C7790 Introduction to Molecular Modelling
TSM Modelling Molecular Structures

Lesson 22
Classification of Interactions

PS/2020 Distant Form of Teaching: Rev1

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Context

macroworld **microworld**

states
(thermodynamic properties, G, T,...)

phenomenological thermodynamics

equilibrium (equilibrium constant)
kinetics (rate constant)

free energy
(Gibbs/Helmholtz)

partition function

statistical thermodynamics

microstates
(mechanical properties, E)
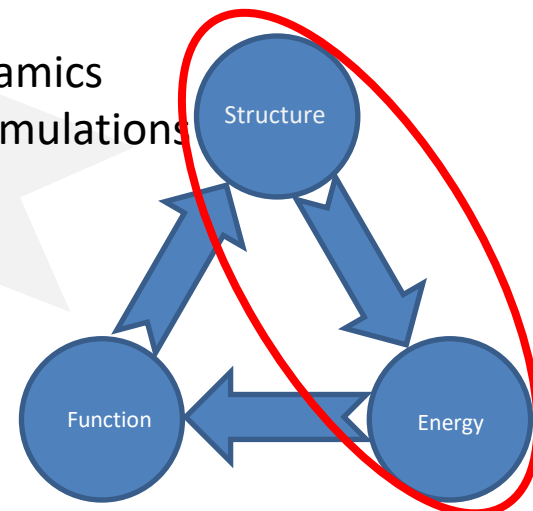
microstate ≠ microworld

Description levels (model chemistry):
- quantum mechanics
  - semiempirical methods
  - ab initio methods
  - post-HF methods
  - DFT methods
- molecular mechanics
- coarse-grained mechanics

Simulations:
- molecular dynamics
- Monte Carlo simulations
- docking
- ...

Structure

Function   Energy

Revision: Schrödinger Equation

Schrödinger equation by its essence provide ultimate description of (bio)chemical systems:

$$\widehat{H}\psi_k(\mathbf{r}, \mathbf{R}) = E_k(\mathbf{R})\psi_k(\mathbf{r}, \mathbf{R})$$

➤ Solution of SR is the **potential energy** E_k and **wavefunction** ψ_k.
  ➤ the potential energy quantify strength of inter-atomic interactions
  ➤ the wavefunction provides further information

Remember: use of SE has some dark sides:
  ➤ one-electron approximation (correlation energy)
  ➤ basis set effects
  ➤ long-tails of some interactions (dispersion energy in HF and DFT calculations)
  ➤ size consistency

By analyzing E_k and ψ_k one can classify interactions between atoms to better understand origin of forces that keep them together. Two major categories of interactions between atoms are:
  ➤ **covalent bonding**
  ➤ **non-covalent interactions**

Covalent Bonding

Covalent Bonding

A **covalent bond** is a chemical bond that involves the **sharing of electron pairs** between atoms.

Notable types of covalent bonds:

➤ σ-bonds (each atom formally contributes by one electron)
➤ π-bonds (each atom formally contributes by one electron)
➤ coordinate covalent bonds (one atom contributes two electrons (a lone pair) and the second atom provides a vacant (empty) orbital)
➤ aromatic bonding
➤ metallic bonding
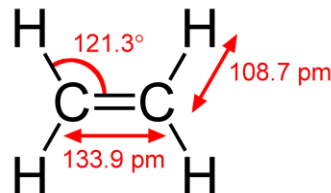➤ three-center two-electron bond (see boron chemistry)
➤ ….

https://en.wikipedia.org/wiki/Covalent_bond

Covalent bonding represents strong interatomic interactions.
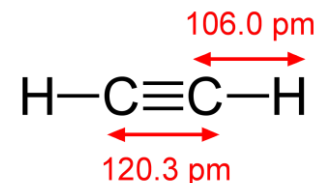
Covalent Bonding, cont.

σ and π covalent bonds:
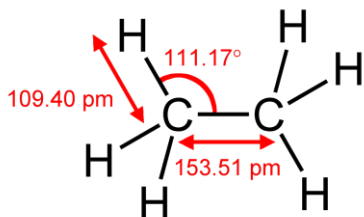
single C-C bond
(1 σ-bond)

double C-C bond
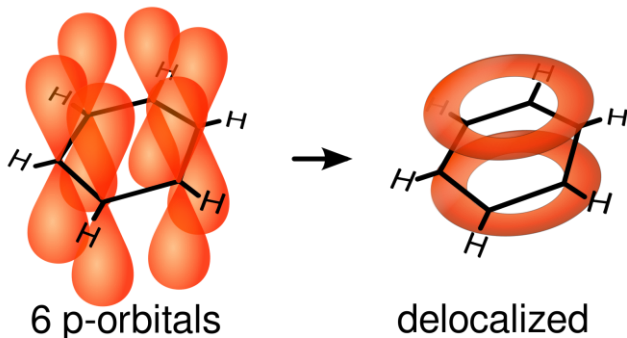(1 σ-bond + 1 π-bond)

triple C-C bond
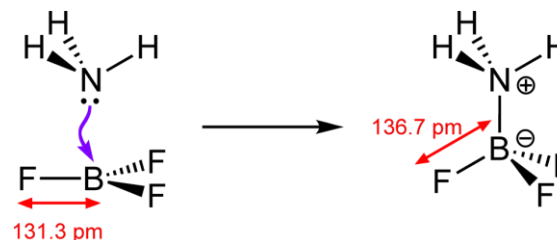(1 σ-bond + 2 π-bonds)

Bond dissociation energies:

~85 kcal/mol

~145 kcal/mol

~200 kcal/mol

Conjugated π-bonds (aromaticity):

6 p-orbitals   delocalized

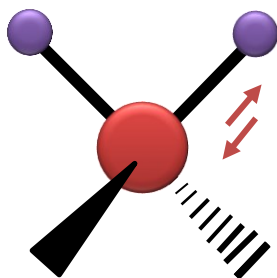**Coordinate covalent bonds:**

https://en.wikipedia.org

Molecular Deformations

➢ Some molecular deformations can be described by vibrational motions.

➢ There is 3N-6(5) unique molecular vibrations, which are called **normal modes**.

➢ A normal vibrational mode is a molecular motion, in which ALL atoms oscillate at the same frequency and phase.

➢ However, some vibrations are more "localized". Meaning that such vibrations exhibit larger amplitudes only on a few atoms, while the rest of the molecule is almost restful.

➢ The other vibrations represent skeletal molecular deformations.

Bond stretching   Model of harmonic oscillator:

characteristic frequency

$$E_V = \left(v + \frac{1}{2}\right)h\upsilon \qquad \upsilon = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \qquad K = \frac{\partial^2 V(r)}{\partial r^2}$$
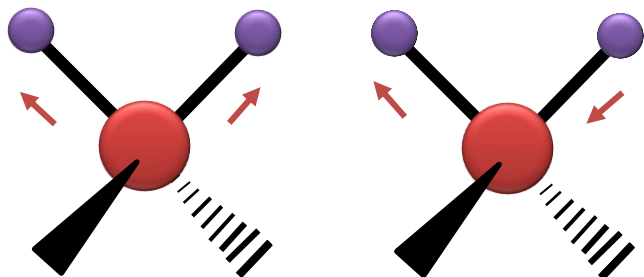
v = 0, 1, 2, …

reduced mass   force constant

curvature of PES at stationary point

Molecular Deformations, cont.

Some types of molecular vibrations
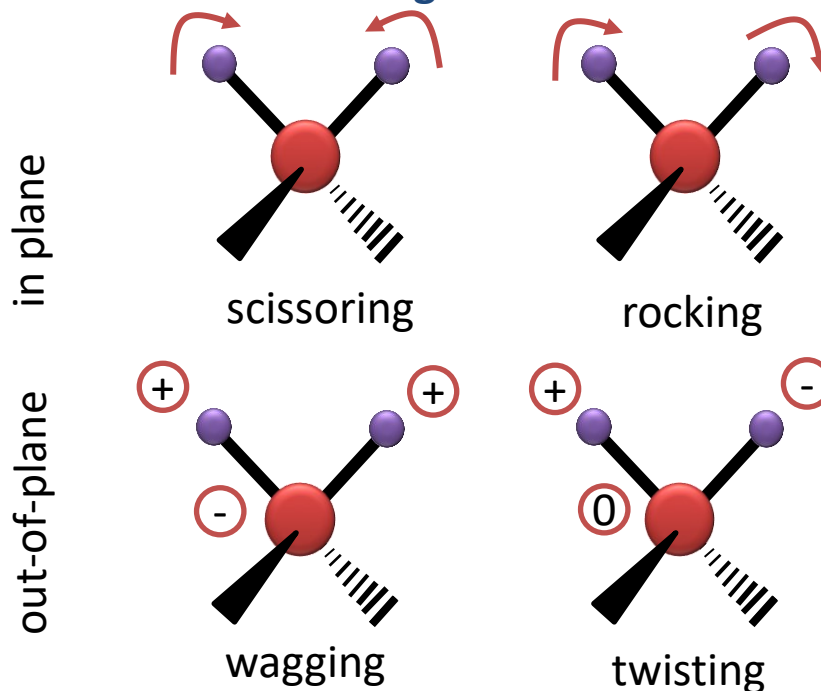
Valence bond stretching

symmetric

asymmetric

Usually, stronger bonds exhibits higher vibrational frequencies and vice versa.

Valence angle deformations

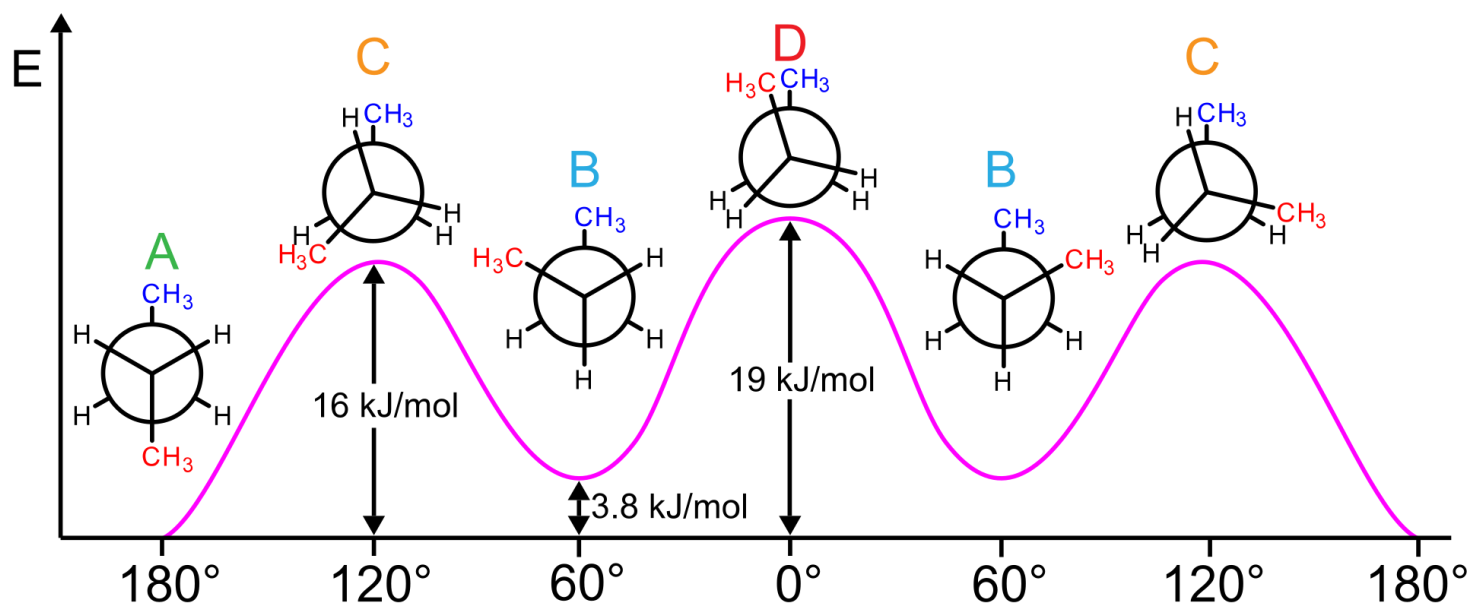in plane

scissoring

rocking

out-of-plane

wagging

twisting

⊕ up
⊖ down
⓪ "no" motion

In chemistry, conformational isomerism is a form of stereoisomerism in which the isomers can be interconverted just by rotations about formally single bonds (refer to figure on single bond rotation).

Non-covalent Interactions

Non-covalent Interactions

Contribution	Additive?	Sign	Comment
Long-range ($E(R) \sim R^{-n}$)			
Electrostatic	Yes	+/-	Strong orientation dependence
Induction	No	-	
Dispersion	Approx.	-	Always present
Resonance	No	+/-	Degenerate states only
Magnetic	Yes	+/-	Very small
Short-range ($E(R) \sim e^{-\alpha R}$)			
Exchange-repulsion	Approx.	+	Dominates at very short range
Exchange-induction	Approx.	+	
Exchange-dispersion	Approx.	+	
Charge transfer	No	-	Donor-acceptor interactions

Stone, A. J.; Oxford University Press. *The Theory of Intermolecular Forces*; Oxford University Press: Oxford, 2016.