2.15: Breaking Symmetries

Local Symmetry

Small modification of the molecule that reduces symmetry will have small effects on the spectra (e.g. H_2CO to CH_3CHO).
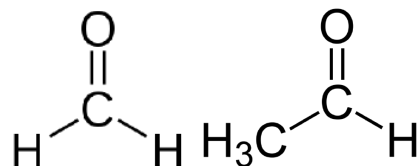

Figure 2.15.1: Formaldehyde (left) and acetaldehyde (right)

This gives same spectra patterns even though the point group of acetaldehyde is Cs, containing only two representations A' and A'' with $x, y = A'$ and $z = A''$. Thus, *all transitions are symmetry allowed*. Because of this, the idea of **local symmetry** is important. Local symmetry is that associated with the **electronically active component** of the molecule only, which is the C=O moiety.
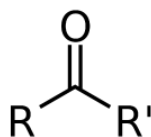
Independent of what R and R' are, provided that they not interact strongly with the C=O bond through conjugation etc. Hence this introduces the concept of a "correlation or coherence length" of the excitation. Hence the UV-Vis spectra of all compounds of this type are similar: acetone, acetaldehyde, cyclopentanone, etc).

Acetone:

- $\pi \to \pi*$ with $\lambda_{max} = 188\,nm$ and $\varepsilon = 1860$
- $n \to \pi^*$ with $\lambda_{max} = 279\,nm$ and $\varepsilon = 15$

vs. formaldehyde

- $\pi \to \pi*$ with $\lambda_{max} = 185\,nm$ and $\varepsilon > 10,000$
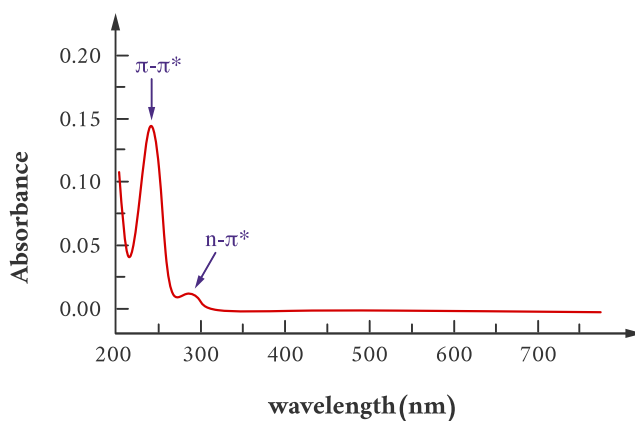- $n \to \pi^*$ with $\lambda_{max} = 270nm$ and $\varepsilon = 100$

Figure 2.15.2: Electronic absorption spectrum of Formaldehyde in water. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Vibronic Coupling

The $^1A_2 \leftarrow {}^1A_1$ transition is forbidden by symmetry selection rules for formaldehyde. Why do we see it in the H_2CO molecule at all? Answer= **Vibronic coupling.** The Born-Oppenheimer approximation is not absolute. There is always some interaction between vibrational and electronic motion in a molecule. This means that the separation

$$|q, r\rangle \approx |r; q\rangle_{el} |q\rangle_{vib}$$

is not always exact. Thus we must consider the transition moment integral in its entirety.

$$\langle q, r|\hat{M}|q, r\rangle^{ex}$$

Let's assume $|q, r\rangle$ is in its ground state for all vibrations ($k_b T <$ all vibrational frequencies). The irreducible representation of all vibrations in non-excited state is A_1. Thus $|q, r\rangle$ has the symmetry of the electron wavefunction itself $|r\rangle$. In general, the symmetry is the direct product of the symmetry representations of $|r\rangle$ and $|q\rangle$.

Now, for the *excited* state wavefunction ($|q, r\rangle^{ex}$), the symmetry is that of the electronic wavefunction ($|r\rangle^{ex}$) **only** if the vibrational state is totally symmetric (i.e. $v' = 0$) for all normal modes or only A_1 vibrations are excited. However, if one-quantum of a non-symmetric vibrational state is excited along with the electronic state (upon absorption of light), then the excited state representation will be:

$$\Gamma_{total} = \underbrace{\Gamma\left(|r\rangle^{rx}\right)}_{\text{vibration symmetry}} \otimes \underbrace{\Gamma\left(|q\rangle^{j^{ex}}\right)}_{\text{electronic symmetry}}$$

If Γ_{total} **contains the same representation as a component of $\hat{M}$ then the transition becomes weakly allowed vibrationally. Important, the appropriate vibrational mode is exited simultaneously with electronic transition.**

> ✔ Example 2.15.1: Formaldehyde
>
> $\hat{M}$ in the C_{2v} point group has the following representations for x, y, and z polarizations:
>
> $$\begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix} = \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix}.$$
>
> Hence, the $^1A_2\,(n, \pi^*) \leftarrow {}^1A_1$ transition in H_2CO transition can be vibronically coupled (allowed) if the quantum of a normal mode with symmetry:
>
> - a_1 giving a z-polarization
> - b_1 giving a y-polarization
> - b_2, giving a x-polarization
>
> is *simultaneously* excited by the absorption of the photon. We can use this to predict the symmetries of the normal modes of vibration that a molecule has. A mode active in inducing an electronic transition (vibronically) is called an **inducing mode** or **promoting mode**.

Symmetry

Assume the electronic (lowest vibrational level) ground state is totally symmetry (e.g., closed shell) is usually the case for organic molecules. A transition may be vibronically induced by exciting one quantum of a vibrational mode of symmetry, , provided the direct produce

$$\Gamma_q \otimes \Gamma_{\hat{M}} \otimes \Gamma_{ex} = A_1 \text{ or } A_{1g}$$

where $\Gamma_{\hat{M}}$ is the symmetry of the $\hat{M}$ operator and Γ_{ex} is the symmetry of the electronic excited state. Of course, the allowed vibrations must contain one of the symmetry Γ_{vib}.
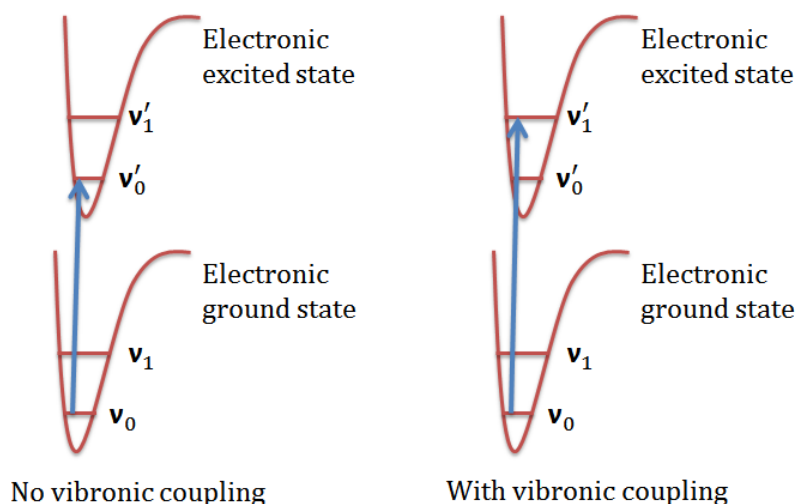
Figure 2.15.3: the 0-0 electronic transition (left) and the 0-1 electronic transition that is coupled with a vibrational transition (right)

The $0 \longrightarrow 0$ band does not appear in a vibrationally-induced electronic transition! This is one of its characteristics other than its reduced oscillator strength.

## Possible vibrational modes for H_2CO

A nonlinear molecule has $3N - 6$ internal degrees of vibrational freedom. These are these many vibrational frequencies, each of which has a symmetry of an irreducible representation for the molecular point group (https://www.chem.purdue.edu/jmol/vibs/form.html). For formaldehyde, with $N = 4$, we have $3 \times 4 - 6 = 6$ vibrational degrees of freedom which are distributed as normal modes comprising of a superposition of local modes. These turn out to (we will discuss later) transform as: $3a_1, b_1, 2b_2$.
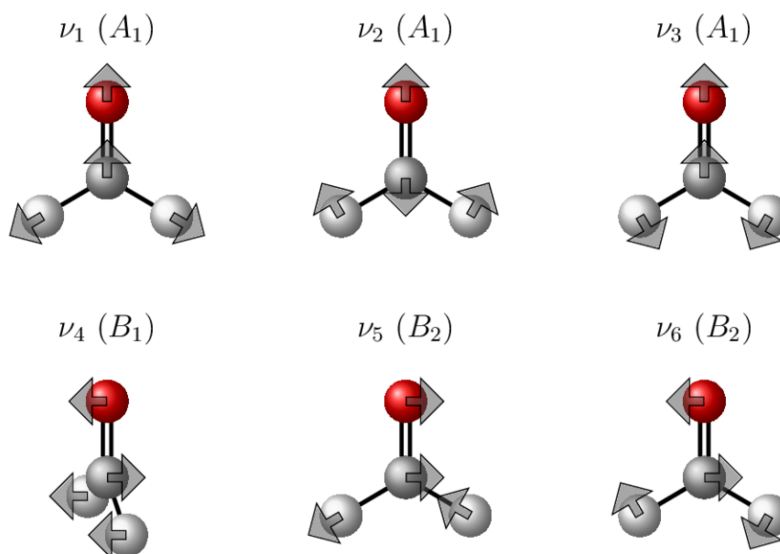
Thus only b_1 and b_2 unsymmetrical modes are possible? We can thus have no Z-polarized vibronic transitions (no a_2 mode in H_2CO), but we can have x- and y-polarized vibronic transition with b_2 and b_1 inducing modes, respectively. Hence, we can use polarization to identify inducing modes for vibronic transitions.

> ✔ Example 2.15.1: Octahedral Transitions Metal Complexes
>
> The d $\longrightarrow$ d transitions in octahedral complexes are electronically forbidden (Laporte forbidden since they are g $\longleftrightarrow$ g), but they can be weakly allowed vibrationally by vibrations that remove the inversion center. Let's consider the $(NH_3)_6 Co^{III}$ complex that has a d^6 configuration (loss of two 4s electrons and one d electron to make the ion).
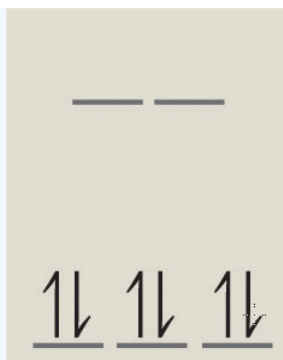
The ground state is t_{2g} and the excited state e_g. Is a d-d transition allowed?

The ground state symmetry is and has a O_h symmetry of ground state configuration due to the octahedral ligand field. Let's consider the potential electronic d $\longrightarrow$ d transition from the t_{2g} orbitals to the e_g orbitals. The excited electronic state symmetries are obtained from the orbital direct product:

$$\Gamma_{t_{2g}} \otimes \Gamma_{e_g} = T_{1g} + T_{2g}$$

(From direct product table for O_h)

Both $^1T_{2g} \leftarrow {}^1A_{1g}$ and $^1T_{1g} \leftarrow {}^1A_{1g}$ transitions are forbidden. Now, $\hat{M}$ or $\{x, y, z\}$ form the basis for a triply degenerate representation T_{1u} in O_h.

O_h	E	8C$_3$	6C$_2$	6C$_4$	3C$_2$ = (C$_4$)^2	i	6S$_4$	8S$_6$	3σ_h	6σ_d	linear functions, rotations	quadratic functions	cubic functions
A$_{1g}$	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2+z^2	-
A$_{2g}$	+1	+1	-1	-1	+1	+1	-1	+1	+1	-1	-	-	-
E$_g$	+2	-1	0	0	+2	+2	0	-1	+2	0	-	(2z^2-x^2-y^2, x^2-y^2)	-
T$_{1g}$	+3	0	-1	+1	-1	+3	+1	0	-1	-1	(R$_x$, R$_y$, R$_z$)	-	-
T$_{2g}$	+3	0	+1	-1	-1	+3	-1	0	-1	+1	-	(xz, yz, xy)	-
A$_{1u}$	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
A$_{2u}$	+1	+1	-1	-1	+1	-1	+1	-1	-1	+1	-	-	xyz
E$_u$	+2	-1	0	0	+2	-2	0	+1	-2	0	-	-	-
T$_{1u}$	+3	0	-1	+1	-1	-3	-1	0	+1	+1	(x, y, z)	-	(x^3, y^3, z^3) [x(z^2+y^2), y(z^2+x^2), z(x^2+y^2)]

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
T_{2u}	+3	0	+1	-1	-1	-3	+1	0	+1	-1	-	-	$[x(z^2-y^2), y(z^2-x^2), z(x^2-y^2)]$

For instance, for the purely electronic transition $^1T_{1g} \leftarrow {}^1A_{1g}$ component,

$$T_{1g} \otimes T_{1u} \otimes A_{1g} = A_{1u} + E_u + T_{1g} + T_{2u}$$

this **does not contain** the A_{1g} symmetry representation (i.e., Laporte forbidden) and is therefore, this is a forbidden electronic transition.

What vibrations will couple these two electronic states? An octahedral complex (7 atoms so there are $3 \times 7 - 6 = 15$ normal modes) has the following vibrational symmetries (discussed later):

$$\Gamma_{vib} = a_{1g} + e_g + 2t_{1u} + t_{2g} + t_{2u}$$

(15 modes here, count them up)

The potential promoting modes are the $2t_{1u}$ and t_{2u} normal modes. The t_{1u} mode will serve as a promoting mode provided

$$T_{1u} \otimes \{T_{1g} \otimes T_{1u} \otimes A_{1g}\} =$$
$$T_{1u} \otimes [A_{1u} + E_u + T_{1u} + T_{2u}] = A_{1g}$$

This turns out to contain A_{1g}, so the t_{1u}'s can serve as a promoting mode for a vibrationally allowed transition. So it turns out, also can the t_{2u} mode.

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