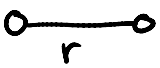
Molecules & bonds

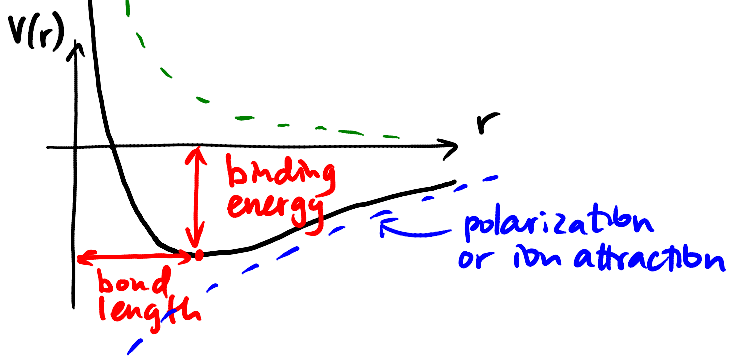
① Potential energy



phenomenologically

$$V(r) = -\frac{A}{r^n} + \frac{B}{r^m}, \quad m > n$$

repulsion dominates @ $r \to 0$
- nuclei repulsion
- exchange interaction



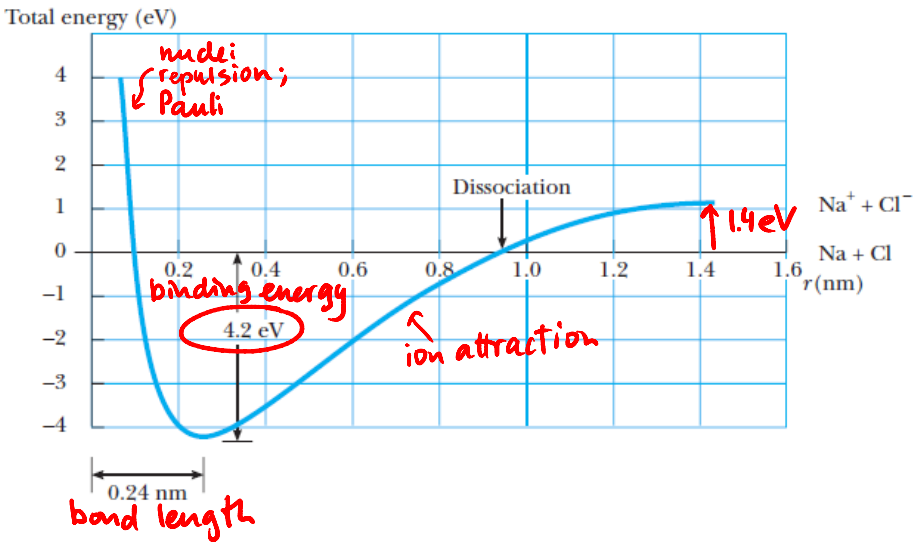
Note: classically, no stable solids are possible ⇒ must be quantum (e.g. Earnshaw's theorem)

② Molecular bonding mechanisms

roughly in order of decreasing strength

I) ionic bond

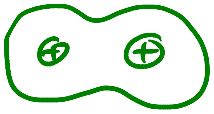
one atom gives up an e^-, the other gets one extra



NaCl : ionization of Na costs 5.1 eV
adding e^- to Cl yields 3.7 eV
"electron affinity"
⇒ activation energy = 1.4 eV (@ $r \to \infty$)

II) Covalent bond (can be very strong = diamond)
e^-'s are shared between atoms
new orbitals formed that replace the old ones

H_2^+



lowest orbital can have
2 electrons
(that's why there is no H_3)

see HW prob.

III) Hydrogen bond
b/w molecules/atoms or inside large molecules such as DNA

H^+ (=p) - positive end of a molecule (unshielded charge)
can come to negative end of another molecule

energy ~ 0.1 eV.

Ex. protein folding (e.g. double-helix structure of DNA)
water boiling @ 100°C (↑ due to H-bonding)

IV) Van der Waals bond
(weakest) molecule dipole-dipole interaction
dipoles: permanent e.g. CO (but not CO_2)
induced e.g. noble gas He-He

Attractive potential $\propto \frac{1}{r^6}$

weaker ↓
perm. - perm.
perm. - induced
induced - induced

③ Molecular excitations

$E = E_{electr.} + E_{vibr.} + E_{rot.} + E_{cm.trans}$

$E_{electr.}$: 2–10 eV

$E_{vibr.}$: 0.2–2 eV

$E_{rot.}$: 10^{-5}–10^{-3} eV

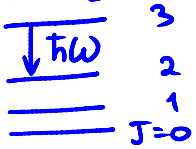
$E_{cm.trans}$: $\frac{p^2}{2M}$, continuous

Rotational

$E_{rot} = \frac{L^2}{2I}$; I – moment of inertia

$I = \mu R_0^2$; $\mu = \frac{m_1 m_2}{m_1 + m_2}$

Quantized $E_{rot} = \frac{\hbar^2}{2I} J(J+1)$, $J = 0, 1, \ldots$



Selection rule: $\Delta J = \pm 1$

molecule must have an electr. dipole (be polar) to emit $\hbar\omega$

$CO \rightarrow$ pure rotational spectrum

$CO_2 \rightarrow$ NO

$\hbar\omega = E_{rot,J} - E_{rot,J-1} = \frac{\hbar^2}{I} J$

Ex. CO

$f = \frac{\omega}{2\pi}$: 1.15×10^{11} Hz, 2.30, 3.46, 4.61 — absorption lines

$\Rightarrow \hbar^2/I = h \times 1.15 \times 10^{11}$ Hz

$I = 1.46 \times 10^{-46}$ kg m^2

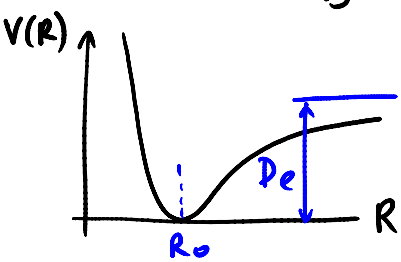
We know masses $C = 12u$, $O = 16u$, $\mu = 6.86u$

$\Rightarrow R_0 = \sqrt{\frac{I}{\mu}} = 1.13 \text{Å}$

a way to measure R_0

Vibrational

Molecular energy depends on R



e.g. $V(R) = D_e\left(1 - e^{-a(R-R_0)}\right)^2$

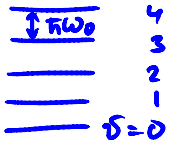
"Morse potential"

$a = \sqrt{\frac{k_e}{2D_e}}$ ← spring const, ← dissociation energy

Expand around minimum: $V(R) = V_0 + \underbrace{\frac{1}{2}k_e(R-R_0)^2}_{\text{SHO}}$

Energy levels: $E_{vibr} = \hbar\omega_0\left(v + \frac{1}{2}\right)$

$\omega_0 = \sqrt{\frac{k_e}{\mu}}$, $v = 0, 1, 2, \ldots$



Selection rule: $\Delta v = \pm 1$

electric dipole must change when atoms vibrate

HCl → yes (said to be "IR active")

N_2 → NO

E.g. CO: $f_0 = \frac{\omega_0}{2\pi} = 6.42 \times 10^{13}$ Hz

$\Rightarrow k_e = 1860$ N/m

zero point motion in CO: $\frac{1}{2}\hbar\omega_0 \sim \frac{1}{2}k_e(\delta R)^2$

$\delta R \sim 0.048$ Å $(\ll R_0)$

Thermal effects

$kT \sim 1/40$ eV @ 300K

$kT \gg \Delta E_{rot}$ → many rotational levels occupied

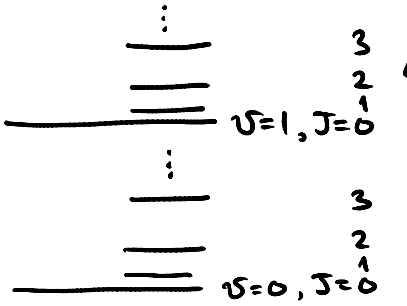
$kT \ll \Delta E_{vibr}$ → most molecules in ground vibrational state

Anharmonicity

at higher energies (= higher T) average separation increases

⇒ thermal expansion of a molecule

Full molecular spectra



rotational - vibrational

if electronic excitation

⇒ also excites a whole set of vibr-rot lines

many close lines → bands