Lecture 16, Feb 16, 2023

IR Spectroscopy

- With infrared light we can see the vibrational motion of atoms in a bond
- A vibrating molecule behaves like two masses joined by a spring
- The potential is $U = \frac{1}{2}kx^2$
  - k is the force constant related to the bond strength – double and triple bonds are stronger and have larger k
  - The same resonant frequency works also in the quantum case
- In a real molecular bond the potential differs, giving it an *anharmonic character*: $E = \left(v + \frac{1}{2}\right) h\nu - x\left(v + \frac{1}{2}\right)^2 h\nu$
  - This allows the states which are otherwise stationary to move
  - The deviation from the harmonic oscillator potential makes different modes coupled which allows for energy transfer
  - $\Delta v = \pm 1$
- Using the absorbance spectrum we can figure out what bonds and structures exist in an atom
  - The width of the lines tell you the lifetime, which comes from the Heisenberg uncertainty principle
- To calculate the number of vibrational modes:
  - Each atom has 3 degrees of freedom
  - For a nonlinear molecule subtract 6 degrees (3 translational + 3 rotational of the base atom)
  - For a linear molecule subtract 5 degrees (3 translational + 2 rotational of the base atom)
- Spin multiplicity selection rule: $\Delta S = 0$

Transitions of an Excited Molecule

- When a vibration is excited, it first undergoes internal conversions (between vibrations), and then falls down back to the ground state via fluorescence from the bottom level
  - With high energy the vibrational energy levels are a lot closer together so energy transition happens very quickly
- The triplet is lower in energy than the singlet (Hund's rule)
  - A singlet state is when an electron undergoes a transition and ends up with opposite spin with another lone electron
  - A triplet state is where both are spin up or down
  - The triplet is always lower energy than the singlet state by Hund's rule
  - Singlet states can flip to the triplet through intersystem crossing, due to the orbital angular motion generating a magnetic field
- Radiative transitions are when photons are absorbed or emitted; non-radiative transitions are when energy is transferred between states in a molecule or to the surroundings (internal conversion)