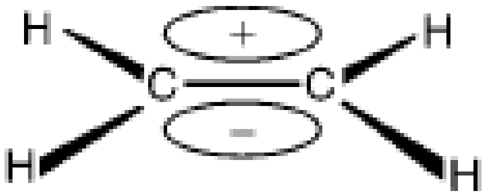
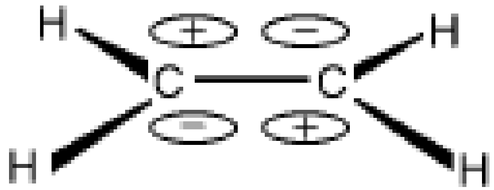
Transition dipole moment
Selection rules: $\mu_{fi} \neq 0$

Ethene:

π

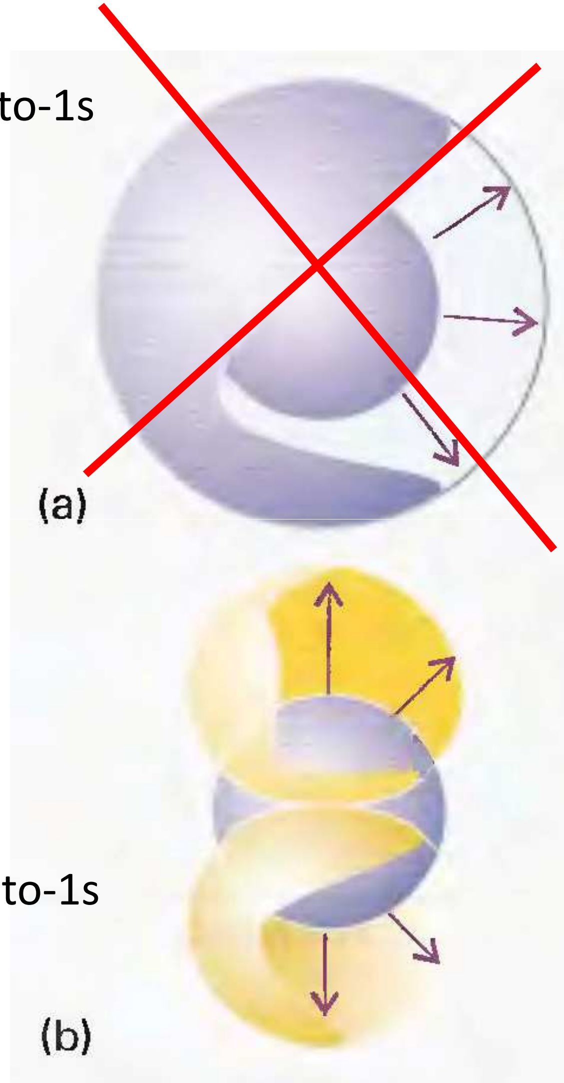


π^*

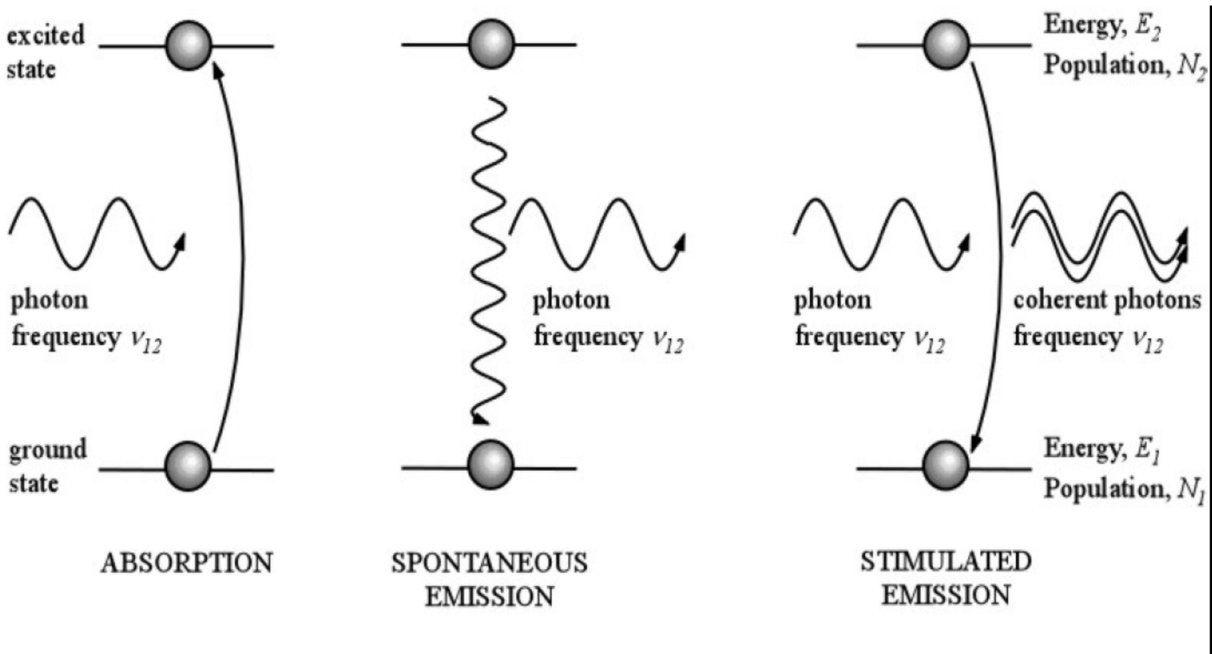


2s-to-1s

2p-to-1s



Einstein coefficients



Non-degenerate two-level (N=2,1) system at thermal equilibrium:

$$\dot{N}_2 = N_1 B_{12}\rho(\tilde{\nu}) - N_2 B_{21}\rho(\tilde{\nu}) - N_2 A_{21} \overset{\text{equil}}{=} 0 \Leftrightarrow \quad (1)$$

$$\rho(\tilde{\nu}) = \frac{A_{21}}{\frac{N_1}{N_2}B_{12} - B_{21}}$$

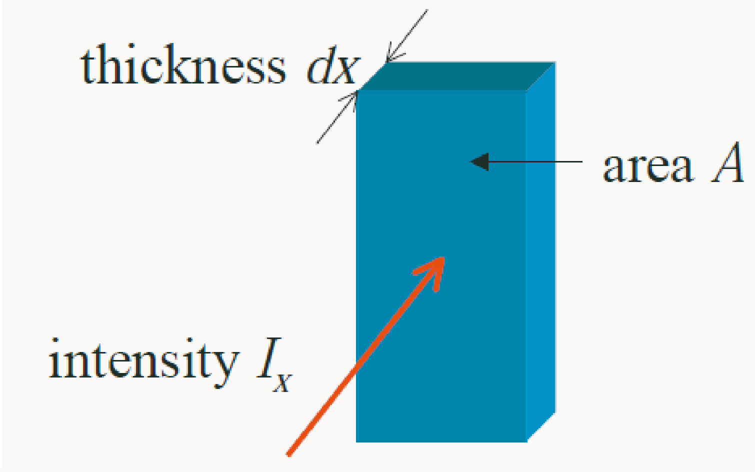
$$\frac{N_1}{N_2} = \frac{e^{-E_1/k_BT}}{e^{-E_2/k_BT}} = e^{(E_2-E_1)/k_BT} = e^{h\nu/k_BT} \quad (2)$$

$$\rho(\tilde{\nu}) \overset{\text{Planck}}{=} \frac{8\pi h\tilde{\nu}_{21}^3}{e^{hc\tilde{\nu}/k_BT} - 1} = \frac{A_{21}}{e^{h\nu/k_BT}B_{12} - B_{21}} \Rightarrow$$

(3)

$$B_{12} = B_{21}$$
$$A_{21} = 8\pi h\tilde{\nu}^3 B_{12}$$

The intensity of spectral bands: Beer-Lambert law



$$-\frac{dI_x}{I_x} = \frac{\sigma C A}{A} dx$$

$\sigma(\tilde{\nu})$

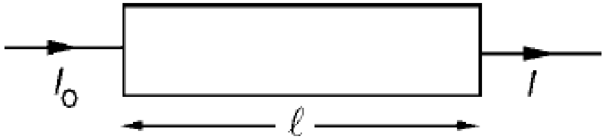
$$I = I_0 e^{-\sigma C x} = I_0 e^{-\mu x}$$

where $\mu = \sigma C$ is the absorption coefficient

- $\sigma \equiv$ absorption cross section [cm^2/molec]
- x $\equiv$ absorption path length [cm]
- C $\equiv$ density of the absorber [molec/cm^3]

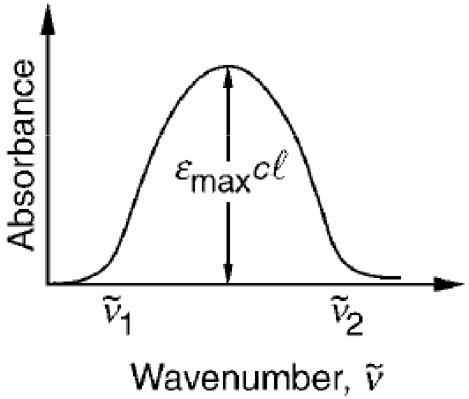
The intensity of spectral bands: Beer-Lambert law

In terms of absorbance A: $A = \log(I/I_0) = \varepsilon(\quad)\, C\, \tilde{\nu}$

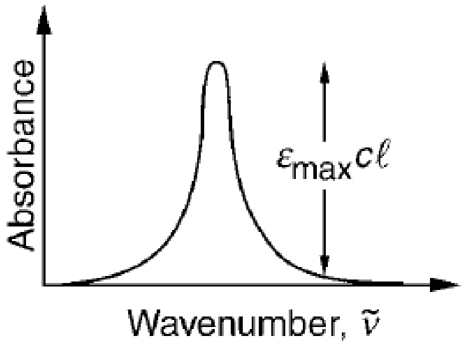


$\varepsilon \equiv$ extinction coefficient [L mol^{-1} cm^{-1}]

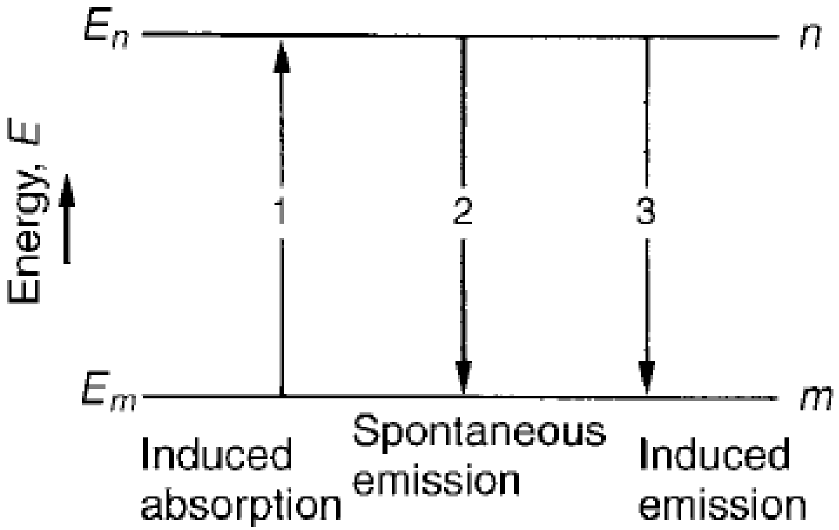
$$\sigma = 1000 \ln(10) \frac{\varepsilon}{N_A} = 3.82 \times 10^{-21} \varepsilon$$



$$A = \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \varepsilon(\tilde{\nu})\, d\tilde{\nu}$$



Lifetime band broadening (Lorentz)



$$-\frac{dN_n}{dt} = kN_n$$

$$\frac{1}{k} = \Delta t$$

$$\frac{dN_n}{dt} = -N_n A_{nm}$$

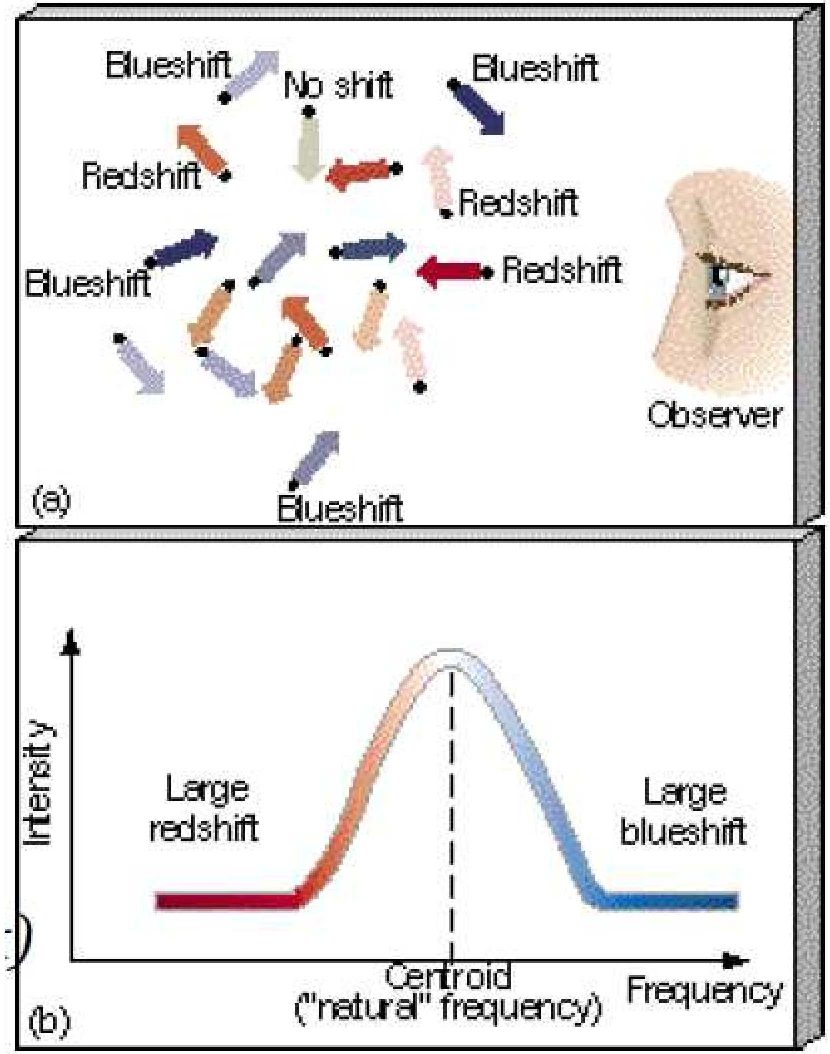
$$k = A_{nm}$$

Heisenberg uncertainity principle: $$\Delta E \Delta t \geq \frac{h}{2\pi}$$

$$\Delta E \Delta t = \Delta h \nu \frac{1}{A_{mn}} \geq \frac{h}{2\pi}$$

$$\Delta \nu \geq \frac{A_{mn}}{2\pi}$$

Doppler broadening (Gauss)



$$\nu_a = \nu\left(1 \mp \frac{v_a}{c}\right)^{-1}$$

Maxwell-Boltzman velocity distribution:

$$P(v) \sim e^{-mv^2/2kT}$$

$$\Delta\nu = \frac{\nu}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2}$$

Spectral band broadening