Molecular Structure 1

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Bonding mechanisms

- Ionic bonds
- Covalent bonds
- van der Waals bonds (several mechanisms)
- The hydrogen bond

General idea

Bonds form because

- of a net attractive force between atoms;
- total $E_{bound} < E_{separate}$.

To break a bond, some energy must be supplied, this is the difference noted above.

Atoms generally attract one another by various mechanisms at large distances, at small separations, repulsive forces dominate.

Potential Energy

A generic expression for two atoms is

$$U = -\frac{A}{r^n} + \frac{B}{r^m}$$

r is internuclear distance, A, n are for attractive forces, B, m for repulsive, n, m are small integers. See figure 11.1.

Ionic bonds

Electrons are transferred from one to another atom. Coulombic due to electrostatic attraction of one ion for other.

$$\mathrm{Na} \xrightarrow{e^-} \mathrm{Cl}$$

so that you have

$$\mathrm{Na}^+ \text{ and } \mathrm{Cl}^-$$

attracting one another.

An *ionization energy* is required to free the electron from Na, and the energy released when the electron is taken on by Cl is the *electron affinity* of Cl.

The difference is the *activation energy* of the NaCl molecule.*

*Chemists don't call ionic associations molecules, but we won't quibble.

At large separations

$$E_{total} = E_{activation}.$$

As the ions approach the energy drops to a minimum, which is

$$-E_{dissasociation}$$

On further approach inner electron shells overlap, which results in repulsion, which is

- partly electrostatic,

- partly due to identity of electrons—fermions cannot occupy same state.

Covalent bonds

Occur when electrons are shared by the two atoms. Stable diatomic atoms often have covalent bonds. An **intermolecular orbital** is formed where one or more electrons are shared at minimum energy.

If two electrons share an intermolecular orbital, they must have antiparallel spins—remember spin provides another quantum number which allows two electrons (fermions) to share the same spatial orbital.

See figures 11.3, 11.4.

van der Waals forces

Molecules can be *polar* (net dipole moment) or *nonpolar* (no permanent net dipole moment).

These attractive forces are due to various *dipole interactions:*

- dipole-dipole force—between polar atoms.

- dipole-induced force—dipole of a polar atom induces a dipole moment on a nonpolar atom.

- dispersion force—nonpolar atoms have random charge fluctuations, which induce effective dipole moments on each other, which are QM *correlated* in time—weak average attractive force.

Van der Waals forces fall off as $1/r^7$ in space.