

Electronic Spectroscopy

Application of Group Theory

- Ψ_{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 excited state (es) is,

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

The state wavefunctions (orbital•vibrational) are:

$$|nv\rangle \equiv \textit{ground state}$$

$$|n'v'\rangle \equiv \textit{excited state}$$

The dipole operator is independent of spin coordinates,
($\mu = e\rho$) $\rho = x, y$ 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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$$\Gamma(n') \otimes \Gamma(xyz) \otimes \Gamma(n) = \Gamma_{\text{totally symmetric}} ?$$

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 or z .

$$\Gamma(n') \otimes \Gamma(n) = \Gamma(xyz) ?$$

Franck-Condon Selection Rule

Short Cut

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

$$\text{if } \Gamma(n') \otimes \Gamma(n) = \Gamma(xyz)$$

$$\text{then } \Gamma(n') \otimes \Gamma(xyz) \otimes \Gamma(n) = \Gamma_{\text{totally symmetric}}$$

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.

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

Note that the difference with respect to the Franck-Condon mechanism is the additional term Γ_{vib} . Actually, we could say that there is a Γ_{vib} in the FC mechanism as well, but it is always totally symmetric by definition. Therefore, Γ_{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 p 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.

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

vibronically-active: $\Gamma_{\text{es}} \Gamma_{\text{vib}} \Gamma_{\text{gs}}$ must transform as Γ_{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 $E_{0-1'}$.

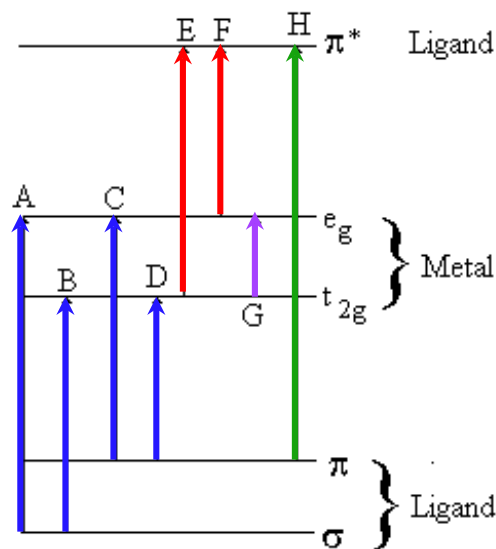
Such peaks are referred to as "false origins"

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 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.