Lecture 17, Feb 17, 2023

Combining Electronic and Vibrational Spectra

- The electronic transition happens much faster than nuclear motion; so this limits where we can land on the upper state
  - This is a vertical transition
  - The favoured transitions are to vibrational states that have the same probabilities before and after the transition (there is more overlap)
  - In the excited state there is a slight distortion; the atoms move further apart because they are higher energy, and electron density between atoms is depleted

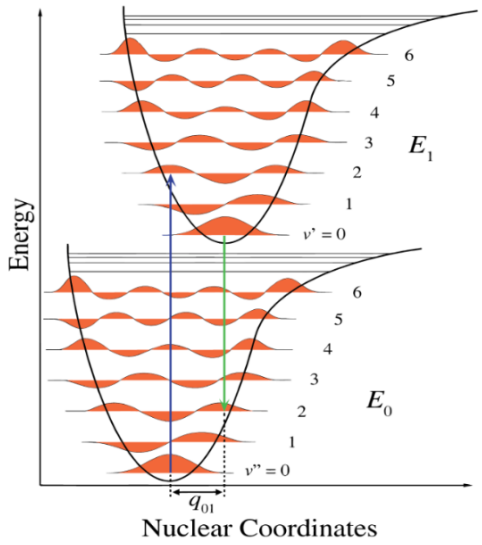

Figure 1: Overlap between vibrational wavefunctions decides transition probability

- After the electronic transition, internal transitions happen between vibrational states
  - This happens very fast because there are a lot of vibrational motions
- After falling to the vibrational ground state, it then falls back down the electronic transition and emits a photon (fluorescence)
  - This transition probabilities is determined in the same way as going up
- Phosphorescence happens after inter system crossing
  - This is much weaker because it's less likely, but it's longer lived
  - e.g. old CRT monitors
- The spectrum of an atom is a sharp line, for a diatomic atom there are multiple lines that begin to merge together, and for a polyatomic atom the lines completely merge together
- As proteins unfold, their spectrum shape changes – we can watch DNA unfold in transcription in real time using this

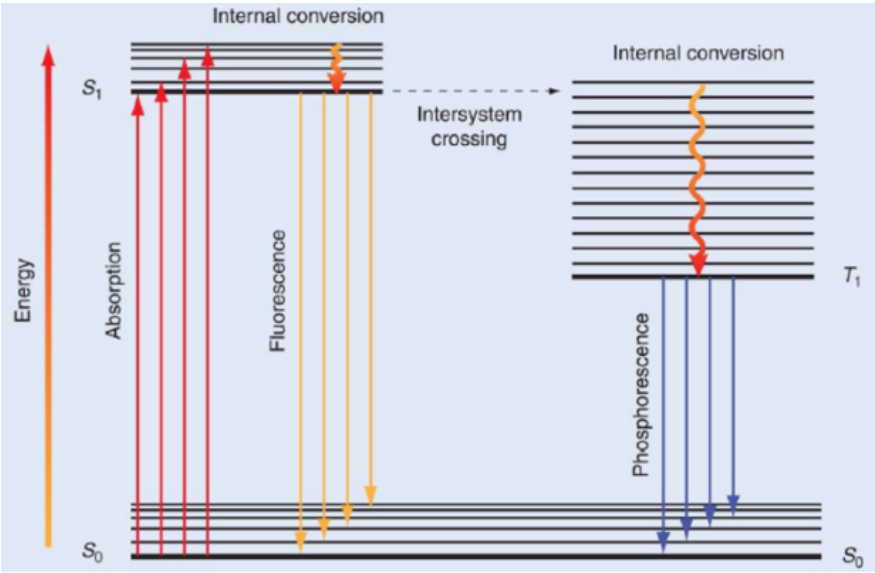

Figure 2: Summary of possible transitions for excited molecules