Lecture 12; CH 101: Inorganic Chemistry

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Selection Rules for Electronic Spectra of Transition Metal Complexes.

The Selection Rules governing transitions between electronic energy levels of transition metal complexes are:

$\Delta S = 0$ The Spin Rule
$\Delta l = +/- 1$ The Orbital Rule (Laporte)

The first rule says that allowed transitions must involve the promotion of electrons without a change in their spin.

Selection Rules for Electronic Spectra of Transition Metal Complexes.

- **Laporte Selection Rule:** In a molecule having center of symmetry, transitions between states of the same parity (symmetry with respect to a center of inversion) are forbidden.

- For example, transitions between states that arise from d orbitals are forbidden (*g*→*g* transitions; d orbitals are symmetric to inversion), but transitions between states arising from d and p orbitals are allowed (*g*→*u* transitions; p orbitals are anti-symmetric to inversion). Therefore, all d-d transitions in octahedral complexes are Laporte-forbidden.

- Laporte-allowed transitions involve $\Delta l = \pm 1$.

Selection Rules for Electronic Spectra of Transition Metal Complexes.

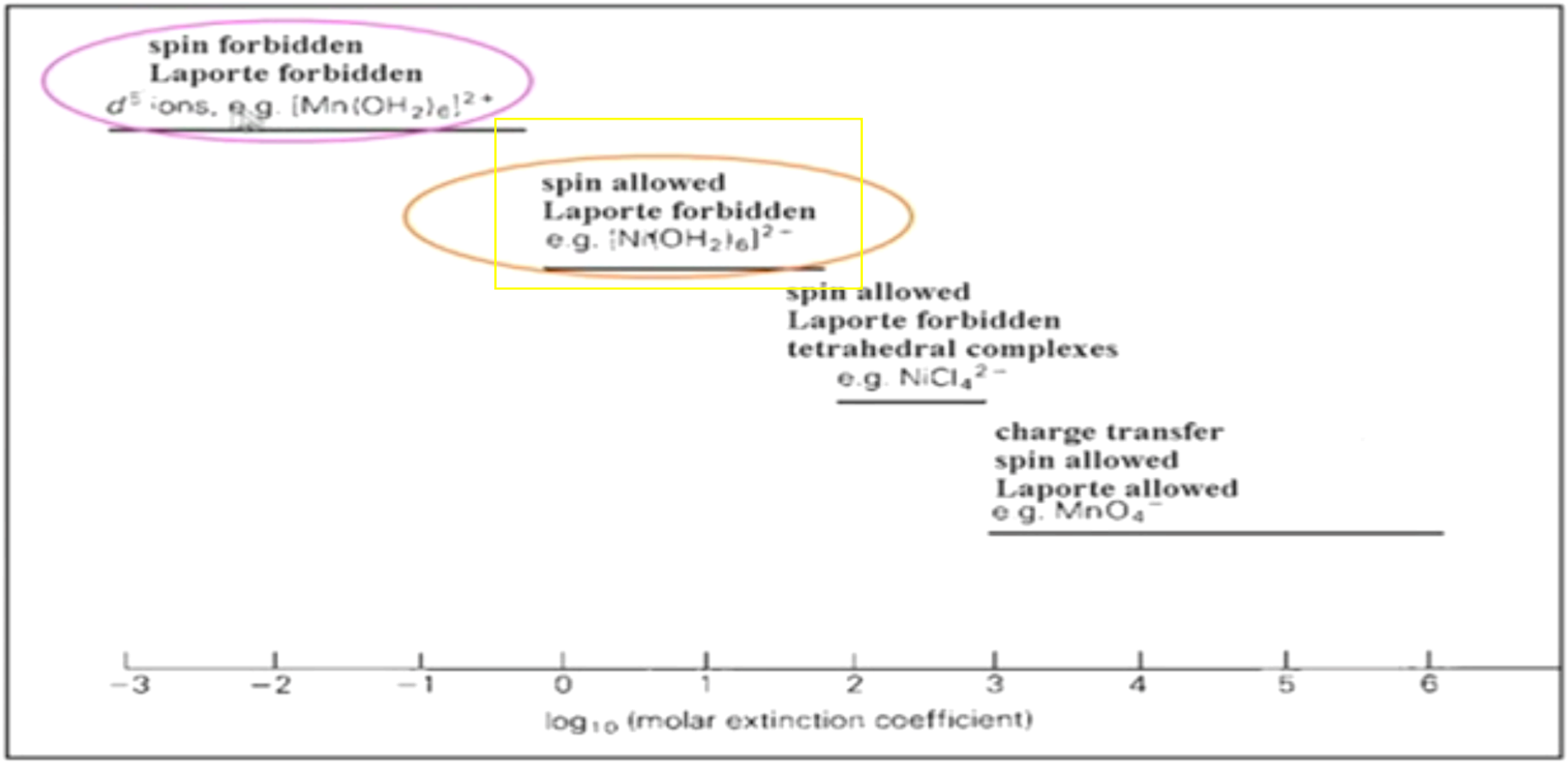
- Some transitions are not allowed does not mean that such a transition will never occur, but that it is less likely and that the intensity (molar absorption coefficient) of such an absorption band is very low.

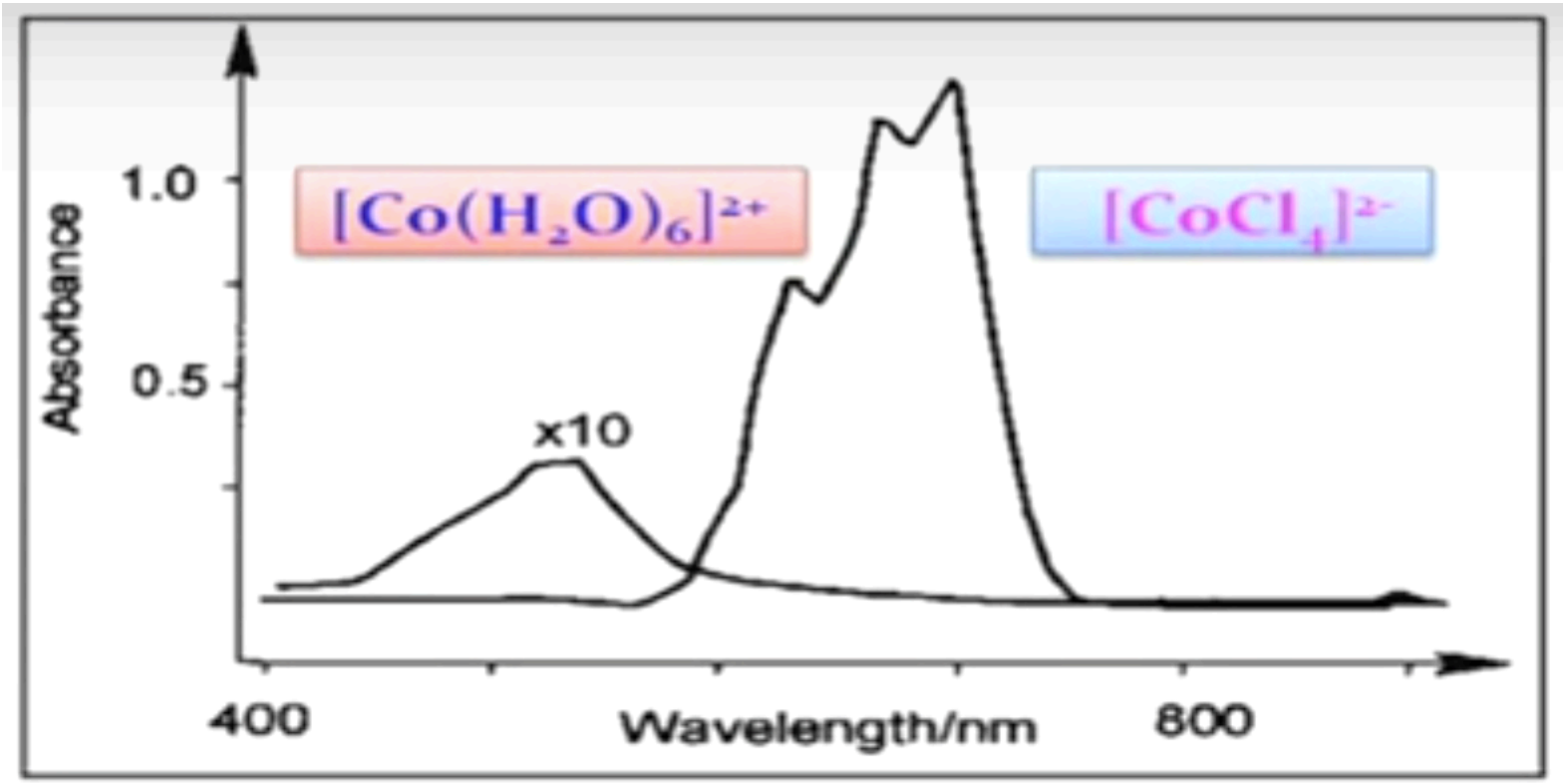
Relaxation of the Rules can occur through:

a) Spin-Orbit coupling - this gives rise to weak spin forbidden bands

b) Vibronic coupling - an octahedral complex may have allowed vibrations where the molecule is asymmetric. Absorption of light at that moment is then possible.

c) π-acceptor and π-donor ligands can mix with the d-orbitals so transitions are no longer purely d-d.


spin forbidden
Laporte forbidden
d^5 ions, e.g. $[Mn(OH_2)_6]^{2+}$
spin allowed
Laporte forbidden
e.g. $[Ni(OH_2)_6]^{2-}$
spin allowed
Laporte forbidden
tetrahedral complexes
e.g. $NiCl_4^{2-}$
charge transfer
spin allowed
Laporte allowed
e.g. MnO_4^-
−3
−2
−1
0
1
2
3
4
5
6
$\log_{10}$ (molar extinction coefficient)


Absorbance
1.0
0.5
[Co(H2O)6]2+
[CoCl4]2-
x10
400
Wavelength/nm
800

Term Symbols.

d^n	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Term Symbol	^2D	^3F	^4F	^5D	^6S	^5D	^4F	^3F	^2D	^1S

Term	Irreducible Representation
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + 2T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

Orgel Diagram.

d^1	d^6	d^4	d^9
T_d	T_d	O_h	O_h
$^2T_2$	$^5T_2$	$^5T_{2g}$	$^2T_{2g}$
^2E	^5E	^5E_g	^2E_g

d^1	d^6	d^4	d^9
O_h	O_h	T_d	T_d
^2E_g	^5E_g	^5E	^2E
$^2T_{2g}$	$^5T_{2g}$	$^5T_2$	$^2T_2$