# 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

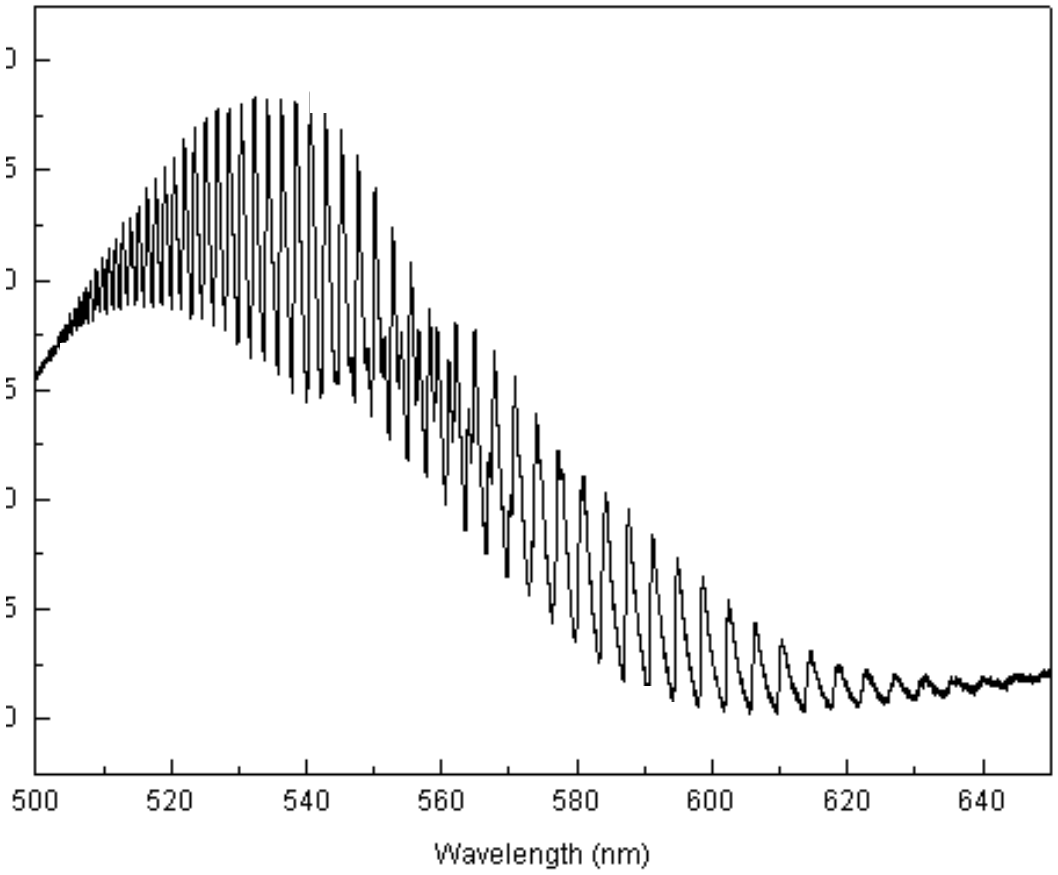
# Vibronic transitions

- Total energy need to include terms from al 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



# Dissociation energy

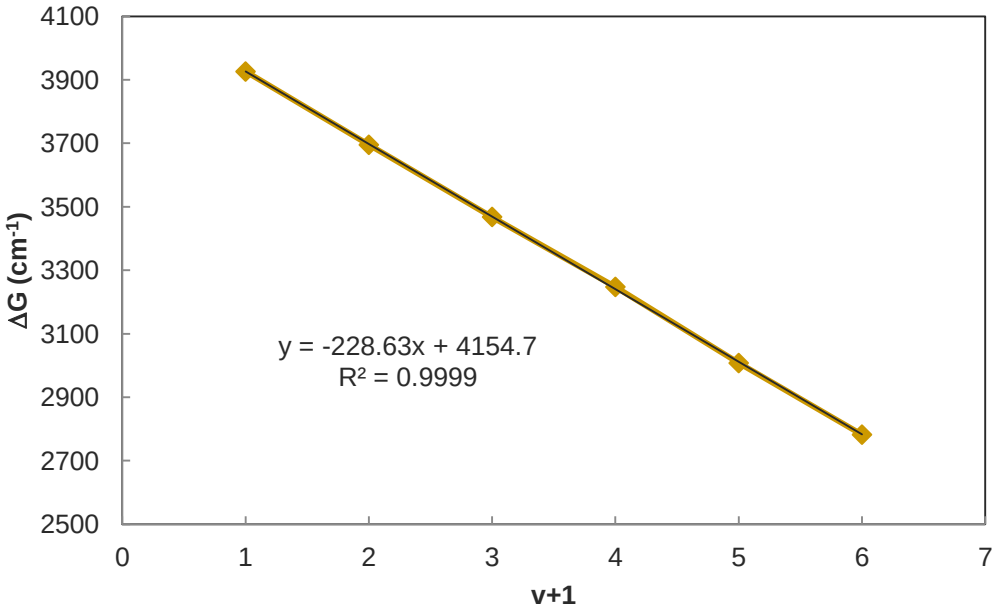
- $D_o$ is dissociation energy.

# Dissociation energies: Example

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

# Iclicker: 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
  - $\tilde{D}_e = \tilde{\nu}_e(1-\tilde{x}_e^2)/4\tilde{x}_e \approx \tilde{\nu}_e/4\tilde{x}_e$
- Using the graph on right, estimate the dissociation energy for $H_2$.



# 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.