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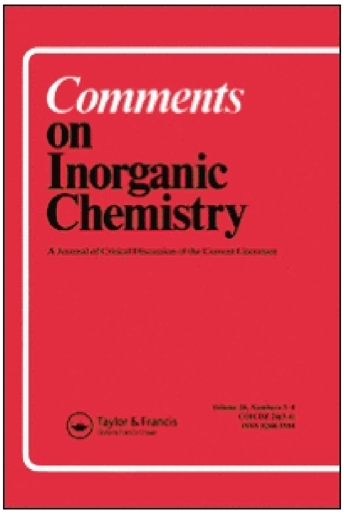

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Electron Paramagnetic Resonance (EPR)

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PART 1. INORGANIC SPECTROSCOPY: BASIC PRINCIPLES AND THE EXPERIMENT

II. ELECTRON PARAMAGNETIC RESONANCE (EPR)

A. The Experiment[1]

In the EPR experiment the total spin ($S = ½$) of the $^2B_{1g}$ ground state is perturbed by the application of an external magnetic field $\vec{H}$ that produces a Zeeman splitting of the $M_s = \pm ½$ levels equal to $g\beta H$. Here β is the Bohr magneton which is a constant equal to 4.67×10^{-5} cm^{-1}/gauss, and g is the quantity of experimental and theoretical interest. The EPR experiment is usually performed with a fixed input microwave energy $h\nu$ (~9 GHz = 0.30 cm^{-1} for X-band and 35 GHz = 1.16 cm^{-1} for Q-band microwave sources). When the scanning magnetic field results in a Zeeman splitting equal to the fixed microwave energy, absorption will occur [Figure II-1 and Eq. (II-1)]. Assuming for now a value of $g = 2$,

$$g\beta H = h\nu \qquad \text{(II-1)}$$

resonance occurs at a magnetic field of ~3300 gauss for an X-band microwave source. For enhanced resolution the EPR spectrum is

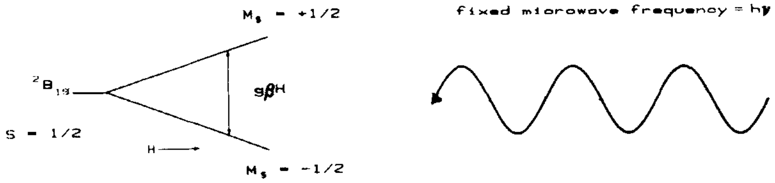

FIGURE II-1 The EPR experiment: Increasing Zeeman splitting of $S = ½$ with increasing magnetic field (H) for fixed input microwave energy ($h\nu$).

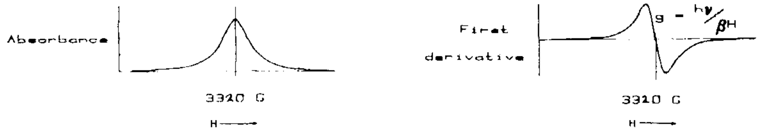

FIGURE II-2 The EPR spectrum: First derivative of the microwave absorption spectrum.

plotted as the first derivative (Figure II-2). The crossover point is at the magnetic field associated with the g value ($= h\nu/\beta H$) of the ground state.

The g value of $CuCl_4^=$ is found[2] to be anisotropic. This means that the Zeeman splitting of the $^2B_{1g}$ ground state depends on the orientation of the complex relative to the external magnetic field. When the $CuCl_4^=$ complex is oriented with its z axis along the magnetic field, microwave absorption occurs at the value of the magnetic field associated with $g_\parallel$, while absorption occurs at $g_\perp$ when the z axis is perpendicular to the external magnetic field. For $CuCl_4^=$, $g_\parallel > g_\perp > 2.00$ (Figure II-3).

For an arbitrary angle θ of the z axis of the complex relative to the external field, one observes absorption at a value of g_{eff} given by the direction cosines in Eq. (II-2):

$$g_{\text{eff}}^2 = g_\parallel^2\cos^2\theta + g_\perp^2\sin^2\theta. \qquad \text{(II-2)}$$

The above is appropriate for a single crystal EPR study where the complex has an orientation defined by the unit cell. Usually, however, one is interested in a sample which is a frozen glass or dilute powder. Here, all orientations of the complex are present. Hence, absorption occurs continually over the region from $g_\parallel$ to $g_\perp$ and is weighted by the number of molecules with a given orientation, which increases in probability toward the perpendicular orientation. This distribution of absorption intensity is given on the left of Figure II-4. The EPR spectrum obtained from the derivative of this intensity distribution is given on the right of Figure II-4.

Finally, copper has a nuclear spin of $I = 3/2$ which couples to the electron spin producing a hyperfine splitting of the EPR spectrum into $2I + 1 = 4$ lines (Figure II-5). Note that $A_\parallel$, which is the hyperfine splitting with the molecular z axis oriented parallel to the

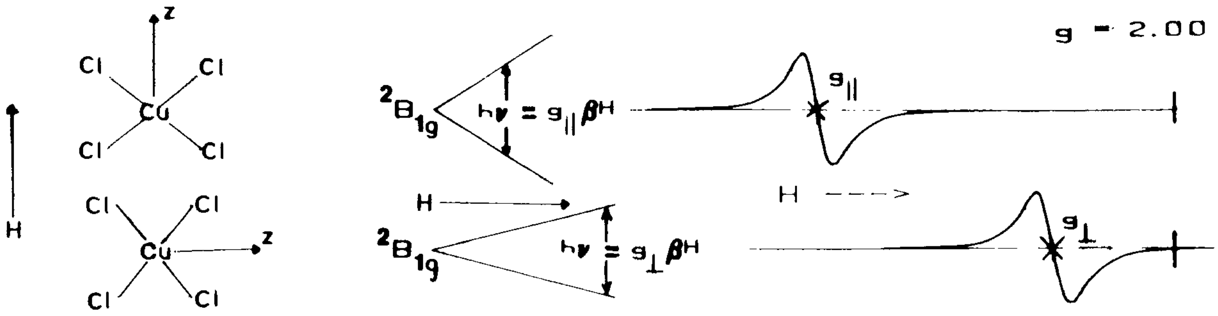

FIGURE II-3 Anisotropic *g* values of D_{4h}–$CuCl_4^=$. Zeeman splitting of $S = \frac{1}{2}$ dependent on orientation of molecule relative to $\vec{H}$. ($g_{\parallel} > g_{\perp} > 2.00$).

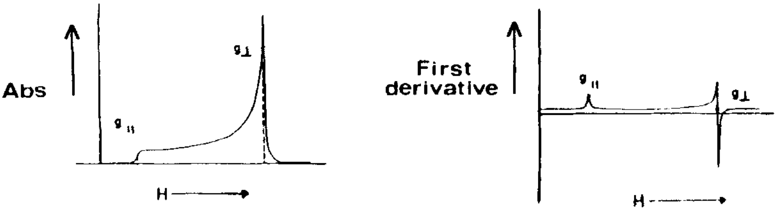

FIGURE II-4 EPR spectrum for $g_{\parallel} > g_{\perp} > 2.00$: First derivative of the powder pattern absorption spectrum.

external magnetic field, is much larger than $A_{\perp}$, the hyperfine splitting for z perpendicular to the field. The origin of hyperfine splitting will be discussed in some detail in Section VII.

B. Basic Principles

We now quantitatively consider the ligand field theoretical origin of the g values. The effects of an external magnetic field (H) on the ground state wavefunction (ψ_g) is given by the Zeeman operator in Eq. II-3 where $\vec{L}$ is the total orbital angular momentum operator and $\vec{S}$ is the total spin angular momentum operator:

$$E_{\text{Zeeman}} = \beta H\langle\psi_g|\vec{L} + 2\vec{S}|\psi_g\rangle. \tag{II-3}$$

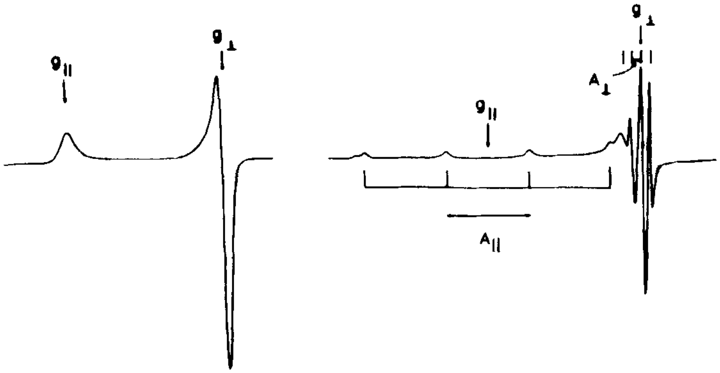

FIGURE II-5 Effects of adding hyperfine coupling to Figure II-4: For D_{4h}-$\text{CuCl}_4^{=}$, $I = 3/2$ and $A_{\parallel} > A_{\perp}$.

First consider a ground state which contains only spin angular momentum, $S = \frac{1}{2}$. Here the ψ_g are $|S,M_s\rangle = |\frac{1}{2}, +\frac{1}{2}\rangle$ and $|\frac{1}{2}, -\frac{1}{2}\rangle$ which split under the application of Eq. (II-3). The splitting is equal to $(2.00)\beta H$ and gives the g value in Figure II-1 as 2.00. Next, consider the free Cu(II) ion which has a ${}^2D_{5/2}$ ground state where the subscript $5/2$ is the value of the total angular momentum $\vec{J} = \vec{L} + \vec{S}$. In addition to spin ($S = \frac{1}{2}$) this state has orbital angular momentum, $L = 2$. Application of Eq. (II-3) to this ground state results in a g value of 1.20, given by the Landé formula in Eq. (II-4)

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \tag{II-4}$$

Here the g value differs significantly from 2.00 due to the presence of orbital angular momentum in the ground state which contributes to the Zeeman splitting through the $\vec{L}$ operator in Eq. (II-3). For $CuCl_4^=$, from Figure I-1, the ground state is ${}^2B_{1g}(x^2 - y^2)$ which has $S = \frac{1}{2}$. The effect of the orbital angular momentum operator on the real d orbitals[3] is given in Table II-1.

Clearly the orbital angular momentum operator in Eq. (II-3) cannot contribute to the Zeeman splitting for the ${}^2B_{1g}(x^2 - y^2)$ ground state since $\langle x^2 - y^2 |\vec{L}|\, x^2 - y^2\rangle = 0$. Thus the g value is again predicted to be the spin only value of 2.00. This type of argument led Van Vleck[4] to the concept that the orbital angular momentum of the free ion is "quenched" by the ligand field. However, in the previous section it was observed experimentally that for $CuCl_4^=$ $g_\parallel > g_\perp > 2.00$. Thus an additional term must be present in the Hamiltonian of the $CuCl_4^=$ complex which modifies the ground state wavefunction by mixing in some orbital angular momentum. This term is the spin-orbit coupling which is given by $\lambda\vec{L} \cdot \vec{S}$ where $\lambda =$

TABLE II-1
Effect of $\hat{L}_i$ on real d orbitals

$\hat{L}_x d_{xz} = -i\, d_{xy}$	$\hat{L}_y d_{xz} = i\, d_{x^2-y^2} - i\sqrt{3}\, d_{z^2}$	$\hat{L}_z d_{xz} = i\, d_{yz}$
$\hat{L}_x d_{yz} = i\sqrt{3}\, d_{z^2} + i\, d_{x^2-y^2}$	$\hat{L}_y d_{yz} = i\, d_{xy}$	$\hat{L}_z d_{yz} = -i\, d_{xz}$
$\hat{L}_x d_{xy} = i\, d_{xz}$	$\hat{L}_y d_{xy} = -i\, d_{yz}$	$\hat{L}_z d_{xy} = -2i\, d_{x^2-y^2}$
$\hat{L}_x d_{x^2-y^2} = -i\, d_{yz}$	$\hat{L}_y d_{x^2-y^2} = -i\, d_{xz}$	$\hat{L}_z d_{x^2-y^2} = 2i\, d_{xy}$
$\hat{L}_x d_{z^2} = -i\sqrt{3}\, d_{yz}$	$\hat{L}_y d_{z^2} = i\sqrt{3}\, d_{xz}$	$\hat{L}_z d_{z^2} = 0$

$\pm\ \zeta_{3d}/2S$, the $+(-)$ being for a less (greater) than half-filled many electron configuration and ζ_{3d} is the one-electron spin-orbit coupling parameter. For Cu(II), $\zeta_{3d} = 830\ \text{cm}^{-1}$, therefore $\lambda = -830\ \text{cm}^{-1}$. The quenching of the orbital angular momentum of the ${}^2B_{1g}(x^2 - y^2)$ ground state derives from the splitting of the fivefold degeneracy of the d orbitals in the free ion due to the square planar ligand field in Figure I-1. Inclusion of spin orbit coupling will partially mix these energetically separated d orbitals into the $d_{x^2-y^2}$ orbital producing the perturbed ground state wavefunction given in Eq. (II-5). Here $E_{x^2-y^2} - E_{xy}$ $(E_{x^2-y^2} - E_{xz,yz})$ is the energy difference between the $x^2 - y^2$ and xy $(x^2 - y^2$ and $xz,yz)$ orbitals in Figure I-1:

$$|{}^2B'_{1g}\rangle = |x^2 - y^2\rangle - \frac{\lambda\langle x^2 - y^2|\vec{L}\cdot\vec{S}|xy\rangle}{E_{x^2-y^2} - E_{xy}}\,|xy\rangle - \frac{\lambda\langle x^2 - y^2|\vec{L}\cdot\vec{S}|xz,yz\rangle}{E_{x^2-y^2} - E_{xz,yz}}\,|xz,yz\rangle. \qquad \text{(II-5)}$$

Application of the Zeeman operator to this perturbed ground state leads to nonzero contributions from the orbital angular momentum operator to the g value; further, these contributions depend on the orientation of the external magnetic field as indicated by

$$E_{\text{Zeeman}} = \beta\vec{H}\langle{}^2B_{1g}'|\underbrace{\vec{L}}_{\hat{L}_x+\hat{L}_y+\hat{L}_z} + 2\vec{S}|{}^2B_{1g}'\rangle. \qquad \text{(II-6)}$$

When the magnetic field is oriented along the z axis, it projects out the $\hat{L}_z$ operator in Eq. (II-6). Application of this operator on ${}^2B_{1g}'$ produces the orbital contribution to $g_\parallel$ given on the right of Eq. (II-7a).

$$g_\parallel = 2 - \frac{8\lambda}{E_{x^2-y^2} - E_{xy}} \qquad \text{(II-7a)}$$

$$g_\perp = 2 - \frac{2\lambda}{E_{x^2-y^2} - E_{xz,yz}} \qquad \text{(II-7b)}$$

For $\vec{H}$ perpendicular to the molecular z axis, only $\hat{L}_{x,y}$ are active, producing the expression for $g_\perp$ given in Eq. (II-7b). Since the energy denominators are positive and λ is negative for Cu(II), Eq. (II-7) gives $g_{\parallel} > g_{\perp} > 2.00$. A general perturbation expression for the g values of any d orbital ground state, ψ_g (derived as indicated above), is given in Eq. (II-8), where $i = x,y,z$, ψ_e are the d orbitals, and

$$g_i = 2(1 - \lambda) \sum_{e \neq g} \frac{\langle \psi_g | L_i | \psi_e \rangle \langle \psi_e | L_i | \psi_g \rangle}{E_g - E_e} \tag{II-8}$$

values for the orbital angular momentum operator are obtained from Table II-1. As the geometry of the complex is changed, the d orbital splitting in Figure I-1 changes and thus the g_i values given by Eq. II-8 change. For example, if the octahedral cupric complex in Figure I-1 were compressed rather than elongated along the z axis, a ${}^2A_{1g}(z^2)$ ground state would eventually occur. Equation II-8 then gives Eq. II-9 with $g_{\perp} > g_{\parallel} = 2.00$.

$$\begin{aligned} g_{\parallel} &= 2.00 \\ g_{\perp} &= 2 - \frac{6\lambda}{E_{z^2} - E_{xz,yz}} \end{aligned} \tag{II-9}$$

Hence the g values are dependent on the nature of the d orbitals contributing to the ground state wavefunction, which in turn results from the geometry of the complex.

C. Comparison of Experiment and Theory

The experimental[2] g values for $CuCl_4^{=}$ are given in Table II-2. Substitution of $\lambda = -830\ cm^{-1}$ and the splittings of the d orbitals (i.e., $E_{x^2-y^2} - E_{xy}$ and $E_{x^2-y^2} - E_{xz,yz}$ obtained from electronic absorption spectroscopy (see Section III)) into Eqs. (II-7a) and (II-7b) gives the crystal-field-theory derived g values also included in Table II-2. Clearly these have greater deviations from $g = 2.00$ than do the experimental values indicating the presence of too much orbital angular momentum contribution to the g values for the $|{}^2B_{1g}'\rangle$ ground state given in Eq. II-5. This arises because the treatment presented in Section II-B has not allowed for covalent mixing of the d orbitals

TABLE II-2
Experimental and theoretical g values for D_{4h}-$CuCl_4^=$

	Exp	Crystal-field theory	SCF-Xα-SW calculations adjusted to experiment
$g_\parallel$	2.221	2.743	2.220
$g_\perp$	2.040	2.177	2.041

with the $3p$ orbitals of the chloride ligands. This mixing allows the unpaired electron in the $d_{x^2-y^2}$ orbital to delocalize onto the ligands which have less spin-orbit coupling, and thus lowers the orbital angular momentum contribution of the ${}^2B_{1g}{}'$ state to the g value. In ligand-field theory the crystal field g values are adjusted to agree with those obtained by experiment, giving an experimental estimate of covalency. An analogous approach[5] of adjusting the results of an SCF-Xα-SW calculation to fit experiment, gives

$$\psi(b_{1g}) = 63\%\ d_{x^2-y^2} + 37\%\ \mathrm{Cl}\ p\sigma \qquad \text{(II-10)}$$

for the b_{1g} orbital of the ground state of $CuCl_4^=$. The unpaired electron is ~35% delocalized onto a linear combination of $p\sigma$ orbitals of the four Cl^- ligands (see Section IV). Thus the ${}^2B_{1g}$ ground state pictured in Figure I-1c must also be modified for covalent interaction with the ligands as shown in Figure II-6.

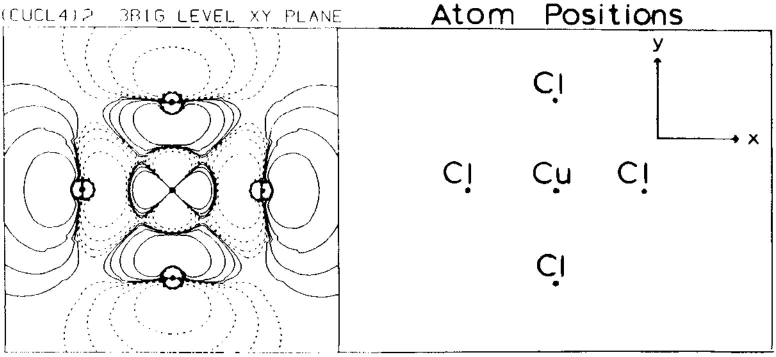

FIGURE II-6 SCF-Xα-SW contour diagram for the ${}^2B_{1g}$ ground state wavefunction of D_{4h}-$CuCl_4^=$.

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III. ELECTRONIC ABSORPTION—LIGAND-FIELD TRANSITIONS

A. Basic Principles

In EPR spectroscopy we focused on the ${}^2B_{1g}$ ground state wavefunction. This was accomplished by perturbing it with an external magnetic field and observing transitions between the Zeeman-split ground state components using radiation in the $\sim$0.3 cm^{-1} region. In electronic absorption spectroscopic studies of the ligand-field transitions,[1] we are probing the splittings of all the d orbitals produced by the ligand field. For $CuCl_4^{=}$, excitation of electrons from the filled d orbitals into the hole in the $b_{1g}(x^2 - y^2)$ orbital produces a number