Electronic spectroscopy:
Electronic transitions

- UV/VIS transitions between discrete electronic states.
- Electrons promoted from ground state to excited state.

- Rotational and vibrational transitions accompany electronic transitions.
Energy level diagram
Vibronic transitions

- Total energy need to include terms from all three transitions.

- Rotational and vibrational terms are comparatively small and not easily resolved.

- Ignoring rotations an expression for excitations between excited state
Vibronic transitions

- Electronic energy spectrum of I$_2$.
- Higher energy transitions become harder to resolve.
- Vibronic progression

![Graph showing electronic energy spectrum of I$_2$.]
Dissociation energy

- \( D_0 \) is dissociation energy.
Dissociation energies: Example

The fundamental line in the infrared spectrum of $^{12}\text{C}^{16}\text{O}$ occurs at 2143.0 cm$^{-1}$, and the first overtone is found at 4260 cm$^{-1}$. Calculate the values of $v_e$ and $v_e x_e$ for $^{12}\text{C}^{16}\text{O}$. 
Icledger: Disociation energies

- The energy difference between two arbitrary levels $\nu$ and $\nu+1$ is
  - $\Delta G = \tilde{\nu}_e (1 - 2\tilde{x}_e (\nu + 1))$

- The dissociation energy can be written as
  - $D_e = \tilde{\nu}_e (1 - \tilde{x}_e^2) / 4\tilde{x}_e \approx \tilde{\nu}_e / 4\tilde{x}_e$

- Using the graph on the right, estimate the dissociation energy for $H_2$. 

---

Graph:

- $y = -228.63x + 4154.7$
- $R^2 = 0.9999$
Electronic excitation intensity pattern

- Intensity pattern of electronic transitions reveals molecular structure.
- Franck-Condon principle
Iclicker: Label the curve

Label the energy curve with:

- Vibration and rotational quantum numbers.
- The zero point energy for the ground electronic state.
- The fundamental vibrational frequency of the ground electronic state.
- The first overtone of the second electronic state.
- The dissociation energy of the second electronic state.
- The P-branch transition from the \( J=1, \nu=0 \) level in the ground electronic state.
- The R-branch transition from the \( J=1, \nu=0 \) level in the ground electronic state.