Spectroscopy

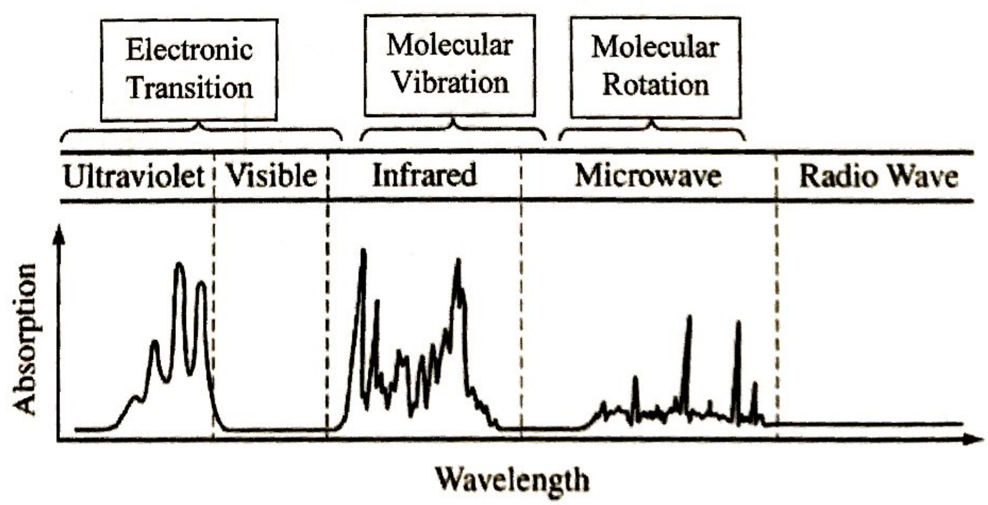
Spectroscopy: a study of the interaction between matter and electromagnetic radiation

- Can be used to determine the atoms, molecules, or structure of a given substance
- So many kinds!!

Types of Spectroscopy

Name of Spectroscopy	Type of Radiation Used	Relative energy	What does it do to the atom/molecule?	What does it tell us?
Photoelectron spectroscopy (PES)	X-ray	very high	Removes electrons (valence and core).	• Identity of element • How tightly electrons are held by the nucleus
UV-Visible spectroscopy (UV-Vis)	Ultraviolet (UV)	high	Excites electrons to jump between energy levels.	• Identity of element or molecule
UV-Visible spectroscopy (Colorimetry)	Visible	medium		• Identity of element or molecule • Concentration of solution
IR (vibrational) spectroscopy	Infrared (IR)	low	Changes vibrations within bonds.	• Types of atoms, bonds, and functional groups within a molecule
Microwave (rotational) spectroscopy	Microwave	very low	Changes the rotation of atoms in bonds.	• Location of hydrogen atoms within a molecule

ABSORPTION SPECTRUM



1. Based on the absorption spectrum shown above, rank the following transitions in order from least to greatest energy required: transition between vibrational states, between rotational states, and between electronic states.

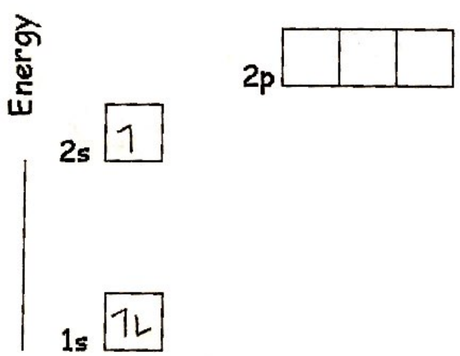
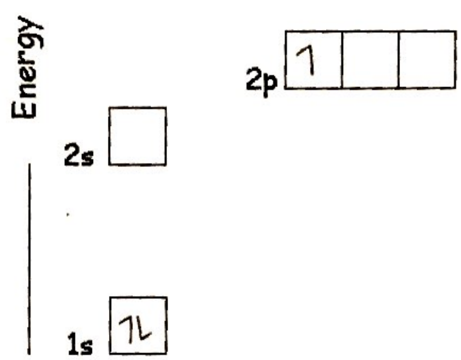
   rotations < vibrations < electronic
   (microwave) (IR) (visible + UV)

2. Which type of spectroscopy have we performed in class? When, and for what purpose?

   Colorimetry! (UV-Vis), to determine concentration of a colored sol'n

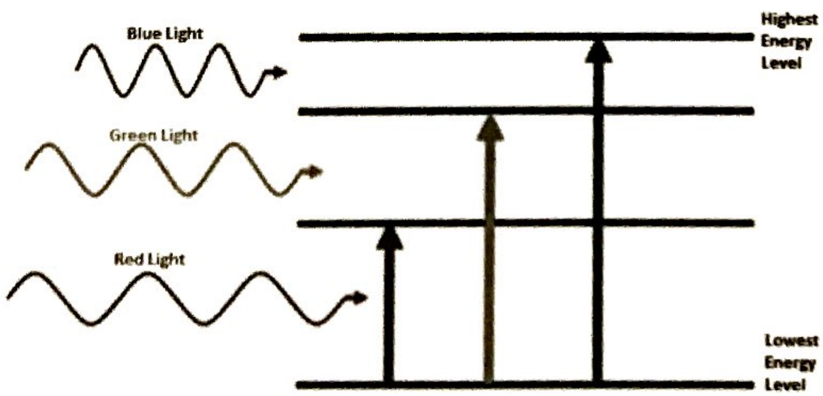
Atomic Absorption/Emission Spectra

Atoms exist in two states in relation to energy.

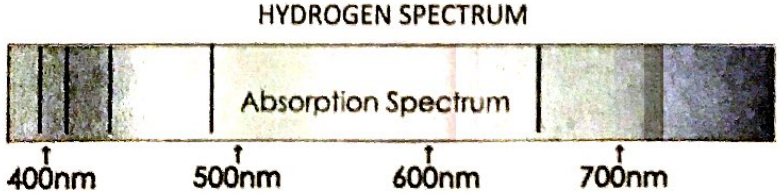
Ground State	Excited State – Added Energy!
Definition: electrons in their lowest energy state	Definition: **when energy is added,** an electron jumps up into a higher energy orbital
Example: lithium ground state $1s^2 2s^1$ 	Example: lithium excited state $1s^2 2p^1$ 

Atomic Absorption Spectra

- Used to determine the concentrations of elements present in a given sample
- Electrons can move to a **higher** energy orbital by absorbing a specific amount, or quantum, of energy.
- As an electron moves from its ground state to an excited state, the atom's potential energy increases.
- The absorption spectrum of an element is the relative intensity of each frequency of electromagnetic radiation absorbed by the atom as the atom's electrons jump **from the ground state to the excited state.**

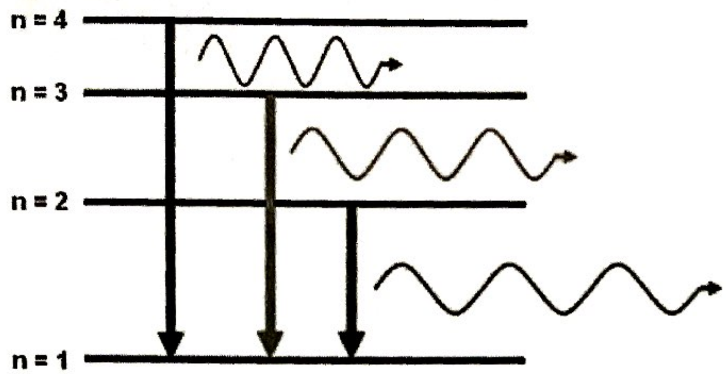


HYDROGEN SPECTRUM

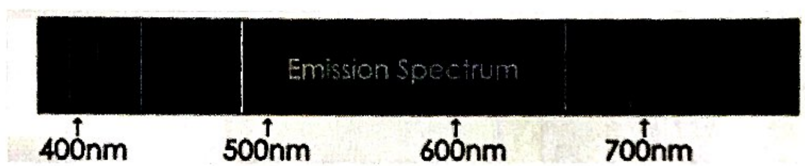


Atomic Emission Spectra (Bright-Line Spectra)

- Used to determine the identities of <u>unknown</u> present in a given sample (emit)
- When electrons fall from an **excited** state back to **ground** state, they <u>release</u> a specific amount, or quantum, of energy.
- The <u>emission</u> spectrum of an element is the relative intensity of each frequency of electromagnetic radiation emitted (released) by the atom as the atom's electrons return from the excited state to the ground state.

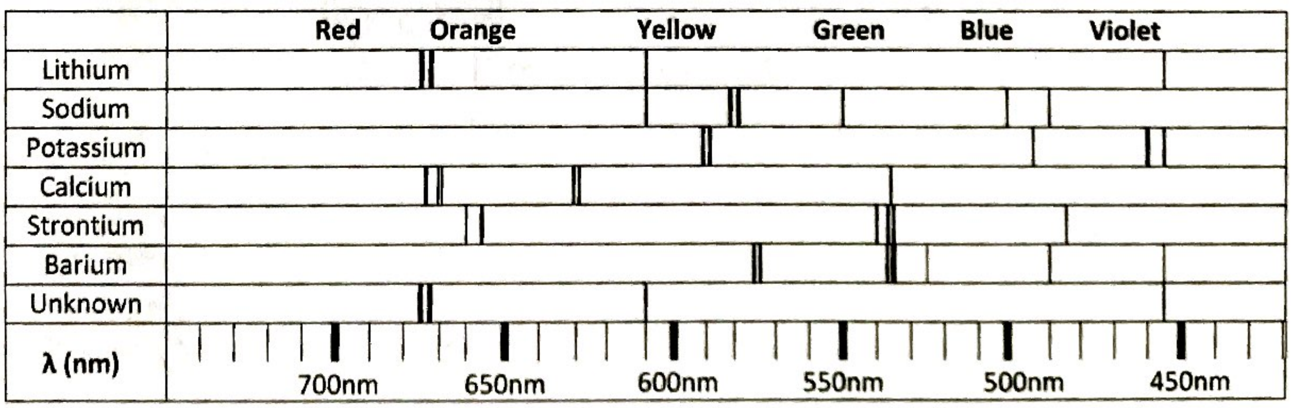


HYDROGEN SPECTRUM



Let's Practice!

1. Using data from the emission spectra below, what is the most likely source of the unknown?



Lithium!

2. Which of the following hydrogen electron transitions will result in the absorption of light with the lowest energy?

   a. n = 2 to n = 3 (b.) n = 3 to n = 4 c. n = 3 to n = 2 d. n = 4 to n = 3

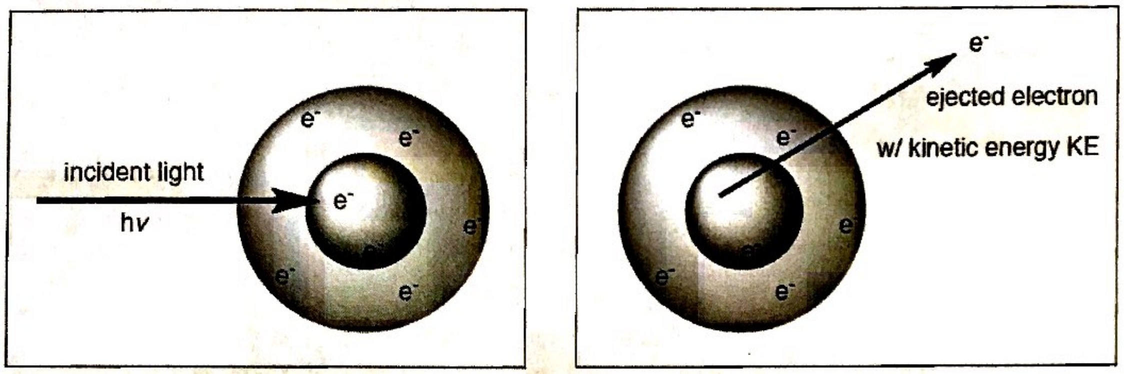
3. Which is an electron configuration of a fluorine atom in the excited state?

   a. $1s^2 2s^2 2p^4$ (b.) $1s^2 2s^2 2p^4 3s^1$ c. $1s^2 2s^2 2p^5$ d. $1s^2 2s^2 2p^5 3s^1$

Photoelectron Spectroscopy (PES)

Photoelectron Spectroscopy (PES): a technique to determine the ionization (or binding) energy of EVERY electron in an atom

- Ionization energy (for PES, more commonly referred to as the **binding energy**): the energy required to remove (ionize) an electron from an atom
- For PES, the binding energy is commonly measured in kJ/mol or MJ/mol.
- Binding energy is plotted on the horizontal axis, with energy decreasing (!!) from left to right (although sometimes this is flipped, so always check)

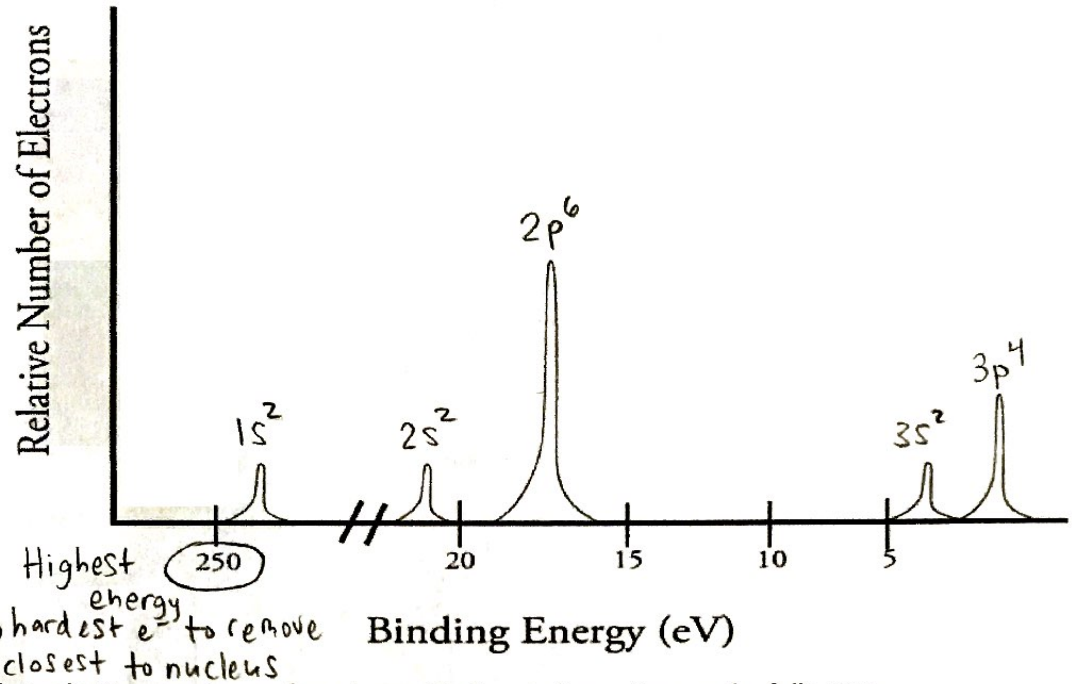


Incoming Radiant Energy = Binding Energy + kinetic energy (of ejected electron)

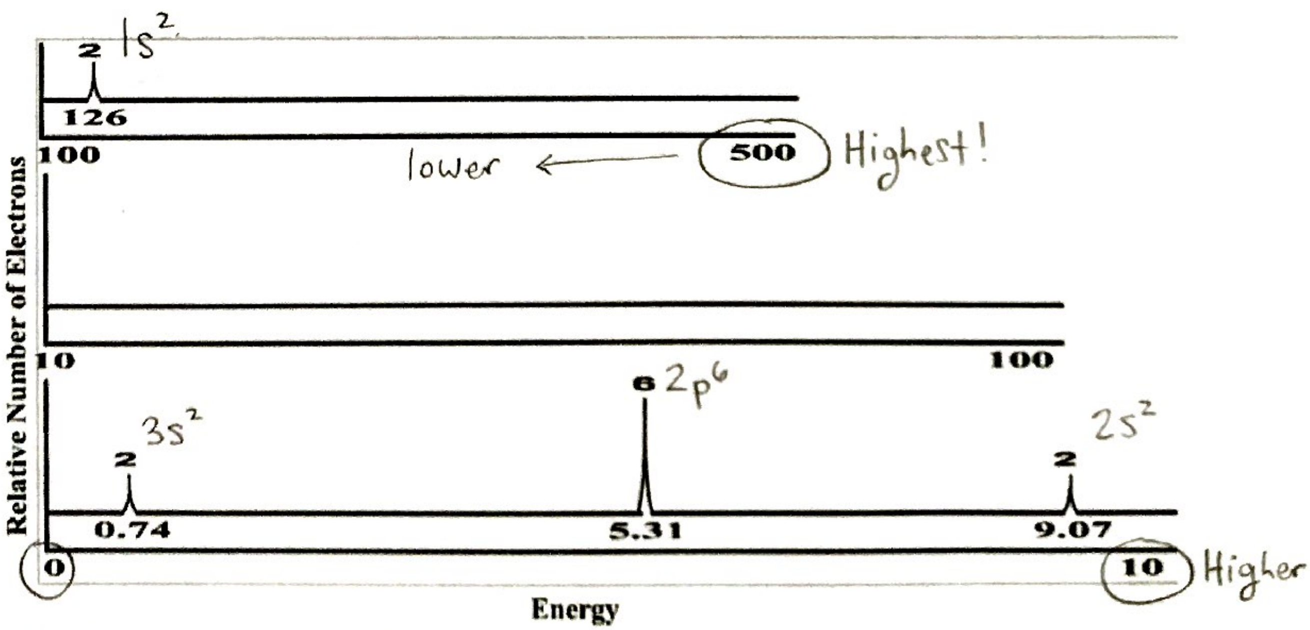
Ionization energy

How to Interpret PES Spectra

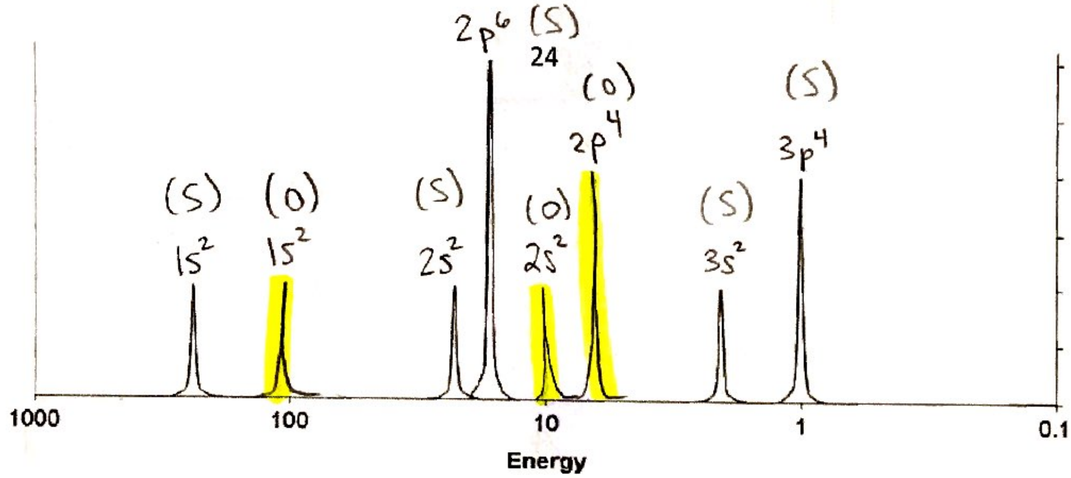
- Peak height corresponds to the relative # of electrons in each sublevel of an atom
- Peak location corresponds to the relative amount of energy required to remove each electron
    - Higher energies = sublevels found closer to the nucleus (1s, 2s, etc)
    - Lower ~~Higher~~ energies = sublevels found farther from the nucleus
- When comparing PES from different atoms:
    - As the number of protons in the nucleus increases (↑), the binding energy will ↑ for electrons in comprable sublevels
    - As the number of e⁻ in a specific sublevel increases (↑), the peak height will ↑ for electrons in comprable sublevels



1. The photoelectron spectrum of an element is shown above. Answer the following:
   a. Label the peaks with their corresponding orbital sublevel AND the number of electrons found.
   b. Identify the element represented by the photoelectron spectrum. Sulfur
   c. Which electrons would be the first to be removed? 3p e^-
   d. Which electrons would be the last electrons to be removed? 1s e^-



2. For the spectrum shown above,
   a. The element is Mg.
   b. It has 2 valence electrons.
   c. Its noble gas configuration is: [Ne]$3s^2$



3. Above is the PES spectrum of sulfur.

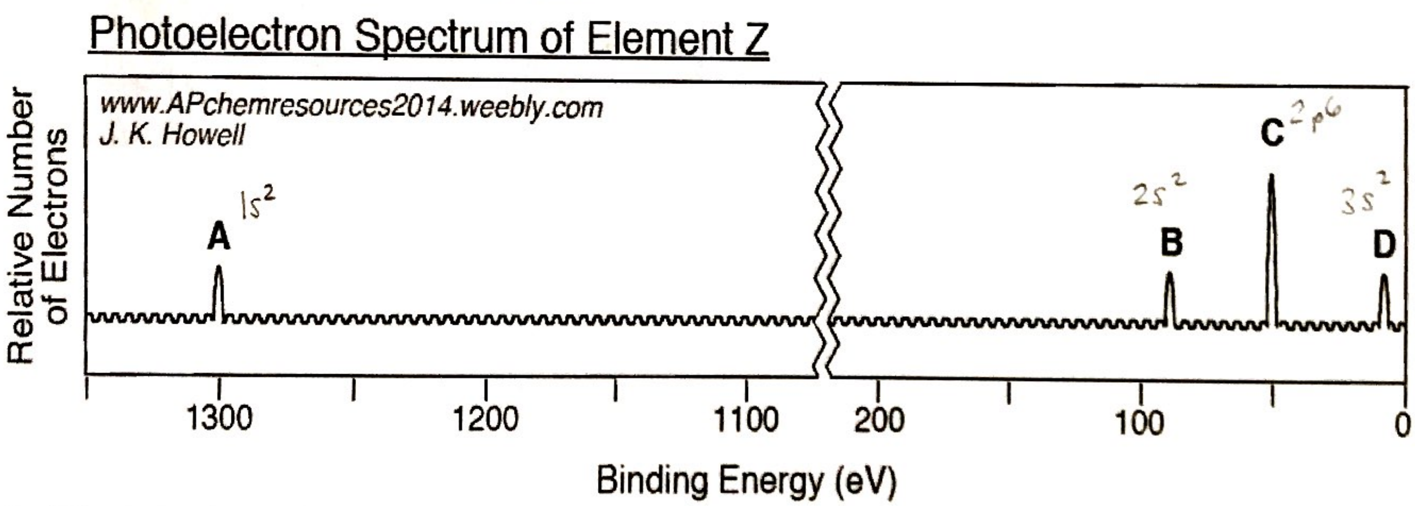
   a. Label each peak in the spectrum to show which subshell it represents, and how many electrons are in it.

   b. On the spectrum, sketch in the relative locations and correct peak heights for the spectrum of oxygen, and label each with the corresponding orbital sublevel and the number of electrons found.

   c. Does it require more or less energy to remove a 2p electron from oxygen compared to a 2p electron from sulfur? Justify in terms of Coulomb's Law.

Less energy: although the e⁻ are in the same main energy in both atoms, S has more p⁺ than O (16 vs 8, respectively), + Coulomb's law states that the energy of attraction is directly proportional to the magnitude of the charges. Less p⁺ = less charge = less attraction to e⁻ = less energy required to remove an e⁻ from the nucleus.

Independent Practice



4. What is the identity of element Z?

   a. Boron b. Carbon c. Neon (d.) Magnesium

5. Label the identity of each peak with principal quantum number, n (energy level), subshell (s, p, d, or f) and a superscript representing the number of electrons found in the subshell.

6. If the PES spectrum above had actually represented the element sodium, what would be different? List at least two differences you would expect to see:

- lower binding energies (Mg = 12 p⁺, Na = 11 p⁺)
- 3s peak ½ height (only 1 e⁻ instead of 2)