be reevaluated

assuming this λ.

The present estimate of D is also compatible with the 1.76 and

$1.89 \ cm^{-1}$ quoted for Rd_{ox}[125,135] and $2.2 \pm 0.3 \ cm^{-1}$ obtained for

desulforedoxin from Mössbauer measurements.[147]
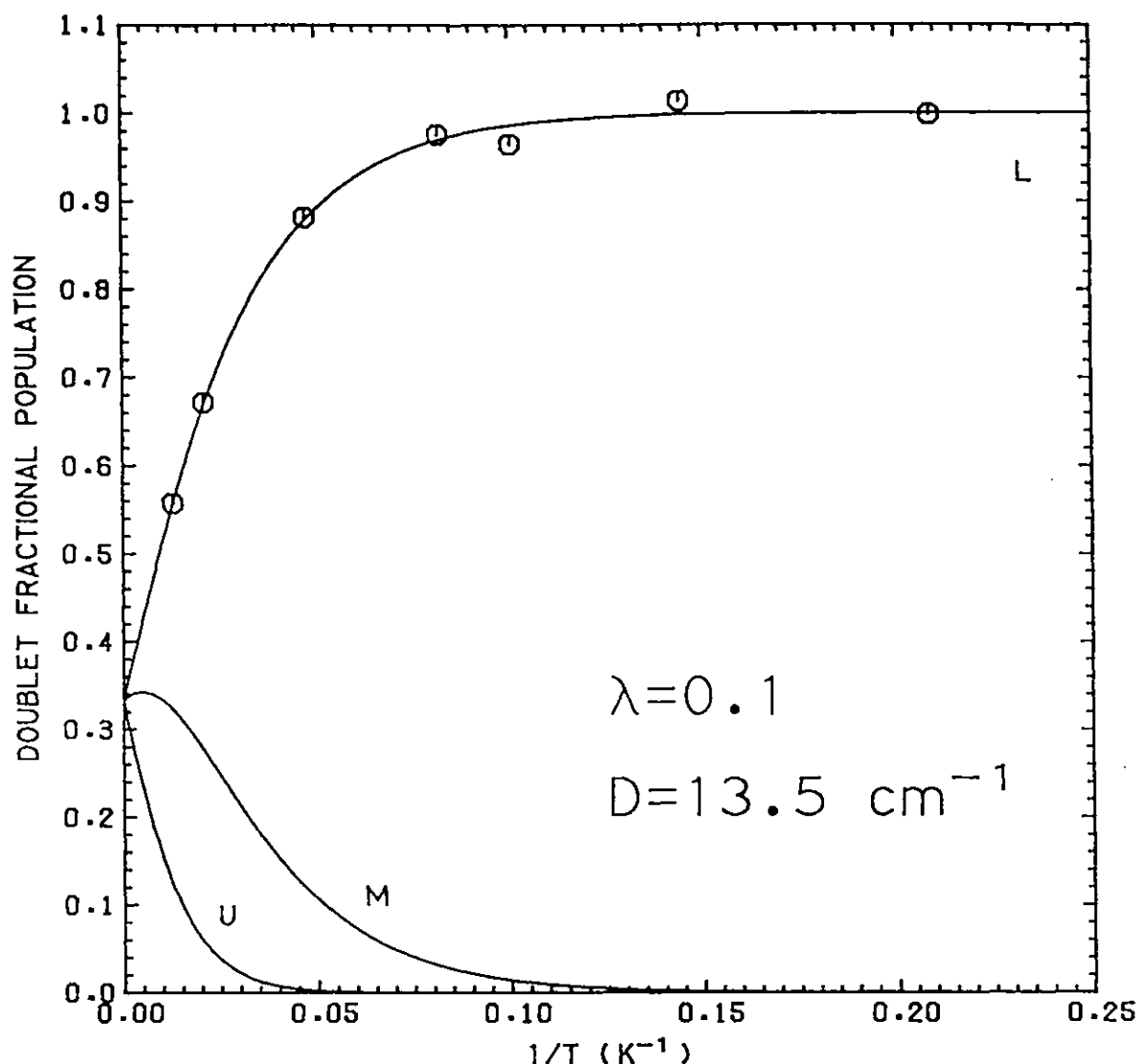
Figure 3.12. Temperature dependence of fractional doublet populations

for the three S = 5/2 doublets with D = 13.5 cm^{-1},

λ = 0.1, compared with experimental normalised intensities

of the sharp g' = 4.3 resonance for $[Fe(S_2-o-xylyl)_2]^-$.

3.5. Origin of the Sharp g' = 4.3 Resonance.

Figure 3.12 shows the temperature variation of the g' = 4.3 peak-intensity in EPR spectra for a $DMF/CH_2C\ell_2$ (3:1) solution of $[Fe(S_2-o-xylyl)_2]^-$. Strong deviation from Curie-law behaviour is observed down to about 10 K after which the curve levels out to the expected horizontal. Using a least squares fitting procedure similar to that described for the g' = 8.4 peak, good agreement with the data is found for D = 13.5 $\pm$ 2 cm^{-1}, Z_1 = 30 $\pm$ 4 cm^{-1} (curve fitting standard deviation 2%) and

with $\lambda = 0.10$, assuming the signal to arise from the lowest doublet

of a Fe(III) species (Figure 3.12). Very similar zero-field splittings

result when λ is constrained to any given value in the range 0 to 1/3

($\lambda = 0$, $Z_1 = 29$ cm^{-1}; $\lambda = 1/3$, $Z_1 = 34$ cm^{-1}).

The ratio of the intensity at $g' = 4.3$ to that for the peak at

lowest field has been found fairly constant when studying solutions

prepared from different samples of the same batch of solid or from

four separate $Et_4N[Fe(S_2\text{-}o\text{-}xylyl)_2]$ syntheses. It would be reasonable

to expect some variation in the ratio if the sharp signal arose from an

impurity. On the other hand, some considerable variation in the intensity

ratio is to be found on comparing spectra obtained with different

solvent systems. Solvent mixtures which solidify in a vitreous state

on cooling, all result in spectra similar to that described for

3:1 $DMF/CH_2C\ell_2$. Some of the solvents which crystallise strongly lead

to a more intense $g' = 4.3$ line, although it is difficult accurately to

assess the situation when the spectrum is also broadened. One possible

explanation of the line is, then, that it results from some aggregation

of the iron-centres, since a strong $g' = 4.3$ line is also observed for

the pure solid. The vitreous samples, however, appear quite trans-

parent showing no signs of crystallisation likely to lead to

precipitation of solid.

If the sharp line results from another species it must arise from

a ground state having an excited state some 30 cm^{-1} higher in energy.

This rules out a species having high λ and D and giving an isotropic

$g' = 4.3$ resonance from its middle Kramers doublet, as such a signal

would be thermally depopulated at low temperatures. An intermediate

spin (S = 3/2) Fe(III) complex with axial symmetry could give rise

to a cross-over line at g' $\sim$ 4 arising from a ground state doublet,

and also possess a well separated higher lying doublet. Such a

$g_\perp$ $\sim$ 4 feature would, however, be broad[148,149] and have an asym-

metric shape connected to a further peak at $g'_{||}$ $\sim$ 2. Thus, this

does not provide a reasonable explanation of the isotropic resonance

observed.

Another potential explanation for the g' = 4.3 line arises from

considering random variations in the spin-Hamiltonian parameters of

the kind already invoked to explain the large high-field linewidths

observed in the spectrum under consideration. Peterson et al.[150,151]

have analysed the situation where the distribution of principal-axis

resonance fields is so large that they overlap, that is become equal.

One intriguing possible consequence with reference to high-spin ferric

characterised by an axial $\underline{D}$ tensor is that resonance spectra might be

dominated by a large " spike" at g' $\sim$ 4, normally considered indicative

of fully rhombic $\underline{D}$ symmetry. The notion is that the $g'_\perp$ $\sim$ 6 and $g'_{||}$ $\sim$ 2

axis-resonance positions from the lowest doublet would be spread out

due to their large anisotropy and the $g_\perp$, $g_{||}$ variation, but that from

a small number of molecules in the distribution having $g_\perp$ $\sim$ $g_{||}$ an

isotropic, and consequently strong, resonance would result midway

between g' = 2 and g' = 6. In a replying letter, Jellison, et al.[152]

have critically described the statistical distributions assumed by

Peterson et al. as hypothetical in view of their lack of attempted

detailed curve fitting for simulated and experimental spectra. Griscom

too has stressed the necessity of using rigorously calculated transition

schemes in assessing the correlation of distribution functions for the variables.[146] Can then a variation in $\underline{D}$ tensor symmetry lead to g' isotropy? Gibson[153] and Griscom[154] have both briefly discussed the specifically axial case by an inspection of D/H plots[132,133] and have concluded the absence of negative $g'_\perp$, $g'_\parallel$ correlation necessary for g' ∿ 4 spiking. Brodbeck[155] has presented a detailed analysis of the angular variation of g' values for S = 5/2, as dependent on D and E. No negative g' correlation is found for lower or upper doublets but in the case of a distribution in λ containing the value λ = 1/3, the middle doublet might give a g' = 4.3 " spike" even though the majority of the molecules are in an environment leading to a near axial $\underline{D}$ tensor. A somewhat obvious conclusion consistent with the early analysis of Castner.[134]

Gibson[153] has suggested that such a distribution in λ for a $\underline{D}$ symmetry slightly lower than fully rhombic might well explain the form of the g' = 4.3 resonance in some Rd_{ox}, for which a sharp line is super-imposed on a broad one.

For $[Fe(S_2\text{-o-xylyl})_2]^-$, where a large λ variation has been suggested to explain the overall lineshape, the identity of some middle doublet principal-axis resonance fields at g' = 4.3 is a distinct possibility. In detail, however, the λ-distribution simulations described in Section 3.2 do not support the production of a sharp line of the shape observed experimentally. Broader spike shaped lines at g' = 4.3 could be produced for certain λ-distributions but the overall fit to the rest of the spectrum would not be retained. It can be seen from Figure 3.6 that the contribution at λ = 1/3 to the simulated lineshape in Figure 3.3 is negligible.

The intensity of a g' = 4.3 spike produced in the manner described by Peterson et al. would be expected, having its origin in an excited state, to deviate negatively from the Curie-law unless considerable thermal variation in λ-distribution resulted in some anomalous effect. The latter is unlikely in view of the temperature invariant lineshape of the g' = 4.3 signal.

The isotropic resonance from the middle doublet predicted when λ = 1/3, arises at g' = 30/7 (4.286) and very closely approaches the g' = 4.28 measured for the sharp line under discussion. As previously indicated this cannot provide an explanation for the sharp line since this must come from resonance in a ground-state doublet. However, if quartic terms make a significant contribution to the spin-Hamiltonian (E 35) an isotropic g' = 30/7 resonance may be calculated to arise from the ground-state, as originally discussed by Kedzie et al.[156]

$$\mathcal{H} = \beta.\underline{H}.\underline{g}.\hat{\underline{S}} + \hat{\underline{S}}.D.\hat{\underline{S}}$$

$$+ \frac{a}{6}.[(\hat{S}_x^4 + \hat{S}_y^4 + \hat{S}_z^4) - \frac{S}{5}(S + 1)(3S^2 + 3S - 1)]$$

$$+\frac{F}{180}[35 \hat{S}_z^4 - 30S(S + 1)\hat{S}_z^2 + 25 \hat{S}_z^2 - 6S(S + 1) + 3S^2(S + 1)^2]$$

$$\text{(E3.5)}$$

Several analyses have been made of the conditions necessary for an isotropic g-tensor in a high spin d^5 system,[131,157,158] but when permutations of axis systems are taken into consideration only two independent sets of conditions corresponding to g' = 30/7 result, and these are adequately summarised by E3.6 given by Kedzie, et al.[156]

$$(a \pm 3a) - F = 6D \qquad \text{(E3.6)}$$

The latter authors have plotted Eigen-values corresponding to these conditions showing the regions where the doublet with isotropic $\underline{g}'$ tensor is lowest in energy. It is readily apparent that in order for the isotropy relationship (E3.6) to be satisfied the magnitudes of either or both $|a|$ and $|F|$ must be equal to or greater than $|D|$. A high value of $|D|$ is indicated by the temperature dependence for the intensity of the sharp line, and it is difficult to accept that quartic spin-Hamiltonian terms could be as large as would seem to be required, since there is no literature precedent for this. The special relationship between coefficients required by E3.6 would seem to be additionally exceptional. Also the absence of any sharp-isotropic feature at $g' = 4.3$ in the Q-band $[Fe(S_2-o-xylyl)_2]^-$ solution spectrum adds further to the inadequacy of this explanation for its appearance at X-band.

3.6. Conclusion.

The EPR spectrum of a solution of $[Fe(S_2-o-xylyl)_2]^-$ has been analysed in terms of a high D value and $\underline{D}$ symmetry intermediate between axial and fully rhombic with a distribution such that $\lambda_0 = 0.13 \pm 0.01$, $\Delta\lambda_{\frac{1}{2}} \sim 0.05$. From the temperature dependent intensity variation of a feature assigned to resonance in the high spin ferric lowest Kramers doublet, D has been estimated at $2.0^{+0.8}_{-0.5}$ cm^{-1}. This D value is unexceptional for sulphur ligation, but the overall $\underline{D}$ tensor symmetry is higher than expected.

If $\underline{D}$ and coordination symmetries are directly related via the crystal field, then the sulphur ligation in Rd_{ox} must be considered to be more aspherically distorted than in $[Fe(S_2-o-xylyl)_2]^-$. It has

been suggested that such additional distortion might be protein

applied leading to a metastable "entactic" state in accordance with

the hypothesis of Valleeand Williams.[159,160] However, EXAFS[161,162]

and Mössbauer[118] investigations show the simple ferric complex to

have a very similar coordination to that in Rd_{ox}. Raman spectroscopy

shows the FeS_4 vibrational unit in $[Fe(S_2-o-xylyl)_2]^-$ to be of low

symmetry (see Section 4).

Disparity between these results and the EPR must be resolved in

terms of the relative sensitivities of the various observational techniques

to the microsymmetry at the iron. In all cases, it is difficult to

translate available spectroscopic differences into actual structural

differences. Over all, on a somewhat empirical comparative basis,

the coordination symmetry in $[Fe(S_2-o-xylyl)_2]^-$ is considered to

closely approach that in Rd_{ox} but to possess less distortion from

tetrahedral.

The possibility of a change in coordination of $[Fe(S_2-o-xylyl)_2]^-$

on dissolution is discounted on the basis that Raman and Mössbauer

spectra are very similar to those for the solid phase. Additionally,

the solution species shows no solvent dependency of its visible

absorption spectrum, or indeed of its EPR spectrum beyond broadening

and changes in relative intensity of the sharp $g' = 4.3$ line. It would

be interesting to obtain spectra for $Et_4N[Fe(S_2-o-xylyl)_2]$ doped into

a suitable host (possibly the ferrous homologue).

EPR measurements for desulforedoxin[147,122] are noted with interest

as the iron is believed to be bound to the protein by four cysteine

residues as in Rd_{ox}, yet the resonance spectrum is characteristic of an

intermediate rhombicity having λ = 0.08. An EXAFS study has been inititiated to probe more deeply into the details of the iron-site geometry for this protein and the results should be instructive in understanding the disparity in the present spectroscopic results outlined above.

No firm conclusion has been reached concerning the origin of the sharp g' = 4.28 resonance for $[Fe(S_2-o-xylyl)_2]^-$. The proximity of g' to the theoretical g' = 30/7 (4.286) isotropic resonances, predicted in a number of circumstances, cannot be considered accidental, although no corresponding signal is seen at Q-band.

At present $[Fe(S_2-o-xylyl)_2]^-$ remains the only well-defined, isolable, synthetic mono-nuclear ferric tetra-mercapto coordinated species available and it will be interesting to see to what extent its properties extend to future $Fe(III)S_4$ complexes in general.

3.6. Experimental.

3.6.1. EPR Measurements.

The $[Et_4N][Fe(S_2-o-xylyl)_2]$ used for the EPR measurements was recrystallised from acetone. Solutions were filtered through a fine sintered frit prior to freezing in quartz tubes. Measurements ca. 100 K and above were made with a quartz dewar insert, employing flowing precooled nitrogen gas as refrigerant. For the temperature range 5-100 K an Oxford-Instruments ESR 10 Helium-flow cryostat with DTC-2 temperature controller was employed. The ESR-10 Au/Fe-chromel thermocouple was extended in a spiral above the He-nozzle/heater-block in order to obtain a more accurate indication of the temperature just below the sample. It was found that although the ESR-10 cryostat was capable of attaining a temperature of 2 K it could not maintain sufficient stability or a small enough thermal gradient in the sample

to allow the accurate measurement of EPR spectra below 5 K. Similar

experience has been reported by other users of this cryostat.[147,163]

3.6.2. Details of Conditions for Spectra in Figures.

Figure 3.2. At temperature 5 K, Power = 36 dB attenuation from

200 mW, Modulation = 16 G, Frequency = 9.12 GHz.

At temperature 100 K, Power = 6 dB, Modulation =

6.3 G, Frequency = 9.12 GHz.

Figure 3.3. Experimental spectrum is same as the 100 K spectrum

of Figure 3.2.

Figure 3.9. Temperature 100 K, Frequency 36 GHz.

The fractional population temperature-dependency curves of Figures

3.11 and 3.12 were calculated using the FORTRAN subroutine below:

```
      SUBROUTINE EBNC(II1,II3)
C
C......THIS ROUTINE FITS INTO PROGRAM SOS.
C      IT GENERATES A FRACTIONAL-POPULATION VECTOR
C      AS A FUNCTION OF A TEMPERATURE VECTOR FOR
C      THREE KRAMERS DOUBLETS FROM AN S=5/2 ION.
C
      COMMON X(1100,5),DATA(100),IB(10)
      COMMON/IN/ICOM,X1,X2,X3,X4,X5,I1,I2,I3,I4,I5
     1,K1,K2,K3,K4,K5,IM,NIN,NLOOP,LOOP1,LOOP2,INU
     2,ARGS(20),IARG,IS,LC,NRUN,JB(7),NSTR,ISTR(40,12)
      DIMENSION FP(3)
      N1=II1
      N3=II3
      N4=MAX0(I4,1)
      N4=MIN0(N4,3)
      NP=X(1100,N1)
      X(1100,N3)=NP
C......LAMBDA VALUE IN DATA(21)
      XLAM=DATA(21)
C......D VALUE IN DATA(22)
      ZFS=DATA(22)/0.695116
      XL=XLAM*XLAM
C
C......MATRIX | DA-X      DD  |
C             |     DB-X  DE  | = 0
C             | DD   DE  DC-X |
C
C......X=ENERGY/D
C
      DA=25.0/4.0
      DB=9.0/4.0
      DC=1.0/4.0
      DD2=10*XL
      DE2=18*XL
```

```
C...... NUMERICAL TRIGONOMETRIC SOLUTION OF THE CUBIC :-
C       X**3 - X**2(DA+DB+DC) + X(DA*DB+DA*DC+DB*DC-DE2-DD2)
C       - (DA*DB*DC-DA*DE2-DB*DD2) = 0
C
      P=-(DA+DB+DC)
      Q=DA*DB+DA*DC+DB*DC-DE2-DD2
      R=-(DA*DB*DC-DA*DE2-DB*DD2)
      SA=Q-P*P/3.0
      SB=2.0*P*P*P/27.0-P*Q/3.0+R
      RT=-SA*SA*SA/27.0
      CTH=-SB/(2.0*SQRT(RT))
      TH=ACOS(CTH)
      TH1=TH/3.0
      RAD=3.1415926536*120.0/180.0
      TH2=TH1+RAD
      TH3=TH2+RAD
      RT=-SA/3.0
      RT=SQRT(RT)*2.0
C......C1,C2,C3 ARE THE ZERO-FIELD DOUBLY DEGENERATE
C      ENERGY ROOTS EXPRESSED IN UNITS OF D.
      C1=COS(TH1)*RT-P/3.0
      C2=COS(TH2)*RT-P/3.0
      C3=COS(TH3)*RT-P/3.0
      ZR=(C1-C3)/(C3-C2)
      IF(ZFS.LT.0.0)ZR=1.0/ZR
      ZR=1.0+ZR
      ZFS=-ABS(ZFS)*(C3-C2)
      FP(1)=1.0
      DO 10 I=1,NP
C......X(I,N1) CONTAINS A TEMPERATURE VECTOR
      FP(2)=EXP(ZFS*X(I,N1))
      FP(3)=FP(2)**ZR
C......FRACTIONAL POPULATION FOR LEVEL N4
   10 X(I,N3)=FP(N4)/(FP(1)+FP(2)+FP(3))
      CALL SET(N3)
      RETURN
      END
```

SECTION 4

RESONANCE RAMAN OF IRON-SULPHUR COMPLEXES
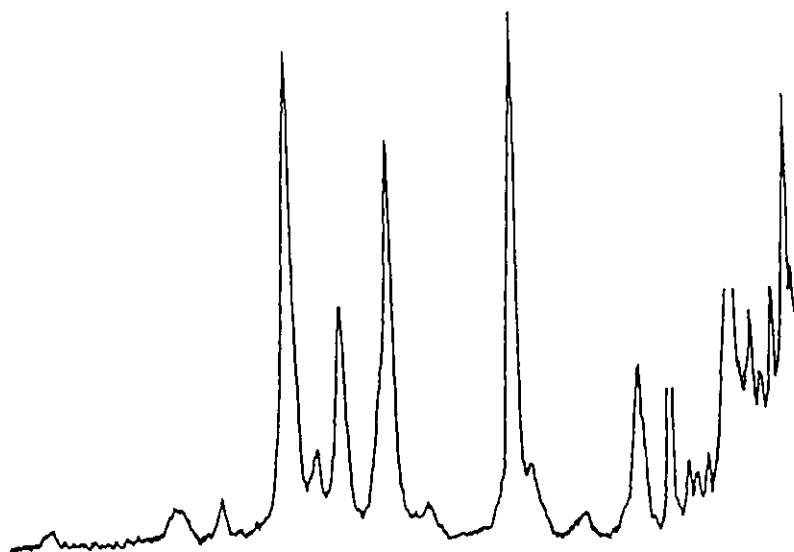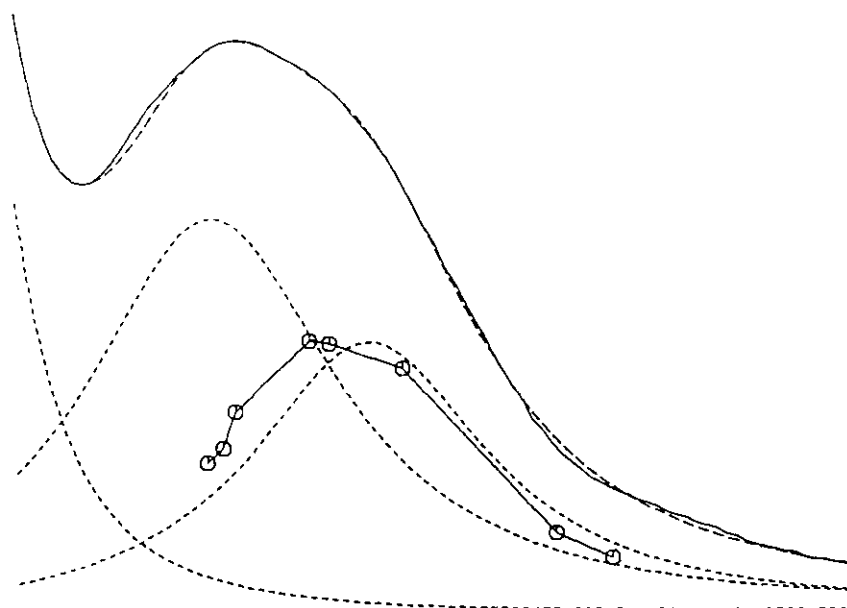
4. RESONANCE RAMAN OF IRON-SULPHUR COMPLEXES.

ABSTRACT

Resonance Raman and infrared studies are presented for 1-Fe, 2-Fe, and 4-Fe model complexes of iron-sulphur protein centres. Medium to strong resonance is observed in the Raman spectra of the complexes when exciting in the visible region, resulting in fairly good quality well-resolved spectra. Partial assignment of observed bands is made according to the normal modes expected for the three major structural types.

For $[Fe(S_2\text{-}o\text{-}xylyl)_2]^-$ the FeS_4 symmetry is found to be degraded from T_d to as low as C_s. It is suggested that in rubredoxins improved Raman spectra should show evidence of a fully split nine-line spectrum.

Spectra for several $[Fe_2S_2(SR)_4]^{2-}$ complexes and their selenium and halogen ligated homologues are described. Fairly extensive cross-correlation of assigned bands is possible. A deconvolution analysis of the visible electronic absorption spectra is given for several of the dimers and comparison made with low resolution excitation profiles of their totally symmetric terminal-ligand stretches. A reassessment is made of previous assignments for protein spectra.

For Raman spectra of $[4Fe\text{-}4S]^{2+}$ proteins, reassignment of some totally symmetric bands is made possible from consideration of the vibrational spectra of $[Fe_4X_4(YR)_4]^{2-}$ (X, Y = S, Se) analogues.

4. RESONANCE RAMAN OF IRON-SULPHUR COMPLEXES.

4.1. INTRODUCTION: RR IN IRON-SULPHUR PROTEINS.

The resonance Raman (RR) process involves laser excitation within an electronic absorption band to produce large and selective enhancement of Raman lines which arise from vibrations of the chromophoric unit.[164] From the presence of intense S→Fe charge transfer absorptions throughout the visible and near-uv spectral regions of iron-sulphur proteins and analogous small inorganic complexes, the enhancement of Fe-S vibrations in RR is to be expected. Since vibrational frequencies are sensitive to geometric and bonding arrangements of localised groups of atoms in a molecule, RR is then a potentially useful technique for the observation of fine structural differences of the iron-sulphur centres. Where the RR transitions can be assigned to specific Fe-S vibrational modes it may additionally be possible, from their frequency dependent intensity enhancement, to determine the origin of the coupled electronic transition. As the inorganic model compounds are more easily well characterised, and may be to some degree subjected to structural design, a comparative analysis of RR spectra for proteins and analogues could lead to a more accurate structural and electronic definition of the iron-sulphur site in its natural environment. For multi-nuclear iron-sulphur centres the vibrational spectra are of interest for additional reasons. Firstly, the spin-lattice relaxation mechanism of the paramagnetic clusters at middle to high temperatures may involve a local vibrational mode directly[101] or as an intermediary to the phonon bath[105,107] (see Section 2), and Raman and IR spectra are important in establishing or invalidating this role.

TABLE 4.1. Vibrational frequencies for iron-sulphur proteins and related synthetic compounds.

Ref.	Molecule	No. Fe	Bands (cm^{-1})	Assignment	Raman excitation (nm)
167,168	Rubredoxin Cl. pasteurianum	1	368 (ρ 0.9) 314 (ρ 0.3) 150 126 (ρ 0.8)	T_2 A_1 T_2 E in T_d symmetry	488.0 632.8
119,169	Rubredoxin P. elsdenii	1	380 362 320 175 w 158 75 w	A_1 E A_1 E A_1 E in C_{3v} symmetry	568.2
170	Adrenodoxin Selena-Adrenodoxin	2Fe 2Fe	397,297 350 355,263 350 all polarised	core modes. terminal ligand mode core modes . terminal ligand mode	488.0 488.0
114	Adrenodoxin	2Fe	390,345,288	Fe-S modes	488.0 476.2 413.1
115	Spinach Fd.	2Fe	395,330,284	Fe-S modes	488.0
171	Adrenodoxin	2Fe	344w, br	Fe-S mode	I.R.
172	C. pasteurianum Fd Chromatium Hipip	4Fe 4Fe	360,345 365,338 250 all polarised	terminal-ligand mode terminal-ligand mode core mode	488.0 488.0
172	[Et$_4$N]$_2$[Fe$_4$S$_4$(SBz)$_4$]	4Fe	332 275 both polarised	terminal-ligand mode core mode	448.0
173	Fe$_2$S$_2$(CO)$_6$	2Fe	329(pol) 314, 267 191 (pol) 554 (pol)	Fe-S sym. str. Fe-S non-sym.mode Fe-Fe str. S-S str.	647.1 676.4
174	Fe(II)[(SPPh$_2$)$_2$N]$_2$	1Fe	283 205	T_2 str. A_1 str. in T_d symmetry	488.0

Secondly, it might be possible to observe Raman transitions involving the manifold of spin states resulting from the antiferromagnetic exchange coupled iron atoms. Such photon-spin interactions have been observed in, for example, FeF_2[165,166] and have also been suggested to explain bands in RR spectra of spinach and adrenal ferredoxins.[114,115] These bands would indicate the energy above the ground state of excited spin levels and lead to an evaluation of the magnitude of the exchange coupling between the iron atoms constituting the bridged cluster.

Whilst measurements of the vibrational properties of iron-sulphur proteins are not extensive, the frequency region where bands from Fe-S modes are expected to lie is well established. Table 4.1 summarises the Fe-S frequencies which have been observed in proteins and synthetic analogues together with some other relevant metal-ligand vibrations. Metal-sulphur stretching frequencies are found in the 480 to 210 cm^{-1} range[175,176]; deformation frequencies are less well catalogued but those which have been described lie between 80 and 150 cm^{-1}.

The RR technique[177, 178] and its application in biochemistry[164,179-181] have been well reviewed.

4.2. Mononuclear Iron-Sulphur Complex; Analogue of Rubredoxins.

4.2.1. RR in Rubredoxins.

The iron-sulphur centres in rubredoxins are comprised of ferric (Rd_{ox}) or ferrous (Rd_{red}) iron approximately tetrahedrally coordinated by four cysteinyl sulphurs. Pronounced ligand field rhombicity has been detected by a number of spectroscopic measurements on both the oxidised and reduced forms.[119] The three dimensional structure of rubredoxin from the bacterium Clostridium pasteurianum is known to a resolution of 1.2Å from X-ray diffraction studies of Jensen and coworkers[182] and the $Fe(III)S_4$ portion of the structure is shown in Figure 4.1. In the structure determination at 1.5Å resolution, approximately the same $\widehat{SFeS}$ angles were found but one abnormally short Fe-S(42) bond length of 2.05Å together with remaining nearly equal lengths of 2.34, 2.32 and 2.24Å had indicated a distortion from tetrahedral more axial than rhombic in character.[183]

Figure 4.1. Crystallographically determined structural data for the FeS_4 site in Rd from C. pasteurianum.[182]
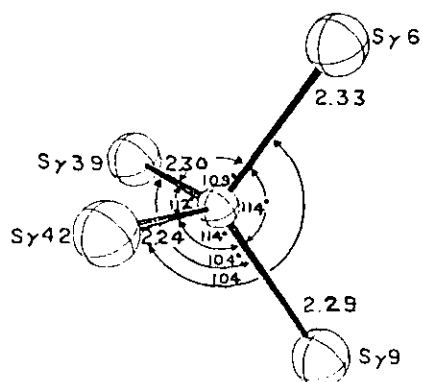
Figure 4.2. Raman spectra for Rd for C. pasteurianum with 488 nm excitation.[167]
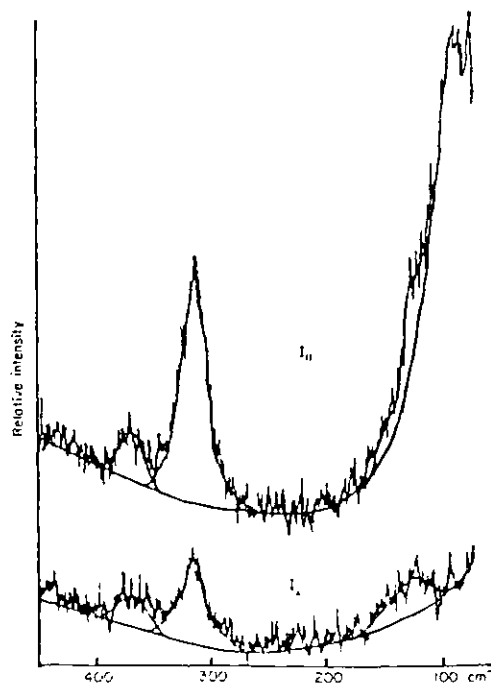
TABLE 4.2. Correlations between the point group T_d and sub-groups.

Site	Vibrational Symmetry			
Group	ν_1 (str)	ν_2 (def)	ν_3 (str)	ν_4 (def)
T_d	A_1^*	E^*	T_2	T_2
T	A^*	E^*	T	T
S_4	A^*	$A^* + B$	$B + E$	$B + E$
D_{2d}	A_1^*	$A_1^* + B_1^*$	$B_2 + E$	$B_2 + E$
C_{3v}	A_1	E	$A_1 + E$	$A_1 + E$
C_3	A	E	$A + E$	$A + E$
C_{2v}	A_1	$A_1 + A_2^*$	$A_1 + B_1 + B_2$	$A_1 + B_1 + B_2$
D_2	A^*	$2A^*$	$B_1 + B_2 + B_3$	$B_1 + B_2 + B_3$
C_2	A	$2A$	$A + 2B$	$A + 2B$
C_s	A'	$A' + A''$	$2A' + A''$	$2A' + A''$
C_1	A	$2A$	$3A$	$3A$

(1) All vibrations are both Raman active and infrared active unless otherwise marked (* = IR inactive).

(2) For a more detailed description of some of the normal modes of vibration see for example Nakamoto.[184]

Table 4.2 describes the group theory predicted metal—ligand-atom vibrational selection rules for four-coordination under eleven possible symmetries. Yamamoto and coworkers have obtained a Raman spectrum of Rd_{ox} from P. elsdenii using 568.2 nm excitation.[169,119] Solution RR spectra show three prominent lines at 370, 320 and 158 cm^{-1}. The 370 cm^{-1} line is split by 18 cm^{-1} and there is evidence for additional bands at 75 and

175 cm^{-1} giving a six-line spectrum and suggesting that the effective

symmetry of the FeS$_4$ complex is less than tetrahedral. Having regard

for the X-ray diffraction structural observations for C.pasteurianum,

at that time only available to 1.5Å resolution, Yamamoto et al., carried

out a normal coordinate analysis for C$_{3v}$ symmetry in keeping with a

trigonal compression along one Fe-S bond. They obtained a good fit to

the observed spectrum with the assignment given in Table 4.1 and by

using valence force constants of 1.74 and 1.44 dynes /Å for the one short

and three long bonds respectively. The optical and EPR spectra of

P. elsdenii and C. pasteurianum rubredoxins are sufficiently similar to

allow the assumption that the stereochemistries of the two FeS$_4$ centres

are essentially the same.

Long, et al. [167,168] have measured Raman spectra for C. pasteurianum

in solid phase with 632.8 nm excitation and in aqueous solution with

488 nm excitation. Figure 4.2 shows the spectrum obtained at 488 nm

and has been interpreted by Long et al. as arising from an FeS$_4$ centre

of T$_d$ symmetry, the assign-ment given is described in Table 4.1. No

splitting of any degenerate transitions was observed, but the non-zero

depolarisation ratio for the symmetrical stretching mode was considered

to indicate a distortion from tetrahedral symmetry. However, the most

recent analysis to 1.2Å resolution of the X-ray diffraction results for

C. pasteurianum, shown diagrammatically in Figure 4.1, indicates that

five of the six $\widehat{SFeS}$ angles of the iron-sulphur centre differ significantly

from the tetrahedral value of 109.5°. The two smallest bond angles,

$\widehat{S(6)FeS}$(42) and $\widehat{S(9)FeS}$(39), both 104°, as well as two of the three largest

angles $\widehat{S(6)FeS}$(9), 114°,and $\widehat{S(39)FeS}$(42), 112°, are related by local

approximate 2-fold axes. Analysis of the X-ray diffractions of rubredoxin

from desulfovibrio vulgaris to 2Å resolution indicates $\widehat{SFeS}$ angles in the range
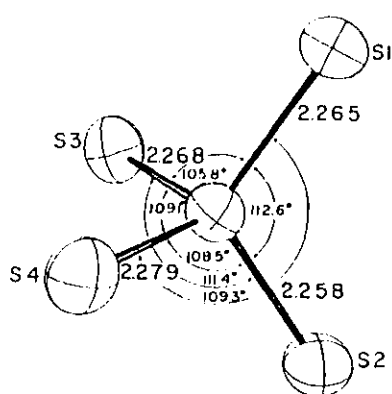
	anion 1	anion 2
	Distance, Å	
Fe–S(1)	2.265 (2)	2.272 (2)
Fe–S(2)	2.258 (2)	2.252 (2)
Fe–S(3)	2.268 (2)	2.265 (2)
Fe–S(4)	2.279 (2)	2.278 (2)
	Angle, deg	
S(1)–Fe–S(2)	112.60 (8)	112.02 (8)
S(1)–Fe–S(3)	105.82 (7)	106.67 (7)
S(1)–Fe–S(4)	109.35 (7)	109.16 (7)
S(2)–Fe–S(3)	111.44 (7)	112.20 (7)
S(2)–Fe–S(4)	108.49 (7)	106.97 (7)
S(3)–Fe–S(4)	109.07 (7)	109.80 (7)

Figure 4.3. Crystallographically determined structural data for the FeS_4 sites in $[Et_4N][Fe(S_2\text{-}o\text{-}xylyl)_2]$.[117,56]

$102\text{-}124°$ (precision $2\text{-}3°$) and Fe–S bond lengths $2.15\text{-}2.35\text{Å}$ (precision 0.1Å)[185] suggesting considerable distortion from T_d symmetry for this protein also.

4.2.2. $[Fe(S_2\text{-}o\text{-}xylyl)_2]^-$ as a model for the iron-sulphur centre in Rd_{ox}.

Ferric and ferrous complexes with the ligand $o\text{-}xylyl\text{-}\alpha,\alpha'\text{-}dithiol$ are well established structurally and spectroscopically as good low molecular weight models of the iron-sulphur centre in rubredoxins.[117,56,118] EXAFS comparisons of these anions with rubredoxins from C. pasteurianum[162] and P. aerogenes[161] reveal very similar absorption edges for corresponding oxidation states, indicating considerable stereochemical equivalence around the iron. The dimensions of the Fe(III)-S₄ group in $[Fe(III)(S_2\text{-}o\text{-}xylyl)_2]^-$ are depicted in Figure 4.3. The coordination approaches T_d microsymmetry with small but definite rhombic distortions evident. Mössbauer[118] and EPR (section 3) measurements in frozen solution indicate that upon release from a crystalline environment a non-cubic stereochemistry persists. The high-spin spherically symmetric Fe(III) ion is devoid of ligand field stabilisation effects on stereochemistry, and in the absence of perturbing

ligand or crystalline forces is expected to adopt strictly regular coord-
ination geometry. $[Fe(S_2-o-xylyl)_2]^-$ is considered to contain an
essentially unconstrained $Fe-S_4$ unit,[117] whose stereochemistry should
closely approach that in Rd_{ox} in the absence of structural constraints
imposed by the protein.

The electronic spectrum of $[Fe(S_2-o-xylyl)_2]^-$ has broad principal bands
at 350, 484 and 640-690 nm with extinction coefficients ranging from
around 8000 to 1600 M^{-1} cm^{-1}. These are similar to those observed in
the proteins and a strong resonant enhancement of Raman bands coupled to
the electronic transitions is expected when irradiating at visible wave-
lengths.

4.2.3. RR spectra of $[Fe(S_2-o-xylyl)_2]^-$.

Raman spectra have been obtained for $Et_4N[Fe(S_2-o-xylyl)_2]$ as solid
(diluted in KBr) and in acetone solution with 482.5, 530.9, 568.2 and
647.1 nm excitations. As with rubredoxin[167,168] the samples are readily
decomposed by excessive exposure to any of the above wavelengths, and
besides the conventional technique of rapid sample rotation it was
necessary to use low powers and, in the case of the solids, low concentrations
and low temperatures in order to obtain optimal signal strength. Prolonged
irradiation also results in an increasing fluorescent background. Table
4.3. lists the observed Raman and IR bands in the range up to 600 cm^{-1},
and Figures 4.4 and 4.5 show examples of spectra obtained using KBr disc
and acetone solution samples. The solid and solution spectra possess very
similar frequency and intensity patterns indicating, as previously observed
by other spectroscopic techniques,[117,56,118] that the coordination stereo-
chemistry is environment-independent for the two phases.

TABLE 4.3.   RR and IR data for $Et_4N[Fe(III)(S_2\text{-}o\text{-}xylyl)_2]$

	RAMAN									IR
	SOLID: KBr DISC				SOLUTION: ACETONE					SOLID: POLYTHENE DISC
Band Maxima cm⁻¹	Intensities at excitation (nm)				Band Maxima cm⁻¹	ρ	Intensities at excitation (nm)			Band Maxima cm⁻¹
	482.5	530.9	568.1	647.1			482.5	568.2	647.1	
75(n)	m	m	1	–						
109	vw	w	1	w						
150	–	1	2	3	145					
160	–		1	3	160		sh	sh		
166	–	2		3						
223	0	w	–	2	222	0.3	0	2	3	
297	10	10	10	10	297	0.35	100	45	15	297vw
320	4	5	4	2	320	0.3	35	15	3	340s
350	2	1	1	4	350	0.2	10	2	5	348sh
373	1	2	1	1	375	∿0.7	10	2	1	371m
450	w	w	vw	w						
467	1	w	w	1	467	prob. pol.	3	1	w	466m
										487w
										559mw
595		1	1	1						596m
OTHER BANDS										
93		w								394vw
280				w						418vw
487			w	w						

4.2.3.1. Fe-S Stretching Vibrations.

A simple analysis in terms of normal modes will be attempted. The most intense and polarised band at 297 cm^{-1} is assigned to the symmetrical stretching ν_1 vibration of Table 4.2. For concentrated samples the IR reveals a weak band at this frequency. Raman lines at 320, 350 and 373 cm^{-1}
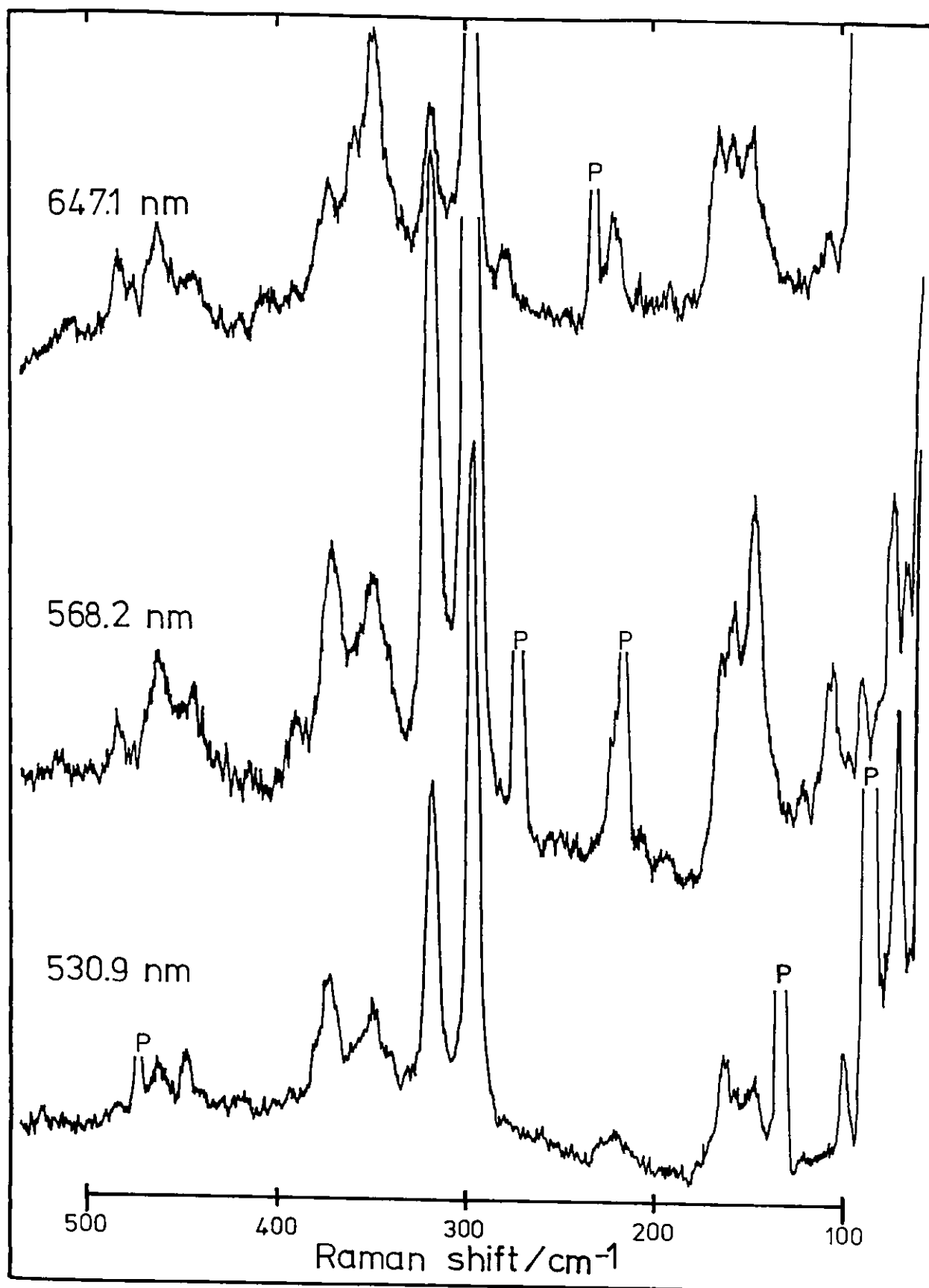
Fig 4.4 Solid—state Raman spectra for [Et₄N][Fe(S₂—o—xylyl)₂] with three excitation frequencies (647.1, 568.2 and 530.9 nm). P = plasma emission line.
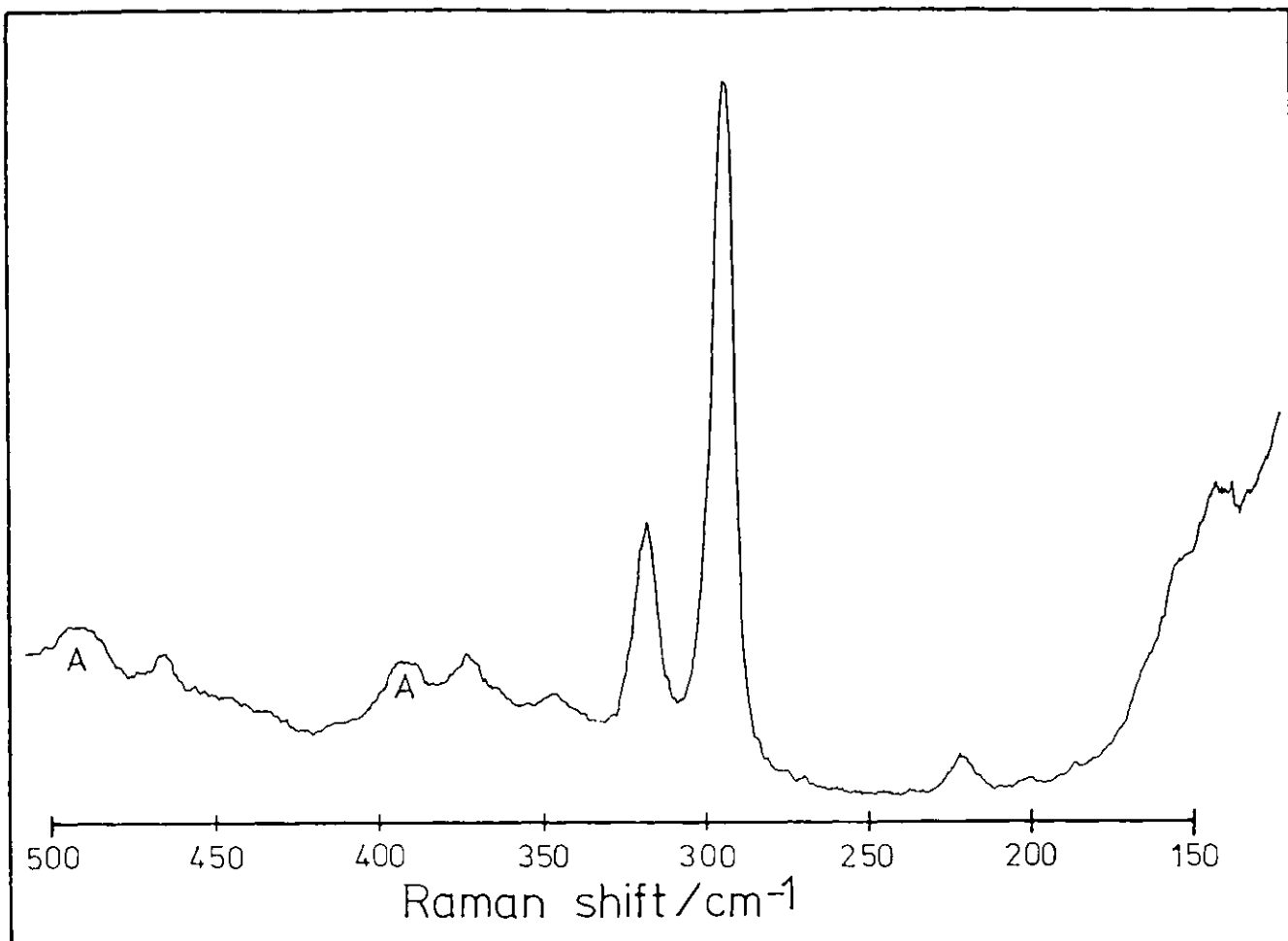
Figure 4.5. Raman spectrum for $[Et_4N][Fe(S_2-o-xylyl)_2]$ in acetone with 568.2 nm excitation. A = acetone peak.

can then be assigned to the v_3 mode triply split by degeneration of tetrahedral symmetry to C_{2v} or lower. Bands corresponding to these stretching vibrations also appear in the infrared. For the Fe-S stretching modes observed in the RR spectra of rubredoxins the most intense line also appears at lowest frequency and is similarly assigned as the vibration of highest symmetry.[167,168,119] With a frequency of 297 cm^{-1} for v_1 an analysis of the ratio of v_1/v_3 for tetrahedral metal chalcogenide anions, MX_4^{n-}, as a function of the ratio of their metal-atom and ligand-atom masses, M_m/M_x, indicates a v_3 frequency of around 350 cm^{-1} for tetrahedrally sulphur-coordinated iron.[186] This value is in keeping with the range 320, 350, 373 cm^{-1} observed for the triply split v_3 mode.

Three of the stretching vibrations appear polarised in the solution

spectrum, thus the iron-sulphur site symmetry must be C_s or lower. If

then the remaining transition at 373 cm^{-1} is depolarised, as seems

probable, the local symmetry would have to be C_s and this band can be

assigned as A" and the 320 and 350 cm^{-1} bands as A'. As in many (and

probably in most) cases the totally symmetric vibrations show the

largest intensities in RR spectra,[177] depolarised bands are often weak

and it is difficult accurately to determine their depolarisation ratios.

It is, of course, for precisely such peaks that accurate depolarisation

data is required in order to distinguish them from polarised bands.

The fact that the 373 cm^{-1} band is only weakly resonance enhanced lends

a little further credance to its assignment as the asymmetic (A") stretch.

No further Fe-S stretching vibrations are expected. The weak Raman

lines at 450 and 467 cm^{-1}, though just low enough in frequency to be

Fe-S stretches, could possibly be bending modes about the methylene

carbons, which, as chelate ring vibrations, might be subject to some

resonance enhancement. This is based on the assumption that the $\widehat{XYZ}$

angle bending frequency is roughly given by the equation

$1/4[\nu(X-Y) + \nu(Y-Z)]$ [see for example, reference 184] with $\nu(Ph-C)$

around 1200 cm^{-1} and $\nu(C-S)$ around 650 cm^{-1}.[110] The 595 cm^{-1} Raman line

is at the frequency where a resonance enhanced overtone of the ν_1 297 cm^{-1}

mode would be expected. The infrared bands at 466, 487, 559 and 596 cm^{-1}

are also found for $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ and $[Fe_2Se_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$

(Table 4.6 and section 4.3.3.1.) with a very similar frequency and

intensity pattern and are attributed to vibrational modes of the chelate

ring atoms; the ligand shows medium strong peaks at 450, 547 and 594

cm^{-1}. The remaining vibrational bands below 250 cm^{-1} in the Raman spectra

are associated with deformations.

4.2.3.2. Fe-S Deformation Vibrations.

For a symmetry of C_{2v} or lower, five Fe-S deformation transitions are expected. Spectral lines in the range 75 to 175 cm^{-1} have been assigned as Fe-S deformations in Rd_{ox}. The polarised band at 222 cm^{-1} seen most strongly when exciting with red light has a rather large Raman shift to be $\delta(\widehat{SFeS})$ in origin and does not correspond to anything observed in Rd_{ox}. The band might possibly be due to a $\delta(\widehat{FeSC})$ mode. The three peaks lying in the 150-166 cm^{-1} frequency interval correlate with the ν_4 (T_2) vibration in T_d symmetry which is triply split for symmetries of C_{2v} or lower. This mode has been assigned to a weak shoulder at 150 cm^{-1} in C. pasteurianum and to lines at 158 and 175 (weak) cm^{-1} in P. elsdenii. The corresponding ν_2 $\delta(\widehat{SFeS})$ vibration has been claimed to give rise to peaks at 126 and 75 cm^{-1} for these two proteins respectively.[167,168,119] [Fe(S$_2$-o-xylyl)$_2$]$^-$ shows Raman bands around 75 and 109 cm^{-1}. The presence of other small peaks and the difficulties inherent in making accurate observations in this region for [Fe(S$_2$-o-xylyl)$_2$]$^-$, due to the sloping Rayleigh scattered background, the presence of strong plasma lines and of possible lattice modes, are felt to make assignment of a split ν_2 mode unjustifiable with the present quality of data. The Raman spectrum of FeCℓ_4^-,[187,188] indicates that ν_2 lines should be expected to lie around 100 cm^{-1}. Theoretical calculations of Weinstock et al.,[189] together with observations on chalcogenometallates indicate that ν_2 must be more intense than ν_4 in the solution Raman of tetrahedral species. This rule may, however, not apply under resonant conditions.

Table 4.4 summarises the assignment of iron-sulphur vibrational modes for [Fe(S$_2$-o-xylyl)$_2$]$^-$.
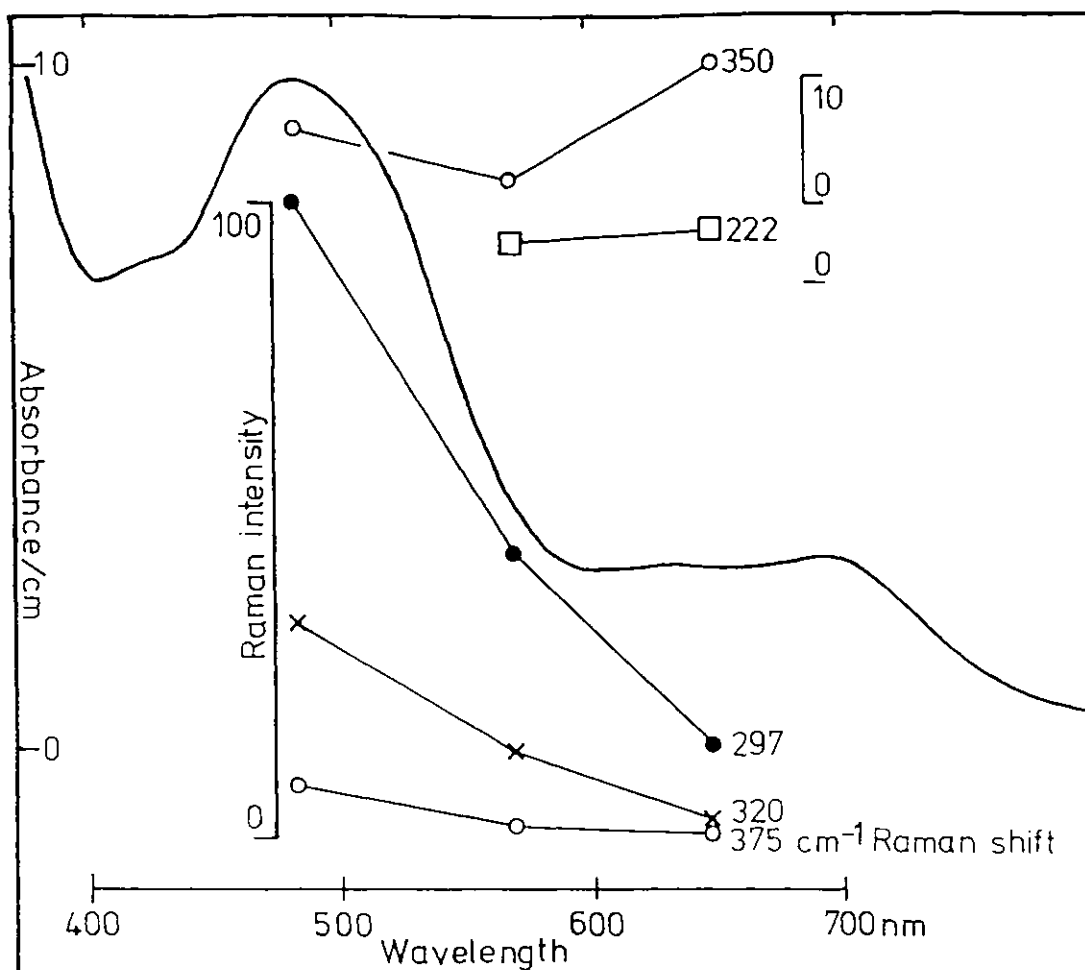
Figure 4.6. Electronic spectrum of [Fe(S$_2$-o-xylyl)$_2$]$^-$ in acetone and

resonance enhancement of several Raman peaks.

TABLE 4.4. RR spectrum of FeS$_4$ core in [Fe(S$_2$-o-xylyl)$_2$]$^-$

Frequency/cm^{-1}	Assignment		
		C$_s$	T$_d$
297	str	A'	A$_1$
320	str	A'	
350	str	A'	T$_2$
373	str	A"	
150	def		
160	def	2A' + A"	T$_2$
166	def		

4.2.3.3. Resonance Enhancement.

Although the variation in excitation frequency in this work is inadequate to obtain excitation profiles for the various resonance enhanced Raman transitions, Figure 4.6 is presented more clearly to demonstrate the intensity changes in comparison with the electronic spectrum for an acetone solution. The bands at 297, 320 and 375 cm^{-1} are clearly coupled to the 484 nm electronic transition. The peak intensities increase by an order of magnitude on going from 647.1 to 482.5 nm irradiation. The Raman peak at 222 cm^{-1} shows post-resonance with the optical absorption to lower energy. All the electronic absorption above at least 400 nm is believed to arise from S$\longrightarrow$ Fe charge transfer transitions.[117]

Taking into account the different concentrations, the 297 cm^{-1} band of $[Fe(S_2-o-xylyl)_2]^-$ is around 3000 times more intense than the 787 cm^{-1} symmetric stretch of the acetone solvent, indicating that a strong resonance effect is involved.

4.2.4. Conclusions.

The analysis of the RR spectra for $[Fe(S_2-o-xylyl)_2]^-$ in terms of an FeS_4 symmetry which is C_s or lower, fits well with the reported X-ray diffraction structure.[56] The situation is somewhat complicated by the existence of two independent anions in the unit cell.[117] Figure 4.3 shows the stereochemistry of the FeS_4 portion for anion 1, and the Fe-S bond length and angles for both anions are printed alongside. It can be seen that for both anions an approximate symmetry plane exists through S(2) & S(4) and the central Fe, bisecting the S(1)FeS(3) angle. The bond lengths Fe-S(1) and Fe-S(3) are nearly equal as are the sets of angles S(1)FeS(2), S(2)FeS(3) and S(1)FeS(4), S(3)FeS(4). The

symmetry closely approaches C_s. The RR spectra for $[Fe(S_2-o-xylyl)_2]^-$ seem capable of revealing this low symmetry.

If $\underline{D}$ and coordination symmetries are directly related via the crystal field, then the EPR analysis of $[Fe(S_2-o-xylyl)_2]^-$ given in Section 3 indicates a higher symmetry than that in Rd_{ox}. In Rd_{ox} from C. pasteurianum the 1.2Å resolution analysis of the X-ray diffraction results show that the FeS_4 centre departs considerably from either C_2 or C_s.[182] The vibrational results obtained in this section would suggest that the RR scattering from this protein should show characteristics of a nine-line spectrum, given adequate resolution and signal to noise ratio, and no adventitious band overlap. The spectra obtained by Long et al.[167,168] may be of insufficient quality to show that the weak ν_3 mode is triply split and that the resulting bands are polarised (a redefinition of the baseline in the published spectra[167] might lead to a depolarisation ratio indicating polarisation of the Raman intensity at round 370 cm^{-1}) The results of Yamamoto et al.[169] come closer to agreement with a low symmetry.

4.3. Binuclear Iron-Sulphur Complexes; Analogues of 2Fe2S Ferredoxins.

4.3.1. RR in 2Fe Ferredoxins.

Critical assessment of the physicochemical data for 2Fe ferredoxins has led to the generally accepted conclusion that the active site has the minimal composition $[Fe_2S_2(SCys)_4]$ and a structure containing two antiferromagnetically coupled tetrahedrally coordinated iron atoms bridged by two sulphides.

The optical absorption spectra of oxidised proteins are adequately summarised by the following λ_{max} (nm) and ε (mM) data 325-333 (12-15); 410-425 (9-10); 455-470 (85-95) [see for example references 190, 191, 49, 171] and resonance enhancement of Raman spectra is expected for visible excitation wavelengths. Two RR studies of adrenodoxin have been reported.[114,170] The technique has also been applied to the ferredoxin from spinach.[115] The results of these studies have been summarised in Table 4.1, together with observations made on adrenodoxin absorption in the far infrared. Iron-sulphur vibrations are found in the 250 to 400 cm^{-1} region. In the Raman only polarised bands due to totally symmetric modes are sufficiently resonance enhanced to be observed above the noisy and

Figure 4.7. Raman spectra for S and Se bridged adrenodoxin with 488 nm excitation.[170]
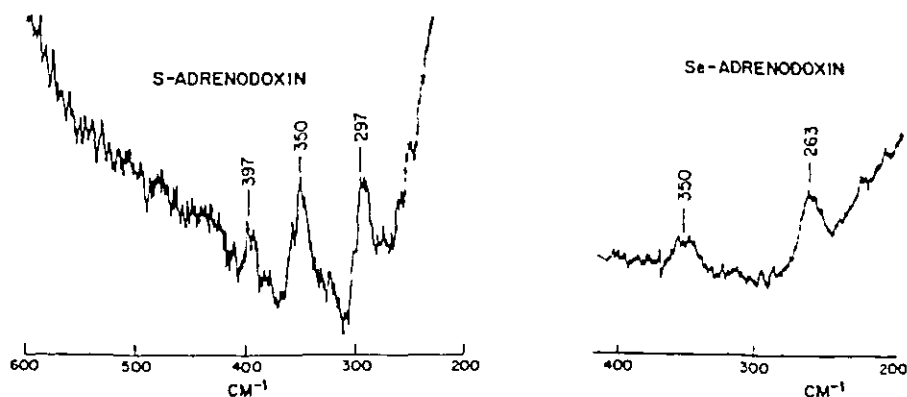
sloping background. The spectra of adrenodoxin and its selenium substituted derivative obtained by Tang, et al.[170] are reproduced in Figure 4.7. The assignment of the 397 and 297 cm^{-1} bands as due to vibrations involving the labile sulphur atoms has been made on the basis of their shift to 355 and 263 cm^{-1} when selenium is substituted as the bridging ligand. Peaks observed at 350 cm^{-1} in both sulphur and selenium adrenodoxin must then correspond to the symmetric stretch of the four terminal cysteine sulphurs.

Iron-sulphur vibrations at around the same three frequencies occur in the RR spectra of adrenal and spinach ferredoxins obtained by Blum and coworkers. Their observations for these two proteins have been made out to 3000 cm^{-1} and weak peaks distributed over this range assigned as arising from transitions within the ladder of spin-states resulting from the antiferromagnetic exchange-coupled irons. Raman scattering by so-called spin-waves in antiferromagnets such as FeF_2 is well documented and the possible mechanisms for spin-phonon interaction have been described.[166,192] Single and multi-flip transitions from both the ground and first excited states are invoked in the interpretation of ferredoxin spectra given by Blum, et al.[114,115] Analysis of the data in this way yields J values of -172 ± 16 cm^{-1} and -74 cm^{-1} for oxidised and reduced spinach ferredoxin and -497 cm^{-1} for adrenodoxin. The Raman process involved has been described as resonant from an examination of the excitation wavelength dependence of the 995 cm^{-1} band intensity in adrenodoxin; this band having been assigned to a $\Delta S = 1$ transition from the ground-state.

4.3.2. RR and IR Spectra of $[Fe_2S_2(SR)_4]^{2-}$.

$[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ and its ligand substitution derivatives,

$[Fe_2S_2(SR)_4]^{2-}$ (R = Ph, pMeC$_6$H$_4$, pCℓC$_6$H$_4$) have been well characterised

and demonstrated to be excellent model compounds for the active sites

of 2Fe ferredoxins.[27,28,38] Halide substitution products, $[Fe_2S_2X_4]^{2-}$

(X = Cℓ, Br, I), have also been synthesised and well characterised.[193,194]

In order to obtain a better understanding of the vibrational spectra for

these iron-sulphur dimers, selenium derivatives have been prepared in

this work. The ligand PhS$^-$ has also been replaced by its selenium

homologue, PhSe$^-$, to give the crystalline salts $[Et_4N]_2[Fe_2S_2(SePh)_4]$

and $[Et_4N]_2[Fe_2Se_2(SePh)_4]$. RR spectra of sulphur and selenium-substituted

ferredoxin analogues have been obtained in solid and, where possible,

solution state; Tables 4.6-11 and Figures 4.10-14.

The starting point for analysis of these spectra is a description

of the 18 fundamental modes of vibration expected for a bridged dimeric

molecule, M_2X_6, of point group D_{2h}. Figure 4.8 illustrates approximately

the character of these normal modes as described by Bell and Longuet-

Higgins[195] and used in their interpretation of vibrational spectra for

diborane. It must be recognised that this description is of limited

value where the masses M and X are comparable, as considerable coupling

of the vibrations is then to be expected with all atoms of the vibrational

unit participating significantly in each normal mode. According to the

selection rules, centrosymmetric modes (those of g-character) are Raman

active, 8 of the u-character vibrations are IR active and the remaining

A_{1u} fundamental is inactive in D_{2h} symmetry. Since in the Fe_2S_6 centre

all the bands corresponding to iron-sulphur vibrations are to be accommodated

in a frequency interval of only some 400 cm^{-1}, strict adherence to the
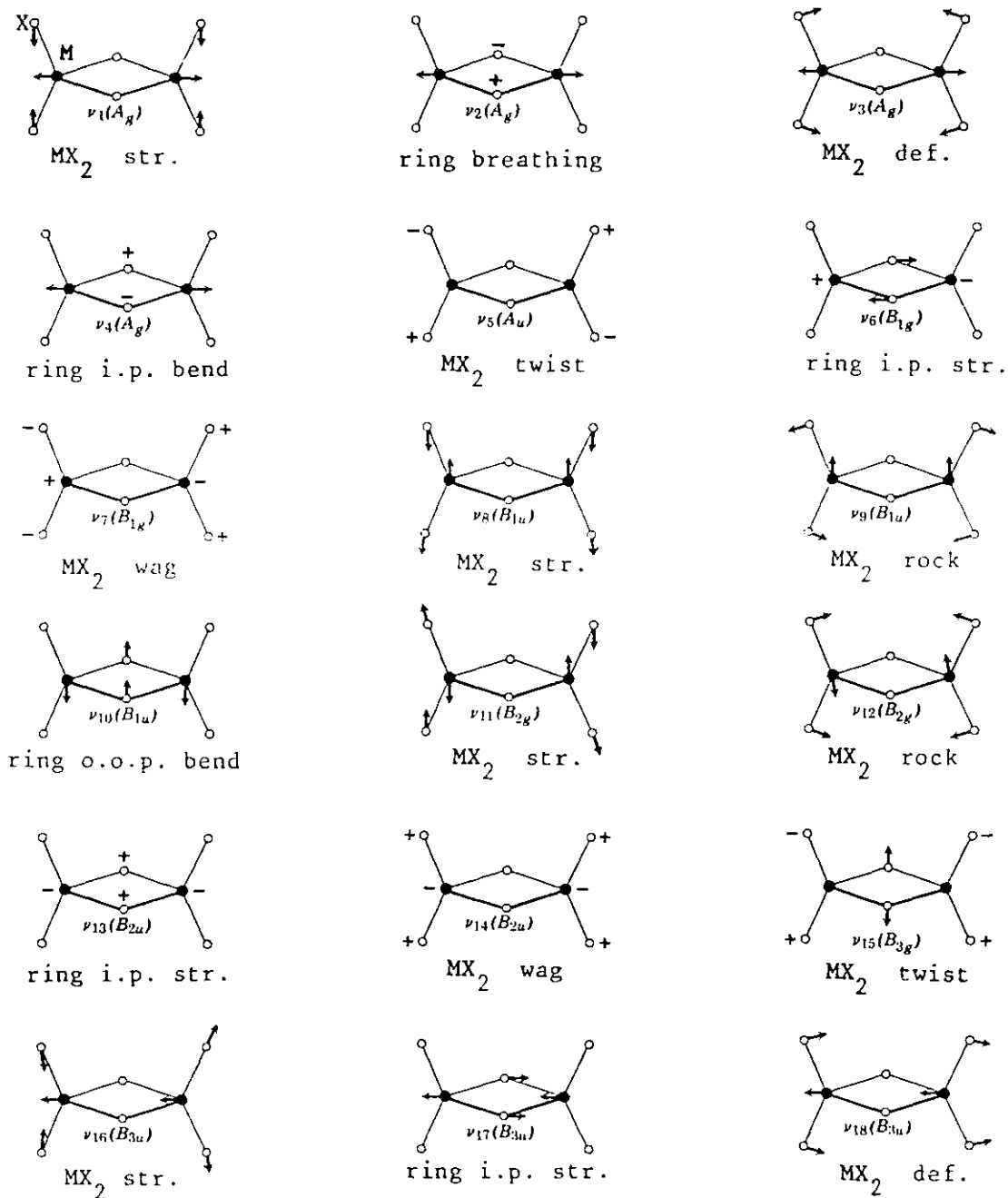
Fig. 4.8. Approximate descriptions of the normal modes of vibration for the bridged dimer M_2X_6

mutual exclusion principle is hardly to be expected in the observed

spectra. Indeed, accidental coincidences or near-coincidences may be

expected for vibrational modes of a similar type.

Ga_2Cl_6, Ga_2Br_6,[196-199] Al_2Cl_6, Al_2Br_6,[197,200,201] and more recently,

Fe_2Cl_6[202-204] have been well studied by Raman, IR and normal coordinate

analyses[205] and consequently represent useful models for the interpretation

of the chalcogenide-ligated bridged diferric complexes. The following

generalised rules have been used in, or deduced from, the assignment of

bands in the dimeric metal halide vibrational spectra. The vibrations

are divided into frequency groups:

(a) Terminal MX_2 stretches [$\nu_1(R)$, ν_8, ν_{11} (R), ν_{16}] at highest frequency

with $\nu_1 \simeq \nu_{16}$, $\nu_8 \simeq \nu_{11}$, $\nu_{11} > \nu_1$ and $\nu_8 > \nu_{16}$. ν_1 more intense than

ν_{11} in Raman.

(b) Ring stretching [$\nu_2(R)$, $\nu_6(R)$, ν_{13}, ν_{17}] at somewhat lower frequency

since M-X bridge linkages are usually weaker than M-X terminal links. ν_2

should be intense, whilst the antisymmetric ring-stretch ν_6 is weak or

not observed.

(c) M-M vibrations [$\nu_4(R)$] in which the M-X bridge bonds are only slightly

stretched but considerable change occurs in the M-M separation. Where

an M-M linkage is possible the frequency and intensity of this band

arising from the ν_4 mode will depend to a large degree on the strength

of the interaction.

(d) Angular motion of terminal MX_2 groups [$\nu_3(R)$, ν_5, ν_7 (R), ν_9, $\nu_{12}(R)$,

ν_{14}, $\nu_{15}(R)$, ν_{18}]. ν_3 and ν_{18} both involve changes in the $X_t\widehat{M}X_t$ angle and

are expected at comparable frequencies high in this group. ν_3 should be

the most intense Raman line in the region. The twisting frequency ν_5 is

inactive in strict D_{2h} symmetry, and ν_{15} is likely to appear very weakly

if at all.

(e) <u>Ring out-of-plane bend</u> (ν_{10}). This IR mode is expected to lie at very low frequency and has been assigned to a band at 24 cm^{-1} in $Fe_2C\ell_6$.[204] Normal coordinate analysis predicts values of 28 and 17 cm^{-1} for $Ga_2C\ell_6$[196] and Ga_2Br_2[199] respectively. The present observations extend down only to 250 cm^{-1} in the IR.

For $Fe_2C\ell_6$ and $Ga_2C\ell_6$ the first two frequency regions are around 500-400 cm^{-1} and 350-250 cm^{-1} $(\nu_6$ may appear lower) respectively, the remaining deformation modes lying below 250 cm^{-1}. Adams and Churchill's extensive normal coordinate analysis for bridged M_2X_6 species indicates that whilst it is often accurate to describe stretching vibrations as terminal, there are fewer instances in which any one mode can be said to be mainly bridge-bond stretching.[205] The use of a bridge-stretch description is, however, considered a reasonable approximation when the M:X mass ratio approaches or exceeds about 2:1. For the Fe_2S_6 core the description of the 18 modes given in Figure 4.8 is expected to be a reasonably good one, as judged by the internal coordinate potential energy distributions available for $Ga_2C\ell_6$ and $A\ell_2C\ell_6$,[205,200] which have M:X ratios above and below that for Fe:S. The corresponding $A\ell$ and Ga bromides show, however, extensive spreading of potential energy among internal coordinate types, and vibrational modes involving iron and selenium, having again an intermediate M:X raio, can not be expected to achieve a good fit to the simple description used here.

X-ray crystallographic structure determinations have been described for three of the sulphur bridged iron dimers synthesised by Holm's group; $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$,[27] $[Fe_2S_2(STol)_4]^{2-}$,[28] and $[Fe_2S_2C\ell_4]^{2-}$,[193] Figure 4.9. Each dimer is centrosymmetric and has a symmetry degraded from D_{2h} to C_{2h}. The reason for the symmetry lowering

Fig. 4.9. Crystal structures for three [2Fe-2S]²⁻ complexes   190

a. $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$

b. $[Fe_2S_2Cl_4]^{2-}$

c. $[Fe_2S_2(STol)_4]^{2-}$

	D_{2h}	$C_{2h}^{-}(Z)$	$C_{2h}^{-}(Y)$	$C_{2h}^{-}(X)$	C_i
v_1	A_{1g}	A_g	A_g	A_g	A_g
v_2	A_{1g}	A_g	A_g	A_g	A_g
v_3	A_{1g}	A_g	A_g	A_g	A_g
v_4	A_{1g}	A_g	A_g	A_g	A_g
v_6	B_{1g}	A_g	B_g	B_g	A_g
v_7	B_{1g}	A_g	B_g	B_g	A_g
v_{11}	B_{2g}	B_g	A_g	B_g	A_g
v_{12}	B_{2g}	B_g	A_g	B_g	A_g
v_{15}	B_{3g}	B_g	B_g	A_g	A_g
v_5	A_{1u}	A_u	A_u	A_u	A_u
v_8	B_{1u}	A_u	B_u	B_u	A_u
v_9	B_{1u}	A_u	B_u	B_u	A_u
v_{10}	B_{1u}	A_u	B_u	B_u	A_u
v_{13}	B_{2u}	B_u	A_u	B_u	A_u
v_{14}	B_{2u}	B_u	A_u	B_u	A_u
v_{16}	B_{3u}	B_u	B_u	A_u	A_u
v_{17}	B_{3u}	B_u	B_u	A_u	A_u
v_{18}	B_{3u}	B_u	B_u	A_u	A_u

(Raman: rows v_1–v_{15}; IR: rows v_5–v_{18})

Fig. 4.5. Symmetry distributions of the normal vibrational modes for five M_2X_6 structures

is different in each case. $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{2-}$ has asymmetric bridge bond lengths (more rigorously terminal Fe-S distances are also slightly unequal lowering the symmetry from effective C_{2h} to C_i); in $[Fe_2S_2(STol)_4]^{2-}$ there is a dihedral angle of $97°$ between Fe-S$_2$ (terminal) and Fe-S$_2$ (bridge) planes; $[Fe_2S_2C\ell_4]^{2-}$ has asymmetric Fe-Cℓ bond lengths. Table 4.5. shows exaggerated skeletal diagrams of the distortions from D_{2h}. The C_2 axes of the resulting three C_{2h} symmetries are mutually perpendicular and lead to different vibrational symmetry distributions as listed in the Table. For a C_i site all Raman active modes are totally symmetric. No other non-centrosymmetric site-groups will be considered, as both the molecular point-group and the space-group have a C_i sub-group, in each of the three structures.

Since the bridge bonds are seen to be shorter than the terminal ligand bonds for each molecule depicted in Figure 4.9 any distinction of frequency regions for the respective vibrations of these bonds, as outlined above, might be expected to be lost or reversed.

Fe-Fe distances of 2.698Å (S$_2$-o-xylyl), 2.691Å (S-Tol) and 2.716Å (Cℓ) are indicative of a stabilising metal-metal interaction and the ν_4 vibration is expected to increase in frequency as the mode takes on more stretching character with increasing bond strength.

4.3.3. Assignment of vibrational spectra.

Vibrational assignments are collected and summarised in Tables 4.12-16 at the end of each section.

4.3.3.1. $[Fe_2X_2(S_2\text{-o-xylyl})_2]^{2-}$ (X = S, Se).

Consistent with the vibrational data for $[Fe(S_2\text{-o-xylyl})_2]^-$ presented in Section 4.2.3, terminal ligand stretching modes are expected in the region 300-370 cm^{-1}. If the polarised band at 327 cm^{-1} in the solution

TABLE 4.6. RR and IR Data for $[Et_4N]_2[Fe_2X_2(S_2-o-xylyl)_2]$ (X = S, Se).

	X = S					X = Se			
	Band maxima (cm^{-1})	INTENSITY/EXCITATION				Band maxima (cm^{-1})	INTENSITY/EXCITATION			
		482.5	530.9	568.2	647.1		482.5	530.9	568.2	647.1
SOLID -RR	139	–	15	15	25	155	6sh	30	40	50
	165	15	25	15	10	165	12	35	20sh	30
	196	25	35	60	40	183		4	3	w
	224	3	4	–	–	228	25	30	20	10
	304	w,sh	4	50	10	261	20	25	15	100
	314sh	w	w	w	w	311	3	6	3	
	321	50	25	40	70	319	6			8
	348	3	w	w	2	339	9	8	6	13
	388	10	20	45	100	349	9	4	3	w,sh
						426		6	3	20

OTHER BANDS

28, 35, 44, 52, 60, 67, 75, 83, 91, 100, 108, 116, 126 (all w-m,n), 145 (w,sh), 278(w), 470(w,br), 548(w), 676(w,br), 865(w), 1230(vw),1490(w,br)	44, 60, 67, 75, 91, 100, 108, 117, 124, 140 (all w-m,n), 520(w), 670 (vw), 865(vw).

SOLUTION RR	160(w,sh), 198(mw,pol), 304(s at 568.2 nm, ρ 0.3),327 (s at 482.5 nm,ρ 0.35)	150(w,sh), 160(w,sh), 226(mw,pol.), 258(vs at 647.1 nm, ρ 0.3), 299 (w,pol),320(w), 427(w)
IR-SELECTED BANDS	265(vw),274(m),300(vw),325(vs), 336(vs), 396(vw,sh),410(w,sh),415 (vs), 464(mw),488(w),500(w,br), 562(w),600(m),675(s),752(m),765(s), 772(m),779(s),861(m),1002(s),1058(m), 1071(m),1172(vs),1187(m),1210(ms), 1222(ms),1262(m),1300(m),1385(s,dl).	278(vw),290(vw,sh),302(mw),320(s), 345(vw,sh), 400(w),464(w),488(w), 525(w,br), 562(w),600(m),675(s), 765(s),772(s),779(s),861(m),1002(s) 1057(m),1071(m),1173(s),1187(m), 1210(m),1222(m),1263(w),1301(m), 1390(s,dl).

TABLE 4.7. RR and IR data for $[Et_4N]_2[Fe_2X_2(SPh)_4]$ (X = S, Se).

	X = S					X = Se			
	Band maxima (cm^{-1})	INTENSITY/EXCITATION				Band maxima (cm^{-1})	INTENSITY/EXCITATION			
		482.5	530.9	568.2	647.1		482.5	530.9	568.2	647.1
SOLID – RR	160	3	4	3	2	140	–	–	2	3
	201	w	1	1		203	10	10	8	10
	244sh	w	w	w		235	2	3	2	–
	256	10	8	9	10	255	1	1	1	1
	320	1	w	1	3	284	1	2	2	3
	351	8	3	3		314	w	w	1	2
	387	4	2	3	8	364	3	2	1	1
	406	1	1	w		410	1	w,sh	w,sh	w,sh
	428	10	10	10	8	428	7	10	10	10
	478	1	–	1 .		475	w	–	1	
	510	1	w	1						

OTHER | BANDS

X = S: 50,60,68,77,84,92,107,116,124 (all m-w, n),985(w),1024(w),1082(m),1126(w), 1473(w),1574(m)

X = Se: 51,60,67,75,83,92,100,108,116, 124 (all m-w,n),996(mw),1025(w), 1082(m),1475(w),1576(mw).

SOLUTION -RR

X = S: 240(w,sh), 253(m, ρ 0.3), 316(w), 354 (w, pol,), 430(vs, ρ 0.3)

X = Se: 190(w,sh), 206(w,sh), 250(w), 282(mw,pol.), 314(w), 429(vs,ρ 0.3)

IR SELECTED BANDS

X = S: 279(w),305(vw,sh),318(s),360(vs,dl), 410(w),424(s),431(m),481(s),698(s) 745(m),794(s),900(w,dl),1027(s),1035(m) 1070(m), 1081(s),1127(mw),1182(s),1303 (m),1395(w),1565(s,br)

X = Se: 260(m),313(ms),359(s),366(m,sh) 400(w,br),428(m),477(ms),690(s,dl), 738(m),787(ms),795(m,sh),888(w), 1023(s),1067(mw,sh),1081(s),1122(w), 1182(s),1304(m),1397(m),1574(s)

TABLE 4.8. RR and IR data for $[Et_4N]_2[Fe_2X_2(SePh)_4]$ (X = S, Se).

		X = S					X = Se			
	Band maxima (cm^{-1})	INTENSITY/EXCITATION				Band maxima (cm^{-1})	INTENSITY/EXCITATION			
		482.5	530.9	568.2	647.1		482.5	530.9	568.2	647.1
SOLID - RR	123	8	6	10	2	187	10	10	10	10
	180br	1	1	1	w	217	3	6	–	8
	214	4	8	–	6	278br	w	1	1	
	242	10	9	5	5	298sh	1	1	w	1
	273	10	8	–	5	309	3	6	10	9
	306	8	10	10	10					
	384	6	2	1	2					
	OTHER 74,82,91,98,108 (all m-w,n), 150(w,sh) 320(w,sh),368(w,sh,br),502(w,br)					BANDS 40,66,75,82,91,99,108,116,124 (all m-w, n),258(w,br),380(w,br), 400(w,br)				
SOLUTION - RR	175(w,sh),215-220(w,sh),243(w, pol.), ∿270(w), ∿290(w), 310(vs, ρ 0.3)					188(w),217(m,pol.),242(w),270(w), 300(w,sh),309(vs, ρ 0.35)				
IR SELECTED BANDS	273(m),307(w),328(s),408(vw),416(s), 465(s),665(s),691(s),740(obsc.), 776(m),788(m),1000(m,dl),1020(s), 1066(s),1171(s),1182(s),1300(ms), 1390(m),1572(s)					274(s), 288(vw),306(mw),320(m) 333(w),400(mw,br), 466(s),665(s), 691(s),740(obsc.),776(mw),789(m), 1002(m),1020(s),1066(s),1172(s), 1180(s),1300(m),1392(m),1572(s)				

TABLE 4.9. RR and IR Data for [Et₄N]₂[Fe₂X₂(STol)₄] (X = S, Se).

	X = S					X = Se			
	Band maxima (cm^{-1})	INTENSITY/EXCITATION				Band maxima (cm^{-1})	INTENSITY/EXCITATION		
		482.5	530.9	568.2	647.1		482.5	530.9	568.2	647.1
SOLID - RR	148	4	6	4	1	192	10	10	8	10
	215	w	2	1		218	2	3	–	1
	241	6	8	10	10	251	w	1	1	1
	320	10	10	7	3	272	2	1	–	4
	375	8	8	7	9	325	2	2	1	2
	386	w	3	6	8	387sh	w	3	5	5
	403	7	9	9	4	398	8	8	10	7
	490	w	1	1	1	630	2	2	3	3
	630	3	4	4						

OTHER BANDS

X = S:
83,92,100,109,117,125,134(all m-w,n), 169(w),640(w,sh),1085(s),1486(m), 1595(m)

X = Se:
68,76,83,100,108,117,124,133,139 167(all m-w,n),294(w),490(w), 590(w),1085(s),1487(m),1595(m).

SOLUTION - RR

X = S:
∿ 210(w,sh), 238(mw,pol.)
305(w, pol.), 325(mw, ρ ∿ 0.3),
378(w,sh), 384(sh)

IR SELECTED BANDS

X = S:
272(vw,br),300(vw,br),325(m,sh),332(s), 374(w,sh),382(mw),396(s),415(ms),490(s) 626(ms),783(m,br),804(vs),998(m),1017(m) 1084(vs),1172(m), 1181(m), 1300(mw,dl), 1390(m), 1590(m,br)

X = Se:
280(vw),304(ms),318(ms),332(m), 384(vw,sh),398(ms,dl), 490(s), 628(s),782(m,br),804(vs),998(ms), 1016(m),1084(vs),1173(ms),1182(mw), 1300(mw,dl),1392(m),1595(m)

TABLE 4.10. RR and IR Data for $[Et_4N]_2[Fe_2S_2(SC_6H_4C\ell)_4]$.

SOLID-RR. Band maxima/cm^{-1} (intensity at 482.5nm excitation): 137(2), 201(2),

221(3),294(9),320(2),342(10),368(8),381(4),401(4).

Other bands: 67,75,107,116(all m-w,n),273(w),542(m),597(w),640(w),1065(mw),

1090(mw),1472(w),1567(w).

SOLUTION-RR: 220(w,sh),286(m, ρ 0.3),320(w),342(vs, ρ 0.36),370(w,sh).

IR - SELECTED BANDS: 274(w),293(ms),323(ms),345(mw),384(s),409(w,sh),418(ms),

450(vw,br),490(s),526(w),543(s),782(m),816(s),821(s),997(m),1007(s),1088(s),

1174(m),1390(m,dl),1565(m).

TABLE 4.11. RR and IR Data for $[Et_4N]_2[Fe_2X_2C\ell_4]$ (X = S, Se) and

$[Et_4N]_2[Fe_2S_2Br_4]$.

$[Fe_2S_2C\ell_4]^{2-}$

SOLID-RR. Band maxima/cm^{-1} (intensity at 482.5nm excitation): 144(4),178(4),

221(w),310(2),333(5),358(w),397(10),450(w,br).

Other bands: 43,48,60,67,76,84,99,108,116,125,132 (all m-w,n),507(w),576(mw),

630(w,br),703(w),730(w),796(w).

IR - SELECTED BANDS: 286(ms),326(w,sh),334(s),345(vs),416(s),800(ms),1008(m),

1032(m),1182(s),1305(m),1368(m),1405(m).

$[Fe_2Se_2C\ell_4]^{2-}$

SOLID-RR. Band maxima/cm^{-1} (intensity at 482.5nm excitation): 150 (1),246(10),

274(1),340(sh,w),348(1),397(1),406(1),435(1),493(2).

Other bands: 45,59,68,76,83,92,100,108,116,124 (all m-w,n),538(w,br),576(w,br),

600(w,br),635(w),683(w),738(w).

IR - SELECTED BANDS: 285-295(w,may be impurity),329(s),342(s),405(w),416(w),

798(ms),1005(m),1030(m),1182(s),1305(m),1368(m),1402(m)

TABLE 4.11 continued.

[Fe$_2$S$_2$Br$_4$]$^{2-}$
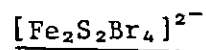
SOLID-RR: Band maxima/cm^{-1} (intensity at 482.5nm excitation) 124(3), 260(1),

274(2),315(1),393(10),410(w,sh).

Other bands: 44,60,74,102,108 (all m-w,n), 134 (568.2nm excitation),

530(m,br,dl), 665(m),788(m).

IR: 263(ms),327(ms),340(w,sh),418(ms),510(w,vbr).

Similar RR spectra are seen at other longer wavelength excitations.

Fig. 4.10 Solid—state Raman spectra of
$[Et_4N]_2[Fe_2X_2(S_2-o-xylyl)_2]$ (X=S,Se) at 530.9nm excitation

$[Fe_2S_2(S_2-o-xyl)_2]^{2-}$

568.2 nm

600   500   400   300   200   100

$[Fe_2Se_2(S_2-o-xyl)_2]^{2-}$

600   500   400   300   200   100

Raman shift/cm^{-1}
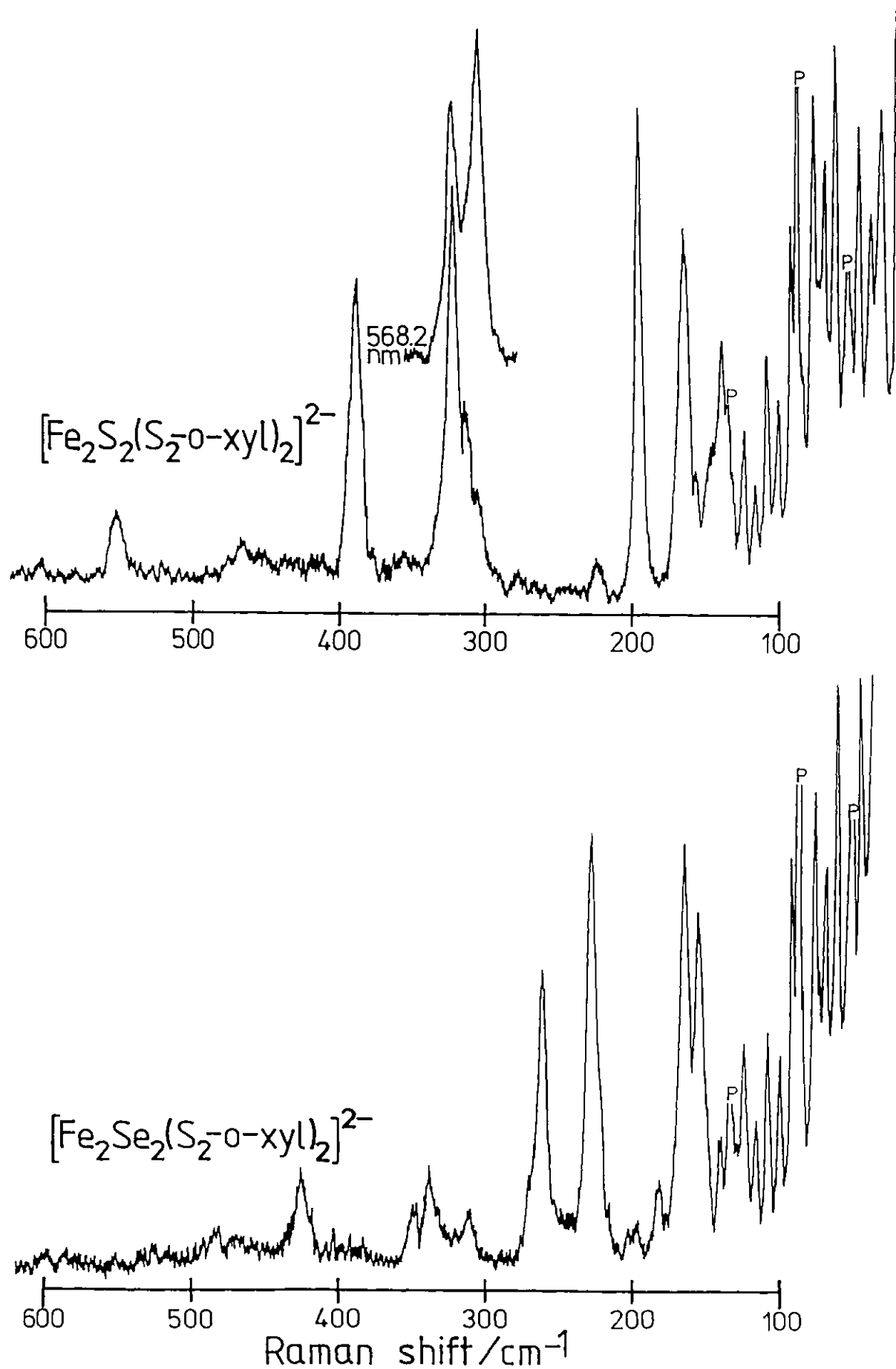
Fig. 4.11 Solid—state infra—red absorption spectra for several dimer complexes

IR Frequency/cm^{-1}

600 500 400 300

$[Fe_2S_2(SPh)_4]^{2-}$

$[Fe_2Se_2(SPh)_4]^{2-}$

$[Fe_2S_2(SePh)_4]^{2-}$

$[Fe_2Se_2(SePh)_4]^{2-}$

$[Fe_2S_2(SC_6H_4Cl)_4]^{2-}$

IR Frequency/cm^{-1}

600 500 400 300

$[Fe_2S_2(STol)_4]^{2-}$

$[Fe_2Se_2(STol)_4]^{2-}$

$[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$

$[Fe_2Se_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$
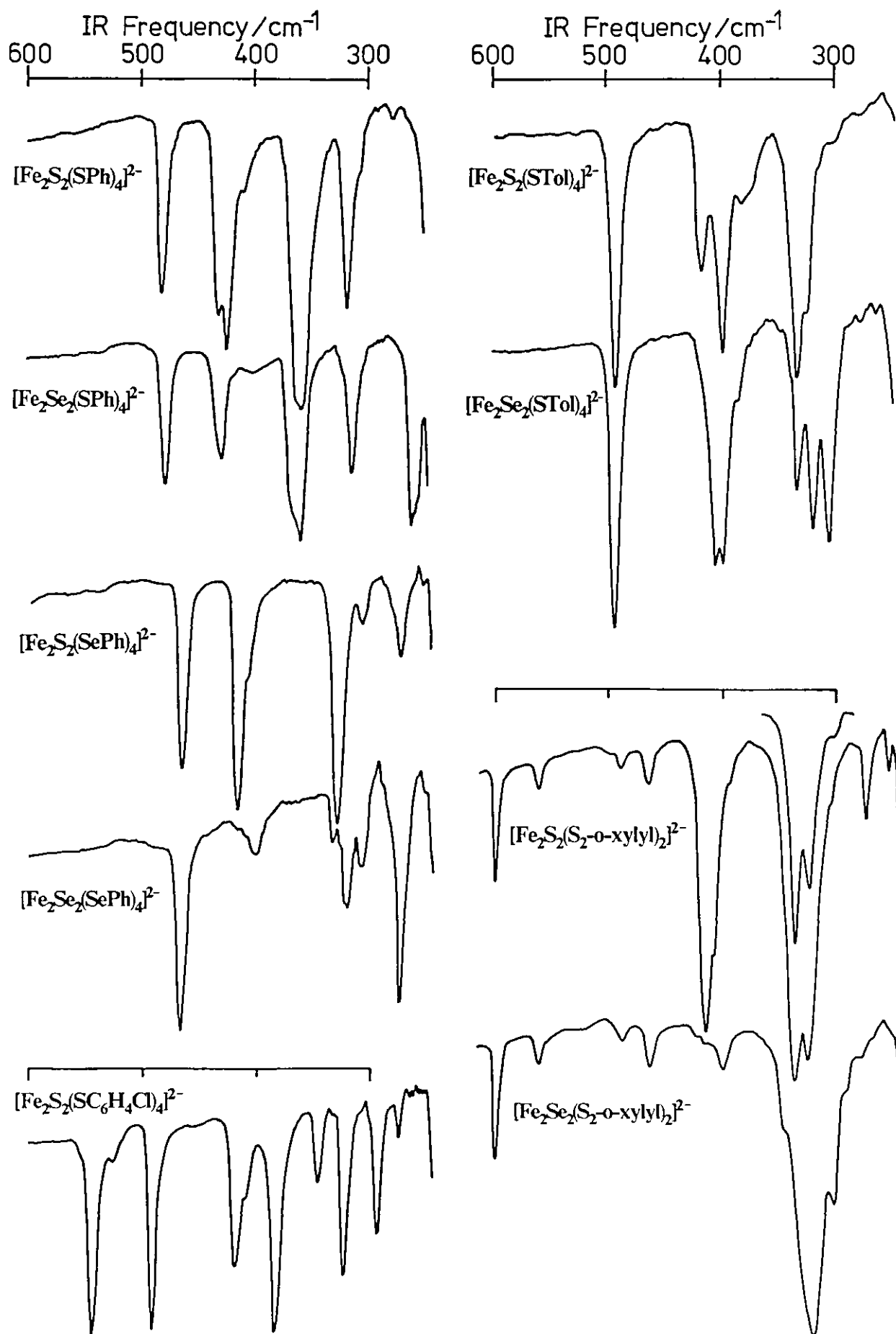
Fig. 4.12 Solid—state Raman spectra of
$[Et_4N]_2[Fe_2X_2(SPh)_4]$ (X=S,Se) at 482.5nm excitation

$[Fe_2S_2(SPh)_4]^{2-}$

P

P

P

600   500   400   300   200   100

$[Fe_2Se_2(SPh)_4]^{2-}$

P

568.2
nm

P

P

600   500   400   300   200   100

Raman shift/cm^{-1}
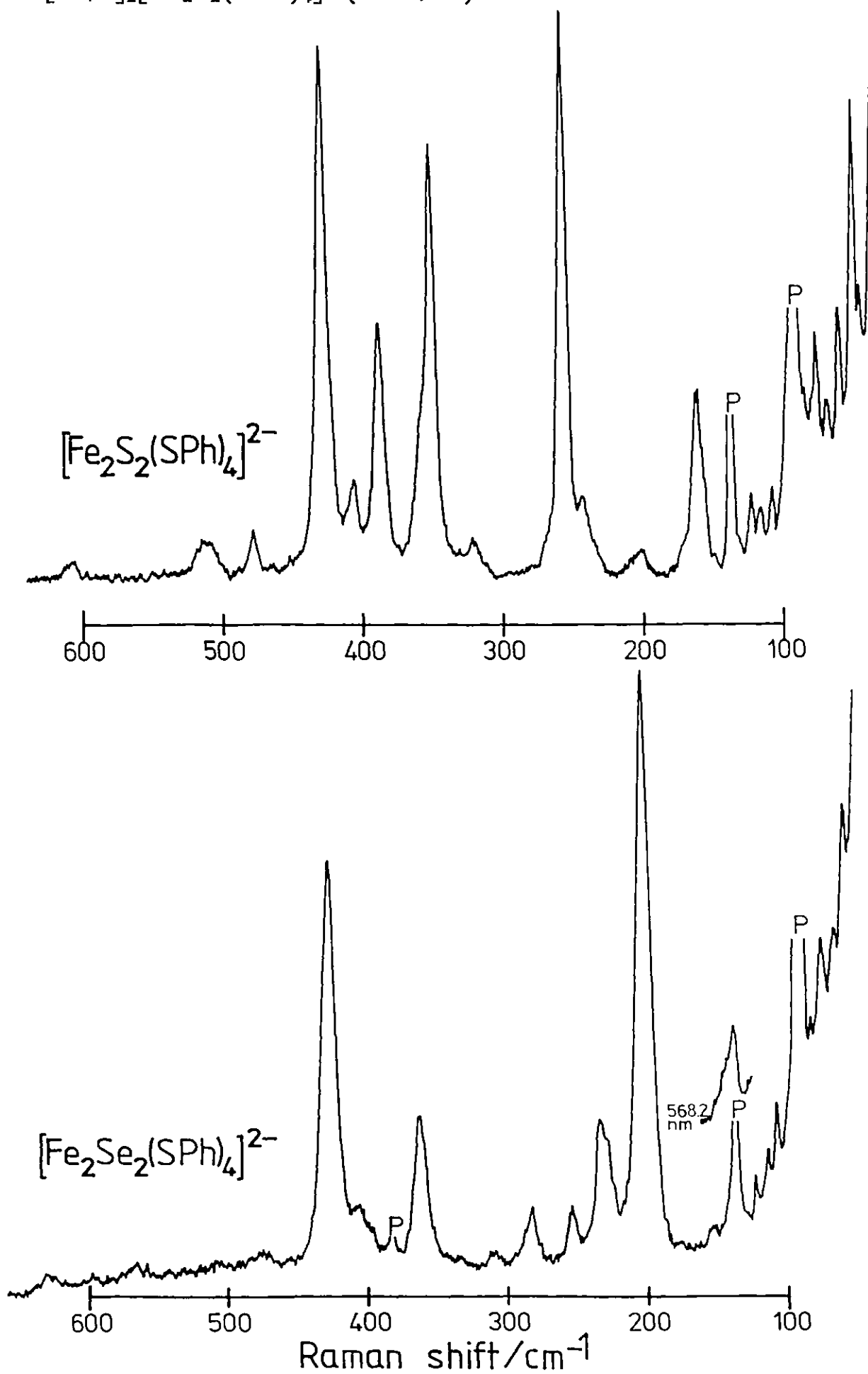
Fig. 4.13
Solid—state Raman spectra of $[Et_4N]_2[Fe_2X_2(SePh)_4]$
at 482.5nm (X=S) and 530.9nm (X=Se) excitation

$[Fe_2S_2(SePh)_4]^{2-}$

$[Fe_2Se_2(SePh)_4]^{2-}$

Raman shift/cm^{-1}
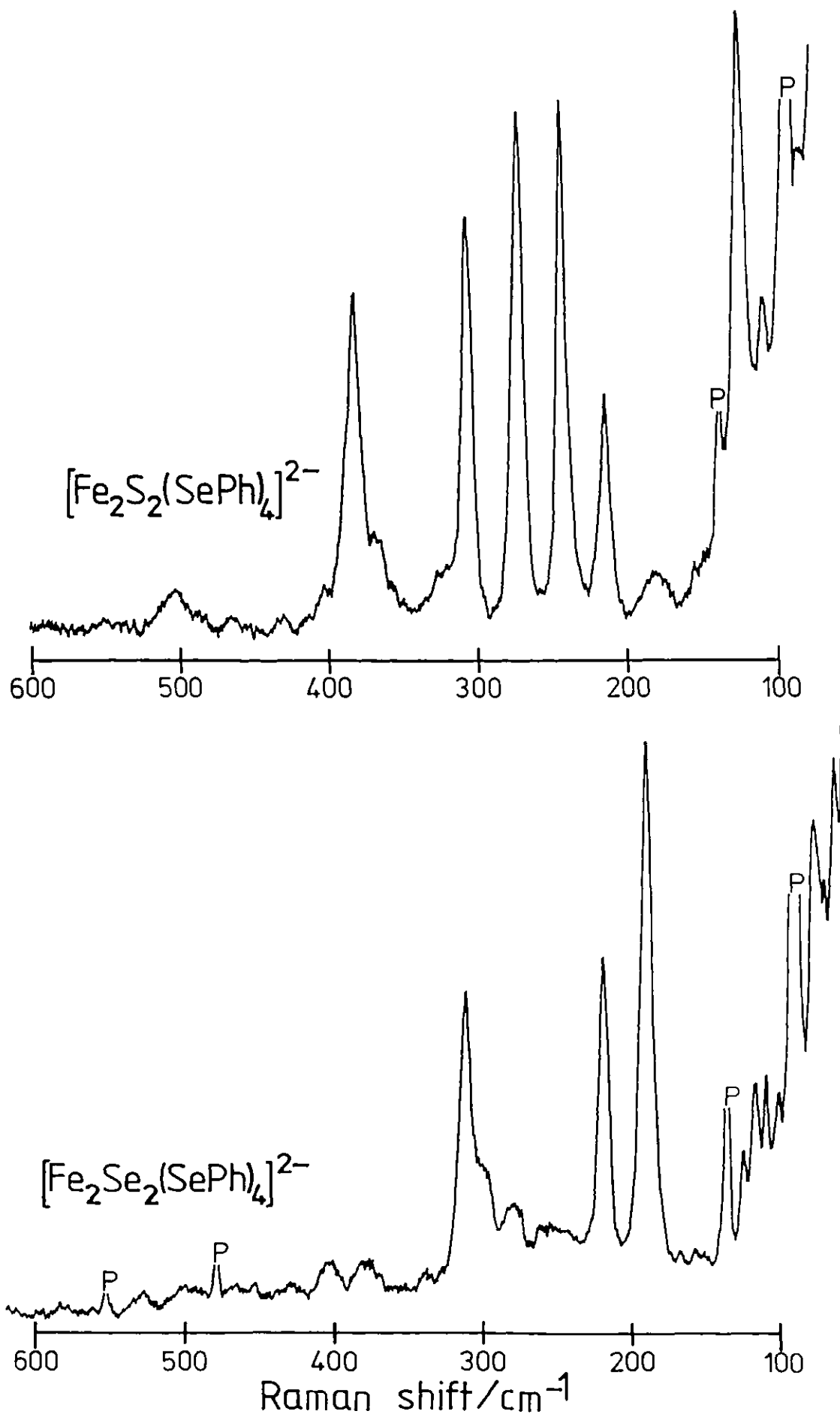
Fig. 4.14 Solid-state Raman spectra of
$[Et_4N]_2[Fe_2X_2(STol)_4]$ (X=S,Se) at 482.5nm excitation

$[Fe_2S_2(STol)_4]^{2-}$

$[Fe_2Se_2(STol)_4]^{2-}$

568.2
nm

Raman shift/cm^{-1}
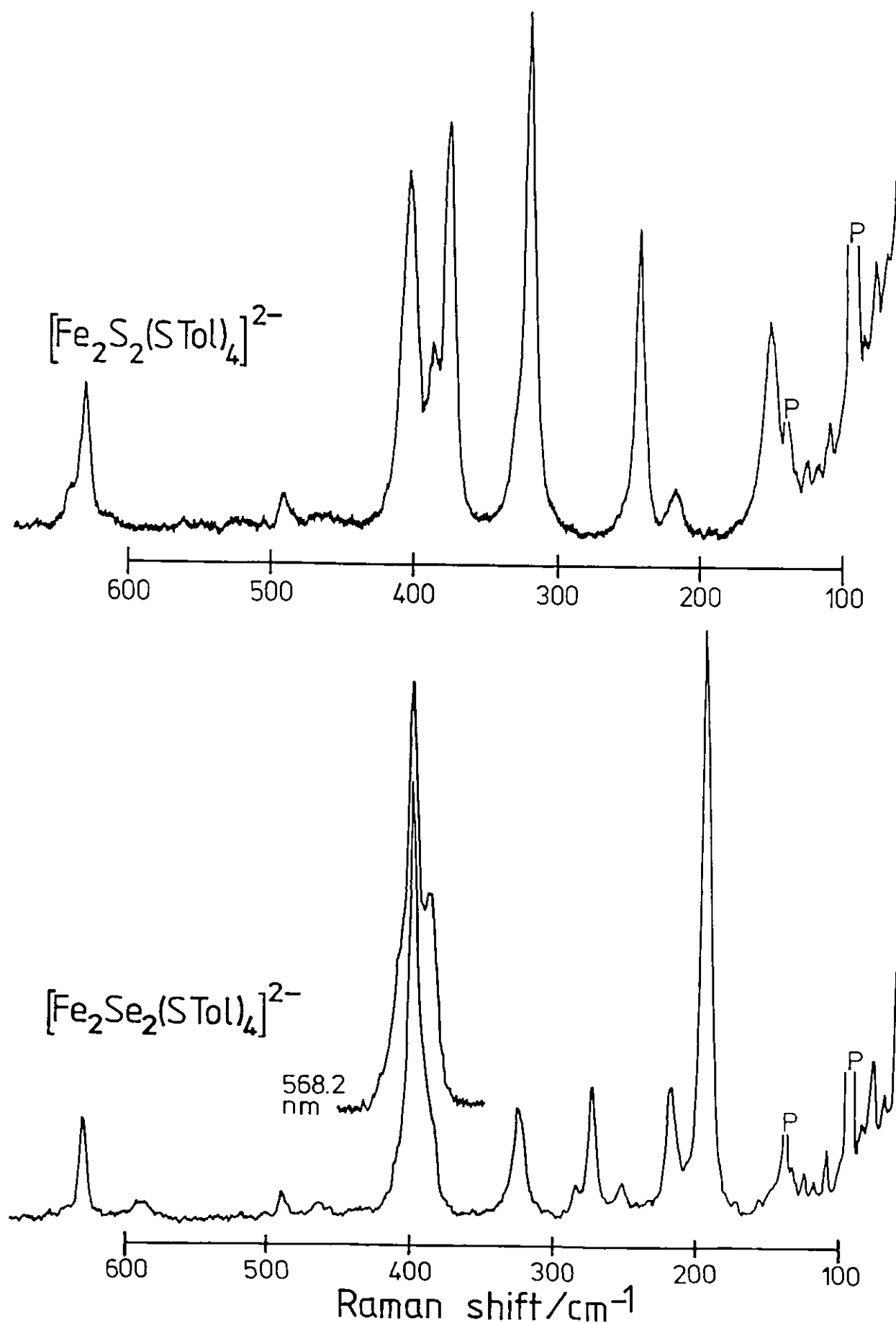
Raman spectrum of $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ corresponds to that at 321 cm^{-1}

in the solid, then this latter peak, and similarly that at 304 cm^{-1},

must be due to a totally symmetric vibration. On the grounds that ν_1 and

ν_{11} are the only bands reasonably expected in this region, the symmetry

would have to be considered degraded to C_i even in solution. Because of

the peculiar resonance effect, with the 304 cm^{-1} peak only having

appreciable magnitude at 568.2 nm excitation, the relative intensities

cannot be used to distinguish which fundamental should correspond to

which band. As both modes are terminal it is unusual that they should

show different resonance effects, and an alternative interpretation is

that the 304 cm^{-1} Raman shift arises from a positive combination of

139 and 165 cm^{-1}. Intensities at these two frequencies are maximal for

excitation at wavelengths relating to different parts of the solid

reflectance spectrum (red and green respectively, see Figure 4.17 and

Section 4.34). The excitation profiles of the 139 and 165 cm^{-1} bands

intersect (Figure 4.17) close to the 568 nm krypton emission, and it is

this exciting line which leads to the large resonance enhancement of the

304 cm^{-1} band. Following this line of argument, and taking ν_1 as the

intense 321 cm^{-1} band it becomes necessary to assign ν_{11} to one of the

weak peaks at 314 and 348 cm^{-1} or to assume coincidence with ν_1.

Generally, $\nu_{11} > \nu_1$ & $\nu_8 > \nu_{16}$ and the strong absorptions at 325 and

336 cm^{-1} in the IR are given the designations ν_{16} and ν_8 respectively.

These frequency orderings may possibly be reversed as $\nu(Fe\text{-}S_b) >$

$\nu(Fe\text{-}S_t)$ and ν_1/ν_{16} mix in some $\nu(Fe\text{-}S_b)$ at low M:X mass ratio, whereas

ν_{11}/ν_8 stay essentially pure $\nu(Fe\text{-}S_t)$.

Given no drastic structural changes on selenium substitution, ν_1 and

ν_{11} should remain in the same frequency region. $[Fe_2Se_2(S_2\text{-o-xylyl})_2]^{2-}$

shows only weakly enhanced Raman lines in the 300-350 cm^{-1} interval.

Because of the poor resolution of the four lines quoted at 311, 319, 339

and 349 cm^{-1} in Table 4.6, and their interplay of relative intensities

as the excitation wavelength varies, the shifts given represent a summary

for spectra obtained on different krypton lines. The surfeit of peaks

presents no difficulty to making correlations with the sulphur bridged

spectra, all are, however, relatively weak. In the IR the strong band

at 320 cm^{-1} is thought to contain both ν_{16} and ν_8 corresponding to the

325 and 336 cm^{-1} absorptions for $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{2-}$.

The intense Raman peak at 388 cm^{-1} in the spectra for the sulphur

bridged molecule is not found in the selenium analogue and is firmly

assigned to ν_2, the ring breathing mode. Asymmetric ring stretches,

ν_{13} and ν_{17} are proposed to give rise to the strong IR absorption around

415 cm^{-1}. If this is so it is surprising that these two vibrations

should occur at around the same frequency, as whilst ν_{13} should be

essentially purely bridge-bond stretching ν_{17} is expected to involve

considerable $S_b\widehat{Fe}S_b$ angle bending. Barring coincidence with ν_{16} or

ν_8, only the medium intensity IR band at 274 cm^{-1} remains and this

would seem to be too low in energy relative to 415 cm^{-1} to be ν_{17}.

Selenium substitution leads to loss of the strong 415 cm^{-1} peak and

appearance of a medium strength absorption at 302 cm^{-1}, whilst in the

Raman new intense lines (polarised in solution) at 228 and 261 cm^{-1}

appear concomitant with the loss of the 388 cm^{-1} peak due to ν_2.

Assigning ν_2 to 261 cm^{-1} for $[Fe_2Se_2(S_2\text{-o-xylyl})_2]^{2-}$, a ratio of 0.67

for $\nu_2(Se):\nu_2(S)$ results and is comparable to that of 0.64 observed on

exchanging bromine for chlorine in the dimeric aluminium and gallium

halides. The latter changes give ratios for $\nu_{13}(Br):\nu_{13}(C\ell)$ and

$\nu_{17}(Br):\nu_{17}(C\ell)$ in the region 0.68 to 0.81. A shift in the IR from 415 cm^{-1} to 302 cm^{-1} for sulphur/selenium bridging in the iron complexes is then compatible with assignment of ν_{13}/ν_{17} to the absorption at 302 cm^{-1}, however, the band is rather weak to contain both modes.

The strong band at 196 cm^{-1} (polarised in solution) in $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{2-}$ is assigned to ν_4, the symmetric in-plane ring deformation. This frequency would imply a medium degree of Fe-Fe interaction, in keeping with the rather long bond length of 2.698Å. In $Fe_2(CO)_6(S_2)$ with a shorter 2.55Å bond length a Raman band at 191 cm^{-1} [173] or 195 cm^{-1} [206] has been described as principally ν(Fe-Fe). Other iron-iron stretching frequencies in dimers fall in the region 190-280 cm^{-1} depending on the degree of bonding interaction,[207-210] lower frequencies are observed where there are no bridging atoms[207] or where no metal-metal interaction exists (e.g., in $Fe_2C\ell_6$ ν_4 = 108 cm^{-1} [202]). In the selenium bridged homologue the 196 cm^{-1} band is absent but new features of comparable intensity appear at 155 and 228 cm^{-1}; a decreased Raman shift would be expected.

Of the remaining unassigned peaks observed in the Raman spectrum of $[Fe_2S_2(S_2\text{-o-xylyl})_2]^{2-}$ the tentative descriptions ν_6 224 cm^{-1}, ν_3 165 cm^{-1} and ν_7 (or ν_{15}) 139 cm^{-1} are suggested.

4.3.3.2. $[Fe_2X_2(YPh)_4]^{2-}$ (X, Y = S, Se).

The analysis for this set of complexes follows to some degree the arguments used in the last section. Bands of totally symmetric origin at 428 cm^{-1} in PhS-ligated dimers are assigned to ν_1 which shifts to 306 cm^{-1} in $[Fe_2S_2(SePh)_4]^{2-}$ and 309 cm^{-1} in $[Fe_2Se_2(SePh)_4]^{2-}$. The similar ν_{16} IR mode is thought to give rise to absorption at 431 cm^{-1} in $[Fe_2S_2(SPh)_4]^{2-}$ and 428 cm^{-1} in $[Fe_2Se_2(SPh)_4]^{2-}$ whilst being shifted

TABLE 4.12. $[Fe_2X_2(S_2\text{-o-xylyl})_2]^{2-}$ (X = S, Se) vibrational assignments.

RR	X = S				X = Se	
$?\nu_7$ or $?\nu_{15}$	139	m	---->	$?\nu_4$	155	ms
$?\nu_3$	165	m	---->	$?\nu_3$	165	m
ν_4	196 p	s -------			183	w
ligand?,$?\nu_6$	224	w			228 p	m
$?\nu_{11}$ or (139+165)	304 p	m	---->	ν_2	261 p	s
	314	sh,w			⎡311	mw
ν_1	321 p	s ----> ?			319	mw
$?\nu_{11}$	348	w			339	mw
ν_2	388	s ------ ----> ?			⎣349	mw
					426	w

IR						
$?\nu_{17}$	274	m	---->	ν_{13} +$?\nu_{17}$ 302		mw
ν_{16}	325	vs	---->	ν_8 + ν_{16} 320		s
ν_8	336	vs			400	w
ν_{13} + $?\nu_{17}$	415	vs ----------				

p - polarised solution counterpart

? - possible assignment

to 273 and 274 cm^{-1} for PhSe-ligation. A double band at 360 cm^{-1} in $[Fe_2S_2(SPh)_4]^{2-}$ correlates with those at 359 and 366 cm^{-1} in $[Fe_2Se_2(SPh)_4]^{2-}$ and is tentatively assigned as ν_8, split perhaps by a solid state effect. Judging by the shift ascribed to ν_{16}, for $[Fe_2S_2(SePh)_4]^{2-}$ ν_8 would be shifted below the range of the present observations.

A second totally symmetric band at 351 cm^{-1} in $[Fe_2S_2(SPh)_4]^{2-}$ is thought to result from ν_2 and to shift to 284 cm^{-1} when selenium is

bridging, giving $\nu_2(Se):\nu_2(S) = 0.81$. Assigning ν_2 for $[Fe_2S_2(SePh)_4]^{2-}$ is less clear, but an increased frequency of 384 cm^{-1} is favoured, being absent in $[Fe_2Se_2(SePh)_4]^{2-}$. Certainly the other nearest possibilities at 273 cm^{-1} or coincidence with ν_1 at 306 cm^{-1} would seem low frequencies. The remaining intense high frequency Raman line at 387 cm^{-1} in $[Fe_2S_2(SPh)_4]^{2-}$ is possibly ν_{11}, occurring at 364 cm^{-1} in $[Fe_2Se_2(SPh)_4]^{2-}$ and shifted to 273 cm^{-1} in $[Fe_2S_2(SePh)_4]^{2-}$. Detailing $\nu_1 > \nu_{11}$ and $\nu_{16} > \nu_8$ is in contention with vibrational analyses for other M_2X_6 bridged structures. This arises from the designation of ν_1 to 428 cm^{-1} because of its low depolarisation ratio in solution. The IR active bridge stretches, ν_{13} and ν_{17}, are tentatively given to 424, 416 and 318, 328 cm^{-1} respectively in $[Fe_2S_2(SPh)_4]^{2-}$, $[Fe_2S_2(SePh)_4]^{2-}$. These are possibly shifted to 313 (ν_{13}) and 260 cm^{-1} (ν_{17}) in $[Fe_2Se_2(SPh)_4]^{2-}$, and 320 cm^{-1} (ν_{13}) in $[Fe_2Se_2(SePh)_4]^{2-}$.

The remaining intense band of totally symmetric origin observed in $[Fe_2S_2(SPh)_4]^{2-}$ at 256 cm^{-1} is thought to be ν_4, shifted considerably to 203 cm^{-1} in $[Fe_2Se_2(SPh)_4]^{2-}$ and less so to 242 cm^{-1} in $[Fe_2S_2(SePh)_4]^{2-}$. For the weak Fe-Fe bonding anticipated in these complexes 256 cm^{-1} is an unusually high frequency for bridge stretching, some 60 cm^{-1} higher than in $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$. As judged by the Fe-Fe distance available for $[Fe_2S_2(STol)_4]^{2-}$ the metallic bonding may well be stronger in the aromatic thiol coordinated complex, but the only way ν_4 could arise at such a large Raman shift is by mixing in some higher frequency vibration such as ν_1.

Whilst moving ever closer to conjecture as the band frequency and intensity drops, the following designations are proffered: $\nu_3 = 160$, 140, 123 cm^{-1} in $[Fe_2S_2(SPh)_4]^{2-}$, $[Fe_2Se_2(SPh)_4]^{2-}$, $[Fe_2S_2(SePh)_4]^{2-}$; $\nu_6 = 244$, 235 cm^{-1} in $[Fe_2S_2(SPh)_4]^{2-}$, $[Fe_2Se_2(SPh)_4]^{2-}$; ν_2, $\nu_4 = 217, 187$ cm^{-1} in $[Fe_2Se_2(SePh)_4]^{2-}$.

TABLE 4.13. $[Fe_2X_2(YPh)_4]^{2-}$ (X, Y = S , Se) Vibrational Assignments.

X = Y = Se			X = Se, Y = S			X = Y = Se			X = S, Y = Se			X = Y = S		
$?\nu_3$	160	m	$?\nu_3$	140	w	$?\nu_4$	187	s	$?\nu_3$	123	s	$?\nu_3$	160	m
	201	w	ν_4	203	s	$?\nu_2$	217p	m		180	w		201	w
$?\nu_6$	244	sh,w	$?\nu_6$	235	m				ligand?	214	m	$?\nu_6$	244	sh,w
ν_4	256p	s		255	w		278	w	ν_4	242p	s	ν_4	256p	s
	320	w	ν_2	284p	mw				$?\nu_{11}$	273	s		320	w
ν_2	351p	m		314	w		298	w	ν_1	306p	s	ν_2	351p	m
$?\nu_{11}$	387	m	$?\nu_{11}$	364	m	ν_1	309p	s	$?\nu_2$	384	m	$?\nu_{11}$	387	m
	406	w		410	w								406	w
ν_1	428p	s	ν_1	428p	s							ν_1	428p	s
	478	w		475	w								478	w
	279	w	$?\nu_{17}$	260	m	ν_{16}	274	s	ν_{16}	273	m		279	w
$?\nu_{17}$	318	s	$?\nu_{13}$	313	ms	ligand?	306	mw	ligand?	307	w	$?\nu_{17}$	318	s
ν_8	360	vs,dl	ν_8	359	s	$?\nu_{13}$	320	m	$?\nu_{17}$	328	s	ν_8	360	vs,dl
	410	w	split	366	sh,ms		333	w					410	w
$?\nu_{13}$	424	s		400	w,br	ligand?	400	mw,br	$?\nu_{13}$	416	s	ν_{13}	424	s
ν_{16}	431	m	ν_{16}	428	m							ν_{16}	431	m

4.3.3.3. [Fe₂X₂(STol)₄]²⁻ (X = S, Se), [Fe₂S₂(SC₆H₄Cℓ)₄]²⁻ and

$$[Fe_2X_2Y_4]^{2-} \text{ (X = S, Se; Y = C}\ell\text{, Br)}.$$

The reasoning behind the assignment of the vibrations for these
complexes (Tables 4.14-16) follows similar lines to those used in the
previous two sections and will not be treated here in detail. For
[Fe₂S₂(SC₆H₄Cℓ)₄]²⁻ interpretation is difficult as there is a greater
number of intense bands, in both the IR and RR spectra, than can easily
be accounted for. The halogen ligated complexes, [Fe₂X₂Cℓ₄]²⁻ (X = S,
Se) and [Fe₂S₂Br₄]²⁻, show a dominant feature in the Raman which has been
assigned to ν_2. The remaining weaker bands are not easily assigned.
No attempt has been made to obtain solution spectra of these complexes
as they are rather less stable than the thiolate coordinated dimers and
additionally the strongest peak in the sulphur bridged compounds would
be obscured by solvent Raman scattering. The Raman and IR results for
[Fe₂S₂Cℓ₄]²⁻ show little similarity with those for Fe₂Cℓ₆.[202-204] The
mean Fe-Cℓ bridge and Fe-Cℓ terminal bonding lengths for the latter have
recently been determined as 2.326 and 2.127Å respectively by vapour phase
electron diffraction.[211] These lengths differ considerably from those
for [Fe₂S₂Cℓ₄]²⁻ (Figure 3.9) and in particular the bridge-terminal
difference is reversed.

4.3.4. Optical spectra and Raman resonance enhancement for the two-
iron complexes.

Figure 4.15 shows overlaid electronic spectra for [Fe₂X₂(YPh)₄]²⁻
(X, Y = S, Se) in DMF solution; peak positions and extinction coefficients
for these and other dimeric complexes are collected in Table 4.17.
Optical data has been reported previously for [Fe₂S₂(SC₆H₄Y)₄]²⁻ (Y = H,
Cℓ, Me) and [Fe₂S₂(S₂-o-xylyl)₂]²⁻ in DMF,[28] and subsequent to this
present work for the selenide-bridged thiolate-coordinated complexes.[29]

TABLE 4.14. $[Fe_2X_2(STol)_4]^{2-}$ (X = S, Se) vibrational assignments.

RR	X = S			X = Se		
$?\nu_3$	148	m	$\dashrightarrow \nu_4$	192	s	
	215	w		218	mw	
ν_4	241p	s	$\dashleftarrow$	251	w	
ν_2	320p	s	$\dashrightarrow \nu_2$	272	mw	
$?\nu_{11}$	375	s		325	mw	
ligand?,$?\nu_{11}$	386	m	$\longrightarrow$ ligand?,$?\nu_{11}$	387	sh,m	
ν_1	403	s	$\longrightarrow \nu_1$	398	s	
	490	w	ligand?	630	m	
ligand?	630	m				
IR						
$?\nu_{17}$	325	sh,m		304	ms	
$?\nu_{17}$	332	s	$\dashrightarrow \nu_{13}$	318	ms	
	374	sh, w		332	m	
ν_8	382	mw	$\longrightarrow \nu_8$ and ν_{16}	398	ms,dl	
ν_{16}	396	s				
ν_{13}	415	ms				

TABLE 4.15. $[Fe_2S_2(SC_6H_4C\ell)_4]^{2-}$ vibrational assignments.

RR			IR		
	137	w		274	w
	201	w	$?\nu_{17}$	293	ms
$?\nu_4$	221	mw	$?\nu_{17},?\nu_8$	323	ms
$?\nu_2,?\nu_4$	294p	s	$?$ligand,$\nu_8?$	345	mw
	320	w	ν_{16}	384	s
$?\nu_2$	342p	s		409	sh,w
ν_1	368	s	ν_{13}	418	ms
ν_{11}	381	m		450	vw,br
	401	m			

TABLE 4.16. [Fe₂X₂Y₄]²⁻ (X = S, Se; Y = Cℓ, Br) vibrational assignments.

[Fe₂Se₂Cℓ₄]²⁻			[Fe₂S₂Cℓ₄]²⁻			[Fe₂S₂Br₄]²⁻		
RR								
	150	w		144	m		124	mw
ν₂	246	s	ν₄	178	m		260	w
	274	w		221	w		274	mw
	340	sh,w	?ν₁₁	310	mw		315	w
	348	w	ν₁	333	m	ν₂	393	s
	397	w		358	w		410	sh,w
	406	w	ν₂	397	s			
	435	w		450w				
	493	mw						
IR								
impurity?	285-95	w		286	ms		263	ms
ν₁₃	329	s		326	sh,vw	ν₁₇	327	ms
ν₈ + ν₁₆	342	s	ν₁₇	334	s		340	sh,w
	405	w	ν₈ +ν₁₆	345	vs	ν₁₃	418	ms
	416	w	ν₁₃	416	s		510	m,vbr

TABLE 4.17. Electronic spectra of [Fe₂X₂(YR)₄]²⁻ (X, Y = S, Se).

IN DMF	λ/nm (ϵ mM); [deconvoluted Lorentzian peaks]
[Fe₂S₂(S₂-o-xylyl)₂]²⁻	293,339(16.9),415(11.4),455(sh),591(5.1)
[Fe₂Se₂(S₂-o-xylyl)₂]²⁻	305,346(18.8),438(11.9),485(sh),628(4.9)
[Fe₂S₂(SPh)₄]²⁻	334(19.0),489(11.3),∿540(br,sh);[480(8.5),559(4.7)]
[Fe₂Se₂(SPh)₄]²⁻	342(20.4),505(12.1); [499(9.5),596(3.9)]
[Fe₂S₂(SePh)₄]²⁻	353(18.8),500(sh),552(11.6);[476(4.0),564(9.9)]
[Fe₂Se₂(SePh)₄]²⁻	355(16.7),540(10.4);[518(6.5),608(5.7)]
[Fe₂S₂(STol)₄]²⁻	334(20.1),496(12.0),∿530(br,sh)
[Fe₂Se₂(STol)₄]²⁻	341(19.5),510(12.0)
IN ACETONE	
[Fe₂S₂(SPh)₄]²⁻	485,∿540(sh); [471, 551]
[Fe₂Se₂(SPh)₄]²⁻	500; [495, 597]
[Fe₂S₂(SePh)₄]²⁻	485, ∿500(sh); [477,563]
[Fe₂Se₂(SePh)₄]²⁻	∿530; [512,604]
[Fe₂S₂(SC₆H₄Cℓ)₄]²⁻	476, ∿540(sh); [480,562]
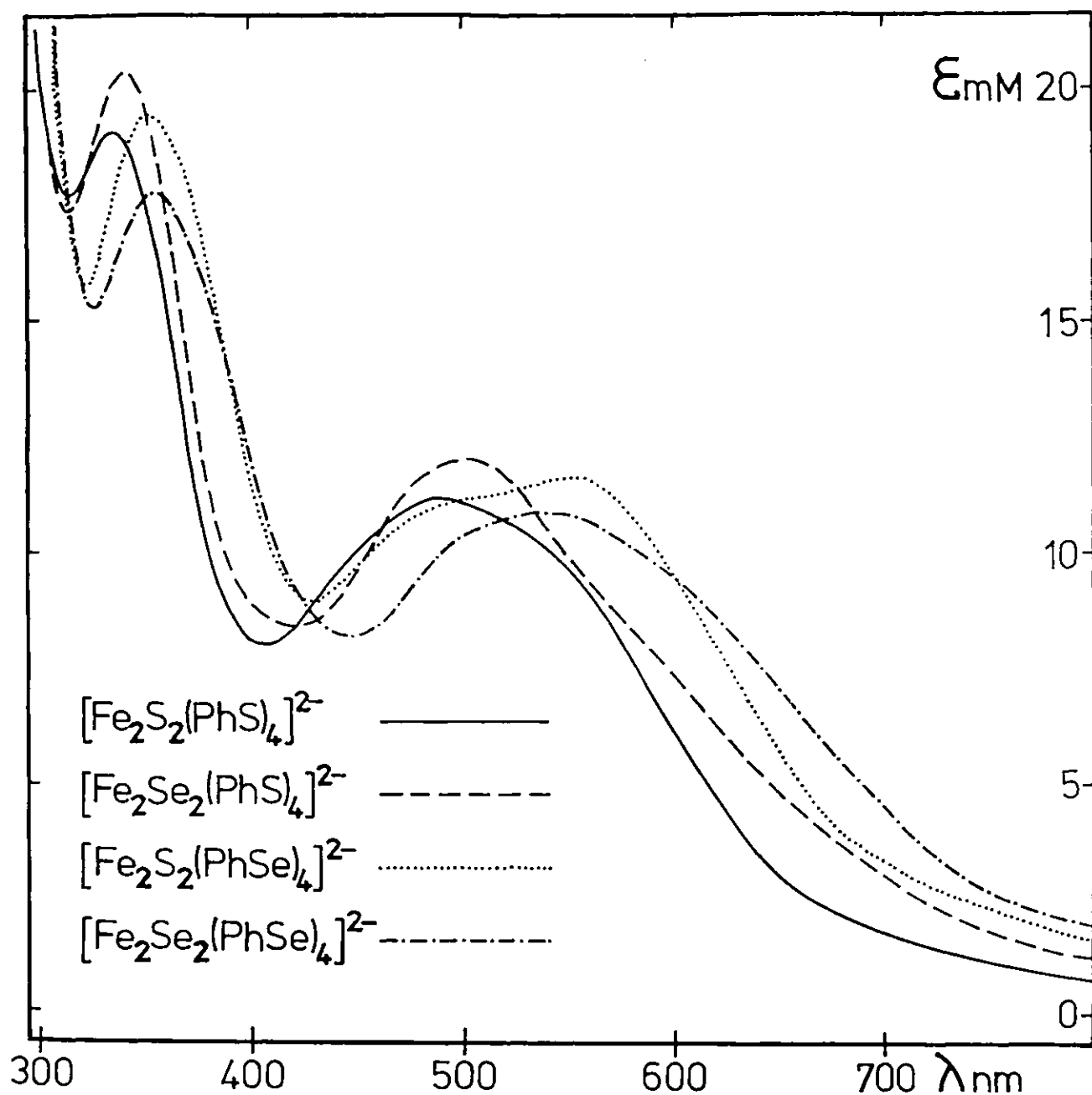
Figure 4.15. Electronic absorption spectra for $[Fe_2X_2(YPh)_4]^{2-}$

(X, Y = S, Se) in DMF.

For $[Fe_2X_2(YPh)_4]^{2-}$ (X, Y = S, Se) the absorption around 500-600 nm has been deconvoluted into two Lorentzian bands by a least-squares fitting procedure. All the bands above 300 nm are charge-transfer in origin and in most cases show red shifts on selenium substitution. Such shifts were also observed in the series of complexes $[Fe_4X_4(YPh)_4]^{2-}$ (X, Y, = S, Se),

being greater for the PhS/PhSe ligand change than for the Fe_4S_4/Fe_4Se_4 core alteration[212]; the reverse seems to be the case for the shifts

in the two low energy bands of the dimeric complexes. Small red shifts

resulting from replacement of coordinated sulphur by selenium, in other-

wise identical complexes, have been observed for several series of compounds

[see references in reference 212]. The very small change in band position

produced on going from PhS- to PhSe-ligation is indicative of comparable

optical electronegativities for the chalcogenides in these ligands.[213,214]

Two-iron ferredoxins reconstituted with bridging selenide, show visible

band bathochromic shifts comparable to those described above for the

analogue complexes.[49,215,83,170]

Figure 4.16 shows optical spectra for five of the dimer complexes

in acetone, together with Lorentzian deconvolution analyses. Raman

intensities for the v_1 assigned symmetric stretching vibrations have

been plotted at Krypton emission frequencies for each complex. These

are normalised using the 787 cm^{-1} acetone solvent peak as a standard.

Allowing for concentration differences the v_1 (Fe-S) modes of $[Fe_2X_2(YPh)_4]^{2-}$

(X, Y, = S, Se) at full resonance range 1300 to 1600 times more intense

than the 787 cm^{-1} acetone symmetric stretch,clearly indicating strong

involvement of a resonance enhancement process. Considering an error

of around 10% in estimation of the relative Raman intensities and an

error of 10 nm or more (depending upon magnitude and width) in evaluating

the deconvoluted band maxima, there appears a reasonable agreement between

the peaks of the excitation profiles and of the lowest energy electronic

bands. Thus, it seems that these probably arise from charge transfer

involving the PhY-Fe bonds. An exception is $[Fe_2Se_2(SPh)_4]^{2-}$ for which

the excitation profile has a peak-value at a wavelength intermediate

FIG 4.16 $[Fe_2X_2(YR)_4]^{2-}$ (X,Y=S,Se:R=Ph,pClPh) IN ACETONE
ELECTRONIC SPECTRA AND RAMAN EXCITATION PROFILES

$[Fe_2S_2(SPh)_4]^{2-}$

EXPT.

CALC.

BANDS

RAMAN

ABSORBANCE →

RAMAN INTENSITY

100

0

WAVELENGTH/nm

400   450   500   550   600   650   700   750   800

$[Fe_2Se_2(SPh)_4]^{2-}$

ABSORBANCE →

RAMAN INTENSITY

100

0

WAVELENGTH/nm

400 450 500 550 600 650 700 750 800

$[Fe_2S_2(SePh)_4]^{2-}$

ABSORBANCE →

RAMAN INTENSITY

100

0

WAVELENGTH/nm

400 450 500 550 600 650 700 750 800

$[Fe_2Se_2(SePh)_4]^{2-}$

ABSORBANCE →

RAMAN INTENSITY

100

0

WAVELENGTH/nm

400 450 500 550 600 650 700 750 800

$[Fe_2S_2(SPhCl-p)_4]^{2-}$

ABSORBANCE →

RAMAN INTENSITY

100

0

WAVELENGTH/nm

400 450 500 550 600 650 700 750 800

between the two deconvoluted bands, though it should be noted that for this case the simulated fit is not very good at the experimental maximum and may indicate an inadequate representation of component lineshapes leading to less accurate resolution of these underlying bands. In most of the remaining complexes the maximum Raman intensity is also observed at higher energy than the low energy deconvoluted shoulder.

Due to solvent obscuration, a study of Raman resonance enhancement for $[Fe_2X_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ (X = S, Se) in DMF, DMSO, or MeCN solvents is not feasible. However, an attempt has been made to correlate intensity variations of the many Raman bands observed for the solid phase with the reflectance spectra for the complexes, diluted in MgO. These electronic spectra are shown in Figure 4.17, together with Raman excitation profiles obtained relative to the symmetric NO_3^- stretch of KNO_3 added as a standard to the supporting KBr matrix. Details of band positions for these reflectance spectra, and also for $[Et_4N]_2[Fe_2S_2(SPh)_4]$, are given in Table 4.18. The spectra are complex, involving many underlying bands. This is in contrast to observations for analogous tetramer compounds [see Section 4.4.2.3.]. Red shifts, comparable to those in solution, are found on going from sulphur to selenium bridging. There is a certain degree of correlation of Raman maximum intensity for several vibrational bands, with the absorption peak around 590 nm in $[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$.

TABLE 4.18. Reflectance spectra of $[Fe_2X_2(SR)_4]^{2-}$ (X = S, Se).

$[Et_4N]_2[Fe_2S_2(S_2\text{-}o\text{-}xylyl)_2]$
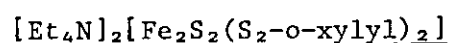
1310(w,br), ∿850(w,br,pr), ∿750(sh), 710, 590, ∿470(br,pr).

$[Et_4N]_2[Fe_2Se_2(S_2\text{-}o\text{-}xylyl)_2]$
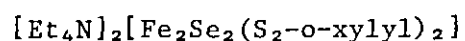
1420(w,br), ∿920(w,br,pr), ∿790(sh), 620, ∿450 and 480 (pr)

$[Et_4N]_2[Fe_2S_2(SPh)_4]$
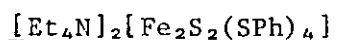
1450(w), ∿900(w,pr), ∿740(sh), 670, ∿580, ∿520(pr)
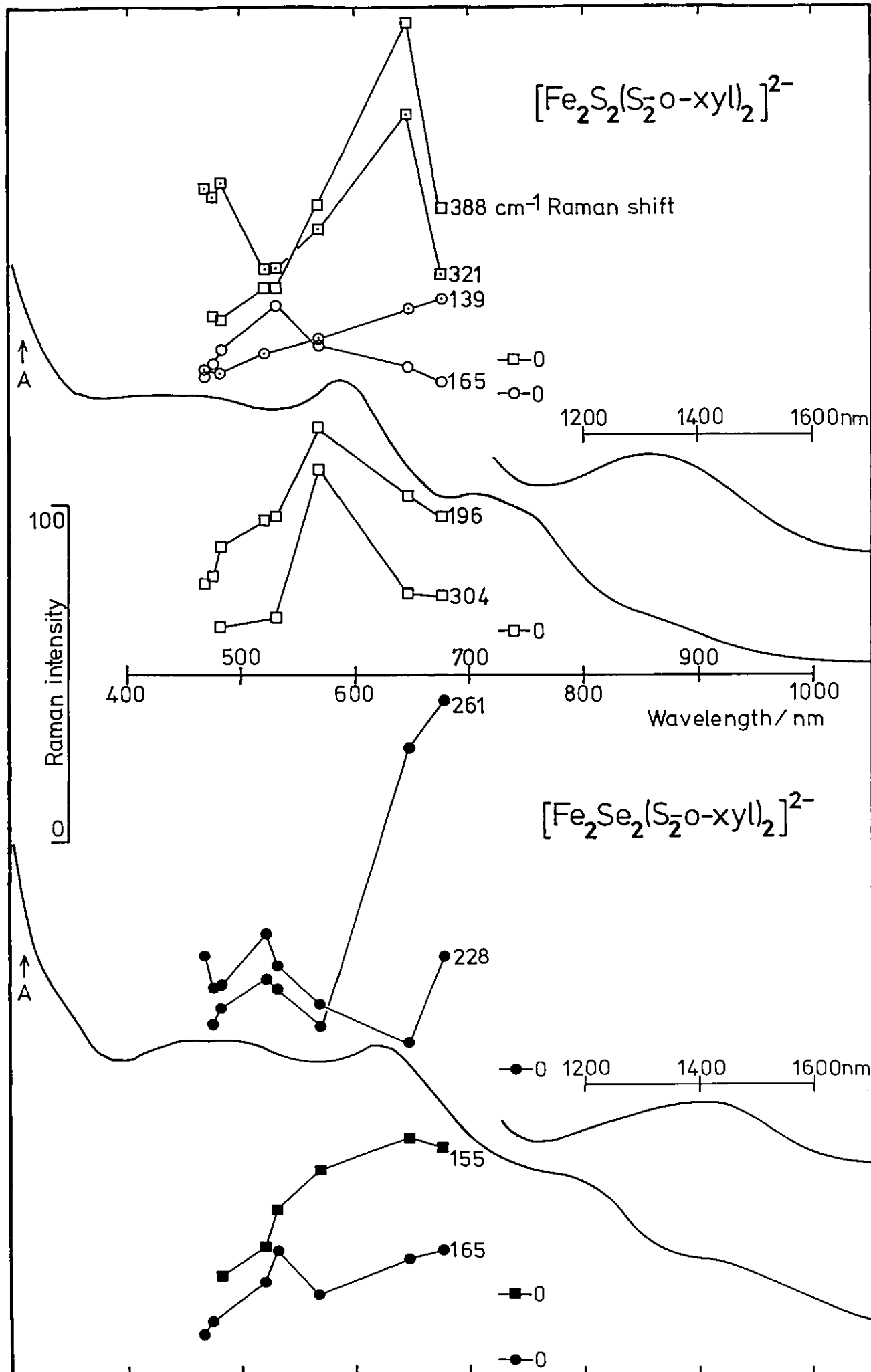
Fig. 4.17 Electronic reflectance spectra and Raman excitation profiles for $[Et_4N]_2[Fe_2X_2(S_2-o-xylyl)_2]$(X=S,Se)

4.3.5. General Conclusions Concerning Dimer Complexes.

Table 4.19 lists by order of mode the vibrational assignments for the twelve dimer complexes studied. Comparing Fe-X vibrations for a given X-atom type, there is quite good agreement for several of the modes assigned in the different compounds. A correlation of ν_4 with Fe-Fe distance is observed for the three complexes for which dimensional structure information is available. As the Fe-Fe separation increases from $2.691\overset{o}{A}$ in $[Fe_2S_2(STol)_4]^{2-}$ to $2.716\overset{o}{A}$ in $[Fe_2S_2C\ell_4]^{2-}$ the frequency assigned to ν_4 decreases from 241 cm^{-1} to 178 cm^{-1} indicative of decreasing bonding interaction .

The bands observed at 330-350 cm^{-1} and 390-395 cm^{-1} in adrenal and spinach ferredoxin Raman spectra[114,115,170] agree reasonably well with those at 321 cm^{-1} (ν_1) and 388 cm^{-1} (ν_2) for $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$. For the other analogue complexes having terminal aryl thiol ligands $\nu_1 > \nu_2$, and thus the alkyl thiol chelated compound seems better to model the protein, in keeping with the cysteine coordination in the latter. The other bridge vibration observed at 284-297 cm^{-1} in the ferredoxins has no counterpart in the $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ Raman spectrum. For selenium bridging ν_2 has been assigned to a strong band at 261 cm^{-1} in $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$, a shift of 127 cm^{-1}. There is a band in selena-adrenodoxin at 263 cm^{-1} which correlates favourably with this interpretation, but this has been tentatively described by Tang et al.[170] as shifted from 297 cm^{-1} in the native protein, a shoulder at $\sim$ 350 cm^{-1} (Se) being identified with shifting of the 397 cm^{-1} (S) peak. For the other terminal thiol ligated analogues the shift of peaks assigned as ν_2, on going from sulphur to selenium bridging, is smaller than for

TABLE 4.19. Correlation of Vibrational Assignments for Dimer Complexes.

Dimer	ν_1	ν_2	ν_3	ν_4	ν_6	ν_8	ν_{11}	ν_{13}	ν_{16}	ν_{17}
$[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$	321	388	165?	196	224?	336	348?	415	325	415 / 274 ?
$[Fe_2S_2(SPh)_4]^{2-}$	428	351	160?	256	244?	360	387?	424	431	318?
$[Fe_2S_2(STol)_4]^{2-}$	403	320	148?	241		382	375 / 386	415	396	325 / 332
$[Fe_2S_2(SCH_4Cl)_4]^{2-}$	368 / 381	342 / 294 ?		294 / 221 ?		323 / 345 ?	368 / 381	418	384	293 / 323 ?
$[Fe_2S_2Cl_4]^{2-}$	333	397		178		345	310?	416	345	334
$[Fe_2Se_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$	319?	261	165?	155?		320	349?	302	320	302?
$[Fe_2Se_2(SPh)_4]^{2-}$	428	284	140?	203	235?	359–366	364?	313	428	260?
$[Fe_2Se_2(STol)_4]^{2-}$	398	272		192		398	387?	318	398	
$[Fe_2Se_2Cl_4]^{2-}$		246				342		329	342	
$[Fe_2S_2(SePh)_4]^{2-}$	306	384?	123?	242			273?	416?	273	328?
$[Fe_2S_2Br_4]^{2-}$		393						418		327
$[Fe_2Se(SePh)_4]^{2-}$	309	217?		187?					320?	274

NOTES: 1. ? = possible assignment; 2. two entries at one frequency for a single compound indicate alternative possible assignments.

$[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$, thus it is difficult to assess from the results

for the model-complexes whether the tentative assignment of Tang et al.

is correct. However, in view of there being similarities between spectra

for $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ and the proteins, assignment of ν_2 to 263 cm^{-1}

in selena-adrenodoxin is favoured here.

No attempt has been made to obtain Raman spectra for the reduced

dimer species reported in Section 1. . It would be necessary to

perform these measurements on frozen solutions using solvents such as

DMF, DMSO, or NMP which scatter strongly in the region of interest.

Gayda, et al.[101] have discussed the possibility of spin-relaxation in

reduced ferredoxins occurring by an Orbach process involving an Fe_2S_6

core vibrational mode, and concluded that this is unlikely in view of the

similarity of Fd_{ox} Raman spectra as against the disparity of EPR temper-

ature-dependence for the same Fe_{red}. More recently, however, Gayda

et al.[107] have suggested that at high temperatures local modes could be

important in determining the efficiency of the Orbach relaxation mechanism

for ferredoxins, in that high frequency modes are not expected to be

able to propagate through the protein. Measurements described in

Section 2 for three of the analogue complexes indicate that any local

mode involved in their spin-relaxation would require a frequency much

higher than anticipated for $[Fe_2S_2(SR)_4]^{3-}$ or observed for any of the

diferric complexes.

The magnetic properties of $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ and $[Fe_2S_2C\ell_4]^{2-}$

have been investigated and antiferromagnetic behaviour demonstrated with

$-J = 149 \pm 8$ cm^{-1} and 158 cm^{-1} respectively.[38,194] For transitions

from ground and first excited states to higher levels of the spin manifold

the following energies are predicted; $[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$ from $S = 0$,

298 ± 16, 894 ± 48, 1788 ± 96, 2980 ± 160 cm^{-1}; from $S = 1$, 596 ± 24,

1490 ± 80, 2682 ± 140 cm^{-1}: $[Fe_2S_2C\ell_4]^{2-}$ from $S = 0$, 316, 948, 1896,

3160 cm^{-1}; from $S = 1$, 632, 1580, 2844 cm^{-1} (errors on this last set

are expected to be higher than quoted for the first). Although in

each case a potential $S = 0 \rightarrow 1$ transition peak occurs around 300 cm^{-1}

and there are weak bands at higher frequencies which correlate, within

the specified error ranges, to the energies predicted from the suscepti-

bility results, no convincing evidence is forthcoming to support the

interpretation of Fd spectra given by Blum et al.[114,115] This conclusion

may be extended to include the Raman results for the other two-iron

clusters studied; assuming the strength of their antiferromagnetic

interactions to be similar.[38] It is difficult to eliminate cation and

ligand vibrations as their intensities and frequencies in the complex and

in control compounds may differ and unassigned bands are in some cases

too weak, in others too numerous, to allow any confidence in fitting

a 0, 2J, 6J, 12J, 20J, 30J pattern, even when allowing a generous error

margin. A similar caution probably applies in judging the validity

of spin-flip Raman assignments made for the proteins.

4.4. Tetranuclear Iron-Sulphur Complexes; Analogues of 4Fe4S Proteins.

4.4.1. RR in 4Fe4S clusters.

Surprisingly little investigation has been made of the vibrational

properties of proteins containing 4Fe4S clusters or of their synthetic

counterparts, $[Fe_4S_4(SR)_4]^{2-}$, first reported almost a decade ago. The

electronic spectra of these is characterised by a prominent absorption

band in the 380-450 nm region, which tails off for around 100 nm to

higher energy. A strong pre-resonance effect is expected for Raman active

vibrations of the iron-sulphur core when exciting with the blue emission

lines available on Argon/Krypton lasers. Figure 4.18 shows RR spectra

obtained for $[Fe_4S_4(SBz)_4]^{2-}$, Chromatium Hipip and C. pasteurianum

ferredoxin by Tang et al.[172] using 488.0 nm excitation. All peaks

observed are polarised, those at frequencies greater than 300 cm^{-1} have

been tentatively assigned to the terminal ligand breathing mode, whilst

those at smaller shifts are assignable to the breathing mode of the Fe_4S_4

Figure 4.18. Raman spectra for three 4Fe-4S centres (488 nm excitation)[172]
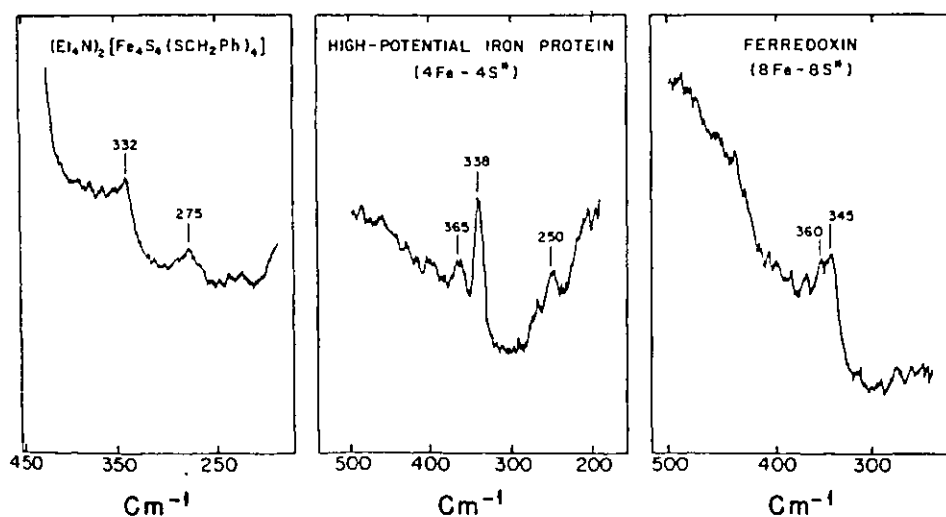
core. The appearance of two polarised bands above 300 cm^{-1} in the

proteins has been interpreted as implying a lowering of symmetry below

T_d.

Subsequent to this present work Holm, et al.[216] have reported that

vibrational analysis of $[Fe_4S_4(SPh)_4]^{n-}$ (n = 2, 3) is underway and that

from preliminary findings ν_{Fe-S} (bridge) = 343 cm^{-1} (dianion), 341 cm^{-1}

(trianion) and ν_{Fe-S} (terminal) $\simeq$ 430 cm^{-1} (dianion and trianion);

though the bands around 340 cm^{-1} do not arise from pure Fe-S_b stretching

modes.

4.4.2. RR and IR spectra of $[Fe_4S_4(SR)_4]^{2-}$.

The properties of $[Fe_4S_4(SR)_4]^{n-}$ (n = 2,3) have been studied in

detail over the past ten years and structurally and spectroscopically

the compounds demonstrated to be true analogues of the clusters present

in 4Fe4S and 8Fe8S proteins. The majority of the investigations have

been performed with the thiolates PhS- and BzS- as terminal ligands.

RR and IR spectra for $[Fe_4S_4(SPh)_4]^{2-}$, $[Fe_4S_4(SBz)_4]^{2-}$ and also for the

corresponding selenium bridged and PhSe- ligated species[212] are described

in Figure 4.19-22 and Tables 4.21-23.

X-ray determined crystal structures are available for $[NMe_4]_2[Fe_4X_4(SPh)_4]$

(X = S, Se),[58,212] and for $[Et_4N]_2[Fe_4S_4(SBz)_4]$.[75] The stereochemistries

of the sulphur bridged tetramers are very similar and manifest D_{2d}

cluster geometry, having a compression along the unique C_2 axis. Carter[217]

has made the observation that the S-S distances for the four thiolate

ligands can be divided into two sets of three, forming a unique base

(mean S-S $\simeq$ 6.3Å) and apex (mean S-S $\simeq$ 6.5Å) of a trigonally distorted

tetrahedron. This distortion, taken together with the tetragonal Fe_4S_4

core distortion eliminates all symmetry elements except the mirror plane and the molecular point group is therefore C_s. The same symmetry reductions can be seen in the Fe_4S_8 core structures of $HIPIP_{red}$ and Fd_{ox}. The core S_4 approximate-tetrahedron is dimensionally larger than the Fe_4 tetrahedron which it interpenetrates. The $Fe_4Se_4S_4$ cluster is devoid of symmetry but closely approaches D_{2d}.

For an $M_4(X_b)_4(X_t)_4$ cubane structure with strict T_d symmetry thirteen normal vibrations are expected. The symmetries and selections rules, together with an approximate description for each vibration, are given in Table 4.20. Twenty-three modes result from losses in degeneracy when the cluster symmetry is degraded to D_{2d}, and the number of totally symmetric vibrations increases from three to six. The symmetry reducing distortions outlined above are not gross, particularly in the case of $[Fe_4S_4(SPh)_4]^{2-}$, and effective T_d symmetry will be assumed in describing vibrational assignments, with due allowance for departure from this where necessary.

Detailed interpretation of the IR and Raman spectra for the tetra-nuclear clusters is not straightforward. This is not unexpected in view of the complexity of the molecules, the comparable masses of the constituent atoms, the close spacing of the vibrational frequencies and the likely similarity of the bond force-constants.

It seems probable that the symmetry coordinate representations will be extensively mixed in the normal modes of vibration. The change in metal: ligand-atom mass ratio from above to below unity on going from sulphur to selenium ligation reduces the interpretive assistance which might other-wise be gained from a comparison of their vibrational spectra. Whilst reasonably firm assignments of the T_d A_1 modes are possible, in the absence of rigorous force field calculations, much of the rest of the brief analysis which follows must be regarded as tentative.

TABLE 4.20. Normal vibrations of $M_4(X_b)_4(X_t)_4$ in T_d and D_{2d} symmetries.

	T_d	Description	D_{2d}
ν_1	A_1	$M-X_t$ breathing.	A_1
ν_2	A_1	$M_4(X_b)_4$ in-phase breathing.	A_1
ν_3	A_1	$M_4(X_b)_4$ out-phase breathing; interior angle deformation or M-M stretch.	A_1
ν_4	E	$M_4(X_b)_4$ elongation-compression.	$A_1 + B_1$
ν_5	E	Interior angle deformation or M-M stretch.	$A_1 + B_1$
ν_6	E	$M-(X_t)$ rocking deformation.	$A_1 + B_1$
ν_7	$T_1(IA)$	$M-(X_b)$ stretch.	$A_2(IA) + E(IR)$
ν_8	$T_1(IA)$	$M-(X_t)$ deformation.	$A_2(IA) + E(IR)$
ν_9	$T_2(IR)$	$M-(X_t)$ stretch.	$B_2(IR) + E(IR)$
ν_{10}	$T_2(IR)$	$M-(X_b)$ stretch.	$B_2(IR) + E(IR)$
ν_{11}	$T_2(IR)$	$M-(X_b)$ stretch.	$B_2(IR) + E(IR)$
ν_{12}	$T_2(IR)$	Interior angle deformation or M-M stretch.	$B_2(IR) + E(IR)$
ν_{13}	$T_2(IR)$	$M-(X_t)$ deformation.	$B_2(IR) + E(IR)$

All modes are Raman active unless labelled inactive (IA).

Vibrational assignments are collected and summarised in Tables 4.24 and 4.25 at the ends of the next two sections.

TABLE 4.21. RR and IR Data for $[Et_4N]_2[Fe_4X_4(PhS)_4]$ (X = S, Se).

	X = S		X = Se	
	Band Maxima (cm^{-1})	Intensity at 530.9 nm excitation	Band Maxima (cm^{-1})	Intensity at 530.9 nm excitation
SOLID -RR	150	w	155	2
	200	w,br	166	w,sh
	240	1	197	1,sh
	267	2	209	5
	280	2	254	2
	338	4	260	w,sh
	382	w	362	1,br
	434	10	382	vw
			431	10
	OTHER 60,68,74,101,109,117,125, 116,172(all m-w,n),360(vw) 406(w,sh),694(w),996(mw), 1014(w),1081(m),1471(w), 1576(m),2330(w)		BANDS 67,75,100,107,115,123 (all m-w,n), ∿280(w,br),382(vw), 885(vw),998(mw),1025(vw), 1081(m),1240(vw),1473(w), 1576(m),2330(w)	
SOLUTION -RR	207(vw),240(vw, ∿ depol.) 268(2, ρ 0.2),288(1,ρ ∿ 0.7),341(4, ρ 0),432 (10, ρ 0.33)		155(w,sh),196(sh,pol.), 209(4, ρ 0.1),255(1,depol.) 270(sh,pol.),432(10, ρ 0.3)	
IR SELECTED BANDS	280(sh),286(m),338(w,sh), 348(s),358(s),377(m), 425(sh),432(m),479(m), 692(s),744(s),782(m),997 (m),1024(s),1080(s),1170(s) 1180(s),1297(m),1389(m), 1575(s)		250(w),262(w),275(w),287(m), 350(s,d1),365(sh),420(sh), 430(m),480(ms),693(s),744 (s),781(m),998(m),1024(s), 1079(s),1170(s),1180(s), 1300(m),1389(m),1575(s)	

TABLE 4.22. RR and IR Data for $[Et_4N]_2[Fe_4X_4(SePh)_4]$ (X = S, Se).

		X = S		X = Se	
		Band Maxima (cm^{-1})	Intensity at 482.5 nm excitation	Band Maxima (cm^{-1})	Intensity at 482.5 nm excitation
SOLID - RR		143	2	150	w
		208	w	204	s
		229	1	215	sh
		247	1	234	s
		270	w	260	w
		288	1	278	m
		309	10	311	s
		362	w	384	vw
		384	1	405	vw
		406	1		
		468	vw		
		OTHER 58,67,64,84,91,101,107,116, 124,132 (all m-w,n)		BANDS 108,116,124 (all m-w,n).	
SOLUTION -RR		228(w),249(1, ρ 0.3), 289 (2, ρ 0), 310 (10,ρ 0.3)		204(9, ρ 0.1), 238 (1), 271(3), 311 (10,ρ 0.3)	
IR-SELECTED BANDS		297(s),312(s),379(s),403(w, sh),466(s),667(s),694(s,) 790(s),902(m),1018(s),1064 (s),1179(s),1230(m,br),1296 (m),1304(m),1395(m),1572(s)		256(mw,)275(m),287(mw), 312 (w),466(s),659(s),688(s), 780(ms,br),993(m),1016(s), 1059(ms),1167(s,br),1560 (ms,br)	

TABLE 4.23. RR and IR Data for $[Et_4N]_2[Fe_4X_4(SBz)_4]$ (X = S, Se).

	X = S		X = Se	
	Band Maxima (cm^{-1})	Intensity at 482.5 nm excitation	Band Maxima (cm^{-1})	Intensity at 482.5 nm excitation
SOLID-RR	245	2	213	m
	268	1	236	s
	334	10	258	s
	356	6	∿370	m,vbr,mlt.
	386	4	474	w
	474	1		
	OTHER BANDS 67,75,83,91,99,107,116, 123,132,140,172 (all m-w,n),293(w,m on 568.2 nm),506(w), 680 (w,vbr),1000(w)			
SOLUTION -RR	245(mw, ρ 0.7 ± 0.2), 271(w, ρ 0.7 ± 0.2), 338(s,ρ 0), 361(w)		214(s, ρ 0.1), 280 (w, ∿ depol.),378 (s, part obsc., pol).	
IR-SELECTED BANDS	332(m),355(s),364(w,sh), 381(m),473(mw),562(mw), 700(m,dl),766(s),778 (m),997(s),1024(m), 1065(m),1170(s),1221(m) 1389(m), 1595(s)		273(s),282(m),328(w),355(s, dl),472(ms),560(m),760(m), 780(m),1000(s),1027(m), 1066(m),1172(s),1198(m), 1222(m),1367(m),1391(s), 1598(s)	

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Fig 4.19 Solid—state Raman spectra of [Et$_4$N]$_2$[Fe$_4$X$_4$(SPh)$_4$](X=S,Se) at 530.9nm excitation

[Fe$_4$S$_4$(SPh)$_4$]$^{2-}$

[Fe$_4$Se$_4$(SPh)$_4$]$^{2-}$

Raman shift/cm^{-1}
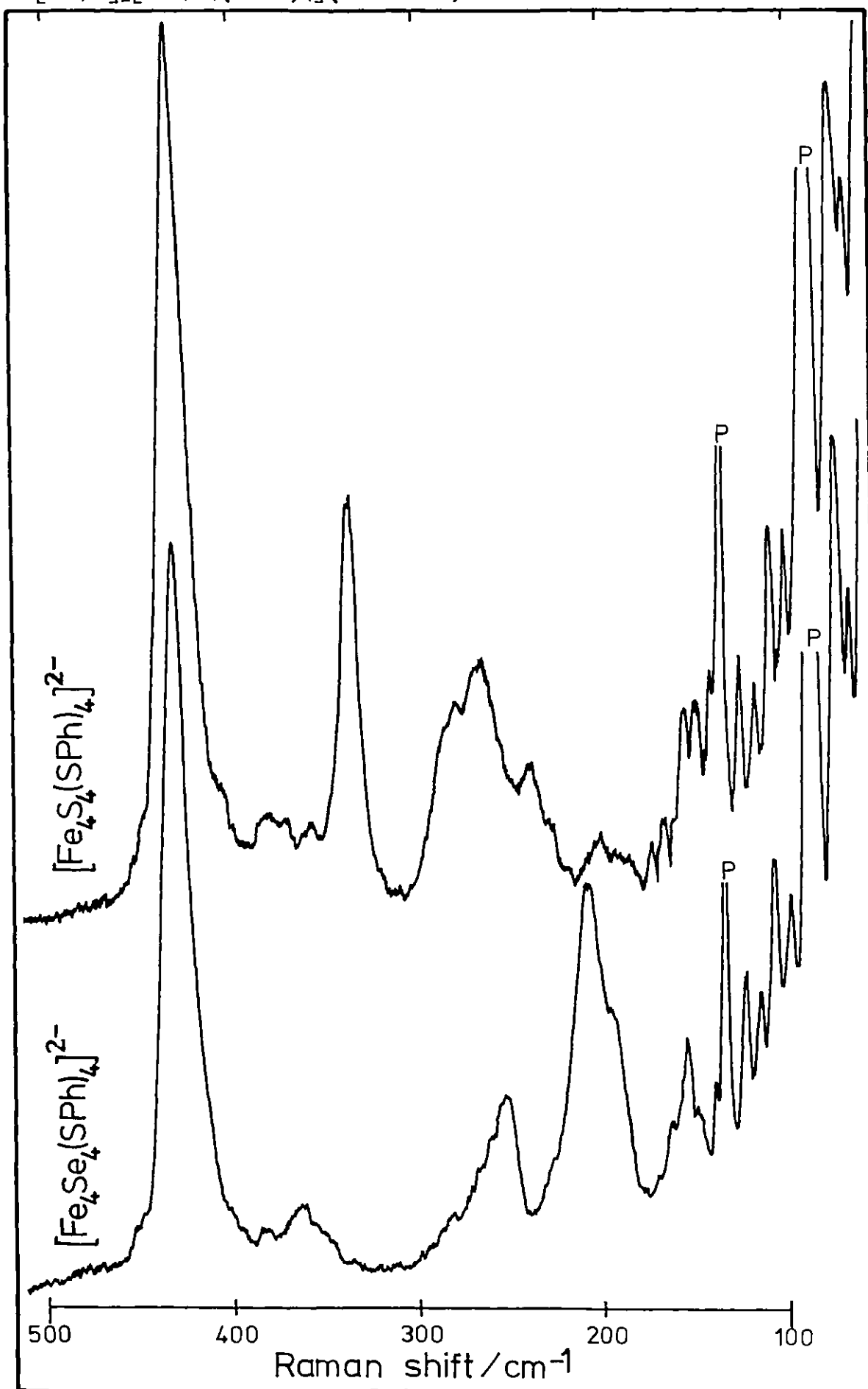
Fig. 4.20 Solid–state infra–red absorption spectra for the tetramer complexes
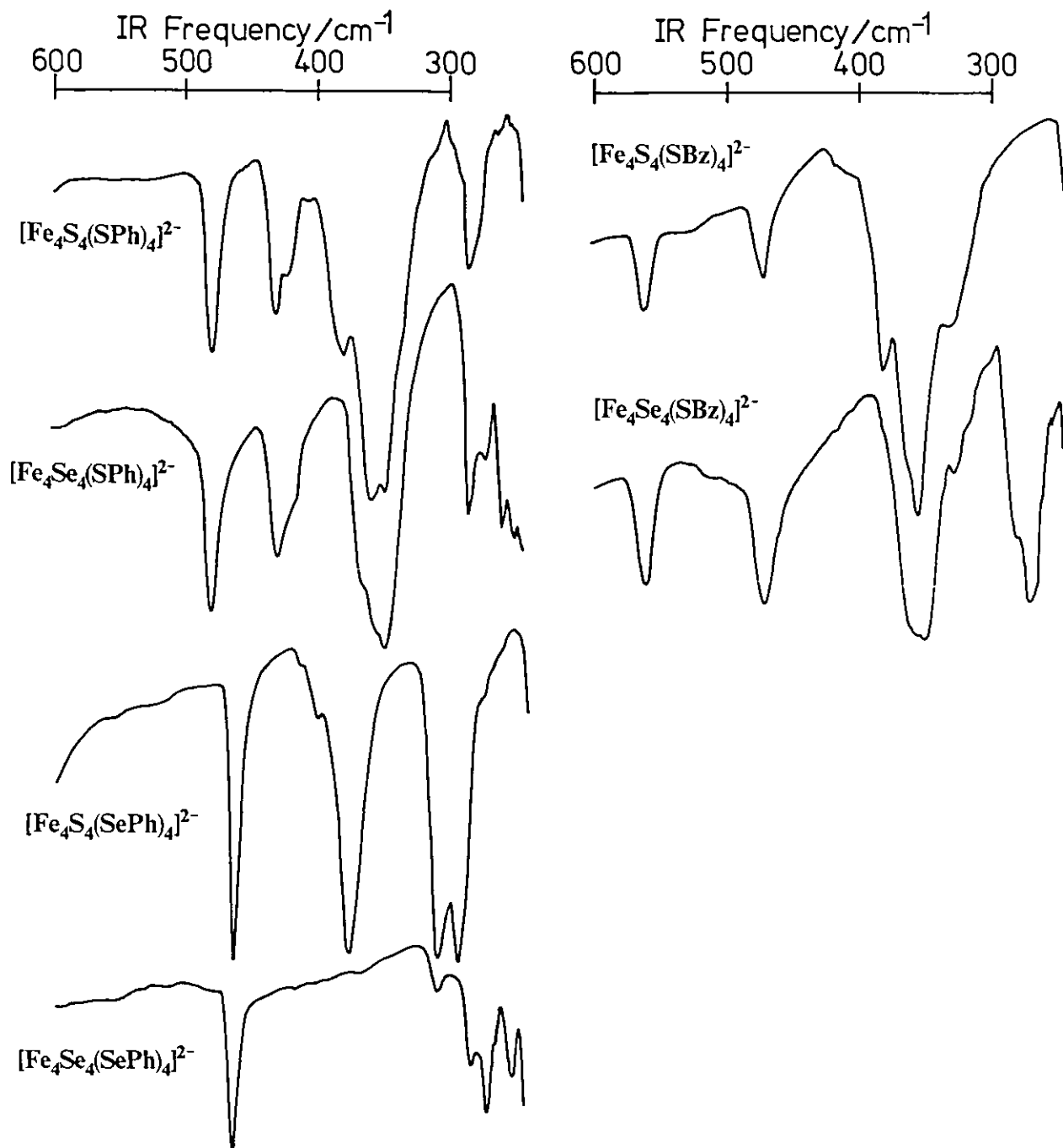
Fig 4.21 Solid−state Raman spectra of
$[Et_4N]_2[Fe_4X_4(SePh)_4](X=S,Se)$ at 482.5nm excitation

$[Fe_4S_4(SePh)_4]^{2-}$

$[Fe_4Se_4(SePh)_4]^{2-}$

P

500   400   300   200   100

Raman shift/cm^{-1}
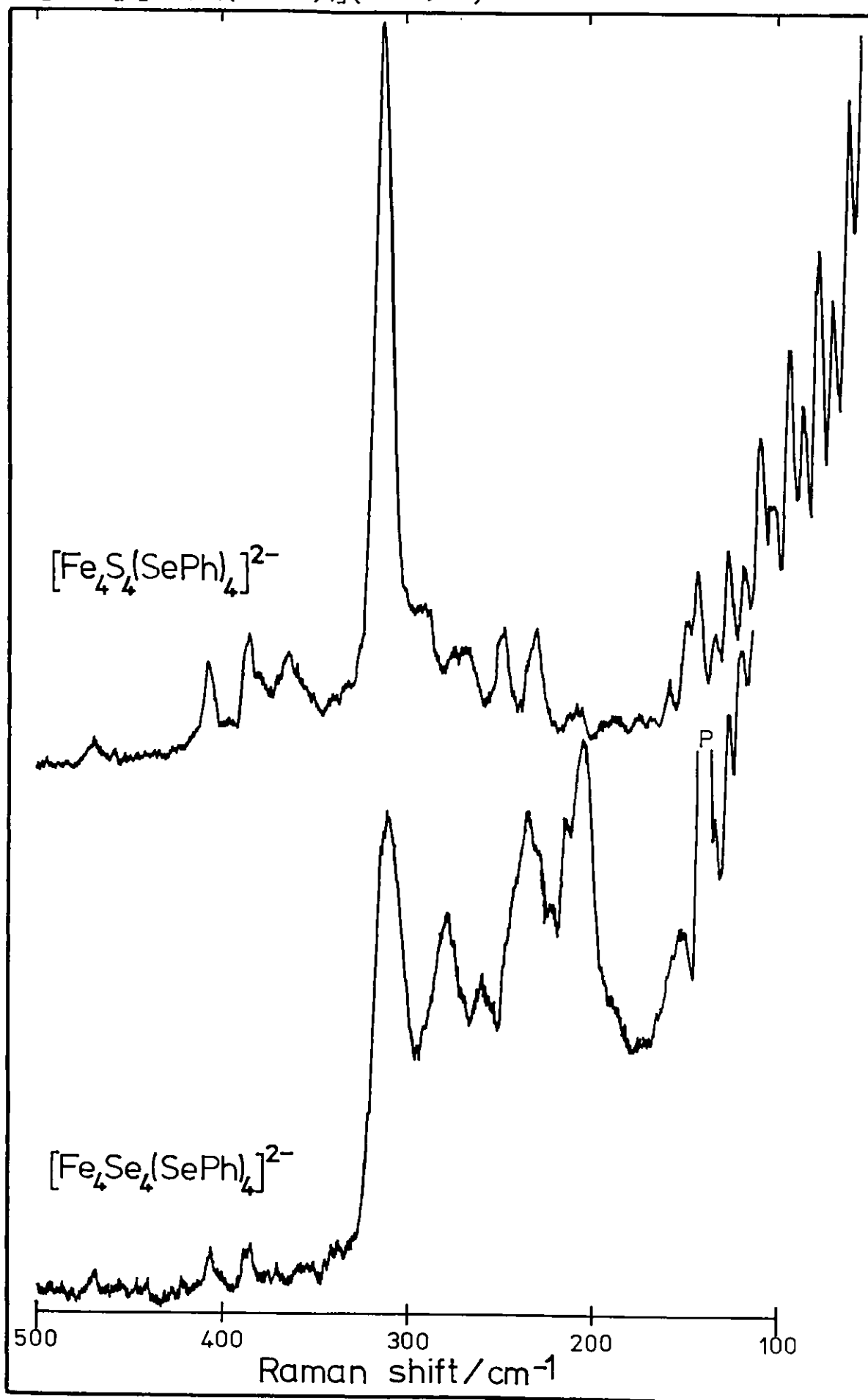
Fig 4.22 Solid—state Raman spectra of
$[Et_4N]_2[Fe_4X_4(SBz)_4](X=S,Se)$ at 482.5nm excitation

$[Fe_4S_4(SBz)_4]^{2-}$

$[Fe_4Se_4(SBz)_4]^{2-}$

500   400   300   200   100
Raman shift / cm⁻¹
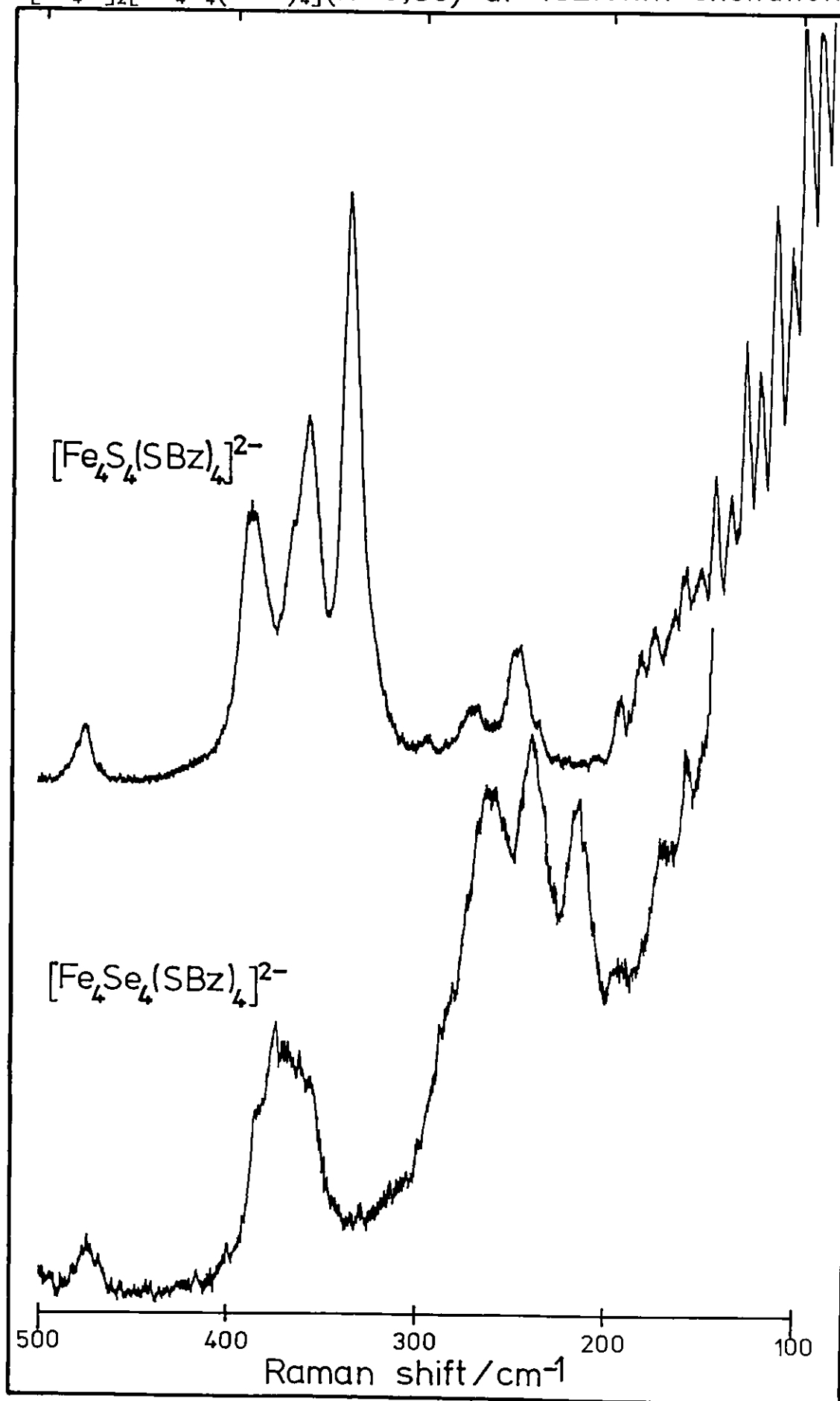
4.4.2.1. [Fe₄X₄(YPh)₄]²⁻ (X, Y = S, Se).

The intense Raman band at 434 cm⁻¹ (polarised in solution) in

$[Fe_4S_4(SPh)_4]^{2-}$ has a counterpart at 431 cm⁻¹ in $[Fe_4Se_4(SPh)_4]^{2-}$ and

is assigned to ν_1. PhSe-ligated derivatives show corresponding peaks

shifted to 309 and 311 cm⁻¹ . These frequencies are comparable to those

observed for the dimer species with phenylchalcogenide ligands (Section

4.3). Similarly the IR spectra for $[Fe_4S_4(SPh)_4]^{2-}$ and $[Fe_4Se_4(SPh)_4]^{2-}$

show bands around 420-430 cm⁻¹; these are attributable to a splitting

of the triply degenerate ν_9 terminal ligand stretch. This vibration

should be weaker in the Raman and is masked by ν_1. Using the change in

ν_1 as a measure of the frequency shift accompanying PhS/PhSe substitution,

either or both IR absorptions at 312 and 297 cm⁻¹ in $[Fe_4S_4(SePh)_4]^{2-}$ are

candidates for ν_9. Weaker bands appear around the same frequencies, 312

and 287 cm⁻¹, in the fully selenium substituted $[Fe_4Se_4(SePh)_4]^{2-}$. The

in-phase cube breathing mode, ν_2, is reasonably assigned to the polarised

338 cm⁻¹ Raman line for $[Fe_4S_4(SPh)_4]^{2-}$, shifted to 209 cm⁻¹ in

$[Fe_4Se_4(SPh)_4]^{2-}$. Comparably, $[Re_4S_4(CN)_{12}]^{4-}$ has this A_1 mode at 335 cm⁻¹

however, the frequency shift is only to 280 cm⁻¹ in $[Re_4Se_4(CN)_{12}]^{4-}$.[218]

The $\nu_2(Se) : \nu_2(S)$ ratio of 0.62 for $[Fe_4S_4(SPh)_4]^{2-}/[Fe_4Se_4(SPh)_4]^{2-}$ is

low but not in gross disagreement with values observed for the μ_2-bridged

iron dimers, which have comparable stretching frequencies. For

$[Fe_4S_4(SePh)_4]^{2-}$ no intense Raman shifts in excess of 309 cm⁻¹ are

observed and it is necessary to assign ν_2 at this frequency in coincidence

with ν_1 . This is not unrealistic in view of the high intensity of this

band and the mixing of ν_1 with the core breathing modes which might be

expected given the relatively high mass of the terminal selenium ligand.

The remaining T_d A_1 vibration, ν_3, can be described as mainly interior cluster-angle deformation or as mainly iron-iron stretching in character.[219] Although at a rather high frequency for this kind of vibration the polarised band at 267 cm^{-1} may be a feasible assignment for ν_3. This out-of-phase breathing mode occurs at 215 cm^{-1} in $[Re_4S_4(CN)_{12}]^{4-}$ [218] and at 214 cm^{-1} in $Cp_4Fe_4(CO)_4$[220]; both compounds have strong metal-metal bonding. $[Pb_4(OH)_4]^{4+}$,[221] $T\ell_4(OEt)_4$[222] and $Pt_4(Me)_{12}X_4$ (X = OH, Cℓ, I)[223] probably possess weak metal-metal interactions, and relatively strong bands in the range 80 to 140 cm^{-1} have been assigned to ν_3. In general, the frequency of ν_3 is expected to increase as the mode becomes more metal-metal stretching in character. The Fe-Fe distance in $[Fe_4S_4(SPh)_4]^{2-}$ averages 2.736[75] and any bonding interaction must be weak. For a high M:X mass ratio where the T_d A_1 vibrational descriptions of Table 4.20 apply the terminal X-ligand atom and M_4 tetrahedra move in phase for ν_2 & ν_3 and out of phase for ν_1 and it is evident that as the M/X masses approach parity the internal coordinate variations used to describe ν_1 will no longer be dominant and will apply to some extent to the descriptions of ν_2 and ν_3 also. Approximate force constant calculations for $Fe_4(CO)_4Cp_4$[220] and the cubic $[(Mo_6C\ell_8)C\ell_6]^{2-}$ [224] reflect a very substantial interaction of the coordinates for ν_3 and ν_1. A greater mixing must be expected in the case of $[Fe_4S_4(SPh)_4]^{2-}$, leading to an increased frequency for ν_3. It is on these grounds that the assignment of ν_3 to 267 cm^{-1} is considered tenable. A high value for this mode is also in keeping with Raman shifts interpreted as out-of-phase bridge breathing vibrations in some of the $[Fe_2S_2(SR)_4]^{2-}$ complexes (Section 4.33).

In $[Fe_4Se_4(SPh)_4]^{2-}$ a polarised line at 197 cm^{-1} is tentatively

assigned to ν_3, possibly on excessive shift from 267 cm^{-1} considering

the arguments invoked above. The mode has an identical frequency in

$[Re_4Se_4(CN)_{12}]^{4-}$.[218] Two weak polarised bands at 247 and 288 cm^{-1}

are candidates for ν_3 in $[Fe_4S_4(SePh)_4]^{2-}$. More mixing of ν_1 and ν_3

might be anticipated for a higher terminal ligand–atom mass, leading to

an increase in ν_3.

An alternative assignment for ν_3 in $[Fe_4S_4(SPh)_4]^{2-}$ is the weak

band of unknown polarisation at the unexceptional frequency of around

200 cm^{-1}. It would then become necessary to assume that the 267 cm^{-1}

line is due to ν_4, which has a totally symmetric component in D_{2d}

symmetry. The low depolarisation ratio and high relative intensity at

268 cm^{-1} do not favour this interpretation.

The $\nu_{12}(T_2)$ and $\nu_5(E)$ vibrations are related to $\nu_3(A_1)$ by similarly

becoming predominantly $\nu(M-M)$ in character with increased tetra-metal

bonding. For an isolated M_4 tetrahedron of like atoms, the frequency

ratios predicted for the Raman active vibrations $A_1:T_2:E$ are $2:\sqrt{2}:1$.[225]

If the 200 cm^{-1} and a further weak peak at 150 cm^{-1} are tentatively

ascribed to ν_{12} and ν_5 the ratios $2:1.5:1.1$ result for $[Fe_4S_4(SPh)_4]^{2-}$.

In view of the considerable mixing of modes which has been suggested

use of this so called 'simple cluster ratio' rule might be considered

unjustified, however, it has been found applicable to the low frequency

vibrations of $[Pb_4(OH)_4]^{4+}$ and $T\ell(OR)_4$[219] for which the weak Pb_4, $T\ell_4$

interactions must lead to considerable coupling with M-O stretching.

The approximate fitting of the simple cluster ratio in $Re(SMe)_4(CO)_{12}$[226]

was considered adventitious, and this may also be the case here for

$[Fe_4S_4(SPh)_4]^{2-}$.

TABLE 4.24. $[Fe_4X_4(YPh)_4]^{2-}$ (X, Y = S, Se) Vibrational Assignments.

X = Y = S			X = Se, Y = S			X = Y = Se			X = S, Y = Se			X = Y = S		
$?\nu_5$	150	w		155	mw		150	w		143	mw	$?\nu_5$	150	w
$?\nu_{12}$	200	w,br		166	sh,w		204 p	s		208	w	$?\nu_{12}$	200	w,br
	240~dp	w	$?\nu_3$	197 p	sh,w		215	sh,w		229	mw		240~dp	w
ν_3	267 p	mw	ν_2	209 p	m		234	s		247 p	mw	ν_3	267	mw
	280~dp	mw		254 dp	mw		260	w		270	w		280~dp	mw
ν_2	338 p	m		260 p	sh,w		278	m	$?\nu_3$	288 p	w	ν_2	338 p	m
	382	w		362	w,br	ν_1	311 p	s	$\nu_1 + ?\nu_2$	309 p	vs		382	w
ν_1	434 p	s		382	vw					362	w	ν_1	434 p	s
			ν_1	431 p	s					384	mw			
										406	mw			
	280	sh,w		250	w		256	mw		297	s		280	sh,w
	286	m		262	w		275	m		312	s		286	m
	338	sh,w		275	w	$?\nu_9$	287	mw		379	s		338	sh,w
	348	s		287	m	ligand?	312	w		403	sh,w		348	s
	358	s		350	s,dl								358	s
	377	m		365	sh,w								377	m
ν_9	425	sh,m		420	sh,m								425	sh,m
	432	m	ν_9	430	m				ν_9				432	m

p - polarised solution counterpart   ,   ? - possible assignment

Returning to the IR spectra, increased difficulty is encountered

in presenting any reasonable interpretation in terms of the simple

descriptions in Table 4.20. The absorption at 377 cm^{-1} in $[Fe_4S_4(SPh)_4]^{2-}$

is present also in $[Fe_4S_4(SePh)_4]^{2-}$ (379 cm^{-1}), but is not seen in

$[Fe_4Se_4(SPh)_4]^{2-}$ (discounting a small shift to the shoulder at 365 cm^{-1}),

and is presumably a stretching vibration involving the bridging chalcogenide.

In $[Fe_4Se_4(SPh)_4]^{2-}$ it is possibly split and shifted to $\sim$ 250-260 cm^{-1}

where two partly obscured bands are observed; a frequency change in keeping

with that observed for v_2 in the Raman. All the remaining IR peaks for

$[Fe_4S_4(SPh)_4]^{2-}$ have close counterparts in the spectra of $[Fe_4Se_4(SPh)_4]^{2-}$

but not in $[Fe_4S_4(SePh)_4]^{2-}$, yet no further terminal ligand stretching

vibrations are anticipated. As in T_d all the IR active modes are of the

same symmetry, and also in D_{2d} the majority are E, intermixing is to be

expected. No further explanation is proffered in the absence of a more

quantitative analysis. It is noted that much of the broad and ill-resolved

weak Raman scattering observed in the spectra of $[Fe_4S_4(SPh)_4]^{2-}$ and

$[Fe_4Se_4(SPh)_4]^{2-}$ between 250 and 400 cm^{-1} correlates with the strong IR

absorptions.

4.4.2.2. $[Fe_4X_4(SBz)_4]^{2-}$ (X = S, Se).

The starting point in interpreting the Raman spectrum of $[Fe_4S_4(SBz)_4]^{2-}$

is the designation of the strong band at 334 cm^{-1} (338 cm^{-1} and polarised

in solution) as v_2, a frequency very similar to that of the corresponding

transition in $[Fe_4S_4(SPh)_4]^{2-}$. A similar S/Se frequency shift to that

ascribed to the thiophenyl ligated tetramers is obtained for this band

if it is assigned at 213 cm^{-1} (polarised in solution) in $[Fe_4Se_4(SBz)_4]^{2-}$.

Tang et al.[172] in their preliminary solution spectra for $[Fe_4S_4(SBz)_4]^{2-}$

(Figure 4.18) tentatively assigned a band at 332 cm^{-1} to the terminal

breathing mode ν_1 and a lower frequency at 275 cm^{-1} to ν_2. The higher

frequency peaks at 356 and 386 cm^{-1}, seen in the spectra of the solid,

are obscured in solution by Raman scattering around 400 cm^{-1}, ubiquitous

for organic solvents. Comparison of the relative intensities of the

bands between 300 and 400 cm^{-1} in $[Fe_4S_4(SBz)_4]^{2-}$ with lines assigned

to ν_1 and ν_2 in $[Fe_4S_4(SPh)_4]^{2-}$ tends to favour the interpretation

$\nu_1 = 332$ cm^{-1}, given by Tang et al. Also for $[Fe(S_2-o-xylyl)_2]^{2-}$ and

$[Fe_2S_2(S_2-o-xylyl)_2]^{2-}$, which like $[Fe_4S_4(SBz)_4]^{2-}$ possess $ArCH_2S-$

coordination,symmetric terminal ligand stretching descriptions have been

attributed to lower frequencies (300-320 cm^{-1}) than for PhS-coordination.

This may be an effect of chelation rather than of the aliphatic nature

of the ligand. The frequency shift on going to selenium bridging, low

intensity at 268 cm^{-1} for assignment to ν_2 and the compatibility with the

corresponding $[Fe_4S_4(SPh)_4]^{2-}$ mode,are felt to present a stronger argument

than the points made above in defence of the asisgnments of Tang, et al.,

and the original designation $\nu_2 = 334$ is favoured. The lines at 356 and 386

cm^{-1} could then be due to ν_1 and,although either is rather intense to be a

T_2 mode, to ν_9.No polarisation data could be obtained and relative intensities

are not a useful criterion for distinguishing which line could belong

to which mode, as whilst the 356 cm^{-1} band is marginally bigger than

that at 386 cm^{-1} with 482.2 nm excitation, the reverse is true when

using 530.9 nm. Both frequencies have close counterparts in the IR,

and on the grounds that the 355 cm^{-1} absorption is stong, as expected,

and a better match to the Raman than the 381 cm^{-1} absorption, which is

shifted on selenium substitution, ν_9 is assigned to 356 cm^{-1} (Raman),

355 cm^{-1} (IR) and ν_1 to 386 cm^{-1} (Raman). In $[Fe_4Se_4(SBz)_4]^{2-}$ the two

modes appear as a broad unresolved Raman feature centred around 370 cm^{-1}

and the T_2 355 cm^{-1} IR absorption is also unshifted from that in·

$[Fe_4S_4(SBz)_4]^{2-}$ whilst being slightly more split. The analysis for the

381 cm^{-1} IR band follows that for the comparable 377 cm^{-1} feature in

$[Fe_4S_4(SPh)_4]^{2-}$, being described as mainly $\nu(Fe-S_b)$ and shifted to

273 , 282 cm^{-1} on selenium substitution. The relative intensities at

381 cm^{-1} in $[Fe_4S_4(SBz)_4]^{2-}$ and 273 , 282 cm^{-1} in $[Fe_4Se_4(SBz)_4]^{2-}$ would

seem to imply that the former band does not contain all the absorption

from ν_{10} and ν_{11} but that a further contribution lies buried in the

poorly resolved envelope between 300 and 400 cm^{-1}.

Following the principles used to interpret the spectrum for

$[Fe_4S_4(SPh)_4]^{2-}$ the Raman lines at 268 and 245 cm^{-1} in $[Fe_4S_4(SBz)_4]^{2-}$

might be considered good candidates for ν_3. Inconsistent with this,

however, a high value of the depolarisation, $\tilde{>} 0.5$, is found at 245 and

271 cm^{-1} in the solution spectrum, although it is not possible to obtain

an accurate estimate of ρ for these bands which are weak and on a high

fluorescent background. Tang et al.[172] consider the band they observe

at 275 cm^{-1} in $[Fe_4S_4(SBz)_4]^{2-}$ to be polarised; however, due to the

lower laser powers necessary in their study of static samples, leading

to less than optimal spectral quality, any determination of ρ is likely

to be subject to a large error.

The origin of the strong Raman lines at 236 and 258 cm^{-1} in

$[Fe_4Se_4(SBz)_4]^{2-}$ is not understood. The weak peak at 474 cm^{-1} in both

BzS-ligated tetramers could arise from a partly resonance-enhanced

$\delta(S-CH_2Ph)$ mode. In the IR spectrum of $[Fe_4S_4(SBz)_4]^{2-}$ the medium

intensity absorption at 332 cm^{-1} appears also in $[Fe_4Se_4(SBz)_4]^{2-}$ at

328 cm^{-1} and could possibly be a splitting from ν_9, though it is not

seen in the Raman for $[Fe_4Se_4(SBz)_4]^{2-}$ and the 338 cm^{-1} band in

$[Fe_4S_4(SBz)_4]^{2-}$ solution spectra has a depolarisation ratio close to zero.

TABLE 4.25. $[Fe_4X_4(BzS)_4]^{2-}$ (X = S, Se) vibrational assignments.

RR	X = S			X = Se	
	245 $\sim$ dp	mw	$\rightarrow \nu_2$	213 p	m
	268 $\sim$ dp	w		236	s
ν_2	334 p	s		258	s
?ν_9	356	s	$\rightarrow \nu_1$ and $\nu_9 \sim 370$ p		m
?ν_1	386	m	ligand 474		w
ligand	474	w			

IR					
	332	m		273	s
ν_9	355	s		282	m
	381	m		328	w
			ν_9	355	s, dl

4.4.2.3. Resonance in the Raman Spectra of the 4Fe Complexes.

In acetone solution the following lowest energy intense bands are observed: 456 nm $[Fe_4S_4(SPh)_4]^{2-}$, 463 nm $[Fe_4Se_4(SPh)_4]^{2-}$, 476 nm $[Fe_4S_4(SePh)_4]^{2-}$, 485 nm $[Fe_4Se_4(SePh)_4]^{2-}$, 417 nm $[Fe_4S_4(SBz)_4]^{2-}$ and 420 nm $[Fe_4Se_4(SBz)_4]^{2-}$. Maxima at similar wavelengths have been reported in DMF.[212] Only for $[Fe_4S_4(SPh)_4]^{2-}$ has the solid reflectance been checked, and in the region of exciting wavelengths used to obtain the Raman spectra reported here this shows a single broad band centred around 500 nm. For $[Fe_4S_4(SBz)_4]^{2-}$ solid state spectra at 5 K show better resolution,
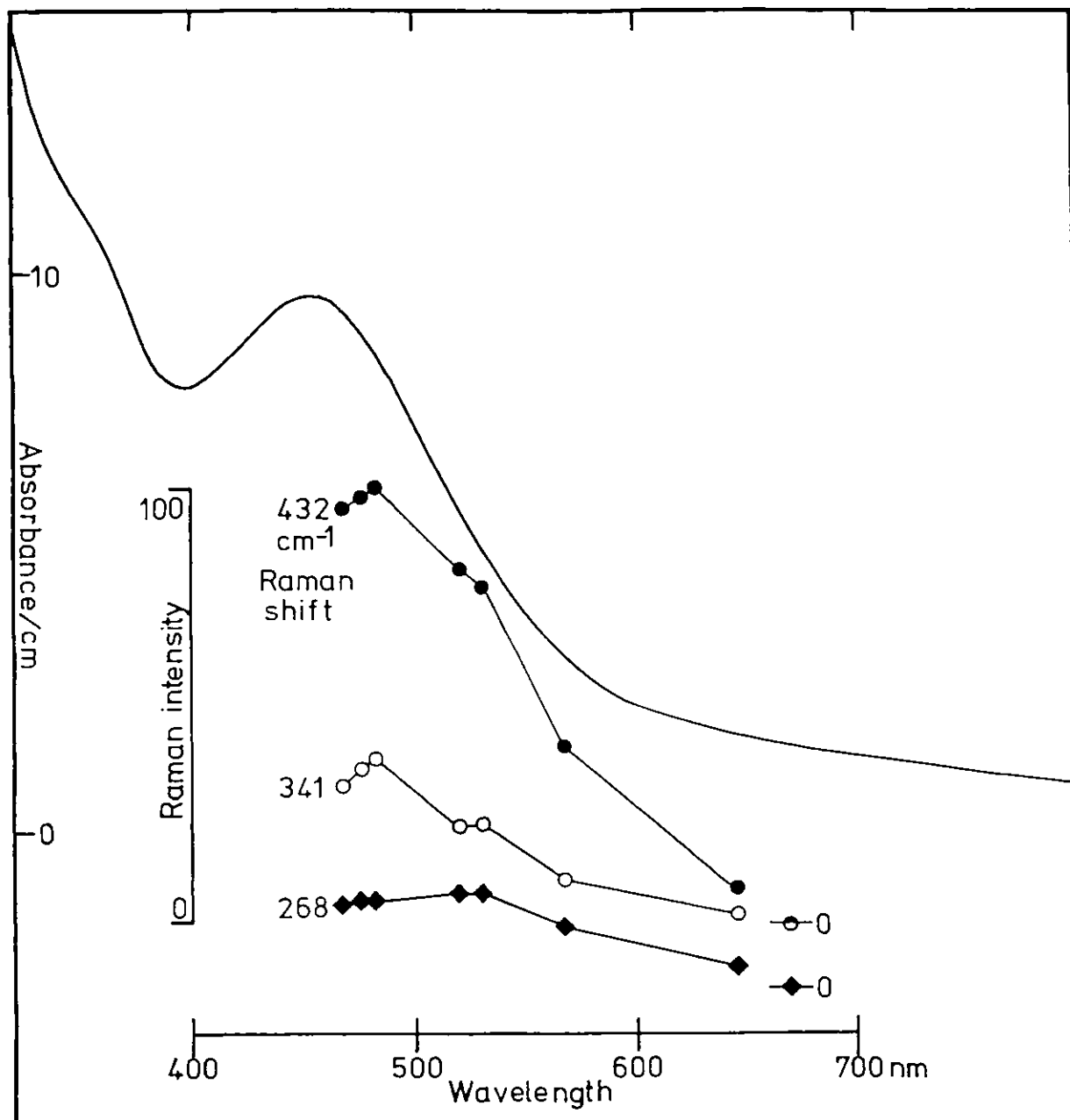
Figure 4.2 3   Electronic spectrum of [Fe₄S₄(SPh)₄]²⁻ in acetone and

resonance enhancement of several Raman peaks.

having a narrow intense band at around 490 nm and weaker features at

600 and 800 nm.[227]

Figure 4.23 shows the relative variation in intensity with excitation

wavelength of the three polarised bands observed for [Fe₄S₄(SPh)₄]²⁻ in

acetone solution. Taking concentrations into account the 432 cm⁻¹ peak

is some 2500 times more intense than the acetone symmetric stretch at

787 cm⁻¹. Whilst the blue lines available on a Krypton laser are

separated by only a small wavelength interval, the decrease in resonance

enhancement on going from 482.5 to 468.0 nm, being reproducible, is felt

to be genuine. For the 432 cm^{-1} peak it is estimated that maximal intensity

would be achieved at $\sim$490 nm. The 310 and 311 cm^{-1} Raman fundamentals

found for acetone solutions of PhSe-ligated tetramers show greatest

resonance enhancement at wavelengths close to the 530.9 nm Krypton

emission, whilst at 482.5 nm respective intensities are comparable to

those at 568.2 nm. Thus, the excitation profiles for the terminal-ligand

stretching modes peak at around 30 to 40 nm higher than the absorption

maxima in the electronic spectra. Unlike the case of the two iron complexes,

the low energy absorptions in the visible spectra of the tetramers show

no evidence of any underlying band at higher wavelength.

4.4.3. General Conclusions Concerning Tetramer Complexes.

The Raman spectra for the $[4Fe-4S]^{2+}$ cluster containing proteins,

Chromatium Hipip and C. Pasteurianum Fd, show similar features to those

described for $[Fe_4S_4(SR)_4]^{2-}$ analogues in the previous two sections.

Bands at 338 and 345 cm^{-1} in the proteins correlate with those at

338 cm^{-1} in $[Fe_4S_4(SPh)_4]^{2-}$ and 334 cm^{-1} (338 in solution) in $[Fe_4S_4(SBz)_4]^{2-}$.

The 356 and 386 cm^{-1} lines observed in $[Fe_4S_4(SBz)_4]^{2-}$ compare with those

at 360 and 365 cm^{-1} and possibly other weak peaks 20 to 40 cm^{-1} higher

in Hipip and Fd. It is fitting that, as in the case of the 2Fe2S results,

the Raman from the aliphatic, as opposed to aromatic, thiol ligated model

complex, more closely resembles that from the protein. As already detailed

the assignment of $\nu_2 = 334$ cm^{-1} for $[Fe_4S_4(SBz)_4]^{2-}$ is in contention with

$\nu_2 = 275$, $\nu_1 = 332$ cm^{-1} given by Tang et al.[172] and this extends to the designations inferred for the proteins in the above comparisons. The appearance of a polarised band to higher frequency close to the most intense line at $\sim$340 cm^{-1} is explained by these authors as resulting from a lowering of cluster symmetry from tetrahedral so as to induce totally symmetric character into an otherwise non-totally symmetric mode. The interpretation indicated by this present work is that these lines are due to ν_1 and that the low frequency polarised 250 cm^{-1} band, seen only in Hipip, is ν_3.

The structure of $[Fe_4S_4(SR)_4]^{2-}$ species in solution has been described as retaining the crystallographically observed D_{2d} distortion of the $[4Fe4S]^{2+}$ core in the solids.[228] No gross structural changes are expected on dissolution and in keeping with this the Raman spectra in solid and solution show very similar peak positions (however, the Raman spectra may be insensitive to small structural changes - see below). On reduction to the trianion a considerable structural change occurs, for $[Fe_4S_4(SPh)_4]^{2-/3-}$ the distortion of the cubane core changes from a compression along one of the C_2 axes into an elongation.[229] Although at present no full description of the Raman for $[Fe_4S_4(SPh)_4]^{2-/3-}$ has been published, Reynolds et al. make reference to preliminary work by Spiro [reference 216; see references and notes 34 to 36] in quoting $\nu_2 = 343$ and 341 cm^{-1} for the dianion and trianion respectively. They have taken this small change in frequency as indicating a weak contribution from core structural rearrangement, to the total free energy of activation for the redox process. The symmetry in $[Fe_4S_4(SBz)_4]^{3-}$ is lower than tetragonal, containing six short (mean 2.302Å) and six long (mean 2.331Å) Fe-S$_b$ core bonds, so arranged as to afford idealised C_{2v} symmetry.[230] This is evidenced in the differences of Mössbauer and magnetic properties for

solid PhS- and BzS-ligated trianions. In solution these properties become
essentially coincident and similar to solid $[Fe_4S_4(SPh)_4]^{3-}$.[228]
Preliminary Raman measurements have been made for $[Et_4N]_3[Fe_4S_4(SBz)_4]$
in solid state and show bands at 235(ms), 338(s), 356(ms), 387(s). The
material presents increased difficulty over $[Et_4N]_2[Fe_4S_4(SBz)_4]$ with
regard to air sensitivity, fluorescent background and photodecomposition.
The low signal to noise ratio necessitated the use of a wide slit program
resulting in poorer resolution; the quality of spectrum being similar to
that for $[Fe_4Se_4(SBz)_4]^{2-}$ in Figure 4.22. In view of the similarity of
the above frequencies to those observed for the dianion it would seem
that Raman is incapable of revealing the changes in structure accompanying
reduction.

Magnetic measurements indicate a J value of $\sim$-230 cm^{-1} in
$[Fe_4S_4(SBz)_4]^{2-}$ and $[Fe_4X_4(SPh)_4]^{2-}$ (X = S, Se).[229] Spin-flip transitions
of the sort invoked by Blum et al.,[114,115] would then be anticipated
from S = 0 at energies around 460, 1380, 2760 cm^{-1} and from S = 1 at
energies around 920, 2300 cm^{-1}. As with the case of the dimers no
satisfactory evidence for Raman scattering by such a process is forth-
coming in the data obtained from tetramer samples.

ADDENDUM

Since completion of the analysis presented in this section, Spiro,

et al. [J. Biol. Chem. 256, 9806 (1981) and J. Biol. Chem. 257, 2447

(1982)] have reported much improved Raman spectra for the $[4Fe-4S]^{2+}$

ferredoxin from C. pasteurianum. They observe bands at 247, 271, 295,

335, 356 and 394 cm^{-1} which correlate well with the Raman shifts at 245,

268, 293, 334, 356 and 386 cm^{-1} described in Table 4.23 for $[Fe_4S_4(SBz)_4]^{2-}$.

Using substitution of core sulphur by ^{34}S the authors have been able

to observe shifts of 4-6 cm^{-1} in bands resulting from Fe_4S_4 core

vibrations. In this way, they too are able to correct the assignment

of ν_2 to $\sim$ 271 cm^{-1} made by Tang et al.,[172] assigning this mode instead

to the most intense peak in C. pasteurianum at 335 cm^{-1}. The other peaks

in the spectrum have only 10-20% the intensity of this band, unlike the

case for $[Fe_4S_4(SBz)_4]^{2-}$ where the features at 356 and 386 cm^{-1} attain

ca.50% or more of the intensity at 334 cm^{-1}. In addition the protein

spectrum lies in a trough of considerable background intensity and

contains additional maxima to those described above, so that the direct

compatibility of the remaining band positions may not be as valid as would

at first appear to be the case from the figures. The protein band at

356 cm^{-1} is assigned to a superposition of ν_1 and ν_9 and the 394 cm^{-1}

band to a T_2 core mode. Although in section 4.4.2.2. ν_9 was assigned

to 356 cm^{-1} in the Raman of $[Fe_4S_4(SBz)_4]^{2-}$ and a T_2 core mode to 381 cm^{-1}

in the IR, for the Raman band at 386 cm^{-1} an assignment as ν_1 was

considered as an alternative possibility to coincidence with ν_9 at

336 cm^{-1}. Whatever the case either band seems rather intense for a single

T_2 mode and a second alternative possibility is that ν_1 = 356 cm^{-1}

whilst the 386 cm^{-1} band is a superposition of ν_9 and a T_2 core mode.

It is peculiar that correspondingly intense T_2 modes are not observed

in the Raman spectra of $[Fe_4S_4(SPh)_4]^{2-}$. This probably reflects the

slightly higher symmetry of the latter compared with $[Fe_4S_4(SBz)_4]^{2-}$.

4.5. Experimental - Sample Preparation.

Synthetic procedures for the compounds studied in this Section
are described in Section 6.

4.5.1. Raman Samples.

Solid state spectra were obtained by the spinning disk technique.
The compound was placed together with about 2 to 3 times the amount of
finely ground dry KBr or KCℓ in a ca. 2 cm diameter screw-capped septum-
sealed sample bottle. This transfer operation was effected rapidly and
the container purged of oxygen by evacuation and N_2-flushing via a
steel needle inserted through the rubber septum at a central hole in
the metal cap. A magnetic bar, with a length only slightly smaller than
the internal diameter of the sample bottle , previously placed in the
container, was used to grind up and mix the solids by rapid rotation
on an efficient magnetic stirrer. A period of 5 to 10 minutes was
usually found sufficient to give an homogeneous fine-grained powder.
This could be rapidly transferred in the open to a die and pressed under
vacuum at 10 tons into a 13 mm disk. Generally, a supportive backing
of pure KBr and KCℓ was used in disk preparation. For the very air
sensitive $[Et_4N]_3[Fe_4S_4(SBz)_4]$ the transfer to the die and pressing
operations were also carried out anaerobically in a plastic bag.

Although in the form of KBr pellets the compounds were found on
the whole to have greatly reduced oxygen sensitivity, they were still
handled anaerobically. The spectrometer (SPEX Ramalog V) sample
compartment was fitted with a small plastic bag extending from the
sample spinner to the collection optics (Figure 4.24). After rapid

RUBBER BAND

PLASTIC BAG

MOTOR
(support not shown)

METAL
PLATE

SAMPLE
SPINNER

COLLECTION OPTICS

N_2

GLASS
INSET

EXCITATION-BEAM
FOCUS
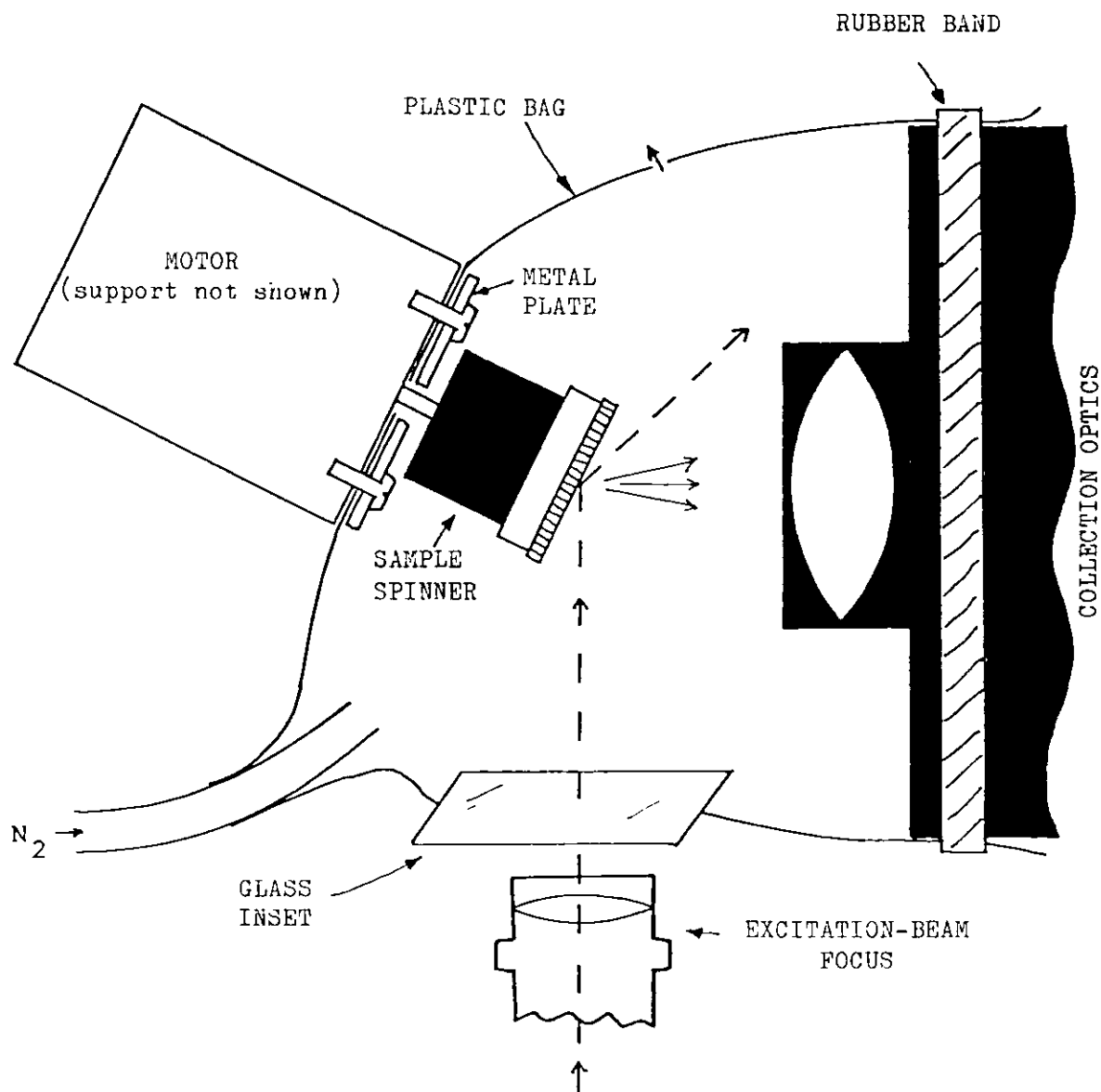
Figure 4.24. Details of Raman spectrometer (SPEX Ramalog V) sample-compartment arrangement for spinning samples in an inert atmosphere.

transfer of the disk to the holder under N_2 flow the plastic bag was fixed in place and purged of O_2 by a rapid stream of N_2. After 5 mins the bag was sealed onto the collection optics with a rubber band and a gentle ingress of N_2 maintained. The laser beam is permitted to enter the bag via a glass microscope slide taped over a hold cut in the lower side.

Solution spectra were obtained in a 2 cm   diameter rotating glass cell, of conventional design, sealed at the top with a cut-down septum.

4.5.2. IR Samples.

Samples for infrared measurements were diluted in spectroscopic polythene powder (Merck) using the magnetic stirrer technique outlined above. Longer stirring times were required to achieve good homogeneous dispersion of the complexes in the polythene. The powder was compressed at 10 tons under vacuum to give 13 mm diameter disks of approximately 0.1 mm thickness. Various concentrations and thicknesses were employed to obtain the maximum information. Measurements were made without further precautions against atmospheric oxidation of the complexes as the polythene gives excellent protection; no spectral differences were found between spectra obtained immediately (ca. 1 min) or after ca. 1 hr. Most spectra were measured within 5 to 10 mins after manufacture of the sample disk.

4.5.3. Selected Ligand Vibrations.

PhSH, Raman: 190ms, 280m, 415s, 619m, 701s, 919m, 1001vs, 1027s, 1094s, 2572s. IR: 466s, 689s, 699m, 733vs, 899m, 917m, 1023s, 1070m, 1091s, 1119ms, 1180mw, 1301mw, 1441s, 1383mw, 1479s, 1583s, 2534ms.

PhSe-SePh, Raman: 72m, 104s, 180w, 190vw, 214s, 265vw, 313s, 616w, 666w, 998s, 1022s. IR: 302mw, 400vw, 460s, 664m, 687s, 731vs, 900m, 998s, 1020s, 1062s, 1178m, 1298ms, 1380m, 1434s, 1570vs.

o-xylyl α,α'-dithiol, Raman: 75s, 108m, 130s, 230m, 332w, 518s, 593w, 670s, 769m, 789ms, 972m, 1047s. IR: 307mw, 393w, 450ms, 547ms, 594ms, 680s, 760s, 970ms, 1050ms, 1088ms, 1189m, 1248s, 1300ms, 1603m.

<u>BzSH</u>, Raman: 269mw, 339mw, 406vw, 474m, 559w, 622s, 682s, 762mw, 794m, 802m, 1003vs, 1032s. IR: 470m, 559m, 697vs, 758ms, 1072m, 1250ms, 1601m, 2565mw.

<u>p-MeC$_6$H$_4$SH</u>, Raman: 115s, 307w, 317w, 368w, 380s, 639ms, 796ms, 1098s. IR: 483s, 629mw, 800s, 914mw, 1019ms, 1099s, 1117m, 1183w, 1210m, 1307mw, 1380w, 1402m, 1494s, 1600w, 2565m.

<u>p-CℓC$_6$H$_4$SH</u>, Raman: 115s, 305mw, 338ms, 343mw, 542w, 630mw, 741mw, 1066mw. IR: 342w, 483s, 525w, 542ms, 743m, 810vs, 1012s, 1095s, 1103s, 1178mw, 1393s, 1478s, 1570w, 2570m.

4.5.4. Conditions and Notes Concerning Figures and Tables.

TABLE 3

1. " -" indicates inability to observe band due to obscuring Rayleigh scattering or fluorescent background, plasma-tube emission line or poor signal to noise ratio (general).

2. Intensity (uncorrected peak height) ratioing is to make largest peak equal to 10 or 100 (general); correlation across excitation wavelengths for the solution is with reference to acetone internal standard 787 cm^{-1} symmetric stretch.

3. Depolarisation ratios, ρ, are for 482.5 nm excitation, excepting 222 cm^{-1} band - 647.1 nm excitation.

4. Solution spectra at 530.9 nm excitation are very poor quality due to large fluorescence.

5. Extra splittings to give many narrow lines in the 100-300 cm^{-1} region together with a large intensity increase of the 103 cm^{-1} peak have been occasionally and irreproducibly observed with 568.2 nm exctn. These are not understood.

<u>Figure 4.</u> IT 1.0s, TC 8s, SS 0.5 cm^{-1}/s, 2 Kcps FS, -150°C.

KBr disc sample.

647.1 nm exctn.   ;   P 100 mW   , SR 5 cm^{-1}

568.2 nm exctn.   ;   P 100 mW   , SR 6 cm^{-1}

530.9 nm exctn.   ;   P 50 mW   , SR 4.5 cm^{-1}

<u>Figure 5.</u> 568.2 nm exctn.   ;   P 170 mW   , SR 5 cm^{-1}

IT 0.5s, TC 8s, SS 0.5 cm^{-1}/s, FS 20 Kcps

<u>Table 6.</u> Correlation of intensities across solid-state RR spectra

at different excitation wavelengths is with reference to

the NO_3^- symmetric stretch of KNO_3 incorporated in the sample.

<u>Figure 10.</u> $[Fe_2X_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$.

X = S   530.9 nm exctn.   ;   P 130 mW   , SR 3 cm^{-1}

IT 1.0s, TC 10s, SS 0.25 cm^{-1}/s, FS 500 cps

X = Se   530.9 nm exctn.   ;   P 150 mW   , SR 3 cm^{-1}

IT 1.0s, TC 10s, SS 0.25 cm^{-1}/s, FS 1 Kcps.

<u>Figure 12.</u> $[Fe_2X_2(SPh)_4]^{2-}$ (X = S, Se).

482.5 nm exctn.   ;   P 50 mW   , SR 2.5 cm^{-1}

IT 1.0s, TC 8s, SS 0.5 cm^{-1}/s

X = S   FS 1 Kcps,

X = Se   FS 2 Kcps

<u>Figure 13.</u> $[Fe_2X_2(SePh)_4]^{2-}$

<u>X = S</u>   482.5 nm exctn.   ;   P 50 mW   , SR 5 cm^{-1}

IT 1.0s, TC 8s, SS 0.5 cm^{-1}/s, FS 1 Kcps

X = Se   530.9 nm exctn.   ;   P 80 mW   , SR 3.5 cm^{-1}

IT 1.0s, TC 8s, SS 0.5 cm^{-1}/s, FS 2 Kcps.

Figure 14. $[Fe_2X_2(STol)_4]^{2-}$

X = S   482.5 nm exctn.   ;   P   50 mW , SR 5 cm^{-1}

          IT 1.0s, TC 8s, SS 0.25 cm^{-1}/s, FS 2 Kcps

X = Se   482.5 nm exctn.   ;   P   50 mW , SR 3 cm^{-1}

          IT 1.0s, TC 8s, SS 0.5 cm^{-1}/s, FS 2 Kcps.

Figure 17. KBr:KNO$_3$: $[Fe_2X_2(S_2-o-xylyl)_2][Et_4N]_2$ $\sim$ 8:4:1 w/w

Figure 19. $[Fe_4X_4(SPh)_4]^{2-}$ (X = S, Se).

          530.9 nm exctn.   ;   P   190 mW , SR 7 cm^{-1}

          IT 1.0s, TC 8s, 0.5 cm^{-1}/s, FS 2 Kcps

          below $\sim$ 180 cm^{-1} SR 3.5 cm^{-1}, FS 1 Kcps

Figure 21. $[Fe_4X_4(SePh)_4]^{2-}$ (X = S, Se).

          482.5 nm exctn.   ;   P   50 mW , SR 5.5 cm^{-1}

          IT 1.0s, TC 10s, 0.25 cm^{-1}/s, FS 1 Kcps.

X = S   below 180 cm^{-1} 476.2 nm exctn., P 50 mW, SR 4 cm^{-1}

Figure 22. $[Fe_4X_4(SBz)_4]^{2-}$ (X = S, Se).

          482.5 nm exctn.   ;   P   50 mW , SR 4 cm^{-1}

          IT 1.0, TC 10, 0.1 cm^{-1}/s, FS 500 cps.

X = S   below 200 cm^{-1} 476.2 nm exctn. P   50 mW

Key   P on Figure = plasma - emission line

         FS   Full scale (cps - counts per second)

         IT   Integration Time

         P   Power

         SR   Spectral Resolution

         SS   Scan Speed

         TC   Time Constant

SECTION 5

TYPE 1 COPPER IN BLUE-COPPER-PROTEINS; β-AMINOTHIONE MODEL COMPLEXES

5. TYPE 1 COPPER IN BLUE-COPPER-PROTEINS; β-AMINOTHIONE MODEL COMPLEXES.

The low temperature synthesis of $Cu(II)N_2S_2$ complexes incorporating N-substituted β-aminothione ligands is described. By varying the bulk of the N-substituent a systematically variable distortion in coordination geometry from square-planar toward tetrahedral may be imposed by means of steric hindrance. The resulting group of complexes represent the most extensive series of 2N2S coordinated Cu(II) currently available. They have been studied by electronic spectroscopy, EPR, resonance Raman spectroscopy and polarography, and comparisons made with corresponding properties of the type 1 centre in blue-copper-proteins.

Two intense absorption peaks are observed in the visible spectra of the complexes in the ranges ca. 600-680 nm and 470-540 nm. These are assigned as charge transfer bands and the former is correlatable with the intense 'blue' $S \longrightarrow Cu$ transition found at similar wavelength in the blue-copper-proteins.

The parallel copper hyperfine splitting in the EPR spectra for frozen solution samples of the complexes varies from ca. 150×10^{-4} cm^{-1} down to 127×10^{-4} cm^{-1} as the steric bulk of the amino-substituent increases. Larger values of this parameter result for Cu(II) doped samples of the corresponding Ni(II) complexes. On the other hand $|A_{||}|$ is greatly decreased in doped Zn(II) complexes, and the lowest values of ca. 100×10^{-4} cm^{-1} approach closely the region for blue-copper-proteins. A plot of $|A_{||}|$ against $g_{||}$ for the 2N2S coordinated Cu(II) complexes shows an inverse relationship for these parameters intermediate between those for 4S and 4N coordination, which may be extrapolated to include several type 1 centres.

Solid state Raman and IR spectra are described for two of the complexes and an attempt made to assign the most intense features to fundamental vibrations of the CuN_2S_2 coordination unit.

Electrochemical measurements for a few of the complexes further establishes a role for 2N2S coordination and tetrahedral distortion in bringing about high redox potentials.

The spectroscopic and redox properties of the model complexes serve further to confirm general pseudo-tetrahedral CuN_2S_2 coordination in type 1 blue-copper-proteins.

5. Type 1 Copper in Blue-Copper-Proteins; β-Aminothione Model Complexes.

5.1. Introduction: Proteins and Models.

The origins of the unusual spectroscopic and redox properties found
for 'Type 1' copper in blue copper-containing proteins have presented
some intriguing problems in biological inorganic chemistry. Three
notably anomalous properties have attracted much interest: (i) an intense
absorption band near 600 nm with an extinction coefficient 10-100 times
greater than found for most Cu(II) complexes; (ii) a very small copper
hyperfine splitting in the EPR spectrum, $|A_{||}| \simeq$ 30-90 x 10^{-4} cm^{-1}; and
(iii) a redox potential appreciably higher than the aqueous Cu(II)/Cu(I)
couple.[231-235]

The type 1 copper centre is found in proteins extracted from a wide
variety of plants, bacteria and mammals. It occurs singly in, for example,
the blue proteins azurin, plastocyanin and stellacyanin. In the larger
enzymes, laccase, ceruloplasmin and ascorbate oxidase it is found in
association with 'type 2' and 'type 3' copper centres, which have
different, but also distinctive properties. An electron-transfer role
has been established for plastocyanin and azurin and this could well be
the function of the type 1 centre in many other single-copper blue proteins
and in the multi-copper enzymes also.

Many physical and chemical techniques have been employed in studying
type 1 centres in an attempt to elucidate the nature of the copper
coordination: amino acid sequence,[236] resonance Raman,[237-239] protein
IR,[240] EXAFS,[241] EPR,[242,243] pulsed EPR,[244-246] linear electric field
effect EPR,[247,244] ENDOR,[248,249] ^{13}C and ^{1}H NMR,[250-258] electronic
absorption, CD and MCD,[259-267,242] XPES,[268-270] electron transfer
kinetics,[271-274] nickel and cobalt substitution.[261,239,275-279] The picture

which has emerged as being consistent with the overall results of these
extensive investigations is of a tetragonally (D_{2d}) distorted tetrahedral
ligation involving a cysteinyl sulphur, two nitrogenous ligands (most
probably histidine imidazole groups) and a fourth methionine, cysteine,
cystine-disulphide or deprotonated peptidylamide ligand. Much effort
has been directed toward the synthesis of simple copper complexes capable
of mimicking the type 1 copper coordination and its unusual properties.
A great diversity of ligand types and coordination stereochemistries
have been employed, but no one complex has been found which represents
an authentic synthetic analogue by modelling all the basic type 1
properties in combination. The particular difficulties inherent in
synthesising analogues of proteins containing single metal atoms coordinated
by a complex polypeptide ligand, which may impose a coordination
environment, have been pointed out by Holm.[1] One problem has been the
incomplete knowledge of the ligand-set in the proteins. In the specific
case of poplar plastocyanin a recent X-ray crystal structure analysis
(2.7 Å resolution) has established that its copper is bound with distorted
tetrahedral stereochemistry (more approximately trigonal than tetrahedral
elongation) to two histidyl nitrogens, a cysteinyl thiolate and a
thioether sulphur from methionine.[242,280] Similar coordination is
indicated for azurin from P. aeruginosa by a lower resolution crystall-
ographic study.[281,282] It is perhaps tempting to generalise this
arrangement to other type 1 copper centres. There probably is not,
however, a unique structure applicable to all type 1 sites; stellacyanin,
for example, contains no methionine[283-286] and a cystine disulphide is
a probable alternative ligand. For this reason, and in view of the insight
gained from comparative studies, the synthesis and investigation of model
compounds continues to be valuable in understanding the detailed geometrical
and electronic structure of type 1 copper.

As has already been indicated a wide variety of copper complexes

have been proposed as modelling some aspect of type 1 coordination,

with equally widely varying degrees of success and applicability, and

just a few of the more useful and informative will be described here.

Some considerable difficulty has arisen in the formulation and inter-

pretation of synthetic model compounds in that the three anomalous

properties of the type 1 copper, listed at the beginning of this section,

may have different, though interrelated, origins. In the light of the

recent crystallographic analyses and subsequent more intensive investi-

gation of the blue-proteins it appears that the intense absorption near

600 nm may be solely a result of S $\rightarrow$ Cu(II) charge transfer[242,259,261,263]

whilst the low $|A_{||}|$ may result solely from a ligand-independent

flattened-tetrahedral stereochemistry where the unpaired electron resides

in an orbital which is a mixture of $3d_{xy}$ and $4p_z$.[248,287,288] The

coordination of the type 1 copper is intermediate between the square-

planar arrangement of hard to soft ligands preferred by Cu(II) and the

tetrahedral soft-ligand environment preferred by Cu(I); this could be

responsible for the observed high redox potential. A major problem

then arises in attempting to synthesise type 1 site analogues because

of the instability of mercapto-copper(II) complexes due to the facile

and essentially irreversible reaction (R1). Any attempt to mimic the

$$2Cu(II) + 2RS^- \longrightarrow 2Cu(I) + RSSR \qquad (R1)$$
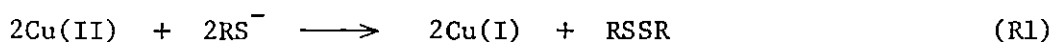
type 1 site must lead to further destabilisation of Cu(II) with respect

to Cu(I) and promote decomposition of the complex via this reaction.

In the proteins this irreversible dissociation tendency may be restricted,

to produce a metastable entactic[159,160] state, by the ability of the peptide to enforce elaborate steric constraints upon the ligands and to protect the site from reactions involving external molecules.

It is clear from several Cu(II)4N[289-294] and Cu(II)4S[295-298] complexes that a small $|A_{||}|$ may result from flattened-tetrahedral coordination, independent of the nature of the ligands. Distortions approaching tetrahedral also lead to low energy d-d transitions of enhanced intensity, characteristic of the type 1 copper sites.[259,263] Intense S $\rightarrow$ Cu(II) charge transfer bands are observed around 600 nm in several copper complexes where there is assumed thiolate coordination.[297,299-304] For thioether coordination absorption bands are also observed around 600 nm in several complexes but there is a degree of conflict in their intensities, being weak for some compounds,[305,306] strong for others[307-309] or intermediate.[310,311]

No structurally characterised four-coordinate N,S-donor cupric complexes have been described which have both low $|A_{||}|$ and intense CT absorption near 600 nm like the blue proteins. The structures S1 (R = $pNO_2-C_6H_4$) and S2 have been crystallographically determined for Cu(I) and there is a distorted tetrahedral coordination.[299,300,306]

(S1)   (S2)

Corresponding Cu(II) complexes, however, have $|A_{||}| \simeq 170 \times 10^{-4}$ cm^{-1}.

A cupric complex similar to S1 but having one pyrazolyl group replaced

by pCH$_3$C$_6$H$_4$S- to give a 2NS(SR) donor set, shows an even larger $|A_{||}|$

$= 187 \times 10^{-4}$ cm^{-1}.[301] On the other hand, a homologue of the ligand in

S2, where the tripodal nitrogen is joined to the pyridine ring by only

one carbon, complexes Cu(II) to give a lower $|A_{||}| = 144 \times 10^{-4}$ cm^{-1},

but a crystal structure determination shows it to be five coordinate.[312]

A recent X-ray structural analysis for the nitrate salt of the cupric form

of S2 shows this too to be five coordinate.[313]

Several reaction products of Cu(II) with small peptides containing

thiol and imidazole groups have been proposed as models for the type 1

copper site since some have $|A_{||}| < 100 \times 10^{-4}$ cm^{-1} and also medium

intensity absorption around 600 nm.[314-317] The reaction products are

stable but have been incompletely characterised, being of unknown

coordination or stereochemistry.

Patterson and Holm[318] have examined a broad series of Cu(II) complexes

to identify specific ligand structural features which might give rise to

Cu(II)/Cu(I) potentials in the blue-copper-protein range, but nearly all

of the 37 complexes studied exhibited negative potentials with respect

to SHE. However, for several cyclic and open-chain polythioether and

aminothioether cupric complexes, substantially positive redox potentials

have been found, comparable to those of the proteins.[295,307,311,319] X-ray

structural information for two such complexes demonstrates in one case

tetragonal and in another square-pyramidal coordination.[309,311] As certain

of these complexes also show reasonably intense visible absorption around

600 nm it has been suggested that distortions from tetragonal geometry

are not requisite for the generation of the spectral and redox properties

which typify blue-copper-proteins.[309] Those of this series for which EPR.

measurements have been made show $|A_{||}| > 160 \times 10^{-4}$ cm^{-1},[295,311] and thus this

parameter at least must make tetrahedral distortion a prerequisite for

complete duplication of type 1 copper properties.

In view of the confusing evidence from the large array of unrelated

model complexes a more systematic approach involving the use of 2N2S

coordination with variable stereochemistry would seem appropriate.

5.2. Cu(II) β-Aminothione Complexes.

5.2.1. Introduction.

The β-difunctional ligand system (S3) (X, Y = O, S, NR, Se) has

shown considerable utility in the comparative investigation of stereo-

(S3)
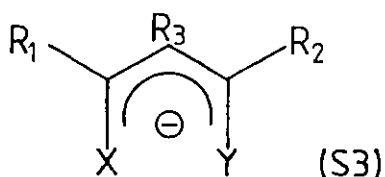
chemical and electronic properties for tetra-coordinate chelates, as

dependent upon donor-atom, metal ion or ligand structure.[320] For X =

NR and Y = O, S, NR distortion from square-planar toward tetrahedral

coordination geometry has been correlated with increased steric bulk of

the R group for a number of metal ions.[321-325,293]

Ni(II) complexes of the N-substituted β-aminothione ligands (S4)

demonstrate a relatively greater stabilisation of planar stereochemistry

(S4) = (RN-R₂R₁S)

(S5) = Cu[(CH₂)ₙ(N-R₂R₁S)₂]
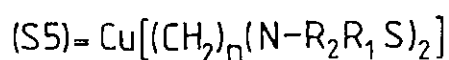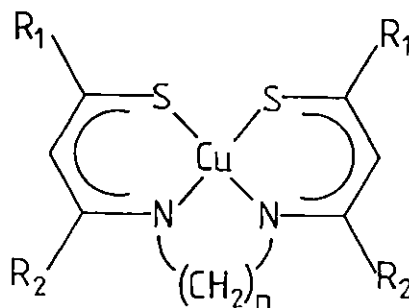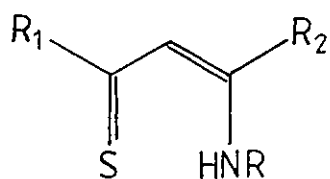
than do corresponding 2N2O coordinated complexes.[322] None-the-less, an

increased tendency toward tetrahedral geometry is apparent as the nitrogen

substituent increases in size.

The only copper complexes reported with this type of 2N2S chelation

have involved quadridentate ligands and are similar to structure (S5).[326-332]

Comparable Cu(II) complexes of the quadridentate ligands (S6) have also

been described by Corrigan et al.,[333] but these authors were unable to

obtain cupric complexes of the corresponding bidentate ligands (S7).

The synthesis of complexes of the latter type has been reported,[334] however,

(S6)

n = 2,3

(S7)
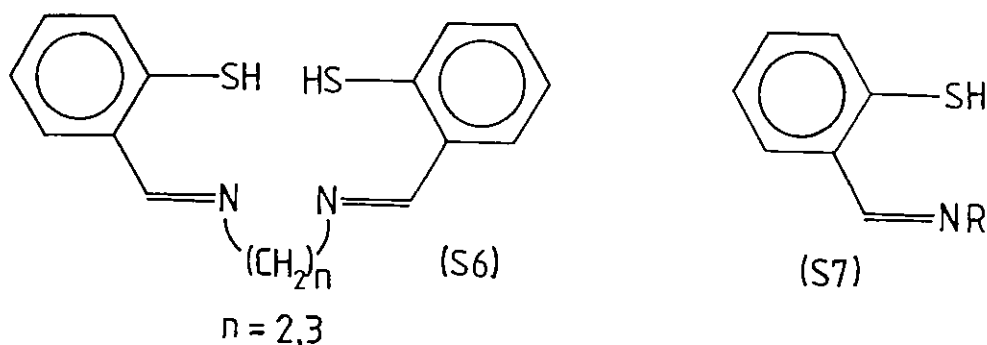
attempts in this present work to obtain these have, like those of

Corrigan et al., failed, leading only to Cu(I) compounds. Similarly,

with the bidentate β-aminothione ligands (S4) only orange coloured Cu(I)

complexes are isolated from anaerobic reactions performed at room

temperature, while intractable dark-brown gums result from prolonged

reaction in the presence of atmospheric oxygen. If, on the other hand,

the coordination of Cu(II) by these ligands is performed at low temperatures

dark-green to dark-blue solutions result from which cupric complexes

may be isolated.

5.2.2. Synthesis of Ligands.

Two approaches have been adopted in ligand (S4) synthesis, as originally employed by Gerlach and Holm[322]:-

R1—C(O)—CH2—C(O)—R2 →(RNH2)→ R1—C(O)—CH=C(HNR)—R2 (S8) →(Et3O⊕)→ R1—C(EtO)=CH—C(HNR⊕)—R2

P4S10 ↓

R1, R2 dithiolium cation (S9), S—S ring ⊕

HS⊖ ↓

(S9) ——RNH2——→ R1—C(S)=CH—C(HNR)—R2 (S4)
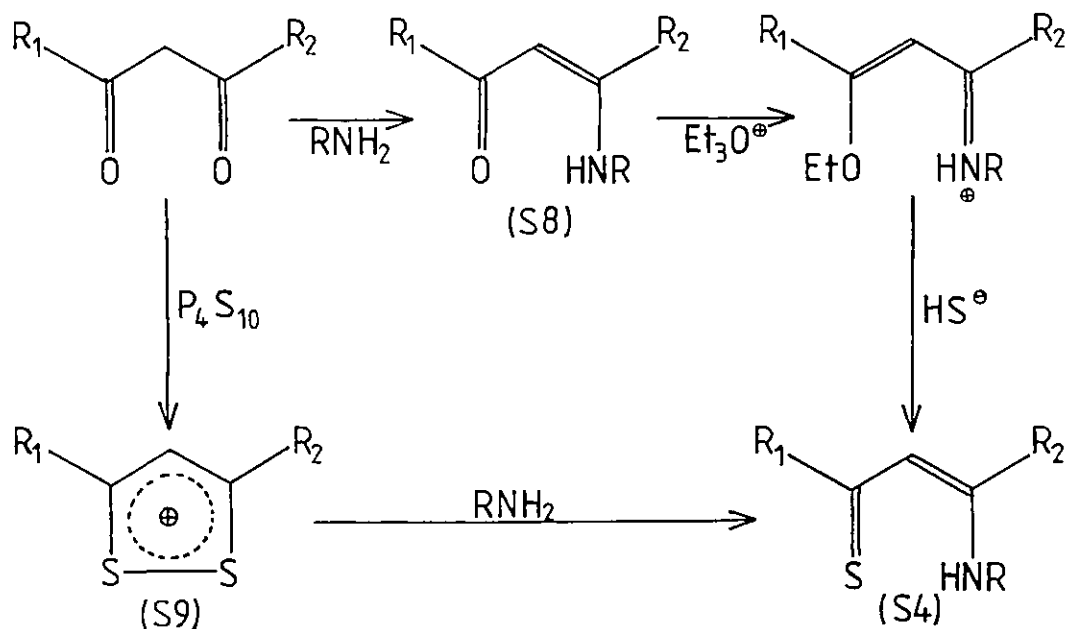
The route via the β-ketoamine (S8) has been used for R_1 = R_2 = Me and R_1 = Ph, R_2 = Me, whilst the second route via the dithiolium cation (S9) has been applied to the synthesis of β-aminothione ligands having R_1 = R_2 = Ph, R_1 = R_2 = tBu, and with a different method of cation preparation,[335] R_1 = Ph, R_2 = H. Only for the RN-MeMeS (i.e., $RN-R_2R_1S$, R_1 = R_2 = Me) ligand has extensive variation of the R group been undertaken, as the members of this series have generally higher solubilities than the phenyl-substituted homologues and involve inexpensive starting materials. Attempts to prepare tBuN-MeMeS or tBuN-tButBuS by the above procedures, were repeatedly unsuccessful.

5.2.3. <u>Synthesis and Characterisation of Cu(II) β-Aminothione Complexes.</u>

Cupric complexes of the β-aminothione ligands have been synthesised by mixing methanolic solutions of ligand and of cupric chloride or cupric acetate at low temperature. The resulting dark green-blue reaction solutions gave darker coloured solid on standing which could be collected by filtration at low temperature. The thermal stability of the solutions and solids formed is greatly dependent on the amino-substituent, R. Thus, for R = Me the complexation reaction may be undertaken at <u>ca</u>. -30°C and the isolated solid is stable for prolonged periods at ambient temperatures. For the more bulky R = iPr substituent, on the other-hand, solutions of the cupric complex must be maintained below <u>ca</u>. -50°C to avoid significant decomposition and the solid may be handled at room temperature for only short periods of time. An electronic effect also appears to be operative in governing the stability of the cupric complexes in that for R = p-YC$_6$H$_4$ far greater tendency towards decomposition to cuprous complexes is found when Y = H or Cℓ than when Y = F, Me or-OMe.

Copper complexation reactions with the β-aminothiones led to orange diamagnetic precipitates when undertaken anaerobically at room temperature. Microanalytical data for a purified complex with PhN-MeMeS demonstrates a one-to-one copper-ligand stoichiometry.

By using dilute reactant solutions and maintaining the reaction solution at <u>ca</u>. -70 to -80°C for several hours it has proven possible to obtain crystalline products with a number of ligands. Notably Cu(II)(iBuN-MeMeS)$_2$ forms dark green needles of a size sufficient to collect X-ray diffraction data, though this has not yet been achieved.

The cupric complexes are soluble in a range of polar organic solvents (DMF, THF, acetone) and their solutions are stable at low temperatures (ca. -50°C). Relative solubilities are dependent upon the R, R_1 and R_2 substituent groups.

The Cu(II)(RN-R_2R_1S)$_2$ complexes have been studied by electronic spectroscopy, EPR, Raman spectroscopy and polarography.

5.3. Electronic Spectra.

Low temperature solution visible spectra and room-temperature solid-state visible-near-IR reflectance spectra have been measured for the cupric β-aminothione complexes. Absorption band maxima and some extinction coefficients are collected in Tables 5.1 and 5.2, and Figures 5.1 and 5.2 show representative spectra. Two intense visible absorption peaks are observed in the ranges ca. 600-680 nm and ca. 470-540 nm for solutions and have close solid-state counterparts. A less intense broad

TABLE 5.1. Visible absorption band maxima of $Cu(II)(RN-R_2R_1S)_2$ in solution.

Ligand	Solvent	Temp./ $^{\circ}C$	λ_{max}/nm [ε/lt cm^{-1}mol^{-1}]
R; $R_1 = R_2 = Me$			
Me	DMF	-60	600 [1500], 480 [2300]
	acetone	RT	610, 480
Et	THF	-50	618 [1400], 481 [1850]
	DMF	-60	613 [1450], 488 [1700]
nPr	THF	-50	610 [1400], 480 [1650]
iPr	THF	-60	679, 500-510 sh
nBu	THF	-55	612 [1400], 475 [1700]
iBu	THF	-50	603 [1400], 470 [1700]
nOct	THF	-60	612 [1400], 475 [1700]
Bz	THF	-60	605 [1500], 487 [1950]
cHx	THF	-60	678 [1400], 504 [∿1000]
pMePh	THF	-55	620 br [1600], 540 br [1600]
pMeOPh	THF	-80	626 [1100], 525 pr [∿1000]
pFPh	THF	-80	630 [1600], 530 [1600]
$-(CH_2)_5-$	THF	-50	∿600 br,sh, 465 pr [∿1500]
EtN-PhPhS	THF	-50	618 [2100], 490 [2600]
EtN-MePhS	THF	-60	621 [2000], 491 [2350]
	DMF	-60	614 [1900], 490 [2350]
EtN-tButBuS	THF	-55	604 [1250], 528 [1350]

pr - poorly resolved; sh - shoulder; br - broad.

FIG. 5.1

ELECTRONIC SPECTRA OF $Cu^{II}(RN-MeMeS)_2$ IN THF OR DMF*

FIG. 5.2
REFLECTANCE SPECTRA OF Cu^{II}(RN—MeMeS)$_2$

R=

Me

iBu

Bz

pFPh

iPr

WAVELENGTH/nm
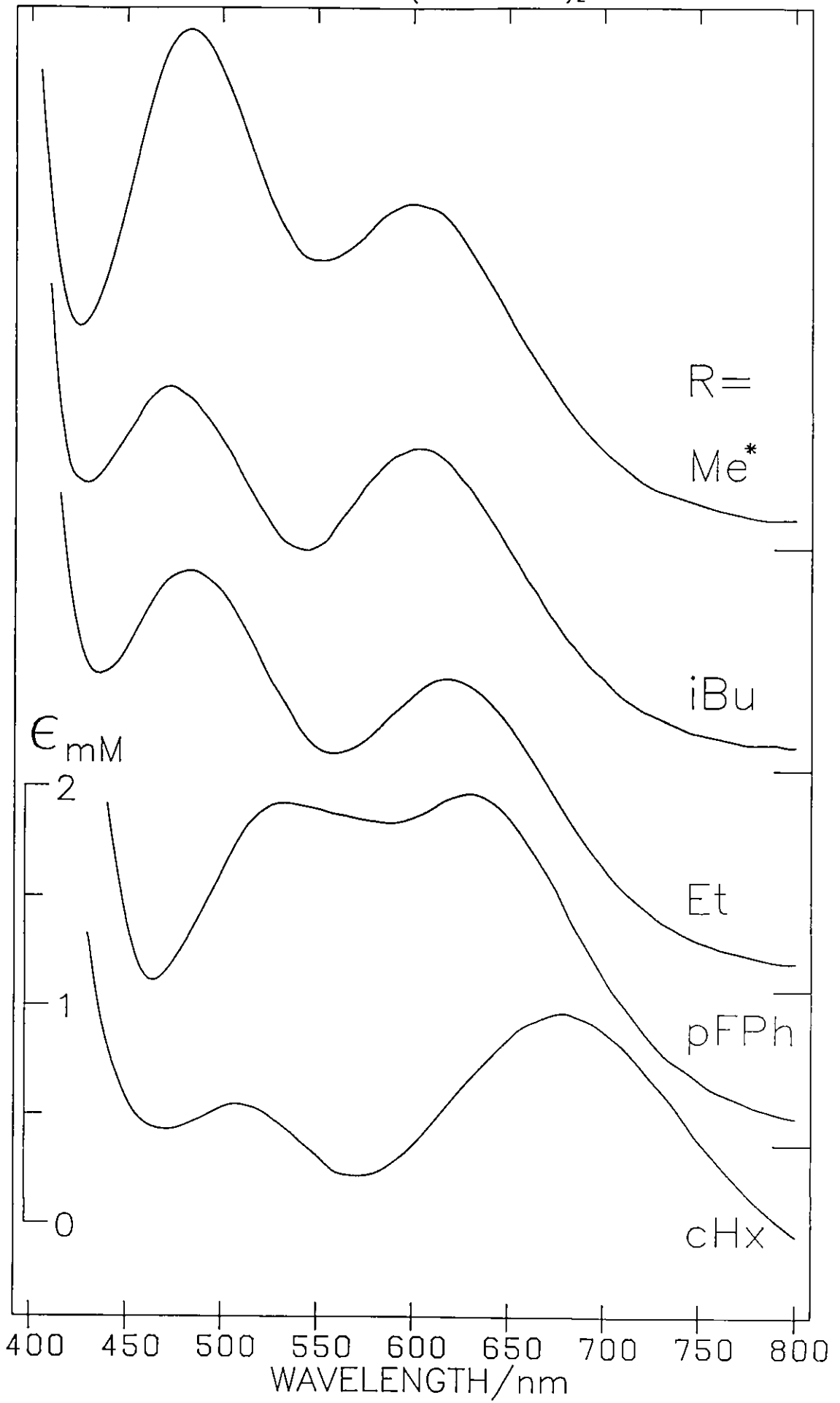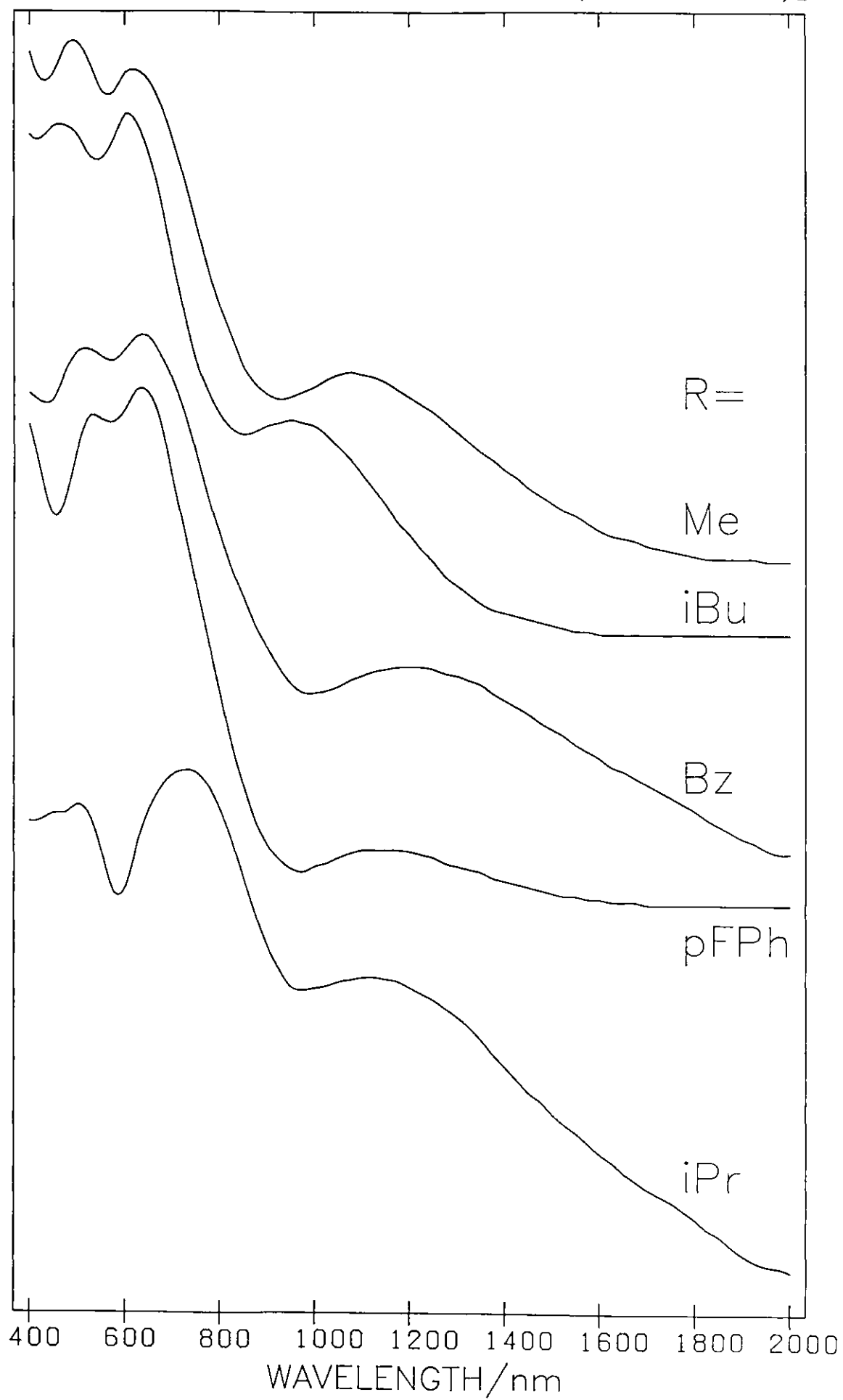
TABLE 5.2. Solid-state reflectance spectra of Cu(II)(RN-R_2R_1S)$_2$;

band maxima at room temperature.

Ligand	λ_{max}/nm
R, R_1 = R_2 = Me	
Me	1075 br, 620, 485
Et	1050 br, 615, 485
nPr	1050 br, 610, 485
iPr	1100 br, 720, 500
nBu	1000 br, 615, 475
iBu	960 br, 600, 460
nOct	980 br, 600, ∿ 500
Bz	1200 br, 635, 510
cHx	960 br, 635, ∿ 430
pMePh	1170 br, 630, ∿ 530
pMeOPh	∿1200> br. pr., 630
pFPh	1130 br, 630, 530
-(CH_2)$_5$-	∿1050 vbr. sh, 610, 490
-(CH_2)$_6$-	∿1000 vbr., 620
EtN-PhPhS	∿ 1200 vbr. pr. sh., ∿850vbr. pr. sh., 620, 510, 420 sh
EtN-HPhS	1130 br., 625, 505, ∿ 430
EtN-tButBuS	910 br., 610, 530

feature is seen in the near IR diffuse reflectance spectra within the range 900-1200 nm. The thermal instability of the Cu(II) complexes presents some difficulty to the accurate determination of molar absorption coefficients for the solution optical bands. Dissolution of the solids must be undertaken at low temperature and the consequent reduced solubility, taken together with the opacity of the resulting

optically dense solutions, makes it difficult to ensure the complexes are
completely dissolved. Dispersal of the solid could, however, be checked
by low temperature filtration on a fine frit prior to spectral measurements.
Decomposition of the chromophore during solution preparation and transfer
to the low temperature cell, was limited as far as possible by the handling
techniques employed, but the extinction coefficients measured, and
reported in Table 5.1, may under-estimate the true values (see also Section
5.8.2. concerning purity of the complexes). The consistency and compati-
bility of the extinction coefficients quoted for the broad selection of
complexes studied indicates reasonable accuracy.

The extinction coefficients of the two bands in the regions 600-680 nm
and 470-540 nm indicate that they are charge-transfer in origin. The
weaker low energy broad band is considered to be d-d, and possibly a
composite of such transitions.

5.3.1. d-d Bands.

For the $Cu(II)(RN-MePhO)_2$ R = Me, iPr complexes with 2N2O coordination
low energy broad features are observed at 625 nm and 725 nm respectively.[325]
The ligand field strength for 2N2S coordination is expected to be weaker,
and the empirical spectrochemical series 4N $\sim$ 4O > 2N2O > 2N2S $\sim$ 2S2O > 4S
has been suggested for the ligand system under consideration.[322] Thus the
observed range of 900-1200 nm would seem reasonable for the lowest energy
d-d transitions in the Cu(II) β-aminothione complexes

Both the position and intensity of d-d bands are expected to be
dependent upon the degree of distortion, if any, from a square-planar ligand
arrangement toward tetrahedral. The average energy of the d-d transitions
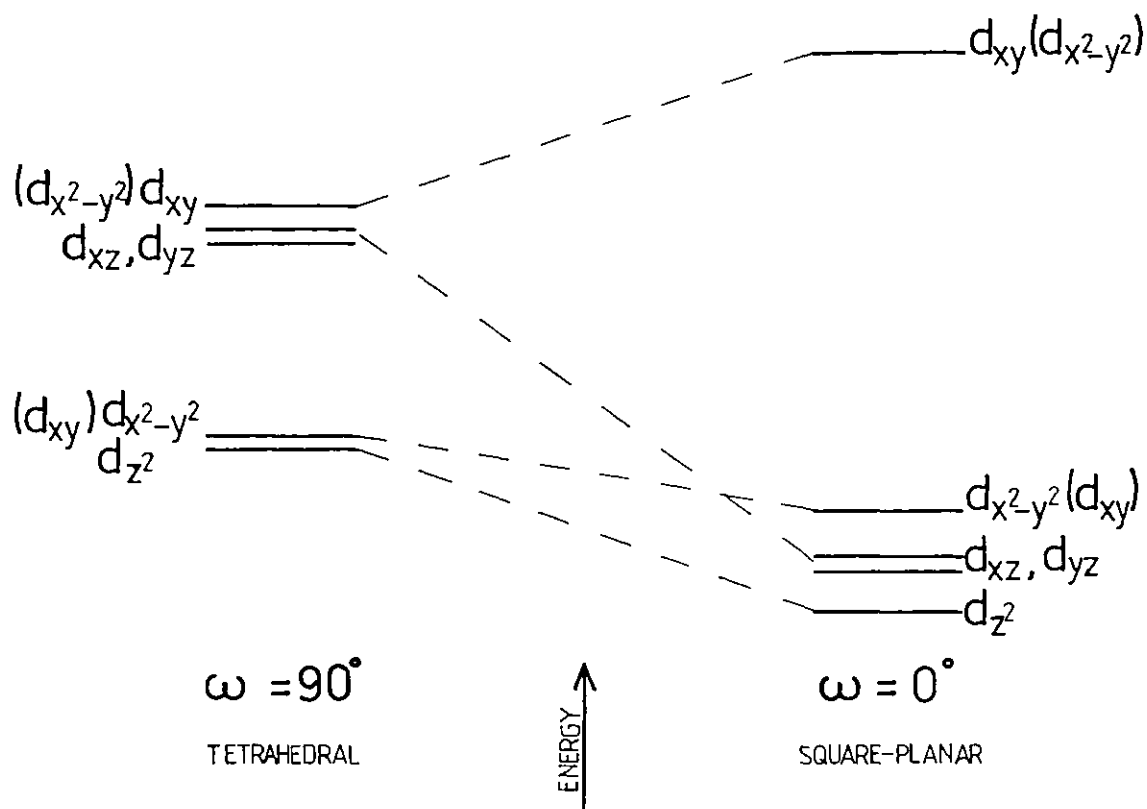
Figure 5.3. Correlation of d-orbital energies for tetrahedral and square-
planar Cu(II) related by a compression along the z-axis.
ω = dihedral angle between pairs of ligand atoms. The
bracketed terms represent the orbitals referred to an
alternative axis system.

will be largest for a square-planar chromophore and least for a regular
tetrahedral chromophore, with a correlation diagram relating the two
extremes as shown in Figure 5.3.

There appears, however, no correlation of the position for the near-
IR absorption maximum with any expected steric bulkiness of the ligand
amino R-group, or of any other spectroscopic parameter thought to be
indicative of tetrahedral distortion (see later). Thus considering the
bulky secondary branch-chain alkyl R-groups, the band occurs at 960 nm
in the $Cu(II)(cHxN-MeMeS)_2$ complex, the shortest wavelength for the
RN-MeMeS series, and at 1100 nm for $Cu(II)(iPrN-MeMeS)_2$. The lowest

energy band maximum is found at 1200 nm for R = Bz which is not

expected to be especially distorted.

Subsequent to the present investigations of bidentate-β-aminothione

Cu(II) complexes Bereman et al. have reported investigations of the

related tetradentate 2N2S coordinated complexes (S5): R_2 = Me, R_1 = Me,

Ph; n = 2, 3[327] and (S10): n = 2,3,4.[328-330]

MeS—S—S—SMe

Cu

N—N

(CH$_2$)$_n$

(S10)
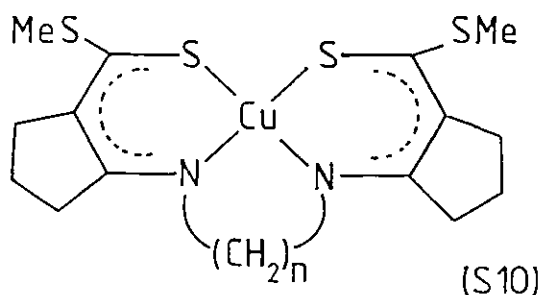
For the latter complexes, crystal structures have been determined for

n = 3 and 4 showing unexpectedly large distortion from planarity involving

dihedral twist angles (ω) of 53° (n = 3) and 57° (n = 4). Accompanying

the tetrahedral distortion along the series n = 2, 3, 4 there is a

decrease in the parallel copper hyperfine splitting (181, 160, 145 x 10^{-4}

cm^{-1}) and an increase in the wavelength of the lowest energy d-d band

(794, 952, 1075 nm). Similar spectroscopic changes are found for the

complexes of structure (S5): R_2 = Me; R_1 = Me (n , λ_{max}= 2, 719 nm; 3,

826 nm); R_1 = Ph (n , λ_{max} = 2, 709 nm; 3, 826 nm).[327]

The copper(II) complexes of the analogous bidentate N,S-ligands studied

here show absorption at lower energies than this latter series of complexes,

indicative of a more tetrahedrally distorted coordination stereochemistry.

It is peculiar, however, that trends in the position of the low energy

electronic bands, similar to those in the above complexes of the quadri-

dentate 2N2S ligands, are not observed, as the Cu(RN-MeMeS)$_2$ complexes

would be expected to show a wider range of stereochemical distortions and indeed demonstrate a broad range of absorption peak-wavelengths.

Enhancement of d-d band intensity may result for tetrahedrally distorted Cu(II) complexes from mixing with allowed 3d-4p transitions made possible by loss of centrosymmetry, or from mixing of the d-d transition with a neighbouring charge-transfer band.[336] The latter mechanism is probably more applicable to the explanation of the relatively high intensities observed in the reflectance spectra of the β-aminothione complexes, though both mechanisms may be operative.

Table 5.3 lists the observed visible and near-IR absorption bands and their assignments for the proteins plastocyanin, azurin and stellacyanin. The most intense d-d bands are found ca. 850-1100 nm. Other weak near-IR absorption maxima in the proteins extend out to ca. 2000 nm.

TABLE 5.3. Electronic spectral parameters for some blue-copper-proteins and their assignments.[259]

λ_{max}/nm [ε/lt cm^{-1} mol^{-1}]			Assignment
Plastocyanin	Azurin	Stellacyanin	
2000*[∿100]	1720*[∿100]	1900*[∿100]	d-d Cu
1070 [200]	980*[∿125]	1140 [∿100]	d-d Cu
847 [1162]		900 [565]	d-d Cu
752 [1289]	779 [686]	789 [341]	(Cys)πS → d$_{xy}$ Cu[†]
606 [4364]	631 [3798]	617 [3549]	(Cys)σS → d$_{xy}$ Cu
552 [1163]	567 [504]		(Met)σS → d$_{xy}$ Cu[†]
		572 [1542]	
450 [300]	481 [198]		πN → d$_{xy}$ Cu
		450 [942]	
428 [∿100]			πN → d$_{xy}$ Cu

*CD band positions ; † These assignments are according to reference 259. More recently, single crystal studies of plastocyanin indicate there to be no degeneracy in the sulphur p-orbitals and the 552 nm band is assigned as S(αS + βp$_z$) → Cu(d$_{xy}$).[242] This has been questioned.[260] (The σ and π designations are carryovers from studies of octahedral complexes in which one ligand p-orbital is σ-bonded and the other two π-bonded to the metal centre.[213])

5.3.2. Charge-transfer bands.

The intense absorption ca. 600-630 nm in blue-copper-proteins,
responsible for the blue colouration wherein is the origin of their
colloquial name, has a well established assignment to a LMCT S(σ) $\rightarrow$
Cu(d_{xy}) transition.[259,242,262] Bands ca. 600-680 nm in the Cu(II)
β-aminothione complexes are, at first sight, reasonably given a similar
assignment . A correlation is noted between the position of this band
and the expected bulkiness of the R-group on the ligand nitrogen. Thus
the series pri-alkyl (600-620 nm) < aryl (620-630 nm) < sec-alkyl (678-
679 nm) connects the increasing steric bulk of R with movement of the
absorption maximum to longer wavelength. The explanation for this trend
is considered to lie in the lowering of the energy of the 'hole' ground-
state d_{xy} (or $d_{x^2-y^2}$) orbital (see Figure 5.3) relative to the ligand
orbital as distortion from square-planar geometry is increased by steric
hindrance from R. The R_1 and R_2 substituents are seen to have relatively
little effect on the position of the band at ca. 600 nm for the complexes
with R = Et. Construction of molecular models shows that these groups are
expected to play little part in causing stereochemical distortion. An
electronic effect is seen, however, in the extinction coefficients of
Cu(EtN-MePhS)$_2$ and Cu(EtN-PhPhS)$_2$ which are significantly larger than
for the corresponding Cu(EtN-MeMeS)$_2$ and Cu(EtN-tButBuS)$_2$ complexes. A
similar intensity enhancement has been observed for phenyl substitution
in the chelate ring of copper(II) N,N'-diaryl-β-iminoamines.[293]

It is less easy to make a categoric assignment of the LMCT bands

observed in the region 470-540 nm, and indeed, determination of the

origin of this absorption casts some doubt on the assignment made for

the peak at ca. 600 nm. Firstly, a N $\rightarrow$ Cu(II) transition would seem

an unlikely origin for the band at ca. 500 nm as the observed extinction

is much higher than would be expected (see, for example, Table 5.3).

It is possible, then, that the 500 nm band should be assigned as

$S(\sigma) \rightarrow Cu(d_{xy})$ and the maximum at ca. 600 nm as $S(\pi) \rightarrow Cu(d_{xy})$, in

contradiction to the assignment given above. Such a blue shift relative

to the peaks assigned to these transitions for the blue-copper-proteins,

would perhaps be indicative of a less distorted coordination geometry.

In the proteins the $S(\pi) \rightarrow Cu(d_{xy})$ band is observed at a much lower

intensity than that attributed to $S(\sigma) \rightarrow Cu(d_{xy})$ CT, whereas comparable

intensities are observed for the two visible LMCT bands in many of the

Cu(II) β-aminothione complexes. This might, however, be due to greater

π-resonance delocalisation in the six membered chelate ring of the

complexes compared to the $S(\pi)$-Cu(II) overlap in the proteins. Substantial

π-delocalisation has been suggested for analogous quadridentate 2N2S

complexes from IR, NMR and X-ray structural data.[326, 328, 329, 332]

An alternative explanation for the bands occurring ca. 500 nm in the

model complexes is that there exists an energy difference in the two $S(\sigma)$

orbitals and that both this and the band at ca.600 nm arise from

$S(\sigma) \rightarrow Cu(d_{xy})$ transitions. Such a view might be supported by the

observation that only a single intense band around 600 nm is found in

the optical spectrum of $Cu(II)[HB(3,5-dimethyl-1-pyrazolyl)_3](pNO_2C_6H_4S)$,[299,30(]

containing only one Cu(II)-S bond, whereas two bands of comparably high

extinction are found for $Cu(II)[S(Ph)_2PNP(Ph)_2S]_2$ at 407 nm and 575 nm.[297]

If this were the case the $S(\pi) \rightarrow Cu(d_{xy})$ transition would be considered

to contribute only to the substantial tailing toward longer wavelengths.

An energy splitting between the two $S(\sigma)$ orbitals of the order 2500-

5000 cm^{-1} would be required, and is rather difficult to justify.

$S(\sigma)$ orbital splittings approaching these have, however, been suggested

and justified for Cu(II) complexes having more than one sulphur-donor

by Amundsen et al.[310]

For some of the complexes a slight asymmetry is seen in the high

energy LMCT band. This could be indicative of assignment of this band to

$S(\sigma) \rightarrow Cu(d_{xy})$ with a small difference in the two $S(\sigma)$ orbital energies

and assignment of the lower energy LMCT band to $S(\pi) \rightarrow Cu(d_{xy})$ as

discussed previously.

Circular dichroism or resonance Raman excitation-profile measurements

might resolve the question of the exact assignment of the LMCT transitions

responsible for the intense visible absorption features of these complexes.

5.3.3. Electronic spectra of nickel(II) β-aminothiones.

Table 5.4 lists band positions and intensities for several Ni(II)

(RN-MeMeS)$_2$ complexes in $CH_2C\ell_2$. All show a d-d band in the region

ca. 640-700 nm. For R = aryl additional near-IR absorption ca. 1200-1600

nm is indicative of a planar-tetrahedral stereochemical equilibrium in

solution.[322] The near-IR absorption is of greatest intensity for R =

2,6-dimethylphenyl, which from considerations of steric bulkiness amongst

the six substituents employed, would be expected to most favour a

tetrahedral coordination geometry. The LMCT bands are found at higher

energy in the nickel complexes compared to the copper. Shifts from 600

and 480 nm in Cu(MeN-MeMeS)$_2$ to 442 and 350 nm in Ni(MeN-MeMeS)$_2$ are

TABLE 5.4. Electronic spectral parameters for Ni(II)(RN-MeMeS)$_2$ Complexes
in $CH_2C\ell_2$.

R	λ_{max}/nm [ε/lt cm^{-1} mol^{-1}]
Me	640 [128], 442 [2090], 350 sh [5600], 310 [9500], 262 [24400]
nOct	650 [118], 445 sh [2100], ∿390 sh, 353 sh [5200], 315 [8440], 255
Octadecyl	645 [113], 445 sh [2000], ∿ 390 sh, 355 sh [5100], 314 [8700], ∿260
Ph	∿1500 sh, 1280 [15], 680 [240], ∿450 br. sh 332 [5000], 276 [9000].
pCℓPh	∿1500 sh, 1270 [15], 678 [250], 460 br.sh, 335 [8000], 280 [10400].
2,6-dimethylphenyl	∿1550 [50], 1330 [50], 704 [304], ∿450 br.sh, 360 sh [10000], 325 sh, 383 [14500]

comparable to those from 621 and 521 nm in native azurin to 439 and
392 nm in the Ni(II) derivative, and are quite compatible with the
expected optical electronegativity differences for Cu(II) and
Ni(II).[261,265,213]

5.4. Electron Paramagentic Resonance.

EPR spectra have been recorded for a wide range of the Cu(II)(RN-R_2R_1S)$_2$ complexes in mobile and frozen solution. For the RN-MeMeS ligand-series measurements have also been made on Cu(II) doped Zn(II), Ni(II) and Cd(II) complexes.

5.4.1   EPR in Solution.

For the complexes isolated as solids, toluene was used as a solvent since it forms an adequate glass when frozen and is expected to be non-coordinating. EPR parameters derived from frozen and mobile solution spectra are reported in Table 5.5. Also to be found in this table are data from spectra recorded for complexes prepared in methanol from Cu(II) and excess deprotonated ligand. This method of sample preparation has been utilised where isotopically pure ^{63}Cu was desired (e.g., 1-Naphthyl-N-MeMeS), where isolation of the solid cupric complex proved difficult or impossible (e.g., tBuN-HPhS) or merely for convenience in order to avoid the lengthy low temperature filtration and drying procedure (e.g., iPrN-tButBuS). In view of the similarity in form of the EPR spectra it is considered a reasonable assumption that the spectra recorded for reaction-solutions result from complexes with similar 2N2S coordination to those which have been isolated and for which other spectroscopic and also analytical data are available. No signals attributable to 2N2S coordination could be obtained from reactions with the ligands tBuN-PhPhS and diphenylmethyl-N-MeMeS, presumably due to the steric opposition to chelation proffered by the bulky amino-substituents.

TABLE 5.5. EPR parameters for Cu(II)(RN-R₂R₁)₂ in solution at 100 K.

Ligand R₁ = R₂ = Me		$g_\parallel$	$-A_\parallel$	g_o	$-A_o$	$^N A_o$	$g_\perp$	$-A_\perp$
R	Solvent							
Me	M	2.147	143					
Me	T	2.148	147	2.070	60	10	2.031	16.5
Et	T	2.146	140	2.071	59	9.5	2.034	18.5
nPr	T	2.144	142	2.070	60	10	2.033	19
iPr	T	2.166	134	2.077	55	nr	2.033	15.5
nBu	T	2.145	142	2.071	60	10	2.034	19
iBu	M	2.150	149	2.067	63	10.5	2.023	20
iBu	T	2.145	149	2.071	64	10.5	2.034	21.5
sBu	M	2.178	131	2.078	56	9	2.028	18.5
sBu	T	2.170	133	2.076	56	9	2.029	17.5
nOct	T	2.146	142	2.071	61	10	2.034	20.5
cHx	M	2.173	130	2.079	56	pr	2.032	19
cHx	T	2.165	139	2.076	56	pr	2.032	14.5
Bz	T	2.141	142	2.071	63	9.5	2.036	23.5
αMeBz	M	2.169	132	2.078	56	pr	2.033	18
1-Naphthyl	M	2.151	143	2.072	62	11.5	2.033	21.5
Ph	M	2.143	134	2.069	56	8.5	2.032	17
pMePh	T	2.139	132	2.069	55	10	2.034	16.5
pMeOPh	M	2.144	133	2.069	55	8.5	2.032	16
pMeOPh	T	2.140	132	2.069	55	8.5	2.034	16.5
pCℓPh	M	2.141	135	2.069	56	8	2.033	16.5
pFPh	T	2.138	133	2.068	55	pr	2.033	16
p(Me₂N)Ph	M	2.143	134	2.065	53	pr	2.026	12.5
2,6-Me₂Ph	M	2.153	128	2.077	55	11.5	2.039	18.5
EtN-MePhS	T	2.144	140	2.070	58	9.5	2.033	17
EtN-PhPhS	T	2.141	143	2.067	60	9	2.030	18.5
nBuN-PhPhS	M	2.144	154	2.066	61	9	2.027	14.5
iPrN-PhPhS	M	2.169	127	2.076	52	nr	2.030	14.5

TABLE 5.5.(continued).

Ligand		$g_\parallel$	$-A_\parallel$	g_o	$-A_o$	$^N A_o$	$g_\perp$	$-A_\perp$
RN-R$_2$R$_1$S	Solvent							
BzN-HPhS	M	2.144	146					
iPrN-HPhS	M	2.141	142	2.072	57	pr	2.038	14.5
tBuN-HPhS	M	2.168	127	2.083	52	nr	2.041	14.5
EtN-tButBuS	T	2.147	151	2.067	67	9.5	2.027	25
iPrN-tButBuS	M	2.157	142	2.070	65	9	2.027	26.5

KEY: Solvents: T = Toluene   nr = not resolved

M = Methanol   pr = poorly resolved

NOTES: 1) $A_\parallel$, A_o and $^N A_o$ in cm^{-1} x 10^{-4} ($\pm$ 1).

2) Cu(II)(1-Napthyl-N-MeMeS)$_2$ $^N A_\parallel$ = 12 x 10^{-4} cm^{-1}

Cu(II)(2,6-dimethylphenyl-N-MeMeS)$_2$ $^N A_\parallel$ = 12.5 x 10^{-4} cm^{-1}

overlapping 1:2:3:2:1 $^N A_\parallel$ structure on the lowest field feature of the latter complex indicates the presence of more than one species or conformation.

3) Frequencies range 9.21 to 9.25 GHz

No 'half-field' (ΔM = 2) transitions, which are indicative of dimer formation, were observed for any of the complexes.

The measured transition fields corresponding to g_o, $|A_o|$ in mobile solution and $g_\parallel$, $|A_\parallel|$ in frozen solution were least-squares fitted according to the second-order equations of Kuska and Rogers[337] and the resultant g and $|A|$ parameters are accurate to about $\pm$ 0.001 and $\pm$ 0.0001 cm^{-1} respectively. $g_\perp$ and $|A_\perp|$ were evaluated via the relationships

$g_o = (g_{||} + 2g_{\perp})/3$ and $A_o = (A_{||} + 2A_{\perp})/3$, neglecting any temperature dependence of g_o and A_o which is probably small with the non-coordinating solvents employed.

5.4.1.1. Lineshapes and simulation.

Figures 5.4-5.6 show a selection of spectra together with some attempted simulations. Most notable is the well resolved $g_{\perp}$ nitrogen superhyperfine structure seen on many of the spectra. Only in the cases of $Cu(II)(1-Naphthyl-N-MeMeS)_2$ and $Cu(II)(2,6-dimethylphenyl-N-MeMeS)_2$ has well resolved superhyperfine splitting been observed on the low field $g_{||}$ features, Figure 5.5. The powder-pattern simulations, parameters for which are collected in Table 5.6, result from a Fortran program 'EPRPOW' which is more fully described in the experimental section (Sec. 6).

TABLE 5.6. EPR parameters used in simulating $^{63}Cu(II)(RN-MeMeS)_2$ solution spectra.

R =	iBu	sBu	1-Naphthyl	pMeOPh
g_x	2.019	2.022	2.018	2.013
g_y	2.041	2.043	2.050	2.040
g_z	2.150	2.178	2.153	2.144
$-A_x$	21	20	22	16
$-A_y$	21	16.5	22	18
$-A_z$	148.5	130.5	141	133
$^N A_x$	12	11	9	9.5
$^N A_y$	11	11	11	9
$^N A_z$	11	9.5	12.3	9
W_x	6	5	10	4
W_y	2.5	3.5	4	3
W_z	6	6	5	12
W-anisotropy	DC	DC	DC	L
Frequency/GHz	9.224	9.238	9.214	9.219
Figure	5.4	5.4	5.5	5.5

W = Gaussian-linewidth (half-height half-width) in gauss.
L = Linear anisotropy, DC = direction cosine anisotropy equation (Sec. 6).
$\underline{A}$ and $^N\underline{A}$ are in $cm^{-1} \times 10^{-4}$.

281

FIG. 5.4

X-BAND EPR SPECTRA IN MeOH AT 100K

282
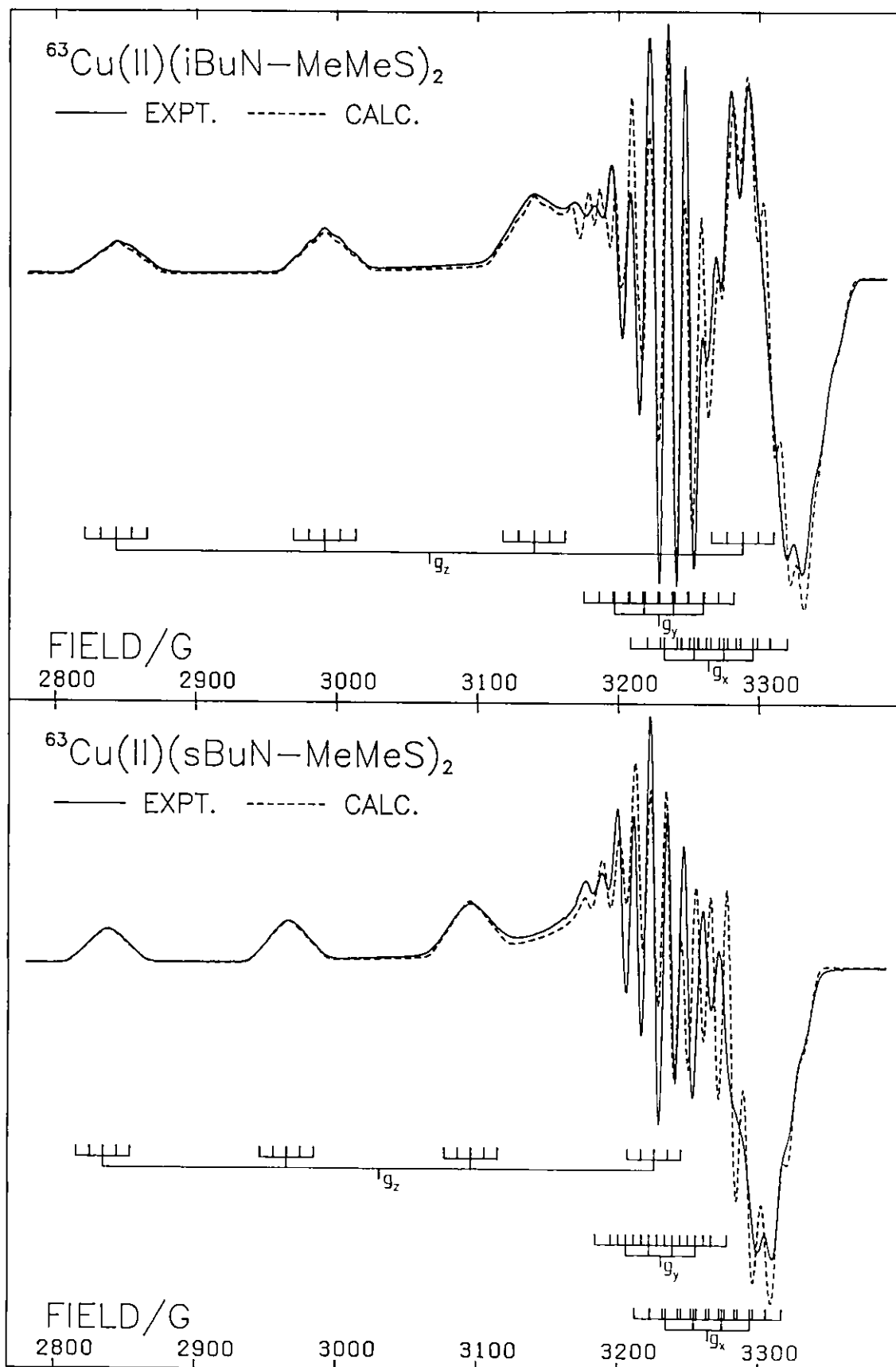
FIG. 5.5
X—BAND EPR SPECTRA IN MeOH AT 100K
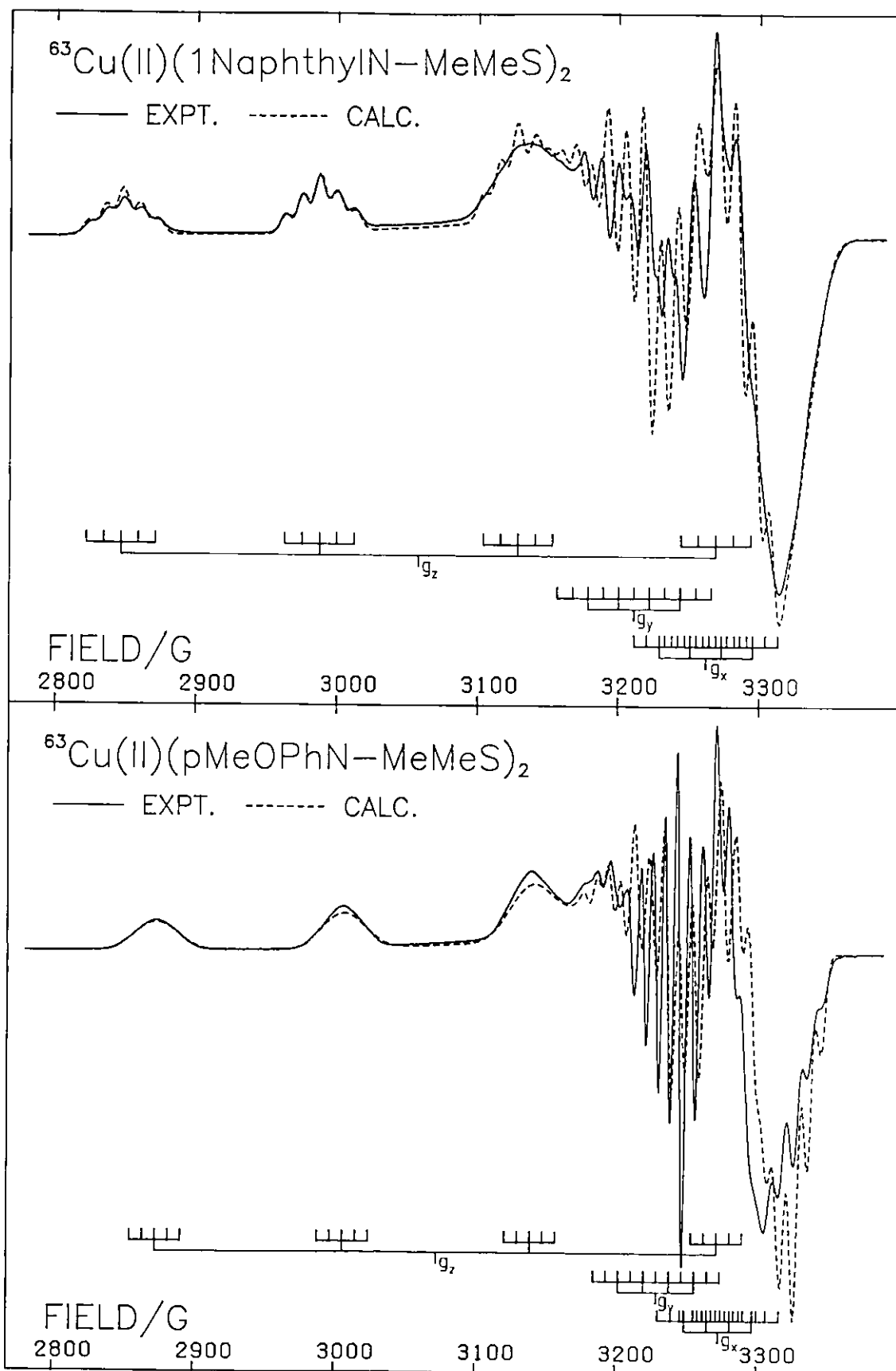
FIG. 5.6
EPR SPECTRA FOR $Cu^{II}(RN-R_2R_1S)_2$ IN MOBILE TOLUENE

$Cu^{II}(iBuN-MeMeS)_2$

$Cu^{II}(sBuN-MeMeS)_2$

$Cu^{II}(EtN-tButBuS)_2$

FIELD/G

3000 3050 3100 3150 3200 3250 3300 3350
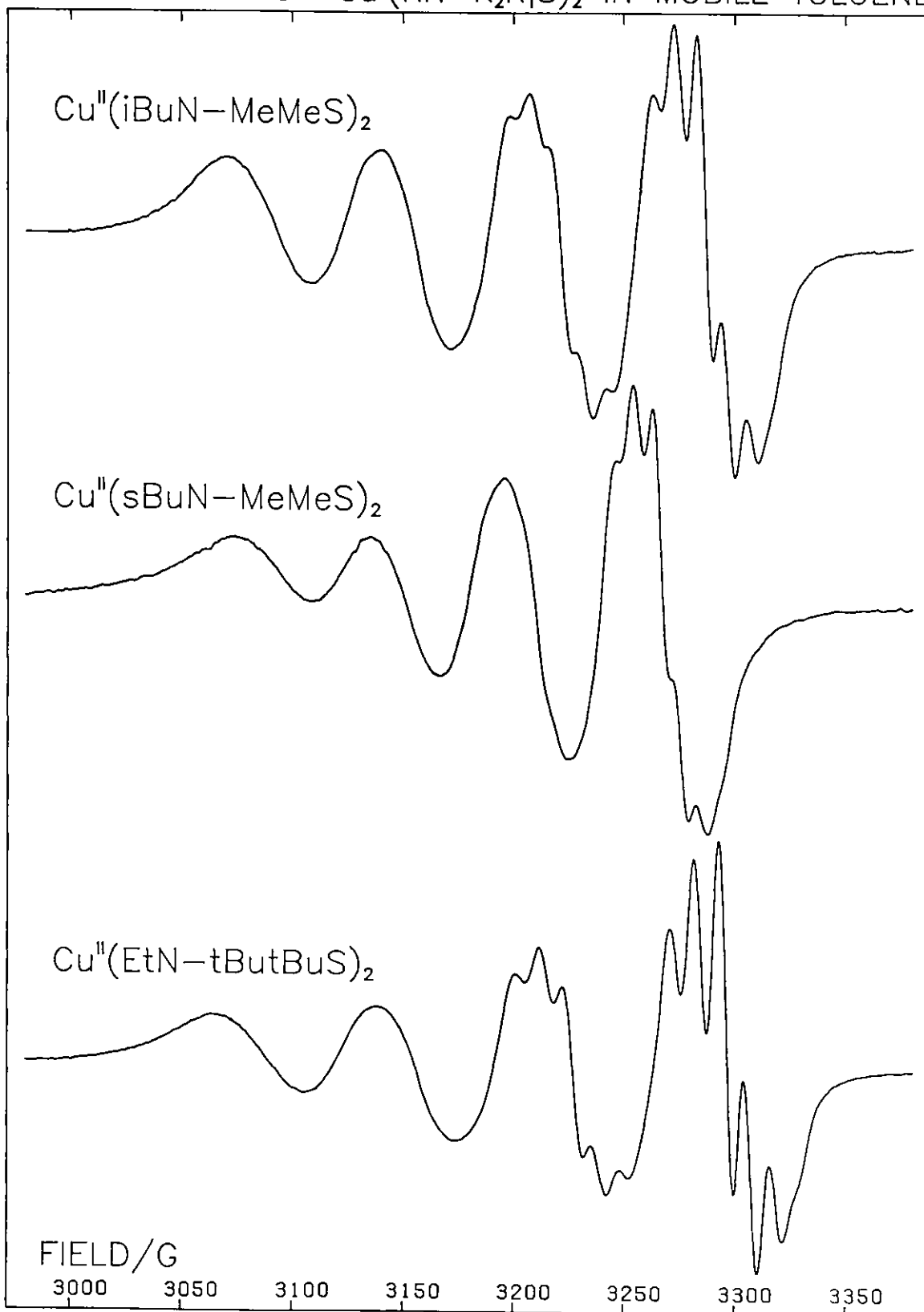
The calculation procedure employs a three-point Gauss-point angular

integration method and second-order perturbation formulae for an

orthorhombic spin Hamiltonian to generate line positions for the primary

transitions. Weighted transition fields have been broadened with both

Gaussian and Lorentzian functions, with width interpolated between three

principal-axis values either linearly or by a direction cosine relation-

ship. In some cases only limited attempts have been made to reproduce

the complex superhyperfine patterns around $g_\perp$ once the general form of

the lineshape was attained, as the restricted capabilities of the program

must be recognised. In particular, the simulation program, as written,

has a simplistic approach to the orientation of the hyperfine and super-

hyperfine tensors. Whilst the primary hyperfine tensor may be rotated

about the unique axis, any remaining hyperfine interactions must assume

the principal axis system of the g-tensor. This means that for the

coordination stereochemistry expected of the β-aminothione Cu(II) complexes

the superhyperfine interaction will only be rigorously calculated when

isotropic. It would be possible to evaluate the orientational dependence

of the splitting from the two nitrogens by introducing three further

parameters into the calculation to specify the relative orientations of

the $^N\!A$ and g tensors together with the angular relationship between the

two Cu-N bonds. No attempt has been made to do this. Accurate x,y-axis

parameters are not, however, required in the discussion that follows,

since no attempt is made to evaluate bonding parameters in the absence

of the d-d energy separations and in view of the difficulties inherent

in estimating the many other unknowns. Despite the above reservations,

together with the additional difficulty of adequately representing line-

width anisotropy and the neglect of quadrupole interactions, quite

acceptable fits to the experimental spectra could be achieved in some

cases.

Thus the simulation of the spectra in terms of superhyperfine

interaction with two nitrogen nuclei, together with the observation

of resolved 1:2:3:2:1 splitting on the low field g_z peaks in some cases,

is strongly indicative of 2N2S coordination, which is assumed for steric

reasons to be trans when projected onto the xy plane.

5.4.1.2. $g_{||}$ vs $|A_{||}|$ Analysis.

Kivelson and Neiman[338] first noted a correlation between Cu(II)

hyperfine splitting and $g_{||}$. Peisach and Blumberg[339] constructed plots

of $A_{||}$ against $g_{||}$ for a substantial range of complexes and established

regions diagnostic of donor-atom coordination, overall charge and electron

delocalisation. The tendency of $g_{||}$ to increase and $|A_{||}|$ to decrease

with an increase in the degree of tetrahedral distortion has been

observed for structurally well-characterised complexes of Cu(II) with

N-alkylsalicylaldiminates,[340,341] bis(pyrazolyl)gallates[291] and dipyrro-

methenates,[292] and explicitly correlated by Addison and co-workers for

complexes with pyrrole-2-carboxaldimates[289] and a wide range of other

four-coordinate donor-sets,[295,296] and by Symons, et al.[342] for Cu(II)

doped pentacyanonitrosylferrate and tetrathiocyanatometallate salts.

$|A_{||}|$ for the β-aminothione Cu(II) complexes has been plotted against

$g_{||}$ in Figure 5.7. The expected anti-parallel relationship between these

parameters is demonstrated by, for example, the change on going from

R = Me, iBu to R = iPr, sBu, cHx, αMeBz in Cu(II)(RN-MeMeS)$_2$, the

increased tetrahedral distortion in members of the latter group over

the former being also manifest in their visible spectra (Sec. 5.3) and

half-wave potentials (Sec. 5.6). There is, however, a wide general

distribution of the points on Figure 5.7 outside an inverse correlation

FIG 5.7 $A_{||}$ vs $g_{||}$ PLOT FOR EPR OF $Cu(II)(RN-R_2R_1S)_2$ IN SOLUTION

$-A_{||}$
$\times 10^4$
(cm^{-1})

160

150

140

130

120

2.130   2.140   2.150   2.160   2.170   2.180

$g_{||}$

	R_1	R_2	R
◆	Me	Me	
◇	Me	Me	Ph
◈	Me	Ph	
◐	Ph	Ph	
⬗	H	Ph	
⬖	tBu	tBu	

◇ Toluene
◇ Methanol

nBu
Et
iBu
iBu
Me
Bz
Et
nPr   nBu   Me
Bz
&iPr nOct
Et   Et
iNaphth
iPr
cHx
iPr
pYPh
sBu
aMeBz
cHx
sBu
2,6-Me$_2$Ph
tBu iPr

~ERROR
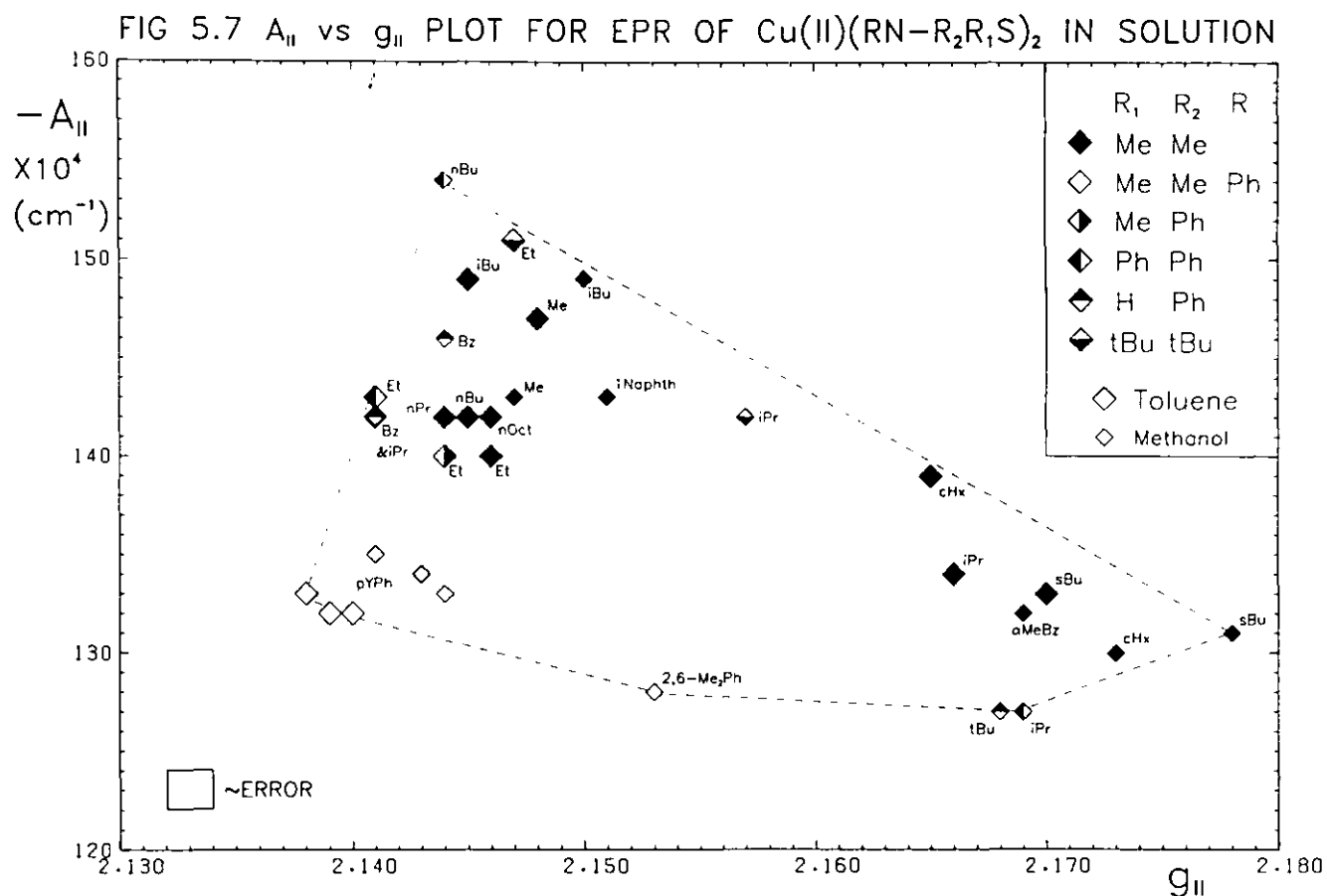
of $|A_{||}|$ and $g_{||}$, particularly noticable in the case of $R = -CH_2R'$ amino-substituents. Furthermore, a displacement toward the lower-left of the plot is observed for parameters of complexes having R = aryl. Thus, in addition to any stereochemical consequences, substantial electronic effects are apparent from changes in the amino and other chelate ring substituents. It must, of course, be noted that the span of $g_{||}$ and $|A_{||}|$ being considered here is not very large and detailed consideration of the interrelation of these parameters will only be given subsequent to a consideration of the wider range of values found for the Cu(II) doped, Zn(II), Ni(II) and Cd(II) β-aminothione complexes.

5.4.2. EPR in Cu(II) doped Zn(II), Ni(II) and Cd(II) β-aminothione

      complexes.

Natural copper(II) or isotopically pure ^{63}Cu(II) has been doped at

low temperature into Zn(II), Ni(II) and Cd(II) EPR-silent complexes of

the RN-MeMeS ligand series. EPR parameters from features corresponding

to resonance along the unique g principal-axis are listed in Tables 5.7,

5.8 and 5.9. Some representative spectra are shown in Figures 5.8 to

5.13, together with attempted simulations. Parameters used for the

simulations are collected in Table 5.10.

A wide range of $|A_{\parallel}|$ values is found (97–184 x 10^{-4} cm^{-1}). Some

of the spectra show excellently resolved 1:2:3:2:1 hyperfine splitting

from two coordinated nitrogens. The $|^{N}A_{\parallel}|$ splittings range from 7–13

x 10^{-4} cm^{-1}. In the case of Cu(II) doped M(II)[(CH$_2$)$_3$(N-MeMeS)$_2$] M =

Zn, Cd splitting is also seen at high field from two protons, 3G for

M = Zn (Figure 5.11) and 4G for M = Cd, presumably arising from the

central bridging methylene group of the ligand.

Despite the reservations about the adequacy of the simulation

procedure expressed in Sec. 5.4.1.1, a very good fit could be achieved

for the X and Q-band spectra of Cu(II) doped Ni(II)[(CH$_2$)$_2$(N-MeMeS)$_2$],

Figure 5.12 (note the stick spectra on all the simulations have no 2nd

order corrections). The agreement of the sets of parameters from best-

fit simulations of spectra at the two frequencies are within experimental

error, Table 5.10. Simulations for other of the doped zinc complexes,

Figures 5.8–10, are less acceptable and no great accuracy can be expected

of the x-y parameters quoted in Table 5.10 as unique fits could not be

attained in this region of the spectra; this is not unusual.[343]

TABLE 5.7. EPR parameters for $^{63}Cu(II)$ doped $Zn(II)(RN-MeMeS)_2$ at 100 K.

R	$g_\parallel$	$-A_\parallel$	$^N A_\parallel$
Me	2.177	115	10
Et	2.162	132	9
nPr	2.174	107	12-13
iPr	2.183	106	pr
nBu	2.161	125	9
iBu	2.172	102	9.5
nOct	2.176	108	pr
cHx	2.194	97	nr
Bz	2.154	132	10
α-MeBz	2.176	110	nr
1-Naphthyl	2.162	100	11
Ph	2.165	106	pr
pMePh	2.155	117	9
pMeOPh	2.153	124	9
pCℓPh	2.146	128	9
pFPh	2.167	108	7
$2,6-Me_2Ph$	2.166	101	12
$2R = -(CH_2)_n-$			
n = 2 (RT)	2.130	159	12
n = 2	2.129	163	12.2
n = 3	2.139	137	10
n = 5	2.148	142	nr
n = 6	2.149	144	nr

Key: nr = not resolved, pr = poorly resolved,

RT = room temperature

Notes: 1) Frequencies in range 9.215 to 9.235 GHz

2) The low field features of R = nPr and

R = 1-Naphthyl are more complicated than

the expected 1:2:3:2:1 $^N A_\parallel$ splitting.

TABLE 5.8. EPR parameters for Cu(II) doped Ni(II)(RN-MeMeS)$_2$ at 100 K.

R	$g_\parallel$	$-A_\parallel$	$^N A_\parallel$	Cu
Me	2.141	160	11.3	63
Et	2.140	165	10	63/65
nOct	2.152	154	10	63/65
$C_{18}H_{37}$	2.155	146	nr	63/65
pMePh	2.144	158		63/65
pCℓPh	2.146	151	10.4	63
2,6-Me$_2$Ph	2.154	147	13-14	63/65
2R = $-(CH_2)_n-$				
n = 2 (RT)	2.111	180.3	12	63
n = 2	2.112	183.3	12.3	63
n = 3	2.132	167	11.5	63

Frequencies range 9.22-9.23 GHz

TABLE 5.9. EPR parameters for Cu(II) doped Cd(II)(RN-MeMeS)$_2$ at 100 K.

R	$g_\parallel$	$-A_\parallel$	$^N A_\parallel$	Cu
Me	2.173	117	12	63
Et	2.166	124		63/65
nOct	2.174	112	12	63/65
pMePh	2.160	135	11.5	63
2R = $-(CH_2)_3-$	2.142	140	10	63

Frequencies range 9.22-9.23 GHz

FIG. 5.8
EPR OF ^{63}Cu(II) DOPED Zn(II)(RN—MeMeS)$_2$ AT 100K

R=cHx

CALC.
Gauss

EXPT.

CALC.
Lorentz

g_z

g_y

g_x

FIELD/G

2800   2900   3000   3100   3200   3300   3400

R=Et

FIELD/G

2800   2900   3000   3100   3200   3300   3400
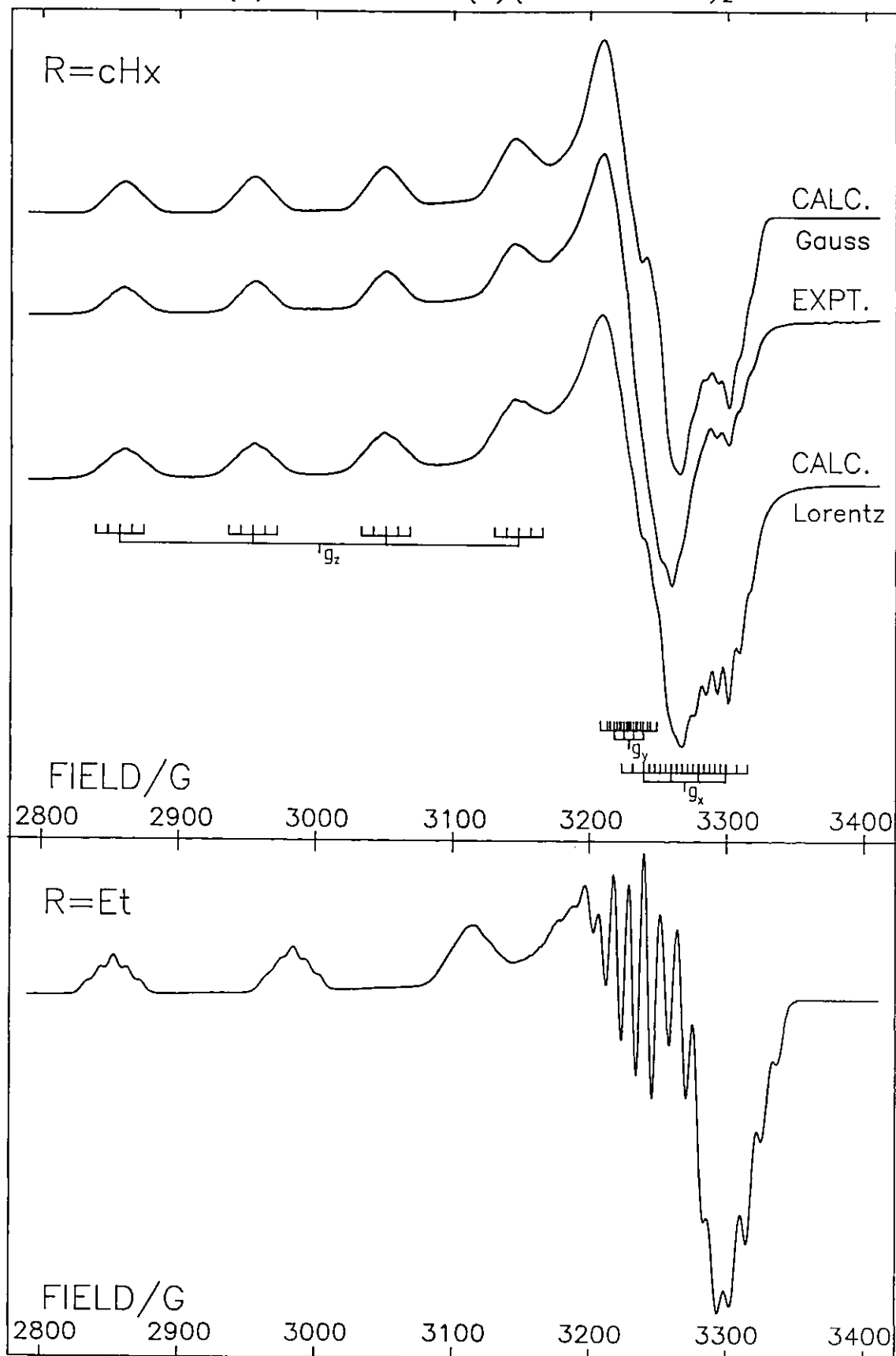
FIG. 5.9
EPR OF ^{63}Cu(II) DOPED Zn(II)(RN−MeMeS)$_2$ AT 100K
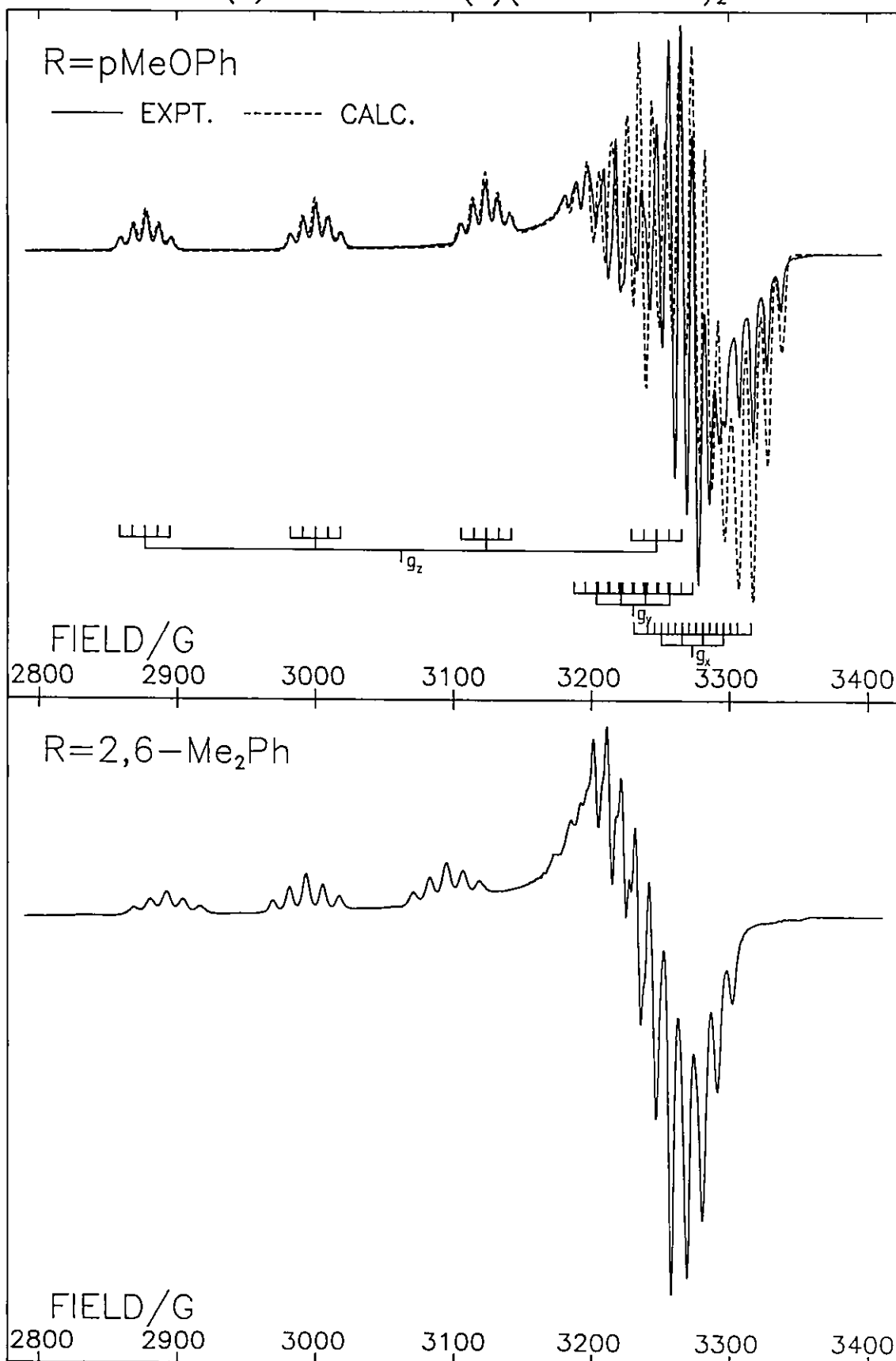
FIG. 5.10
EPR OF ^{63}Cu(II) DOPED M(II)(MeN−MeMeS)$_2$ AT 100K

M=Zn

$^{I}g_z$

——— EXPT.
------- CALC.

$^{I}g_y$
$^{I}g_x$

FIELD/G

| 2800 | 2900 | 3000 | 3100 | 3200 | 3300 | 3400 |

M=Cd

FIELD/G

| 2800 | 2900 | 3000 | 3100 | 3200 | 3300 | 3400 |
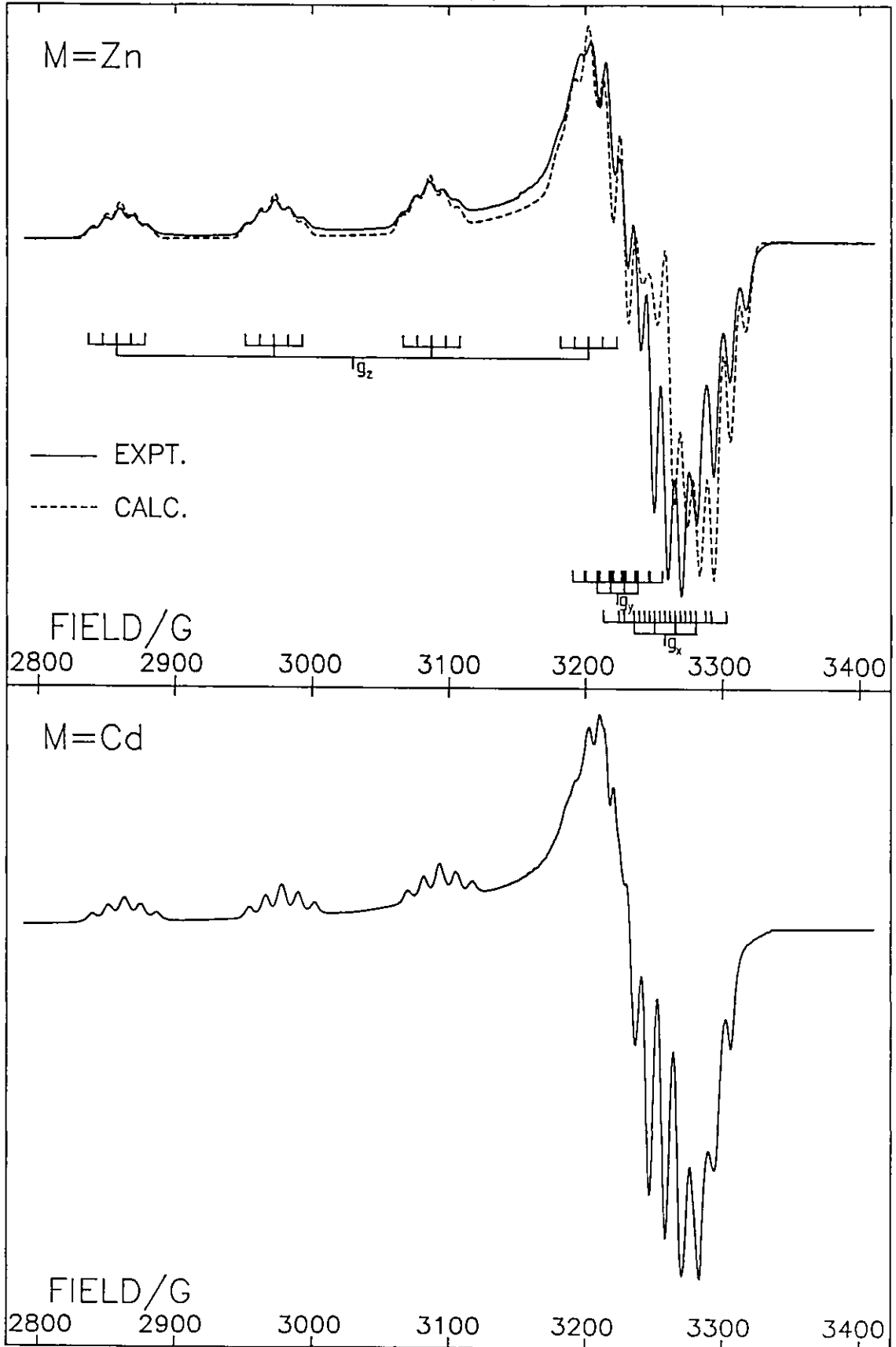
FIG. 5.11

EPR OF $^{63}Cu(II)$ DOPED $Zn(II)((CH_2)_n(N-MeMeS)_2)$ AT 100K

n=2

FIELD/G

2800   2900   3000   3100   3200   3300   3400

n=3

2× ^1H

3330   3340   3350

FIELD/G

2800   2900   3000   3100   3200   3300   3400
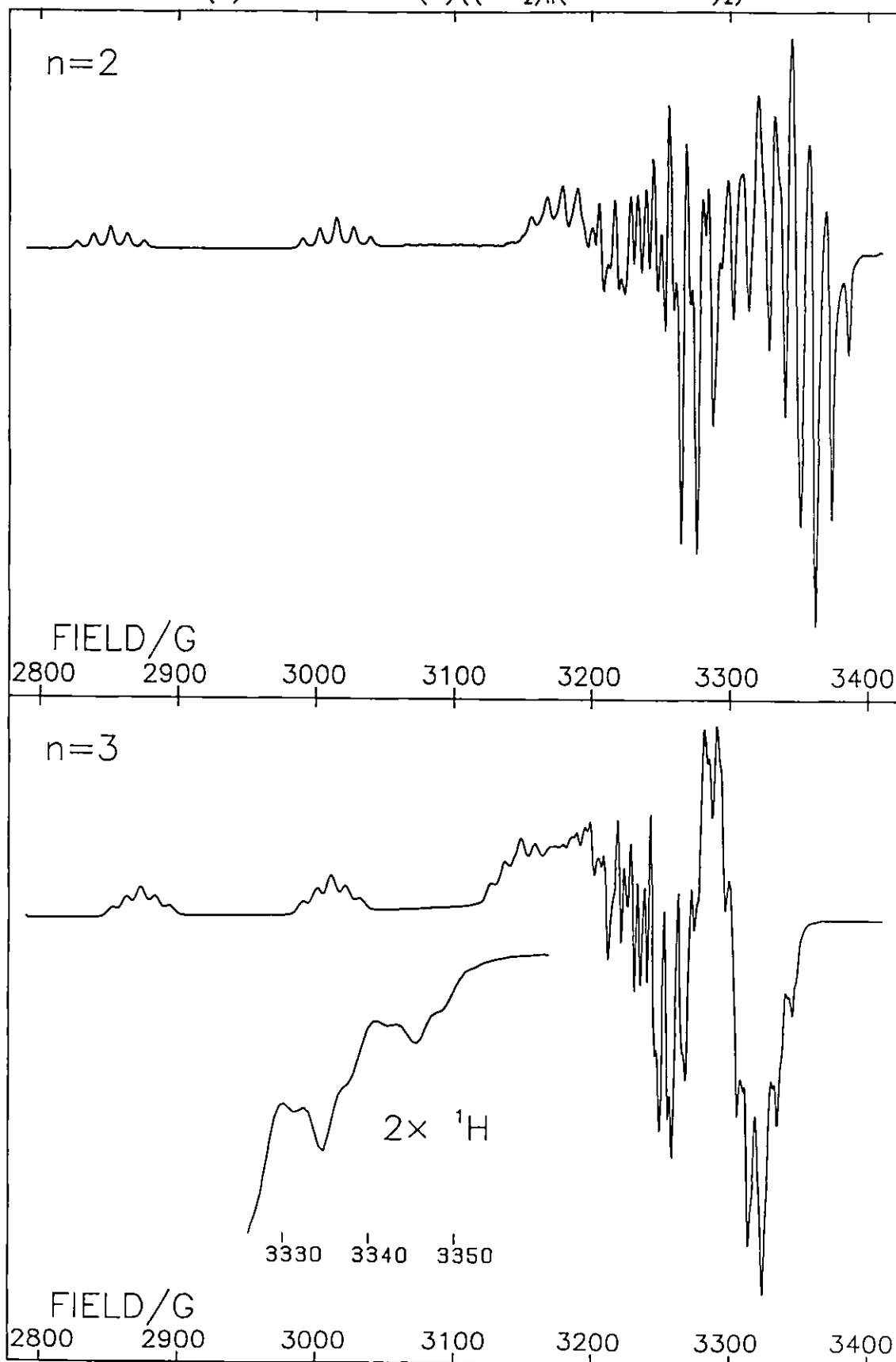
FIG. 5.12

EPR OF ^{63}Cu(II) DOPED Ni(II)((CH$_2$)$_2$(N−MeMeS)$_2$) AT 100K

X−BAND   9.23 GHz
——— EXPT.   -------- CALC.

FIELD/G
2800   2900   3000   3100   3200   3300   3400

Q−BAND   36.0 GHz
——— EXPT.   ------- CALC.

FIELD/G
11900 12000 12100 12200 12300 12400 12500 12600 12700 12800
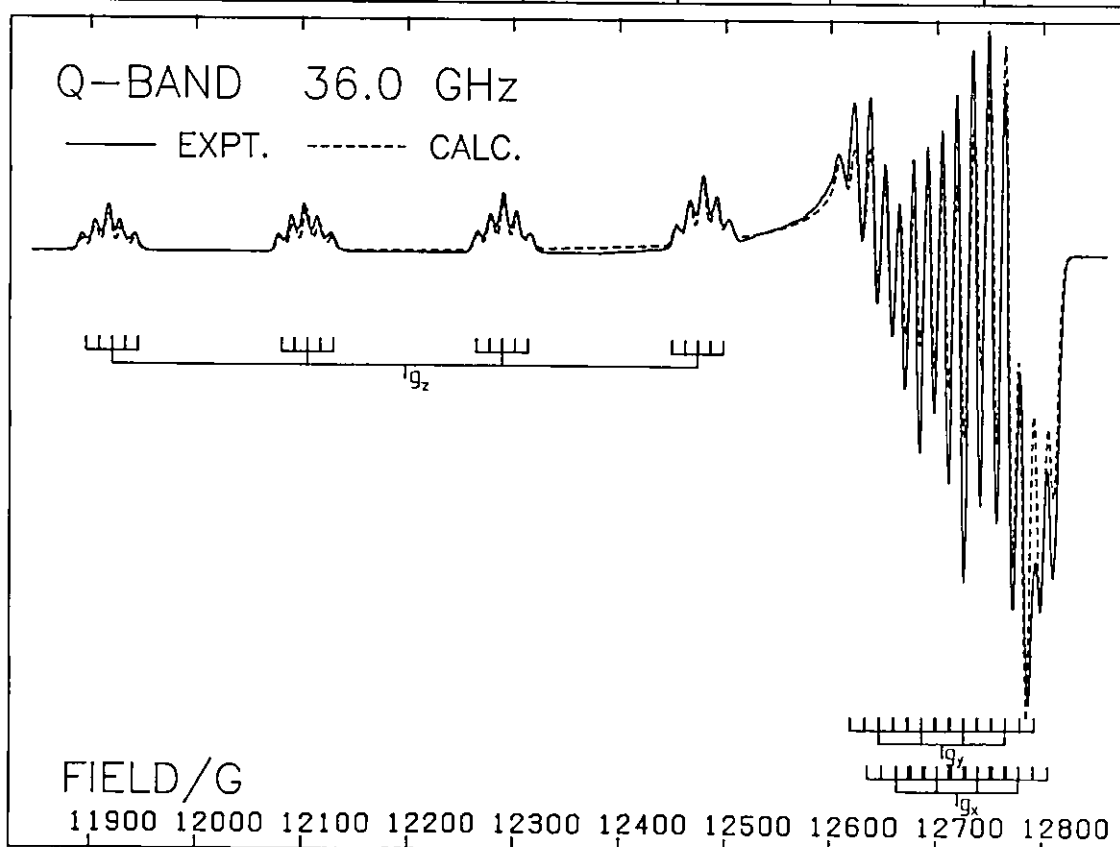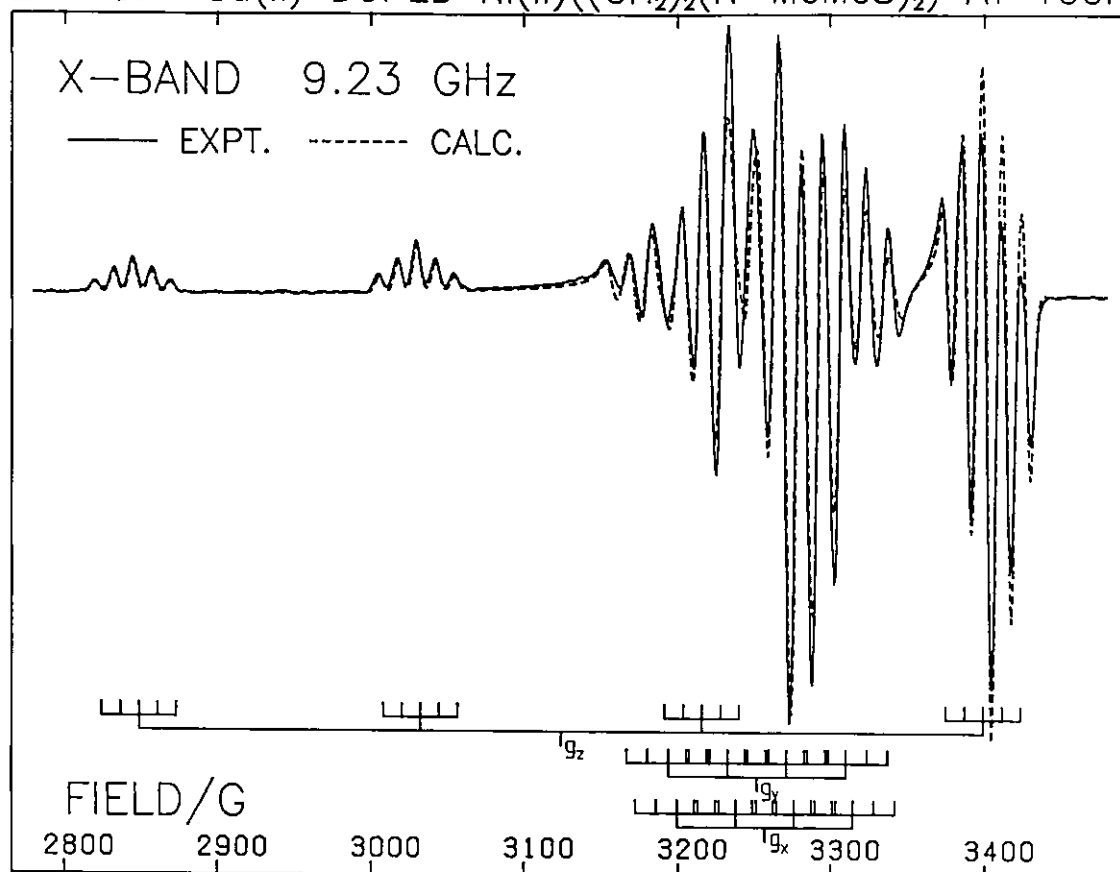
FIG. 5.13
EPR OF Cu(II) DOPED Ni(II)(RN—MeMeS)$_2$ AT 100K

R=C$_{18}$H$_{37}$

FIELD/G

2800 2900 3000 3100 3200 3300 3400

R=pClPh ^{63}Cu

2970   3000   3030

FIELD/G

2800 2900 3000 3100 3200 3300 3400
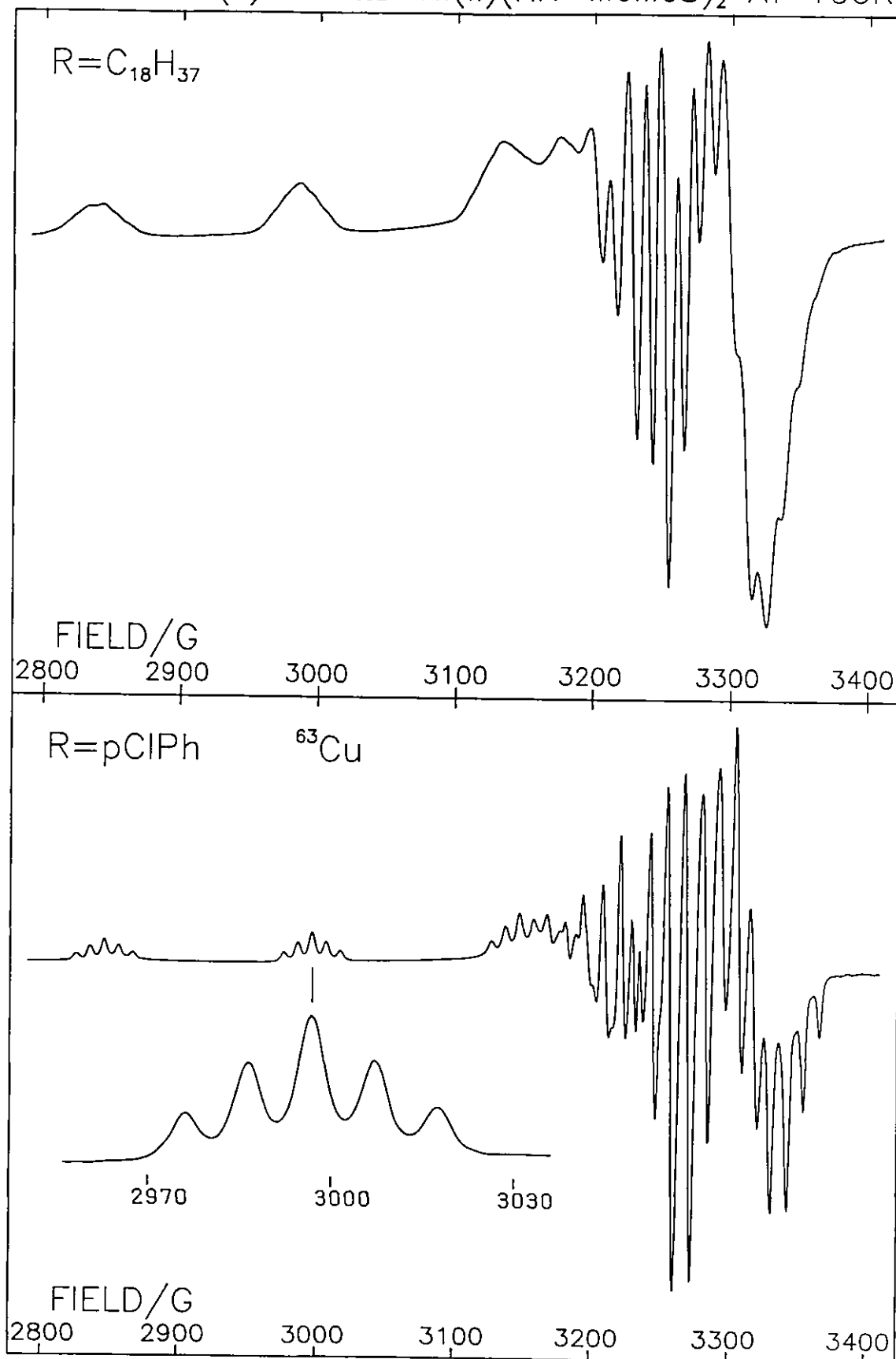
TABLE 5.10. EPR parameters used in simulating spectra of [63]Cu(II) doped M(II)(RN-MeMeS)$_2$ (M = Zn, Ni)

| | M=Zn; R- | | | M=Ni; 2R=-(CH$_2$)$_2$- | |
	Me	pMeOPh	cHx	X-band	Q-band
g_x	2.024	2.014	2.017	2.024	2.024
g_y	2.046	2.045	2.043	2.027	2.026
g_z	2.176	2.153	2.196	2.111	2.111
$-A_x$	15	15	20	38.4	38.4
$-A_y$	10	17.8	7	38.8	39.5
$-A_z$	115	123.6	97	183.5	184.5
^NA_x	11.2	10	8	13.6	13.6
^NA_y	9	8.2	5	13.6	13.6
^NA_z	10.4	9.1	8.8	12.2	12.2
W_x	3.9	3.0	4.5*	4.5	5.0
W_y	3.9	2.5	7.0*	4.0	4.5
W_z	4.4	3.0	6.4*	3.0	4.0
W-anisotropy	L	L	L	DC	DC
Frequency/GHz	9.228	9.225	9.229	9.228	36.03
Figure	5.10	5.9	5.8	5.12	5.12

See footnotes to Table 5.6

*Lorentzian widths W_x = 5, W_y = 8, W_z = 7 Gauss.

FIG 5.14 $A_\parallel$ vs $g_\parallel$ PLOT FOR EPR OF Cu(II) DOPED M(II)(RN–MeMeS)$_2$ (M=Zn,Ni,Cd)

$-A_\parallel$
$\times 10^4$
(cm^{-1})

	Zn	Ni	Cd
R	■	●	▲
Aryl	□	○	△
(CH$_2$)$_n$	□	○	△

Frozen–solution region

□ ~ERROR

$g_\parallel$
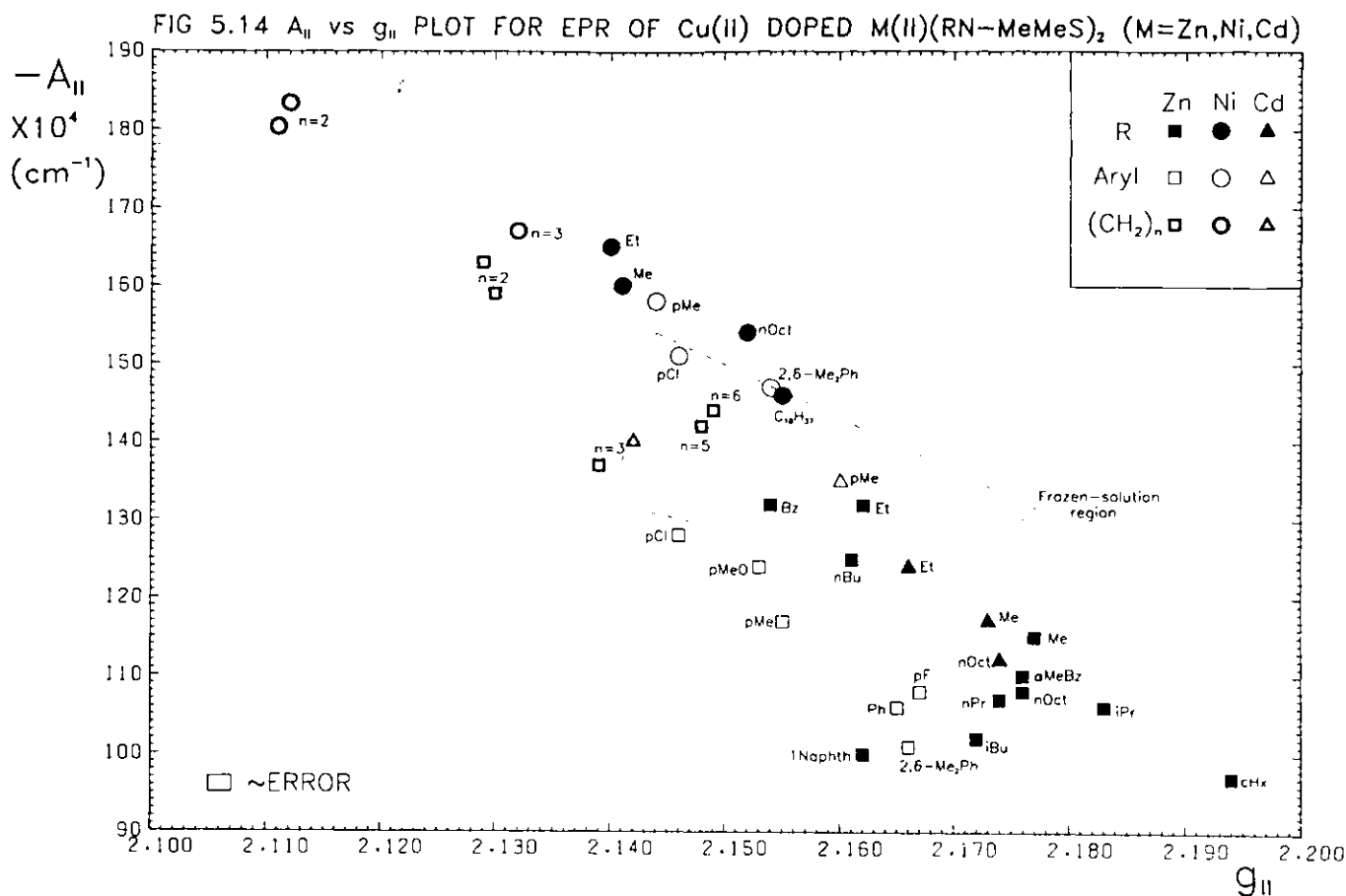
$|A_{\parallel}|$ values for the doped complexes are plotted against $g_{\parallel}$ in

Figure 5.14. The $|A_{\parallel}|$, $g_{\parallel}$ region for the solution parameters is also

outlined. An approximate halving of $|A_{\parallel}|$ is apparent on going from the

Cu(II) doped Ni[(CH$_2$)$_2$(N–MeMeS)$_2$] extreme to Cu(II) doped Zn(cHxN–MeMeS)$_2$,

and complexes with intermediate $|A_{\parallel}|$ values lie close to a line connecting

these two complexes on the $|A_{\parallel}|$ vs $g_{\parallel}$ plot, albeit with a fair scatter.

Other lines, connecting corresponding Ni(II)–Zn(II) and Ni(II)–Cd(II)

Cu(II) doped complexes of a given specific ligand, in many cases closely

parallel this trend, e.g., for R = Me, Et, nOct, $-(CH_2)_2-$ and $-(CH_2)_3-$.

A steeper $|A_{\parallel}|$ vs $g_{\parallel}$ slope is found on going from Ni(II) to Zn(II) host

when R = aryl, most notably for R = pCℓPh where there is a 23×10^{-4} cm^{-1}

decrease in $|A_{\parallel}|$ but no change in g-value.

FIG 5.15 $A_{\parallel}$ vs $g_{\parallel}$ PLOT FOR EPR OF Cu(II) 2N2S COMPLEXES AND BLUE-COPPER-PROTEINS
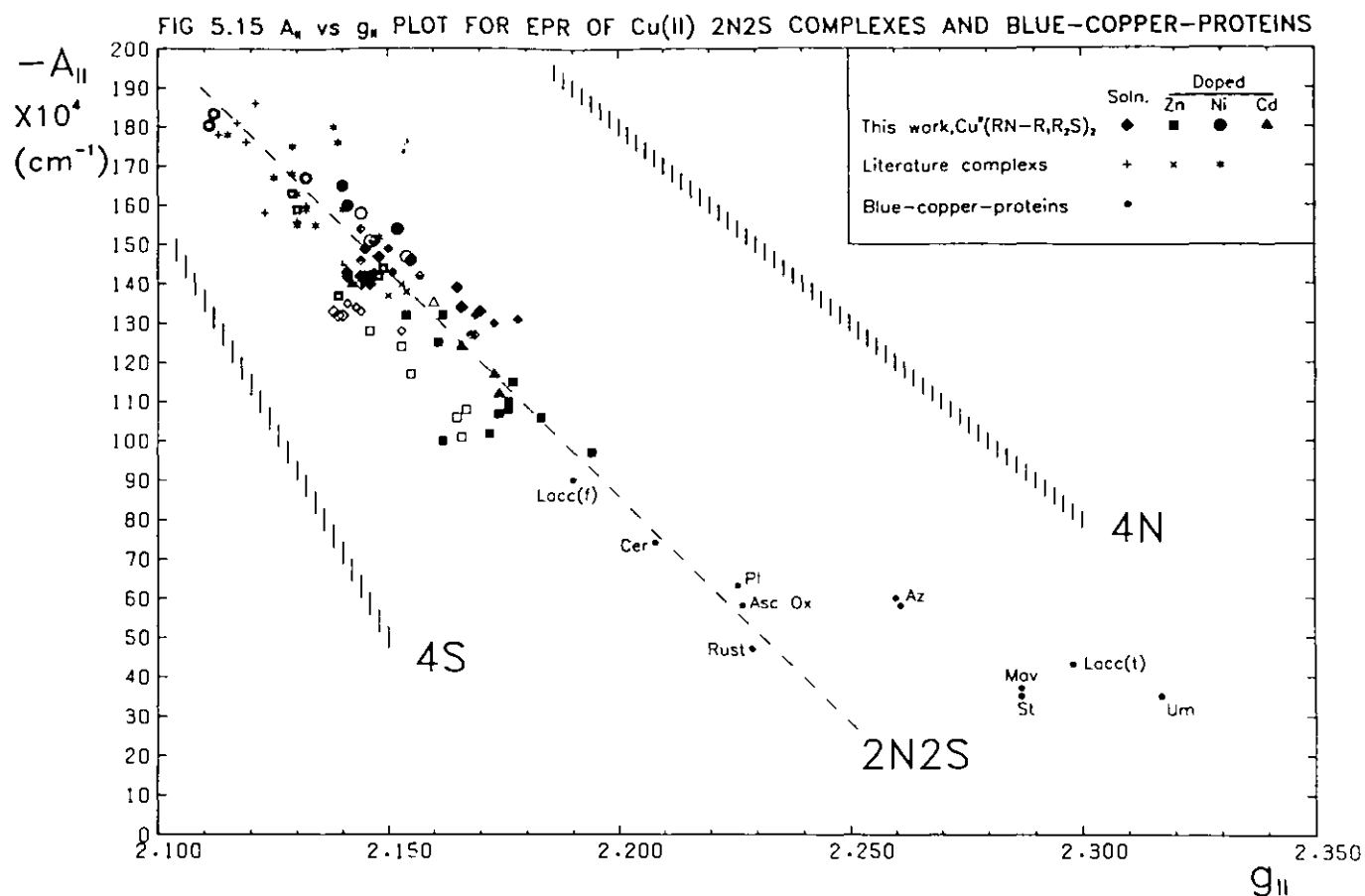
5.4.3. Discussion of EPR parameters.
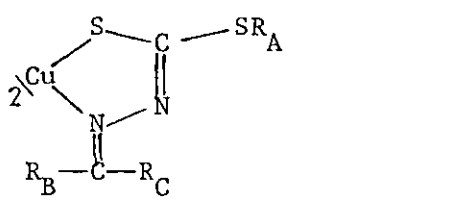
The plotting of $|A_{\parallel}|$ vs $g_{\parallel}$ is extended in Figure 5.15 to include all the compounds previously tabulated (Tables 5.5, 5.7-5.9), other 2N2S complexes in solution or doped into Zn(II) or Ni(II) hosts (Table 5.11) and type 1 blue-copper-protein centres (Table 5.12), together with the previously established relationships between the two parameters for 4N and 4S coordination.[289,295,296,339]

Qualitative descriptions of trends on the $|A_{\parallel}|$ vs $g_{\parallel}$ plots have been compiled by Sakaguchi and Addison.[295]

(1) Tetrahedral distortion from square-planar causes the $(g_{\parallel}, A_{\parallel})$ point for a CuX_4 coordination centre to be shifted down and to the right.

(2) Replacement of 'hard' or class-a donor atoms by 'soft' or class-b donors tends to shift a CuX_4 centre of given geometry down and to the left.

TABLE 5.11. $g_{\parallel}$ and $|A_{\parallel}|$ parameters for previously reported 2N2S copper(II)

complexes.

Complex	Solvent or host	ref.	$g_{\parallel}$	$\mid A_{\parallel} \mid /cm^{-1} \times 10^{-4}$
Cu[(CH$_2$)$_2$-(N-MeMeS)$_2$]			2.118	177
Cu[(CH(CH$_3$).CH$_2$)-(N-MeMeS)$_2$]		327	2.119	176
Cu[(CH$_2$)$_3$-(N-MeMeS)$_2$]			2.130	156
Cu[(CH$_2$)$_2$-(N-MePhS)$_2$]			2.113	178
Cu[(CH$_2$)$_3$-(N-MePhS)$_2$]			2.123	158
	50:50 DMF:CH$_2$Cl$_2$			
Structure (S10) n = 2		328	2.117	181
n = 3		329	2.132	160
n = 4			2.140	145
Structure (S6) n = 2	2:3 CHCl$_3$:DMF	333	2.121	186
Cu(II)bis-(5-ethyl-2-mercapto-3-thenylidene)ethylenediamine	Ni(II)	331	2.115	178

R$_A$	R$_B$	R$_C$				
Me	2-Naphthyl	Me	Ni(II)		2.130	163
Me	mNO$_2$Ph	Me	Ni(II)		2.129	168
Me	Ph	Me	Ni(II)		2.132	159
Me	p-tolyl	Me	Ni(II)	344	2.134	155
Me	pNO$_2$Ph	Me	Ni(II)		2.130	155
Me	Ph	H	Ni(II)		2.138	180
Me	H	o-tolyl	Ni(II)		2.129	175
Me	H	m-tolyl	Ni(II)	345	2.139	176
Me	H	o-ClPh	Ni(II)		2.125	167

TABLE 5.11 (continued).

Complex			Solvent or host	ref.	$g_\parallel$	$\|A_\parallel\|/cm^{-1} \times 10^{-4}$
R_A	R_B	R_C				
Bz	Me	Ph	Ni(II)	⎫	2.148	152
Bz	Me	p-tolyl	Ni(II)	⎪	2.140	143
Bz	Me	2-naphthyl	Ni(II)	⎬ 345	2.140	159
Me	H	o-tolyl	Zn(II)	⎪	2.150	137
Me	Me	p-tolyl	Zn(II)	⎪	2.153	140
Me	Me	Ph	Zn(II)	⎭	2.154	138

TABLE 5.12   EPR parameters for blue-copper-proteins.

Protein	ref.	$g_\parallel$	$\|A_\parallel\|/cm^{-1} \times 10^{-4}$	$g_\perp$	$\|A_\perp\|/cm^{-1} \times 10^{-4}$
Azurin (Az) Ps.fluorescens	346	2.261	58	2.052	∼ 0
Ps.aeruginosa	"	2.260	60	2.052	∼ 0
Stellacyanin (St) R.vernicifera	347	2.287	35	x 2.025	x 57
				y 2.077	y 29
Plastocyanin (Pl)	348				
Chenopodium album		2.226	63	2.023	<20
Umecyanin (Um)	349	2.317	35	2.05	
Armoracia lapathifolia					
Mavicyanin (Mv)	350	2.287	37	x 2.025	x 54
Cucurbita pepo medullosa				y 2.077	y 28
Rusticyanin (Rust)	351	2.229	47	x 2.019	x 61
Thiobacillus ferro-oxidans				y 2.064	y 19
Laccase [Lacc(t)] R.vernicifera	347	2.298	43	2.047	17
[Lacc(f)] P.versicolor	352	2.190	90	2.042	10
Ceruloplasmin (Cer) Human	353	2.208	74	2.050	
Ascorbate oxidase (Asc.ox)	⎡354	2.27	58	x 2.036	x 5
Curcurbita pepo medullosa	⎣355			y 2.058	y 5

(3) Increasing nett charge on the CuX_4 moiety, increasing ligand electron donation or increasing electron delocalisation tends to decrease $g_{||}$ and increase $|A_{||}|$.

No ready general confirmation of the expected electronic effects (point 3) of substituents is forthcoming from the results on the present complexes.

Point 2 is illustrated by the intermediate position of the $g_{||}$, $|A_{||}|$ region containing the 2N2S complexes with respect to the regions established for complexes having 4N and 4S coordination. The shift to smaller g-values on going to 'softer' donor-atoms is indicative of increased delocalisation of the unpaired spin-density away from the copper nucleus, interpreted as increased covalency in the metal-ligand bonds.

The increase in $g_{||}$ and decrease in $|A_{||}|$ with increasing distortion from square-planar toward tetrahedral coordination (point 1 above) has already been described for the complexes, but is now more clearly seen in Figure 5.15. Although no direct, for example crystallographic, evidence can be presented to indicate the relative degree of tetrahedral distortion in any of the β-aminothione complexes, the trends in $g_{||}$, $|A_{||}|$ do follow those expected from considering the stereochemical distortions anticipated from the steric bulk of substituents and/or structural imposition by host lattice, and have ample precedent in comparable series of complexes. Thus to reiterate, complexes having α-branched amino-substituents giving steric hinderance[289,340,292,291,341] and/or Zn host lattices[342,344,345] are expected more closely to approach tetrahedral coordination stereochemistries than those having α-unbranched substituents and/or Ni hosts, and the ($g_{||}$, $|A_{||}|$) points for the former appear, in general, down and to the right of those for the latter.

X-ray crystallographic structure determinations for $Zn(II)[(CH_2)_n$-$(N-MeMeS)_2]$, n = 2, and 4 demonstrate the adoption of a pseudo-tetrahedral Zn coordination geometry,[356,357] whilst for $Ni(II)[(CH_2)_2$-$(N-MeMeS)_2]$ the expected square-planar geometry has been spectroscopically confirmed.[326] All of the nickel complexes used as hosts are considered to be predominantly planar in solution by comparison with similar compounds,[322] although as mentioned in Sec. 5.3.3 the presence of near-IR absorption for the R = aryl complexes is indicative of some tetrahedral form also, Table 5.4. Reflectance spectra of the solids did not show near-IR features, and were not helpful in determining the crystalline stereochemistry. Reflectance measurements were also made on several of the more intensely coloured Cu(II) doped $Zn(RN-MeMeS)_2$ complexes in an attempt to correlate electronic and EPR parameters, but no correlation of the band maxima with $|A_{||}|$ or $g_{||}$ was apparent.

Solution visible and polarographic results presented in other parts of this section indicate more tetrahedrally distorted coordination geometry in the bidentate β-aminothione Cu(II) complexes than in related complexes (see Table 5.11) having quadridentate 2N2S ligands, and this is borne out in their relative positions in Figure 5.15. A similar spectroscopic and polarographic distinction between members of the dissolved bidentate β-aminothione Cu(II) complex series concerning α-branching of the amino substituent has already been pointed out in Sec. 5.4.1.2.

From the orbital magnetic contribution of $g_{||}$ to $|A_{||}|$ a direct antiparallel relationship is anticipated between these two parameters, and such an explanation has been invoked to interpret the behaviour of certain series of copper(II) complexes.[243,342] The trends in $g_{||}$ and $|A_{||}|$ on passing from square-planar to tetrahedral stereochemistry may thus be qualitatively understood in similar terms; the energy separation of the electronic levels decreasing and leading to increasing g-values.

Indeed, evaluation of the orbital coupling contribution to $\underline{A}$, by

diagonalisation of the spin-orbit coupling perturbation matrix (all

order perturbation), has been considered by Bertini, et al.[358] entirely

sufficient to account for the copper-hyperfine and $\underline{g}$-tensor parameters

when the distortion from square-planar is not too severe. For distortions

of large extent the admixture of 4p and 4s orbital character into the

ground state, permitted by loss of a coordination sphere inversion centre,

becomes increasingly important. The expressions for the EPR $\underline{g}$ and $\underline{A}$

tensor parameters as obtained from 2nd order perturbation theory, after

considering linear combinations of copper 3d, 4s and 4p orbitals and

ligand orbitals pertinent to D_{2d} symmetry, are too complex to allow any

analysis in terms of a simple direct relationship between $|A_{||}|$ and $g_{||}$

for the present series of complexes.[287-289,359,360] Decrease in $|A_{||}|$

due to 3d-4p and 3d-4s orbital mixing was first suggested by Bates[287] to

account for the very small $\underline{A}$ values found for the cupric complex of

$(\alpha,\alpha'\text{-bromo})$dipyrromethane. Mixing of 4p and 4s character into the ground-

state is favourable where there is a tetrahedral distortion from square-

planar since it leads to a lowering of energy. The spin distribution in

the admixed orbital produces a magnetic field at the nucleus which is

opposite in direction to that from the d_{xy} orbital and the resultant

reduced field leads to a small hyperfine splitting. Sharnoff[359] suggested

that the unpaired electron in the tetrachlorocuprate anion spends 12% of

its time in a 4p(Cu) orbital, in order to explain the low value of

25×10^{-4} cm^{-1} found for $|A_{||}|$. A 19% 4p contribution to the ground

state in azurins was proposed by Brill and Bryce[288] to account for the

unusual characteristics of both EPR and electronic spectra. However,

although the reduction of $|A_{||}|$ by 3d-4p and 3d-4s orbital mixing has

become well established in interpreting EPR parameters from tetrahedrally

distorted copper complexes,[291,298,340,361,362] the validity of invoking

large mixing coefficients is not without dispute. On the basis of

the wide variation of $|A_{\parallel}|$ observed in cupric complexes having similar

pseudo-tetrahedral structures, Bencini et al.[363] have proposed that the

$|A_{\parallel}|$ values for $CuCl_4^{2-}$ and type 1 copper-proteins are essentially due to

covalency of copper-ligand interactions and large spin-orbit coupling of

the ligand donor-atoms. Similarly, the unexpectedly high $|A_{\parallel}|$ values

of Cu(II) N,N'-diaryl-β-iminoamines (considering their expected degree

of tetrahedral distortion from square-planar) has been cited as indicating

that 3d-4p mixing may not be so dominant a factor in decreasing $|A_{\parallel}|$ for

pseudo-tetrahedral copper(II).[293] It is difficult, however, to accept

the view of Bencini et al.[363] that covalency is important in reducing $|A_{\parallel}|$

since in Cu(TPP), for example, the unpaired electron wave-function has a

high proportion of ligand character but the copper hyperfine splitting is

large and anisotropic.[364] and refs. therein

For the present series of complexes $|A_{\parallel}|$ falls too low to be accounted

for purely by coupling of the orbital momentum with the nuclear spin and

thus some additional contribution to the hyperfine splitting must be

present. Drastic changes in covalency of the metal-ligand interactions

are neither manifested in trends in the superhyperfine ^{14}N splittings nor

anticipated in view of the constant 2N2S coordination, and the mechanism

for reduction of $|A_{\parallel}|$ proposed by Bencini, et al.[363] is rejected. The

lowering of $|A_{\parallel}|$ by 4p and 4S mixing into the ground level, which has

increasing effectiveness as the coordination geometry distorts more toward

tetrahedral, is considered, together with the orbital contribution to $|A_{\parallel}|$,

to be a correct interpretation of the behaviour of the present compounds

as depicted in Figure 5.15.

The $(g_{\parallel}, |A_{\parallel}|)$ points for many of the type 1 copper proteins are found in a region which is an extension to the trend of decreasing $|A_{\parallel}|$ with increasing $g_{\parallel}$ for the 2N2S model complexes. Distorted tetrahedral 2N2S coordination sites have been crystallographically established for plastocyanin[280] and azurin[281] and seem reasonable assumptions for fungal laccase, ceruloplasmin, ascorbate oxidase and rusticyanin on the basis of the results in Figure 5.15. This coordination may also be appropriate to tree laccase, stellacyanin, umcyanin and mavicyanin since although the $(g_{\parallel}, |A_{\parallel}|)$ points for these appear at some distance from the 2N2S delineator constructed in Figure 5.15, the present results give no real indication of the behaviour of the $g_{\parallel}$ vs. $|A_{\parallel}|$ relationship at such remote values.

A large tetrahedral distortion in the copper centres of all type 1 proteins is believed to be a necessary, and probably sufficient, condition to explain their unusual copper $\underline{A}$-tensors. The z-axis EPR parameters for Cu(II) doped Zn(II)(cHxN-MeMeS)$_2$ represent the closest approach to date by a 2N2S coordinated complex to those for the type 1 proteins and are quite comparable to the values observed for fungal laccase (Table 5.12).

5.5. Vibrational Spectra.

5.5.1. Raman and IR spectra for Cu(RN-MeMeS)₂ (R = Me, iBu).

The thermal instability of the cupric complexes, together with their intense absorption in the visible presents some considerable difficulty to the measurement of Raman spectra. Using the technique of spinning samples at low temperature, described in Appendix B, spectra of reasonable quality have been obtained for the most stable solids, $Cu(II)(MeN-MeMeS)_2$ and $Cu(II)(iBuN-MeMeS)_2$. Band positions and relative intensities at several excitation wavelengths are reported in Tables 5.13 and 5.14 and Figure 5.16 shows some representative spectra obtained for solid

TABLE 5.13. Raman spectral parameters for $Cu(II)(MeN-MeMeS)_2$ at $-140^{\circ}C$ (KBr disc).

Band maxima (cm⁻¹) and intensities vs. excitation (nm)								Ligand	
647.1		568.2		530.2		482.5			
						97	2	77	8
108	w	108	~7					112	4
		124	2					185	10
151	4	149	3	150	3	151	2	298	br,w
		167	1	166	vw			334	br,w
191	3	193	w	185	br,w	191	1	372	br,w
242	9	241	9	242	2	242	5	471	5
294	4	291	4	293	2	293	1	630	2
317	10	315	3	317	1	318	2	715	2
365	2	260	w					844	w
380	2	376	10	376	10	376	10	1023	w
395	1							1035	w
440	w							1069	w
486	4	485	3						
500	2	495	w						
		566	3						
598	4	598	w						

Other w-m bands observed on 647.1 nm at 665, 704, 802, 840, 864, 986, 1022 and 1060 cm⁻¹.

$Cu(II)(MeN-MeMeS)_2$ in acetone at $-75^{\circ}C$ 647.1 nm excitation:244(m,ρ0.35), 320 (m,ρ0.25),~190(w),~151(w). 482.5 nm excitation:~250(w),~380 (w)

TABLE 5.14. Raman Spectral Parameters for Cu(II)(iBu-MeMeS)$_2$ at -140°C

(KBr disc).

Band maxima (cm^{-1}) and intensities vs. excitation (nm)								Ligand	
647.1		568.2		530.9		482.5			
		107	10	106	1			96	7
		123	3					177	10
154	s	155	10	157	5	155	mw	290	2
		196	1					331	2
221	m	208	6	220	br,1	231	w	389	1
253	m	252	9	255	3	254	w	452	3
		290	4	286	2	286	w	476	1
300	m	300	4	300	2	300	vw	499	3
						340	w	522	1
380	mw	380	2	381	10	381	s	637	2
				476	2			717	2
485	m	485	4	488	1			814	w
514	ms	513	6	513	w			840	w
				550	w			950	w
				602	2			1025	w
				658	2			1073	2

TABLE 5.15. Low frequency IR data for Cu(II)(RN-MeMeS)$_2$ (R = Me, iBu).

MeN-MeMeS		iBuN-MeMeS	
Cu(II) Complex	Ligand	Cu(II) Complex	Ligand
257w		263m	
288w	300w	290m,dl	292m
317w		330w	338m
	335vw	370s,dl	
370m	371br,w		393w
∿ 480sh,vw	472mw	457vw	
498m		478sh,w	477m,dl
	512m	488w	
598mw	597m	512m	510m
	628m	532ms	
663mw		600m	594s
700mw			629ms
	718s	658m	
798s	806s		

Fig. 5.16 Raman spectra of solid
$Cu(II)(MeN-MeMeS)_2$ at $-140°C$
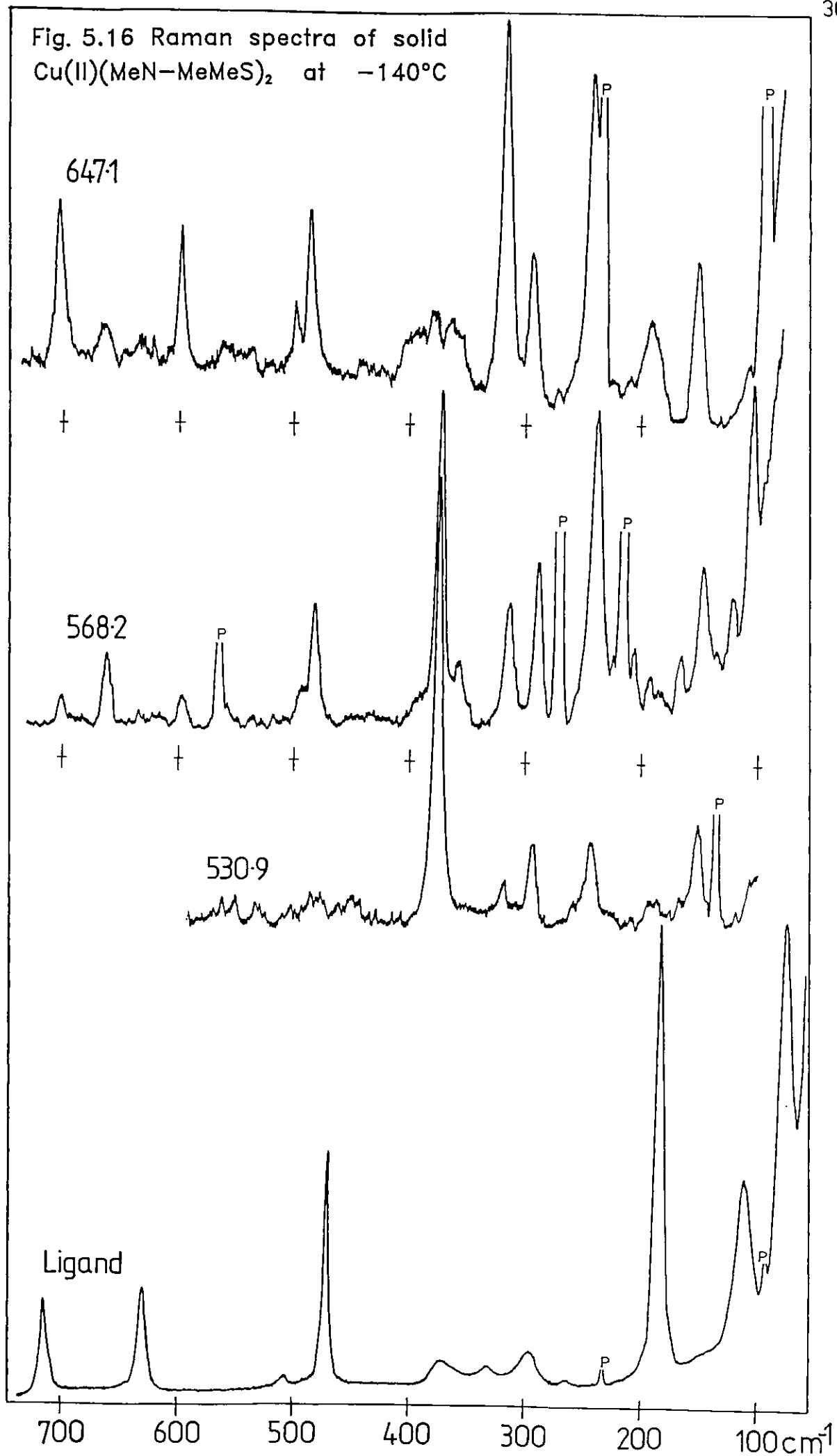
Cu(MeN-MeMeS)$_2$. Measurements have also been made on an acetone solution

of the latter complex and are of sufficient quality to indicate the polar-

isation of two bands which correlate with shifts observed for the solids.

Attempts to obtain spectra for a few of the other less stable complexes

were frustrated by excessive fluorescent emission leading to extremely

poor signal to noise ratio. Low frequency IR spectral details for

Cu(MeN-MeMeS)$_2$ and Cu(iBuN-MeMeS)$_2$ in polythene are given in Table 5.15.

5.5.2. Assignment.

Table 5.16 presents the group-theoretically predicted symmetries and

selection rules for the normal modes of a trans-planar and a tetrahedral

or tetrahedrally-distorted planar CuN_2S_2 vibrational unit. In each case

TABLE 5.16. Symmetries and selection rules for normal modes of CuN_2S_2.

trans-planar, C_{2h}		tetrahedral, C_{2v}	
$2A_g$	ν(R)	$2A_1$	ν(R+IR)
$2A_g$	δ(R)	$2A_1$	δ(R+IR)
$1A_u$	δ(IR)	A_2	δ(R)
$1B_g$	δ(R)	B_1	ν(R+IR)
$2B_u$	ν(IR)	B_1	δ(R+IR)
$1B_u$	δ(IR)	B_2	ν(R+IR)
		B_2	δ(R+IR)

ν - stretch; δ - deformation

R - Raman active;   IR - infrared active

two polarised Raman active stretching frequencies are anticipated. Two bands at 242 cm^{-1} and 317 cm^{-1} in Cu(II)(MeN-MeMeS)$_2$ have polarised solution counterparts at 244 cm^{-1} ($\rho \simeq 0.35$) and 320 cm^{-1} ($\rho \simeq 0.25$), and do not appear in the ligand spectrum. These bands are reasonably assigned as mainly metal-donor-atom stretching in character, probably predominantly ν(Cu-S). The 317 cm^{-1} shift correlates with a weak IR absorption at an identical frequency and from the selection rules of Table 5.16 would tend to suggest, as expected, a departure from square-planar geometry; unless this were to be cis, which is unlikely for steric reasons.

For Cu(II)(iBuN-MeMeS)$_2$ corresponding medium-strong lines are observed in the Raman at 253 cm^{-1} and 300 cm^{-1}. The Raman bands at 376 cm^{-1} in Cu(II)(MeN-MeMeS)$_2$ and 381 cm^{-1} in Cu(II)(iBuN-MeMeS)$_2$, seen most strongly with blue-green excitation wavelengths, have no plausible strong ligand counterparts and are considered also to be metal-ligand vibrations, probably mainly ν(Cu-N). An IR absorption at 370 cm^{-1} seen in both metal complexes may be due to the same mode, though a weaker absorption at a very similar frequency is also seen in the MeN-MeMeS ligand and presents an alternative explanation for the Cu(MeN-MeMeS)$_2$ band.

Barring coincidence, a fourth metal-ligand stretching mode is anticipated and Raman bands at 293, 486 and 500 cm^{-1} in Cu(II)(MeN-MeMeS$_2$) and 286, 485 and 514 cm^{-1} in Cu(II)(iBuN-MeMeS)$_2$ would seem reasonable candidates. Correlatable absorptions at 288, 480, 498 cm^{-1} for Cu(MeN-MeMeS)$_2$ and 290, 488 and 512 cm^{-1} (also additional candidate at 532 cm^{-1}) for Cu(iBuN-MeMeS)$_2$ are seen in the IR. Most have close ligand counterparts in the Raman or IR. The higher frequencies would be expected to involve considerable mixing with ligand modes due to rigidity of the chelate ring conferred by electron delocalisation, and resonance enhancement of Raman

active ligand vibrations is not unexpected. No categorical assignment is attempted here.

Looking to lower frequencies, the Raman shifts of 151 cm^{-1} and 155 cm^{-1} in $Cu(MeN-MeMeS)_2$ and $Cu(iBuN-MeMeS)_2$ respectively are probably primarily CuN_2S_2 deformations of totally symmetric character. The band at 191 cm^{-1} in $Cu(MeN-MeMeS)_2$ is noted to have a very intense ligand counterpart at 185 cm^{-1}

The intense Raman lines at 242, 317 and 376 cm^{-1} in $Cu(MeN-MeMeS)_2$ are matched by similar intense features at 259, 317 and 384 cm^{-1} in $Ni(MeN-MeMeS)_2$.

Metal sulphur stretches have been assigned by normal-coordinate analysis to around 290 cm^{-1} and 380 cm^{-1} in metal dithioacetylacetonates[365] but to around 250 cm^{-1} and 190 cm^{-1} in metal monothioacetylacetonates.[366]

5.5.3. Raman assignments in blue-copper-proteins.

Several papers have been published reporting or discussing Raman spectra of blue-copper-proteins.[237-239,367-371] Table 5.17 summarises the main bands which have been observed at low frequencies. The bands have been categorised as $\nu[Cu-S(Cys)]$, $\nu[Cu-S(Met)]$ or $\nu(Cu-N)$ according to the general concensus in the literature, and in light of the available X-ray structural information for plastocyanin and azurin. The division of the observed protein bands into these categories must, however, be regarded as tentative. Originally, the weak line ~ 260 cm^{-1} was considered to be primarily $\nu[Cu-S(cys)]$ but the $\nu[Cu-S(Met)]$ assignment seems now to be generally preferred in view of Raman studies on cupric thioether complexes[369] and on anion binding in ceruloplasmin.[368] $\nu[Cu-S(thiolate)]$ bands have been assigned at 375 and 427 cm^{-1} in the cis-planar copper D-penicillamine

TABLE 5.17. Raman spectral data for blue-copper-proteins.

Protein	Assigned Stretching Vibration				
	Cu-S(Met)		mainly Cu-S(Cys)		mainly Cu-N(His)
Azurin[239]	262w		372		407,425
Azurin[237]	260w		374		412,422,462w
Plastocyanin[237]	265w		382		415,434
Plastocyanin[238]	262w		379		407,426
Ceruloplasmin[238]	250w	325w	350w,375		400,450w
Ceruloplasmin[237]	280w		355w,375w		395,425
Ceruloplasmin Ia[368]	270w	340w	380		415
Ceruloplasmin Ib[368]	270w,		360,		402,415
Tree laccase[238]	259w	331w	360w,383,		408,419,485w
Ascorbate oxidase[238]	260w		350w,383		$\overline{407,417,429}$,488w
Stellacyanin[238]	267w		350,388		410w,424w,444w

2N2S complex.[372] In $Cu[HB(3,5-dimethyl-1-pyrazolyl)_3](pNO_2C_6H_4S)$, however, a polarised band at 276 cm^{-1} has been reasonably assigned as $\nu(Cu-S)$[299] and would tend to support a $\nu[Cu-S(Cys)]$ assignment for the $\underline{ca}$. 260 cm^{-1} shift in the proteins.

Solomon $\underline{et\ al.}$[259] have estimated from the shape of the 606 nm electronic absorption band in plastocyanin that a vibrational mode of frequency 240 $\pm$ 60 cm^{-1} is coupled to the $S(\sigma) \rightarrow Cu(II)$ CT transition. Similarly, for the 617 nm absorption in stellacyanin a frequency of 290 $\pm$ 80 cm^{-1} is calculated. However, the shape of the 631 nm band in azurin indicates a vibronically coupled mode of frequency 390 $\pm$ 150 cm^{-1}.

As an elongation of the Cu-S bond is expected to be the dominant distortion

in the $S(\sigma) \rightarrow Cu(d_{x^2-y^2})$ excited state, the coupled vibrational

frequencies should provide rough estimates of the Cu-S stretching

frequencies in the proteins.

The observation of bands at 242 cm^{-1} in Cu(II)(MeN-MeMeS)$_2$ and

253 cm^{-1} in Cu(II)(iBuN-MeMeS)$_2$ assigned to predominantly ν(Cu-S), demon-

strates that copper-sulphur stretching vibrations other than those for

copper-thioether bonds may reasonably be expected at such low frequency.

It must be recognised, however, that the β-aminothione cupric complexes

may have rather different CuN$_2$S$_2$ vibrational properties from the blue-

copper-proteins, in that they are expected to possess a more rigid

chelating ring structure. The 242 and 253 cm^{-1} bands of the Cu(II)-

(RN-MeMeS)$_2$ (R = Me, iBu) complexes feature amongst the most intense

lines in their respective Raman spectra, and it is the weakness of the

scattering ca. 260 cm^{-1} in the proteins, compared with that at higher

frequencies, which most militates against assignment as ν[Cu-S(Cys)],

since this mode should be most strongly coupled to the $S(\sigma) \rightarrow Cu(II)$ CT

band within which the Raman excitation wavelength lies.

The high intensity of the bands assigned as predominantly ν(Cu-N)

in the proteins, compared with the intensity of bands considered to be

mainly ν[Cu-S(Cys)], is surprising. Attempts have been made to rationalise

this observation in terms of metal-ligand orbital-overlap criteria.[237,238]

For Cu(MeN-MeMeS)$_2$ the Raman lines considered to be mainly ν(Cu-S) are

only the most intense features in the spectrum when exciting with light

of wavelength 647.1 nm. At shorter wavelengths, the 376 cm^{-1} feature,

thought to be mainly ν(Cu-N), becomes most intense. ν(Cu-N) modes, together with certain ligand modes, are expected to be resonance enhanced to some degree, when exciting within the S(σ) $\rightarrow$ Cu(II) CT absorption contour, due to extensive mixing with the ν(Cu-S) vibration. However, unless, for example, the electronic absorption with maximum around 480 nm were considered to be N(σ) $\rightarrow$ Cu(II) in origin, which seems unlikely, the relative intensities of the Raman bands is, as in the proteins, difficult to understand completely.

5.6. Electrochemistry.

Initial investigative measurements have been made on the electro-
chemical properties of a few of the cupric β-aminothione complexes in DMF
solution. Reduction processes have been studied at low temperature using
a rapid-dropping-mercury-electrode (RDME), a hanging-mercury-drop-electrode
(HMDE) and at stationary and rotating platinum electrodes; all referenced
to an aqueous SCE via a double electrolyte junction. Table 5.18 summarises
electrochemical data for $Cu(II)(RN-MeMeS)_2$ R = Me, Et, nOct, iPr and also
for $Cu(II)[(CH_2)_2(N-MeMeS)_2]$. Figure 5.17 shows cyclic voltammograms for
$Cu(II)(MeN-MeMeS)_2$ at platinum and mercury-drop electrodes.

TABLE 5.18. Electrochemical data for $Cu(II)(RN-MeMeS)_2$ (R = Me, Et, nOct,
iPr and en/2) at ca. $-35^{\circ}C$.

R	$E_{\frac{1}{2}} \pm 0.02$/V	slope[a]/mV	ΔE[b]/mV
Me (Hg)	-0.67		-65
Me (Pt)			-90
Et (Hg)	-0.64	-28	-80
nOct (Hg)	-0.67	-27	-80
iPr	-0.50		
en[c·] (Hg)	-1.09	-29	-60
en[c·] (Pt)			-90

NOTES: a. E vs. $\ln[(i_d-i)/i]$ plot.

b. cathodic peak - anodic peak; 5-10 mV/s scan rate

c. measured at $20^{\circ}C$.

FIG. 5.17
Cyclic voltammograms
of Cu(II)(MeN–MeMeS)$_2$
in DMF

Pt electrode

HMDE
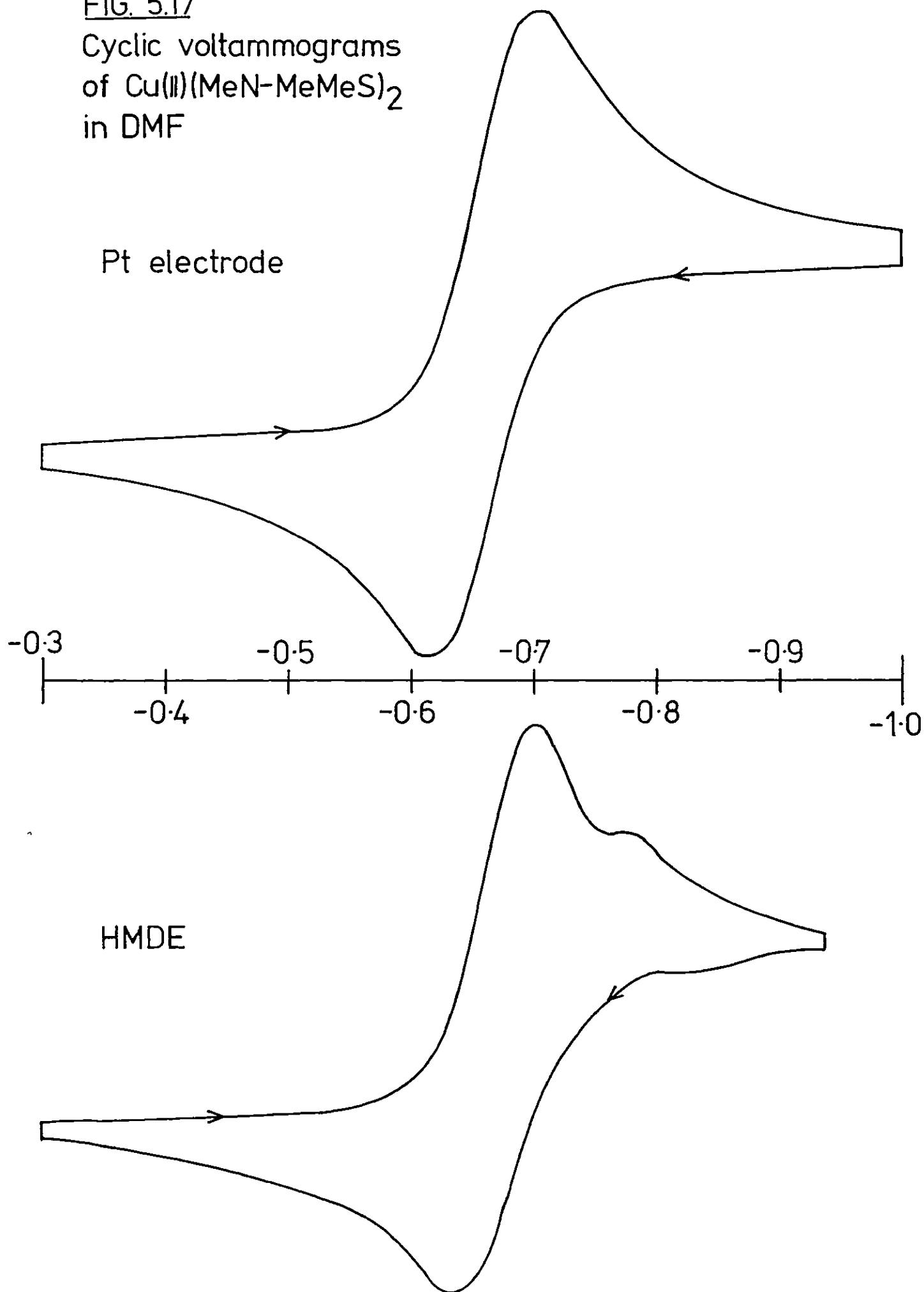
5.6.1. Difficulties in measurements.

Voltammetry of $Cu(MeN-MeMeS)_2$ at platinum is complicated to some degree by electrode kinetics at the scan-rate used, as is demonstrated by the anodic peak to cathodic peak potential separation of 90 mV. At mercury the peak potential separation is 65 mV and closely approaches that expected for reversible one-electron redox processes. Quasi-reversibility of the reduction at platinum was also observed for $Cu(II)[(CH_2)_2(N-MeMeS)_2]$ [see also ref. 373] and further departure from reversible behaviour was found for $Cu(II)(nOctN-MeMeS)_2$, thus the HMDE was favoured for general use. This necessitated the use of a sample-solution temperature in excess of $-40^{\circ}C$ to avoid solidification of the electrode. Decomposition half-lives of the less stable complexes having nOct- and iPr-ligand amino-substituents, are considerably shortened above $-30^{\circ}C$ and so a temperature of ca. $-35^{\circ}C$ was maintained and electrochemical analysis performed within a short time from preparation of the electrolyte solution. Any cuprous decomposition products would be stable under the anaerobic measurement conditions and would not be expected to undergo reduction in the potential range investigated.

An additional problem encountered with the HMDE was the presence of non-Faradaic (adsorption) processes, probably exacerbated by the use of low temperatures. This may be seen in the cyclic voltammograms of $Cu(MeN-MeMeS)_2$, Figure 5.17. A post reduction peak is seen on the cathodic scan. Similar but more intense peaks were observed for the other $Cu(II)(RN-MeMeS)_2$ complexes and are indicative of medium to strong reactant adsorption.[374] Typical of the behaviour of such systems, where the adsorbed layer is of constant amount but the material diffusing to the electrode surface is time- and concentration-dependent, the post-peak increases in intensity, relative to the cathodic peak current, with increasing scan-rate and with dilution. The adsorption effects were thus

minimised by using solutions near saturation in the copper complex and employing low voltage sweep rates of 5-10 mV/s.

In polarographic measurements the adsorption effect manifests itself as a post-wave of constant height (i_a) 100-200 mV more negative than the wave for the diffusing complex (i_d'), such that the total diffusion current $i_d = i_d' + i_a$. Since $i_a \propto h$ (height of mercury column) whilst $i_d' \propto \sqrt{h.c}$ (concentration)[375,376] it proves possible to verify that the second wave is due to adsorption by observing the ratio of $i_a : i_d'$ as h and c are varied. The evidence for adsorption from such measurements was, however, less conclusively convincing than that from the stationary electrode voltammetry, as the estimation of i_d' involved a large degree of uncertainty due to the poor resolution of the two waves.

5.6.2. Analysis of polarographic data.

For Cu(II)(nOctN-MeMeS)$_2$ only a single wave was resolved, Figure 5.18, though the cyclic voltammogram reveals a post peak due to adsorption. Analysis of this polarographic wave in terms of equation E5.1[377] is given in Figure 5.18.

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} \cdot \ln[(i_d - i)/i] \qquad\qquad E\ 5.1$$

Deviation from linearity in the $\ln[(i_d - i)/i]$ vs. E plot cathodic of ca. -0.7 V could be due to adsorption of the Cu(II)(nOctN-MeMeS)$_2$ on the HMDE. The slope of -27 mV approaches the theoretical -26 mV expected for a reversible one-electron redox reaction. A similar analysis for Cu(II)(EtN-MeMeS)$_2$, where there is a reasonably well defined post wave, using i_d' in place of i_d yields a $\ln[(i_d' - i)/i]$ vs. E slope of -28 mV.
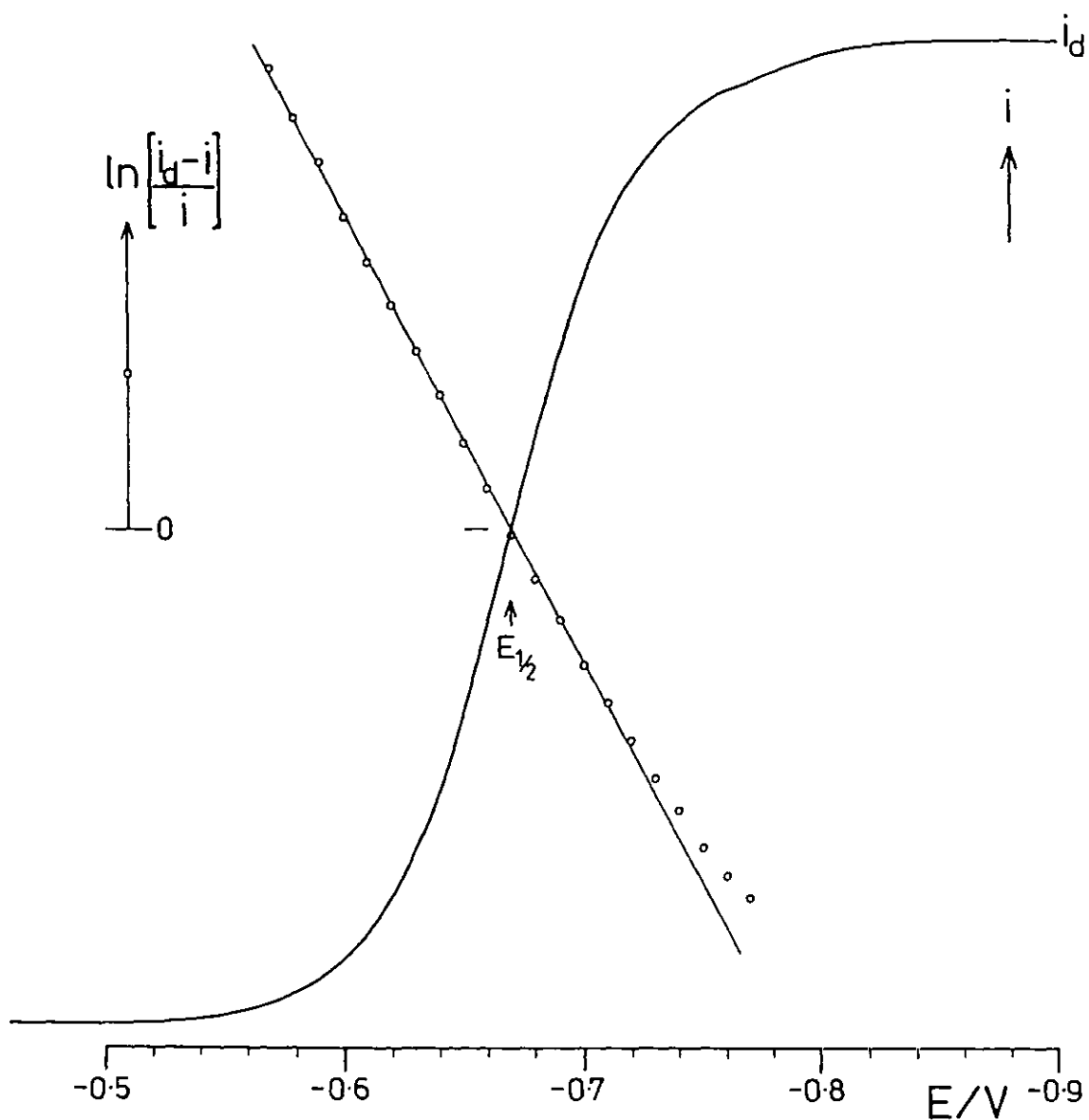
Figure 5.18. Polarogram of Cu(II)(nOctN-MeMeS)$_2$ in DMF at a RDME.

Cyclic voltammetric cathodic-anodic peak potential separations of 80 mV observed for these two complexes, indicate, on the other hand, some departure from reversibility. Thus the coefficient RT/nF in equation E5.18 may be modified by a reduced transfer coefficient.[377]

Several electrochemical studies of the Cu(II)[(CH$_2$)$_2$(N-MeMeS)$_2$] complex have been reported: (electrode, solvent, $E_\frac{1}{2}$/V, ΔE/mV); Pt, MeCN, -1.09, 80[378]; Hg, DMF, -1.07, 68[318]; Pt, DMA, ---, 70[379]; Hg, MeCN,-1.18, 58[373]. A comparable half-wave potential is found in this present work, Table 5.18.

5.6.3. Comparison of $E_{\frac{1}{2}}$ with those of other complexes.

Patterson and Holm[318] in a study of the electrochemical properties of a wide range of Cu(II) coordination environments have made the following general observations:

1. Planar Cu(II) + e⁻ $\rightleftharpoons$ non-planar Cu(I): $E_{\frac{1}{2}}$ = -0.6 to -1.5 V

non-planar Cu(II) + e⁻ $\rightleftharpoons$ non-planar Cu(I): $E_{\frac{1}{2}}$ = -0.46 to -0.88 V
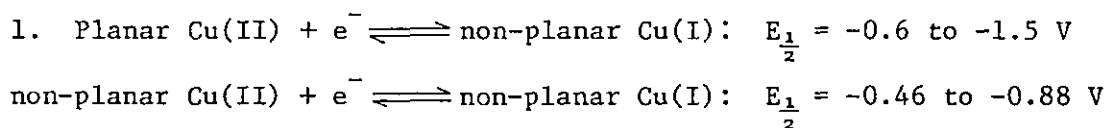
2. Increasing stereochemical distortion from planarity in a series of Cu(II) complexes involving a common ligand type results in progressive raising of $E_{\frac{1}{2}}$; interpreted in terms of destabilisation of the Cu(II) complex, relative to the real or hypothetical sterically unstrained planar geometry, toward the non-planar Cu(I) reduction product. Thus, in the idealised scheme:
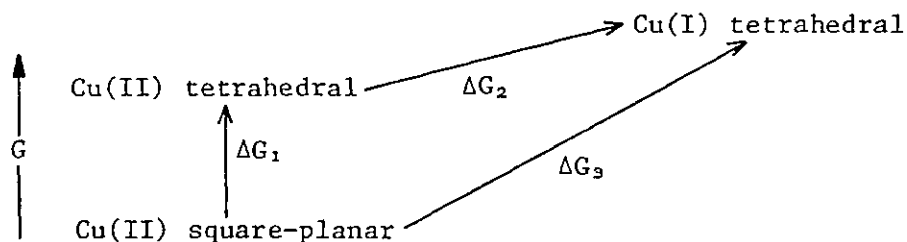
$\Delta G_2 < \Delta G_3$

3. For Cu(II) complexes where only the donor atom portion of the ligand is varied the order of increasing anodic potential is 4N < 2N2O < 2N2S.

4. Increasing electron-releasing tendency in chelate-ring substituents is reflected in cathodic potential shifting of $E_{\frac{1}{2}}$, provided there are no dominating structural changes.

Some of these observations are confirmed for 2N2S coordination in the β-aminothione complexes studied. On going from $Cu(II)[(CH_2)_2(N-MeMeS)_2]$, which must be considered as essentially planar, to $Cu(II)$ $(RN-MeMeS)_2$ (R = Me, Et, nOct) an anodic shift in $E_{\frac{1}{2}}$ of 420 to 450 mV occurs and is interpreted as resulting from a tetrahedral distortion from square-planar geometry in the latter series of complexes. The trend is extended on going to $Cu(II)(iPrN-MeMeS)_2$ where the shift in $E_{\frac{1}{2}}$ from the planar reference value approaches 600 mV, in keeping with increased stereochemical distortion due to the sterically bulky iPr group. Patterson and Holm[318] observed comparable anodic $E_{\frac{1}{2}}$ shifts of 450 and 630 mV respectively in the analogous oxygen-donor β-ketoaminate complexes $Cu(II)(MeN-MePhO)_2$ and $Cu(II)(iPrN-MePhO)_2$, when compared to the planar reference $Cu(II)[(CH_2)_2(N-MePhO)_2]$. Yokoi and Addison[289] have correlated $E_{\frac{1}{2}}$ with $g_{\parallel}$ in cupric pyrrole-2-carboxaldiminates (4N) and salicylaldiminates (2N2O) for a range of pseudo-tetrahedral coordination symmetries. For the Cu(II) β-aminothione complexes the paucity of data does not permit analysis in any detail, but the trend of increasing $E_{\frac{1}{2}}$ potential with increasing $g_{\parallel}$ is noted in the series $Cu(II)[(CH_2)_2(N-MeMeS)_2]$, $Cu(II)(RN-MeMeS)_2$ (R = Me, Et, nOct), $Cu(II)(iPrN-MeMeS)_2$. The steric bulk of the amino-substituents on the ligands appears to dominate any electronic inductive effects, as found for other series of Cu(II) Schiff-base complexes.[289,318]

A nearly constant anodic shift of ca. 0.4 V was noted by Patterson and Holm[318] upon replacing oxygen by sulphur in complexes with otherwise identical ligands. They were unable, however, to study complexes containing both a 2N2S donor set and non-planar stereochemistry. Comparison of $Cu(II)(MeN-MeMeS)_2$ with $Cu(II)(MeN-MePhO)_2$ and $Cu(II)(iPrN-MeMeS)_2$ with $Cu(II)(iPrN-MePhO)_2$[318] indicates 2N2O — 2N2S anodic shifts of 290 and 280 mV respectively. An additional 80-90 mV is probably appropriate to these figures however, due to the electronic effect of the Ph chelate ring substituent for the 2N2O complexes.[318]

5.6.4. Comparison of $E_{\frac{1}{2}}$ with blue-copper-proteins.

Redox potentials for type 1 Cu(II) in proteins vary widely from ca. 0.0 to 0.6 V[231] relative to the SCE. Thus, the highest potential found for the β-aminothione copper complexes (-0.5 V) falls 500 mV short of the protein range, though it is the least negative observed for this type of β-difunctional ligand system. The revealed trends of increasing redox potential with distortion from planar symmetry and with adoption of 2N2S as opposed to 2N2O or 4N coordination, must, however, be considered appropriate in view of the known and speculated type 1 coordination environments for the blue-copper-proteins. What additional factors lead to the highly facilitated reduction found for the type 1 Cu(II) centre remains to be fully investigated and understood, as does the origin of the wide difference in potentials found amongst the individual proteins which have otherwise very similar spectroscopic parameters. Rather unexpectedly, the highest potentials are found for proteins with largest $|A_{||}|$ and lowest $g_{||}$.[380]

Notable in respect of their ability to reproduce redox potentials comparable to the full range found in the proteins, are Cu(II) complexes of quadridentate and macrocyclic ligands involving thioether donors.[295,307,311,319] The reasons for the low potentials have not been fully elucidated.

5.7. Concluding Remarks and Summary.

The complexes described in this section represent the most extensive series of 2N2S coordinated copper with systematically variable stereochemistry at present available. Spectroscopic and redox measurements on the complexes are consistent with pseudo-tetrahedral 2N2S geometry in which the degree of tetrahedral distortion is dependent upon the steric bulk of the amino-substituent. In solution the complexes show the lowest $|A_\parallel|$ values yet observed for this type of coordination in synthetic compounds. Constrained as impurities in Zn(II) complexes of the same ligand, z-axis EPR parameters closely approaching those found for type 1 copper proteins are observed, further supporting the belief that the coordination of the latter is near tetrahedral and predominantly, if not exclusively, 2N2S. Intense absorption bands in the visible spectra of the complexes are attributable to sulphur to copper charge transfer and are correlatable with similar features in type 1 protein spectra. The results give further evidence of the need for sulphur coordination and at least some degree of tetrahedral distortion from square-planar in order to reproduce in model compounds the intense protein 'blue' bands.

Redox potentials for the complexes deviate substantially negative of the type 1 centres, but are indicative of a role for tetrahedral distortion in bringing about high potentials.

Thus, the series of β-aminothione complexes serve to confirm some trends extrapolated from the extensive studies of other type 1 model complexes and to support the present-day understanding of the type 1 coordination site as revealed by the detailed and wide ranging investigations made during the past decade.

5.8. EXPERIMENTAL

5.8.1. Preparation of α,β-unsaturated β-aminothione ligands and their precursors.

The β-aminothione ligands were prepared by nucleophilic reactions of primary amines with 1,2-dithiolium salts (R_1, R_2 = Ph,Ph; Ph, H; tBu, tBu) or of hydrosulphide ion with O-alkylated β-ketoamine salts (R_1, R_2 = Me, Me; Ph, Me).[322 and refs. therein]

5.8.1.1. Preparation via 1,2-dithiolium salts.

Phenyl-1,2-dithiolium perchlorate (R_1, R_2 = Ph, H) was prepared by the method of Klingsberg.[335] The other two dithiolium cations were prepared by fusion of the corresponding β-diketones with excess P_4S_{10}.[381] The preparation of 2,2,6,6-tetramethyl-5-ethylamino-4-heptane dione (EtN-tButBuS) from 2,2,6,6-tetramethyl-3,5-heptanedione, which has not previously been reported, is outlined below as an example.

5 g of dipivaloylmethane and 10 g of P_4S_{10} were warmed to 120°C under N_2. After an initial vigorous reaction the mixture was maintained at ca. 130°C for 15 mins. with occasional stirring, and then extracted by refluxing with 50 ml of ca. 2 M HCℓ for 1 hr. After cooling and filtering the solution was treated with excess perchloric acid and the precipitated dithiolium perchlorate salt collected and recrystallised from MeOH/Et$_2$O. Yield 60% white plates; Mpt. 288-290°C; Anal. calc. C 41.94; H, 6.09; S, 20.38; Cℓ, 11.26%. Found C, 42.18; H, 6.07; S, 20.35; Cℓ, 11.82%.

1 g of the above dithiolium salt and 2 ml of a 33% ethanolic solution of EtNH$_2$ together with 10 ml of hexane, were stirred and gently warmed for 15 mins. A small amount of charcoal was added to the yellow reaction solution which was then filtered. The solvent was removed in vacuo and

the β-aminothione product recrystallised (low temperature) from 40-60

petroleum ether. Yield, ca. 50% yellow needles; Mpt. 69-73°C; Anal.

Calc. C, 68.72; H, 11.01; N, 6.17; S, 14.10. Found, C, 68.80; H, 11.21;

N, 6.17; S, 14.29.

Other β-aminothione ligands were prepared by reactions of the

corresponding dithiolium cation and primary amine in MeOH, Et_2O, hexane

or mixtures of these solvents.

5.8.1.2. Preparation via β-ketoamines.

β-Ketoamine precursors were synthesised by refluxing component β-

diketone and primary amine in Et_2O over 3Å molecular sieves. The

separated Schiff's bases were treated successively with $Et_3O^+BF_4^-$ [382] in

dry CH_2Cl_2 and NaSH in dry EtOH, as described by Gerlach and Holm.[322]

The resulting pale yellow to deep orange solutions were filtered and

solvent removed in vacuo. The crude aminothione products could generally

be purified by recrystallisation from petroleum ether, Et_2O, MeOH or

mixtures of these solvents. In some cases chromatography on Al_2O_3 with

toluene as solvent was necessary in order to separate the products from

some β-ketoamine reactant.

No conversion to thione could be achieved by this reaction method when

the alkylamino-substituent had a tertiary branched α-carbon(t-butylamine,

1-adamantanylamine or 1,1,4,4-tetramethyl-1,4-butane diamine).

Compounds not subjected to elemental analyses were identified by

their PMR spectra. Many of the compounds have not previously been

described, and characterisation data are presented in Tables 5.19 and

5.20.

TABLE 5.19. PMR data for β-aminothione ligands - (RN-R₂R₁S).

R	δ(R₁=Me)	δ(R₂=Me)	δ(β-H)	δ(NH)	δ(R)
Me	2.51	2.08	6.16	14.0	CH₃ 3.08(d)
Et	2.50	2.09	6.10	14.0	CH₃ 1.35(t),CH₂ 3.41(m)
iPr	2.47	2.10	6.01	14.2	CH₃ 1.33(d),CH 3.92(m)
nBu	2.55	2.11	6.18	14.2	CH₃ 0.98(t),-(CH₂)₂-1.66(m),N-CH₂ 3.45(m).
iBu	2.55	2.11	6.25	14.3	CH₃ 1.06(d),CH∿2.0(m), CH₂ 3.30(∿t).
sBu	2.55	2.13	6.12	14.3	CH₃ 1.32(d),CH 3.76(m), CH₂-CH₃ 1.00(t),1.7(m).
nOctyl	2.59	2.12	6.25	14.2	CH₃ 0.90(t),-(CH₂)₆- ∿ 1.3>,NCH₂ 3.49(m).
C₁₈H₃₇	2.51	2.10	6.03	14.0	CH₃ 0.90,-(CH₂)₁₆- ∿ 1.3, N-CH₂ ∿3.4(m).
cHx	2.53	2.12	6.12	14.3	-(CH₂)₅- 1.5 to 1.9, CH 3.7br.
Bz	2.62	2.10	6.30	14.5	Ph 7.48,CH₂ 4.69
αMeBz	2.57	1.97	6.16	14.6	Ph 7.37,CH₃ 1.65(d), CH 4.89(m)
αPhBz	2.59	2.02	6.20	14.8	Ph 7.39,CH 5.96(d)
1-Naphthyl	2.73	2.00	6.50	16.0	Naphthyl ∿7.3 to 8.2
Ph	2.50	2.05	6.24	15.6	Ph ∿7.25
pMePh	2.61	2.10	6.32	15.7	Me 2.37,Ph 7.17(m)
pMeOPh	2.60	2.08	6.31	15.6	Me 3.83,Ph 7.05(m)
pCℓPh	2.64	2.12	6.36	15.7	Ph 7.33(m)
pFPh	2.64	2.12	6.41	15.6	Ph ∿7.3
p(NMe₂)Ph	2.59	2.08	6.29	15.5	Me 3.02, Ph 6.98
2,6-Me₂Ph	2.64	1.82	6.43	15.5	Me 2.23,Ph 7.25
2R=-(CH₂)₅-	2.58	2.12	6.21	14.3	-(CH₂)₃- 1.78(br), N-CH₂ 3.52(d)
2R=-(CH₂)₆-	2.55	2.12	6.20	14.4	-(CH₂)₄- ∿1.7(br), N-CH₂ ∿3.45
EtN-MePhS	Ph∿7.4(m)	Me 1.93	6.40	14.3	CH₃ 1.18(t),CH₂ 3.25(m)
iPrN-PhPhS	Ph∿7.5(m)	Ph∿7.5(m)	6.52	14.7	CH₃ 1.28(d),CH 3.7(m)
EtN-HPhS	Ph∿7.6(m)	H∿7.6*	6.56(d)	13.9	CH₃ 1.36(t),CH₂ 3.48(m)
iPrN-HPhS	Ph∿7.5(m)	H∿7.5*	6.46(d)	13.8	CH₃ 1.34(d),CH 3.66(m)
EtN-tButBuS	tBu 1.39	tBu 1.29	6.56	15.2	CH₃∿ 1.5(m),CH₂ 3.77(m)
iPrN-tButBuS	tBu∿1.4	tBu∿1.4	6.48	15.4	Me∿1.4,CH 4.35

CDCℓ₃ - solvent; shifts(δ) in ppm; *hidden in Ph resonance;
Ph resonances - approximate centre of multiplet; d - doublet, t - triplet,
m - multiplet.

TABLE 5.20. Elemental microanalyses for β-aminothione ligands - $(RN-R_2R_1S)$.

$R, R_1=R_2=Me$		C	H	N	S	Mpt./$^\circ$C
Me	C	55.77	8.58	10.84	24.81	90–91
	F	55.67	8.62	10.78	24.84	
Et	C	58.69	9.15	9.78	22.38	43–44
	F	58.87	9.27	9.77	22.59	
nPr	C	61.09	9.61	8.91	20.39	28.5–30.5
	F	61.09	9.62	8.86	20.30	
nBu	C	63.10	10.00	8.18	18.72	33–34
	F	63.00	10.18	8.32	18.91	
iBu	C	63.10	10.00	8.18	18.72	38
	F	63.46	10.17	8.23	18.77	
sBu	C	63.10	10.00	8.18	18.72	oil
	F	63.30	10.20	8.10		
nOctyl	C	68.66	11.08	6.16	14.01	30–31.5
	F	68.60	11.27	6.25	13.55	
$C_{18}H_{37}$	C	75.13	12.34	3.81	8.73	
	F	75.99	12.74	3.87		
cHx	C	66.95	9.70	7.10	16.25	66.5–68
	F	66.94	9.83	7.09	16.22	
Bz	C	70.20	7.36	6.82	15.62	46–7
	F	70.11	7.55	6.82	15.58	
αMeBz	C	71.18	7.81	6.39	14.62	
	F	71.55	7.92	6.40	13.54	
αPhBz	C	76.82	6.81	4.98	11.39	
	F	77.06	6.83	5.07	10.96	
1-Naphthyl	C	74.65	6.26	5.80	13.28	97–98
	F	74.74	6.35	5.80	13.41	
Ph	C	69.07	6.85	7.32	16.76	61.5–63
	F	68.97	6.78	7.26	16.47	
pCℓPh	C	58.53	5.36	6.20	14.20	76–77
	F	58.75	5.39	6.22	14.22	
pFPh	C	63.13	5.78	6.69	15.32	32–33
	F	63.06	5.80	6.68	15.77	
2,6-Me$_2$Ph	C	71.18	7.81	6.39	14.62	76.5–78
	F	71.27	7.87	6.41	14.94	
Et-MePh	C	70.20	7.36	6.82	15.61	
	F	70.22	7.32	6.80		
tBu-PhPh	C	72.24	7.16	4.74	10.85	136–138
	F	76.96	7.16	4.81	11.07	
Et-HPh	C	69.07	6.85	7.32	16.76	
	F	68.73	6.81	7.25	17.05	
Et-tButBu	C	68.66	11.08	6.18	14.10	69–73
	F	68.80	11.21	6.17	14.29	

Other Mpts: - iPrN-MeMeS 31.5-33°C; pMePhN-MeMeS 33-35°C; pMeOPhN-MeMeS 50-51.5°C; EtN-PhPhS 80-81.5°C; BzN-HPhS 85-86; iPrN-HPhS 67.5-68.5°C; tBuN-HPhS 63-64°C.

5.8.2. Preparation of cupric β-aminothione complexes.

The concentration of ligand and the temperature and duration of reaction used in any specific preparation were dependent upon the solubility of the ligand and the stability of the product copper complex, as determined by the substituent groups R, R_1 and R_2. An exemplary preparation is outlined below.

80 ml of MeOH was carefully added to 2 mmol of ligand and 10 mmol of NaH (5 fold excess). The NaOMe generated in situ serves to deprotonate the ligand. This solution was filtered, cooled to ca. -60°C and then added to 1 mmol of $CuCl_2.2H_2O$ in 40 ml of MeOH at the same temperature. The mixture on stirring generally developed a dark green-blue colouration. Further, sometimes prolonged, cooling to -80°C led to a dark coloured precipitate or microcrystalline solid. This could be collected by filtration at ca. -70°C and washed well with MeOH and sometimes with Et_2O. Drying was accomplished by initially sucking N_2 through the filtered solid at low temperature and then, after replacing the filtrate collection vessel with a dry one, applying a vacuum and allowing the temperature to rise gradually to room temperature. Collected solids were stored at -30°C. A cooling bath of industrial methylated spirits was used in preparations, contained in a 8 x 30 cm Dewar and refrigerated by careful addition of liquid nitrogen. Such a bath could be maintained below -70°C for up to 24 hrs, if desired, by storage in a freezer at -30°C. Solutions were handled in tubes 20-30 cm long and 3-5 cm in diameter. The filtration apparatus is shown in Figure 5.19 and may be immersed up to the B34 joint in the cooling bath.

Microanalytical data for the complexes is given in Table 5.21. Good

analyses were obtained for several of the compounds, but for the less

stable complexes the results are less good. The microanalysis samples

were maintained at low temperature prior to weighing, but it is difficult

to assess to what extent decomposition with weight change may have taken

place whilst the individual samples were awaiting analysis within the

automatic loading mechanism of the machine. Difficulty in attaining

good microanalytical data of thermally unstable copper-thiolate complexes

has been expressed by others.[299] Where the CHN analyses are in substantial

error the deviation is generally found to be negative but the C:H:N ratio

is close to that expected for the ligand,this may be indicative of

Figure 5.19. Low temperature filtration apparatus.
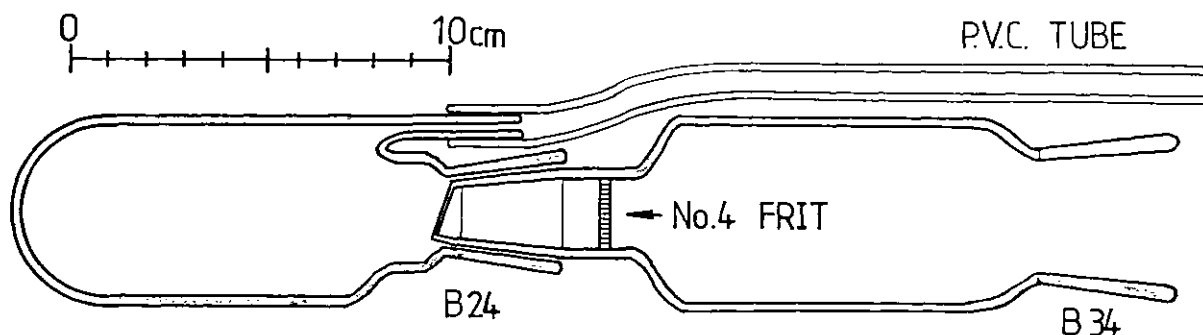
TABLE 5.21. Elemental microanalyses for cupric β-aminothione complexes

Cu(II)(RN-R_2R_1S)$_2$.
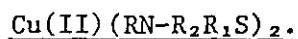
R	R_2	R_1		C	H	N
Me	Me	Me	C	45.04	6.30	8.76
			F	44.93	6.18	8.49
iBu	Me	Me	C	53.50	7.98	6.93
			F	53.54	8.04	6.93
Bz	Me	Me	C	61.05	5.98	5.93
			F	60.63	5.96	5.86
pMePh	Me	Me	C	61.05	5.98	5.93
			F	60.62	5.93	5.90
Et	Me	Ph	C	61.05	5.98	5.93
			F	61.03	5.97	5.84
Et	tBu	tBu	C	60.48	9.37	5.43
			F	60.40	9.25	5.29
Et	Me	Me	C	48.32	6.95	8.05
			F	46.39	6.26	7.23
nPr	Me	Me	C	51.10	7.50	7.45
			F	48.73	6.96	6.93
iPr	Me	Me	C	51.10	7.50	7.45
			F	46.18	6.93	6.57
nBu	Me	Me	C	53.50	7.98	6.93
			F	51.74	7.86	6.65
nOct	Me	Me	C	60.48	9.37	5.43
			F	56.90	8.31	5.00
cHx	Me	Me	C	57.92	7.95	6.14
			F	55.85	7.56	5.86
pFPh	Me	Me	C	55.04	4.62	5.84
			F	53.59	4.51	5.62
pMeOPh	Me	Me	C	57.18	5.60	5.56
			F	56.37	5.50	5.53
Et	Ph	Ph	C	68.48	5.41	4.70
			F	65.72	5.20	4.50
Et	H	Ph	C	59.50	5.44	6.31
			F	57.35	5.34	5.97

contamination by $Cu(I)(RN-R_2R_1S)_2$. The $Cu(II)(RN-R_2R_1S)_2$ formulae assigned to those compounds having elemental analyses in good agreement, are reasonably extended to other complexes isolated on the basis of the spectroscopic evidence (EPR in particular) presented in the previous sections.

5.8.3. Preparation of samples for spectroscopy.

5.8.3.1. Visible and near-IR.

Solution electronic spectra were measured for samples maintained at ca. -50 to $-80^{\circ}C$ in a Beckman RIIC variable temperature accessory with glass windows. The sample was sucked through the optical cell (1 mm path length, mounted on a low temperature finger within an evacuated case) via wide-bore PTFE tubing, until the tubing was well cooled and the absorption at one of the band maxima was constant.

For solid state reflectance spectra samples of pure or MgO diluted powders were applied to a supported piece of filter paper and protected by a glass microscope cover slide.

5.8.3.2. EPR.

Frozen solution EPR samples were contained in 200 x 5 mm (o.d.) quartz tubes having small holes at the end which is normally sealed. Low temperature solutions could be easily sucked into these tubes (precooled in liquid nitrogen) with a Pasteur pipette bulb, and then frozen in place and stored in liquid nitrogen.

Mobile solution samples were loaded into flat cells 0.5 x 3 x 40 mm in a similar manner and placed in the spectrometer cavity with the smallest cell dimension perpendicular to the magnetic field.

5.8.3.3. Raman.

Solids diluted in KBr and pelleted under pressure, and acetone solutions were investigated using the apparatus described in Appendix B.

5.8.3.4. Electrochemistry.

Polarographic and cyclic-voltammetric measurements in DMF with 0.1 M nBu$_4$NCℓO$_4$ supporting electrolyte, were performed on a Beckman Electroscan 30. A three electrode configuration was employed with the platinum counter electrode partitioned by a frit from the bulk solution. The saturated calomel reference electrode was separated from the sample via a nBu$_4$NCℓO$_4$/DMF bridge with fumed-silica gel junction, then a Et$_4$NCℓ/H$_2$O bridge with a frit junction, then a KCℓ/H$_2$O bridge with a fibre junction. For DC polarography a Metrohm E354 drop-knocker was employed at 5-6 drops/sec.

5.8.4. Zn(II), Ni(II) and Cd(II) complexes.

The Cu(II) doped Zn(II) and Cd(II) β-aminothione complexes were prepared in a similar manner to the cupric complexes (Sec. 5.8.2.) but using zinc and cadmium acetates plus ca. 0.5 to 1.0 mole % Cu(II). For some of the complexes it was necessary to maintain the reaction solution at low temperature (ca. -80°C) for 1-2 days in order to obtain a good yield. For the quadridentate ligands having 2R = -(CH$_2$)$_n$- (n = 2,3) the reactions were performed at room temperature, as the cupric complexes are stable; where n = 5,6 the reactions were performed in a freezer at ca. -30°C and acetone was added to the ligand solution to prevent precipitation prior to reaction.

For the Ni(II) complexes, which are generally more soluble, preparations of pure products were carried out in MeOH at room temperature. These were then dissolved in acetone together with a little deprotonated ligand, cooled, and a methanolic Cu(II) solution added. The doped complexes formed from these solutions were collected by low temperature filtration as described for the Cu(II) complexes. Doping of the nickel complexes having $2R = -(CH_2)_n-$ $n = 2,3$ was undertaken at room temperature. For $n = 3$ a green and a brown form of the solid Ni(II) complex were collected, the EPR parameters reported in Table 5.8 were common to both forms.

Microanalytical results for these complexes are reported in Table 5.22.

TABLE 5.22. Elemental microanalyses for zinc, nickel and cadmium β-amino-
thione complexes M(II)(RN-MeMeS)$_2$.

M = Zn; R =		C	H	N	S
Me	C	44.79	6.26	8.71	
	F	45.00	6.33	8.73	
Et	C	48.06	6.91	8.01	
	F	48.05	7.01	8.04	
nPr	C	50.85	7.47	7.41	
	F	50.73	7.49	7.33	
nBu	C	53.26	7.95	6.90	
	F	53.45	8.08	6.89	
iBu	C	53.26	7.95	6.90	
	F	53.44	8.06	6.91	
nOct	C	60.27	9.34	5.41	
	F	60.25	9.50	5.50	
Bz	C	60.82	5.95	5.91	
	F	60.68	5.92	5.97	
Ph	C	59.25	5.42	6.38	14.38
	F	59.48	5.39	6.29	14.71
pFPh	C	54.83	4.60	5.81	
	F	54.38	4.63	5.71	
2R = -(CH$_2$)$_2$-	C	45.07	5.67	8.76	
	F	44.99	5.63	8.66	
2R = -(CH$_2$)$_3$-	C	46.78	6.04	8.39	
	F	47.08	6.14	8.38	
M = Ni; R =					
Me	C	45.74	6.40	8.89	
	F	45.61	6.45	8.84	
nOct	C	61.05	9.46	5.48	
	F	60.83	9.61	5.49	
C$_{18}$H$_{37}$	C	69.76	11.20	3.54	
	F	70.48	11.36	3.68	
pCℓPh	C	52.00	4.36	5.51	
	F	52.06	4.38	5.48	
2,6-Me$_2$Ph	C	63.04	6.51	5.65	12.94
	F	63.38	6.54	5.70	12.93
2R = -(CH$_2$)$_2$-	C	46.03	5.79	8.95	20.48
	F	46.27	5.83	8.96	20.17
2R = -(CH$_2$)$_3$-	C	47.73	6.16	8.56	
	F	47.49	6.12	8.44	

TABLE 5.22 (continued.)

M = Cd; R =		C	H	N	S
Me	C	39.08	5.47	7.60	
	F	38.86	5.44	7.50	
Et	C	42.37	6.10	7.06	
	F	42.25	5.99	6.92	
$C_{18}H_{37}$	C	55.25	8.56	4.96	
	F	55.36	8.66	4.94	
2R = $-(CH_2)_3-$	C	41.00	5.29	7.36	
	F	40.75	5.20	7.22	

5.8.5.   Experimental details for Figures.

5.8.5.1.   EPR.

Fig. 4.   EPR of ^{63}Cu(II)(RN-MeMeS)$_2$ in MeOH. R = iBu; P 20, MA 2.5, RG 800

ν9.224.   R = sBu; P 20, MA2, RG 800, ν9.238.

Fig. 5.   EPR of ^{63}Cu(II)(RN-MeMeS)$_2$ in MeOH.

R = 1-Naphthyl; P20, MA 4, RG 800, ν9.214

R = pMeOPh; P 20, MA 1.6, RG 1250, ν9.219

Fig. 6.   EPR in mobile toluene, temperature ca. $-30°C$.

Cu(II)(iBuN-MeMeS)$_2$; P 0, MA 1, RG 250, ν9.245

Cu(II)(sBuN-MeMeS)$_2$; P 0, MA 1.6, RG 630, ν9.247

Cu(II)(EtN-tButBuS)$_2$; P 0, MA 1.6, RG 400, ν9.242

Fig. 8.   EPR of Zn(II)[Cu(II)](RN-MeMeS)$_2$.

R = cHx; P 20, MA 1, RG 320, ν9.229

R = Et; P 30, MA1, RG 1250, ν9.228

Fig. 9.   EPR of Zn(II)[Cu(II)](RN-MeMeS)$_2$.

R = pMeOPh; P 30, MA 0.8, RG 630, ν9.225

R = 2,6-dimethylphenyl; P 20, MA 3.2, RG 1600, ν9.225

Fig. 10. EPR of M(II)[Cu(II)] (RN-MeMeS)$_2$.

M = Zn; P 30, MA 1, RG 630, ν9.228.

M = Cd; P 20, MA 1.6, RG 320, ν9.230.

Fig. 11. EPR of Zn(II)[Cu(II)][(CH$_2$)$_n$(N-MeMeS)$_2$]

n = 2; P 20, MA 0.63, RG 200, ν9.227

n = 3; P 20, MA 0.8, RG 400, ν9.217.

Fig. 12. EPR of Ni(II)[Cu(II)][(CH$_2$)$_2$(N-MeMeS)$_2$]

X-Band; P 30, MA 0.8, RG 500, ν9.228.

Fig. 13. EPR of Ni(II)[Cu(II)](RN-MeMeS)$_2$.

R = C$_{18}$H$_{37}$, P 20, MA 2, RG 800, ν9.227

R = pCℓPh, P 22, MA 0.63, RG 250, ν9.228.

NOTES. P = Power/dB attenuation from 200 mW, MA = modulation amplitude/G,

RG = receiver gain, ν = microwave frequency/GHz.

5.8.5.2. Raman.

Fig. 16. Cu(II)(MeN-MeMeS)$_2$ at -140°C.

647.1 nm exctn., P 200 mW, SR 6 cm^{-1}, IT 1.0s, TC 8s, SS 0.6 cm^{-1}/s, FS 2 Kcps.

568.2 nm exctn., P 130 mW, SR 7 cm^{-1}, IT 1.0s, TC 8s, SS 0.5 cm^{-1}/s, FS 2 Kcps.

530.9 nm exctn., 100 mW, SR 6 cm^{-1}, IT 1.0 s, TC 7s, SS 0.5 cm^{-1}/s, FS 5 Kcps

Ligand at room temperature

647.1 nm exctn., SR 4 cm^{-1}, IT 0.5s, TC 3s, SS 0.5 cm^{-1}/s, FS 100 Kcps.

NOTES. P on figure = plasma-emission line, FS - full scale (cps counts per

sec.), IT - integration time, P - power, SR - spectral resolution, SS - scan

speed, TC - time constant.

5.8.5.3. Electrochemistry.

Fig. 17. Pt electrode- scan rate = 5 mV/s at -41°C.

HMDE - scan rate = 10 mV/s at -38°C

Fig. 18. Scan rate 2 mV/s at -36°C.

SECTION 6

EXPERIMENTAL

6. EXPERIMENTAL.

6.1. Preparative chemistry of iron-sulphur complexes.

All manipulations were carried out in an atmosphere of oxygen-free dinitrogen or argon, purified by passage through a hot tower containing BASF catalyst R3-11 and dried in a second tower of P_2O_5 supported on molecular sieves.

Solvents: MeOH, EtOH, DMSO and acetone were AR grade and not further purified; THF, Et_2O and HMPA were distilled from sodium under N_2; MeCN, PhCN, DMF and $CH_2C\ell_2$ were distilled from P_2O_5; NMP was distilled from molecular sieves under vacuum. The solvents were freed of dissolved dioxygen by prolonged purging with N_2 and/or by repeated evacuation/gas flushing cycles whilst shaking.

$Et_4N[Fe(S_2-o-xylyl)_2]$ was prepared as by Lane et al.[56] but using ethanol in place of acetonitrile, and recrystallised from hot acetone. $[Et_4N]_2[Fe_2S_2(S_2-o-xylyl)_2]$ from $Et_4N[Fe(S_2-o-xylyl)_2]$ as by Cambray et al.[45] $[Et_4N]_2[Fe_2Se_2(S_2-o-xylyl)_2]$ as for the sulphur bridged complex, but using sodium hydroselenide[383] in place of sodium hydrosulphide. $[Et_4N]_2[Fe_2X_2-(SC_6H_4Y)_4]$ (X = S, Se; Y = H, Me, $C\ell$) by ligand substitution from $[Et_4N]_2[Fe_2X_2(S_2-o-xylyl)_2]$ in acetonitrile.[28] $[Et_4N]_2[Fe_2S_2Y_4]$ (Y = $C\ell$, Br) as Wong et al.[193] similarly for $[Et_4N]_2[Fe_2Se_2C\ell_4]$. $[Et_4N]_2[Fe_4S_4(SR)_4]$ (R = Ph, Bz) as Averill et al.[58] (see also reference 384). $[Et_4N]_2[Fe_4Se_4-(SR)_4]$ (R = Ph, Bz), $[Et_4N]_2[Fe_4X_4(SePh)_4]$ (X = S, Se) as Bobrik et al.[212] (see also reference 385). $[Et_4N]_2[Fe_4Se_4(SBz)_4]$ has a tendency to separate as an oil and is best recrystallised by slow addition of MeOH to a saturated room temperature acetonitrile solution, followed by slow cooling.

[Et₄N][Fe₂X₂(SePh)₄] (X = S, Se) were prepared in a similar manner

to the PhS- ligated complexes. To a stirred slurry of around 1.5 mmol

of [Et₄N]₂[Fe₂X₂(S₂-o-xylyl)₂] in 50 ml of acetonitrile a solution of

30 mmol of PhSeSePh[386] in 200 ml of acetonitrile was added. After about

15 mins the reaction mixture developed a dark purple/black colouration

and was stirred overnight. Reduction of the solvent volume to around

150 ml resulted in separation of excess ligand and after filtration on

Celite the crude product was precipitated with ca. 200 ml THF. Filtering

again on Celite separates the product from a grey-brown filtrate,

spectralexamination of which revealed the presence of a large amount of

tetramer dianion [Fe₄X₄(SePh)₄]²⁻. The black solid collected in the Celite

was dissolved out with acetonitrile at room temperature, concentrated by

removal of solvent in vacuo, and recrystallised by slow addition with

stirring of room-temperature THF. X = S yields 40% of purple-black needles.

X = Se yields 25% of small purple-black crystals.

Microanalyses are given for previously unreported complexes only:-

[Et₄N]₂[Fe₂Se₂(S₂-o-xylyl)₂]: Calc.; C, 44.35; H, 6.51; N, 3.23. Found;

C, 44.87; H, 6.54; N, 3.45. [Et₄N]₂[Fe₂Se₂(SPh)₄]; Calc.; C, 49.69;

H, 6.26; N, 2.90. Found; C, 50.03; H, 6.40; N, 2.91. [Et₄N]₂[Fe₂Se₂(STol)₄]:

Calc.; C, 51.66; H, 6.70; N, 2.74. Found: C, 51.67; H, 6.72; N, 2.88.

[Et₄N]₂[Fe₂S₂(SePh)₄]: Calc.; C, 45.43; H, 5.72; N, 2.65. Found: C, 45.11;

H, 5.66; N, 2.79. [Et₄N]₂[Fe₂Se₂(SePh)₄]: Calc.; C, 41.62; H, 5.24;

N, 2.43. Found: C, 41.85; H, 5.30; N, 2.40. [Et₄N]₂[Fe₄Se₄(SBz)₄]:

Calc.; C, 40.89; H, 5.30; N, 2.17. Found: C, 40.55; H, 5.29; N, 2.33.

Subsequently Reynolds and Holm[29] have published details concerning

preparation of the selenium bridged dimers by a different direct route.

6.2. Instrumentation.

X-band EPR measurements were made with a Varian E12 spectrometer operating at about 9.2 GHz. For low temperature measurements, samples were cooled in a stream of N_2 gas the temperature of which was regulated by a Varian variable temperature accessory. The Q-band machine has a Varian 36 GHz microwave bridge, cavity, detection electronics and field-controller, together with a Newport instruments 12 inch type-F magnet powered by a C905 rotary generator. Fields were calibrated using proton and lithium nuclear magnetic resonances.

Raman spectra were obtained using a Spex Ramalog V instrument with a cooled RCA gallium-asenide photomultiplier and DPC-2 photon counter. A CRL-52 Krypton-ion laser was used with excitation wavelengths blue (468.0 nm, 476.2 nm, 482.5 nm), green (520.8 nm, 530.9 nm), yellow (568.2 nm) and red (647.1 nm, 676.4 nm). Plasma emission lines and $CC\ell_4$ were used to calibrate the monochromator frequency scale.

Infrared spectra were recorded using Perkin-Elmer 597 and 683 spectrometers.

NMR spectra were obtained with Perkin-Elmer R12A and R32 machines.

Electronic spectra were measured with Perkin-Elmer 551 and Cary 14 spectrophotometers.

6.3. "EPRPOW"; EPR Powder Simulation Program for S = 1/2.

The following program has been employed in this work in simulating the EPR spectra of reduced $[Fe_2S_2(SR)_4]^{2-}$ (Sec. 1) and Cu(II) β-aminothiones (Sec. 5) and in calculating component spectra for simulation of the solution spectrum of $[Fe(S_2\text{-}o\text{-}xylyl)_2]^-$ (Sec. 3). The equations and methodology of the calculation are based on a program originally written by Belford and White[387] but the algorithm has been completely re-written for faster, shorter and interactive execution. Additional linewidth and lineshape options have been incorporated.

The program is similar to that of Pilbrow and co-workers.[343,388,389]

The powder EPR spectrum is a summation of hyperfine (m) peaks over all

θ and ϕ molecular orientations with respect to field (Figure 6.1):-

$$F(H) = \sum_{\theta} \sum_{\phi} \sum_{m} P(\theta,\phi).G(H,m,\theta,\phi). \sin \theta. \Delta\theta\Delta\phi \qquad \text{E6.1}$$

Figure 6.1. Relations between the g and A tensor coordinate systems

$(g_x, g_y, A_x$ and A_y are coplanar).
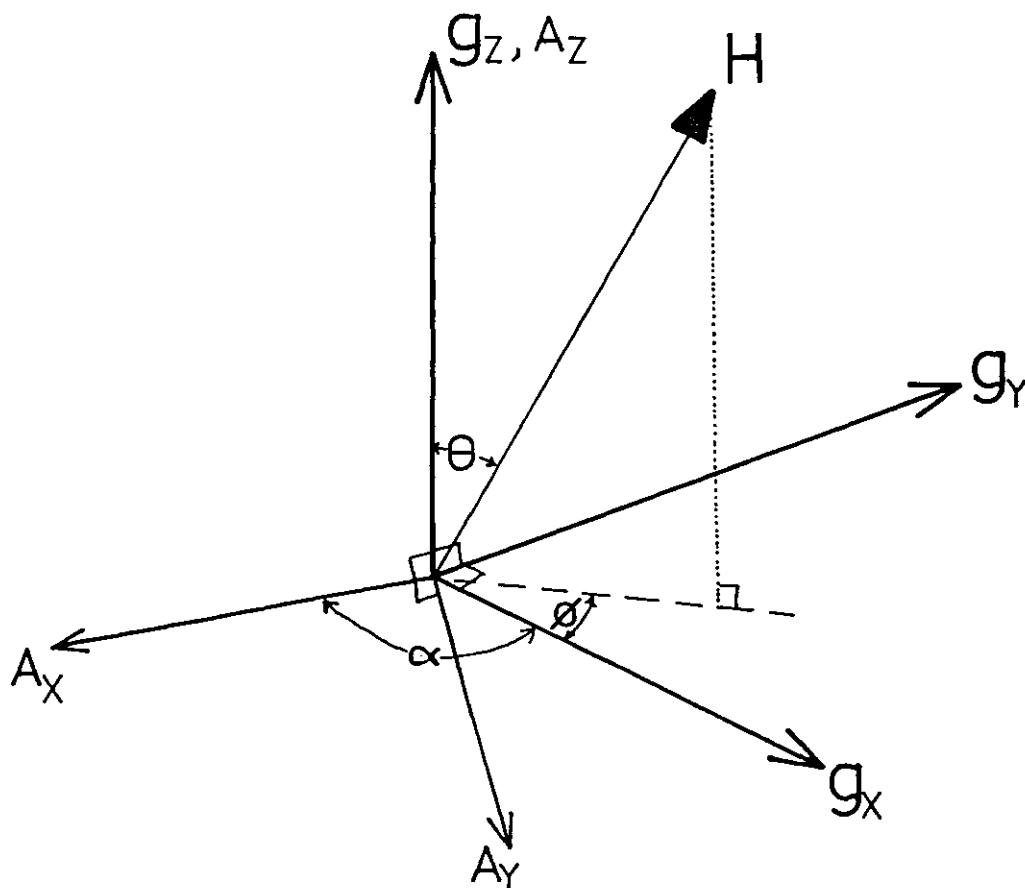
The summation is performed by a three-point Gauss-point approximation.[390]

Positions, $H(m,\theta,\phi)$ of the primary transitions are generated from second-order perturbation formulae for an orthorhombic spin Hamiltonian:

$$\hat{\mathcal{H}}_s = \beta(g_x \cdot H_x \cdot \hat{S}_x + g_y \cdot H_y \cdot \hat{S}_y + g_z \cdot H_z \cdot \hat{S}_z) + A_x \cdot \hat{S}_x \cdot \hat{I}_x + A_y \cdot \hat{S}_y \cdot \hat{I}_y + A_z \cdot \hat{S}_z \cdot \hat{I}_z$$

E6.2

$\underline{g}$ and $\underline{A}$ tensors are assumed coincident about the z-axis but misalignment by an angle α (see Figure 6.1) is allowed in the x-y plane (see references 388 and 389 for detailed equations on $\underline{g}$ - $\underline{A}$ non-coincidence and second order hyperfine formulae).

Transitions are weighted by the anisotropic probability:-

$$P(\theta,\phi) = [g_x{}^2 g_y{}^2 (1 - \ell_z{}^2) + g_y{}^2 g_z{}^2 (1 - \ell_x{}^2) + g_z{}^2 g_x{}^2 (1 - \ell_y{}^2)]/2g^3$$

E6.3

where $g^2 = g_x{}^2 \ell_x{}^2 + g_y{}^2 \ell_y{}^2 + g_z{}^2 \ell_z{}^2$, and the direction cosines ℓ_x, ℓ_y, ℓ_z are given by $\ell_x = \sin\theta\cos\phi, \ell_y = \sin\theta\sin\phi$ and $\ell_z = \cos\phi$. This transition probability factor differs from those originally used by White and Belford[387] and Pilbrow and co-workers[343,388,389] in having an additional g denominator, in keeping with the analysis of Aasa and Vânngård.[391]

Ligand superhyperfine splitting is treated only to first order with an anisotropy equation:

$$A^2 = (A_x{}^2 g_x{}^2 \ell_x{}^2 + A_y{}^2 g_y{}^2 \ell_y{}^2 + A_z{}^2 g_z{}^2 \ell_z{}^2)/g^2 \qquad \text{E6.4}$$

The transitions are broadened by a Lorentzian or Gaussian function, $G(H,m,\theta,\phi)$ of anisotropic width. The form of the function used depends on whether an absorption or derivative resultant lineshape presentation is desired:-

Lorentzian: $Y = Y_{max} \cdot \; \delta^2/[\delta^2 + (H-H_o)^2]$

$Y' = -2(H-H_o) \cdot Y^2/\delta^2$

Gaussian: $Y = Y_{max} \cdot \exp[(-\ln2)(H-H_o)^2/\delta^2]$

$Y' = -2(\ln2)(H-H_o) \cdot Y/\delta^2$

where

$Y_{max} = 1/\pi\delta$, δ = halfwidth at half-height,

H_o = central field position of the function

Mixed convolution products of these Lorentzian and Gaussian functions may be used, though this is more time consuming. To save calculation time the broadening functions are cut off where they have low intensity (default cut-offs in terms of half-height half-widths are $\pm$ 3 for Gaussian and $\pm$ 10 for Lorentzian).

Four linewidth anisotropy formulae are available. The simplest, and possibly the most useful, makes no recourse to any theory, using a linear interpolation by field between principal axis values. A second is similar but uses a parabolic interpolation formula. The third is based upon an assumption of unresolved hyperfine splitting as the main reason for broadening and uses equation E6.4 with the linewidth in place of A.[388,389] The last is useful if a linear variation in a g-distribution, Δg, is dominant in defining the linewidth. In this case the anisotropy formula is a quadratic in H, with the three coefficients replacing the role of the principal-axis linewidth values used in the other three formulae.

The number of θ,ϕ divisions required to obtain a satisfactory computed lineshape depends on the degree of anisotropy in $\underline{g}$ and $\underline{A}$ and on the component linewidth and spectral resolution. Typically 50 θ intervals and

12 ϕ intervals were found adequate in the case of the 400 point spectrum of reduced $[Fe_2S_2(SPh)_4]^{2-}$ in Figure 1.11, whilst a 180 by 15 θ,ϕ grid was used for the 600 point simulation of the $Cu(II)(iBuN-MeMeS)_2$ spectrum in Figure 5.4. The respective times for these two calculations on a CDC Cyber 174 were 3.2 secs. and 150 secs. The former is sufficiently low to allow least squares fitting of an experimental lineshape, but the latter is too high by around two orders of magnitude.

```
      SUBROUTINE EPRPOW
C
C......A ROUTINE TO CALCULATE AN EPR LINESHAPE
C......USING SPATIAL INTEGRATION                        C......GAUSSIAN WIDTHS
C                                                          WG(1)=DATA(27)/DPH
C......BASED ON A NUMERICAL ALGORITHM DEVELOPED           WG(2)=DATA(28)/DPH
C     BY L.K.WHITE & R.L.BELFORD OF THE SCHOOL OF         WG(3)=DATA(29)/DPH
C     CHEMICAL SCIENCES OF THE UNIVERSITY OF ILLINOIS.  C......G-TENSOR ORDERING
C     COMPUTATIONAL ALGORITHM REWRITTEN AND               GX=DATA(21)
C     FURTHER DEVELOPED BY P.BEARDWOOD (CHEM. DEPT.,      IF(GX.EQ.0.0)CALL ERROR(13,0,0,0)
C     IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY).        GY=DATA(22)
C                                                         GZ=DATA(23)
      REAL LX,LY,LZ                                       IF(GY.GT.0.0)GO TO 255
      COMMON XI(1100),TOTL(1100),X2(2200),TLG(1100)       GY=GX
     1,DATA(100),IO,ID(9)                                 WL(2)=WL(1)
      COMMON/REFVAB/DUM(426),IDUM(28),INTO(20),INT(20,4)  WG(2)=WG(1)
      DIMENSION HG(2),AG2(2),HL(2),AHL(2),SIG(2),SN(2)  255 IF(GZ.GT.0.0)GO TO 256
      DIMENSION D(9),THETA(9),PHI(9)                      GZ=GX
      DIMENSION A(3,4),GG(3),HA(4),WL(3),WG(3),HM(3)      WL(3)=WL(1)
      DATA HG(2),AG2(2),HL(2),AHL(2),SIG,SN(2)/6*1.0,-1.0/  WG(3)=WG(1)
C......ARRAY 'DATA' CONTAINS INPUT PARAMETERS          C......HTOG CONVERTS FIELDS TO G-VALUES
C......STARTING FIELD                                  256 GX=HTOG(GX)
      HS=DATA(9)                                          GY=HTOG(GY)
C......ENDING FIELD                                      GZ=HTOG(GZ)
      HE=DATA(10)                                         GXX=GX*GX
C......NUMBER OF POINTS                                  GYY=GY*GY
      NPS=DATA(11)                                        GZZ=GZ*GZ
      DPH=(HE-HS)/FLOAT(NPS-1)                            GXXYY=GXX*GYY
C......FREQUENCY                                         GYYZZ=GYY*GZZ
      HVB=DATA(12)*714.4843012                            GZZXX=GZZ*GXX
      IF(HVB.EQ.0.0)CALL ERROR(25,2HNU,0,0)             C......CONVOLUTION FUNCTION TYPE
C......NUMBER OF PHI INTERVALS                         C......LORGAU= 0 FOR LORENTZIAN
      NN=DATA(13)                                       C......        1 FOR GAUSSIAN
C......NUMBER OF THETA INTERVALS                       C......        2 FOR LORENTZIAN ON GAUSSIAN
      MM=DATA(14)                                       C......        3 FOR GAUSSIAN ON LORENTZIAN
C......DERIVATIVE=0                                       LORGAU=DATA(41)+1.0
      NDL=DATA(42)+1.0                                    GO TO(21,22,23,24)LORGAU
      NDG=DATA(43)+1.0                                 21 ASSIGN 401 TO IGL3
C......CONVOLUTION FUNCTION CUTOFFS                       GO TO 28
      CUTL=DATA(46)                                    22 ASSIGN 402 TO IGL3
      CUTG=DATA(47)                                       GO TO 28
      CUTLG=DATA(48)                                   23 ASSIGN 403 TO IGL3
      IF(CUTL.EQ.0.0)CUTL=10.0                            ASSIGN 50 TO IGL4
      IF(CUTG.EQ.0.0)CUTG=3.0                             SI=SIG(NDL)
      IF(CUTLG.EQ.0.0)CUTLG=1.0                           GO TO 28
C......LORENTZIAN WIDTHS                               24 ASSIGN 404 TO IGL3
      WL(1)=DATA(24)/DPH                                  ASSIGN 80 TO IGL4
      WL(2)=DATA(25)/DPH                                  SI=SIG(NDG)
      WL(3)=DATA(26)/DPH                                  GO TO 28
```

```
C......LINEWIDTH ANISOTROPY
C......LWFN=  0 FOR LINEAR ANISOTROPY
C......      1 FOR PARABOLIC ANISOTROPY
C......      2 FOR DIRECTION COSINE ANISOTROPY
C......      4 FOR QUADRATIC ANISOTROPY
  28   LWFN=DATA(44)
C......DIRECTION COSINE LINEWIDTH ANISOTROPY
       IF(LWFN-2)250,251,252
 251   IF(LORGAU.EQ.1)GO TO 264
       WGXG=WG(1)*WG(1)*GXX
       WGYG=WG(2)*WG(2)*GYY
       WGZG=WG(3)*WG(3)*GZZ
       ASSIGN 650 TO IGL1
       ASSIGN 211 TO IGL2
       IF(LORGAU.EQ.2)GO TO 29
       ASSIGN 550 TO IGL2
       GO TO 267
 264   ASSIGN 550 TO IGL1
 267   WGXL=WL(1)*WL(1)*GXX
       WGYL=WL(2)*WL(2)*GYY
       WGZL=WL(3)*WL(3)*GZZ
       GO TO 29
C......QUADRATIC LINEWIDTH ANISOTROPY
 252   IF(LORGAU.EQ.1)GO TO 253
       ASSIGN 640 TO IGL1
       ASSIGN 211 TO IGL2
       IF(LORGAU.EQ.2)GO TO 29
       ASSIGN 540 TO IGL2
       GO TO 29
 253   ASSIGN 540 TO IGL1
       GO TO 29
C......LINEAR AND PARABOLIC LINEWIDTH ANISOTROPY
 250   HM(1)=HVB/GX
       HM(2)=HVB/GY
       HM(3)=HVB/GZ
       IMAX=1
       IF(HM(2).GT.HM(1))IMAX=2
       IF(HM(3).GT.HM(IMAX))IMAX=3
       IMIN=1
       IF(HM(2).LT.HM(1))IMIN=2
       IF(HM(3).LT.HM(IMIN))IMIN=3
       IMID=1
       IF(HM(2).LT.HM(IMAX).AND.HM(2).GT.HM(IMIN))IMID=2
       IF(HM(3).LT.HM(IMAX).AND.HM(3).GT.HM(IMIN))IMID=3
       HX=HM(IMAX)
       HY=HM(IMID)
       HZ=HM(IMIN)
       IF(LORGAU.EQ.1)GO TO 260
       WX=WG(IMAX)
       WY=WG(IMID)
       WZ=WG(IMIN)
       IF(LWFN.EQ.0)GO TO 261
C......PARABOLIC
       ASSIGN 670 TO IGL1
       ASSIGN 211 TO IGL2
       CALL INTPL(HZ,HY,HX,WZ,WY,WX,CG1,CG2,CG3)
       IF(LORGAU.EQ.2)GO TO 29
       ASSIGN 570 TO IGL2
       GO TO 260
C......LINEAR
 261   ASSIGN 660 TO IGL1
       ASSIGN 211 TO IGL2
       CALL INTPL(HX,HX,HY,WX,0.0,WY,CG1,CG2,0.0)
       CALL INTPL(HY,HY,HZ,WY,0.0,WZ,CG3,CG4,0.0)
       IF(LORGAU.EQ.2)GO TO 29
       ASSIGN 560 TO IGL2
 260   WX=WL(IMAX)
       WY=WL(IMID)
       WZ=WL(IMIN)
       IF(LWFN.EQ.0)GO TO 263
C......PARABOLIC
       CALL INTPL(HZ,HY,HX,WZ,WY,WX,CL1,CL2,CL3)
       IF(LORGAU.EQ.1)ASSIGN 570 TO IGL1
       GO TO 29
C......LINEAR
 263   CALL INTPL(HX,HX,HY,WX,0.0,WY,CL1,CL2,0.0)
       CALL INTPL(HY,HY,HZ,WY,0.0,WZ,CL3,CL4,0.0)
       IF(LORGAU.EQ.1)ASSIGN 560 TO IGL1
  29   IF(DATA(71).EQ.0.0)GO TO 265
C......LINEWIDTH ANISOTROPY DRAWN INSTEAD OF SPECTRUM
       ASSIGN 309 TO IGL3
       DO 280 I=1,NPS
 280   X2(I)=0.0
       AL=0.0
       AG=0.0
 265   IF(DATA(15).GT.0.0)GO TO 41
C......PRIMARY-HYPERFINE PARAMETERS
       INTO(1)=1
       NHLO=1
       SPINO=0.0
       SPN=0.0
       CA=0.0
       CB=0.0
```

```
       ZG=0.0
       ASSIGN 52 TO IHYP1
       ASSIGN 52 TO IHYP2
       GO TO 46
C......NUMBER OF HYPERFINE LINES
  41   NHLO=DATA(15)
C......PRIMARY-HYPERFINE TENSOR
       AX=DATA(30)
       AY=DATA(31)
       AZ=DATA(32)
       IF(AY.EQ.0.0)AY=AX
       IF(AZ.EQ.0.0)AZ=AX
       AXX=AX*AX
       AYY=AY*AY
       AZZ=AZ*AZ
C......A-TENSOR NON-COINCIDENCE ANGLE: ROTATION ABOUT Z
       ALP=DATA(40)*0.01745329252
       SALP=SIN(ALP)
       CALP=COS(ALP)
C......SECOND-ORDER PRIMARY-HYPERFINE CONSTANTS
       TXX=AXX*CALP*CALP+AYY*SALP*SALP
       TYY=AXX*SALP*SALP+AYY*CALP*CALP
       TXY=(AXX-AYY)*CALP*SALP
       GTXX=GXX*TXX
       GTYY=GYY*TYY
       GTXY=2.0*GX*GY*TXY
       GXYT=GX*GY*(TYY-TXX)+(GXX-GYY)*TXY
       GXYT=GXYT*GXYT
       TXXYYXY=TXX*TYY-TXY*TXY
       SPINO=(DATA(15)+1.0)/2.0
       SPN=SPINO*(SPINO-1.0)
       CALL INTIN(0,NHLO)
       ASSIGN 53 TO IHYP1
       ASSIGN 53 TO IHYP2
C......SECONDARY-HYPERFINE PARAMETERS
  46   DO 200 I=1,4
 200   IF(DATA(49+I*5).GT.0.0)GO TO 45
       DO 90 I=1,4
       HA(I)=0.0
  90   INT(1,I)=1
       NHL1=1
       NHL2=1
       NHL3=1
       NHL4=1
       SPIN1=0.0
       SPIN2=0.0
       SPIN3=0.0
       SPIN4=0.0
       GO TO 42
  45   ASSIGN 51 TO IHYP1
       NHL1=AMAX1(DATA(54),1.0)
       NHL2=AMAX1(DATA(59),1.0)
       NHL3=AMAX1(DATA(64),1.0)
       NHL4=AMAX1(DATA(69),1.0)
       SPIN1=(DATA(54)+1.0)/2.0
       SPIN2=(DATA(59)+1.0)/2.0
       SPIN3=(DATA(64)+1.0)/2.0
       SPIN4=(DATA(69)+1.0)/2.0
       ND=50
       GG(1)=GXX
       GG(2)=GYY
       GG(3)=GZZ
       DO 300 I=1,4
       IHL=DATA(ND+4)
       IF(IHL.EQ.0)GO TO 301
       CALL INTIN(I,IHL)
       DO 400 K=1,3
       A(K,I)=DATA(ND+K)*DATA(ND+K)*GG(K)
 400   IF(A(K,I).EQ.0.0)A(K,I)=A(1,I)
       GO TO 300
 301   DO 500 K=1,3
 500   A(K,I)=0.0
       INT(1,I)=1
 300   ND=ND+5
  42   NSN=1
       DO 100 I=1,1100
 100   TOTL(I)=0.0
       NN=MAX0(NN,3)
       MM=MAX0(MM,3)
       NN3=3*NN
       MM3=3*MM
C......3-POINT GAUSS-POINT INTEGRATION SET UP
       IF(GX.EQ.GY.AND.GZ.EQ.GY)GO TO 89
       D(1)=0.22222222
       D(2)=1.02497166
       D(3)=0.75280612
       D(4)=0.55555555
       D(5)=0.88888888
       D(6)=D(4)
       D(7)=D(3)
       D(8)=D(2)
       D(9)=D(1)
       C1=1.570796327
```

```
      C2=0.77459667
      C3=1-0.28989794
      C4=1+0.88989794
      C5=3.141592654
      SINT=C1*0.5/NN
      GSINT=SINT*C2
      THETA(1)=0.0
      THETA(2)=SINT*C3
      THETA(3)=SINT*C4
      THETA(4)=SINT-GSINT
      THETA(5)=SINT
      THETA(6)=SINT+GSINT
      THETA(7)=C1-THETA(3)
      THETA(8)=C1-THETA(2)
      THETA(9)=C1
      SINT=SINT*2.0
      IF(GX.EQ.GY.OR.GZ.EQ.GY)GO TO 82
      IF(DATA(40).EQ.0.0)C5=C5*0.5
      SINP=C5*0.5/MM
      GSINP=SINP*C2
      PHI(1)=0.0
      PHI(2)=SINP*C3
      PHI(3)=SINP*C4
      PHI(4)=SINP-GSINP
      PHI(5)=SINP
      PHI(6)=SINP+GSINP
      PHI(7)=C5-PHI(3)
      PHI(8)=C5-PHI(2)
      PHI(9)=C5
      SINP=SINP*2.0
      GO TO 81
89    NN3=1
      D(1)=1.0
      THETA(1)=0.0
      SINT=0.0
      NSN=2
82    MM3=1
      PHI(1)=0.0
      SINP=0.0
81    NN1=MAX0((NN3-3),1)
      MM1=MAX0((MM3-3),1)
      NPS=NPS+2
C......LOOP FOR THETA INTEGRATION: XY-Z
      DO 108 I=1,NN3
      IX=MAX0((I-3),0)
      IX=MIN0(IX,1)
      IY=MAX0((I-NN1),0)
      IY=MIN0(IY,1)
      NPB=MOD((I+2),3)+3*(IX+IY)+1
      IF=(I-1)/3
      FL=FLOAT(IX-IY)*IF
      TETA=THETA(NPB)+SINT*FL
      CS=COS(TETA)
      CS2=CS*CS
      SN(1)=SIN(TETA)
      SN2=SN(1)*SN(1)
      DD=D(NPB)*SN(NSN)
C......LOOP FOR PHI INTEGRATION: XY PLANE
      DO 108 M=1,MM3
      IX=MAX0((M-3),0)
      IX=MIN0(IX,1)
      IY=MAX0((M-MM1),0)
      IY=MIN0(IY,1)
      MPB=MOD((M+2),3)+3*(IX+IY)+1
      IF=(M-1)/3
      FL=(IX-IY)*IF
      FI=PHI(MPB)+SINP*FL
      CC=COS(FI)
      CC2=CC*CC
      SS=SIN(FI)
      SS2=SS*SS
      SSCC=SS*CC
C......DIRECTION COSINES
      LX=SN2*CC2
      LY=SN2*SS2
      LZ=CS2
      GLX=GXX*LX
      GLY=GYY*LY
      GLZ=GZZ*LZ
      G2=GLX+GLY+GLZ
      G=SQRT(G2)
      GB=0.4668598728*G
      GGB=G*GB
C......TRANSITION PROBABILITY
      U=(GXXYY*SN2+GYYZZ*(SS2+CS2*CC2)+GZZXX*(CC2+CS2*SS2))/(G*G2)
C......"W"-INCLUDES INTEGRATION AND SITE WEIGHTING FACTORS
      W=U*DD*D(MPB)
      H=HVB/G
      GO TO IHYP1(51,52,53)
C......SECONDARY-HYPERFINE
51    DO 47 K=1,4
47    HA(K)=(SQRT(LX*A(1,K)+LY*A(2,K)+LZ*A(3,K)))/GGB
      GO TO IHYP2(52,53)
```

```
C......SECOND-ORDER PRIMARY-HYPERFINE
53    GPERP2=GXX*CC2+GYY*SS2
      AZG=TXX*GLX+TYY*GLY+AZZ*GLZ+GTXY*SN2*SSCC
      ZZ=AZG/G2
      ZG=SQRT(ZZ)/GB
      APERP2=(GTXX*CC2+GTYY*SS2+GTXY*SSCC)/GPERP2
      ABCDE2=SSCC*SSCC*GXYT/(ZZ*G2*GPERP2)
      AA=APERP2*AZZ/ZZ
      AB=TXXYYXY/APERP2
      AC=ABCDE2*AZZ*GZZ*CS2/(APERP2*GPERP2)
      AD=GZZ*GPERP2*((APERP2-AZZ)**2)*SN2*CS2/(ZZ*G2*G2)
      AE=ABCDE2*SN2
      GBBH=GB*GB*H
      CA=(AA+AB+AC)/(4*GBBH)
      CB=(AD+AE)/(2*GBBH)
C......GAUSSIAN LINEWIDTH
52    GO TO IGL1(540,550,560,570,640,650,660,670)
C......QUADRATIC ANISOTROPY
640   AG=WG(1)+WG(2)*H+WG(3)*H*H
      GO TO 600
C......DIRECTION COSINE ANISOTROPY
650   AG=(SQRT(WGXG*LX+WGYG*LY+WGZG*LZ))/G
      GO TO 600
C......LINEAR ANISOTROPY
660   IF(H.LT.HY)GO TO 661
      AG=CG1+H*CG2
      GO TO 600
661   AG=CG3+H*CG4
      GO TO 600
C......PARABOLIC ANISOTROPY
670   AG=CG1+H*(CG2+H*CG3)
600   AGI=1.0/AG
      AG2(1)=AGI*AGI*0.69314718
      ICOG=CUTG*AG+0.5
      FCOG=ICOG
      FGI=AGI*AG2(NDG)*W
C......LORENTZIAN WIDTHS
      GO TO IGL2(211,540,550,560,570)
C......QUADRATIC ANISOTROPY
540   AL=WL(1)+WL(2)*H+WL(3)*H*H
      GO TO 700
C......DIRECTION COSINE ANISOTROPY
550   AL=(SQRT(WGXL*LX+WGYL*LY+WGZL*LZ))/G
      GO TO 700
C......LINEAR ANISOTROPY
560   IF(H.LT.HY)GO TO 561
      AL=CL1+H*CL2
      GO TO 700
561   AL=CL3+H*CL4
      GO TO 700
C......PARABOLIC ANISOTROPY
570   AL=CL1+H*(CL2+H*CL3)
700   AL2=AL*AL
      ICOL=CUTL*AL+0.5
      FCOL=ICOL
      FLI=AL*W
C......SECONDARY-HYPERFINE LOOPS
211   DO 98 I4=1,NHL4
      H4=H+HA(4)*(FLOAT(I4)-SPIN4)
      DO 98 I3=1,NHL3
      H3=H4+HA(3)*(FLOAT(I3)-SPIN3)
      DO 98 I2=1,NHL2
      H2=H3+HA(2)*(FLOAT(I2)-SPIN2)
      DO 98 I1=1,NHL1
      H1=H2+HA(1)*(FLOAT(I1)-SPIN1)
C......PRIMARY-HYPERFINE LOOP
      DO 98 IO=1,NHLO
      SPINM=FLOAT(IO)-SPINO
      HO=H1-SPINM*(ZG+SPINM*(CB-CA))-CA*SPN
      HSTAR=((HO-HS)/DPH)+2.0
      IM=HSTAR+0.5
      HF=INTO(IO)*INT(I1,1)*INT(I2,2)*INT(I3,3)*INT(I4,4)
C......BROADENING FUNCTIONS
      GO TO IGL3(401,402,403,404,309)
C......GAUSSIAN
402   CALL LIMITS(L1,L2,ICOG,1,IM,NPS)
      FG=FGI*HF
      DO 20 L=L1,L2
      HG(1)=HSTAR-FLOAT(L)
      AHG=AG2(1)*HG(1)*HG(1)
      AHG=AMIN1(AHG,700.0)
20    TOTL(L)=TOTL(L)+FG*HG(NDG)/EXP(AHG)
      GO TO 98
C......LORENTZIAN
401   CALL LIMITS(L1,L2,ICOL,1,IM,NPS)
      FL=FLI*HF
      DO 30 L=L1,L2
      HL(1)=HSTAR-FLOAT(L)
      AHL(1)=AL2+HL(1)*HL(1)
30    TOTL(L)=TOTL(L)+FL*HL(NDL)/(AHL(1)*AHL(NDL))
      GO TO 98
C......LORENTZIAN ON GAUSSIAN
403   J1=IM-ICOG
```

```
        J2=IM+ICOG
        L2=MINO(ICOL,NPS)+1
        DO 40 L=1,L2
        HL(1)=L-1
        AHL(1)=ALZ+HL(1)*HL(1)
40      TLG(L)=AL*HL(NDL)/(AHL(1)*AHL(NDL))
        TLG(1)=TLG(1)*0.5
        FG=FGI*HF
        HG(1)=HSTAR-FLOAT(J1)
        AHG=AG2(1)*HG(1)*HG(1)
        AHG=AMIN1(AHG,700.0)
        TG1=FG*HG(NDG)/EXP(AHG)
        COL1=AL*CUTLG/TG1
        DO 50 J=J1,J2
        HG(1)=HSTAR-FLOAT(J)
        AHG=AG2(1)*HG(1)*HG(1)
        AHG=AMIN1(AHG,700.0)
        TGL=FG*HG(NDG)/EXP(AHG)
        ICOLG=AMIN1((ABS(TGL*COL1)+0.5),FCOL)
        GO TO 306
50      CONTINUE
        GO TO 98
C......GAUSSIAN ON LORENTZIAN
404     J1=IM-ICOL
        J2=IM+ICOL
        L2=MINO(ICOG,NPS)+1
        FG=FGI*HF
        DO 70 L=1,L2
        HG(1)=L-1
        AHG=AG2(1)*HG(1)*HG(1)
        AHG=AMIN1(AHG,700.0)
70      TLG(L)=FG*HG(NDG)/EXP(AHG)
        TLG(1)=TLG(1)*0.5
        HL(1)=HSTAR-FLOAT(J1)
        AHL(1)=ALZ+HL(1)*HL(1)
        TL1=AL*HL(NDL)/(AHL(1)*AHL(NDL))
        COG1=AG*CUTLG/TL1
        DO 80 J=J1,J2
        HL(1)=HSTAR-FLOAT(J)
        AHL(1)=ALZ+HL(1)*HL(1)
        TGL=AL*HL(NDL)/(AHL(1)*AHL(NDL))
        ICOLG=AMIN1((ABS(TGL*COG1)+0.5),FCOG)
        GO TO 306
80      CONTINUE
98      CONTINUE
108     CONTINUE
        GO TO 91
C......LOOP EXTERNAL
306     CALL LIMITS(K1,K2,ICOLG,1,J,NPS)
        JI=MAXO(J,K1)
        JP=MINO(JI,(K2+ICOLG))+1
        JI=MINO(JI,K2)
        JM=MINO(J,K2)
        JM=MAXO(JM,(K1-ICOLG))-1
        DO 60 K=K1,JI
60      TOTL(K)=TOTL(K)+TGL*TLG(JP-K)
        TGL=TGL*SI
        DO 61 K=JI,K2
61      TOTL(K)=TOTL(K)+TGL*TLG(K-JM)
        GO TO IGL4(50,80)
C......END OF LOOPS
91      NPS=NPS-2
        DO 500 I=1,NPS
500     TOTL(I)=TOTL(I+1)
        TOTL(1100)=NPS
        TOTL(1098)=HS
        TOTL(1099)=HE
        TOTL(1095)=1.0
C......NORMALISE SPECTRUM
        CALL NORMAL(2,2)
        IF(IB(6).NE.0)CALL DRAW(2,0.0,0.0,0,0)
        IF(DATA(71).EQ.0.0)RETURN
        DATA(71)=0.0
        DO 320 I=1,NPS
320     TOTL(I)=X2(I)
        GO TO 91
309     TOTL(IM)=AL
        X2(IM)=AG
        GO TO 108
        END
CHTOG
        FUNCTION HTOG(X)
C
C......FIELD:G-VALUE INTERCONVERSION
C
C......IF X +VE  RESULT IS A G-VALUE
C......IF X -VE  RESULT IS A FIELD
C......IF X<10   X IS ASSUMED TO BE A G-VALUE
C......IF X>10   X IS ASSUMED TO BE A FIELD
C
        COMMON S(5500),DATA(100)
        HTOG=ABS(X)
        IF(X.LT.0.0)GO TO 1


        IF(HTOG.LE.10.0)RETURN
2       FREG=DATA(12)
        IF(FREG.EQ.0.0)CALL ERROR (25,4HFREG,0,0)
        HTOG=714.484301*FREG/HTOG
        RETURN
1       IF(HTOG.GT.10.0)RETURN
        GO TO 2
        END
CINTPL
        SUBROUTINE INTPL (XX,XY,XZ,YX,YY,YZ,C1,C2,C3)
C
C......EVALUATES COEFFICIENTS OF PARABOLIC INTERPLOATION
C......AND EXTRAPLOATION EQUATION- Y=C1+C2X+C3X*X USING
C......CRAMERS RULE.
C
C......X-VALUES
        VX=XX
        VY=XY
        VZ=XZ
C......Y-VALUES
        AX=YX
        AY=YY
        AZ=YZ
        VV=ABS((VY-VZ)*(VX-VY))
        IF(VV.LT.0.0000001)GO TO 4
        GO TO 3
4       VV=ABS(VZ-VX)
        IF(VV.LT.0.0000001)GO TO 1
        GO TO 2
1       C1=AX
        CZ=0.0
        C3=0.0
        RETURN
2       DENOM=VZ-VX
        DELX=VZ*AX-AZ*VX
        DELY=AZ-AX
        C1=DELX/DENOM
        C2=DELY/DENOM
        C3=0.0
        RETURN
3       VXZ=VX*VX
        VY2=VY*VY
        VZZ=VZ*VZ
        DENOM=VZZ*(VY-VX)+VYZ*(VX-VZ)+VXZ*(VZ-VY)
        DELX=VZZ*(AX*VY-AY*VX)+VYZ*(AZ*VX-AX*VZ)+VXZ*(AY*VZ-AZ*VY)
        DELY=VZZ*(AY-AX)+VYZ*(AX-AZ)+VXZ*(AZ-AY)
        DELZ=VZ*(AX-AY)+VY*(AZ-AX)+VX*(AY-AZ)
        C1=DELX/DENOM
        C2=DELY/DENOM
        C3=DELZ/DENOM
        RETURN
        END
CINTIN
        SUBROUTINE INTIN(I,IHL)
C......SET HYPERFINE PARAMETERS
        COMMON X(5500),DATA(100),IO,IO(9)
        COMMON/REFVAB/DUM(426),IDUM(28),INT(20,5)
        COMMON/IN/ICOM,X1,X2,X3,X4,X5,IDUM2(10),IM
       1,NIN,NLOOP,LOOP1,LOOP2,INU,ARGS(20),IARG,JO(10)
       2,NSTR,ISTR(40,12)
        N=I+1
        INTX=DATA(N*5+45)
C......INTX= 0 - READ IN VALUES
C......INTX> 0 - SET ALL VALUES TO INTX
C......INTX=-1 - USE PREVIOUS INPUT VALUES
        IF(INTX.EQ.-1)RETURN
        NHL=IHL
        IF(INTX.EQ.0)GO TO 1
        DO 10 K=1,NHL
10      INT(K,N)=INTX
        RETURN
1       WRITE(IO,1000)N,NHL
1000    FORMAT(*HYPERFINE INTENSITIES FOR SET*,I3,* -ENTER*,I3,*  VALUES*)
        CALL PRINT
        READ(INU,*)(INT(K,N),K=1,NHL)
        IF(EOF(INU))1,2
2       DATA(N*5+45)=-1.0
        RETURN
        END
CLIMITS
        SUBROUTINE LIMITS(L1,L2,ICO,IS,IM,IE)
C
C......EVALUATES RANGE(L1 TO L2) FOR BROADENING FUNCTION.
C......THE FUNCTION IS CLIPPED AT THE CUTOFF(ICO) OR AT
C......THE START AND END POINTS(IS,IE)
C
        L1=MAXO((IM-ICO),IS)
        L1=MINO(L1,IE)
        L2=MINO((IM+ICO),IE)
        L2=MAXO(L2,IS)
        RETURN
        END
```

APPENDICES

APPENDIX A
=========

An Interactive Spectral Manipulation Program.

A.1. Introduction.

During the course of this work a program has been developed which has general utility for manipulation of spectra and related data, with particular emphasis on EPR. The overriding principle employed in designing the programs' mode of operation has been to put the maximum amount of control at the users disposal and to maintain a high level of default on the available options. The aim has been to achieve flexibility and generality in the program's applications and to maximise the speed of user/program interaction, but at the same time to ensure a simplicity of operation, with adequate error recovery, so that basic manipulations may be performed without difficulty by an infrequent user. To this end virtually all input is taken in response to a single prompt as character information (A - format) and interpreted by a routine ('SYNTAX') which defines the syntax for a command-orientated language.

A.2. Commands.

Input commands take the general form:

COMMAND: P1/P2 = P3*P4+P5 (S1) (S2)

'COMMAND' is an alpha-identifier of up to 10 characters, P1 to P5 are parameters which may be (1) signed or unsigned integer or floating point numbers (2) alpha-numeric strings up to 10 characters in length (3) alpha

identifiers from the data-set (see below). The separators '/ = * +'

may occur in any order and thus need only be entered if their respective

parameters P2-P5 are to be specified. The ':' separator is optional

unless P1 begins with an alpha character. Further sequential parameters

or long character strings may be attached to the command with the

optional terminating parenthetical terms, S1 and S2.

Commands may be strung together in sentences by separating with ','

or ';', and are then processed sequentially. Such a sentence may form

a line of input with up to 100 characters. If the operation performed

by a command is to be repeated with new parameters then it is implicitly

assumed following ',' without being re-entered. The ';' delimiter also

causes retention of the parameter values P2-P5, unless they are respecified

by the input.

A.3. Data-Identifiers.

A data set of 100 elements is available at any one time for use as

data, switches, registers, etc. These are allotted names of up to 10

alpha—characters and may be set using the general form of the command

input:

DATAID   P1*P4/P2+P5

or   DATAID = P3*P4/P2+P5

where the separators now take their normal mathematical meanings. Unlike

the usual form of the command, if after a data entry and ',' or ';' the

command field is left unspecified, data entry to the next element in the

data set is assumed, thus allowing rapid sequential setting of blocks of

adjacent elements.

A.4. Spectra.

Up to five spectra (intensities at equally spaced monotonic values of some spectroscopic variable) may be retained in central memory, each having a small updatable data-set of its own. Additional random access storage is available for 100 spectra and/or main data-sets on each of three files.

A.5. Some Examples.

A.5.1. Data identifiers;- GX, GY, GZ and NU

GX   2.001

GY = GX + 0.03

NU   9.21

GZ = 714.5 * NU/3030

A.5.2. Commands DRAW, READ, SMOOTH

DRAW 1 * 2.5 - draw spectrum 1 at 2.5 times normal intensity

READ 3/2 = 4 - read record 3 on file 2 into spectrum 4

SMOOTH 2 = 3 * 4 - smooth spectrum 2 4 times and place result in spectrum 3.

A.6. Strings.

A group of commands up to 300 characters in length may be collected together and given a new name using the command 'STRING/P2(S1)'. The string of commands between the brackets, S1, is stored and may be executed by simply naming P2 in the normal way for a command. Any parameters (P1-P5) in this string of commands may be replaced by '?' and variably specified at execution of the string-command as parenthetical arguments. A string may call another string, or indeed itself.

Example.

STRING/RASD (READ?/2, ?/3 = 2, ADD 1 = 3, 2* -1.5, SMOOTH 3, DRAW 3)
RASD (1,1), RASD (1,3)

- reads two spectra from different files, subtracts 1.5 of one from the
other, smooths the result and draws it.

A.7. Editor.

The contents of character strings of this sort may be modified
using a built in editor. Commands to this editor take the same form as
the general command input and may thus be interspersed with any other
command. The following string editor commands are available:

P   - print the string

A(S1)   - add the substring S1 to the end

C(S1)(S2)- change all occurrences of substring

          S1 to S2

M   - print the string and receive modification

          instructions on the next line

A.8. Command File.

Any number of lines of commands may be collected into a file and
input may be switched to read from this file instead of the keyboard.
In this way it is possible to write a subprogram in the spectroscopic
language defined by the Fortran program, and to have it executed in
interpreter fashion. Movement in and modification of this file is made
possible via the editor; the relevant additional commands being:

```
N P1        - move forward P1 lines

GOTO P1     - move to line P1

T           - move to top of file

B           - move to bottom of file

L(S1)       - locate first occurrence of string S1

D P1        - delete P1 lines

I P1        - insert P1 lines

SOSRUN P1*P4 - move to line P1 and execute P4 lines
```

A particularly useful feature of this command file, in connection with the screen-display, is the 'PIC' command. This, together with associated commands 'UNPIC' and 'REPIC', automatically controls the writing and reading of the command file, where plot space positional information is also stored, allowing a complex picture easily to be built-up on the screen and modified.

A.9 . Examples of Program Applications.

The following string and command files demonstrate the syntax and some of the commands outlined above. The examples are taken from the work in this thesis. Many of the figures in this manuscript have been produced entirely using the graphical capabilities of the program, e.g., Figures 0.2, 1.4, 1.9, 2.6, 3.7, 5.4, and 5.15.

Example 1.

The following set of strings were used in the fitting and plotting of the composite band analysis for $[Fe_2S_2(SR)_4]^{2-}$ electronic spectra, Figure 4.16, Table 4.17.

```
$...RENAME DATA-ID ELEMENTS
$...FX-WAVELENGTH , LX-LINEWIDTH , HX-HEIGHT
$...X=A,B,C - THREE BANDS
RENAME/AXA=FA,/AXB=FB,/AXC=FC,/AYA=LA,/AYB=LB,/AYC=LC
/AZA=HA,/AZB=HB,/AZC=HC
$...CALCULATE COMPONENT BANDS, DRAW, ADD INTO ACCUMULATOR
$...AND DRAW RESULT AT END
STRING8/SS(LTYP2,ADD=3,COMPSET3/INTL=BL,GZ=FA,LZL=LA,AX=HA,CC,
GZ=FB,LZL=LB,AX=HB,CC,GZ=FC,LZL=LC,AX=HC,CC,SPEC2=3,LTYP,DRAW2)
STRING9/CC(GOFF,ISO,GON,TDATA2/SIG=AX,COMPSET2/INTL=BL,ADD2,DRAW2)
$...ITERATIVE FITTING
STRING10/RR(REFINE(FA?,FB?,FC?,LA?,LB?,LC?,HA?,HB?,HC?,
GZ=FA,LZL=LA,ISO,COMPSET2/INTL=BL,TDATA2/SIG=HA,ADD2=3
GZ=FB,LZL=LB,ISO,COMPSET2/INTL=BL,3,TDATA2/SIG=HB,ADD2,
GZ=FC,LZL=LC,ISO,COMPSET2/INTL=BL,TDATA2/SIG=HC,ADD2,SPEC2=3))
$...PRINT PEAK-WAVELENGTH,WIDTHS AND HEIGHTS
$...OF COMPONENT BANDS
STRING11/PP(PVAL/FA*3,/FB*3,/FC*3)
```

<u>Example 2.</u>

The command file and strings below were used in generating the

simulation of the solution EPR spectrum for $[Fe(S_2-o-xylyl)_2]^-$ depicted

in Figure 3.3. and described in Section 3.

```
$...CALCULATION STRING
STRING12/SS(POW,INTCOR2,AX=AX+1,STOSPEC:AX=2/3)
AX,GOFF
$...DATA FOR LOWER THEN MIDDLE DOUBLET(S=5/2)
$...AT INCREASING VALUES OF LAMBDA
GX3262.4,1132.7,1045.4,NPC40,10,SS
GX10000.0,9312.8,1086.2,NPC20,1,SS
GX3279.4,1182.9,1007.7,NPC40,10,SS
GX10000.0,8025.8,1088.2,NPC20,1,SS
GX3307.6,1237.9,973.6,NPC40,10,SS
GX10000.0,6849.7,1091.4,NPC20,1,SS
GX3347.2,1298.1,942.7,NPC40,10,SS
GX10000.0,5837.6,1095.9,NPC20,1,SS
GX3398.3,1363.7,914.8,NPC40,10,SS
GX10000.0,5009.6,1101.6,NPC20,1,SS
GX3460.9,1435.2,889.6,NPC40,10,SS
GX5760.3,4352.1,1108.4,NPC20,1,SS
GX3535.2,1512.9,866.9,NPC40,10,SS
GX4605.8,3835.4,1116.3,NPC20,1,SS

       ...        ...        ...
       ...        ...        ...
                  ETC
       ...        ...        ...
       ...        ...        ...
GX8688.5,5320.6,684.0,NPC40,10,SS
```

```
GX1642.6,1550.0,1421.1,NPC20,1,SS
GX9217.3,5648.1,681.5,NPC40,10,SS
GX1616.5,1539.7,1439.0,NPC20,1,SS
GX9798.2,5999.2,679.3,NPC40,10,SS
GX1592.2,1531.9,1457.3,NPC20,1,SS
GX10441.5,6356.6,677.2,NPC40,10,SS
GX1526.3,1569.2,1475.9,NPC20,1,SS
GX11160.2,6738.5,675.3,NPC40,10,SS
GX1547.6,1522.7,1494.8,NPC20,1,SS
GX11974.8,7139.6,673.6,NPC40,10,SS
GX1527.1,1521.1,1514.0,NPC20,1,SS
$...CALCULATE GAUSSIAN INTENSITY DISTRIBUTION
$...PLACING RESULT IN SPEC 4
STRING8/GG(RDATA2,PDATA2,PAUSE,PDATA2,GOFF,ISO,GON,PSPEC2*40=NH,SPEC4=2,RDATA1)
$...ADD LOWER THEN MIDDLE DOUBLET SPECTRA OVER THE
$...ENTIRE LAMBDA RANGE USING A GAUSSIAN DISTRIBUTION
$...OF INTENSITIES(SPEC 4),AND STORE THE TWO RESULTING SPECTRA
STRING9/AA(AX=-1,AY1,ADD=3,HE15000,CC,STORE1/2=3,AX,AY1,ADD=3,CC,STORE2/2=3)
STRING10/CC(AX=AX+2,RSPEC:AX/3=2,AY=AY+1,TDATA/AZ=AY*4,/AXC=INT*2,AXC=AZ/AXC,
ADD2+M*AXC,IF65*AX/GT,CC)
$...ADD TOGETHER LOWER AND MIDDLE DOUBLET SPECTRA
$...INCORPORATING BOLTZMANN DISTRIBUTION FACTOR 'INT'
STRING11/II(HE6000,RSPEC1/2=2,ADD2=2+M,RSPEC2/2=3,ADD3+M*INT,TDATA2/SIG=1)
```

Example 3.

This command file constructs Figure 3.11.

```
$...READ EXPERIMENTAL TEMPERATURES AND INTENSITIES
RSPEC1/2,READ2/2=2
$...PLOT AXES, EXPERIMENTAL POINTS AND CALCULATED
$...LINES FOR THE THREE DOUBLETS(S=5/2).
XAX,DECPL1,YAX,PLOT1*2,EQNC,LINE5*3,EQNC*2,LINE5*3,EQNC*3,LINE5*3
$...MARK DOUBLETS WITH IDENTIFIERS
$...NAME FOLLOWED BY ITS LOCATION WRITTEN AFTER
PIC,ANOTATE=W(L);(M);(U)
$L
$  23.275269617204231   17.295526315789516     X
$M
$  23.275269617204231    4.556710526315840     X
$U
$  23.275269617204231     .810000000000073     X
$...AXIS NAMES
PIC,ANOTATE=W+90(DOUBLET FRACTIONAL POPULATION)
$DOUBLET FRACTIONAL POPULATION
$  -2.230106726881615    6.055394736842231     X
PIC,ANOTATE=W(1/T (K$+-1$=))
$1/T (K$+-1$=)
$  10.372043810752757   -1.834736842105144     X
$...FURTHER ANNOTATION OF GRAPH
PIC,ANOTATE=W*2($4K$==0.13),=W*2(D=2.0 $2CM$=$+-1)
$$4K$==0.13
$   1.683871767742005   22.540921052631698     X
$D=2.0 $2CM$=$+-1
$   1.683871767742005   20.557368421052729     X
```

```
********************************************
A.10  COMMANDS AND THEIR PARAMETERS:PROGRAM SOS
      ********************************************
```

```
        CONTROL
        *******

        START                    INITIALISE FOR GRAPHICS VDU.
        END                      TERMINATE PROGRAM EXECUTION.
        KMAT                     INITIALISE FOR MICROFILM OR KINGMATIC PLOTTING.
        FAST                     ENABLE HIGH SPEED OUTPUT ON GRAPHICS VDU.
        SLOW                     DISABLE HIGH SPEED OUTPUT ON GRAPHICS VDU.
        DATA P1=P3*P4/P2+P5       SET DATA-SET ELEMENT P1 TO (P3*P4/P2+P5).
        TABLE P1=P3               USE TABLE P1 FOR CHECKING INPUT COMMANDS AND/OR(P3)
                                 DATA-IDENTIFIERS.
        RENAME/P2=P3             TEMPORARILY CHANGE COMMAND-NAME OR DATA-IDENTIFIER P2 TO P3.
        DOSTR P1                 EXCECUTE STRING P1.
        SOSRUN P1*P4             READ AND PROCESS P4 LINES OF INPUT FROM FILE 'SOSRUN'
                                 STARTING AT LINE P1.
        PAUSE                    TEMPORARILY DIVERT FROM 'STRING' OR 'SOSRUN' PROCESSING
                                 TO 'INPUT'.
        CONT                     AFTER 'PAUSE' RETURN TO ORIGINAL COMMAND/DATA STRING.
        ABORT P1                 AFTER 'PAUSE' ABORT ORIGINAL COMMAND STRING BY P1 LEVELS.
        IF P1*P4/P2              AS FORTRAN - IF(P1.P2.P4)CONTINUE,OTHERWISE AS 'CONT'.
        PIC P1/P2                INSERT INPUT STRING IN FILE 'SOSRUN'.P1&P2 GOVERN
                                 POSITION.SPECIAL CONDITIONS ARE SET UP FOR X-WIRES INPUT
                                 WHICH IS ALSO WRITTEN TO 'SOSRUN'.
        UNPIC P1                 REMOVE LINE P1 AND ASSOCIATED X-WIRE INPUT.
        REPIC P1                 REGENERATE LINE P1 AND ASSOCIATED X-WIRES INPUT.
        PRINT P1                 SET PRINT QUANTITY CONTROL SWITCH TO P1.


        SPECTRA STORAGE FILES
        *********************

        READ P1/P2=P3            READ RECORD P1 ON FILE P2 INTO SPEC P3 AND MAIN DATA-SET.
        RSPEC P1/P2=P3           READ RECORD P1 ON FILE P2 INTO SPEC P3.
        RDATA P1/P2              READ RECORD P1 ON FILE P2 INTO MAIN DATA-SET.
        STORE P1/P2=P3           STORE SPEC P3 AND MAIN DATA-SET AS RECORD P1 ON FILE P2.
        STOSPEC P1/P2=P3         STORE SPEC P3 AS RECORD P1 ON FILE P2.
        STODATA P1/P2            STORE MAIN DATA-SET AS RECORD P1 ON FILE P2.
        CATALOG P1=P3            PRINT CATALOG OF FILE P1; P3=DUMP SUPPRESSES OUTPUT.
        OPEN P1                  OPEN FILE P1.
        UNPACK P1/P2=P3          UNPACK 'PACK' FILE, STORING SPECTRA P1-P2(INCLUSIVE)
                                 ON FILE P3.


        SPECTRAL MANIPULATION
        *********************

        SPEC P1=P3/P2*P4+P5      COPY SPECTRUM P3 INTO P1 FROM ELEMENT P2 TO P4 ADDING P5
                                 TO EACH VALUE.
        SPECIN P1/P2=P3*P4       MODIFY ELEMENT P2 OF SPEC P3 TO VALUE P1; P4=IN-INSERT,
                                 P4=OUT-REMOVE.
        PSPEC P1/P2*P4=P3        PRINT DATA-SET OF SPEC P1,AND P4 ELEMENT-VALUES STARTING
                                 AT ELEMENT P2; P3=DUMP SUPPRESSES OUTPUT.
        INTEG P1=P3*P4           INTEGRATE SPEC P1 P4 TIMES PUTTING RESULT IN SPEC P3.
        DERIV P1=P3*P4           DIFFERENTIATE SPEC P1 P4 TIMES PUTTING RESULT IN SPEC P3.
```

```
SMOOTH P1=P3*P4                 SMOOTH SPEC P1 P4 TIMES PUTTING RESULT IN SPEC P3.
FILTER P1=P3/P2*P4              DIGITALLY FILTER SPEC P1 P4 TIMES ACCORDING TO CONVOLUTION
                                SHAPE SPECIFIED BY P2, PUTTING RESULT IN SPEC P3.
NOISE P1=P3*P4/P2+P5            ADD NOISE OF S/N=P4 TO SPEC P1 FROM ELEMENT P2 TO P5
                                PUTTING RESULT IN P3.
LEVEL P1=P3*P4/P2+P5            SUBTRACT LINEAR BASELINE (<1ST. P2 POINTS>-<LAST P2 PTS.>)*P4
                                FROM P1 PUTTING RESULT IN SPEC P3.
NORMAL P1=P3                    NORMALISE SPEC P1 PUTTING RESULT IN SPEC P3.
ALIGN P1=P3/P2*P4+P5            INTERPOLATE SPEC P1 WITH POLYNOMIAL ORDER P4 ACCORDING TO
                                MAIN DATA-SET OR SPEC P2 PUTTING RESULT IN SPEC P3; P5-NEW
                                MICROWAVE FREQUENCY.
REVERSE P1=P3                   REVERSE ORDER OF POINTS FOR SPEC P1 PUTTING RESULT IN SPEC P3.
ADD P1=P3/P2*P4+P5              ADD P4 TIMES SPEC P1 INTO SPEC P3 AFTER COMPARISON WITH
                                SPEC P2; P5=M-EMPLOY 'MATCH' MODE.
EDIT=P3                         EDIT SPECTRUM P3 USING X-WIRES INPUT.
EXPACT P1=P3/P2*P4+P5           EXPAND OR CONTRACT SPEC P1 AT FIELD POSITION P2 BY AMOUNT P5
                                PUTTING RESULT IN SPEC P3; P4- VALUE TO INSERT IN EXPANSION.
HSHIFT P1=P3/P2*P4              SHIFT SPEC P1 BY AMOUNT P4 PUTTING RESULT IN SPEC P4; P2-
                                POLYNOMIAL INTERPOLATION ORDER.
INTCOR P1=P3                    USE G-VALUES IN DATA-SET TO EVALUATE INTEGRATED-INTENSITY
                                CORRECTION FACTOR, APPLY TO SPEC P1 AND ENTER VALUE IN
                                DATA-SET ELEMENT P3.
TDATA P1/P2=P3*P4               SET DATA-SET ELEMENT P2 FROM DATA-SET ELEMENT P3; P1&P4=0
                                FOR MAIN DATA-SET OR =SPEC-NUMBER FOR SPEC DATA-SETS.
XDATA P1/P2=P3*P4               EXCHANGE DATA-SET ELEMENTS P2 AND P3; P1&P4=0 FOR MAIN
                                DATA-SET OR =SPEC-NUMBER FOR SPEC DATA-SETS.


GRAPHICAL
*********

DRAW P1/P2*P4+P5                DRAW SPEC P1 IN COMPARISON TO SPEC P2, Y-SHIFTED BY P5
                                AND MULTIPLIED BY P4.
PLOTPT P1/P2=P3                 PLOT POINT AT X=P1,Y=P2 WITH SYMBOL TYPE P3; P3=0
                                FOR NO SYMBOL; P3 -VE FOR NO LINE FROM LAST POINT.
AXIS P1/P2=P3*P4+P5(S1)(S2)     DRAW X-AXIS WITH START AND END VALUES DETERMINED BY
                                MAIN DATA-SET OR BY SPEC P1 OR BY,P2&P3; P4 CONTROLS
                                SIZE AND ORIENTATION OF MARKINGS; P5 CONTROLS NUMBERING
                                FORMAT; S1-ALTERNATIVE AXIS NAME; S2-ALTERNATIVE
                                MARKING POSITIONS.
MARK P1/P2=P3*P4+P5(S1)(S2)     MARK FIELD OR G-VALUE POSITION P1 WITH ARROW; P2,P3
                                S1 AND S2 CONTROL LABELLING; P4 CONTROLS SIZE; P5 CONTROLS
                                Y-SHIFT.
BASELINE P1/P2                  DRAW BASELINE OF SPEC P1 WITH LINETYPE P2.
BOX P1/P2=P3*P4(S1)             SET BOX P1 WITH X-Y SIDES RATIO P2 AND P3 X-BOXES BY
                                P4 Y-BOXES; S1- FOUR SEQUENTIAL VALUES CONTROL X,Y-FRAME
                                SIZE AND X,Y-BOX INTERNAL PLOT SPACE.
DRAWBOX P1/P2=P3*P4+P5(S1)      ESTABLISH TEMPORARY BOX STRUCTURE (PARAMETERS AS 'BOX'),
                                AND DRAW BOX P1; P5 CONTROLS BOX NUMBERING.
GRID P1*P4/P2                   DRAW GRID WITH P1 X-DIVISIONS, P4 Y-DIVISIONS AND LINETYPE P2.
ANOTATE P1/P2=P3*P4+P5(S1)      PLOT CHARACTERS IN S1 OR 'STRING' P1/P2 WITH SIZE P4 AND AT
                                ANGLE P5; P3 GOVERNS CHARACTER SET TO BE USED.
VECTOR P1                       DRAW LINES OF TYPE P1 USING X-WIRES INPUT.
OBLONG P1                       DRAW OBLONG WITH LINE TYPE P1 USING X-WIRES INPUT.
ASIZE P1/P2=P3*P4               MARK OUT A(P1) PAPER SIZE ACCORDING TO FORMAT P2,P3; P4=0
                                FOR X-WIRES ORIGIN INPUT.
ORIGIN P1=P3/P2*P4              REDEFINE ORIGIN AT X-WIRES INPUT (OR AT X=P2,Y=P4) WITH
                                ROTATION P1; P3=ROT FOR NO ORIGIN TRANSLATION.
MAG P1                          REDEFINE MAGNIFICATION AS P1.
HARDON                          ENABLE MICROFILM GENERATION.
HARDOFF                         DISABLE MICROFILM GENERATION.
HARD                            GENERATE MICROFILM.
GON                             ENABLE GRAPHICS.
GOFF                            DISABLE GRAPHICS.
```

CALCULATION AND CURVE FITTING
****

(CALCULATED SPECTRA ARE PLACED IN SPEC 2)

```
ISO                         ISOTROPIC SPECTRUM.
KNEUB                       ANISOTROPIC EPR SPECTRUM ACCORDING TO ANALYTICAL SOLUTION
                            OF KNEUBUHL (JCP VOL.33,PG.1074(1960)).
POW                         POWDER EPR SPECTRUM BY SPATIAL INTEGRATION.
CONV                        CONVOLUTE SPEC 4 WITH LORENTZIAN-GAUSSIAN LINESHAPE.
CALC                        USER SUPPLIED CALCULATION ROUTINE.
FUNC P1/P2=P3*P4+P5         EVALUATE RMS PER CENT DIFFERENCE FUNCTION VALUE FOR SPECTRA
                            P1 AND P2 USING MASK IN SPEC P4; P3 AND P5 ARE SPECTRA TO
                            RECEIVE ALIGNED SPECTRA FROM P1 AND P2.
REFINE P1/P2=P3*P4+P5(S1)   FIND MINIMUM VALUE OF 'FUNC'-LEAST SQUARES FIT,FOLLOWING
                            EXCECUTION OF STRING S1; PARAMETERS AS 'FUNC', DATA VALUES
                            TO BE VARIED ARE SPECIFIED BY '?' WITHIN S1.
```

STRINGS AND EDITOR
****

```
STRING P1=P3/P2(S1)         DEFINE 'STRING' P1 WITH NAME P2 AS S1 OR AS 'STRING' P3.
PSTR P1/P2                  PRINT 'STRING' P1/P2.
SEDIT P1                    EDIT 'STRING' P1.
TEDIT                       EDIT 'SOSRUN' FILE.
   FOR FOLLOWING EDITOR COMMANDS P2=NP SUPPRESSES OUTPUT; PARENTHETICAL INPUT
   STRINGS MAY BE REPLACED WITH STORED 'STRINGS' BY SPECIFYING P2=S1 AND P5=S2
   IN THE ABSENCE OF S1,S2,P2,P5 AN INPUT REQUEST IS PROMPTED.
A P1(S1)                    ADD STRING S1 TO NEXT P1 LINES.
B                           MOVE TO BOTTOM OF FILE.
C P1(S1)(S2)                LOCATE STRING S1 IN P1 LINES AND CHANGE TO S2.
D P1                        DELETE P1 LINES.
I P1(S1)                    INSERT P1 LINES OF STRING S1.
L P1(S1)                    LOCATE STRING S1 IN P1 LINES.
M P1(S1)                    MODIFY NEXT P1 LINES ACCORDING TO S1; IF S1 NOT SPECIFIED.
                            THE LINE IS PRINTED AND MODIFICATION INSTRUCTIONS ARE
                            RECEIVED ON NEXT LINE.
N P1                        MOVE P1 LINES DOWN FILE.
P P1                        PRINT P1 LINES.
T                           MOVE TO TOP OF FILE.
W                           PRINT SEQUENCE NUMBER OF PRESENT LINE.
GOTO P1                     MOVE TO LINE P1.
LNON                        ENABLE AUTO-LINE NUMBERING.
LNOFF                       DISABLE AUTO-LINE NUMBERING.
```

TWO AXIS GRAPHS
****

```
XAX P1                      SET X-AXIS ACCORDING TO VECTOR P1 AND DRAW.
YAX P1                      SET Y-AXIS ACCORDING TO VECTOR P1 AND DRAW.
PLOT P1*P4/P2               PLOT POINTS X-VECTOR=P1 AGAINST Y-VECTOR=P4 USING SYMBOL P2.
LINE P1*P4                  JOIN POINTS X-VECTOR=P1 PLOTTED AGAINST Y-VECTOR=P4 WITH LINE.
GRAPH P1*P4/P2              DRAW X-AXIS ACCORDING TO VECTOR P1 AND Y-AXIS ACCORDING TO
                            VECTOR P4 PLOTTING POINTS USING SYMBOL P2 JOINED BY A LINE.
SET P1                      SET MAX. AND MIN IN DATA-SET OF VECTOR P1.
ORDER P1/P2                 SET ELEMENTS OF VECTOR P1 IN ASCENDING OR DESCENDING(P1 -VE)
                            ORDER OF MAGNITUDE; VECTORS P2(EG. 235) ARE ALSO ORDERED
                            RETAINING POSITION OF ELEMENTS RELATIVE TO P1.
EGNA P1/P2=P3               USER SUPPLIED ROUTINE USING VECTOR P1 TO GENERATE NEW
                            VECTOR P3; IF P1=0 A VECTOR OF EQUALLY SPACED POINTS IS
                            CREATED IN P2 AND USED TO GENERATE P3.
EGNB P1/P2=P3               AS EGNA.
EGNC P1/P2=P3               AS EGNA.
```

MISCELLANEOUS
****

SIZE P1	ON GRAPHICS VDU- SET CHARACTER SIZE P1.
SKIP P1	ON GRAPHICS VDU- SKIP P1 LINES ON SCREEN.
NEW	ON GRAPHICS VDU- CLEAR PAGE.
TITLE P1(S1)	APPLY TITLE S1 TO SPECTRUM P1 OR TO MAIN DATA-SET(P1=0).
PDATA P1=P3	PRINT FORMATTED SELECTION OF MAIN DATA-SET ELEMENT VALUES; P1 CONTROLS QUANTITY; P3=DUMP SUPPRESSES OUTPUT.
PFILE/P2	PRINT CONTENTS OF 'DUMP' FILE; IF P2=R REWIND FILE AFTERWARDS.
PVAL P1/P2=P3*P4	PRINT P4 VALUES OF MAIN DATA-SET OR SPECTRAL DATA-SET(P1>0) STARTING AT VALUE P2; P3=DUMP SUPPRESSES OUTPUT.
PF(S1)	PERMANENT FILE OPERATING-SYSTEM STATEMENT S1 EXCECUTED FROM WITHIN PROGRAM.
CTIME	PRINT CENTRAL PROCESSOR SECONDS USED SINCE LOGON.
BELL	RING BELL.
XIN P1=P3	INPUT FIELD OR G-VALUE TO MAIN(P1=0) OR SPECTRAL(P1>0) DATA-SET USING X-WIRES; X-WIRES CONTROL CHARACTERS:- C=CONTINUE,D=DIFFERENCE,G=G-VALUE,E=END.
YIN P1=P3	AS XIN BUT X-WIRES INPUT IS A Y-MAGNITUDE.
HVAL P1/P2=P3	CONVERT FIELD VALUE P1/P2 TO G-VALUE AND PUT RESULT IN MAIN DATA-SET POSITION P3.
GVAL P1/P2=P3	CONVERT G-VALUE P1/P2 TO FIELD-VALUE AND PUT RESULT IN MAIN. DATA-SET POSITION P3.
COMPSET P1/P2=P3	SET COMPARISON POINTS FOR SPEC P1 OR MAIN DATA-SET(P1=0); P2=POSN,INTL,INTU; P3=BL,MAX,MIN,HS,HE OR NUMERIC FIELD.
HELP/P2	PROVIDE INFORMATION ABOUT THE PROGRAM OR ITS COMMANDS(P2).

APPENDIX B

A Variable Temperature Cryostat for Rapidly-Rotating Raman Samples.

For highly absorbing solid and solution Raman samples, intense local heating, which may lead to decomposition or solvent cavitation, can often be avoided by rapidly rotating the sample relative to the exciting laser beam. A device has been described which uses a rotating lens to circularly scan the laser beam across a static sample, the scattered light being collected by the same lens.[392] In the latter case it proves possible to study samples cryostated at low temperatures. The rotational mechanism and alignment of the optical components for this sample technique are, however, more complicated than for the conventional sample-spinning arrangement employed at ambient temperatures. A cryostat for spinning-samples is described here which is of fairly simple construction and which is easily optically aligned. Solid or solution samples may be rotated with several thousand r.p.m. at temperatures in the range ca. 100-300 K. The ability to use low temperatures may be essential when studying compounds which are not stable at room temperature, and for other samples which are very susceptible to thermal or photolytic decomposition by the laser beam,may allow the use of higher incident excitation power levels, leading to enhanced signal to noise ratio.

The main cryostat is a double surface evacuated container of Pyrex construction. Gaseous nitrogen, precooled by passage through a spiralled 5 mm copper tube immersed in liquid nitrogen refrigerant, flows continually

through the cryostat and around the sample, figure B.1. Controlled

dilution of the cooled N_2 with gas at ambient temperature allows a

wide range of intermediate temperatures to be selected to an accuracy

of ca. 1-2 K. Solid samples are prepared as thin 13 mm alkali-halide

compressed discs and held in contact with a brass heat sink by a nylon

retaining cap. Liquids are contained in 15 mm o.d. cylindrical quartz

cells. Both samples are spun by a small 10-20 V motor having ball-

race bearings and an extended axle. The motor is supported in a B19

side-arm of the cryostat. The exciting beam enters perpendicularly

Figure B.1. Cryostat, solution sample spinner and refrigeration method.
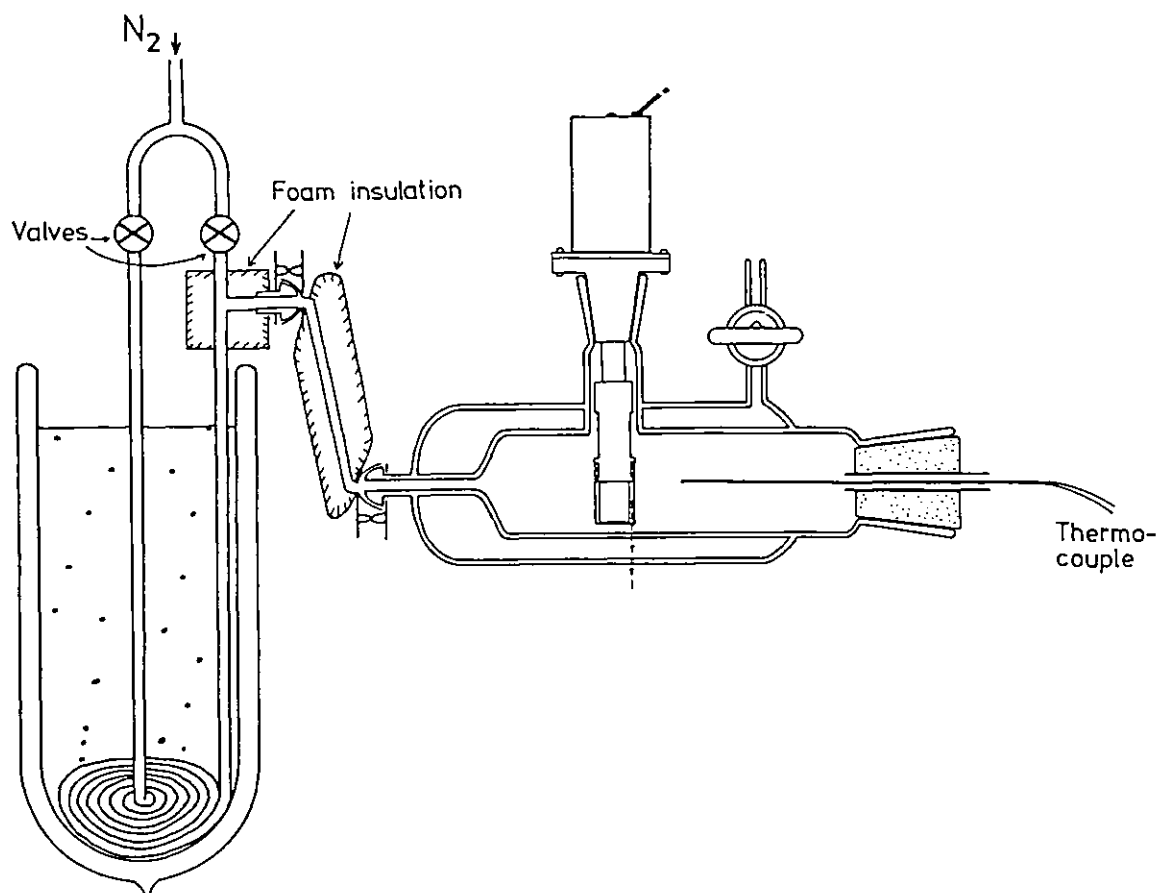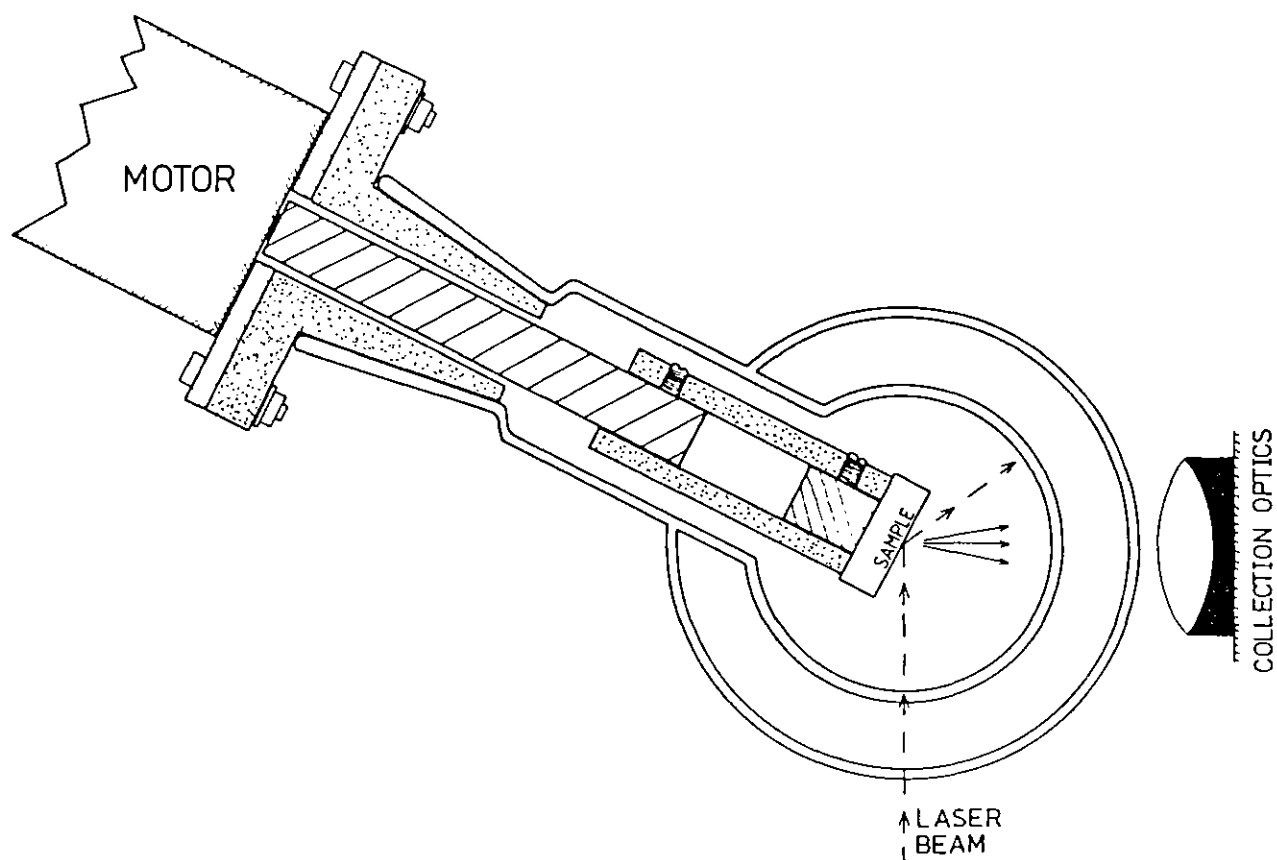
Figure B.2. Cross sectional view of cryostat and solid-sample spinner

through the side of the cryostat and Raman scattered light is collected

at 90° after further transmition through the cryostat wall. The

arrangement for solid samples is such that scattered light is trans-

mitted without distortion, being perpendicular to the glass wall, since

the sample is located on the axis of the cylindrical cryostat, Figure

B.2.

The cryostat has been used in this work to achieve greatly improved

S/N ratio in Raman spectra of the intensly absorbing [Et$_4$N][Fe(Ⅲ)(S$_2$-o-

xylyl)$_2$] and Cu(II)(RN-MeMe)$_2$ [R = Me, iBu] solids at ca. 130 K [Sections

4.2 and 5.5, Figures 4.4 and 5.16]. For Cu(II)(MeN-MeMe)$_2$ in solution,

where thermal instability would preclude measurements at room temperature,

Raman spectra have been obtained in acetone at ca. 200 K.
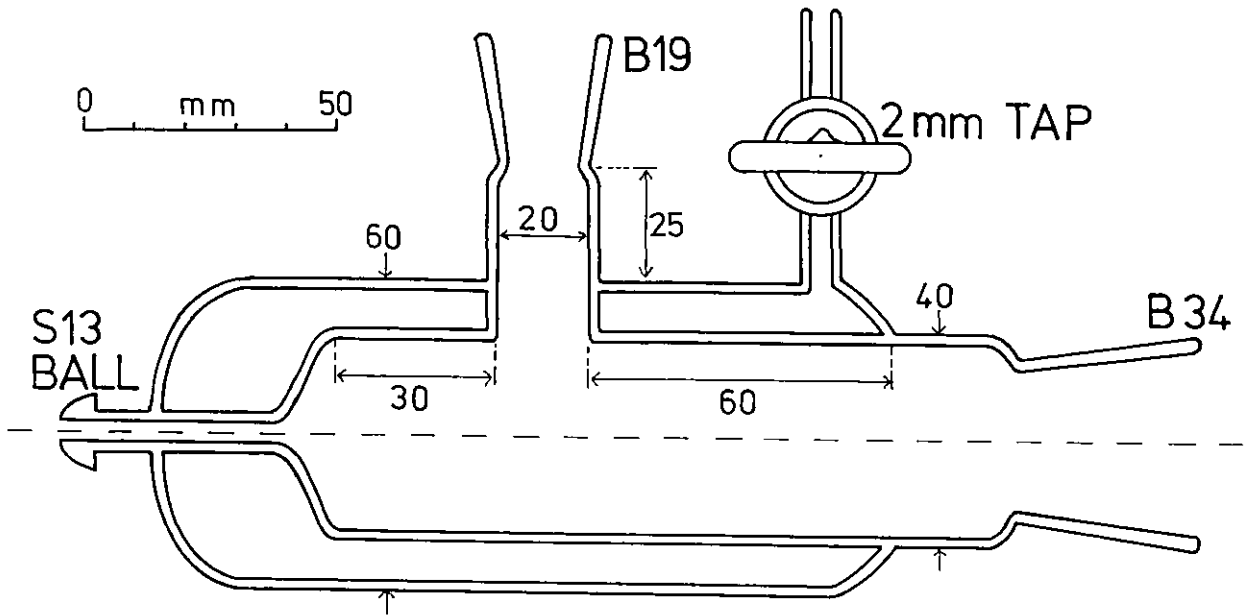
FIG. B.3   Pyrex cryostat body
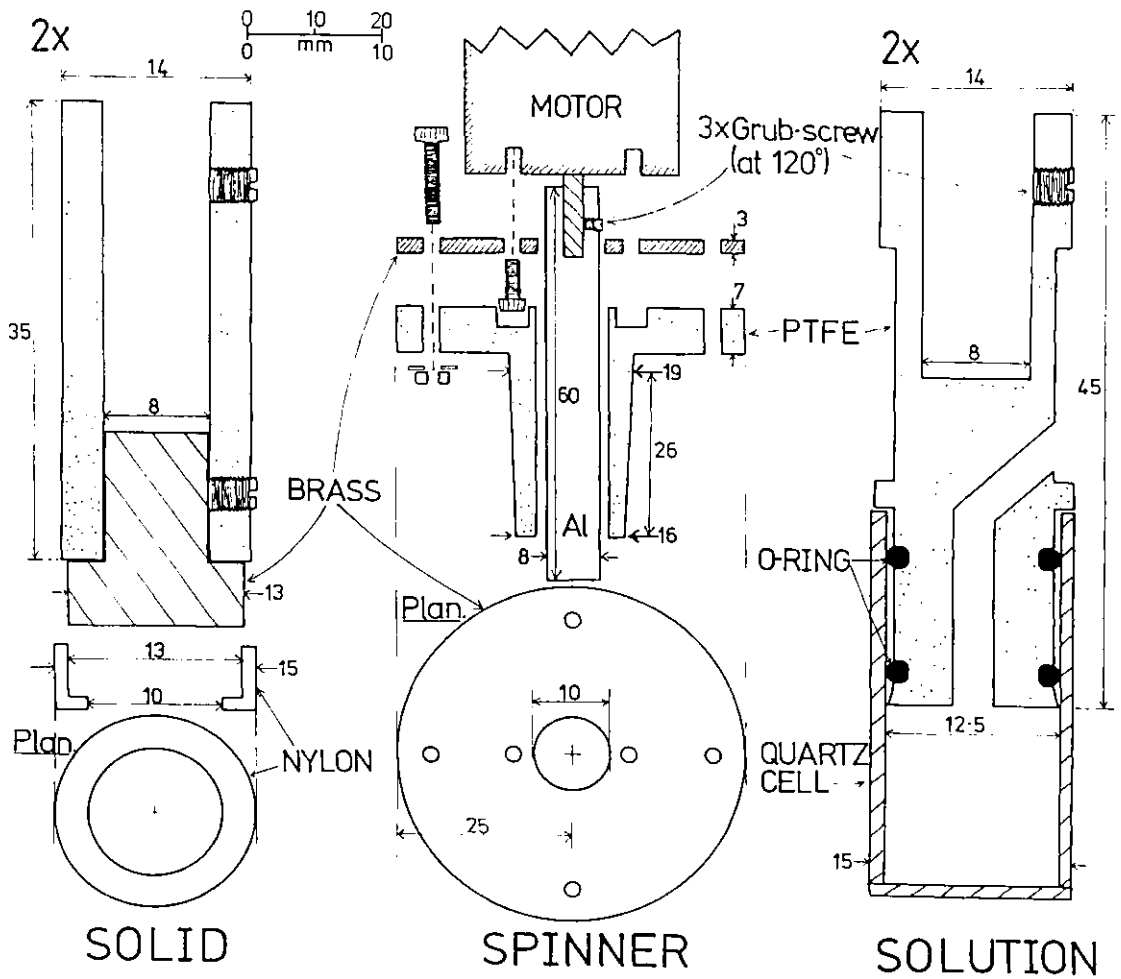
FIG. B.4   Details of the sample spinners.

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Like one, that on a lonesome road
Doth walk in fear and dread,
And having once turned round, walks on,
And turns no more his head;
Because he knows a fightful fiend
Doth close behind him tread.