7.9.1: Biology - Polarizability of Biologically Significant Atoms

Our next goal is to understand *"noncovalent interactions"*. Noncovalent interactions hold together the two strands DNA in the double helix, convert linear proteins to 3D structures that are necessary for enzyme activity, and are the basis for antibody-antigen association. More importantly, noncovalent interactions between water molecules are probably the feature of water that is most important for **biogenesis** (the beginnings of life in the aqueous environment). Obviously, the topics of the next few sections, are of crucial importance to Biology. But in order to understand *noncovalent interactions*, we first need to develop a better understanding of the nature of bonds ranging from **purely covalent** to **ionic**.

In other sections, chemical bonds are divided into two classes: covalent bonds, in which electrons are shared between atomic nuclei, and ionic bonds, in which electrons are transferred from one atom to the other. However, a sharp distinction between these two classes cannot be made. Unless both nuclei are the same (as in H_2), an electron pair is never shared *equally* by both nuclei. There is thus some degree of electron transfer as well as electron sharing in most covalent bonds. On the other hand there is never a *complete* transfer of an electron from one nucleus to another in ionic compounds. The first nucleus always maintains some slight residual control over the transferred electron.

Pure Covalent Bonds

Pure Covalent Bonds are those in which electrons are shared equally between the two atoms involved. This can only happen for pairs of identical atoms. Iodine is a purple/black solid made up of \(\ce{I2}\) molecules, which should have a pure covalent bond by sharing 5p electrons. It's toxic and, in solution, used as a bacteriocide. The net charge on each atom is 0, meaning that the charge is the same as if it were an isolated I atom.

The element iodine$_2$

Another way of showing charge distribution is with an **electrostatic potential map**, where blue indicates positive charge and red indicates negative charge in regions of space around the two nuclei. Notice that the charge distribution is identical on the two iodines, although it is not uniformly distributed on either one (there's a positive region on the ends of the molecule, which probably results from electrons along the axis being drawn into the bond between the nuclei:
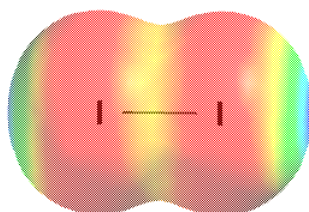
Electrostatic surface map for I_2

Diagram of two spheres merging. There is a gradient of colors spread throughout the sphere. The color is blue on the end of each sphere. This transitions to green then to a minor strip of yellow then to a major portion which is red. The area around where the two sphere merges is yellow.

It is curious that the iodine molecule, with no net charges on either atom, should attract other iodine molecules to make a solid. This exemplifies one kind of attraction important in biomolecules, the *van der Waals attraction,* and we'll discuss that a lot more later. It's not the most important kind of attraction, however. To see how stronger attractions between molecules arise, we need to see what happens when we change the I_2 molecule slightly.

Polarizability of iodine atoms

Suppose we now change one I atom to atoms in Group I: a Li atom, Na atom, and Cs atom in succession. The products, lithium iodide (LiI), sodium iodide (NaI), and cesium iodide (CsI) look like typical ionic compounds; they are all white crystalline solids. NaI is used as a source of "iodine" (actually iodide) for "iodized salt", and looks just like NaCl. But the relatively low melting point of LiI ($459^{\circ}C$) is suggestive of covalent bonding. It is important to realize that all of these compounds exist as crystal lattices, not individual molecules, under ordinary conditions. The individual molecules that we're discussing are gas phase species, modeled in a vacuum. LiI and its crystal lattice are shown here:


Lithium iodide crystals
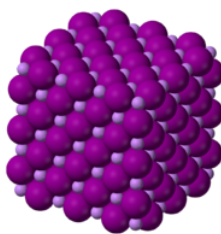
LiI crystal lattice

Three dimensional lithium iodide lattice is made up of a regular pattern of alternating dark purple spheres and light purple spheres. The light purple sphere is significantly smaller than the darker purple sphere.

The electrostatic potential surface confirms that there is sharing of electrons in LiF, because there is only a slight minimum in electron density between the atoms, and Li has clearly distorted the spherical distribution of electrons on I, showing that electrons are shared. In a purely ionic compound, there would be virtually no electron density between the two *spherical* electron clouds of the ions.
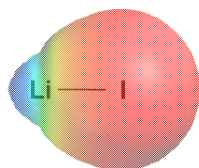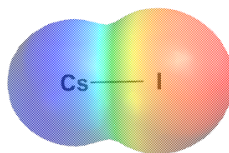
Electrostatic surface map for LiI

A small sphere in blue, labeled "L" "i" merges with a larger sphere, labeled "I", which is red. The region in between has a greenish yellow hue.
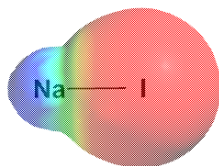
Electrostatic surface map for NaI

A small sphere in blue, labeled "N" "a" merges with a larger sphere, labeled "I", which is red. The region in between has a greenish yellow hue.

Electrostatic surface map for CsI

A sphere in blue, labeled "C" "s" merges with a slightly larger sphere, labeled "I", which is red. The region in between has a greenish yellow hue.

We say that the small Li^+ ion distorts, or **polarizes** the large electron cloud of I^-. Large anions (negative ions) are easily polarized, while smaller ones, like F⁻ are much less polarizable because the electrons are held more tightly. We see that small cations (positive ions) like Li^+ are strong polarizers, while larger cations, like Na^+ or Cs^+ are less effective polarizers.

Because Cs^+ is least effective in polarizing I^-, CsI is the most ionic of the three. The electron cloud around the I^- is almost spherical (undistorted), and there is a definite decrease in electron density in the region between Cs and I. But there is still some sharing of electrons in CsI, because we do not see a region of zero electron density between two spherical ions. This is, in part, due to the fact that Cs is large (near the bottom of Group I), so it is also slightly polarized by the iodine core.

Dipole Moments

The extent of polarization in LiI can be confirmed experimentally. An ion pair like LiI has a negative end (I^-) and a positive end (Li^+). That is, it has two electrical "poles," like the north and south magnetic poles of a magnet. The ion pair is therefore an electrical **dipole** (literally "two poles"), and a quantity known as its dipole moment may be determined from experimental measurements. The **dipole moment** μ is proportional to the size of the separated electrical charges Q and to the distance r between them:

$$\mu = Qr \tag{7.9.1.1}$$

In the LiI ion pair the two nuclei are known to be separated by a distance of 239.2 pm.
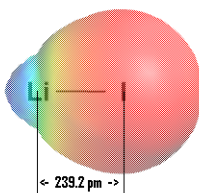
Li-I bond distance

If the bond were completely ionic, there would be a net charge of -1.6021×10^{-19} C (the electronic charge) centered on the I nucleus and a charge of $+1.6021 \times 10^{-19}$ C centered on the Li nucleus:

The dipole moment would then be given (via Equation 7.9.1.1):

$$\mu = Qr$$
$$= 1.6021 \times 10^{-19} C \times 239.2 \times 10^{-12}\, m$$
$$= 3.832 \times 10^{-29}\, C\, m$$

The measured value of the dipole moment for the LiH ion pair is 2.43×10^{-29} C m, which is only about 64% of this value. This can only be because the negative charge is *not* centered on the I nucleus but shifted somewhat toward the Li^+ nucleus. This shift brings the opposite charges closer together, and the experimental dipole moment is smaller than would be expected.

As the bond becomes less polarized, there is less electron sharing and the bond becomes more ionic. In the case of CsI, the charge is 0.822 e, so the dipole moment is 82% of the theoretical value for a totally ionic species. The bond distance is 270.0 pm, so the dipole moment is

$$\mu = Qr$$
$$= 0.822\, e \times 1.6021 \times 10^{-19} C/e \times 270.0 \times 10^{-12} m$$
$$= 3.56 \times 10^{-29}\, C\, m$$

The polarization of the bond in LiI gives it very different properties than the nonpolar I_2. It's interesting that the blood/brain barrier allows nonpolar molecules, like O_2 to pass freely, while more polar molecules may be prohibited. Ionic species, like the Li^+ and I^- that result from dissolving LiI in water, require special carrier-mediated transport mechanism which moderates the ion levels in the brain, even when plasma levels fluctuate significantly.