Selection rules

$0 \longrightarrow n$ vibrations

$$\langle \psi_0 | \mu_x | \psi_n \rangle = \underbrace{\mu_0 \langle \psi_0 | \psi_n \rangle}_{0} + \left.\frac{d\mu}{dx}\right|_{x=0} \langle \psi_0 | x | \psi_n \rangle$$

Need $\left.\frac{d\mu}{dx}\right|_{x=0} \neq 0$ and $\langle \psi_0 | x | \psi_n \rangle \neq 0$

$$\langle \psi_0 | x | \psi_n \rangle = A_0 A_n \int_{-\infty}^{\infty} H_0 \, x \, H_n \, e^{-\alpha x^2} dx$$

Nonzero only if $n=1$

Absorption only $\Delta n = 1$ $(0 \to 1)$ allowed

emission only $\Delta n = -1$ $(1 \to 0)$, $(2 \to 1)$, $(3 \to 2)$, etc. allowed.

If the potential is harmonic.

N_2, H_2, O_2: 99.9% of atmosphere

do not absorb IR radiation emitted by earth.

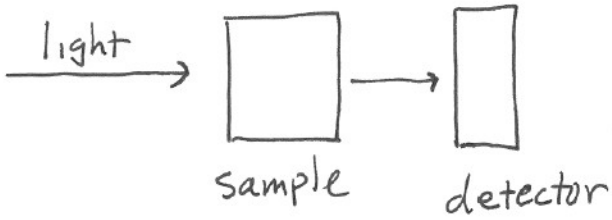
so most IR radiation escapes into space

CO_2, CH_4 absorb, emit IR radiation

greenhouse gases

Beer's law: $I(\lambda) = I_0(\lambda)\, e^{-\varepsilon(\lambda) m L}$

m = concentration
L = path length
ε = molar absorption coefficient



often have mirrors to reflect light → increase path length

monochromator – generates light of known wavelength, generally tunable.

How many vibrations in a polyatomic molecule?

$$\left.\begin{array}{ll} \text{nonlinear} & 3n-6 \\ \text{linear} & 3n-5 \end{array}\right\} \quad n = \#\text{ atoms}$$

H_2O $\quad 3 \cdot 3 - 6 = 3$

CH_4 $\quad 3 \cdot 5 - 6 = 9$

C_6H_6 $\quad 3 \cdot 12 - 6 = 30$ ⟶ 20 distinct frequencies after allowing for degeneracies