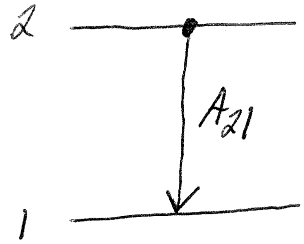
Lifetime of excited state



Consider spontaneous decay from level 2:

$$\frac{dN_2}{dt} = -N_2 A_{21}$$

Solution is $\quad N_2(t) = N_{20}\, e^{-A_{21}t} = N_{20}\, e^{-t/\tau_{21}}$

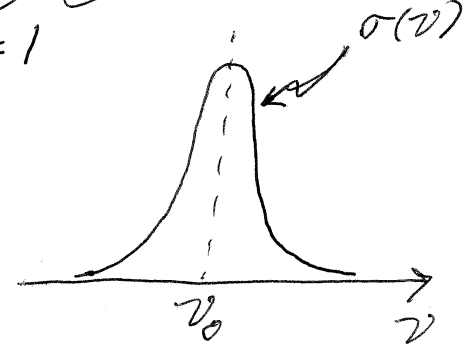
where $\quad \tau_{21} = \dfrac{1}{A_{21}} \quad$ is radiative lifetime

Can relate τ_{21} to $\sigma(\nu)$:

$$\sigma(\nu) = \frac{1}{\tau_{21}} \frac{\lambda^2}{8\pi n^2}\, g(\nu)$$

$$\int \sigma(\nu)\, d\nu = \frac{1}{\tau_{21}} \frac{\lambda^2}{8\pi n^2} \underbrace{\int g(\nu)\, d\nu}_{=1}$$

$$\therefore \quad \boxed{\tau_{21} = \frac{\lambda^2}{8\pi n^2 \int \sigma(\nu)\, d\nu}}$$



Oscillator strength:

$$f \equiv (4\pi\epsilon_0) \frac{mc}{\pi e^2} \int \sigma(\nu)\, d\nu$$

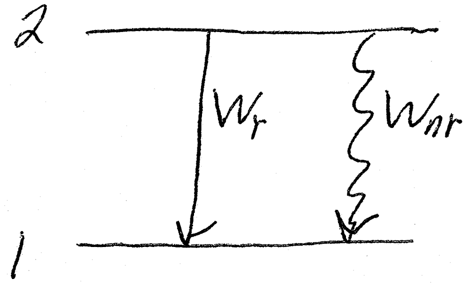
$f \sim 1$ allowed transition

$\tau_{21} \sim$ 1-10 ns

Quantum Yield

An excited state may decay nonradiatively as well as radiatively:

- collisional de-excitation in gases
- phonon emission in solids
- energy transfer



$W_r \equiv \frac{\text{prob}}{\text{time}}$ for radiative decay

$W_{nr} \equiv \frac{\text{prob}}{\text{time}}$ for nonradiative decay

$W_{tot} = W_r + W_{nr} = \frac{\text{prob}}{\text{time}}$ for any decay.

Define $W_r \equiv \frac{1}{\tau_r}$ $\qquad W_{tot} \equiv \frac{1}{\tau}$

$W_{nr} \equiv \frac{1}{\tau_{nr}}$

Quantum yield $\quad \phi \equiv \frac{W_r}{W_{tot}}$ probability that atom emits radiatively.

$$\phi = \frac{1/\tau_r}{1/\tau} = \frac{\tau}{\tau_r}$$

measure τ directly
must calculate τ_r

Lineshape function

Two types of line broadening processes:

1) Homogeneous broadening (same for every atom)

$$\Delta\nu_{1/2} = \frac{1}{2\pi \Delta t} \qquad \Delta t = \text{uninterupted radiation time}$$

a. Lifetime broadening ("natural" linewidth)

b. Pressure broadening (collisions in gases)

c. Phonon broadening (vibrations in solids)

$$\boxed{g(\nu) = \frac{1}{\pi} \frac{\Delta\nu/2}{(\nu-\nu_0)^2 + (\Delta\nu/2)^2}}$$

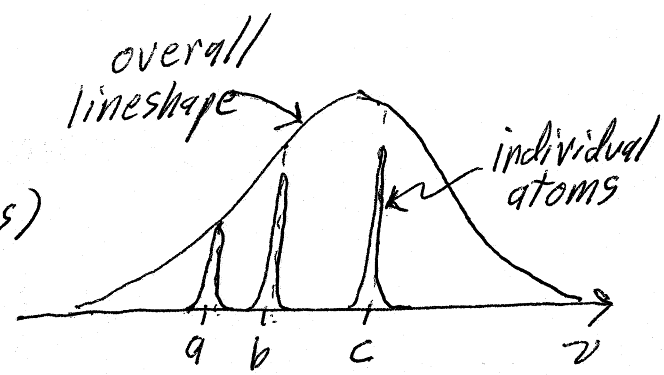
Lorentzian lineshape

$$g_{max} = \frac{2}{\pi \Delta\nu} \qquad \Delta\nu = \text{FWHM}$$

2) Inhomogeneous broadening

a. Doppler broadening (gases)

b. Different lattice sites (solid)



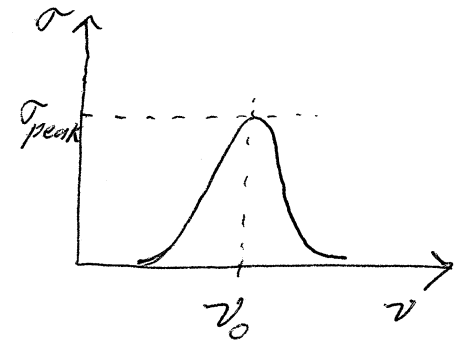
$$\boxed{g(\nu) = a\, e^{-b(\nu-\nu_0)^2}}$$

Gaussian lineshape

$$a = \frac{1}{\Delta\nu}\sqrt{\frac{4\ln 2}{\pi}} \qquad g_{max} = a = \frac{1}{\Delta\nu}\sqrt{\frac{4\ln 2}{\pi}}$$

$$b = \frac{4 \ln 2}{(\Delta\nu)^2}$$

Calculating Peak Cross Section



$$\sigma(\nu) = A_{21} \frac{\lambda^2}{8\pi} g(\nu)$$

$$\sigma_{peak} = A_{21} \frac{\lambda^2}{8\pi} g_{max}$$

For any lineshape, $g_{max} \sim \frac{1}{\Delta\nu}$ since $\int g(\nu)\,d\nu = 1$

Exact result for:

<u>Lorentzian</u> $\quad g_{max} = \frac{2}{\pi\,\Delta\nu} \qquad \Delta\nu$ is FWHM

<u>Gaussian</u> $\quad g_{max} = \frac{2}{\Delta\nu}\sqrt{\frac{\ln 2}{\pi}}$

Area under cross section curve is found from

$$\frac{\sigma(\nu)}{\sigma_{peak}} = \frac{g(\nu)}{g_{max}}$$

$$\int \sigma(\nu)\,d\nu = \int \sigma_{peak} \frac{g(\nu)}{g_{max}}\,d\nu$$

$$= \frac{\sigma_{peak}}{g_{max}} \int g(\nu)\,d\nu$$

$$= \frac{\sigma_{peak}}{g_{max}}$$

For Lorentzian,

$$\int \sigma(\nu)\,d\nu = \frac{\pi}{2}\,\sigma_{peak}\,\Delta\nu$$