PART TWO: Electrostatic Interactions

• In the first section of this course, we were more concerned with structural aspects of molecules. In this section the emphasis is on bonding.

• Bonds in molecules are formed by the interactions between electrons.

• One way of probing the bonds is to “look” at the electrons in the bonds. We can do this by the process of ionization.

[Def] Ionization is the process of removing or adding an electron from an atom or molecule to produce a charged species.

Ionization (oxidative) is the basis of Photoelectron Spectroscopy (PES). You will meet this again in 19-2070 (Structure and Spectroscopy). When light (photons) of energy $E = h\nu$ strikes a material (solid, liquid, gas, solution, etc.) it can cause electrons to move from an occupied (lower lying) orbital to an unoccupied (higher lying) orbital. ⇒ This is called excitation.
If the energy $E = h\nu$ is high enough, the electron can be ejected from the material.

This is called **ionization**.

For the hydrogen atom, the ionization process is:

$$\text{H}(g) + h\nu \rightarrow \text{H}^+(g) + e^- \left( \frac{1}{2}m_e \nu^2 \right)$$

Energy must be conserved in any system, so the energy input (on the left side of the equation) must be equal to the sum of resulting energies (right side).

Conservation of energy means that:

$$h\nu = \Delta E_H(= E_{n\|} - E_{n\perp}) + \frac{1}{2}m_e \nu^2$$

Any “extra” energy left over after the energy required to ionize is accounted for is converted into the **Kinetic Energy** of the ejected electron, $\frac{1}{2}m_e \nu^2$. 
[Def] The ionization potential, $IP$, of an atom or molecule is the minimum energy required to remove an electron from the gaseous atom or molecule in its ground state.

In our H atom example, the following equation is true if the H atom is in the gas phase and is in its ground state electronic configuration ($1s^1$) when ionized:

$$IP = \Delta E_H = E_{nII} - E_{nI}$$

where $nI = 1$; i.e., ground state H
and $nII = \infty$; i.e., electron ejected to form $H^+$

**NOTE:** Because $H^+$ is simply a proton (no electrons), no relaxation occurs after the ionization process. In multi-electron systems, removing an electron from an atom/molecule usually results in a cation in an excited state and a relaxation process is then necessary to attain the cation ground state. This relaxation process is often vibrational/rotational (i.e., thermal transfer energy to surroundings) but other relaxation mechanisms are also possible (e.g., luminescence = emission of a photon).

The ionization potential of the H atom: $IP_H = 13.60 \text{ eV}$
Prof. Albert Einstein correctly explained the *Photoelectric Effect*, for which he won the Nobel Prize in Physics (1921).

*Einstein Photoelectric Law*: \( h\nu = IP + \frac{1}{2}m_e v^2 \)

When Ionization occurs as a result of the interaction of photons with the molecule, it is called *photoionization*. The resulting electrons are called *photoelectrons*.

*Figure 1-8* If a photon of sufficient energy impinges on the hydrogen atom, the result is ionization. The energetics of the ionization are governed by the Einstein photoelectric effect, which states that any photon energy not required to carry out the ionization process, \( IE \), will be manifested as kinetic energy of the ejected electron \((\frac{1}{2}m_e v^2)\).
The principle behind *Photoelectron Spectroscopy* (PES) (see CHEM 2070)

If we know the photon energy $h\nu$ (i.e., we choose the wavelength of light used) and can detect and measure the KE of the ejected electron, we can deduce the ionization potential $IP$.

Let’s look again at the equation:

$$IP = \Delta E_H = E_{nII} - E_{nI}$$

where $nI = 1$; i.e., ground state H

and $nII = \infty$; i.e., electron ejected to form $H^+$

$E_{nI} = E_1$ is then the energy of the gaseous H atom *ground state*. This will be a negative number. (Recall: lower energy = more stable)

$E_{nII} = E_\infty$ is the energy of the “gaseous H atom when the electron is excited to the $n = \infty$ orbital with radius $r = \infty$”, which is just a confusing way of saying it is the energy of the resulting ionized H atom (i.e., $H^+$).

In the case of the H atom, $E_{nII} = E_\infty = 0$

$\therefore IP_{nI} = - E_{nI}$
\[ IP_{nI} = - E_{nI} \]

**Meaning:** the ionization potential is equal to the negative of the orbital energy.

\[ IP_H = 13.60 \text{ eV} \]
and the energy of the 1s orbital for a gaseous H atom is \( E_{1s} = -13.60 \text{ eV} \).

This is known as **Koopmans’ Theorem**.

**WARNING!!!:**
The simple equation \( IP_{nI} = - E_{nI} \) is **exactly true only for 1 electron systems**!

*Koopmans’ Theorem* states that the above equation holds true for multielectron systems if the orbitals of the resulting ion \( M^+ \) are unchanged from those of the neutral molecule or atom \( M \).

\[ \Rightarrow \] This statement is called the “**frozen orbital**” approximation.

Remember that this is just an approximation and must be applied with caution.
The *photoelectron spectroscopy* experiment: a schematic diagram

Typical photon source: HeI source

\[ h\nu = 21.22 \text{ eV} \]

Voltage on the cylindrical analyzer plates is scanned in order to focus e⁻'s of different KE onto the detector.

*Figure 4-20* Schematic diagram of a photoelectron spectrometer. Adapted with permission from H. Bock and P.D. Mollère, *J. Chem. Educ.* 51: 506 (1974).
A note about units…

Ionization Potentials are almost always given in $eV = \text{electron volts}$
This is a useful unit of energy.

[Def] The *electron volt* is the energy acquired by an electron when it is accelerated by a potential difference of 1 Volt.

$1 \text{ eV} = 8065.479 \text{ cm}^{-1}$

$1 \text{ eV particle}^{-1} = 23.060362 \text{ kcal mol}^{-1} = 96.49 \text{ kJ mol}^{-1}$

The Ionization Potential for H is 13.60 eV.

(This is sometimes called a *Rydberg.*)
In all atoms except H, further ionizations are possible.

Example: Li has the ground state configuration 1s\(^2\)2s\(^1\).

\[
\begin{align*}
\text{Li}_{(g)} (1s^22s^1) &\rightarrow \text{Li}^+_{(g)} (1s^2) + e^- & IP_1 = 5.392 \text{ eV}; \quad \text{1}\textsuperscript{st} e^- \text{ ejected from 2s} \\
\text{Li}^+_{(g)} (1s^2) &\rightarrow \text{Li}^{2+}_{(g)} (1s^1) + e^- & IP_2 = 75.638 \text{ eV}; \quad \text{2}\textsuperscript{nd} e^- \text{ ejected from 1s} \\
\text{Li}^{2+}_{(g)} (1s^1) &\rightarrow \text{Li}^{3+}_{(g)} \text{ (nucleus)} + e^- & IP_3 = 122.45 \text{ eV}; \quad \text{3}\textsuperscript{rd} e^- \text{ ejected from 1s}
\end{align*}
\]

It is also possible to remove the 1\textsuperscript{st} electron from the 1s orbital.

\[
\begin{align*}
\text{Li}_{(g)} (1s^22s^1) &\rightarrow \text{Li}^+_{(g)} (1s^12s^1) + e^- & IP_{1s} = 64.84 \text{ eV}; \quad \text{1}\textsuperscript{st} e^- \text{ ejected from 1s}
\end{align*}
\]

**Question**: Why are there three different energies for ejecting electrons from 1s?
TRENDS in $IP$ values across and down the periodic table.
For example, let’s look at the values of $IP_1$ for alkali metals.

Li$_{(g)}$ → Li$_{(g)}^+$ + e$^-$  $IP_1 = 5.392$ eV  [He]$2s^1$
Na$_{(g)}$ → Na$_{(g)}^+$ + e$^-$  $IP_1 = 5.139$ eV  [Ne]$3s^1$
K$_{(g)}$ → K$^+_{(g)}$ + e$^-$  $IP_1 = 4.341$ eV  [Ar]$4s^1$
Rb$_{(g)}$ → Rb$^+_{(g)}$ + e$^-$  $IP_1 = 4.177$ eV  [Kr]$5s^1$
Cs$_{(g)}$ → Cs$^+_{(g)}$ + e$^-$  $IP_1 = 3.894$ eV  [Xe]$6s^1$

Let’s look at the values of $IP_1$ for the 3$^{rd}$ row elements.

Na$_{(g)}$ → Na$_{(g)}^+$ + e$^-$  $IP_1 = 5.139$ eV  [Ne]$3s^1$
Mg$_{(g)}$ → Mg$_{(g)}^+$ + e$^-$  $IP_1 = 7.646$ eV  [Ne]$3s^2$
Al$_{(g)}$ → Al$_{(g)}^+$ + e$^-$  $IP_1 = 5.986$ eV  [Ne]$3s^23p^1$
Si$_{(g)}$ → Si$_{(g)}^+$ + e$^-$  $IP_1 = 8.151$ eV  [Ne] $3s^23p^2$
P$_{(g)}$ → P$^+_{(g)}$ + e$^-$  $IP_1 = 10.486$ eV  [Ne] $3s^23p^3$
S$_{(g)}$ → S$_{(g)}^+$ + e$^-$  $IP_1 = 10.360$ eV  [Ne] $3s^23p^4$
Cl$_{(g)}$ → Cl$_{(g)}^+$ + e$^-$  $IP_1 = 12.967$ eV  [Ne] $3s^23p^5$
Ar$_{(g)}$ → Ar$_{(g)}^+$ + e$^-$  $IP_1 = 15.759$ eV  [Ne] $3s^23p^6 = [Ar]$
Figure 2-2 Variation of atomic ionization energy, $IE_1$, with atomic number. Notice that maximum ionization energies in a given row occur for the noble gases and that the ionization energies of the transition elements are similar.