Solutions to End-of-Chapter Exercises
Chapter 6

Fundamental constants & properties of nuclei

$c = 2.997 \times 10^{8}$ m s^{-1}
$e = 1.602 \times 10^{-19}$ C
$k = 1.381 \times 10^{-23}$ J K^{-1}
$h = 6.626 \times 10^{-34}$ J s

Mass

Electron = $9.109\,390 \times 10^{-31}$ kg
Proton = $1.672\,622 \times 10^{-27}$ kg

$\mu_0 = 4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1} (= T^{2} J^{-1} m^{3})
$\mu_B = 9.274 \times 10^{-24}$ J T^{-1}
$\mu_N = 5.050\,784 \times 10^{-27}$ J T^{-1}
$g_e = 2.0023\,193$ (electron g factor)
$g_p = 5.585\,694\,7$ (proton g factor)
$\gamma_e = 1.761 \times 10^{11}$ s^{-1} T^{-1}

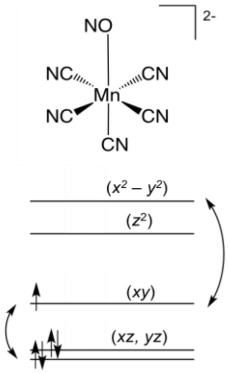
Properties for other common nuclei

	g_N	ν_N / MHz	γ / 10^{7} s^{-1} T^{-1}
^{1}H	5.5857	14.9021	26.752
^{2}H	0.8574	2.2876	4.107
^{13}C	1.4048	3.7479	6.728
^{14}N	0.4038	1.0772	1.934
^{31}P	2.2632	6.0380	10.839

ν_L (in units of MHz) for $B = 0.35$ T

Exercise 6.1) The EPR spectrum of a low spin $[Mn^{II}(CN)_5(NO)]^{2-}$ complex in C_{4v} symmetry is characterised by axial g values ($g_{\|} = 1.9892$, $g_{\perp} = 2.0265$). Using this information, account for the likely d-orbital splitting arrangement of the complex and hence explain the magnitude of the g values.

ANSWER



The likely d-orbital splitting arrangement is shown in the scheme opposite. Note in this case (similar to the LS Cr(I) presented on page 66), d_{xz} and d_{yz} will lie below the SOMO (so $E_{xz,yz} - E_{xy}$ is small and positive), while d_{x2-y2} is empty and much higher in energy (so E_{x2-y2} is large and negative). Hence one of the g values should be higher then g_e and one ($g_{zz} = g_{\|}$) should be lower (arising from promotion of the electron from d_{xy} into the empty d_{x2-y2} orbital).

$$\text{Hence } g_{xx,yy} = g_e + \frac{2\lambda}{E_{xy}-E_{yz,xz}} \text{ and } g_{zz} = g_e - \frac{8\lambda}{E_{xy}-E_{x^2-y^2}}$$

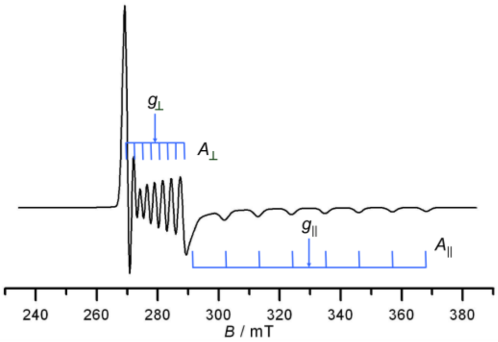
Exercise 6.2) The frozen solution X-band EPR spectrum (recorded at 9.5 GHz) of a square planar Co(II) complex bearing an axially coordinated substrate, $[Co^{II}(L_2)_2](X)$, is shown in Fig. 6.19. By analysing the spectrum, determine the anisotropic g and A values.

ANSWER

The anisotropic g and A values are $g_{\perp} = 2.430$, $A_{\perp} = 25$ G, $g_{\|} = 2.061$, $A_{\|} = 110$ G. The A values are extracted from the separation between the hyperfine lines. The g values are determined, by finding the central field position of each pattern, and by using this B value in the resonance equation:

$$\text{eg., } g_{||} = \frac{(6.626 \times 10^{-34}\ \mathrm{Js}) \times (9.5 \times 10^{9}\ \mathrm{s}^{-1})}{(9.274 \times 10^{-24}\ \mathrm{JT}^{-1}) \times (3300 \times 10^{-4}\ \mathrm{T})} = 2.057$$

The solution is shown in the figure below. ^{59}Co has a nuclear spin of $I = 7/2$, hence $2nI + 1 = 8$ lines are expected in both the parallel and perpendicular directions. As frequently observed in polycrystalline systems, the hyperfine lines may be overlapped, and hence not all components of the hyperfine will be visible.
Extraction of the spin Hamiltonian should be obtained *via* simulation of experimental spectra. Further examples of analysing powder spectra can be found in www.EPRsimulator.org.

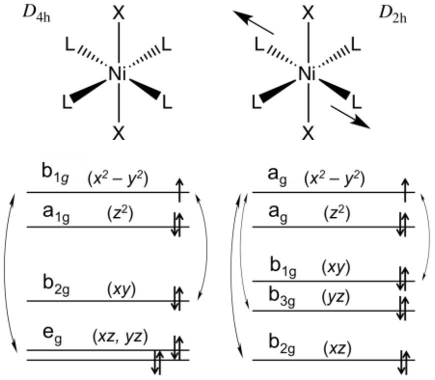


Exercise 6.3) Predict the relative magnitude and anisotropy of the g values for the two d^9 Ni(I) complexes given below, i.e., *trans*-$[Ni^{I}(L_4)X_2]$ and trigonally distorted *trans*-$[Ni^{I}(L_4)X_2]$.

ANSWER

A few quick points can be noted before analysis of the spectra;
Firstly, the D_{4h} complex should produce an axial EPR spectrum, while the D_{2h} should produce a rhombic spectrum (caution; at X-band frequency the anisotropy in g may not be visible, so the spectrum could still appear axial). Secondly, since all orbitals are filled (apart from the SOMO), positive g shifts are expected.

The likely d-orbital splitting arrangement for the two symmetries are shown below.



D_{4h} symmetry; This is analogous to the elongated D_{4h} case discussed on page 64 for Cu(II). As a result the predicted g values are:

$$g_{xx,yy} = g_e + \frac{2\lambda}{E_{x^2-y^2} - E_{yz,xz}} \quad \text{and} \quad g_{zz} = g_e + \frac{8\lambda}{E_{x^2-y^2} - E_{xy}}$$

Therefore $g_{zz} > g_{yy} = g_{xx} > 0$

D_{2h} symmetry: Consider the symmetry representations R_x, R_y, R_z for this D_{2h} case (refer to appropriate Character tables).

For R_z, $A_g \times B_{1g} = B_{1g}$, $E_{x2\text{-}y2} - E_{xy}$ where $n = 8$ (see Fig 6.4) $\Longrightarrow g_{zz} = g_e + \frac{8\lambda}{E_{x^2-y^2} - E_{xy}}$

For R_x, $A_g \times B_{3g} = B_{3g}$, $E_{x2\text{-}y2} - E_{yz}$ where $n = 2$ (see Fig 6.4) $\Longrightarrow g_{xx} = g_e + \frac{2\lambda}{E_{x^2-y^2} - E_{yz}}$

For R_y, $A_g \times B_{2g} = B_{2g}$, $E_{x2\text{-}y2} - E_{xz}$ where $n = 2$ (see Fig 6.4) $\Longrightarrow g_{yy} = g_e + \frac{2\lambda}{E_{x^2-y^2} - E_{xz}}$

Therefore $g_{zz} > g_{xx} > g_{yy} > 0$

Exercise 6.4) γ-irradiation of dimethyl glyoxime at low temperature generates an iminoxy radical with the following proposed formulation (shown on 75). Assuming the CN•O fragment of this radical can be considered as possessing C_{2v} symmetry, and given the spin Hamiltonian parameters of the radical were determined to be $g_{xx} = 2.0095$, $g_{yy} = 2.0063$, $g_{zz} = 2.0026$, $A_{xx} = \pm 2.5$, $A_{yy} = \pm 2.5$, $A_{zz} = \pm 4.5$ mT, estimate the value of the $C\widehat{N}O$ angle (ϕ).

ANSWER

For C_{2v} symmetry, a rhombic **g** and **A** tensor is expected (the experimental g/A value are consistent with this). The sign of the hyperfine cannot be determined from the experimental powder EPR spectrum. However, investigation of the possible sign combinations leads to the following solution for a_{iso} and the dipolar component T:

$$\begin{bmatrix} 2.5 & & \\ & 2.5 & \\ & & 4.5 \end{bmatrix} = 3.167 + \begin{bmatrix} -0.667 & & \\ & -0.667 & \\ & & 1.333 \end{bmatrix}$$

$$\rho^s = C_s^2(N) = \frac{a_{iso}}{A_0} = \frac{3.167}{64.6} = 0.049$$

$$\rho^p = C_p^2(N) = \frac{b}{b_0} = \frac{0.667}{1.98} = 0.337$$

$$\text{Since } \lambda^2 = C_p^2/C_s^2 = \frac{0.337}{0.049} = 6.8775$$

$$\text{But the dihedral angle is then given as } \phi = 2\cos^{-1}(\lambda^2+2)^{-\frac{1}{2}} = 140.8^\circ \text{ for } \mathrm{C\widehat{N}O}.$$

Exercise 6.5) The anisotropic g and A values for a surface stabilised $^{13}CO_2^-$ radical were determined to be $g_{xx} = 2.0026$, $g_{yy} = 1.9965$, $g_{zz} = 2.0009$, $A_{xx} = \pm18.1$, $A_{yy} = \pm17.7$, $A_{zz} = \pm22.4$ mT. Using this information, estimate the ^{13}C unpaired spin density and orbital occupancy. Comment on the anisotropy of the **g** tensor with respect to the symmetry of the radical.

ANSWER

In this case, one must analyse the ^{13}C hyperfine in order to find the orbital spin densities:

$$\begin{bmatrix} 18.1 & & \\ & 17.7 & \\ & & 22.4 \end{bmatrix} = 19.4 + \begin{bmatrix} -1.3 & & \\ & -1.7 & \\ & & 3.0 \end{bmatrix}$$

In this case, unlike the previous example(exercise 6.4), the dipolar contribution now does not reduce to zero, implying a fraction of the $2p_z$ spin density is allocated to a 2p orbital perpendicular to the molecular plane. The dipolar component must now be decomposed into a larger (T) and smaller (T') traceless form:

$$\begin{bmatrix} -1.3 & & \\ & -1.7 & \\ & & 3.0 \end{bmatrix} = \begin{bmatrix} -1.595 & & \\ & -1.595 & \\ & & 3.190 \end{bmatrix} + \begin{bmatrix} 0.29 & & \\ & -0.14 & \\ & & -0.14 \end{bmatrix}$$

Note: in the above two equations we are solving for x,y,z using the general analytical expression $x = a + 2b - c$; $y = a - b + 2c$; $z = a - b - c$. Although more than one solution is possible, not all solutions will be meaningful (eg., one must consider the sign of a_{iso}, and the magnitude of T). In the above case, A_{xx}, A_{yy}, $A_{zz} > 0$.

Since $a_{iso} = 19.4$ mT, $T = 1.595$ mT and $T' = 0.14$ mT, the corresponding spin densities can be determined as follows:

$$\rho^{2s} = \frac{a_{iso}}{A_0} = \frac{19.4}{134.7} = 0.144$$

$$\rho^{2p_z} = \frac{b}{b_0} = \frac{1.595}{3.8} = 0.4197$$

$$\rho^{2p_x} = \frac{b}{b_0} = \frac{0.14}{3.8} = 0.0368$$

The total spin density on ^{13}C is therefore 0.144 + 0.4197 + 0.0368 = 0.60, leaving the remaining spin density of the oxygen atoms (which would be visible using ^{17}O enriched CO_2).