

Lecture : 4

Types of Bonding (part II) (16-31)

Primary bonding: e^- are transferred or shared
Strong (100-1000 KJ/mol or 1-10 eV/atom)

- Ionic: Strong Coulomb interaction among negative atoms (have an extra electron each) and positive atoms (lost an electron). Example - Na^+Cl^-
- Covalent: electrons are shared between the molecules, to saturate the valency. Example - H_2
- Metallic: the atoms are ionized, losing some electrons from the valence band. Those electrons form an electron sea, which binds the charged nuclei in place

Secondary Bonding: no e^- transferred or shared
Interaction of atomic/molecular dipoles
Weak (< 100 KJ/mol or < 1 eV/atom)

- Fluctuating Induced Dipole (inert gases, H_2 , Cl_2 ...)
- Permanent dipole bonds (polar molecules - H_2O , HCl ...)
- Polar molecule-induced dipole bonds (a polar molecule induces a dipole in a nearby nonpolar atom/molecule)

Re

Ionic Bonding (I)

Ionic Bonding is typical for elements that are situated at the horizontal extremities of the periodic table.

Atoms from the left (metals) are ready to give up their valence electrons to the (non-metallic) atoms from the right that are happy to get one or a few electrons to acquire stable or noble gas electron configuration.

As a result of this transfer mutual ionization occurs: atom that gives up electron(s) becomes positively charged ion (cation), atom that accepts electron(s) becomes negatively charged ion (anion).^e

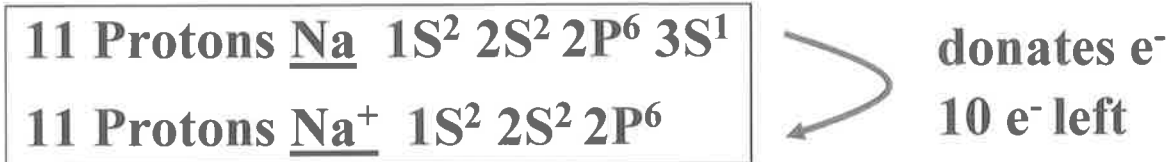
Formation of ionic bond:

1. Mutual ionization occurs by electron transfer (remember electronegativity table)
 - Ion = charged atom
 - Anion = negatively charged atom
 - Cation = positively charged atom
2. Ions are attracted by strong coulombic interaction
 - Oppositely charged atoms attract each other
 - An ionic bond is non-directional (ions may be attracted to one another in any direction)

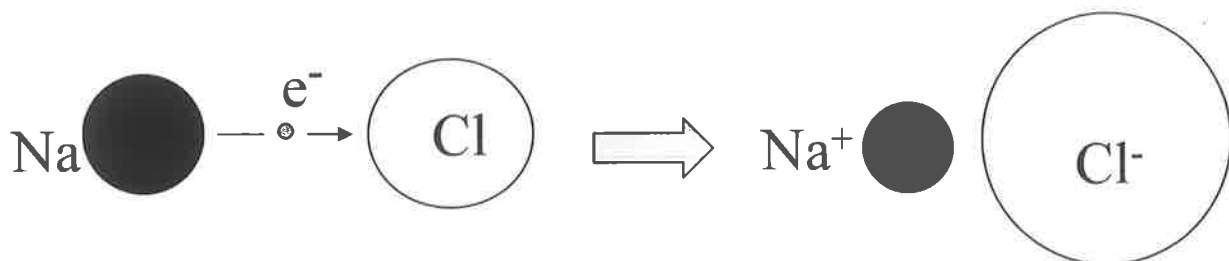
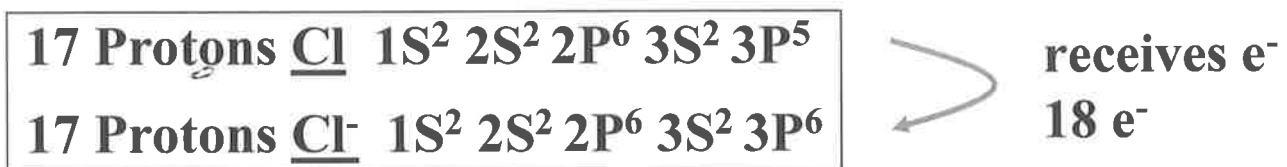
Ionic Bonding (II)

Example: table salt (NaCl)

Na has 11 electrons, 1 more than needed for a full outer shell (Neon)



Cl has 17 electron, 1 less than needed for a full outer shell (Argon)

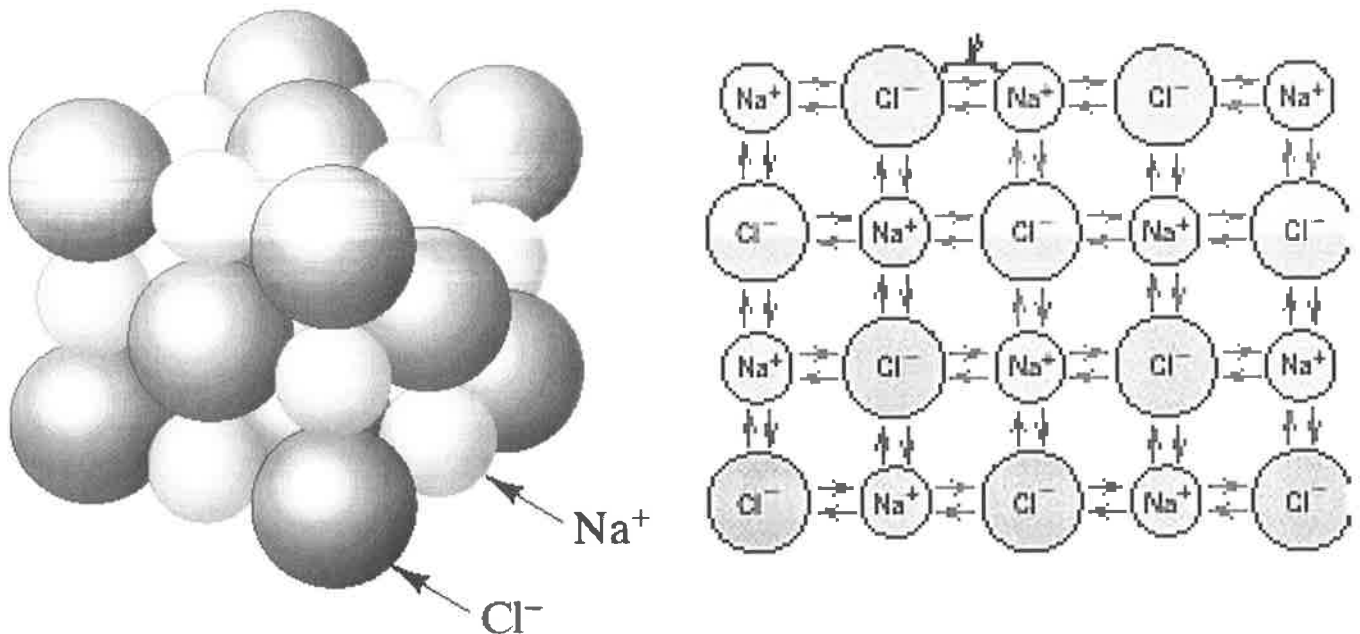


- Electron transfer reduces the energy of the system of atoms, that is, electron transfer is energetically favorable
- Note relative sizes of ions: Na shrinks and Cl expands

Ionic Bonding (III)

A strong electrostatic attraction between positively charged Na^+ ions and negatively charged Cl^- atoms along with Na^+ - Na^+ and Cl^- - Cl^- repulsion result in the NaCl crystal structure which is arranged so that each sodium ion is surrounded by Cl^- ions and each Na^+ ion is surrounded by Cl^- ions, see the figure on the left.

Any mechanical force that tries to disturb the electrical balance in an ionic crystal meets strong resistance: ionic materials are strong and brittle. In some special cases, however, significant plastic deformation can be observed, e.g. NaCl single crystals can be bent by hand in water.



Ionic bonds: very strong, nondirectional bonds

Ionic Bonding (IV)

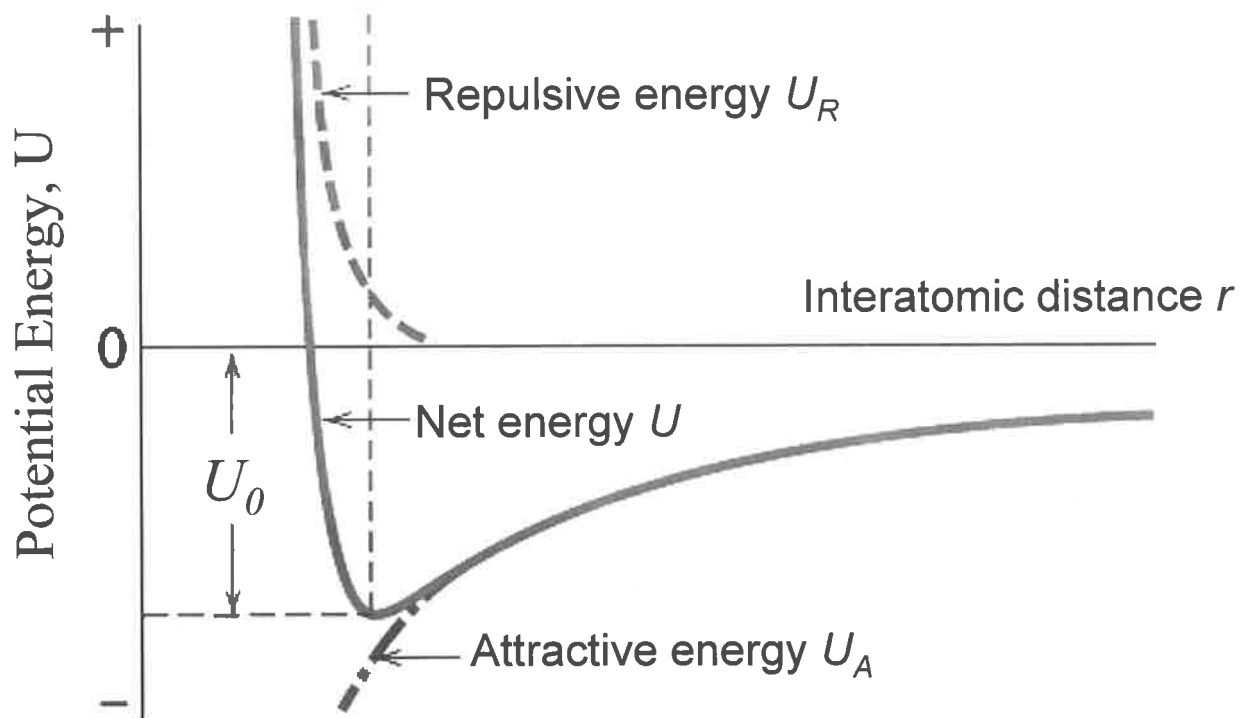
Attractive coulomb interaction between charges of opposite sign:

$$U_A = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_1 q_2}{r} = -\frac{A}{r}$$

Repulsion due to the overlap of electron clouds at close distances (Pauli principle of QM):

$$U_R = \frac{B}{r^n}$$

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



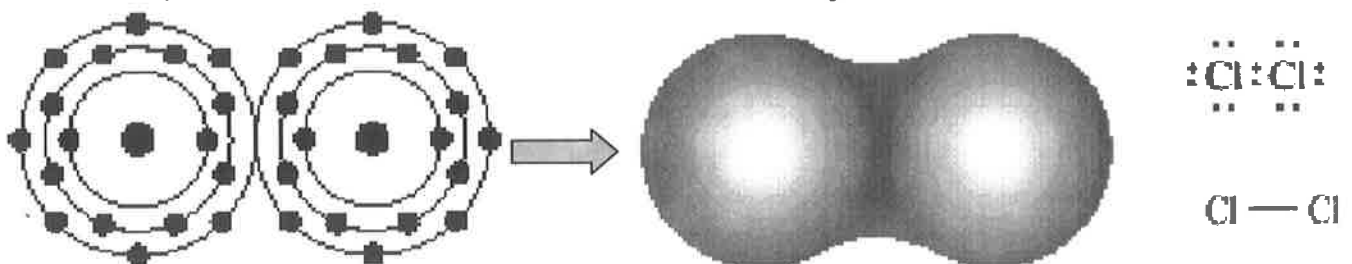
Covalent Bonding (I)

In covalent bonding, electrons are shared between the molecules, to saturate the valency. In this case the electrons are not transferred as in the ionic bonding, but they are localized between the neighboring ions and form directional bond between them. The ions repel each other, but are attracted to the electrons that spend most of the time in between the ions.

Formation of covalent bonds:

- Cooperative sharing of valence electrons
- Can be described by orbital overlap
- Covalent bonds are HIGHLY directional
- Bonds - in the direction of the greatest orbital overlap
- Covalent bond model: an atom can covalently bond with at most $8 - N'$, $N' =$ number of valence electrons

Example: Cl_2 molecule. $Z_{\text{Cl}} = 17$ ($1\text{S}^2 2\text{S}^2 2\text{P}^6 3\text{S}^2 3\text{P}^5$)
 $N' = 7$, $8 - N' = 1 \rightarrow$ can form only one covalent bond

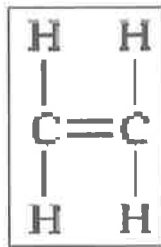


Covalent Bonding (II)

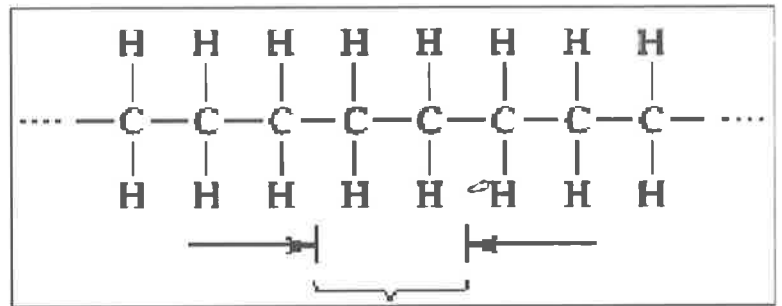
Example: Carbon materials. $Z_c = 6$ ($1S^2 2S^2 2P^2$)

$N' = 4$, $8 - N' = 4 \rightarrow$ can form up to four covalent bonds

ethylene molecule:



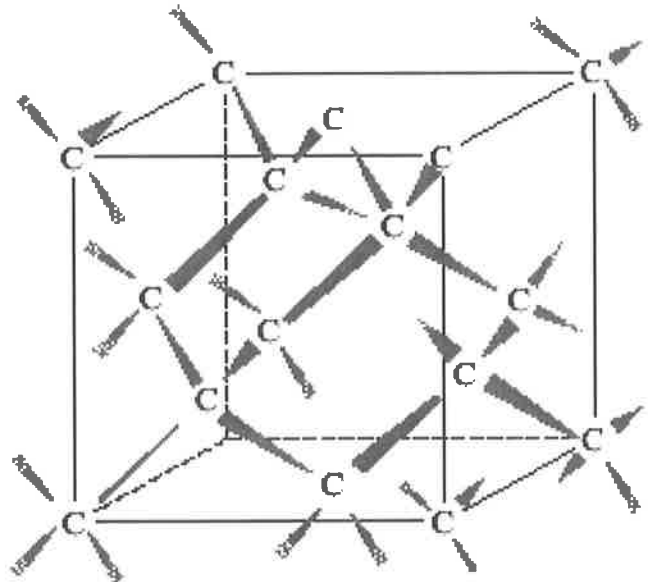
polyethylene molecule:



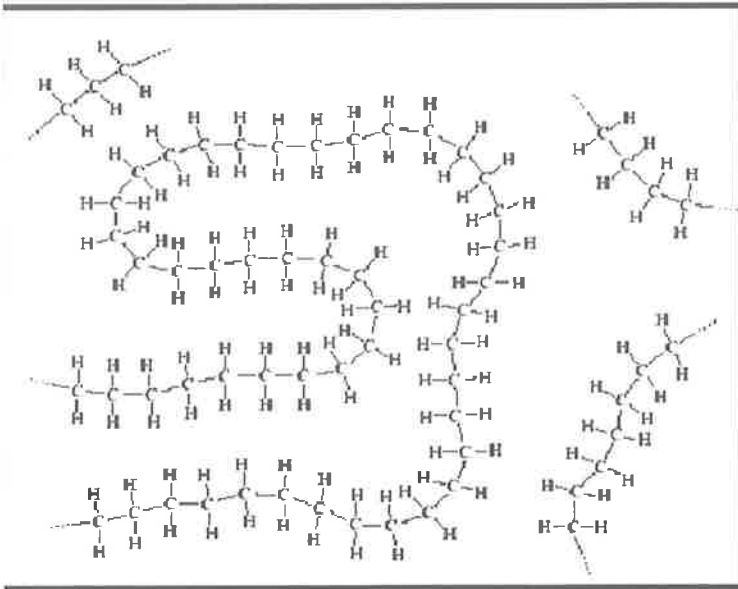
ethylene mer

diamond:

(each C atom has four covalent bonds with four other carbon atoms)

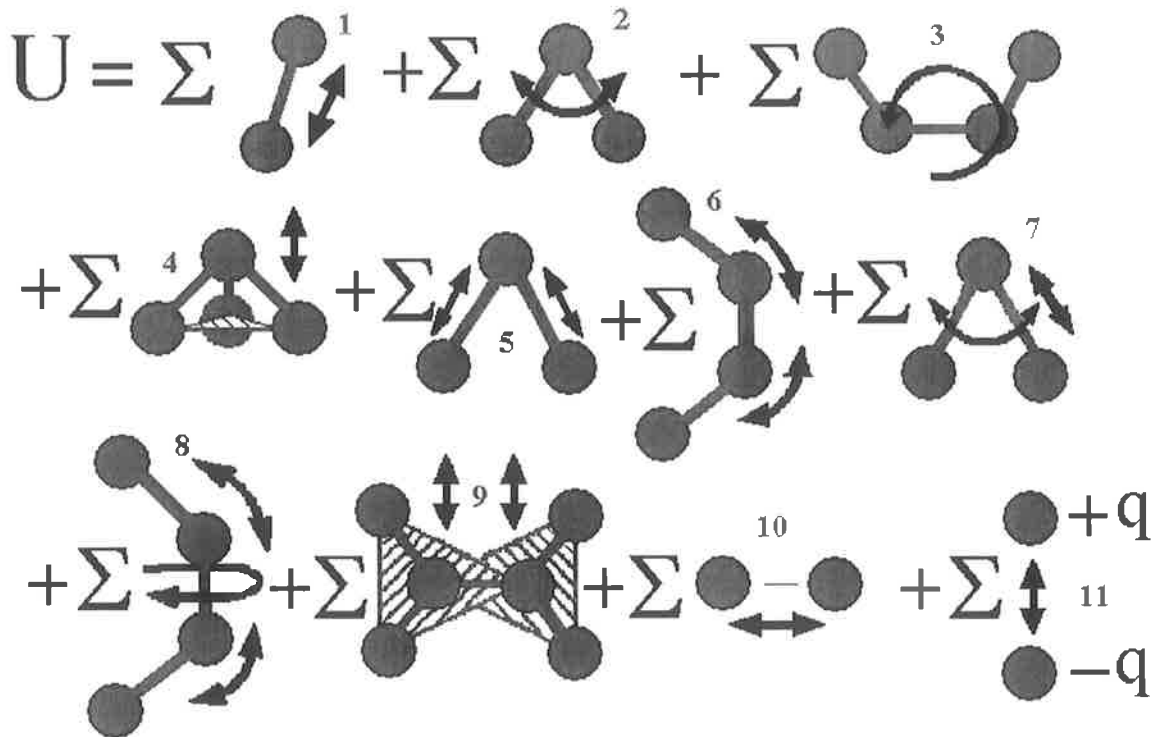


Covalent Bonding (III)



2-D schematic of the “spaghetti-like” structure of solid polyethylene

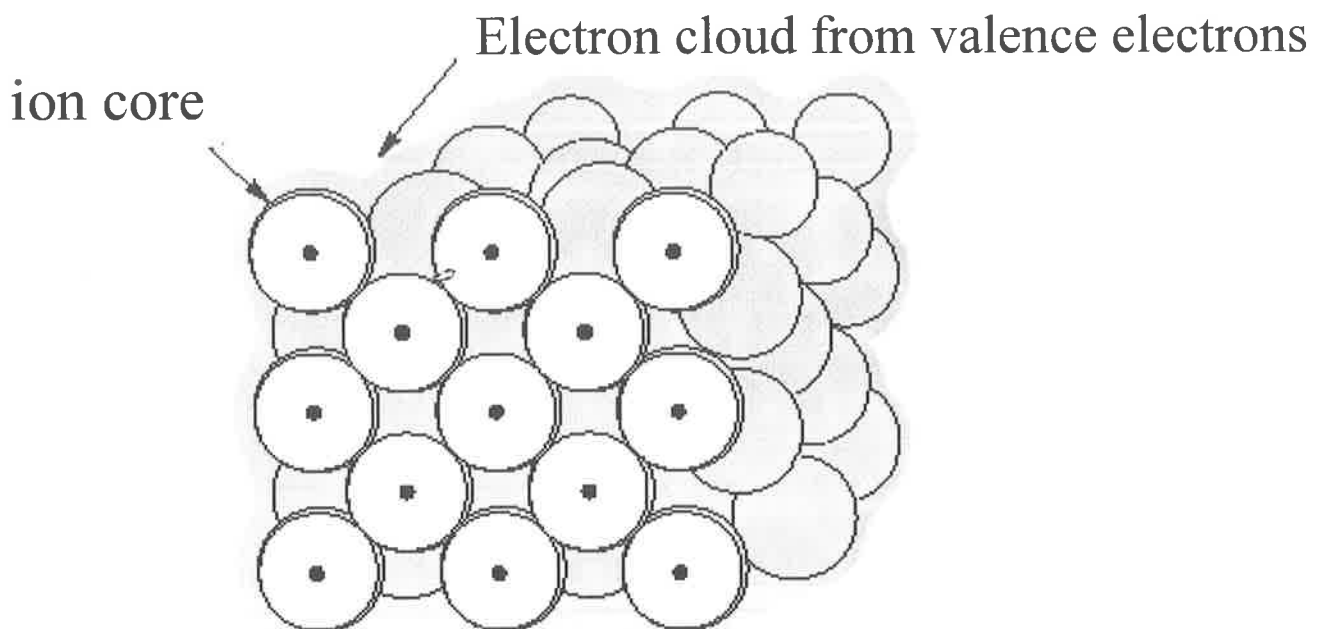
The potential energy of a system of covalently interacting atoms depends not only on the distances between atoms, but also on angles between bonds...



Metallic Bonding

Valence electrons are detached from atoms, and spread in an 'electron sea' that "glues" the positive ions together.

- A metallic bond is non-directional (bonds form in any direction) → atoms pack closely



The “bonds” do not “break” when atoms are rearranged – metals can experience a significant degree of plastic deformation.

Examples of typical metallic bonding: Cu, Al, Au, Ag, etc. Transition metals (Fe, Ni, etc.) form mixed bonds that are comprising of metallic bonds and covalent bonds involving their 3d-electrons. As a result the transition metals are more brittle (less ductile) than Au or Cu.

Secondary Bonding (I)

Secondary = van der Waals = physical (as opposite to chemical bonding that involves e^- transfer) bonding results from interaction of atomic or molecular dipoles and is weak, ~ 0.1 eV/atom or ~ 10 kJ/mol.



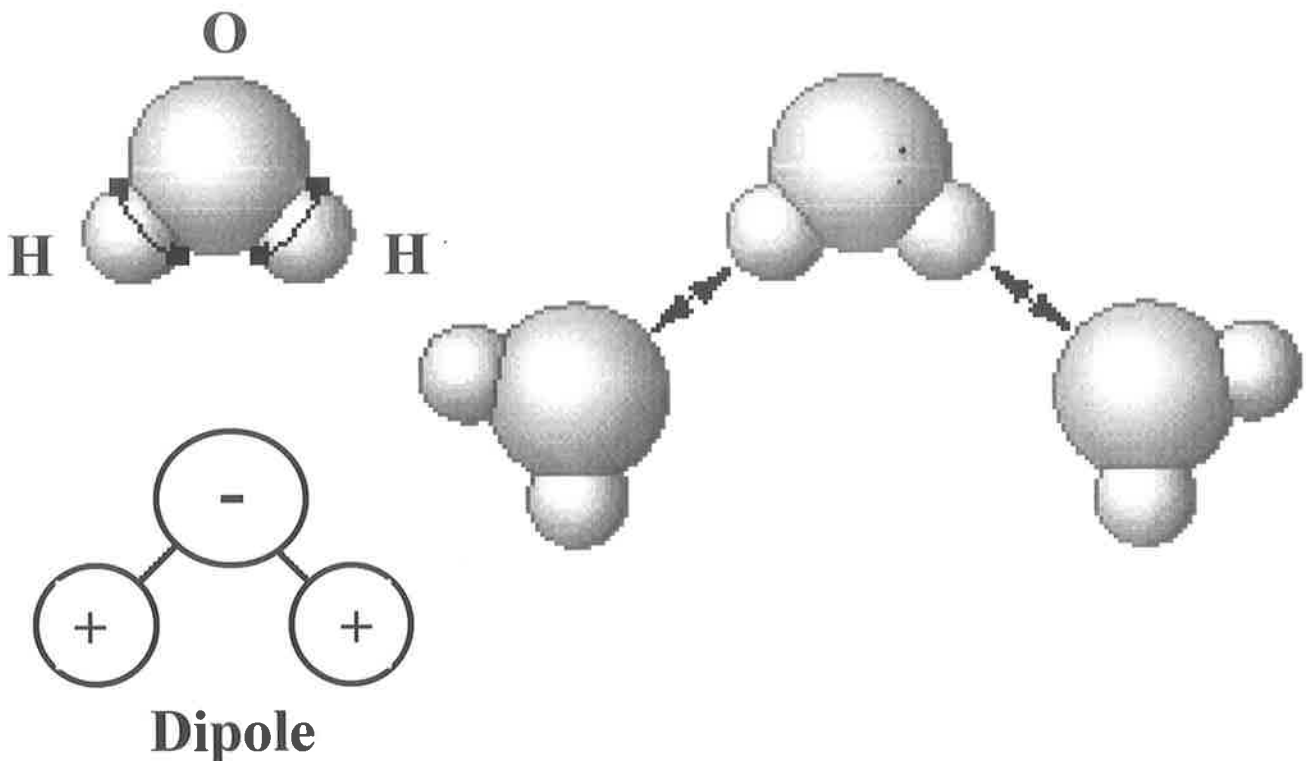
Permanent dipole moments exist in some molecules (called **polar molecules**) due to the asymmetrical arrangement of positively and negatively regions (HCl, H₂O). Bonds between adjacent polar molecules – **permanent dipole bonds** – are the strongest among secondary bonds.

Polar molecules can induce dipoles in adjacent non-polar molecules and bond is formed due to the attraction between the permanent and induced dipoles.

Even in electrically symmetric molecules/atoms an electric dipole can be created by fluctuations of electron density distribution. Fluctuating electric field in one atom A is felt by the electrons of an adjacent atom, and induce a dipole momentum in this atom. This bond due to fluctuating induced dipoles is the weakest (inert gases, H₂, Cl₂).

Secondary Bonding (II)

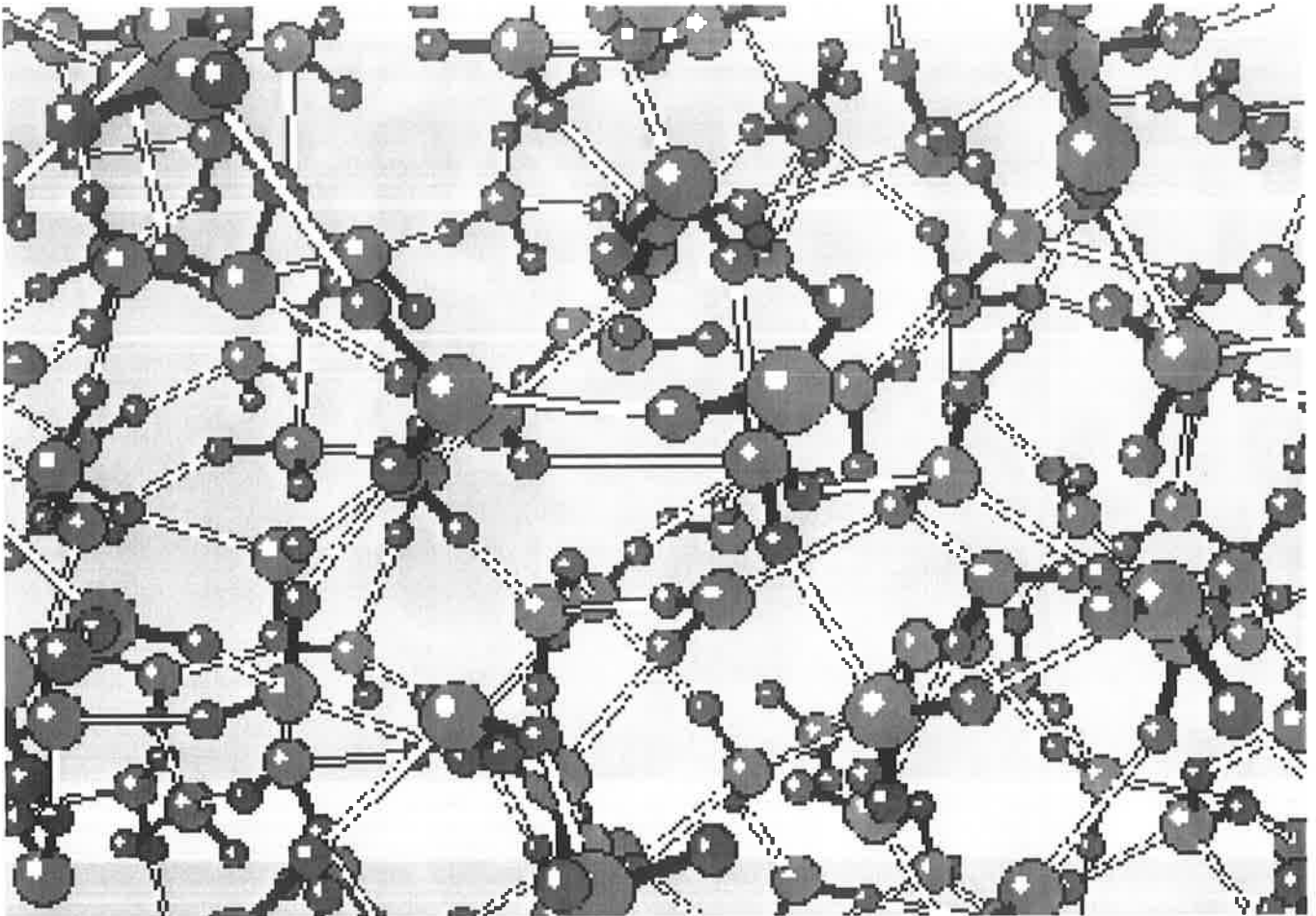
Example: hydrogen bond in water. The H end of the molecule is positively charged and can bond to the negative side of another H₂O molecule (the O side of the H₂O dipole)



“Hydrogen bond” – secondary bond formed between two **permanent dipoles** in adjacent water molecules.

Secondary Bonding (III)

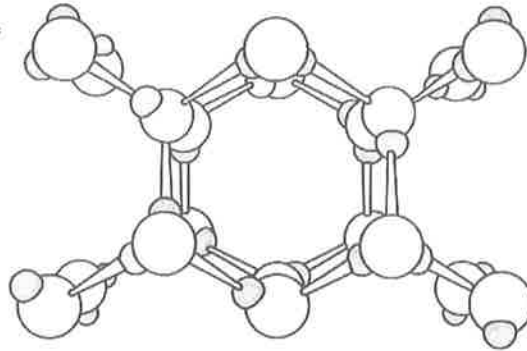
Hydrogen bonding in liquid water
from a molecular-level simulation



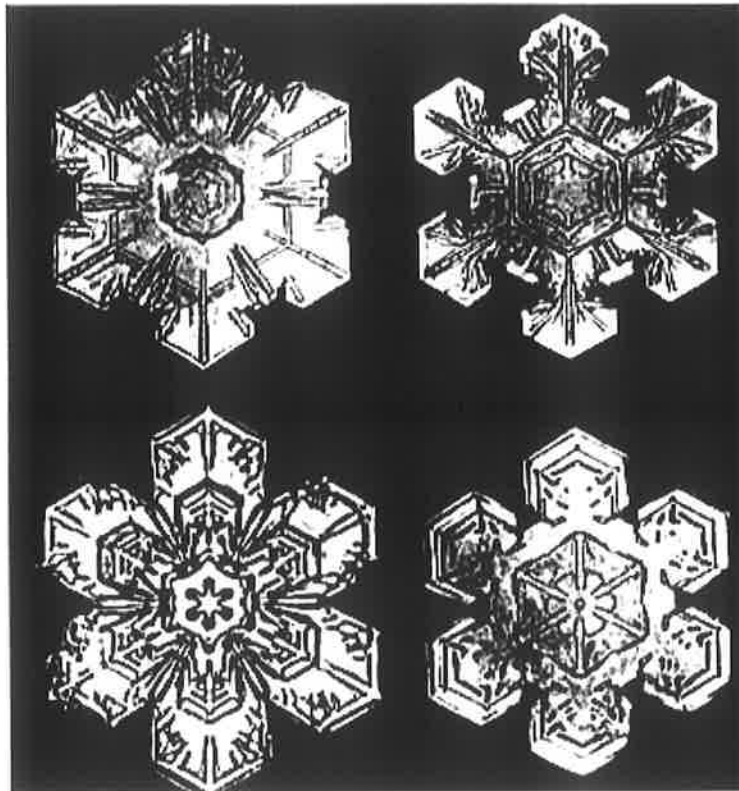
Molecules: Primary bonds inside, secondary bonds among each other

Secondary Bonding (IV)

The Crystal Structures of Ice



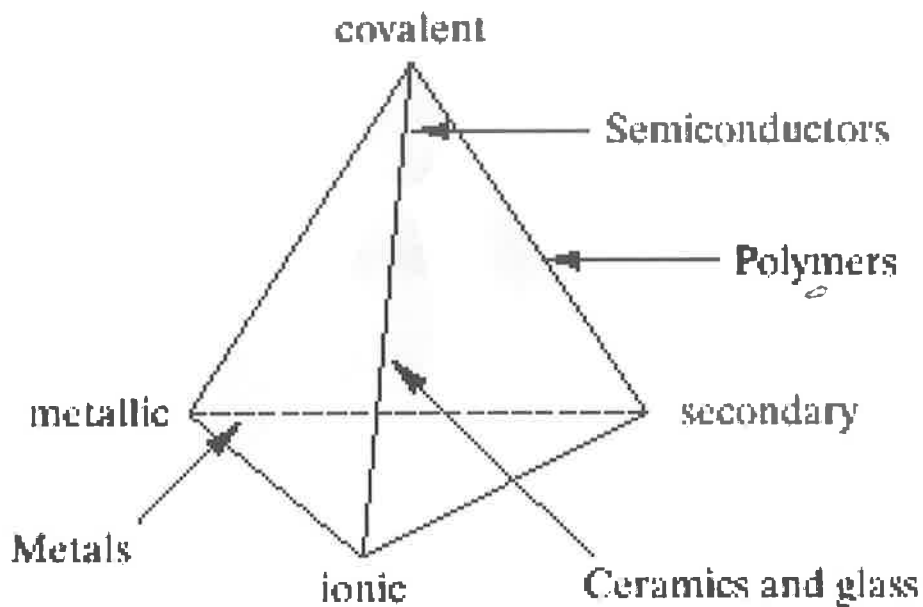
Hexagonal Symmetry of Ice Snowflakes



Figures by Paul R. Howell

Bonding in real materials

In many materials more than one type of bonding is involved (ionic and covalent in ceramics, covalent and secondary in polymers, covalent and ionic in semiconductors).



Examples of bonding in Materials:

Metals: Metallic

Ceramics: Ionic / Covalent

Polymers: Covalent and Secondary

Semiconductors: Covalent or Covalent / Ionic

Correlation between bonding energy and melting temperature

Table 2.3 Bonding Energies and Melting Temperatures for Various Substances

<i>Bonding Type</i>	<i>Substance</i>	<i>Bonding Energy</i>		<i>Melting Temperature (°C)</i>
		<i>kJ/mol (kcal/mol)</i>	<i>eV/Atom, Ion, Molecule</i>	
Ionic	NaCl	640 (153)	3.3	801
	MgO	1000 (239)	5.2	2800
Covalent	Si	450 (108)	4.7	1410
	C (diamond)	713 (170)	7.4	>3550
Metallic	Hg	68 (16)	0.7	-39
	Al	324 (77)	3.4	660
	Fe	406 (97)	4.2	1538
	W	849 (203)	8.8	3410
van der Waals	Ar	7.7 (1.8)	0.08	-189
	Cl ₂	31 (7.4)	0.32	-101
Hydrogen	NH ₃	35 (8.4)	0.36	-78
	H ₂ O	51 (12.2)	0.52	0

Summary

Make sure you understand language and concepts:

- Atomic mass unit (amu)
- Atomic number
- Atomic weight
- Bonding energy
- Coulombic force
- Covalent bond
- Dipole (electric)
- Electron state
- Electronegative
- Electropositive
- Hydrogen bond
- Ionic bond
- Metallic bond
- Mole
- Molecule
- Periodic table
- Polar molecule
- Primary bonding
- Secondary bonding
- Van der Waals bond
- Valence electron