28 Feb 2020

Electron Paramagnetic Resonance of Transition metal ion complexes



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Electron Paramagentic Resonance (EPR)

Electron Paramagnetic Resonance Electron Spin Resonance or Electro Magnetic Resonance

Detects the unpaired electron in the sample under investigation and its electronic structure around it

What is an EPR spectrum?

It is usually a plot of first derivative of absorption of microwave frequency radiation against the magnetic field intensity.





Why EPR ?



EPR imaging in cardiology Defects in diamond Dosimetry applied to teeth TM = transition metals, Ln = lanthanides.

Wide application of EPR in many branches of Science?



Electron Paramagentic Resonance (EPR)



What are the main features of an EPR spectrum?

Main parameters and features of EPR spectrum:

- 1. Position of absorption: Magnetic field value at which the absorption takes place
- 2. Number, Separation, relative intensity of the lines
- 3. Width and Shape of the line

Structure of the species under investigation Their interaction with environment Dynamic process associated with it.

Electron spin in a magnetic field (Zeeman effect)





- v frequency (GHz or MHz)
- g g-factor (approximately 2.0023)
- β Bohr magneton (9.2741 x 10⁻²¹ erg.Gauss⁻¹)
- B magnetic field (Gauss or mT)

EPR is the resonant absorption of microwave radiation by paramagnetic systems in the presence of an applied magnetic field



 $h\nu = g\beta B$ v= (g β /h)B = 2.8024 x B MHz

for B = 3480 G	ν	= 9.75 GHz	(X-band)
for B = 420 G	ν	= 1.2 GHz	(L-band)
for B = 110 G	ν	= 300 MHz	(Radiofre

Spin lattice relaxation

Spin-Lattice relaxation time (T_1) : This relates the characteristic **lifetime of the electronic state** and is **determined by the exchange of energy via thermal vibrations of the lattice**.



Spin-Spin relaxation (T₂)

Spin-Spin relaxation is concerned with mutual spin flips caused by dipolar and exchange interaction between the assembly of spins making up the sample.

Due to spin-spin interactions, often the EPR lines obtained are broad, within that fine structural details are buried. Example: Hyperfine interactions (which will give us the atoms surrounded by the metal ions)

Fundamentals

- 1. g values
 - Spin-orbit coupling
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- 3. Hyperfine interaction
- 4. Isotropic and anisotropic EPR Spectra

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Spin-orbit coupling in transition metal ion

Spin-orbit coupling in transition metal ions

In gaseous ion all five d-orbitals are degenerate and splits in octahedral field as below



When will you observe Spin-orbit coupling?

When Orbital contribution arises ?

In order that an electron can have orbital angular momentum, it must be possible to transform the orbital <u>that it occupies</u> into an exactly equivalent and degenerate orbital by rotation.

The electron is then effectively rotating about the axis used for the orbital rotation.

Spin-Orbit coupling:

- Degenerate orbital
- Orbitals with similar shape (or interconvertible by symmetry operation)
- Unsymmetrically filled t₂g orbitals or transition metal complexes with spectroscopic term symbol as T2g or T.





The unsymmetrical filling of e_g orbital cannot/weakly contribute to spin-orbit coupling. (Jahn-Teller distortion prevails)

Orbital contribution to the magnetic moment: dⁿ configuration

d¹ e.g. Octahedral Ti(III)



Possible t_{2g} arrangements = 3

The ground state electronic configuration that contribute to orbital angular momentum (first order orbital angular momentum)

High spin Oh	Low spin Oh	Td
d ¹ , d ² , d ⁶ , d ⁷	d⁴, d⁵	d ³ , d ⁴ , d ⁸ , d ⁹ ,

What about the other dⁿ configuration?: Second order orbital contribution

Other dⁿ configurations such as Oh d³, d⁸ or Td d⁷

In these cases, orbital angular momentum arises due to the mixing of orbital singlet ground state with the excited states.



The extent of mixing is depends on

- Energy gap between the ground and excited state (smaller the gap larger the mixing)
- Mixing is totally governed by the symmetry of the molecule

How does this spin-orbit coupling affect the g-value?

 \blacktriangleright For free or isolated electron, the *g*-value is determined as 2.0023



- Presence of orbital angular momentum can interact with spin angular momentum constructively or it may oppose each other. In such cases, the observed magnetic moment either higher than or lower than (respectively) compare to free electron. Hence there will be change in g-value of complex.
- Magnetic field in linear relationship with magnetic moment, ie larger the moment, splitting of moment in magnetic field will be higher.
- From g-value we can deduce the electronic environment of an atom or ion.

How g-value changes by spin-orbit coupling?

Where

a denotes **covalency**, usually a² will be < 1 (if an unpaired electron delocalized, the spin-orbit coupling will be reduced.

- $\lambda~$ = Spin orbit coupling constant
- ΔE = Energy gap between the orbitals

(Bigger $\Delta E \rightarrow$ less mixing \rightarrow smaller shift of g from g_e. Note ΔE corresponds to an **electronic dd transition**!)

n = depends on the identity of orbitals which are being mixed

Metal ion d^n configuration λ/cm^{-1}	$ \begin{array}{c} \mathrm{Ti}^{3+}\\ d^{1}\\ \mathrm{155} \end{array} $	V^{3+} d^2 105	Cr^{3+} d^{3} 90	$\frac{\mathrm{Mn}^{3+}}{d^4}$ 88	Fe^{2+} d^{6} -102	$\begin{array}{c} \text{Co}^{2+} \\ d^7 \\ -177 \end{array}$	Ni^{2+} d^{8} -315	$\begin{array}{c} \mathrm{Cu}^{2+} \\ d^9 \\ -830 \end{array}$
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λ = Positive for less than half filled orbitals

λ = Negative for more than half filled orbital

Hence, the *g*-value is higher than the free electron *g*-value (g_e) for more than half filled electronic configuration and the same will be less the free electron *g*-value (g_e) for less than half filled d-orbital.

$$\Delta E = hv = g\mu B$$
$$g = hv/\mu B \quad or \ g \propto 1/B$$

$$g = g_e - \frac{a^2 n \lambda}{\Delta E}$$

Prediction of n value from Magic Pentagon



Example of d¹ case (one unpaired electron system): Importance of symmetry (point group)

(V=O)²⁺ complex: axially compressed, therefore D_{4h} symmetry Vanadium in +4 oxidation state (d¹ configuration)



and contribute to magnetic moment)

Determining mixing of orbital? (Magnetic field orientation dependent mixing of orbital based on symmetry of a molecule)

	E	$2C_4$ (z)	с 2	2C'2	2C"2	i	28 ₄	σ _h	2σ _v	^{2σ} d	linears, rotations	quadratic
A _{lg}	1	1	1	1	1	1	1	1	1	1		$x^{2}+y^{2}, z^{2}$
A _{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R _z	
Blg	1	-1	1	1	-1	1	-1	1	1	-1		x ² -y ²
B _{2g}	1	-1	1	-1	1	1	-1	1	-1	1		ху
Eg	2	0	-2	0	0	2	0	-2	0	0	(R _x , R _y)	(xz, yz)
A _{lu}	1	1	1	1	1	-1	-1	-1	-1	-1		
A _{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B _{lu}	1	-1	1	1	-1	-1	1	-1	-1	1		
B _{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
Eu	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

estor table for D _ name or



$$g_{\perp} = 2.0023 - 2k' \lambda \Delta E_{xz,yz}$$

 $B_{2g}R_x = 2$ 0 -2 0 0 2 0 -2 0 0 (corresponds to E_g) (xz,yz orbital will mix and contribute to magnetic moment)

Axial and rhombic epr spectrum

 $hv = g\beta H$; since g-parallel and g-perpendicular are different, expect to have two different EPR signals



V=O²⁺ ion epr spectrum



There are supposed to be two EPR lines. The more lines are due to hyperfine interaction $(I_{vanadium} = 7/2)$. Both $g_{parallel}$ and g_{\perp} lines split into 8 lines each (total 16 lines). Due to overlapping of some EPR signals less than 16 lines observed.

Electronic structure of axially elongated Cu²⁺ ion



$$d_{z^2}$$

$$d_{xz} d_{yz} \xrightarrow{\uparrow} \downarrow \downarrow \downarrow$$

Character table for D _{4h} point group												
	E	2C ₄ (z)	с 2	2C'2	2C"2	i	28 ₄	σ _h	2σ _v	^{2σ} d	linears, rotations	quadratic
Alg	1	1	1	1	1	1	1	1	1	1		x ² +y ² , z ²
A _{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R _z	
B _{lg}	1	-1	1	1	-1	1	-1	1	1	-1		x ² -y ²
B _{2g}	1	-1	1	-1	1	1	-1	1	-1	1		ху
Eg	2	0	-2	0	0	2	0	-2	0	0	(R _x , R _y)	(xz, yz)
A _{lu}	1	1	1	1	1	-1	-1	-1	-1	-1		
A _{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	Z	
B _{lu}	1	-1	1	1	-1	-1	1	-1	-1	1		
B _{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
Eu	2	0	-2	0	0	-2	0	2	0	0	(x, y)	



B _{1g}	1	-1		1	1	-1	1	-1	1	1	-1	
R _z	1	1		1	-1	-1	1	1	1	-1	-1	
B_{1g} . R_{z}	1	-1		1	-1	1	1	-1	1	-1	1	B _{2g} (xy)
B _{1g}		1	-1	1	1	-1	1	-1	1	1	-1	
$R_x \text{ or } R_y$		2	0	-2	0	0	2	0	-2	0	0	
$B_{1g}.R_{z}$	Ĩ	2	0	-2	0	0	2	0	-2	0	0	E _g (xz, yz)

$$g_{parallel} = g_e \, - \, rac{a^2 n \lambda}{\Delta E} \, egin{array}{c} g_\perp = g_e \, - \, rac{a^2 n \lambda}{\Delta E} \ \end{array}$$

 $g_{parallel} ~and ~g_{\perp} > ~g_e; \ {
m also} g_{parallel} > g_{\perp}$

Simple Cu(II) monomeric complexes EPR spectrum



Rule of thumb

g-value change (spin-orbit coupling):

- Transition from an orbital to an empty orbital contribute negatively to g-value i.e g < g_e
- Transition from an orbital to half-filled orbital contribute positively to g-value i.e g
 > g_e



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Hyperfine interaction and hyperfine coupling constant

Splitting of EPR signal due to coupling with nuclear spin called Hyperfine interaction, and the distance between the signal due to nuclear coupling is called hyperfine constant.





When electron interacting with I = ½ nucleous: (2I+1) levels generated



When electron interacting with I = 1 nucleous:



Selection rule: to observe epr signal $\Delta M_s = \pm 1$ $\Delta M_l = 0$

Intensity of EPR lines when $I_i = \frac{1}{2}$ (*i* = 1, 2, 3 etc..)







Intensity of EPR lines when $I_i = \frac{1}{2}$ (*i* = 1, 2, 3 etc..)

(a)		$I_i = 1/2$ (<i>i</i> = 1,	,2, , <i>n</i>)
No.of nuclei <i>n</i>	No. of lines 2/ + 1	First-order line positions/ <i>a</i> o <i>M_I</i>	Binomial intensity ratios
0	1	0	1
1	2	1/2 1/2	1 1
2	3	1 0 1	1 2 1
з	4	3/2 1/2 1/2 3/2	1 3 3 1
4	5	2 1 0 1 2	1 4 6 4 1
5	6	5/23/21/2 1/23/25/2	1 5 10 10 5 1
6	7	3 2 1 0 1 2 3	1 6 15 20 15 6 1
•	•	· · ·	
			· · · ·

Intensity of EPR lines when $I_i = 1$ (i = 1, 2, 3 etc..)

(b)		l _i = 1 (i = 1,2, ,n)																		
No.of nuclei <i>n</i>	No. of lines 2/ + 1	First-order line positions/ <i>a</i> o <i>M_I</i>					Multinomial intensity ratios													
0	1					0										1				
1	3				1	0	1								1	1	1			
2	5			2	1	0	1	2						1	2	3	2	1		
з	7		3	2	ī	0	1	2	з				1	3	6	7	6	з	1	
4	9	4	3	2	1	0	1	2	3	4		1	4	10	16	19	16	10	4	1
				•		·		·						:		·		•		
				•		÷		•								:		:		

Predict the / value of nucleus





 CH_3 - CH_2 .



Number of EPR lines (2nI +1) (2mI+1) where n and m are Chemically inequivalent nuclei with non-zero nuclear spin.

Nuclear Spin Value of important 3d ions

Properties of 3d Isotopes

Isotope	Spin	Abundance
⁴⁵ Sc	7/2	100.%
⁴⁶ Ti, ⁴⁸ Ti, ⁵⁰ Ti	0	87.2
⁴⁷ Ti	5/2	7.3
⁴⁹ Ti	7/2	5.5
51 _V	7/2	100.
⁵⁰ Cr, ⁵² Cr, ⁵⁴ Cr	0	90.5
⁵³ Cr	3/2	9.6
⁵⁵ Mn	5/2	100.
⁵⁴ Fe, ⁵⁶ Fe, ⁵⁸ Fe	0	97.8
57 _{Fe}	1/2	2.2
⁵⁹ Co	7/2	100.
⁵⁸ Ni, ⁶⁰ Ni, ⁶² Ni, ⁶⁴ Ni	0	98.9
61 _{Ni}	3/2	1.2
⁶³ Cu	3/2	69.1
⁶⁵ Cu	3/2	30.9

Simple Mn(II) monomeric complexes EPR spectrum

Mn(II) isotropic EPR spectrum

S = 5/2 and I = 5/2



Simple vanadyl complexes EPR spectrum



The ESR spectrum shows eight well-defined isotropic signals which confirm that no delocalization occurs between the metal centres.

Polyhedron., 2013, 53, 8

Simple V(IV) monomeric complexes EPR spectrum



No of lines (2nI+1).(2mI+1) (2X1X7/2+1).(2X2X1/2+1) 8X3 = 24 lines

In the second derivative spectrum, a superhyperfine coupling of the unpaired electron of the vanadium atom with the N imido group (¹⁴N nucleus, I = 1) gives rise to a typical 1:1:1 triplet

Parameters contributes to hyperfine splitting

The hyperfine coupling constant depends on:



As in g-tensor, **dipolar coupling** results in anisotropy in hyperfine tensor i.e the strength of hyperfine interaction vary in different direction (A_{II} and A_{\perp} (or) A_z , A_y , A_x)

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Fine structure

The appearance of more than one epr signal (for $S > \frac{1}{2}$) or line is known as fine structure.



Where this is the case if *S* level **does not have zero field splitting** (only one signal will be observed as the splitting of energy level will be similar ie.. At any point the transition from -1 to 0 and 0 to +1 will always be equal.

Zero field splitting

Zero field splitting will be observed system containing more than one unpaired electrons.

In general, species with S spin has the total of (2S+1) energy state characterized by quantum number M_s

In the absence of external magnetic field all these states are degenerate.

However, the degeneracy of these states removed through electrical field produced by other atoms which act via spin-orbit coupling even in the absence of magnetic field ie zero field called Zero field splitting (D).

Consider a system with S = 1 (contains two unpaired electron) $M_s = (2S+1) = 3$, which are ± 1 and 0.



Zero field splitting (ZFS) in S = 1 system



EPR spectroscopy quantitatively predicts the zero field splitting experimentally.

Effect of hv Vs D for S = 1 system



Calculating the energy gap between the M_s states in various ground state

$$E_{Ms} = D\left[S_z^2 - \frac{S(S+1)}{3}\right]$$

For system with negative zero field splitting (highest M_s level will be lowest in energy)

Energy of particular state is calculated by DS²



Zero field splitting and hv (relationship)



System with ZFS, will give 2S (where S = n/2) number of signals.



EPR is an excellent tool to predict the sign of D



 $[Co(X)_2(tm-tu)_2]$ where X = Br or I

X band EPR @ 5 K: Proof for easy axis anisotropy

[Co_{0.02}Zn_{0.98}(Br)₂(tm-tu)₂]



 $g_{eff}^{z} = 6.69; g_{eff}^{y} = 3.05; g_{eff}^{x} = 1.87$

 A_z (MHz) = 570; A_v = 100; A_x = 20



 $g_{eff}^{z} = 6.70; g_{eff}^{y} = 2.55; g_{eff}^{x} = 1.68$ A_z (MHz) = 473; A_y = 85; A_x = 10

The allowed effective g-values with \pm D





Gatteschi, Benelli and Bencini, Structure and Bonding 1982, 52, 38-86

Take home message

- ✓ EPR is an excellent tool to investigate the electronic structure of metal complex.
- ✓ The g-value of transition metal complexes deviates from free electron g-value due to Spin-orbit coupling.
- ✓ The g-value of less than half-filled transition metal ion is always smaller than the free electron g-value.
- ✓ The g-value of more than half-filled transition metal ion is always larger than the free electron g-value.
- ✓ Spin orbit coupling is responsible for anisotropy in g-values (axial or rhombic spectrum)
- ✓ Spin orbit coupling is also a predominant factor in lifting the degeneracy of Ms level in the absence of external magnetic field. (D)
- ✓ Magnitude of D (if D << hv) can be predicted accurately and sign of D-can be determined from X or Q-band spectroscopy.
- ✓ Dipolar coupling results in anisotropy in hyperfine interaction

Text and Reference books:

- 1. Electron paramagnetic Resonance: A practitioner's tool kit
 - Marina Brustolon and Elio Giamell
- 2. Electron Paramagnetic Resonance

- John A Weil and James R. Bolton

3. NMR, NQR, EPR and Mossbauer spectroscopy in Inorganic Chemistry

- R. V. Parish

4. Electron Spin Resonance: Theory and Application

- N. M. Atherton

5. Electron Paramagnetic Resonance

- Victor Chechik, Emma Carter, Damien Murphy

