Electronic Spectrum of a Transition Metal Complex

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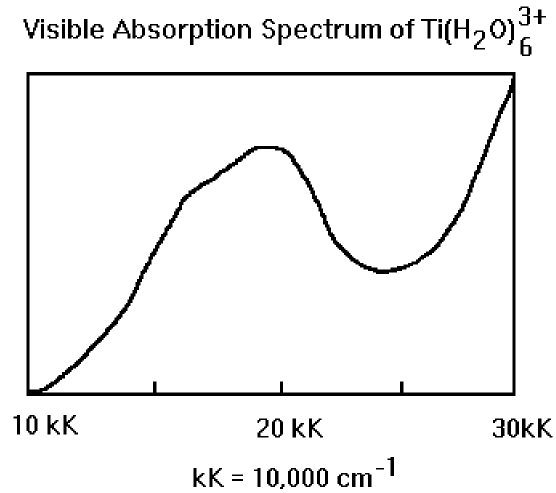
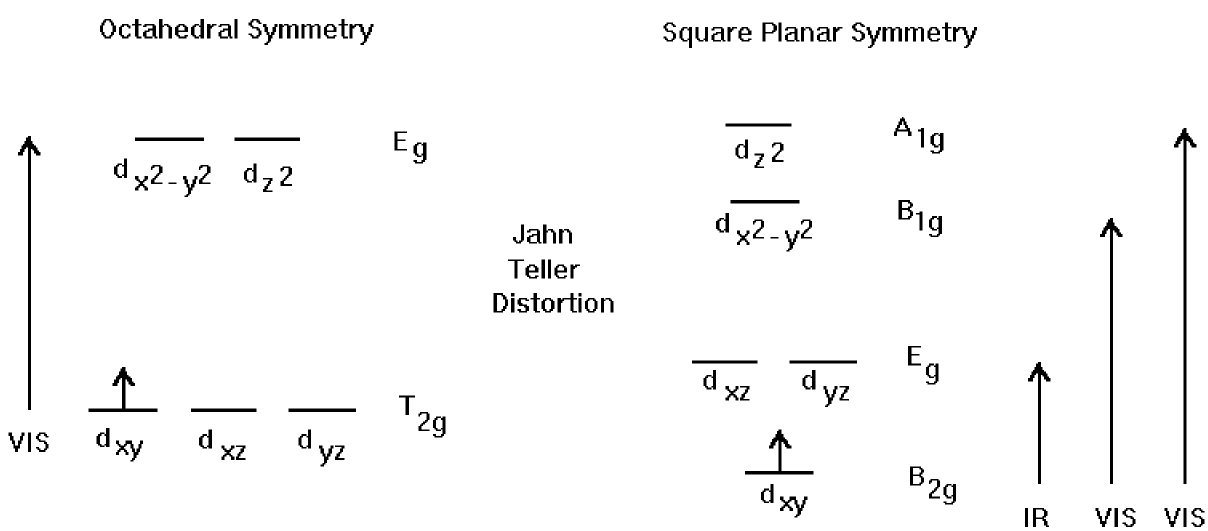
This spectroscopy exercise deals with the interpretation of the visible spectrum of $Ti(H_20)_6^{3+}$ shown below.



The analysis begins with the assumption that $Ti(H_20)_6^{3+}$ has octahedral, O_h, 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 from octahedral 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 the following predictions would be plausible. 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 predicted electronic transitions is orbitally allowed, but they are observed through the agency of vibronic coupling. Furthermore the square planar geometry is in better agreement with the experimental spectrum than octahedral symmetry.

Because of the importance of vibronic coupling to electronic transitions in this example the determination of the symmetry of the vibrational degrees of freedom is essential. In the vibrational analysis the water ligands will be treated as composite entities. We will only consider the titanium water molecule vibrational modes and ignore the internal vibrations of the water molecule.

$Ti(H_20)_6^{3+}$ - Octahedral Symmetry

$$C_{Oh} := \begin{array}{c} \begin{matrix} E & C_3 & C_2 & C_4 & C_2 & i & S_4 & S_6 & \sigma_h & \sigma_d \end{matrix} \\ \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 \\ 2 & -1 & 0 & 0 & 2 & 2 & 0 & -1 & 2 & 0 \\ 3 & 0 & -1 & 1 & -1 & 3 & 1 & 0 & -1 & -1 \\ 3 & 0 & 1 & -1 & -1 & 3 & -1 & 0 & -1 & 1 \\ 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 \\ 1 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 \\ 2 & -1 & 0 & 0 & 2 & -2 & 0 & 1 & -2 & 0 \\ 3 & 0 & -1 & 1 & -1 & -3 & -1 & 0 & 1 & 1 \\ 3 & 0 & 1 & -1 & -1 & -3 & 1 & 0 & 1 & -1 \end{pmatrix} \end{array} \begin{array}{l} A_{1g}:\ x^2+y^2+z^2 \\ A_{2g} \\ E_g:\ 2z^2-x^2-y^2,\ x^2-y^2 \\ T_{1g}:\ Rx, Ry, Rz \\ T_{2g}:\ xy, xz, yz \\ A_{1u}: \\ A_{2u} \\ E_u \\ T_{1u}:\ x, y, z \\ T_{2u} \end{array}$$

$$Oh := \begin{pmatrix} 1 \\ 8 \\ 6 \\ 6 \\ 3 \\ 1 \\ 6 \\ 8 \\ 3 \\ 6 \end{pmatrix} \qquad \Gamma_{uma} := \begin{pmatrix} 7 \\ 1 \\ 1 \\ 3 \\ 3 \\ 1 \\ 1 \\ 1 \\ 5 \\ 3 \end{pmatrix}$$

$$A_{1g} := \left(C_{Oh}{}^T\right)^{\langle 1 \rangle} \qquad A_{2g} := \left(C_{Oh}{}^T\right)^{\langle 2 \rangle} \qquad E_g := \left(C_{Oh}{}^T\right)^{\langle 3 \rangle} \qquad T_{1g} := \left(C_{Oh}{}^T\right)^{\langle 4 \rangle}$$

$$T_{2g} := \left(C_{Oh}{}^T\right)^{\langle 5 \rangle} \qquad A_{1u} := \left(C_{Oh}{}^T\right)^{\langle 6 \rangle} \qquad A_{2u} := \left(C_{Oh}{}^T\right)^{\langle 7 \rangle} \qquad E_u := \left(C_{Oh}{}^T\right)^{\langle 8 \rangle}$$

$$T_{1u} := \left(C_{Oh}{}^T\right)^{\langle 9 \rangle} \qquad T_{2u} := \left(C_{Oh}{}^T\right)^{\langle 10 \rangle} \qquad h := \sum Oh \qquad \Gamma_{tot} := \overrightarrow{\left(\Gamma_{uma} \cdot T_{1u}\right)}$$

$$\Gamma_{tot}{}^T = (21\ \ 0\ \ -1\ \ 3\ \ -3\ \ -3\ \ -1\ \ 0\ \ 5\ \ 3) \qquad \Gamma_{vib} := \Gamma_{tot} - T_{1u} - T_{1g}$$

Determine which irreducible representations contribute to Γ_{vib}:

$$i := 1 .. 10 \qquad Vib_i := \frac{\sum \overrightarrow{\left[Oh \cdot \left(C_{Oh}{}^T\right)^{\langle i \rangle} \cdot \Gamma_{vib}\right]}}{h} \qquad Vib = \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 2 \\ 1 \end{pmatrix} \begin{array}{l} A_{1g}:\ x^2+y^2+z^2 \\ A_{2g} \\ E_g:\ 2z^2-x^2-y^2,\ x^2-y^2 \\ T_{1g}:\ Rx, Ry, Rz \\ T_{2g}:\ xy, xz, yz \\ A_{1u}: \\ A_{2u} \\ E_u \\ T_{1u}:\ x, y, z \\ T_{2u} \end{array}$$

Thus we see that the vibrational modes have the following symmetry: $\Gamma_{vib} := A_{1g} + E_g + T_{2g} + 2 \cdot T_{1u} + T_{2u}$

Inspection of the character table shows that in octahedral symmetry the degeneracy of the d-orbitals is split into a three-fold degenerate T_{2g} (d_{xy}, d_{xz}, d_{yz}) level and a two-fold degenerate E_g (d_{z^2}, $d_{x^2-y^2}$) level. Electrostatic arguments (see your general chemistry text) predict that the T_{2g} level is lower in energy. Thus, according to this model Ti^{3+} has one d-electron in the T_{2g} level. As the spectrum above shows, the complex absorbs in the visible region at 20,000 cm^{-1} (500 nm). However, the T_{2g} ---> E_g transition is orbitally forbidden as is shown below.

$$\int \Psi_{ex}\cdot\mu_e\cdot\Psi_{eg}\,d\tau_e = 0 \qquad\qquad \frac{\sum\overrightarrow{\left(Oh\cdot E_g\cdot T_{1u}\cdot T_{2g}\right)}}{h} = 0$$

On the left we have the transition moment integral expressed in the language of integral calculus (see any quantum chemistry text) and on the right we have the same integral in the group-theoretical vector-matrix representation.

In calculating the transition moment for T_{2g} ---> 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 the vibrational state of the molecule. 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.

$$\int\int \Psi_{ex}\cdot\Psi_{vx}\cdot\mu_e\cdot\Psi_{eg}\cdot\Psi_{vg}\,d\tau_e\,d\tau_v$$

The calculations below show that vibronic transitions involving the T_{1u} and T_{2u} vibrational modes are allowed because the transition moment is not zero. It is important to note that the ground states of all vibrational modes of all point groups have A_{1g} symmetry. (See F. A. Cotton, *Chemical Applications of Group Theory*, J. Wiley, 1963, p. 262.)

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

The A_{1g}, E_g and T_{2g} modes do not provide vibrational assistance as is shown below.

$$\frac{\sum\overrightarrow{\left(Oh\cdot A_{1g}\cdot E_g\cdot T_{1u}\cdot T_{2g}\cdot A_{1g}\right)}}{h} = 0 \qquad \frac{\sum\overrightarrow{\left(Oh\cdot E_g\cdot E_g\cdot T_{1u}\cdot T_{2g}\cdot A_{1g}\right)}}{h} = 0 \qquad \frac{\sum\overrightarrow{\left(Oh\cdot T_{2g}\cdot E_g\cdot T_{1u}\cdot T_{2g}\cdot A_{1g}\right)}}{h} = 0$$

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

$Ti(H_20)_6^{3+}$ - 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, splitting the degeneracy of both the octahedral T_{2g} ground state and its E_g excited state. Electrostatic arguments provide a suitable rationale for the degeneracy splitting caused by the tetragonal distortion.

$$C_{D4h} := \begin{array}{c} \begin{array}{cccccccccc} E & C_4 & C_2 & C_2' & C_2'' & i & S_4 & \sigma_h & \sigma_v & \sigma_d \end{array} \\ \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 & 1 & -1 \\ 1 & -1 & 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 \\ 2 & 0 & -2 & 0 & 0 & 2 & 0 & -2 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 \\ 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & 1 & 1 \\ 1 & -1 & 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 2 & 0 & -2 & 0 & 0 & -2 & 0 & 2 & 0 & 0 \end{pmatrix} \end{array} \begin{array}{l} \\ A_{1g}\text{: } x^2 + y^2, z^2 \\ A_{2g}\text{: } Rz \\ B_{1g}\text{: } x^2 - y^2 \\ B_{2g}\text{: } xy \\ E_g\text{: } (Rx, Ry), (xz, yz) \\ A_{1u}\text{: } \\ A_{2u}\text{: } z \\ B_{1u} \\ B_{2u} \\ E_u\text{: } (x, y) \end{array} \qquad D4h := \begin{pmatrix} 1 \\ 2 \\ 1 \\ 2 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 2 \end{pmatrix} \qquad \Gamma_{uma} := \begin{pmatrix} 7 \\ 3 \\ 3 \\ 3 \\ 1 \\ 1 \\ 1 \\ 5 \\ 5 \\ 3 \end{pmatrix}$$

$$A_{1g} := \left(C_{D4h}{}^T\right)^{\langle 1 \rangle} \quad A_{2g} := \left(C_{D4h}{}^T\right)^{\langle 2 \rangle} \quad B_{1g} := \left(C_{D4h}{}^T\right)^{\langle 3 \rangle} \quad B_{2g} := \left(C_{D4h}{}^T\right)^{\langle 4 \rangle} \quad E_g := \left(C_{D4h}{}^T\right)^{\langle 5 \rangle}$$

$$A_{1u} := \left(C_{D4h}{}^T\right)^{\langle 6 \rangle} \quad A_{2u} := \left(C_{D4h}{}^T\right)^{\langle 7 \rangle} \quad B_{1u} := \left(C_{D4h}{}^T\right)^{\langle 8 \rangle} \quad B_{2u} := \left(C_{D4h}{}^T\right)^{\langle 9 \rangle} \quad E_u := \left(C_{D4h}{}^T\right)^{\langle 10 \rangle}$$

$$h := \sum D4h \qquad \Gamma_{tot} := \overrightarrow{\left[\Gamma_{uma} \cdot \left(A_{2u} + E_u\right)\right]} \qquad \Gamma_{tot}{}^T = (21 \;\; 3 \;\; -3 \;\; -3 \;\; -1 \;\; -3 \;\; -1 \;\; 5 \;\; 5 \;\; 3)$$

Symmetry of the vibrational modes. $\Gamma_{vib} := \Gamma_{tot} - A_{2g} - E_g - A_{2u} - E_u$

$$Vib_i := \frac{\sum \overrightarrow{\left[D4h \cdot \left(C_{D4h}{}^T\right)^{\langle i \rangle} \cdot \Gamma_{vib}\right]}}{h} \qquad Vib = \begin{pmatrix} 2 \\ 0 \\ 1 \\ 1 \\ 1 \\ 0 \\ 2 \\ 0 \\ 1 \\ 3 \end{pmatrix} \begin{array}{l} A_{1g}\text{: } x^2 + y^2, z^2 \\ A_{2g}\text{: } Rz \\ B_{1g}\text{: } x^2 - y^2 \\ B_{2g}\text{: } xy \\ E_g\text{: } (Rx, Ry), (xz, yz) \\ A_{1u}\text{: } \\ A_{2u}\text{: } z \\ B_{1u} \\ B_{2u} \\ E_u\text{: } (x, y) \end{array}$$

$$\Gamma_{vib} := 2 \cdot A_{1g} + B_{1g} + B_{2g} + E_g + 2 \cdot A_{2u} + B_{2u} + 3 \cdot E_u$$

The D_{4h} energy level diagram shows three possible electronic transitions, one IR transition and two transitions in visible region of the spectrum. The following calculations show that all three are formally forbidden. Again, vibronic coupling is invoked to explain the appearance of the two electronic transitions in the visible region.

$$\frac{\sum \overrightarrow{\left[D4h \cdot E_g \cdot (A_{2u} + E_u) \cdot B_{2g}\right]}}{h} = 0 \qquad \frac{\sum \overrightarrow{\left[D4h \cdot B_{1g} \cdot (A_{2u} + E_u) \cdot B_{2g}\right]}}{h} = 0 \qquad \frac{\sum \overrightarrow{\left[D4h \cdot A_{1g} \cdot (A_{2u} + E_u) \cdot B_{2g}\right]}}{h} = 0$$

An A_{1u} or E_u vibrational mode can provide vibronic coupling for the B_{2g} --> B_{1g} transition. Again it is important to recall that the ground states of all vibrational modes have A_{1g} symmetry.

$$\frac{\sum \overrightarrow{\left[D4h \cdot A_{1u} \cdot B_{1g} \cdot (A_{2u} + E_u) \cdot B_{2g} \cdot A_{1g}\right]}}{h} = 1 \qquad \frac{\sum \overrightarrow{\left[D4h \cdot E_u \cdot B_{1g} \cdot (A_{2u} + E_u) \cdot B_{2g} \cdot A_{1g}\right]}}{h} = 1$$

A B_{1u} or E_u vibrational mode can provide vibronic coupling for the B_{2g} --> A_{1g} transition.

$$\frac{\sum \overrightarrow{\left[D4h \cdot B_{1u} \cdot A_{1g} \cdot (A_{2u} + E_u) \cdot B_{2g} \cdot A_{1g}\right]}}{h} = 1 \qquad \frac{\sum \overrightarrow{\left[D4h \cdot E_u \cdot A_{1g} \cdot (A_{2u} + E_u) \cdot B_{2g} \cdot A_{1g}\right]}}{h} = 1$$

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.

Primary reference: Daniel C. Harris and Michael D. Bertolucci, "Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy." Dover Publications, Inc., New York, 1989.