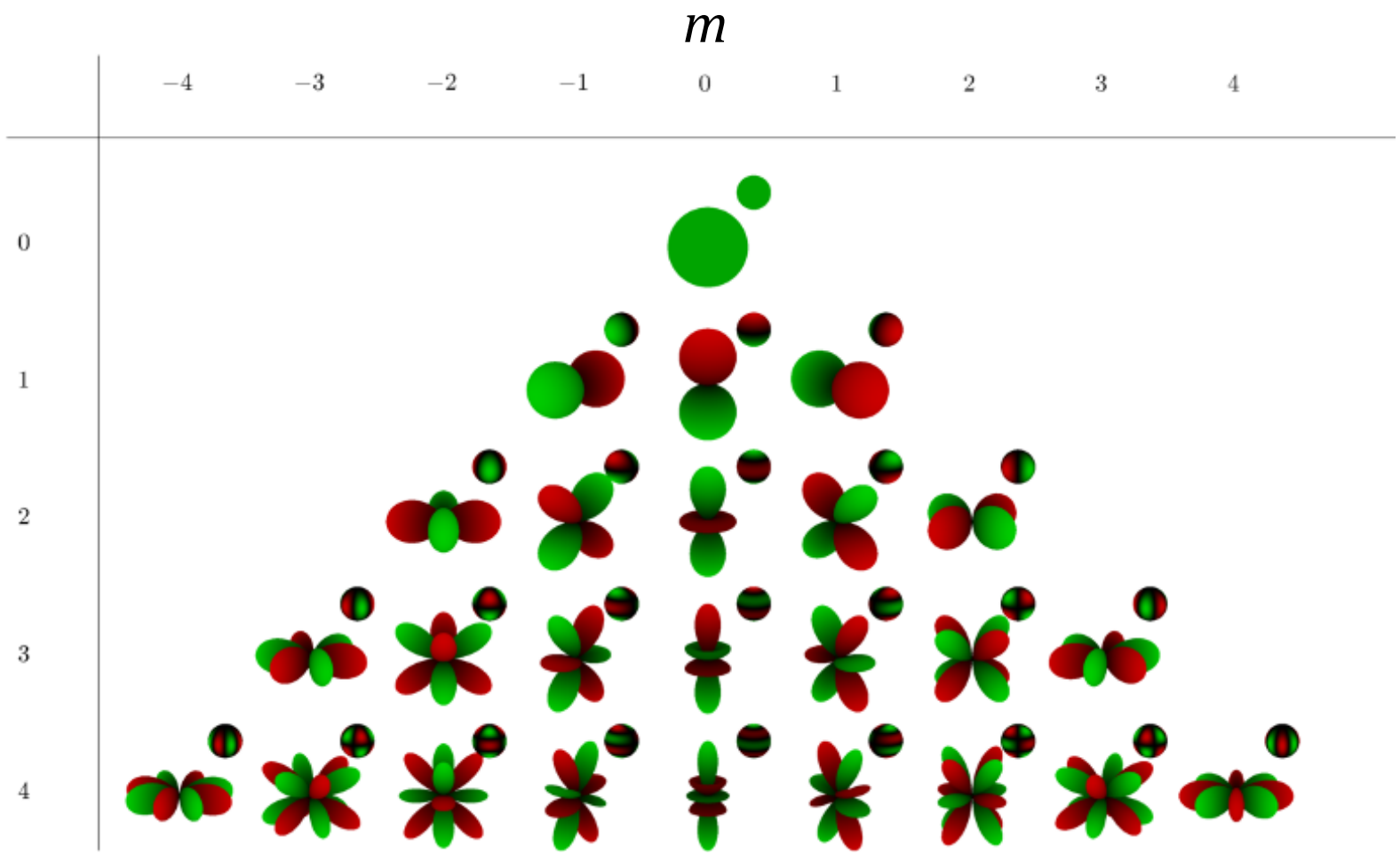
Take another look at the spatial distributions of the wavefunction solutions to the rigid rotor Hamiltonian - the spherical harmonics.

A. What information does the quantum number *J* encode?

B. What information does the quantum number *m* encode?

$$Y_J^m(\theta, \phi)$$



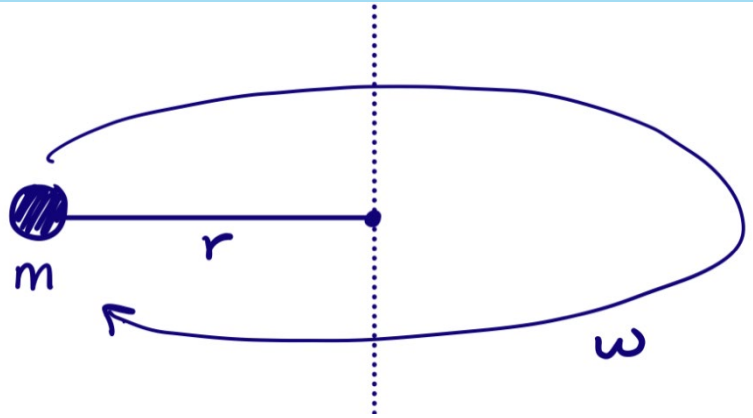
CHM 305 The Quantum World

Lecture 13: Molecular Spectroscopy

McQuarrie Ch. 5, 6

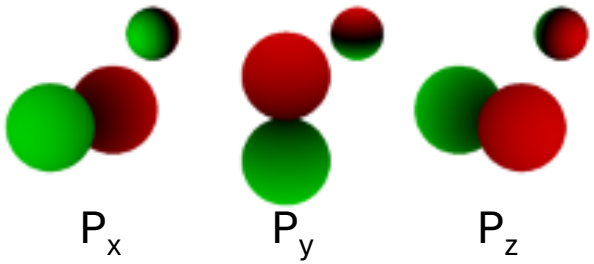
Last time we talked about: angular momentum

- Lay out definitions for classical circular motion and angular momentum
- Discuss rotations of classical and quantum mechanical rigid bodies
- Write down the Schrodinger equation and its solutions for the quantum rigid rotor in spherical coordinates
- Make connections to rotations of diatomic molecules and the hydrogen atom



$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2$$

$$\hat{H}\psi(\theta,\phi) = E\psi(\theta,\phi)$$



Road map for today's lecture

Overall goal: use harmonic oscillator and rigid rotor to model the frequencies of light that molecules absorb

1. Harmonic oscillator ↔ vibrational/infrared spectroscopy
   transition energies, selection rules

2. Rigid rotor ↔ rotational/microwave spectroscopy
   transition energies, selection rules



2. Harmonic oscillator-rigid rotor ↔ rovibrational spectroscopy
   and rotation-vibration interaction

In Part 2 after fall break, Prof. Kunin will cover deviations from these models, and more on light-matter interactions & spectroscopic selection rules

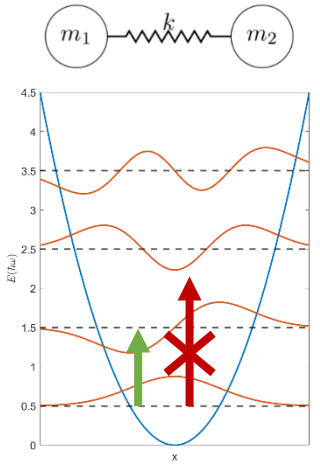
The basic principle of absorption spectroscopy

source of light with tunable energy

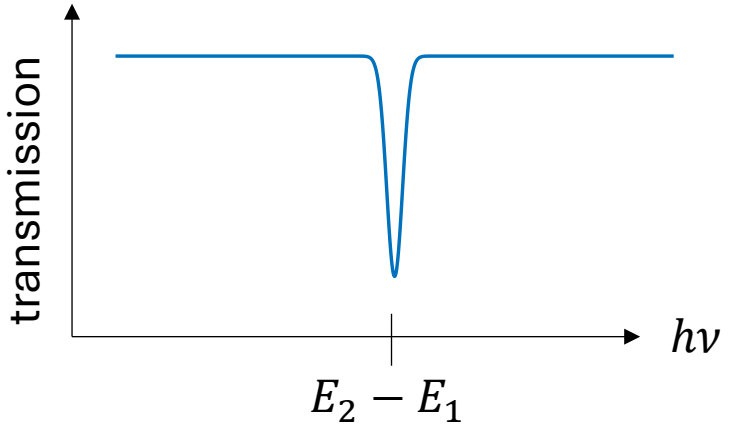
$E = h\nu$

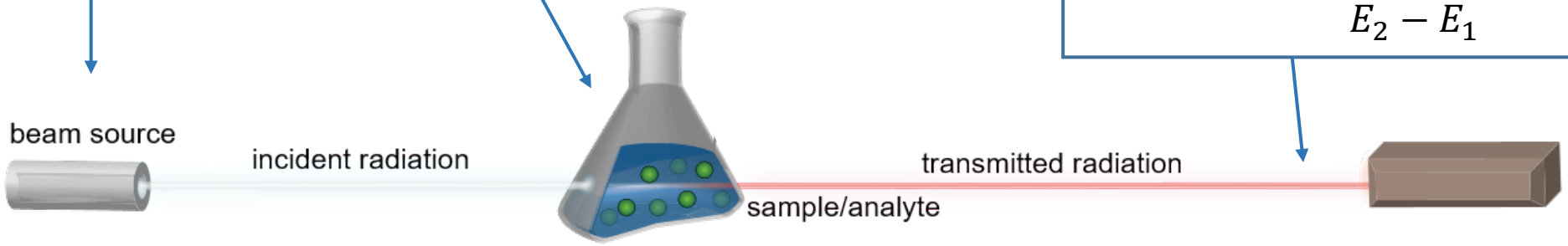
light can drive a transition between states 1 and 2 if

$E_2 - E_1 = h\nu$



scan the frequency of light to record an absorption spectrum

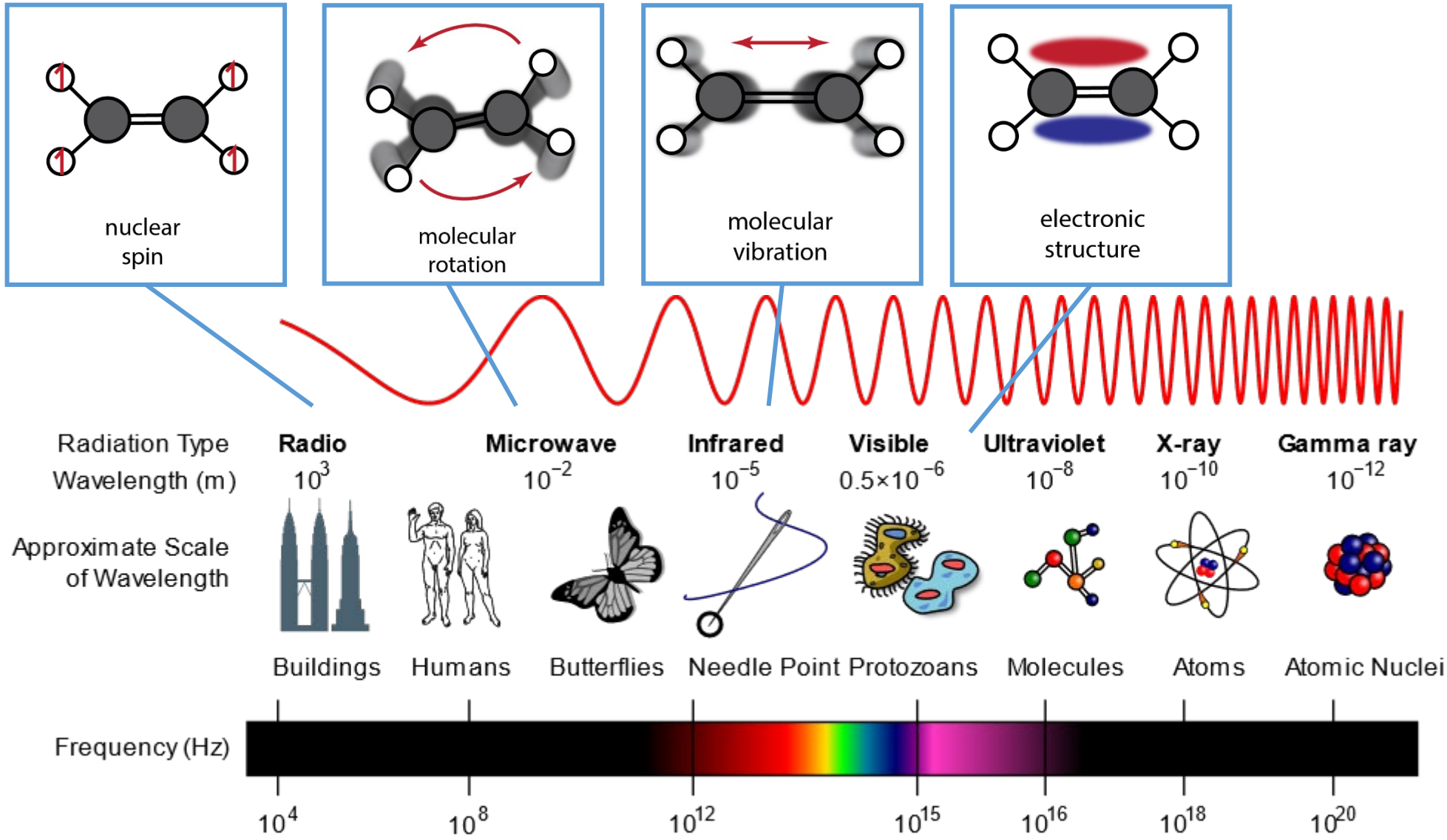




Emission **Absorption** **Transmission** **Detection**

https://commons.wikimedia.org/w/index.php?curid=12659294

Different frequencies of light drive different molecular transitions

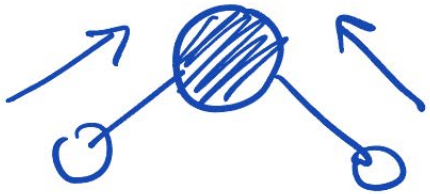


Practice Problem #1

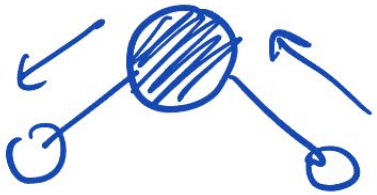
Sketch the vibrational absorption spectrum of the HCl molecule, which has a harmonic vibrational frequency of $2886\,\mathrm{cm}^{-1}$. Treat the system just within the harmonic oscillator approximation.

Practice Problem #2

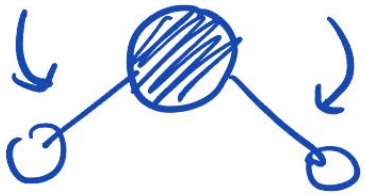
Sketch the vibrational absorption spectrum of the water molecule, treating it as a harmonic oscillator. Water has three IR-active vibrations with frequencies near 1595, 3652, and 3756 cm^{-1}. Treat each vibration of the system within the harmonic oscillator approximation.



symmetric stretch ($3652\ \text{cm}^{-1}$)



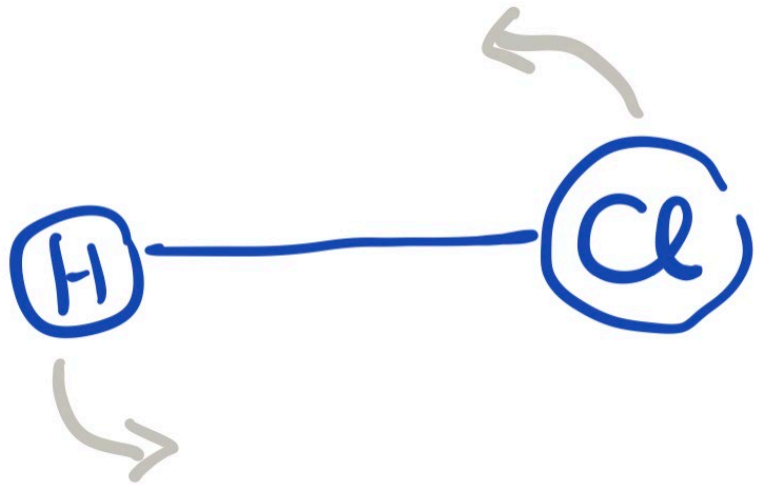
asymmetric stretch ($3756\ \text{cm}^{-1}$)



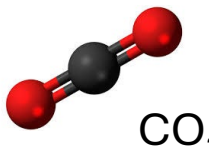
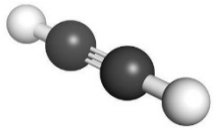
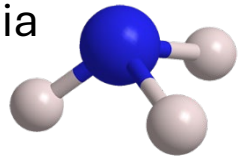
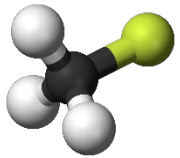
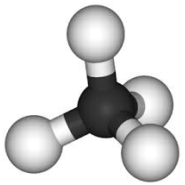
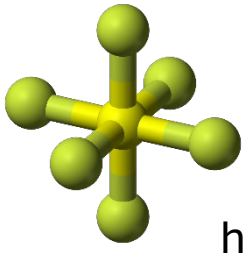
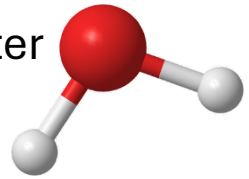
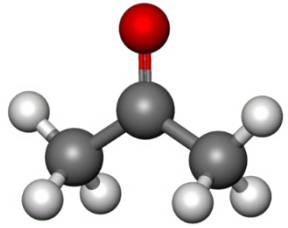
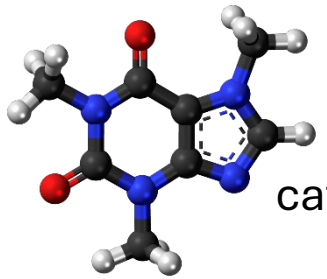
bending ($1595\ \text{cm}^{-1}$)

Practice Problem #3

Sketch the microwave spectrum of the HCl molecule within the rigid rotor approximation, given that it has a rotational constant $B = 10.6\,\mathrm{cm}^{-1}$.



Rotational spectra of polyatomics are more complex!

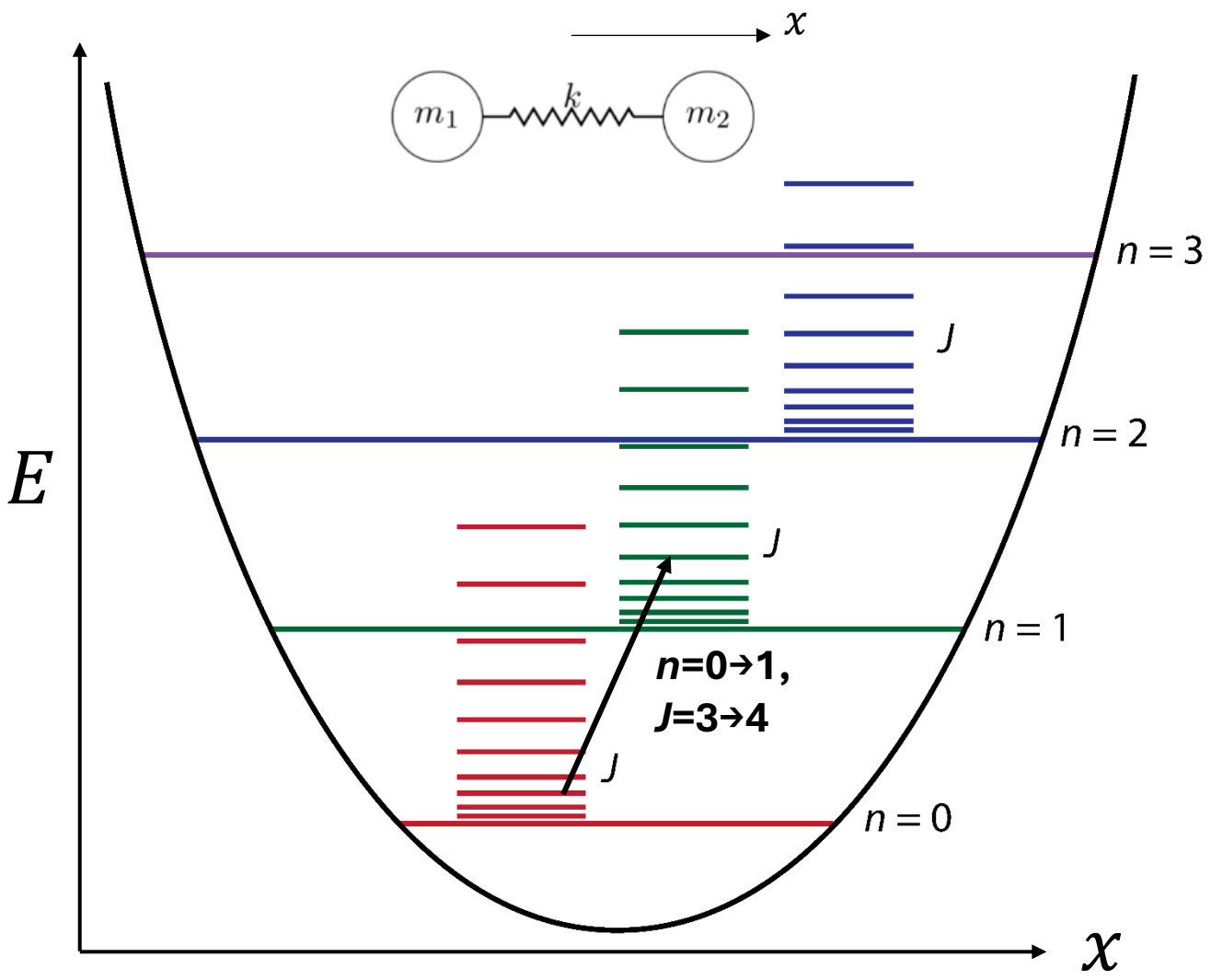
molecule type:	linear	symmetric top	spherical top	asymmetric top
	 CO_2  acetylene	ammonia   fluoro-methane	methane   sulfur hexafluoride	water  acetone   caffeine
	$I_A = 0$ $I_B = I_C$	$I_A \neq 0$ $I_B = I_C$	$I_A = I_B = I_C$	$I_A \neq I_B \neq I_C$

high symmetry, relatively simple rotational spectra

no permanent dipole moment, no rotational spectrum!

most complicated! (and most common)

Rotational-vibrational transitions



Rotations

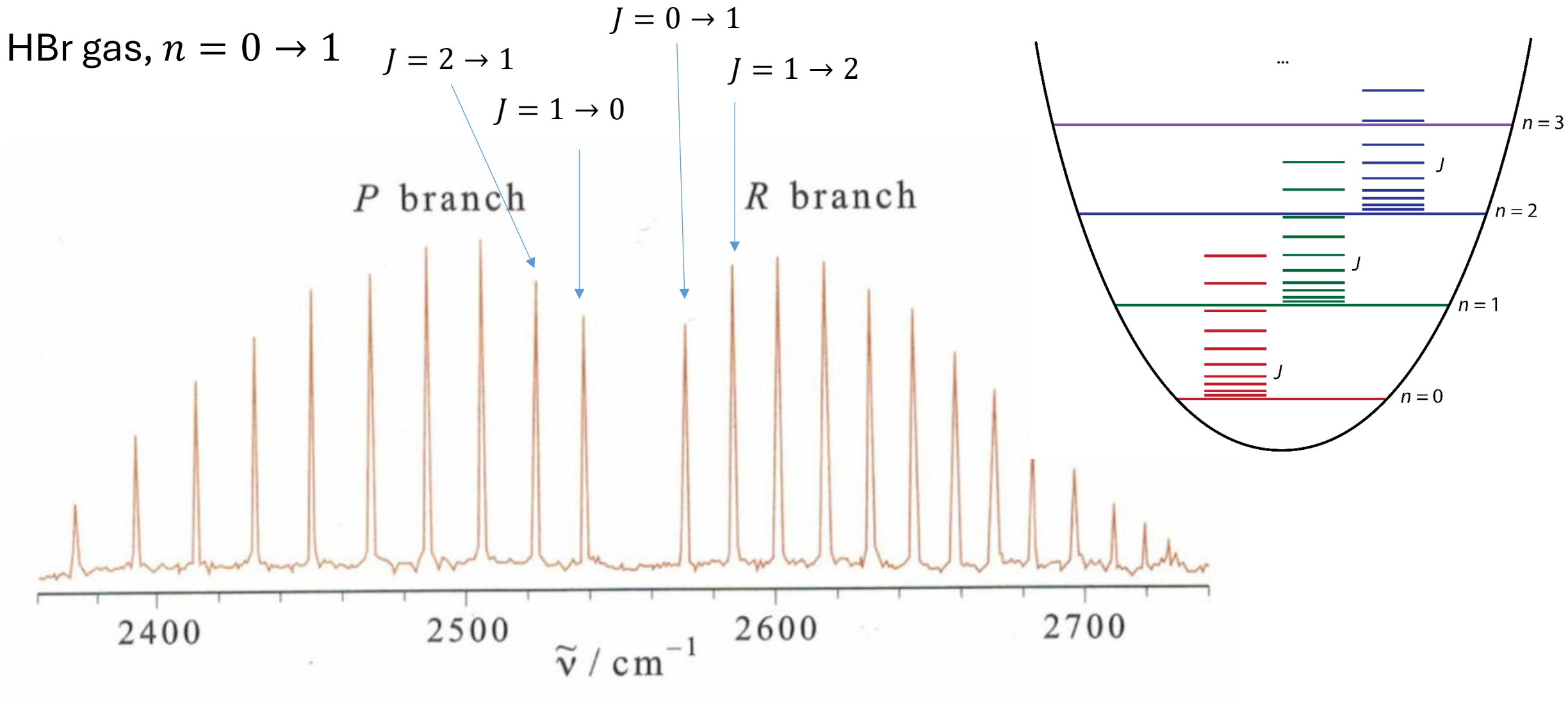
- Rigid rotor model
- Transitions driven by microwave light = microwave spectroscopy

Vibrations

- Harmonic oscillator model
- Transitions driven by infrared light = IR spectroscopy
- **Complete description involves "rovibrational" transitions that change both *n* and *J* quantum numbers**

P- and R-branches in rovibrational spectra

HBr gas, $n = 0 \rightarrow 1$



Wrapping up

- **After the break:** Spectroscopy Part 2: deviations from H.O. and R.R. models in real spectra, angular momentum and selection rules

- **Today's reading:** McQuarrie Ch. 5, 6