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>I</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		
Р	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)

Answer: The first ionization energy of sulfur matches the furthest-right peak on the PES. The different peaks in PES represent the effort needed to evict an electron in different subshells of a neutral sulfur atom. In contrast, the ionization energy chart represents the energy needed to evict the most easily removed electron from a neutral sulfur atom (IE1), an S^+ ion (IE2), an S^{2+} ion (IE3), etc. These two data sets have only one point of overlap, which is IE1 on the chart and the lowest-energy peak on the PES. None of the peaks in the PES relate to removing an electron from a sulfur cation, and, likewise, none of the successive ionization energies concern removing an electron from other than the highest subshell.

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.



Answer: For this element, there is no conflict. The Bohr model shows 2 electrons in the lowest orbit and 1 electron in a higher orbit. The PES shows electrons at two energy levels, with the more tightly held level having twice as many electrons as the other.

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.



Answer: For this element, the PES is not consistent with the Bohr model. The PES shows electrons at three different energy levels, while the Bohr model has only two energy levels.

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

Photo Electron Spectra



a. Why are the fluorine peaks to the left of the boron peaks? Answer: Fluorine has a greater nuclear charge, causing the electrons in all the subshells to

be held more tightly.b. Why is there one peak in fluorine that is so much taller than all the others?

Fluorine has 4 more electrons than boron; all the additional electrons are in the 2p subshell, giving it 5 in all, causing that peak to be much higher than 1s or 2s, which each have 2 electrons.

- 5. Below is shown the PES spectrum of sulfur (atomic number = 16).
- a. Write the full electron configuration of sulfur. $1s^2 2s^2 2p^6 3s^2 3p^4$
- b. Label each peak in the spectrum to show which subshell it represents (i.e., 1s, 2s, etc.) They go in order from left to right as written in the electron configuration above.
- 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. All the aluminum peaks should be shifted to the right relative to the same peak in sulfur because aluminum has a smaller nuclear charge. The heights should all be the same as in sulfur, except the 3p peak, which should be half the height of the 1s, 2s, and 3s peaks.
- d. Draw a circle around the sulfur peak whose energy is equal to the first ionization energy of sulfur. It's the 3p peak.

