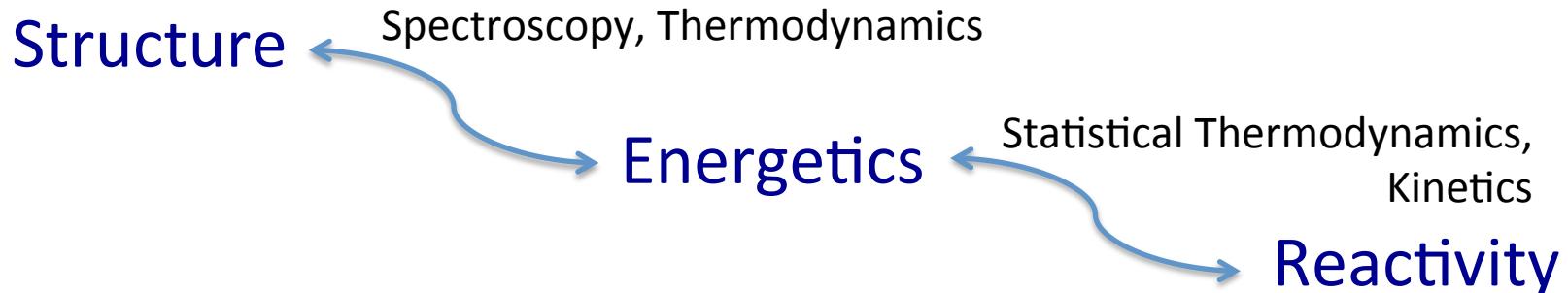


Ch 1b Lecture 6

January 17th, 2013

How are molecular structures deduced, and how might we sense compounds remotely or follow reactions?



Next few lectures – *Light/matter interactions*, or,
An Introduction to Spectroscopy.

Reading: Review OGC sections 4.5-4.7 as needed, OGC sections 20.1-20.3; RC Sections 9-4 to 9-7, 9-9

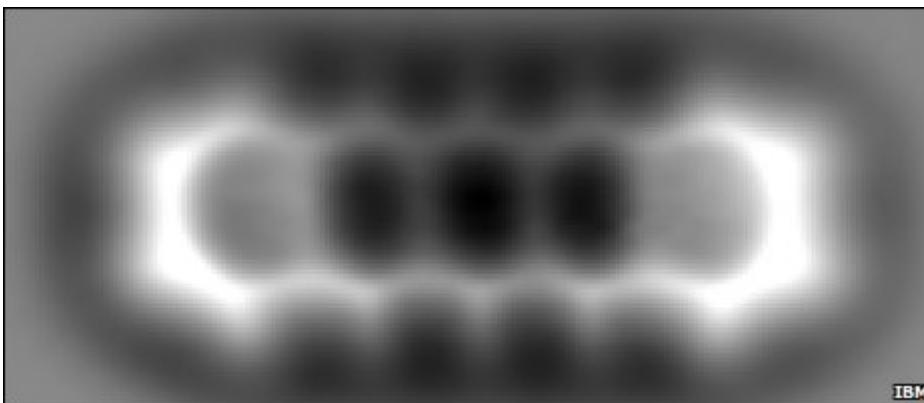
Ranger says: “Come visit us in the MOSH Pit after dinner!”



In the past, chemistry texts would begin: “We cannot see molecules, but we know they exist...”

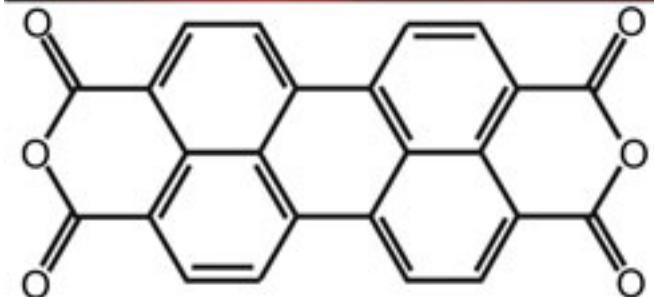
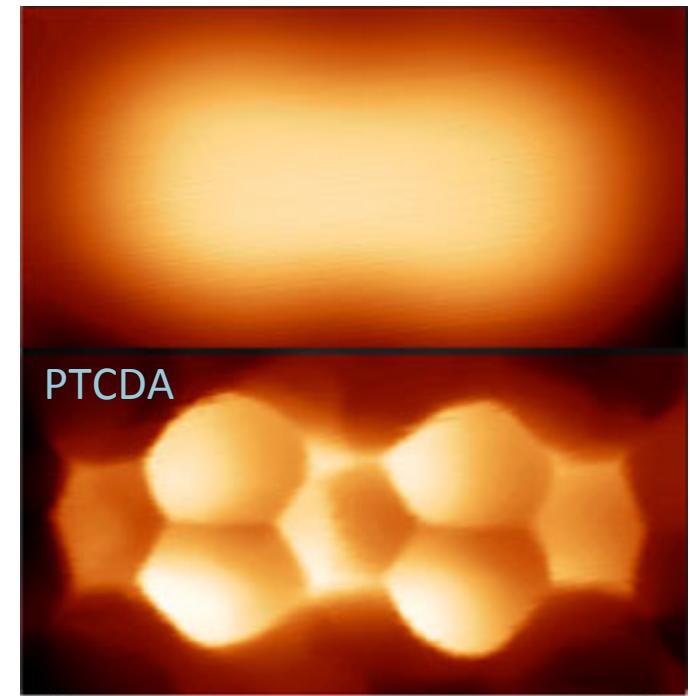
Thanks to STM/AFM (Nobel Prize, 1986), they now say: “We know molecules exist, and here are the pictures to prove it!”

Science 325, 1110 (28 Aug 2009)



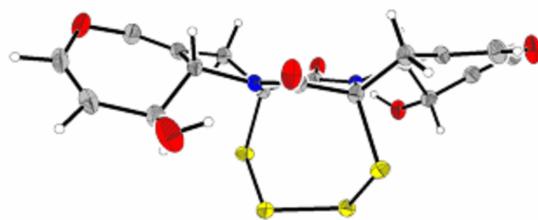
<http://news.bbc.co.uk/2/hi/8225491.stm>

Phys. Rev. Lett. 105, 086103 (2010)

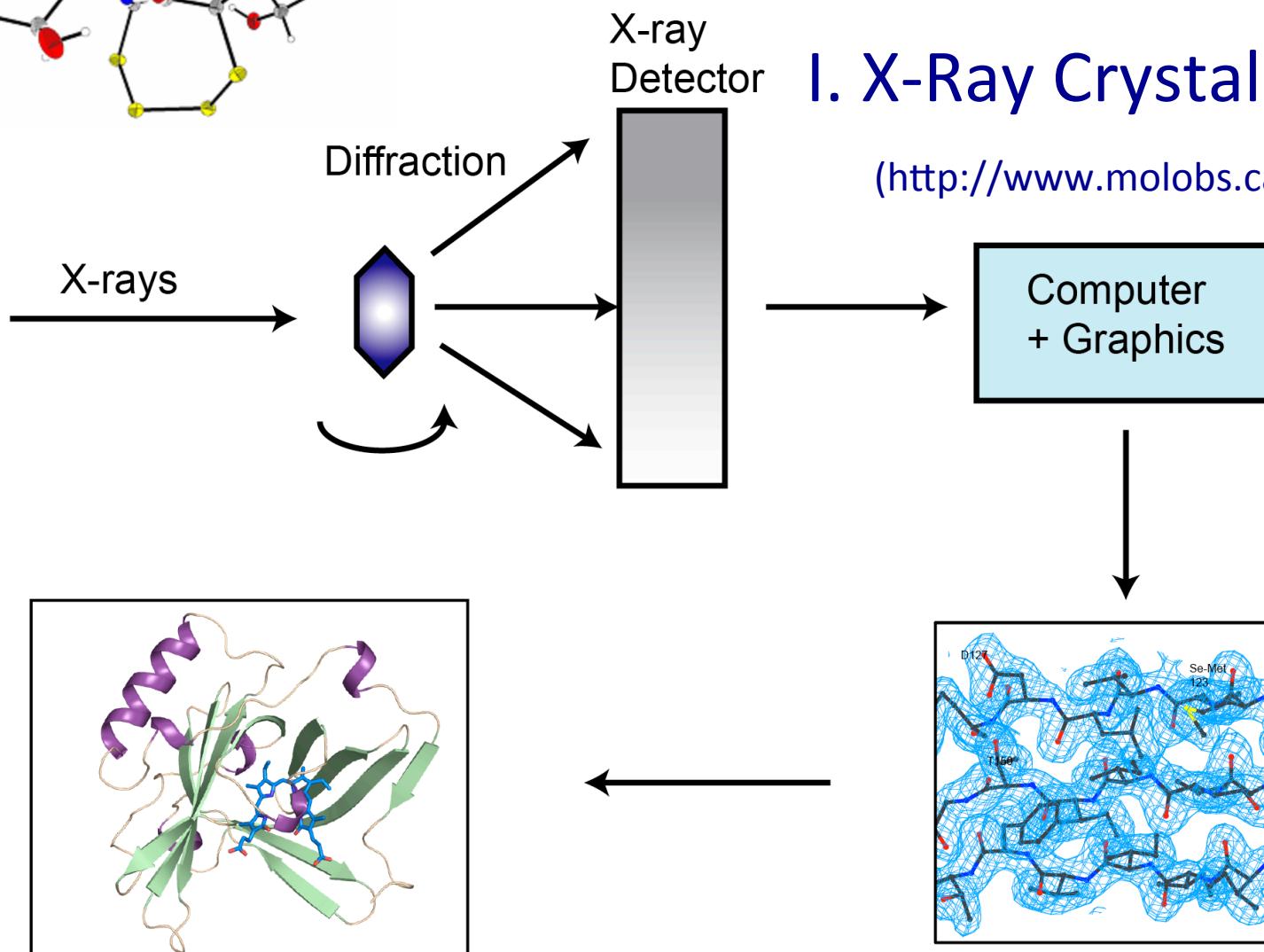


<http://physics.aps.org/story/v26/st8>

Other approaches to molecular structure?



Tetrasulfide intermediate (acetylaranotin), Reisman Lab



I. X-Ray Crystallography

(<http://www.molobs.caltech.edu/>)

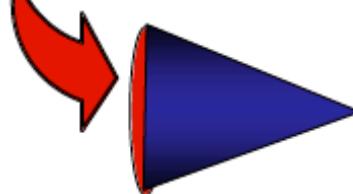
Protein Model

Electron Density Map

Other approaches to molecular structure?

II. Mass spectrometry

Sample



Ionization

Electron ionization (EI)

Chemical ionization (CI)

Photoionization

Fast atom bombardment

Field ionization

Atmospheric pressure CI

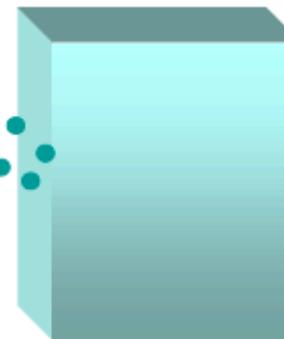
Particle impact

Electrospray

MALDI

DART (most recent)

(gives mass & fragmentation, more next week)



Mass Analysis

Magnetic sector

Quadrupole filter

Ion trap (linear)

Time-of-flight

FTMS

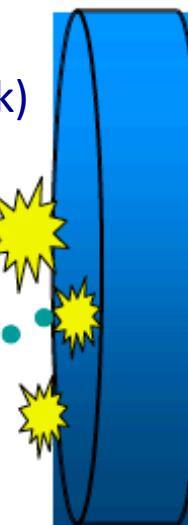
Orbitrap

Tandem and hybrids

Triple quad, TOF-TOF

Q-trap and q-TOF

....



Detection

Electron multiplier

Channeltron

Microchannel plate

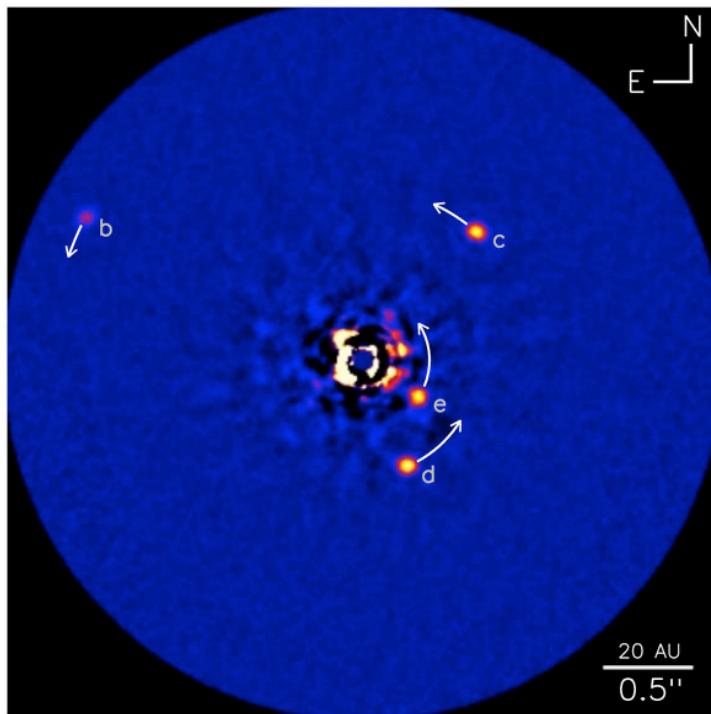
Faraday cup

Photomultiplier

....

HR 8799

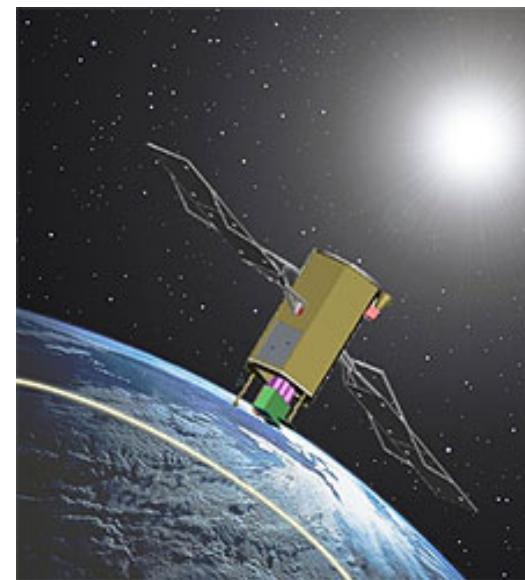
C. Dartois et al. (2011)



First extrasolar planetary system imaged

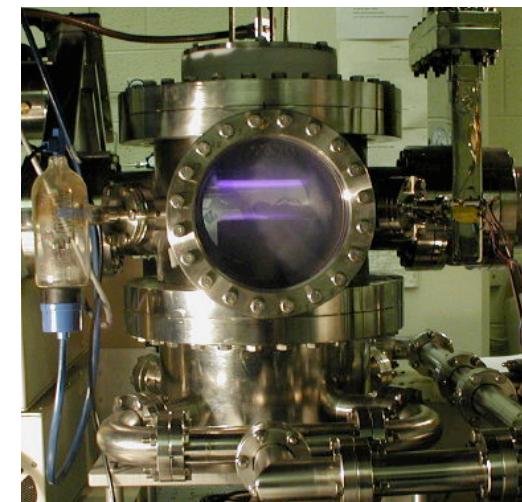
When you cannot access a sample directly, how do you probe what is going on?

Orbiting Carbon Observatory (OCO)



Global climate, carbon cap & trade

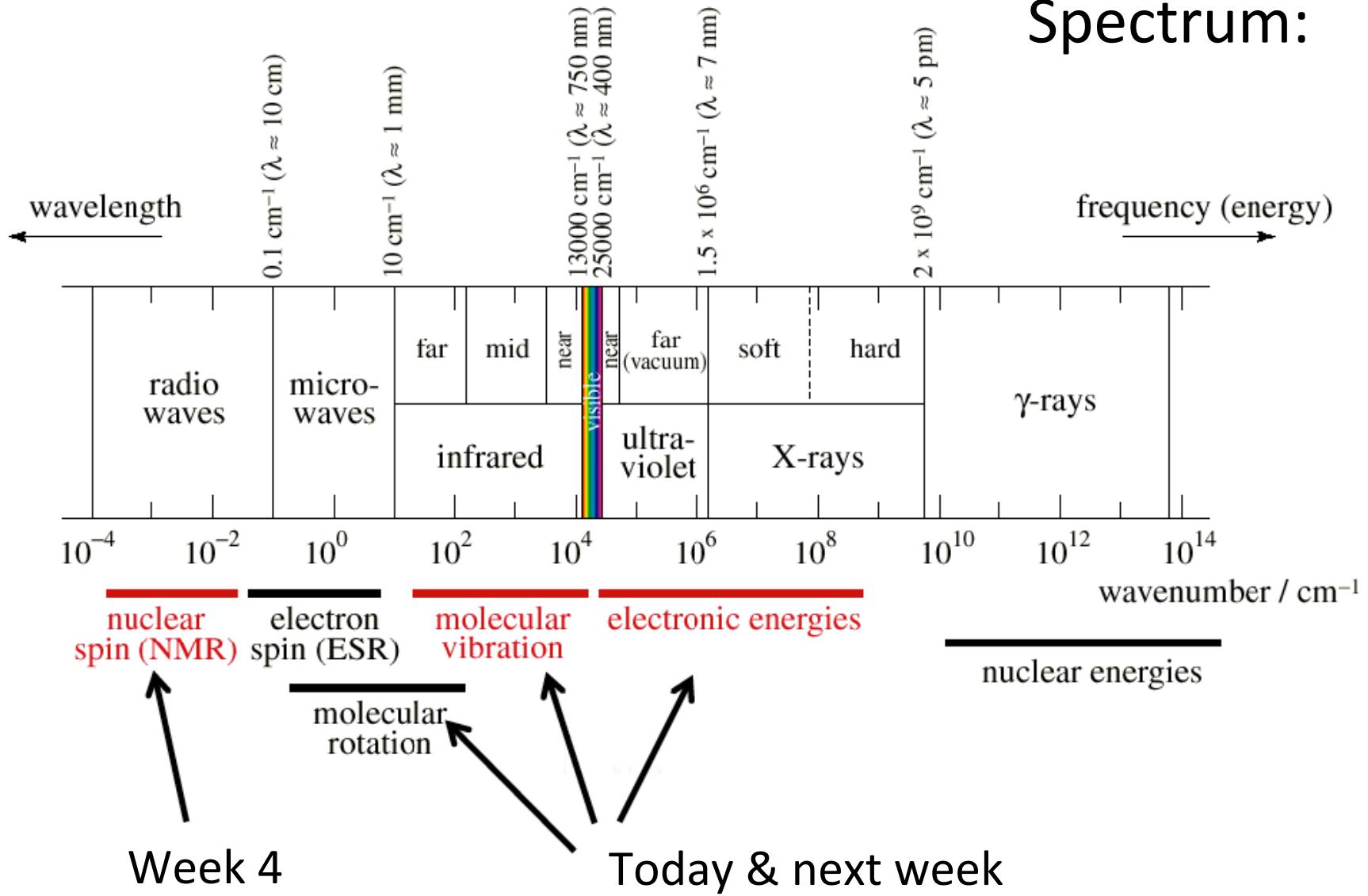
CVD Plasma



Thin film, device fabrication

Use photons!

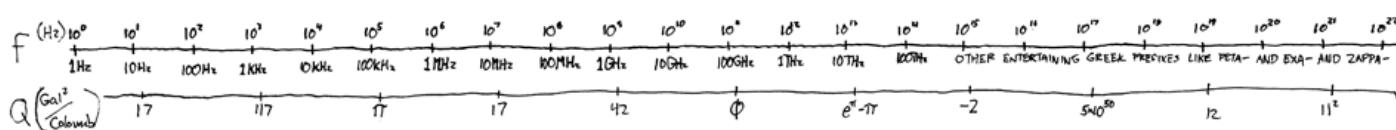
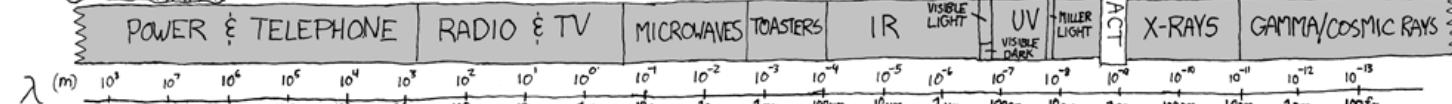
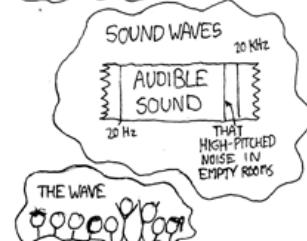
The Electromagnetic Spectrum:



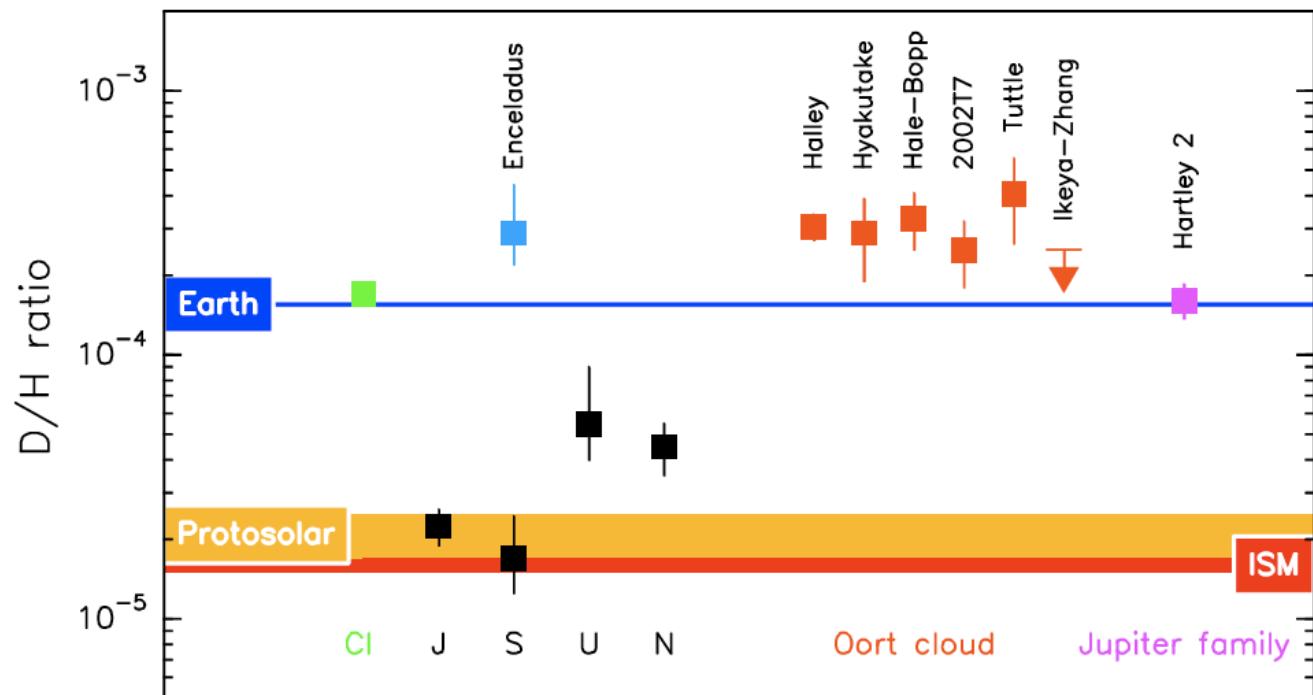
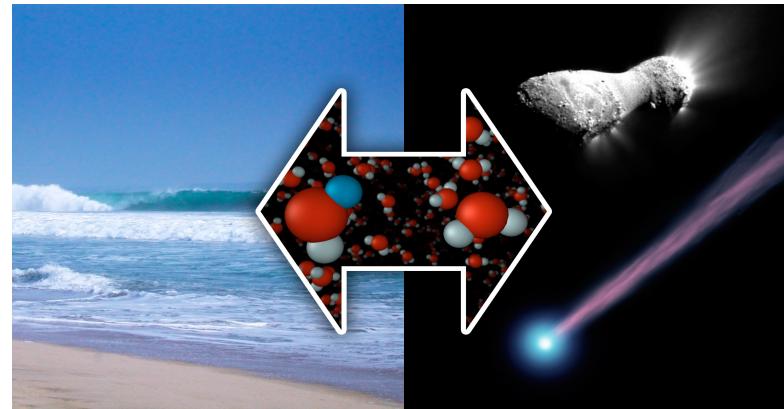
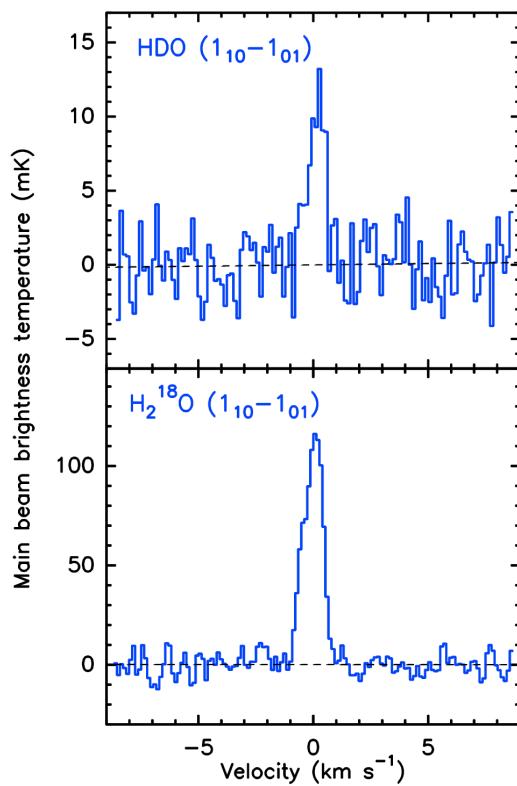
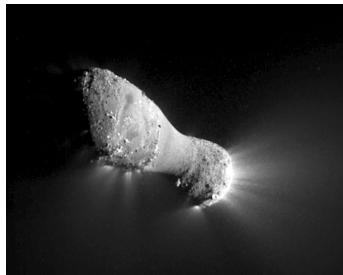
THE ELECTROMAGNETIC SPECTRUM

THESE WAVES TRAVEL THROUGH THE ELECTROMAGNETIC FIELD. THEY WERE FORMERLY CARRIED BY THE AETHER, WHICH WAS DECOMMISSIONED IN 1897 DUE TO BUDGET CUTS.

OTHER WAVES:



Key Point About Molecular States/Spectra:



Features can be sharp,
and thus highly diagnostic.

Hartogh et al. 2011, *Nature* **478**, 7367

We are familiar with continuum/classical mechanics...



A happy Erwin Schrödinger, without his cat.

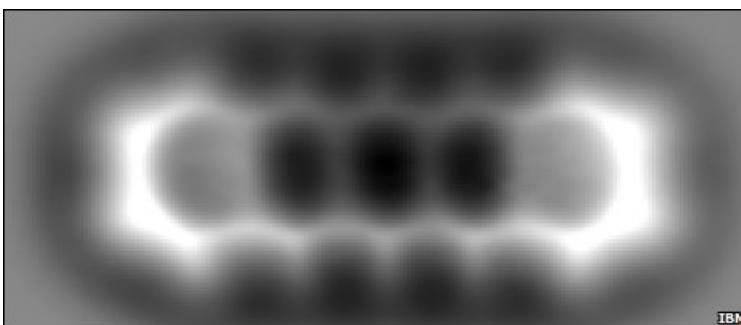
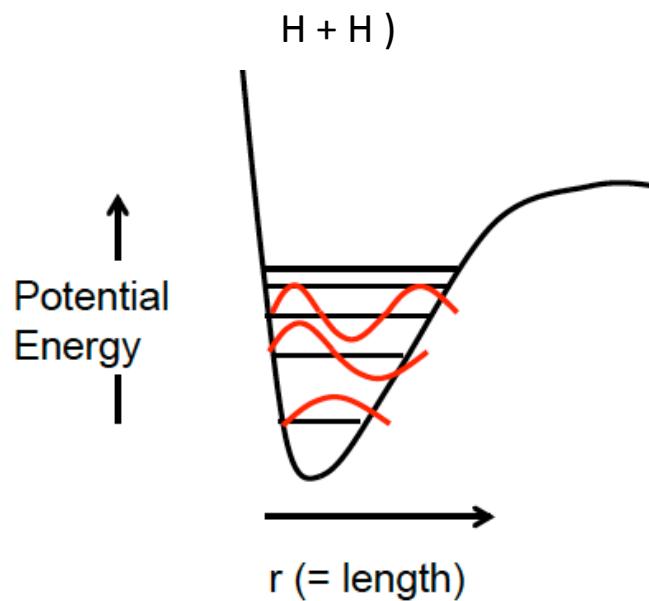


$H\Psi = E\Psi$, $H=K.E.+P.E.$
for stationary states.

The quantum world can be weird (Max Planck Institut für Quanten Optik)!

What spatial and temporal scales do we care about?

A realistic potential well (i.e.



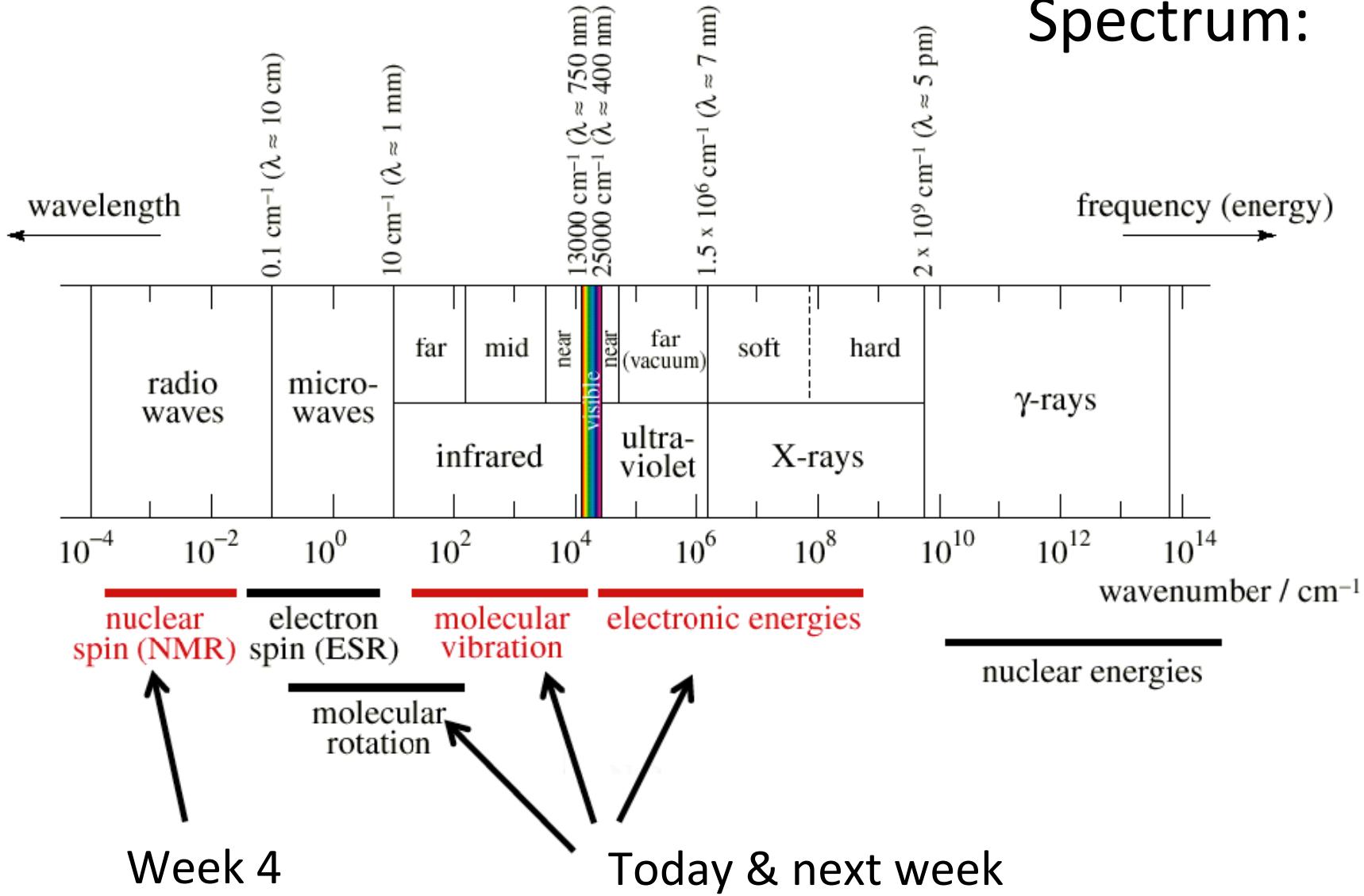
- Distances are Å.
- Velocities are $\geq 10^4$ cm/s (more later).

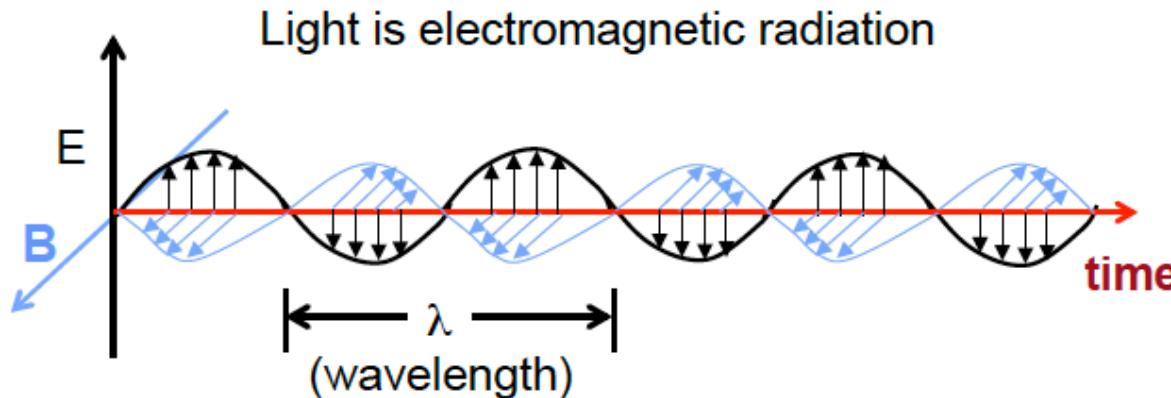
So, free atoms or molecules will travel 10 Å in 10 picoseconds.

For a diatomic molecule, there are six spatial degrees of freedom (x, y, z /atom); and so 3 trans, 1 vib, 2 rot.

Use photons!

The Electromagnetic Spectrum:





Spectroscopy Units

wavenumbers cm^{-1}

A wavenumber is simply $1/\lambda$, with λ in cm's.

Recall that Energy = $E = h\nu = hc/\lambda$, so $1/\lambda$ ($= \text{cm}^{-1}$) is an energy ν , or frequency (cycles per second) is also an energy

$$c \approx 3.0 \times 10^{10} \text{ cm}\cdot\text{s}^{-1} = 3.0 \times 10^8 \text{ m}\cdot\text{s}^{-1} = \text{speed of light in vacuum}$$

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} = (kg \cdot m^2 \cdot s^{-1}) = \text{Planck's constant}$$

Spectroscopy Units

wavenumbers cm^{-1}

A wavenumber is simply $1/\lambda$, with λ in cm's.

Recall that $E = h\nu = hc/\lambda$, so $1/\lambda$ ($= \text{cm}^{-1}$) is an energy
 ν , or frequency (cycles per second) is an energy

Also, electron volts eV $1 \text{ eV} \approx 8000 \text{ cm}^{-1} = 1.6 \times 10^{-19} \text{ J}$

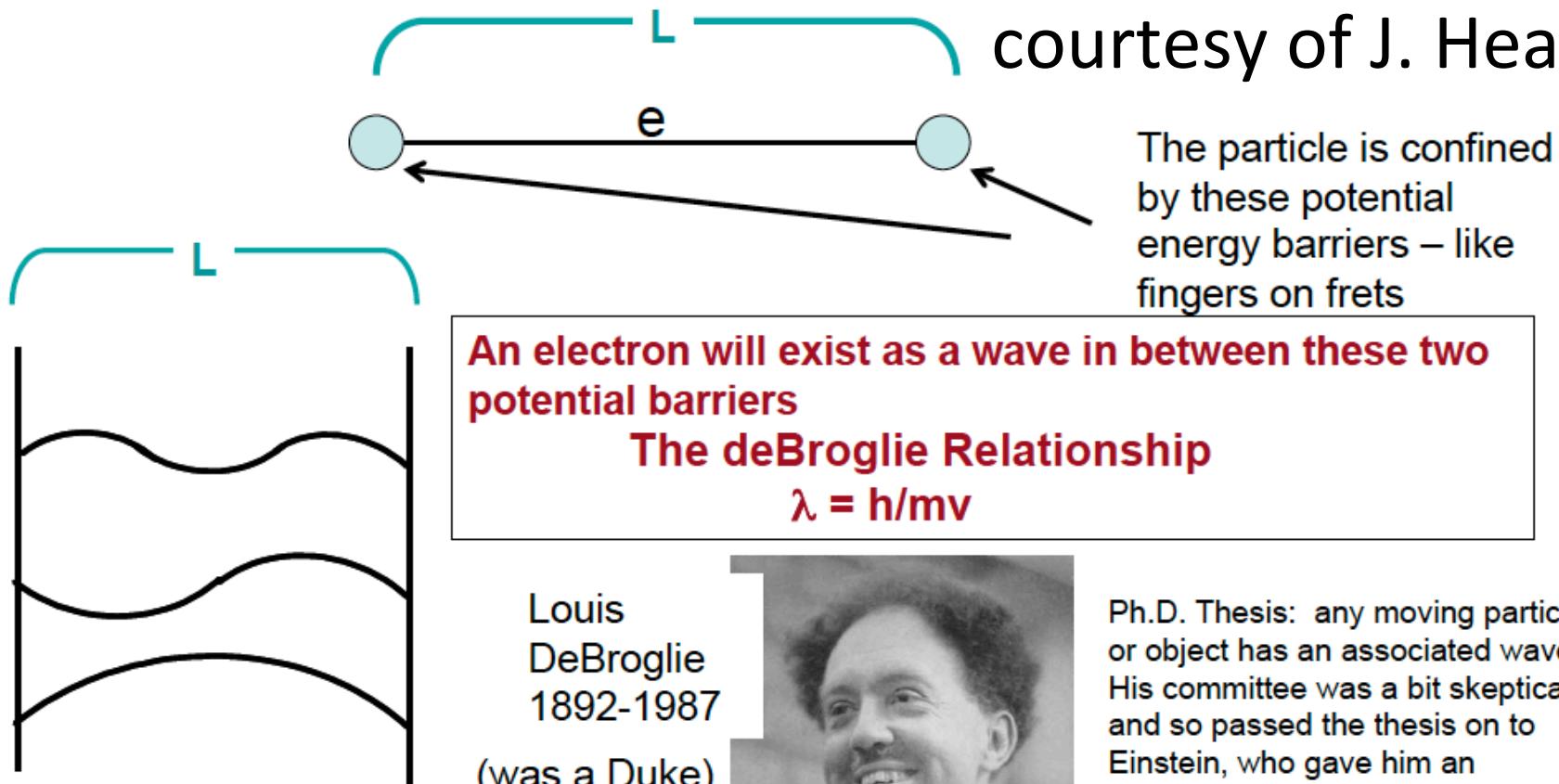
1 eV is the kinetic energy an electron has after being accelerated through a 1 volt electric field

Visible light $\approx 13000 - 25000 \text{ cm}^{-1} \approx 1.5 - 3 \text{ eV}$

eV's are a manageable unit for describing visible & UV light and hence chemical bond energies

$c \approx 3.0 \times 10^{10} \text{ cm} \cdot \text{s}^{-1} = 3.0 \times 10^8 \text{ m} \cdot \text{s}^{-1}$ = speed of light in vacuum
 $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ ($\text{kg m}^2 \text{ s}^{-1}$) = Planck's constant

From whence quantization? (A guitar analogy, courtesy of J. Heath)



A guitar string and its resonant frequencies. Notice that all frequencies are integral multiples of the fundamental frequency, shown at the bottom of the drawing.



Ph.D. Thesis: any moving particle or object has an associated wave. His committee was a bit skeptical, and so passed the thesis on to Einstein, who gave him an enthusiastic pass. He later got a Nobel Prize.

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} (\text{kg m}^2 \text{s}^{-1}) = \text{Planck's constant}$$

$$m_e = \text{mass of an electron} = 9.109 \times 10^{-31} \text{ kg}$$

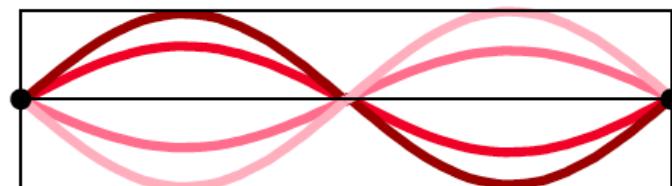
From whence quantization? (A guitar analogy, courtesy of J. Heath)

This should look familiar, here's a slide from Ch 1a:

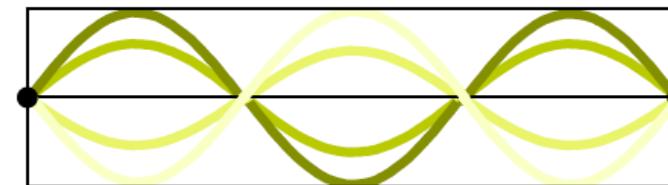
Other Allowed Standing Waves



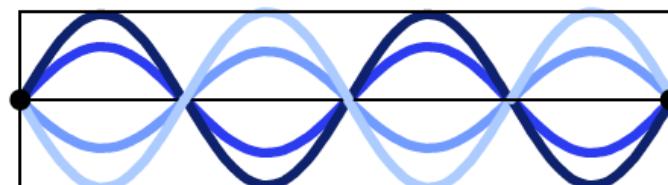
No nodes



One node (at $x = \frac{d}{2}$)

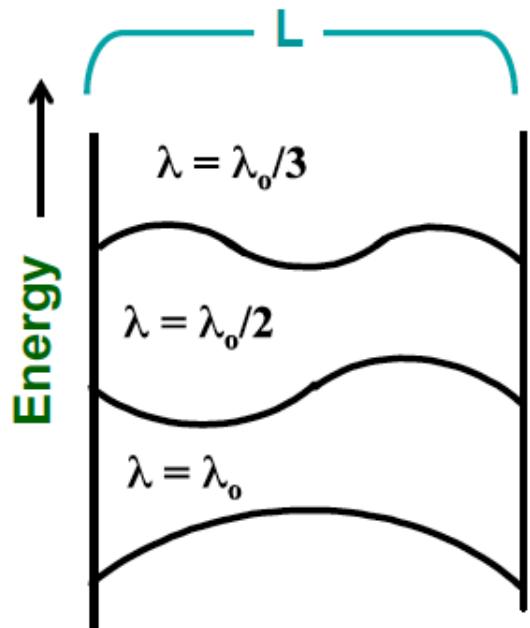


Two nodes ($x = \frac{d}{3}, \frac{2d}{3}$)



Three nodes ($x = \frac{d}{4}, \frac{d}{2}, \frac{3d}{4}$)

Particle in a box (PiB), via the S.E. (OGC):



$$E_n = n^2 \hbar^2 / (8m_e L^2)$$

$$E_3 = 9\hbar^2 / (8m_e L^2) = \text{energy of quantum state } \Psi_3$$

$$E_2 = 4\hbar^2 / (8m_e L^2) = \text{energy of quantum state } \Psi_2$$

$$E_1 = \hbar^2 / (8m_e L^2) = \text{energy of quantum state } \Psi_1$$

The energy levels of the wavefunctions are controlled by:

Key Point:

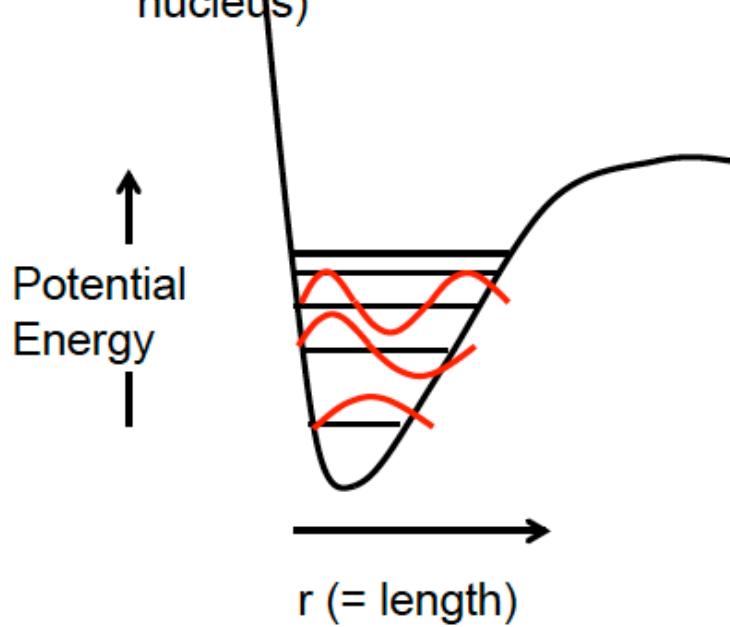
Mass – heavier masses = more closely spaced E_n levels

Potential energy – without the potential energy barriers, λ is infinite and there is no quantization

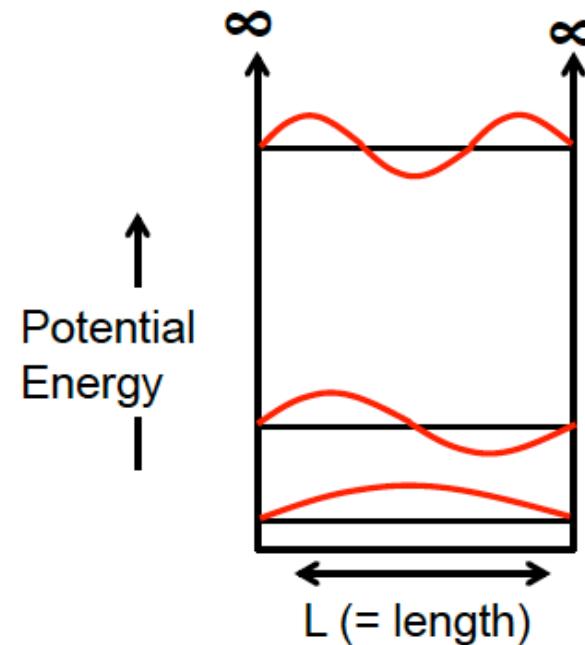
Length – Smaller ‘boxes’ = larger E_n spacings

Potential Energy and Ψ_n and E_n

A **realistic potential well** (i.e. an electron encircling a nucleus)



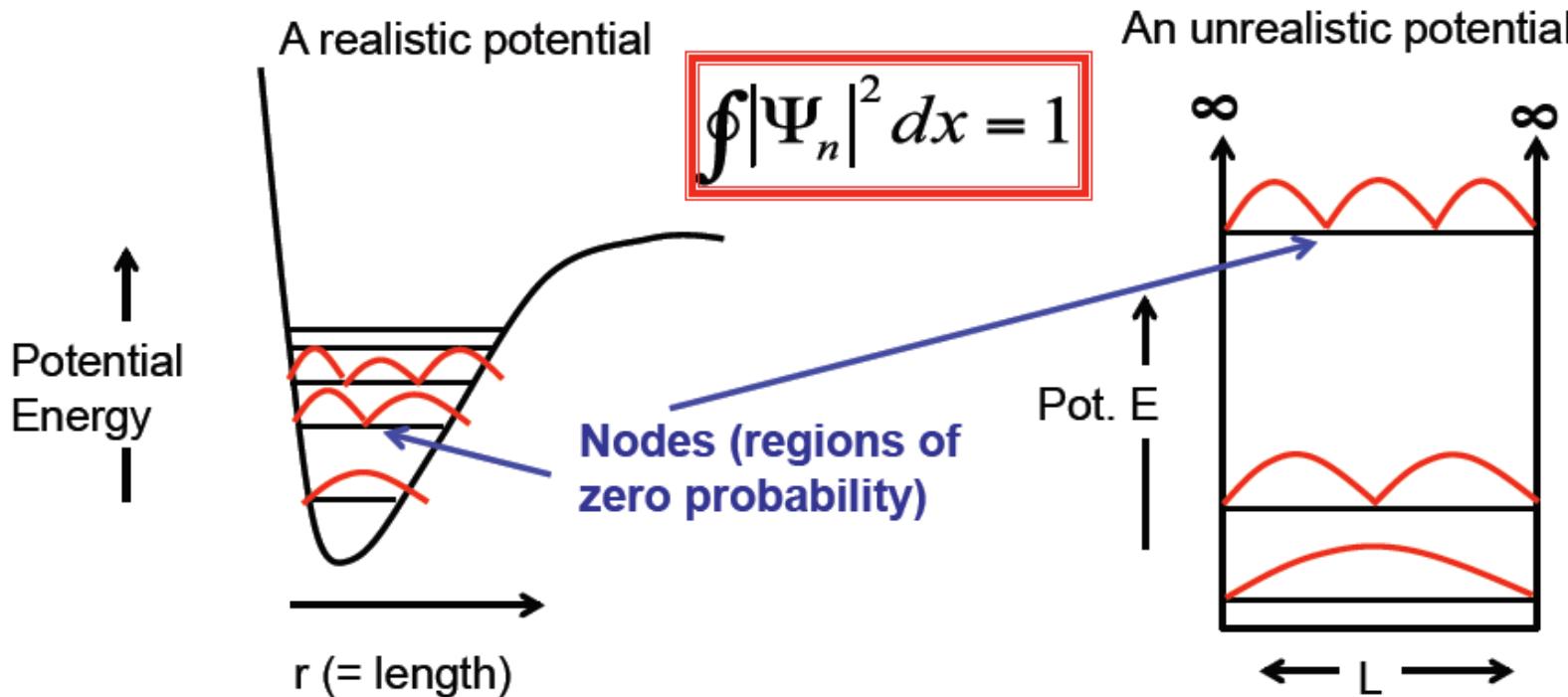
An **unrealistic potential well** (i.e. Potential Energy goes to infinity at edges (particle in a box))



What is Common to the Unrealistic and Realistic Potential Energy Wells

- One degree of freedom = one quantum number (n)
- Confining a particle within a 'potential' directly leads to quantized energy levels (*from deBroglie hypothesis*)
- Wavefunctions are wave-like (i.e. sinusoidal-type functions)

Probability Distributions of $\Psi = |\Psi|^2$

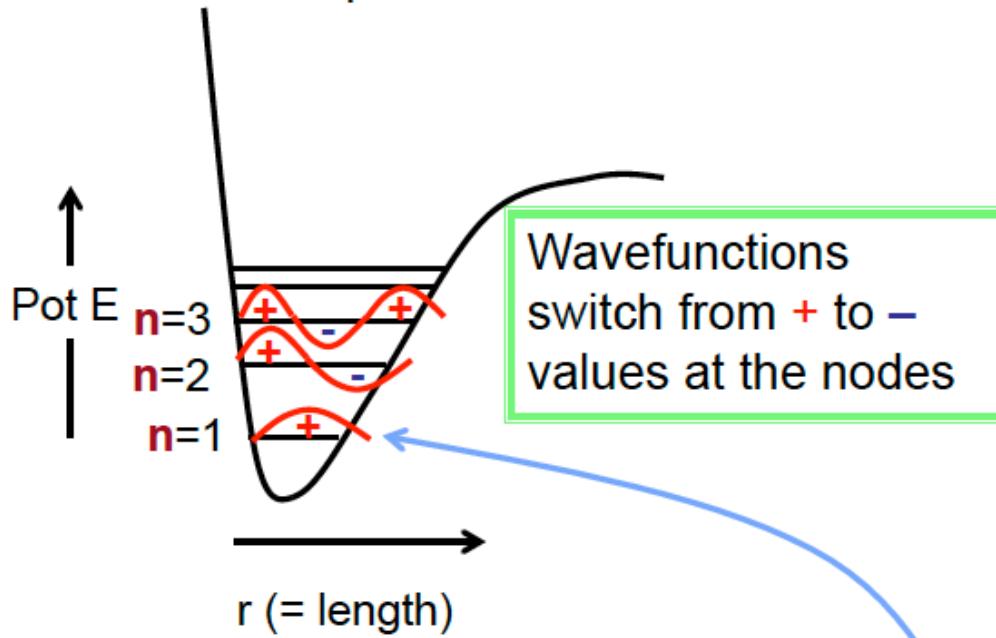


Probability distributions

- Higher energy quantum states have more nodes (a 1s orbital has 0 nodes, a 2s orbital and a 2p orbital both have 1 node, 3s and 3p orbitals have 2 nodes each)
- Probability distribution maps out the places where the particle is likely to exist
- For the ‘realistic’ potential, there is finite probability outside of the potential energy surface
- The equation (above middle) means that the integrated probability of finding a particle somewhere within the wavefunction is equal to unity.

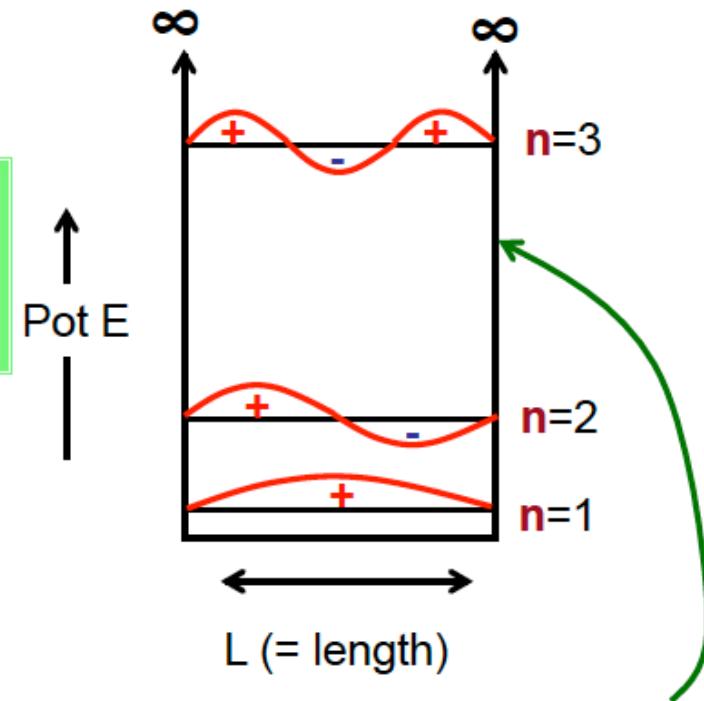
Potential Energy and Ψ_n and E_n

A realistic potential



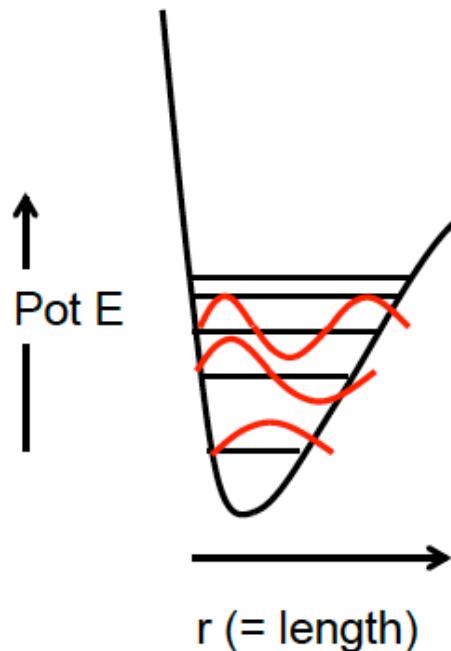
- Level spacing decreases with increasing n
levels are continuous (non-quantized) at limit of large n (all real systems are like this)
- Wave function spill-over boundaries of potential well (*leads to phenomena such as quantum mechanical tunneling*)

An unrealistic potential



Level spacing increases as n^2
Wave functions end sharply at limits of potential well

The Heisenberg Uncertainty Principle



An electron, at position x , traveling through space

$p = mv = \text{momentum}$

Measure x and measure p
Our measurements will have an uncertainty in them –
i.e. we measure $x \pm \Delta x$ where Δx is the uncertainty.

Heisenberg says the best we can do is:

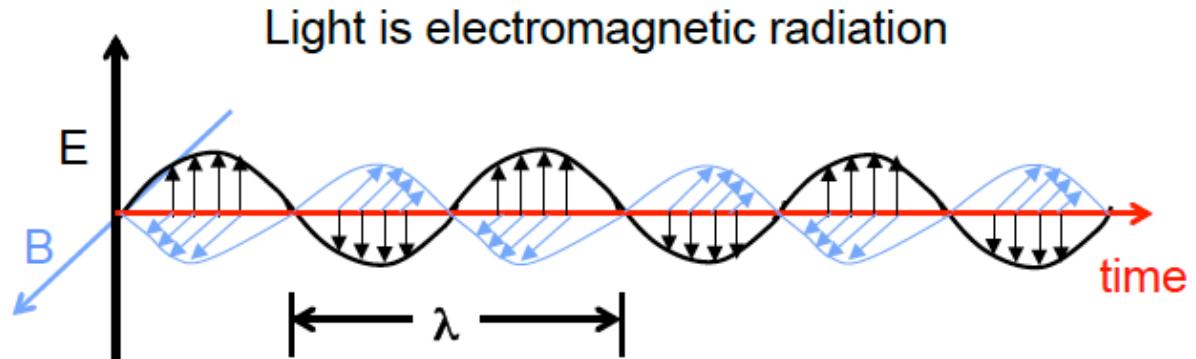
$$\Delta p \Delta x = \Delta(mv) \Delta x \geq h/4\pi$$

Problem: Let's say that we have done a measurement that shows that an electron is located within the nucleus of an atom. Assume the nucleus has a diameter of 10^{-13} m . This implies that $\Delta x = 10^{-13} \text{ m}$, then how well do we know the kinetic energy of the electron? **Good problem to work out**

There is a similar relationship for ΔE and Δt .

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} (\text{kg m}^2 \text{ s}^{-1}) = \text{Planck's constant}$$

Spectroscopy

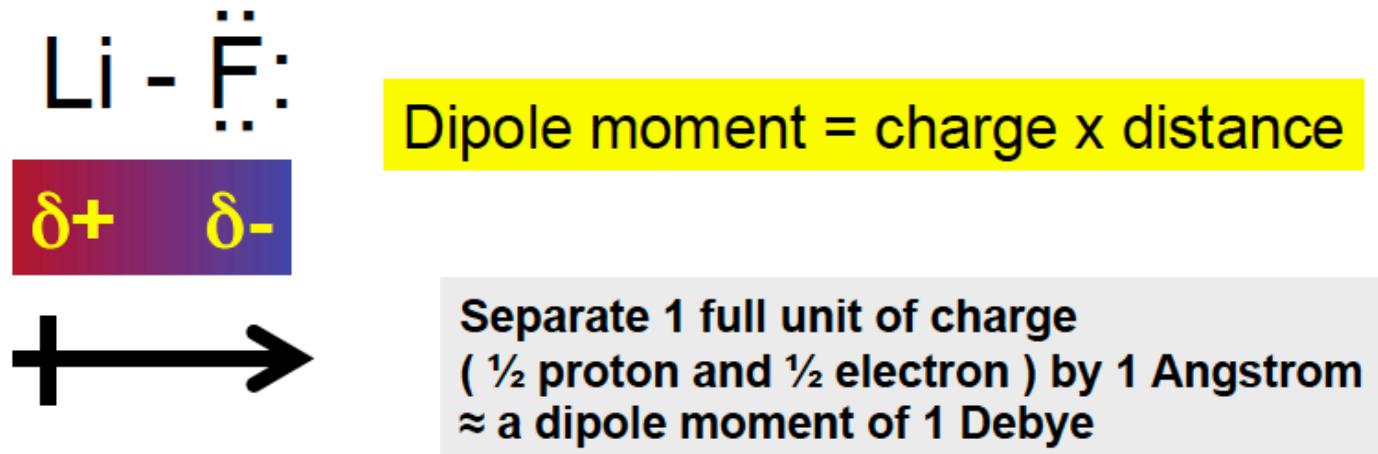


It is a field with an electric component and, at right angles, a magnetic component, that sinusoidally varies in time

Key Point:

Anything that exhibits a periodically varying electric field
(an alternating electric field)
can resonantly interact with the light and absorb or emit radiation

Some molecules have a permanent electric field that is associated with them – this field is described by their dipole moment

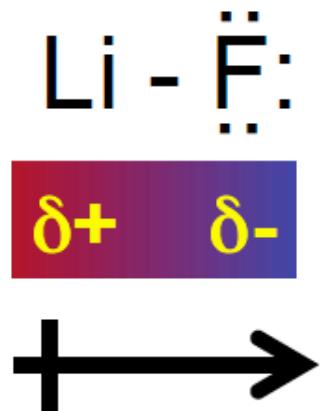


Fluorine is substantially more electronegative than Li
The Fluorine atom has a partial negative charge
The Li-atom has a partial positive charge

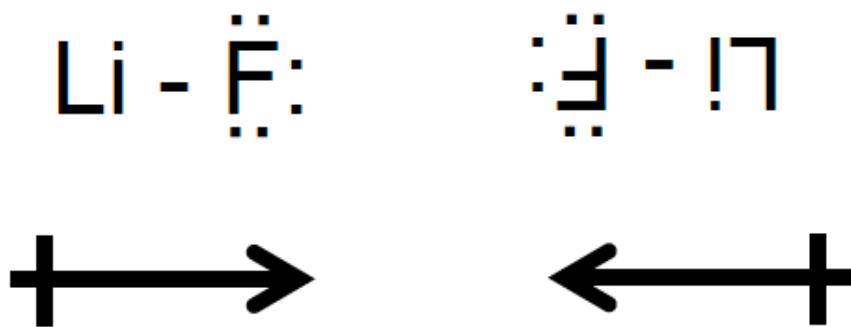
Thus, LiF has a permanent electric field.

Molecules can also have a temporary electric field

Ways to generate an alternating electric field from this molecule



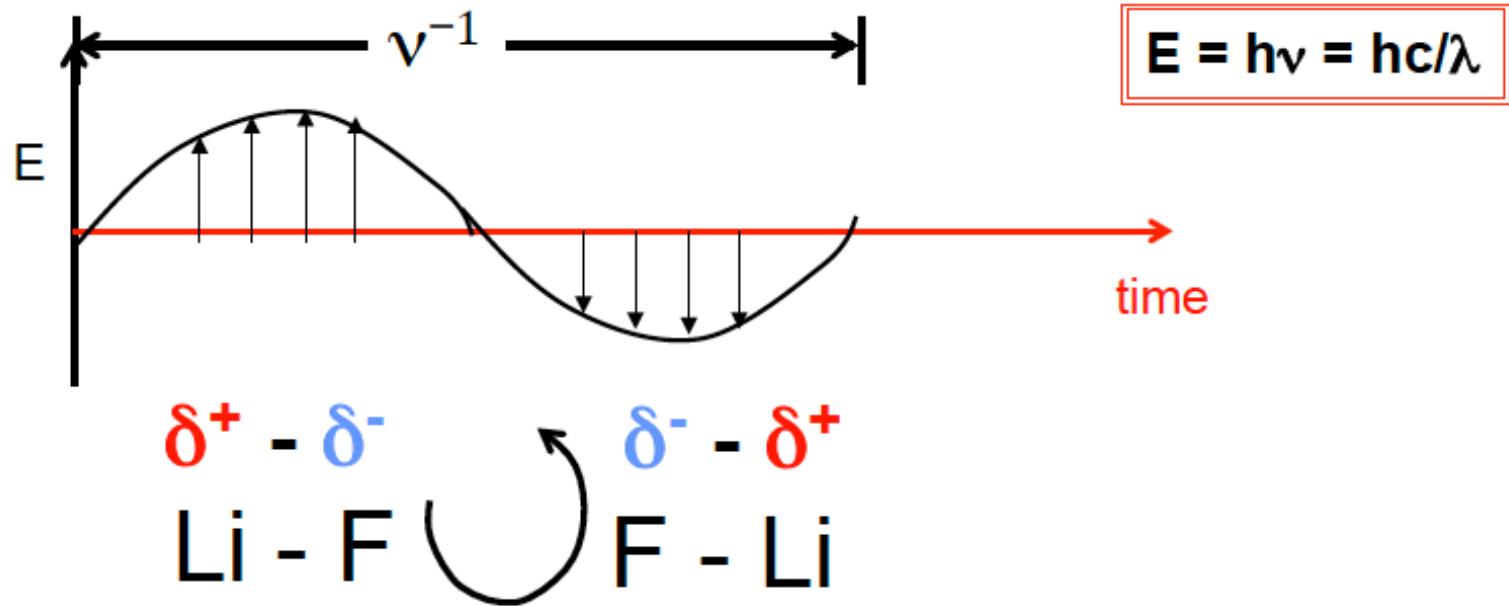
1. Rotate the molecule



Field switches direction when molecule rotates

The result is an alternating electric field

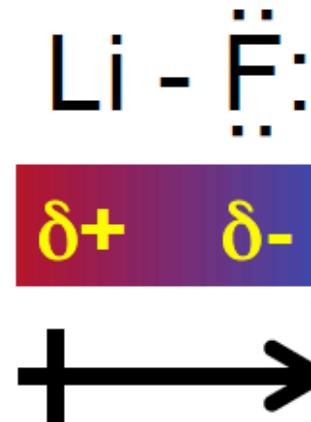
Molecular Rotational Spectroscopy



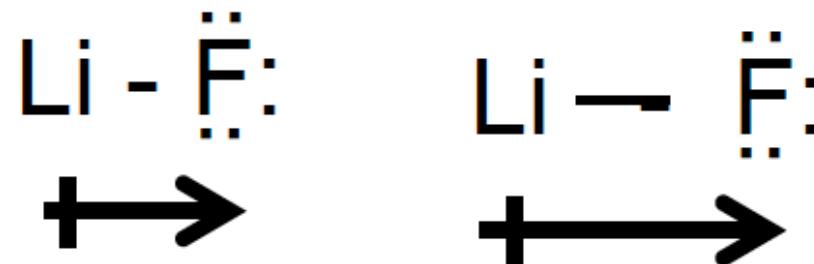
Molecules can absorb or emit light at their frequencies of rotation

What if molecule doesn't have a dipole?

Ways to generate an alternating electric field from this molecule



2. Stretch (vibrate) the molecule



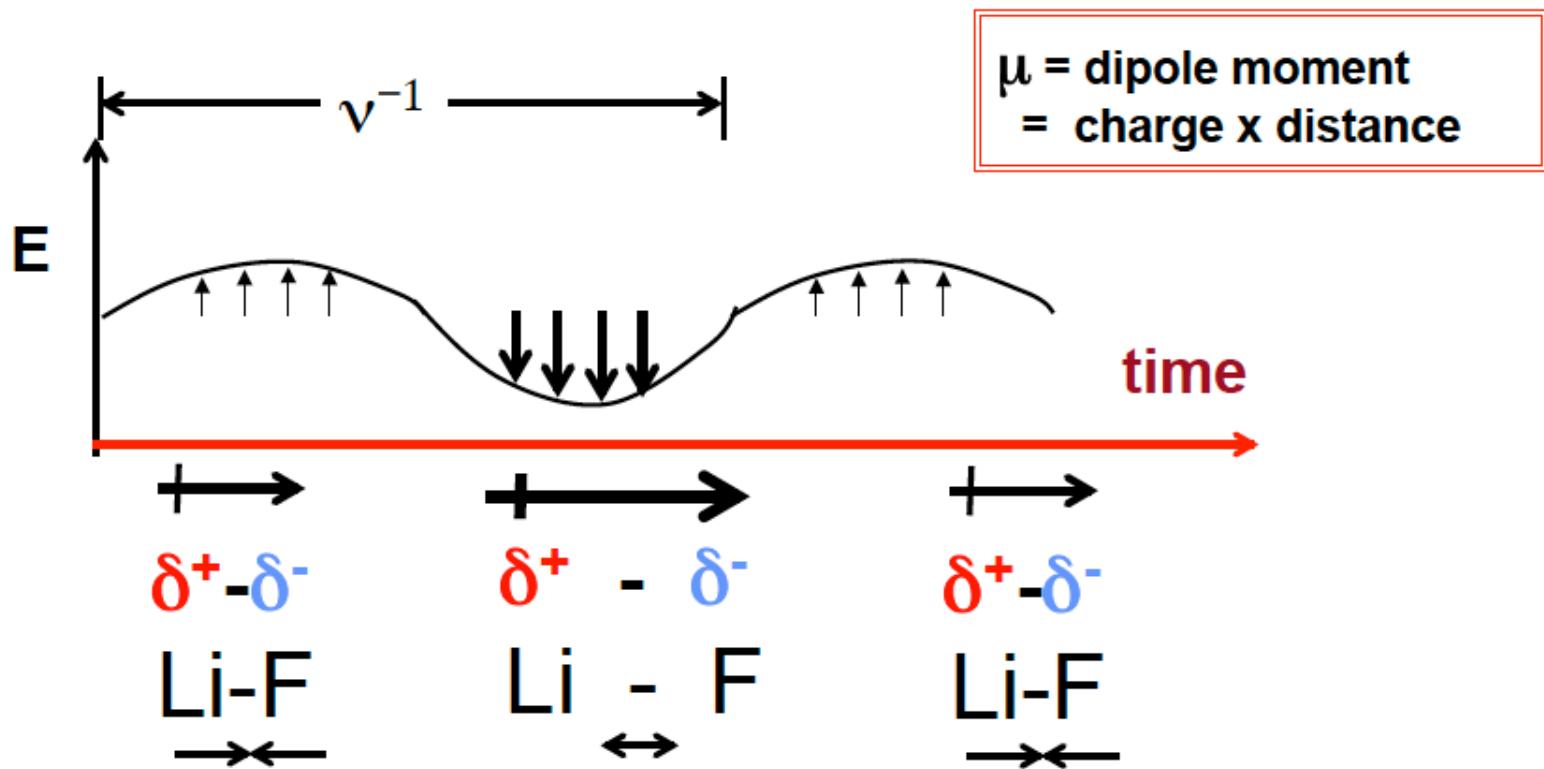
Dipole Moment describes the magnitude of electric field

Dipole moment = charge \times distance

If bond distance increases, then dipole moment increases

Result is an alternating electric field as the molecule vibrates

Molecular Vibrational Spectroscopy



$\mu = \text{dipole moment}$
 $= \text{charge} \times \text{distance}$

Molecules can absorb or emit light
 at their frequencies of vibration

What if molecular vibration doesn't change dipole moment?

Ways to generate an alternating electric field from this molecule

3. Change bonding structure within molecule

Triple bond
1 σ , 2 π bonds

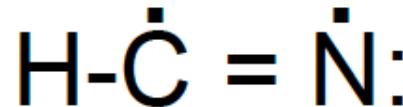


$\delta+$ $\delta-$



Remove one
bond by placing
1 electron into a
 π^* orbital

Double bond
1 σ , 1 π bonds



$\delta+$ $\delta-$

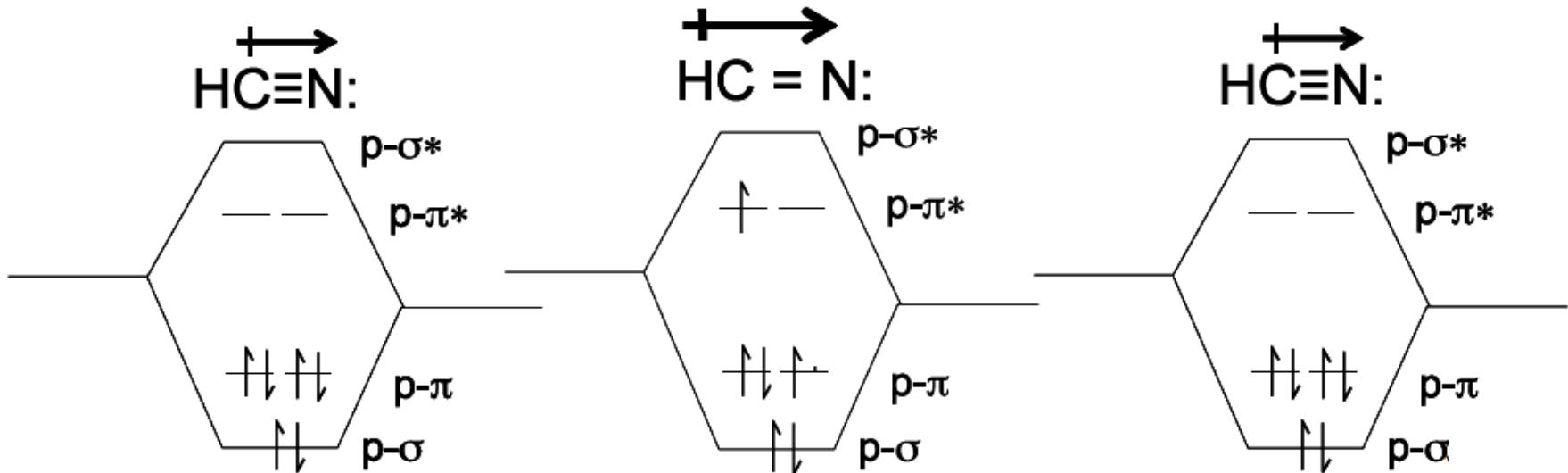
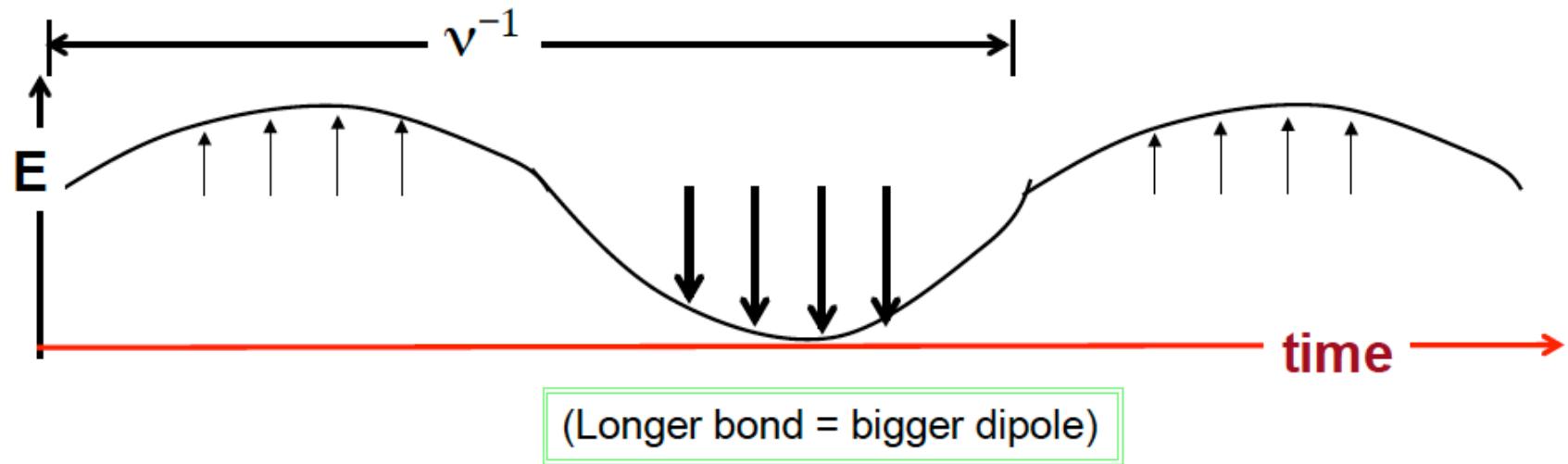


Bond length increases

The 1st approximation is that dipole moment changes – this is correct!

By how much? We would need to more deeply understand how charge is distributed in each of these two different electronic configurations of the same molecule

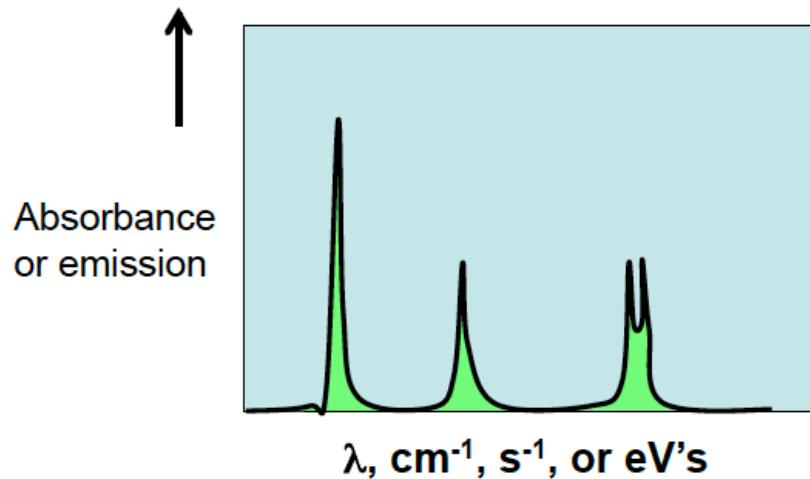
Molecular Electronic Spectroscopy



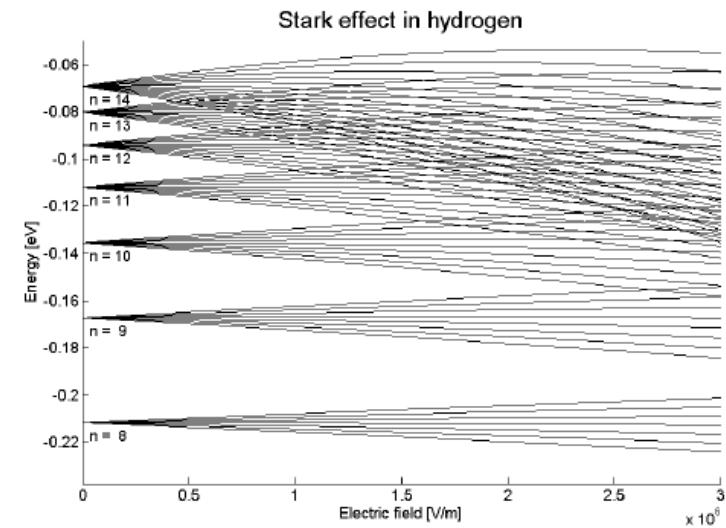
Where molecules can absorb light

| Wavelength of Light | Molecular Interaction | Spectroscopy Name |
|--|---|--|
| Radiowaves 1.meter and longer wavelengths | Nuclear spins flip from up to down, or from down to up | Nuclear magnetic resonance (NMR) Information about local chemical environments as well as global structure |
| Microwaves Millimeter wavelengths | Molecules rotate | Molecular rotation spectroscopy Information about dipole moments and bond lengths and angles. |
| Infrared 1.– 40 micrometers 1 micrometer = 10^{-6} meters | Molecules vibrate | Molecular vibrational spectroscopy Information about the functional groups present on a molecule, the symmetry of the molecule, the structure of the molecule |
| Visible/ultraviolet 1000 to 100 nanometers | Electrons move from one electronic configuration to another | Electronic Spectroscopy Information about the molecular orbitals |

Beyond dipole moments, when we see a discrete spectrum, what determines the intensities of the various features?

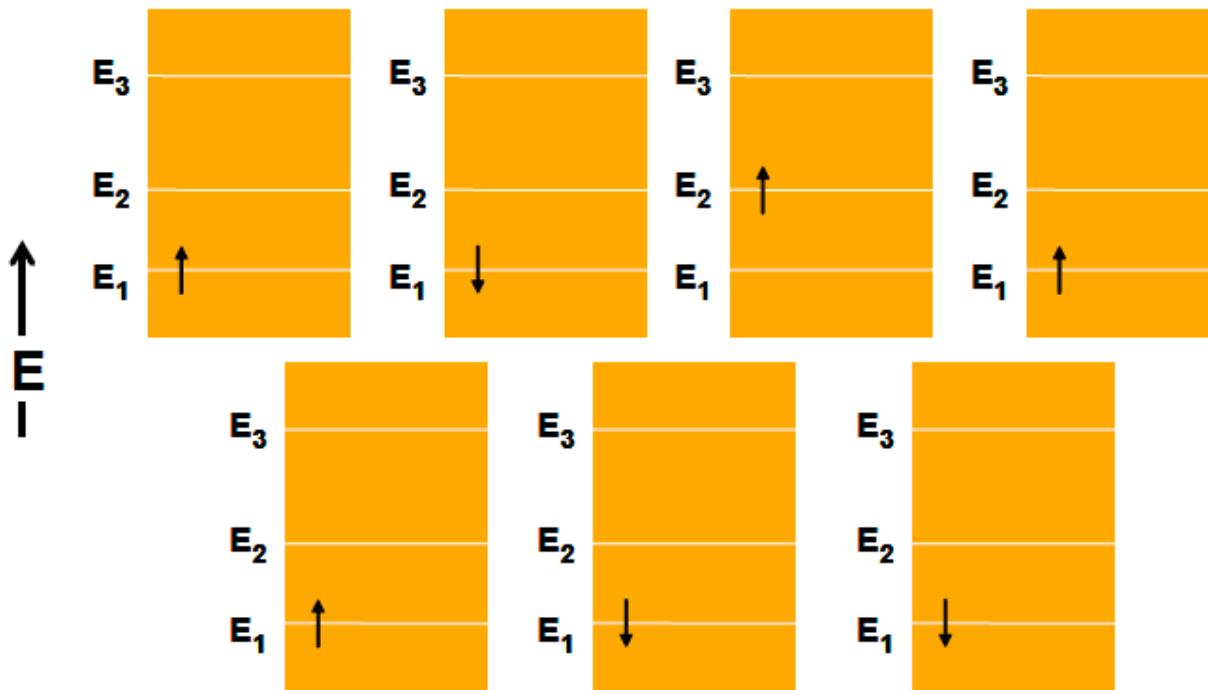


The answer is complicated, here we will just worry about degeneracies, which you encountered in atomic hydrogen (energy depends only on n , not l or m_l).



Degeneracies & Populations of Quantum Levels

7 particle in a box systems at temperature T



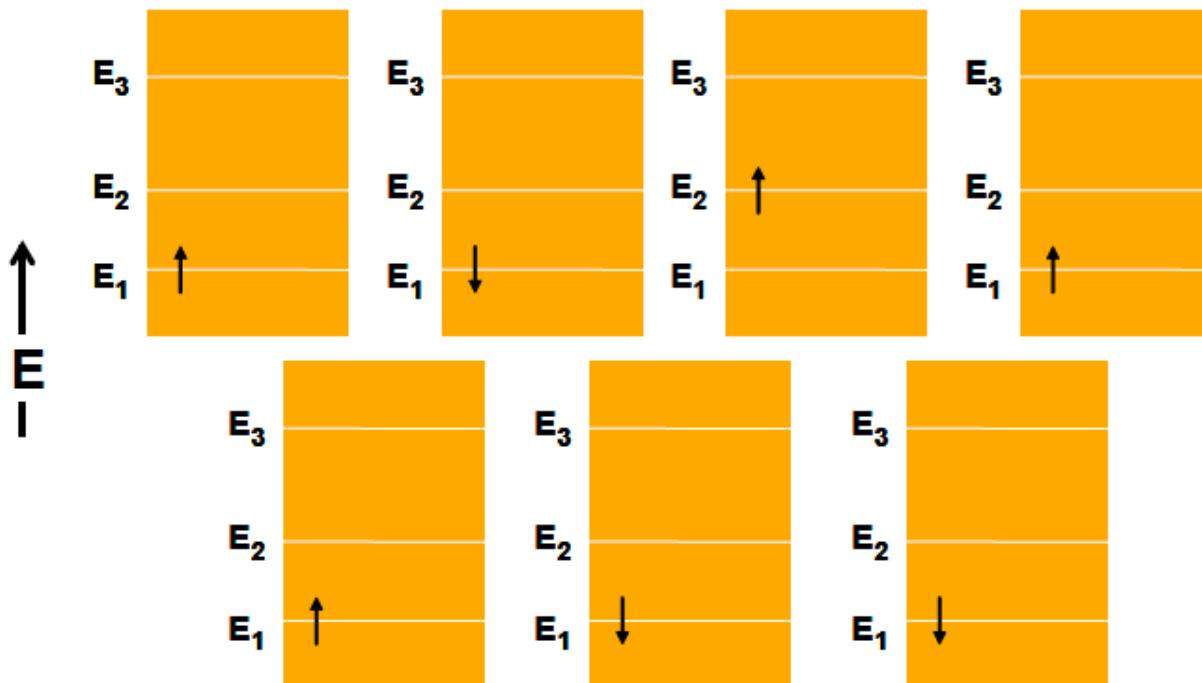
The lowest energy state is the ground state

An electron in this state can be spin up or spin down –

these two possibilities imply that the degeneracy of the ground state is 2. We say that $g_{\text{1}} = 2$, where **1** means we are referring to the $n=1$ quantum state.

Degeneracies & Populations of Quantum Levels

7 particle in a box systems at temperature T



If we have a statistical number (> than the 7 shown) P in a Box systems.

At temperature T, what fraction of these systems have an electron in the n=2 state?

Degeneracies & Populations of Quantum Levels

1st molecule 2nd molecule 3rd molecule



$g_k = 2$ for each level shown here

For an energy level E_k , the population of that level (for the case above, the probability that that level is occupied) is given by:

$$n_k \propto g_k e^{\frac{-E_k}{k_B T}}$$

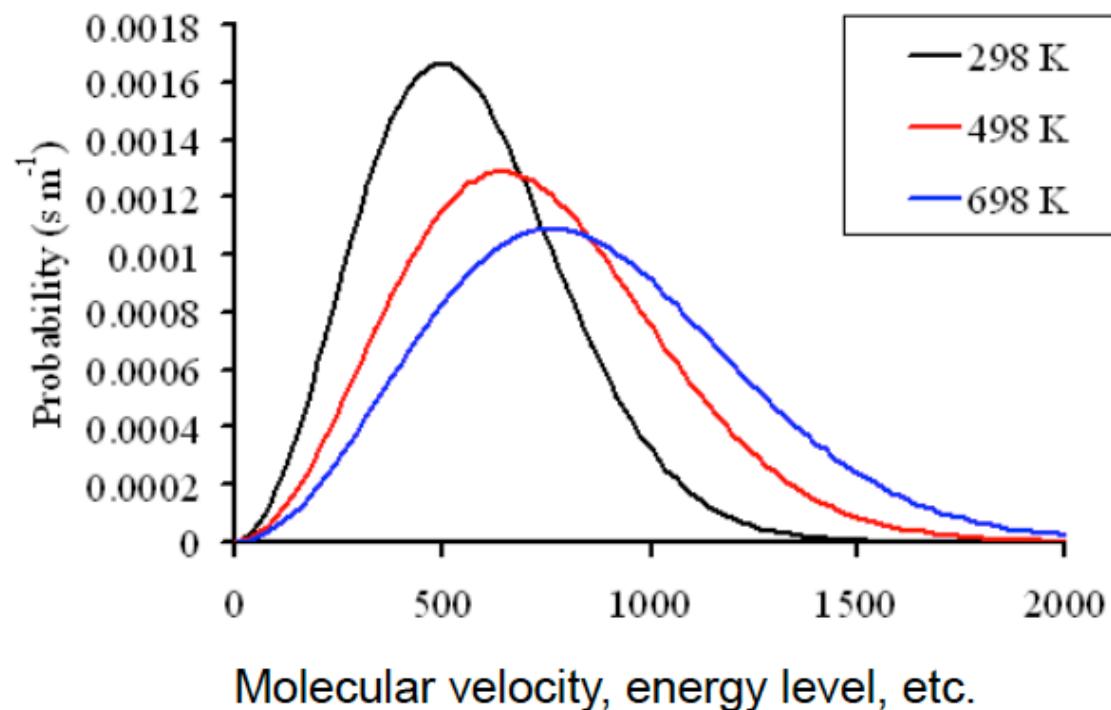
↗

This exponential function leads to what is called a Boltzmann distribution – very important in many fields – Chem Eng; Chem; Physics; Astronomy, (even Biology) etc.

$$h = 6.626e-34 \text{ J}\cdot\text{s} \quad (\text{kg m}^2 \text{ s}^{-1}) = \text{Planck's constant}$$

$$k_B = 1.381e-23 \text{ J}\cdot\text{K}^{-1} \quad T = \text{temperature (in K)}$$

Boltzmann Distributions



We'll come back to this when we cover the kinetic theory of gases...

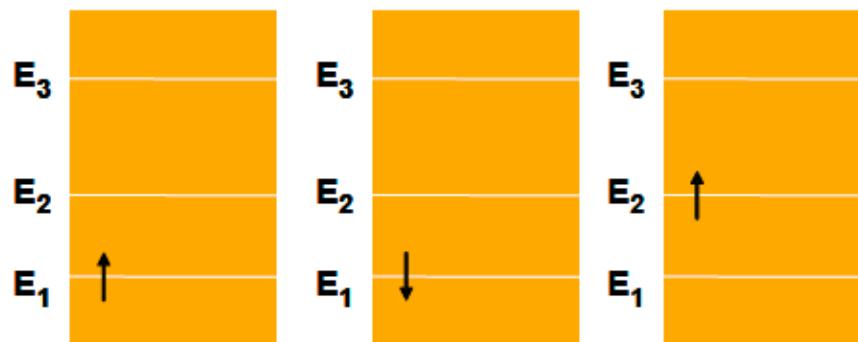


Ludwig Boltzmann
(shown here smiling)

Degeneracies & Populations of Quantum Levels

35

1st molecule 2nd molecule 3rd molecule



$$k_B T \text{ at } 298\text{K} \approx 200 \text{ cm}^{-1}$$

$$\Delta E_{1,2} = E_2 - E_1$$

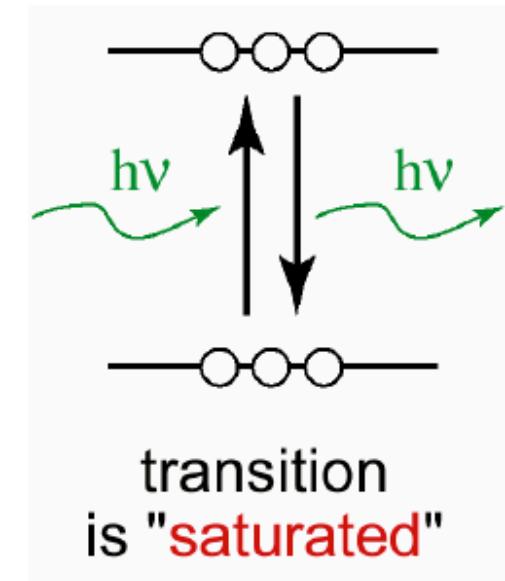
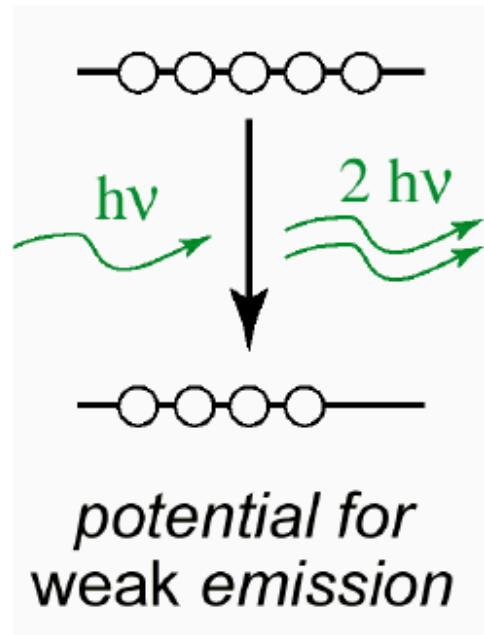
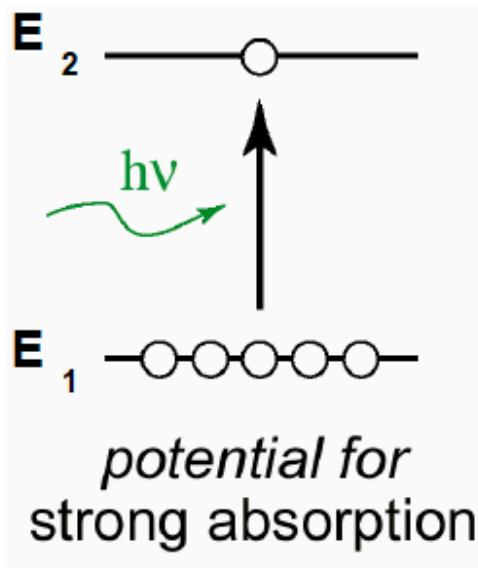
Key Point:

A more relevant number is the population ratio between the ground and excited states, since this is what is typically measured:

If we plotted this for all of the states Ψ_n of energy E_n , we would have the Boltzmann distribution

$$\frac{n'}{n''} = \frac{g'}{g''} e^{\frac{-\Delta E}{k_B T}}$$

$$h = 6.626e-34 \text{ J}\cdot\text{s} \quad (\text{kg m}^2 \text{ s}^{-1}) = \text{Planck's constant}$$
$$k_B = 1.381e-23 \text{ J}\cdot\text{K}^{-1} \quad T = \text{temperature (in K)}$$



$$A_{\lambda} = -\log_{10} \left(\frac{I_S}{I_R} \right) = c \epsilon_{\lambda} l$$

Beer-Lambert Law

I_R = intensity w/no sample
 I_S = intensity w/sample
 c = concentration
 l = cell length
 ϵ_{λ} = molar extinction coeff.

The role of the Boltzmann Distribution and the importance of degeneracies varies widely across the major forms of spectroscopies

Recall that $k_B T$ (at 300K) = 200 cm⁻¹

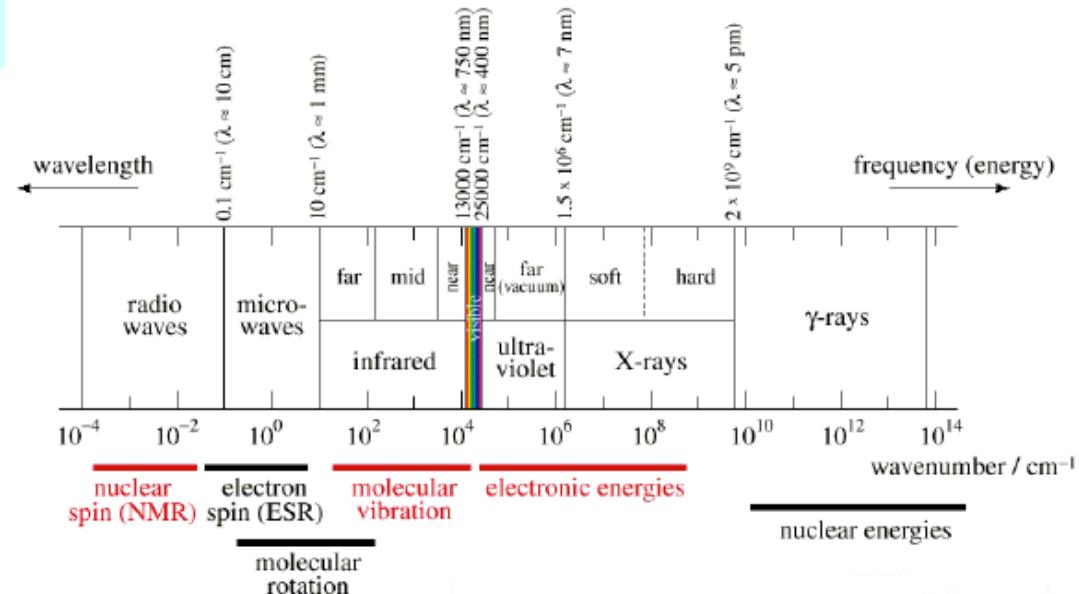
Nuclear Magnetic Resonance levels ~ small fractions of a cm⁻¹

Rotational energy level ~ few cm⁻¹

Vibrational energy level ~ 10² – 10³ cm⁻¹

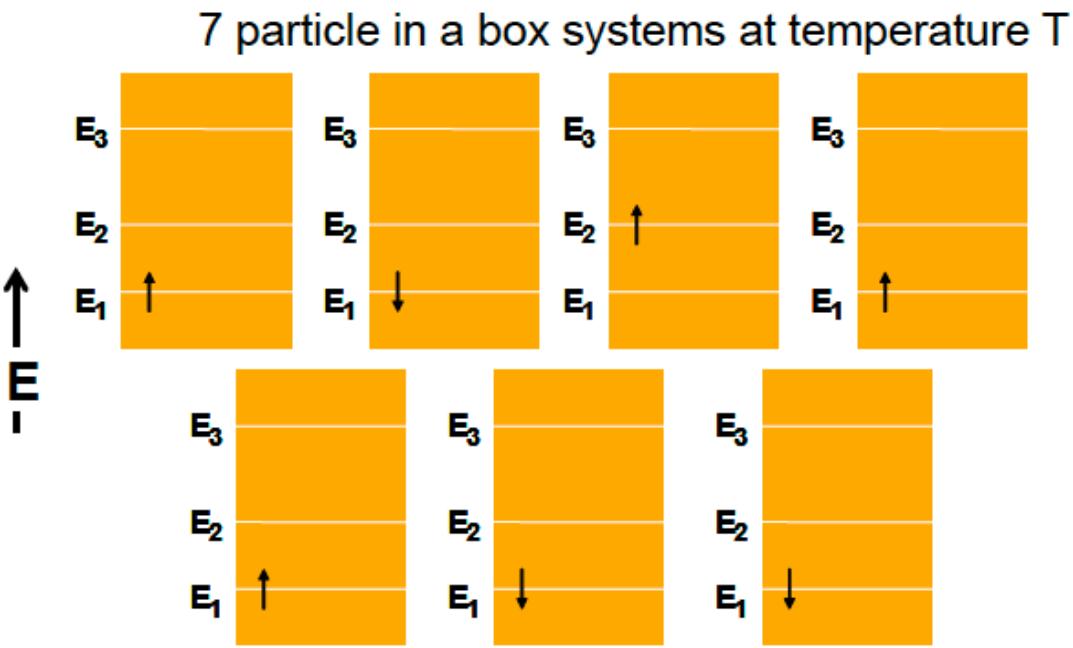
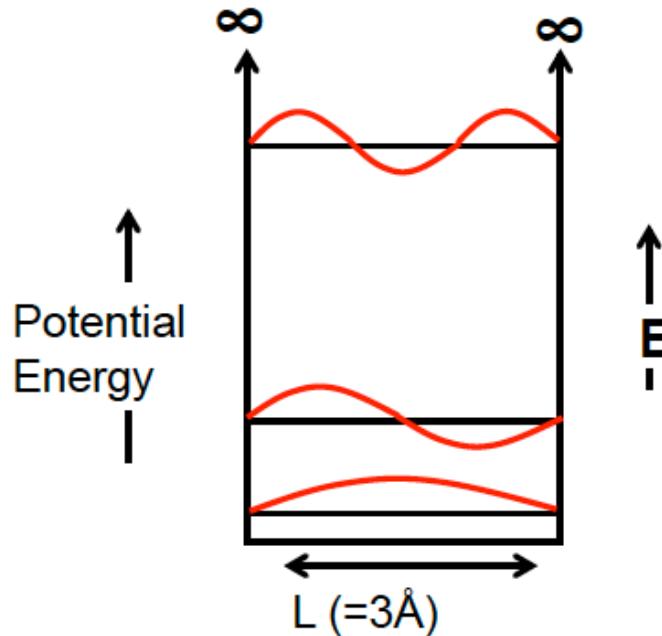
Electronic Energy level ~10⁴ cm⁻¹

$$\frac{n'}{n''} = \frac{g'}{g''} e^{\frac{-\Delta E}{k_B T}}$$



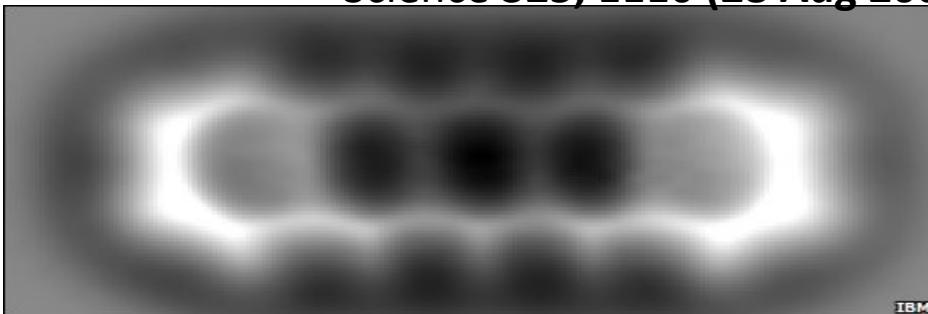
Here is a pretty good problem to work out:

Take a particle-in-a-1D-box system, at room temperature, in which the particle is an electron, and the 1D box is 3 Angstroms (\AA) long. Outside of this 3 \AA length, the potential energy is infinite, and within the box, it is 0. What fraction of PiB systems are going to have the electron in the E_2 (first excited) state relative to the ground state? How big would the box have to be before 5% of the systems had their electron in the E_2 state?



Are there molecular examples that can be treated as a PiB?

Science 325, 1110 (28 Aug 2009)



<http://news.bbc.co.uk/2/hi/8225491.stm>

Go to larger molecules, esp.
those with that are aromatic to
delocalize the electrons (think
about the PiB solutions).

Create “artificial atoms”:
CdSe Quantum Dots



Simultaneous excitation at 365 nm

