

**COMMONWEALTH OF AUSTRALIA**

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## Schedule

- Lecture 1: Electronic absorption spectroscopy  
Jahn-Teller effect and the spectra of  $d^1$ ,  $d^4$ ,  $d^6$  and  $d^9$  ions
- Lecture 2: Interpreting electronic spectra  
Interelectron repulsion and the nephelauxetic effect
- Lecture 3: Interpreting electronic spectra  
Selection rules and charge transfer transitions

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## Summary of Last Lecture

### d-d spectroscopy

- For  $d^2$ ,  $d^3$ ,  $d^7$  and  $d^8$ , the effect of repulsion between the d-electrons must be considered through the Racah parameter B
- Three transitions are predicted in their ligand-field spectra

### Band Shapes

- Exciting d-electrons usually increases the bond length
- This leads to broad bands

### Today's lecture

- Selection rules

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## Energies of d-d Transitions

Octahedral  $d^1$ ,  $d^4$ ,  $d^6$  and  $d^9$ :  
1 band      energy =  $\Delta_{\text{oct}}$

3 bands      Octahedral  $d^2$ :  
 $\Delta_{\text{oct}}$  and B from calculation

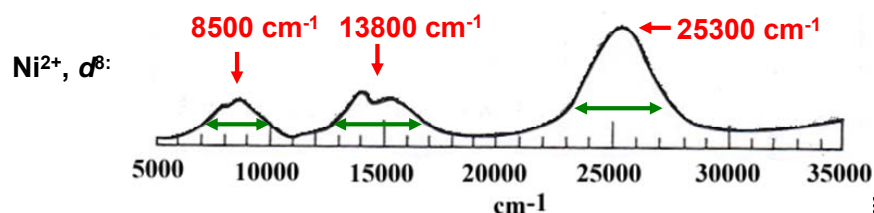
3 bands      Octahedral  $d^7$ :  
 $\Delta_{\text{oct}} = \nu_2 - \nu_1$       B from calculation

3 bands      Octahedral  $d^3$  and  $d^8$ :  
 $\nu_1 = \Delta_{\text{oct}}$       B from calculation

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## Features of an Electronic Spectrum

- The **frequency**, **wavelength** or **energy** of a transition relates to the energy required to excite an electron:
  - depends on  $\Delta_{\text{oct}}$  and B for ligand-field spectra
  - decides **colour of molecule**
- The **width** of a band relates to the vibrational excitation that accompanies the electronic transition:
  - narrow bands: excited state has similar geometry to the ground state
  - broad bands: excited state has different geometry to the ground state
- The **height** or **area** of a band relates to the number of photons absorbed
  - depends on concentration and path length
  - transition probability
  - decides **intensity or depth of colour**



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## Transition Probability

- When light is shined on a sample, some of the light may be absorbed and some may pass straight through
  - the proportion that is absorbed depends on the 'transition probability'
- To be absorbed, the light must interact with the molecule:
  - the oscillating electric field in the light must interact with an oscillating electric field in the molecule
- During the transition, there must be a change in the **dipole moment** of the molecule:
  - if there is a large change, the light / molecule interaction is strong and many photons are absorbed:  
**large area or intense bands → intense colour**
  - if there is a small change, the light / molecule interaction is weak and few photons are absorbed:  
**low area or weak bands → weak colour**
  - If there is no change, there is no interaction and **no** photons are absorbed

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## Selection Rules

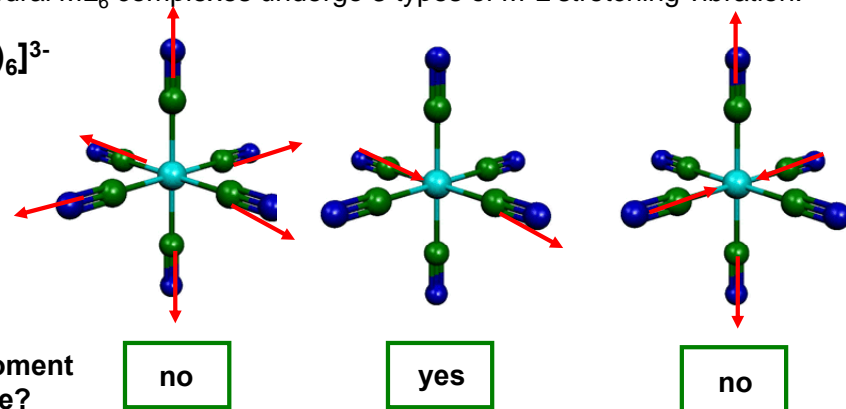
- During the transition, there must be a change in the **dipole moment** of the molecule:
  - if there is a large change, the light / molecule interaction is strong and many photons are absorbed:  
**large area or intense bands → intense colour**
  - if there is a small change, the light / molecule interaction is weak and few photons are absorbed:  
**low area or weak bands → weak colour**
  - If there is no change, there is no interaction and **no** photons are absorbed

Selection rules tell us which transitions give no change in dipole moment and hence which will have zero intensity

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## Selection Rules - IR

- During the transition, there must be a change in the **dipole moment** of the molecule
- Octahedral  $\text{ML}_6$  complexes undergo 3 types of M-L stretching vibration:

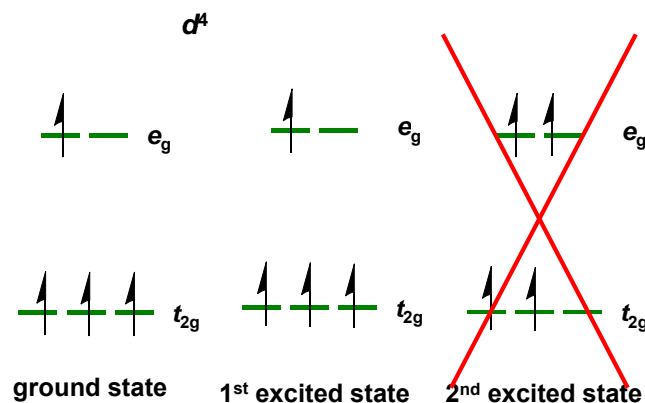


- There is **one** band in the M-L stretching region of the IR spectrum

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## Selection Rules – Spin Selection Rule

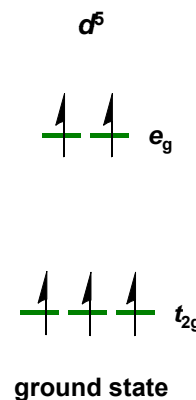
The spin cannot change during an electronic transition



Only one  
spin allowed  
transition

## Selection Rules – Spin Selection Rule

The spin cannot change during an electronic transition



NO spin allowed transitions  
for high spin  $d^6$

## Selection Rules – Orbital Selection Rule

- A photon has 1 unit of angular momentum
- When a photon is absorbed or emitted, this momentum must be conserved

$\Delta l = \pm 1$  or:

' $s \leftrightarrow p$ ', ' $p \leftrightarrow d$ ', ' $d \leftrightarrow f$ ' etc allowed ( $\Delta l = \pm 1$ )

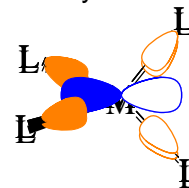
' $s \leftrightarrow d$ ', ' $p \leftrightarrow f$ ' etc forbidden ( $\Delta l = \pm 2$ )

' $s \leftrightarrow s$ ', ' $p \leftrightarrow p$ ', ' $d \leftrightarrow d$ ', ' $f \leftrightarrow f$ ' etc forbidden ( $\Delta l = 0$ )

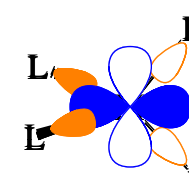
...so why do we see ' $d-d$ ' bands?

## 'Relaxing' The Orbital Selection Rule

- The selection rules are **exact** and cannot be circumnavigated
- It is our **model** which is too simple:
  - the ligand-field transitions described in Lectures 2 and 3 are in molecules not atoms
  - labelling the orbitals as ' $d$ ' (atomic orbitals) is **incorrect** if there is any covalency



A metal  $p$ -orbital overlaps  
with ligand orbitals



A metal  $d$ -orbital overlaps  
with the same ligand orbitals

Through covalent overlap with the ligands,  
the metal ' $d$ ' and ' $p$ ' orbitals are mixed

## 'Relaxing' the Orbital Selection Rule

Through covalent overlap with the ligands, the metal '*d*' and '*p*' orbitals are mixed

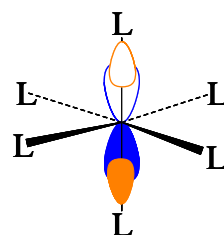
- As the molecular orbitals are actually mixtures of *d* and *p*-orbitals, they are actually **allowed** as  $\Delta l = \pm 1$
- But**, if covalency is small, mixing is small and transitions have **low intensity**

In tetrahedral complexes, the '*d-d*' transitions become allowed through covalency but the '*d-d*' bands are still weak as covalency is small

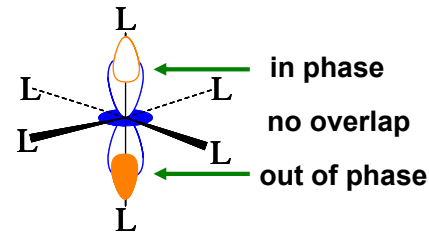
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## Laporte Selection Rule

- This way of 'relaxing' the orbital selection rule is not available in octahedral complexes



A metal *p*-orbital overlaps with ligand orbitals



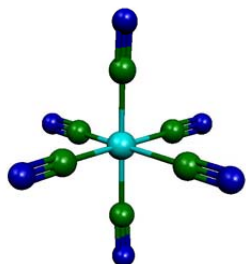
A metal *d*-orbital **cannot** overlap with the same ligand orbitals

In general, no mixing of the '*d*' and '*p*' orbitals is possible if the molecule has a centre of inversion (Laporte rule)

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## 'Relaxing' the Laporte Selection Rule

- Again our model is deficient:
  - molecules are not rigid but are always vibrating



During this vibration, centre of inversion is temporarily lost: *d-p* mixing can occur

- Vibrational amplitude is small so deviation and mixing is small:
  - octahedral complexes have lower intensity bands than tetrahedral complexes
  - the intensity of the bands increases with temperature as amplitude increases

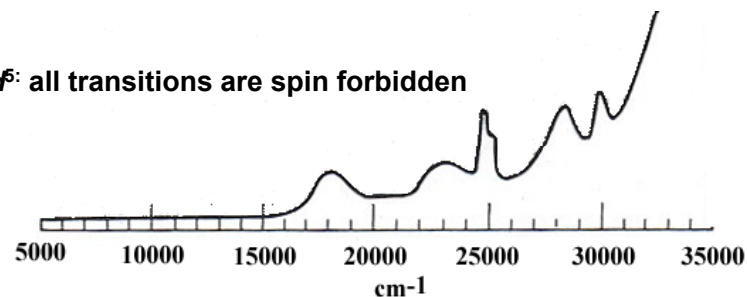
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## 'Relaxing' the Spin Selection Rule

- Again our model from lectures 1 and 2 is deficient:
  - electrons can have magnetism due to the spin and orbital motions
  - this coupling allows the spin forbidden transitions to occur

spin-orbit coupling: the interaction between spin and orbital magnetism

- $\text{Mn}^{2+} d^5$ : all transitions are spin forbidden



spin-orbit coupling gets stronger as elements get heavier and so spin forbidden transitions get more important

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## Charge Transfer Transitions

- As well as 'd-d' transitions, the electronic spectra of transition metal complexes may 3 others types of electronic transition:
  - Ligand to metal charge transfer (**LMCT**)
  - Metal to ligand charge transfer (**MLCT**)
  - Intervalence transitions (**IVT**)
- All complexes show LMCT transitions, some show MLCT, a few show IVT

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## Ligand to Metal Charge Transfer

- These involve excitation of an electron from a ligand-based orbital into a d-orbital



- This is always possible but LMCT transitions are *usually* in the ultraviolet
- They occur in the visible or near-ultraviolet if
  - metal is easily **reduced** (for example metal in high oxidation state)
  - ligand is easily **oxidized**

If they occur in the visible or near-ultraviolet, they are much more intense than 'd-d' bands and the latter will not be seen

## Ligand to Metal Charge Transfer

- They occur in the visible or near-ultraviolet if
  - metal is easily **reduced** (for example metal in high oxidation state)

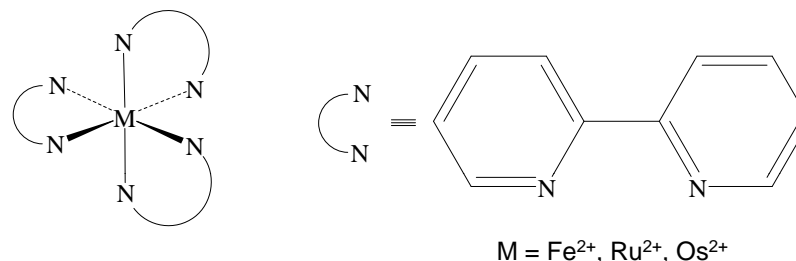
$d^0$	<b>TiO<sub>2</sub></b> Ti <sup>4+</sup>	<b>VO<sub>4</sub><sup>3-</sup></b> V <sup>5+</sup>	<b>CrO<sub>4</sub><sup>2-</sup></b> Cr <sup>6+</sup>	<b>MnO<sub>4</sub><sup>-</sup></b> Mn <sup>7+</sup>
	in far UV <b>white</b>	~39500 cm <sup>-1</sup> <b>white</b>	~22200 cm <sup>-1</sup> <b>yellow</b>	~19000 cm <sup>-1</sup> <b>purple</b>

→ more easily reduced

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## Metal to Ligand Charge Transfer

- They occur in the visible or near-ultraviolet if
  - metal is easily **oxidized** and ligand has low lying **empty** orbitals

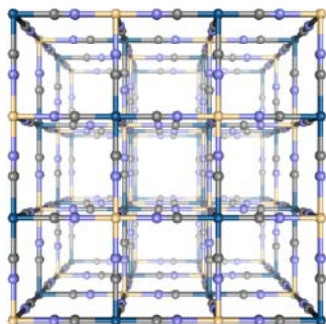


- Sunlight excites electron from M<sup>2+</sup> ( $t_{2g}$ )<sup>6</sup> into empty ligand  $\pi^*$  orbital
  - method of capturing and storing solar energy

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## Intervalence Transitions

- Complexes containing metals in two oxidation states can be coloured due to excitation of an electron from one metal to another



**"Prussian blue"**  
contains  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$

- Colour arises from excitation of an electron from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$

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## Selection Rules and Band Intensity

- The height of the band in the spectrum is called the 'molar extinction coefficient' - symbol  $\epsilon$ :

	$\epsilon$ ( $\text{mol}^{-1} \text{cm}^{-1}$ )	type of transition	type of complex
<div>very pale colours</div> <div>↓</div> <div>intense colours</div>	$10^{-3} - 1$	spin forbidden orbitally forbidden, Laporte forbidden	octahedral $d^5$ complexes (e.g. $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ )
	$1 - 10$	spin forbidden orbitally forbidden,	tetrahedral $d^5$ complexes (e.g. $[\text{MnCl}_4]^{2-}$ )
	$10 - 10^2$	spin allowed, orbitally forbidden Laporte forbidden	octahedral and square planar complexes
	$10 - 10^3$	spin allowed, orbitally forbidden	tetrahedral complexes
	$> 10^3$	LMCT, MLCT, IVT	

## Summary

### By now, you should be able to ....

- Explain that the spin cannot change during an electronic transition
- Explain that pure ' $d-d$ ' transitions cannot occur
- Explain that  $d-p$  mixing in complexes without centre of inversion (e.g. tetrahedron) 'relaxes' this rule
- Explain that ' $d-p$ ' mixing for complexes with a centre of inversion (e.g. octahedron or square planar) can only occur due to molecular vibrations
- Explain that origin of LMCT, MLCT and IVT transitions
- Predict the relative intensities of spin, Laporte and orbitally forbidden transitions

## Practice

- Solutions of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ions are pale green but the chromate ion  $[\text{CrO}_4]^{2-}$  is an intense yellow. Characterize the origins of the transitions and explain their relative intensities.
- Common glass used for windows and many bottles is green because of  $\text{Fe}^{2+}$ . It is decolourized by addition of  $\text{MnO}_2$  to form  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$ . Why is the glass decolourized?
- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  exists in two isomeric forms.
  - Draw the structures of these isomers
  - Predict which isomer will give rise to the more intense ' $d-d$ ' bands

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