ChemActivity 7

Photoelectron Spectroscopy

(What Is Photoelectron Spectroscopy?)

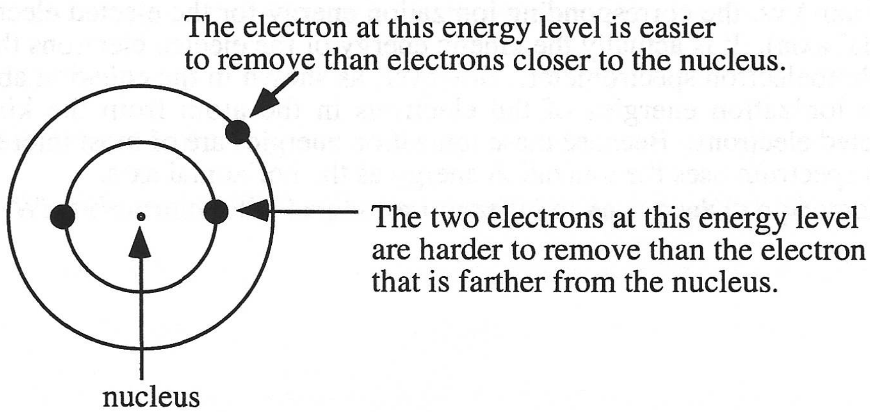
Information

From our previous examination of the ionization energies of the atoms, we proposed a shell model of the atom, and noted that the number of valence electrons in the outermost shell is related to the position of the element in the periodic table, and therefore is an important factor in determining the physical and chemical properties of the element. Within this model, the electrons in an atom are arranged in shells about the nucleus, with the successive shells being farther and farther from the nucleus. The ionization energy described previously is the minimum energy needed to remove an electron from the atom. The most easily removed electron always resides in the valence shell, since that is the shell that is the farthest from the nucleus. For atoms with many electrons, we would expect that the energy needed to remove an electron from an inner shell would be greater than that needed to remove an electron from the valence shell, because an inner shell is closer to the nucleus and is not as fully shielded as the outer valence electrons. Thus, less energy is needed to remove an electron from an $n = 2$ shell than from an $n = 1$ shell, and even less is needed to remove an electron from an $n = 3$ shell. But do all electrons in a given shell require precisely the same energy to be removed? In order to answer this question, we must consider ionization energies in greater detail.

Photoelectron Spectroscopy

From Coulomb's Law, we know that an electron in a given shell will require a certain energy to be separated from the atom. Thus, an electron can be said to occupy an **energy level** in an atom. Within our model, each electron must be in a shell at a particular distance from the nucleus, and the energy levels corresponding to these shells are **quantized**—that is, only certain discrete energy levels should be found.

Figure 1. Each electron within an atom is found at a particular energy level.



Ionization energies may be measured by the electron impact method, in which atoms in the gas phase are bombarded with fast-moving electrons. These experiments give a value for the ionization energy of the electron that is most easily removed from the atom—in other words, the ionization energy for an electron in the highest occupied energy level. An alternative, and generally more accurate, method that provides information on all the occupied energy levels of an atom (that is, the ionization energies of all electrons in the atom) is known as photoelectron spectroscopy; this method uses a photon (a packet of light energy) to knock an electron out of an atom. Electrons obtained in this way are called photoelectrons.

Very high energy photons, such as very-short-wavelength ultraviolet radiation, or even x-rays, are used in this experiment. The gas phase atoms are irradiated with photons of a particular energy. 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, $\frac{1}{2} mv^2$, where v is the velocity of the ejected electron. In other words, the speed of the ejected electron depends on how much excess energy it has received. So, if IE is the ionization energy of the electron and KE is the kinetic energy with which it leaves the atom, we have

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

or, upon rearranging the equation,

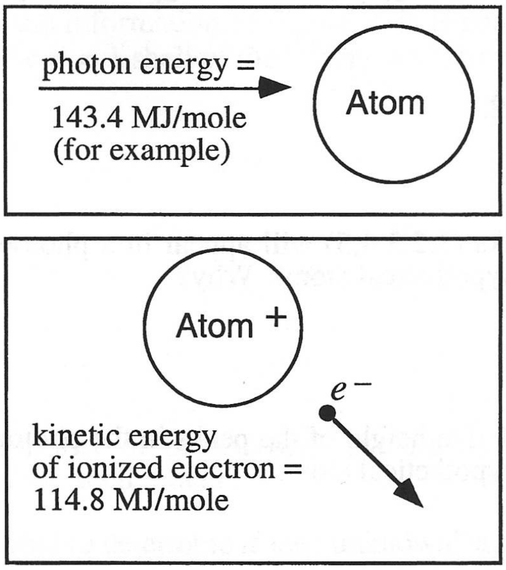
$$IE = E_{photon} - KE$$

Thus, we can find the ionization energy, IE, if we know the energy of the photon and we can measure the kinetic energy of the photoelectron. The kinetic energy of the electrons is measured in a photoelectron spectrometer.

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 energy levels of the atom. Also, because the photons used all have the same energy, electrons ejected from a given energy 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*. This is essentially a plot of the number of ejected electrons (along the vertical axis) vs. the corresponding ionization energy for the ejected electrons (along the horizontal axis). It is actually the kinetic energy of the ejected electrons that is measured by the photoelectron spectrometer. However, as shown in the equation above, we can obtain the ionization energies of the electrons in the atom from the kinetic energies of the ejected electrons. Because these ionization energies are of most interest to us, a photoelectron spectrum uses the ionization energy as the horizontal axis.

Model 1: Photoelectron Spectroscopy.



IE of electron = 28.6 MJ/mole

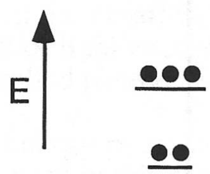
Critical Thinking Questions

1. Show that the IE of the electron in the model is 28.6 MJ/mole.

2. What is meant by the term "energy level"?

3. What determines the height (or intensity) of each peak in a photoelectron spectrum?

4. A *hypothetical* atom in a galaxy far, far away has 2 electrons at one energy level and 3 electrons at another energy level (see energy level diagram below).

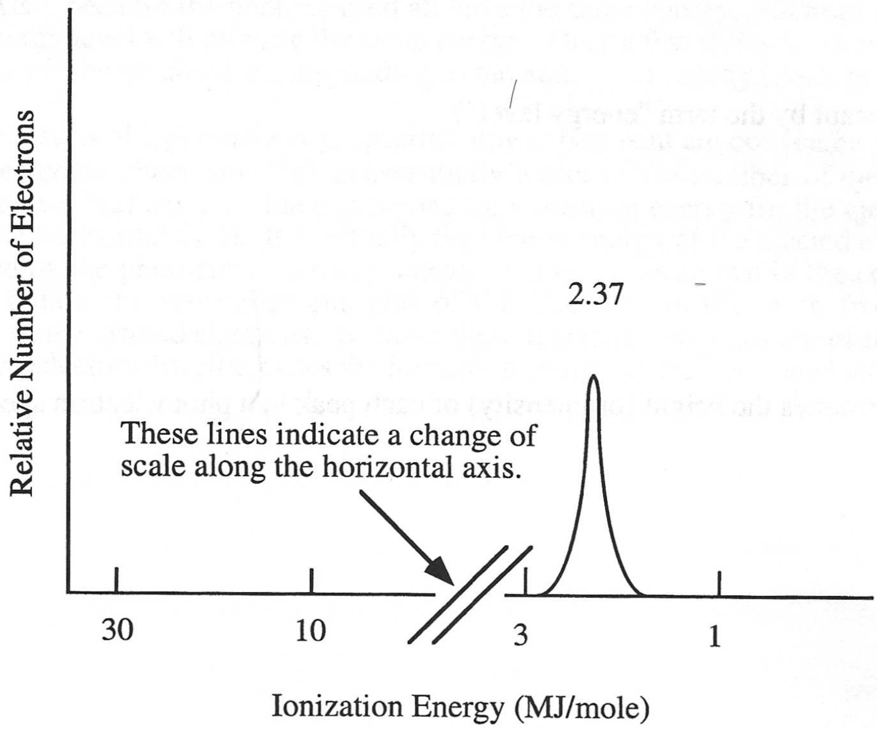


   a) How many peaks (1,2,3,4,5) will appear in a photoelectron spectrum of a sample of this hypothetical atom? Why?

   b) Describe the relative height of the peaks in the photoelectron spectrum of a sample of this hypothetical atom.

5. What determines the position of each peak (where along the horizontal axis the peak is positioned) in a photoelectron spectrum?

Figure 2. A simulated photoelectron spectrum of an "unknown" atom.



Critical Thinking Questions

6. Based solely on the information in Figure 2, is it possible to determine *how many* electrons are in the $n = 1$ shell of the "unknown" atom? Why or why not?

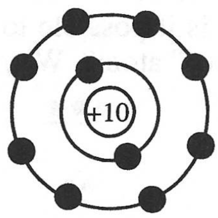
7. Based on the number of peaks (one) and its intensity in Figure 2 and your understanding of the shell model:

   a) Is it possible to determine if the "unknown" atom is H or He? Explain.

   b) Explain why the "unknown" atom cannot be Li.

8. Based on the value of the IE given in Figure 2, identify the "unknown" atom.

Model 2: The Neon Atom.



Let us now predict what the photoelectron spectrum of Ne will look like, based on our current model of the Ne atom. In this model, there are 2 electrons in the n =1 shell, and 8 electrons in the n = 2 shell of a Ne atom. Assuming that all of the electrons in each of the shells has the same energy, we would expect two peaks in the photoelectron spectrum. One peak, from the electrons in the n = 2 shell, should appear at an energy of 2.08 MJ/mole, because that is the first ionization energy of Ne as determined previously. The second peak should be at a significantly higher energy, because it corresponds to the ejection of electrons from the n = 1 shell, which is significantly closer to the nucleus. At this point we do not have any good way of estimating what that energy is, but we know that it will be a lot higher than 2.08 MJ/mole. Finally, we also can predict the relative sizes of the two peaks—that is, the relative areas under the two curves on the spectrum. Recall that in photoelectron spectroscopy, the bombarding photon ejects an electron *at random* from each of the atoms in the sample. Thus, of the 10 electrons in Ne, we would expect that 2/10 of the time the electron is ejected from the n = 1 shell, and 8/10 of the time it is ejected from the n = 2 shell. The size of the peak in the spectrum is determined by the relative **number** of electrons with that IE that are ejected. Thus, the peak at 2.08 MJ/mole should be 4 times as large as the peak at a much higher energy, which corresponds to the ejection of electrons from the n = 1 shell. *To summarize, our prediction is that the photoelectron spectrum of Ne should consist of two peaks, one at an energy of 2.08 MJ/mole and one at much higher energy, and the relative sizes of these two peaks should be 4:1.*

Critical Thinking Questions

9. Why is it expected that 2/10 of the ejected electrons will come from the n = 1 shell, and 8/10 of the electrons from the n = 2 shell?

10. The peak due to the n = 1 shell is predicted to be at a much higher energy than the n = 2 peak because the n = 1 shell is "significantly closer to the nucleus." Why is the distance of the shell from the nucleus important in determining the corresponding peak position in the photoelectron spectrum?

11. Make a sketch of the predicted photoelectron spectrum of Ne based on the description given above. Indicate the relative intensity (peak size) and positions of the two peaks.

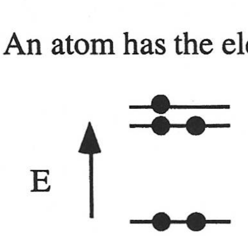
Exercises

1. In a photoelectron spectrum, photons of 165.7 MJ/mole impinge on atoms of a certain element. If the kinetic energy of the ejected electrons is 25.4 MJ/mole, what is the ionization energy of the element?

2. The ionization energy of an electron from the first shell of lithium is 6.26 MJ/mole. The ionization energy of an electron from the second shell of lithium is 0.52 MJ/mole.
   a) Prepare an energy level diagram (similar to the one in CTQ 4) for lithium; include numerical values for the energy levels.

   b) Sketch the photoelectron spectrum for lithium; include the values of the ionization energies.

3. An atom has the electrons in the energy levels as shown below:



Make a sketch of the PES of this element.

CHEMISTRY

A Guided Inquiry

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