Lecture C3a Microscopic to Macroscopic, Part 3: Hydrogen Bonding and Metal-Ligand Bonding

Last time we examined various types of noncovalent intermolecular interactions:

Type of interaction	Typical energy (kJ⋅mol ⁻¹)	Interacting species
ion-ion	250	ions only
ion-dipole	15	ions and polar molecules
dipole-dipole	2	stationary polar molecules
	0.3	rotating polar molecules
dipole-induced dipole	2	at least one molecule must be polar
London (dispersion) [†]	2	all types of molecules
hydrogen bonding	20	molecules containing N, O, F; the link is a shared H atom

TABLE 5.1 Interionic and Intermolecular Interactions*

*The total interaction experienced by a species is the sum of all the interactions in which it can participate.

[†]Also known as the induced-dipole–induced-dipole interaction.

C-H covalent bond in $CH_4 = 440 \text{ kJ mol}^{-1}$

Last time we examined various types of noncovalent intermolecular interactions...

- a. ion-ion
- b. ion-dipole
- c. electric dipole-electric dipole
- d. magnetic dipole-magnetic dipole
- e. dispersion forces
- f. hydrogen bonding
- g. metal-ligand bonding

Let's look at hydrogen bonding next!

f. hydrogen bonding



Hydrogen Fluoride, HF

HF hydrogen bond energy - a whopping 40 kJ mol⁻¹

f. hydrogen bonding



carboxylic acid dimer

Hydrogen bonds are formed by electronegative atoms (e.g., O, N, F) sharing their lone pair electrons with hydrogen atoms. The electronegative donor creates a positively charged H atom that can then interact with the electronegative acceptor. Both the donor and acceptor need to be a highly electronegative atom: e.g., O, N, F



f. hydrogen bonding



The H-bond donor shares the Hydrogen atom; the acceptor shares the lone pair. OH stretching frequencies in Hydrogen Bonds



carboxylic acid dimer

Formic Acid (R=H): OH 3570 cm-I monomer OH 3080 cm-I dimer

 $\Delta v = 490 \text{ cm}^{-1}$



HF HF 3960 cm-1 monomer HF 3450 cm-1 hydrogen bonded $\Delta v = 510 \text{ cm}^{-1}$

Frequency decreases (smaller k), but the Intensity increases : $\Delta\mu/\Delta x$ is substantially larger when H-bonding occurs

Hydrogen Bonding Networks



Water is highly hydrogen bonded

There are 15 known phases of ice. Here is the crystal structure for the most familiar to us, Ice I_h (hexagonal ice).



This structure was obtained from a combination of x-ray diffraction (for the oxygen atoms) and neutron diffraction (for the hydrogen atoms). Glucose is a molecule that has a lot of OH groups (5): $C_6H_{12}O_6$ or $C_6H_7O(OH)_5$



A six-membered ring sugar or carbohydrate molecule. Other sugars: fructose, sucrose, ribose. Cellulose is a polymer molecule created by linking many glucose units together.



Cellulose polymers can hydrogen bond with themselves in many ways, giving rigidity to the solid. Proteins can have many hydrogen bonds as well: e.g., beta sheet (anti-parallel) structure





Every sugar unit has one of four nitrogenous bases attached:

- G Guanine C - Cytosine A - Adenine
- T Thymine



three hydrogen bonds

R



two hydrogen bonds





3D structure of DNA is a double helix.

James Watson and Francis Crick first proposed the double helix model in 1953.

Their double-helix model was based on an X-ray diffraction image taken by Rosalind Franklin and Raymond Gosling in 1952.





We now call this the Watson-Crick model of DNA.

- a. ion-ion
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Final topic: lets's look at metal-ligand bonding!

Is it covalent or non-covalent?

g. metal-ligand bonding

Lone pairs of small molecules can interact with the d and f electrons of metals to form complexes. The small molecules are called "ligands."



In aqueous solution:

 $[Ni(H_2O)_6]^{2+}$ is green.

 $[Ni(NH_3)_6]^{2+}$ is violet.

Multi-Ligand Molecules:

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••
NH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>
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Ethylene diamine - en





 $M^{n+} + Y^{4-} \longrightarrow MY^{n-4}$

Ethylene diamine tetraacetic acid (EDTA) has six ligands and is a great metal chelator.

g. metal-ligand bonding

Metal-CO (metal-carbonyls) are strong ligand bonds





CO HOMO (5σ)

CO LUMO $(I\pi^*)$

Both the CO HOMO and LUMO are involved in metal ligand bonding

g. metal-ligand bonding

Metal Carbonyls: "Pi back bonding"



Both the CO HOMO and LUMO are involved in metal ligand bonding

g. metal-ligand bonding

Back bonding to the HOMO reduces the bond order of CO, so a the CO stretching frequency is lowered in the complexes



Infrared Spectroscopy!

Compound	v _{co}
со	2143 cm ⁻¹
Ti(CO) ₆ ⁻²	1748 cm ⁻¹
V(CO) ₆ ⁻¹	1859 cm ⁻¹
Cr(CO) ₆	2000 cm ⁻¹
Mn(CO) ₆ +	2100 cm ¹
Fe(CO) ₆ ²⁺	2204 cm ⁻¹

CO infrared stretch:

2143 cm⁻¹ gas phase

g. metal-ligand bonding

Nickel Tetracarbonyl

CO infrared stretch:

2143 cm⁻¹ gas phase

2059 cm⁻¹ complex



Ni: 4s²3d⁸

 $10 + (4 \times 2) = 18$ electron rule!

g. metal-ligand bonding

Iron Pentacarbonyl

Fe(CO)₅

CO infrared stretch:

2143 cm⁻¹ gas phase 2022 and 2000 cm⁻¹ complex



 $8 + (5 \times 2) = 18$ electron rule!

g. metal-ligand bonding

Chromium Hexacarbonyl

 $Cr(CO)_6$

CO infrared stretch:

2143 cm⁻¹ gas phase

2000 cm⁻¹ complex



Cr: 4s¹3d⁵

 $6 + (6 \times 2) = 18$ electron rule!

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Metal carbonyl bonds in 18e systems range in energy from 100-200 kJ mol⁻¹



There are many types of metal-ligand bonds, varying from very weak to very strong. This is called Inorganic Chemistry!