Photoelectron Spectroscopy (PES) **ANSWER KEY**

1. In a photoelectron spectrum, photons of 165.7 MJ/mol strike atoms of an unknown element. If the kinetic energy of the ejected electrons is 25.4 MJ/mol, what is the ionization energy of the element?

IE = Energy if Photons – KE of electrons = 165.7 MJ/mol – 25.4 MJ/mol = 140.3 MJ/mol

1. What determines the position and the height (intensity) of each peak in a photoelectron spectrum?

Position = Ionization Energy, height = relative number of electrons

1. Why is the distance of the energy level from the nucleus important in determining the corresponding peak position in the photoelectron spectrum?

When electrons are further from the nucleus, the interactions (Coulombic attractions)

between the electrons and nucleus are weaker, so less energy is needed to remove them.

1. Based on the information provided below, draw a photoelectron spectrum for argon. Indicate the relative intensities and positions of all peaks.

Signal Intensity (Rel. # of e-s)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| e- conf | 1s2 | 2s2 | 2p6 | 3s2 | 3p6 |
| IE (MJ/mol) | - 309.0 | - 31.5 | - 24.1 | - 2.83 | - 1.52 |

-24.1

-1.52

Ionization Energy (MJ/mol)

-309

-31.5

-2.83

Signal Intensity (Rel. # of e-s)

1. Identify the element which produced the photoelectron spectrum shown below. Briefly explain your reasoning. Label each peak with the portion of the electron configuration that it represents.

Magnesium. Three peaks represent 2 electrons each, the third peak is about three times as high. 2 + 2 + 6 + 2 = 12

Magnesium. Three peaks represent 2 electrons each (the 1st, 2nd, and 4th from the left) and the other peak (3rd from left) is about three times as high. 2 + 2 + 6 + 2 = 12, which is the number of electrons in Magnesium. **OR…** The way the peaks correspond to electron configuration reveals that this is magnesium.

2p6

3s2

2s2

1s2

127 125 9 7 5 2 0

Ionization Energy (MJ/mol)

1. Identify if either of the following statements is correct. Briefly explain your reasoning:
2. The PES of Mg2+ is expected to be identical to the photoelectron spectrum of Ne.

FALSE - These two species are isoelectronic, so they will have the same electron configuration which will produce a similar pattern of peaks in the PES, however, since magnesium has two more protons, the attractions between the electrons and the nucleus will be stronger, so the peaks will occur at different energies.

1. The photoelectron spectrum of 35Cl is identical to the PES of 37Cl.

TRUE – The structures of these two isotopes of chlorine only differ in the number of neutrons which do not play a role in the electron configuration nor in the ionization energies, so they will show no differences in the PES.

1. Is it possible to deduce the electron configuration for an atom from its photoelectron spectrum? If so, explain how. If not, explain why not.

Yes, usually. If the entire PES is given the first peak will always represent electrons in the 1s. If there is ONLY the 1s peak, it would be difficult to tell whether the element is hydrogen or helium, because there are no other peaks to establish relative height. If there are multiple peaks, the first one will establish a relative height for two electrons. Moving to the right, each successive peak represents the next energy sublevel, and its height, relative to the first peak, tells us how many electrons in that sublevel. Only the last peak will represent a partially filled sublevel, except in cases of electron promotion.

Signal Intensity (Rel. # of e-s)

**Simulated Photoelectron Spectrum of Potassium**

2.38

29.1

37.1

347

3.93

0.42

347 345 37 35 33 31 29 4 2 0

Ionization Energy (MJ/mol)

1. Why is the peak at 0.42 MJ/mol in the K photoelectron spectrum identified as being in the 4th energy level? On the diagram above, label the portion of the electron configuration represented by each peak.

Higher ionization energy (appearing further to the left on the graph) is a characteristic of electrons which are closer to the nucleus (greater Coulombic attraction due to shorter distance, E=Q1Q2/r), so the 1st peak represents the first energy sublevel in the atom (1s), and the second peak represents the 2s, 3rd peak=2p, 4th= 3s, 5th=3p, etc., Although the 4s is filled during electron arrangements before the 3d, the reverse is NOT true when removing electrons, so in atoms with more than 20 electrons, the 6th peak would represent the 3d, but since potassium and calcium do not have any d electrons, the 6th peak represents the 4s.

1. Circle the element which is most likely to have these ionization energies (listed in kJ/mol) and explain your choice; **1st IE** = 1086 **2nd IE** = 2390 **3rd IE** = 4620 **4th IE** = 6220 **5th IE** = 37820 **6th IE** = 46990

**Al Br C P S Big jump between 4th and 5th IE shows there are 4 valence e-s**

1. On a piece of graph paper, sketch the PES for the following elements; Na, Fe, Si and S. The x axis may show breaks in scale, but relative positions and relative heights of peaks are important.

Signal Intensity (Rel. # of e-s)

Simulated Photoelectron Spectrum for Sulfur

3p4

3p2

Simulated Photoelectron Spectrum for Silicon

3s1

Simulated Photoelectron Spectrum for Sodium

4s2

3d6

3p6

3s2

2p6

2s2

Simulated Photoelectron Spectrum for Iron

1s2

Ionization Energy (MJ/mol)

Signal Intensity (Rel. # of e-s)

1s2

Ionization Energy (MJ/mol)

3s2

2p6

2s2

Signal Intensity (Rel. # of e-s)

3s2

2p6

2s2

Signal Intensity (Rel. # of e-s)

1s2

Ionization Energy (MJ/mol)

2p6

2s2

Ionization Energy (MJ/mol)

1s2