Electronic states, Jablonski diagram and Franck-Condon principle.

We have shown that everything lights up with SE:

$$\hat{H}\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\vec{r})\Psi = E\Psi$$

$$\Downarrow$$

$$E \sim \frac{\hbar^2}{m} \quad \text{or} \quad E \sim \frac{\hbar^2}{mr^2}$$

It all depends on mass and size of the particle.

$m_H \sim 1.67 \cdot 10^{-27}$ kg

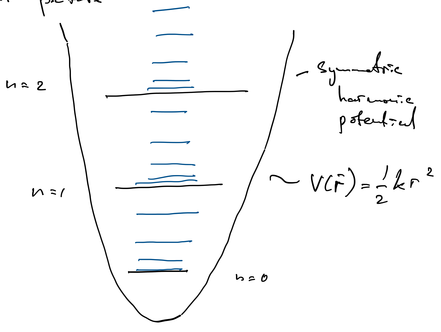
$m_e \sim 9.11 \cdot 10^{-31}$ kg $\quad 10^4$!

rotation $\longrightarrow$ $10^{-1} - 10^2$ cm^{-1} (THz)

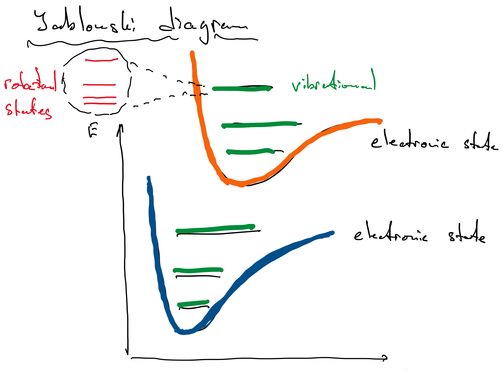
vibration $\longrightarrow$ $10^2 - 10^3$ cm^{-1} (IR)

electronic $\longrightarrow$ $10^3 - 10^5$ cm^{-1} (UV-VIS)

Final picture



Jablonski diagram



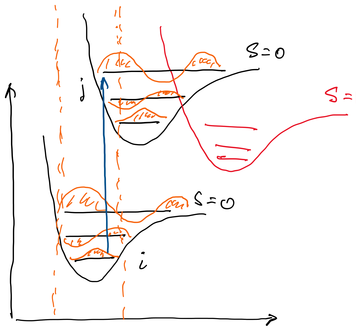
Which transitions will be allowed?

Rotation and vibration selection rules:

$$\Delta n = \pm 1 \quad \Delta l = \pm 1 \quad \Delta m = 0$$

Electronic states:

$$\Delta S = 0 \quad \text{- spin} \begin{cases} \uparrow \\ \downarrow \end{cases}$$



Besides selection rules $\begin{cases} \Delta n = \pm 1 \\ \Delta l = \pm 1 \\ \Delta m = 0 \\ \Delta S = 0 \end{cases}$

we need to see where wavefunctions overlap:

$$\int \Psi_i^* \mu \Psi_j \neq 0$$

Franck-Condon principle:

1) Overlap between two conformations must exist in $\vec{r}$

2) Only vertical transitions are allowed

This has two reasons:

a) transition bond length to remain constant

or

b) time of transitions infinitely shorter than vibration.