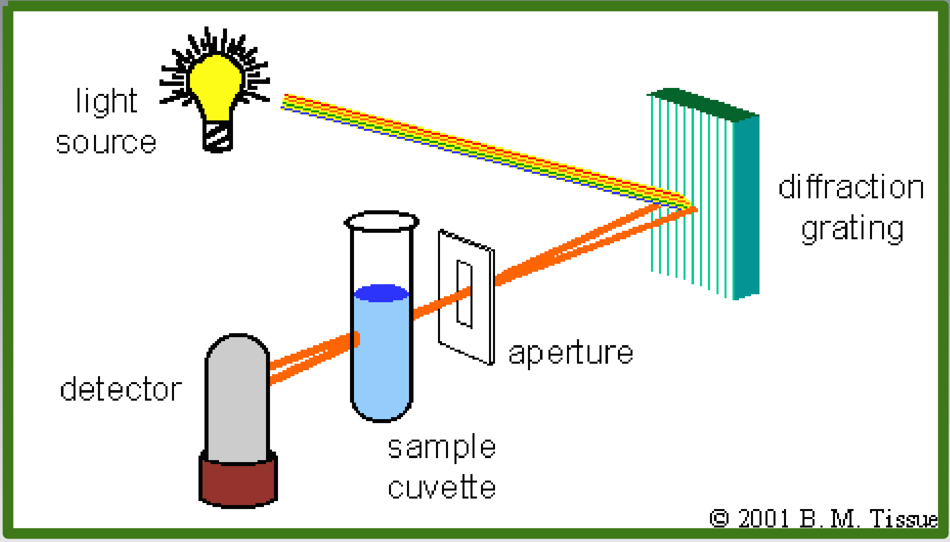
Spectroscopy…

- Spectroscopy is an analytical technique which helps determine structure and therefore identity.
- It involves shining light or energy of various wavelengths through matter to see the interaction that takes place.
- It destroys little or no sample.
- The amount of light absorbed by the sample is measured and graphed.

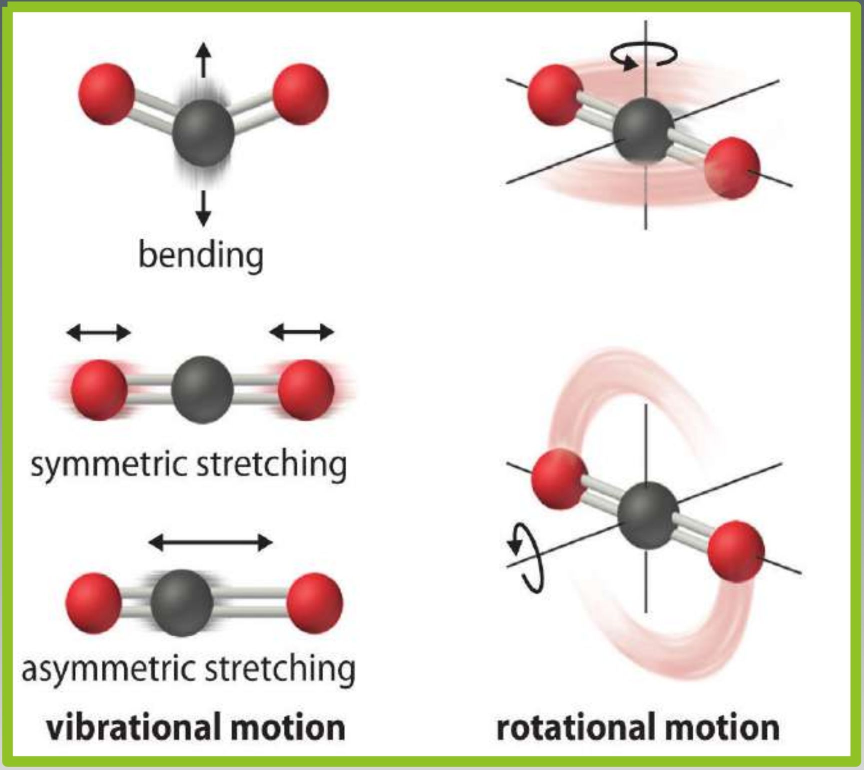


Types of Spectroscopy

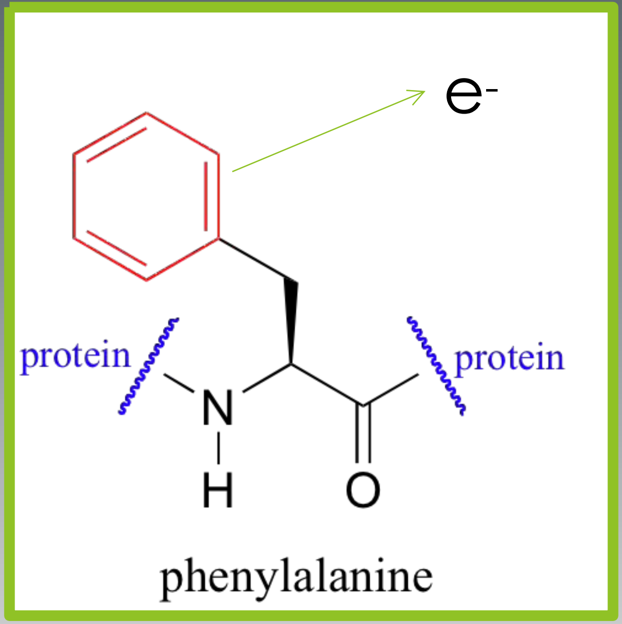
- Microwave spectroscopy excites entire small molecules to rotate and is used to determine the identity of small molecules.
- Infrared (IR) spectroscopy excites the vibrations of flexible bonds in organic molecules and is used to determine the functional group of an organic molecule.
- Ultraviolet (UV) spectroscopy excites electrons to move to higher energy levels to identify organic compounds, especially aromatic ones (with benzene) like in proteins and amino acids.
- Nuclear magnetic resonance (NMR) spectroscopy detects signals from protons in hydrogen atoms and can be used to identify organic molecules very accurately.
- Mass spectrometry (MS) fragments the molecule and measures the masses of each fragment, thereby identifying the original compound.

What happens to the molecule when hit with different types of energy......

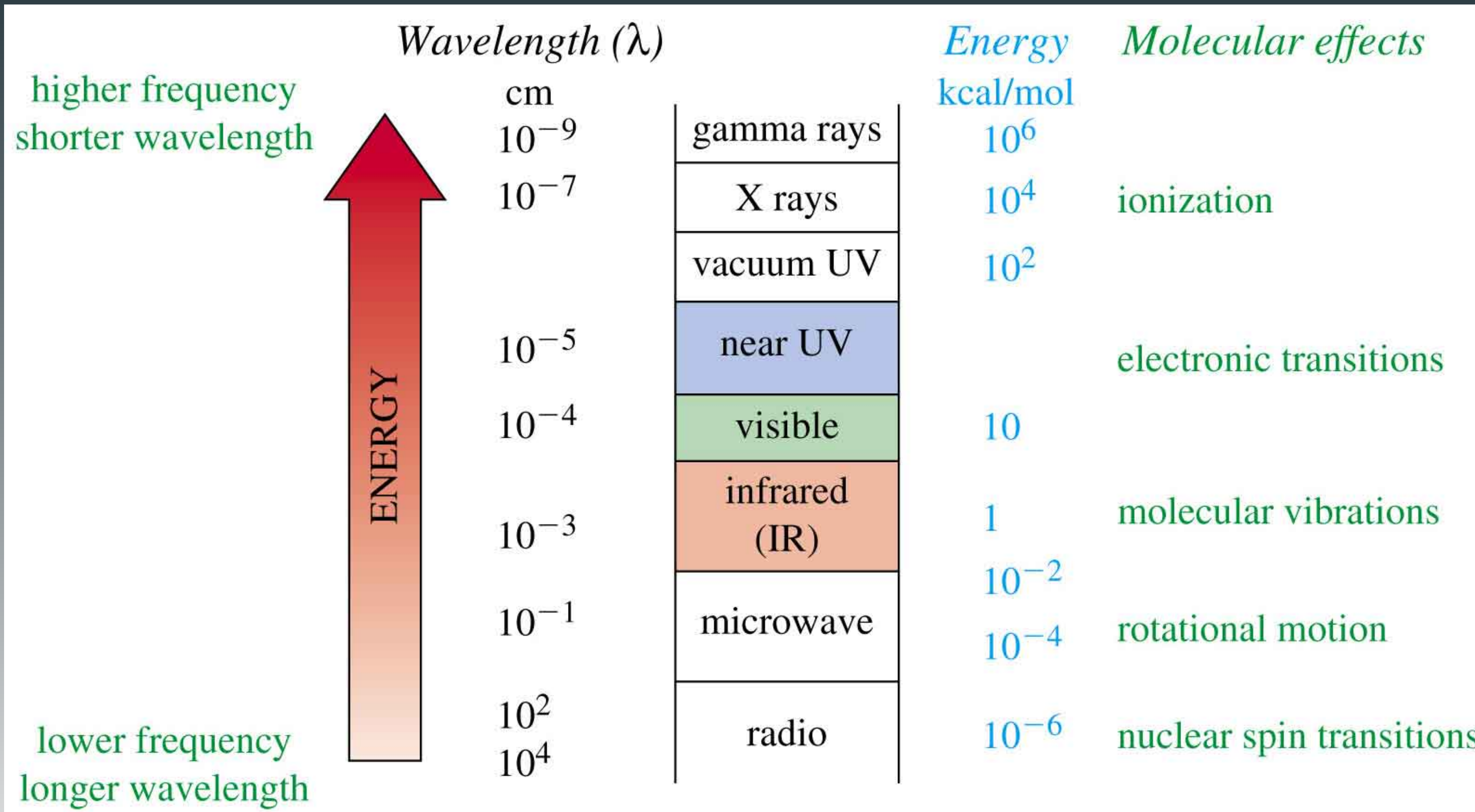
IR Spectroscopy **Microwave Spectroscopy**



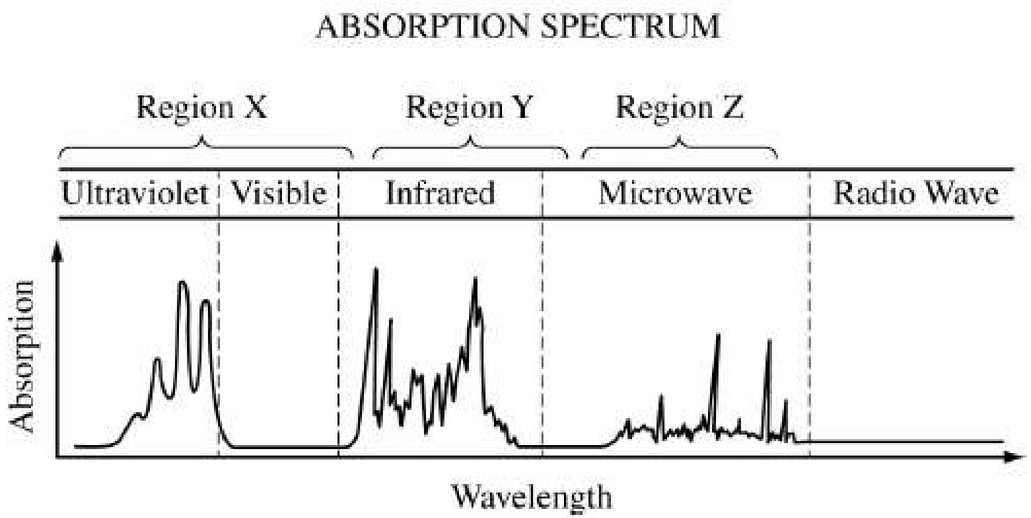
UV Spectroscopy



Energy and its effect on molecules



Sample AP problem......

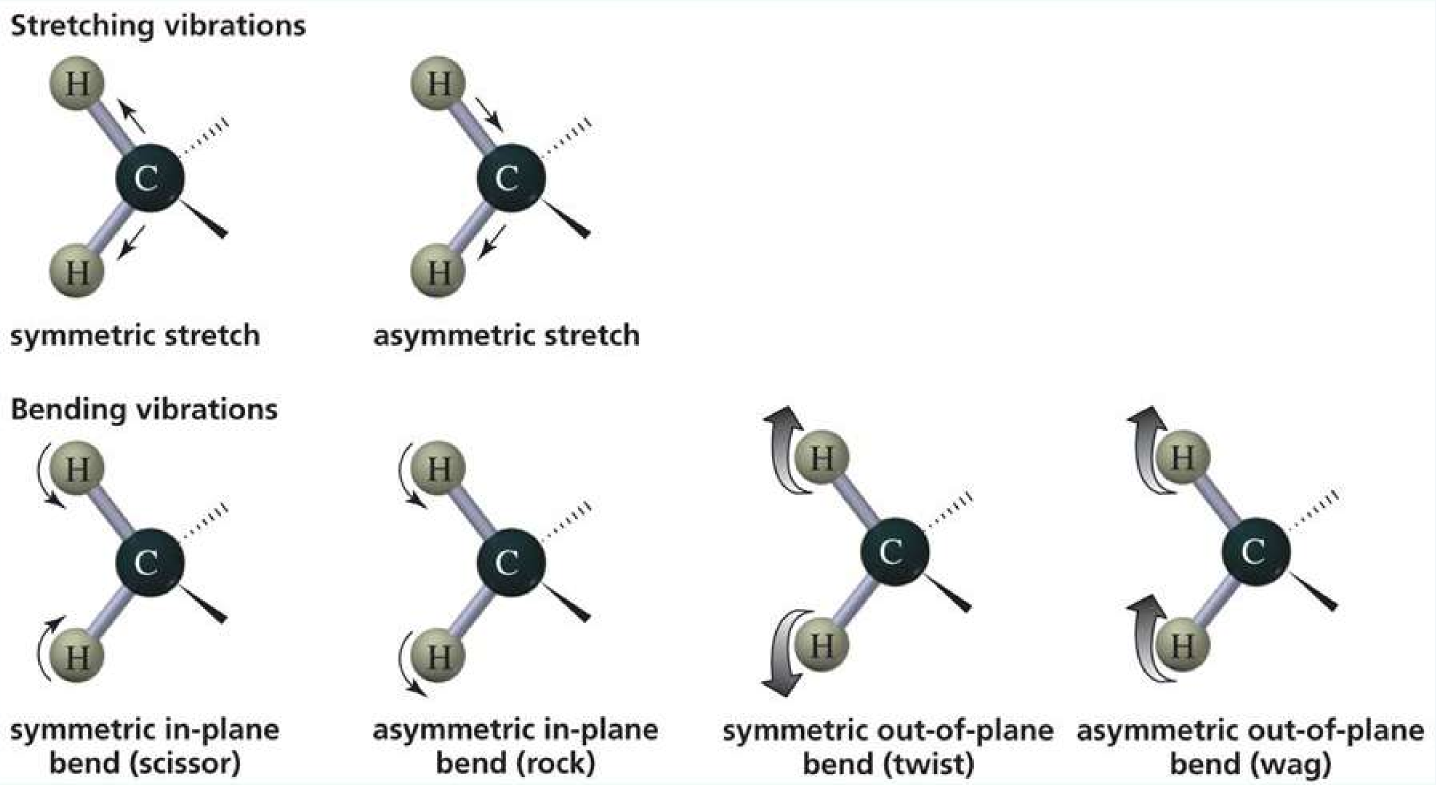


50. The diagram above represents the absorption spectrum for a pure molecular substance. Which of the following correctly indicates the type of transition observed for the substance in each of the regions of the absorption spectrum?

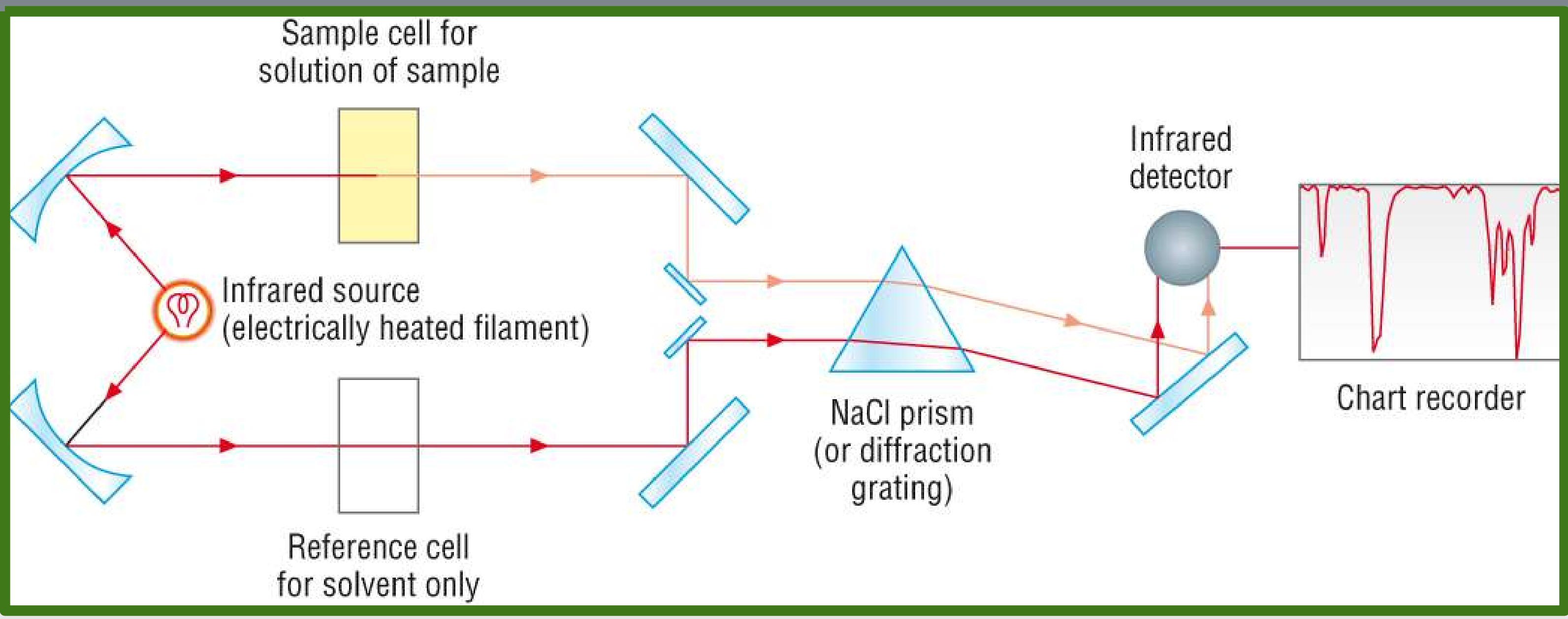
	Region X	Region Y	Region Z
(A)	Molecular vibration	Molecular rotation	Electronic transition
(B)	Electronic transition	Molecular rotation	Molecular vibration
(C)	Molecular rotation	Molecular vibration	Electronic transition
(D)	Electronic transition	Molecular vibration	Molecular rotation

IR Spectroscopy

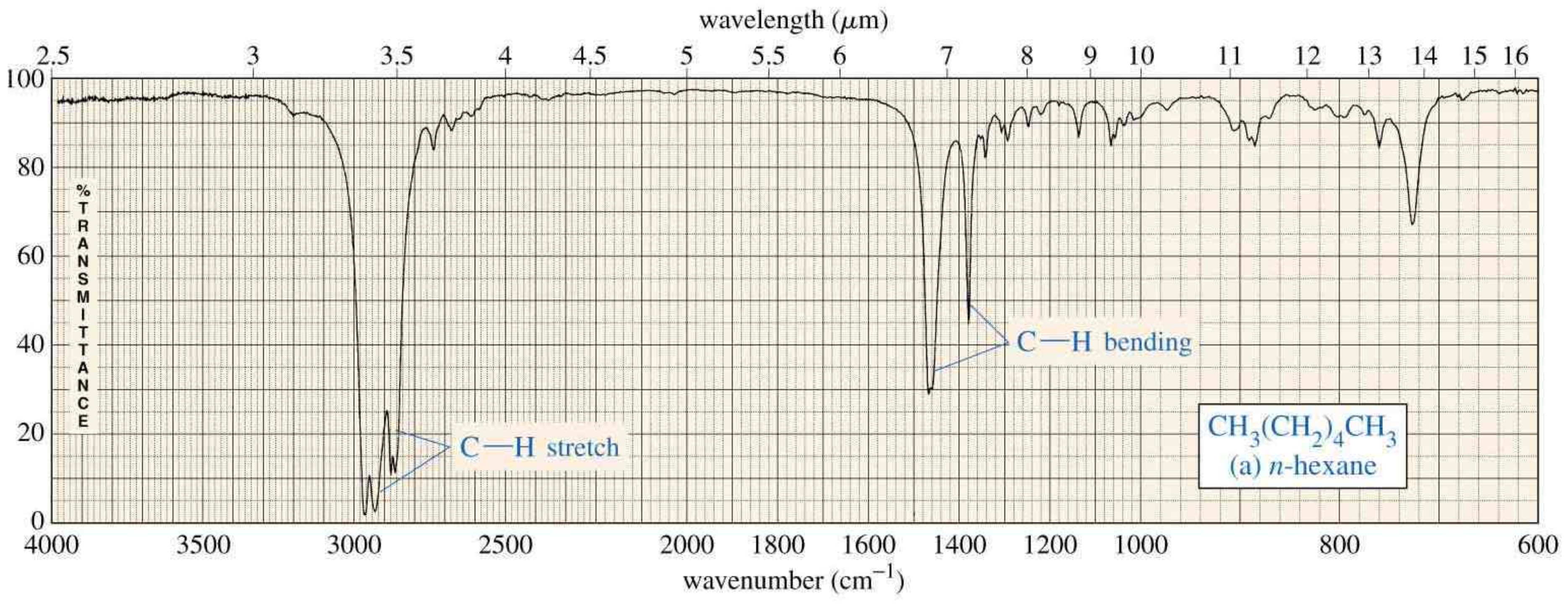
- Infrared light or energy causes the bonds in organic molecules to vibrate, stretch and bend
- No two molecules will give exactly the same IR spectrum



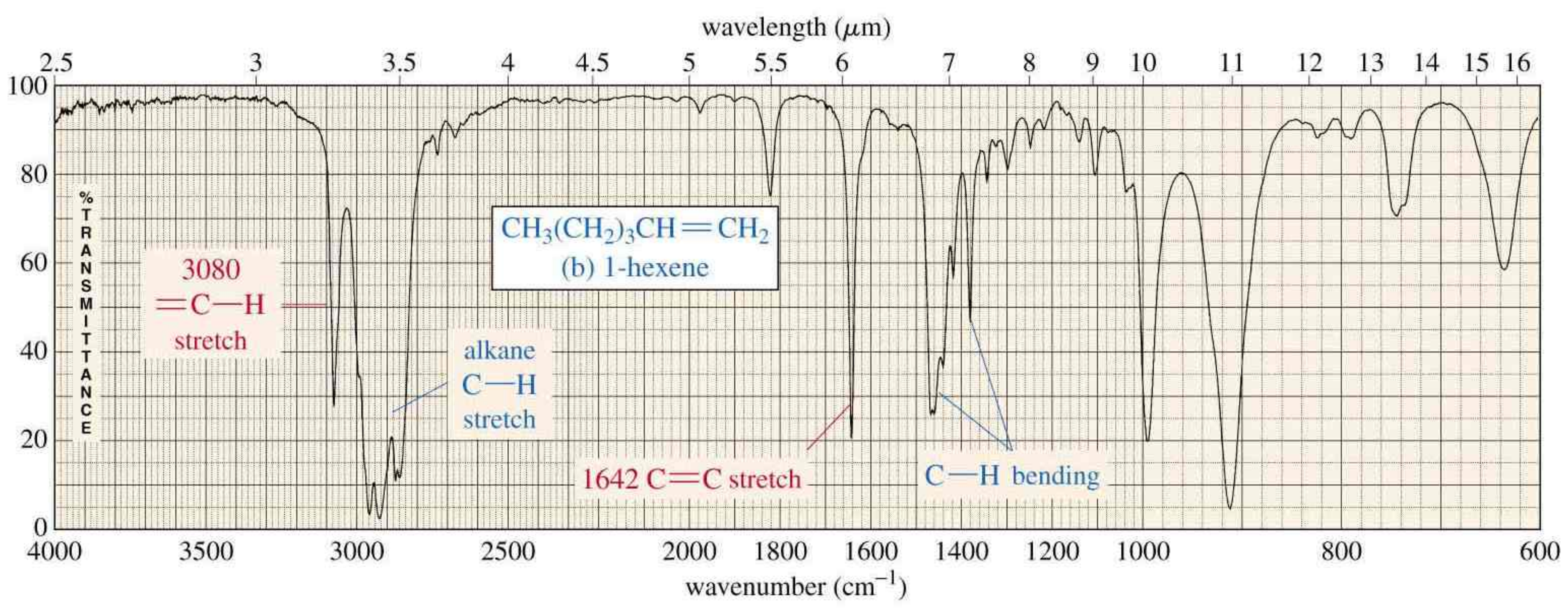
An Infrared Spectrometer



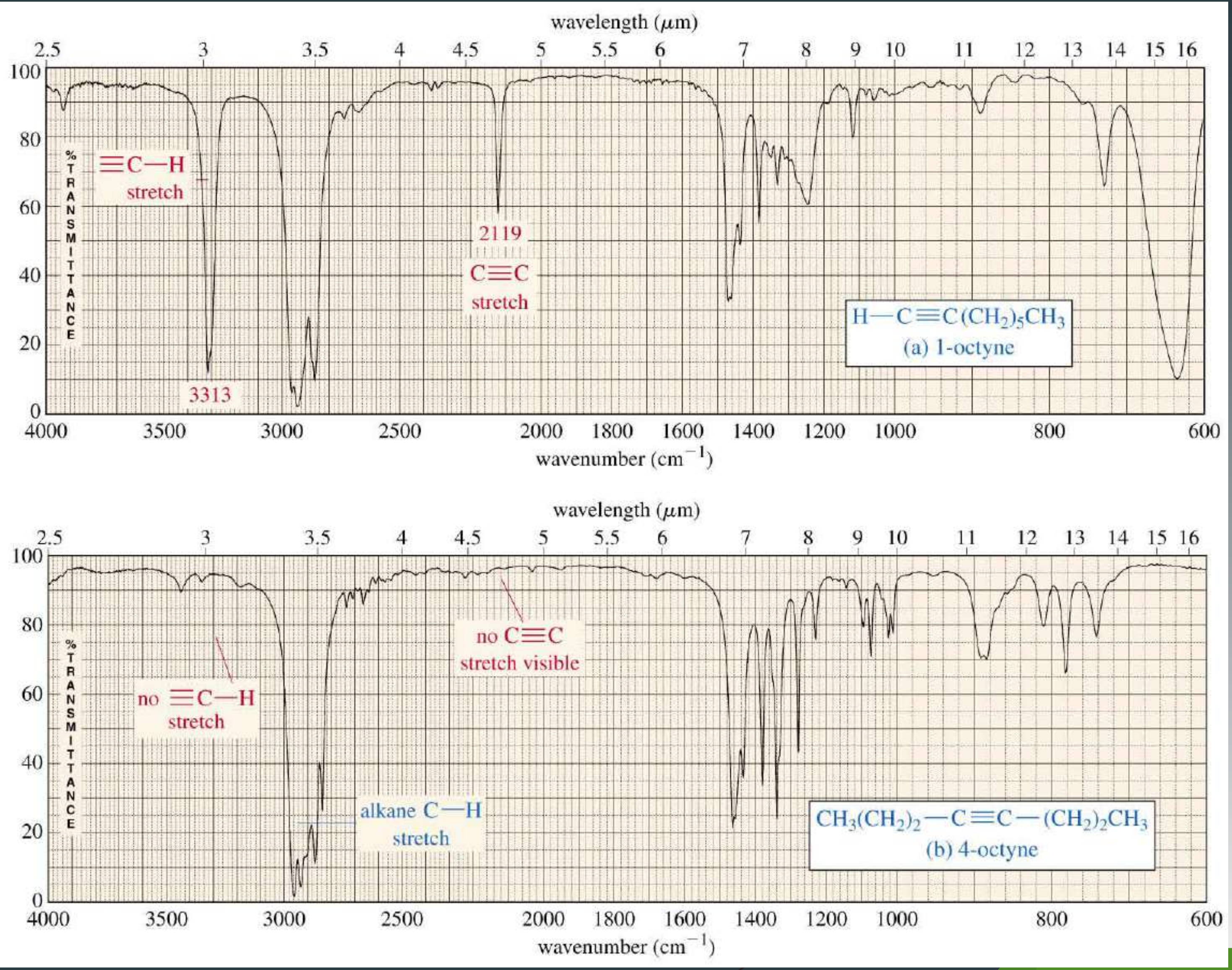
An Alkane IR Spectrum



An Alkene IR Spectrum

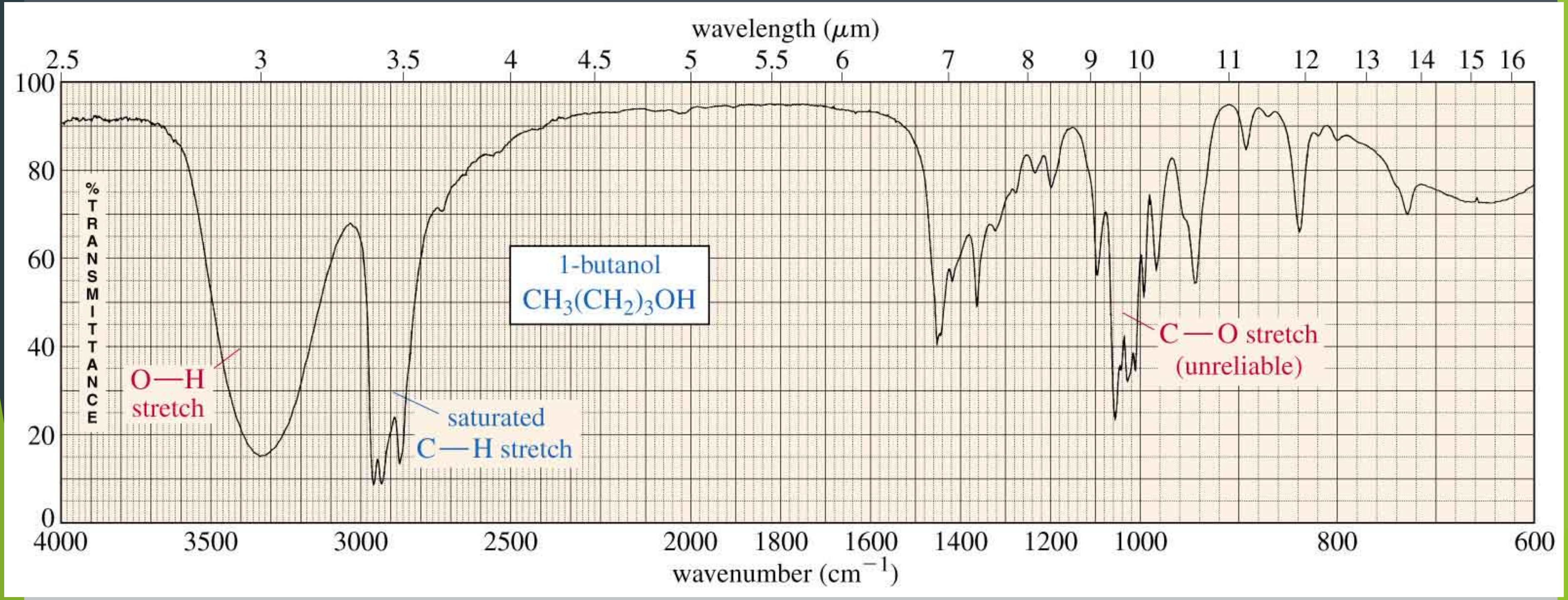


An Alkyne IR Spectrum



Ch

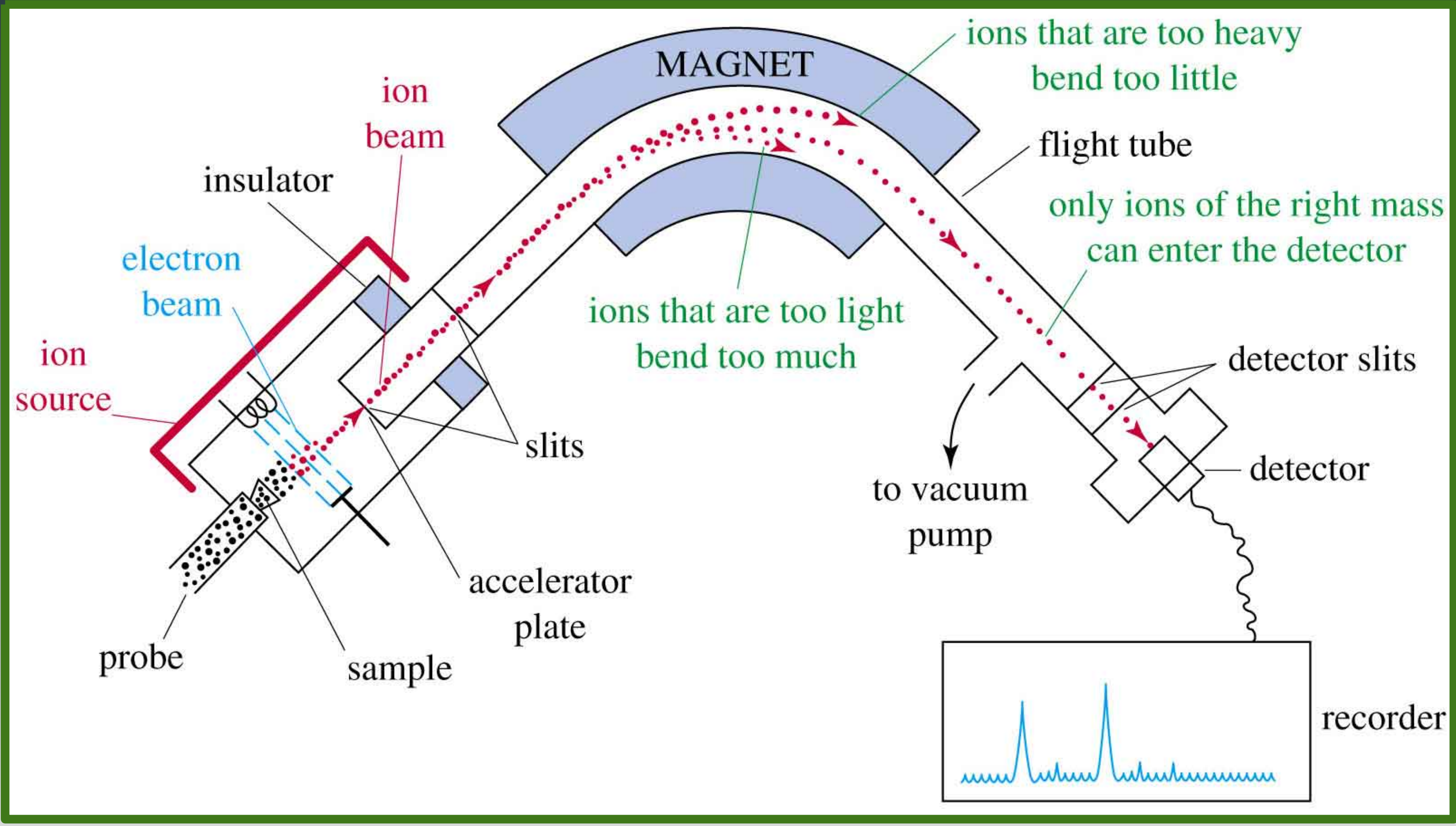
An Alcohol IR Spectrum



Mass Spectrometry

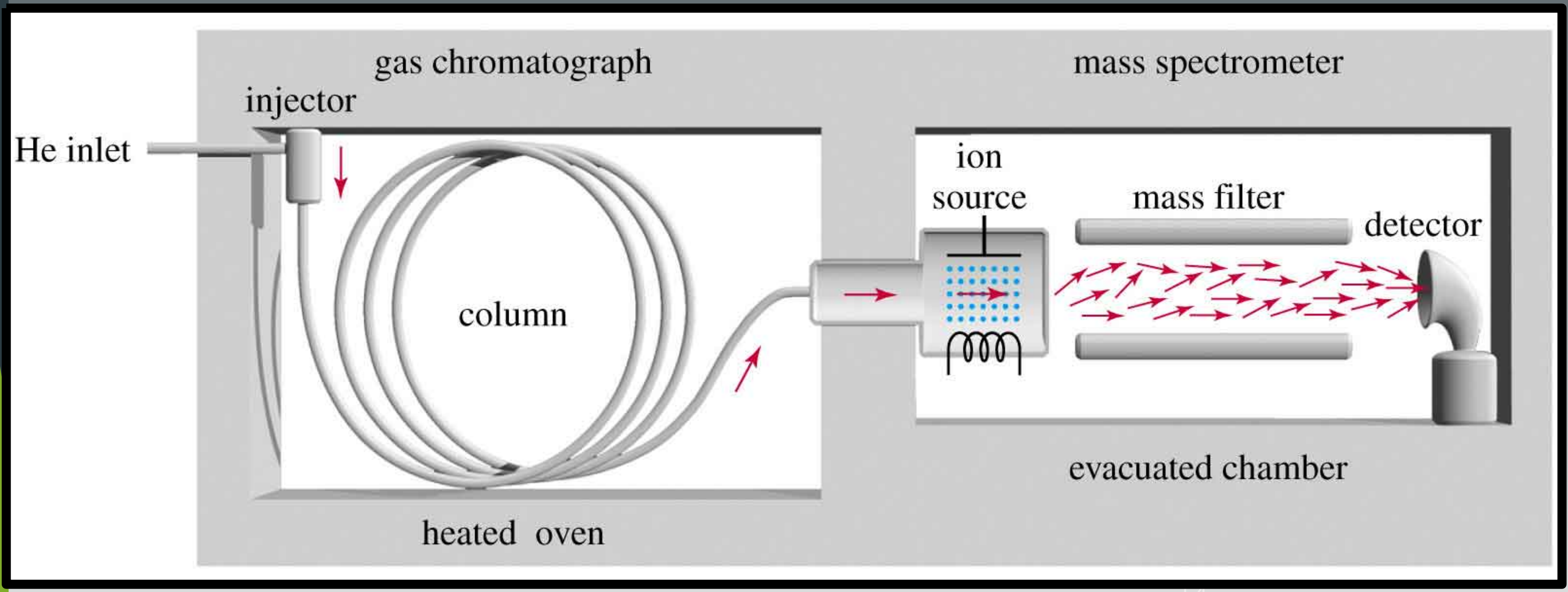
- Molecular mass can be determined from analyzing a very small sample.
- It does not involve the absorption or emission of light.
- A beam of high-energy electrons breaks the molecule apart into fragments, usually into cations.
- A magnetic field moves the molecules to a detector.
- Only the cations are deflected by the magnetic field.
- Amount of deflection depends on ***m/z*** (mass/charge)
- The masses of the fragments and their relative abundance reveal information about the structure or formula of the molecule.

Mass Spectrometer



The GC-MS

The gas chromatograph vaporizes the compound into a gas, and then the sample is bombarded with electrons. The electrons fragment the molecule into smaller pieces, and even ions!



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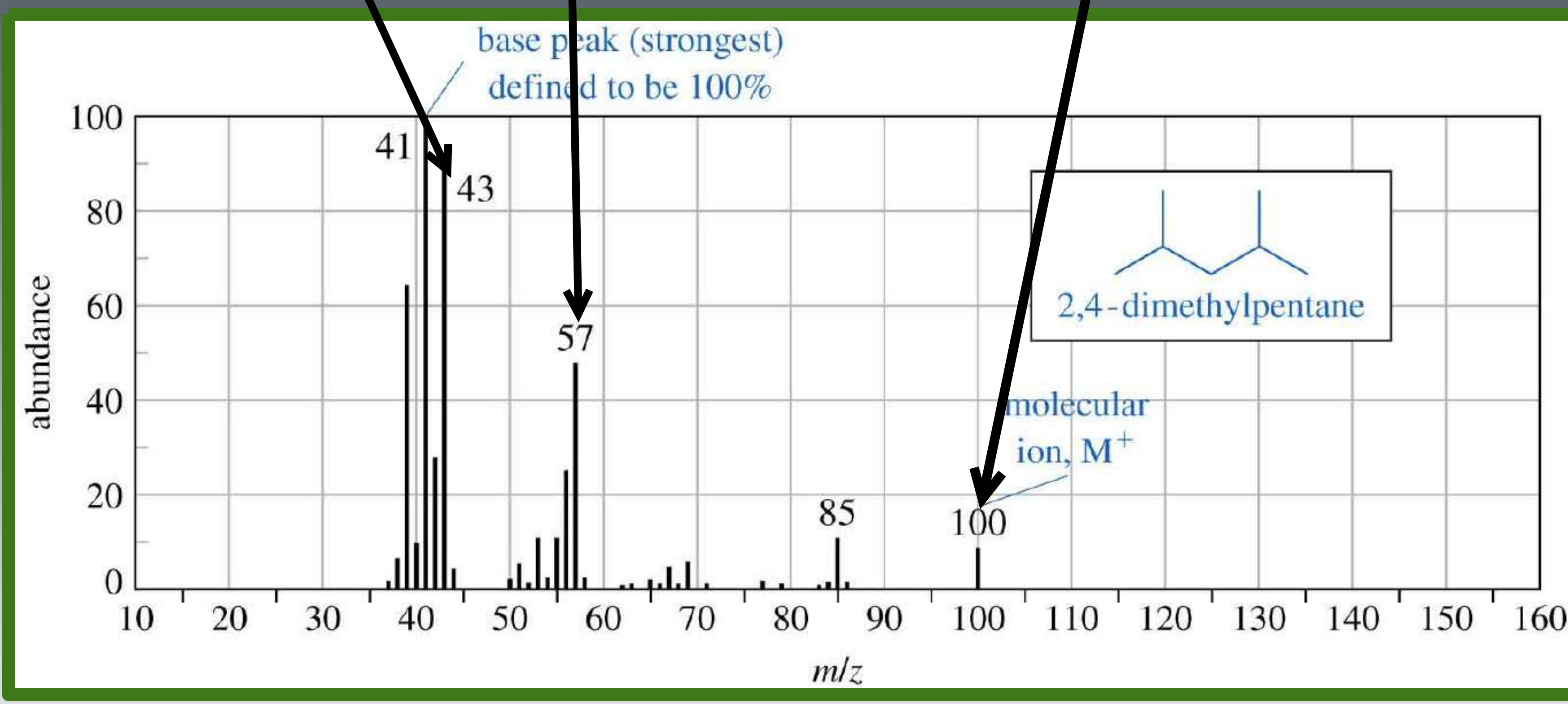
Most important peak is here – this identifies the molecule!

CH_3
|
CH_3-CH^+

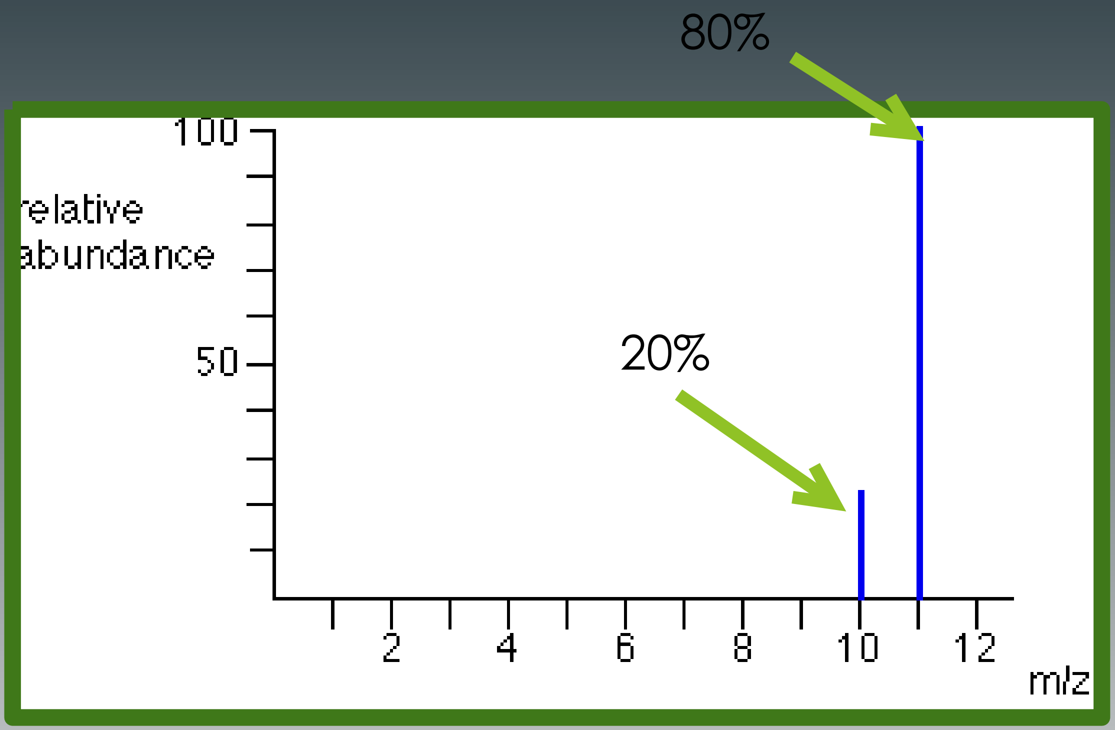
CH_3
|
+CH_2-CH-CH_3

CH_3 CH_3
| |
CH_3-CH-CH_2-CH-CH_3

2, 4 dimethylpentane



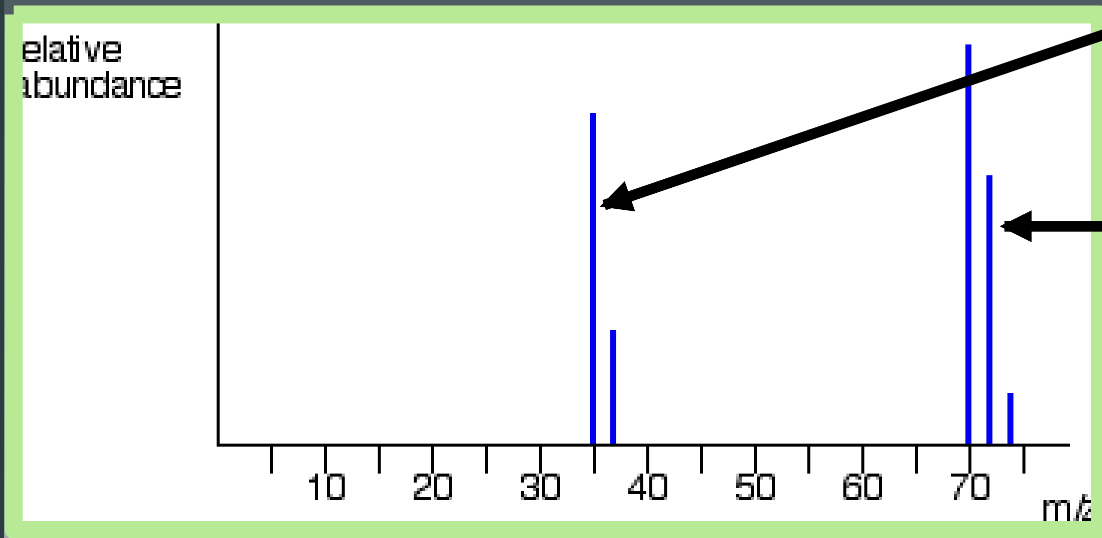
We can also determine isotopes and relative abundances of elements with mass spectrometry…



What element is this?

1. Look at the two largest peaks – the average atomic mass will be between these two peaks!
2. The height of each peak tells us the relative abundance of each isotope of the element!
3. What element has an average atomic mass between 10 and 12?

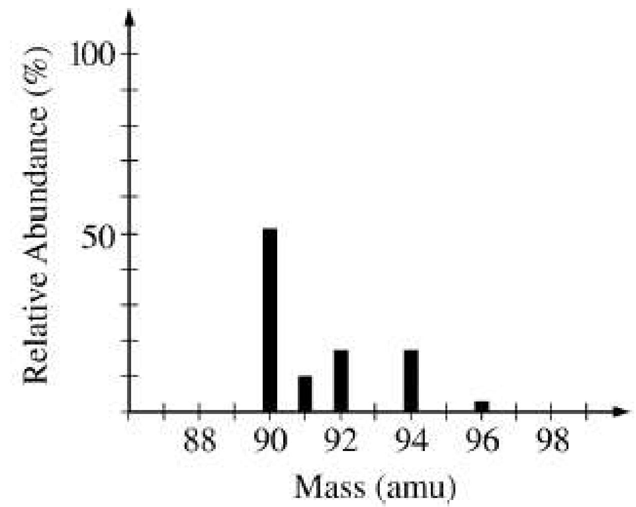
Problems with diatomic elements……



1. **What element is this?**
2. **Hint – why are there two areas that have peaks?**
3. **This element is diatomic!**
4. **The first set of peaks represents the diatomic atoms being separated into single atoms**
5. **The second set of peaks represents the diatomic elements left whole in the mass spectrometer**
6. **What element has an approximate atomic mass of 35, with the diatomic form having a mass of approximately 71?**

Sample AP problem……

- What element is this?
- How many isotopes does it have?
- What is the average atomic mass, and why?

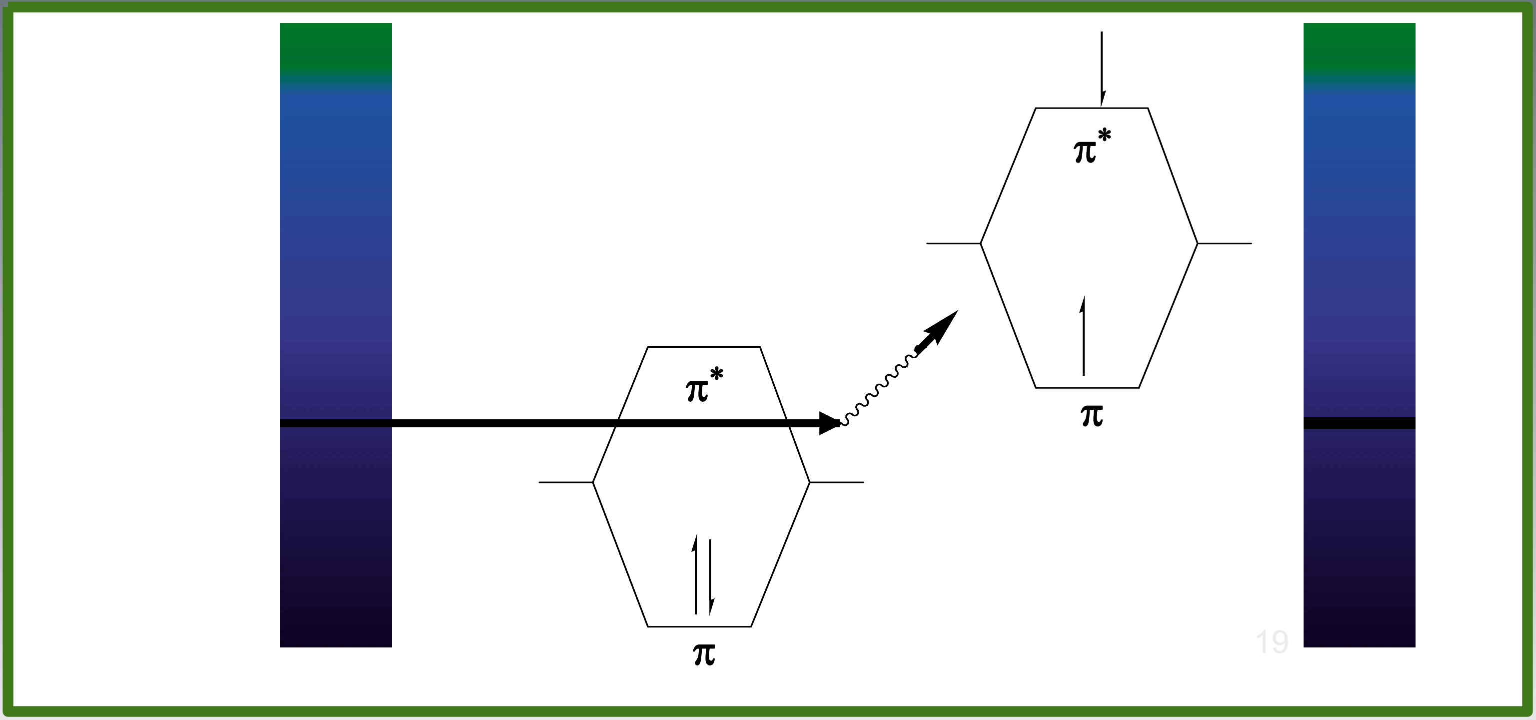


3. The mass spectrum of element X is presented in the diagram above. Based on the spectrum, which of the following can be concluded about element X?

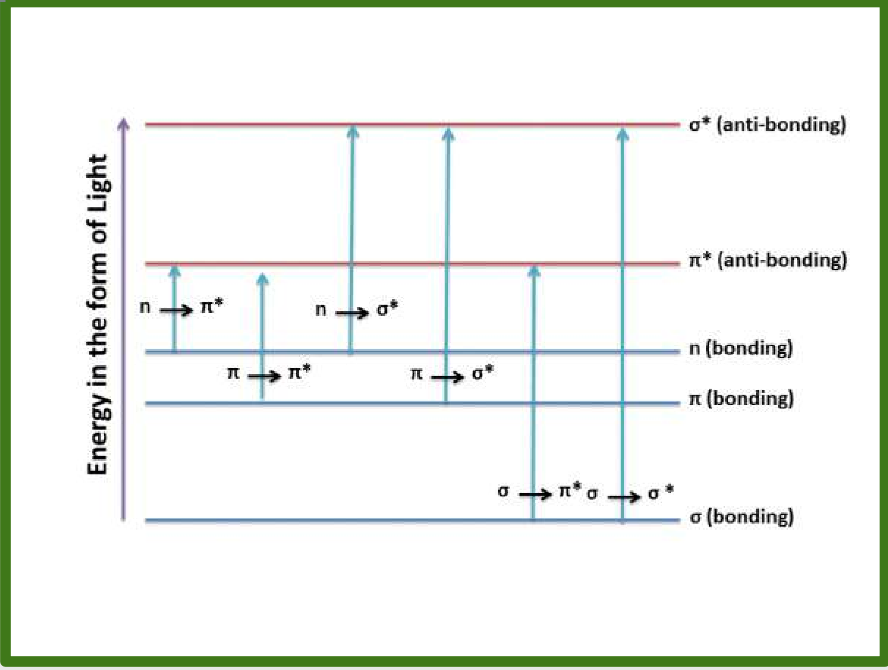
   (A) X is a transition metal, and each peak represents an oxidation state of the metal.
   (B) X contains five electron sublevels.
   (C) The atomic mass of X is 90.
   (D) The atomic mass of X is between 90 and 92.

UV Spectroscopy....

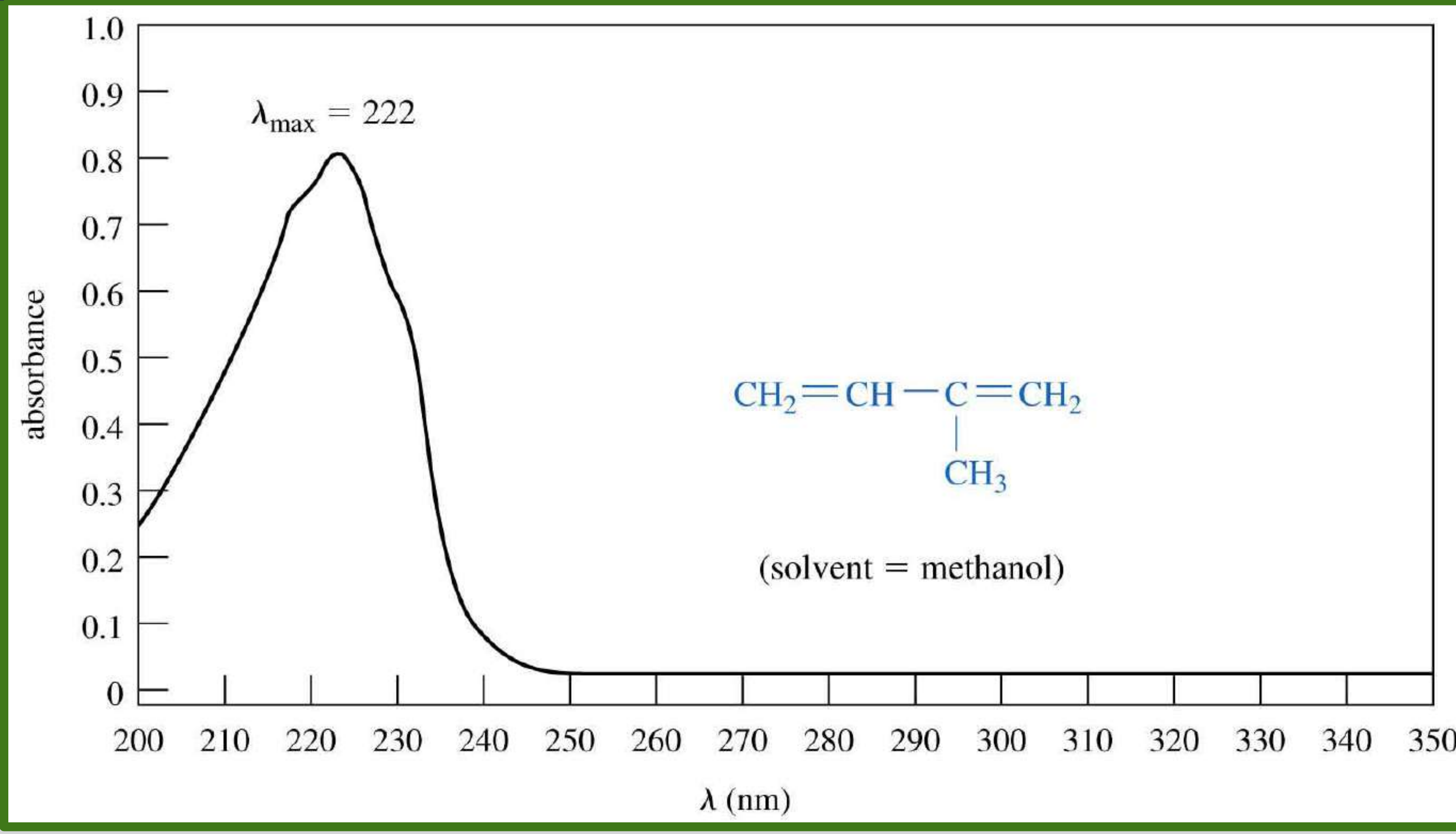
1. In UV spectroscopy, the sample is energized with broad spectrum UV energy
2. If a particular electronic transition matches the energy of a certain UV wave, the UV wave be absorbed by the electron and the electron will be excited
3. The remaining UV light passes through the sample and is observed
4. From this residual UV light a spectrum is obtained with "gaps" at these discrete energies – this is called an absorption spectrum
5. Molecular orbital theory is very important in understanding UV spectroscopy!



Transition	Example	Cause/Source	λ (ηm)
$\sigma \rightarrow \sigma^*$	hexane	alkanes	< 200
$\pi \rightarrow \pi^*$	C_2H_4, 1,4-pentadiene	unconjugated, unsaturated cpds.	<200
$\pi \rightarrow \pi^*$	1,3-pentadiene	conjugated systems	210 -250
$\pi \rightarrow \pi^*$	benzenes	double bonds in benzenoids	230 -280
$\pi \rightarrow \pi^*$	benzenes	double bonds in benzenoids	180 - 190
$\pi \rightarrow \pi^*$	benzenes	double bonds in benzenoids	~ 200
$n \rightarrow \sigma^*$	CH_3NH_2, CH_3OH, CCl_4	most heteroatoms in saturated cpds.	160 - 190
$n \rightarrow \pi^*$	acetone, methyl ethyl ketone	heteroatoms in unsaturated cpds.	> 250



UV Spectrum of Isoprene



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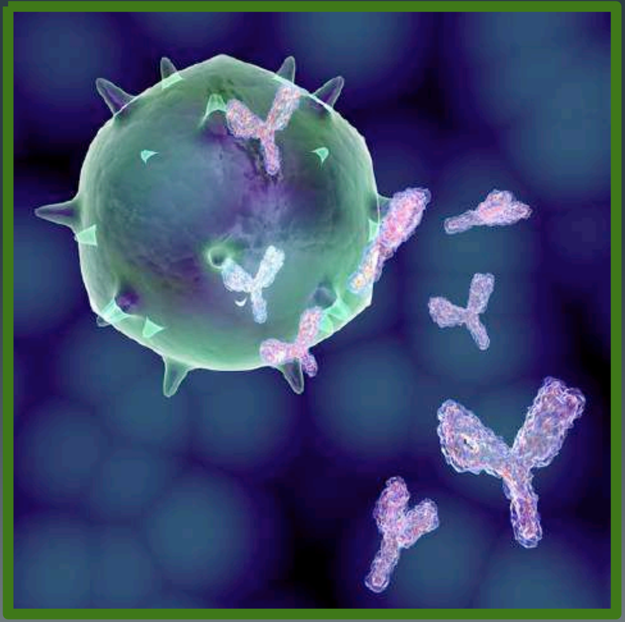
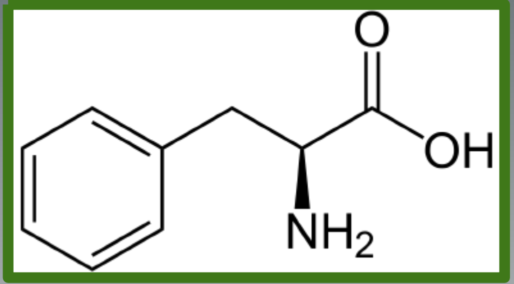
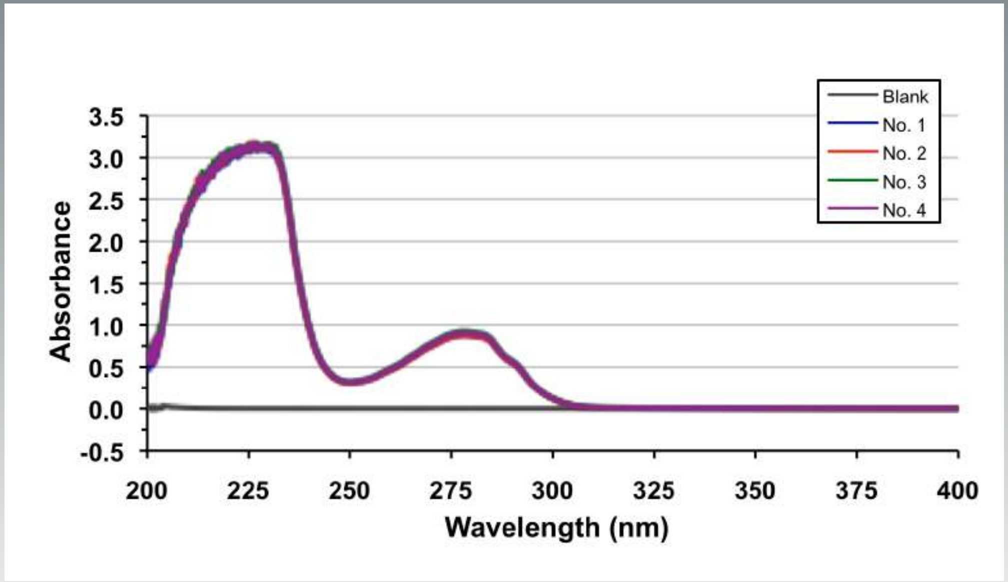
•Quantitative analysis using UV spectroscopy is used in biochemical labs to measure the concentration of proteins or enzymes in biological reactions
•Shown below is the concentration of an antibody in solution
•Antibodies are proteins or enzymes that identify and destroy foreign entities in the body
•Phenylalanine, tryptophan, tyrosine, and histidine are all amino acids with aromatic hydrocarbons (contains a benzene ring) – these absorb UV energy the best
•Proteins that possess these amino acids can be quantitatively measured with UV spectroscopy

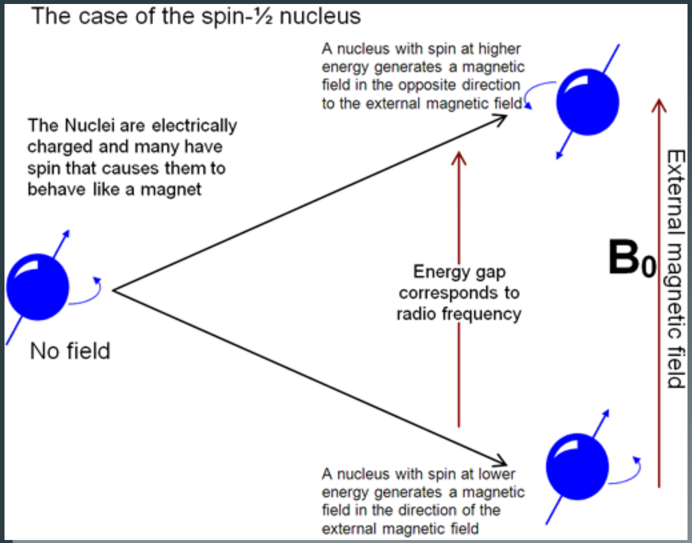






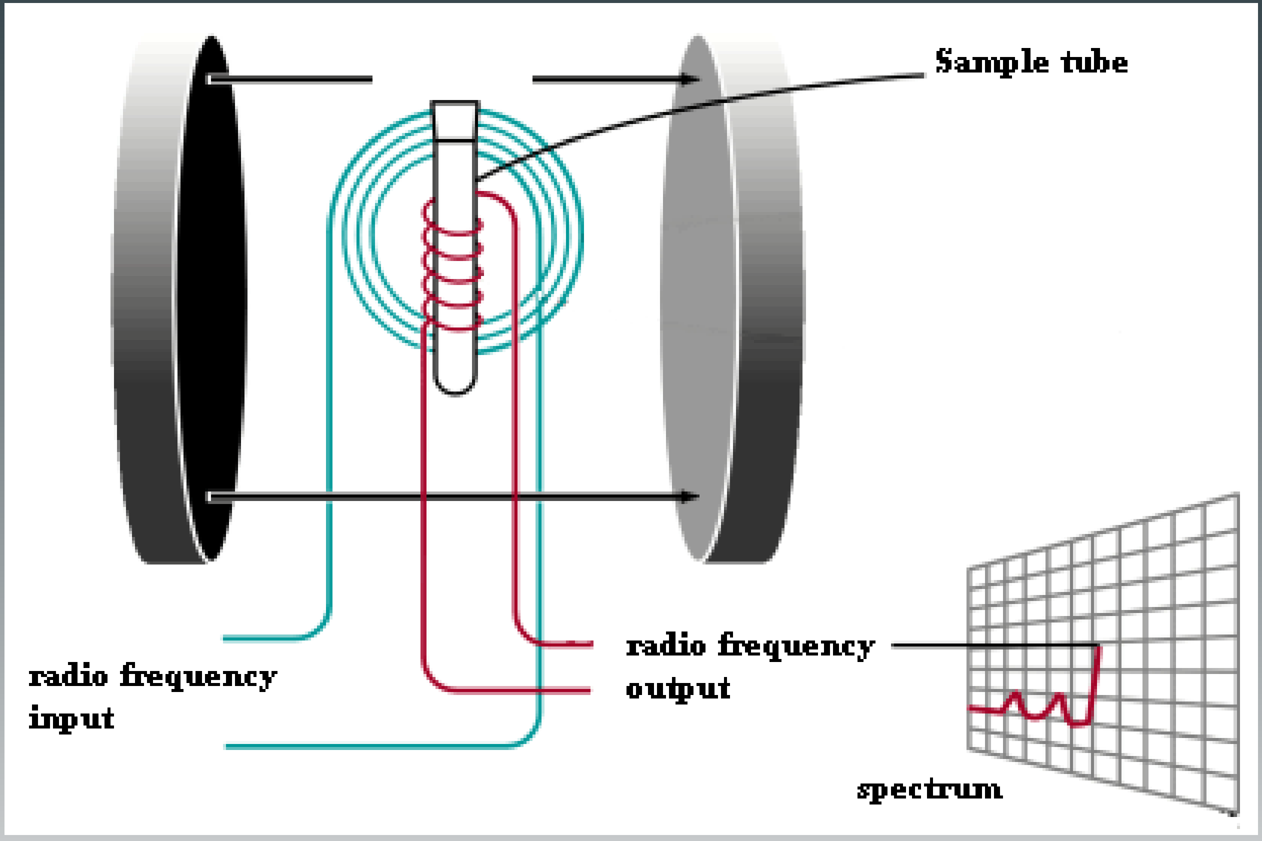
$A = \varepsilon \times l \times c$
A = absorbance
ε= molar absorptivity
C = concentration

Proton Nuclear Magnetic Resonance (1H-NMR)

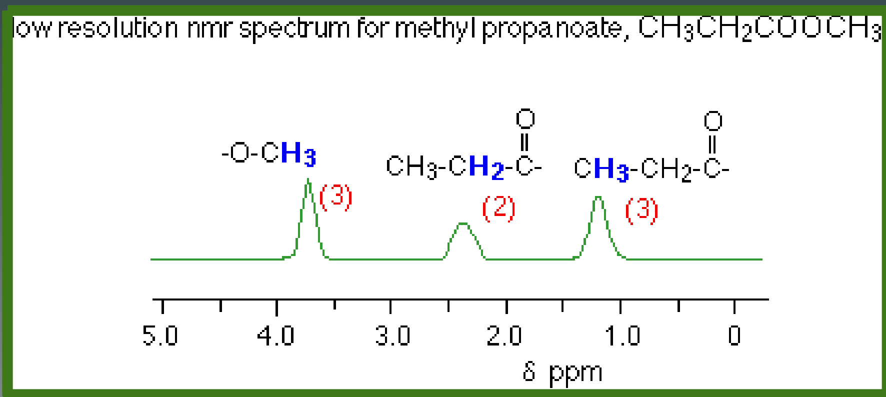


- Hydrogen nuclei have one proton
- These protons behave like little magnets and point either north or south
- An external magnetic field can align these protons either with the magnetic field or against it
- You can flip this proton back and forth with magnets with energies equal to that of radio waves (60-100 MHz)

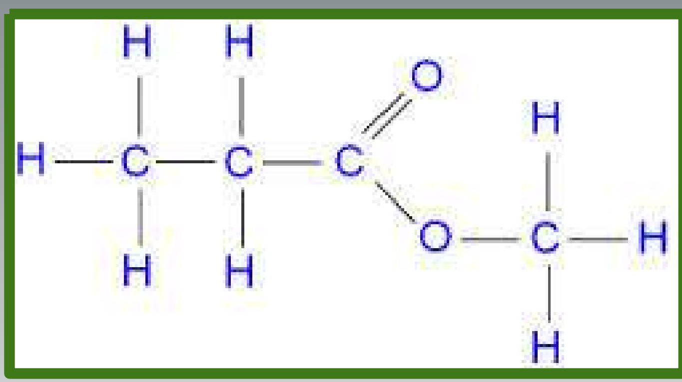
How an NMR works…..



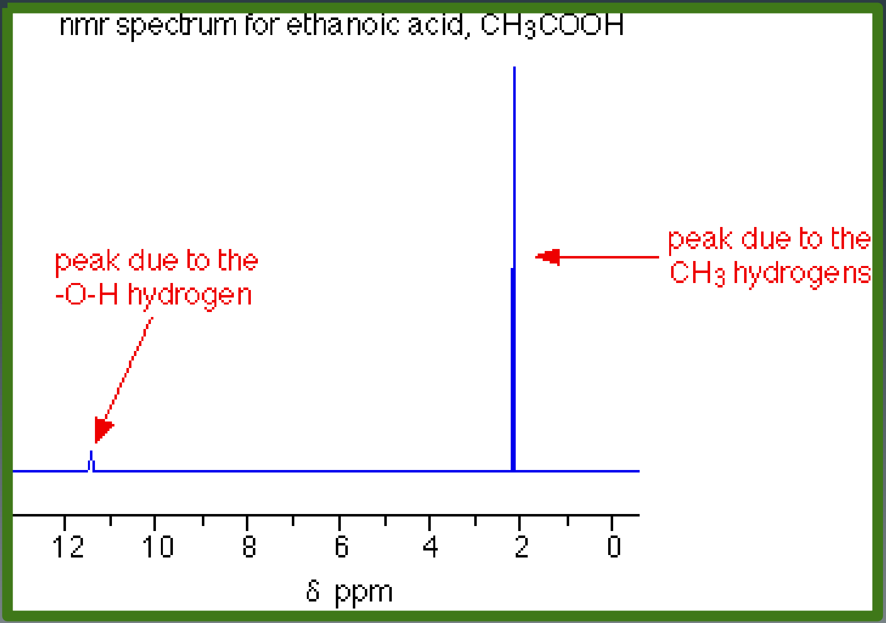
Low resolution NMR….



The position of the peaks tells you useful things about what groups the various hydrogen atoms are in. In any exam, you will be given a table of chemical shifts if you need them.



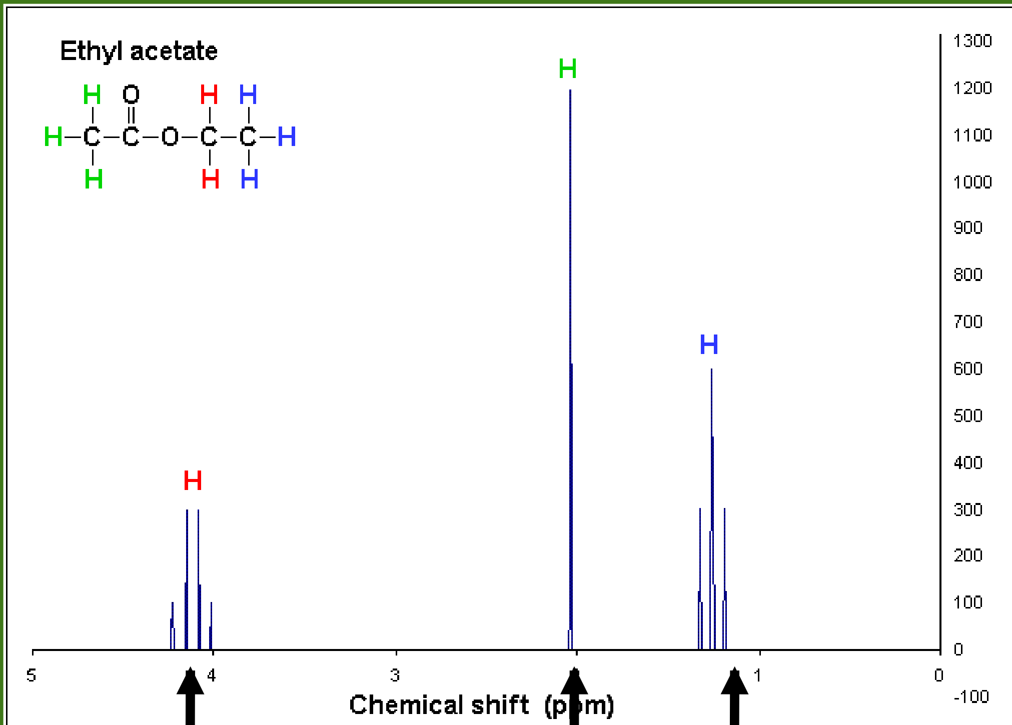
	chemical shift, δ
R-CH_3	0.7 - 1.6
-O-CH_3	3.3 - 4.3
R-CH_2-C(=O)-	2.0 - 2.9



Size of the peaks….

The sizes of the two peaks gives important information about the numbers of hydrogen atoms in each environment. It isn't the height of the peaks that matters, but the ratio of the areas under the peaks. If you could measure the areas under the peaks in the diagram above, you would find that they were in the ratio of 3 (for the larger peak) to 1 (for the smaller one). That shows a ratio of 3:1 in the number of hydrogen atoms in the two environments - which is exactly what you would expect for CH_3COOH.

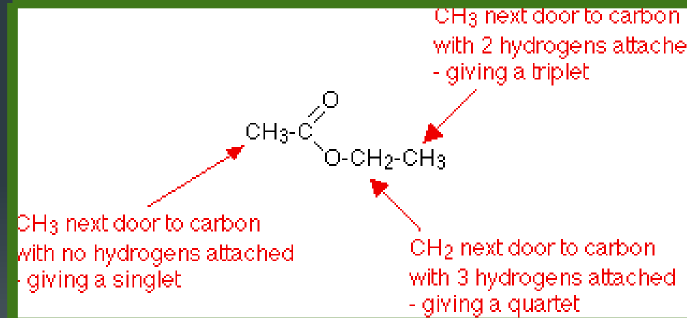
High resolution NMR….



quartet

singlet

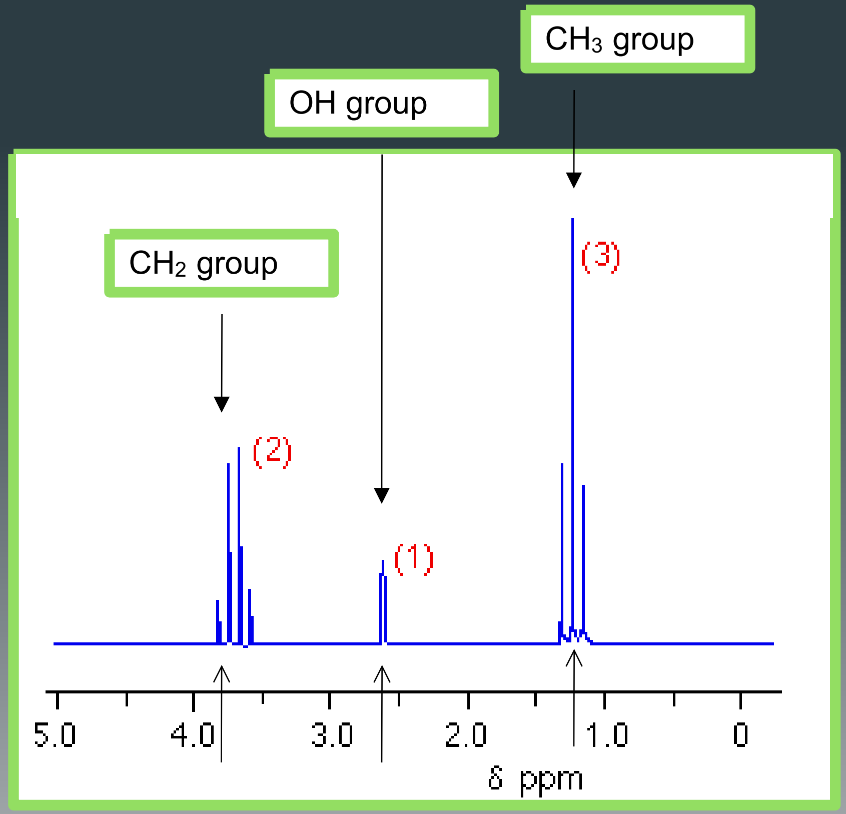
triplet



The n+1 rule:

- Nearby hydrogen atoms interfere with the magnetic field of hydrogen atoms
- This is called splitting
-The amount of splitting tells you about the number of hydrogens attached to the carbon atom or atoms next door to the one you are currently interested in.
- The number of sub-peaks in a cluster is one more than the number of hydrogens attached to the next door carbon(s).
- So - on the assumption that there is only one carbon atom with hydrogens on next door to the carbon we're interested in:
- singlet next door to carbon with no hydrogens attached
-doublet next door to a CH group
-triplet next door to a CH_2 group
-quartet next door to a CH_3 group

How do we identify functional groups….?



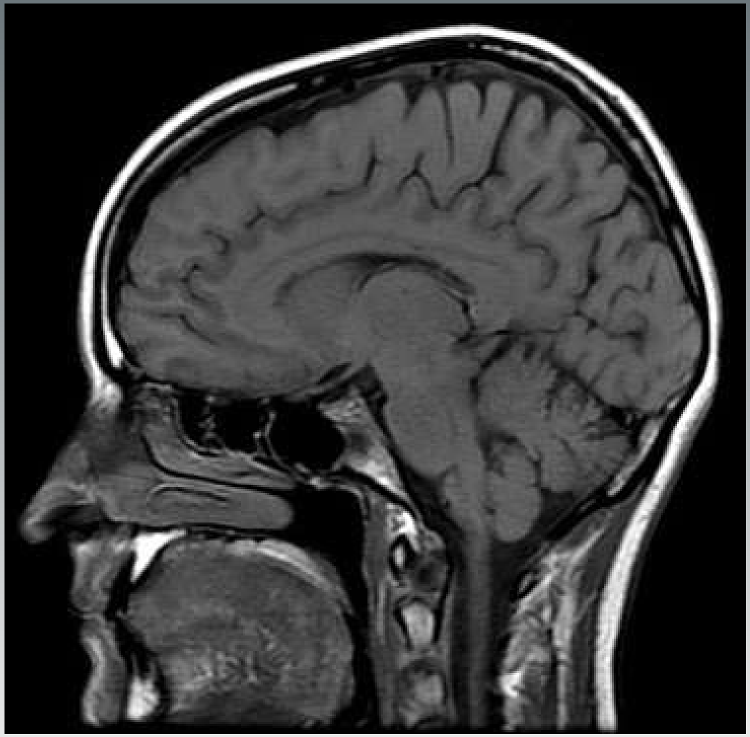
quartet

singlet

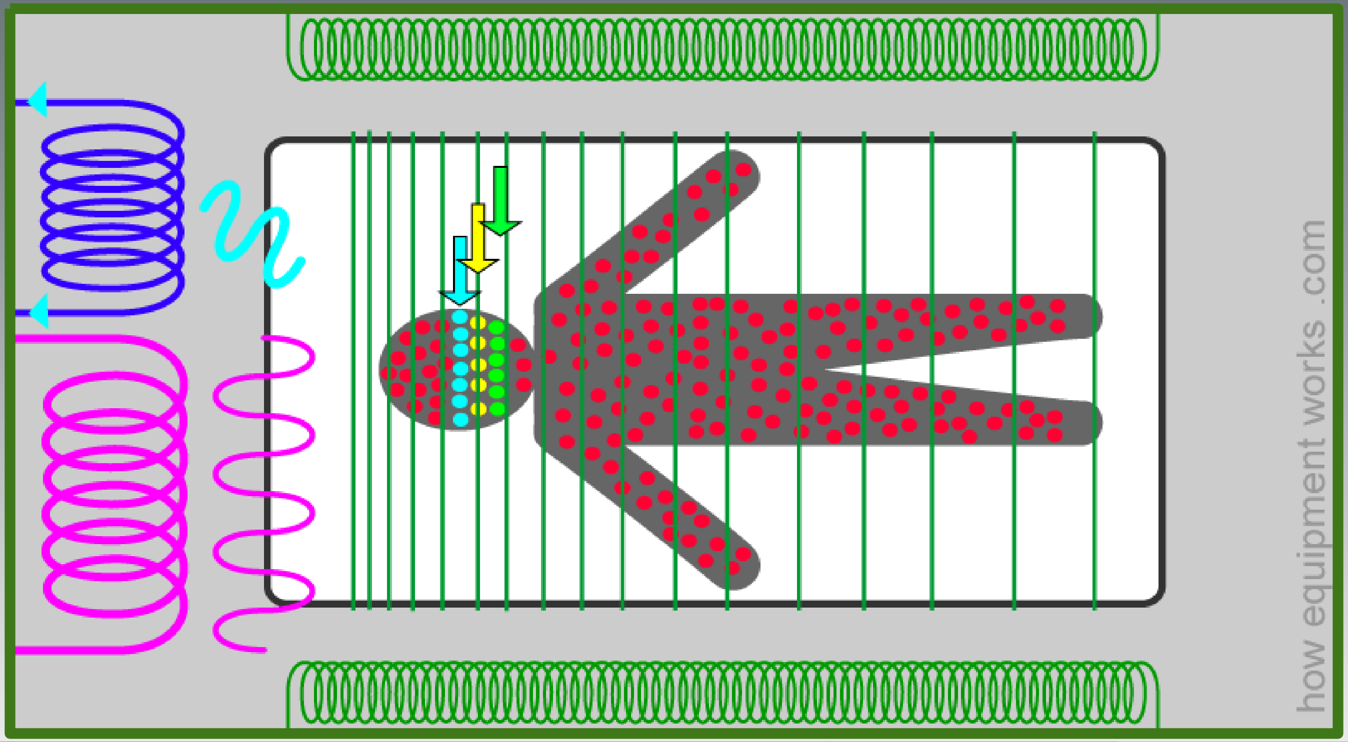
triplet

CH_3CH_2OH

An MRI machine......

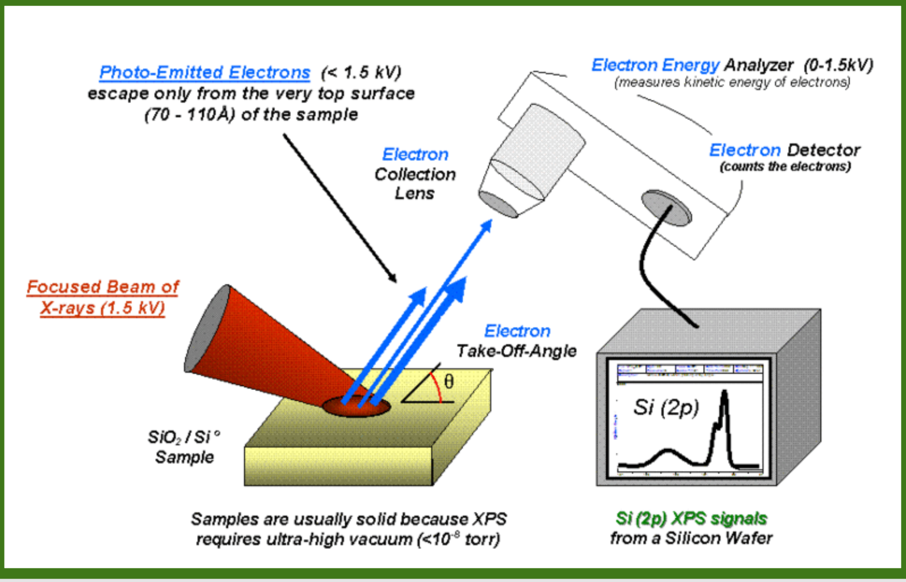


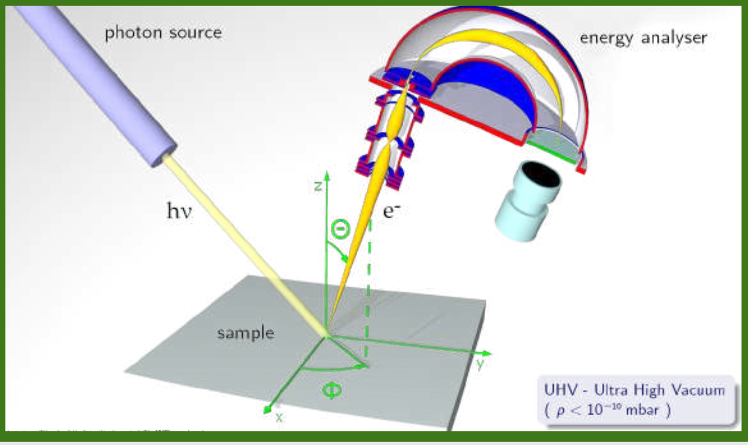
- An MRI machine is an NMR machine....they changed the name because people were getting freaked out when they heard the term “nuclear”.....
- Same principle – protons in the nucleus of hydrogen atoms (a main component of water, which the body is comprised of) are spun, and the energy that is given off is interpreted by a computer as an image!

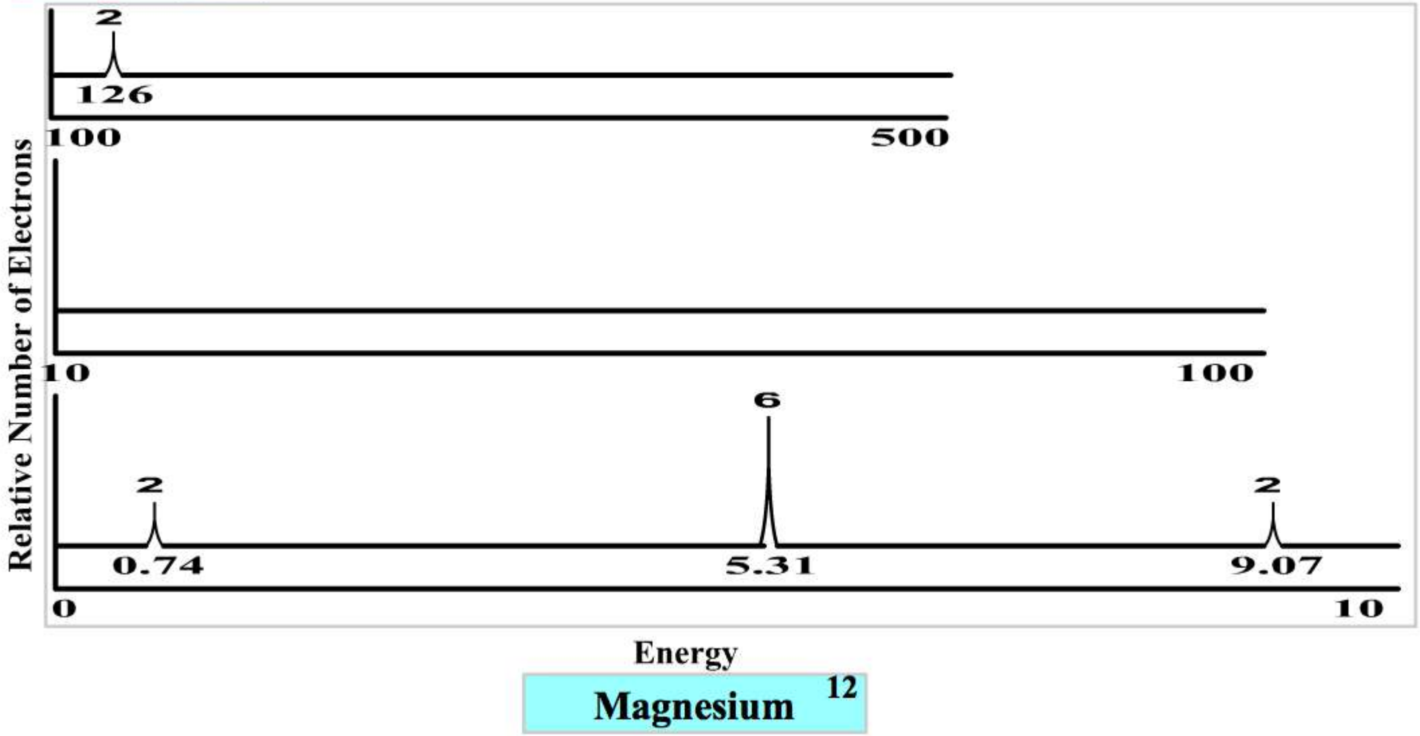


Photoelectron Spectroscopy……

- Photoelectron Spectroscopy determines the ionization energies of electrons in atoms or molecules by bombarding them with high energy waves and detecting the kinetic energy of the electron as it escapes from the surface
- This utilizes the photoelectric effect from Einstein – E=hv
- An electron must be hit with enough energy to remove it from the surface and give it kinetic energy
- $E_{light} = hv = E_{kinetic} + E_{binding}$



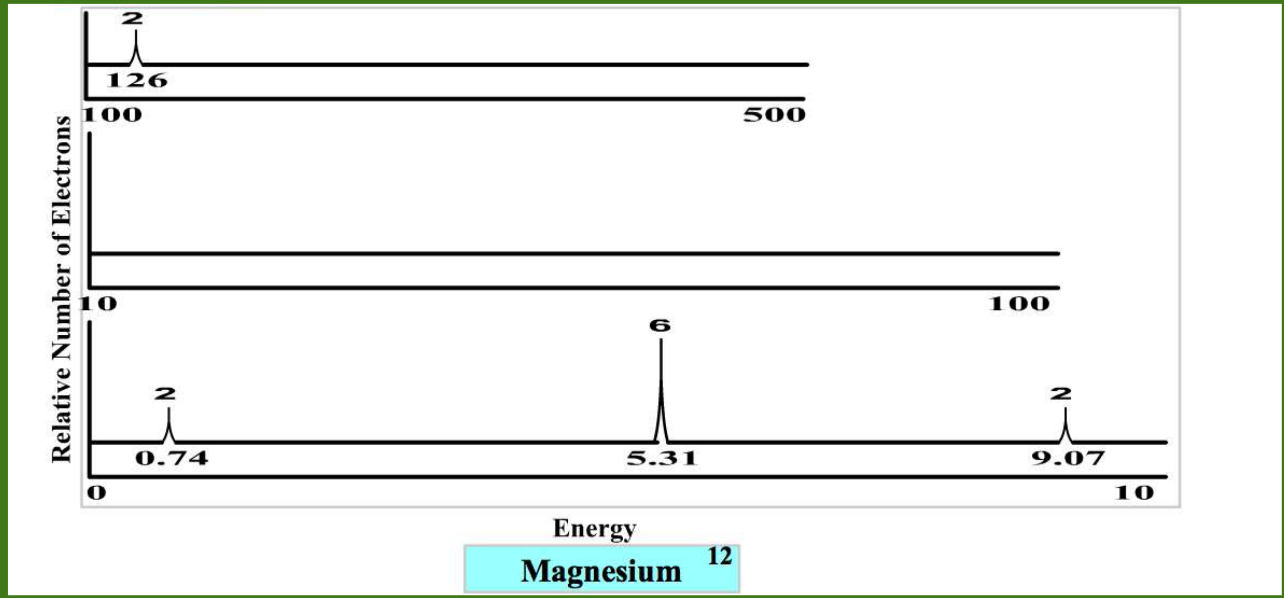




If the question flagged Mg as the element in question:

a. Which peak in the spectrum represents electrons that are closest to the nucleus?
b. What is the relevance of the relative height of the peaks at 5.31 eV and 9.07 eV?
c. Why is there such a large difference in energy between the peaks at 0.74, 5.31 and 9.07 eV, and the peak at 126 eV?

Sample AP problem….

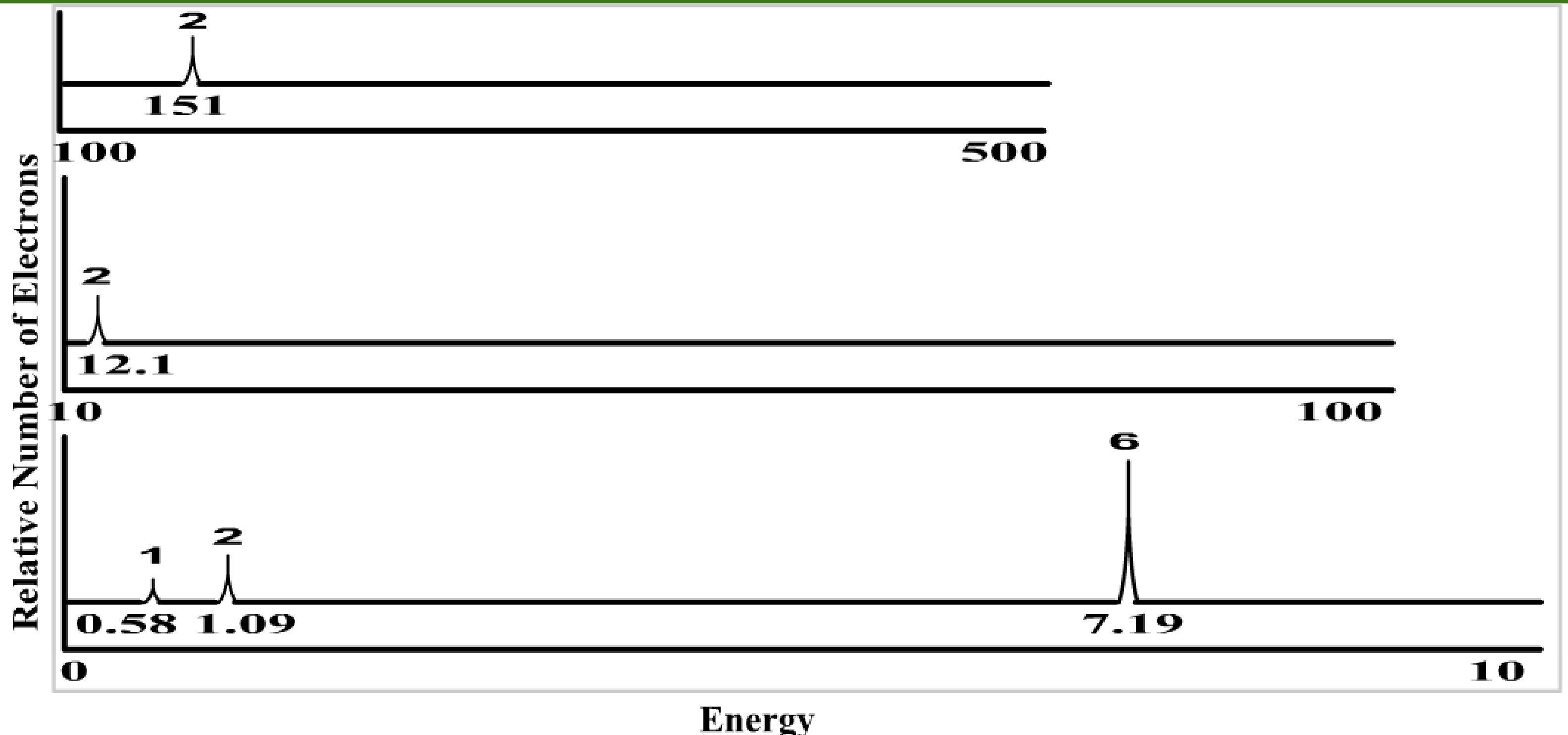


Sample AP problem….

The peak marked 126 eV represents the two electrons in the 1s sublevel – these electrons would take the most energy to remove from the atom, since they are closest to the nucleus!

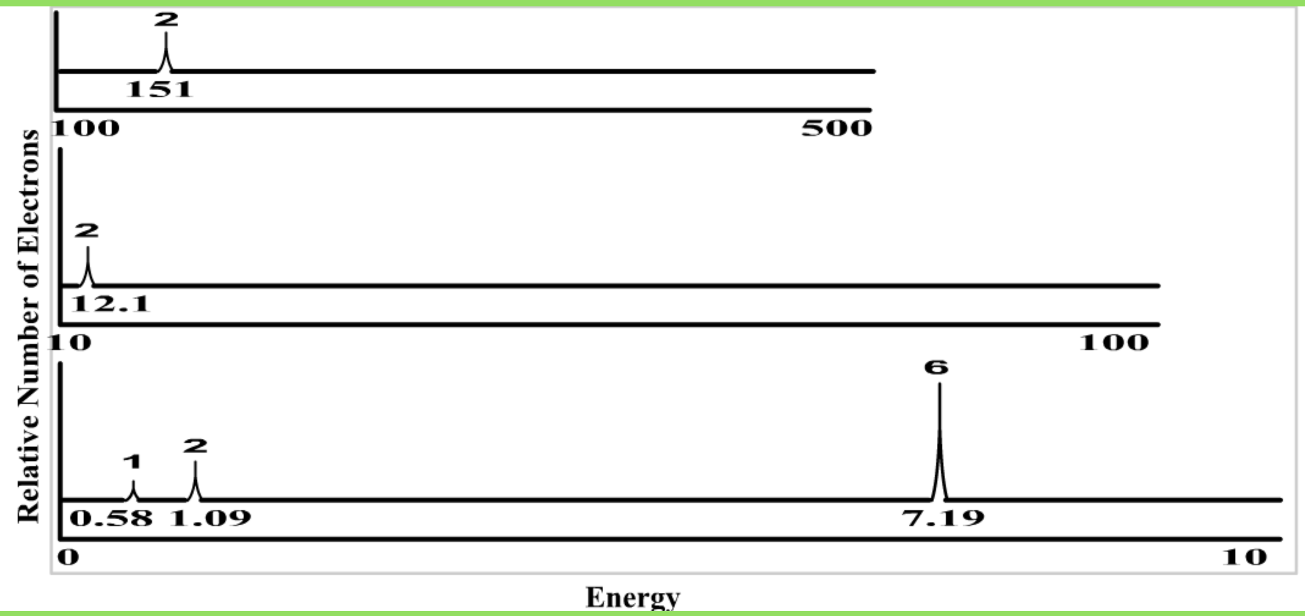
The height of the peaks represent the number of electrons that are being removed from that sublevel – the peak marked 5.31 eV represents the 2p sublevel electrons, and since the peak is three times the height of the electrons at 9.07 eV, and is marked 6, we know that there are 6 electrons being removed from the 2p sublevel. The peak at 9.07 eV represents the 2 electrons being removed from the 2s sublevel. It takes more energy to remove these electrons, because they are in a more stable sublevel, and are a bit closer to the nucleus.

When removing electrons from an atom, the atom becomes positively charged. This causes the atom to attract its remaining electrons with greater attractive or coulombic force. Once the valence electrons are removed (.74 eV peak – 3s electrons), and then the 2nd energy level electrons are removed (5.31 eV peak – 2p electrons, 9.07 eV – 2s electrons), the atom has a +10 charge. It takes an incredible amount of energy to remove the remaining 2 electrons. Additionally, those electrons are close to the nucleus, with no shielding at all. The 1s electrons take 126 eV of energy to be removed because of this.



a. Assuming that the PES data shows ALL of the electrons present in the atom, identify the element.
b. Still applying the assumption in a., which specific electrons are associated with the peak at 151 eV?
c. What does a relatively low value of energy tell you about the relative position of the electrons within any atom?

Sample AP problem….

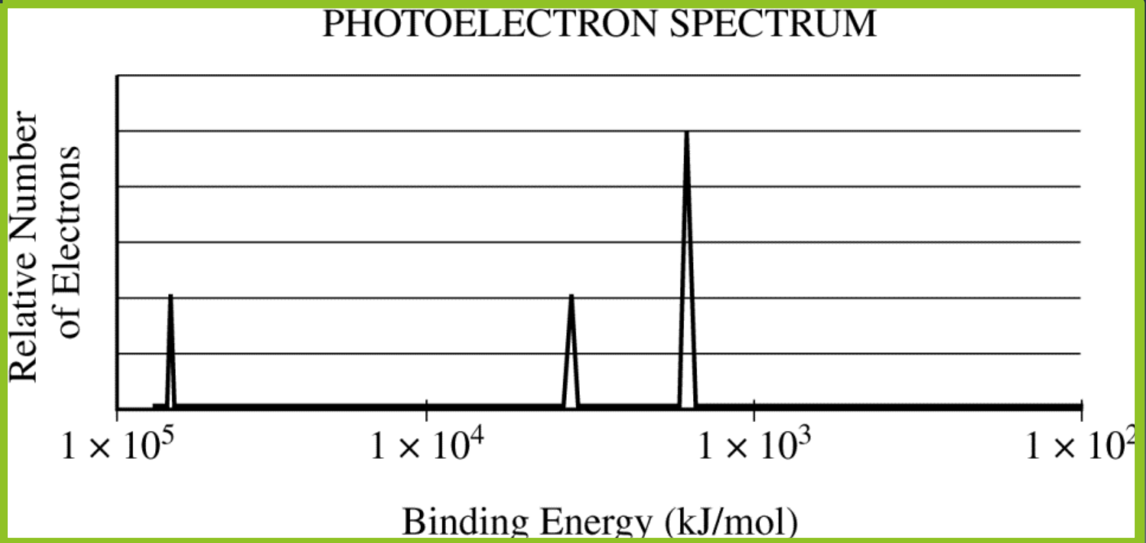


Sample AP problem….

This element is aluminum. If the relative peaks are examined (and assigned numbers, which this graph has already done), in total the peaks add to 13 total electrons.

The peak at 151 eV represents the electrons in an Al atom that require the largest amount of energy to remove. These would be the electrons with the least amount of shielding, or are closest to the nucleus, representing the 1s electrons.

The lower the relative energy value of a peak, the farther away from the nucleus the electrons are. With increased shielding, the electrons have a lower ionization energy, and therefore are easier to remove from the atom. The peaks at .58 eV and 1.09 eV respectively represent the 3 valence electrons of aluminum!



Sample AP problem….

Peak 1	Peak 2	Peak 3
6.72×10^4 kJ/mol	3.88×10^3 kJ/mol	1.68×10^3 kJ/mol

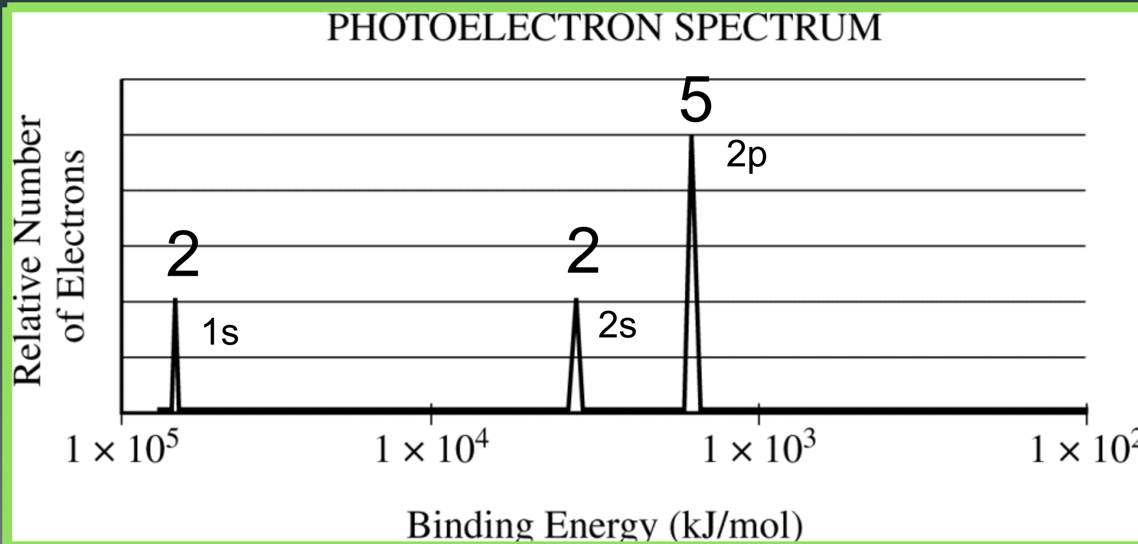
Answer these questions!

The complete photoelectron spectrum of an unknown element is shown above.

A student examines the spectrum and proposes that the second ionization energy of the element is 3.88×10^3 kJ/mol. To refute the proposed interpretation of the spectrum, identify the following:

(i) The subshell from which an electron is removed in the second ionization of an atom of the element

(ii) The subshell that corresponds to the second peak of the photoelectron spectrum above

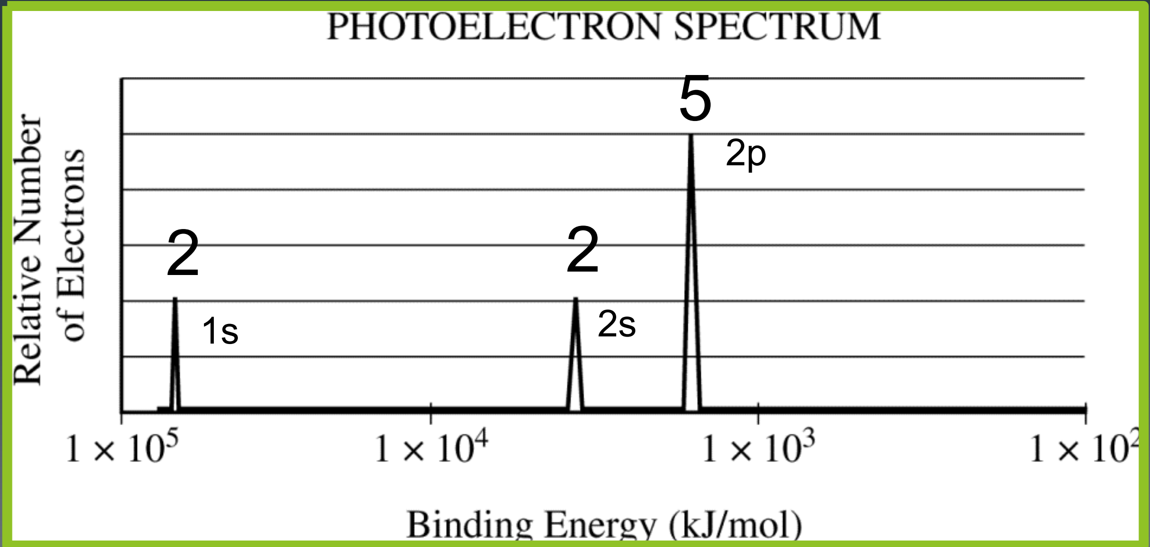


Sample AP problem….

Peak 1	Peak 2	Peak 3
6.72×10^4 kJ/mol	3.88×10^3 kJ/mol	1.68×10^3 kJ/mol

First, realize that the x axis is *backwards* – the energy goes from high to low! The relative height of each peak has been labeled – if asked, we could identify this element as fluorine.

The first peak shown represents the electrons that require the *most* energy to remove – the 1s electrons. The second peak represents the 2s electrons, which would require the second highest energy to remove. The last peak represents the 2p electrons, which would require the *least* energy to remove.



Sample AP problem….

Peak 1	Peak 2	Peak 3
6.72×10^4 kJ/mol	3.88×10^3 kJ/mol	1.68×10^3 kJ/mol

(i) 3.88×10^3 kJ/mol cannot be the second ionization energy. It is peak 2, which has been identified already as the 2s sublevel, which would not include the second electron removed from the atom – the 2p sublevel would contain that. Since the last peak represents the *least* amount of energy required to remove electrons, these electrons would be the first to leave the atom, corresponding to the valence electrons with the weakest attraction to the nucleus, or the most unstable electrons – which would represent the 2p electrons.

(ii) The second peak, as identified, represents the 2s electrons – which would not contain the second electron removed from the atom.

When to use each?

• IR is good for determining what functional groups are present in an organic molecule, but not how they are connected
• Mass spectrometry gives you an exact molecular mass, and is good for inorganic molecules. It can also determine all of the isotopes of an element present.
• NMR determines the number of hydrogens present on carbon atoms, and where they are present in a molecule – can be used in conjunction with mass spec and IR.
• UV spectroscopy can measure very accurately the concentration of organic molecules – specifically proteins – in solution .
• PES is used to determine the identity of an element based on its ionization energies, and can be used to determine various ionization energies of electrons in certain elements