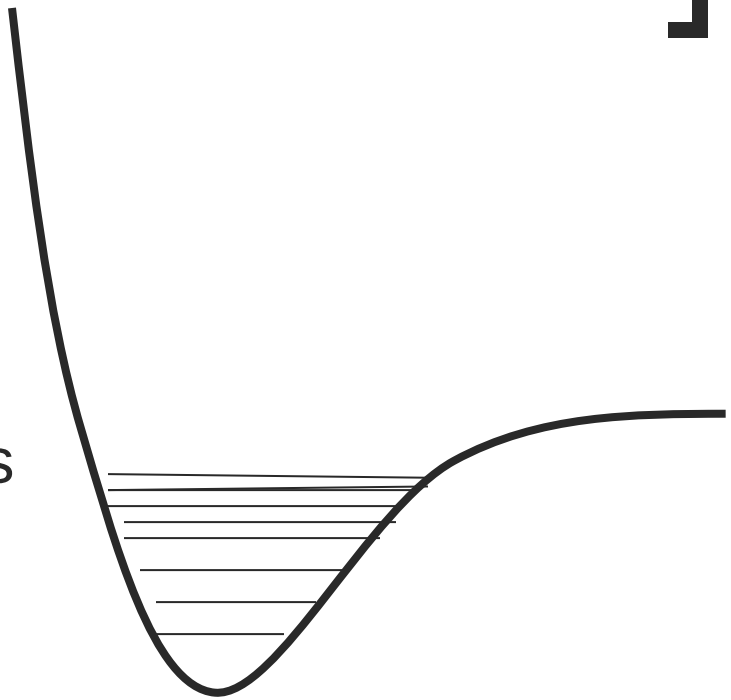
Molecular Spectroscopy:

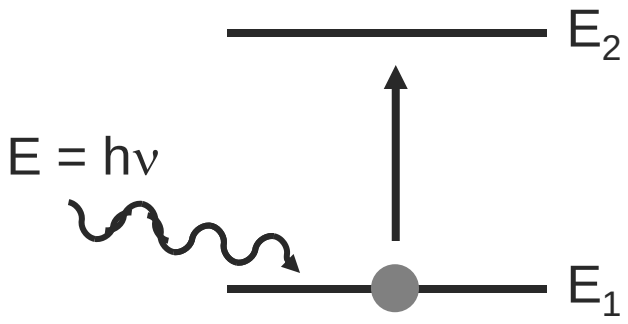
Molecular Spectroscopy

- How are some molecular parameters determined?



- What are the practical applications of spectroscopic knowledge?
- Can molecules (or components thereof) be identified based on differences in energy levels?

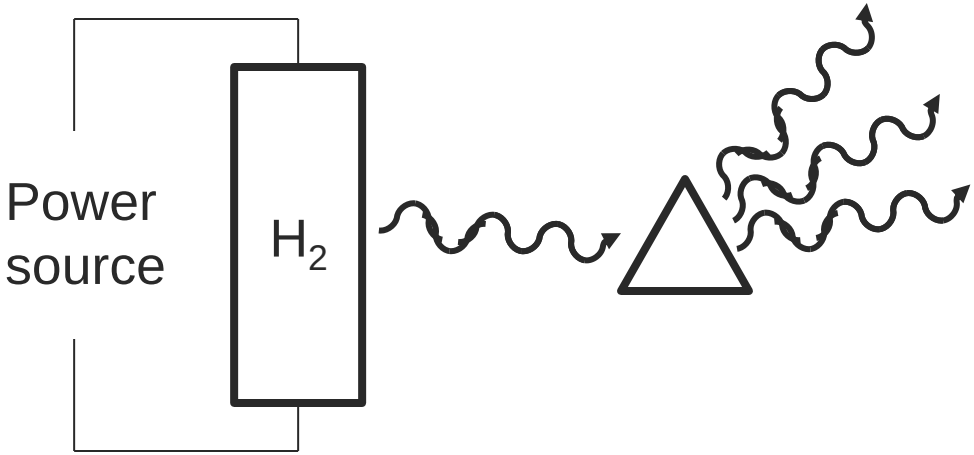
Molecular Spectroscopy



	ΔE	**ν,λ**	**Selection rule**
Electronic	10^{-18} – 10^{-19}J	UV/VIS 200 – 800 nm	Franck-Condon overlap
Vibration	10^{-20} – 10^{-21} J	IR 0.2 – 4 μm	$\Delta\nu = \pm 1$
Rotation	10^{-23} – 10^{-24} J	Microwave 3mm – 10 cm	$\Delta J = \pm 1$

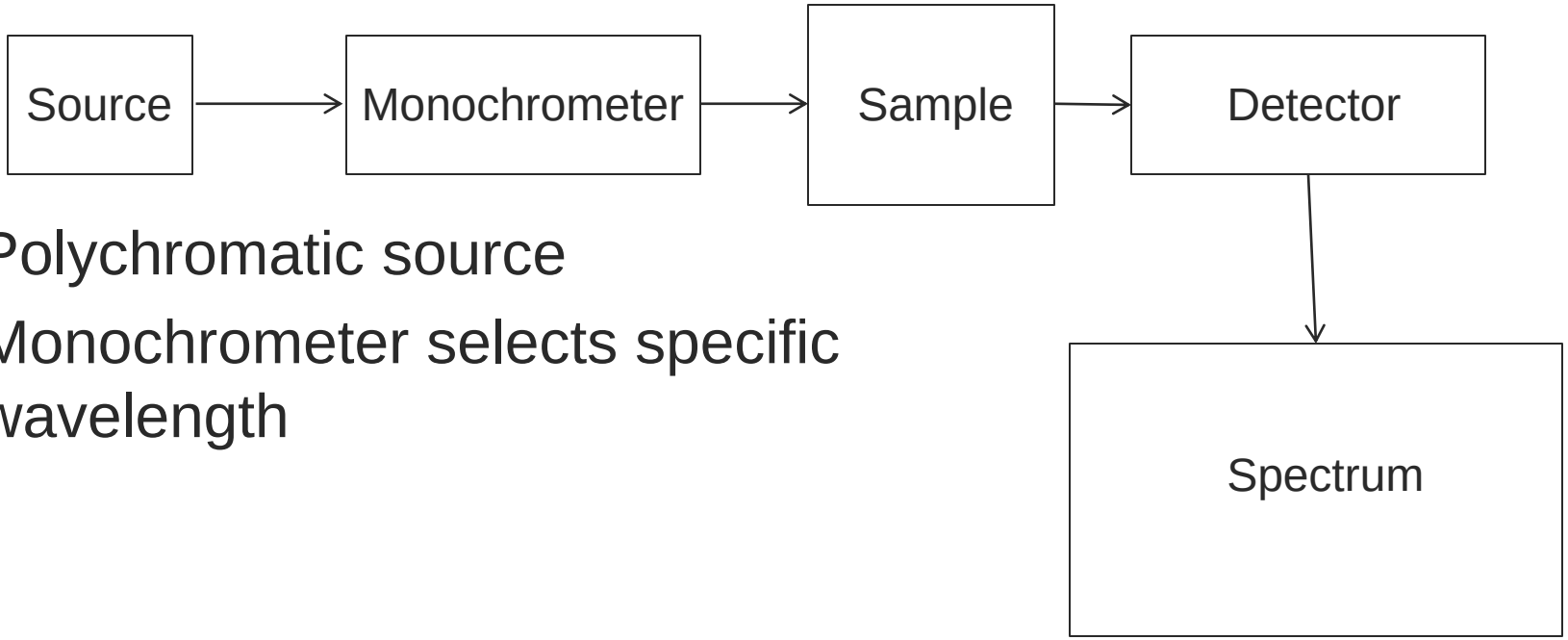
Molecular Spectroscopy

- Quantum mechanics developed to overcome shortcomings in classical physics



- Electronic excitation of H_2
  - $H_2 \rightarrow H_2^* \rightarrow H_2 + h\nu$
- Probe energy levels of a molecule using electromagnetic radiation

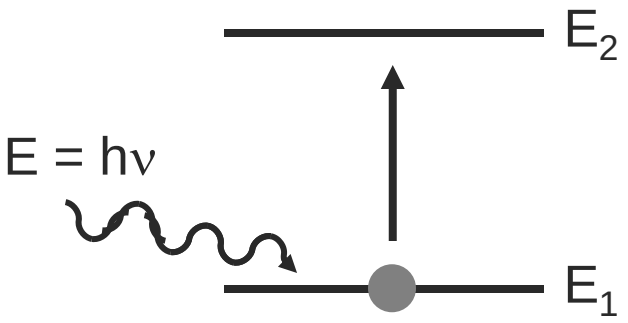
General Spectrometer



- Polychromatic source
- Monochrometer selects specific wavelength
-
-
- Bohr frequency must be satisfied
- Different types of spectrometers to probe different “types” of states

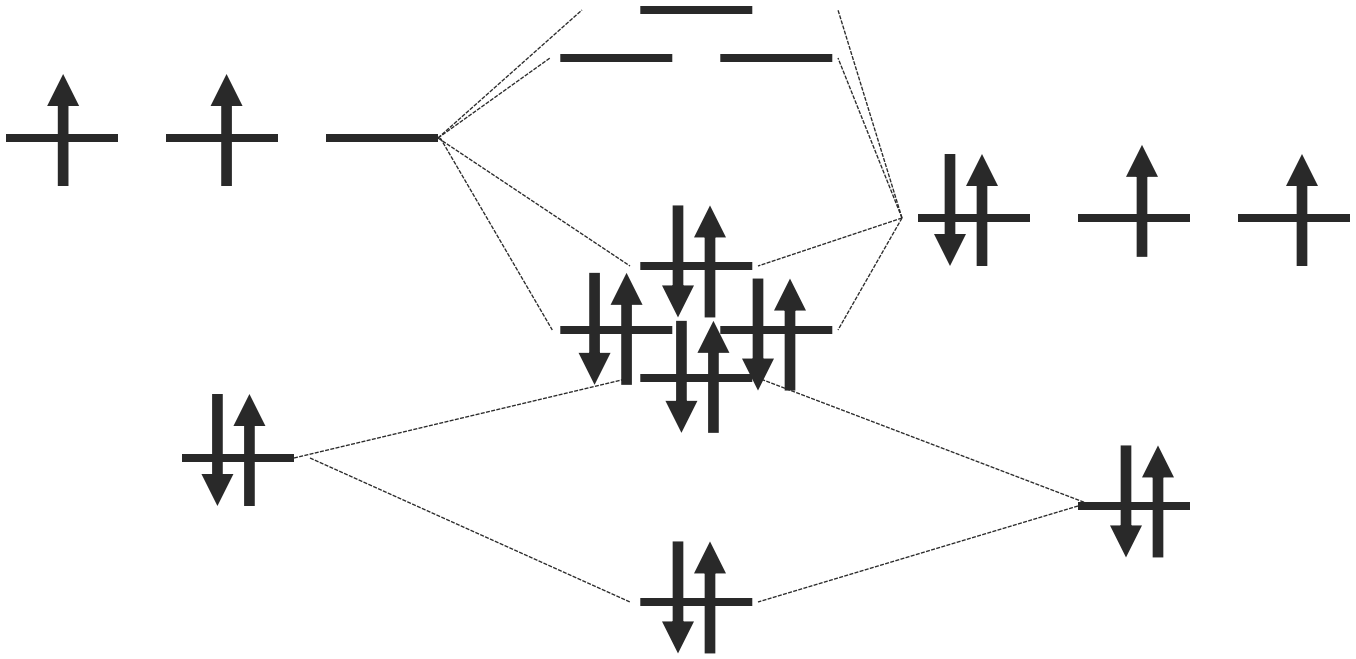
Bohr frequency condition

- Energy absorbed or emitted is the result of transitions between discrete energy states.
- Bohr frequency condition
- h is Planks constant



Electronic Spectroscopy

- Excitations between electronic states – CO molecule.



- Energy of transition

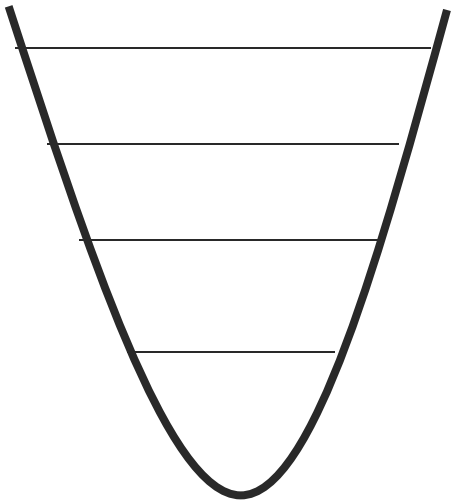
Iclicker: Beta carotene

- Beta carotene absorbs strongly in visible wavelengths. Assume the electronic states can be represented by a simple particle-in-a-box with energy levels of:

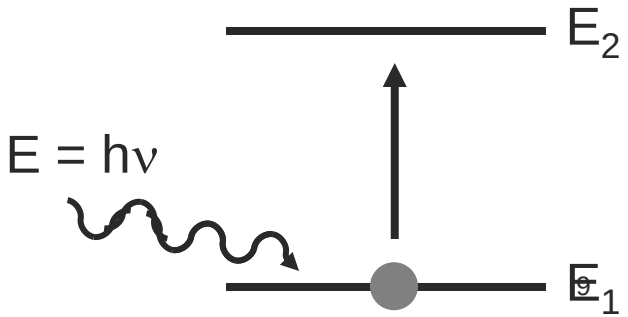
  If the absorption can be represented by a transition between the 11 and 12 electronic energy state and the molecule is roughly 18.3 A long determine the wavelength of the absorption.

Vibrational spectroscopy

- Quantized vibrational states.
- Modeled with harmonic oscillator.
- Energy levels



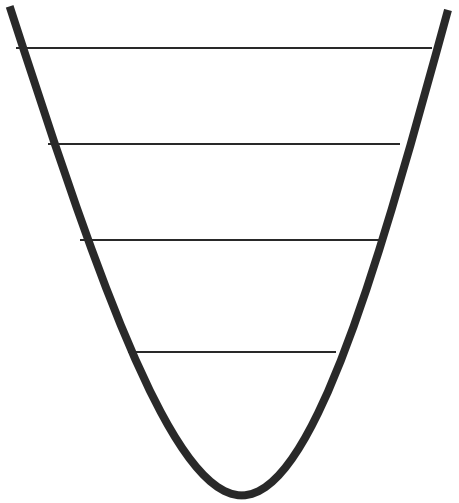
- Ground state is n=0 state

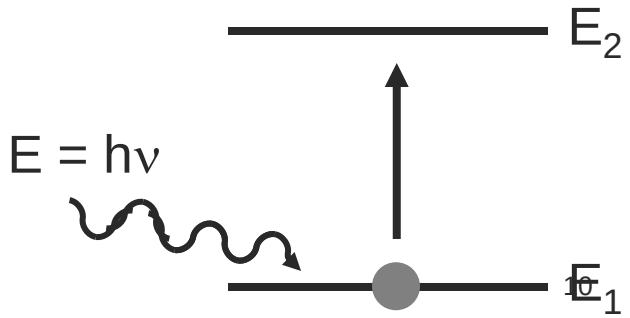


Vibrational spectroscopy

- Energy difference between adjacent states

- For CO, the n=0 to n=1 transition is at 2143 cm^{-1}.



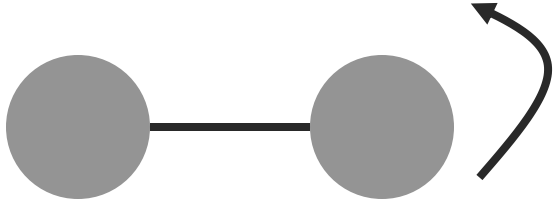


Iclicker: CO vibration

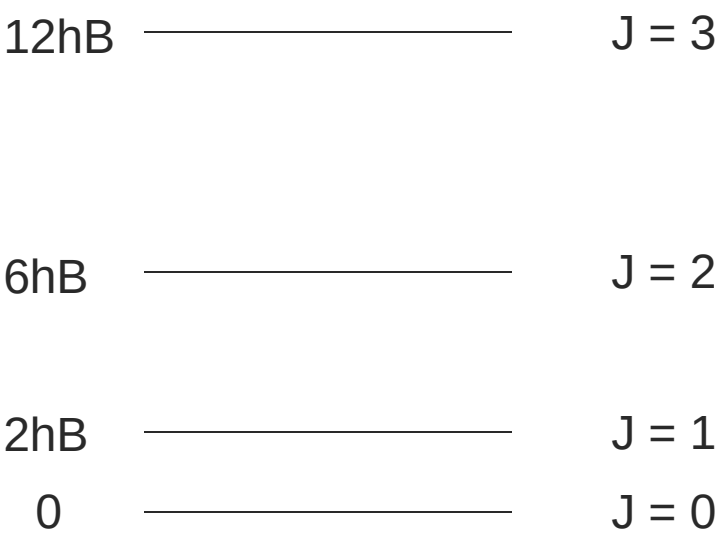
- What is bond force constant in CO molecule?

Rotational Spectroscopy

- Rigid rotor approximation



- Energy levels of a rigid rotator



- g_j – degeneracy of levels

Rotational Spectroscopy

- Assuming a simple rigid rotor, B for $^{12}C^{16}O$ is 57.65 GHz. Sketch the absorption spectrum if the first three rotational transitions are observed ($0 \rightarrow 1$, $1 \rightarrow 2$, and $2 \rightarrow 3$)

Iclicker: $^{12}C^{16}O$

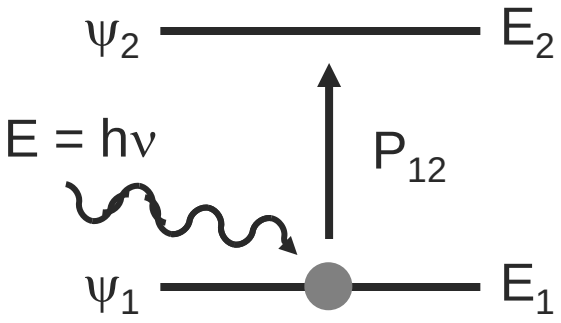
- The pure rotational spectrum of $^{12}C^{16}O$ has two adjacent transitions at 3.863 and 7.725 cm-1. Calculate the internuclear distance
  - A – 56.5 pm
  - B – 113 pm
  - C – 226 pm
  - D – 452 pm
  - E – 904 pm

Iclicker: $^{13}C^{16}O$

- What is the transition frequency for the J = 0 $\rightarrow$1 transition of $^{13}C^{16}O$ assuming the same internuclear spacing as $^{12}C^{16}O$?
  - A – 101.1 GHz
  - B – 104.3 GHz
  - C – 107.5 GHz
  - D – 110.4 GHz
  - E – 112.6 GHz

Selection Rules

- Energy separation determines needed frequency range.
- Available transitions determined by quantum mechanics summarized in selection rules.



- Quantum mechanics also defines intensities of transitions

All together

- Energy levels that have been discussed in isolation are all available in spectroscopy studies.
- Electronic spectra contain virbational and rotational excitations, vibrational spectra contain information on rotational levels, …