Self-Study / Tutorial / Exam Preparation Problems

- Is a (dxy) HOMO to LUMO transition allowed for $[Pt(CN)_4]^{2-}$? Will vibronic coupling make any difference? $\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$
  - Pt is group 10 so d^{10} in zero oxidation state, CN are negative ligands removing 4e while the charge adds 2e, thus this is a Pt d^8 complex
  - the ligands are strong field ligands so we can assume a strong field energy level splitting
  - the structure will be square planar and the point group will be D_{4h}
  - the energy ordering of orbitals will follow the pattern given in **Figure 1**, ie the dz^2 is stabilised substantially and falls below the dxy orbital. Thus the HOMO is the dxy based MO
  - this is a spin paired complex so the multiplicity will be S=0 2S+1=1
  - we need to evaluate the transition dipole moment

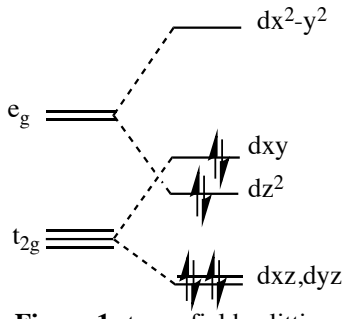

Figure 1 strong field splitting

$$\Gamma^A \in \left\{ \Gamma^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma^{|i\rangle} \right\}$$

  - as all orbitals are fully occupied the ground electronic state $\Gamma^{|i\rangle} = A_{1g}$
  - a single excitation will put one electron into the dx^2-y^2 based MO, under the D_{4h} point group the dxy has B_{2g} symmetry and the dx^2-y^2 has B_{1g} symmetry. The direct product of the electrons not in completely filled MOs gives the symmetry of the excited state $\Gamma^{<f|}=B_{1g}\otimes B_{2g}=A_{2g}$
  - under D_{4h} the dipole moment spans the E_u and A_{2u} IR
  - putting all of this information together:

$$\Gamma^A \in \left\{ \Gamma^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma^{|i\rangle} \right\}$$
$$\left\{ \Gamma^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma^{|i\rangle} \right\} = \left\{ A_{1g} \otimes \left\{ A_{2u}, E_u \right\} \otimes A_{2g} \right\}$$
$$A_{1g} \notin \left\{ A_{1u}, E_u \right\}$$

  - thus the ground to first excited state transition will not occur.
  - we have been given $\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$ (if you want the practice you could evaluate this for yourself!)
  - to determine if vibronic coupling will allow a transition we need to evaluate:

$$\Gamma^A \in \left\{ \Gamma_{elec}^{\langle f|} \Gamma_{vib}^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma_{elec}^{|i\rangle} \Gamma_{vib}^{|i\rangle} \right\}$$
$$\Gamma^A \in \Gamma_{vib}^{\langle f|} \otimes \left\{ \Gamma_{elec}^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma_{elec}^{|i\rangle} \Gamma_{vib}^{|i\rangle} \right\}$$
$$\Gamma_{elec}^{|i\rangle} \Gamma_{vib}^{|i\rangle} = A_{1g} \otimes A_{1g}$$
$$\left\{ \Gamma_{elec}^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma_{elec}^{|i\rangle} \Gamma_{vib}^{|i\rangle} \right\} = \left\{ A_{1u}, E_u \right\}$$
$$\Gamma_{vib}^{\langle f|} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$$
$$A_{1g} \in \left\{ A_{1g}, B_{1g}, B_{2g}, A_{2u}, B_{2u}, \boxed{E_u} \right\} \otimes \left\{ A_{1u}, \boxed{E_u} \right\}$$

- we require now that IR on the LHS be the same as those on the RHS for the totally symmetric IR to be generated
- this is true for the E_u IR thus vibronic coupling will allow a band for the HOMO-LUMO transition to occur in the spectrum.

- What order should be expected for the intensity of the d-d transitions in $[MCl_6]^{2-}$, *trans*-$M(H_2O)_4Cl_2$ and *cis*-$M(H_2O)_4Cl_2$?
  - $[MCl_6]^{2-}$ is octahedral and so all transitions will be parity forbidden
  - *trans*-$M(H_2O)_4Cl_2$ has a reduced symmetry but will belong to the D_{4h} point group which still contains a centre of symmetry and thus will still have a centre of inversion
  - *cis*-$M(H_2O)_4Cl_2$ will belong to the C_{2v} point group which has no centre of symmetry and so the parity selection rule will be circumvented
  - intensities could be expected to vary *cis*-$M(H_2O)_4Cl_2$ > *trans*-$M(H_2O)_4Cl_2$ > $[MCl_6]^{2-}$
- In the self-study problems for last lecture it was noted that a Jahn-Teller distortion or vibronic coupling within $[Ti(H_2O)_6]^{3+}$ broadened the spectrum. The formally forbidden transition was $(t_{2g})^1(e_g)^0 \rightarrow (t_{2g})^0(e_g)^1$, use the full transition dipole moment to show why this transition is vibronically allowed.
  - the ground state is $^2T_{2g}$, the excited state is ^2E_g and the octahedral dipole moment has T_{1u} symmetry
  - thus we can immediately deduce that the transition is forbidden by parity

$$\Gamma^A \in \left\{\Gamma^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma^{|i\rangle}\right\}$$
$$A_{1g} \in \left\{E_g \otimes T_{1u} \otimes T_{2g}\right\} = \left\{(T_{1u} + T_{2u}) \otimes T_{2g}\right\}$$
$$= \left\{(A_{2u} + E_u + T_{1u} + T_{2u}), (A_{1u} + E_u + T_{1u} + T_{2u})\right\}$$
$$\in \left\{A_{1u}, A_{2u}, E_u, T_{1u}, T_{2u}\right\} \notin A_{1g}$$

  - the vibrational components for an octahedral complex are $\Gamma_{vib} = A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$
  - thus forming the full transition dipole moment, we need to evaluate if the final vibrational state has any of the same IR as the quantity on the right hand side of the equation given below:

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

$$\Gamma^{|i\rangle}_{elec}\Gamma^{|i\rangle}_{vib} = T_{2g} \otimes A_{1g} = T_{2g}$$
$$\Gamma^{\langle f|}_{elec} = E_g \quad and \quad \Gamma^{\mu} = T_{1u}$$
$$\left(\Gamma^{\langle f|}_{elec} \otimes \Gamma^{\mu} \otimes \Gamma^{|i\rangle}_{elec}\Gamma^{|i\rangle}_{vib}\right) \in \left\{A_{1u}, A_{2u}, E_u, T_{1u}, T_{2u}\right\}$$

  - thus comparing the IR components of both sides we find that there are two components that are the same and thus the transition is vibronically allowed

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