DIPOLE MOMENTS

When non-identical atoms are joined in a covalent bond, the electron pair will be attracted more strongly to the atom that has the higher electronegativity. As a consequence, the electrons will not be shared equally; the center of the negative charges in the molecule will be displaced from the center of positive charge. Such bonds are said to be polar and to possess partial ionic character, and they may confer a polar nature on the molecule as a whole.

A polar molecule acts as an electric dipole which can interact with electric fields that are created artificially or that arise from nearby ions or polar molecules. Dipoles are conventionally represented as arrows pointing in the direction of the negative end. The magnitude of interaction with the electric field is given by the permanent electric dipole moment of the molecule. The dipole moment corresponding to an individual bond (or to a diatomic molecule) is given by the product of the quantity of charge displaced q and the bond length r:

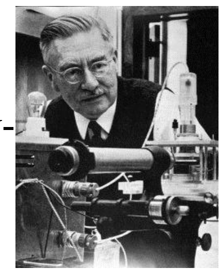
$$\mu = q \times r$$

In SI units, q is expressed in coulombs and r in meters, so μ has the dimensions of C-m. If one entire electron charge is displaced by 100 pm (a typical bond length), then

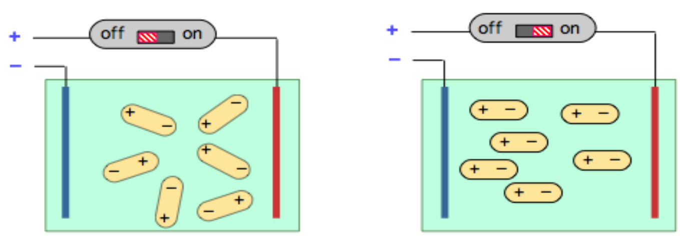
$$\mu = (1.6022 \times 10^{-19}\ \mathrm{C}) \times (10^{-10}\ \mathrm{m}) = 1.6 \times 10^{-29}\ \mathrm{C\text{-}m} = 4.8\ \mathrm{D}$$

The quantity denoted by D, the Debye unit, is still commonly used to express dipole moments. It was named after Peter Debye (1884-1966), the Dutch-American physicist who pioneered the study of dipole moments and of electrical interactions between particles; he won the Nobel Prize for Chemistry in 1936.

<u>How dipole moments are measured</u>

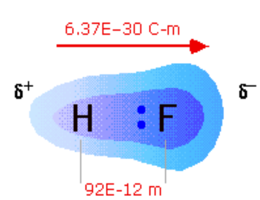


When a solution of polar molecules is placed between two oppositely-charged plates, they will tend to align themselves along the direction of the field. This process consumes energy which is returned to the electrical circuit when the field is switched off, an effect known as electrical capacitance.



Measurement of the capacitance of a gas or solution is easy to carry out and serves as a means of determining the magnitude of the dipole moment of a substance.

Problem Example 1



Estimate the percent ionic character of the bond in hydrogen fluoride from the experimental data shown at the right.

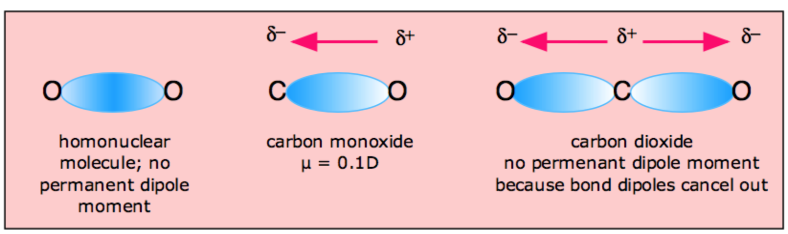
Solution:

$$\frac{6.37\text{E}-30 \text{ C-m}}{92\text{E}-12 \text{ m}} = 6.92 \text{ E}-20 \text{ C} \quad \text{(charge displaced)}$$

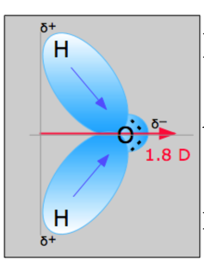
$$\frac{6.92 \text{ E}-20 \text{ C}}{1.60\text{E}-19 \text{ C/electron}} = 0.43 \text{ (ionic character of bond)}$$

<u>Dipole moments as vector sums</u>

In molecules containing more than one polar bond, the molecular dipole moment is just the vector combination of what can be regarded as individual "bond dipole moments". Being vectors, these can reinforce or cancel each other, depending on the geometry of the molecule; it is therefore not uncommon for molecules containing polar bonds to be nonpolar overall, as in the example of carbon dioxide:

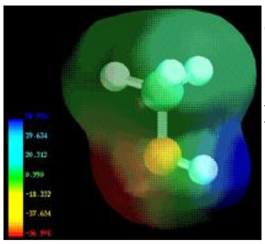


The zero dipole moment of CO_2 is one of the simplest experimental methods of demonstrating the linear shape of this molecule.



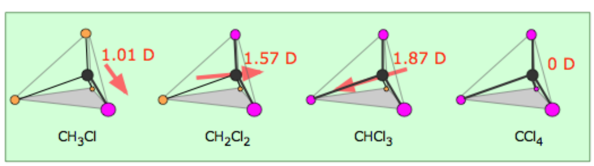
H_2O, by contrast, has a very large dipole moment which results from the two polar H–O components oriented at an angle of 104.5°. The nonbonding pairs on oxygen are a contributing factor to the high polarity of the water molecule.

In molecules containing nonbonding electrons or multiple bonds, the elecronegativity difference may not correctly predict the bond polarity. A good example of this is carbon monoxide, in which the partial negative charge resides on the carbon, as predicted by its negative formal charge.



Electron densities in a molecule (and the dipole moments that unbalanced electron distributions can produce) are now easily calculated by molecular modelling programs. In this example [source] for methanol CH3OH, the blue area centered on hydrogen represents a positive charge, the red area centered where we expect the lone pairs to be located represents a negative charge, while the light green around methyl is approximately neutral.

The manner in which the individual bonds contribute to the dipole moment of the molecule is nicely illustrated by the series of chloromethanes:



(Bear in mind that all four positions around the carbon atom are equivalent in this tetrahedral molecule, so there are only four chloromethanes.)

Source: http://www.chem1.com/acad/webtext/chembond/cb04.html