Electronic Spectroscopy
Application of Group Theory

• $\Psi_{Tot}$ assumed to be separable

$$\Psi_{tot} = \psi_{elec}\chi_{vib} = |n\rangle|v\rangle$$

• If a transition is not allowed by symmetry then vibronic coupling can be invoked as a perturbation. We can use group theory for both Franck-Condon and vibronic spectroscopy.
Selection Rules

Transition moment integral for ground state \((gs) \Rightarrow \text{excited state} \,(es)\) is,

\[ M_{ge} = \langle gs | \mu | es \rangle \]

The state wavefunctions (orbital\(\cdot\)vibrational) are:

\( |nv\rangle \equiv \text{ground state} \)

\( |n'v'\rangle \equiv \text{excited state} \)

The dipole operator is independent of spin coordinates,

\((\mu = e\rho) \; \rho = x, y \text{ or } z\)

\[ M_{ge} = \langle nv | e\rho | n'v' \rangle \]

The result after separation of electronic and nuclear terms is:

\[ M_{ge} = \langle n | e\rho | n' \rangle \langle v | v' \rangle \]
For electronic transitions, the initial vibrational state will *usually* be \( v = 0 \) and \( v' \) in the excited state

\[
M_{ge} = \langle n|e\rho|n'\rangle\langle 0|v'\rangle
\]

The intensity of the transition is proportional to \( M_{ge}^2 \), so,

\[
I \propto |M_{ge}|^2 = \langle n|e\rho|n'\rangle^2\langle 0|v'\rangle^2
\]

• \( \langle n'|e\rho|n\rangle \) gives rise to the orbital or symmetry selection rules. If the direct product \( \Gamma(n') \Gamma(n) \) transforms as \( x, y, \) or \( z \) the electronic transition is said to be “\( x \)-polarized”, “\( y \)-polarized” or “\( z \)-polarized”, respectively.

• \( \langle 0|v'\rangle \) is the overlap of the vibrational wavefunctions in the ground (\( v=0 \)) and excited electronic states. The \( \langle v|v'\rangle^2 \) terms are referred to as the Franck-Condon factors and can modulate the intensity of the electronic transition.
Franck-Condon Selection Rule

There are two ways to look at the Franck-Condon active selection rule. First, we can ask whether the direct product of the ground (n) and excited (n’) states combined with electromagnetic radiation (x, y or z) contains the totally symmetric representation:

\[ \Gamma(n') \otimes \Gamma(xyz) \otimes \Gamma(n) = \Gamma_{\text{totally symmetric}} \]
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\[
\Gamma(n') \otimes \Gamma(\text{xyz}) \otimes \Gamma(n) = \Gamma_{\text{totally symmetric}}?
\]

If the answer is affirmative then the transition is allowed. An alternative method is to ask whether the direct product of ground and excited states contains \(x, y \text{ or } z\).

\[
\Gamma(n') \otimes \Gamma(n) = \Gamma(\text{xyz})?
\]
The short cut method is to ask whether the direct product of ground and excited states contains x, y or z.

\[ \Gamma(n') \otimes \Gamma(n) = \Gamma(xyz) ? \]

If the answer is yes, then the transition is allowed. The idea here is that any irrep times itself is totally symmetric. Therefore if \( \Gamma(n') \otimes \Gamma(n) = \Gamma(xyz) \) then \( \Gamma(n') \otimes \Gamma(xyz) \otimes \Gamma(n) = \Gamma \) totally symmetric
Vibronic Coupling Selection Rule

If a distortion of the molecule is required to permit a transition to occur then we refer to the transition as vibronic. We can understand the process as a state mixing of higher lying states into the excited state. In this case the symmetry of the vibronic mode also enters into consideration. The symmetry of vibronic states given by the direct product of the orbital and vibrational irreps dictate the selection rules.

\[ \Gamma_{es} \otimes \Gamma_{vib} \otimes \Gamma_{xyz} \otimes \Gamma_{gs} = \Gamma_{\text{totally symmetric}} \]

Note that the difference with respect to the Franck-Condon mechanism is the additional term \( \Gamma_{vib} \). Actually, we could say that there is a \( \Gamma_{vib} \) in the FC mechanism as well, but it is always totally symmetric by definition. Therefore, \( \Gamma_{vib} \) in the FC case does not play a role in the direct product.
Vibronic Coupling Selection Rule
Short Cut

We can use the same logic applied the Franck-Condon case to make our task easier. We take the direct product of the electronic states and the non-totally symmetric vibration that couples them. If this direct product contains $x$, $y$ or $z$ then the transition is vibronically allowed. The condition is:

$$\Gamma_{es} \otimes \Gamma_{vib} \otimes \Gamma_{gs} = \Gamma_{xyz}$$

This short cut makes it easy to do a quick search using the character table. One can test a number of vibronic modes to see whether they have the correct symmetry to couple two electronic states.
In centrosymmetric molecules, d-orbitals are always *gerade* while m is always *ungerade* so d-d transitions are orbitally or Laporte forbidden $\langle g | e \rho | g \rangle = 0$. However, these transitions can be *vibronically allowed* through *ungerade* vibrations since in the $v=1$ level of an *ungerade* vibration, the molecule loses its center of symmetry and thus the selection rule is relaxed.

$$\Gamma_{es} \Gamma_{vib} \Gamma_{xyz} \Gamma_{gs} = \Gamma_{\text{totally symmetric}}$$

**Vibronically-active:** $\Gamma_{es} \Gamma_{vib} \Gamma_{gs}$ must transform as $\Gamma_{xyz}$

In cases like this, the $v = 0 \rightarrow v' = 0$ band (the “origin” or 0-0’ band) is not observed and the lowest energy peak maximum will be at $E_{0-0'}$ plus one quantum of excited state vibrational energy, i.e. at $E_{0-1'}$.

**Such peaks are referred to as "false origins"**
The lowest energy electric dipole *allowed* transition is from the \( v' = 0 \) vibrational level of the ground electronic state to the \( v = 0 \) vibrational level of the lowest energy excited electronic state. This transition is called the origin, or 0-0’ (“zero-zero”) band.

The lowest energy electric dipole *forbidden* transition is from the \( v = 0 \) vibrational level of the ground electronic state to the \( v' = 1 \) vibrational level of a vibronically-active mode of the lowest excited electronic state. This transition is called a false origin.

To be vibronically-active, the direct product of a mode with the irreps of \( m \) *and* with the excited state irrep must transform as the ground state irrep.
Vibronic Transitions in Metal Complexes

A-D: ligand to metal charge transfer bands (LMCT)
E-F: metal to ligand charge transfer bands (MLCT)
G: d-d (Ligand Field) bands
H: ligand $\pi \rightarrow \pi^*$

Vibronic Transitions in Aromatic Molecules

The particle on a circle model shows us that there are allowed and forbidden transitions for aromatic molecules. These are known as B and Q bands, respectively. They are $\pi - \pi^*$ transitions observed in every aromatic molecule.
Vibronic Transitions involving Heteroatoms

The lone pair on N, O, S and other heteroatoms in aromatic molecules give rise to $n-\pi^*$ transitions, which have out-of-plane character. These are usually forbidden transitions. We have considered the example of formaldehyde in our Introduction to vibronic coupling.