Pure Electronic Selection Rules

- now we have all the necessary background to evaluate if an electronic transition will occur
- we know that the totally symmetric A_{1g} must be contained within the direct product of the term symbols of the ground state, the excited state and the dipole moment

$$\Gamma^{A} \in \left\{\Gamma^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma^{|i\rangle}\right\} \qquad \text{Equation 1}$$

- we can predict the ground state term from the Orgel or Tanabe-Sugano diagrams, which also identify excited states of the correct multiplicity
- we know the multiplicity must not change
- we know that the irreducible representation of the dipole moment in the O_h point group, this is T_{1u}, however for TM we also know the ground and excited states are always garade
- but for a transition to occur we know that the parity of the initial and final states must change, thus the d-d transitions can never be parity allowed

$$A_{1g} \notin \left\{\Gamma_{g}^{\langle f|} \otimes T_{1u} \otimes \Gamma_{g}^{|i\rangle}\right\} \qquad \text{Equation 2}$$

- nevertheless for d-d transitions we also know the rules can be broken since TM complexes can be highly coloured, this will be covered shortly
- complexes don't need to be octahedral, the same principles apply to lower symmetry systems
- if the centre of inversion is not present then the parity selection rule is no longer active and transitions can take on a greater intensity, this is particularly true for tetrahedral molecules

- For example for a d^2 complex the ground state is $^3T_{1g}$ symmetry, using the Tanabe-Sugano diagram we can expect three transitions to states $^3T_{2g}$, $^3A_{2g}$, and $^3T_{1g}(P)$
  - including parity the selection rules show that transitions to the T_{2g} and T_{1g} states are forbidden, the direct products will always generate an ungerade symmetry.

$$\Gamma^{A} \in \left\{\Gamma^{\langle f|} \otimes \Gamma^{\mu} \otimes \Gamma^{|i\rangle}\right\} == T_{1g} \otimes T_{1u} \otimes T_{2g} \notin A_{1g} \qquad \text{Equation 3}$$

Vibronic Transitions and Vibrational fine Structure

- so far we have focused on the inner part of the transition dipole moment integral, the electronic component.
- when light is absorbed by a molecule it excites the system from the ground to the excited electronic state, however some of the light can also vibrationally excite the molecule, **Figure 1**
- **vibronic transitions** occur when transitions are between different electronic *and* vibrational states.

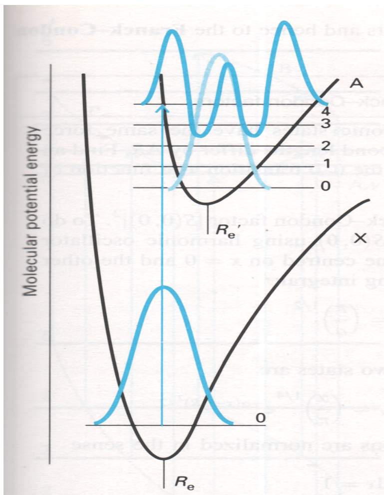

Figure 1 showing good overlap between the vibrational functions. diagram from Molecular Quantum Mechanics by Atkins and Friedman.

$$\begin{aligned}\mu_{fi} &= \int \chi_f \left[\int \psi_f (\mu_e) \psi_i d\tau_e \right] \chi_i d\tau_n \\ &= \langle \chi_f \psi_f | \mu_e | \psi_i \chi_i \rangle \qquad \text{Equation 4} \\ &= \langle \psi_f | \mu_e | \psi_i \rangle \langle \chi_f | \chi_i \rangle = \mu_{fie} S_{fi}\end{aligned}$$

- it is assumed the electronic transition dipole moment is essentially insensitive to the nuclear displacements allowing separation of the components.
- S_{fi} is the **vibrational overlap integral**, in general $S_{fi} \neq 0$ because of the displacement of the electronic potential energy surfaces, **Figure 1**

IMPORTANT

- vibrational states on a single electronic potential are orthogonal, however *vibrational states on different electronic states are not orthogonal*

- **Figure 2** shows the resultant vibrational fine structure in a UV-vis spectrum. The depicted calculation is determining the vibrational wavenumber generating the fine structure. Also shown is the graphical abstract from a paper by J. Houmøller, S. Kaufman, K. Støchkel, L. Tribedi, S. Nielsen and J. Weber, "On the Photoabsorption by Permanganate Ions in Vacuo and the Role of a Single Water Molecule. New Experimental Benchmarks for Electronic Structure Theory" *ChemPhysChem*, **2013**, Vol 14(6), p1133-1137, DOI: 10.1002/cphc.201300019.

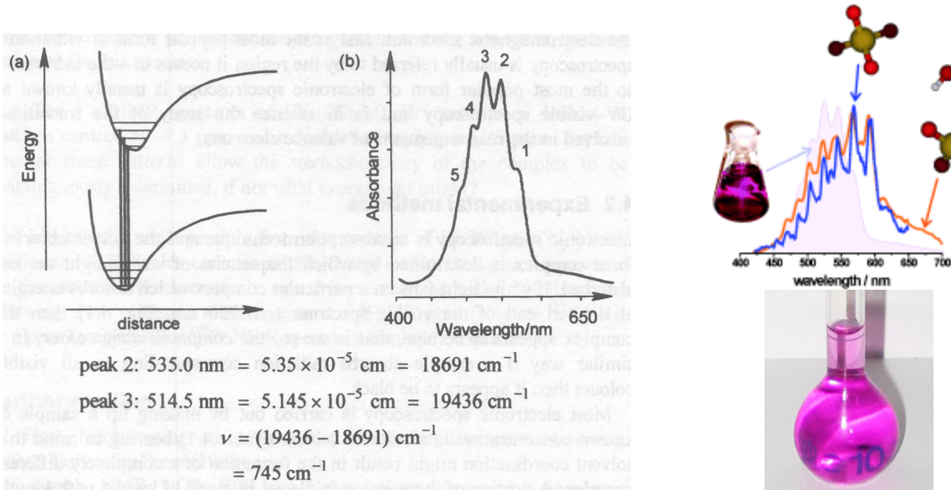

Figure 2 Vibrational fine structure on the electronic absorption band of $[MnO_4]^-$.[1]

- typically the vibrational fine structure is not clearly resolved in a UV-vis spectrum, however the vibronic coupling significantly broadens the beaks to the order of 1000 cm^{-1} wide. (What is the width of your average vibrational peak in an IR spectrum?)
- the intensity of a vibronic transition is proportional to $|S_{fi}|^2$ (the square of the magnitude of S_{fi}) . $|S_{fi}|^2$ is called the **Franck-Condon factor**
  - you have met Franck-Condon factors before particularly in relation to photochemistry (**Figure 3**)

[1] Image from Inorganic Spectroscopic Methods by Alan Brisdon, (b) abstract image from http://onlinelibrary.wiley.com/doi/10.1002/cphc.v14.6/issuetoc (c) $KMnO_4$ solution from http://www.sciencebrothers.org/the-chemical-chameleon/, 25 Feb 2015

- both the Franck-Condon factor (FC) and the electronic transition dipole moment μ_{fie} =V are very important for determining the rate of photochemical and electron transfer events, they are key components in Fermi's Golden Rule:

$$k = \frac{2\pi}{h} FC \bullet V^2 \qquad \text{Equation 5}$$

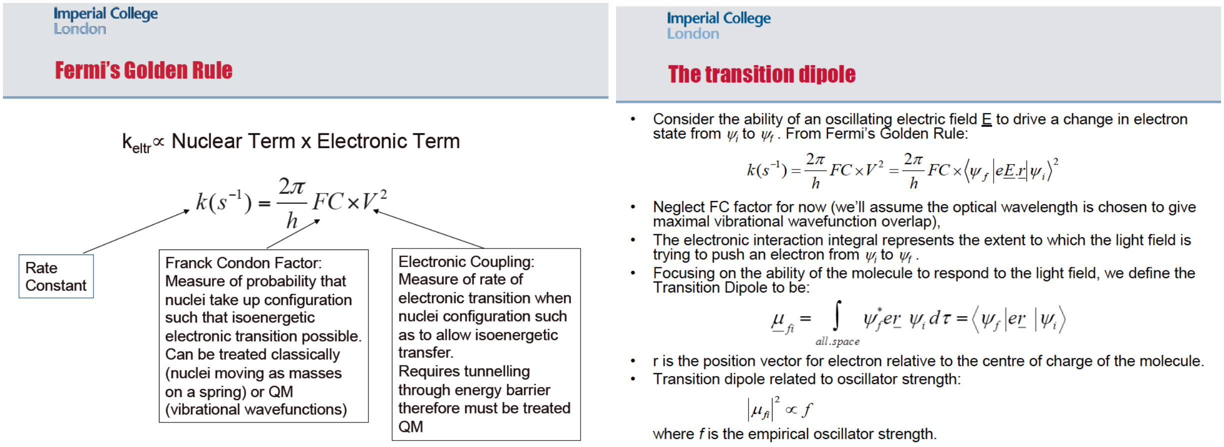

Figure 3 Slides from the photochemistry course of Saif Haque

Breaking the Electronic Selection Rules

- the colour of transition metal complexes indicates that while transitions may be formally forbidden they are still occurring. What is happening?
- if **vibronic coupling** occurs we now need to evaluate if a more complex transition dipole moment is zero or non-zero

$$\mu_{fi} = \int \chi_f \left[\int \psi_f \mu \psi_i d\tau_e \right] \chi_i d\tau_n \qquad \text{Equation 6}$$

- the process is similar to that covered previously, we need to determine the symmetry of all the components and ensure that the integrand contains a totally symmetric IR.
- in the following we will assume that the spin multiplicity is unchanged, ie that the transition is spin allowed
- let us consider a spin-allowed transition for a d^1 system
  - the ground electronic state is $^2T_{2g}$ and the ground vibrational state is always totally symmetric $\Gamma_{elec}\Gamma_{vib} = T_{2g} \otimes A_{1g} = T_{2g}$
  - the dipole moment is T_{1u}
  - the final excited state is a little more complex to evaluate
  - the electronic final state will be ^2E_g (ie a t_{2g} to e_g transition)
  - there are 3N-6 vibrations possible, for an octahedral complex with 6 ligands N=7 and so there are 3*7-6=15 possible vibrations these have $\Gamma_{vib} = A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$ (using the reduction formula and projection operator). The final vibrational state could have the symmetry of any one of these vibrational wavefunctions; any of these vibrations could lead to vibronic coupling and a weak transition.

$$
\begin{aligned}
&\left(E_g\right)\otimes\left(A_{1g},E_g,T_{1u},T_{2g},T_{2u}\right)\\
&=\left\{\left(E_g\right),\left(A_{1g}+A_{2g}+E_g\right),\left(T_{1u}+T_{2u}\right),\left(T_{1g}+T_{2g}\right),\left(T_{1u}+T_{2u}\right)\right\}\\
&\in\left\{A_{1g},A_{2g},E_g,T_{1u},T_{2u},T_{1g},T_{2g}\right\}
\end{aligned}
$$

Equation 7

- this leads to:

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

Equation 8

- we do not need to evaluate this daunting direct product, because we know that the A_{1g} is contained in the product of any two identical IRs, thus we need to only look for "matching" IRs on both sides of the direct product
- we do find this in the T_{1u} and T_{2u} components, thus this transition is vibronically allowed.
- however while we can say that a transition is allowed we cannot currently say anything about its intensity!

- vibronic coupling essentially allows ungerade terms into the final wavefunction which then satisfies the requirement that the transition involve a g->u symmetry change. This is often "explained" as the vibrational motion of the molecule temporarily removing the centre of symmetry or inversion centre.

<u>In Notes Activity</u>

- 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,

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

More Vibronic Transitions

- there are other ways the formal selection rules can be circumvented, the physics/mathematics behind this is complex and so I will only just touch on the basic concepts behind the breakdown
- even if the μ_{fi} is zero by symmetry there is still the possibility of a transition arising
  - when we derived the equations for infrared and Raman spectroscopy we expanded the dipole moment in terms of the normal modes.

$$\mu = \mu_0 + \sum_k \left(\frac{\partial \mu}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum_k \left(\frac{\partial^2 \mu}{\partial Q_k^2} \right)_0 Q_k^2 + \cdots \qquad \text{Equation 9}$$

  - we said the important term was the first order term

$$\mu_{fi} = \sum_k \left(\frac{\partial \mu}{\partial Q_k} \right)_0 \langle \chi_f | Q_k | \chi_i \rangle \qquad \text{Equation 10}$$

  - the first time we did this we assumed the electronic and nuclear wavefunctions were separable, and we were only considering vibrations on a single electronic state
  - however if the nuclear and electronic motion are not separated or we are treating an excitation between different electronic states we must use the full equation:

$$\mu_{fi} = \int\int \chi_f \psi_f \, \mu \psi_i \chi_i d\tau_e d\tau_n \quad \textit{and} \quad \mu = \mu_0 + \sum_k \left(\frac{\partial \mu}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum_k \left(\frac{\partial^2 \mu}{\partial Q_k^2} \right)_0 Q_k^2 + \cdots$$

$$\mu_{fi} = \int \chi_f \left[\int \psi_f \left(\mu_0 + \sum_k \left(\frac{\partial \mu}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum_k \left(\frac{\partial^2 \mu}{\partial Q_k^2} \right)_0 Q_k^2 + \cdots \right) \psi_i d\tau_e \right] \chi_i d\tau_n$$

$$\mu_{fi} = \langle \psi_f | \mu_0 | \psi_i \rangle \langle \chi_f | \chi_i \rangle + \sum_k \langle \psi_f | \left(\frac{\partial \mu}{\partial Q_k} \right)_0 | \psi_i \rangle \langle \chi_f | Q_k | \chi_i \rangle$$
$$+ \frac{1}{2} \sum_k \langle \psi_f | \left(\frac{\partial^2 \mu}{\partial Q_k^2} \right)_0 | \psi_i \rangle \langle \chi_f | Q_k^2 | \chi_i \rangle + \cdots$$

Equation 11

  - remember that the differential is a *number* (the change in dipole evaluated around the equilibrium geometry of the mode), thus even though it might appear dependent on the nuclear motions (ie dependent on Q) it is brought into the electronic integral.
  - you should recognise the zero order term of μ_{fi} as the one leading to vibronic transitions discussed above

$$\langle \psi_f | \mu_0 | \psi_i \rangle \langle \chi_f | \chi_i \rangle \qquad \text{Equation 12}$$

  - I will refer in the following to the first order as the *linear* term, and to the second order term as the *quadratic* term

first: $\sum_k \langle \psi_f | \left(\frac{\partial \mu}{\partial Q_k} \right)_0 | \psi_i \rangle \langle \chi_f | Q_k | \chi_i \rangle$ second: $\frac{1}{2} \sum_k \langle \psi_f | \left(\frac{\partial^2 \mu}{\partial Q_k^2} \right)_0 | \psi_i \rangle \langle \chi_f | Q_k^2 | \chi_i \rangle$

Equation 13

- so far we have assumed that the potential energy surface is harmonic, however in reality the potential is anharmonic
  - for example the potential can take on the form of a Morse potential
  - if vibrations are large they will extend out of the "harmonic" region of a potential
  - anharmonicity can have significant and multiple effects

An Anharmonic Wavefunction

- first the nuclear wavefunction or vibrational solutions change slightly, however the new solutions can be expanded in terms of original HO functions
  - the main effect is to "reduce" the restriction of the $\Delta v \pm 1$ selection rule for vibrations in the first order term

$$\chi_i' = \sum_{\alpha} c_\alpha \chi_\alpha \quad \chi_f' = \sum_{\beta} c_\beta \chi_\beta$$

$$\langle \chi_f | Q_k | \chi_i \rangle \neq 0 \qquad \text{Equation 14}$$

$$\left\langle \sum_{\beta} c_\beta \chi_\beta \middle| Q_k \middle| \sum_{\alpha} c_\alpha \chi_\alpha \right\rangle = \sum_{\alpha,\beta} c_\beta c_\alpha \langle \chi_\beta | Q_k | \chi_\alpha \rangle$$

An Anharmonic Potential

- next because the potential is not harmonic we cannot assume that the second order term is small or zero, these terms can contribute and $\mu_{fi} \neq 0$

$$\frac{1}{2}\sum_k \langle \psi_f | \left(\frac{\partial^2 \mu}{\partial Q_k^2} \right)_0 | \psi_i \rangle \langle \chi_f | Q_k^2 | \chi_i \rangle \qquad \text{Equation 15}$$

  - the electronic component can be non-zero
  - in addition the vibrational selection rule changes and we have the requirement that $\Delta v \pm 2$, the nuclear component
  - components in the third order and higher term of μ_{fi} can also contribute allowing for some intensity in formally forbidden transitions

Non-diagonal Hessian

- so far we have still assumed that the Hessian is a diagonal matrix, if the diagonalisation of the Hessian is not complete and there are a few (small) **off-diagonal terms** left then
  - these contribute to the second order terms, this combining of the vibrational (normal modes) Q allows for some intensity in formally forbidden transitions
  - again the electronic component can be non-zero

$$\frac{1}{2}\sum_k \langle \psi_f | \left(\frac{\partial^2 \mu}{\partial Q_i \, \partial Q_j} \right)_0 | \psi_i \rangle \langle \chi_f | Q_i Q_j | \chi_i \rangle \qquad \text{Equation 16}$$

Charge Transfer

  - excitations are not limited to d-d transitions, the lower (occupied) and higher energy (vacant) ligand based orbitals are also available
  - ligands with π-donor or π-acceptor orbitals have these in the right region for absorption to occur in the visible range

- these are called LMCT or *ligand to metal charge transfer* or MLCT or *metal to ligand charge transfer* bands
- transitions are "angular momentum" and parity allowed and are intense
- MLCT occur from dAO dominated MOs to ligand dominated MOs, they tend to be high energy and on the blue to UV end of the spectrum for 3d TMs (<400nm) however for the 4d and 5d TMs they can occur in the visible region
- LMCT require empty metal orbitals and thus occur for high oxidation states or for TM to the left of the periodic table, in this process the ligand can be formally oxidised and the metal reduced
- ligand to ligand transitions can also occur, and you have seen these ligands referred to as **chromophores**. The ligands tend to be π-conjugated or aromatic, although SCN, NO_2 and NO_3 also have strong transitions in the visible region.

Explicit consideration of the vibrational wavefunction (not examined)

- The total vibrational wavefunction is a **product** of the $\varphi_i(Q_i)$

$$\chi_n = \prod_i \varphi_i(Q_i) = \varphi_{v1}(Q_1)\varphi_{v2}(Q_2)\varphi_{v3}(Q_3)\cdots \qquad \text{Equation 17}$$

- in the ground state each of these wavefunctions contributes the lowest level quanta of vibrational energy to the molecule, ν_1, ν_2, ν_3 …=0 (the zero-point energy of the molecule).
- when the molecule is excited by interaction with light individual modes are excited and can have more quanta of energy, for example ν_1=1 and ν_2, ν_3 …=0.
- the ν_i=0 level is called the fundamental mode, and the ν_i=1 level is called the "first overtone"
- it is normal to move over to a Dirac notation, where the order within the Dirac bra-ket brackets indicates which mode is being considered
- below is an example using just two vibrational functions
- we assume that initially all modes are in their ground vibrational state (quantum no) ν=0, after the interaction one mode (Q_1) is excited by a single quantum to ν=1.

$$\begin{aligned}
\chi_i &= \varphi_{v1}(Q_1)\varphi_{v2}(Q_2) = [0\,0] \\
\chi_f &= \varphi_{v1}(Q_1)\varphi_{v2}(Q_2) = [1\,0] \\
\mu_{fi} &= \int \varphi_{v1}(Q_1)\varphi_{v2}(Q_2)\mu\varphi_{v1}(Q_1)\varphi_{v2}(Q_2)dQ_1dQ_2 \\
\mu_{fi} &= \langle 1\,0\,|\mu|0\,0\,\rangle
\end{aligned} \qquad \text{Equation 18}$$

- it is easy to see how this can be generalised to more vibrational states

$$\mu_{fi} = \langle 1\,0\,0\cdots|\mu|0\,0\,0\cdots\rangle \qquad \text{Equation 19}$$

- and we can generalise further, to consider the excitation of the vibrational wavefunction associated with coordinate Q_i which is initial in quantum state ν=n and is excited to state ν=n'

$$\mu_{fi} = \langle 0\,0\cdots n_i'\cdots 0|\mu|0\,0\cdots n_i\cdots 0\rangle \qquad \text{Equation 20}$$

- now consider the excitation of a single mode in isolation

- expand out the linear term of the transition dipole moment
- the initial individual modes Q are in their lowest energy states
- after the absorption one vibrational mode Q_1 has been excited, all others remain in their ground state

$$\sum_k \langle \psi_f | \left(\frac{\partial \mu}{\partial Q_k} \right)_0 | \psi_i \rangle \langle \chi_f | Q_k | \chi_i \rangle$$

$$notation \; \langle \psi_f | \left(\frac{\partial \mu}{\partial Q_k} \right)_0 | \psi_i \rangle = \left(\frac{\partial \mu'}{\partial Q_k} \right)_0 \qquad \text{Equation 21}$$

$$\chi_i = | \; 0 \;\; 0 \;\; 0 \;\; \cdots \; \rangle \quad \chi_f = | \; 1 \;\; 0 \;\; 0 \;\; \cdots \; \rangle$$

$$\begin{aligned}
&\sum_k \langle \psi_i | \left(\frac{\partial \mu}{\partial Q_k} \right)_0 | \psi_i \rangle \langle \chi_f | Q_k | \chi_i \rangle \\
&= \left(\frac{\partial \mu'}{\partial Q_1} \right)_0 \langle \; 1 \;\; 0 \;\; 0 \;\; \cdots | Q_1 | \; 0 \;\; 0 \;\; 0 \;\; \cdots \rangle + \left(\frac{\partial \mu'}{\partial Q_2} \right)_0 \langle \; 1 \;\; 0 \;\; 0 \;\; \cdots | Q_2 | \; 0 \;\; 0 \;\; 0 \;\; \cdots \rangle + \cdots \\
&= \left(\frac{\partial \mu'}{\partial Q_1} \right)_0 \langle 1 | Q_1 | 0 \rangle \underbrace{\langle 0 | 0 \rangle}_{=1} \underbrace{\langle 0 | 0 \rangle}_{=1} \cdots + \left(\frac{\partial \mu'}{\partial Q_2} \right)_0 \underbrace{\langle 1 | 0 \rangle}_{=0} \langle 0 | Q_2 | 0 \rangle \underbrace{\langle 0 | 0 \rangle}_{=1} \cdots + 0 \cdots \\
&= \left(\frac{\partial \mu'}{\partial Q_1} \right)_0 \langle 1 | Q_1 | 0 \rangle \neq 0
\end{aligned}$$

Equation 22

- after eliminating all the terms that are zero due to the orthogonality of vibrational wavefunctions we are left with a single term in Equation 22

- now we can consider the effect of multiple excitations, in this case both Q_1 and Q_2 are excited

$$\begin{aligned}
&\chi_i = | \; 0 \;\; 0 \;\; 0 \;\; \cdots \; \rangle \quad \chi_f = | \; 1 \;\; 0 \;\; 0 \;\; \cdots \; \rangle \\
&\sum_k \langle \psi_i | \left(\frac{\partial \mu}{\partial Q_k} \right)_0 | \psi_i \rangle \langle \chi_f | Q_k | \chi_i \rangle \\
&= \left(\frac{\partial \mu'}{\partial Q_1} \right)_0 \langle \; 1 \;\; 1 \;\; 0 \;\; \cdots | Q_1 | \; 0 \;\; 0 \;\; 0 \;\; \cdots \rangle + \left(\frac{\partial \mu'}{\partial Q_2} \right)_0 \langle \; 1 \;\; 1 \;\; 0 \;\; \cdots | Q_2 | \; 0 \;\; 0 \;\; 0 \;\; \cdots \rangle + \cdots \\
&= \left(\frac{\partial \mu'}{\partial Q_1} \right)_0 \langle 1 | Q_1 | 0 \rangle \underbrace{\langle 1 | 0 \rangle}_{=0} \underbrace{\langle 0 | 0 \rangle}_{=1} \cdots + \left(\frac{\partial \mu'}{\partial Q_2} \right)_0 \underbrace{\langle 1 | 0 \rangle}_{=0} \langle 1 | Q_2 | 0 \rangle \underbrace{\langle 0 | 0 \rangle}_{=1} \cdots + 0 \cdots \\
&= 0
\end{aligned}$$

Equation 23

- if there are two excitations the terms reduce to zero and thus multiple excitations cannot contribute to the first order term
- however if we consider the effects of incomplete diagonalisation of the hessian, and again consider both Q_1 and Q_2 are excited, then the result can be non-zero, thus multiple excitations can contribute to the second order term!

$$
\begin{aligned}
&\sum_{k,j}\left\langle \psi_f \right|\left(\frac{\partial^2 \mu}{\partial Q_k\,\partial Q_j}\right)_0 \left|\psi_i\right\rangle \left\langle \chi_f \middle| Q_k Q_j \middle| \chi_i\right\rangle + \cdots \neq 0 \\
&= \left(\frac{\partial^2 \mu'}{\partial Q_1\,\partial Q_2}\right)_0 \left\langle\; 1 \;\; 1 \;\; 0 \;\; \cdots \;\middle| Q_1 Q_2 \middle|\; 0 \;\; 0 \;\; 0 \;\; \cdots \;\right\rangle + \left(\frac{\partial^2 \mu'}{\partial Q_1\,\partial Q_3}\right)_0 \left\langle\; 1 \;\; 1 \;\; 0 \;\; \cdots \;\middle| Q_1 Q_3 \middle|\; 0 \;\; 0 \;\; 0 \;\; \cdots \;\right\rangle + \cdots \\
&= \left(\frac{\partial^2 \mu'}{\partial Q_1\,\partial Q_2}\right)_0 \langle 1|Q_1|0\rangle\langle 1|Q_2|0\rangle\underbrace{\langle 0|0\rangle}_{=1} + \left(\frac{\partial^2 \mu'}{\partial Q_1\,\partial Q_3}\right)_0 \langle 1|Q_1|0\rangle\underbrace{\langle 1|0\rangle}_{=0}\langle 0|Q_3|0\rangle + 0\cdots \\
&= \left(\frac{\partial^2 \mu'}{\partial Q_1\,\partial Q_2}\right)_0 \langle 1|Q_1|0\rangle\langle 1|Q_2|0\rangle
\end{aligned}
$$

Equation 24

Key Points

- be able to evaluate if a d-d transition is allowed or forbidden for spin, parity, symmetry or angular momenta
- be able to describe, using appropriate equations and diagrams, vibronic transitions, and how they are evidenced in spectra.
- be able to write equations deriving the Frank-Condon factors, be able to discuss how strong vibrational overlap integrals arise, and the link with Fermi's Golden Rule
- be able to determine if a forbidden transition is vibronically allowed via coupling of the nuclear and electronic wavefunctions
- be able to briefly describe other ways in which the selection rules can be circumvented
- be able to explain and illustrate on a MO diagram charge transfer excitations

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? $\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$
- 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*-$M(H_2O)_4Cl_2$?
- 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.