With the aid of a labelled diagram, briefly describe how the operation of the Jahn-Teller effect may give rise to an axially compressed tetragonal geometry in the complexes of a d⁹ metal ion.

Tetragonal compression of an octahedron corresponds to shortening two, trans related metal-ligand bonds. This has the effect of increasing the repulsion experienced by an electron in a d₅z² orbital, as its electron density is directed towards these shortened bonds. There is also an increase in repulsion felt by electrons in the dₓz and dᵧz orbitals although the effect is much smaller.

The d-orbital splitting diagram is therefore:

\[
\begin{align*}
\Delta_{\text{oct}} & \quad \text{octahedron} & \quad \text{tetragonally compressed} \\
& \quad \text{octahedron} & \\
\end{align*}
\]

Note that, unless the distortion is very large, Δₒct >> δ₁ > δ₂. (Although the dₓz and dᵧz₂ orbitals are not directly affected by the compression, their energies are shown as shifting up. This is simply to keep the average splitting as zero to maintain zero LFSE for d⁹, d⁵ and d¹⁰).

The LFSE in the octahedral complex is:

\[
\text{LFSE} = 6 \times (-0.4 \Delta_{\text{oct}}) + 3 \times (+0.6 \Delta_{\text{oct}}) = -0.6 \Delta_{\text{oct}}.
\]

The LFSE in the distorted complex is:

\[
\text{LFSE} = 4 \times (-0.4 \Delta_{\text{oct}} - \frac{1}{3} \delta_2) + 2 \times (-0.4 \Delta_{\text{oct}} + \frac{1}{2} \delta_2) + 2 \times (+0.6 \Delta_{\text{oct}} - \frac{1}{2} \delta_1) + 1 \times (+0.6 \Delta_{\text{oct}} + \frac{1}{2} \delta_1) \\
= -0.6 \Delta_{\text{oct}} - \frac{1}{2} \delta_1
\]

As far as the ligand-field part of the overall energy is concerned, the complex is more stable in tetragonally distorted geometry than it is in the octahedral geometry.
Consider the high-spin complexes, \([\text{Mn(OH}_2\text{)}_6]^{3+}\) and \([\text{Mn(OH}_2\text{)}_6]^{2+}\). The lowest energy d-d band in the spectrum of the \([\text{Mn(OH}_2\text{)}_6]^{3+}\) complex is at 476 nm.

**Relevant constants and conversions:** \(c = \text{speed of light} = 3.00 \times 10^8 \text{ m s}^{-1}\); \(h = \text{Planck’s constant} = 6.63 \times 10^{-34} \text{ J s}\); \(N_A = \text{Avogadro’s constant} = 6.02 \times 10^{23} \text{ mol}^{-1}\); Faraday’s constant = 96,485 C mol\(^{-1}\).

**(i)** Give the d-electron configuration for each of the Mn centres; and draw appropriate d-orbital energy diagrams and illustrate the distributions of the d electrons within them.

The complexes contain octahedrally coordinated Mn\(^{2+}\)(aq) (d\(^5\)) and Mn\(^{3+}\)(aq) d\(^4\). As water is a fairly weak-field ligand, both complexes will be high spin.

\[
\begin{align*}
\Delta_{\text{oct}} &\quad \begin{array}{c}
\text{Mn}^{2+} \\
\text{O}_2
\end{array} &\quad \begin{array}{c}
\text{eg} \\
d_{x^2} & d_{x^2-y^2} \\
\Delta_{\text{oct}} &\quad \begin{array}{c}
\text{Mn}^{3+} \\
\text{O}_2
\end{array} &\quad \begin{array}{c}
\text{eg} \\
d_{x^2} & d_{x^2-y^2}
\end{array} \\
\begin{array}{c}
d_{xz} \quad d_{yz} \quad d_{xy} \\
\text{t}_{2g}
\end{array} &\quad \begin{array}{c}
d_{xz} \quad d_{yz} \quad d_{xy} \\
\text{t}_{2g}
\end{array}
\end{align*}
\]

The higher charge on Mn\(^{3+}\) leads to shorter Mn-O bond lengths and a larger value of \(\Delta_{\text{oct}}\).

**(ii)** Explain which of the two complexes has Jahn-Teller distortions and how this will effect the electronic absorption spectrum of the complex with such a distortion.

The octahedrally coordinated Mn\(^{3+}\)(aq) ion has a degenerate ground state, as eg electron can occupy either of the orbitals. It is therefore susceptible to a Jahn-Teller distortion.

The octahedral complex has one spin-allowed transition, \((t_{2g})^3(\text{eg})^3 \rightarrow (t_{2g})^2(\text{eg})^2\). The distortion will provide a small splitting of the t\(_{2g}\) orbitals and a large splitting of the eg orbitals (see above). Assuming an tetragonally compressed distortion, three transitions are possible (see figure overleaf). As \(\Delta_{\text{oct}} \gg \delta_1 > \delta_2\), the transitions are in the order shown.

The first excitation requires energy equal to \(\delta_1\). As \(\delta_1\) is quite small, this is likely to be in infrared and the transition is likely to be invisible underneath the more intense vibrational bands.
The second and third transitions have energies of approximately $\Delta_{\text{oct}}$ and differ by an amount equal to $\delta_2$. As $\delta_2$ is very small, it is unlikely that two separate bands will be observed. In fact, the size of $\delta_2$ means that a single band will result, without any evidence of there being two transitions.

(iii) **Calculate the Ligand-Field Stabilization Energy (LFSE) in kJ mol$^{-1}$ for each of the above complexes.**

The LFSE for the d$^2$ ion is zero.

As the t$_{2g}$ orbitals are stabilized by 0.4 $\Delta_{\text{oct}}$ and the e$_g$ orbitals are destabilized by 0.6 $\Delta_{\text{oct}}$ by the ligand-field, the LFSE for the d$^4$ ion is:

$$\text{LFSE} = 3 \times (-0.4 \Delta_{\text{oct}}) + 1 \times (0.6 \Delta_{\text{oct}}) = -0.6 \Delta_{\text{oct}}.$$  

As $E = \frac{hc}{\lambda}$, 476 nm corresponds to a energy in J molecule$^{-1}$ of:

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34}) \times (3.00 \times 10^9)}{(476 \times 10^{-9})} = 4.18 \times 10^{-19} \text{ J molecule}^{-1}.$$  

Or,

$$E = (4.18 \times 10^{-19}) \times (6.02 \times 10^{23}) = 252000 \text{ J mol}^{-1} = 252 \text{ kJ mol}^{-1}.$$  

For a d$^4$ ion, the energy of the single ligand-field transition corresponds to $\Delta_{\text{oct}}$, so $\Delta_{\text{oct}} = 252$ kJ mol$^{-1}$ and:

$$\text{LFSE} = -0.6 \times \Delta_{\text{oct}} = (-0.6 \times 252) = -151 \text{ kJ mol}^{-1}.$$  

*Note that for the d$^1$ ion considered in lecture 1, the Jahn-Teller distortion lead to two overlapping bands. This was due to the excitation of an electron to the two split e$_g$ orbitals giving an energy difference of $\delta_1$. In the d$^5$ case, the two transitions are to the same upper level and are only split by $\delta_2$. 