

MAGNETIC RESONANCE STUDIES
OF SILVER AND RELATED METAL SYSTEMS

by

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A Thesis submitted for the degree of
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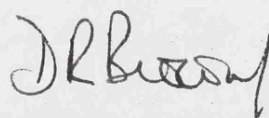


Statement

The work described in this thesis was carried out by the author in the Department of Chemistry of Leicester University during the period March 1974 to December 1976.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by references.

No part of this thesis is concurrently being submitted for another degree in this or any other University.



D.R. Brown

December 1976

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Chapter One

Introduction

Silver has the electronic configuration $\text{Kr}4\text{d}^{10}5\text{s}^1$. It exists as the monovalent cation in most of its compounds but there are a large number in which it is stable in the divalent 4d^9 form. The monovalent ion, Ag^+ , is diamagnetic but the paramagnetism of the Ag^{2+} ion and of silver atoms (Ag^0), and the favourable magnetic moment of the silver nucleus make them most suitable for study by Electron Spin Resonance (ESR).

Chemically prepared Ag^{2+} compounds and silver atoms do exhibit ESR spectra but for this work paramagnetic silver species have generally been produced by high energy irradiation of samples containing the silver(I) ion. The Ag^+ ion can act in many environments as both an electron source and trap and both Ag^{2+} and Ag^0 are frequently detected simultaneously, between them providing much information on the environment of the parent Ag^+ ion.

The ability of Ag^+ to capture electrons is utilised in the photographic process where silver halides are photolytically reduced to silver metal. The ESR of irradiated pure silver halides however, yields no information on the nature of the traps and sources of the photo-electrons¹, although there is speculation that clusters of silver ions rather than individual ions may be the primary electron traps.

With a view to clarifying the nature of these electron traps and holes, radiolytically produced silver centres have been studied in a range of media. Mixtures of silver halides and alkali halides are examined in Chapter Two and frozen solutions of the silver(I) ion in a range of protic and aprotic solvents in Chapter Three.

Irradiated silver nitrate, in contrast to the halides, exhibits a well resolved ESR spectrum²; the principal hole trap

is Ag^{2+} , and NO_3^{2-} , or more correctly AgNO_3^- , the major electron trap. In Chapter Five the products of irradiation of a range of other-d¹⁰ and-s²p⁶ metal nitrates are compared with those of silver nitrate.

The silver(I) ion is generally considered to solvate weakly and in water there is some doubt as to its solvation number. The unique results amongst the solvents used in Chapter Three for frozen aqueous silver(I) solutions give some indication as to how Ag^+ might be solvated in water. In Chapter Four NMR has been used to study silver(I) and other-d¹⁰ metal ions in water and methanol with the purpose of relating the solvation of the other-d¹⁰ cations, zinc, mercury and cadmium to that of the silver ion.

1.1 Principles of Electron Spin Resonance

This section is not intended as a full description of the fundamental theory of ESR. This is covered in a number of books³⁻⁹ on the subject. In this Section only those aspects of the theory that will be encountered in later chapters is discussed.

The Spin Hamiltonian

Electron spin resonance involves the absorption of energy during the stimulated inversion of an electron spin in a magnetic field; it is therefore natural to discuss the energies involved as eigenvalues of a Hamiltonian involving spin operators; this is referred to as the Spin Hamiltonian. The

General Hamiltonian describing the energy of an ion in a crystalline environment contains terms of widely ranging magnitudes, and it is by the application of Perturbation Theory that we can legitimately consider the Spin Hamiltonian in the absence of the other much larger terms that appear in the General Hamiltonian.

The Spin Hamiltonian is written:

$$\mathcal{H}_s = g\beta H \cdot S + S \cdot a \cdot I - g_N \beta_N H \cdot I . \quad 1.1$$

$g\beta H \cdot S$ is the Electronic Zeeman term describing the interaction between the electron angular momentum and the magnetic field. $S \cdot a \cdot I$ describes the magnetic interaction between an electron and a nucleus.

$g_N \beta_N H \cdot I$ is the Nuclear Zeeman term describing the interactions between the nuclear angular momentum and the applied field. The Nuclear Quadrupole term has been ignored. This term equals zero unless $I > \frac{1}{2}$ and even then its exclusion can readily be allowed for in the Spin Hamiltonian.

The g Tensor

If an electron is not associated with a magnetic nucleus then the Spin Hamiltonian reduces to:

$$\mathcal{H}_s = g\beta H \cdot S . \quad 1.2$$

g is the Landé g factor and equals 2.0023 for a free electron; H is the applied magnetic field vector; β is the Bohr Magneton and S is the Electron Spin Operator. In this system there are two possible spin states defined by their m_S quantum numbers. These are the $|\frac{1}{2}\rangle$ state and the $|\frac{-1}{2}\rangle$ state. Operating on these two spin states with the Spin Hamiltonian (1.2) yields two

energy levels separated by $g\beta H$. Interaction of an electron in one state with microwave radiation of the correct frequency will cause inversion of the spin; the resonance condition is thus defined:

$$h\nu = g\beta H. \quad 1.3$$

The value of g for an electron with no angular momentum other than that due to its spin is 2.0023; if an electron has orbital angular momentum in addition then the g value will vary from this 'free spin value'. The shifts in the resonance position associated with this g value variation are often small and to a first approximation may then be thought of as stemming from an additional small perturbing field arising from a very slight induced orbital motion. This adds to or subtracts from the external field giving a negative ($-\Delta g$) or a positive ($+\Delta g$) shift.

Clearly the g factor need not be isotropic and the symmetry of the g factor is defined by the symmetry of the molecular orbital the electron occupies. It is normally described by a tensor (defined with respect to a reference frame such that it is diagonal) and the Hamiltonian should be written:

$$\mathcal{H}_s = \beta \begin{pmatrix} H_x & H_y & H_z \end{pmatrix} \begin{bmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{bmatrix} \begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix}$$

$$\mathcal{H}_s = \beta \left[H_x g_{xx} S_x + H_y g_{yy} S_y + H_z g_{zz} S_z \right]. \quad 1.4$$

The magnitude of the g shift (Δg) from its free spin value and the symmetry of the g tensor depend on the type and symmetry of the orbital the unpaired electron occupies in its ground state and also on the nature of the excited state;

experimental g values are used to obtain information on these properties.

The Hyperfine Constant (a Tensor)

If an electron is associated with a magnetic nucleus then in addition to the external field the electron will experience a field associated with the magnetic moment of the nucleus. The Hyperfine Coupling Constant arises from the interaction between the electron and the nuclear magnetic moments.

a , like g , in the general case is orientation dependent and a tensor quantity, (normally diagonalised in the same reference frame as g), but in the treatment following, both g and a will be considered isotropic for simplicity.

The Spin Hamiltonian (1.1) can be expanded when the applied magnetic field is along the z direction:

$$\mathcal{H}_s = g\beta H S_z + a(S_x I_x + S_y I_y + S_z I_z) - g_N \beta_N H I_N \quad 1.5$$

and in terms of shift operators:

$$\mathcal{H}_s = g\beta H S_z + a \left[\frac{1}{2}(S_+ I_- + S_- I_+) + S_z I_z \right] - g_N \beta_N H I_N. \quad 1.6$$

A system of one unpaired electron associated with one nucleus with $I=\frac{1}{2}$ will be considered; to determine the energy levels associated with the system a set of basis states must be chosen; these are normally defined as $|m_S, m_I\rangle$ and for this particular system are:

$$|+\frac{1}{2}+\frac{1}{2}\rangle; |+\frac{1}{2}-\frac{1}{2}\rangle; |-\frac{1}{2}+\frac{1}{2}\rangle; |-\frac{1}{2}-\frac{1}{2}\rangle.$$

By operating on each of these states with the Hamiltonian (1.6) it is possible to obtain an energy matrix H , where:

$$H_{ij} = \langle i | \mathcal{H} | j \rangle. \quad |i\rangle \text{ and } |j\rangle \text{ are basis states.}$$

The matrix obtained is:

$$\begin{array}{c}
 |+\frac{1}{2}+\frac{1}{2}\rangle \\
 |+\frac{1}{2}-\frac{1}{2}\rangle \\
 |-\frac{1}{2}+\frac{1}{2}\rangle \\
 |-\frac{1}{2}-\frac{1}{2}\rangle
 \end{array}
 \begin{vmatrix}
 \frac{1}{2}(G-N+\frac{1}{2}a) & 0 & 0 & 0 \\
 0 & \frac{1}{2}(G+N-\frac{1}{2}a) & \frac{1}{2}a & 0 \\
 0 & \frac{1}{2}a & -\frac{1}{2}(G+N+\frac{1}{2}a) & 0 \\
 0 & 0 & 0 & -\frac{1}{2}(G-N-\frac{1}{2}a)
 \end{vmatrix}$$

where $G=g\beta H$ and $N=g_N\beta_N H$.

If a is small compared to G then the off diagonal elements can be neglected. If the Nuclear Zeeman term is also taken as being small then the roots of the Secular Determinant yield four energy levels.

$$\begin{aligned}
 E_1 &= \frac{1}{2}g\beta H + \frac{1}{4}a \\
 E_2 &= \frac{1}{2}g\beta H - \frac{1}{4}a \\
 E_3 &= -\frac{1}{2}g\beta H + \frac{1}{4}a \\
 E_4 &= -\frac{1}{2}g\beta H - \frac{1}{4}a
 \end{aligned}
 \tag{1.7}$$

The allowed transitions are given by:

$$\begin{aligned}
 h\nu &= E_1 - E_4 = g\beta H + \frac{1}{2}a \\
 h\nu &= E_2 - E_3 = g\beta H - \frac{1}{2}a.
 \end{aligned}
 \tag{1.8}$$

Since in the ESR experiment the microwave frequency is kept constant and the magnetic field swept the resonance field positions for these two transitions are given by:

$$\begin{aligned}
 H_1 &= H_0 - \frac{1}{2}A \\
 H_2 &= H_0 + \frac{1}{2}A
 \end{aligned}
 \tag{1.9}$$

where $H_0 = h\nu/g\beta$ and $A = a/g\beta$. (A is the hyperfine constant measured in Gauss).

This situation represents the 'high field assumption'. The hyperfine constant A can be measured directly from the separation of the two transitions in Gauss and g can be calculated from the midpoint of the two transitions. At high field coupling between S and I is broken down and both S and I are quantised independently along the axis of H , and m_S and m_I are said to be 'good' quantum numbers. The basis states described by $|m_S, m_I\rangle$ are then the true basis states and S and I can be replaced in the Spin Hamiltonian (1.1) by m_S and m_I . If, however, I and S are not fully decoupled as occurs at low field and $a/2$ is not small enough to be ignored, the basis states chosen using m_S and m_I are not the real basis states. In this situation a new set of energy levels emerge as roots of the Secular Determinant and the ESR parameters cannot then be lifted directly from the experimentally observed resonance field position. Calculations of the correction necessary to the experimental data appear in the appendices.

The hyperfine tensor A is not always isotropic and in general is made up of an isotropic and an anisotropic component. For the frequently encountered axially symmetric system the hyperfine tensor can be written:

$$\begin{bmatrix} A_{\parallel} & 0 & 0 \\ 0 & A_{\perp} & 0 \\ 0 & 0 & A_{\perp} \end{bmatrix} = \begin{bmatrix} A_{\text{iso}} + 2B & 0 & 0 \\ 0 & A_{\text{iso}} - B & 0 \\ 0 & 0 & A_{\text{iso}} - B \end{bmatrix} \quad 1.10$$

where $A_{\parallel} = A_{zz}$ and $A_{\perp} = A_{xx} = A_{yy}$.

The isotropic contribution A_{iso} arises from the Fermi contact interaction and is related directly to the spin density in an s or a σ type orbital, only orbitals of this type having non zero wave functions at the nucleus. The theoretical isotropic

hyperfine splitting for an atom with a single unpaired electron in an ns orbital is given by³;

$$A_{\text{iso}}^0 = -\left(\frac{8\pi}{3}\right)g_N\beta_N h \left|\psi_{\text{ns}}^2(0)\right|^2 \quad (\text{Gauss}) \quad 1.11$$

and from the experimental value of A_{iso} the electron density in the ns orbital can be found from³:

$$A_{\text{iso}} = A_{\text{iso}}^0 \times c_{\text{ns}}^2 \quad 1.12$$

where c_{ns}^2 = spin density in the ns orbital.

The anisotropic contribution 2B arises from the dipolar interaction between the electron and the nuclear magnetic dipole moments. This quantity is related to the spin density in a p orbital by an equation analogous to equation 1.12. The theoretical value for $2B^0$ is given by³:

$$2B^0 = \frac{4}{5}g_N\beta_N \langle r^{-3} \rangle_{\text{np}} \quad (\text{Gauss}) \quad 1.13$$

By extracting A_{iso} and 2B from the hyperfine tensor it is usually possible to identify the type of orbital an electron occupies, and in the case of a paramagnetic species containing more than one nucleus the values of A_{iso} and of 2B corresponding to the coupling to each nucleus make it possible to identify which atomic orbitals each atom in a molecule contributes to the molecular orbital in which the unpaired electron resides.

In the following Chapters, ESR parameters have been obtained from experimental resonance field positions using the solutions to the eigenvalue equation that appear in Appendix One.

1.2 Experimental details of the ESR measurements

The Spectrometer

Most of the spectra in Chapters Two, Three and Five were run either on a Varian E3 or a Varian E109 spectrometer. Both these instruments operate in the X-band region of the microwave spectrum ($\nu=9$ GHz) and both employ 100 KHz field modulation and phase sensitive detection in their normal modes of operation, producing a first derivative of the absorption spectrum. The spectra were calibrated using a suitable g marker in the sample such as DPPH and the microwave frequency could be measured accurately using a Hewlett Packard 5246L frequency counter.

X-band spectra of samples at 77K were run using a quartz Dewar flask containing liquid nitrogen inserted in the cavity. The annealing experiments were carried out by decanting the liquid nitrogen and allowing the sample to warm up slowly in the bottom of the Dewar flask; when any significant changes in the spectrum were observed the sample was recooled with liquid nitrogen. More precise control of the temperature from about 85K upwards was possible by the use of a Variable Temperature Accessory in which nitrogen gas, first cooled by passing through a coil immersed in liquid nitrogen was heated to a preset temperature and blown over the sample, normally sealed in a glass tube, in the spectrometer cavity. Spectra were also run at 4.2K (or just above) by blowing helium gas from liquid helium over the sample, again sealed in a glass tube in the sample cavity.

Spectra at Q-band (35 GHz) frequency were recorded on an instrument built by Mr J.A. Brivati and described fully elsewhere¹⁰.

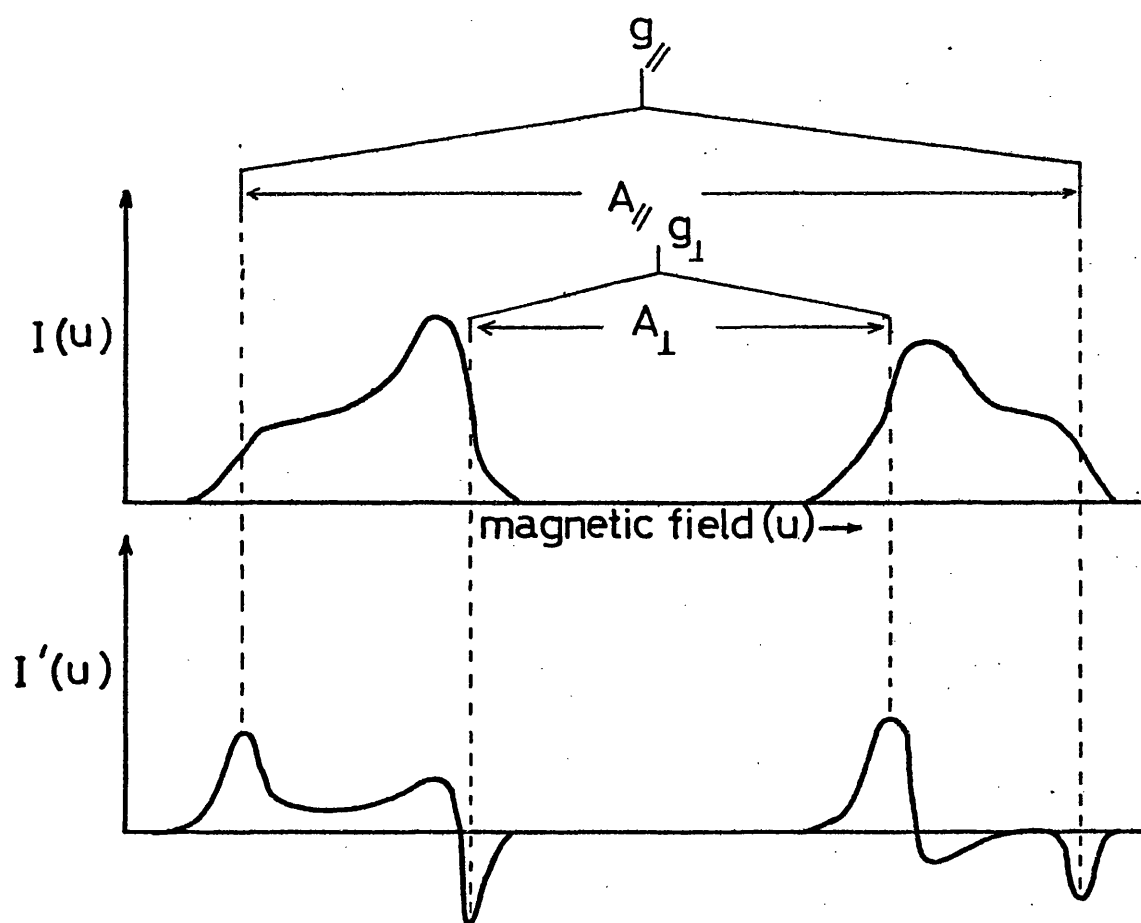


Figure 1.1 Absorption and first derivative curves for the powder spectrum of an axially symmetric radical containing one magnetic nucleus, $I=\frac{1}{2}$.

Sample Irradiation

The technique used to prepare the radicals for this study was to expose diamagnetic material to ^{60}Co γ rays in a Vickrad source. This source provided a dose rate of about 1.6 M.Rad per hour. The samples were irradiated at 77K by lowering a Dewar vessel of liquid nitrogen containing the samples into the Gamma cell.

Powder spectra

The use of powder (glassy or polycrystalline) samples for ESR studies is a simpler and a more convenient method for

studying a sample than to use a single crystal. Often, because of the nature of the material being studied (frozen solutions for example) a powder spectrum is the only type that can be obtained.

The analysis of powder spectra is dealt with by Atkins and Symons⁹ and by Kneubuhl¹¹ but Figure 1.1 shows a typical spectra for a radical with axially symmetric g and A tensors containing one magnetic nucleus with $I=\frac{1}{2}$ and it can be seen from this figure, assuming I and S are decoupled, how the A and g values are extracted from the spectrum.

Powder spectra arising from more than one paramagnetic species often cannot be assigned unambiguously because of their complexity. In such cases there are many parameters that can be adjusted such as the γ dose given to the sample, the temperature, the microwave power and the use of Q-band instead of X-band frequency so that the features arising from each type of radical can be recognised and picked out of a complicated spectrum.

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Chapter Two

Electron Spin Resonance studies

of Silver doped Alkali Halides

According to a widely held point of view, the basis of the modern photographic process is the photochemical dissociation of silver halide salts¹.

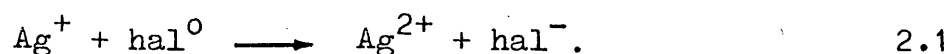
When photons are absorbed in silver halide crystals, electron-hole pairs are first formed. The electrons may then combine with silver ions in interstitial or other suitable defect sites with the formation of silver atoms. It is generally supposed that it is this process that leads to the formation of the latent image.

Mechanisms have been suggested to explain this behaviour by Mitchell and Mott^{2,3} and they suggest that deep traps for photo-electrons of the type Ag_4^+ and Ag_3^+ arise on exposure of a silver halide crystal to light and it is from these centres that the latent image is formed. Species of this type are frequently paramagnetic and might be expected to be detectable by ESR. Indeed, Ag_2^+ , Ag_3^{2+} and Ag_4^{3+} have been detected in frozen solutions in the work reported in Chapter Three and by Forbes and Symons⁴. Unfortunately, attempts to detect such centres in pure silver halides have failed and irradiated pure silver halides in general have been shown to provide quite uninformative ESR spectra⁵.

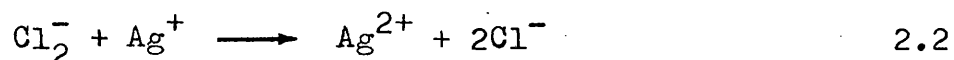
When silver chloride is dilutely doped into potassium chloride and the crystal exposed to X or γ rays at 77K silver atoms (Ag^0) are formed and have been detected by ESR⁶. It was hoped in this work that this technique of doping silver halides could be used to get a better idea of the nature of the electron traps in photolysed silver halides.

It is known that the hole left following expulsion of a photoelectron is equivalent to a halogen atom at the surface of a silver halide crystal because for instance, bromine is

evolved on photolysis of a silver bromide crystal⁷, but inside the crystal at low temperatures it is thought that the hole may exist as Ag^{2+} , the self trapped hole. Although Ag^{2+} has not been detected by the ESR of irradiated pure silver halides, silver chloride crystals doped with suitable electron traps such as sulphide, selenide or ferric ions do yield the Ag^{2+} spectrum⁸. The formation of Ag^{2+} in preference to halogen atoms within the crystal reflects the effect the crystal field has on the orbital energies of the ions. The energy level of a 4d electron of a silver ion in the crystal lattice is higher than for the ion in a vacuum because of the surrounding negatively charged ions. Conversely the 3p level of a lattice chloride ion is lower than for the ion in a vacuum. Thus the chloride 3p level is lower than the 4d of the silver and the electron is associated with the chloride and the hole with the silver. The process can be represented by:



The hole trap formed in $\text{KCl}:\text{AgCl}$ crystals is the familiar V_K centre, Cl_2^- . Warming up demonstrates the stability of Ag^{2+} in a crystal lattice as the Cl_2^- ESR signal diminishes to be replaced by the Ag^{2+} signal, Cl_2^- gaining sufficient mobility to move to and react with an Ag^+ impurity ion.



It appears, therefore, that the major electron loss centre in silver halides may be the Ag^{2+} ion and there is ESR evidence strongly in favour of this idea^{6,8}. The nature of the electron trap centre is less clear however and it was primarily for this reason that this extension to the study of silver doped alkali

halides was carried out.

2.1 Experimental Details

Silver chloride and bromide were prepared by precipitation from an aqueous solution of silver nitrate or perchlorate using an appropriate alkali halide solution. The precipitate was washed with deionised water several times and recrystallised from concentrated ammonia solution. After further washing the precipitate was dried at ca. 60°C. In addition, silver halides of 99.999% purity provided by Koch-Light Ltd. were used. Alkali halides were of Analar grade and were all recrystallised from water before being used. Silver fluoride was prepared from silver carbonate and hydrofluoric acid as described by Anderson, Bak and Hillebert⁹. All silver salts were handled under safe-light conditions. Trace amounts of nitrate ion, found in virtually all the silver halides used were very difficult to remove and ESR spectra showing nitrate ion radiation damage products invariably arose. It was assumed, however, that the use of high purity and recrystallised reagents would keep the impurity level down to a tolerable minimum.

The silver doped alkali halides were prepared from the melt. The alkali halide and silver halide were weighed out to the required composition and then ground up together. The powder was then melted in a silica glass tube under nitrogen in a vertical tubular furnace as shown in Figure 2.1. The furnace temperature was maintained at ca. 20° above the melting point of the alkali halide using a C.N. Instruments Proportional Temperature Controller. The sample was maintained above

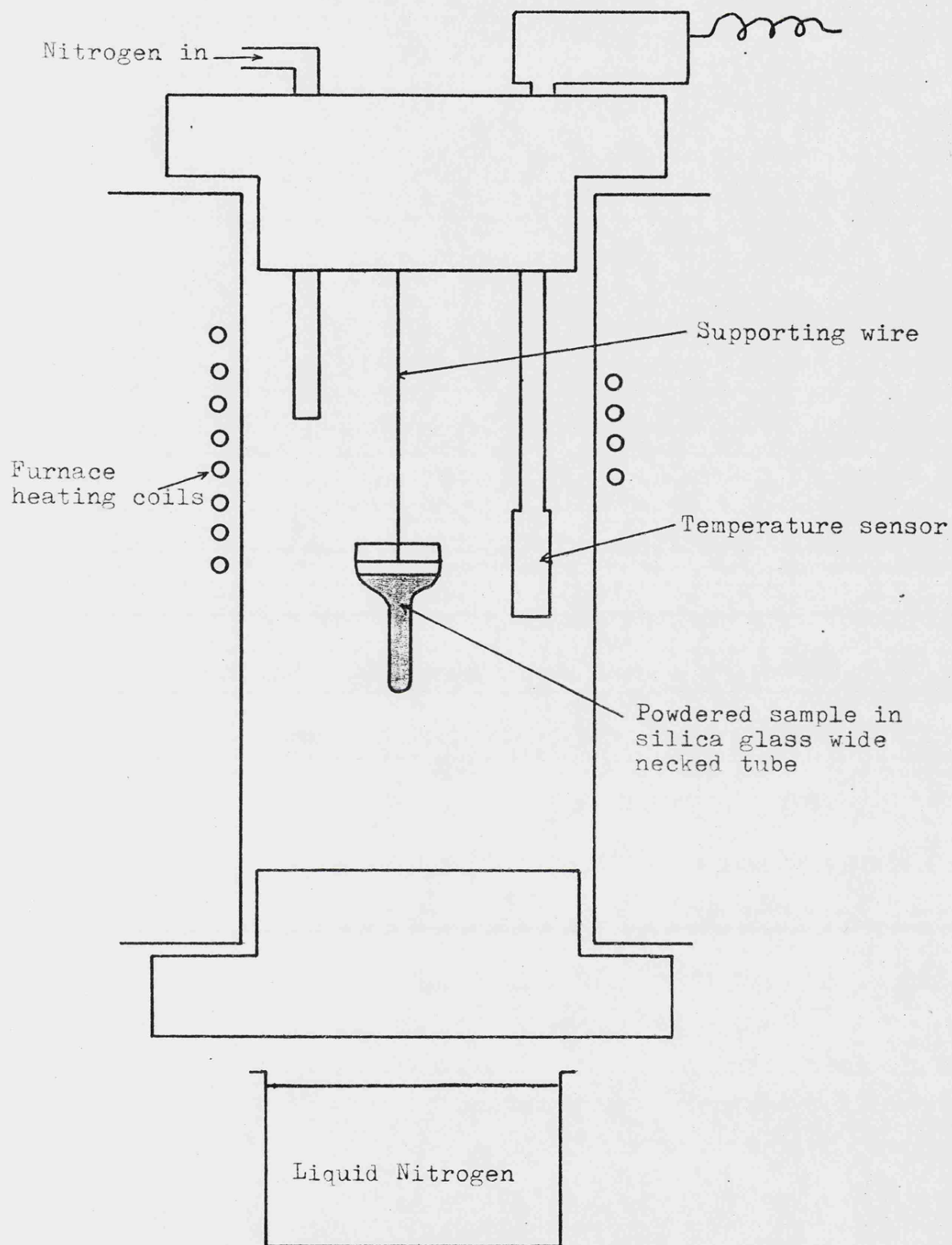


Figure 2.1 Experimental apparatus for melting and freezing quickly silver halide/alkali halide mixtures

its melting point for an hour and then it was very rapidly frozen by releasing the supporting wire and allowing the glass tube containing the molten solid to fall into liquid nitrogen in an insulated vessel. The tube was then annealed to room temperature, the glass broken away and the sample ground to a fine powder. This technique was used to avoid phase separation as the melt cooled down; KCl:AgCl mixtures for instance, tend to separate into a KCl rich phase (as studied by Delbecq et al⁶) and an AgCl rich phase, and although for this particular system the rapid quenching did not prevent this happening, mixtures of NaCl:AgCl could be prepared by this method for the complete AgCl mole fraction (MF) range. It was surprising that no other mixtures could be made in the intermediate concentration range; it seems reasonable to suppose that the similarity in the lattice parameters of NaCl and AgCl¹⁰ enables the mixture to be stably maintained in the solid phase and it might be expected that NaBr:AgBr mixtures would be equally stable but this does not seem to be the case.

The homogeneity of these solid mixtures was determined from their X-ray powder photographs. These were compared with those from powders of the constituents; a homogeneous mixture gave rise to a new powder photograph whereas phase separation was characterised by the superimposition of two photographs similar to those of the constituent materials.

Silver fluoride dopes had to be prepared in a platinum crucible and consequently the rapid quenching technique was not applicable. Dilute KF:AgF mixtures were prepared successfully using this method but it was uncertain whether Ag^+ could be incorporated into the NaF lattice. ESR results indicate that it might not have been.

The following mixtures were prepared for this study:

NaCl:AgCl - all concentrations.

KCl:AgCl - impurity level silver concentration only.

KBr:AgBr - " " " " "

NaBr:AgBr - " " " " "

KF:AgF - " " " " "

Silver doped alkali iodides could not readily be prepared although Mel'nikov et al.¹¹ do appear to have prepared and studied them.

Attempts to grow single crystals of KBr and NaBr containing AgBr from aqueous solution were also unsuccessful.

All the ESR spectra reported are of powdered samples; all samples were irradiated with ^{60}Co γ rays either at 77K or at room temperature and generally doses of about 15 M.Rads were given at 77K and about 30 M.Rads at room temperature. Photolysis using visible and UV light was carried out on all the powders made at both 77K and room temperature but this process rarely yielded sufficient paramagnetic products to produce an ESR spectrum; where it did it is reported.

A difficulty was encountered when high silver concentration NaCl:AgCl mixtures were studied. When samples containing ~ 0.7 MF $[\text{Ag}^+]$ were irradiated at low temperature and then held in the spectrometer cavity it was not possible to tune the microwave bridge, the sample appeared to be absorbing too much microwave power. This characteristic was directly associated with the high field $g=1.891$ feature discussed later and when it was lost by annealing the bridge could be tuned normally.

2.2 Results and Discussion

Firstly the processes that occur in KCl:AgCl crystals after exposure to X or γ rays at 77K as studied by Delbecq et al.⁶ will be outlined and then the ESR results for the other systems studied here will be compared to those from the KCl:AgCl system.

To aid the interpretation of the spectra the magnetic properties of the more important nuclei studied are summarised in Table 2.1.

Table 2.1 Magnetic properties of silver, chlorine, bromine and fluorine nuclei

Nucleus	Isotopic Abundance	Nuclear Spin	Magnetic Moment*
^{109}Ag	48.7 %	$\frac{1}{2}$	-0.130
^{107}Ag	51.3	$\frac{1}{2}$	-0.113
^{35}Cl	75	$\frac{3}{2}$	0.821
^{37}Cl	25	$\frac{3}{2}$	0.683
^{79}Br	51	$\frac{3}{2}$	2.099
^{81}Br	49	$\frac{3}{2}$	2.263
^{19}F	100	$\frac{1}{2}$	2.627

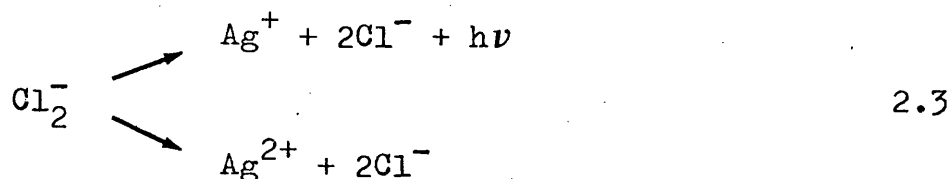
*in multiples of the Nuclear Magneton

KCl:AgCl exposed to γ rays at 77K

The formation of the two species, Cl_2^- and Ag^0 , as detected by ESR accounts for essentially all the trapped electrons and holes; electrons produced by the γ rays move through the conduction band and are captured by Ag^+ forming Ag^0 . The hole

associated with the electron is thought to move only a short distance before being captured to form Cl_2^- .

Warming the crystal or powder to 208K allows Cl_2^- to migrate and either it encounters Ag^0 in which case both are lost forming Ag^+ and 2Cl^- or it reacts with Ag^+ forming trapped Ag^{2+} and Cl^- .



A powder ESR spectrum of the $\text{KCl}:\text{AgCl}$ system following low temperature irradiation and an anneal to 208K showing Ag^{2+} features and reduced Ag^0 features appears in Figure 2.2.

Further warming of the crystal to 373K results in the concurrent disappearance of both Ag^0 and Ag^{2+} ; it is thought that this mutual annihilation occurs when Ag^0 releases an electron into the conduction band which is then captured by Ag^{2+} .

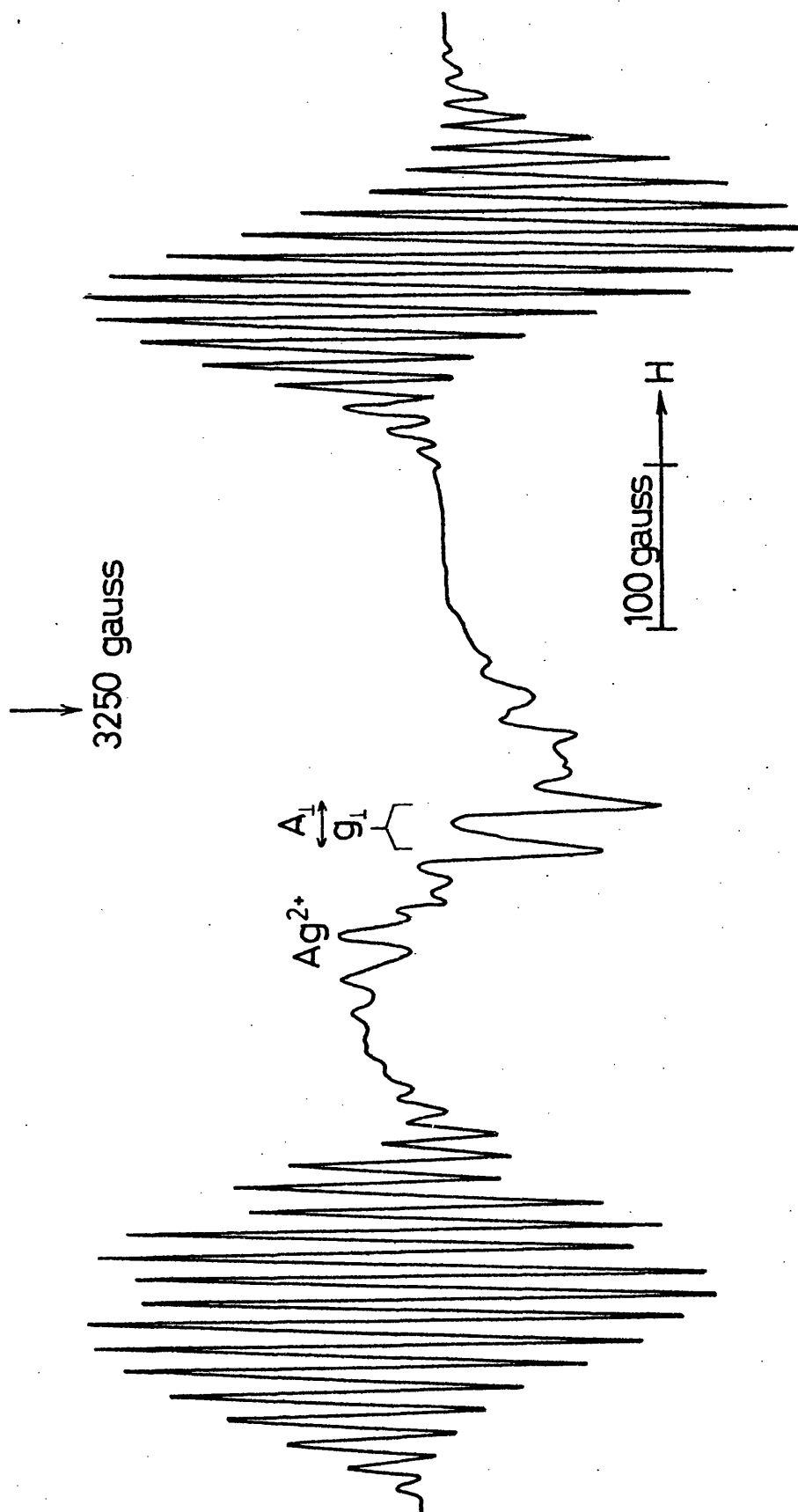
The paramagnetic silver centres produced in this system are Ag^0 and Ag^{2+} . A few salient features of these two species are summarized below:

Ag^0 :-

The silver atom is formed in a substitutional cationic lattice site. The unpaired electron resides in a molecular orbital composed predominantly of a silver 5s atomic orbital with contributions from the 3p orbitals of six surrounding chloride ligands arranged octahedrally around the silver ion. The electron spin is delocalised onto the chloride ligands to an extent of approximately 1.3% of the electron spin on each.

ESR parameters obtained in this study from the powder spectrum of Ag^0 agree within experimental error with those

Figure 2.2 The ESR powder spectrum of KCl:AgCl at 77K following low temperature irradiation and annealing showing chlorine SHFS on the Ag^0 features and on the Ag^{2+} perpendicular features. The Ag^{2+} parallel features are hidden under the $\text{Ag}^0(m_I = -\frac{1}{2})$.



found by Delbecq⁶ and are as follows:

$$^{109}\text{Ag}^0 \quad g=2.000\pm0.003 \quad A_{\text{iso}}(\text{Ag})=-640\pm5 \text{ G} \quad A_{\text{iso}}(\text{Cl})=13.3\pm0.2 \text{ G}$$

$$^{107}\text{Ag}^0 \quad g=2.000\pm0.003 \quad A_{\text{iso}}(\text{Ag})=-557\pm5 \text{ G} \quad A_{\text{iso}}(\text{Cl})=13.3\pm0.2 \text{ G}$$

Any anisotropy in the chlorine super hyperfine structure (SHFS) is within the line width of a powder spectrum so only A_{iso} values are quoted.

Ag^{2+} :-

The electronic ground state of Ag^{2+} is $-4d^9$ or a 2D state. An octahedral crystal field splits the D level into an orbital triplet and an orbital doublet, the doublet being of higher energy. Jahn Teller¹² distortion of the lattice may then occur, splitting this triplet and doublet further. The doublet corresponds essentially to the d_z^2 and the $d_{x^2-y^2}$ silver atomic orbitals and the unpaired electron resides in one of these, depending on the nature of the distortion. The ESR parameters found by Delbecq⁶ and reproduced in this work indicate that the electron is in a $d_{x^2-y^2}$ rather than a d_z^2 orbital and therefore Jahn Teller distortion must occur by extension of two axial Ag-Cl bond lengths and the compression of four equatorial Ag-Cl bond lengths. The ESR parameters indicate that there is a hyperfine interaction with the nuclei of four chloride ligands in the plane perpendicular to the symmetry axis and the crystal study⁶ shows hyperfine interaction with two chlorine nuclei in the direction of the symmetry axis. The ESR parameters for Ag^{2+} obtained by Delbecq are as follows:

$$g_{//} = 2.193 \pm 0.003$$

$$g_{\perp} = 2.035 \pm 0.003$$

$$A_{//}(\text{Ag}) = -38 \pm 2 \text{ G}$$

$$A_{\perp}(\text{Ag}) = -32 \pm 2 \text{ G}$$

$$A_{\perp}(\text{Cl}) \cong 5 \text{ G}$$

$$A_{//}(\text{Cl}) = 32 \pm 2 \text{ G}$$

Warming the powdered samples up results in loss of the resolved parallel and perpendicular features and they are replaced by a broad isotropic singlet at approximately $g=2.09$. This is due to the dynamic nature of the Jahn Teller distortion. The orientation of each Ag^{2+} and its ligands is frozen in at 77K but at higher temperatures the distortion can resonate about the x, y and z axes. The Ag^{2+} unpaired electron then exhibits an average g value, and if resolution allowed, would be seen to be delocalised onto six equivalent chloride ligands. The well resolved spectrum associated with the frozen orientation showing parallel and perpendicular features is recovered when the powder is recooled to 77K.

Similar ESR parameters have been obtained by Höhne and Stasiw⁸ for Ag^{2+} formed by irradiation of an AgCl crystal doped with suitable electron trapping agents. They claim that Ag^+ ions, well removed from the impurity centres in the crystal, act as hole traps, in other words Ag^+ ions in an environment no different from that in pure silver chloride. This is in contrast to the Ag^+ ion in KCl:AgCl which is an impurity centre acting as a hole trap. The parameters for Ag^{2+} found in AgCl:S,Se are:

$$g_{//} = 2.165 \pm 0.002$$

$$g_{\perp} = 2.041 \pm 0.001$$

$$A_{//} = -35 \pm 2 \text{ G}$$

$$A_{\perp}(\text{Ag}) = -23 \pm 2 \text{ G}$$

$$A_{//}({}^{35}\text{Cl}) = 32 \pm 2 \text{ G}$$

$$A_{//}({}^{37}\text{Cl}) = 27 \pm 2 \text{ G}$$

KCl:AgCl exposed to γ rays at room temperature

Ag^0 is again found as the principal electron trap centre having ESR parameters identical with those of Ag^0 formed at 77K. Correlation of ESR measurements with optical absorption data has led to the identification of two further types of silver atom by Mel'nikov et al^{13,14} which are formed by subsequent UV or visible irradiation into specific absorption bands.

Ag_f^0 :-

This centre comprises a neutral silver atom in a cationic site adjacent to an anionic vacancy.

$$g_{\text{iso}} = 1.998 \pm 0.002 \quad A_{\text{iso}}(^{109}\text{Ag}) = -466 \pm 3 \text{ G}$$

Ag_a^0 :-

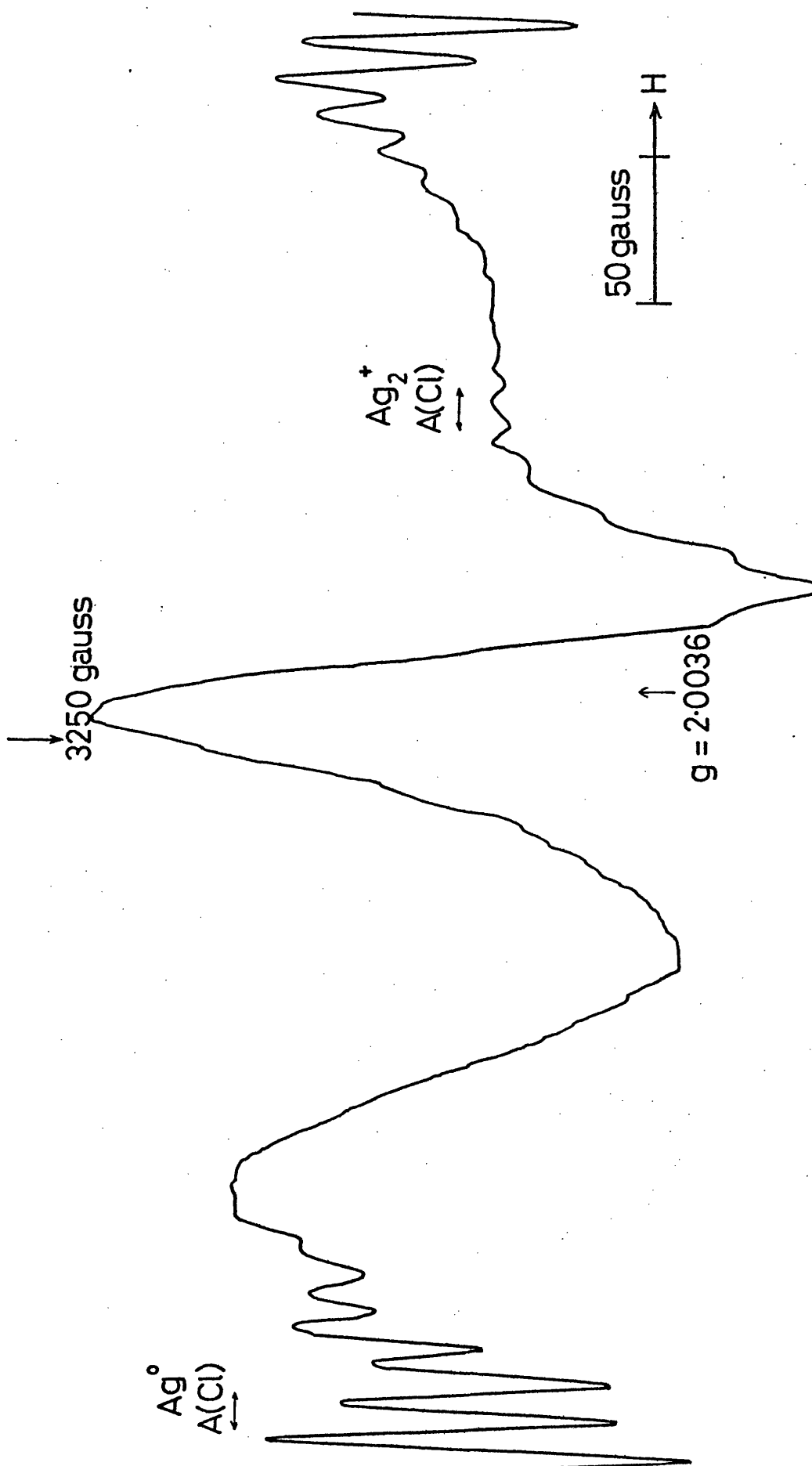
This is postulated as being a neutral silver atom at an anionic site.

$$g_{\text{iso}} = 1.997 \pm 0.002 \quad A_{\text{iso}}(^{109}\text{Ag}) = -515 \text{ G}$$

In addition, Ag_2^+ is detected in the KCl:AgCl system after room temperature irradiation. It has been identified by Zhitnikov¹⁵ who used isotopically enriched silver compounds. In this study enriched compounds were not used which means resolution is poor and the spectrum complex for any species containing more than one silver nucleus but in Figure 2.3 the resolved SHFS on the central Ag_2^+ feature from chloride ligands can be seen. The similarity in superhyperfine coupling constants for chloride coupled to Ag_2^+ and to Ag^0 strongly indicates that the Ag_2^+ species occupies one cationic site and is probably

Figure 2.3 The ESR powder spectrum of $\text{KCl}:\text{AgCl}$ at room temperature following room

temperature irradiation showing the chlorine SHFS on the Ag_2^+ central feature and the dynamically broadened Ag^{2+} isotropic line at $g=2.009$.



surrounded by six chloride ligands in a similar way to Ag^0 .

SHF coupling constants to Cl are as follows:

Ag_2^+ (ref.15) c.f.	Ag^0
$A_{\text{iso}} = 15 \pm 1 \text{ G}$	$A_{\text{iso}} = 13.3 \pm 0.2 \text{ G}$
$2B = 1.9 \pm 0.5 \text{ G}$	

That aggregates of more than two silver nuclei have not been detected in this system reinforces the idea that Ag_2^+ is stabilised in a single cationic lattice site; steric constraints would prevent the formation of larger aggregates.

The hole trap is Ag^{2+} after room temperature irradiation. This is expected from the behaviour of crystals that have been irradiated at 77K and subsequently annealed.

NaCl:AgCl exposed to γ rays at 77K

NaCl:AgCl mixtures with a low silver content (0.02 MF AgCl) behave similarly on low temperature irradiation to the analogous potassium chloride mixtures. Ag^0 and Cl_2^- are the initial products and on warming Ag^{2+} becomes the major hole trap replacing Cl_2^- . The resolution of the ESR spectra, however, is reduced because of the higher magnetic moment of ^{23}Na over ^{40}K .

ESR parameters for Ag^0 and Ag^{2+} derived from the powder spectrum are as follows:

Ag^0	$g_{\text{av}} = 2.000 \pm 0.005$	(Separate resonances from
	$A_{\text{av}} = -590 \pm 20 \text{ G}$	the individual silver
	$A(\text{Cl}) = 24 \pm 5 \text{ G}$	isotopes are not resolved)

$$\begin{array}{lll}
 \text{Ag}^{2+} & g_{//} = 2.197 \pm 0.002 & g_{\perp} = 2.041 \pm 0.002 \\
 & A_{//}(\text{Ag}) = -36 \pm 2 \text{ G} & A_{\perp}(\text{Ag}) = -27 \pm 2 \text{ G} \\
 & A_{\perp}(\text{Cl}) \leq 10 \text{ G} & A_{//}(\text{Cl}) = 32 \pm 5 \text{ G}
 \end{array}$$

These results agree with those of Sierro¹⁶ who studied similar mixtures as single crystals. The powder ESR spectrum of NaCl:AgCl following low temperature irradiation and annealing appears in Figure 2.4 and shows features assigned to Ag^{2+} and to the depleted concentration of Ag^0 .

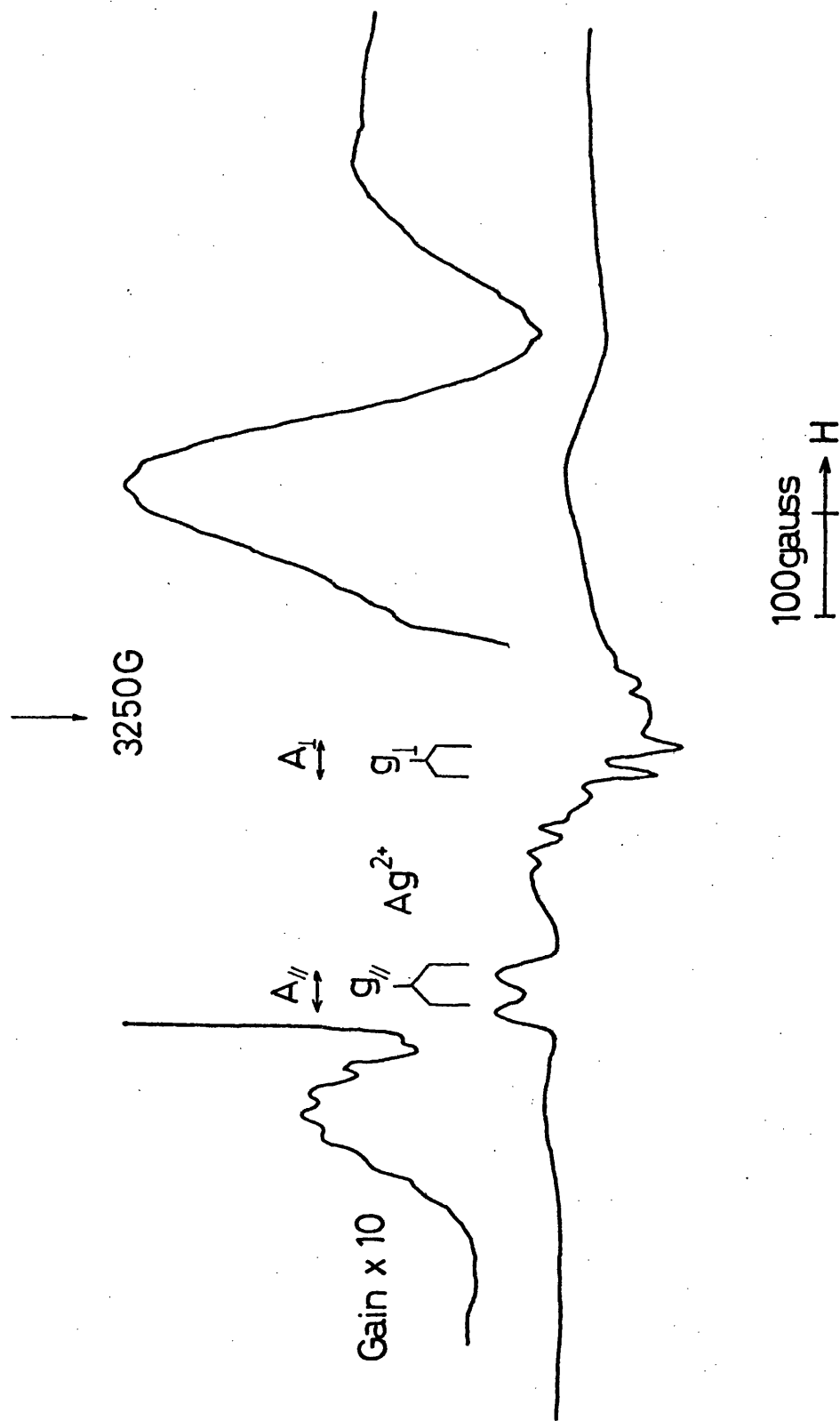
On low temperature irradiation of mixtures containing more than 0.02 MF AgCl the initial hole trap is Ag^{2+} . The ESR parameters for this species are essentially similar to those of Ag^{2+} formed as a secondary product in the more dilute systems except that $g_{//}$ tends to decrease slightly (presumably towards the value found by H6hne and Stasiw⁸) as the silver concentration $[\text{Ag}^+]$ is increased. The parameters for Ag^{2+} in a mixture containing 0.62 MF AgCl are:

$$\begin{array}{lll}
 g_{//} = 2.185 \pm 0.005 & g_{\perp} = 2.040 \pm 0.002 & \\
 A_{//}(\text{Ag}) = -35 \pm 2 \text{ G} & A_{\perp}(\text{Ag}) = -27 \pm 2 \text{ G} & \\
 A_{\perp}(\text{Cl}) < 10 \text{ G} & A_{//}(\text{Cl}) = 32 \pm 5 \text{ G} &
 \end{array}$$

Ag^{2+} was found to be slightly less stable in NaCl than in KCl; on warming up above room temperature Ag^{2+} is lost with an accompanying blue luminescence and loss of pink colour in the powder at a somewhat lower temperature than in KCl:AgCl.

The principal electron trap is Ag^0 until the silver concentration is higher than ca. 0.05 MF AgCl when a new asymmetric feature appears in the $g=1.891$ region which grows in intensity, shifts slightly to lower g value and loses its asymmetry as $[\text{Ag}^+]$ is increased. Annealing the irradiated powders

Figure 2.4 The ESR powder spectrum of NaCl:AgCl (0.01 MF AgCl) at 77K following irradiation at 77K and annealing showing Ag^0 and Ag^{2+} features.



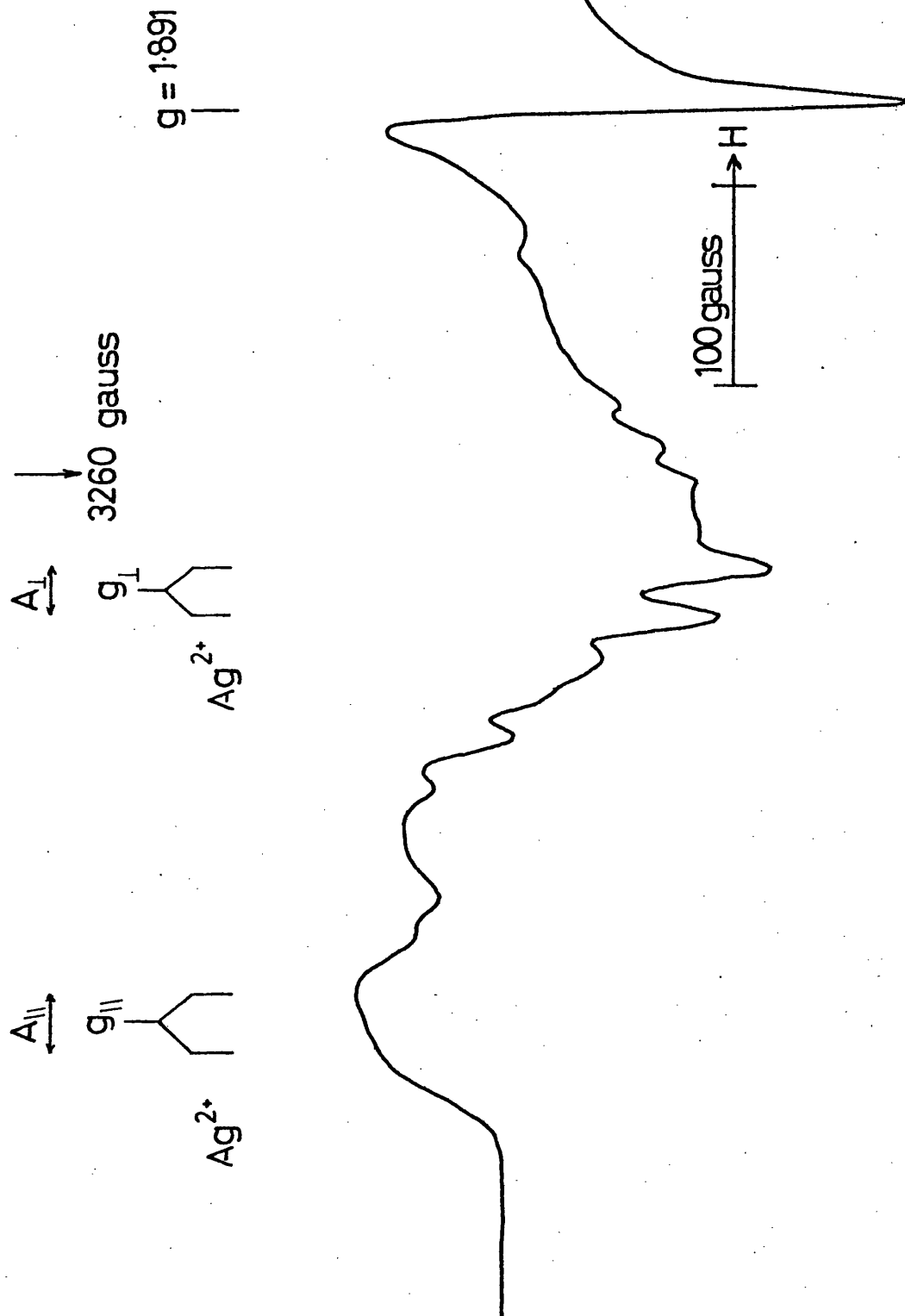
results in an irreversible narrowing of the line followed by its rapid decay at ca. 170K. The Ag^0 concentration rapidly falls to zero in this MF region¹⁷. In Figure 2.5 the $g=1.891$ feature can be seen along with the self trapped hole, Ag^{2+} .

It seems likely that the $g=1.891$ species, which is reproducibly formed in the AgCl concentration range 0.05 - 0.7 MF, is the electron capture centre, but its apparent intensity is only a small fraction of that of the electron loss centre. This can be understood if the single line detected is really part of a complex spectrum of many lines, all others being undetectable. This could arise for two reasons; (a) the other features are dynamically broadened or (b) none of them have precise locations. The former concept seems improbable because the spectrum is unaltered at 4.2K. The latter, (b), however arises naturally from the following model.

As $[\text{Ag}^+]$ increases there is a tendency for clustering. Initially units containing two, three or four Ag^+ ions would trap electrons to give centres resembling the $\text{Ag}_2^+(g_{\text{av}}=1.983)$, $\text{Ag}_3^{2+}(g_{\text{av}}=1.973)$ and $\text{Ag}_4^{3+}(g_{\text{av}}=1.970)$ centres previously detected⁴ and studied in Chapter Three. Such features, present in relatively low concentrations, would have features largely hidden by the main Ag^0 and Ag^{2+} features, and could well be present. It is noteworthy that g_{av} shifts to low values in this series. As the number of Ag^+ ions involved in a cluster increases, so g_{av} would be expected to reach a limiting value (as the number of peripheral Ag^+ ions becomes small compared to the inner ions). The hyperfine features from ^{109}Ag and ^{107}Ag are expected to comprise a multiplet covering a range of ca. 500-600 G. For centres containing an even number of equivalent Ag^+ ions there should always be a central line which should be narrow when the

Figure 2.5 The ESR powder spectrum of NaCl:AgCl (0.2 MF AgCl) at 77K following low

temperature irradiation showing poorly resolved Ag^{2+} features and the $g=1.891$ species.



hyperfine coupling to each Ag^+ is small. However, no other features from these clusters will coincide unless the clusters are equivalent.

A wide range of cluster sizes might be expected and only the central feature in the limiting g value region would be detected. The asymmetric broadening to the low field side of the singlet in the low concentration region and the slight shift in g value as the $[\text{Ag}^+]$ increases, as seen in Table 2.2, accord with this model.

Table 2.2 g value variation of the high field singlet with $[\text{Ag}^+]$ as found in $\text{NaCl}:\text{AgCl}$ after γ irradiation at 77K

$[\text{Ag}^+]$ MF	g^*
0.09	1.8917 ± 0.0003
0.13	1.8918
0.17	1.8917
0.29	1.8911
0.62	1.8906

*measured as if feature isotropic

From this model it is concluded that excess electrons in silver chloride are not initially trapped and localised by the formation of discrete Ag_2^+ or Ag_4^{3+} centres but are delocalised over many Ag^+ ions.

$\text{NaCl}:\text{AgCl}$ exposed to γ rays at room temperature

The high $[\text{Ag}^+]$ mixtures showed no paramagnetic centres after room temperature irradiation; they were blackened by irradiation however, and it is probable that clusters of ions

acting as electron traps are mobile at this temperature and that they aggregate to form colloidal silver metal immediately. In addition this process appears to prevent the formation of the self trapped hole, Ag^{2+} . Mixtures containing low $[\text{Ag}^+]$ exhibit similar spectra to their KCl analogue although features from Ag_2^+ and Ag^0 are ill defined again as a result of the high magnetic moment of ^{23}Na .

KBr:AgBr and NaBr:AgBr exposed to γ rays

Both of these mixtures could only be prepared with low silver bromide contents. γ irradiation of both systems produces similar results with the spectra of the NaBr:AgBr showing the poorer resolution.

Br_2^- is the initial hole centre after irradiation at 77K and the electron trap is Ag^0 . The strong nuclear magnetic moments of both bromine isotopes make for a complex spectrum in which the bromine SHFS on Ag^0 spreads across the signal from Br_2^- . ESR parameters derived from the powder spectrum for Ag^0 are as follows:

$$^{109}\text{Ag}^0 \quad g=2.000\pm0.005 \quad A_{\text{iso}}(\text{Ag})=-630\pm10\text{G} \quad A_{\text{iso}}(\text{Br})=78.3\pm0.2\text{G}$$

$$^{107}\text{Ag}^0 \quad g=2.000\pm0.005 \quad A_{\text{iso}}(\text{Ag})=-548\pm10\text{G} \quad A_{\text{iso}}(\text{Br})=78.3\pm0.2\text{G}$$

These parameters agree reasonably well with those of Mel'nikov¹¹ who has additionally determined the anisotropy in the bromine SHFS at 4.2K:

$$A_{\text{iso}}(\text{Br}) = 78.8\pm0.5 \text{ G} \quad 2B(\text{Br}) = 7.2\pm0.2 \text{ G}.$$

These figures represent a similar distribution of unpaired electron spin density to that on Ag^0 in a KCl lattice.

On annealing Br_2^- is lost and $[\text{Ag}^0]$ diminishes slightly but Ag^{2+} could not be detected; were it present it would be hidden under the bromine SHFS on the Ag^0 signal. A single crystal study would help in the identification but it was not found possible to coprecipitate a single crystal of KBr:AgBr from aqueous solution. Sierro¹⁶ claims to have produced Ag^{2+} in KBr:AgBr crystals by irradiating with γ rays at 77K and then bleaching Br_2^- centres, but using powder samples neither thermal bleaching nor optical bleaching using 'F' light¹⁸ revealed Ag^{2+} , the bromine SHFS on Ag^0 invariably dominating the region of the spectrum in which Ag^{2+} is expected.

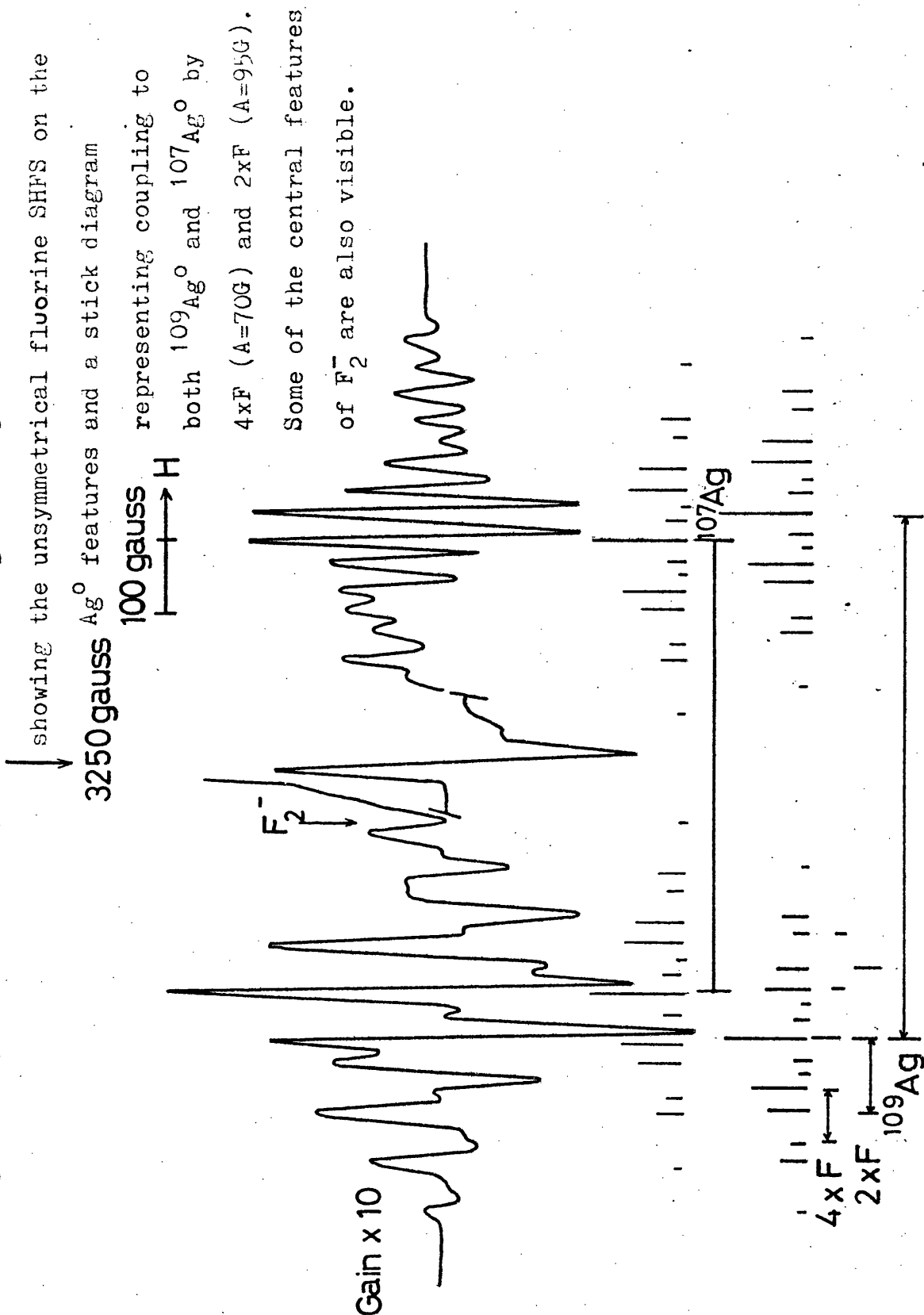
No paramagnetic centres were detected by ESR following room temperature irradiation of these mixtures.

KF:AgF exposed to γ rays at 77K

Only mixtures containing low silver fluoride concentrations could be prepared for this system because the rapid quenching technique was not applicable.

The ESR spectrum of KF:AgF powder following γ irradiation at 77K appears in Figure 2.6. F_2^- is the principal hole trap exhibiting a spectrum similar to that found in $\text{LiF}^{19,20}$ and Ag^0 is the major electron trap although an F centre may also be present accounting for the very strong central feature; the colour of the irradiated powder, yellow, could conceivably be related to an F centre although such a colour is more likely due to silver atoms. The strong central feature prevents the observation of Ag^{2+} , if it is formed, when the powder is allowed to warm up. The interpretation of the Ag^0 spectrum as seen in Figure 2.6 indicates that the orbital in which the

Figure 2.6 The ESR powder spectrum of $\text{KF}:\text{AgF}$ at 77K following low temperature irradiation



electron resides is composed largely of a silver 5s atomic orbital but that there is some contribution from orbitals of the fluoride ligands. Analysis of the SHFS associated with the ligands indicates that the delocalisation of the spin into ligand orbitals is unsymmetrical and that delocalisation onto two of the fluorides is greater than onto the other four. The two strongly coupled ligands split the Ag^0 features into triplets which are further split into quintets by the less strongly coupled ligands. The ESR parameters derived from the powder spectrum are:

$$\begin{array}{lll}
 {}^{109}\text{Ag}^0 & g=1.999\pm0.003 & A_{\text{iso}}(\text{Ag})=-710\pm5 \text{ G} \\
 & & A_{\text{iso}}(2\text{xF})=95\pm3 \text{ G} \\
 & & A_{\text{iso}}(4\text{xF})=70\pm3 \text{ G} \\
 \\
 {}^{107}\text{Ag}^0 & g=1.999\pm0.003 & A_{\text{iso}}(\text{Ag})=-605\pm5 \text{ G} \\
 & & A_{\text{iso}}(2\text{xF})=95\pm3 \text{ G} \\
 & & A_{\text{iso}}(4\text{xF})=70\pm3 \text{ G.}
 \end{array}$$

The very high $A_{\text{iso}}(\text{Ag})$ value is indicative of almost unit occupancy by the spin of the silver 5s orbital and the $A_{\text{iso}}(\text{F})$ values reflect about 0.55% spin density on each of the two strongly coupled ligands and about 0.41% spin density on the four more weakly coupled ligands.

The higher spin density on silver in the $\text{KF}:\text{AgF}$ system than in the $\text{KCl}:\text{AgCl}$ system is expected and due to the ionic nature of the Ag-F bond compared to the Ag-Cl bond. The unsymmetrical coupling to fluorine nuclei is unexpected however, and difficult to explain, particularly because the very high $A_{\text{iso}}(\text{Ag})$ precludes much spin occupancy of silver p orbitals which might be expected if unsymmetrical coordination were occurring.

Such a distortion of the octahedron surrounding the silver atom is the only way of explaining the fluorine coupling and this also raises the question of why the fluorine SHFS is apparently isotropic.

A Jahn Teller distortion could be invoked if the unpaired electron occupied a silver orbital with some d character as it might if excited states were mixed in with the $^2S_{1/2}$ ground state. Again, the high $A_{iso}(Ag)$ value indicates no such mixing and distortion would not be expected to arise. In any case, warming the sample up, while reducing the signal intensity does not change the form of the spectrum; if Jahn Teller distortion were frozen in at 77K then warming would result in the distortion being averaged out and coupling to six equivalent fluoride ions would be expected.

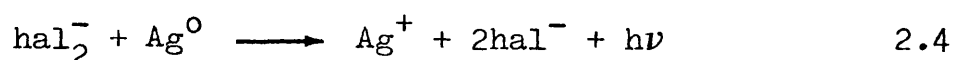
It would have been useful to have compared this result with those from other alkali fluorides doped with silver but AgF could not readily be incorporated into either LiF , CsF or NaF using the method described earlier.

2.3 Conclusion

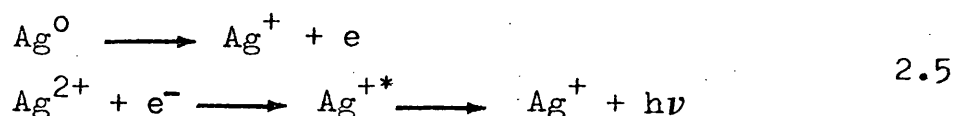
The hole trap, Ag^{2+} , has been detected in a number of environments; it has been shown to be a primary product of irradiation of silver nitrate crystals^{21,22} and in Chapter Three it is found in many of the irradiated frozen silver(I) solutions. In this work and in that of Höhne and Stasiw⁸ its stability in silver chloride has been demonstrated; it has not however, been positively identified when other halides have been used instead of chloride.

This may be because a dynamic Jahn Teller distortion is being effective in broadening the signal at 77K in the bromide, iodide and fluoride lattices which is not so effective in the chloride, in which case cooling the samples to 4K might quench the distortion sufficiently to resolve the signal. Alternatively, if the Jahn Teller distortion only produces a small splitting in the e_g levels then the hole may have sufficient thermal energy at 77K to jump from the $d_{x^2-y^2}$ to the d_{z^2} orbital again causing line broadening. An ESR study of these systems at 4K is necessary to determine whether these are real explanations although the complexity of the ligand SHFS might, even then, prevent the observation of the Ag^{2+} resonance.

Thermoluminescence has been observed by Delbecq et al⁶ and Starkie²³ in silver doped alkali halides that have been irradiated at 77K as they warm up and frequently changes in the ESR spectra can be correlated with emissions. For instance the reaction (2.4) can be associated in KCl, KBr and KI



with a yellow or yellow-green luminescence in the 455-550 nm region. Similarly the loss of Ag^0 and Ag^{2+} by reactions (2.5) can be associated in NaCl with a blue emission at 400 nm.



A similar emission is reported in the NaBr:AgBr, LiBr:AgBr and NaI:AgI systems which is absent when the undoped alkali halides are examined and if this emission is related to the existence of, and subsequent decomposition of Ag^{2+} this is at least partial evidence for the existence of Ag^{2+} in doped

alkali halides other than the alkali chlorides.

If the work of Höhne and Stasiw⁸ could be repeated, doping silver bromide and iodide with suitable electron traps and Ag^{2+} detected in these crystals then the evidence favouring Ag^{2+} as the major hole trap centre in all the silver halides used in the photographic process would be very strong indeed.

The positively identified electron traps in this chapter are Ag^0 , coordinated to Cl, Br and F ligands, Ag_2^+ , observed only under the unique conditions of two silver ions plus an electron occupying one cationic lattice site and the new $g=1.891$ species for which a model has been suggested. If the model of very large clusters of Ag^+ ions acting as electron traps is correct then it is surprising that no paramagnetic aggregates of three and four silver nuclei have been detected in NaCl:AgCl at any silver concentration. These are shown in Chapter Three to possess particular stability in a number of frozen solvents and indeed Mitchell and Mott^{2,3} do suggest that aggregates of the type Ag_4^+ and Ag_3^+ may be responsible for electron trapping in pure silver halides.

References for Chapter Two

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Chapter Three

Radiation Damage in frozen Aqueous and
Non Aqueous Silver Solutions as studied
by Electron Spin Resonance

A notable difference between cations having an outer electron configuration ns^2np^6 and those having the configuration $ns^2np^6nd^{10}$ is that only the latter capture electrons in irradiated fluid or rigid solutions. Ag^+ readily gives Ag^0 on irradiation but even Al^{3+} shows no tendency to capture an electron to form Al^{2+} . One possible contributory factor could be the greater polarisability of the d^{10} ions which ensures that only for this group can an electron become weakly trapped by a suitable polarisation long enough to permit the relaxation of the ligands necessary to form a deep trap.

Radiolytic formation of Ag^0 has been well established both in fluids by optical spectroscopy¹, and in the solid state by both optical² and ESR spectroscopy³⁻⁵. An important facet of these studies has been the formation of radical ion clusters such as Ag_2^+ , Ag_3^{2+} and Ag_4^{3+} , which have been identified by ESR^{3,4,6}.

In this work the formation of silver atoms and clusters is studied in a range of frozen solvents. In addition the hole centre Ag^{2+} , formed in many solvents alongside Ag^0 , is studied. Between them, the ESR spectra of these centres provide considerable information on the environment of the parent Ag^+ ion.

Conclusions regarding ion pairing in methyl cyanide solutions of silver nitrate are drawn from these studies and considerable information is forthcoming on the nature of solvation of the Ag^+ ion in this solvent from spectra of irradiated silver perchlorate solutions. ESR spectra of frozen aqueous solutions reflect the mode of solvation of Ag^+ in this medium, the Ag^0 spectrum arising from electron capture by a number of discrete types of solvate of the parent

Ag^+ ion.

The ESR spectra of silver centres in most non aqueous solvents however, are less well resolved and the mode of interaction of the parent ion with the solvent molecules cannot so readily be established.

A preliminary study of the soluble $\text{Aghal}_n^{(n-1)-}$ complex ions is also reported. It was hoped that the way these complex ions solvate could be compared to the way free Ag^+ ions solvate.

In the following Sections frozen aqueous systems are dealt with first. Section 3.2 contains a study of ion pairing in silver nitrate/methyl cyanide solutions and then the contrasting behaviour of silver perchlorate/methyl cyanide solutions is discussed in Section 3.3. Some results regarding aggregate formation by silver ions and atoms, and silver adduct formation in primary alcohols is reported in Section 3.4. In the same Section trends in the spectra and ESR parameters of silver centres formed in the range of solvents studied are discussed and finally in Section 3.5 the preliminary results of the study of soluble $\text{Aghal}_n^{(n-1)-}$ ions are presented.

Most of the ESR data is tabulated in Appendix Three.

3.1 Radiation Damage in Aqueous Silver Solutions

Silver ions have been shown by Bales and Kevan^{8,9} and others^{3,5} to capture electrons in frozen aqueous solution to form a range of distinct Ag^0 centres displaying low (ca.80%) atom character. Although in capturing an electron the charge is lost from Ag^+ , the ligands remain a significant part of the trap and the Ag^0 centres formed in rigid solution are in contrast to Ag^0 trapped in a water matrix from the gas phase which have hyperfine coupling constants and g values very close to the gas phase value (Table A3.1).

It was hoped that a study of Ag^0 and Ag^{2+} formed from Ag^+ in aqueous glasses might yield information about the solvation of the parent Ag^+ cation.

Thermodynamic measurements indicate that the solvation of Ag^+ is weak and that the solvation number is low¹⁰, although the NMR study of Akitt¹¹, which deduces a solvation number of 0.6 and is discussed more fully in Chapter Four, is dismissed as being without physical significance. The NMR results reported in Chapter Four support the conclusion reached here, in that a solvation number for Ag^+ somewhat greater than the commonly supposed value of two is favoured in aqueous solution.

3.1a Experimental

Water was doubly distilled from alkali potassium permanganate. Deuterated water was 99.8% pure and supplied by Nuclear Magnetic Resonance Ltd. Salts were all Analar grade

and were used as supplied except silver fluoride which was prepared by the method of Anderson, Bak and Hillebert¹².

Samples for irradiation were prepared by freezing small droplets of solution in liquid nitrogen. They were irradiated at 77K as described in Chapter One. Silver ion concentrations were studied in the range $0.001-2 \text{ mol kg}^{-1}$ and except where stated otherwise silver nitrate was the silver salt used.

3.1b Results and Discussion

The results are summarized in the Figures and in Table A3.1.

Ag^{2+} Centres in Water

In general poorly defined parallel features are detected at 77K after relatively high radiation doses (Fig. 3.1a). Also the $m_I = -\frac{1}{2}$ component of the perpendicular features is detected before annealing, on the low field side of the intense central feature. (In general, separate components from the two silver isotopes, ^{107}Ag and ^{109}Ag , are not resolved in the Ag^{2+} spectrum, although they are in the Ag^0 spectrum). On annealing above 77K the parallel features become far better defined (Fig. 3.1b). The form of the g tensor of these Ag^{2+} centres is typical of complexes in which the unpaired electron is in a silver $d_{x^2-y^2}$ orbital. Were the unpaired electron in a silver d_z^2 orbital, low field perpendicular features would be observed. This latter configuration would be expected if linear solvates were present so it is concluded that such

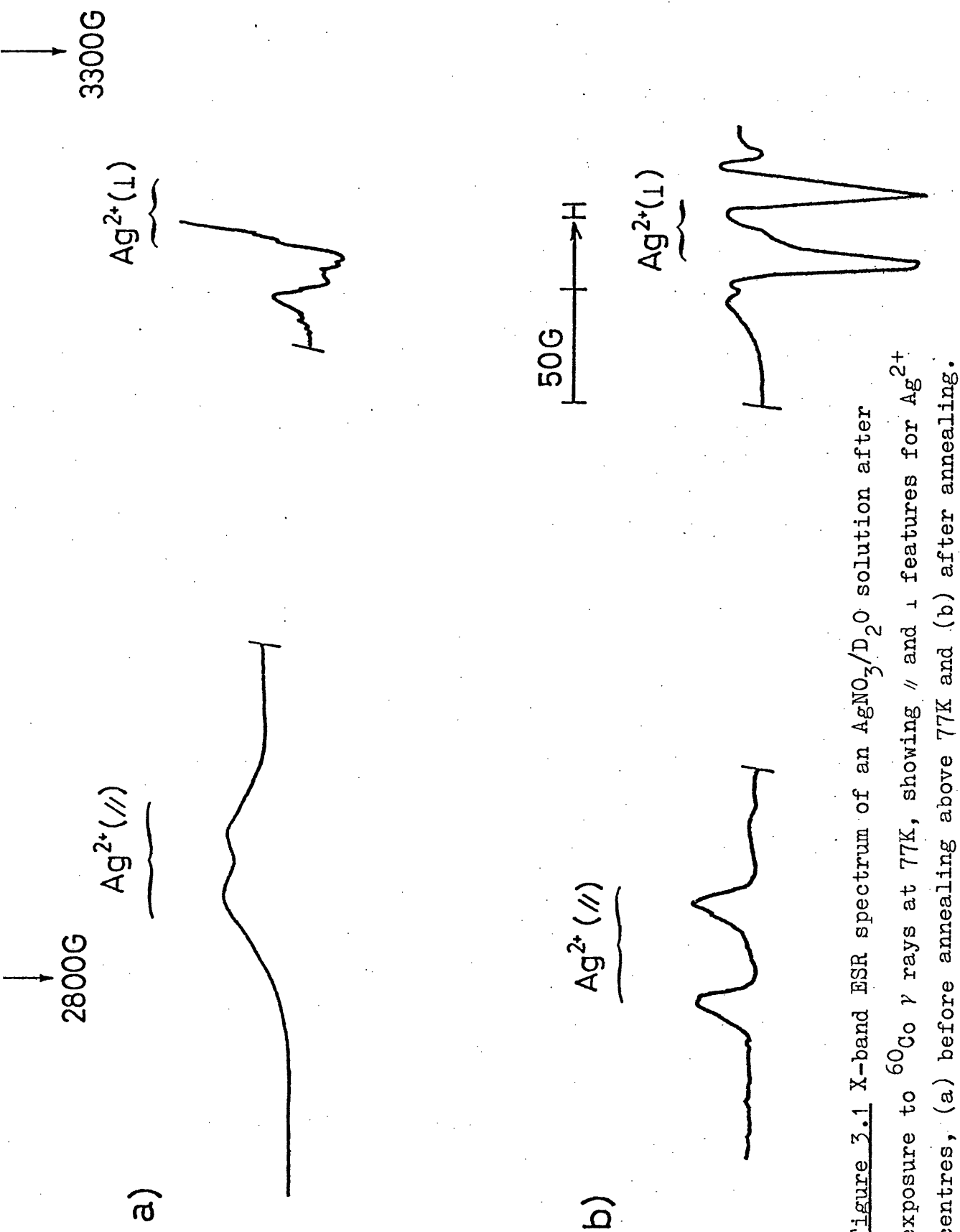
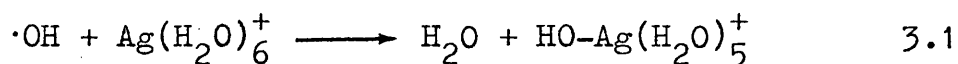


Figure 3.1 X-band ESR spectrum of an $\text{AgNO}_3/\text{D}_2\text{O}$ solution after exposure to ^{60}Co γ rays at 77K, showing $\parallel$ and $\perp$ features for Ag^{2+} centres, (a) before annealing above 77K and (b) after annealing.

solvates are not important components of any of the solutions studied here. Unsymmetrical solvates that still favour a $d_{z^2}^1$ configuration would show two low field (x and y) components with the z component in the free spin region. Again, no such species is detected.

The results could be accommodated in terms of octahedral coordination by solvent molecules with a linear Jahn Teller distortion involving elongation along the z axis⁵, but were this the case it would likely be a dynamic distortion as observed for Ag^{2+} in alkali halides¹³. This would result in an isotropic doublet centred on g_{av} . Such a feature is not detected on warming the beads, even up to the softening point.

This suggests that Ag^{2+} has a built in, rather than a Jahn Teller induced, distortion. This could arise because the solvates that lose electrons preferentially are those that already have the required distortion. A five coordinated solvate having a structure close to square pyramidal would give the required results directly or alternatively reactions such as (3.1)



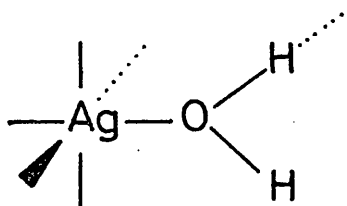
would give rise to the required configuration. There are many other possibilities. It seems reasonable to suggest that the initial broad features stem from a range of different types of Ag^+ solvate, all of which favour distortion to give a $4d_{x^2-y^2}^1$ configuration and that on annealing further distortion occurs around the Ag^{2+} ion to give the most stable configuration of solvent molecules, most likely square planar.

Ag⁰ Centres in Water

As was shown by Bales and Kevan⁸, frozen aqueous silver nitrate solutions exposed to low doses of γ rays give a predominating Ag⁰ centre (A) which exhibits an extra 6G doublet splitting. This splitting is lost when D₂O solutions are used and hence must stem from a single proton (Fig. 3.2a). They offered no explanation for the presence of this unique proton.

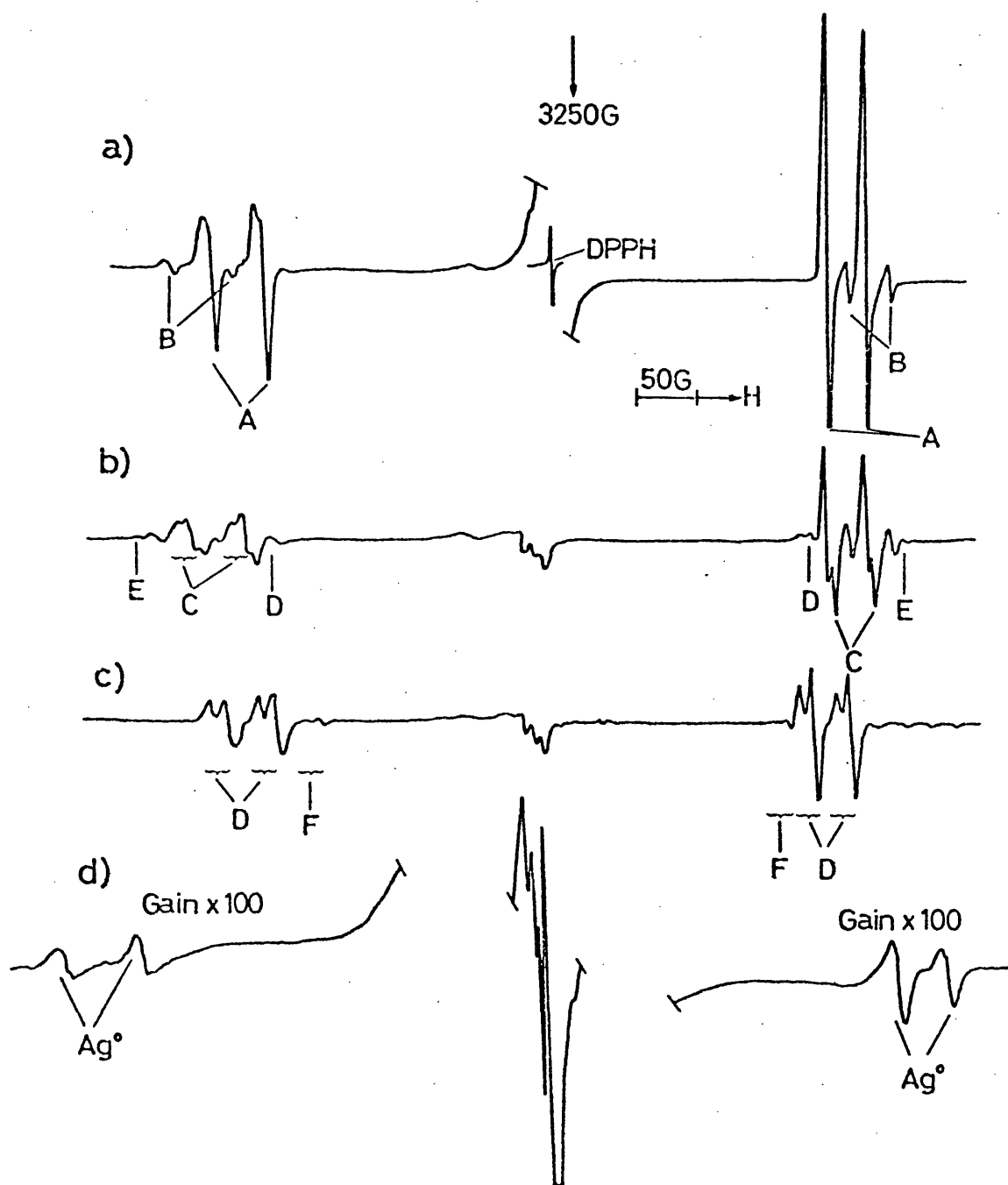
Although the initial rate of formation of A is high, it soon falls to zero and other centres, especially C, dominate (Figs. 3.2b and 3.4). Annealing results in the loss of A, B and C and the gain of D and F (Figs. 3.2c and 3.4). Both of these observations regarding centre A lead to the following model.

A small percentage of Ag⁺ ions in solution have one water molecule in their solvation shell that is hydrogen bonded to the surrounding water by only one of its protons as shown below.



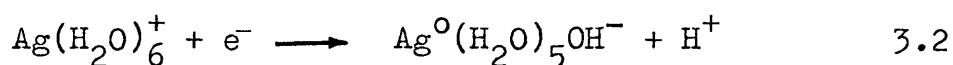
These cations are then thought to be slightly better electron traps than the remainder, for which all the ligand water protons are hydrogen bonded. The non hydrogen bonded proton must then be the unique proton whose hyperfine coupling is detected by ESR. This unique water molecule will be less

Figure 3.2 X-band ESR spectrum of an $\text{AgNO}_3/\text{D}_2\text{O}$ solution after low temperature irradiation, showing features for $^{109}\text{Ag}^\circ$ and $^{107}\text{Ag}^\circ$ centres, (a) after a low γ ray dose, showing only centres A and B; (b) after a higher dose (ca. 3 MRad), showing features for centres C, D and E; (c) after annealing to give predominant signals from centres D and F, and (d) for solutions containing $\text{Mg}(\text{ClO}_4)_2$, showing features for atom like Ag° ; (deuterium atom signals not shown).



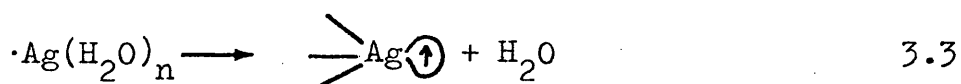
strongly bonded to silver than the remainder, because it is less basic¹⁴, and hence this solvate might be expected to be a better electron trap. Since the total number of $(\text{OH})_{\text{free}}$ groups is low in aqueous solution, such centres are soon reduced to low concentrations, and the electrons are trapped elsewhere.

Alternatively, the formation of a unique proton could be explained in terms of proton loss.



To test this, the effect on the yield of centre A of increasing the pH of the solution was studied. No change was observed so this possibility is discounted.

Identification of the other centres is impossible, but some general conclusions can be drawn. The symmetrical centres, B and E, are formed in low yield, but this may reflect a low capture cross section rather than a low abundance of the appropriate solvated ion. Possibly the tetrahedral $\text{Ag}(\text{H}_2\text{O})_4^+$ and octahedral $\text{Ag}(\text{H}_2\text{O})_6^+$ hydrates are responsible. The other major primary asymmetric centre is C, and both A and C appear to anneal to give the more asymmetric centre D. It is suggested that D is formed by actual loss of one water molecule from the original coordination sphere.



If the remaining water molecules remain approximately in their original locations this will provide a low energy site for the excess electron.

Centre C exhibits asymmetry and it would appear that the parent ion from which C is formed must also have a built

in well defined asymmetry. The solvates $\text{Ag}(\text{H}_2\text{O})_3^+$ and $\text{Ag}(\text{H}_2\text{O})_5^+$ are possible candidates.

Approximate estimates of the 5s and 5p orbital populations can be obtained from the hyperfine constants in Table A3.1. The 5s population for centre A is ca.75% for example, based on an atomic value of $A_{\text{iso}}^0(^{109}\text{Ag})$ of -706G. The anisotropies detected are difficult to estimate accurately and the large errors make calculation of 5p character highly approximate. However, based on a $2B^0(^{109}\text{Ag})$ value of 9.5G^{15} it can be concluded that all the Ag^0 centres, save the isotropic centres, possess appreciable spin density in the silver 5p orbitals.

Ag^0 Centres in ^{17}O enriched D_2O

In order to learn more about the structure of these Ag^0 centres, solutions in D_2O enriched with ca.12% ^{17}O were studied. Silver nitrate enriched with ^{109}Ag was also used to simplify the spectra. Such a study was only really possible on centre A and the results demonstrate the presence of D_2^{17}O in the primary solvation shell, but quantitative estimations of solvation numbers are made difficult by the presence of minor Ag^0 species absorbing in the same region (Fig. 3.3), and the impossibility of estimating accurately the proper anisotropy of the ^{17}O hyperfine coupling. The ^{17}O nucleus has $I=5/2$ and for 12% enrichment only six components are expected from a set of equivalent oxygen nuclei. In addition, they will be broadened by the anisotropy of the ^{17}O coupling so that the $\pm 5/2$ features should be broader than the $\pm 3/2$ features which in turn will be broader than the $\pm 1/2$ features. The analysis of the spectrum in Figure 3.3 is somewhat approx-

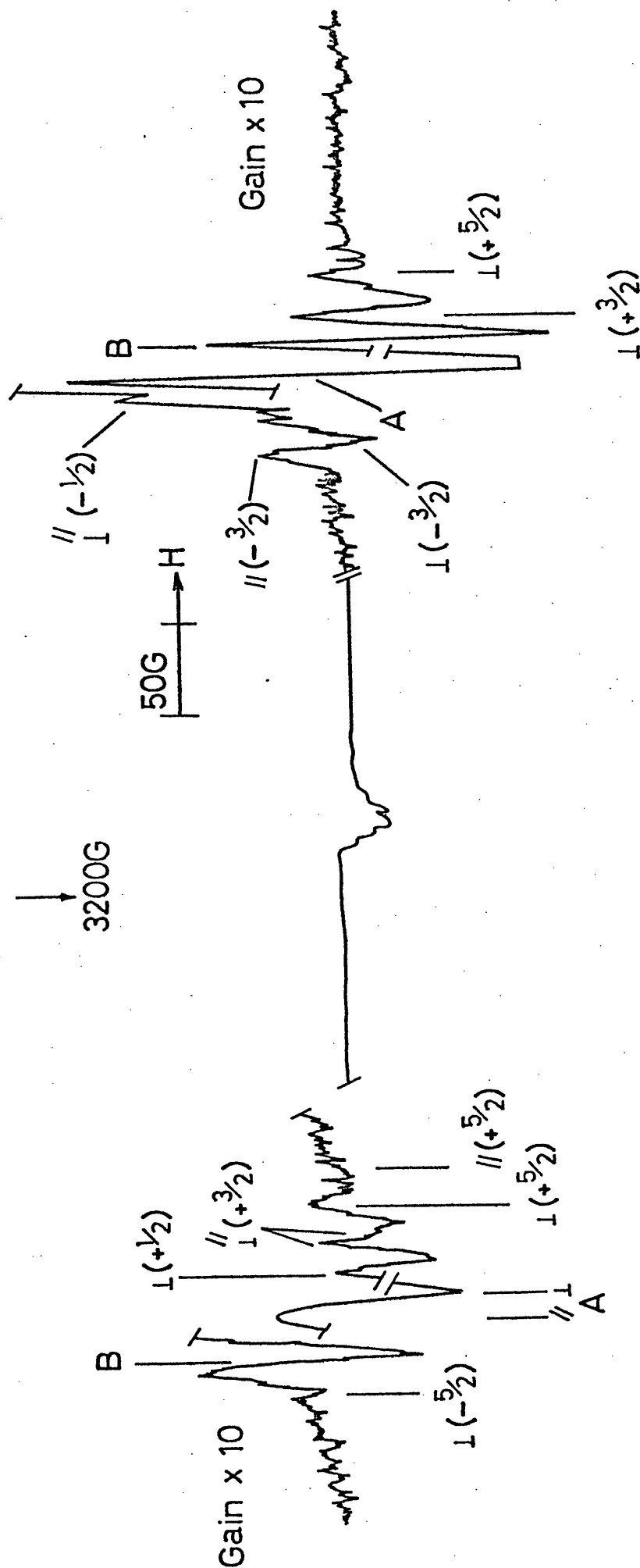


Figure 3.2 X-band ESR spectrum of a $^{109}\text{Ag}^+/\text{D}_2\text{O}$ solution enriched by 12% D_2^{17}O , after low temperature irradiation showing Ag^0 centres A and B and satellite lines assigned to Ag^0 centres containing D_2^{17}O .

imate but from it the following parameters are estimated:

$$\begin{aligned} A_{\parallel}({}^{17}\text{O}) &\cong 28\text{G} & A_{\perp}({}^{17}\text{O}) &\cong 21\text{G} \\ A_{\text{iso}} &\cong 23.3\text{G} & 2B &\cong 4.7\text{G} \end{aligned}$$

These values can be converted into rough spin densities using values for unit population of the 2s(1660G) and 2p(104G) orbitals of oxygen¹⁶. Thus it is concluded that there is ca.5% delocalisation onto each water molecule.

It is not easy to gauge the number of equivalent water molecules from the relative intensities of the ¹⁷O satellite lines because of the broadening imposed by their anisotropies and because of overlap with minor features from other Ag⁰ centres. However, reconstructions favour the presence of four or possibly six (but probably not two) equivalent water molecules for centre A.

The Aquation of Ag⁺

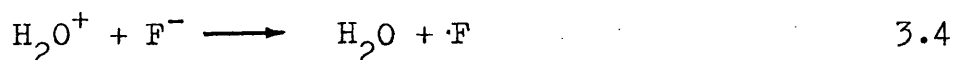
Two important conclusions can be drawn. One is that solvation is not "switched off" when Ag⁺ ions are converted to atoms. This contrasts with the results for anionic centres at 77K, for which well defined solvation is "switched on", despite the rigidity of the glass. For example, electron capture by O₂ in aqueous or alcoholic glasses at 77K results in ESR spectra showing solvation to be as complete as it is in fluid solutions of O₂⁻ frozen to this temperature¹⁷.

The other important conclusion is that aqueous solutions of Ag⁺ contain a range of at least six types of solvate that differ from one another in a well defined way. These differences are quantised rather than being smeared over a wide

range of different structures, since this would simply confer broadening to the lines. Instead, they must differ either in the number of primary, or the number of secondary, solvent molecules.

The Effect of Additives

The results are independent of the anion (F^- , NO_3^- or ClO_4^-), and hence contact ion pairing is unimportant. The distribution of Ag^0 types formed is unaltered on the addition of a range of salts, although changes in the overall yield of Ag^0 and other centres are obtained. This was noted by Bales and Kevan⁹ in the case of added KF. They ascribed the 10-fold increase in total yield of Ag^0 to reaction 3.4 which effectively traps the hole centres, thereby



suppressing electron return. The enhanced yield in the presence of F^- is confirmed in this work and the yield of $\cdot OH$ (or $\cdot OD$) is also found to increase (2-3-fold) as is the yield of Ag^{2+} centres. However, the interpretation embodied in equation 3.4 is suspect for the following reasons.

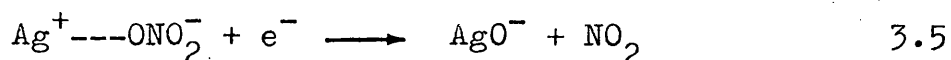
1) Electron loss by aquated F^- is not expected to be any easier than loss from water itself. This is supported by the absence of any detectable CTTS absorption for fluoride ions in water¹⁸.

2) It has previously been shown¹⁹ that irradiated halide solutions form $HOhal^-$ radicals at 77K, but in the particular case of $HO F^-$, the centre closely resembles the hydroxyl radical and is only detectable when $[F^-]$ is high. In contrast, $HO Cl^-$,

and especially HOBr^- and HOI^- are formed in preference to $\cdot\text{OH}$ radicals, and hence only Cl^- , Br^- and I^- really act as hole traps.

It is suggested that the effect of added KF is physical, not chemical, and is merely to promote glass formation rather than phase separation on freezing the solutions. The yellow colour characteristic of Ag^0 has a speckled appearance in the absence of KF but is uniformly distributed in its presence. The Mn(II) test for glass formation¹⁹ was applied to the system and this establishes phase separation in the absence of KF and glass formation when KF is present.

Phase separation occurs into glassy regions and ice crystals. (The absence of a pure AgNO_3 phase is shown by the absence of any detectable features from the $\text{Ag}^+ \text{---} \text{NO}_3^{2-}$ centres found therein^{20, 7}). The ice crystals give $\cdot\text{OH}$ in low yield as the only detectable species and this phase absorbs the γ rays, reducing their ability to interact with the glassy regions. Furthermore, it is shown later that concentrated solutions of silver nitrate tend to form NO_2 and NO_3^{2-} in competition with Ag^0 centres, probably because of reactions such as (3.5) thus reducing still further the potential yield

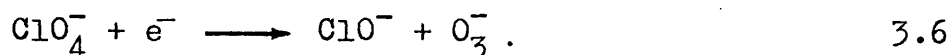


of Ag^0 .

When the phase separated solids are replaced by glasses, the ejected electrons are efficiently trapped by Ag^+ ions to give only Ag^0 centres since the nitrate ion pairs are now absent. This also accounts for the gain in $[\cdot\text{OH}]$ since back reactions are suppressed, and for the drop in $[\text{NO}_2 + \text{NO}_3^{2-}]$. The increase in $[\text{Ag}^{2+}]$ follows from the above argument. Electrons

are trapped efficiently and some positive holes migrate to Ag^+ to give Ag^{2+} .

Addition of $\text{Mg}(\text{ClO}_4)_2$ in high concentration ($\geq 2 \text{ mol kg}^{-1}$) also gives good glasses, and enhanced yields of Ag^0 centres, though to a smaller extent (ca. 3-fold). The smaller yield reflects the ability of ClO_4^- to react with electrons²¹:

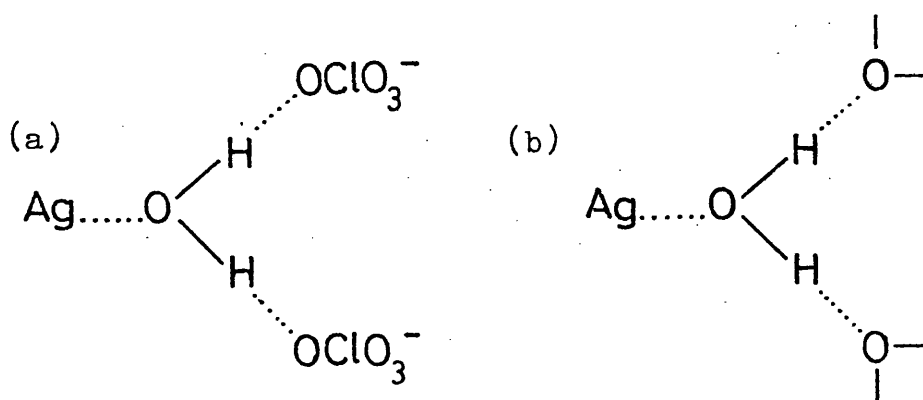


The presence of an enhanced central feature suggests the presence of O_3^- in these glasses.

In contrast to the fluoride glasses, these perchlorate glasses give a new Ag^0 centre more akin to the normal atom (Table A3.1 and Fig. 3.2d). The Ag^0 spectrum is similar to that found in 6M aqueous sulphuric acid glasses³.

The formation of atom like Ag^0 in 6M sulphuric acid can be explained in terms of desolvation of the parent Ag^+ ion by the large excess of H^+ and HSO_4^- ions which will coordinate the water molecules. In a similar way Mg^{2+} would coordinate the available water preferentially over Ag^+ but in view of the weak solvation associated with the ClO_4^- ion it might be thought that there would be ample water available for coordination to Ag^+ when Mg^{2+} is present, even at a concentration of $\sim 3 \text{ mol kg}^{-1}$.

An alternative explanation stems from the weak coordinating ability of the perchlorate ion. In the presence of a high concentration of ClO_4^- the Ag^+ ions in solution will be solvated by water molecules that are also coordinated to ClO_4^- ions as in (a). The weak hydrogen bond between the water and the ClO_4^- ion would weaken the $\text{Ag} \cdots \text{OH}_2$ bond relative to the $\text{Ag} \cdots \text{OH}_2$ bond in (b), in which the water is hydrogen



bonded to other water molecules. This would effectively desolvate the Ag^+ ion and electron capture would result in a more atom like Ag^0 centre.

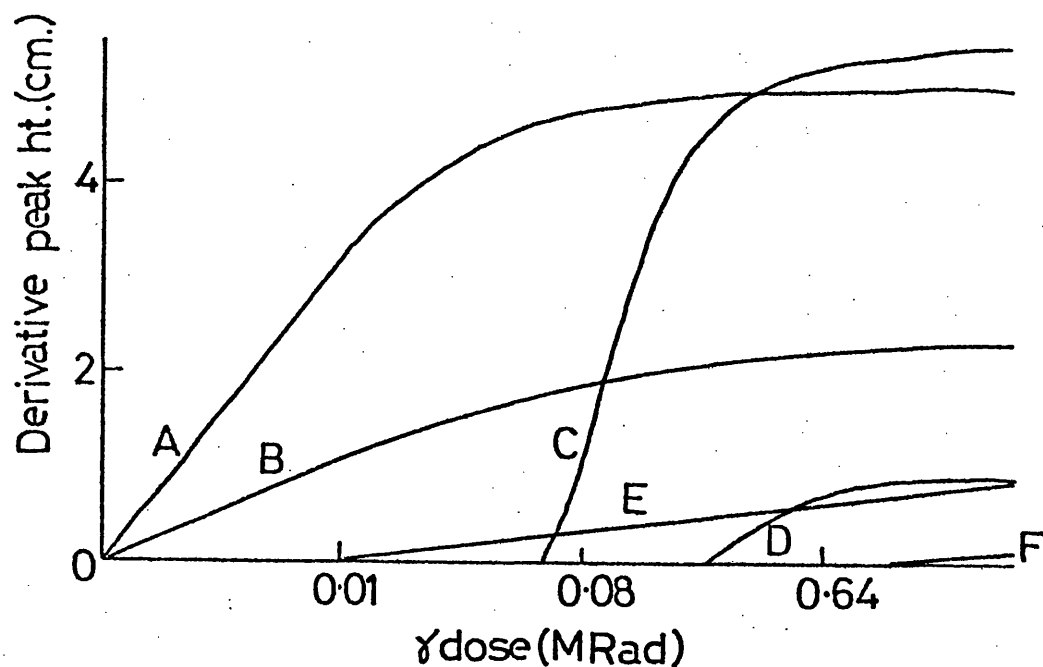
This idea accommodates the fluoride results because added F^- would not, when bonded to the primary solvation shell, appreciably weaken the $\text{Ag}^+ \cdots \text{OH}_2$ bond and hence no atom like Ag^0 would be expected.

Dose, Thermal and Concentration Effects

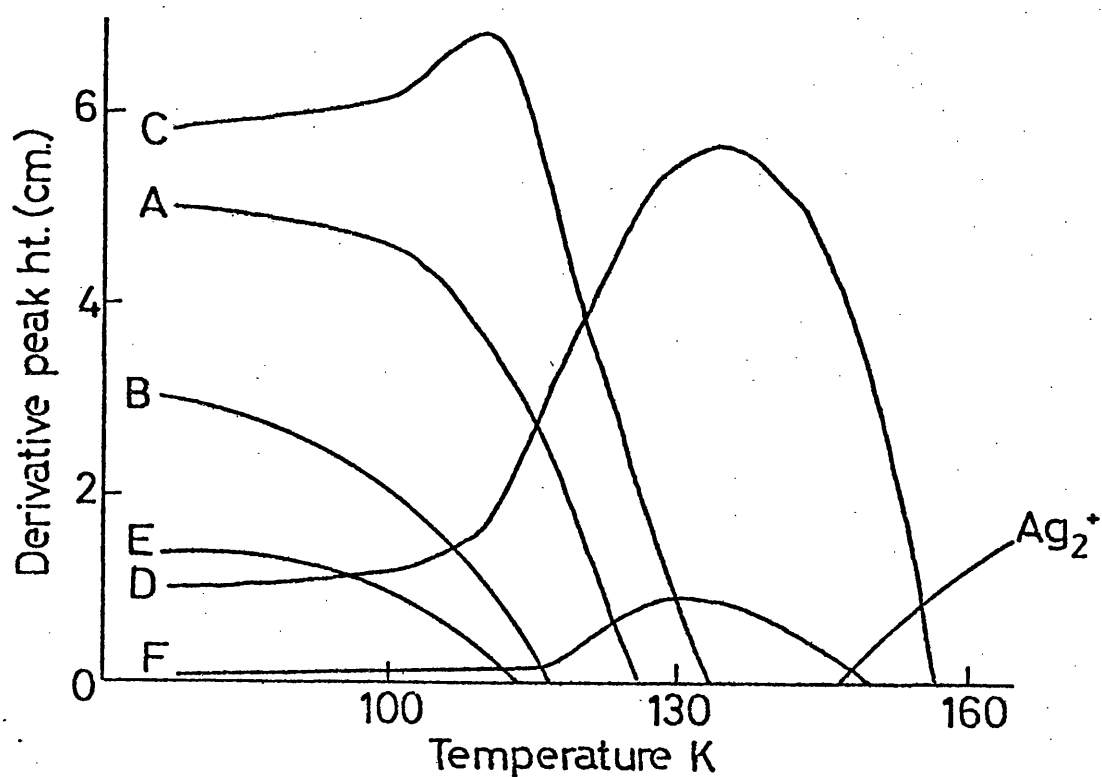
These have been extensively studied by Bales and Kevan^{8,9} and the results of this work in general confirm theirs. Changes in the distribution of Ag^0 centres with dose must reflect trapping powers and concentrations of the different solvates, as discussed above for centre A. Thermal effects can again be understood in terms of selective desolvation. In Figure 3.4 the concentration of the individual Ag^0 types is plotted, a) against the γ dose received and, b) after a γ dose of 3 MRad, against temperature. The plots are only comparative as radical concentrations are measured as the peak height on a first derivative spectrum.

It is notable that high γ doses result in the formation of a new, hitherto unmentioned Ag^0 centre. The low accuracy

Figure 3.4 Comparative yields of Ag^0 centres (measured as first derivative peak heights) in an $\text{AgNO}_3/\text{D}_2\text{O}$ solution (1 mol kg^{-1}), (a) vs. ^{60}Co γ ray dose at 77K;



(b) vs. temperature (following a γ ray dose of ca. 3MRad at 77K).



with which the parameters for this centre can be measured precludes the drawing of any conclusions regarding its nature.

The relative yields of the various Ag^0 centres is found to be fairly independent of $[\text{Ag}^+]$ in the range 0.001–2 mol kg^{-1} , and in view of the phase separation any conclusions regarding concentration effects would be suspect.

Ag_2^+ Centres in Water

As with sulphuric acid glasses³, these centres are formed on annealing above 77K, but never in high yield. (Fig. 3.5) The features are remarkably narrow and do not change in width on going from $\text{H}_2\text{O} \rightarrow \text{D}_2\text{O}$ matrices. This suggests that the unpaired electron is rather strongly confined to the σ bond between the two silver atoms, and avoids the anti-bonding solvation region.

Higher aggregate centres such as Ag_4^{3+} are only detected in magnesium perchlorate glasses. This is probably linked to the higher mobility of the atom like Ag^0 centres in this matrix.

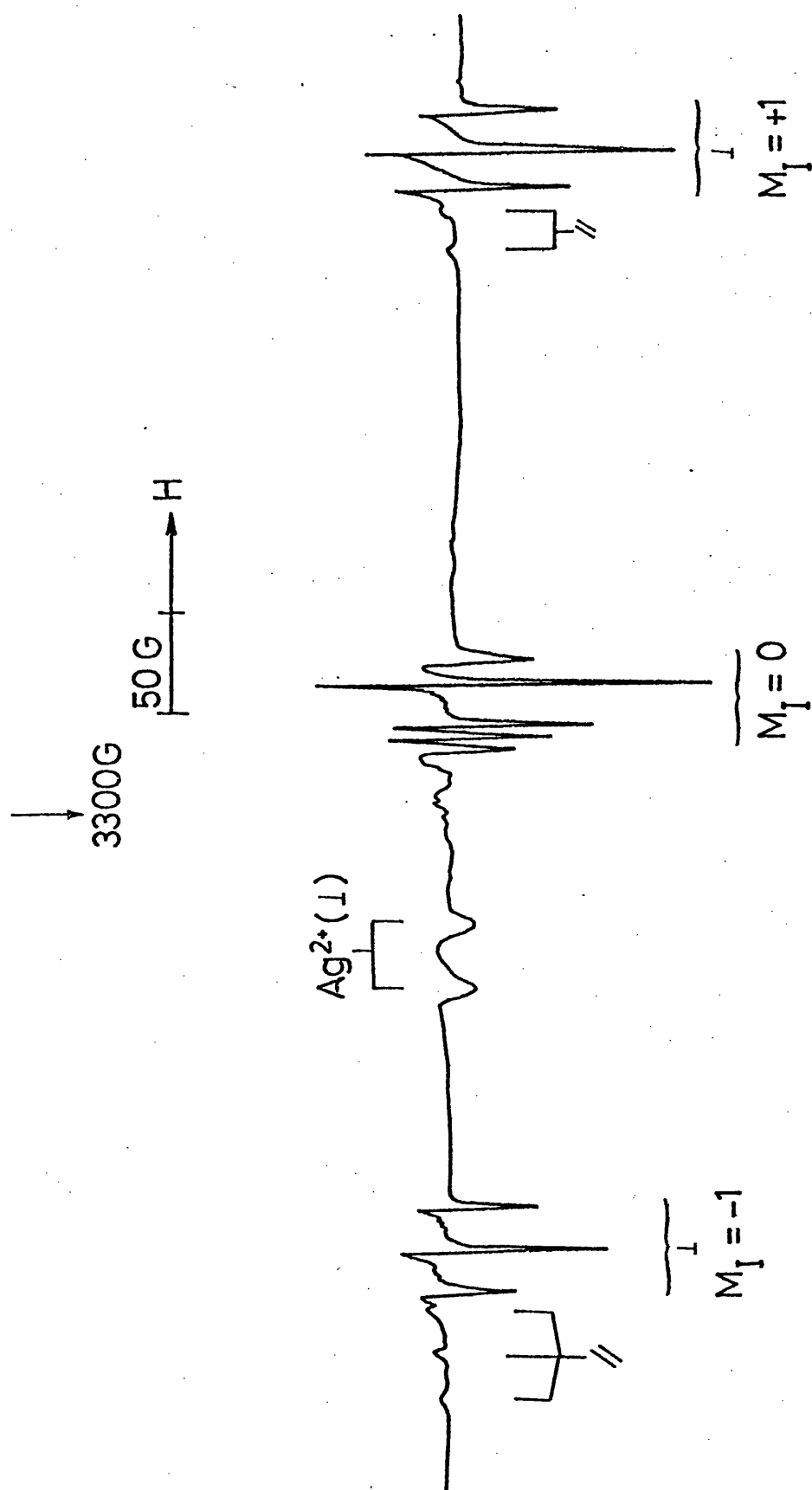


Figure 3.5 X-band ESR spectrum of an $\text{AgNO}_3/\text{D}_2\text{O}$ solution following low temperature irradiation and prolonged annealing, showing features assigned to Ag_2^+ ions.

3.2 An ESR and IR Study of Ion Pairing in Silver Nitrate/Methyl Cyanide Solutions⁷

This system was chosen for study by ESR primarily to reinforce evidence collected by Dr. T.J.V. Findlay⁷ using IR and Raman spectroscopy for the existence of ion pairs and clusters of silver ions in methyl cyanide solutions of silver nitrate.

Irish et al.²² have studied solutions of silver nitrate in methyl cyanide using Raman spectroscopy to monitor changes in the symmetrical (ν_0) and other nitrate vibrational modes. They largely confirmed the earlier work of Janz et al.²³ that there is a slight shift in ν_0 as $[\text{Ag}^+]$ increases, followed by a larger shift at high concentrations. The former was attributed to ion pair formation and the latter to the formation of clusters. They failed to monitor the more definitive ν_3 band because the solvent is optically black in this region. Since this can give more intimate details of ion pair formation it was decided to study the ν_3 band using CD_3CN as solvent.

It was hoped that the formation of ion pairs and clusters could be confirmed by ESR of the irradiated frozen solutions. An additional aim of this study was to compare electron capture processes in a system in which two centres, Ag^+ and NO_3^- can compete, either as separate units or when weakly complexed together, for electrons.

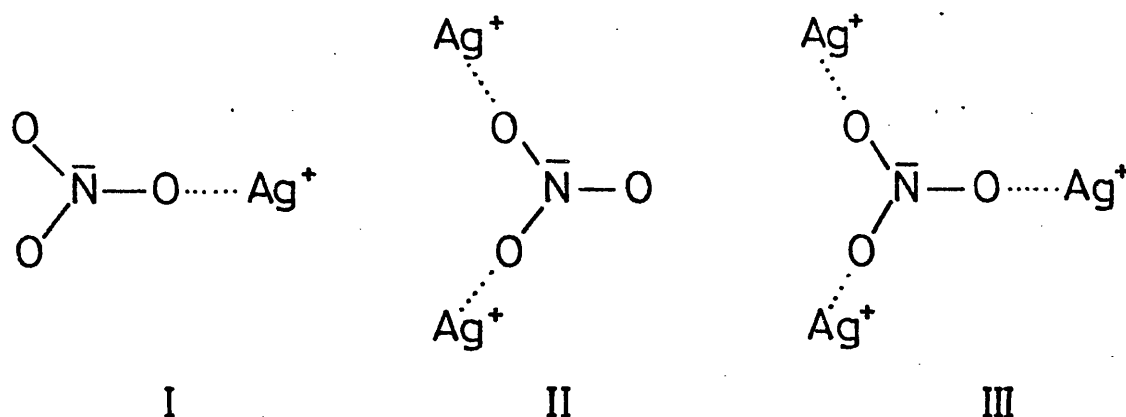
3.2a Experimental

Silver nitrate was Analar grade and used as supplied. Methyl cyanide d-3 was supplied by Nuclear Magnetic Resonance Ltd. and was of 99.5% purity. Solutions were prepared by weight under water free conditions. Beads for irradiation were prepared by pipetting small droplets of solution into liquid nitrogen; irradiation and ESR measurements were carried out as described in Chapter One. Radiation doses at 77K were typically 3 MRad.

3.2b Results and Discussion

Vibrational Spectroscopy

Findlay has observed the nitrate ν_3 band in the Infrared spectrum of $\text{AgNO}_3/\text{CD}_3\text{CN}$ solutions. This band is better resolved than those bands studied by Irish²². In dilute solution a central peak at $\sim 1360 \text{ cm}^{-1}$ dominates; this corresponds to the value for solvated nitrate ions in the solvent. However, at all concentrations this band is flanked by a doublet (~ 1420 and $\sim 1307 \text{ cm}^{-1}$) which has been assigned to the contact ion pair, $\text{Ag}^+ \cdots \text{ONO}_2^-$, the doublet arising because of the decrease in symmetry of the nitrate ion on forming the ion pair. As the concentration increases the central line is not lost but its intensity goes through a minimum in the 1-2 mol kg^{-1} region and then increases. It has been suggested⁷ that this is indicative of cluster formation. Of the structures I, II and III below, I and II would give doublets whereas



III would give a singlet.

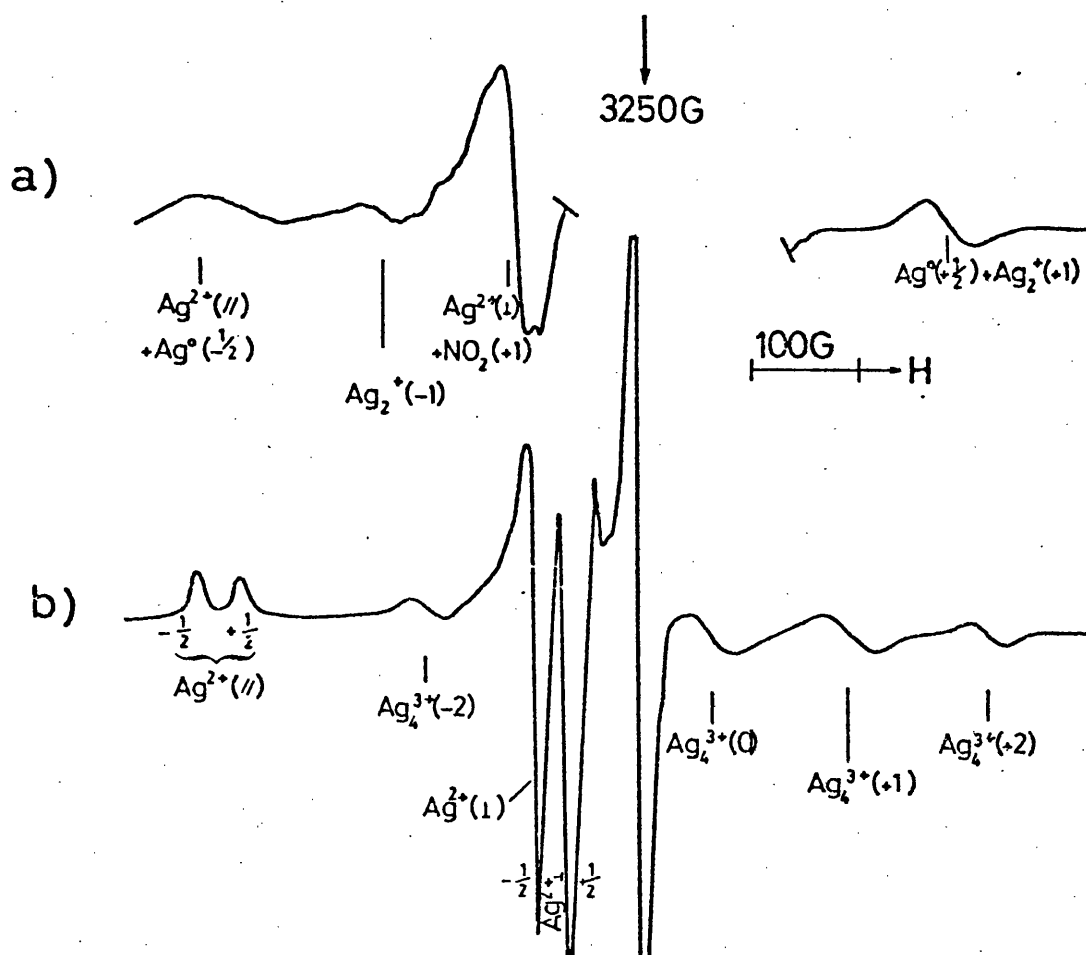
ESR Spectroscopy

Radicals formed from deuterated and undeuterated methyl cyanide have been extensively studied^{24,25} and will not be discussed here. The ESR data is summarized in Table A3.2 and in Figure 3.6.

Nitrate radiation damage products are principally NO_2 and NO_3^{2-} , little NO_3 being observed. In contrast to solutions of tetra n-butylammonium nitrate which give only NO_3^{2-} on irradiation at 77K at all salt concentrations, NO_2 is detected following irradiation of even dilute silver nitrate solutions. The features from NO_2 probably obscure the NO_3^{2-} features in the low concentration region, but it is concluded that NO_2 is the preferentially formed product. Dilute solutions also give features from silver hyperfine coupling analysed in terms of Ag^0 and Ag_2^+ .

As $[\text{Ag}^+]$ increases Ag^0 is lost and the dominant electron capture species becomes Ag_2^+ . At concentrations $\geq 3.5 \text{ mol kg}^{-1}$ the dominant features become those for Ag_4^{3+} . It is quite possible that broad features for Ag_3^{2+} are also present but they are never clearly resolved.

Figure 3.6 X-band ESR spectrum of an $\text{AgNO}_3/\text{CD}_3\text{CN}$ solution

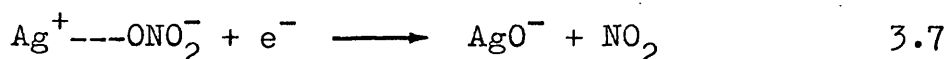


(0.4 mol kg^{-1}) following low temperature irradiation, (a) at 77K, showing outer features for Ag^0 , Ag_2^+ and Ag^{2+} and (b) after annealing, showing features for Ag^{2+} and Ag_4^{3+} .

Features assigned to Ag^{2+} sharpen and become more intense on annealing and recooling to 77K (Table A3.2 and Fig. 3.6). Features from NO_3 are probably also present but are poorly defined because of overlap with the central features from methyl cyanide damage.

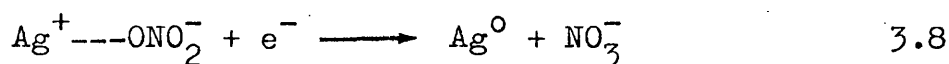
The effect of γ rays on powdered silver nitrate crystals has also been studied and the results of Mosley and Moulton²⁰ confirmed that the only significant electron capture product is NO_3^{2-} .

These results lead to the following model. Solvated nitrate ions give NO_3^{2-} in direct competition with solvated Ag^+ ions which give Ag^0 . The contact ion pairs (I) would seem to react at least in part by reaction 3.7.



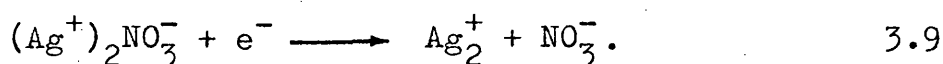
This reaction is in general accord with Symons and Zimmerman²⁶ and Shields⁵ who attribute NO_2 formation in aqueous solution to an electron capture, rather than an electron loss, process by NO_3^- .

It is possible that reaction 3.8 competes with reaction



3.7, but since $[\text{NO}_2]$ is always high it is suggested that reaction 3.7 dominates.

Species such as II and III can, it seems, on adding an electron extrude Ag_2^+ and the preferred path for such aggregates is then:

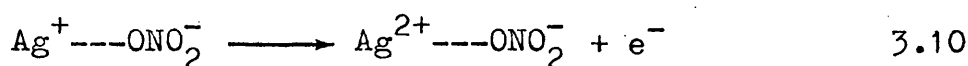


It is surprising that neither reaction 3.7 nor 3.9

occur in pure silver nitrate crystals. The crystal forces must favour the bending distortion that leads to NO_3^{2-} rather than the movement of two silver ions leading to Ag_2^+ .

Electron Loss Centres

These are solvent radicals, NO_3 and Ag^{2+} . Again, there must be competition between Ag^+ and NO_3^- . The large increase in $[\text{Ag}^{2+}]$ as $[\text{AgNO}_3]$ increases might suggest that Ag^{2+} formation is favoured from Ag^+ involved in ion pairs rather than free solvated Ag^+ .



Unlike the features in the spectrum from electron gain centres, Ag^{2+} exhibits a well resolved spectrum with parameters normal for silver with a configuration $-\text{d}_{\text{z}}^2 \text{d}_{\text{x}}^1 \text{d}_{\text{y}}^2$. That no super-hyperfine structure (SHFS) is seen in either the parallel or the perpendicular regions of the spectrum from coupling to solvent MeCN molecules via ^{14}N must mean that electron loss is favoured by Ag^+ which is coordinated to a maximum number of nitrate ions, since these would not be expected to give any resolved ^{14}N splitting. This is in marked contrast to Ag^{2+} formed following irradiation of frozen silver perchlorate/methyl cyanide solutions discussed next. In this system Ag^{2+} exhibits parameters typical of a silver $-\text{d}_{\text{z}}^2 \text{d}_{\text{x}}^1 \text{d}_{\text{y}}^2$ configuration and in addition coupling to ^{14}N nuclei is seen on both parallel and perpendicular features (Fig. 3.7a).

3.3 An ESR Study of Solvation in Silver Perchlorate/Methyl Cyanide Solutions

By replacing the nitrate ion with the perchlorate ion it was hoped that the amount of Ag^+ involved in ion pairing in methyl cyanide might be reduced. The ESR spectra associated with this system indicate that this is so (Fig. 3.7). The formation of silver ion aggregates does not seem to occur at 77K and, when deuterated methyl cyanide is used, the spectra of both Ag^0 and Ag^{2+} exhibit well resolved coupling to solvent molecules via ^{14}N .

3.3a Experimental

The sample preparation, irradiation and ESR measurements were performed exactly as in 3.2a substituting Analar grade silver perchlorate for silver nitrate.

3.3b Results and Discussion

The results are summarized in Figures 3.7 and 3.8 and Table A3.2.

Ag^{2+} Centres in CD_3CN

On both the parallel and the perpendicular features superhyperfine structure (SHFS) is detected from coupling to

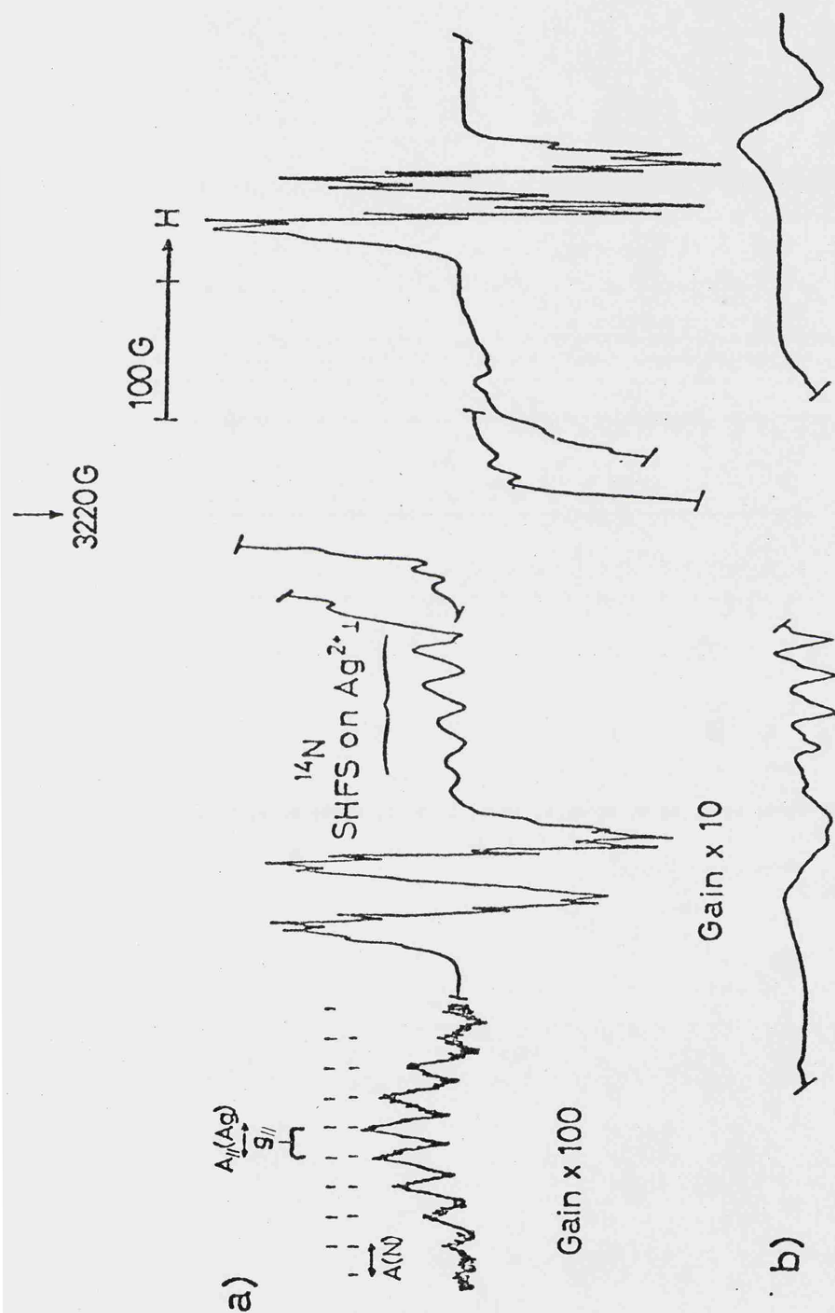


Figure 3.7 X-band ESR spectrum of an $\text{AgClO}_4/\text{CD}_3\text{CN}$ solution (0.5 mol kg^{-1}) following low temperature irradiation, (a) at 77K, showing Ag^0 and Ag^{2+} features, both with well resolved nitrogen superhyperfine structure and (b) after annealing, showing broad features for Ag_2^+ .

solvent molecules via ^{14}N . A tentative interpretation of the SHFS on the parallel features is shown in Figure 3.7 and suggests coupling to four roughly equivalent solvent molecules. The SHFS cannot unambiguously be assigned, however, until the precise extent of the peripheral ^{14}N satellite lines has been established and at X-band microwave frequency overlap with the $m_I = -\frac{1}{2} \text{Ag}^0$ features makes this difficult.

That the parallel features are at low field and the perpendicular features are just below free spin is indicative of a silver electronic configuration of $-d_z^2 d_{x^2-y^2}^1$. The perpendicular features are not fully revealed even after annealing although a value for the hyperfine coupling constant to ^{14}N is estimated at $A(\text{N}) \sim 23\text{G}$. This value is slightly higher than $A(\text{N})$ on the parallel features ($\sim 21\text{G}$) and indicates that the coordination is slightly asymmetric. Indeed, some type of 'frozen in' distortion has to be invoked to explain the form of the g tensor, there being no evidence for the distortion being dynamic; even when the beads are annealed to the softening point the parallel and perpendicular features maintain their positions in the ESR spectrum.

A necessary experiment with this system is to examine the spectrum at Q-band microwave frequency. This will shift both the parallel and the perpendicular features well away from the other signals in the spectrum and more, or hopefully all, of the SHFS in the perpendicular region will be revealed. The peripheral lines on the parallel features would also be clearly defined and a more exact analysis of the spectrum possible.

On the basis of the X-band spectrum a suitable model would involve Ag^+ coordinated to four solvent molecules in

a distorted tetrahedral configuration. A spectrum at Q-band frequency is essential for a precise interpretation but the proposed model does bear credence particularly in view of the analysis of the nitrogen SHFS on the Ag^0 features discussed later.

The large increase in $[\text{Ag}^{2+}]$ as $[\text{AgClO}_4]$ is increased indicates that the same factor is controlling $[\text{Ag}^{2+}]$, independent of whether NO_3^- or ClO_4^- is the anion. If, as proposed in Section 3.2, Ag^{2+} is formed from ion pairs, then the SHFS on the Ag^{2+} parallel features might be expected to be due to a solvation shell of methyl cyanide molecules, at least one of which is replaced by a perchlorate ion.

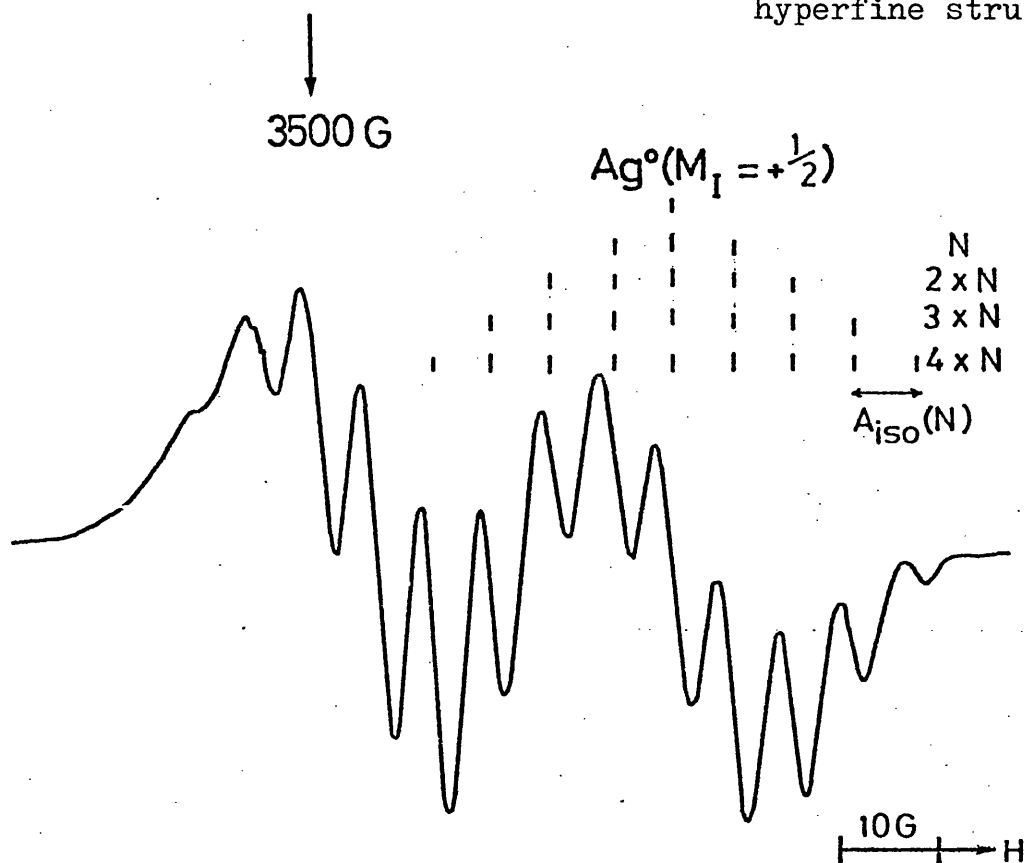
Such an interpretation of the SHFS may be possible; a Q-band spectrum would provide the definitive answer. If coupling to three instead of four nitrogens in the parallel region were invoked it would mean $A_{\parallel}(\text{Ag}^{2+})$ is larger than the value quoted in Table A3.2 (ca. -20G). This is not an unreasonable suggestion as -20G is low in comparison with values of $A_{\parallel}(\text{Ag}^{2+})$ in other media.

Ag^0 Centres in CD_3CN

Well resolved spectra indicate that little or none of the Ag^0 arises from ion pairs. The ^{14}N SHFS on both the $m_I = +\frac{1}{2}$ and $m_I = -\frac{1}{2}$ features is analysed unambiguously in terms of coupling to four equivalent ^{14}N nuclei ($A_{\text{iso}}(\text{N}) = 6.3\text{G}$), each Ag^0 feature being split into nine lines (Fig. 3.8a). The SHFS is slightly anisotropic and this supports the concept of a distorted tetrahedral solvation shell. The isotropic coupling to silver ($A_{\text{iso}}(\text{Ag}) = -534\text{G}$) and to nitrogen accounts

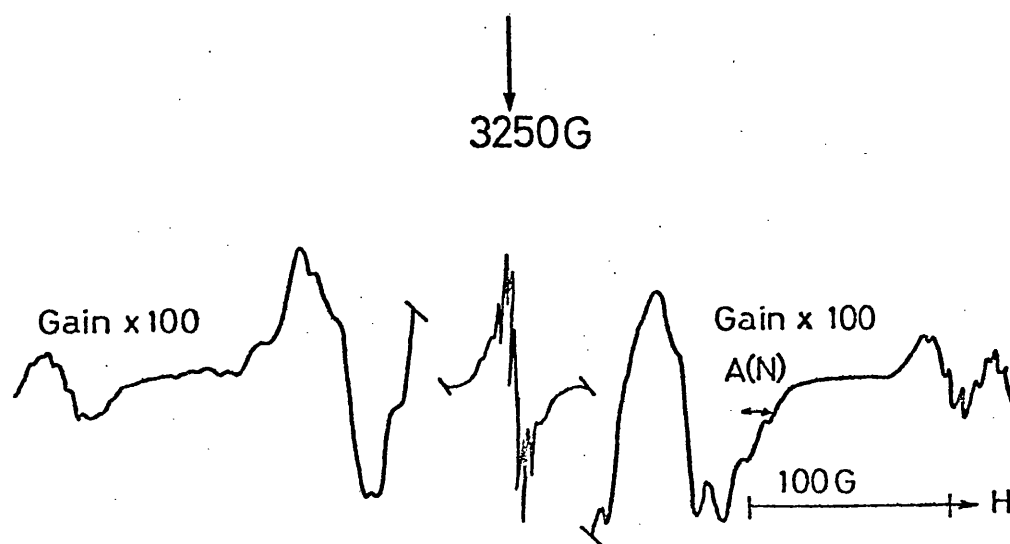
Figure 3.8 X-band ESR spectrum of an $\text{AgClO}_4/\text{CD}_3\text{CN}$ solution (2 mol kg^{-1}) following low temperature irradiation, (a) at 77K, showing $\text{Ag}^\circ m_I = +\frac{1}{2}$ features and the associated ^{14}N superhyperfine structure;

a)



(b) at 77K, showing doublet assigned to $(\text{CD}_2\text{CN-Ag})^+$.

b)



for approximately 80% of the unpaired spin density. Even allowing for some spin density on other nuclei within the solvent molecules an appreciable amount of anisotropy has to be invoked to accomodate all the unpaired spin. The negative g shift is consistent with some spin occupancy of the silver 5p orbitals.

On annealing Ag_2^+ and Ag_4^{3+} are formed (Table A3.2), although no nitrogen SHFS is observed on their spectra (Fig.3.7b).

When solutions are studied with high $[\text{AgClO}_4]$ ($\geq 2 \text{ mol kg}^{-1}$), an additional paramagnetic species is observed characterised by a doublet in the ESR spectrum centred approximately on free spin (Fig. 3.8b). The form of this doublet is unchanged on going from $\text{CD}_3\text{CN} \rightarrow \text{CH}_3\text{CN}$ matrices and it appears to show fine structure that may be associated with ^{14}N nuclei. Its approximate ESR parameters are:

$$g_{\text{iso}} \cong 2.000 \quad A_{\text{iso}} \cong -87\text{G} \quad A_{\text{iso}}(\text{N}) \cong 7\text{G} .$$

It is difficult to gauge the number of nitrogen nuclei involved in the SHFS as anisotropy may well be present. Again, a spectrum at Q-band frequency would clarify the situation but a preliminary assignment to a species of the type $\text{Ag}^+-\text{CD}_2\text{CN}$ is suggested, similar to the $\text{Ag}^+-\text{CD}_2\text{OD}$ adduct species detected in frozen alcoholic solution, and discussed later.

The Solvation of Ag^+

Silver frequently favours a coordination number of two²⁷ and such a coordination number is exhibited in the linear $\text{Ag}(\text{CN})_2^-$ ion. $\text{Ag}(\text{NH}_3)_2^+$ is also linear²⁸, and this ion

is thought to be a major component in ammoniacal silver solutions although recent evidence from Raman spectroscopic studies indicates that Ag^+ is solvated by four ammonia molecules in liquid ammonia²⁹. Indeed, four coordination to silver is not uncommon with nitrogen containing ligands²⁷, including methyl cyanide³⁰, and ESR has been used as a tool with some of these, notably the silver dipyriddy ion³¹, to establish the configurations of ligand molecules around the parent silver ion.

The results reported here clearly indicate that Ag^+ is coordinated by four solvent molecules. It appears that the solvation number is not changed when the monopositive charge on Ag^+ is either increased (to form Ag^{2+}), or lost completely (to form Ag^0) at 77K, although the superhyperfine constants from ^{14}N coupling do indicate a reduced delocalisation of spin onto the ligands when the charge is lost (Ag^0) compared to when it is increased (Ag^{2+}).

Four coordinated silver generally exhibits sp^3 tetrahedral geometry when the ligand-metal bond is ionic²⁷. A more covalent ligand-metal bond leads to dsp^2 hybridisation on the silver ion and square planar coordination is favoured. The relatively high basicity of methyl cyanide would therefore suggest tetrahedral coordination and this is consistent with the model of a distorted tetrahedral solvation shell proposed earlier to explain the observed spectra.

A marked difference between these results and those from frozen aqueous silver solutions is that in methyl cyanide the Ag^0 seems to arise from only one type of Ag^+ solvate and there is no need to invoke the idea of quantised, discrete solvate types, needed to explain the various types of Ag^0

formed in aqueous solution.

Further experiments on silver perchlorate solutions in mixed methyl cyanide/water solvents might prove informative. In changing gradually from an aqueous to a methyl cyanide solvent, a link might be established between the different types of solvation in the two solvents.

3.4 Silver Centres formed in Other Aqueous and Non Aqueous Systems

In contrast to the ESR spectra of frozen aqueous and methyl cyanide solutions, most non aqueous solutions exhibit poorly defined Ag^0 and Ag^{2+} spectra. Aggregation is generally facile in non aqueous solvents and frequently Ag_2^+ and Ag_4^{3+} are detected and sometimes Ag_3^{2+} is also seen. It is notable that aggregates of more than four silver nuclei are not detected in these frozen solutions.

A study of radiolytically produced silver centres in frozen alcoholic solutions and a comparison with aqueous systems has been carried out by Shields⁵. The Ag^0 species do not exhibit such well resolved spectra as in aqueous solution and there is clearly less delocalisation of the spin onto the ligands but nevertheless, structure is visible on the Ag^0 features; whether this is caused by anisotropy as proposed by Shields, or by the existence of two types of Ag^0 is discussed later.

This study was initiated before the work on the silver perchlorate/methyl cyanide system, reported in Section 3.3, was carried out. Following the work on the silver nitrate/methyl cyanide system, and because no hyperfine coupling to Ag^0 or Ag^{2+} from the solvent was detected, it was decided to study radiolytically produced silver centres in a range of solvents of varying basicities. Although information from this study on the solvation of the parent Ag^+ ion is not forthcoming there are aspects of the results that are novel.

3.4a Experimental

Solutions were prepared using solvents of Spectrograde or the highest available purity. Silver nitrate and perchlorate were Analar grade and were used as supplied. Silver solutions were studied, where possible, in the concentration range $0.001 \rightarrow 5.0 \text{ mol kg}^{-1}$. Beads of frozen solution were prepared and irradiated as described earlier.

3.4b Results and Discussion

The results are summarized in Tables A3.3-A3.6. The solvent systems will be discussed in turn.

Silver Centres in Primary Alcohols

Hydrogen bonding is less pronounced in alcohols than in water and the solvent structures are somewhat less rigid. Irradiation of frozen silver perchlorate/alcohol solutions produces Ag^0 centres with substantially higher spin densities in the silver 5s orbital than are found in aqueous solutions (Table A3.3 and ref. 5). In methanol, Shields^{5,32} has interpreted the spectrum of Ag^0 in terms of one predominating species exhibiting an axially symmetric hyperfine tensor. In this work a similar spectrum has been observed but it is interpreted in terms of two predominant isotropic species rather than one of axial symmetry (Fig. 3.9a and Table A3.3), for the following reasons. (1) The relative yields of the two species (A and B) are dependent on $[\text{Ag}^+]$, A being in rel-

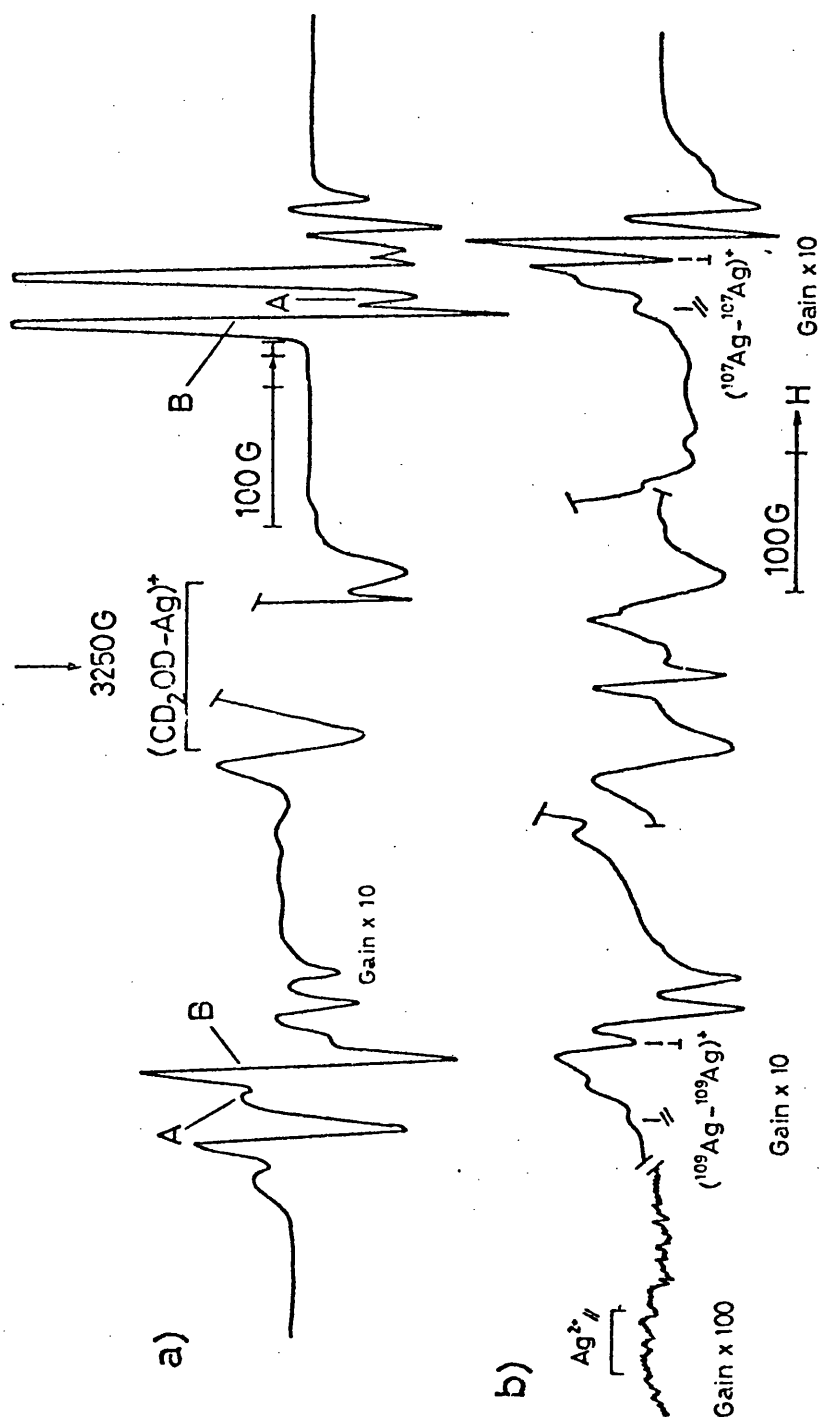


Figure 3.9 X-band ESR spectrum of an $\text{AgClO}_4/\text{CD}_3\text{OD}$ solution (0.1 mol kg^{-1}) following low temperature irradiation, (a) at 77K showing features assigned to the $(\text{CD}_2\text{OD-Ag})^+$ centre and the Ag° centres A and B, (b) after annealing showing Ag_2^+ features and intensified $(\text{CD}_2\text{OD-Ag})^+$ features.

atively higher abundance when $[\text{Ag}^+]$ is low. (2) When n-butanol is used instead of methanol, two similar species occur but in this medium B is the overwhelmingly predominant product and its ESR spectrum is clearly isotropic.

Similar Ag^0 species are formed in methyltetrahydrofuran (MeTHF) solution (Table A3.3).

That two types of Ag^0 predominate fits these systems between aqueous systems, in which at least six types of Ag^0 are formed, and the methyl cyanide system in which only one type of Ag^+ solvate yields Ag^0 . It is not possible to predict the structures of the two solvates A and B, although the two symmetrical tetrahedral and octahedral solvates are obvious possibilities.

The $(\text{Ag}-\text{Ag}_3)^{3+}$ Centre:

On annealing methanolic glasses, the formation of Ag_2^+ is readily detected by ESR (Fig. 3.9b), and this is followed by Ag_4^{3+} . Ag_4^{3+} is characterised by five broad, evenly spaced lines which are observed at all $[\text{Ag}^+]$, but superimposed on this is a further spectrum consisting of four sets of doublets (Fig. 3.10). The intensity of this new spectrum reaches a maximum when $[\text{Ag}^+] = 1-2 \text{ kg mol}^{-1}$ and decreases to unobservably low levels at $<0.1 \text{ mol kg}^{-1}$ and $>5 \text{ mol kg}^{-1}$ whence it is completely hidden in the Ag_4^{3+} spectrum. It is ascribed to an unsymmetrical Ag_4^{3+} unit, written $\text{Ag}_3^{2+}-\text{Ag}^+$, and its parameters are as follows.

$$g_{\text{iso}} = 1.963 \pm 0.003 \quad A_{\text{iso}}(3x\text{Ag}) = -141 \pm 2\text{G}$$

$$A_{\text{iso}}(\text{Ag}) = -57 \pm 2\text{G}$$

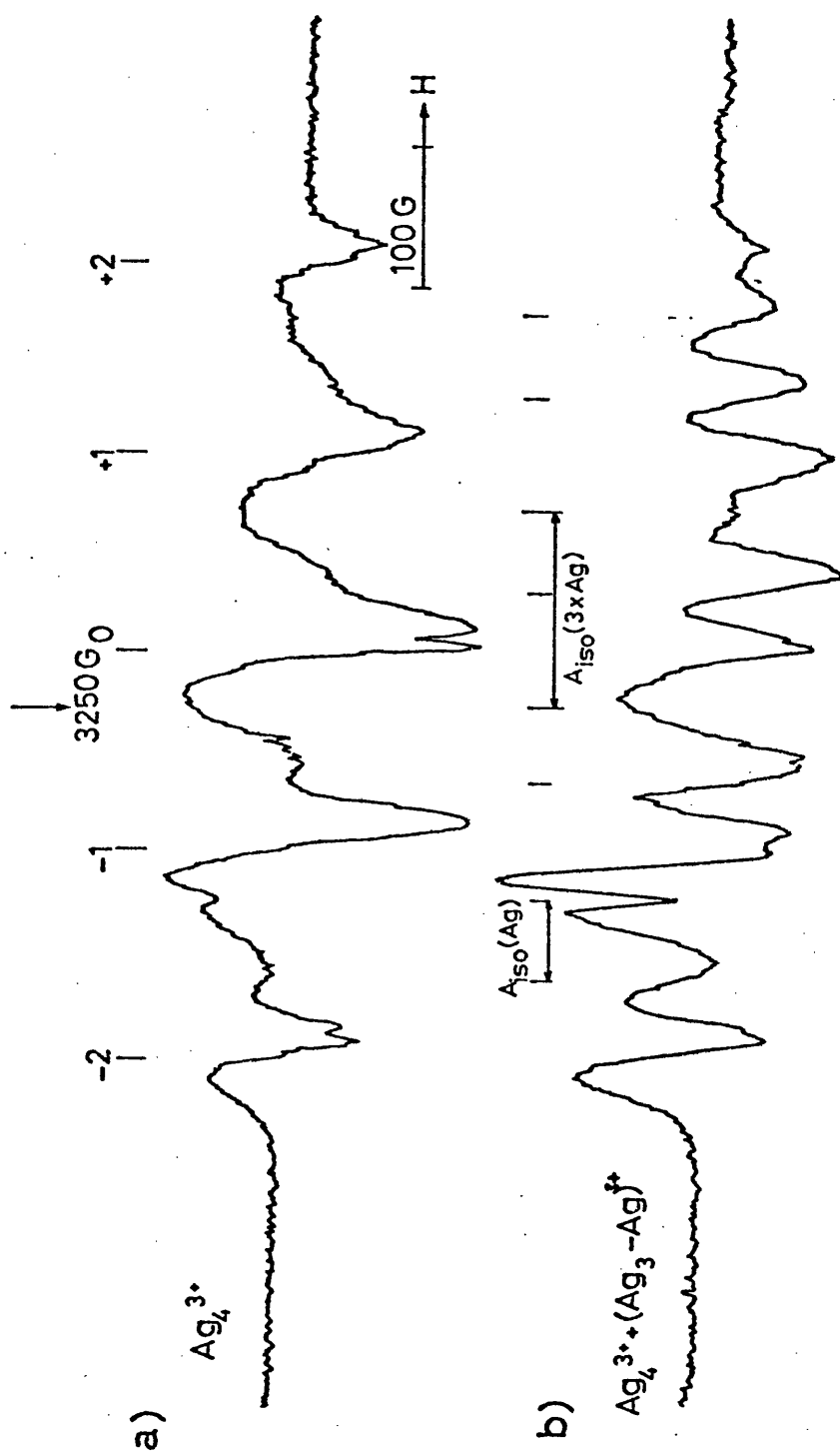


Figure 3.10 X-band ESR spectrum of an $\text{AgClO}_4/\text{CD}_3\text{OD}$ solution following low temperature irradiation, after annealing, (a) when $[\text{AgClO}_4] = 0.2\text{ mol kg}^{-1}$ showing features from Ag_4^{3+} and (b) when $[\text{AgClO}_4] = 1.2\text{ mol kg}^{-1}$ showing additional features from $(\text{Ag}_3 - \text{Ag})^{3+}$.

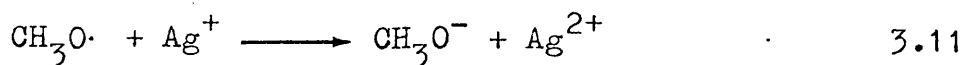
An identical spectrum is detected in the anneal of n-butanol glasses. The significance of this species is not understood, but its concentration dependence suggests that its formation may be related to the degree of ion pairing in the solvent. A crude possibility would be that it is one Ag^+ involved in a contact ion pair sharing an unpaired electron with three normally solvated Ag^+ ions. Such a model does not, however, accomodate its low yield at high $[\text{AgClO}_4]$, particularly relative to the high yield of Ag_4^{3+} at these concentrations.

The $(\text{Ag}-\text{CH}_2\text{OH})^+$ Centre:

A further species detected in these systems is characterised by an isotropic doublet, which appears and increases in intensity as the beads are annealed concurrently with the disappearance of the signal attributed to $\cdot\text{CH}_2\text{OH}$ (or $\cdot\text{CD}_2\text{OD}$ in deuterated methanol)³³. This doublet is centred on free spin (Fig. 3.9). The ESR parameters are almost independent of whether methanol or n-butanol is used and are as follows.

	g_{iso}	A_{iso}
MeOH	2.002 ± 0.002	$-127 \pm 3 \text{ G}$
n-BuOH	2.002 ± 0.005	$-130 \pm 5 \text{ G}$

These features have been assigned by Eachus and Symons³³ to the AgOCH_3^+ ion, formed following tautomeric rearrangement of the $\cdot\text{CH}_2\text{OH}$ to the $\text{CH}_3\text{O}\cdot$ radical. This assignment is questioned because the relatively high stability of CH_3O^- would lead one to expect the products of reaction 3.11 to be significant contributors to the structure of AgOCH_3^+ , and ESR parameters for such a species would be more characteristic of Ag^{2+} .



In contrast, AgH^+ , the analogous species, has been identified by the same authors³³ in 7.2M sulphuric acid and this seems a reasonable identification; the products of reaction 3.11, if $\text{CH}_3\text{O}\cdot$ were replaced by $\cdot\text{H}$, would be unstable and Ag^{2+} would not be expected.

A more reasonable assignment for the doublet in alcoholic glasses is the adduct $(\text{CH}_2\text{OH-Ag})^+$ with coupling to the Ag^+ via carbon. Proton coupling might be expected if such a species were the correct one and although it is not seen, it may be present but hidden in, and to some extent responsible for, the line width. That replacing CH_3OH with CD_3OD reduces the line widths supports this view.

Any anisotropy in the hyperfine tensor of this species is hidden in the line width but a value for the spin density in the silver 5s orbital is estimated at ca.20%. This compares³³ with ca.50% occupancy in AgH^+ and the difference is a function of the relative electronegativities of the H and the $\cdot\text{CH}_2\text{OH}$ radicals.

Silver Centres in Dipolar Aprotic Solvents

Silver centres are detected in all the dipolar aprotic solvents studied. These were dimethylsulphoxide (DMSO), hexamethylphosphoramide (HMPA), methyl cyanide and ethyl cyanide. With the exception of methyl cyanide all the solvents were undeuterated and the ESR spectra are poorly resolved and uninformative regarding the solvation of Ag^+ .

Ag^0 is invariably formed and silver aggregate species can also be detected either by using high $[\text{Ag}^+]$ or by annealing

the irradiated beads made from more dilute solutions. The ESR parameters for Ag^0 , Ag_2^+ and Ag_4^{3+} formed in these media are in Tables A3.3-A3.5.

Ag^{2+} , the hole centre, is often formed and invariably exhibits parameters indicating that the unpaired spin is in a $d_{x^2-y^2}$ orbital. The parameters for these centres are in Table A3.6.

Silver Centres in Amine Solutions

The solvents used were 35% aqueous NH_3 solution, pyridine, ethylenediamine and a number of primary amines. ESR spectra from silver perchlorate solution in t-butylamine show the best resolution.

Hyperfine constants for Ag^0 are generally small (Table A3.3), reflecting the strong coordination of ligand molecules to the parent Ag^+ ion. SHFS is visible on Ag^0 features from t-butylamine solution but it is not clear enough to determine the extent of delocalisation onto individual ligands or the coordination number. Spectra from deuterated amines might show better resolution.

Aggregation to Ag_4^{3+} is facile in 35% NH_3 solution and possibly in t-butylamine, although in pyridine and ethylenediamine aggregation appears to stop once Ag_3^{2+} has been formed.

Ag^{2+} is detected in most of these solvents, invariably exhibiting spectra characteristic of a $d_z^2 d_{x^2-y^2}^1$ configuration.

Some Conclusions on Silver Electron Excess Centres

From the data in Table A3.3 it seems that on removing

the charge on Ag^+ at 77K solvation is retained around Ag^0 atoms in many solvents; the delocalisation of the unpaired spin onto solvent ligands (as measured by the decrease in $A_{\text{iso}}(\text{Ag})$ relative to the free atom value) is at least roughly related to the Lewis basicity of the solvent and hence to its solvating power towards Ag^+ , itself a Lewis acid.

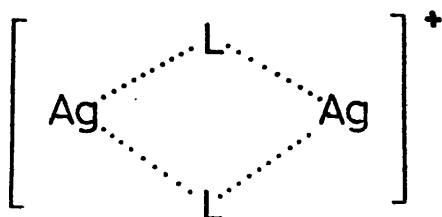
There are similarities between these results for Ag^0 (Table A3.3) and those recently reported by Catterall³⁴ for alkali metals in frozen hexamethylphosphoramide (HMPA). When fluid solutions of alkali metals in HMPA are frozen a range of paramagnetic species are detected having up to ~70% atom character. Such values for the atom character indicate that interaction between solvent molecules and uncharged atoms is significant and suggest that the balance between strongly solvated cations and weakly solvated atoms is a subtle one.

The spectra of the irradiated frozen Ag^+ solutions can be categorised with respect to the resolution of the Ag_2^+ features detected. There are three categories.

- (1) Those of very high resolution; aqueous are the only systems in this category (Fig. 3.5).
- (2) Those of intermediate resolution, where parallel and perpendicular features and the 1:2:1 pattern from the two silver isotopes can be detected, but line widths are significantly larger than in ice; frozen solutions in methanol, HMPA, MeTHF, benzene and 6M H_2SO_4 fall into this category (Fig. 3.9).
- (3) Those of poor resolution, where signals from Ag^0 , Ag_2^+ and Ag^{2+} merge. Ag_2^+ appears as a broad, single, isotropic feature both at low and high fields; DMSO, t-butylamine and methyl cyanide solutions provide such spectra (Fig. 3.7).

As a consequence of these categories, two distinct types of Ag_2^+ are postulated. It is suggested that Ag_2^+ exists in ice, methanol and the rest of the solvents constituting category (2) above as a contact pair with the unpaired electron in a σ bond between the silver nuclei. Formation of such a pair is accompanied by a rearrangement of the solvation shells to accomodate the Ag_2^+ entity.

By way of contrast the ESR signal from Ag_2^+ in frozen methyl cyanide, DMSO and t-butylamine can be explained in terms of silver nuclei separated by solvent molecules as shown below. The unpaired electron would then be in a some-



what more diffuse molecular orbital delocalised onto solvent molecules as well as silver. Such a model explains the apparent lack of anisotropy and the line widths associated with the Ag_2^+ features in these solvents.

It is more difficult to postulate such models for the formation of larger aggregates. The smaller hyperfine constants and the 1:3:3:1 or 1:4:6:4:1 patterns from the two silver isotopes superimposed on each feature mean that the spectra are always poorly resolved and solvents cannot be categorised as they can on the basis of the Ag_2^+ features.

3.5 Silver/Halogen Complex Centres in Aqueous and Other Solvents

It is generally acknowledged that Ag^+ ions exist in solutions containing halide ions as complex ions of the type $\text{AgHal}_n^{(n-1)-}$, but most of the evidence for their existence is thermodynamic³⁵⁻³⁷. It was decided to include such complexes in this study and to compare the results pertaining to the solvation of such complex ions to those of systems containing free and normally solvated Ag^+ ions.

3.5a Experimental

Solvents used were Spectrograde or of the highest available purity. Silver salts were halides (Koch Light Ltd.). Excess halide was added either as alkali halides (Analar) or as tetraalkylammonium halides (Eastman Kodak Ltd.). Solutions were prepared by dissolving the required amount of halide in the solvent and then refluxing in the presence of silver halide. The solutions were allowed to cool overnight and were then frozen and irradiated at 77K in the usual way.

3.5b Results and Discussion

Several systems were studied but it was found that only those containing the chloride ion provide well resolved spectra.

The best resolved spectra from aqueous systems are achieved using D_2O solutions, and of the non aqueous systems studied, solutions in methyltetrahydrofuran (MeTHF) exhibit the clearest spectra. Solutions in other non aqueous solvents exhibit broadly similar, but less clearly defined, spectra.

$AgCl_n^{(n-1)-}$ Centres in D_2O

From the equilibrium constants for the formation of $AgCl_n^{(n-1)-}$ complex ions in water³⁷ the concentration of each $AgCl_n^{(n-1)-}$ species can be calculated as a function of chloride ion concentration.

$[Cl^-]$ mol l^{-1}	$[Ag^+]$	$[AgCl_{aq}]$	$[AgCl_2^-]$	$[AgCl_3^{2-}]$
0.2	4.4×10^{-10}	2.25×10^{-7}	3.4×10^{-6}	6×10^{-7}
1	8.8×10^{-11}	2.25×10^{-7}	1.7×10^{-5}	1.5×10^{-5}
4	2.2×10^{-11}	2.25×10^{-7}	6.9×10^{-5}	2.5×10^{-4}
~6(satd.)	1.5×10^{-11}	2.25×10^{-7}	1.0×10^{-4}	5.5×10^{-4}

On irradiating a range of frozen solutions of sodium chloride and silver chloride in D_2O the major paramagnetic products are $\cdot OD$, Cl_2^- and Ag^0 . The Cl_2^- features are similar to those found in solid KCl ³⁸ and the $\cdot OD$ features similar to those found in pure D_2O . The Ag^0 features represent a reduced spin density in the silver 5s orbital compared to uncomplexed Ag^0 in water and, following an anneal and a recool to 77K, superhyperfine structure (SHFS) on the Ag^0 features from delocalisation onto chlorine nuclei is resolved (Fig. 3.11).

The form of the Ag^0 spectrum is independent of $[Cl^-]$ but it is only clearly detected at high $[Cl^-]$ and saturated sodium chloride solutions provide the most intense spectra.

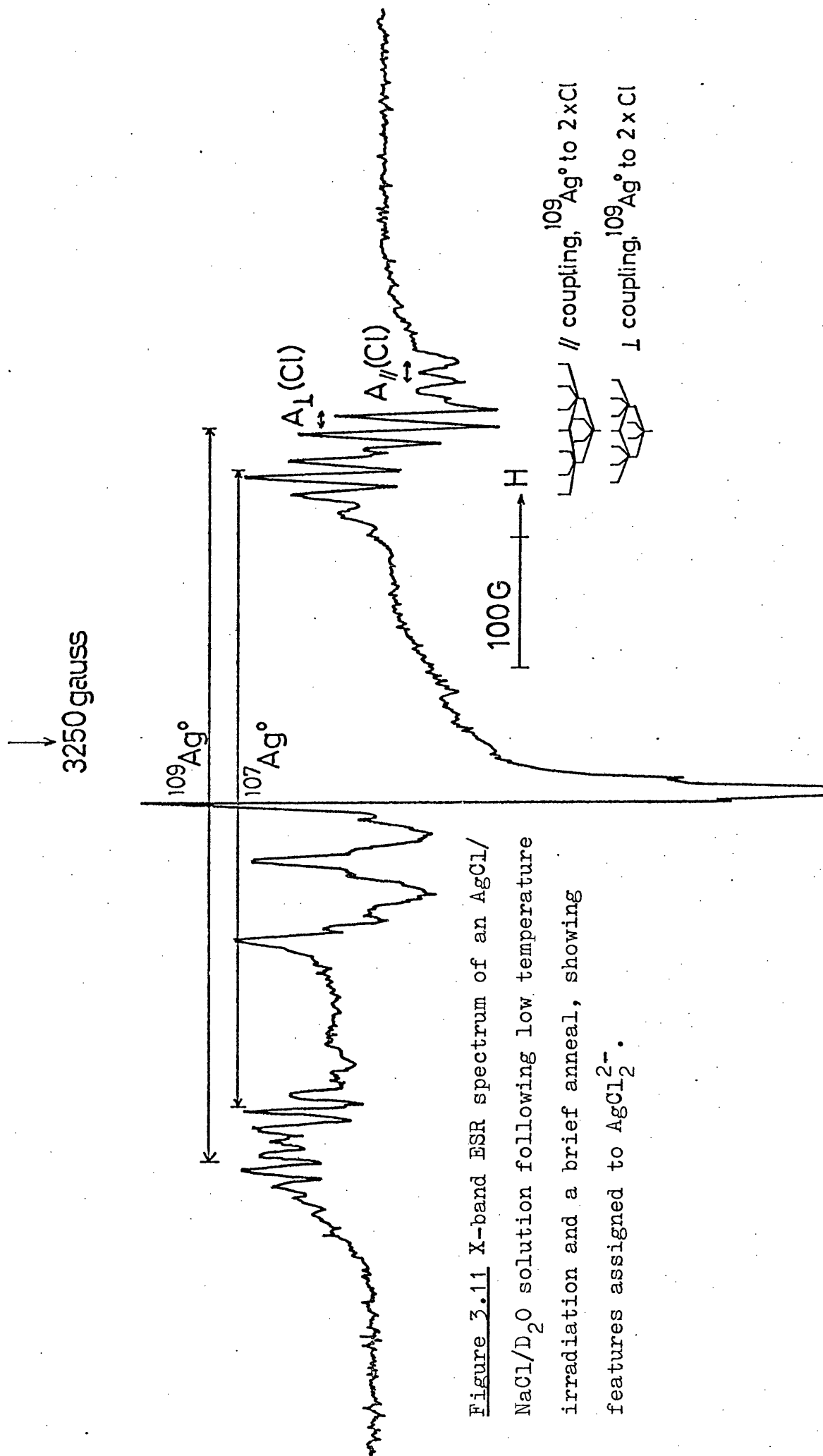


Figure 3.11 X-band ESR spectrum of an $\text{AgCl}/\text{NaCl}/\text{D}_2\text{O}$ solution following low temperature irradiation and a brief anneal, showing features assigned to $\text{AgCl}_2^{\cdot -}$.

The SHFS is interpreted in terms of anisotropic coupling to two chlorine nuclei. Although the SHFS as seen in Fig. 3.11 cannot be fitted exactly to a predicted spectrum from Ag^0 coupled to two chlorine atoms, it is an appreciably better fit than is obtained if coupling to one, three or four chlorines is proposed. The species can be written AgCl_2^{2-} and its parameters are as follows.

$^{109}\text{Ag}^0$	$g_{\text{iso}}=1.995\pm0.003$	$A_{\text{iso}}(\text{Ag})=-500\pm3\text{G}$	$A_{//}(\text{Cl})=14\pm1\text{G}$
			$A_{\perp}(\text{Cl})=11\pm1\text{G}$
$^{107}\text{Ag}^0$	$g_{\text{iso}}=1.995\pm0.003$	$A_{\text{iso}}(\text{Ag})=-438\pm3\text{G}$	$A_{//}(\text{Cl})=14\pm1\text{G}$
			$A_{\perp}(\text{Cl})=11\pm1\text{G}$

This species is presumably the product of electron capture by AgCl_2^- . It can be seen above that AgCl_3^{2-} is usually in significantly higher concentration than AgCl_2^- , so it is suggested that AgCl_2^- is the preferred site for electron capture of the two. The low concentration of AgCl_{aq} in these solutions would prevent the detection of a spectrum from AgCl^- (although it may be present, incurring line broadening on the major features).

The hyperfine constants for AgCl_2^{2-} bear comparison with those for Ag^0 coordinated to six chlorine ligands in a potassium chloride crystal¹³. The chlorine superhyperfine constants reflect a similar unpaired spin density on chlorine in the two environments.

$\text{AgCl}_2^{2-}/\text{D}_2\text{O}$	$\text{AgCl}_6^{6-}/\text{KCl}$
$A_{\text{iso}}(\text{Cl})=12\pm0.5\text{G}$	$A_{\text{iso}}(\text{Cl})=13.3\pm0.2\text{G}$
$2B=2\text{G}$	

Based on atomic values for A_{iso} and $2B^{39}$, an A_{iso} value of 12G represents a chlorine 3s spin density of ca.0.7%, and a 2B value of 2G a 3p spin density of ca.2%. Because it is difficult to estimate the anisotropy in the silver hyperfine coupling, an accurate spin density on silver cannot be calculated. The A_{iso} value (-500G) however, while being a little lower than that for normally solvated Ag^0 (~-505G), suggests that the unpaired spin densities on Ag^0 (solvated) and Ag^0 (complexed) are comparable. The low spin density on the chloride ligands then implies that the extent of delocalisation in the two environments onto solvent molecules is similar.

The tendency for silver to form linear²⁷, two coordinated⁴⁰ complexes would indicate that the AgCl_2^- (or AgCl_2^{2-}) complex ion is also linear and anisotropy might be expected in the g and A tensors. The hyperfine coupling to silver however, is no more anisotropic than that found for normally hydrated Ag^0 . This suggests that coordination by water molecules on the positions around the central Ag^+ ion not occupied by chloride ligands, is sufficiently similar to coordination by chloride to maintain an even distribution of spin throughout the silver $5p_x$, $5p_y$ and $5p_z$ orbitals.

The inability of $\text{Ag}(\text{hal})_n^{(n-1)-}$ to easily lose electrons is demonstrated by the absence of any Ag^{2+} features. In addition, aggregation of silver ions or atoms is not observed when the beads are annealed. This reflects the decreased mobility of the complex ions compared to free Ag^+ ions or Ag^0 atoms.

$\text{AgCl}_n^{(n-1)-}$ in Non Aqueous Solvents, particularly MeTHF

Data on the solubility of these complex ions in non aqueous solvents is not readily available. Their solubility in ethanol/water mixtures has been studied³⁶ but features attributable to electron capture by $\text{AgCl}_n^{(n-1)-}$ ions in such media are found to be ill defined.

Of the solvents studied only frozen MeTHF solutions provide well defined spectra (Fig. 3.12). The silver electron capture centre differs markedly from Ag^0 formed in irradiated silver perchlorate/MeTHF beads, showing a much reduced hyper-fine coupling to silver ($A_{\text{iso}} \sim 450\text{G}(^{109}\text{Ag})$). There is also well defined fine structure on the Ag^0 features but this has not so far been adequately interpreted. Spectra run at Q-band frequency indicate that there is little g anisotropy associated with the species, so it is concluded that the fine structure is due to delocalisation of the spin onto chloride ligands, and not anisotropy in the silver g and A tensors. The ESR spectrum would be clarified considerably if ^{109}Ag enriched silver chloride were used.

The absence of Ag^{2+} features and the reluctance to aggregate on the part of the silver atoms and ions are further notable differences from the behaviour of uncomplexed Ag^+ ions in MeTHF and point strongly to the detected species being formed from a complex ion of the type $\text{AgCl}_n^{(n-1)-}$.

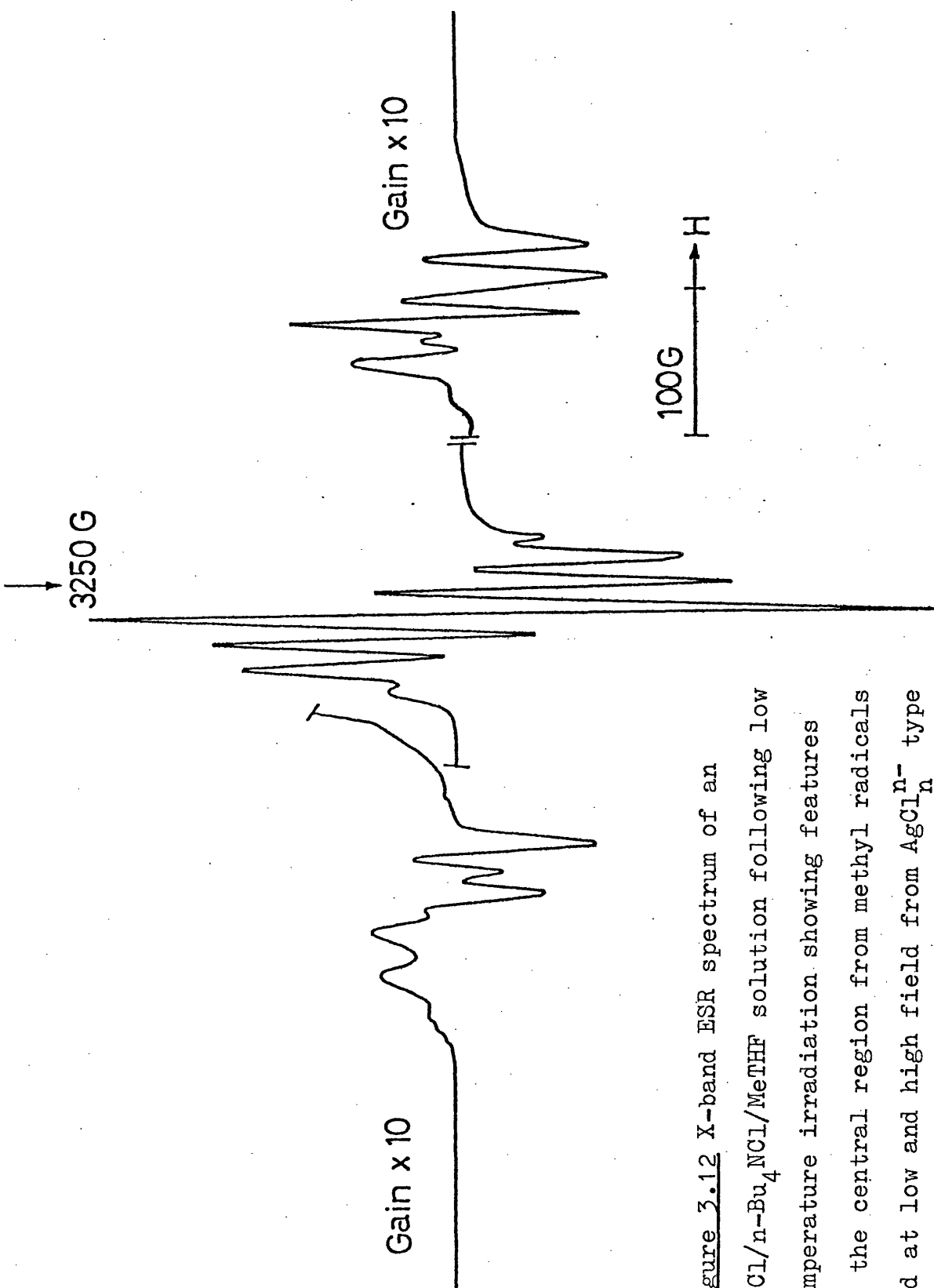


Figure 3.12 X-band ESR spectrum of an $\text{AgCl}/n\text{-Bu}_4\text{NCl}/\text{MeTHF}$ solution following low temperature irradiation showing features in the central region from methyl radicals and at low and high field from AgCl_n^{n-} type species.

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Chapter Four

Solvation of Silver and other $-d^{10}$ Cations

as studied by Nuclear Magnetic Resonance

The nature of hydration of the silver(I) ion is uncertain¹. Vapour pressure measurements made on silver nitrate solutions for example indicate that the water of hydration is only weakly held² but do not give directly a value for the solvation number. Other methods indirectly point to the solvation number of the silver(I) ion being low^{3,4}, and this view is supported to some extent by the tendency of the ion to form low coordination number complexes, particularly of the AgL_2 type, although it is noticeable that silver(I) often exhibits a coordination number of four with simple σ bonding ligands. The most recent estimate, by Akitt⁵, calculated from the shifts induced in the NMR hydroxyl proton resonance of water by silver(I) ions puts the solvation number at ca.0.6 and presupposes an asymmetric solvation shell. Neither of these conclusions are well founded; the calculation is based on a method by Malinowski⁶ which is suspect as will be shown later and accepting the invalidity of this method removes the need to involve asymmetric solvation.

The ESR measurements in Chapter Three on frozen aqueous silver solutions indicate that most of the silver ions in aqueous solution are solvated by between four and six water molecules and seem to rule out the possibility of linear solvation as a significant occurrence. A recent study of the Raman spectra of silver in liquid ammonia indicates that here also silver(I) exhibits a solvation number of four⁷ and the work reported in this chapter was carried out to lend weight to the evidence in favour of a solvation number of four or more for silver(I) ions in aqueous and methanolic solution⁸. It was intended that by extending the study of solvent NMR shifts to other $-d^{10}$ cations and by the use of methanol in addition to water any behavioural trends might be used to postulate the

nature of hydration of the silver(I) ion.

4.1 Experimental

Water was doubly distilled from alkaline permanganate. Methanol (Hopkins and Williams, Carl Fischer Reagent Grade) was dried over calcium hydride. Salts were all perchlorates of the highest available purity. They were dried in a vacuum oven at ca. 40°C and any residual water was estimated by standard procedures. For methanol studies salts were recrystallised from methanol solutions that had been dried over molecular sieve. In some cases a trace of perchloric acid was added to stabilise the solutions. Mercuric perchlorate was not sufficiently soluble in water to give reliable shifts. Salt concentrations were checked using EDTA and suitable indicators.

NMR spectra were recorded on a Jeol 100 MHz spectrometer equipped with a Jeol JNM-VT temperature controller. For aqueous solutions, tetramethylammonium perchlorate and sodium 3-trimethylsilylpropanesulphonate were used as internal markers and the good agreement obtained for these was taken as evidence that they were not seriously perturbing the solvents. The C-H proton peak was used as a reference for methanolic solutions. Measured shifts are all related to the value for the hydroxyl resonance of the pure solvent under identical conditions in the Table and the Figures, down-field shifts being taken as negative.

Shifts were studied in the concentration range zero to ca. 1M, and four to five measurements were made in this range for each system. The shifts were all closely linear and the

data given in the Table were obtained from the best straight line through the origin and the data points.

Solutions of cadmium perchlorate in methanol were studied just above the melting point in the hope of resolving a separate peak for the cation solvation shell, but to no avail. Similarly, aqueous solutions containing various aprotic solvents such as acetone were studied close to their solidification temperature but again, no separate resonance could be detected.

4.2 Results

Following the observation of separate hydroxyl proton resonance in the NMR spectrum of magnesium perchlorate in methanol at low temperatures⁹ attributable to the solvent molecules in the hydration sphere of the cation, it has been possible to establish molal shifts for a number of individual ions in methanol¹⁰. Hence molal shifts of salts measured in methanol can be split into a contribution from the cation and from the anion. The cation shifts reported here are calculated from the overall molal shift of the relevant perchlorate salt taking the contribution to the shift attributable to the perchlorate ion as $+0.125$ ppm at 204K ¹⁰ and $+0.166$ ppm at 313K ¹⁰. These two values are quoted as being accurate to ± 0.016 ppm and a similar reproducibility was observed for the salt shifts measured here, so the molal cation shifts, which are composite results of these two measurements are considered accurate to ± 0.025 ppm.

The calculation of absolute molal ion shifts in water is more difficult. The low temperature at which a separate signal for the cation hydration shell can be observed can only be

achieved by the use of high salt concentration or by the addition of cosolvents¹¹. By extrapolation of the results obtained under these conditions to higher temperature and lower salt concentration, values for absolute shifts under normal conditions can be obtained. This has been done for the chloride ion¹² and the result compared with the shift calculated by an independent method involving the comparison of molal shifts due to mono- and di-valent metal chlorides where the absolute chloride shift is treated as a parameter that can be adjusted until the mono- and di-valent cation shifts all lie on a smooth curve when plotted against the charge/radius ratio. The close agreement of the two methods leads to absolute chloride ion molal shifts at a number of temperatures¹². All the individual ion shifts in water quoted are based on these values and in this study the contribution to the overall salt shift from the perchlorate ion is taken as +0.115 ppm at 273K and as +0.099 ppm at 298K, both accurate to ± 0.01 ppm. The absolute cation shifts in the Table are thus estimated to be accurate to ± 0.015 ppm.

The absolute molal ion shifts for the $-d^{10}$ cations studied and for Ca^{2+} and Ba^{2+} appear in the Table. The results for the Hg^{2+} ion are suspect as it was very difficult to dehydrate the perchlorate and the water content of the methanolic solutions was quite possibly high, despite attempts to reduce it.

Table 4.1 Molal ion NMR shifts in ppm for water and methanol hydroxyl protons for a range of metal perchlorates.

Cation	In H ₂ O		In MeOH	
	at 273K	at 298K	at 204K	at 313K
Ag ⁺	-0.030	-0.013	-0.040	-0.066
Cd ²⁺	-0.165	-0.178	-0.250	-0.562
Hg ²⁺			-0.26	-0.45
Zn ²⁺	-0.192	-0.175	-0.316 ^a	-0.537
Ca ²⁺	-0.030 ^b	-0.062 ^b	-0.144	-0.245
Ba ²⁺	+0.020 ^b	-0.015 ^b	-0.120	-0.117

a. Data from ref.13. b. Data from ref.12.

In Figures 4.1 and 4.2 the molal ion shifts are plotted against the charge/radius ratio of the cations at two temperatures in each solvent and compared with similar data for a number of s^2p^6 ions^{10,12}. The Pauling radius scale is used in all cases except for the alkylammonium ions for which the ionic radii are calculated from bond lengths within the ions.

4.3 Discussion

The solvation number of ca.0.6 for the silver(I) ion calculated by Akitt⁵ is based on the method of Malinowski⁶. This is summarized as follows.

The Malinowski method⁶

The single resonance signal of a proton in an aqueous electrolyte solution is a weighted average dependent on its

Figure 4.1 Molal Cations Shifts in Methanol as a Function of

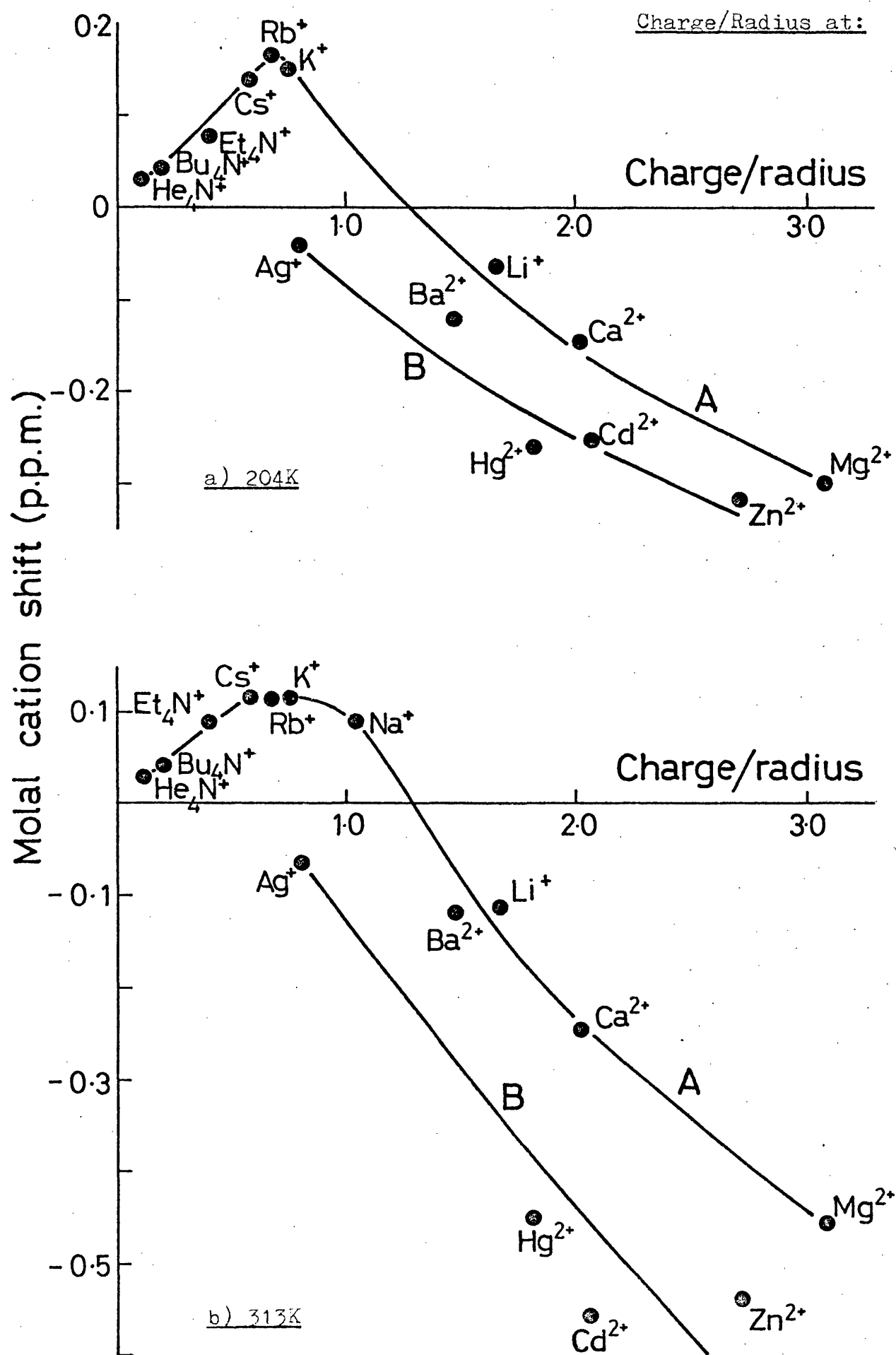
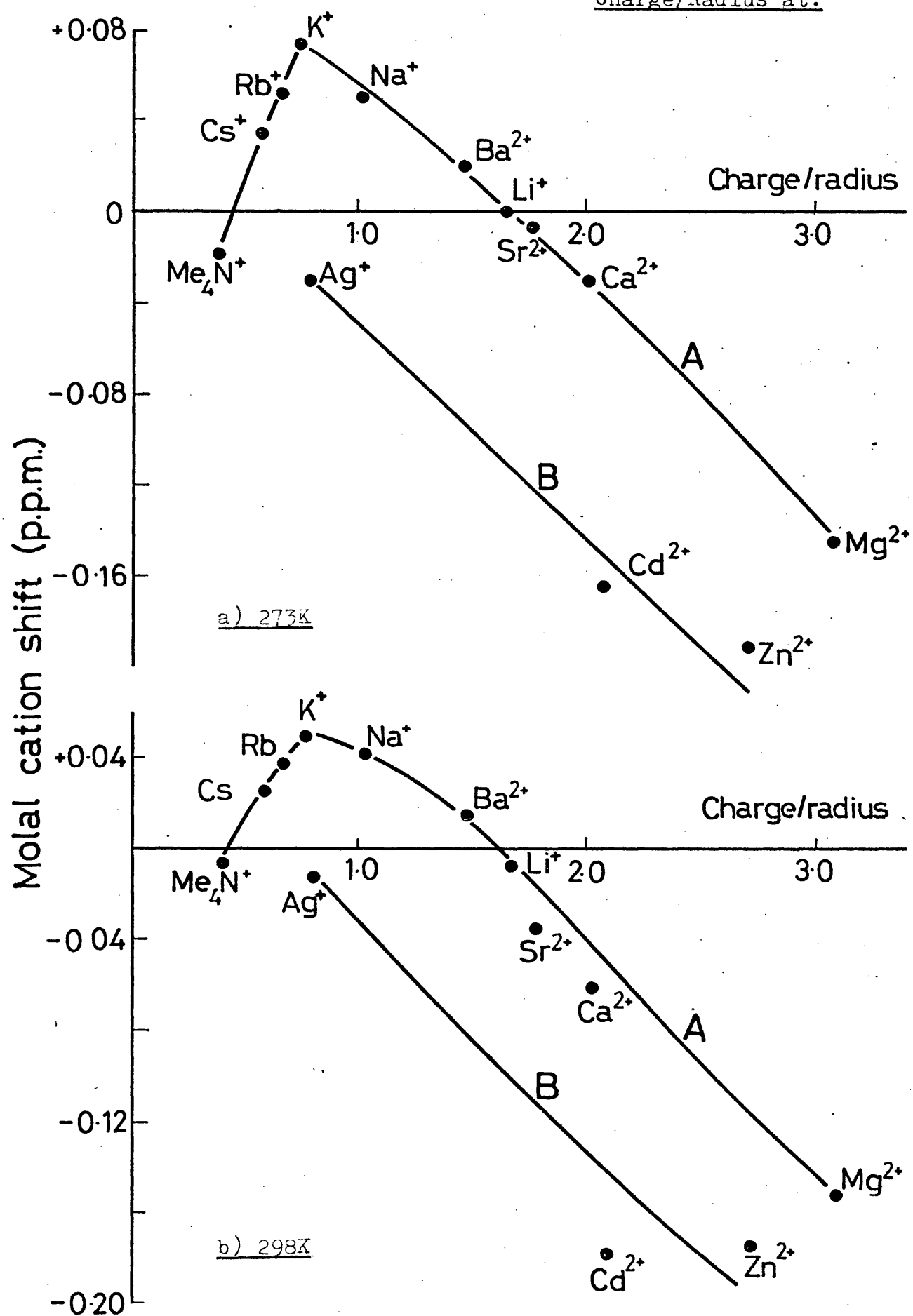


Figure 4.2 Molal Cation Shifts in Water as a Function of

Charge/Radius at:

various possible environments. When the proton resides in a complexed (hydrated) water structure its resonance position differs from that of pure water and an average shift, δ_S is assigned to the protons in the hydrated form. δ_N is assigned to the protons in bulk water and δ_{sol} is assigned to the net shift of the solution. If X_N and X_S are the mole fractions of protons in normal water and hydrated water respectively, then

$$\delta_{sol} = X_N \delta_N + X_S \delta_S. \quad 4.1$$

If h represents the total effective solvation number - the moles of water per stoichiometric mole of salt, and m represents the stoichiometric molality, equation 4.1 can be rewritten:

$$\delta_{sol} = (hm/55.55)(\delta_S - \delta_N) + \delta_N. \quad 4.2$$

If the shift associated with a solution, δ_{sol} , is plotted against temperature and δ_N , the shift associated with pure solvent is also plotted against temperature, they are both found to be linear and if extrapolated to high temperature will converge. The temperature of convergence is independent of salt concentration and at this temperature $\delta_{sol} = \delta_N$; in other words, from equation 4.2, $\delta_S = \delta_N$. δ_N can readily be calculated at this temperature from the established temperature dependence in the pure solvent and hence a value for δ_S obtained.

$$\delta_N = 0.0102T - 4.38 \text{ ppm} \quad 4.3$$

Equation 4.2 can be rearranged:

$$h = (55.55/m) (\delta_{sol} - \delta_N) / (\delta_S - \delta_N). \quad 4.4$$

Once δ_S has been established for an electrolyte system and if

it is then assumed that δ_S is independent of temperature; by measuring δ_{sol} and calculating δ_N , at any temperature and for any concentration, h , the effective hydration number of the salt can be obtained from equation 4.4.

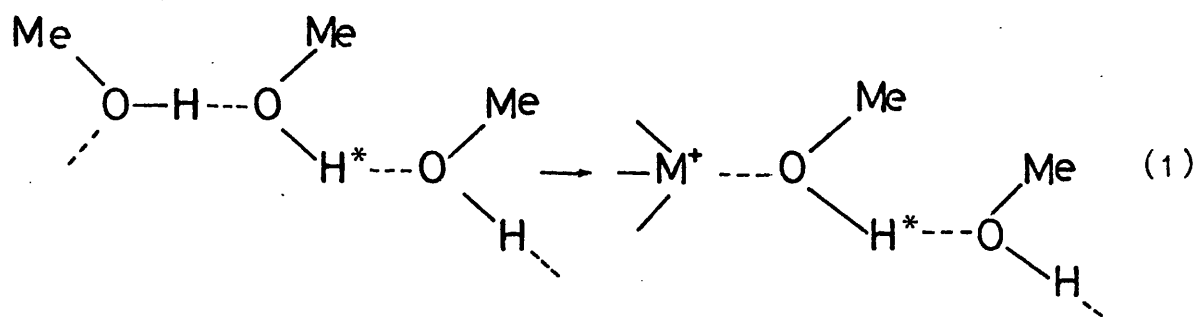
The temperature at which $\delta_S = \delta_N$ from the extrapolated plots is generally well above 100°C so its significance is doubtful. The main doubt concerning the preceding argument however, lies in the temperature independence of δ_S , the shift attributable to protons in the hydration shell.

It can be argued that the results for ions such as Mg^{2+} in methanol, for which primary solvent shells give rise to resolved resonances support the claim that these resonances are relatively insensitive to temperature⁸. They are certainly less temperature sensitive than the hydroxyl resonance of the pure solvent¹⁴ but this reflects the fact that hydrogen bonding linking primary and secondary solvent molecules is stronger in these cases than the hydrogen bonding in the bulk solvent. It seems reasonable to suggest that hydroxyl resonances associated with solvent shell molecules in which hydrogen bonding between the primary and secondary solvent shells is not so radically different from that in the bulk solvent (as is presumably the case for most of the ions studied, which do not shift the hydroxyl resonance as much as Mg^{2+}), should exhibit a temperature dependence more akin to that found in the pure solvent.

There seems, therefore, little foundation in the assumption that δ_S is temperature independent, particularly for a cation like Ag^+ , which has such a small effect on the overall hydroxyl proton resonance position of its solvent and it is concluded that the solvation number of 0.6 calculated by this method has little physical significance.

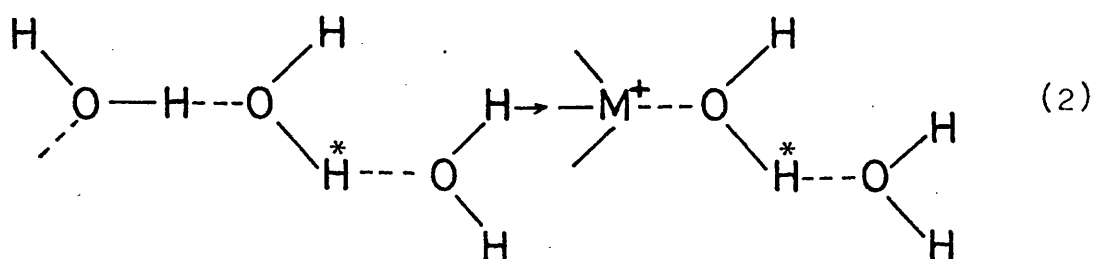
Cation shifts

The curves marked A in Figure 4.1 are readily explained in terms of process (1) without any need to invoke the concept of structure breaking¹⁰. Replacing the methanol molecule indicated with a cation will either increase the acidity of the (starred) proton in which case the overall deshielding this entails will lead to a net downfield shift in the hydroxyl resonance, or decrease the acidity resulting in an upfield shift. The former behaviour is observed for small ions



with high charge density such as Mg^{2+} , whereas the latter is observed for larger cations such as the alkali metal ions (other than lithium). As the size increases, ultimately such bonding to the cation becomes unimportant and the methanol molecules revert to their normal state; this explains the decreasing effect on the molal shift the alkylammonium ions have as they move from the tetraethyl- to the tetrahexyl- ion.

A similar explanation can be offered to explain the curves marked A in Figure 4.2 with process (2) being analogous

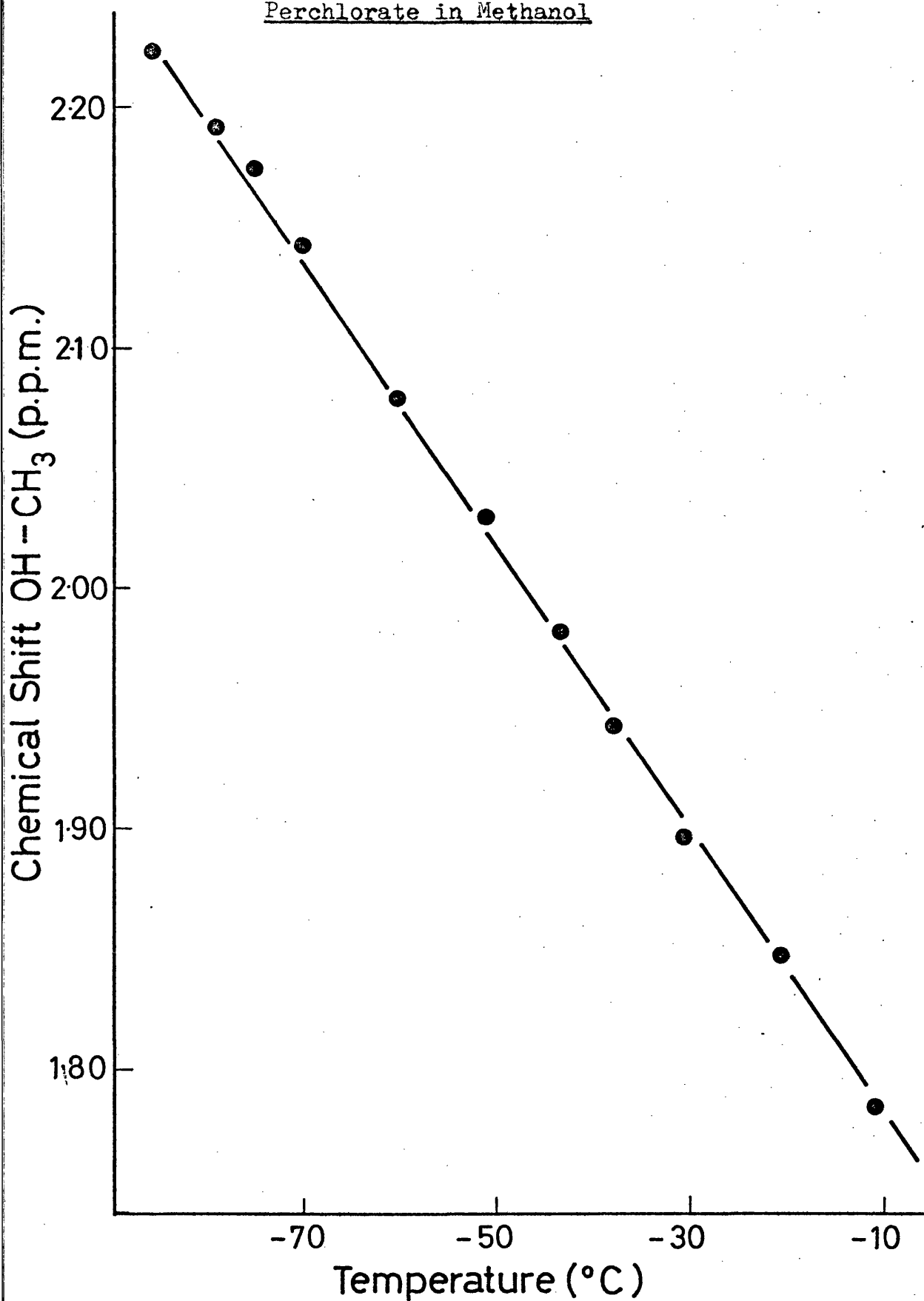


to process (1)¹²; the similarity in the behaviour of the cations in water and methanol reflects the similarity of the two solvents. For the large alkylammonium ions however, a structuring effect is detected in water at low temperatures which results in the unexpected down-field shifts associated with these ions¹².

The anomalous down-field shift shown by solvent coordinated to silver(I) ions compared to that shown by solvent coordinated to alkali metal ions of similar radius and explained by Akitt in terms of a solvation number of unity or less is also observed for the other ions of $-d^{10}$ configuration. The curves marked B in Figures 4.1 and 4.2 show how the shifts associated with Ag^+ , Hg^{2+} , Cd^{2+} and Zn^{2+} are consistently down-field compared to those arising from ions of $-s^2p^6$ configuration. The results for Zn^{2+} are noteworthy since this ion has an established solvation number of six¹³ (in methanol) and is probably solvated symmetrically. From the consistent behaviour of the other $-d^{10}$ cations with Zn^{2+} there is no reason to suppose that either Hg^{2+} , Cd^{2+} or Ag^+ exhibit a solvation number any lower than that of Zn^{2+} .

It was hoped that a solvation number for Cd^{2+} might be forthcoming from a low temperature study of a methanolic solution of cadmium perchlorate to clarify the situation further but no separate resonance for the cation solvation shell could be detected. Figure 4.3 shows the chemical shift of the hydroxyl proton as a function of temperature. If the solvation shell hydroxyl resonance were independent of the bulk hydroxyl peak at low temperature then a step in the plot might be expected at the temperature above which exchange is sufficiently rapid for all the hydroxyl protons to contribute to the same

Figure 4.3 Chemical Shift, $\text{OH}-\text{CH}_3$, as a Function of
Temperature for a 1.46 Molal Solution of Cadmium
Perchlorate in Methanol



peak. No such step is visible so it must be concluded that the solvation shell is not sufficiently tightly bound to Cd^{2+} to result in a separate resonance at any temperature above the melting point.

It is probable that the reason why the curves marked B are displaced down-field from the curves marked A stems from the degree of charge transfer or covalency in the cation-solvent σ bonds. Covalent contributions are undoubtedly small for ions such as Na^+ , but are appreciable for Ag^+ even when octahedrally coordinated by chloride ions¹⁶. This will have the effect of increasing the acidity of the protons of the ligand solvent molecules and hence will give rise to an extra down-field shift.

It is noticeable in Figures 4.1 and 4.2 that Zn^{2+} generally does not exhibit such a large relative down-field shift as the other $-d^{10}$ cations. If this covalency concept is correct then this is not unexpected since Zn^{2+} does show a smaller tendency to form covalent bonds than Ag^+ , Hg^{2+} and Cd^{2+} .

In conclusion it can be said that there is no NMR evidence in favour of an abnormally low solvation number for Ag^+ and the results in the Chapter support those in Chapter Three in suggesting that it is probably not less than four on average in water and methanol. The extra down-field shift associated with $-d^{10}$ cations is ascribed to covalency effects rather than to a low solvation number.

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Chapter Five

An Electron Spin Resonance Study of Radiation Damage in some Inorganic Nitrates

It has been seen in the preceding Chapters how the Ag^+ ion can both capture and lose electrons, frequently in the same matrix. In a silver nitrate crystalline matrix however, the NO_3^- ion competes successfully with Ag^+ for photo-produced electrons and no Ag^0 is produced¹. This is in contrast to frozen solutions of silver nitrate, in which electrons are successfully trapped by Ag^+ ions^{2,3}. The primary electron capture centre in crystalline silver nitrate is an NO_3^{2-} unit, but with the unpaired spin delocalised appreciably onto a neighbouring Ag^+ ion (ca.2%). Clearly, the preference for NO_3^{2-} over Ag^0 as the electron capture centre is a slight one.

This subtle balance between electron capture by cation or by anion suggested that a study of the nitrates of other -d¹⁰ cations might be informative, particularly with respect to the mechanisms involved in the γ radiolysis of the nitrate ion. Depending on the cation, the nitrate ion will itself trap either electrons ($-\text{NO}_3^{2-}$) or holes ($-\text{NO}_3$) or both.

The three radiation damage products of the nitrate ion, NO_3^{2-} , NO_3 and NO_2 have been fairly conclusively characterised by their ESR spectra⁴. NO_3^{2-} and/or NO_3 are formed as primary products at 77K by electron capture and electron loss respectively. NO_2 is thought to be only formed as a secondary product.

As well as these three products another species has been detected in a number of irradiated nitrates^{5,6,7}. It exhibits ESR parameters similar to, but distinctly different from, those of NO_3 and has been tentatively identified⁷ as NO_4^{2-} . In this work the same species is detected in some -d¹⁰ metal nitrates and is studied in more depth in sodium and

potassium nitrates. It would appear that this species takes over from 'normal' NO_3 as a major electron loss centre when high radiation doses are employed.

5.1 Experimental

Nitrate salts were of the highest available purity, and were recrystallised from water. Mercurous nitrate was prepared from an excess of mercury and moderately concentrated nitric acid as described by Aylett⁸. Single crystals, when used, were prepared from aqueous solution. The nitrates were dried and/or dehydrated in a vacuum oven at up to 150°C .

Crystals and powders were irradiated at 77K and room temperature with ^{60}Co γ rays and ESR spectra were obtained as described in Chapter One. Radiation doses were typically 3 MRad at 77K and 30 MRad at room temperature, except for sodium and potassium nitrates, which were exposed to a range of doses.

5.2 Results and Discussion

5.2a -d¹⁰ Metal Nitrates

The results are summarized in the Figures and the Tables in Appendix Four.

Silver Nitrate

The results reported here largely confirm those from the single crystal study of Mosley and Moulton¹. γ irradiation at 77K produces Ag^{2+} as the principal hole centre and $\text{Ag}^+-\text{NO}_3^{2-}$ as the electron trap centre. The data obtained from the powder spectrum is in close agreement with that from the single crystal spectrum¹ (Table A4.1).

Cadmium Nitrate

Anhydrous cadmium nitrate and the tetrahydrate were prepared⁹ and their composition checked by 'H' and 'N' analysis (C.H.N. Ltd. Wigston). Attempts to prepare the dihydrate¹⁰ were unsuccessful.

Low temperature irradiation of the tetrahydrate yields broad, poorly resolved spectra, the main products being NO_3^{2-} , NO_3 and NO_2 (Fig. 5.1). Although the crystal structure of the tetrahydrate is well known¹¹, no link can be drawn between it and the ESR spectrum, the features all being too poorly defined to deduce anything about the relative configurations of the ions.

Annealing the powder results in signals from NO_3 and NO_3^{2-} being lost and NO_2 growing in. Irradiation at room temperature results in a high yield of NO_2 immediately.

In contrast, the anhydrous salt, on low temperature irradiation, exhibits NO_3 and NO_3^{2-} spectra but very little NO_2 (Fig. 5.2a). The features are much better resolved than for the hydrate and if the powder is allowed to warm up to ca.200K superhyperfine structure (SHFS) becomes clearly visible

Figure 5.1 X-band ESR powder spectrum of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, measured at 77K, following exposure to ^{60}Co γ rays at 77K, showing poorly resolved features for NO_2 , NO_3^{2-} and 'normal' NO_3 .

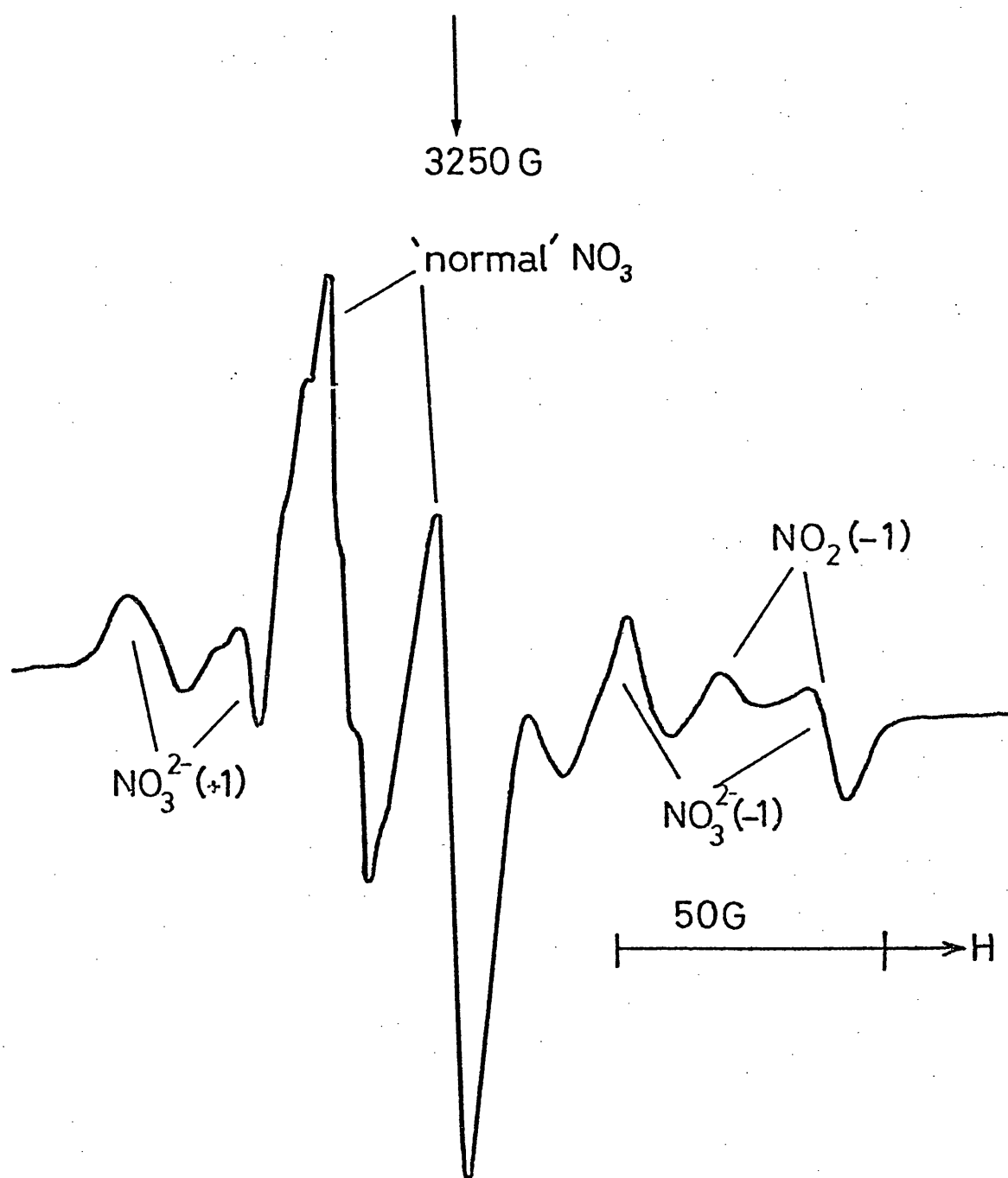
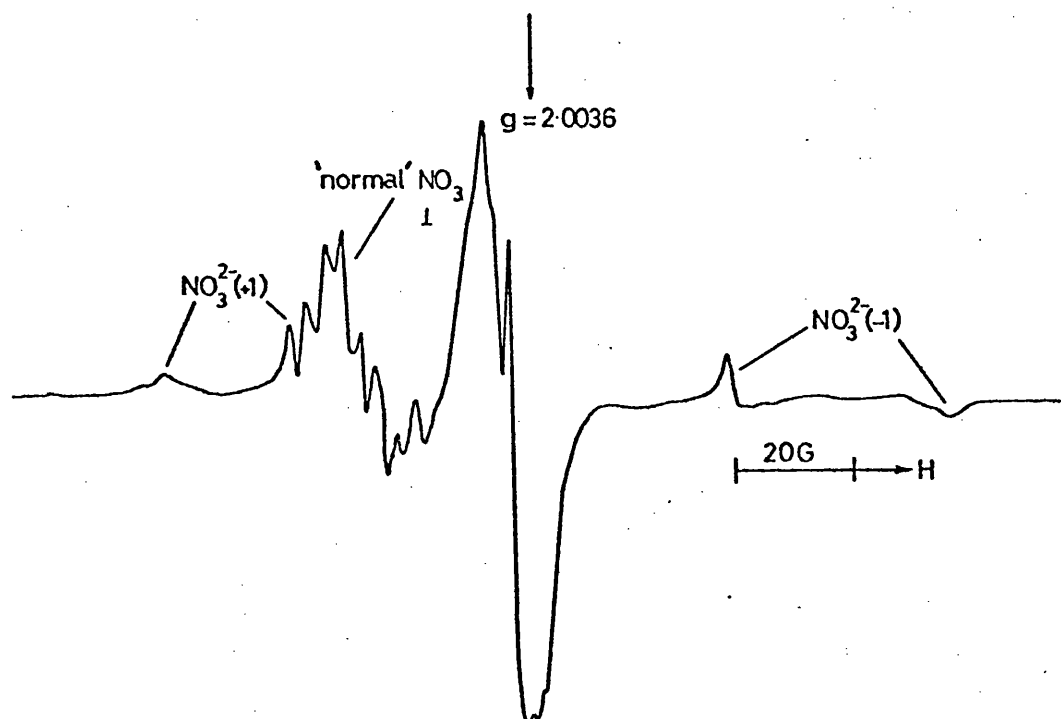
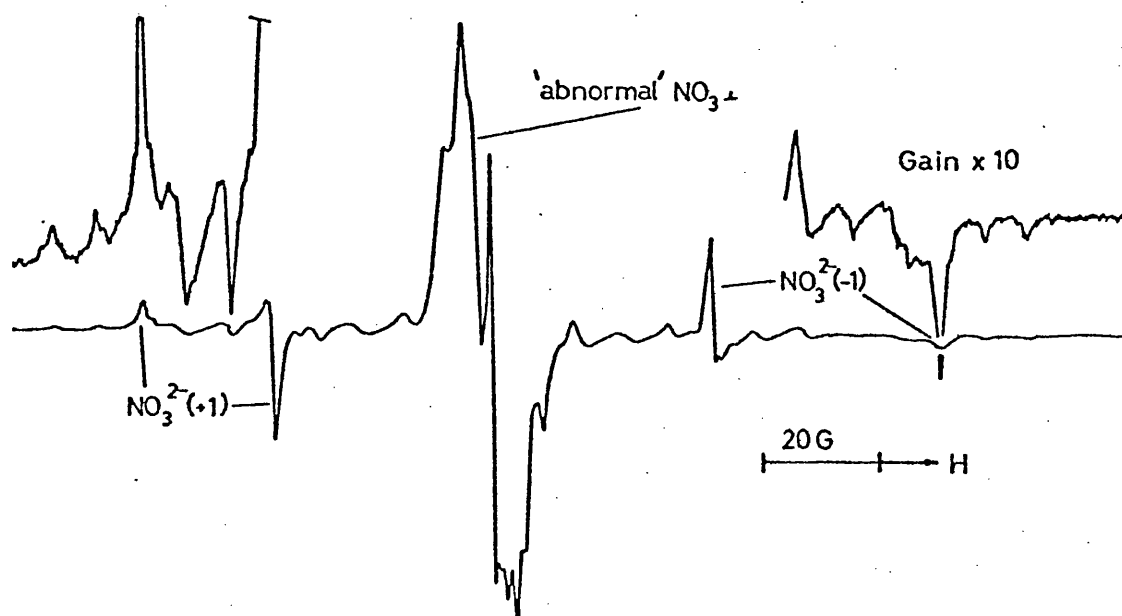


Figure 5.2 X-band ESR powder spectrum of anhydrous $\text{Cd}(\text{NO}_3)_2$ following low temperature irradiation; (a) at 77K, showing superhyperfine structure (SHFS) on the 'normal' NO_3 features;



(b) at 200K, showing well resolved NO_3^{2-} features plus the associated SHFS and features assigned to 'abnormal' NO_3 .



on the NO_3^{2-} spectrum (Fig. 5.2b). Cadmium has two abundant isotopes with nuclear spin, ^{113}Cd ($I=\frac{1}{2}$, 12.3%) and ^{111}Cd ($I=\frac{1}{2}$, 12.9%). The SHFS is analysed in terms of coupling of NO_3^{2-} to two inequivalent cadmium ions. Such an interpretation is supported by the ratios of the satellite peak heights to those of the central lines. Coupling of NO_3^{2-} to a third cadmium nucleus with a smaller splitting is also conceivable. The values of $A(\text{Cd})$ indicate a very low spin density on cadmium (Table A4.1). Based on an atomic value for $A_{\text{iso}}(\text{Cd})$ of 5200G^{12} , and bearing in mind the anisotropy in the cadmium SHFS, a total spin density on cadmium of, at most, a few per cent is envisaged.

Unfortunately a detailed crystal structure of anhydrous cadmium nitrate, to which these results could be linked, is not available¹³.

NO_3 is a primary product at 77K, exhibiting $g_{\parallel}$ and $g_{\perp}$ values typical of 'normal' NO_3^4 . Fine structure is clearly resolved on the perpendicular features but its source is so far unexplained. It is too intense to be from coupling to cadmium ions in view of the low abundance of the cadmium isotopes with nuclear spin, unless coupling to a number of equivalent cadmium ions is envisaged. The intensities could be explained by coupling to five or more cadmium nuclei with superhyperfine coupling constants of ca. 6G along the perpendicular symmetry axis and of $\leq 1\text{G}$ along the parallel axis. This explanation however, as well as being intuitively unlikely, is difficult to rationalise in view of the SHFS on the NO_3^{2-} spectrum described previously.

Annealing the anhydrous nitrate results in the loss of 'normal' NO_3 and its associated blue colour and features are

revealed that are akin to those previously assigned⁷ to NO_4^{2-} . Similar features are detected in potassium and sodium nitrates and they will be discussed later. The species responsible for these features will be referred to as 'abnormal' NO_3 . Interestingly, the hydrated salt, while exhibiting a 'normal' NO_3 spectrum at 77K, does not reveal the 'abnormal' NO_3 spectrum when annealed.

Zinc Nitrate

It was found that low temperature irradiation of zinc nitrate powder results in an ESR spectrum, the form of which is virtually independent of whether the anhydrous or the hexahydrate salt is used. (The anhydrous nitrate was prepared from zinc metal plus dinitrogen tetroxide⁸). Poorly resolved spectra characteristic of NO_3 , NO_3^{2-} and NO_2 are obtained at 77K and the NO_2 yield is 4-5 times greater for the hydrated than for the anhydrous salt. Annealing results in a loss of NO_3 and NO_3^{2-} and an increase in NO_2 concentration. No 'abnormal' NO_3 is observed.

Mercury (II) Nitrate

Mercury (II) nitrate hydrates with 0.5 or 1 molecule of water depending on conditions⁸. The material used was dried at various temperatures and pressures prior to irradiation but this made little difference to the ESR spectra. It is concluded that the samples used at all times contained an indefinite amount of water of hydration.

The ESR spectrum, following low temperature irradiation,

exhibits high field features attributable to Hg^+ (Fig. 5.3). Mercury has two naturally abundant isotopes with nuclear spin, ^{201}Hg ($I=3/2$, 13.34%) and ^{199}Hg ($I=1/2$, 16.8%). The large mercury hyperfine coupling constants (Table A4.3) indicate that the unpaired electron is confined largely to one mercury nucleus and SHFS, seen on both the central feature (from $^{200}\text{Hg}^+$) and on the two high field features (from $^{199}\text{Hg}^+$ and $^{201}\text{Hg}^+$), is interpreted in terms of delocalisation of the spin to a very small extent onto surrounding mercury nuclei. From the relative intensities of the satellite lines it is concluded that coupling is to 3 ± 1 equivalent mercury ions with $A(\text{Hg})=15.5\text{G}$. The lack of anisotropy in the SHFS implies that each Hg^+ ion is coupled to four surrounding Hg^{2+} ions arranged tetrahedrally about the Hg^+ ion. Presumably such a unit is an integral feature of the crystal structure of mercuric nitrate. The mercury superhyperfine coupling constant indicates a spin density of $<0.5\%$ on each of these surrounding cations.

(When A values are small, only satellite lines from coupling to ^{199}Hg will be observed; the $m_I=\pm 1/2$ features from ^{201}Hg will be small and/or hidden and the $m_I=\pm 3/2$ features will overlap with those from ^{199}Hg).

Additional features are detected under certain conditions from an Hg^+ species exhibiting larger hyperfine coupling, broader lines and no SHFS (Fig. 5.3). It must be assumed that they arise from Hg^{2+} ions in a less well defined environment than those that lead to the structured Hg^+ features. The line width does not arise from coupling to hydrogen nuclei in the water molecules as might be expected, (mercuric nitrate recrystallised from D_2O exhibits identical features). However, that the features are not always reproducible from sample to

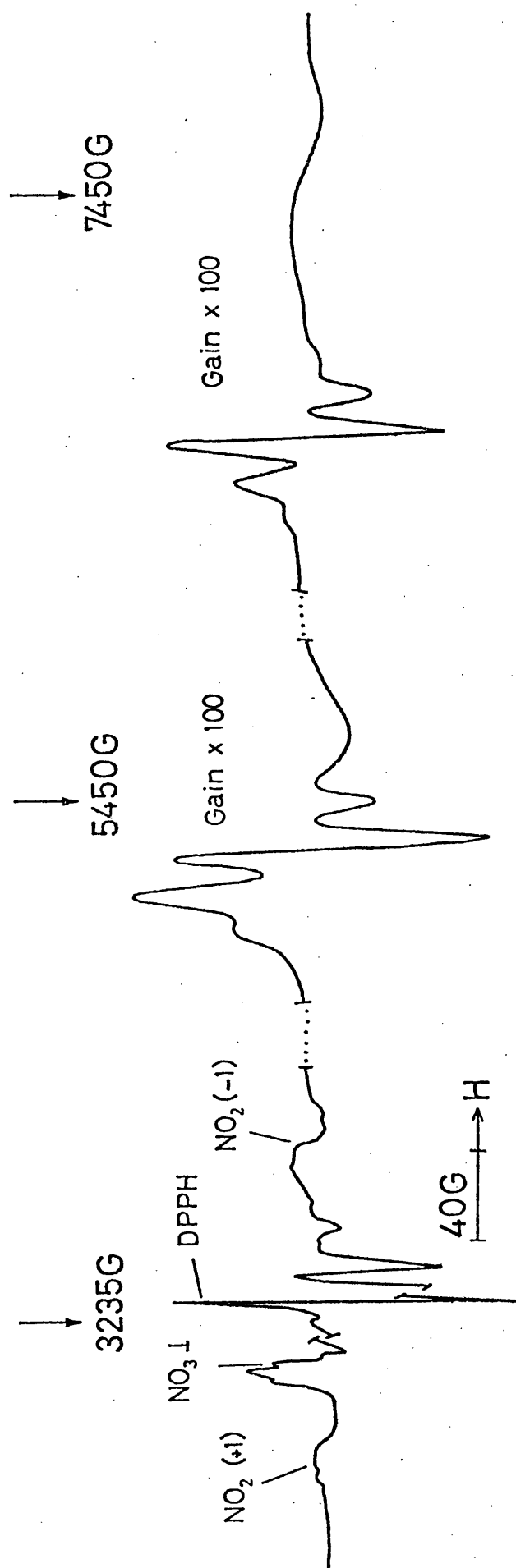


Figure 5.3 X-band ESR powder spectrum of $\text{Hg}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ following low temperature irradiation, showing features assigned to NO_2 and NO_3 in the free spin region, and features from the two types of Hg^+ in the 5400G and the 7400G regions. Features in the former region are assigned to $^{199}\text{Hg}^+$ and in the latter to $^{201}\text{Hg}^+$.

sample does indicate that their detection depends critically on the extent of hydration.

NO_2 and NO_3 Centres:

Little or no NO_3^{2-} is detected following irradiation at 77K. NO_2 is formed at 77K and exhibits fine structure, presumably through coupling to mercuric cations, but the powder spectrum is too complex and poorly resolved to be interpreted.

'Normal' NO_3 is also formed and this, too, exhibits SHFS. Annealing results in the loss of 'normal' NO_3 and a possible increase in NO_2 concentration. It is uncertain whether 'abnormal' NO_3 is formed as well.

Anhydrous mercuric nitrate can be prepared from dinitrogen tetroxide and mercuric oxide¹⁴ and a study of this might be informative on the nature of the two types of Hg^+ formed. In addition, NO_2 would not be expected as a primary product in the anhydrous salt and this would aid interpretation of any SHFS on the NO_3 features.

Mercury (I) Nitrate Dihydrate

In general, mercurous salts contain the Hg_2^{2+} unit and mercurous nitrate is no exception. It is diamagnetic, two electrons occupying the highest filled molecular orbital, a σ orbital largely confined to the internuclear region. Mercury is not a d^{10} cation when in its monovalent state but it is included in this study principally because Hg_2^{2+} can act as an electron capture (or loss) centre, and the spectra bear comparison with those from Hg^+ , formed in mercuric nitrate.

The $\text{Hg}_2^{+/3+}$ Centre:

At 77K high field lines are detected which are analysed in terms of anisotropic coupling of the unpaired spin to ^{201}Hg and ^{199}Hg in an Hg_2 unit. The hyperfine constants are calculated as described in Appendix One and using the programme in Figure A1.4, and are thus quoted to appropriately large uncertainties (Table A4.3 and Fig. 5.4).

Whether the unit is the electron capture centre Hg_2^+ or the loss centre Hg_2^{3+} is uncertain. The hyperfine constants are similar to those found for the $\text{Hg}_2^{+/3+}$ species in frozen sulphuric acid¹⁵ and thus the same process would appear to be occurring in the two media. Attempts were made to identify the species in sulphuric acid by including the electron scavengers, nitrate and selenate ions, in the solution but they were found to have no effect on the yield of $\text{Hg}_2^{+/3+}$.

Were both Hg_2^+ and Hg_2^{3+} formed, they could readily be identified. Hg_2^+ , with an unpaired electron in a σ^* orbital, would exhibit a larger isotropic contribution to the hyperfine tensor and a smaller anisotropic contribution than would Hg_2^{3+} , where the unpaired electron would be in a σ orbital confined more to the internuclear region.

No $\text{Hg}_2^{+/3+}$ species is detected following low temperature irradiation of mercurous sulphate. Because NO_3^- is a better electron scavenger than SO_4^{2-} this might suggest that the $\text{Hg}_2^{+/3+}$ species formed in a nitrate environment is the electron loss centre Hg_2^{3+} . This is not substantial evidence however; many other factors may be influencing electron capture and loss in the sulphate crystal.

The major evidence for electron capture being responsible for $\text{Hg}_2^{+/3+}$ formation lies in the fact that NO_3^{2-} is not detected

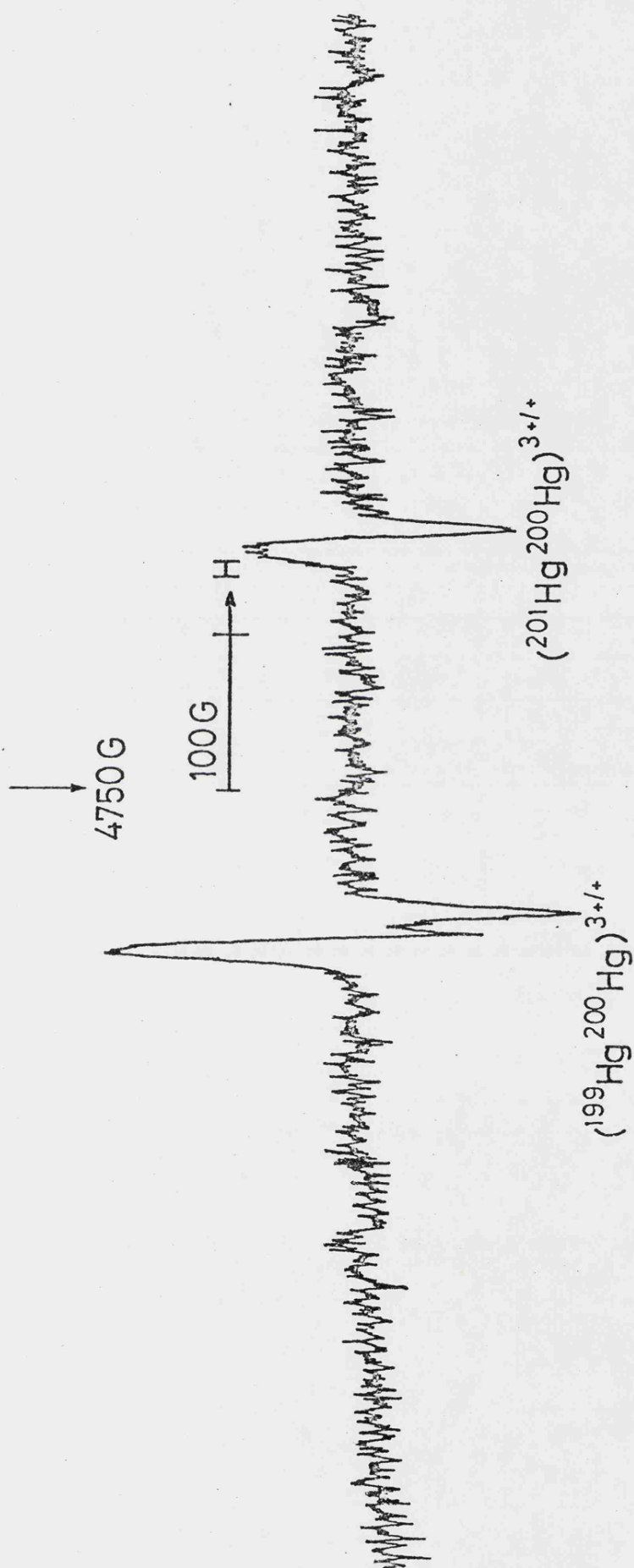


Figure 5.4 Part of the X-band ESR powder spectrum of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ following low temperature irradiation, showing anisotropic features at high field assigned to the $\text{Hg}_2^{+/3+}$ ion.

at 77K. This puts mercurous nitrate in line with mercuric and thallic nitrates, in both of which the cation is the major electron capture centre, and in conclusion this is the favoured view, that the $\text{Hg}_2^{+/3+}$ species is in fact Hg_2^+ , the electron excess centre.

NO_2 Centres:

The principal paramagnetic radiation damage products from the nitrate ion are NO_2 and NO_3 . NO_2 is formed at 77K and exhibits satellite lines through coupling to mercury nuclei (Fig. 5.5). Immediately following radiolysis a coupling constant of ca. 115G is calculated to one mercury nucleus and it must be concluded that the coupling to the other mercury nucleus in the Hg_2 unit is small ($\leq 7\text{G}$). The anisotropy in the SHFS is not clear.

After a short anneal and recool to 77K the NO_2 features show improved resolution and satellite lines that are interpreted in terms of coupling to three distinct types of mercury nuclei. Two types of mercury are responsible for the satellite lines that appear on the next anneal, and after an anneal to room temperature coupling to one type of mercury only is observed. At none of these stages can a realistic estimate of the anisotropy in the mercury SHFS be made.

This chain of reproducible events in the mercurous nitrate crystal, summarized in Figure 5.5 and Table 5.1, must be due to quantised rearrangement of the NO_2 radical relative to the Hg_2^{2+} units as the crystal is annealed.

Figure 5.5 The free spin region of the X-band ESR powder spectrum of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ following low temperature irradiation, showing predominant features from NO_2 and the associated mercury satellite features; (a) at 77K, immediately after radiolysis, (b) and (c) after successively longer anneals and (d) after an anneal to room temperature.

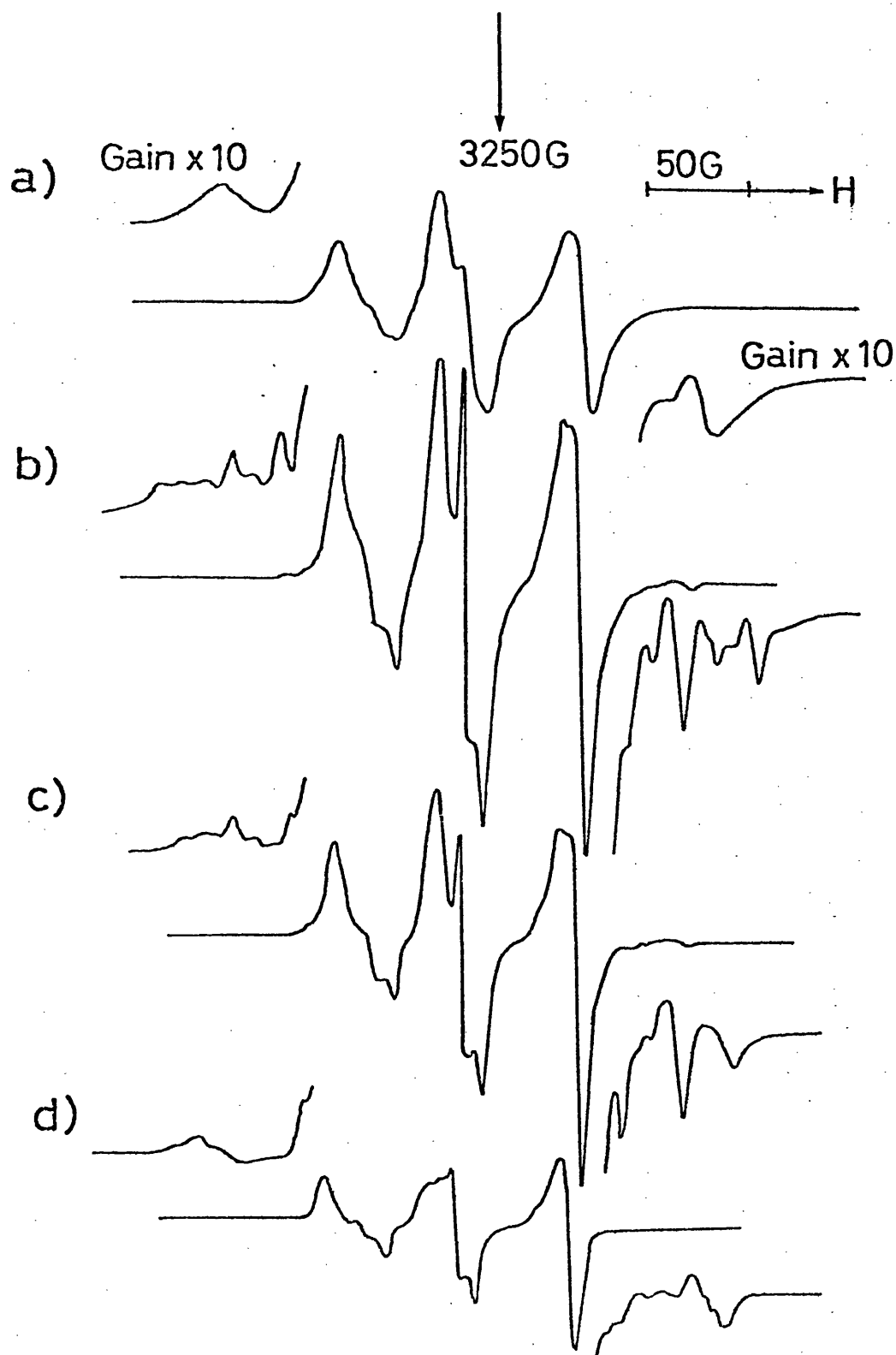
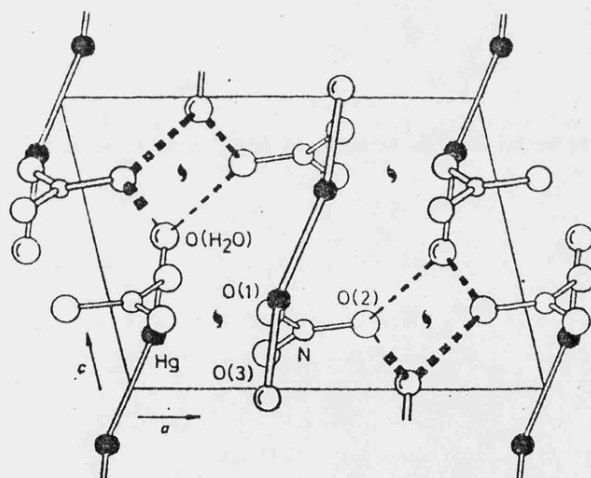


Table 5.1 ^{199}Hg Satellite Lines in the NO_2 ESR Spectrum of
Irradiated Mercurous Nitrate Dihydrate (measured at 77K).

	$A_{\text{iso}}(\text{Hg})$
Immediately after radiolysis	115(± 5)G
After 1st anneal	125(± 5), 185(± 5) + 103(± 5)G
After 2nd anneal	150(± 5) + 100(± 5)G
After anneal to RT	145(± 5)G

The crystal structure is well known¹⁶ and it can be seen from the projection below that NO_3^{2-} ions (and hence NO_2 radicals) are in close contact with a number of $\text{H}_2\text{O}-\text{Hg}-\text{Hg}-\text{OH}_2$ units. Indeed, there are three nitrate oxygen atoms at 2.68, 2.75 and 2.81 Å from, and within the coordination sphere of, each mercury atom.



Projection of the crystal structure on the ac plane.

Only one oxygen atom from each nitrate ion is involved in hydrogen bonding to water molecules and it seems likely that this would be the oxygen lost in the formation of NO_2 . It is clear that NO_2 , once formed, would be in the proximity of more than one mercury atom and that it may, given more

mobility than it has at 77K, rearrange to new, thermodynamically more stable configurations. From the discrete way the mercury SHFS changes as mercurous nitrate is annealed it is concluded that there are a number of such configurations, each one quantised according to the energy required by the NO_2 radical to attain it.

Indium and Gallium Nitrates

Neither of these nitrates can readily be prepared anhydrous.¹⁷ The gallium nitrate used was in the form $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and indium nitrate was the trihydrate $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$. On low temperature irradiation both salts yield poorly resolved spectra, characteristic of NO_2 , NO_3 ('normal' only) and NO_3^{2-} (largely hidden under NO_2 features). Annealing results in the loss of NO_3 and NO_3^{2-} and a gain in the yield of NO_2 .

Thallic Nitrate

Thallic (III) nitrate trihydrate is the subject of a preliminary investigation by Zimmerman¹⁸. On irradiation it appears that Tl^{3+} acts as the preferential electron trap and high field features attributable to Tl^{2+} are detected. Some SHFS is seen on these features but it is as yet uninterpreted. NO_2 and 'normal' NO_3 are also formed at 77K. NO_3 exhibits SHFS, presumably through coupling to Tl^{3+} ions.

Electron Capture Centres in d^{10} Metal Nitrates

From the results reported in this Chapter it can be

seen that radiolytically produced electrons at 77K can be captured either at anion (nitrate) sites or at cation sites. The competition between NO_3^- and the cation for electrons is a close one, and in AgNO_3 and $\text{Cd}(\text{NO}_3)_2$ the cation participates in the electron capture site to a small extent. In the same way, it is likely that the unpaired electron on Hg^+ , formed from Hg^{2+} , is delocalised to a small extent onto the anion (as well as other Hg^{2+} ions), although the SHFS from nitrogen nuclei would be very small and hidden in the line widths.

The ability of Hg^{2+} to capture electrons more readily than Zn^{2+} or Cd^{2+} reflects the unique chemistry mercury exhibits in this group, sometimes explained in terms of the 'inert pair' effect, and is consistent with the large positive Standard Redox Potential of mercury¹⁹.

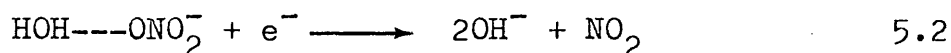
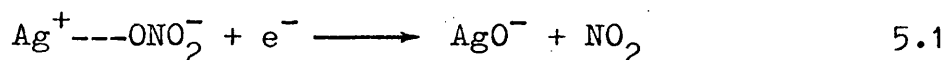
	zinc	cadmium	mercury
E_o for $\text{M}^{2+} + 2\text{e}^- \rightarrow \text{M}$	-0.762V	-0.402V	+0.854V

The 'inert pair' effect is also held responsible for the reduced stability of trivalent thallium compared to trivalent indium and gallium¹⁹. The trend, therefore, of electron capture transferring from being at an anionic site to being at a cationic site on moving down this group would not be unexpected. Such a trend cannot be positively identified however, because of the broad signals associated with gallium and indium nitrates which preclude the positive identification of NO_3^{2-} . In addition, the high magnetic moments and high nuclear spins of these two metals might well prevent the detection of the cation electron capture centres, were they formed.

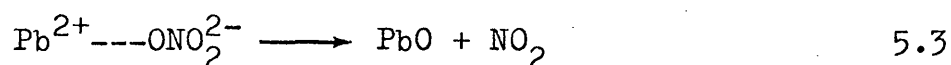
NO₂ Centres

These are almost invariably formed on room temperature irradiation of inorganic nitrates. The ESR spectrum at room temperature consists of an isotropic triplet indicative of a rotating NO₂ radical.

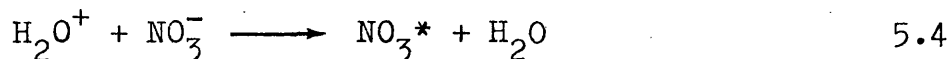
At 77K it is unlikely that NO₂ is formed as a primary product from the nitrate ion. It has been seen however, how NO₂ is formed at 77K in a number of irradiated nitrates, notably hydrated nitrates. It has been suggested that NO₂ formation at 77K follows electron capture by nitrate ions that are involved either in ion pairs (5.1)³, or in hydrogen bonding with water molecules (5.2)⁷.



In irradiated lead (II) nitrate crystals, the first formed NO₃²⁻ ions have been shown to give NO₂ on annealing, reaction 5.3 being proposed as a reasonable mechanism⁵.

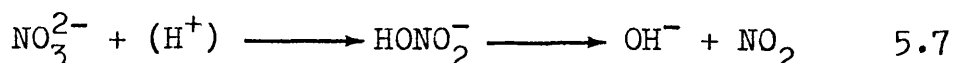


An alternative view depicts NO₂ as an electron loss centre, and a favoured process for its formation is via reaction with H₂O⁺.^{20,21}



Whether NO₂ formation is through electron loss or electron capture by the nitrate ion is uncertain. Symons

and Zimmerman⁷ favour the electron capture process (5.2), because there appears to be no compelling reason why loss of an electron by a nitrate ion should leave an NO_3 molecule with enough energy to break a strong N-O bond (reaction 5.5). Electron capture, followed by protonation and then decomposition to NO_2 , in their view, is a preferable mechanism.



In this work, the formation of NO_2 at 77K is only observed in hydrated nitrates, anhydrous cadmium and silver nitrates only exhibit NO_2 spectra on annealing. NO_2 formation is clearly linked to the presence of water molecules and this fact is consistent with both of the proposed mechanisms of formation. The argument above⁷ favours electron capture as the process involved but the large yields of NO_2 observed as primary products in irradiated mercury (I) and (II) nitrates and thallic nitrate suggest otherwise. These are the three nitrates, of those studied, in which electron capture is principally at the cation and the increased yields of NO_2 associated with all three of these over the other nitrates is indicative of an electron loss process being responsible for its formation.

Electron Loss Centres in $\sim 10^{-10}$ Metal Nitrates

Other than Ag^{2+} , which is the electron loss centre in irradiated silver nitrate, the principal electron loss centre is NO_3 , characterised by Atkins and Symons⁴. This is a primary product at 77K in all the other nitrates studied (Table A4.1),

as well as in alkali nitrates²² and aqueous solutions⁷.

The formation, in anhydrous cadmium nitrate, of 'abnormal' NO_3 is not unique; it is also detected in frozen aqueous nitrate solutions and alkali nitrates and is discussed more fully in the next Section.

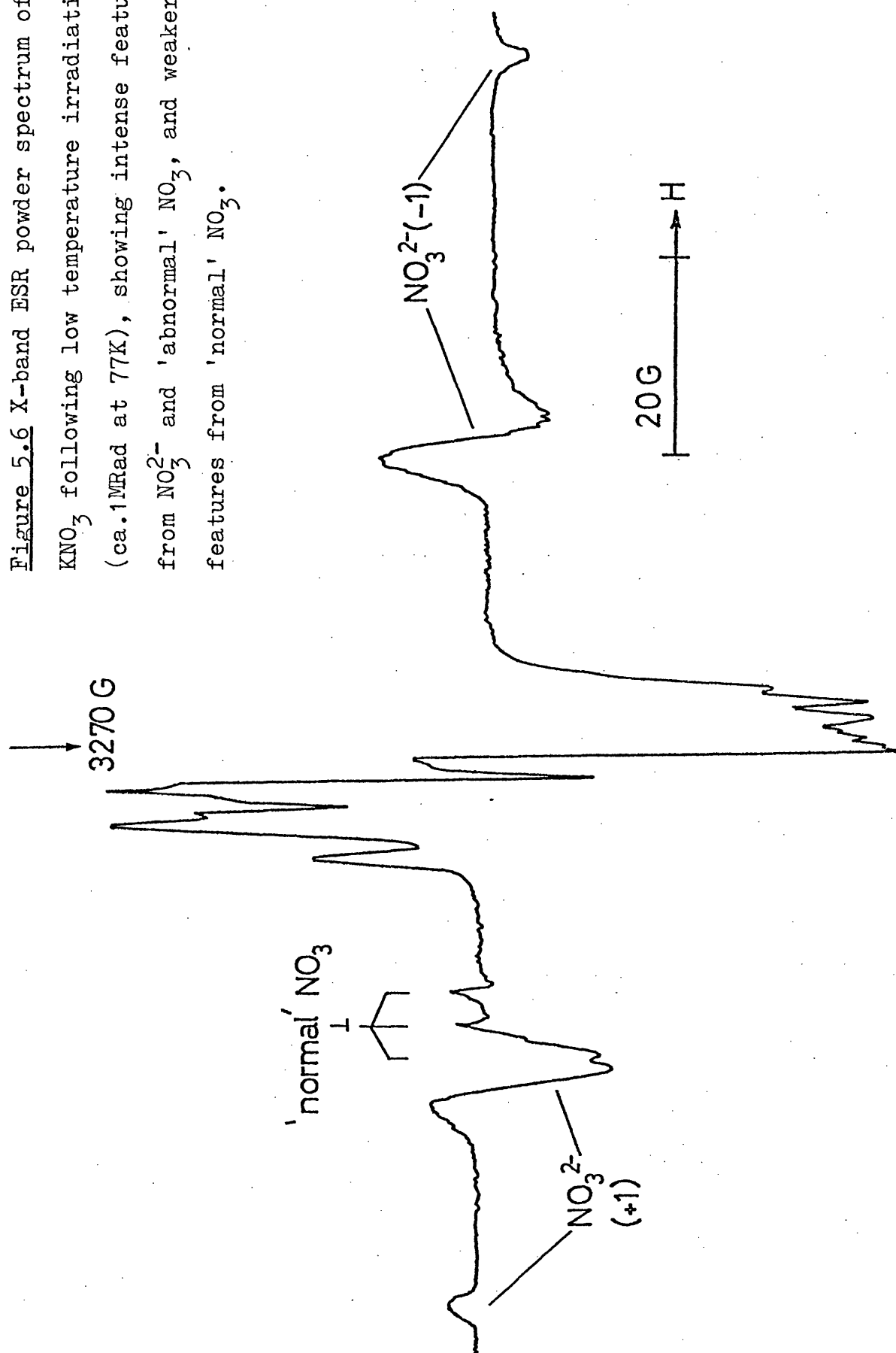
5.2b Sodium and Potassium Nitrates

Irradiated potassium nitrate has been studied in detail, using ESR, by Livingston and Zeldes²²⁻²⁴; they have identified 'normal' NO_3 and NO_3^{2-} as primary products at 77K and NO_2 as a secondary product, formed on suitable treatment of the irradiated crystals. Irradiated sodium nitrate has been studied by a number of authors²⁵⁻²⁸. NO_3 and NO_3^{2-} are again the primary products and NO_2 can be formed in much the same way as in potassium nitrate.

The NO_3 Centre

In this study the main interest is in NO_3 formation. In potassium nitrate, following low radiation doses (≤ 0.003 MRad) at 77K, NO_3^{2-} and 'normal' NO_3 are formed (Table A4.4). As the radiation dose increases, the rate of increase of the yield of 'normal' NO_3 rapidly falls to zero and new features appear with similar, but distinctly different, ESR parameters (Fig. 5.6). These new features are almost identical to those found in aqueous potassium nitrate solution⁷ and very close to those found in crystalline lead nitrate⁵, thallous nitrate⁶ and cadmium nitrate. They have been assigned tentatively to

Figure 5.6 X-band ESR powder spectrum of KNO_3 following low temperature irradiation (ca. 1 MRad at 77K), showing intense features from NO_3^{2-} and 'abnormal' NO_3 , and weaker features from 'normal' NO_3 .



the NO_4^{2-} species⁷ but in this work the species has been referred to simply as 'abnormal' NO_3 .

The ESR data indicates that the species is almost axially symmetrical but suffers a slight distortion from this symmetry: a preliminary single crystal study reveals that the 'parallel' symmetry axis is the same as that for 'normal' NO_3 and NO_3^{2-} . It appears to have a particular stability, signals from 'abnormal' NO_3 disappearing at a higher temperature than those from 'normal' NO_3 .

In a semi-quantitative way it seems that 'abnormal' NO_3 takes over from 'normal' NO_3 as the principal electron loss centre when the yield of 'normal' NO_3 reaches its limit. It was wondered whether one or other was an impurity centre but recrystallising the salts was found not to affect the yield of either type of NO_3 .

The small values for the hyperfine coupling constant to ^{14}N in 'abnormal' NO_3 (Table A4.4) suggest that this species, like 'normal' NO_3 , has no direct unpaired electron density on nitrogen, and a reasonable conclusion is that the species must be an oxide or oxyion of nitrogen with a hole in an orbital confined to one or more oxygen ligands.

The evidence suggests that 'abnormal' NO_3 is an electron loss centre. This could be substantiated by doping the nitrates with suitable electron scavengers and observing the effect on the 'abnormal' NO_3 yield but on the assumption that it is true the assignment⁷ to NO_4^{2-} , which is an electron excess centre, can be discounted.

It is impossible to derive the parameters for 'abnormal' NO_3 by invoking specific librations or hindered rotations for 'normal' NO_3 . The idea that 'abnormal NO_3 ' is really the

normal form of NO_3 can be discounted principally because the species designated 'normal' NO_3 , as formed in most inorganic nitrates, is always accompanied by a blue colour and its visible spectrum corresponds closely to the known spectrum for NO_3 in the gas phase²⁹, 'Abnormal' NO_3 is accompanied by no such colour.

A clue to the nature of 'abnormal' NO_3 may lie in the fact that it is only formed in anhydrous nitrates. Irradiated cadmium nitrate tetrahydrate exhibits ESR spectra characteristic of 'normal' NO_3 only, whereas in the anhydrous salt 'abnormal' NO_3 is also detected. The results of Symons and Zimmerman⁷ for frozen aqueous potassium nitrate solution are so similar to those for crystalline potassium nitrate that phase separation into an ice and a potassium nitrate phase must be considered as a possibility; this would be consistent with 'abnormal' NO_3 formation being associated with a water free phase.

NO_3 formation in sodium nitrate follows a similar pattern. Features are poorly defined however, because of the higher magnetic moment of ^{23}Na over ^{40}K .

The NO_3^{2-} Centre

The spectrum of NO_3^{2-} has been identified at 77K in crystalline potassium nitrate^{30,22} and the parameters found in this study agree with those of Cunningham³⁰.

NO_3^{2-} formation in sodium nitrate is not so well documented and although its formation is not a surprising result, the NO_3^{2-} features are notably different from those in potassium nitrate in that they show well resolved ^{23}Na SHFS (Fig. 5.7).

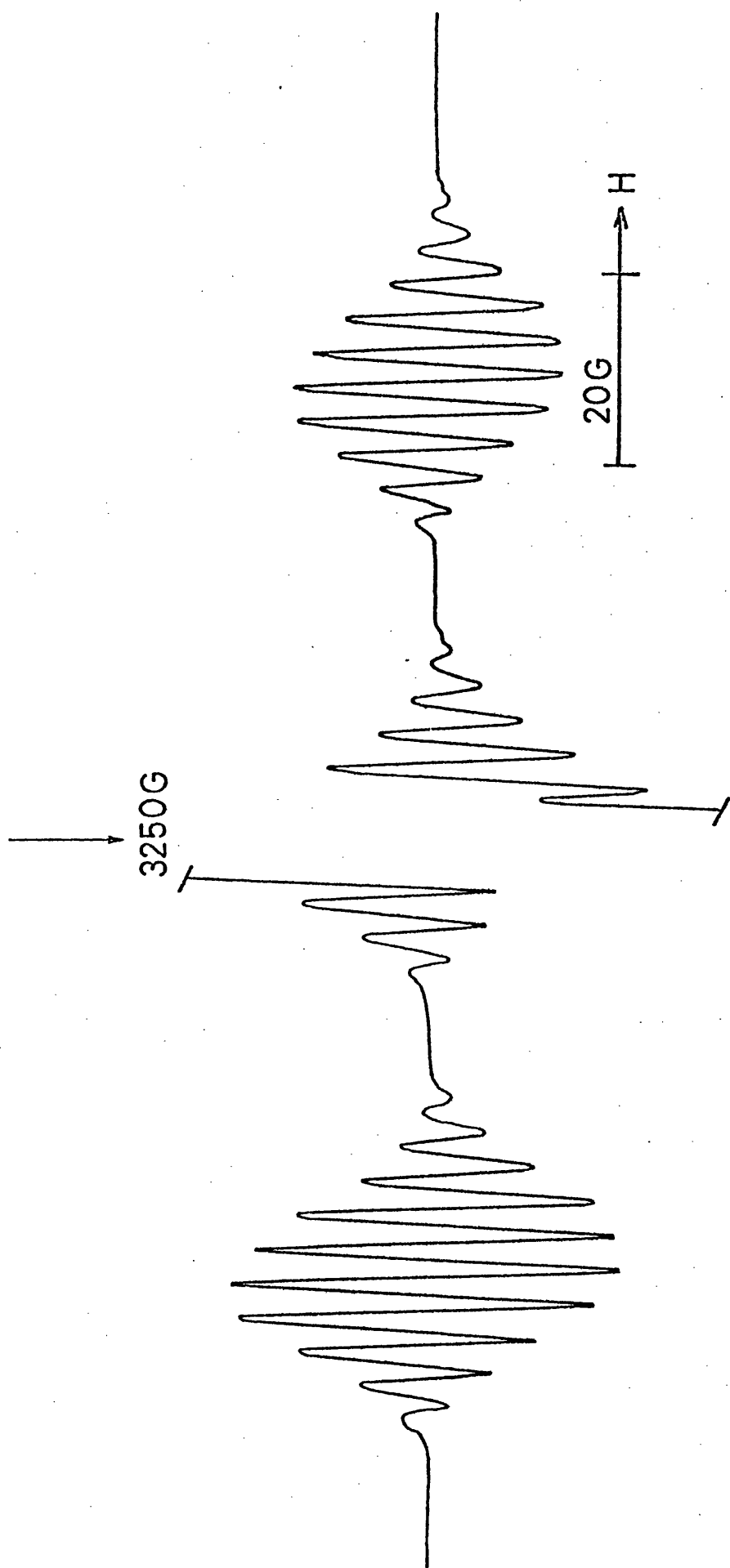
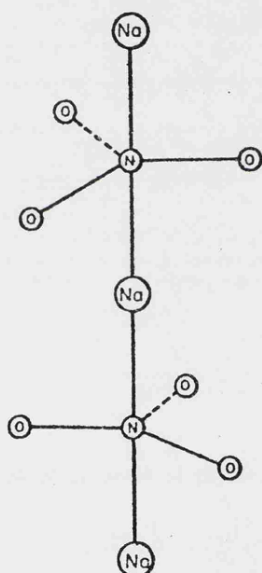


Figure 5.7 X-band ESR spectrum of an irradiated single crystal of NaNO_3 (at 77K) in an arbitrary orientation, measured during an anneal, showing features from NO_3^{2-} and clearly resolved ^{23}Na SHFS.

The SHFS is interpreted in terms of coupling to three equivalent ^{23}Na nuclei along both parallel and perpendicular symmetry axes with relatively little anisotropy in the sodium coupling (Table A4.4).

The unpaired electron in NO_3^{2-} is largely confined to a nitrogen orbital⁴, and in view of the crystal structure of sodium nitrate³¹, a section of which is shown below, coupling to two rather than three equivalent ^{23}Na nuclei might be expected.



Arrangement of atoms in NaNO_3 crystal.

From the hyperfine parameters for NO_3^{2-} a p:s ratio for the orbital in which the electron is formally sited can be calculated. The value found, of 9.2, indicates that a small deviation from planarity occurs when NO_3^{2-} is formed from NO_3^- . Such a deviation, although small ($10\text{--}20^\circ$), might conceivably be sufficient to bring three sodium ions into equivalent positions relative to the unpaired spin.

The O_2^- Centre

After a sufficiently long anneal and a recool to 77K, irradiated potassium nitrate exhibits a spectrum attributed to O_2^- . It appears to be a primary product of low temperature irradiation but the signal is largely hidden initially by those from NO_3^- and NO_3^{2-} . Comparison of the g values with those for O_2^- in potassium chloride (Table 5.2) indicates that in potassium nitrate O_2^- is librating; indeed, when the powder is allowed to warm up further reversible averaging of the g values is observed.

Table 5.2 ESR Parameters for O_2^- Centres

	g_1	g_2	g_3
in KNO_3 (77K)	2.0400	2.0092	2.0013
in KCl ³²	2.436	1.955	1.951
in NaO_2 ³³	2.175	2.00	2.00

O_2^- formation could be explained by electron capture by NO_3^- ions and the subsequent decomposition of excited NO_3^{2-} (5.8).



Alternatively, O_2^- could be formed from an impurity centre, such as trapped oxygen, in the potassium nitrate used. The latter view is favoured, principally because O_2^- is not detected in irradiated sodium nitrate which, in other respects, exhibits almost identical behaviour to irradiated potassium nitrate.

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Appendix One

The Calculation of g and a Values for Systems

with Large Nuclear Hyperfine Constants

In Chapters Two, Three and Five paramagnetic centres frequently arise whose hyperfine coupling constants are sufficiently large that the parameters cannot be obtained directly from the observed resonance positions. Notable in this respect are Ag^0 , Ag_2^+ , Hg^+ and $\text{Hg}_2^{+/3+}$. The methods which have been used in this work to calculate the ESR parameters for these systems are outlined below.

A1.1 g and a value calculations for Ag^0 like species

Generally, in the ESR spectra of Ag^0 both the high field ($m_I = +\frac{1}{2}$) and the low field ($m_I = -\frac{1}{2}$) transitions occur at convenient magnetic fields. For this reason a calculation is required to extract the g and a values from measurements of these two transitions. Atkins and Symons¹ have performed such a calculation.

In Section 1.1 the Spin Hamiltonian is defined in terms of shift operators:

$$\mathcal{H}_S = g\beta H_Z S_Z + a \left[\frac{1}{2} (S_+ I_- + S_- I_+) + S_Z I_Z \right] . \quad \text{A1.1}$$

The Nuclear Zeeman term, which is small, has been omitted. If this Hamiltonian operates on the basis states of an anisotropic system of one unpaired electron associated with one nucleus of spin $I = \frac{1}{2}$, then, with the applied field in the z direction the energy matrix this gives is:

$$\begin{array}{ccccc}
\langle m_S m_I | & \langle +\frac{1}{2} +\frac{1}{2} | & \langle +\frac{1}{2} -\frac{1}{2} | & \langle -\frac{1}{2} +\frac{1}{2} | & \langle -\frac{1}{2} -\frac{1}{2} | \\
\langle +\frac{1}{2} +\frac{1}{2} | & \left[\begin{array}{ccccc} \frac{1}{2}(G+a_z) & 0 & 0 & \frac{a_x-a_y}{4} \\ 0 & \frac{1}{2}(G-a_z) & \frac{a_x+a_y}{4} & 0 \\ 0 & \frac{a_x+a_y}{4} & -\frac{1}{2}(G+a_z) & 0 \\ \frac{a_x-a_y}{4} & 0 & 0 & -\frac{1}{2}(G-a_z) \end{array} \right] & & & \\
\langle +\frac{1}{2} -\frac{1}{2} | & & & & \\
\langle -\frac{1}{2} +\frac{1}{2} | & & & & \\
\langle -\frac{1}{2} -\frac{1}{2} | & & & &
\end{array} \quad A1.2$$

where $G = g_z \beta H_z$.

If the off diagonal elements are not small enough to be ignored then the roots of the Secular Determinant

$$|H-E| = 0 \quad A1.3$$

provide four energy levels and although not strictly correct because S and I are not decoupled they can be assigned to eigenstates described approximately by the basis states $\langle m_S m_I |$.

$$\begin{aligned}
E_1 \langle +\frac{1}{2} +\frac{1}{2} | &= \frac{a_z}{4} + \frac{1}{4} \left[4G^2 + (a_x - a_y)^2 \right]^{\frac{1}{2}} \\
E_2 \langle -\frac{1}{2} -\frac{1}{2} | &= \frac{a_z}{4} - \frac{1}{4} \left[4G^2 + (a_x - a_y)^2 \right]^{\frac{1}{2}} \\
E_3 \langle +\frac{1}{2} -\frac{1}{2} | &= -\frac{a_z}{4} + \frac{1}{4} \left[4G^2 + (a_x + a_y)^2 \right]^{\frac{1}{2}} \\
E_4 \langle -\frac{1}{2} +\frac{1}{2} | &= -\frac{a_z}{4} - \frac{1}{4} \left[4G^2 + (a_x + a_y)^2 \right]^{\frac{1}{2}}
\end{aligned} \quad A1.4$$

From the selection rule $\Delta m_S = \pm 1$ the allowed transitions can be written as:

$$h\nu = E_1 - E_4 = E_3 - E_2 \quad A1.5$$

A more rigorous determination of the eigenstates and the transition probabilities between them would reveal that the two allowed transitions predicted in A1.5 are the two with by far the highest probabilities under typical conditions.

Thus two equations can be written down relating the resonance field positions to the hyperfine coupling constants and g values.

$$\begin{aligned} h\nu &= \frac{a_z}{2} + \frac{1}{4} \left[\left[4(g_z \beta H_1)^2 + (a_x - a_y)^2 \right]^{\frac{1}{2}} + \left[4(g_z \beta H_1)^2 + (a_x + a_y)^2 \right]^{\frac{1}{2}} \right] \\ h\nu &= -\frac{a_z}{2} + \frac{1}{4} \left[\left[4(g_z \beta H_2)^2 + (a_x - a_y)^2 \right]^{\frac{1}{2}} + \left[4(g_z \beta H_2)^2 + (a_x + a_y)^2 \right]^{\frac{1}{2}} \right] \end{aligned} \quad \text{A1.6}$$

where H_1 and H_2 are the low and high field resonance line positions respectively.

The corresponding expressions, for the resonance line positions in the directions of the x and y components of the g and a tensors can be derived by setting up similar energy matrices. The resulting expressions are analogous to A1.6 with the x and y components interchanged with the z components.

If the low and high field resonance fields corresponding to each of the principal directions of the a and g tensors can be measured then the values of the a and g tensors in these directions can be calculated using a computer programme similar to the one listed in Figure A1.1.

This programme, written by Dr R.J. Booth, starting with estimated values for a_x , a_y and a_z calculates approximate values for g_x , g_y and g_z and then refines the values of all six variables by iterative use of equations A1.6 until they are self consistent.

A1.2 g and a value calculations for Ag_2^+ like species

A calculation of the eigenvectors and eigenstates for a system of one unpaired electron associated with two equivalent nuclei, both of spin $I=\frac{1}{2}$ was not available so the details of the calculation carried out in this work will be summarized here.

[The treatment used by Shields and Symons² to describe Ag_2^+ is an approximation in that 1) it uses the equations of Bleaney³ that were derived for mono-nuclear species and 2) it treats the species as if isotropic].

Neglecting the Nuclear Zeeman terms, the Spin Hamiltonian used to describe the Ag_2^+ spin states is:

$$\mathcal{H}_S = g\beta H \cdot S + S \cdot a \cdot I + S \cdot a \cdot I' \quad . \quad \text{A1.7}$$

This can be written, with H along the z direction and in terms of raising and lowering operators:

$$\begin{aligned} \mathcal{H}_z = & G S_z + S_z I_z a_z + \frac{a_x + a_y}{4} (S_+ I_- + S_- I_+) + \frac{a_x - a_y}{4} (S_+ I_+ + S_- I_-) \\ & + S_z I'_z a_z + \frac{a_x + a_y}{4} (S_+ I'_- + S_- I'_+) + \frac{a_x - a_y}{4} (S_+ I'_+ + S_- I'_-) \quad . \quad \text{A1.8} \end{aligned}$$

Similar operators can be constructed along the x and y directions. I =spin of nucleus 1; I' =spin of nucleus 2; $G=g\beta H$. By operating on the basis states described by $\langle m_S m_I m_{I'} |$ the following energy matrix is obtained.

$\langle m_S m_I m_I' $	$\langle +\frac{1}{2}+\frac{1}{2}+\frac{1}{2} $	$\langle +\frac{1}{2}+\frac{1}{2}-\frac{1}{2} $	$\langle +\frac{1}{2}-\frac{1}{2}+\frac{1}{2} $	$\langle +\frac{1}{2}-\frac{1}{2}-\frac{1}{2} $	$\langle -\frac{1}{2}+\frac{1}{2}+\frac{1}{2} $	$\langle -\frac{1}{2}+\frac{1}{2}-\frac{1}{2} $	$\langle -\frac{1}{2}-\frac{1}{2}+\frac{1}{2} $	$\langle -\frac{1}{2}-\frac{1}{2}-\frac{1}{2} $
$\langle +++ $	$\frac{G_z + a_z}{2} \frac{z}{2}$	0	0	0	0	$\frac{a_x - a_y}{4}$	$\frac{a_x - a_y}{4}$	0
$\langle ++- $	0	$\frac{G_z}{2}$	0	0	$\frac{a_x + a_y}{4}$	0	0	$\frac{a_x - a_y}{4}$
$\langle +-+ $	0	0	$\frac{G_z}{2}$	0	$\frac{a_x + a_y}{4}$	0	0	$\frac{a_x - a_y}{4}$
$\langle --- $	0	0	0	$\frac{G_z - a_z}{2} \frac{z}{2}$	0	$\frac{a_x + a_y}{4}$	$\frac{a_x + a_y}{4}$	0
$\langle -++ $	0	$\frac{a_x + a_y}{4}$	$\frac{a_x + a_y}{4}$	0	$-\frac{G_z - a_z}{2} \frac{z}{2}$	0	0	0
$\langle +- - $	$\frac{a_x - a_y}{4}$	0	0	$\frac{a_x + a_y}{4}$	0	$-\frac{G_z}{2}$	0	0
$\langle --+ $	$\frac{a_x - a_y}{4}$	0	0	$\frac{a_x + a_y}{4}$	0	0	$-\frac{G_z}{2}$	0
$\langle --- $	0	$\frac{a_x - a_y}{4}$	$\frac{a_x - a_y}{4}$	0	0	0	0	$-\frac{G_z + a_z}{2} \frac{z}{2}$

A1.9

Ag_2^+ has axial symmetry so:

$$a_z = a_{//} = a_1$$

$$a_x = a_y = a_{\perp} = a_2$$

A1.10

The energy matrix can be rewritten:

$\langle m_S m_I m_I' $	$\langle --- $	$\langle +++ $	$\langle ++- $	$\langle +-+ $	$\langle -++ $	$\langle +-- $	$\langle -+- $	$\langle --+ $
$\langle --- $	$-\frac{G_z + a_1}{2} \frac{z}{2}$							
$\langle +++ $		$\frac{G_z + a_1}{2} \frac{z}{2}$						
$\langle ++- $			$\frac{G_z}{2}$	$\frac{a_2}{2}$				
$\langle +-+ $			$\frac{G_z}{2}$	$\frac{a_2}{2}$				
$\langle -++ $			$\frac{a_2}{2}$	$\frac{a_2}{2}$	$-\frac{G_z - a_1}{2} \frac{z}{2}$			
$\langle +-- $					$\frac{G_z - a_1}{2} \frac{z}{2}$	$\frac{a_2}{2}$	$\frac{a_2}{2}$	
$\langle -+- $					$\frac{a_2}{2}$	$-\frac{G_z}{2}$		
$\langle --+ $					$\frac{a_2}{2}$		$-\frac{G_z}{2}$	

A1.11

By treating each block of this matrix separately, eigenvalues can be obtained as roots of each Secular Determinant:

$$|H-E| = 0$$

This immediately provides two eigenvalues and their associated eigenvectors.

$$\begin{aligned} \Psi_7 &= \langle -\frac{1}{2} - \frac{1}{2} - \frac{1}{2} | & E_7 &= \frac{-G_z + a_1}{2} \\ \Psi_8 &= \langle +\frac{1}{2} + \frac{1}{2} + \frac{1}{2} | & E_8 &= \frac{G_z + a_1}{2} \end{aligned} \quad A1.12$$

The two remaining 3x3 matrices can be diagonalized using a Jacobi diagonalization matrix of the form:

$$R = \begin{bmatrix} \cos\theta \cos\alpha & -\sin\theta & \cos\theta \sin\alpha \\ \sin\theta \cos\alpha & \cos\theta & \sin\theta \sin\alpha \\ -\sin\alpha & 0 & \cos\alpha \end{bmatrix} \quad A1.13$$

such that:

$$R^{-1} \cdot M \cdot R = \begin{bmatrix} E_1 & & \\ & E_2 & \\ & & E_3 \end{bmatrix} \quad A1.14$$

Six new eigenstates emerge with their associated eigenvalues.

$$\begin{aligned} \Psi_1 &= \cos\theta \cos\alpha |++\rangle + \sin\theta \cos\alpha |+-\rangle - \sin\alpha |-++\rangle \\ \Psi_2 &= -\sin\theta |++\rangle + \cos\theta |+-\rangle \\ \Psi_3 &= \cos\theta \sin\alpha |++\rangle + \sin\theta \sin\alpha |+-\rangle + \cos\alpha |-++\rangle \\ \Psi_4 &= -\sin\theta |+-\rangle + \cos\theta \cos\alpha |--\rangle + \sin\theta \cos\alpha |--\rangle \\ \Psi_5 &= \cos\alpha |+-\rangle + \cos\theta \sin\alpha |+-\rangle + \sin\theta \sin\alpha |--\rangle \\ \Psi_6 &= -\sin\theta |+-\rangle + \cos\theta |--\rangle \\ E_1 &= \frac{G_z}{2} (\cos^2\alpha - \sin^2\alpha) - \frac{a_1}{2} \sin^2\alpha - a_2 \cos\alpha \sin\alpha (\cos\theta + \sin\theta) \end{aligned} \quad A1.15$$

$$E_2 = \frac{G_z}{2} \sin^2 \theta + \frac{G_z}{2} \cos^2 \theta$$

$$E_3 = \frac{G_z}{2} (\sin^2 \alpha - \cos^2 \alpha) + a_2 \sin \alpha \cos \alpha (\cos \theta + \sin \theta) - \frac{a_1}{2} \cos^2 \alpha$$

$$E_4 = \frac{G_z}{2} (\sin^2 \phi - \cos^2 \phi) - a_2 \sin \phi \cos \phi (\cos \theta + \sin \theta) - \frac{a_1}{2} \sin^2 \phi$$

$$E_5 = \frac{G_z}{2} (\cos^2 \phi - \sin^2 \phi) + a_2 \cos \phi \sin \phi (\cos \theta + \sin \theta) - \frac{a_1}{2} \cos^2 \phi$$

$$E_6 = -\frac{G_z}{2} \sin^2 \theta - \frac{G_z}{2} \cos^2 \theta$$

where: $\theta = 45^\circ$

$$\tan 2\phi = \frac{\sqrt{2}a_2}{G_z - \frac{a_1}{2}}$$

A1.16

$$\tan 2\alpha = -\frac{\sqrt{2}a_2}{G_z + \frac{a_1}{2}}$$

The spin transition is induced by the oscillating magnetic field associated with the microwave radiation. The experimental conditions are such that the microwave magnetic vector is perpendicular to the static field. If the latter is H_z , the oscillating field is H_x which couples with the S_x component of the spin angular momentum. The transition probability is thus proportional to the matrix element:

$$|\langle \Psi_i | 2S_x | \Psi_1 \rangle|^2 \quad \text{A1.17}$$

and since $2S_x = (S_+ + S_-)$ this can be written:

$$|\langle \Psi_i | S_+ + S_- | \Psi_1 \rangle|^2 \quad \text{A1.18}$$

The transition probabilities are shown below. Typical numerical

estimates reveal that there are four transitions that are considerably stronger than the others.

transition	transition probabilities	
Ψ_4/Ψ_1	$\cos^2\phi \cos^2\alpha$	(strong)
Ψ_4/Ψ_3	$\cos^2\phi \sin^2\alpha$	
Ψ_5/Ψ_1	$\cos^2\alpha \sin^2\phi$	
Ψ_5/Ψ_3	$\sin^2\phi \sin^2\alpha$	
Ψ_6/Ψ_2	1	(strong)
Ψ_7/Ψ_4	$\sin^2\phi$	
Ψ_7/Ψ_5	$\cos^2\phi$	(strong)
Ψ_8/Ψ_1	$\sin^2\alpha$	
Ψ_8/Ψ_3	$\cos^2\alpha$	(strong)

The four strong transitions can be described by:

$$\begin{aligned} \Psi_4/\Psi_1 \quad h\nu = \frac{g_z\beta H}{2} \left[(\sin^2\phi - \cos^2\phi) - (\cos^2\alpha - \sin^2\alpha) \right] + \frac{a_1}{2} (\sin^2\phi + \sin^2\alpha) \\ + \sqrt{2}a_2 (\cos\alpha \sin\alpha - \sin\phi \cos\phi) \end{aligned}$$

$$\Psi_6/\Psi_2 \quad h\nu = g_z\beta H$$

A1.19

$$\Psi_7/\Psi_5 \quad h\nu = g_z\beta H \cos^2\phi - \frac{a_1}{2} (1 + \cos^2\phi) + \sqrt{2}a_2 \cos\phi \sin\phi$$

$$\Psi_8/\Psi_3 \quad h\nu = g_z\beta H \cos^2\alpha + \frac{a_1}{2} (1 + \cos^2\alpha) - \sqrt{2}a_2 \sin\alpha \cos\alpha$$

By inspection it can be seen that Ψ_7/Ψ_5 will be the high field transition and Ψ_8/Ψ_3 the low field transition and since these are the two transitions that experimentally can be clearly seen they form the basis of the rest of the calculations.

The equivalent procedure, substituting a_2 for a_1 , g_1 for g_z (g_z) and $\frac{a_1+a_2}{2}$ for a_2 yields the transitions in the

perpendicular direction. This represents an approximation in that $\frac{a_1 - a_2}{2}$ terms in the energy matrix are ignored but these represent inaccuracies in the energy levels within experimental error for the system used. They could most easily be included by treating them as perturbations on the energy levels found after diagonalization.

There are thus four equations on which the programme in Figure A1.2 is based.

$$\begin{aligned}
 // \left\{ \begin{aligned} \Psi_7/\Psi_5 \quad v &= G_1 \frac{\beta W \cos^2 \phi}{h} - \frac{a_1}{2h} (1 + \cos^2 \phi) + \frac{2a_2 \sin \phi \cos \phi}{h} \\ \Psi_8/\Psi_3 \quad v &= G_1 \frac{\beta Y \cos^2 \alpha}{h} + \frac{a_1}{2h} (1 + \cos^2 \alpha) - \frac{2a_2 \sin \alpha \cos \alpha}{h} \end{aligned} \right. \quad A1.20 \\
 \perp \left\{ \begin{aligned} \Psi_7/\Psi_5 \quad v &= G_2 \frac{\beta X \cos^2 \phi'}{h} - \frac{a_2}{2h} (1 + \cos^2 \phi') + \frac{2(a_1 + a_2) \sin \phi' \cos \phi'}{2h} \\ \Psi_8/\Psi_3 \quad v &= G_2 \frac{\beta Z \cos^2 \alpha'}{h} + \frac{a_2}{2h} (1 + \cos^2 \alpha') - \frac{2(a_1 + a_2) \sin \alpha' \cos \alpha'}{2h} \end{aligned} \right.
 \end{aligned}$$

where: $G_1 = g_{//}$ and $G_2 = g_{\perp}$;

W = high field $//$ field position; Y = low field $//$;

X = high field $\perp$; Z = low field $\perp$.

ϕ and α are as defined in Equation A1.16 and ϕ' and α' are obtained from ϕ and α by substituting $\frac{a_1 + a_2}{2}$ for a_2 , a_2 for a_1 and G_2 for G_1 .

By iterative use of equations A1.20 the programme refines values of the hyperfine constants $a_{//}$ and $a_{\perp}$ and the g values, $g_{//}$ and $g_{\perp}$ until they are self consistent.

An alternative method of calculating the corrected energy levels is to apply second order Perturbation Theory. This has

been done as a check on the exact calculation.

The perturbation on the first order eigenvalues can be represented by¹:

$$E |++\rangle = \langle ++ | \mathcal{H}_1 | ++ \rangle - \sum_{n=1}^{\infty} \frac{|\langle ++ | \mathcal{H}_1 | n \rangle|^2}{E_{|n\rangle}^0 - E_{|++\rangle}^0} \quad A1.21$$

This gives a set of corrected energy levels associated with the zeroeth order eigenvectors.

$$\begin{aligned} |++\rangle \quad E &= \frac{G_z}{2} + \frac{a_z}{2} + \frac{(a_x - a_y)^2}{8G_z + 4a_z} \\ |+-\rangle \quad E &= \frac{G_z}{2} + \frac{(a_x + a_y)^2}{16G_z + 8a_z} + \frac{(a_x - a_y)^2}{16G_z - 8a_z} \\ |+-\rangle \quad E &= \frac{G_z}{2} + \frac{(a_x + a_y)^2}{16G_z + 8a_z} + \frac{(a_x - a_y)^2}{16G_z - 8a_z} \\ |+-\rangle \quad E &= \frac{G_z}{2} - \frac{a_z}{2} + \frac{(a_x + a_y)^2}{8G_z - 4a_z} \\ |--\rangle \quad E &= -\frac{G_z}{2} - \frac{a_z}{2} - \frac{(a_x + a_y)^2}{8G_z + 4a_z} \\ |--\rangle \quad E &= -\frac{G_z}{2} - \frac{(a_x + a_y)^2}{16G_z - 8a_z} - \frac{(a_x - a_y)^2}{16G_z + 8a_z} \\ |--\rangle \quad E &= -\frac{G_z}{2} - \frac{(a_x + a_y)^2}{16G_z - 8a_z} - \frac{(a_x - a_y)^2}{16G_z + 8a_z} \\ |--\rangle \quad E &= -\frac{G_z}{2} + \frac{a_z}{2} - \frac{(a_x - a_y)^2}{8G_z - 4a_z} \end{aligned} \quad A1.22$$

where $G_z = g_z \beta H$

From the selection rule $\Delta m_S = \pm 1$ there are four allowed transitions and by considering the situation where the magnetic field is along the x or y direction, four equations analogous to equations A1.20 can be obtained describing the low and the high field parallel and perpendicular transitions.

$$\begin{cases} \nu = G_1 H_1 \frac{\beta}{h} + \frac{a_1}{h} + \frac{a_2^2}{2G_1 H_1 \beta + a_1 h} \\ \nu = G_1 H_2 \frac{\beta}{h} - \frac{a_1}{h} + \frac{a_2^2}{2G_1 H_2 \beta - a_1 h} \end{cases}$$

A1.23

$$\begin{cases} \nu = G_2 H_3 \frac{\beta}{h} + \frac{a_2}{h} + \frac{(a_1 - a_2)^2 + (a_1 + a_2)^2}{8G_2 H_3 \beta + 4a_2 h} \\ \nu = G_2 H_4 \frac{\beta}{h} - \frac{a_2}{h} + \frac{(a_1 - a_2)^2 + (a_1 + a_2)^2}{8G_2 H_4 \beta - 4a_2 h} \end{cases}$$

where $G_1 = g_{//}$ and
 $G_2 = g_{\perp}$

The programme in Figure A1.3 calculates a and g values from the high and low field resonance field positions by iterative use of equations A1.23 in a similar way to the programme in Figure A1.2.

g and a values calculated using both programmes are found to be in good agreement and within the limits of accuracy imposed by the use of second order Perturbation Theory.

ESR parameters quoted for Ag_3^{2+} and Ag_4^{3+} are uncorrected and taken direct from the experimental resonance positions. It is assumed that the corrections would be small compared to the accuracy with which the line positions can be measured; Ag_3^{2+} and Ag_4^{3+} spectra are invariably poorly resolved.

A1.3 g and a value calculations for the species Hg^+ and $Hg_2^{+/3+}$

In the ESR studies of mercury(I) and mercury(II) nitrates in Chapter Five, the a values of the Hg^+ and $Hg_2^{+/3+}$ species

encountered are such that only one ESR transition for each of the two mercury isotopes possessing nuclear spin is observed. These are approximately described as the $m_I = -\frac{1}{2}$ transition for the ^{199}Hg isotope ($I = \frac{1}{2}$) and the $m_I = +\frac{3}{2}$ transition for the ^{201}Hg isotope ($I = \frac{3}{2}$). That 70% of naturally occurring mercury has no nuclear spin means that the g values for these systems can be found directly from the signal associated with the ^{200}Hg isotope ($I = 0$). Once g values have been established, a values can be readily calculated from the single resonances associated with each of the magnetic isotopes.

The treatment of Atkins and Symons¹ outlined in Section A1.1 dealing with an anisotropic system of one unpaired electron ($S = \frac{1}{2}$) associated with one nucleus having $I = \frac{1}{2}$ can be simplified for axially symmetric systems⁴. The two high field transitions corresponding to the magnetic field parallel to, and perpendicular to the symmetry axis can be represented by:

$$h\nu = \frac{g_{\parallel}\beta H_1}{2} - \frac{a_1}{2} + \frac{1}{2} \left[(g_{\parallel}\beta H_1)^2 + a_2^2 \right]^{\frac{1}{2}} \quad \text{A1.24}$$

$$h\nu = \frac{1}{2} \left[(g_{\perp}\beta H_2)^2 + \left(\frac{a_1 - a_2}{2} \right)^2 \right]^{\frac{1}{2}} - \frac{a_2}{2} + \frac{1}{2} \left[(g_{\perp}\beta H_2)^2 + \left(\frac{a_1 + a_2}{2} \right)^2 \right]^{\frac{1}{2}}$$

where H_1 = high field resonance with $H \parallel$ to the symmetry axis.

H_2 = high field resonance with $H \perp$ to the symmetry axis.

$a_1 = a_{\parallel}$ and $a_2 = a_{\perp}$.

A similar treatment of the system of one unpaired electron associated with one nucleus having $I = \frac{3}{2}$ has been performed by Lin and McDowell⁵ and for an axially symmetric system the high field transitions with the field parallel to and perpendicular to the symmetry axis can be represented by⁴:

$$h\nu = \frac{g_{\parallel}\beta H_3}{2} - a_3 + \frac{1}{2} \left[(g_{\parallel}\beta H_3 - a_3)^2 + 3a_4^2 \right]^{\frac{1}{2}} \quad \text{A1.25}$$

$$h\nu = \frac{g_{\perp}\beta H_4}{2} - a_4 + \frac{1}{2} \left[(g_{\perp}\beta H_4 - a_4)^2 + 3 \left(\frac{a_3 + a_4}{2} \right)^2 \right]^{\frac{1}{2}}$$

where H_3 , H_4 , a_3 and a_4 are equivalent to H_1 , H_2 , a_1 and a_2 in equations A1.24.

Equations A1.24 describe the situation of an electron associated with a single ^{199}Hg nucleus ($I=\frac{1}{2}$) and equations A1.25 an electron associated with a single ^{201}Hg nucleus ($I=\frac{3}{2}$).

Hg^+ :

Hg^+ , as studied in Chapter Five is isotropic. The g value can be obtained from the signal from non magnetic $^{200}\text{Hg}^+$ and then the a values calculated from simplified versions of equations A1.24 and A1.25.

For an isotropic system equations A1.24 reduce to:

$$A(\text{Gauss}) = \frac{2H_0(H_1 - H_0)}{2H_0 - H_1} \quad \text{A1.26}$$

where $H_0 = \frac{h\nu}{g\beta}$; H_1 = resonance field; A = hyperfine constant (Gauss). Equations A1.25 reduce to:

$$A(\text{Gauss}) = \frac{2H_0(H_3 - H_0)}{4H_0 - H_3} \quad \text{A1.27}$$

Thus, the A_{iso} values for $^{199}\text{Hg}^+$ and $^{201}\text{Hg}^+$ can be calculated from the two observable transitions using equations A1.26 and A1.27 respectively.

Hg_2^+ :

Hg_2^+ , like Ag_2^+ , possesses axial symmetry.

The relatively low natural abundance of both mercury isotopes that possess nuclear spin means that Hg_2^+ is likely to exist either as $^{200}\text{Hg}_2^+$ (no nuclear spin), $(^{199}\text{Hg} - ^{200}\text{Hg})^+$ (one nucleus ^{199}Hg , with $I=\frac{1}{2}$) or $(^{201}\text{Hg} - ^{200}\text{Hg})^+$ (one nucleus ^{201}Hg , with $I=\frac{3}{2}$). The high field transitions associated with the latter two species are described by equations A1.24 and A1.25.

It might be expected that $^{200}\text{Hg}_2^+$ would yield a sufficiently strong signal in the centre-field region for $g_{\parallel}$ and $g_{\perp}$ to be extracted directly from the spectrum. Were this so the hyperfine constants could be easily obtained from equations A1.24 and A1.25. $g_{\parallel}$ and $g_{\perp}$ cannot normally however, be unambiguously determined from the central region of the spectrum because of the strong signals associated with other radicals in the system.

If $g_{\parallel}$ and $g_{\perp}$ are estimated the resulting values of $a_{\parallel}$ and $a_{\perp}$ for the two isotopes are usually invalidated because the simple equation

$$\frac{^{199}a_{\parallel}}{^{199}a_{\perp}} = \frac{^{201}a_{\parallel}}{^{201}a_{\perp}} \quad \text{A1.28}$$

is not satisfied.

The data quoted in Chapter Five has been obtained using the programme in Figure A1.4. In this programme $g_{\perp}$ is estimated from the spectrum and by iterative use of equations A1.24, A1.25 and A1.28, $g_{\parallel}$ and the hyperfine constants are calculated.

A more satisfactory programme would use an estimate of $g_{\parallel}$, which might be expected to approximate to the 'free spin value' to calculate the hyperfine constants and $g_{\perp}$; attempts to write such a programme failed however, because the refined values of the parameters could not be made to converge.

By using the programme in Figure A1.4 and by adjusting the estimate of $g_{\perp}$, keeping it within experimentally imposed limits, such that $g_{\parallel}$ takes up values fairly close to free spin and again within the experimentally observed centre-field absorption, values for $a_{\parallel}$ and $a_{\perp}$ for $(^{199}\text{Hg} - ^{200}\text{Hg})^+$ and $(^{201}\text{Hg} - ^{200}\text{Hg})^+$ are forthcoming and are quoted in Chapter Five with appropriately large uncertainties.

References for Appendix One

1. P.W. Atkins and M.C.R. Symons, 'The Structure of Inorganic Radicals', Elsevier, Amsterdam, 1967.
2. L. Shields and M.C.R. Symons, Mol.Phys., 1966, 11, 57.
3. B. Bleaney, Phil.Mag., 1951, 42, 441.
4. Jun-Ichi Isoya and Shizuo Fujiwara, Bull.Chem.Soc.Japan, 1972, 45, 2182.
5. W.C. Lin and C.A. McDowell, Mol.Phys., 1964, 7, 223.

Figure A1.1 Computer programme in BASIC to calculate a_x , a_y , a_z and g_x , g_y , g_z for a system of one unpaired electron associated with one nucleus ($I=\frac{1}{2}$) from the lowfield and the highfield x, y and z resonance positions; typically used for Ag^0 .

```

10 PRINT "INPUT MICROWAVE FREQUENCY IN M.Hz."
20 INPUT V
30 PRINT "INPUT LOW FIELD X,Y & Z TRANSITION FIELDS"
40 INPUT A,B,C
50 PRINT "INPUT HIGH X,Y & Z TRANSITION FIELDS"
60 INPUT D,E,F
70 LET X=(D-A)/2
80 LET Y=(E-B)/2
90 LET Z=(F-C)/2
130 LET K=1.399611
140 LET D1=2*V-X+Y*Z/(2*V-X)
150 LET D2=2*V+X+Y*Z/(2*V+X)
160 LET G1=SQR((D1*D1+D2*D2-2*(Y+Z)*(Y+Z))/(D*D+A*A))/(2*K)
170 LET D1=4*G1*G1*K*K*D*D+(Y-Z)*(Y-Z)
180 LET D2=4*G1*G1*K*K*D*D+(Y+Z)*(Y+Z)
190 LET D3=4*G1*G1*K*K*A*A+(Y-Z)*(Y-Z)
200 LET D4=4*G1*G1*K*K*A*A+(Y+Z)*(Y+Z)
210 LET X1=.25*(SQR(D3)+SQR(D4)-SQR(D1)-SQR(D2))
220 LET D1=2*V-Y+X1*Z/(2*V-Y)
230 LET D2=2*V+Y+X1*Z/(2*V+Y)
240 LET G2=SQR((D1*D1+D2*D2-2*(X1+Z)*(X1+Z))/(E*E+B*B))/(2*K)
250 LET D1=4*G2*G2*K*K*E*E+(X1-Z)*(X1-Z)
260 LET D2=4*G2*G2*K*K*E*E+(X1+Z)*(X1+Z)
270 LET D3=4*G2*G2*K*K*B*B+(X1-Z)*(X1-Z)
280 LET D4=4*G2*G2*K*K*B*B+(X1+Z)*(X1+Z)
290 LET Y1=.25*(SQR(D3)+SQR(D4)-SQR(D1)-SQR(D2))
300 LET D1=2*V-Z+X1*Y1/(2*V-Z)
310 LET D2=2*V+Z+X1*Y1/(2*V+Z)
320 LET G3=SQR((D1*D1+D2*D2-2*(X1+Y1)*(X1+Y1))/(F*F+C*C))/(2*K)
330 LET D1=4*G3*G3*K*K*F*F+(X1-Y1)*(X1-Y1)
340 LET D2=4*G3*G3*K*K*F*F+(X1+Y1)*(X1+Y1)
350 LET D3=4*G3*G3*K*K*C*C+(X1-Y1)*(X1-Y1)
360 LET D4=4*G3*G3*K*K*C*C+(X1+Y1)*(X1+Y1)
370 LET Z1=.25*(SQR(D3)+SQR(D4)-SQR(D1)-SQR(D2))
380 IF ABS((X-X1)*(Y-Y1)*(Z-Z1))<=.1 THEN 430
390 LET X=X1
400 LET Y=Y1
410 LET Z=Z1
420 GOTO 140
430 PRINT"G & A (M.Hz.) VALUES FOR X,Y & Z ARE"
440 PRINT "X",G1,X1
450 PRINT "Y",G2,Y1
460 PRINT "Z",G3,Z1
470 STOP
480 END

```

Figure A1.2 Computer programme, in BASIC to calculate $a_{//}$, $a_{\perp}$, $g_{//}$ and $g_{\perp}$ for a system of one unpaired electron associated with two equivalent nuclei, both $I=\frac{1}{2}$, from the low field and the high field parallel and perpendicular resonance positions; typically used for Ag_2^+ . This programme is based on an exact solution of the Eigenvalue equation.

```

10 PRINT "INPUT MICROWAVE FREQUENCY IN M.HZ"
20 INPUT V
30 PRINT "INPUT LOW FIELD PARALLEL, LOW FIELD PERPENDICULAR"
31 PRINT "HIGH FIELD PARALLEL, HIGH FIELD PERPENDICULAR"
40 INPUT Y,Z,W,X
50 LET G1=2
60 LET G2=2
70 LET A1=1000
80 LET A2=1000
95 LET U=0
99 LET B1=1.3996106
100 LET P=0.5*(ATN((1.4142*A2)/(G1*B1*W-0.5*A1)))
110 LET Q=0.5*(ATN((-1.4142*A2)/(G1*B1*Y+0.5*A1)))
120 LET R=0.5*(ATN((0.7071*A1+0.7071*A2)/(G2*B1*X-0.5*A2)))
130 LET S=0.5*(ATN(-(0.7071*A1+0.7071*A2)/(G2*B1*Z+0.5*A2)))
140 LET B=0.5*(COS(Q)*COS(Q)-COS(P)*COS(P))
150 LET C=2.8284*(SIN(Q)*COS(Q)-SIN(P)*COS(P))
151 LET C=0.5*C
160 LET D=1.3996*(W*COS(P)*COS(P)+Y*COS(Q)*COS(Q))
170 LET E=1.3996*(W*COS(P)*COS(P)-Y*COS(Q)*COS(Q))
180 LET F=2.8284*(SIN(P)*COS(P)+SIN(Q)*COS(Q))
181 LET F=0.5*F
190 LET G=0.5*(2+COS(Q)*COS(Q)+COS(P)*COS(P))
200 LET H=0.5*(COS(S)*COS(S)-COS(R)*COS(R))
210 LET J=1.4142*(SIN(S)*COS(S)-SIN(R)*COS(R))
211 LET J=0.5*J
220 LET K=1.3996*(X*COS(R)*COS(R)+Z*COS(S)*COS(S))
230 LET L=1.3996*(X*COS(R)*COS(R)-Z*COS(S)*COS(S))
240 LET M=1.4142*(SIN(R)*COS(R)+SIN(S)*COS(S))
241 LET M=0.5*M
250 LET N=0.5*(2+COS(S)*COS(S)+COS(R)*COS(R))
251 IF U=1 GOTO 270
252 IF U=2 GOTO 280
253 IF U=3 GOTO 290
260 LET G3=(2*V-B*A1+C*A2)/D
261 LET G1=G3
262 LET U=1
263 GOTO 100
270 LET A3=(E*G1+F*A2)/G
271 LET A1=A3
272 LET U=2
273 GOTO 100
280 LET G4=(2*V-H*A2+J*(A1+A2))/K
281 LET G2=G4
282 LET U=3

```

```
283 GOTO 100
290 LET A4=(L*G2+M*A1)/(N-M)
300 IF ABS(A4-A2)<=.001 THEN 400
310 LET A2=A4
320 PRINT "ROUGH VALUES" G1,A1,G2,A2
330 GOTO 95
400 PRINT "G AND A(M.HZ) VALUES ARE"
410 PRINT "PARALLEL" G1,A1
420 PRINT "PERPENDICULAR" G2,A2
430 STOP
440 END
```

Figure A1.3 Computer programme, in BASIC to calculate $a_{\parallel}$, $a_{\perp}$, $g_{\parallel}$ and $g_{\perp}$ for a system of one unpaired electron associated with two equivalent nuclei, both $I=\frac{1}{2}$, from the low field and the high field parallel and perpendicular resonance positions; typically used for Ag_2^+ . This programme is based on Eigenvalues calculated from Second order Perturbation theory.

```

10 PRINT "INPUT MICROWAVE FREQUENCY IN M.HZ"
20 INPUT V
30 PRINT "INPUT LOW FIELD PARALLEL, LOW FIELD PERPENDICULAR"
31 PRINT "HIGH FIELD PARALLEL, HIGH FIELD PERPENDICULAR"
40 INPUT H1,H3,H2,H4
50 LET G1=2
60 LET G2=2
70 LET A1=1000
80 LET A2=1000
95 LET U=0
99 LET B=1.39961
251 IF U=1 GOTO 270
252 IF U=2 GOTO 280
253 IF U=3 GOTO 290
260 LET G3=(2*V-(0.5*A2*A2*(H2+H1)))/(G1*B*H1*H2)/(B*(H1+H2))
261 LET G1=G3
262 LET U=1
263 GOTO 99
270 LET A3=(B*G1*(H2-H1))/2-(A2*A2*0.25*(H2-H1))/(G1*B*H1*H2)
271 LET A1=A3
272 LET U=2
273 GOTO 99
280 LET G4=(2*V-(0.25*(A1*A1+A2*A2)*(H4+H3)))/(G2*B*H4*H3)/(B*(H3+H4))
281 LET G2=G4
282 LET U=3
283 GOTO 99
290 LET A4=(B*G2*(H4-H3))/2+(0.25*(A1*A2+A2*A2)*(H3-H4))/(2*G2*B*H3*H4)
300 IF ABS(A4-A2)<=.001 THEN 400
310 LET A2=A4
320 PRINT "ROUGH VALUES" G1,A1,G2,A2
330 GOTO 95
400 PRINT "G AND A(M.HZ) VALUES ARE"
410 PRINT "PARALLEL" G1,A1
420 PRINT "PERPENDICULAR" G2,A2
430 STOP
440 END

```

Figure A1.4 A computer programme, in BASIC to calculate $a_{\parallel}$, $a_{\perp}$ and $g_{\parallel}$ from an estimate of $g_{\perp}$ and the high field parallel and perpendicular resonance positions associated with the two systems, 1) an unpaired electron associated with one nucleus of spin $I=\frac{1}{2}$, typically ($^{200}\text{Hg}-^{199}\text{Hg}$)⁺ and 2) an unpaired electron associated with one nucleus of spin $I=\frac{3}{2}$, typically ($^{200}\text{Hg}-^{201}\text{Hg}$)⁺.

```

5 PRINT "USE HIGH FIELD AXIAL LINES OF BOTH MERCURY ISOTOPES."
10 PRINT "INPUT MW IN MHZ"
20 INPUT V
30 PRINT "INPUT MERCURY 199 HI. FIELD PARALLEL, PERPENDICULAR(G)"
40 INPUT H3,H4
41 PRINT "INPUT MERCURY 201 HI. FIELD PARA.,PERP,."
42 INPUT M3,M4
50 LET A1=1000
51 LET A2=1000
55 PRINT "GUESS G.PARA., ESTIMATE G.PERP.,THE PROGRAM HOLDS
  G.PERP"
56 PRINT "AND ADJUSTS G.PARA. UNTIL PARAMETERS FOR BOTH"
57 PRINT "ISOTOPES ARE CONSISTENT."
60 LET B1=50
61 PRINT "INPUT G PARA.,G PERP"
62 LET B2=50
65 INPUT G1,G2
90 LET U=0
100 IF U=1 GOTO 300
101 IF U=2 GOTO 400
102 IF U=3 GOTO 450
103 IF U=4 GOTO 500
104 IF U=5 GOTO 550
110 LET C=SQR(G1*H3*G1*H3*86.0089+B1*B1)
120 LET A3=G1*H3*9.2741-2*6.6262*V+C
130 LET A1=A3
140 LET U=1
150 GOTO 100
300 LET D=SQR(86.0089*G2*G2*H4*H4+0.25*(A1-B1)*(A1-B1))
310 LET E=SQR(86.0089*G2*G2*H4*H4+0.25*(A1+B1)*(A1+B1))
320 LET B3=D-2*6.6262*V+E
340 LET B1=B3
360 LET U=3
370 GOTO 100
400 LET F=SQR((G1*9.2741*M3-A2)*(G1*9.2741*M3-A2)+3*B2*B2)
410 LET G3=(A2-0.5*F+6.6262*V)/(4.63705*M3)
420 LET G1=G3
430 LET U=4
440 GOTO 100
450 LET J=G2*9.2741*M4-B2
460 LET K=0.75*(A2+B2)*(A2+B2)
470 LET B4=G2*M4*4.63705-6.6262*V+0.5*SQR(J*J+K)
480 LET B2=B4
490 LET U=5
491 GOTO 100
500 LET G2=G2

```

```
530 GOTO 90
550 LET A4=A1*B2/B1
560 IF ABS(A4-A2)<=.001 THEN 600
570 LET A2=A4
580 U=2
590 GOTO 100
600 PRINT "G.PARA.=" G1
610 PRINT "G.PERP.=" G2
611 LET A1=A1/(9.2741*G1)
612 LET B1=B1/(9.2741*G2)
620 PRINT "MERCURY 199"
630 PRINT "A1=(GAUSS)A PARA." A1
640 PRINT "B1=(GAUSS)A PERP." B1
650 PRINT "MERCURY 201"
660 LET A2=A2/(9.2741*G1)
670 LET B2=B4/(9.2741*G2)
680 PRINT "A2=A.PARA.="A2
690 PRINT "B2=A.PERP.="B2
700 STOP
710 END
```


Appendix Two

The ESR Spectrum of Irradiated

Dinitrogentetroxide

For the work reported in Chapter Five, anhydrous zinc nitrate was prepared from zinc metal and dinitrogen tetroxide. In the course of the preparation, amorphous dinitrogen tetroxide was irradiated at 77K and examined by ESR; this led to a more detailed study of the radiolysis of N_2O_4 .

Dinitrogen tetroxide is thermally unstable and has been the source of NO_2 in a variety of ESR studies of this radical^{1,2}, but radicals of the type N_2O_4^- have not previously been detected by ESR. Similar σ^* radicals can often be prepared however, by electron addition to the corresponding diamagnetic dimers, typical examples being:



N_2O_4^- formation might, therefore, be expected on radiolysis of N_2O_4 but the electron loss product N_2O_4^+ , which might also be formed, would exhibit a similar ESR spectrum. How these two species can be distinguished on the basis of their ESR spectra is discussed later.

A2.1 Experimental

Amorphous solid N_2O_4 was obtained from the liquid by pipetting small droplets directly into liquid nitrogen. Single crystals were grown in capillary tubes having extremely fine bore tips, filled under vacuum with liquid N_2O_4 . These were lowered slowly into a Dewar flask containing partially solidified ethanol.

Beads were irradiated with ^{60}Co γ rays, and ESR spectra

were measured as described in Chapter One.

A2.2 Results and Discussion

Irradiation of the amorphous solid gives centres A, B and C (Fig. A2.1). The group of features labelled A suggest that there are two or more different sites for this species, and this is confirmed by the single crystal results. Centre B comprises a set of five asymmetric features, assigned to hyperfine coupling to two equivalent ^{14}N nuclei. The ± 1 components of the powder spectrum overlap with those for centre A, but the single crystal spectra leave no doubt that there are five rather than three lines, and even reveal the second order splitting of the inner features (Fig. A2.2). A second set of features, labelled B', are sometimes detected after irradiation of the amorphous material. This centre is only a minor component, and is not detected in the irradiated single crystal. However, irradiation of a solution of N_2O_4 in a CD_3OD glass gives B' rather than B, together with features assigned to centre A. Features for $\cdot\text{CD}_2\text{OD}$ radicals are also clearly resolved but the absence of a violet colour shows that e_t^- formation is largely suppressed.

A third set of lines is also obtained from the amorphous and the crystalline material. These, labelled C in Figures A2.1 and A2.2, are considerably broader than, and partially hidden by, the more intense features from A and B. Nevertheless, there are clearly five components and tentative hyperfine parameters can be extracted. It is firmly concluded that the overall hyperfine interaction with ^{14}N is considerably

Figure A2.1 X-band ESR spectrum of amorphous N_2O_4 after exposure to ^{60}Co γ rays at 77K, showing features from centres A, B and C.

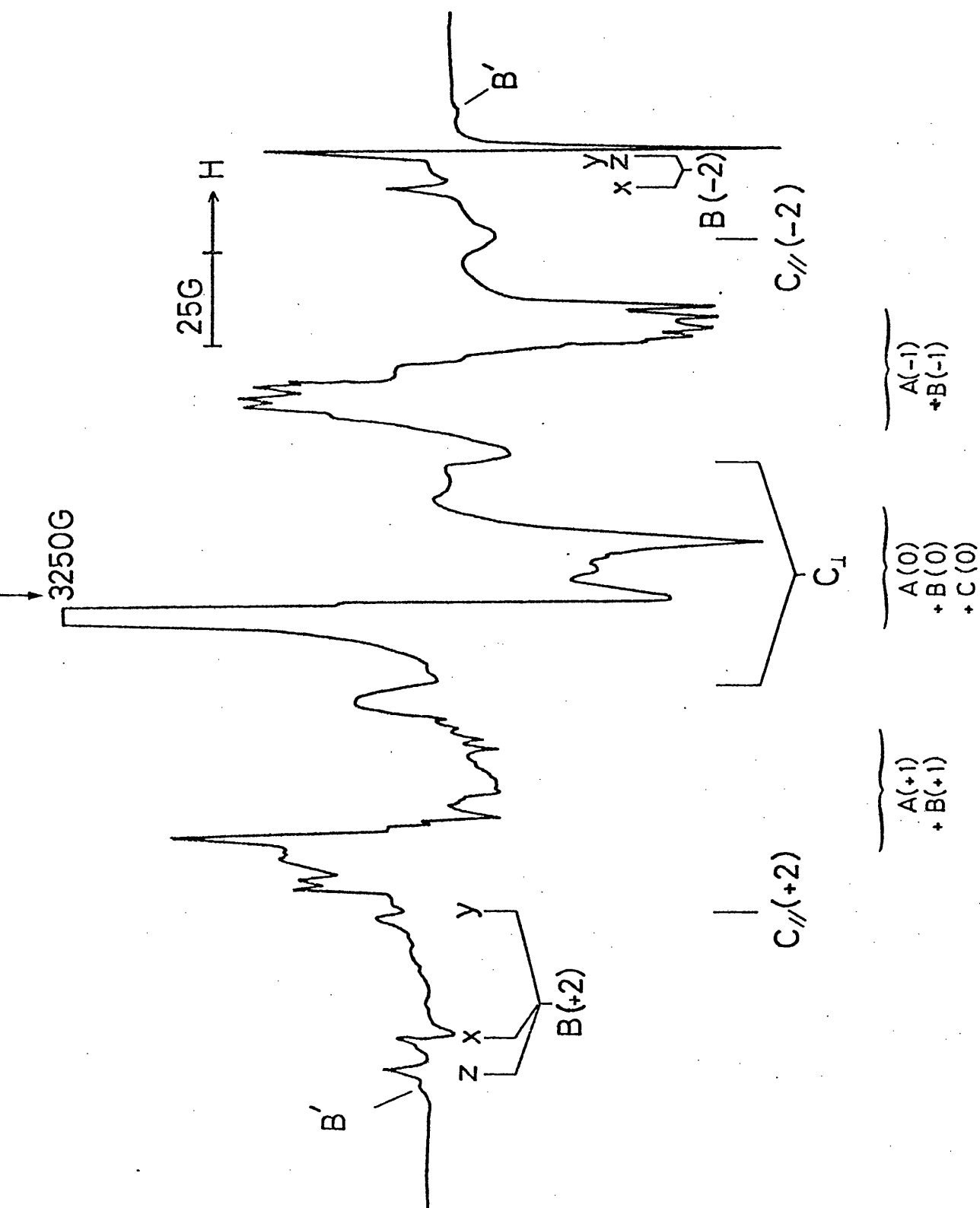
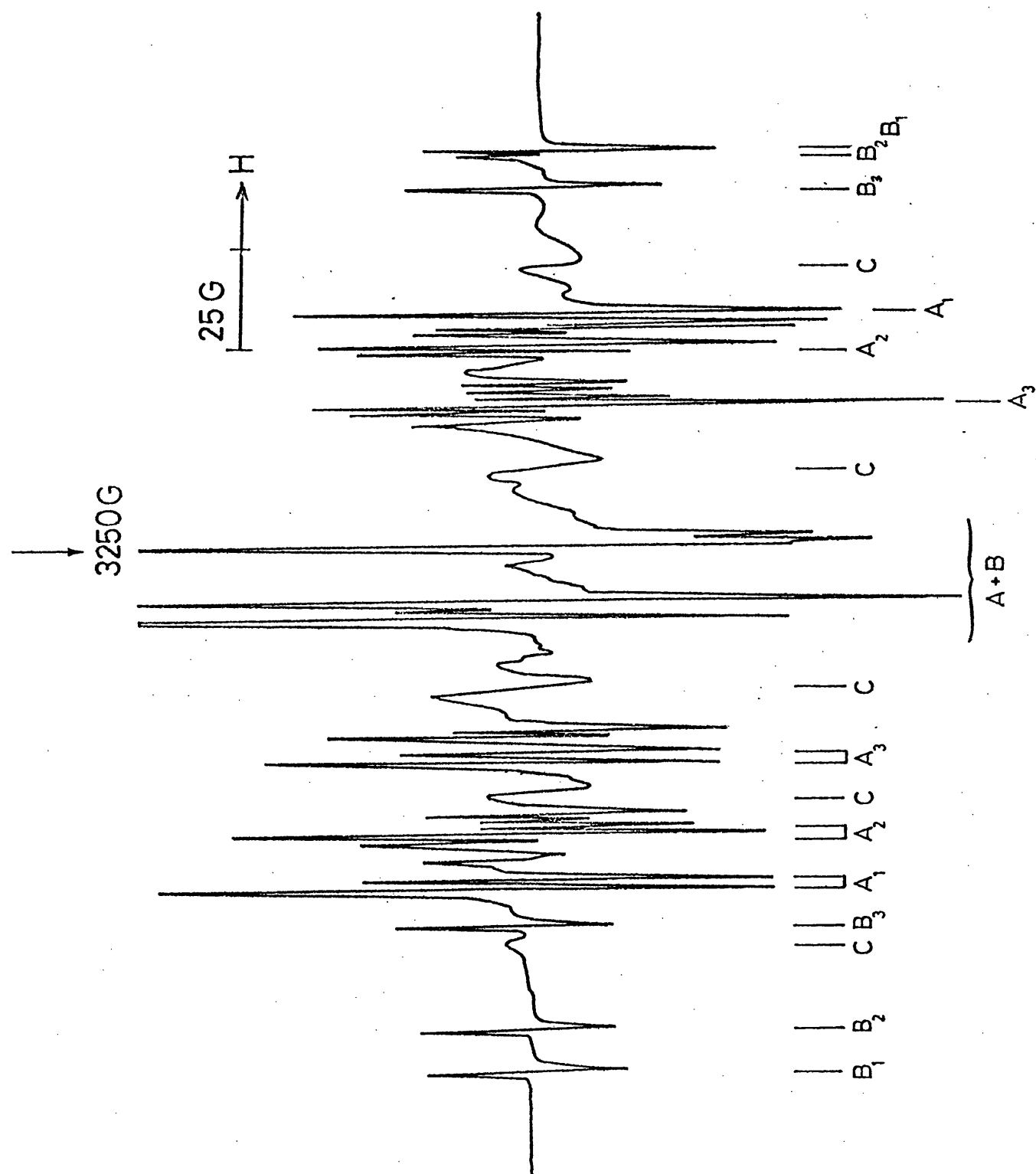


Figure A2.2 X-band ESR spectrum of a single crystal of N_2O_4 in an arbitrary orientation following low temperature irradiation, showing three sets of lines close to the x, y and z positions for centres A and B.

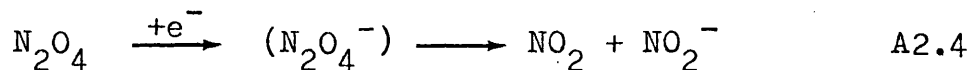
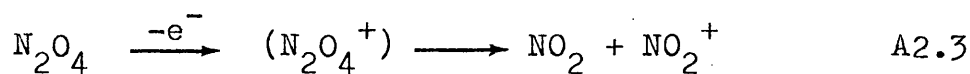


less than that for centre B.

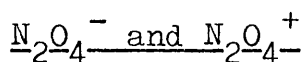
ESR parameters for A, B, B' and C appear in Table A2.1.

Identification

Centre A is clearly NO_2 . Its formation can be visualised as being either through electron loss or through electron capture.



Reactions A2.3 and A2.4 are presumably in competition with the distortions that yield stable primary ions, but the two reactions do suggest that two types of NO_2 can be formed, one adjacent to NO_2^+ and one adjacent to NO_2^- . NO_2^- would have a considerably smaller O-N-O bond angle than NO_2^+ (which might be expected to be linear) and NO_2 radicals would have different librational properties when next to these two ions. The single crystal spectra show six sets of lines for NO_2 and three for centre B. Since there are three distinct N_2O_4 molecules per unit cell this is consistent with the possibility of two types of NO_2 being formed from N_2O_4 .



Centre B could be either N_2O_4^+ or N_2O_4^- . The parameters for B' derived from methanolic solutions clearly relate to B, since A_{iso} , g_{av} , A_y and g_y are almost identical. This means that the centre in N_2O_4 is librating about the y axis, resulting in partial averaging of the x and z parameters. Since formation

Table A2.1 ESR Data for NO_2 , N_2O_4^- and N_2O_4^+ in a solid N_2O_4 Matrix

	g values			hyperfine interaction (G)			
	g_x	g_y	g_z	A_{iso}	B_x	B_y	B_z
N_2O_4^- (B) ^b	2.003(1)	1.991(5)	2.003(0)	51.8	+0.1	-4.7	+ 4.6
N_2O_4^- (B') ^b	2.005(5)	1.991(3)	2.000(9)	51.5	-3.7	-5.1	+ 8.8
N_2O_4^+ (C)	2.00	2.00	1.98	ca.30	~-5	~-5	~+10
NO_2 (A) ^a	2.002(1)	2.005(6)	1.992(0)	52.8	+11.9	-5.0	- 6.9
NO_2 (ice matrix) ^c	2.0022	2.0066	1.992(0)	56.9	+13.33	-6.28	-7.24
NO_2 ($\text{Pb}(\text{NO}_3)_2$) ^d	2.0029	1.9910	1.9982	53.7	-5.2	-7.7	+12.9
NO_2 (NaNO_2) ^e	2.0057	1.9910	2.0015	54.7	-5.27	-7.95	+13.22
NO_2 (gas) ^f	2.0062	1.9910	2.0020	52.59	-6.46	-7.71	+14.17

a. Parameters taken from unique species left after anneal of low γ dose samples.

b. Libration in xz plane reduced on going from B $\rightarrow$ B'.

c. Ref. 2.

d. M.C.R. Symons, D.X. West and J.G. Wilkinson, J.Chem.Soc.(Dalton), 1974, 2247.

e. H. Zeldes and R. Livingston, J.Chem.Phys., 1961, 35, 563.

f. Ref. 1.

of e_t^- is suppressed in CD_3OD along with centre C, it seems probable that B and B' are electron gain centres.

If B is the electron gain centre, $N_2O_4^-$, then the unpaired electron might be expected to be in a σ^* orbital having relatively more 2s character than in NO_2 and probably greater $2p_z$ character as well. These expectations are borne out by the data in Table A2.2. The increase in overall spin density on nitrogen in $N_2O_4^-$ relative to NO_2 and the decrease in the hybridisation ratio λ^2 are consistent with an unpaired electron in a σ^* orbital of the dimer and reflect the expected decrease in the O-N-O bond angle, θ .

Table A2.2 Nitrogen 2s and 2p Orbital Occupancy and Hybridisation Ratios in NO_2 , $N_2O_4^-$ and $N_2O_4^+$

	c_{2s}^2	c_{2p}^2	λ^2
NO_2 (gas phase)	9.56%	45.4%	4.75
$N_2O_4^-$ (B')	9.4	29.0	3.1
$N_2O_4^+$ (C)	5.5	31.0	5.6

Centre C is then presumably the electron loss centre, $N_2O_4^+$. The data in Table A2.2 indicates that the total 2s character is virtually unchanged relative to NO_2 but that the $2p_z$ character is increased. This accomodates the expected increase in θ (since NO_2^+ is linear), and it indicates that the total spin density on nitrogen is again increased relative to NO_2 , as would be expected for an unpaired electron localised in a σ orbital.

The Structure of N_2O_4

The N_2O_4 molecule is planar in the gaseous and the solid states and has an unusually long N-N bond³. There have been three recent molecular orbital calculations⁴⁻⁶ on N_2O_4 but the calculations of Howell and Van Wazell⁵ are the most satisfactory for interpreting the results.

They predict the uppermost filled orbital in N_2O_4 to be of $6a_g$ symmetry and to be principally comprised of an anti-bonding combination of oxygen $2p_z$ orbitals. However, the ESR parameters for $N_2O_4^+$ (centre C) indicate that the unpaired spin is in a σ orbital comprising largely s-p hybrids on nitrogen. To explain this apparent anomaly it is suggested that in $N_2O_4^+$ the $4a_g$ σ bonding orbital is raised above the $6a_g$ orbital by N-N stretching and an increase in θ .

The lowest empty orbital in N_2O_4 is given as $6b_{1u}\sigma^*$ involving 2s and $2p_z$ nitrogen orbitals. The ESR parameters for $N_2O_4^-$ (centre B) are consistent with an unpaired electron in such an orbital and there is no need to invoke any change in orbital levels when $N_2O_4^-$ is formed from N_2O_4 .

References for Appendix Two

1. R.M. Lees, R.F. Curl Jr. and J.G. Baker, J.Chem.Phys., 1966, 45, 2037.
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3. B. Cartwright and J.H. Robertson, Chem.Comm., 1966, 3, 82.
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5. J.M. Howell and J.R. Van Wazen, J.Amer.Chem.Soc., 1974, 96, 7902.
6. R.L. Griffiths, R.G.A.R. MacLagan and L.F. Philips, Chemical Physics, 1974, 3, 451.

Appendix Three

ESR Data for Silver Centres
in Irradiated Frozen Solutions

Table A3.1 ESR Data for Silver Centres in Irradiated Frozen Aqueous Solutions (at 77K)

	Matrix	g values ^a			hyperfine interaction (G) ^a			
		g_x	g_y	g_z	A_x	A_y	A_z	A_{iso}
Ag ⁰	gas ^b							-706
	H ₂ O ^c (condensed from gas phrase)							-715.5
	6M H ₂ SO ₄ ^d							-702
	D ₂ O(frozen solutions)							
	A	1.995(9)	1.995(9)	1.999(7)	-534.5	-534.5	-540.5	-536.5
	B							-585.4
	C	1.995(8)	1.995(8)	1.999(6)	-548.2	-548.2	-554.2	-550.2
	D	2.003(6)	1.996(6)	1.992(8)	-496.7	-492.5	-490.0	-493.1
	E ^e							-608.9
	F(¹⁰⁷ Ag) ^e	1.992	1.992	2.001	-370	-370	-382	-374
	F(¹⁰⁹ Ag) ^e est.	1.992	1.992	2.001	-428	-428	-442	-433

(contd.)

Table A3.1 contd.

	Matrix	g values ^a			hyperfine interaction (G) ^a			
		g_x	g_y	g_z	A_x	A_y	A_z	A_{iso}
Ag_2^+	$3M Mg(ClO_4)_2/D_2O$							-705
	D_2O	1.976	1.976	1.997	-280.5	-280.5	-291.0	-284.0
	D_2O (after anneal and recool)	2.059	2.059	2.338	-30(± 1)	-30(± 1)	-38(± 1)	-32.7

a. All data, except where stated, refers to the ^{109}Ag isotope.

b. N.F. Ramsey, 'Molecular Beams', Clarendon Press, Oxford, 1955.

c. R.A. Zhitnikov, N.V. Kolesnikov and V.I. Kosyakov, Sov.Phys. JETP., 1963, 17, 815.

d. Ref. 3 (Chapter Three).

e. Parameters for E and F are of limited accuracy because of overlap of stronger signals.

Table A3.2 ESR Data for Silver Centres in Irradiated Methyl
Cyanide Solutions (at 77K)

$\text{AgNO}_3/\text{CD}_3\text{CN}$

	g values			hyperfine interaction (G)		
	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel}$	$A_{\perp}$	A_{iso}
Ag^0			1.997^{a}			-630^{a}
Ag_2^+			1.981			-266
Ag_4^{3+}			1.960			-130
Ag^{2+}	2.283	2.058	2.133	-42	-30	-34
$\text{AgClO}_4/\text{CD}_3\text{CN}$						
Ag^{ob}			1.997			-534.2 $6.3(\text{N})$
Ag_2^+			1.981			-267
Ag_4^{3+}			1.955			-134
Ag^{2+}	2.314	-	-	-20^{c} $21(\text{N}) \sim 23(\text{N})$	-	-

- a. Some uncertainty due to overlap of Ag^0 with Ag_2^+ and Ag^{2+} features.
- b. Data for ^{109}Ag isotope.
- c. An accurate analysis of the peripheral lines in the nitrogen SHFS on the Ag^{2+} parallel feature is required before a definitive value for $A_{\parallel}(\text{Ag}^{2+})$ can be obtained.

Table A3.3 ESR Data for Ag° Centres in Irradiated Frozen Solutions (at 77K)

Matrix	$g_{\text{av}}(^{109}\text{Ag}^\circ)$ $g_{\text{av}}(^{107}\text{Ag}^\circ)$ g values	hyperfine interaction (G) $A_{\text{iso}}(^{109}\text{Ag}^\circ)$ $A_{\text{iso}}(^{107}\text{Ag}^\circ)$	
Gas ^a	2.002	-706	
6M H_2SO_4 ^b	2.000	-702	
Ice ^c (Deposited from gas phase)	2.0020 2.0021	-715.5 -619.8	
D_2O (Frozen solution)	av ~1.999 av ~1.999	av ~-505 av ~-435	
CD_3OD A B	2.001 2.001 2.000 2.000	-651 -561 -615 -533	[A] $\approx$ [B]
n-Butanol A B	2.001 2.001 2.000 2.000	-648 -560 -613 -530	[B] $\gg$ [A]
MeTHF ^d A B	2.001 2.001 2.000 2.000	-620 -535 -585 -506	[A] $\approx$ [B]
CD_3CN (AgNO_3)	~1.997	~-630	Broad features
CD_3CN (AgClO_4)	1.997 1.997	-534 -459 6.3(N) 6.3(N)	Well resolved
$\text{C}_2\text{H}_5\text{CN}$ (AgClO_4)	1.997 1.997	-567 -490	

(contd.)

Table A3.3 contd.

Matrix	g values		hyperfine interaction (G)	
	$g_{av}(^{109}\text{Ag}^0)$	$g_{av}(^{107}\text{Ag}^0)$	$A_{iso}(^{109}\text{Ag}^0)$	$A_{iso}(^{107}\text{Ag}^0)$
DMSO ^d (AgNO ₃)	~2.00		~-520	
HMPA ^d	1.998	1.998	-551	-477
Adamantane	2.000	2.000	-601	-520
35% aq. NH ₃	1.999	1.999	-443	-374
t-butylamine	2.000	2.000	-466	-413
Pyridine	~2.000		~-470	
Formamide	~2.000		~-540	
Ethylenediamine	~2.000		~-390	
				Well resolved
				Well resolved
				Broad features
				Poorly resolved ¹⁴ N SHFS
				Broad features
				Broad features
				Broad features

a. N.F. Ramsey, 'Molecular Beams', Clarendon, Oxford, 1955.

b. Ref. 3 (Chapter Three).

c. R.A. Zhitnikov, N.V. Kolesnikov and V.I. Kosyakov, Sov.Phys. JETP., 1963, 17, 815.

d. DMSO=Dimethylsulphoxide; HMPA=Hexamethylphosphoramide; MeTHF=Methyltetrahydrofuran.

Table A3.4 ESR Data for Ag_2^+ Centres in Irradiated Frozen Solutions^a (at 77K)

Matrix	g values		hyperfine interaction (G)		
	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel}$	$A_{\perp}$
(1) ^b $\text{D}_2\text{O} + \text{H}_2\text{O}$	1.997	1.976	1.983	-291.0	-280.5
$\text{CD}_3\text{OD} + \text{CH}_3\text{OH}$	1.997	1.970	1.979	-316.5	-307.0
n-Butanol	1.999	1.971	1.980	-319.5	-308.0
MeTHF ^d		1.971			-306.0
HMPA ^d	1.999	1.973	1.982	-294.9	-280.0
6M H_2SO_4	1.999	1.973	1.982	-322.2	-313.6
Benzene	1.999	1.983	1.988	-372.1	-363.5
(3) ^c CD_3CN			~1.981		~-280
DMSO ^d			~1.985		~-275
Ethylenediamine			~1.985		~-220

a. Solvents divided into categories (1), (2) and (3) according to the resolution of Ag_2^+ features (see Chapter Three).

b. Data for $^{109}\text{Ag}_2^+$.

c. Features from individual silver isotopes are unresolved.

d. Abbreviations explained in Table A3.3.

Table A3.5 ESR Data for Ag_3^{2+} and Ag_4^{3+} Centres in Irradiated Frozen Solutions (at 77K)

	Matrix	g_{av}^a	$A_{\text{av}}^a(\text{G})$
Ag_3^{2+}	Toluene ^b	1.973	-203
	Pyridine	1.976	-153
	Ethylenediamine	1.980	-105
Ag_4^{3+}	6M H_2SO_4	1.973	-150
	Benzene ^b	1.970	-147
	CD_3OD	1.967	-150
	n-Butanol	1.973	-140
	CD_3CN	1.960	-137
	$\text{C}_2\text{H}_5\text{CN}$	1.977	-142
	MeTHF ^c	1.976	-137
	DMSO ^c	1.975	-134
	HMPA ^c	1.979	-126
	35% aqueous NH_3	1.970	-126
	Formamide	1.960	-130
$(\text{Ag}_3-\text{Ag})^{3+}$	CD_3OD	1.963	-141 (3xAg)
			-57 (Ag)

a Features associated with the individual Ag isotopes and with anisotropy are invariably unresolved.

b Ref. 6 (Chapter Three).

c Abbreviations explained in Table A3.3

Table A3.6 ESR Data for Ag^{2+} Centres in Irradiated Frozen Solutions (at 77K)

Matrix	g values ^a		hyperfine interaction (G) ^a		
	$g_{\parallel}$	$g_{\perp}$	g_{iso}	$A_{\parallel}$	$A_{\perp}$
D_2O	2.338 (± 0.001)	2.059 (± 0.001)	2.152	-38(± 2)	-30(± 2)
6M H_2SO_4	2.310 (± 0.01)	2.061 (± 0.004)	2.144	-25(± 15)	-27.5(± 4)
CD_3OD	2.334 (± 0.006)	2.063 (± 0.004)	2.153	-32(± 5)	-26(± 4)
CD_3CN (AgNO_3)	2.283 (± 0.004)	2.058 (± 0.004)	2.133	-42(± 2)	-30(± 2)
$\text{C}_2\text{H}_5\text{CN}$	2.271 (± 0.004)	2.057 (± 0.002)	2.128	-37.5(± 2)	-27.5(± 3)
DMSO	2.288 (± 0.007)	2.058 (± 0.005)	2.135	-27(± 6)	-25(± 10)
Adamantane	2.322 (± 0.008)	2.058 (± 0.004)	2.143	-40(± 12)	-30(± 1)
Formamide	2.280 (± 0.01)	2.050 (± 0.002)	2.130	-35(± 6)	-33(± 3)

a. Features from the two isotopes, ^{107}Ag and ^{109}Ag , are unresolved.

Appendix Four

ESR Data for Nitrogen and Other Centres
in Some Irradiated Inorganic Nitrates

Table A4.1 ESR Data for NO_3^- ('Normal') and NO_3^{2-} in Some Irradiated -d^{10} Metal Nitrates (at 77K)

Matrix	g values			hyperfine interaction (G)		
	g_1	g_2	g_3	A_1	A_2	A_3
<u>NO_3^- in:</u>						
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2.009	2.021	2.021	~3	~4	~4
$\text{Ca}(\text{NO}_3)_2$	2.007(5)	2.023(5)	2.023(5)	~3	~5	~5
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.006	2.018(5)	2.018(5)	~3	3.5	3.5
$\text{Hg}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	2.008	2.022	2.022	3.3	~3	~3
$\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	2.003	2.020	2.020	~3	~3	~3
$\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	2.002	2.019(5)	2.019(5)	~3	~3	~3

(contd.)

Table A4.1 contd.

Matrix	g values			hyperfine interaction (G)		
	g_1	g_2	g_3	A_1	A_2	A_3
NO_3^{2-} in:						
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.001	2.006	2.006	66.0	32.0	32.0
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2.001	2.004(5)	2.004(5)	67.0	32.5	32.5
$\text{Ca}(\text{NO}_3)_2$	2.000(5)	2.005(5)	2.005(5)	67.0	36.5	36.5
				15.0(Cd1)	16.0(Cd1)	16.0(Cd1)
				30.0(Cd2)	32.0(Cd2)	32.0(Cd2)
				~3 (Cd3)	~2 (Cd3)	~2 (Cd3)
AgNO_3 (powder)	2.002	2.005	2.005	67.5	36.9	36.9
				16.3(Ag)	14.4(Ag)	14.4(Ag)
AgNO_3^a (crystal)	2.000	2.002	2.007	67.4	35.8	37.1
				16.8(Ag)	13.5(Ag)	14.5(Ag)

a. Ref. 1 (Chapter Five).

Table A4.2 ESR Data for NO_2 in Some Irradiated $-\text{d}^{10}$ and Related Metal Nitrates (at 77K)

Matrix	g values			hyperfine interaction (G)		
	g_1	g_2	g_3	A_1	A_2	A_3
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.002	2.005	1.992	69.5	52.0	48.0
$\text{Cd}(\text{NO}_3)_2$ (following anneal and recool)	2.000	2.005	1.992	65.5	48.0	45.5
$\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	2.001	2.005	1.992	66.0	51.5	47.0
$\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	2.001	2.005	1.991	68.0	50.0	47.0
$\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	2.002	2.005	1.992	67.0	52.5	46.5
$\text{Pb}(\text{NO}_3)_2^{\text{a}}$	1.9982	2.0029	1.9910	66.6	48.5	46.0
NaNO_2^{b}	2.0015	2.0057	1.9910	67.92	49.43	46.75
AgNO_3^{c}	2.0039	2.0090	1.9975	69.6	50.7	48.5

a. Ref. 5 (Chapter Five).

b. R. Livingston and H. Zeldes, J.Chem.Phys., 1961, 35, 563.

c. Ref. 1 (Chapter Five).

Table A4.3 ESR Data for Mercury Centres in Irradiated Mercury (I) and (II) Nitrates (at 77K)

Species	Matrix	g values			hyperfine interaction ^a (G)	
		$g_{ }$	$g_{\perp}$	g_{av}	A_{iso}	2B
$^{199}\text{Hg}^+$	$\text{Hg}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$			2.000	13100(± 50) 15.5(4xHg)	0
$^{199}\text{Hg}^+$ (broad line)	$\text{Hg}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$			2.000	13750(± 50)	0
$^{201}\text{Hg}^+$	$\text{Hg}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$			2.000	4700(± 20) 15.5(4xHg)	0
$^{201}\text{Hg}^+$ (broad line)	$\text{Hg}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$			2.000	4940(± 20)	0
$(^{199}\text{Hg}^{200}\text{Hg})^{+}/3+$	$\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	2.00	1.97 ^b	1.98	3900(± 500)	160(± 50)
$(^{201}\text{Hg}^{200}\text{Hg})^{+}/3+$	$\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	2.00	1.97 ^b	1.98	1450(± 200)	60(± 20)

a. Calculated using methods outlined in Appendix One.

b. $g_{\perp}$ value estimated so that programme A1.4 calculates a reasonable value for $g_{||}$.

See Appendix One.

Table A4.4 ESR Data for Nitrogen Centres in Irradiated Sodium and Potassium Nitrates (at 77K)

Matrix	g values			hyperfine interaction (G)		
	g_1	g_2	g_3	A_1	A_2	A_3
<u>'Normal' NO_3^- in:</u>						
KNO_3^a	2.003(1)	2.023(2)	2.023(2)	4.31	3.46	3.46
NaNO_3	2.004(7)	2.023(9)	2.023(9)	5.2	4.0	4.0
<u>'Abnormal' NO_3^- in:</u>						
KNO_3	2.002(7)	2.010(2)	2.007(5)	1.6	3.25	3.0
satd. $\text{KNO}_3/\text{D}_2\text{O}^b$	2.0002	2.0083	2.0057	1.60	3.30	3.15
NaNO_3	2.004(2)	2.009(2)	2.009(2)	2	3	3
<u>NO_3^{2-} in:</u>						
KNO_3	2.000(9)	2.006(7)	2.006(7)	63.0	31.75	31.75
satd. $\text{KNO}_3/\text{D}_2\text{O}^b$	2.0014	2.0059	2.0059	64.3	30.8	30.8
NaNO_3	1.999(1)	2.005(9)	2.005(9)	67.25	30.75	30.75
				3.75(3xNa)	3.40(3xNa)	3.40(3xNa)

a. In agreement with Livingston and Zeldes, (ref. 22, Chapter Five).

b. Ref. 7 (Chapter Five).

Summary

Electron Spin Resonance is used to detect radiolytically produced silver centres in a range of alkali halide:silver halide mixtures. A new silver aggregate electron excess centre is detected in mixtures of NaCl:AgCl containing high $[Ag^+]$ and a silver atom species is detected in a KF lattice where it appears to be coordinated asymmetrically to six fluoride ligands. The stability of Ag^{2+} as a hole centre in halide lattices is demonstrated.

Silver centres in irradiated frozen solutions, as studied by ESR, can provide information on the solvation of the parent Ag^+ ion. A solvation number of four for Ag^+ in methyl cyanide is found and a solvation number of four or six in water seems likely. The spectra associated with other solvents are less informative, but some general conclusions regarding solvation and ion pairing are made. Silver atom-ion aggregates are frequently detected in these systems although aggregates of more than four silver nuclei are not found in any of the solvents studied.

NMR results for cation induced shifts in the hydroxyl proton resonance in aqueous and methanolic solutions of a range of $-d^{10}$ metal cations support the view that the solvation number for Ag^+ in these media is between four and six.

An ESR study of radiation damage in a range of inorganic nitrates reveals a new paramagnetic nitrogen oxide or oxy-ion. So far unidentified, it appears to be similar to, but distinctly different from, NO_3 . Electron capture is studied in $-d^{10}$ metal nitrates where there is a subtle balance between capture at cation and at anion sites; the paramagnetic centres in

these nitrates often exhibit superhyperfine structure that can be linked to the crystal structures.

The radiolysis of dinitrogen tetroxide and the formation of N_2O_4^+ and N_2O_4^- is also studied.