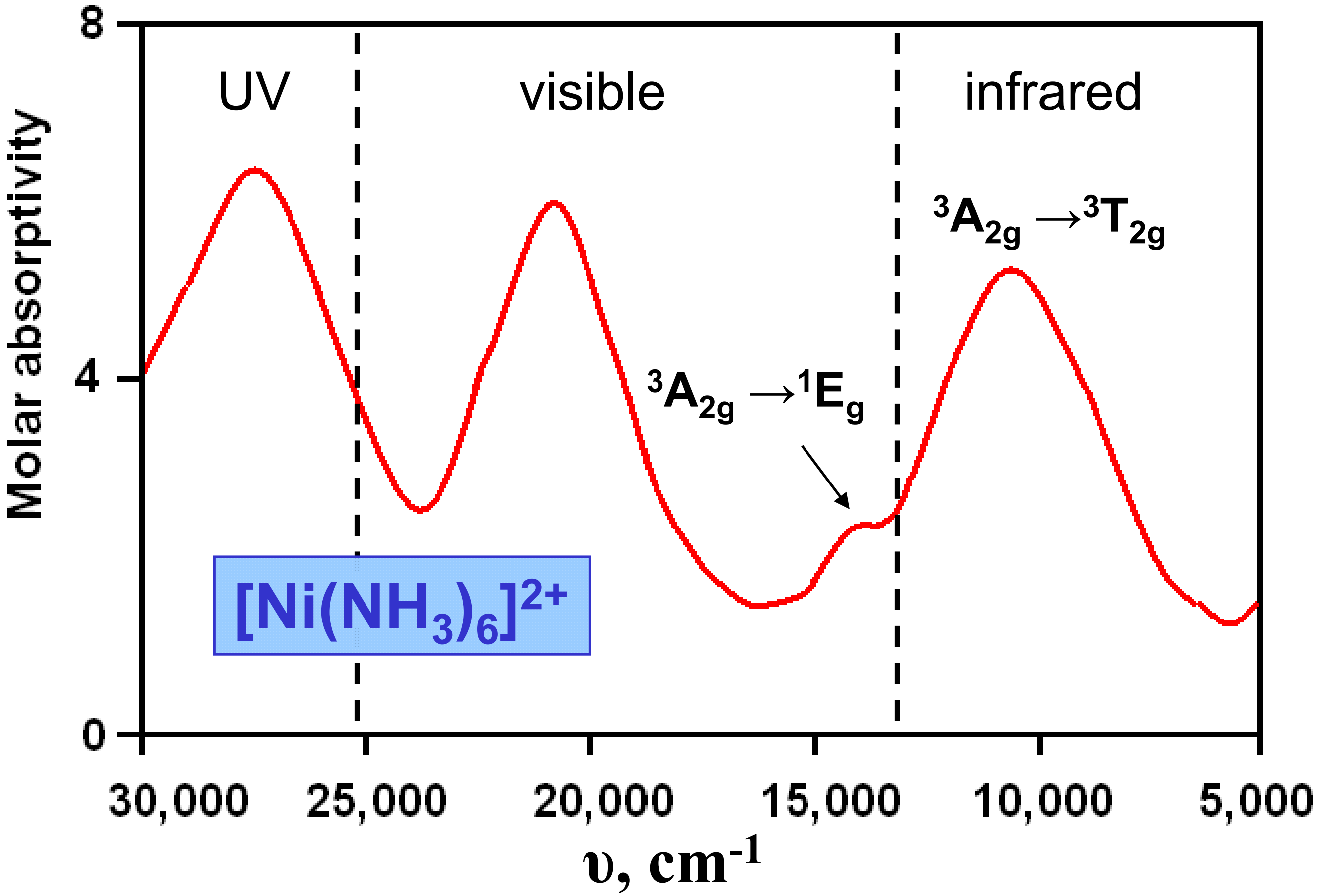
# ELECTRONIC SPECTRA

**Dr. G. VIGNESH**
**Assistant Professor**
**St.Xavier's College(Autonomous)**
**Palayamkottai**

# d-d spectra :


8
4
0
Molar absorptivity
UV
visible
infrared
$^3A_{2g} \rightarrow {}^3T_{2g}$
$^3A_{2g} \rightarrow {}^1E_g$
$[Ni(NH_3)_6]^{2+}$
30,000
25,000
20,000
15,000
10,000
5,000
υ, $cm^{-1}$

# The electronic spectra of d-block complexes:

The features of electronic spectra that we need to be able to master are:

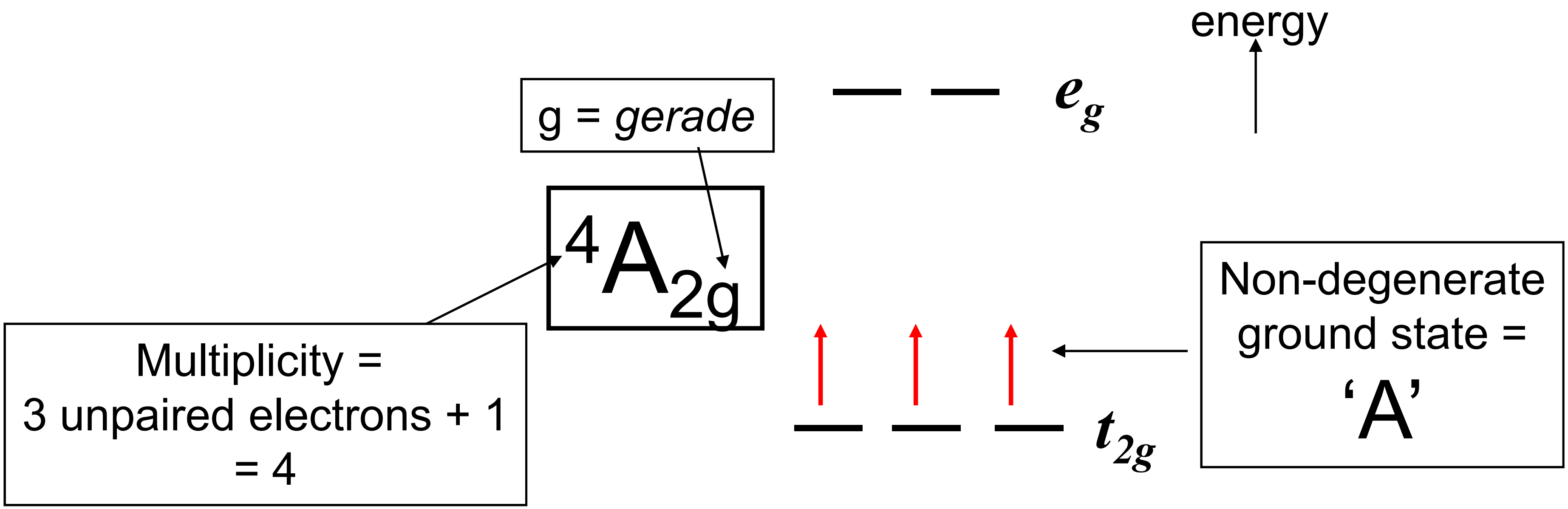
1) naming of electronic states and d-d transitions, e.g.$^3A_{2g}$, or $^3A_{2g} \rightarrow {}^1E_g$

2) Explanation of relative intensities of bands in the spectra of complexes of d-block metal ions. (The Laporte and spin selection rules)

3) calculation of the crystal field splitting parameters from energies of d-d bands

# Naming of electronic states:

In names of electronic states, e.g. $^4A_{2g}$, the labels A, E, and T, stand for non-degenerate, doubly degenerate, and triply degenerate, while the numeric superscript stands for the multiplicity of the state, which is the number of unpaired electrons plus one. Note that the electronic states can be ground states (states of lowest energy) or excited states:



energy

$e_g$

g = *gerade*

$^4A_{2g}$

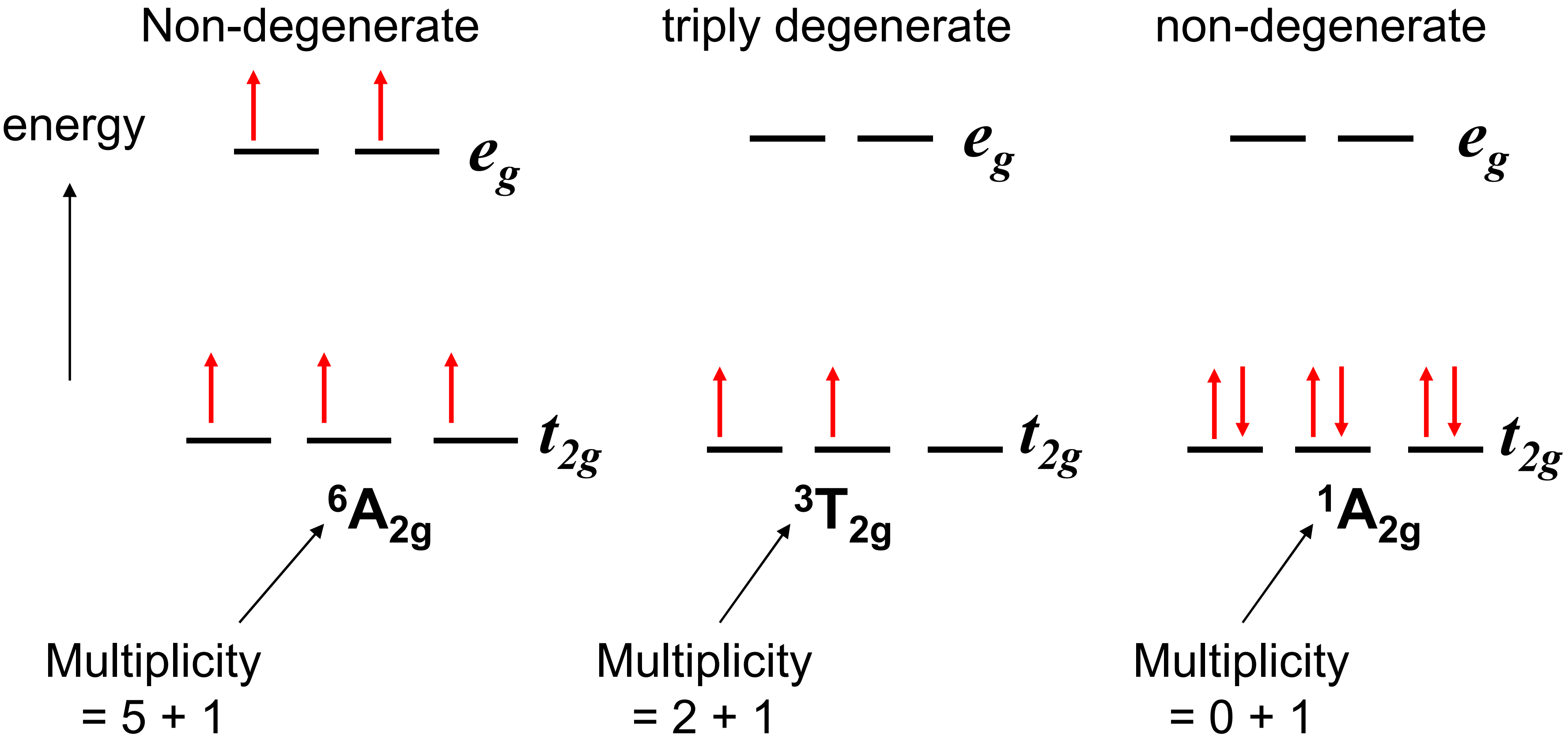
Multiplicity =
3 unpaired electrons + 1
= 4

$t_{2g}$

Non-degenerate
ground state =
'A'

# Naming of electronic states (contd.):

NOTE: In determining degeneracy, one can re-arrange the electrons, but the **number of unpaired electrons must stay the same**, and the **number of electrons in each of the $e_g$ and $t_{2g}$ levels must stay the same**.



energy

Non-degenerate

$e_g$

$t_{2g}$

$^6A_{2g}$

Multiplicity = 5 + 1

triply degenerate

$e_g$

$t_{2g}$

$^3T_{2g}$

Multiplicity = 2 + 1

non-degenerate

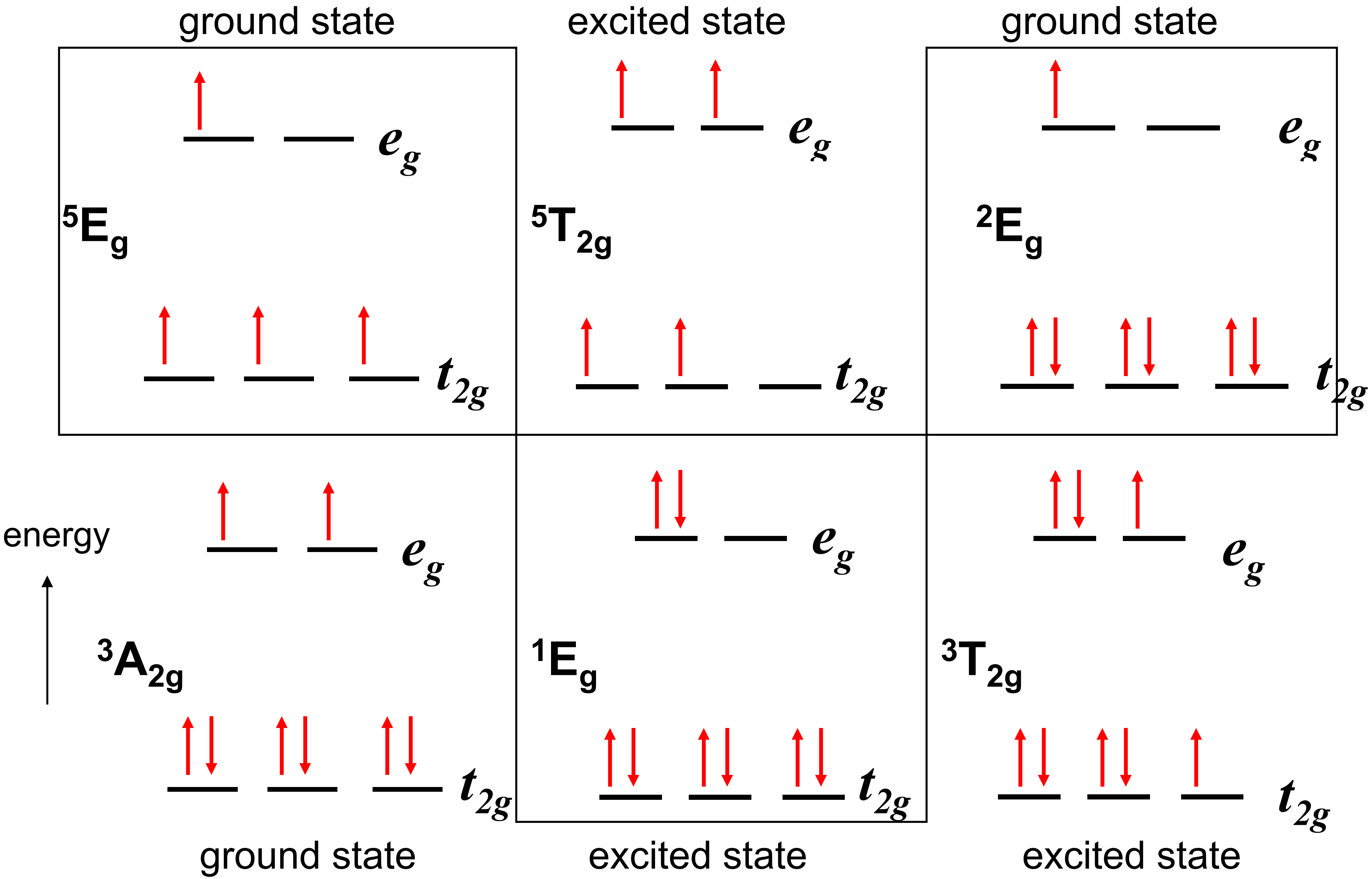
$e_g$

$t_{2g}$

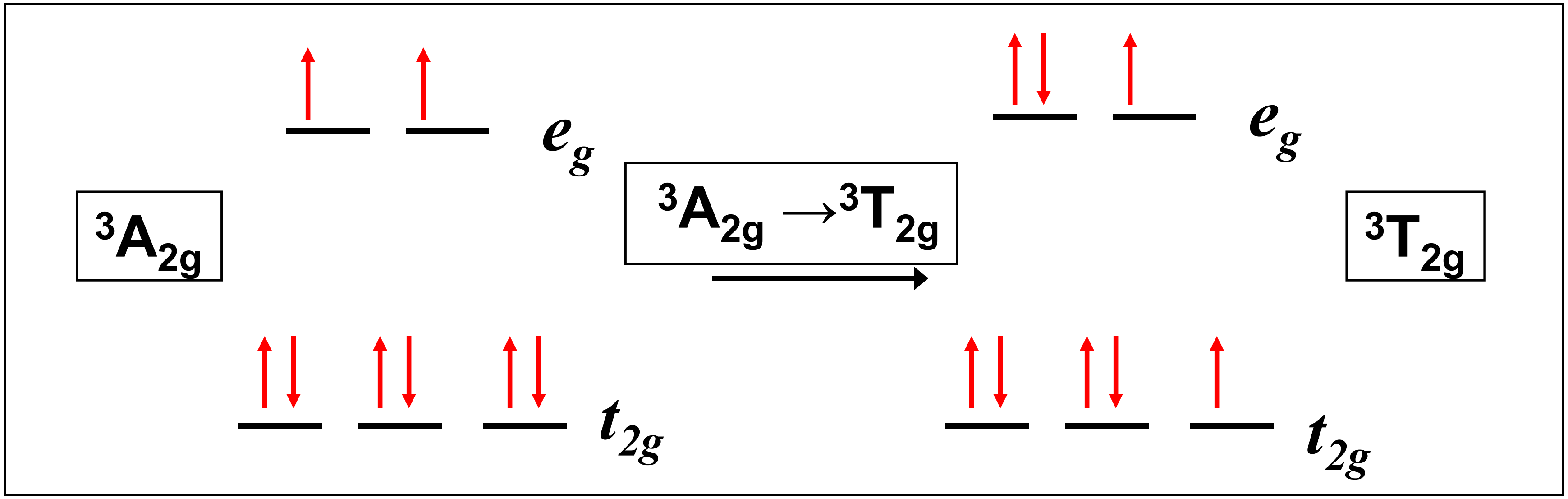
$^1A_{2g}$

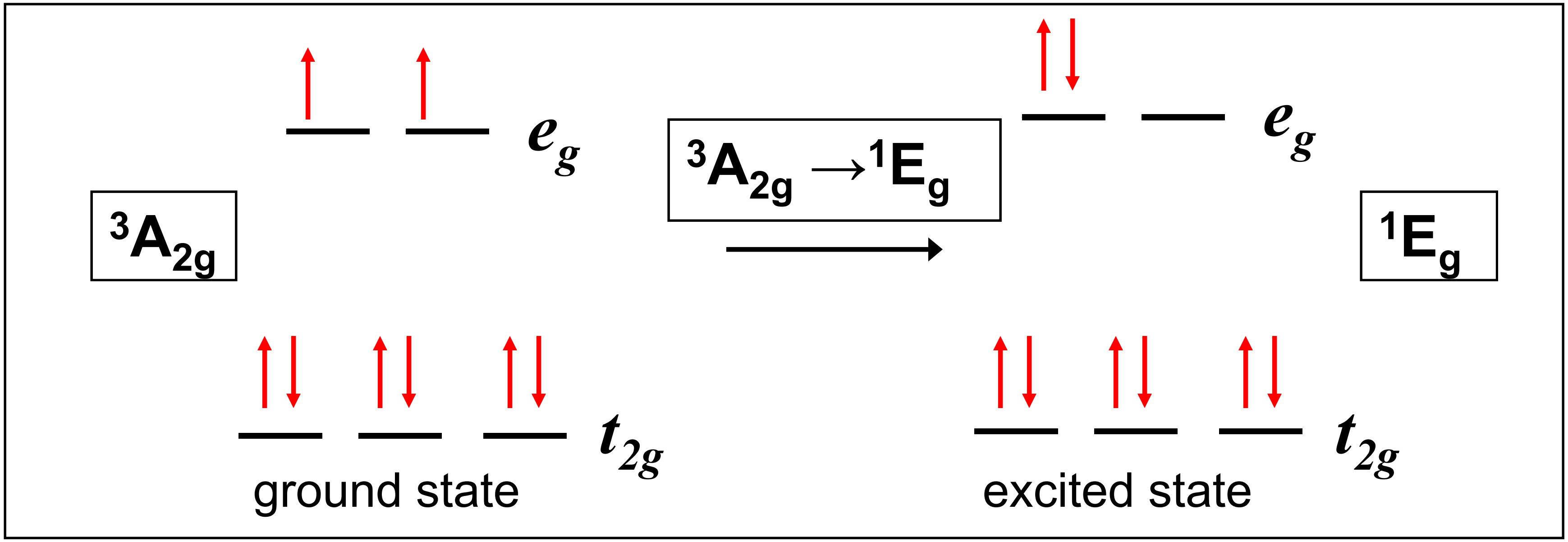
Multiplicity = 0 + 1

# Naming of electronic states (contd.):



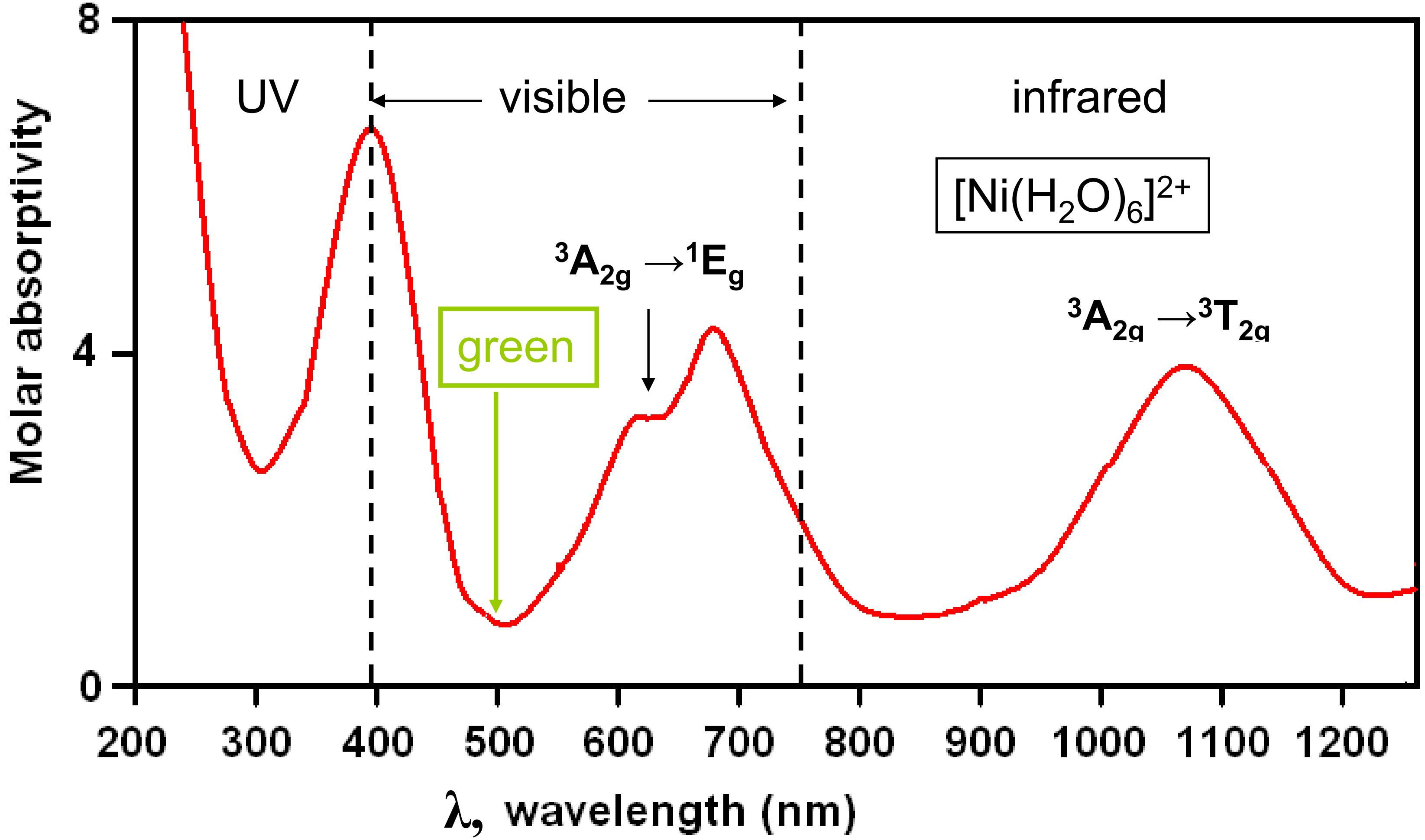
# Electronic transitions:





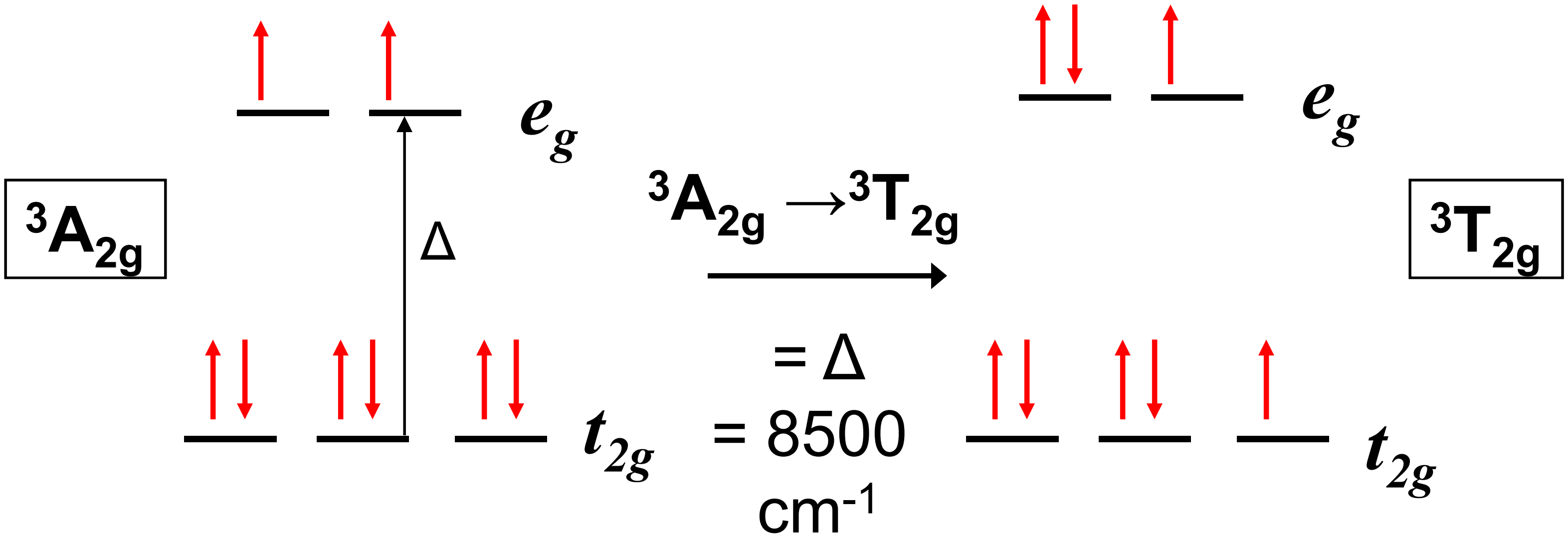
# The electronic spectrum of $[Ni(H_2O)_6]^{2+}$:

The complex looks green, because it absorbs only weakly at 500 nm, the wavelength of green light.



# The electronic spectrum of $[Ni(H_2O)_6]^{2+}$:

On the previous slide we saw the two bands due to the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^1E_g$ transitions. The band at $\lambda = 1180$ nm which is the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition shown below, corresponds to $\Delta$ for the complex. This is usually expressed as $\Delta$ in $cm^{-1} = (1/\lambda(nm)) \times 10^7 = 8500\ cm^{-1}$.



$\boxed{{}^3A_{2g}}$

$e_g$

$\Delta$

$t_{2g}$

${}^3A_{2g} \rightarrow {}^3T_{2g}$

$= \Delta$

$= 8500$ $cm^{-1}$

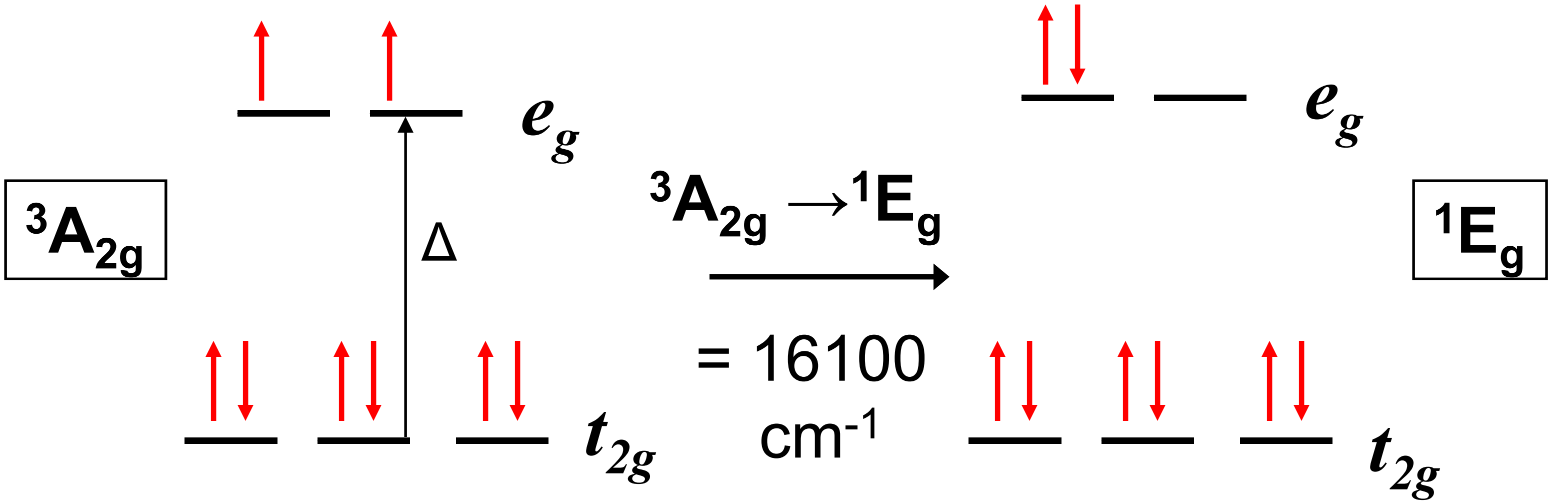
$e_g$

$t_{2g}$

$\boxed{{}^3T_{2g}}$

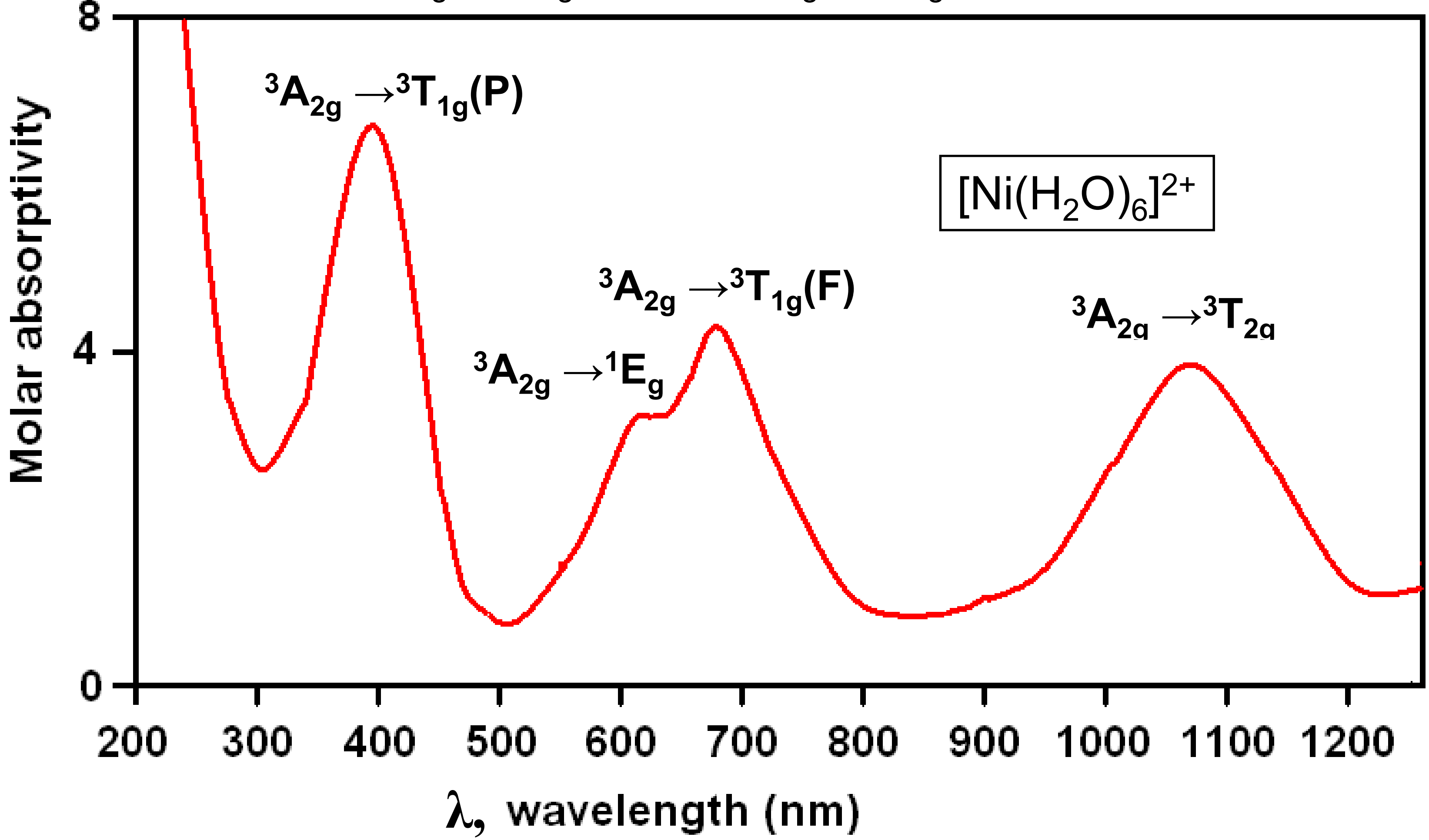
# The electronic spectrum of $[Ni(H_2O)_6]^{2+}$:

Note the weak band at 620 nm that corresponds to the $^3A_{2g} \rightarrow {}^1E_g$ transition. The electron that is excited moves within the $e_g$ level, so that the energy does not involve Δ, but depends on the value of P, the spin-pairing energy. The point of interest is why this band is so weak, as discussed on the next slide.



# The electronic spectrum of $[Ni(H_2O)_6]^{2+}$:

The two peaks at higher energy resemble the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition, but involve differences in magnetic quantum numbers of the d-orbitals, and are labeled as $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ to reflect this:



# The Intensity of bands in complexes of d-block ions:

The three types of bands present in e.g. $[Ni(H_2O)_6]^{2+}$ are:

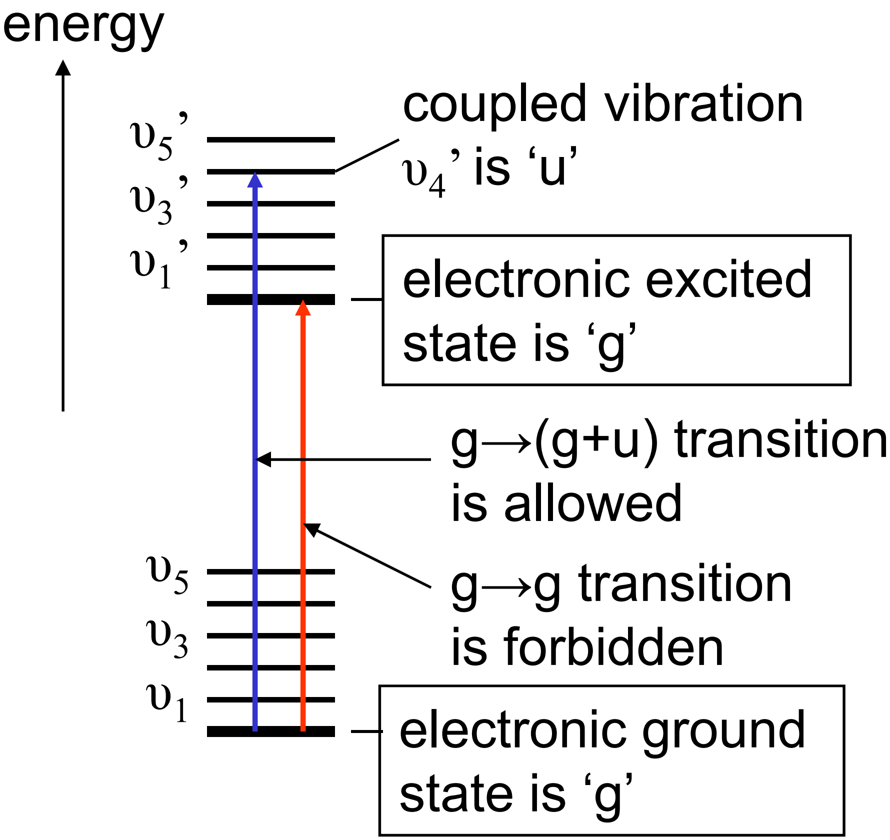
1) Laporte-allowed plus spin allowed charge transfer bands of very high intensity

2) Laporte-forbidden plus spin-allowed d→d transitions (e.g. $^3A_{2g} \rightarrow {}^3T_{2g}$) of moderate intensity

3) Laporte forbidden plus spin-forbidden d→d transitions ($^3A_{2g} \rightarrow {}^1E_g$) of very low intensity.

# Vibronic coupling:

Electronic transitions are coupled to vibrations of various symmetries, and the latter may impart opposite parity to an electronic state and so help overcome the Laporte selection rule:



coupled vibration $\upsilon_4'$ is 'u'

electronic excited state is 'g'

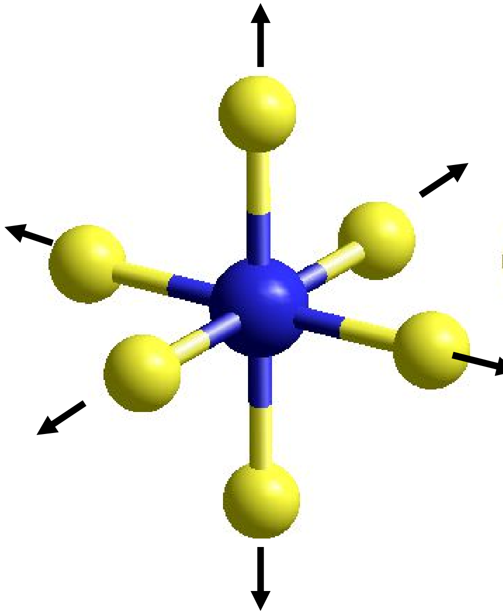
g→(g+u) transition is allowed

g→g transition is forbidden

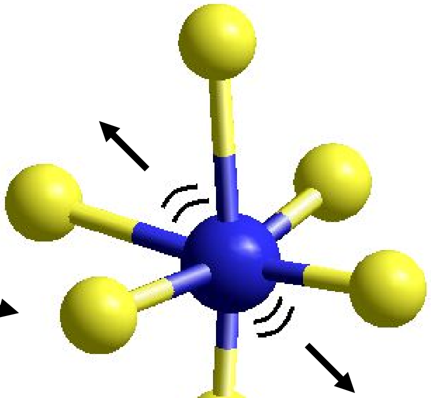
electronic ground state is 'g'

Electronic transitions, as seen in the spectra of complexes of Ni(II) shown above, are always very broad because they are coupled to vibrations. The transitions are thus from ground states plus several vibrational states to excited states plus several vibrational states ($\upsilon_1$, $\upsilon_2$, $\upsilon_3$), so the 'electronic' band is actually a composite of electronic plus vibrational transitions.

# Symmetry of vibrational states, and their coupling to electronic states:

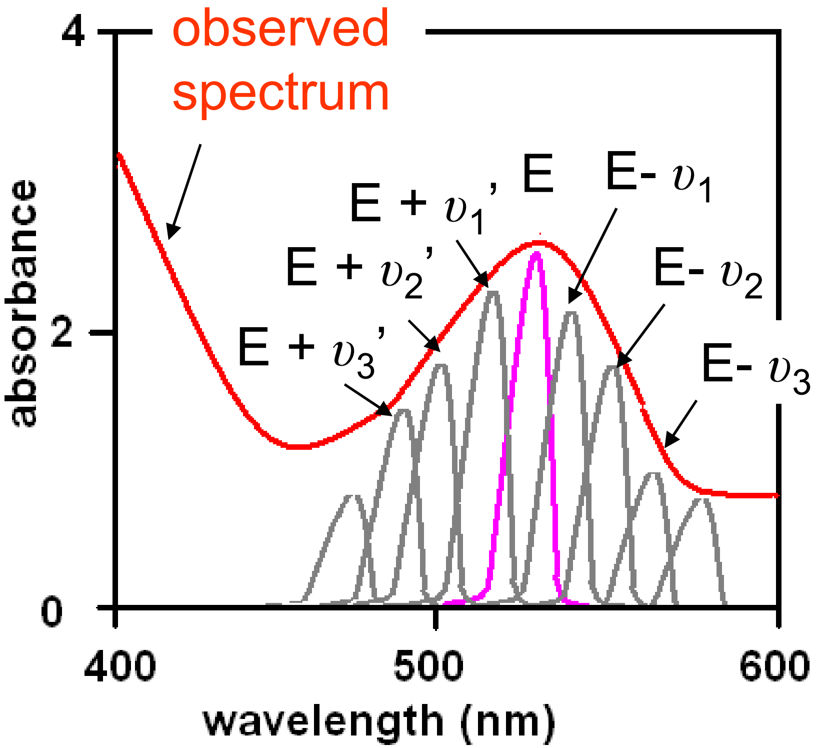


$A_{1g}$
symmetry
vibration



$T_{1u}$
symmetry
vibration

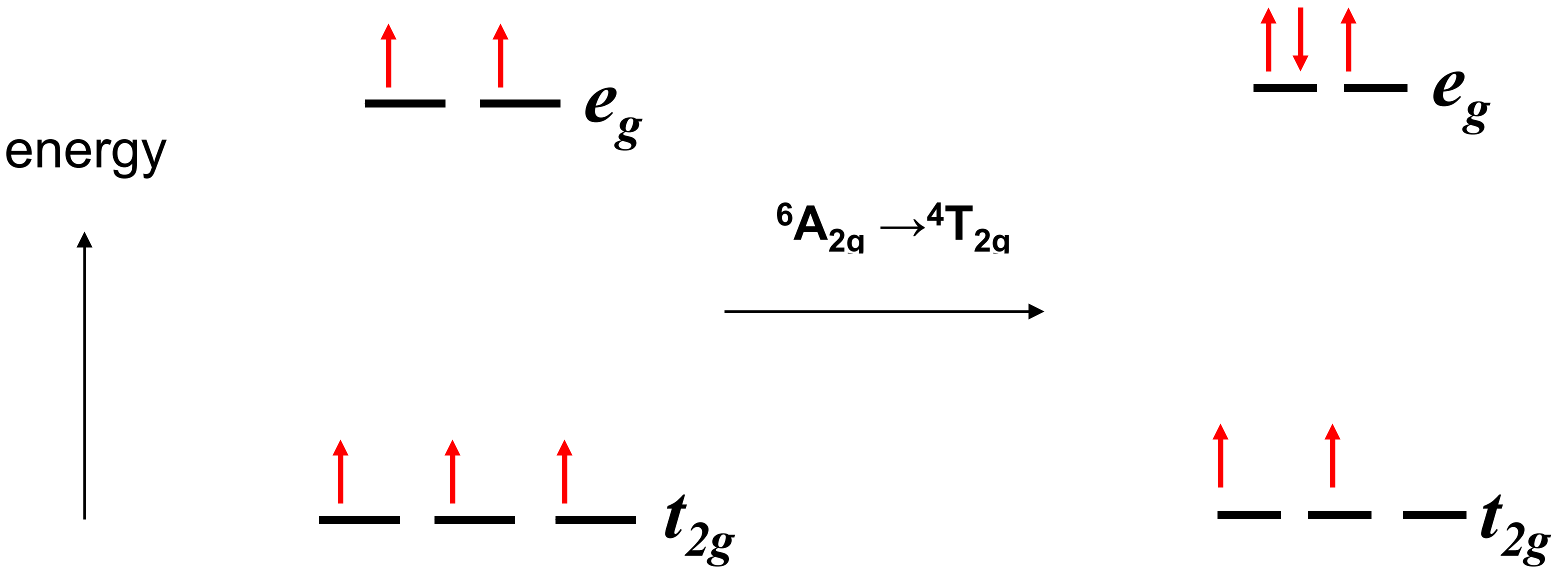
(symbols have same meaning for vibrations: A = non-degenerate, T = triply degenerate, g = gerade, u = ungerade, etc.)



The band one sees in the UV-visible spectrum is the sum of bands due to transitions to coupled electronic (E) and vibrational energy levels ($\upsilon_1$, $\upsilon_2$, $\upsilon_3$)

# The spectra of high-spin $d^5$ ions:

For high-spin $d^5$ ions all possible d-d transitions are spin-forbidden. As a result, the bands in spectra of high-spin complexes of Mn(II) and Fe(III) are very weak, and the compounds are nearly colorless. Below is shown a d-d transition for a high-spin $d^5$ ion, showing that it is spin-forbidden.

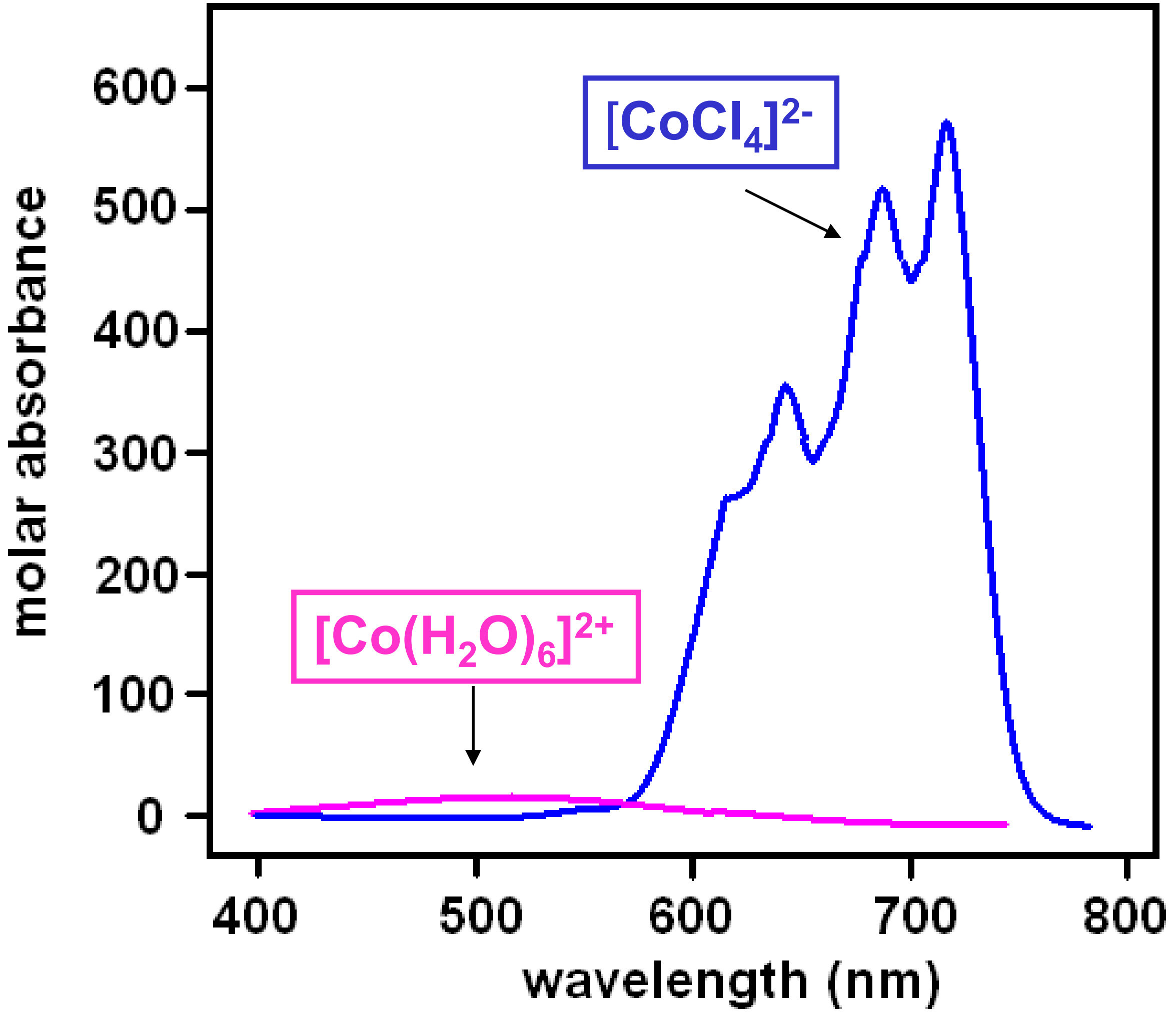


Complexes of Gd(III) are colorless, while those of other lanthanide M(III) ions are colored, except for La(III) and Lu(III). Why is this?

# The spectra of complexes of tetrahedral metal ions:

As we have seen, a tetrahedron has no center of symmetry, and so orbitals in such symmetry cannot be *gerade*. Hence the d-levels in a tetrahedral complex are $e$ and $t_2$, with no '*g*' for *gerade*. This largely overcomes the Laporte selection rules, so that tetrahedral complexes tend to be very intense in color. Thus, we see that dissolving $CoCl_2$ in water produces a pale pink solution of $[Co(H_2O)_6]^{2+}$, but in alcohol tetrahedral $[CoCl_2(CH_3CH_2OH)_2]$ forms, which is a very intense blue color. This remarkable difference in the spectra of octahedral and tetrahedral complexes is seen on the next slide:

# The spectra of octahedral $[Co(H_2O)_6]^{2+}$ and tetrahedral $[CoCl_4]^{2-}$ ions:



The spectra at left show the very intense d-d bands in the blue tetrahedral complex $[CoCl_4]^{2-}$, as compared with the much weaker band in the pink octahedral complex $[Co(H_2O)_6]^{2+}$. This difference arises because the $T_d$ complex has no center of symmetry, helping to overcome the $g \not\rightarrow g$ Laporte selection rule.