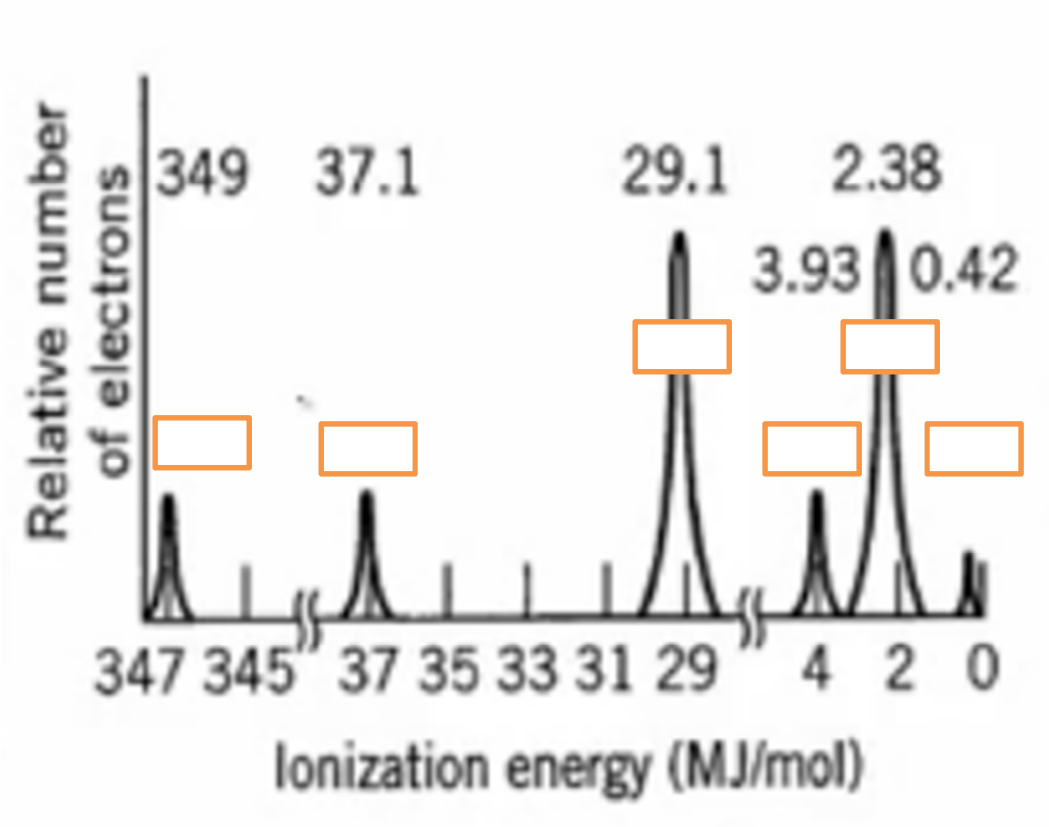
Photoelectron Spectroscopy (PES)

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=NRIqXeY1R_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.

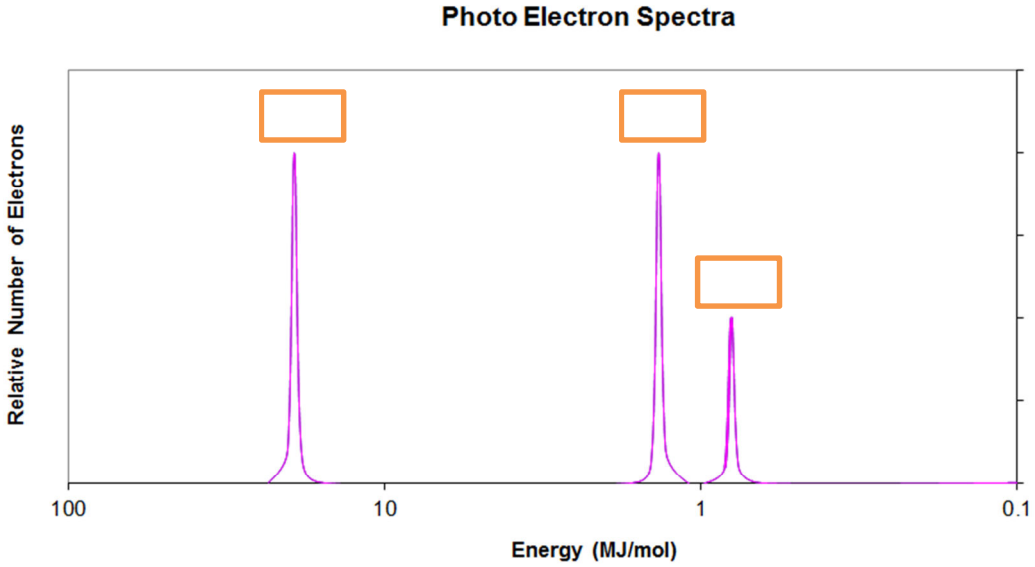
A few points to note:

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

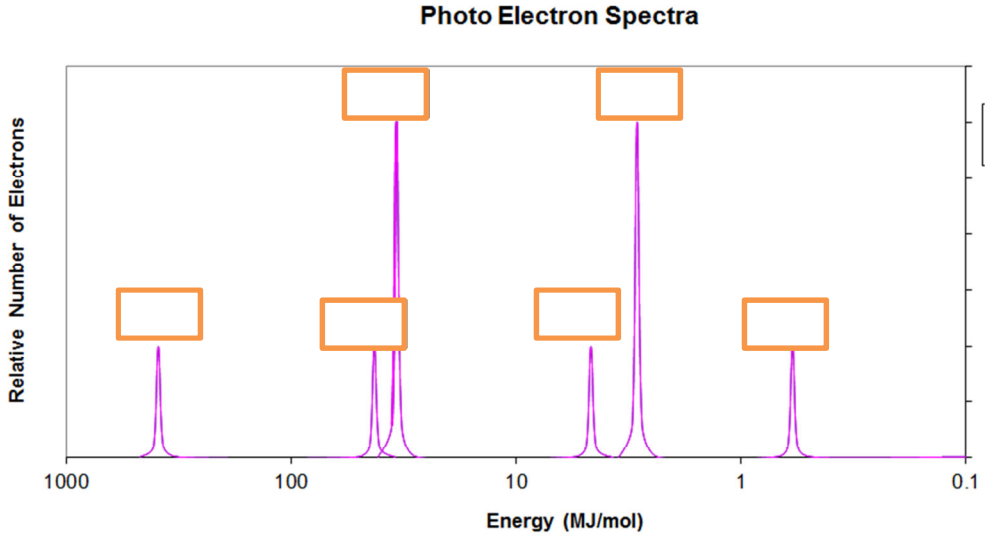
3d electrons would typically have a higher ionization energy than 4p electrons because 3d electrons are closer to the nucleus and therefore have a stronger Coulombic force holding them than 4p electrons. You can identify whether a peak represents 3d or 4p electrons by viewing the relative height of a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

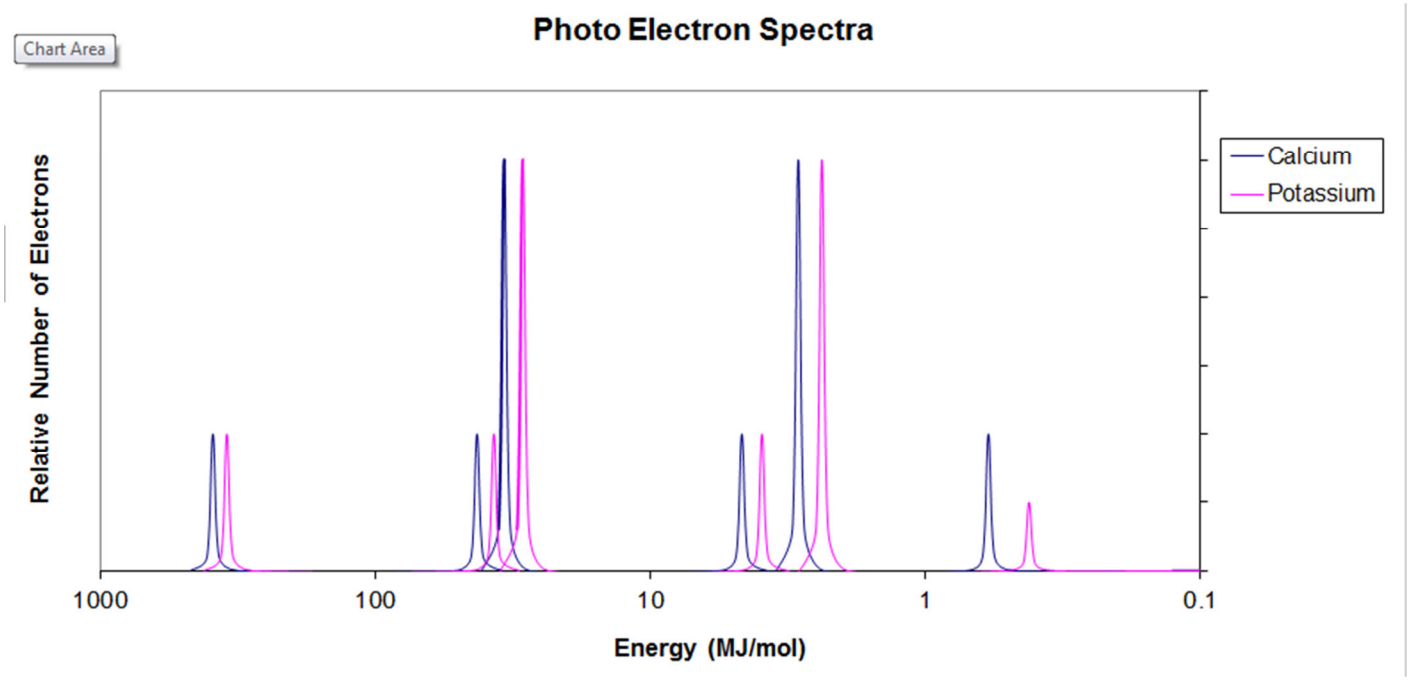


The element is



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.