Nephelauxetic Effect

M. Sc. : CC – 3 (Inorganic Chemistry)

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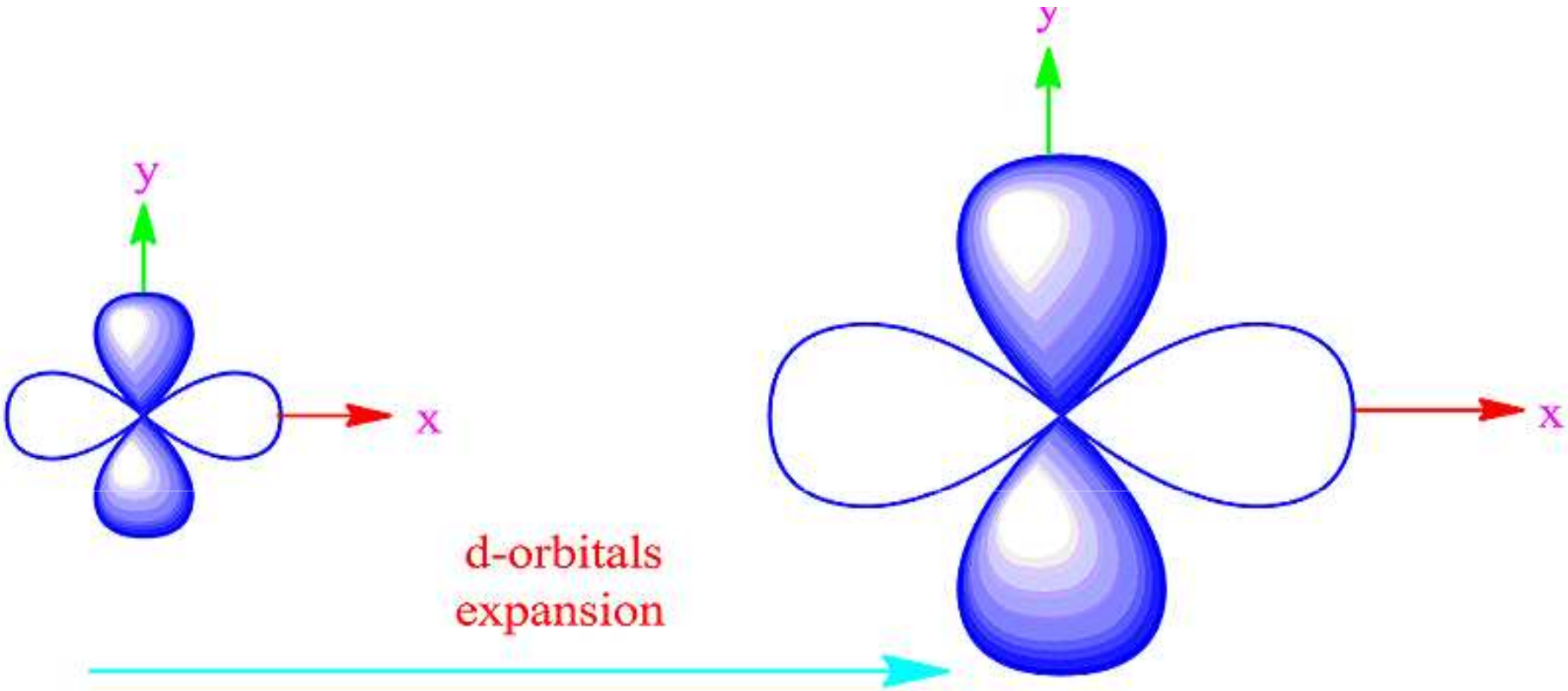
Nephelauxetic Effect/

Electron cloud expension/Nephelauxetic Parameter

- It is electron repulsion found in complexes due to e-e repulsion.
- It is denoted by ß (Nephelauxetic parameter)
- It is expressed by $ß = \frac{\text{B complex}}{\text{B free ion}}$
- ß is always less than 1
- It means B complex is less than B free ion.
- It means energy gap between two terms in free ion is greater than that of its complex form.
- i.e. e-e repulsion between two electrons in free ion is greater than its complex.
- When ligand approaches to the free ion than e-e repulsion is decreased & hence nephelauxetic parameter is decreased.
- It determines covalent character in complex compound & is directly proportional to the NE.

Free Metal ion

In complex



In free ion ee repulsion is greater than that of complex. So NE is increased but nephelauxetic ratio $\beta = \frac{\text{B complex}}{\text{B free ion}} < 1$.

Nephelauxetic effect $\propto \frac{1}{\text{Ele Repuls}} \propto$ 1/ Nephelauxetic ratio

Calculation of ß

We know that

$$ß = \frac{\text{B complex}}{\text{B free ion}}$$ or, 1-ß=1-$$\frac{\text{B complex}}{\text{B free ion}}$$ = red. of ee rep.

B ion – B complex / B ion = h.k

% red. of e-e rep.=1$$\frac{\text{B complex}}{\text{B free ion}}$$ X 100=h.k X 100

where h & k are constant for ligand & metal respectively & its value is fixed in free state

here ,

h = 0.1, k =1.0

% red. Of e-e rep.= 0.1 x 1.0 x 100 = 10%

Reduction of N ratio (parameter) indicates increase covalent character in complexes

Cloud expansion ↑ NE ↑ ß ↓ Covalent Character ↑ delocalization ↑

Factors Affecting ß Value

Nephelauxetic effect depends upon both types of ligand and types of central metal ion.

A series of ligands arranged in descending order from the highest value of nephelauxetic parameter (ß) to lowest value is called nephelauxetic series

$$F^- > H_2O > NH_3 > en > OX^{--} > NCS^- > Cl^- > CN^- > Br^- > I^-$$

h=	0.8	1.0	1.4	1.55	1.55	1.98	2.0	2.1	2.3	2.7

NE increases, NP decreases, % redu. e-e rep. increases covalent character increases.

Example: 1

$[NiF_6]^{-4}$

Here,

h=0.8 therefore B=843 cm^{-1}

$[NiBr_6]^{-4}$

h=2.3 therefore B=600 cm^{-1}

Similarly NS of metal ion are as

Ni(II) ≈ Co(II) < Mo(II) < Re(IV) < Fe(III) < Ir(III) < Pt(IV) < Pd(IV)

K= 0.07 0.12 0.12 0.18 0.24 0.26 0.6 0.7

NE ↑, ß ↓, CC ↓, e-e rep. ↑

Example: 2

$[FeF_6]^{3-}$

K= 0.24x0.8 = 0.192 = % reduction = 19.2

$[Cr(NH_3)_6]^{3+}$

k_{Cr}= 0.21

h_{NH3} = 1.4

So k.h = 0.294 therefore % reduction = 29.4

Significance of NE

NE determines electron expending nature, % reduction of e-e rep., covalent character in complex, nature of EPR peaks etc.

As we know that

1. Reduction of N ratio (parameter) indicates increase covalent character in complexes

Cloud expansion ↑ NE ↑ ß ↓ Covalent Character ↑ delocelization ↑

So covalent character increases with increasing NE & decreasing ß value

$$F^- > H_2O > NH_3 > en > OX^{--} > NCS^- > Cl^- > CN^- > Br^- > I^-$$

h=	0.8	1.0	1.4	1.55	1.55	1.98	2.0	2.1	2.3	2.7

NE increases from left to right

ß decreases left to right

Cloud expansion increases from left to right

Covalent character increases from left to right

Oxidation states of metal (Depends upon size of cation)

$$M^0 > M^+ > M^{+2} > M^{+3}$$

NE increases from left to right

ß decreases left to right

Cloud expansion increases from left to right

Covalent character increases from left to right

If B=B- then complex 100% ionic

if B-<B then complex is not pure ionic & have covalent character

For $[Co(en)3]^{3+}$

$B' = 1400(1 - 0.35 \times 1.5)\ cm^{-1}$ $B' = 665\ cm^{-1}$

This experimental value of B for $[Co(en)3]^{3+}$ is 568 cm^{-1}.

The values of Racah parameter (B) for transition metal ion in the gaseous state can be noted from the table given below.

Metal	M^0	M_{1+}	M_{2+}	M_{3+}	M_{4+}
Ti	560	681	719	-	-
V	579	660	765	860	-
Cr	790	710	830	1030	1040
Mn	720	872	960	1140	-
Co	789	879	1117	-	-
Ni	1025	1038	1080	-	-
Cu	-	1218	1239	-	-
Fe	805	870	1059	-	1144


Thank You