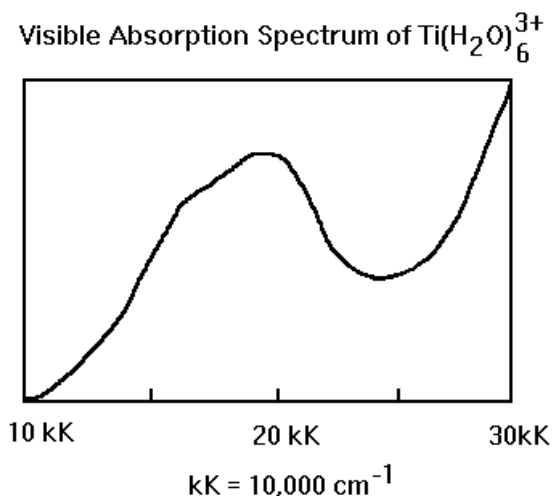
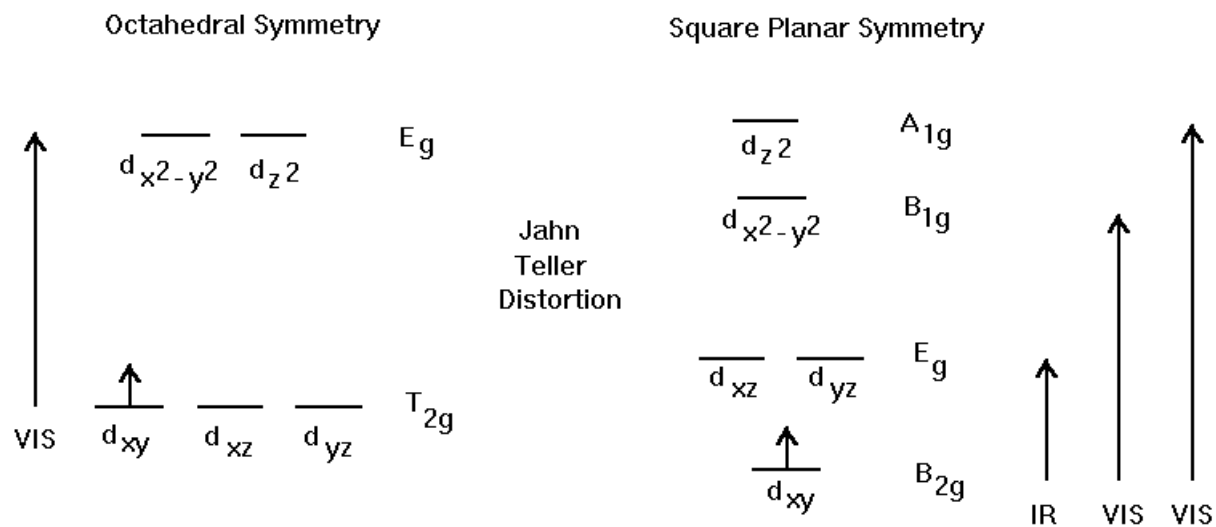


Electronic Spectrum of a Transition Metal Complex

This exercise has to do with the interpretation of the visible spectrum $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ which is shown below.



The analysis will begin by assuming that $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ has octahedral symmetry. This assumption accounts for the gross features of the spectrum, but does not explain the shoulder that appears on the main absorption peak. The hexaaquatitanium(III) complex is orbitally degenerate and is therefore subject to a Jahn-Teller distortion which reduces the symmetry to square planar. It will be shown that D_{4h} symmetry is fully consistent with the experimental spectrum. The d-orbital energy level diagrams for O_h and D_{4h} symmetry are shown below and will be referred to later in the analysis.



On the basis of these energy level diagrams we would make the following predictions. For octahedral symmetry there is one electronic transition in the visible region. For square planar symmetry there are two electronic transitions in the visible region and one in the infrared. In the analysis that follows it will be shown that none of the electronic transitions is orbitally allowed, but they are allowed through vibronic coupling. Further more the square planar geometry is in better agreement with the experimental spectrum than octahedral symmetry.

Ti(H₂O)₆³⁺ - Octahedral Symmetry

COh :=	$\begin{matrix} E & C_3 & C_2 & C_4 & C_2 & i & S_4 & S_6 & \sigma_h & \sigma_d \\ \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 \\ 2 & -1 & 0 & 0 & 2 & 2 & 0 & -1 & 2 & 0 \\ 3 & 0 & -1 & 1 & -1 & 3 & 1 & 0 & -1 & -1 \\ 3 & 0 & 1 & -1 & -1 & 3 & -1 & 0 & -1 & 1 \\ 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 \\ 1 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 \\ 2 & -1 & 0 & 0 & 2 & -2 & 0 & 1 & -2 & 0 \\ 3 & 0 & -1 & 1 & -1 & -3 & -1 & 0 & 1 & 1 \\ 3 & 0 & 1 & -1 & -1 & -3 & 1 & 0 & 1 & -1 \end{bmatrix} \end{matrix}$		Oh :=	
		$A_{1g}: x^2 + y^2 + z^2$ A_{2g} $E_g: 2z^2 - x^2 - y^2, x^2 - y^2$ $T_{1g}: R_x, R_y, R_z$ $T_{2g}: xy, xz, yz$ A_{1u} A_{2u} E_u $T_{1u}: x, y, z$ T_{2u}	$\begin{bmatrix} 1 \\ 8 \\ 6 \\ 6 \\ 6 \\ 3 \\ 1 \\ 6 \\ 8 \\ 3 \\ 6 \end{bmatrix}$	$\Gamma_{uma} := \begin{bmatrix} 7 \\ 1 \\ 1 \\ 1 \\ 3 \\ 3 \\ 1 \\ 1 \\ 1 \\ 5 \\ 3 \end{bmatrix}$

$A_{1g} := (\text{COh}^T)^{\langle 1 \rangle}$	$A_{2g} := (\text{COh}^T)^{\langle 2 \rangle}$	$E_g := (\text{COh}^T)^{\langle 3 \rangle}$	$T_{1g} := (\text{COh}^T)^{\langle 4 \rangle}$
$T_{2g} := (\text{COh}^T)^{\langle 5 \rangle}$	$A_{1u} := (\text{COh}^T)^{\langle 6 \rangle}$	$A_{2u} := (\text{COh}^T)^{\langle 7 \rangle}$	$E_u := (\text{COh}^T)^{\langle 8 \rangle}$
$T_{1u} := (\text{COh}^T)^{\langle 9 \rangle}$	$T_{2u} := (\text{COh}^T)^{\langle 10 \rangle}$	$h := \sum \text{Oh}$	$\Gamma_{tot} := \overrightarrow{(\Gamma_{uma} \cdot T_{1u})}$
$\Gamma_{tot}^T = (21 \ 0 \ -1 \ 3 \ -3 \ -3 \ -1 \ 0 \ 5 \ 3)$		$\Gamma_{vib} := \Gamma_{tot} - T_{1u} - T_{1g}$	

Determine which irreducible representations contribute to Γ_{vib} :

$$i := 1..10 \quad X_i := \frac{\sum_h \left[\text{Oh} \cdot (\text{COh}^T)^{\langle i \rangle} \cdot \Gamma_{vib} \right]}{h} \quad X^T = (1 \ 0 \ 1 \ 0 \ 1 \ 0 \ 0 \ 0 \ 2 \ 1)$$

Thus we see that: $\Gamma_{vib} := A_{1g} + E_g + T_{2g} + 2 \cdot T_{1u} + T_{2u}$

Inspection of the character table shows that in octahedral symmetry the d-orbitals are split into a lower T_{2g} (d_{xy}, d_{xz}, d_{yz}) level and an upper E_g ($d_{z^2}, d_{x^2-y^2}$) level. Ti^{3+} has one d-electron in the T_{2g} level. As the spectrum below shows, the complex absorbs in the visible region at $20,000 \text{ cm}^{-1}$ (500 nm). However the $T_{2g} \rightarrow E_g$ transition is orbitally forbidden as is shown below.

$$\int \Psi_{ex} \cdot \mu_e \cdot \Psi_{eg} \, d\tau = 0 \quad \frac{\sum_h (\text{Oh} \cdot E_g \cdot T_{1u} \cdot T_{2g})}{h} = 0$$

In calculating the transition moment for $T_{2g} \rightarrow E_g$ electronic transition it has been assumed that there was no change in the vibrational state of the molecule. However, it is possible for formally forbidden electronic transitions to become allowed through coupling to changes in vibrational state. In other words pure electronic transitions do not actually occur, because the vibrational (and rotational) states of the molecule change at the same time. These are called vibronic transitions and they are allowed if the integral shown below is nonzero.

$$\int \int (\Psi_{ex} \cdot \Psi_{vx} \cdot \mu_e \cdot \Psi_{eg} \cdot \Psi_{vg}) \, d\tau \, d\tau_v$$

The calculations below show that vibronic calculations involving the T_{1u} and T_{2u} vibrational modes are allowed because the transition moment is not zero.

$$\frac{\sum(\text{Oh} \cdot T_{1u} \cdot E_g \cdot T_{1u} \cdot T_{2g} \cdot A_{1g})}{h} = 2 \qquad \frac{\sum(\text{Oh} \cdot T_{2u} \cdot E_g \cdot T_{1u} \cdot T_{2g} \cdot A_{1g})}{h} = 2$$

At this point we have shown that the vibrationally assisted $T_{2g} \rightarrow E_g$ electronic transition is allowed. However, the shoulder on the experimental spectrum suggest that more than one electronic transition is occurring. In the next section we will see that a reduction to square planar symmetry under the Jahn-Teller effect leads to an d-orbital energy level diagram that is consistent with the experimental spectrum.

Ti(H₂O)₆³⁺ - Square Planar Symmetry

The Jahn-Teller effect predicts a tetragonal distortion of the octahedral complex to the lower D_{4h} square planar symmetry. The energy level diagram is shown above - essentially the ligands on the z-axis move in toward the titanium ion.

$CD_{4h} :=$	$E \ C_4 \ C_2 \ C_2' \ C_2'' \ i \ S_4 \ \sigma_h \ \sigma_v \ \sigma_d$		$D_{4h} :=$		$\Gamma_{uma} :=$
$\begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 & 1 & -1 \\ 1 & -1 & 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 \\ 2 & 0 & -2 & 0 & 0 & 2 & 0 & -2 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 \\ 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & 1 & 1 \\ 1 & -1 & 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 2 & 0 & -2 & 0 & 0 & -2 & 0 & 2 & 0 & 0 \end{bmatrix}$	$A_{1g}: x^2 + y^2, z^2$ $A_{2g}: R_z$ $B_{1g}: x^2 - y^2$ $B_{2g}: xy$ $E_g: (R_x, R_y), (xz, yz)$ $A_{1u}:$ $A_{2u}: z$ B_{1u} B_{2u} $E_u: (x, y)$	$\begin{bmatrix} 1 \\ 2 \\ 1 \\ 1 \\ 2 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 2 \end{bmatrix}$	$\begin{bmatrix} 5 \\ 1 \\ 1 \\ 3 \\ 1 \\ 1 \\ 1 \\ 5 \\ 3 \\ 1 \end{bmatrix}$		

$$A_{1g} := (CD_{4h}^T)^{\langle 1 \rangle} \quad A_{2g} := (CD_{4h}^T)^{\langle 2 \rangle} \quad B_{1g} := (CD_{4h}^T)^{\langle 3 \rangle} \quad B_{2g} := (CD_{4h}^T)^{\langle 4 \rangle} \quad E_g := (CD_{4h}^T)^{\langle 5 \rangle}$$

$$A_{1u} := (CD_{4h}^T)^{\langle 6 \rangle} \quad A_{2u} := (CD_{4h}^T)^{\langle 7 \rangle} \quad B_{1u} := (CD_{4h}^T)^{\langle 8 \rangle} \quad B_{2u} := (CD_{4h}^T)^{\langle 9 \rangle} \quad E_u := (CD_{4h}^T)^{\langle 10 \rangle}$$

$$h := \sum D_{4h} \quad \Gamma_{tot} := (\Gamma_{uma} \cdot (A_{2u} + E_u)) \quad \Gamma_{tot}^T = (15 \ 1 \ -1 \ -3 \ -1 \ -3 \ -1 \ 5 \ 3 \ 1)$$

Symmetry of the vibrational modes.

$$\Gamma_{vib} := \Gamma_{tot} - A_{2g} - E_g - A_{2u} - E_u \quad i := 1..10 \quad Y_i := \frac{\sum [D_{4h} \cdot (CD_{4h}^T)^{\langle i \rangle} \cdot \Gamma_{vib}]}{h}$$

$$Y^T = (1 \ 0 \ 1 \ 1 \ 0 \ 0 \ 1 \ 0 \ 1 \ 2) \quad \Gamma_{vib} := A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2 \cdot E_u$$

The energy level diagram above shows three possible electronic transitions, one IR transition and two transitions in visible region of the spectrum. The calculations below show that all three are formally forbidden. Vibronic coupling is invoked to explain the appearance of the two electronic transitions in the visible region.

$$\frac{\sum \overrightarrow{(D4h \cdot E_g \cdot (A2u + Eu) \cdot B2g)}}{h} = 0 \quad \frac{\sum \overrightarrow{(D4h \cdot B1g \cdot (A2u + Eu) \cdot B2g)}}{h} = 0 \quad \frac{\sum \overrightarrow{(D4h \cdot A1g \cdot (A2u + Eu) \cdot B2g)}}{h} = 0$$

A A_{1u} or E_u vibrational mode can provide vibronic coupling for the $B_{2g} \rightarrow B_{1g}$ transition

$$\frac{\sum \overrightarrow{(D4h \cdot A1u \cdot B1g \cdot (A2u + Eu) \cdot B2g \cdot A1g)}}{h} = 1 \quad \frac{\sum \overrightarrow{(D4h \cdot E_u \cdot B1g \cdot (A2u + Eu) \cdot B2g \cdot A1g)}}{h} = 1$$

A B_{1u} or E_u vibrational mode can provide vibronic coupling for the $B_{2g} \rightarrow A_{1g}$ transition

$$\frac{\sum \overrightarrow{(D4h \cdot B1u \cdot A1g \cdot (A2u + Eu) \cdot B2g \cdot A1g)}}{h} = 1 \quad \frac{\sum \overrightarrow{(D4h \cdot E_u \cdot A1g \cdot (A2u + Eu) \cdot B2g \cdot A1g)}}{h} = 1$$

A close examination of the experimental spectrum indicates the presence of two electronic transitions of similar energy (shoulder). So the energy level diagram and the vibronic analysis are consistent with the actual spectrum.