PHOTOELECTRON SPECTROSCOPY

Background Information:

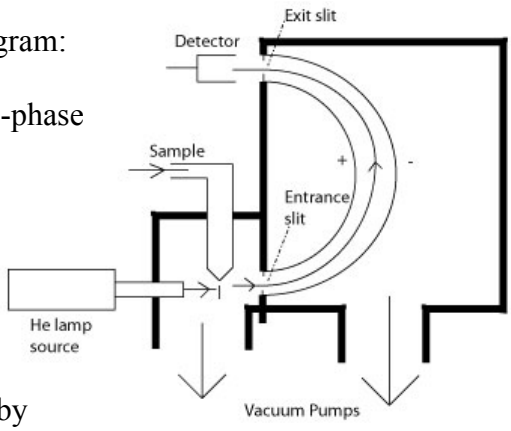
In photoelectron spectroscopy (PES), one can determine the identity of a substance by measuring the amount of energy needed to remove electrons from the substance's component electrons. For the purposes of AP Chemistry, we will only be considering the atoms of one element at a time.

If photons of great enough energy are used, ANY electron in the atom is vulnerable to being ionized, not just the "least tightly bound" ones. A PES "spectrum" will end up showing the **ionization energies of every electron** in a given atom, as well as the **relative abundances of electrons with a given IE**.

The "trick" is how to determine those ionization energies.

Well, if the Energy of the photon (E_{photon}) is known, all we need to do is to determine the kinetic energy of a given, ejected electron ($KE_{electron}$) . The **difference** between those two energies MUST be the energy needed to "dislodge" the electron from it's nucleus. $IE_{electron} = E_{photon} - KE_{electron}$

This is all done in a device like that represented in the following diagram:



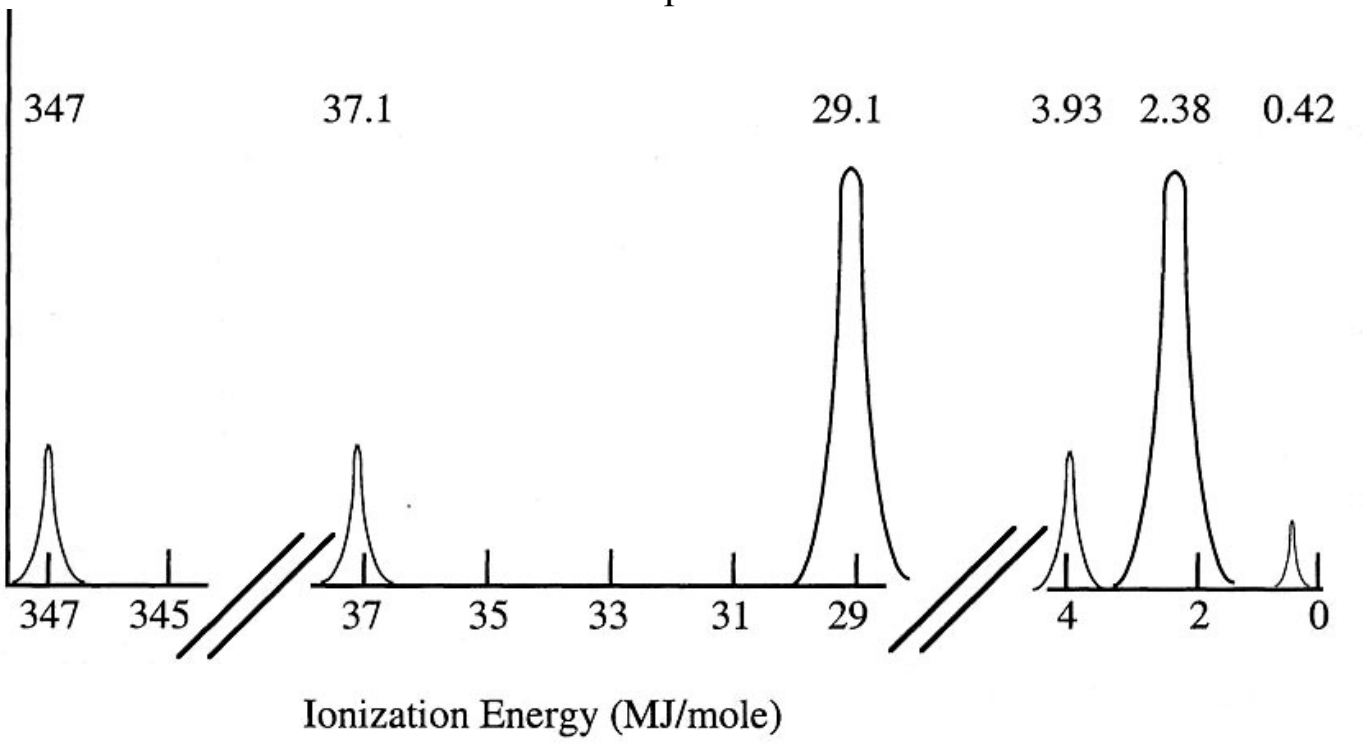
The helium lamp is the source of photons of a **known energy**. A gas-phase atom comes into the path of a photon, and an "unlucky" electron is hit and absorbs all of the energy from the photon. That electron is ejected from the atom (because it has been given enough energy to escape the "pull" of its nucleus), is deflected by an electromagnet, and hits a detector that not only "**counts**" that electron, but also **determines the kinetic energy** of that electron based on how hard it hits the detector. (That ionized atom, by the way, has been whisked off by the vacuum pump, so it can't have another one of its electrons kicked off. ***This is important***, as the "beauty" of PES is that each electron detected has been ejected from a "regular", neutral atom… not an atom that has been fundamentally changed by already having had an electron or seventeen removed!)

PES Spectra

The photoelectron spectrum is a plot of the relative number of electrons emitted versus their ionization energy. In the diagram below, the "X" axis is labeled high to low energies so that you think about the XY intersect as being the nucleus. Since all the orbitals of a given subshell are "degenerate" (equal energy), then the ionization energy of each electron within a given subshell is the same… MEANING… **that each peak observed on the spectrum is that of a single subshell** (2s, 3p, etc.). And since the y axis represents relative numbers of electrons, the peak height (relative to other peak heights) indicates the number of electrons in that subshell. In other words… PES is conclusive, experimental confirmation of the orbital "filling" order for electron configurations.

Interpretations from the data:

Photoelectron Spectra for **Potassium**



1. Place "relative intensity" values on the y axis in the tables above.

2. Label each peak on the graphs above with the subshell each represents (1s, etc).

3. Which electron will be removed from a neutral atom of potassium to form K^+? _____
Explain, using the information provided by the above spectrum:

4. Superimpose your best estimate of what the PES spectrum of calcium would be on top of potassium's spectrum above. (Don't forget to take into account that not only does calcium have one more electron than potassium… it also has one more PROTON.)

5. The next question contains the **actual** ionization values for Calcium. Compare them to the values that you assigned them in the last question. How did you do? Did you at least understand that all of calcium's values should be shifted LEFT of potassium's values? (These questions are rhetorical. I will be giving you a chance to explain why these values are shifted left in a later question.)

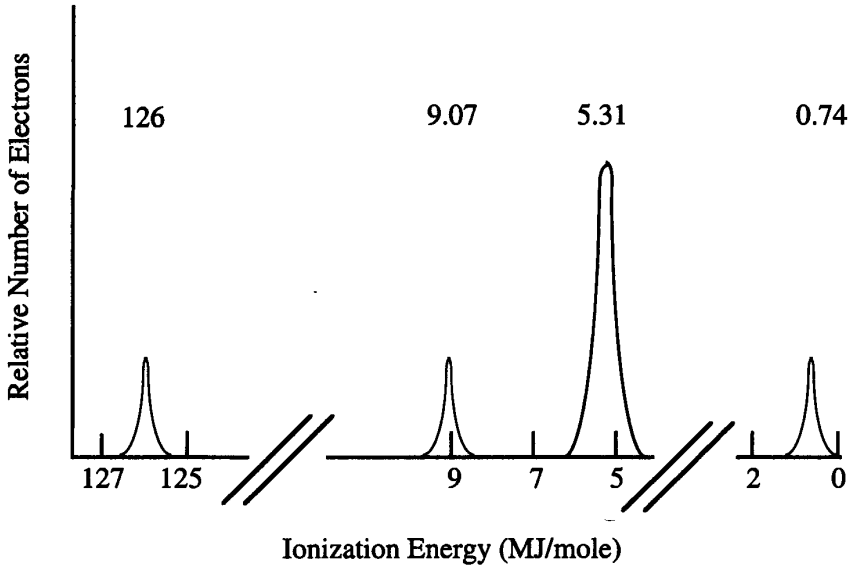
6. There are three basic "trends" that can be gleaned from the table below. What are they?

Table 1. Ionization energies (MJ/mole) for selected elements.

Element	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*
K	347	37.1	29.1	3.93	2.38		0.42
Ca	390	42.7	34.0	4.65	2.90		0.59
Sc	433	48.5	39.2	5.44	3.24	0.77	0.63

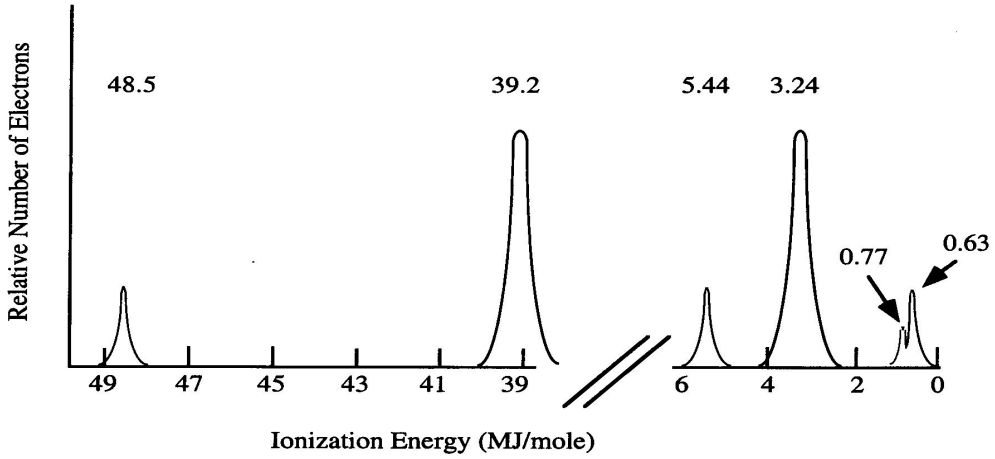
7. **Why** do you think the ionization energy for an electron in the 4s orbital in calcium greater than the ionization energy of an electron in the 4s orbital in potassium?

8. What element could have the following spectrum? _____



9. Examine the graph below. (It is IMPORTANT to read the note that is right above the graph!)

Figure 2. Simulated photoelectron spectrum of scandium. The 1s peak occurs at 433 MJ/mole and is not shown in this spectrum.



a) Which subshell is represented by the 0.77 peak?_____

b) Which subshell is represented by the 0.63 peak? _____

c) How **sure** are you about your answers to "a" and "b"? Did you write the electron configuration for scandium and make sure that your answers correspond to what is known about scandium's electronic structure?

d) How can this graph be used as **proof** that the 4s subshell "fills" before the 3d subshell?

e) Scandium loses two electrons when forming Sc^{2+}. Which electrons are most likely to be removed? Justify your answer:

10. Sketch a spectrum of **bromine** (label the "Y" axis quantitatively but not the "X")

PES questions from Russ Maurer

1. Below is the PES of sulfur, and a table of successive ionization energies. The energy scale for the PES is in MJ/mol (1 MJ = 1000 kJ). There is exactly one peak on this graph whose energy corresponds to an ionization energy in table 7.2. What is it? Why doesn't anything else match up?

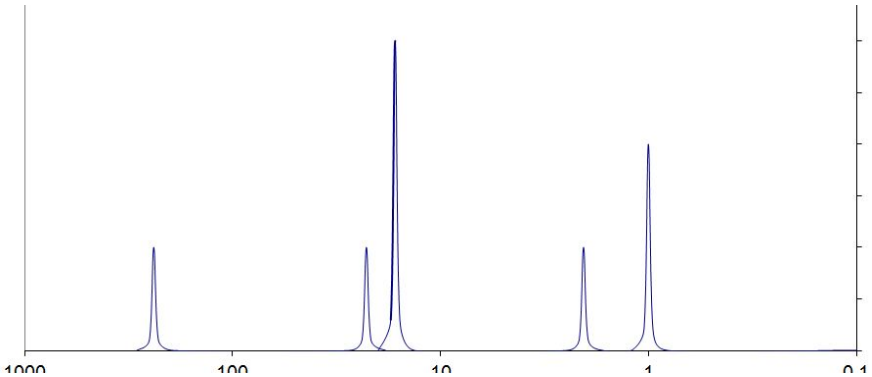


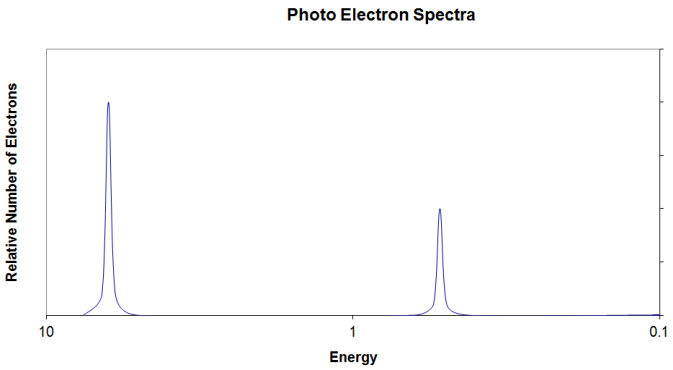
TABLE 7.2 • Successive Values of Ionization Energies, *I*, for the Elements Sodium through Argon (kJ/mol)

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4562	(inner-shell electrons)				
Mg	738	1451	7733				
Al	578	1817	2745	11,577			
Si	786	1577	3232	4356	16,091		
P	1012	1907	2914	4964	6274	21,267	
S	1000	2252	3357	4556	7004	8496	27,107
Cl	1251	2298	3822	5159	6542	9362	11,018
Ar	1521	2666	3931	5771	7238	8781	11,995

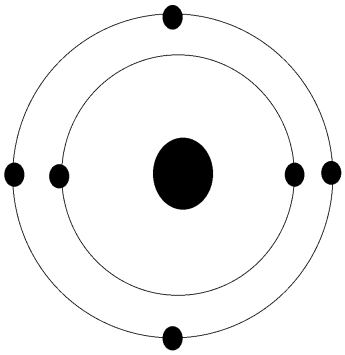
(From Brown et al., Chemistry the Central Science 12 ed., copyright Pearson Prentice Hall)

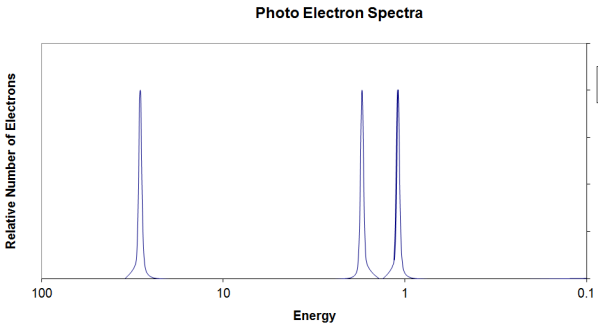
2. Here is a picture of the original Bohr model of lithium (Z=3), and next to it, the PES of lithium. Is there anything in the PES data for this element that requires revision of the Bohr model? Explain.

Lithium (Li)
Bohr Model

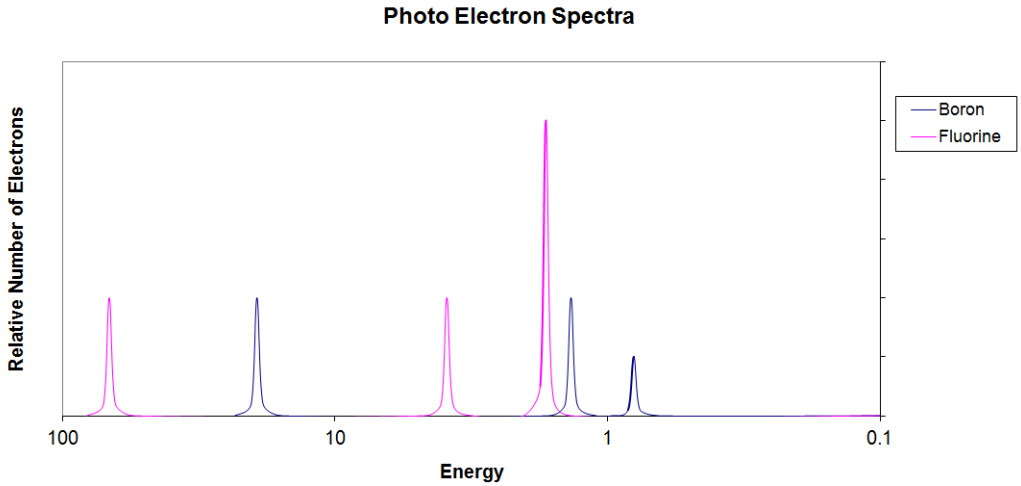


3. Similarly, here is the original Bohr model of carbon and the corresponding PES. Is there anything in the PES data for this element that requires revision of the Bohr model? Explain.





4. Here is a PES spectrum of boron (Z=5; blue) superimposed on that of fluorine (Z=9; pink)



a. Why are the fluorine peaks to the left of the boron peaks?
b. Why is there one peak in fluorine that is so much taller than all the others?

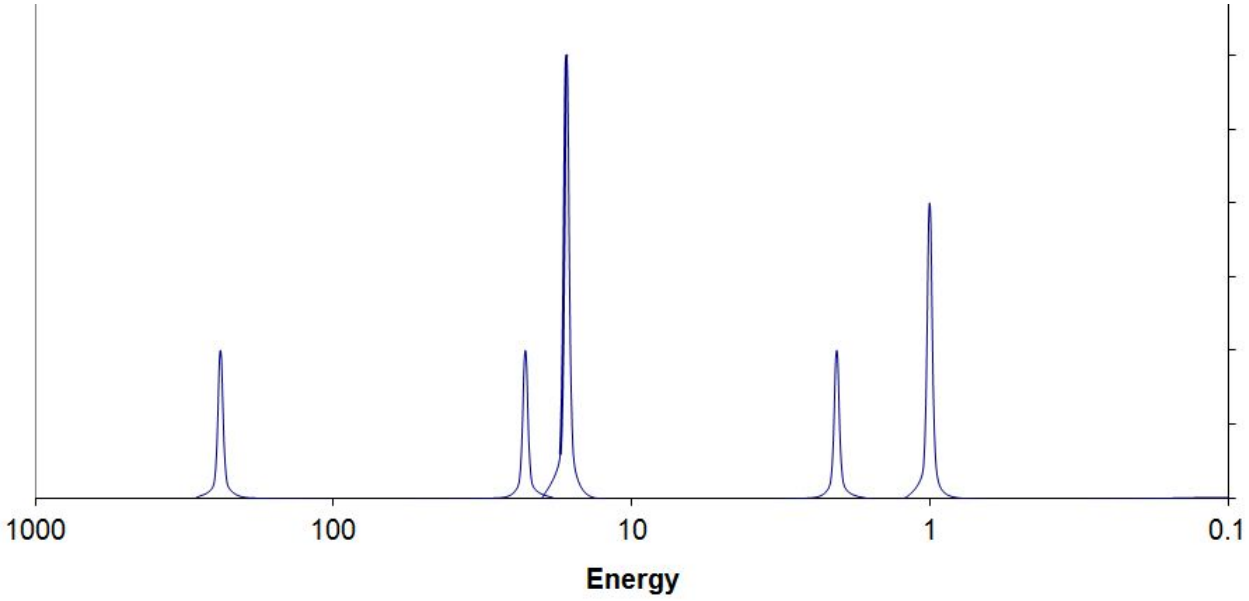
5. Below is shown the PES spectrum of sulfur (atomic number = 16).

a. Write the full electron configuration of sulfur.

b. Label each peak in the spectrum to show which subshell it represents (i.e., 1s, 2s, etc.)

c. On the spectrum, sketch in the relative locations and correct peak heights for the spectrum of aluminum (atomic number = 13). By relative location, I mean correctly to the left or right of the same subshell peak in the sulfur spectrum.

d. Draw a circle around the sulfur peak whose energy is equal to the first ionization energy of sulfur.


1000
100
10
1
0.1
Energy