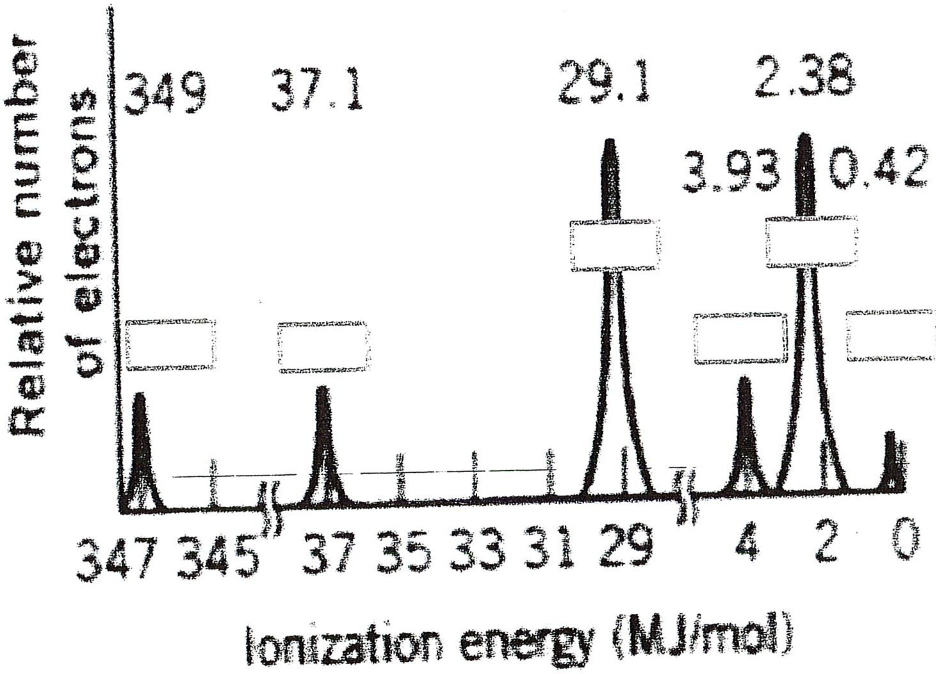
Chapter 7: Atomic Structure and Periodicity.

PES
Quantum #'s

Photoelectron Spectroscopy (PES)

PES is a method used to identify the placement of electrons for a SINGLE atom. Data from PES experiments are displayed as follows: (Note that these are ionization energies for different electrons in the SAME atom)



from https://www.youtube.com/watch?v=NRlqXeY1R_I

Note that the y axis shows the relative number of electrons in each peak. The peak heights therefore show how many electrons would have a given ionization energy relative to another peak. Recall that the closer an electron is to the nucleus, the more energy would be needed to remove that electron from an atom. In the diagram above, the peak at 349 represents electrons CLOSEST to the nucleus, therefore, in the 1st shell. We know from electron configurations that 2 electrons can fit into the 1s sublevel, so we can surmise that the peak at 349 represents two 1s electrons ($1s^2$).

The next peak at 37.1 MJ/mol would represent electrons in the ______ shell. Note the height of this peak is the same as the height of the first peak, so the peak should represent ______ electrons. What sublevel should this be? ______ with a configuration of ______ The next peak at 29.1 MJ/mol should be the ______ electrons. Note how large this peak is compared to the prior peak. The peak at 29.1 MJ/mol represents ______ The peak at 3.93 MJ/mol represents two ______ electrons. The peak at 2.38 MJ/mol represents ______ electrons (note the height of this peak is the same as the height for the six 2p electrons at 29.1 MJ/mol). The last peak at 0.42 MJ/mol would be for electrons in the ______ sublevel. Based on the height of this peak, the number of electrons is ______ because the height of the peak is ½ the height of the peaks at 3.93 MJ/mol, 37.1 MJ/mol and 349 MJ/mol.

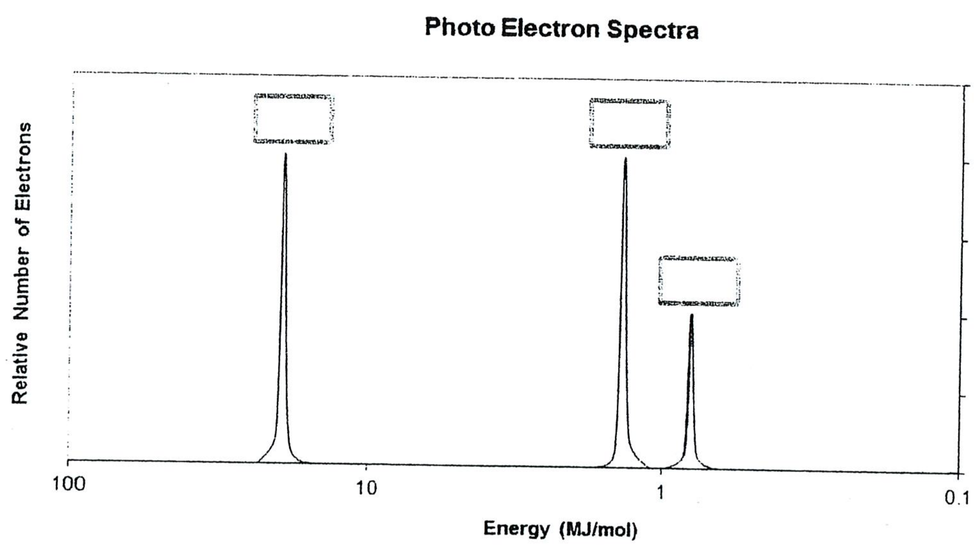
A few points to note:

Sometimes the innermost electrons are not shown on a diagram because the scale would be too large.

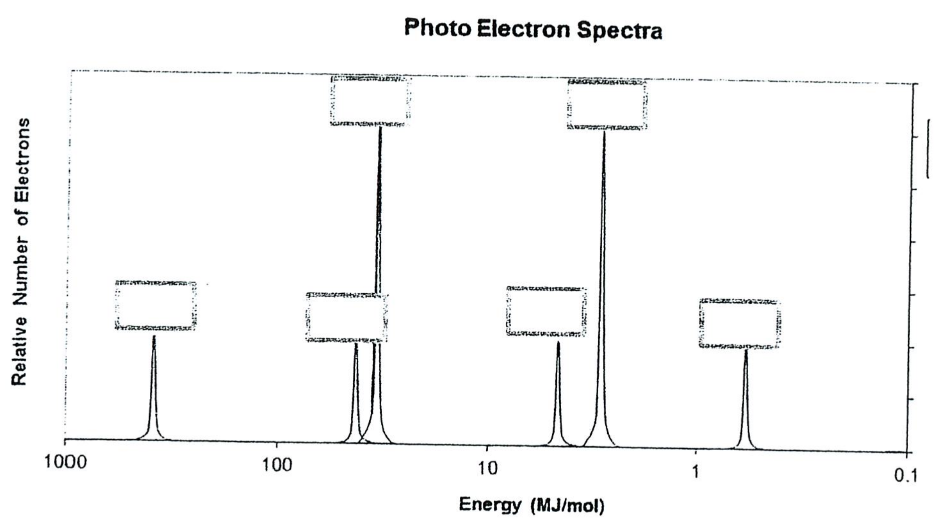
3d electrons would typically have a higher ionization energy than 4p electrons because 3d electrons are closer to the nucleus and therefore have a stronger Coulombic force holding them than 4p electrons. You can identify whether a peak represents 3d or 4p electrons by viewing the relative height of a peak and noting what the electron configuration for an atom should be.

Your turn:

What element is this: Identify the sublevel and number of electrons for each peak.

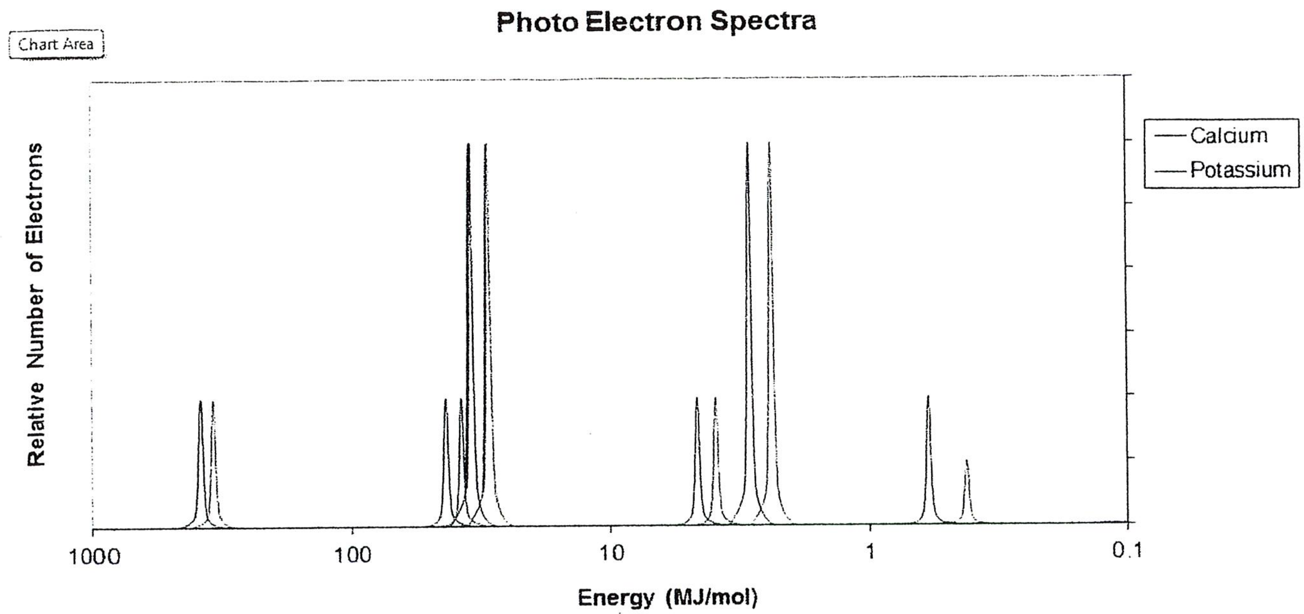


The element is



The element is

Comparing spectra for different elements



Why are Calcium's peaks slightly higher in energy (x-axis) than potassium's peaks?

Draw an approximate sketch (just showing relative sizes of peaks and whether they are high or low ionization energy for:

a) Silicon

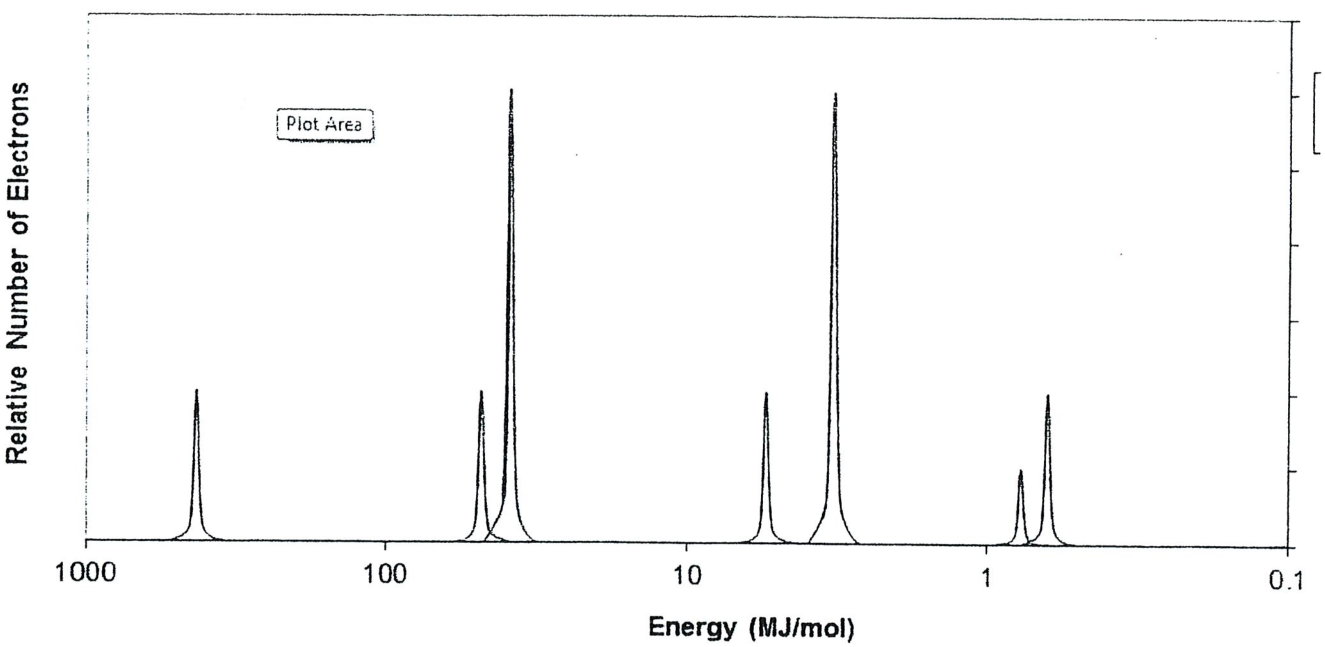
b) nitrogen

Explain whether each of the following is true or false.

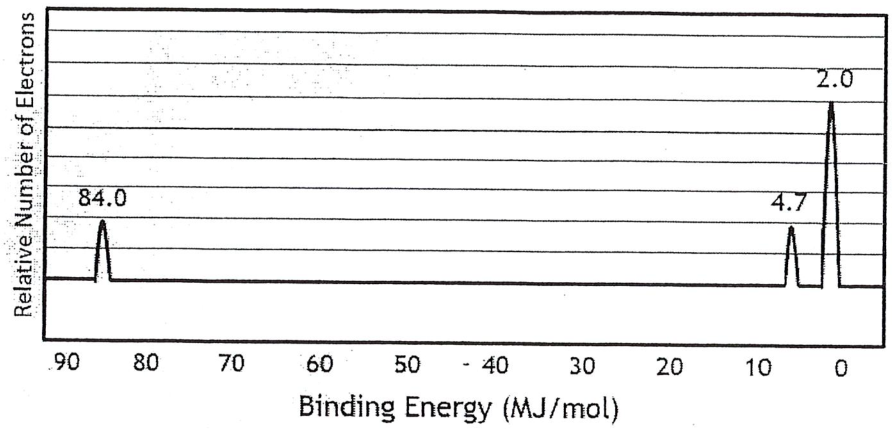
1) The photoelectron spectrum of Ca^{2+} and Ar should be the same.

2) The photoelectron spectrum of ^{16}O and ^{18}O should be the same.

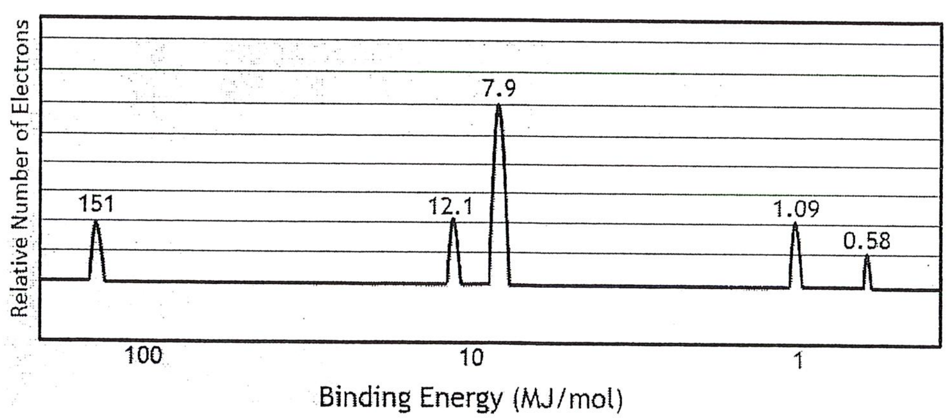
The photoelectron spectrum of Scandium is below. Explain why the peak just to the right of 1.0 is assigned to the 3d orbital and not the 4p orbital.



Analyzing data from PES (slide 30)



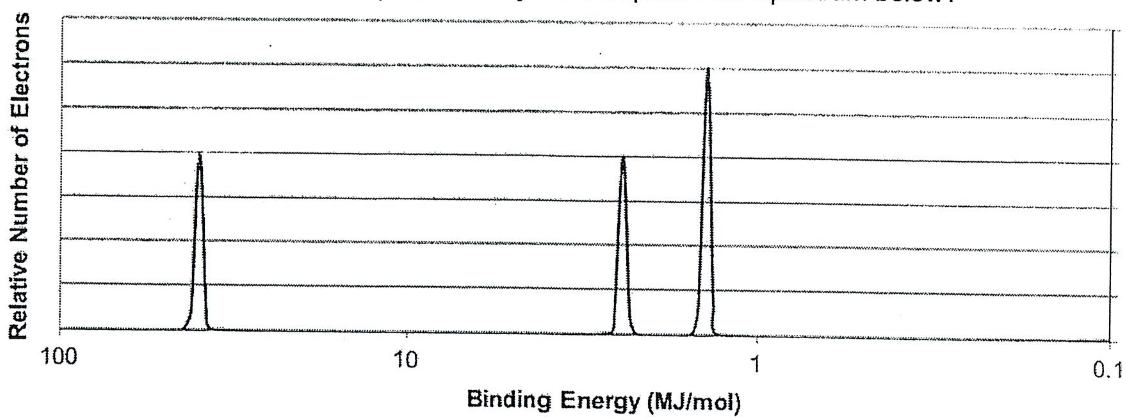
1. Which of the following elements might this spectrum represent?
   (A) He
   (B) N
   (C) Ne
   (D) Ar



2. Given the spectrum above, identify the element and its electron configuration:
   (A) B
   (B) Al
   (C) Si
   (D) Na

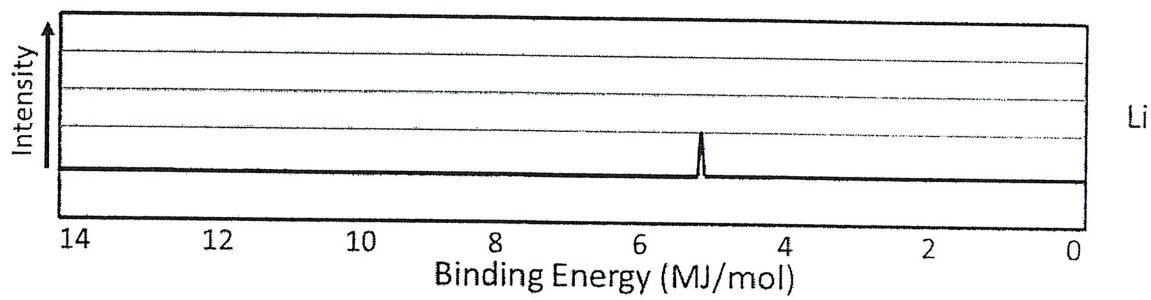
Sample Questions

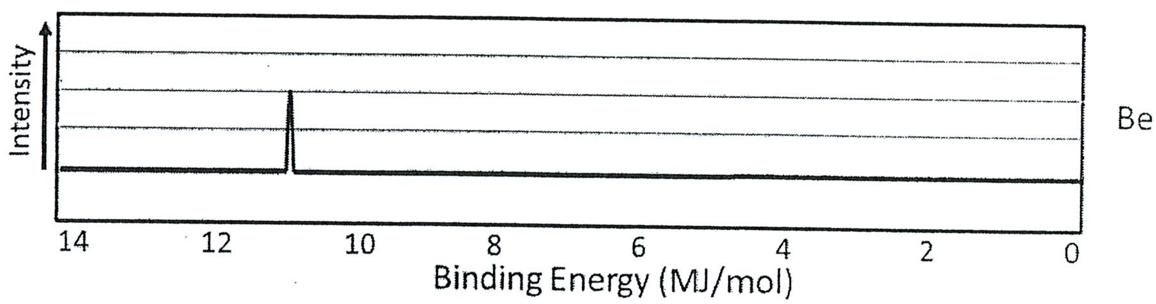
1. Which element could be represented by the complete PES spectrum below?



   a. Li
   b. B
   c. N
   d. Ne

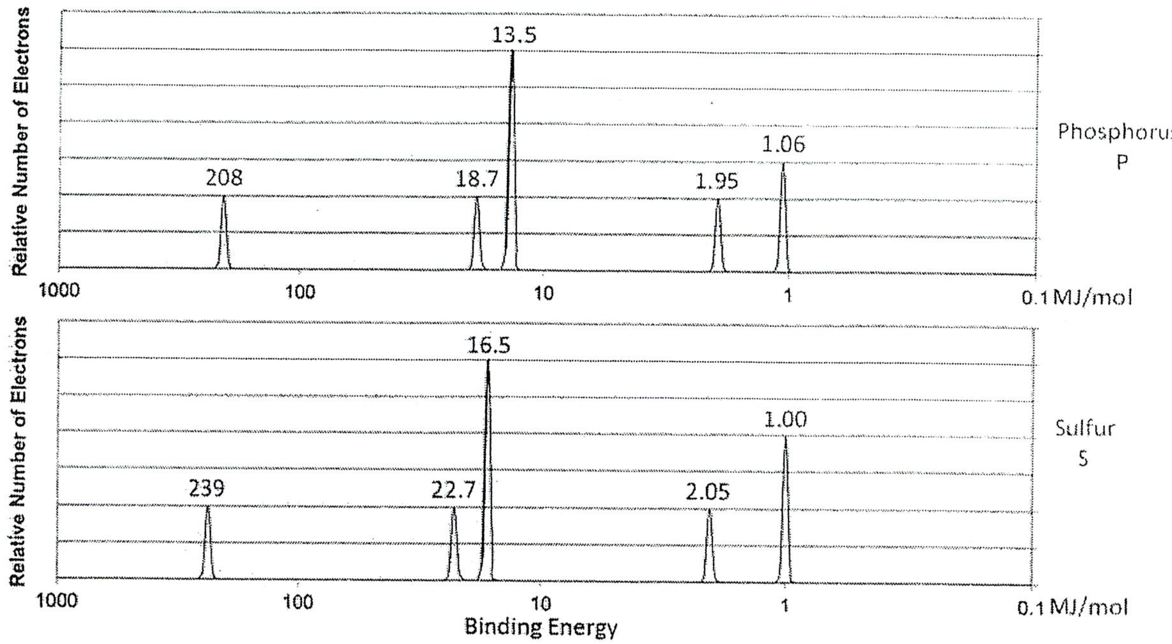
2. Which of the following best explains the relative positioning and intensity of the 2s peaks in the following spectra?



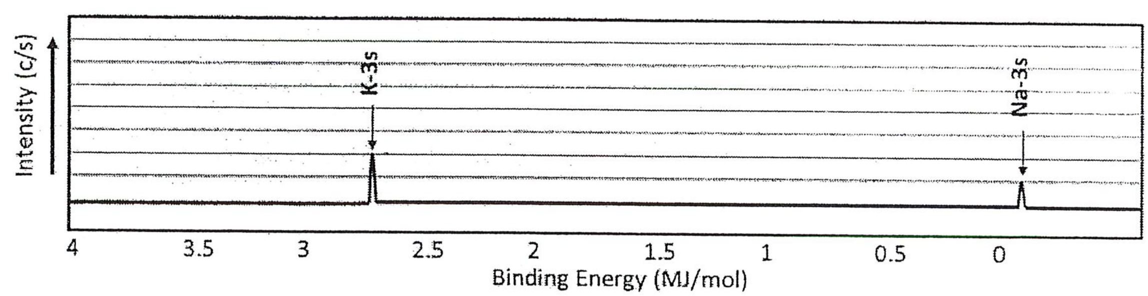


   a. Be has a greater nuclear charge than Li and more electrons in the 2s orbital
   b. Be electrons experience greater electron-electron repulsions than Li electrons
   c. Li has a greater pull from the nucleus on the 2s electrons, so they are harder to remove
   d. Li has greater electron shielding by the 1s orbital, so the 2s electrons are easier to remove

6

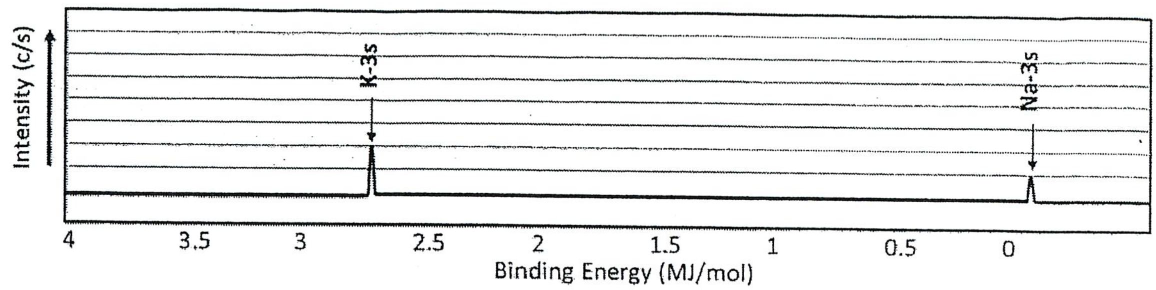


3. Given the photoelectron spectra above for phosphorus, P, and sulfur, S, which of the following best explains why the 2p peak for S is further to the left than the 2p peak for P, but the 3p peak for S is further to the right than the 3p peak for P?
   a. S has a greater effective nuclear charge than P, and the 3p sublevel in S has greater electron repulsions than in P.
   b. S has a greater effective nuclear charge than P, and the 3p sublevel is more heavily shielded in S than in P.
   c. S has a greater number of electrons than P, so the third energy level is further from the nucleus in S than in P.
   d. S has a greater number of electrons than P, so the Coulombic attraction between the electron cloud and the nucleus is greater in S than in P.

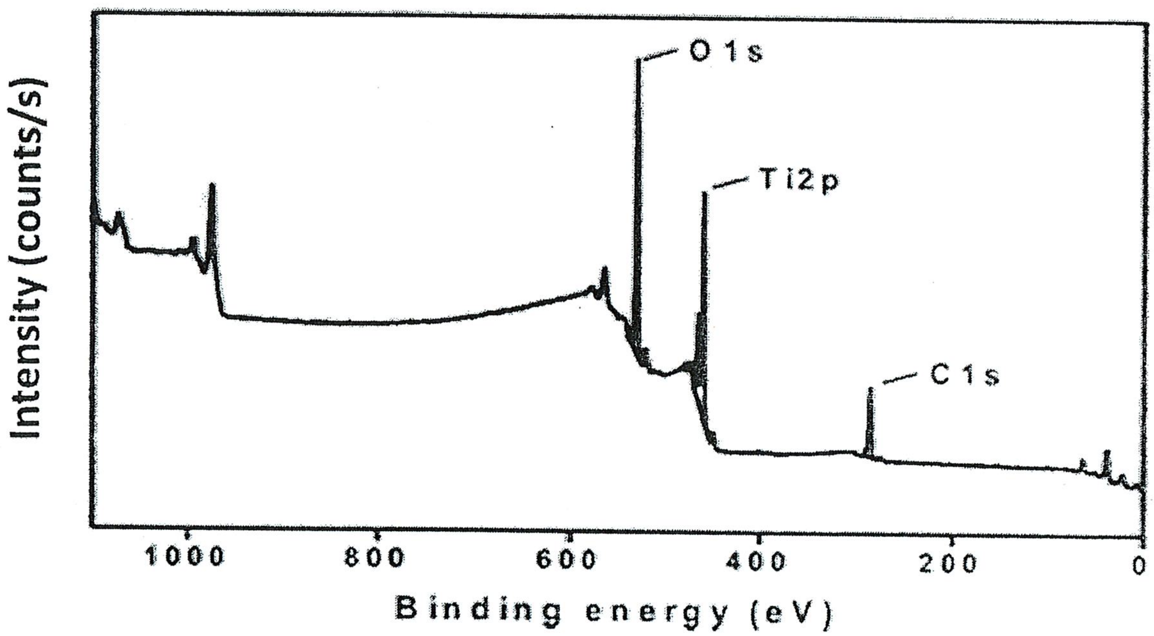


4. Looking at the spectra for Na and K above, which of the following would best explain the difference in binding energy for the 3s electrons?
   a. K has a greater nuclear charge than Na
   b. K has more electron-electron repulsions than Na
   c. Na has one valence electron
   d. Na has less electron shielding than K

7

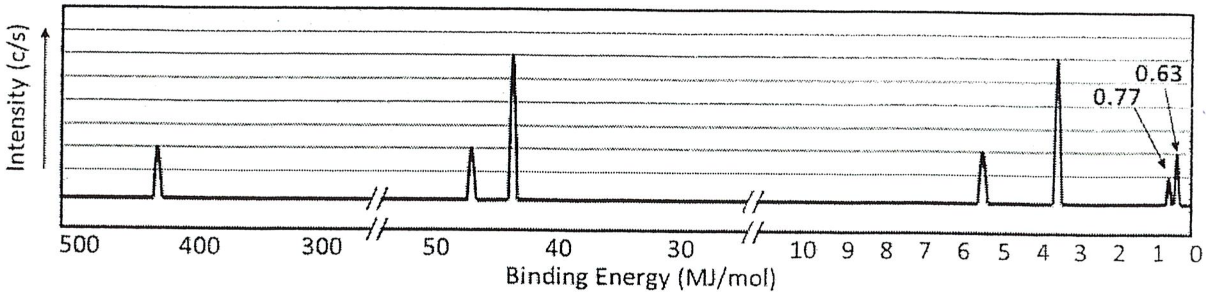


5. Looking at the spectra for Na and K above, which of the following would best explain the difference in ***signal intensity*** for the 3s electrons?
   a. K has a greater nuclear charge than Na
   b. K has more electron-electron repulsions than Na
   c. Na has one valence electron
   d. Na has less electron shielding than K

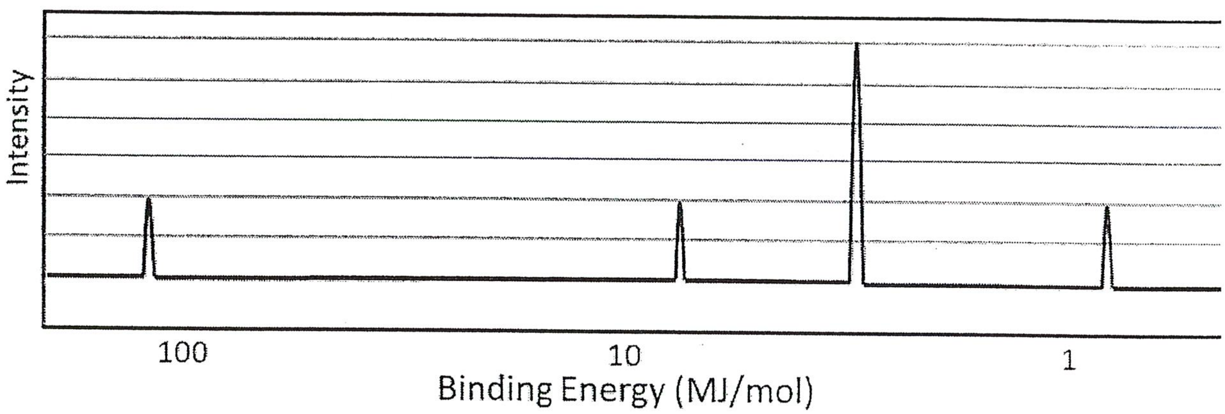


6. Given the photoelectron spectrum above, which of the following best explains the relative positioning of the peaks on the horizontal axis?
   a. O has more valence electrons than Ti or C, so more energy is required to remove them
   b. O has more electron-electron repulsions in the 2p sublevel than Ti and C
   c. Ti atoms are present in a greater quantity than O than C in the mixture.
   d. Ti has a greater nuclear charge, but the 2p sublevel experiences greater shielding than the 1s sublevel.

8



7. Given the photoelectron spectrum of Scandium above, which of the following best explains why Scandium commonly makes a 3+ ion as opposed to a 2+ ion?
   a. Removing 3 electrons releases more energy than removing 2 electrons.
   b. Scandium is in Group 3, and atoms only lose the number of electrons that will result in a noble gas electron configuration
   c. The amount of energy required to remove an electron from the 3d sublevel is close to that for the 4s sublevel, but significantly more energy is needed to remove electrons from the 3p sublevel.
   d. Removing 2 electrons alleviates the spin-pairing repulsions in the 4s sublevel, so it is not as energetically favorable as emptying the 4s sublevel completely.



8. On the photoelectron spectrum for magnesium given above, draw the spectrum for aluminum.

9

Part 1

Name ______________________________
Partner's name ______________________________
Period ______
Date ______________________________

Photoelectron Spectroscopy (PES): An Investigation

Sources:

Chemistry: A Guided Inquiry, 4th edition, by Richard S. Moog and John J. Farrell (John Wiley & Sons, 2008).

Annis Hapkiewicz, AP Chemistry workshop leader, December 2012.

John Gelder, Oklahoma State University, draft version of PES Activity, presented by Alice Putti at the APSI, Grandville, MI, June, 2013.

Introduction: We have learned that ionization energy is the minimum energy required to remove an electron from an atom. The most easily removed electron always resides in the valence level of the atom since that is the level farthest away from the nucleus. The following chart gives the first ionization energies for the first 20 elements, in units of megajoules/mole (MJ/mol).

$_{1}H$	1.31	$_{6}C$	1.09	$_{11}Na$	0.50	$_{16}S$	1.00
$_{2}He$	2.37	$_{7}N$	1.40	$_{12}Mg$	0.74	$_{17}Cl$	1.25
$_{3}Li$	0.52	$_{8}O$	1.31	$_{13}Al$	0.58	$_{18}Ar$	1.52
$_{4}Be$	0.90	$_{9}F$	1.68	$_{14}Si$	0.79	$_{19}K$	0.42
$_{5}B$	0.80	$_{10}Ne$	2.08	$_{15}P$	1.01	$_{20}Ca$	0.59

An interesting question we could ask, that cannot be answered from the experimental data of the first ionization energy, is: Do all electrons in the same level require the same amount of energy to remove? We can answer this question if we look at photoelectron spectroscopy (PES) data for the atoms.

In photoelectron spectroscopy, high energy photons (such as ultraviolet radiation or x-rays) are directed at a gaseous element and the kinetic energies of the ejected electrons are measured. If the energy of the photon is greater than the energy necessary to remove an electron from the atom, an electron is ejected with the excess energy appearing as kinetic energy. So, if IE is the ionization energy of the electron and KE is the kinetic energy with which it leaves the atom, then

$$E_{photon} = IE + KE$$

or, upon rearranging the equation,

$$IE = E_{photon} - KE$$

The kinetic energy of the electrons is measured in a photoelectron spectrometer.

For example, before photon interaction, suppose the photon energy = 143.4 MJ/mol and after the photon interaction, the kinetic energy of the ionized electron = 114.8 MJ/mol. The ionization energy would be: 143.4 – 114.8 = 28.6 MJ/mol.

If photons of sufficient energy are used, an electron may be ejected from *any* of the energy levels of an atom. Each atom will eject only one electron, but every electron in each atom has an (approximately) equal chance of being ejected. Thus, for a large group of identical atoms, the electrons ejected will come from all possible levels of the atom. Also, because the photons used all have the same energy, electrons ejected from a given level will all have the same energy. Only a few different energies of ejected electrons will be obtained corresponding to the number of energy levels in the atom.

The results of a photoelectron spectroscopy experiment are conveniently presented in a **photoelectron spectrum.** Examples of photoelectron spectra data are available at http://www.chem.arizona.edu/chemt/Flash/photoelectron.html. You will use the PES data provided to answer the following questions.

Investigation

1. Open the web page given above. To display the first spectrum, click on hydrogen on the periodic table.

    a. The label on the x-axis is energy and the units are megajoules/mole. What is the label on the y-axis?

    b. In the lab you did on the Hydrogen Spectrum, the first ionization energy was determined to be 1312 kJ/mol. How does that relate to the photoelectron spectrum for hydrogen?

2. Helium is next, but before looking at its photoelectron spectrum, answer these questions:

    a. How many electrons does helium have in its first level?

    b. On the chart given in the introduction, what is the value of the first ionization energy of helium?

    c. Describe (predict) what the PES would look like if the same amount of energy is required to remove each of the electrons.

    d. Describe (predict) what the PES would look like if different amounts of energy are required to remove each electron.

    e. Now look at the actual PES for helium. Compare it to the predictions you made. Describe what you see and comment about the relative energy of the peak(s) and the number of electrons for each peak in the PES for He and the PES for H.

3. The next element is lithium, but don't look at its PES yet!

a. How many electrons does lithium have and in what levels are these electrons found?

b. Before looking at the PES for lithium predict what you believe the spectrum will look like. Note: you do not have to predict the exact energies of each electron but you can make reasonable estimates based on the first ionization energy for lithium and the PES for helium.

c. Now look at the actual PES for lithium. For each peak in the PES identify the energy level the electrons represented by that peak occupy. Explain why the two peaks are different heights. Which electron in lithium requires the least amount of energy to remove?

Sketch the spectrum for lithium:

4. The next element is beryllium, don't look at its PES yet!

a. How many electrons does beryllium have and in what levels do these electrons occupy?

b. Before looking at the PES for beryllium predict what you believe the spectrum will look like. Note: you do not have to predict the exact energies of each electron but you can make reasonable estimates based on the first ionization energy for beryllium and the PES for lithium.

c. Now look at the actual PES for beryllium. First note that instead of having one long x-axis, it is divided into two regions, 0-10 MJ/mol and 10-100 MJ/mol.

For each peak in the PES identify the energy level the electrons represented by that peak occupy. How does the PES of beryllium compare to the PES of lithium. (You can put both of them on the screen by using the "Dual" mode instead of the "Mono" mode.)

5. The next element is boron. Of course, you shouldn't look at its PES yet!

a. How many electrons does boron have and what levels do those electrons occupy?

b. Before looking at the PES for boron, predict how many peaks it will have, the number of electron(s) for each peak and estimate the relative energies.

c. Now look at the PES for boron and briefly describe how to interpret the PES for boron. How does the PES for boron support the idea that there are two different sublevels in the second energy level?

6. Look at the PES for the rest of the second period elements (carbon through neon). Answer the following questions after looking at these spectra.

a. Would you agree or disagree with the following statement? Explain.

"The electrons in the second energy level all have the same energy."

b. How many "sublevels" are found in the second level? How many "sublevels" are found in the first level?

c. How many electrons are in each sublevel in the second level? In the first level?

d. Moving systematically from lithium to neon:

i. How many electrons are in the first level?

ii. What happens to the energy required to remove an electron in the first level moving from left to right in the second period? Support your answer with a meaningful explanation.

iii. What happens to the energy of the electrons in the outermost level?

7. Look at the PES for the elements in the third period (sodium to argon) and briefly describe your observations. Any surprises? Briefly explain your observations.

8. A notation has been agreed upon for writing an electron configuration to identify the location of the level and sublevel of each electron in an atom. Levels are labeled with a number: 1, 2, 3, etc. and sublevels are labeled with letters: *s, p, d,* and *f.* Every sublevel contains an *s* sublevel.

a. Write the complete electron configuration for the first ten elements in the periodic table.

b. Look at the PES for potassium, calcium, and scandium. Something very interesting happens when we look at the PES for scandium that has not occurred in any element prior to scandium. Briefly explain.

c. If one electron is removed from scandium, which electron (identify the level and sublevel) requires the least amount of energy to remove?

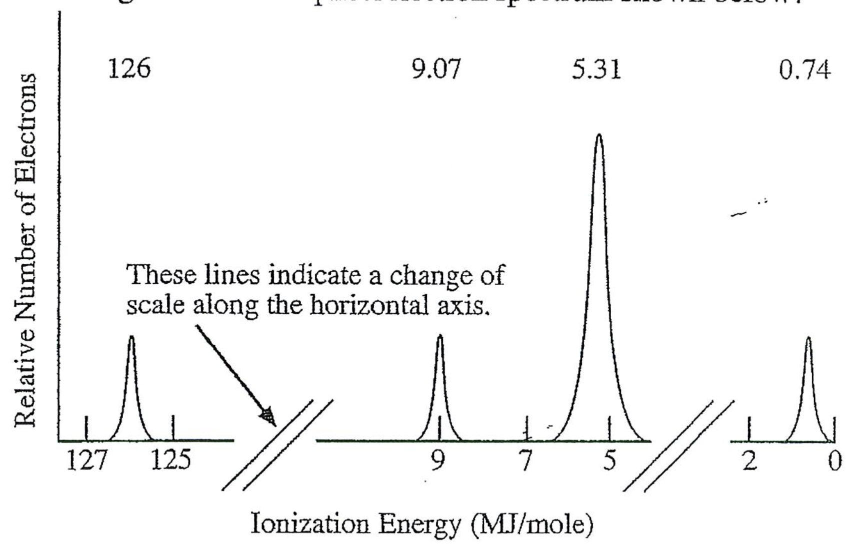
9. Sketch the PE spectrum of (a) oxygen and (b) scandium. Label each peak with the appropriate sublevel.

Part II

Name ______________________________
AP Chemistry   Ms. Kitzmann   Period _____
Date ______________________________
PES: Review Questions

Based on the investigation you did of PES, you should be able to answer the following questions. One of the things to pay attention to is that PES spectra do not always look the same, or are they labeled the same way every time!

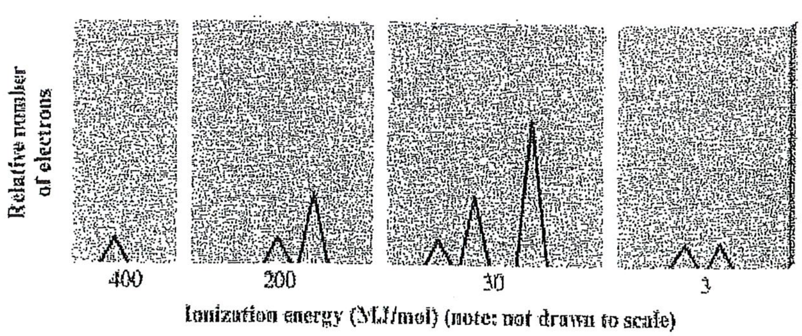
1. What element do you think would give rise to the photoelectron spectrum shown below? Explain your reasoning.



2. Indicate whether each of the following is true or false and explain your reasoning:
(a) The photoelectron spectrum of Mg^{2+} is expected to be identical to the photoelectron spectrum of Ne.

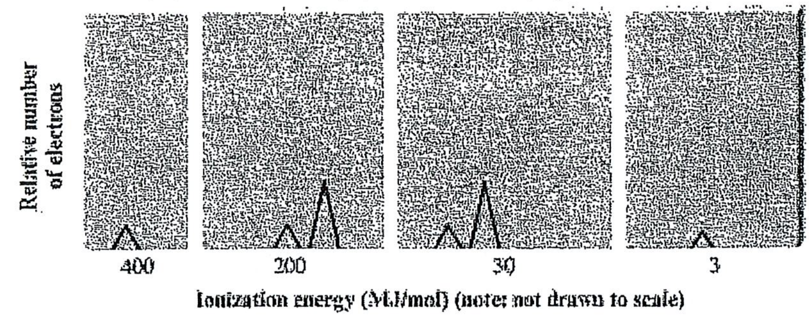
(b) The photoelectron spectrum of ^{35}Cl is identical to the photoelectron spectrum of ^{37}Cl.

3. Identify the element whose photoelectron spectrum is shown below:
(A) O   (B) Ca   (C) Ti   (D) Ge



4. Identify the element whose photoelectron spectrum is shown below:

(A) N (B) K (C) Ca (D) Sc



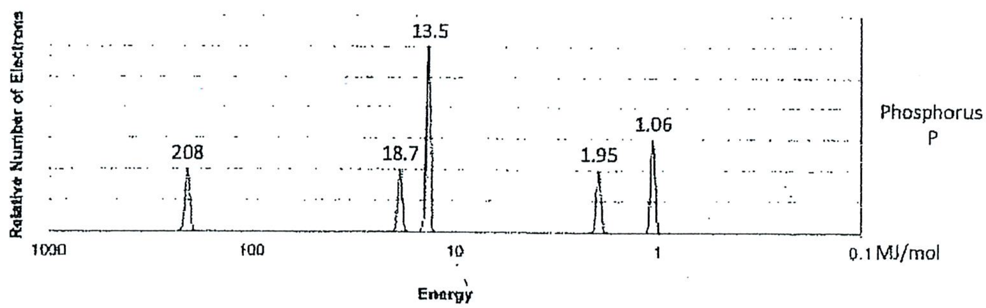
5. Given the photoelectron spectra for phosphorus, P, and sulfur, S, which of the following best explains why the 2p peak for S is further to the left than the 2p peak for P, but the 3p peak for S is further to the right than the 3p peak for P?

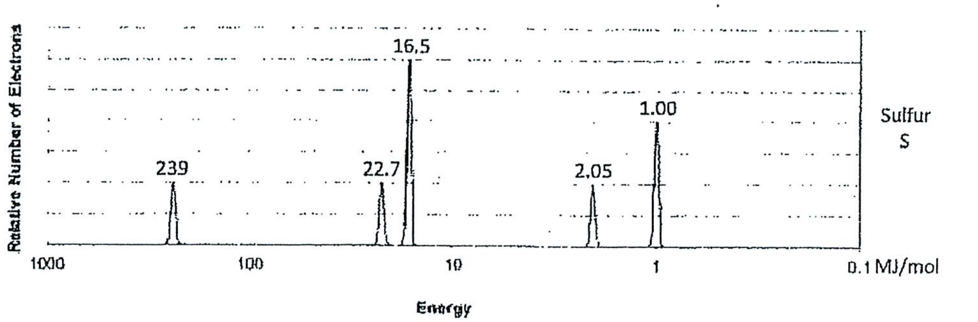
(A) S has a greater effective nuclear charge than P, and the 3p sublevel in S has greater electron repulsions than in P.

(B) S has a greater effective nuclear charge than P, and the 3p sublevel is more heavily shielded in S than in P.

(C) S has a greater number of electrons than P, so the third energy level is further from the nucleus in S than in P.

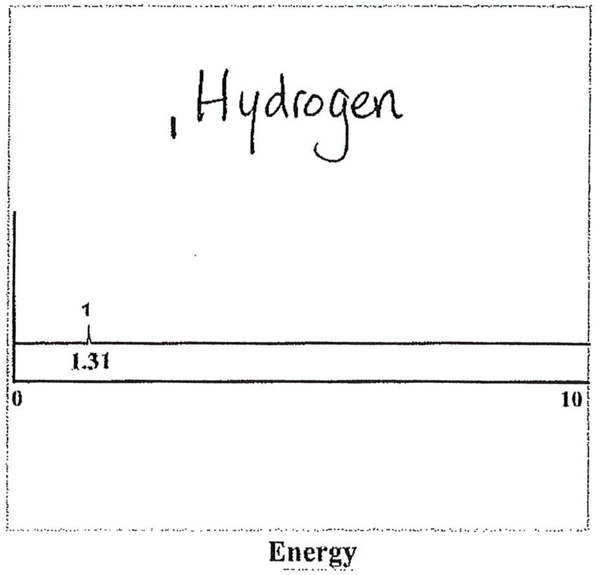
(D) S has a greater number of electrons than P, so the Coulombic attraction between the electron cloud and the nucleus is greater in S than in P.

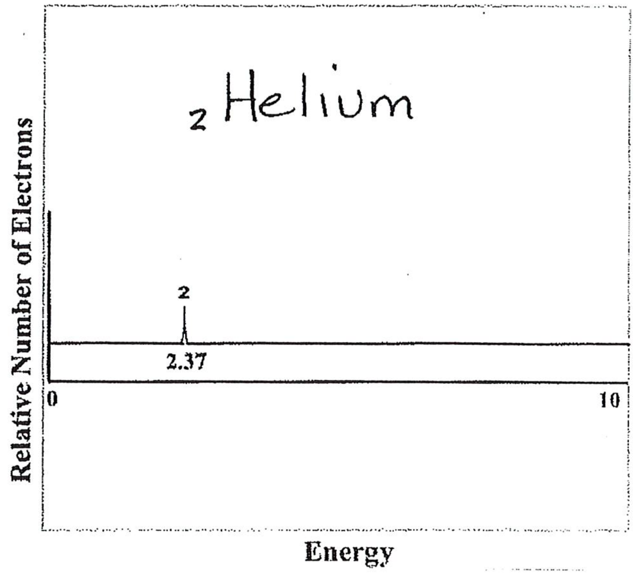


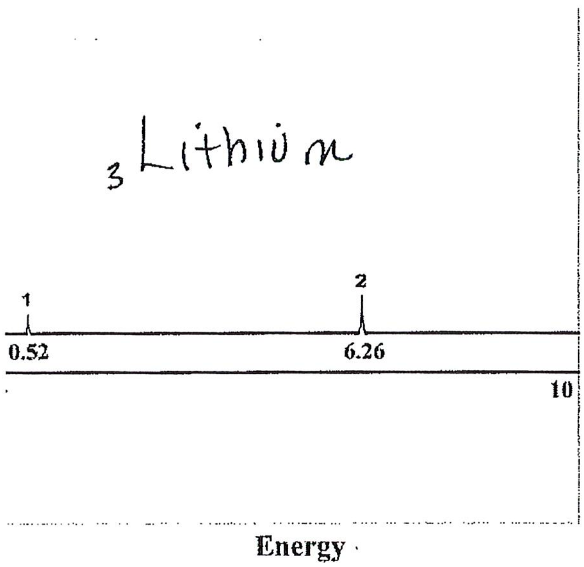


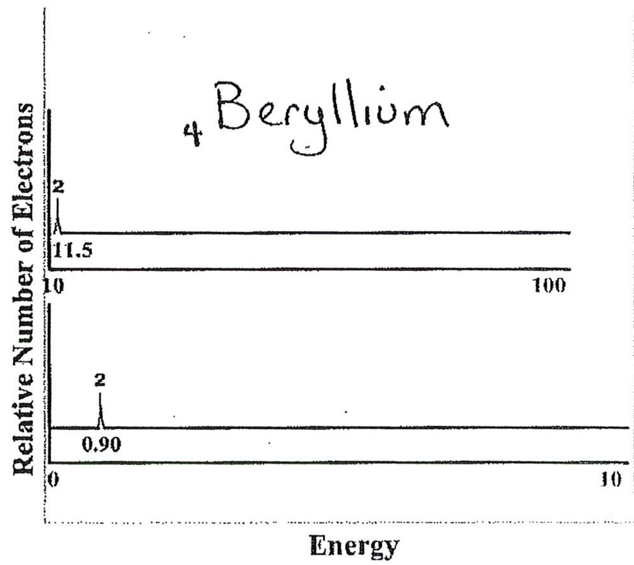
6. What are some differences between how these spectra are portrayed and the ones shown in the PES Investigation?

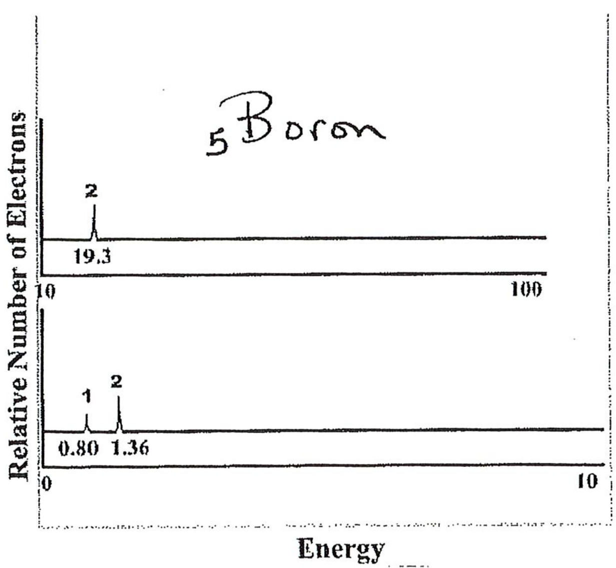
PE Spectra from Arizona website

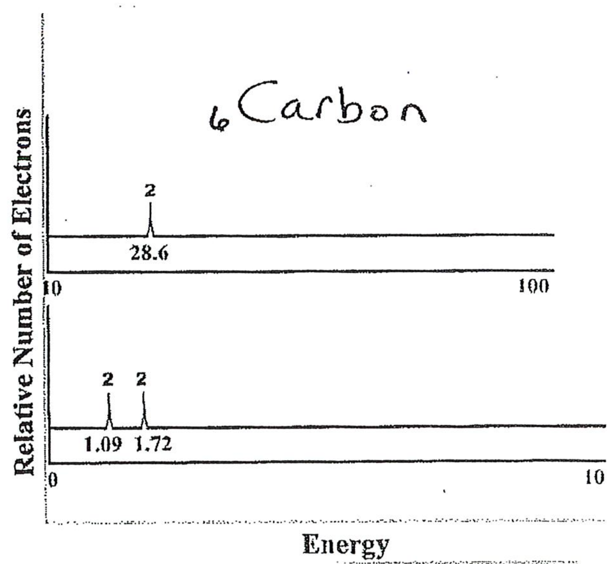


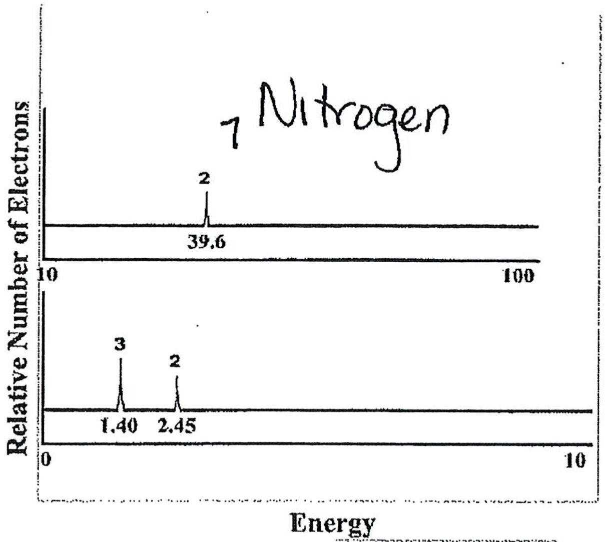


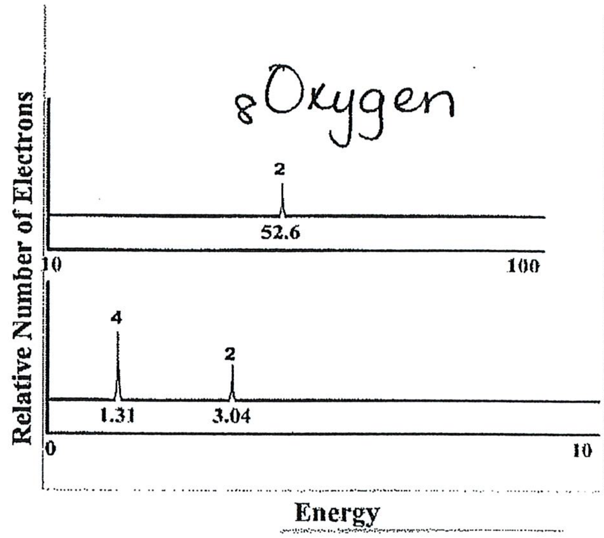


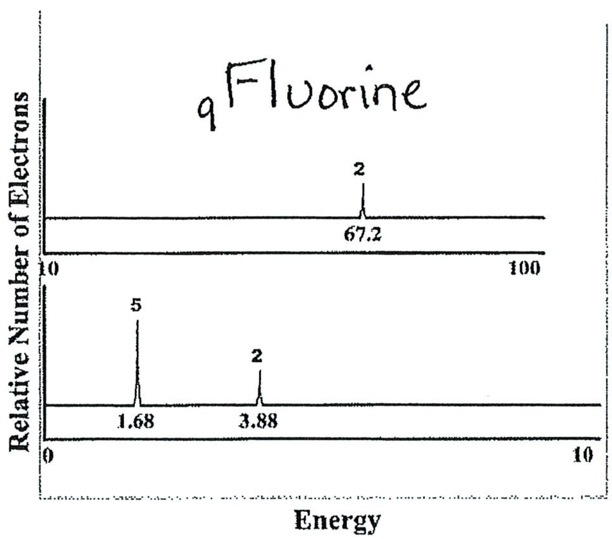


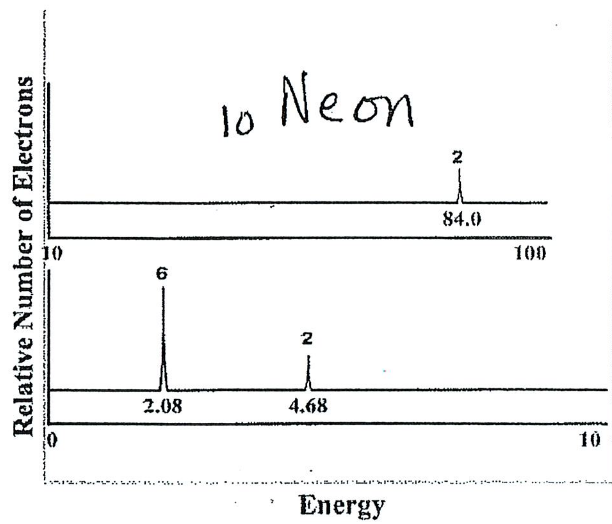


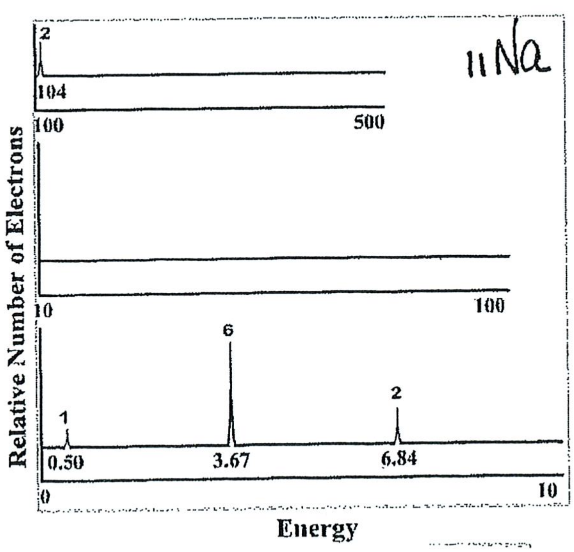


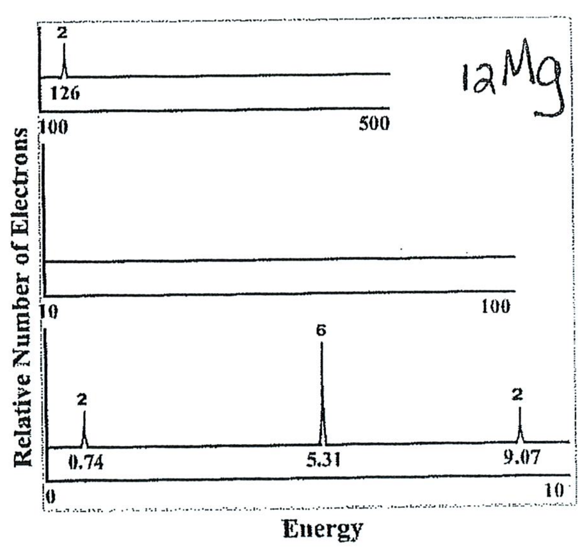

7 Nitrogen
Relative Number of Electrons
2
39.6
10
100
3
2
1.40
2.45
0
10
Energy

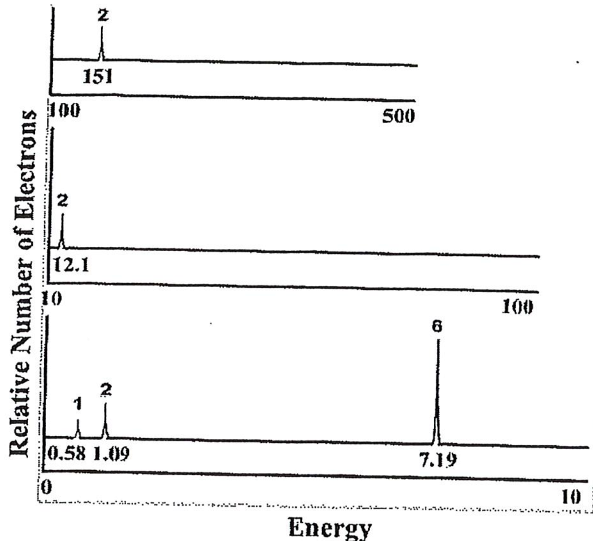

8 Oxygen
Relative Number of Electrons
2
52.6
10
100
4
2
1.31
3.04
0
10
Energy


9 Fluorine
Relative Number of Electrons
2
67.2
10
100
5
2
1.68
3.88
0
10
Energy

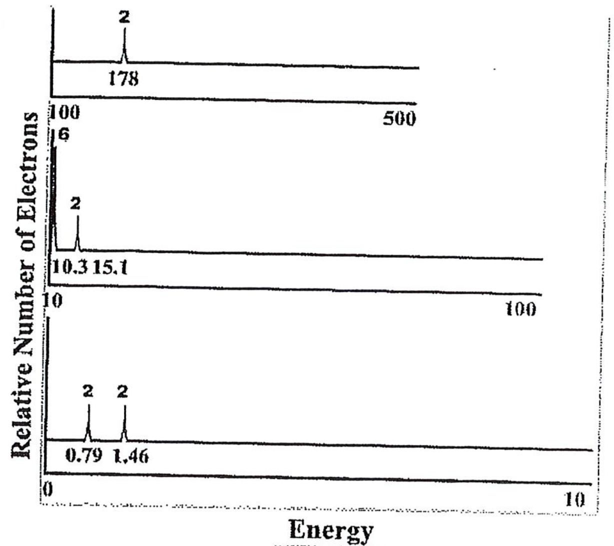

10 Neon
Relative Number of Electrons
2
84.0
10
100
6
2
2.08
4.68
0
10
Energy


11 Na
Relative Number of Electrons
2
104
100
500
10
100
1
6
2
0.50
3.67
6.84
0
10
Energy

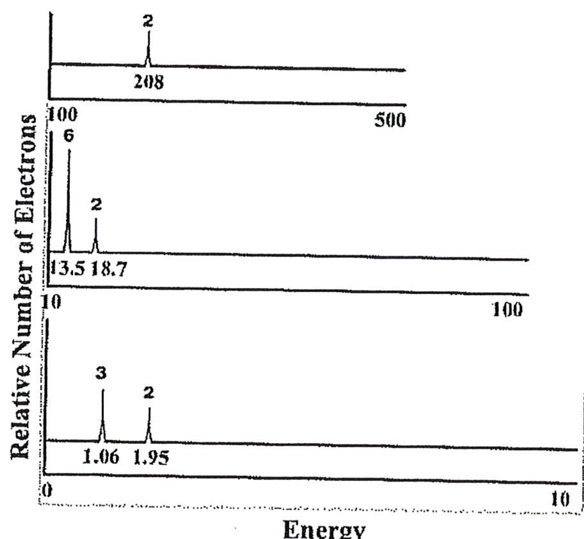

12 Mg
Relative Number of Electrons
2
126
100
500
10
100
2
6
2
0.74
5.31
9.07
0
10
Energy



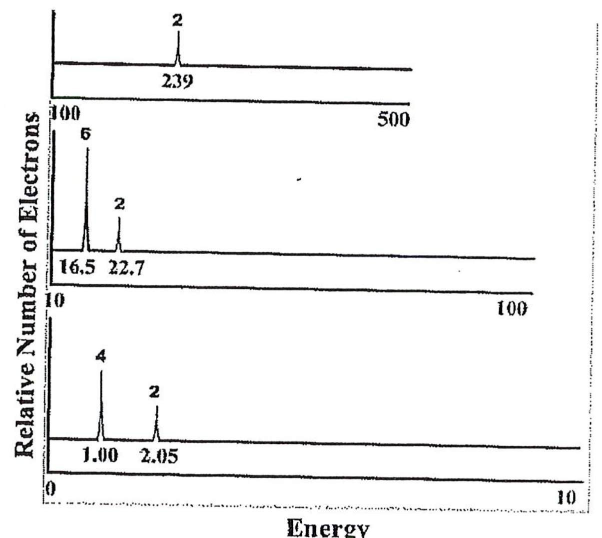
Activate1 **Aluminum** 13



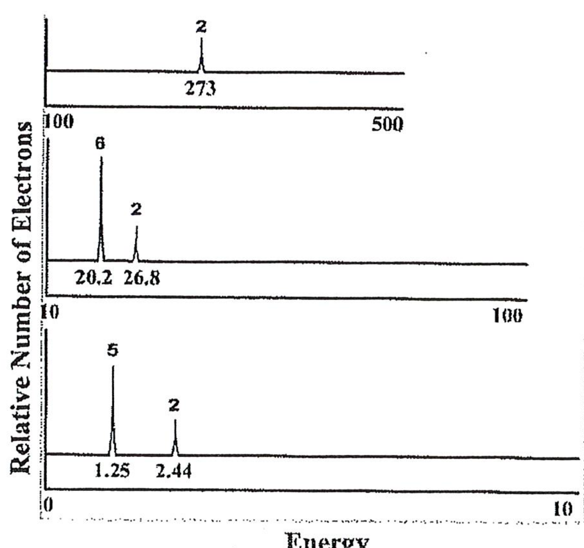
Activate2 **Silicon** 14



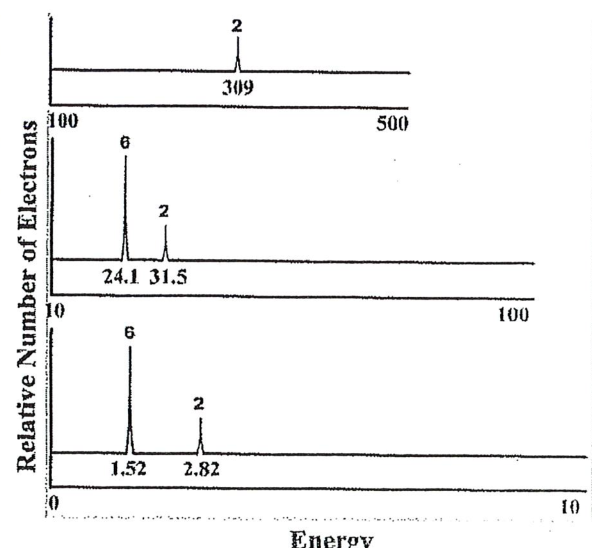
Activate1 **Phosphorus** 15



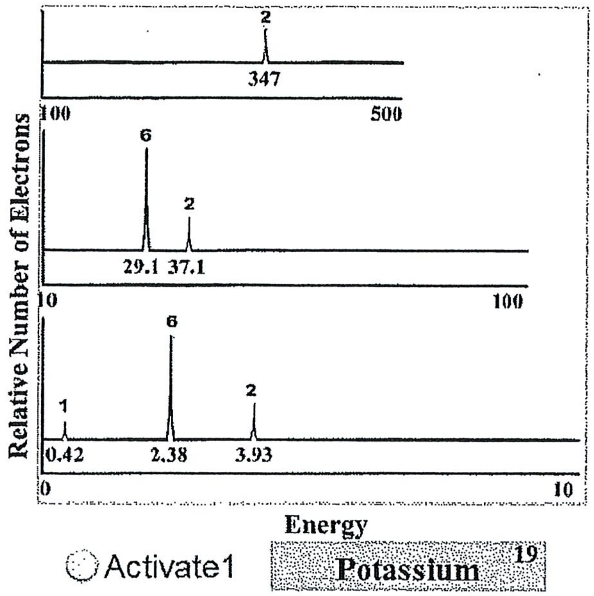
Activate2 **Sulfur** 16

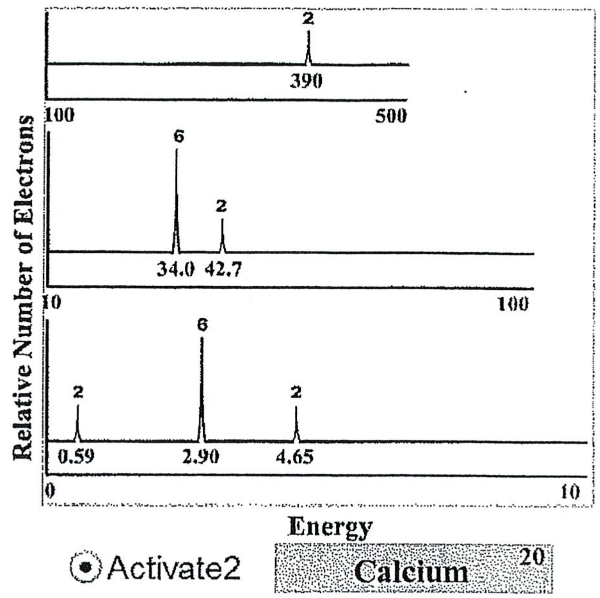


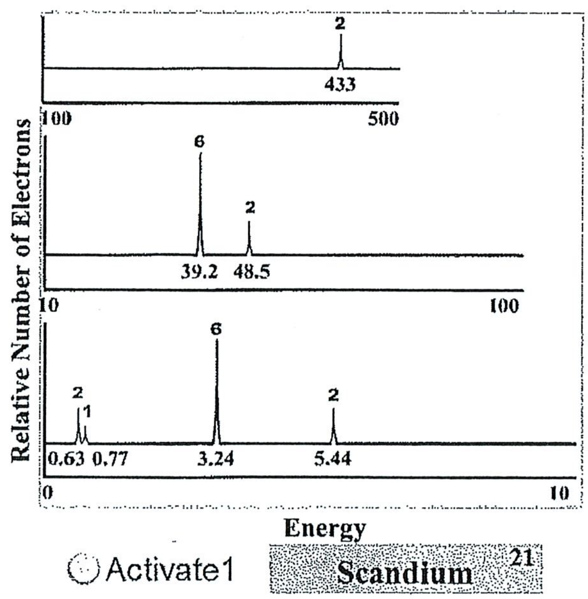
Activate1 **Chlorine** 17



Activate2 **Argon** 18


2
347
100
500
Relative Number of Electrons
6
2
29.1 37.1
10
100
6
1
2
0.42
2.38
3.93
0
10
Energy
Activate1
Potassium
19


2
390
100
500
Relative Number of Electrons
6
2
34.0 42.7
10
100
6
2
2
0.59
2.90
4.65
0
10
Energy
Activate2
Calcium
20


2
433
100
500
Relative Number of Electrons
6
2
39.2 48.5
10
100
6
2
1
2
0.63 0.77
3.24
5.44
0
10
Energy
Activate1
Scandium
21

Name:______________________________Class:____________Date:______

Periodic Trends Worksheet

1.) Rank the following elements by increasing atomic radius: carbon, aluminum, oxygen, potassium.

2.) Rank the following elements by increasing electron affinity: sulfur, oxygen, neon, aluminum.

3.) What is the difference between electron affinity and ionization energy?

4.) Why does fluorine have higher ionization energy than iodine?

5.) Why do elements in the same family generally have similar properties?

6.) In the modern periodic table, elements are ordered according to

___________________ _____________ __________.

7.) Mendeleev notice that properties of elements appeared at regular intervals when elements were arranged in order of increasing __________.

8.) The discovery of noble gases changed Mendeleev's periodic table by adding a new ________________ (period, series, group, sublevel block).

9.) The most distinctive property of noble gases is that they are ___________ (metallic, radioactive, metalloids, largely unreactive).

10.) What is the name of the group that Lithium belongs to. __________

11.) On the periodic table, a horizontal row is a ______________ a vertical column is a ______________.

12.) Explain the distinction between atomic mass and atomic number.

13.) When an electron is added to a an atom in the ground state, energy is

always absorbed   always released   absorbed and released.

14.) The energy required to remove an electron is ____________________

15.) The trend for the above property is (Use arrows and words).

16.) The energy required to add an electron is _________________

17.) The trend for the above property is (Use arrows and words).

18.) What happens to atomic radii as you move from left to right across the period? (Use arrows and words).

19.) Why is this? (Use complete sentences)

20.) Name the following:

Halogen with the least negative electron affinity __________

Alkaline earth metal with the highest ionization energy ___________

Element in period three with the smallest atomic radii ___________

21.) Compare and explain the size of Ca^{+}, Ca^{-}, and Ca. (use complete sentences)

22.) Which element has the greater ionization energy?

Ca or Mg

Te or I

23.) What is the relationship between atomic radii and ionization energy?

24.) Which element has a greater Electron affinity?

Cl or S Si or C

25.) Write the electron configuration (short or long way) for the following.

Na

Na^{+}

O^{2-}

Cl

Cl^{-}

26.) Compare the electron configuration of F^{-}, Ne , and Na^{+}

27.) DRAW THE ORBITAL DIAGRAM FOR THE FOLLOWING AND PREDICT WHETHER EACH ELEMENT IS EXPECTED TO BE PARAMAGNETIC OR DIAMAGNETIC.

1. argon

2. silicon