Cohesion: The Lennard-Jones(12,6) Potential

In summary:

Table 16.3 *Interaction potential energies*

Interaction type	Distance dependence of potential energy	Typical energy/ (kJ mol^{-1})	Comment
Ion-ion	$1/r$	250	Only between ions
Ion-dipole	$1/r^2$	15	
Dipole-dipole	$1/r^3$	2	Between stationary polar molecules
	$1/r^6$	0.3	Between rotating polar molecules
London (dispersion)	$1/r^6$	2	Between all types of molecules

The energy of a hydrogen bond X—H···Y is typically 20 kJ mol^{-1} and occurs on contact for X, Y = N, O, or F.

$$V = -\frac{C}{r^6}$$

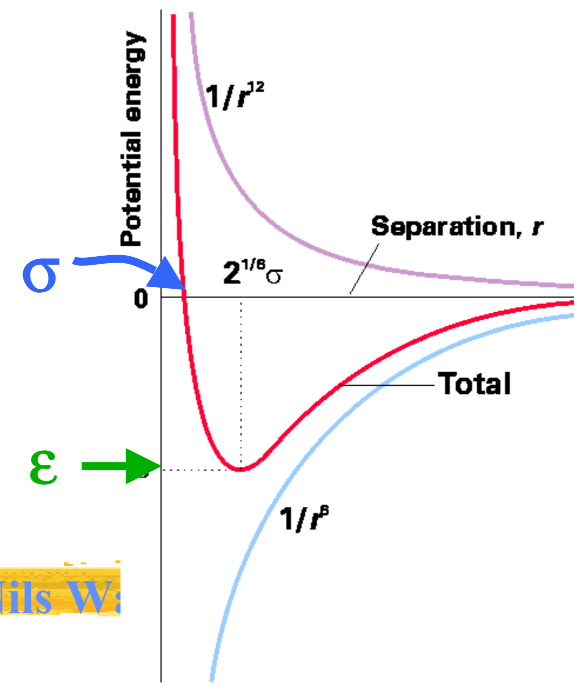
Attractive forces

Repulsive forces (Pauli exclusion principle!)

$$V \approx +\frac{C^*}{r^n}; \quad n > 6$$

Easiest to compute: n = 12

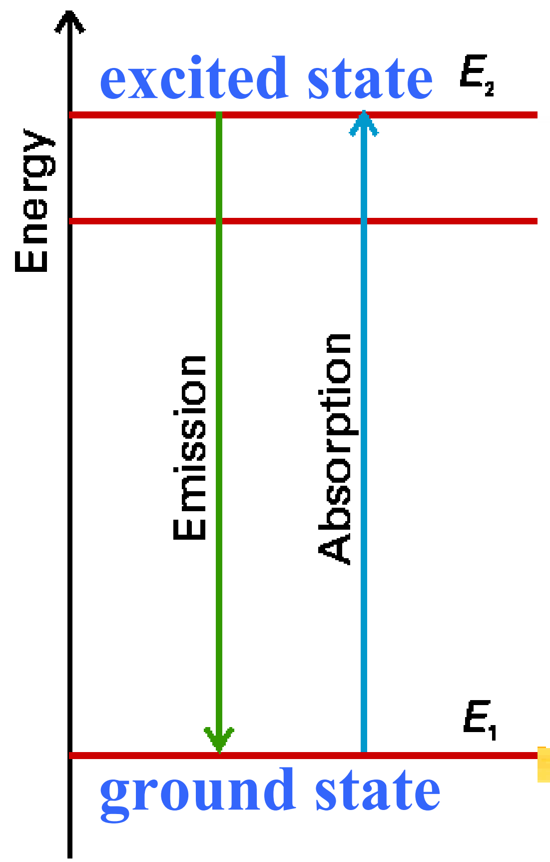
$$\Rightarrow \quad V = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$



The application of quantum mechanics: Spectroscopy

Atkins, Chapter 17

Transitions between defined energy states



Bohr frequency condition

$$h\nu = |E_1 - E_2|$$

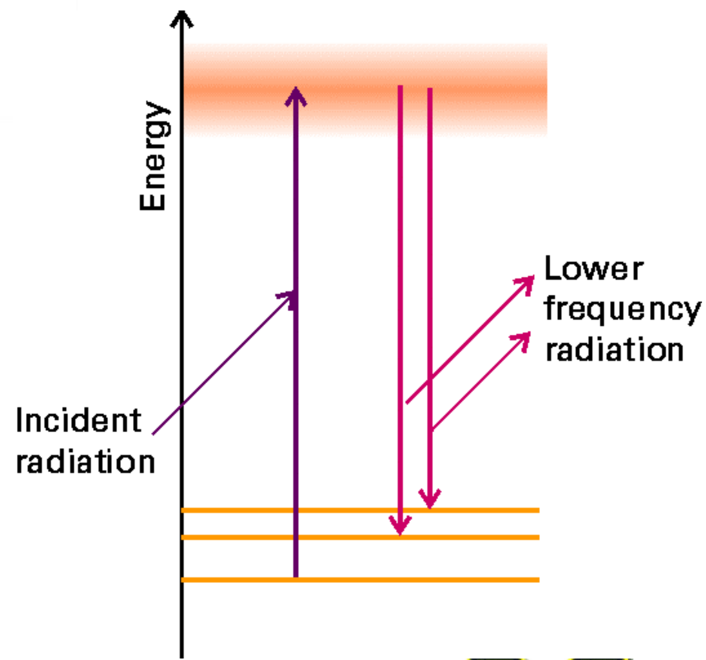
wavelength

$$\lambda = \frac{c}{\nu}$$

wavenumber [cm^{-1}]

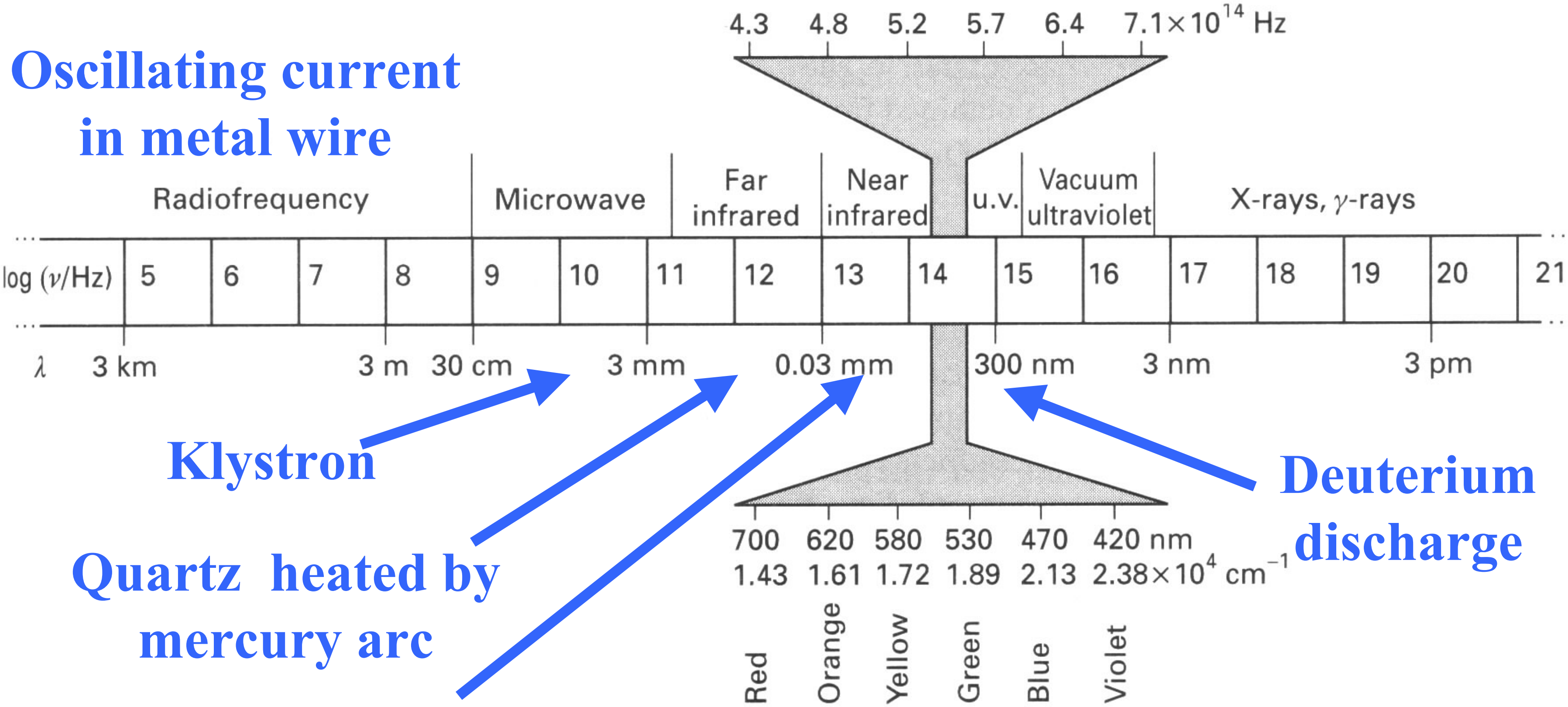
$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

Exception: Raman scattering



The electromagnetic spectrum

Oscillating current in metal wire



Klystron

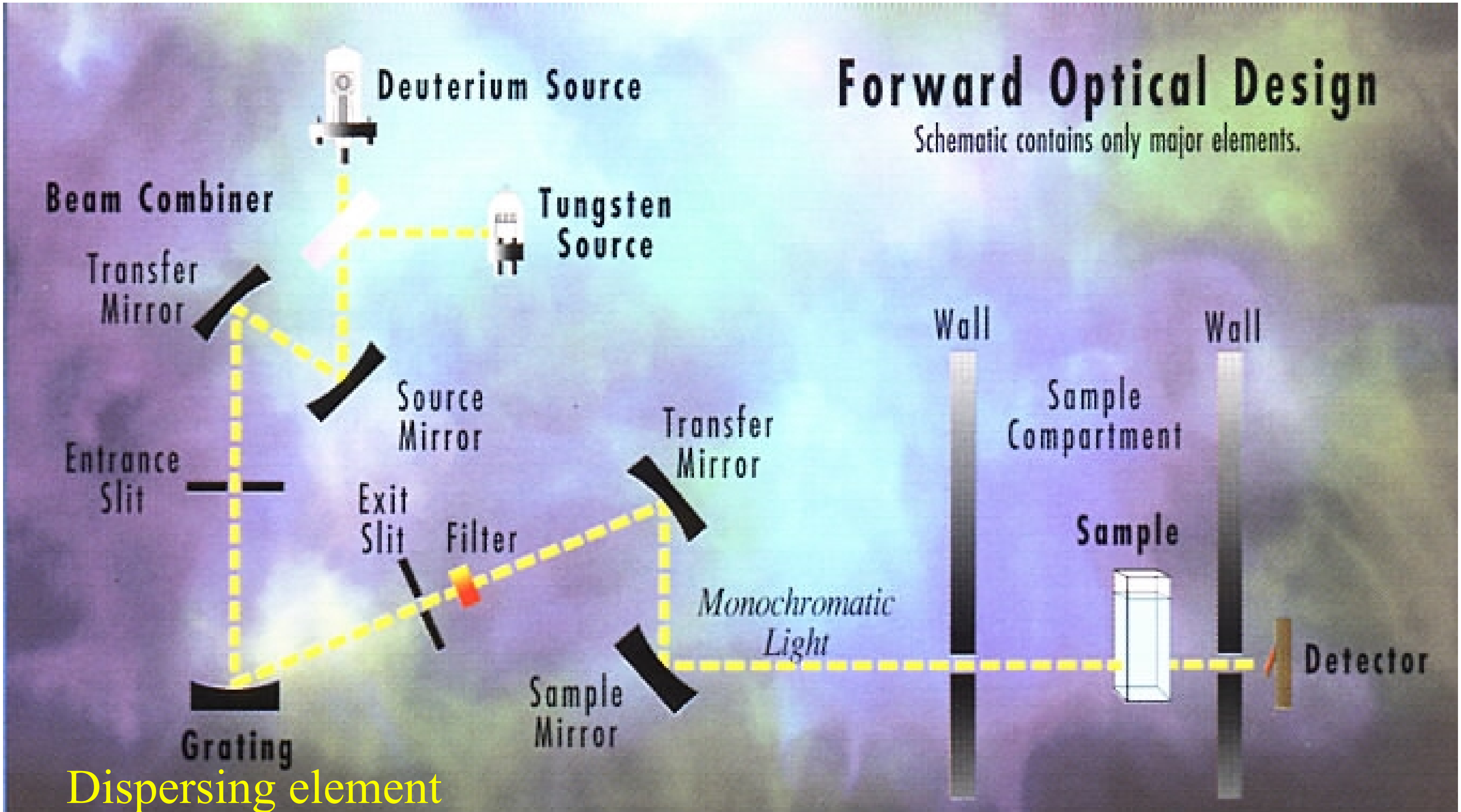
Quartz heated by mercury arc

Nernst filament (black body)

Deuterium discharge

Tungsten-iodine lamp

A spectrophotometer



Resolution limits: 1. Line broadening through the Doppler effect

Radiation source receding from observer:

$$\nu' = \left(\frac{1 - s/c}{1 + s/c}\right)^{1/2} \nu$$

speed

Radiation source approaching observer:

$$\nu' = \left(\frac{1 + s/c}{1 - s/c}\right)^{1/2} \nu$$

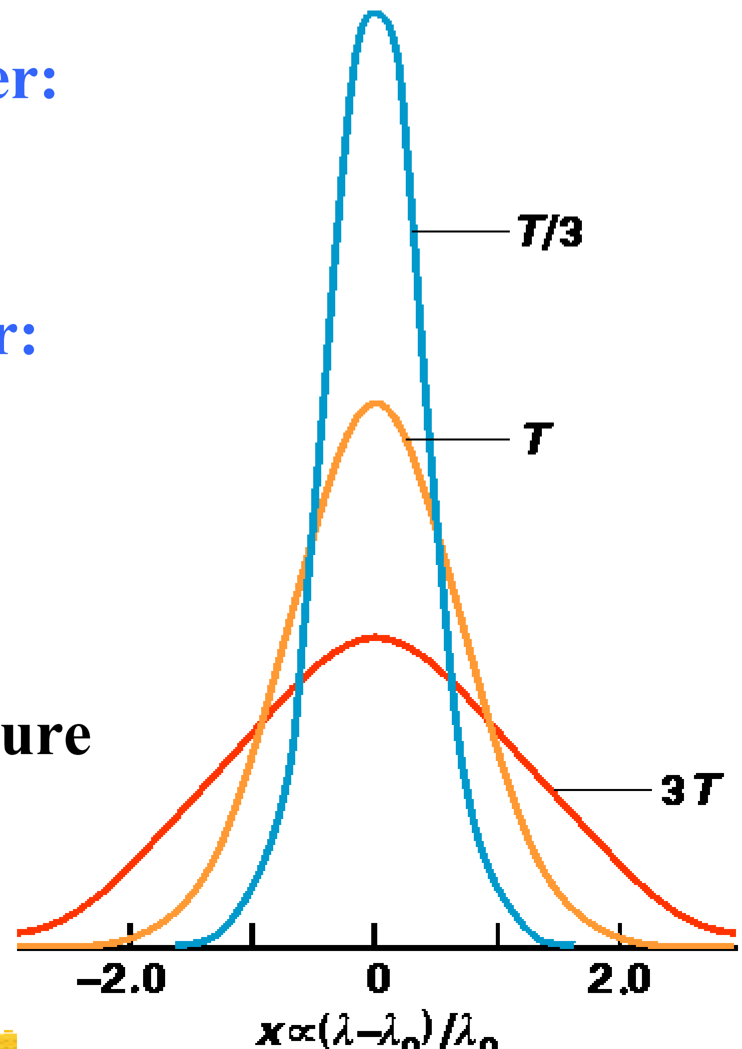
Overall effect on the linewidth:

$$\delta\lambda = \frac{2\lambda}{c}\left(\frac{2RT\ln 2}{M}\right)^{1/2}$$

temperature

mass

→ **particularly in gases**



Resolution limits: 2. Collision broadening

Particle collision

$\Downarrow$

deformation of involved particles

$\Downarrow$

changes in electronic, vibrational, rotational states

$\Downarrow$

transitions less well defined

$\Downarrow$

line broadening

→ particularly in liquids or gases under high pressure

Resolution limits - the bottom line: 3. Lifetime broadening

Solving the time-dependent Schrödinger equation reveals the energy-time form of **Heisenberg's uncertainty principle:** $\delta E \approx \frac{\hbar}{\tau} \Rightarrow \delta\tilde{\nu} \approx \frac{5.3\ \text{cm}^{-1}}{\tau/\text{ps}}$

practical

Lifetime of excited state; determined by collisional deactivation and spontaneous emission

Gases @ low pressure enable high-resolution spectroscopy

unchangeable
⇒ natural linewidth