
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

Summary of Last Lecture

d-d spectroscopy

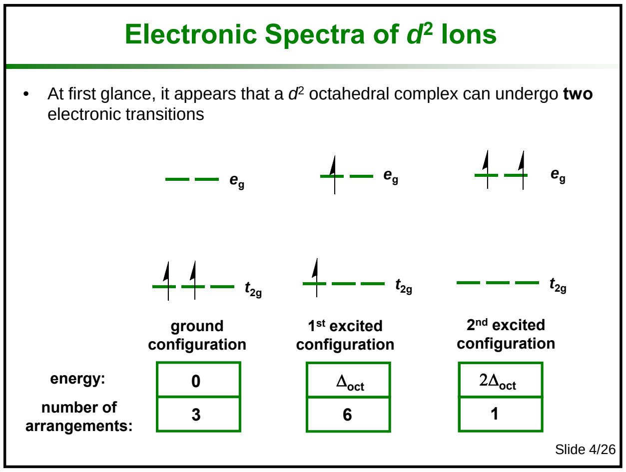
- For d^1, high spin d^4, high spin d^6 and d^9 complexes, there is a single band in visible spectrum
- The energy of the band is equal to Δ_{oct}

Jahn-Teller effect

- High spin d^4, low spin d^7 and d^9 octahedral complexes are always distorted
- The effect also leads to broadening of bands

Today's lecture

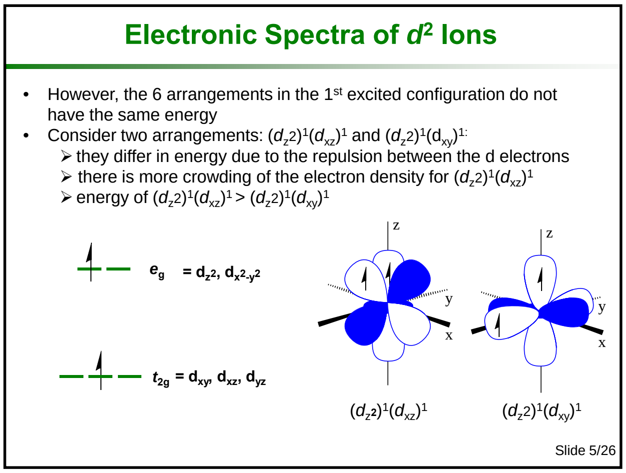
- Effects of interelectron repulsion



Electronic Spectra of d^2 Ions

- At first glance, it appears that a d^2 octahedral complex can undergo **two** electronic transitions

	ground configuration	1st excited configuration	2nd excited configuration
energy:	0	Δ_{oct}	$2\Delta_{oct}$
number of arrangements:	3	6	1



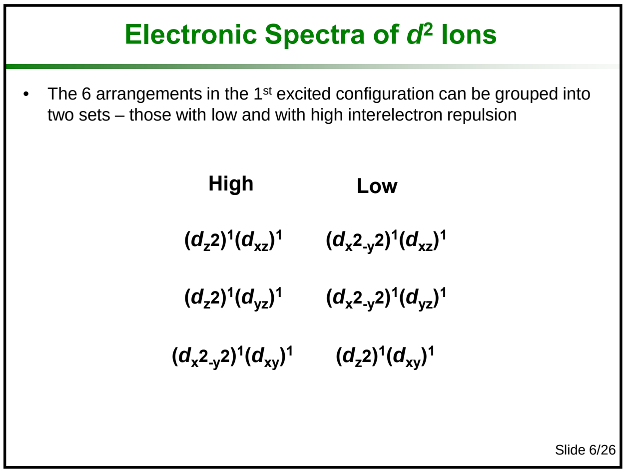
Electronic Spectra of d^2 Ions

- However, the 6 arrangements in the 1st excited configuration do not have the same energy
- Consider two arrangements: $(d_{z^2})^1(d_{xz})^1$ and $(d_{z^2})^1(d_{xy})^1$:
  - ➢ they differ in energy due to the repulsion between the d electrons
  - ➢ there is more crowding of the electron density for $(d_{z^2})^1(d_{xz})^1$
  - ➢ energy of $(d_{z^2})^1(d_{xz})^1 > (d_{z^2})^1(d_{xy})^1$

$e_g = d_{z^2}, d_{x^2-y^2}$

$t_{2g} = d_{xy}, d_{xz}, d_{yz}$

$(d_{z^2})^1(d_{xz})^1$ $(d_{z^2})^1(d_{xy})^1$



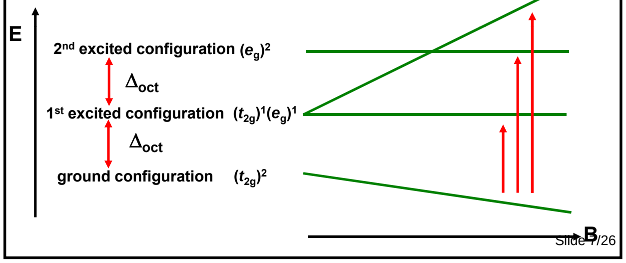
Electronic Spectra of d^2 Ions

- The 6 arrangements in the 1st excited configuration can be grouped into two sets – those with low and with high interelectron repulsion

High	Low
$(d_{z^2})^1(d_{xz})^1$	$(d_{x^2-y^2})^1(d_{xz})^1$
$(d_{z^2})^1(d_{yz})^1$	$(d_{x^2-y^2})^1(d_{yz})^1$
$(d_{x^2-y^2})^1(d_{xy})^1$	$(d_{z^2})^1(d_{xy})^1$

Electronic Spectra of d^2 Ions

- The size of the interelectron repulsion is measured with the **Racah parameter, B**
- The interelectron repulsion effect is **large** – it is of similar importance to the ligand-field splitting
- The splitting of the 1st excited configuration into 2 sets leads to there being **3 d-d transitions**

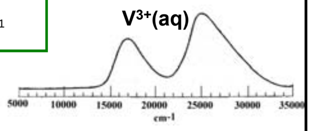


Electronic Spectra of d^2 Ions

- The energy of the transitions depends on **both the ligand-field splitting parameter, Δ_{oct}, and the interelectron repulsion parameter, B**
- The calculation is best performed on a spreadsheet or computer
  - For V^{3+}(aq), only two transitions are actually observed in the visible spectrum – the third is hidden by charge transfer bands*

➢ v_1 ~ 17800 cm^{-1}, v_2 ~ 25700 cm^{-1}

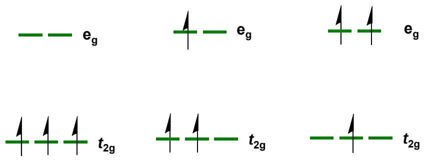
➢ Δ_{oct} ~ 19200 cm^{-1}, B ~ 620 cm^{-1}



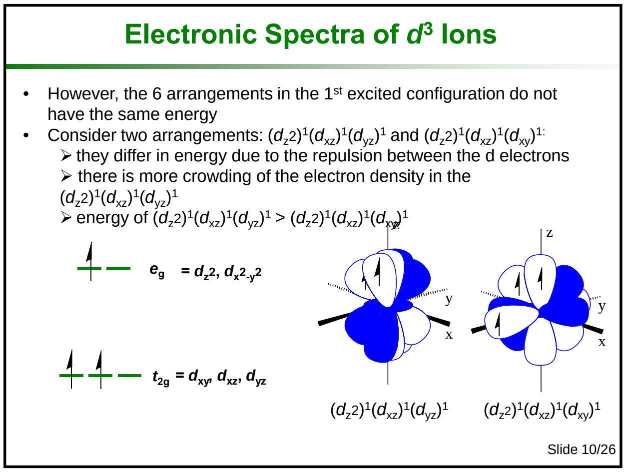
* see lecture 3

Electronic Spectra of d^3 Ions

- Similar arguments can be applied for d^3:
- At first glance, it appears that a d^3 octahedral complex can also undergo **two** electronic transitions



	ground configuration	1st excited configuration	2nd excited configuration
energy:	0	Δ_{oct}	$2\Delta_{oct}$
number of arrangements:	1	6	3



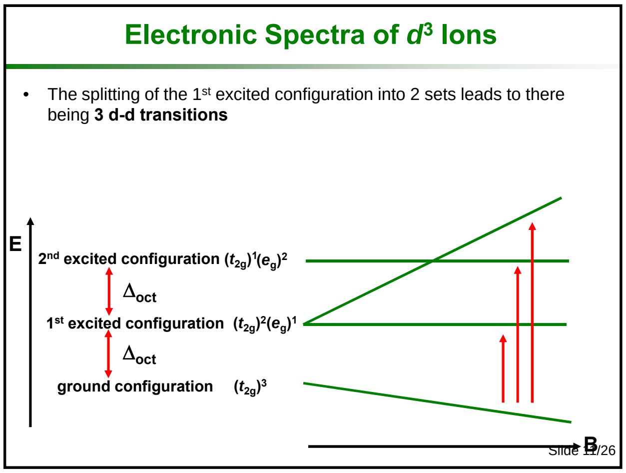
Electronic Spectra of d^3 Ions

- However, the 6 arrangements in the 1st excited configuration do not have the same energy
- Consider two arrangements: $(d_{z}2)^1(d_{xz})^1(d_{yz})^1$ and $(d_{z}2)^1(d_{xz})^1(d_{xy})^1$:
    - ➢ they differ in energy due to the repulsion between the d electrons
    - ➢ there is more crowding of the electron density in the $(d_{z}2)^1(d_{xz})^1(d_{yz})^1$
    - ➢ energy of $(d_{z}2)^1(d_{xz})^1(d_{yz})^1 > (d_{z}2)^1(d_{xz})^1(d_{xy})^1$

$e_g = d_{z^2}, d_{x^2-y^2}$

$t_{2g} = d_{xy}, d_{xz}, d_{yz}$

$(d_{z}2)^1(d_{xz})^1(d_{yz})^1$ $(d_{z}2)^1(d_{xz})^1(d_{xy})^1$



Electronic Spectra of d^3 Ions

- The splitting of the 1st excited configuration into 2 sets leads to there being **3 d-d transitions**

E

2nd excited configuration $(t_{2g})^1(e_g)^2$

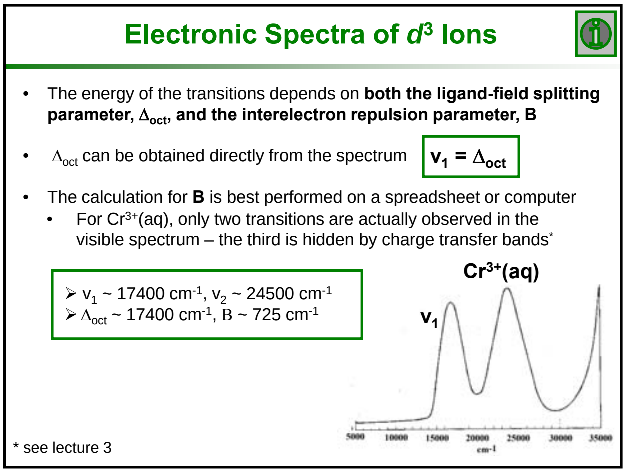
Δ_{oct}

1st excited configuration $(t_{2g})^2(e_g)^1$

Δ_{oct}

ground configuration $(t_{2g})^3$

B



Electronic Spectra of d^3 Ions

- The energy of the transitions depends on **both the ligand-field splitting parameter, Δ_{oct}, and the interelectron repulsion parameter, B**
- Δ_{oct} can be obtained directly from the spectrum **$\nu_1 = \Delta_{oct}$**
- The calculation for **B** is best performed on a spreadsheet or computer
    - For Cr^{3+}(aq), only two transitions are actually observed in the visible spectrum – the third is hidden by charge transfer bands*

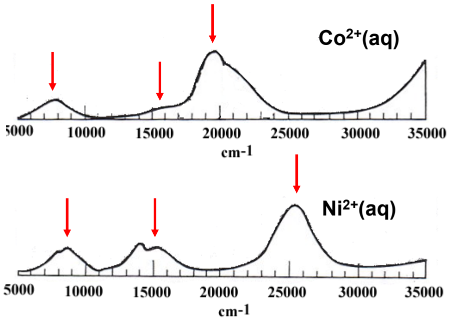
➢ ν_1 ~ 17400 cm^{-1}, ν_2 ~ 24500 cm^{-1}
➢ Δ_{oct} ~ 17400 cm^{-1}, B ~ 725 cm^{-1}

Cr^{3+}(aq)

* see lecture 3

Electronic Spectra of *d*^{7} and *d*^{8} Ions

- Similar arguments can be applied for d^7:and d^8 ocahedral ions
- In both cases, three transitions are predicted



Calculation of Δ_{oct} and B

- To calculate Δ_{oct} and B from the spectrum:

Octahedral *d*^{1}, *d*^{4}, *d*^{6} and *d*^{9}:
1 band energy = Δ_{oct}

Octahedral *d*^{2}:
3 bands Δ_{oct} and B from calculation

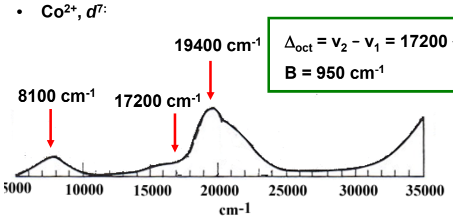
Octahedral *d*^{7}:
3 bands $\Delta_{oct} = v_2 - v_1$ B from calculation

Octahedral *d*^{3} and *d*^{8}:
3 bands $v_1 = \Delta_{oct}$ B from calculation

Calculation of Δ_{oct} and B

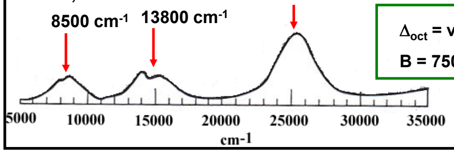
- **Co^{2+}, *d*^{7}:**

$\Delta_{oct} = v_2 - v_1 = 17200 - 8100 = 9100$ cm^{-1}
B = 950 cm^{-1}



- **Ni^{2+}, *d*^{8}:**

$\Delta_{oct} = v_1 = 8500$ cm^{-1}
B = 750 cm^{-1}



Spectrochemical Series

- The value of Δ_{oct} obtained from the spectra of complexes is found to depend on the metal ion and the ligand
- The position of a ligand in the series depends on its σ and π-bonding

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O$

weak field – poor σ-donors, π-donors

$< NCS^- < CH_3CN < NH_3 <$ en

Intermediate field – good σ-donors, π-neutral

< bipy < phen $< -NO_2^- < PPh_3 < CN^- <$ CO

strong field – good σ-donors, π-acceptors

Nephelauxetic Effect and Series

- The value of **B**, the interelectron repulsion parameter, is found to be *smaller* in complexes than in free atoms and ions
- Covalent overlap with the ligand orbitals, delocalizes the d-electron density reducing the repulsion

B (complex) < B (free ion)

Nephelauxetic or 'cloud expanding' effect

- Reduction in B is related to covalency of M-L bond:

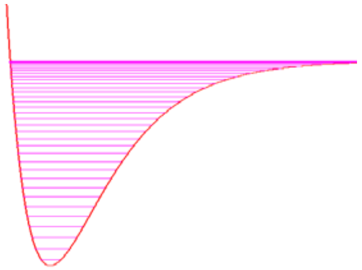
$F^- > H_2O >$ urea $> NH_3 > NH_2CH_2CH_2NH_2$

$> OCCO_2^{2-} = CO_3^{2-} > NCS^- > Cl^- = CN^- > Br^-$

$> N^{3-} > I^- > S^{2-}$

Band Widths

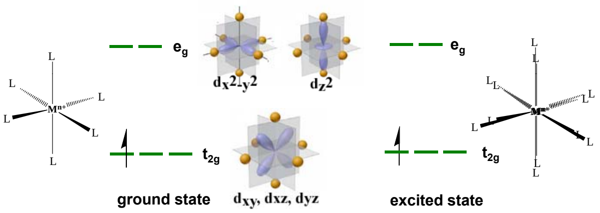
- Each electronic state has a set of associated vibrational energy levels
- These levels get closer together as the energy increases
- When the electronic excitation occurs, the vibrational energy can also change – the shape and width of the band depends on the change in vibrational energy



See CHEM2401

Bond Lengths in Excited States

- In the electronic transitions, the electrons are excited from t_{2g} to e_g
- The excited state has more electrons in e_g: antibonding levels (in d-orbitals which repel the ligands)



•The bond lengths in the excited state are almost always ***longer***

The Franck-Condon Principle

- However, the electronic transition takes place *very* rapidly – much faster than the nuclei can respond:

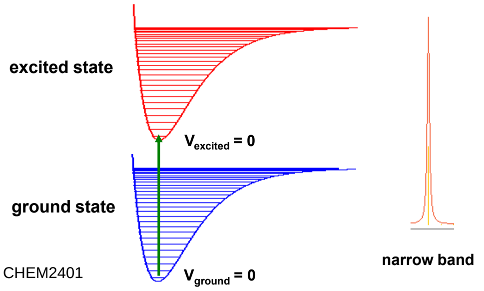
- The excitation occurs 'vertically' from the lowest vibrational level in the ground state, without change in the bond length
- The excited state is formed with the geometry of the ground state: **the Franck-Condon principle**
- After excitation, it can relax to the true bond length of the excited state

- Depending on the bond lengths in the ground and excited states, there are two common possibilites:

See CHEM2401

The Franck-Condon Principle

- If the equilibrium bond length in the excited state is ***the same*** as in the ground state,
  - the vertical transition hits the lowest vibrational level in the excited state and a narrow band results



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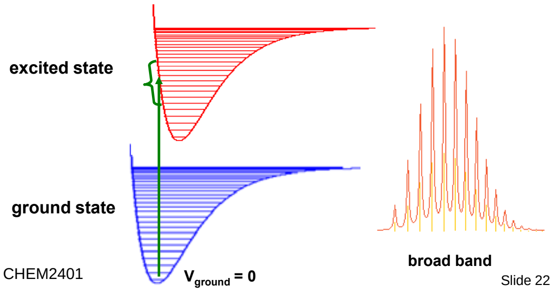
The Franck-Condon Principle

- If the equilibrium bond length in the excited state is ***longer*** than in the ground state,
  - ➢ the vertical transition hits the a number of vibrational level in the excited state and a broad band results



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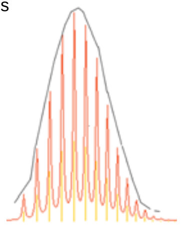
Shapes of d-d Bands

- From slide 19, most d-d transitions lead to excited states with longer bonds than in the ground state
  - ➢ usually the bands are broad
  - ➢ sometimes the separate vibrational lines can be seen, usually the bands are featureless



resolved vibrational structure

broad band

See CHEM2401

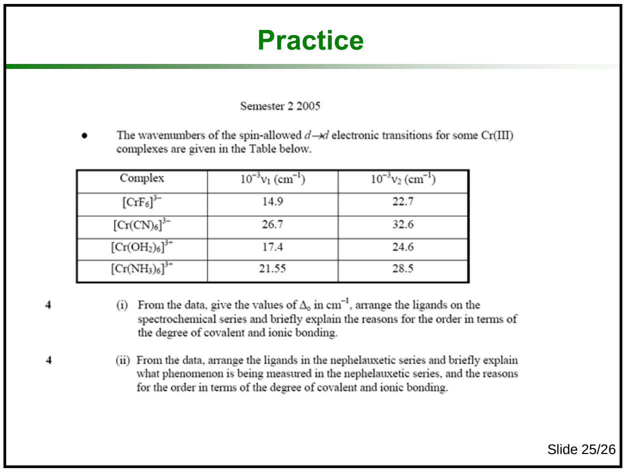
Summary

By now you should be able to....

- Show the effect of repulsion between the *d*-electrons on the spectrum of octahedral d^2, d^3, d^7 and d^8
- Explain the origin of the presence of 3 bands in the spectrum of these ions
- Obtain Doct from the spectrum of octahedral d^1, d^3, high spin d^4, d^6, d^7, d^8 and d^9 complexes
- Explain why exciting *d*-electrons usually increases the bond length
- Explain why this leads to broad bands in spectra

Next lecture

- Selection rules



Practice

Semester 2 2005

- The wavenumbers of the spin-allowed *d*→*d* electronic transitions for some Cr(III) complexes are given in the Table below.

Complex	$10^{-3}\nu_1$ (cm^{-1})	$10^{-3}\nu_2$ (cm^{-1})
$[CrF_6]^{3-}$	14.9	22.7
$[Cr(CN)_6]^{3-}$	26.7	32.6
$[Cr(OH_2)_6]^{3+}$	17.4	24.6
$[Cr(NH_3)_6]^{3+}$	21.55	28.5

4 (i) From the data, give the values of Δ_o in cm^{-1}, arrange the ligands on the spectrochemical series and briefly explain the reasons for the order in terms of the degree of covalent and ionic bonding.

4 (ii) From the data, arrange the ligands in the nephelauxetic series and briefly explain what phenomenon is being measured in the nephelauxetic series, and the reasons for the order in terms of the degree of covalent and ionic bonding.