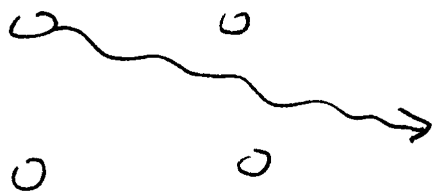
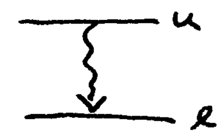
The Meaning of Spontaneous Radiation

Let us consider a system with no incident radiation + few photons so that we can ignore absorption + stimulated emission.



$$\frac{dn_u}{dt} = -A_{ul}\, n_u$$ 1st order kinetics



$$n_u(t) = n_u(0)\, e^{-A_{ul} t}$$ exponential decay

More fundamental idea: each atom decays randomly, but fewer are left in "u" as time goes by.

Half Life: $\frac{1}{2} = e^{-A_{ul} \tau_{1/2}}$ $\qquad \ln 2 = A_{ul} \tau_{1/2}$

$$\tau_{1/2} = (A_{ul})^{-1} \ln 2 \propto \nu_{ul}^{-3}$$

$\boxed{\tau = A_{ul}^{-1} \text{ relaxation time}}$

For dipole-allowed transitions:

$\tau_{1/2}$ (s)	Transition	ΔE (eV)	λ region
$10^{-9} - 10^{-6}$	electronic e.g. $H(2p \to 1s)$	2–10 (1000 Å – 5000 Å)	uv/visible
$10^{-2} - 10^{0}$	vibrational	1/10 – 1/2 (800 – 4000 cm^{-1})	IR
$10^{3} - 10^{7}$	rotational	0.0002–0.001 (0.8 – 8.0 cm^{-1}) (25 – 250 GHz)	μwave

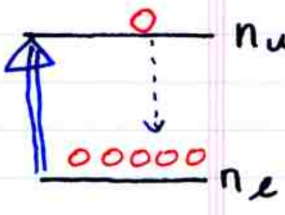
$$\Delta E = h\nu = h\frac{c}{\lambda} = hc\tilde{\nu}\,(cm^{-1})$$

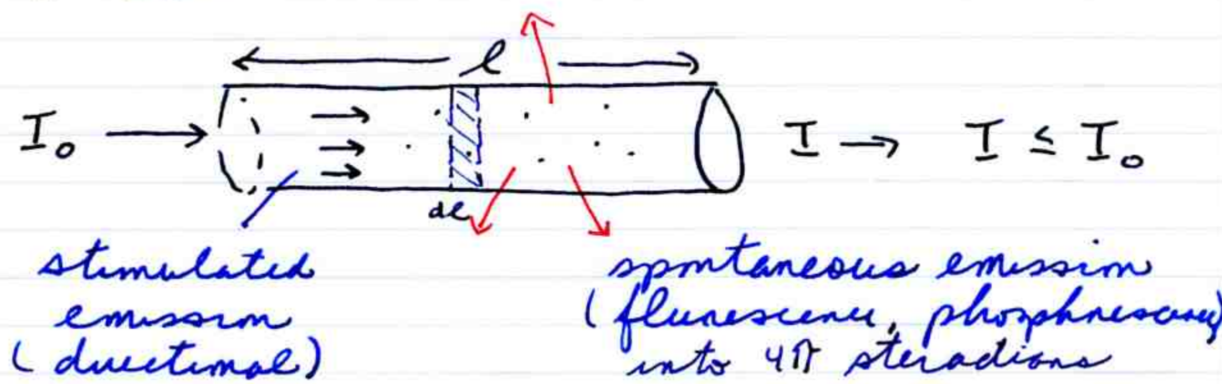
Fully-Allowed Transitions

Transition	ΔE (eV)	$\lambda, \tilde{\nu}, \nu$	Region	$\tau_{1/2}$ (s)
Electronic i.e. H(2p → 1s)	2 - 10	1000 Å - 5000 Å 100 nm - 500 nm	visible/UV	$10^{-9} - 10^{-6}$
Vibrational e.g. CO (n = 1 → 0)	0.1 - 0.5	800 - 4000 cm^{-1} 2.5 - 12.5 μm	IR	$10^{-2} - 10^{0}$
Rotational CO J = 1 → 0	0.0001 - 0.001	0.8 - 8.0 cm^{-1} 25 - 250 GHz 1.2 - 12 mm	μwave	$10^{3} - 10^{7}$

III. Absorption Coefficients (Experimental)

The majority of spectroscopic experiments are performed in absorption by shining radiation into a sample of gas in which $n_\ell > n_u$. If, on the other hand, a population inversion can be achieved & maintained ($n_u > n_\ell$) stimulated emission dominates and we can have a laser.





Beer-Lambert Law / Law of Radiative Transfer

$$dI(\nu) = -I(\nu)\,K_\nu\,d\ell \qquad K_\nu: \text{absorption coefficient } (cm^{-1})$$

ignores spontaneous emission
(can contain stimulated emission by reduction of K_ν)

$$I(\nu) = I_0(\nu)\,e^{-K_\nu \ell} \qquad \tau_\nu = K_\nu \ell \text{ "optical depth"}$$

exponential decay — unitless

$$K_\nu = \underbrace{\sigma_\nu}\,(cm^2)\,n_\ell\,(cm^{-3}) \quad \text{or} \quad n_\ell - n_u = n_\ell\left(1 - e^{-h\nu_{ul}/kT}\right)$$

cross section "effective area of target"

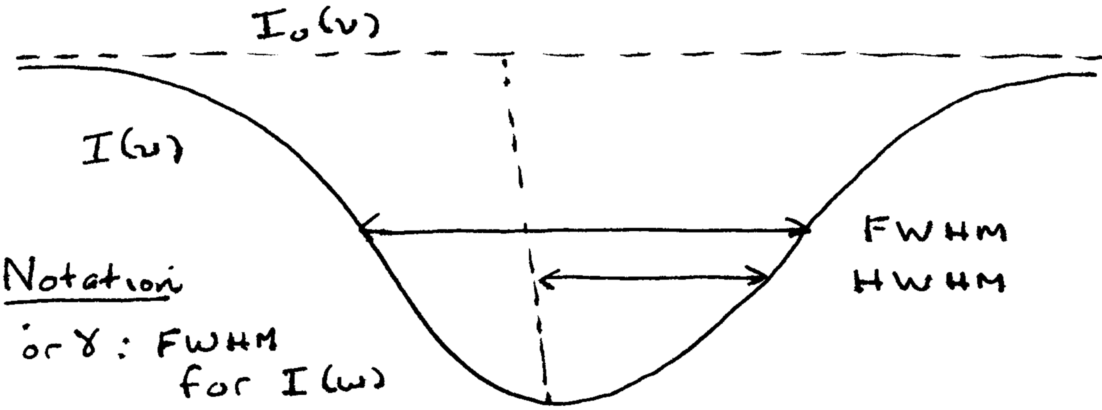
Can we relate $K_\nu, \sigma_\nu, \tau_\nu$ to the Einstein B coefficients or to $|\langle\mu\rangle_{ul}|^2$?

One immediate problem is that even in low pressure gases, absorption does not occur at just a single frequency or wavelength, but over a range of them.

The effect can be caused by instrumental factors, but even with a perfectly monochromatic instrument, "broadening" occurs. Consider the optically thin case:

$$\tau_\nu < 1 \quad K_\nu \ell < 1 \quad \sigma_\nu n_\ell \ell < 1$$

$$I(\nu) \cong I_o(\nu)\left[1 - K_\nu \ell + \cdots\right] = I_o(\nu) - \underbrace{K_\nu \ell I_o(\nu)}_{\text{absorbed intensity at } \nu}$$



<u>Notation</u>

Γ or γ : FWHM for $I(\omega)$

$\Delta\nu$: FWHM for $I(\nu)$ $\quad$ ν_{ul} (resonance) $K_\nu = K_\nu^{max}$

<u>Types of Profiles (ν)</u>

$$K_\nu = K_\nu^{max} P(\nu) \qquad P(\nu = \nu_{ul}) = 1$$

$$K_\nu = K\, g(\nu - \nu_{ul}) \qquad \int_{-\infty}^{\infty} g(\nu - \nu_{ul})\, d(\nu - \nu_{ul}) = 1$$

$$\int K_\nu \, d\nu = K$$

K ← integrated absorption coefficient

or $\int \sigma_\nu \, d\nu = \sigma$

a) <u>Homogeneous Broadening</u>

each atom can absorb or emit over entire range

Lorentzian Profile : $$P_L(\nu) = \frac{(\Delta\nu/2)^2}{(\nu - \nu_{ul})^2 + (\Delta\nu/2)^2}$$

or $$g_L(\nu - \nu_{ue}) = \frac{\Delta\nu / 2\pi}{(\nu - \nu_{ue})^2 + (\Delta\nu/2)^2}$$

For example: $\nu = \nu_{ue} + \frac{\Delta\nu}{2}$ $P_L = \frac{1}{2}$.

In terms of ω:

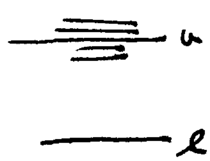
$$g_L(\omega - \omega_{ue}) = \frac{\Gamma / 2\pi}{(\omega - \omega_{ue})^2 + (\Gamma/2)^2}$$

$\Gamma = 2\pi\,\Delta\nu$ so that $\int_{-\infty}^{\infty} g_L(\omega - \omega_{ue})\, d(\omega - \omega_{ue}) = 1$ as well

(Γ: FWHM)

Homogeneous broadening arises when a population decays experimentally with a rate of decay Γ. ($e^{-\Gamma t}$)
(Fourier analysis)

(1) natural line broadening



HUP $\Gamma = A_{ue}$ $\Delta\nu = \frac{1}{2\pi} A_{ue}$

only important for electronic transitions

(2) pressure broadening

Collisional Rate out of either state $= k_{coll}\, n_{gas}$

$\Gamma = k_{coll}\, n_{gas}$ $\Delta\nu = \frac{1}{2\pi} k_{coll}\, n_{gas} = \gamma P(\text{torr})$

$k_{coll} = \sigma_{coll} \langle v \rangle$

1 - 10 MHz/Torr
"pressure-broadening coefficient"

DECAY $\rightarrow$ FINITE TIME TO MEASURE $\rightarrow$ WIDTH BY HUP

Γ $\Delta E \Delta t \sim \hbar$ $\Delta E = \hbar\Gamma$

$\Delta E / \Gamma \sim \hbar$ $\Delta\omega \sim \Gamma$

b) inhomogeneous broadening: need full ensemble of atoms

Doppler broadening: caused by motions of atoms with respect to radiation source. Each atom 'sees' a different frequency.

$v > 0$ ⟶ ← • blue shifted

$v < 0$ ⟶ • ⟶ red shifted

$$\frac{\nu - \nu_{ul}}{\nu_{ul}} = \frac{v}{c}$$

1-D Maxwell-Boltzmann distribution ⟹ Gaussian profile

$$P_G(\nu) = e^{-mv^2/2kT} = \exp\left\{-mc^2(\nu-\nu_{ul})^2/2\nu_{ul}^2 kT\right\}$$

also, by definition of $\Delta\nu$:

$$P_G(\nu) = \exp\left\{-(\ln 2)(\nu-\nu_{ul})^2/(\Delta\nu/2)^2\right\}$$

normalized version $g_G(\nu-\nu_{ul})$

Voigt Profile: convolution of Lorentzian & Gaussian shapes

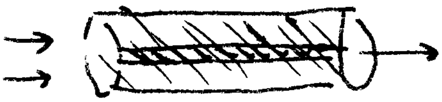
Expt vs Theory: Use of Integrated Parameters

$$I_{abs} = \int K_\nu \, l \, I_0 \, d\nu \qquad \text{optical thinness}$$

$$= l I_0 \underbrace{\int K_\nu \, d\nu}_{K \ \ cm^{-1} s^{-1}} = l I_0 n_l \underbrace{\int \sigma_\nu \, d\nu}_{\sigma \ \ cm^2 s^{-1}}$$

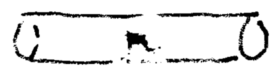
K, σ integrated parameters independent of line shape

What exactly is I_{abs}? It is the energy absorbed throughout the cell per second per steradian:



In terms of theory:

$$\underset{\text{cm}^2\ \text{s ster}}{\underline{\text{energy}}} \qquad I_{abs} = \underbrace{\frac{1}{4\pi}}_{\text{per steradian}} \Big[\underbrace{B_{u\leftarrow\ell}\, \rho_0(\nu_{u\ell})\, n_\ell}_{\text{volume absorption rate cm}^{-3}\,\text{s}^{-1}} \Big] \underbrace{h\nu_{u\ell}}_{\text{energy}}\ \ell$$



$$I_{abs} = \ell I_0 \int K_\nu\, d\nu$$

$$I_0(\nu_{u\ell}) = \frac{c}{4\pi}\rho_0(\nu_{u\ell}) \Longrightarrow \rho_0(\nu_{u\ell}) = 4\pi I_0(\nu_{u\ell})/c$$

$$\cancel{\ell}\,\cancel{I_0}\int K_\nu\, d\nu = \frac{1}{\cancel{4\pi}} B_{u\leftarrow\ell}\frac{\cancel{4\pi}\,\cancel{I_0}}{c}\, n_\ell\, h\nu_{u\ell}\,\cancel{\ell}$$

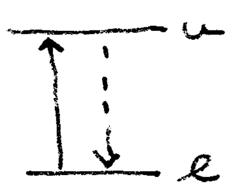
$$K = \int K_\nu\, d\nu = \frac{1}{c}\left[B_{u\leftarrow\ell}\, n_\ell\, h\nu_{u\ell}\right] = \sigma n_\ell$$

$$B_{u\leftarrow\ell} = \frac{2\pi}{3\hbar^2}\left|(\mu)_{u\leftarrow\ell}\right|^2 = \frac{8\pi^3}{3h^2}\left|(\mu)_{u\leftarrow\ell}\right|^2$$

$$\therefore\ K = \frac{8\pi^3}{3hc}\,\nu_{u\ell}\, n_\ell \left|(\mu)_{u\leftarrow\ell}\right|^2$$

$$\sigma = \frac{8\pi^3}{3hc}\,\nu_{u\ell}\left|(\mu)_{u\leftarrow\ell}\right|^2$$

<u>Stimulated Emission Correction</u>, $\int K_\nu\, d\nu$



replace $B_{u\leftarrow\ell}\, n_\ell$ with $B_{u\leftarrow\ell}\, n_\ell - B_{u\rightarrow\ell}\, n_u$

$n_u > n_\ell$ $\int K_\nu d\nu$ "gain"

Oscillator Strength

$$\sigma \equiv \frac{\pi e^2}{m_e c} f_{u\ell} \; ; \quad f_{u\ell} = \frac{8\pi^2 m_e \nu_{u\ell}}{3 h e^2} \left| \langle \mu \rangle_{u-\ell} \right|^2$$

used in atomic physics $f_{u\ell} \lesssim 1$ unitless

Physics: Equation of Radiative Transfer

K_ν : contains stimulated emission correction

$$I(\nu) = I_0(\nu) e^{-K_\nu \ell} + I(\nu, T) \left[1 - e^{-K_\nu \ell} \right]$$

if optically thin:

$$I(\nu) = I_0(\nu) \left[1 - K_\nu \ell \right] + I(\nu, T) K_\nu \ell$$