In Class Activity

- A low spin $Co^{3+}$ complex has an ${}^1A_{1g}$ ground state and excited states of ${}^1T_{1g}$ and ${}^1T_{2g}$. Does vibronic coupling allow these transitions to occur?
  - Hint: in this case as the final electronic state is changing it is easier to work out the direct products in the following sequence,

$$A_{1g} \in \left\{ \Gamma^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma^{|i\rangle} \right\}$$
$$\Gamma^{\langle f|} = \Gamma_{vib}^{\langle f|} \otimes \Gamma_{elec}^{\langle f|}$$
$$\Gamma^{|i\rangle} = \Gamma_{elec}^{|i\rangle} \otimes \Gamma_{vib}^{|i\rangle}$$
$$A_{1g} \in \left\{ \Gamma_{vib}^{\langle f|} \otimes \Gamma_{elec}^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma_{elec}^{|i\rangle} \otimes \Gamma_{vib}^{|i\rangle} \right\}$$
$$A_{1g} \in \left\{ \Gamma_{elec}^{\langle f|} \otimes \left( \Gamma_{vib}^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma_{elec}^{|i\rangle} \otimes \Gamma_{vib}^{|i\rangle} \right) \right\}$$

  - Co is $d^9$ and the overall charge is +3 therefore in this complex the Co is $d^6$. We are told the complex is low-spin so from the Tanabe-Sugano diagram the ground state is ${}^1A_{1g}$ or alternatively we know the $t_{2g}$ levels are completely filled which must be ${}^1A_{1g}$. The Tanabe-Sugano diagram tells us that the two lowest excitations (preserving the multiplicity) are ${}^1T_{1g}$ and ${}^1T_{2g}$.

$$A_{1g} \in \left\{ \Gamma_{elec}^{\langle f|} \otimes \left( \Gamma_{vib}^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma_{elec}^{|i\rangle} \otimes \Gamma_{vib}^{|i\rangle} \right) \right\}$$
$$\Gamma_{elec}^{|i\rangle} \otimes \Gamma_{vib}^{|i\rangle} = {}^1A_{1g} \otimes {}^1A_{1g} = {}^1A_{1g}$$
$$\Gamma^{\mu} = T_{1u}$$
$$\Gamma_{vib}^{\langle f|} = \left( A_{1g}, E_g, T_{1u}, T_{2g}, T_{2u} \right)$$
$$\left( \Gamma_{vib}^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma_{elec}^{|i\rangle} \otimes \Gamma_{vib}^{|i\rangle} \right) = \left\{ \left( A_{1g}, E_g, T_{1u}, T_{2g}, T_{2u} \right) \otimes T_{1u} \otimes A_{1g} \right\}$$
$$= \left\{ \begin{array}{l} T_{1u}, (T_{1u} + T_{2u}), (A_{1g} + E_g + T_{1g} + T_{2g}), \\ (A_{2u} + E_u + T_{1u} + T_{2u}), (A_{2g} + E_g + T_{1g} + T_{2g}) \end{array} \right\}$$
$$\left( \Gamma_{vib}^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma_{elec}^{|i\rangle} \otimes \Gamma_{vib}^{|i\rangle} \right) \in \left\{ A_{1g}, A_{2g}, A_{2u}, E_g, E_u, T_{1u}, T_{2u}, T_{1g}, T_{2g} \right\}$$
$$\Gamma_{elec}^{\langle f|} \in \left\{ {}^1T_{1g}, {}^1T_{2g} \right\}$$
$$A_{1g} \in \left\{ \boxed{T_{1g}}, \boxed{T_{2g}} \right\} \otimes \left\{ A_{1g}, A_{2g}, A_{2u}, E_g, E_u, T_{1u}, T_{2u}, \boxed{T_{1g}}, \boxed{T_{2g}} \right\}$$

  - we only to look for "matching" IRs on both sides of the direct product, which we do find, this in the $T_{1g}$ and $T_{2g}$ components, thus this transition is vibronically allowed.