Absorption coefficient, absorption cross-section and oscillator strength

Recall ;

$$dF = W(N_2 - N_1)dz = -\sigma(N_1 - N_2)Fdz \qquad (*)$$

Where F is the photon flux (number of photon per unit area per unit time)

$$F = \frac{I}{h\nu}$$

And

$$W = \frac{2\pi^2}{3n\varepsilon_o c_0 h^2}|\mu_{21}|^2 I\, g(\Delta\nu)$$

Now multiply (*) by $h\nu$;

$$\therefore dI = -\sigma(N_1 - N_2)Idz = -\alpha I\, dz$$

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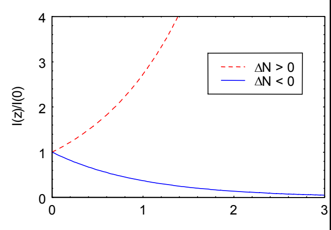
$$\therefore \frac{dI}{dz} = -\alpha I \quad \Rightarrow \quad I(z) = I(0)e^{-\alpha z} = I(0)e^{-\sigma(N_1 - N_2)z}$$

$$\therefore \alpha \equiv absorption\ coefficient = \sigma(N_1 - N_2)$$

$$\because W \equiv \sigma F = \frac{\sigma I}{h\nu} \quad \Rightarrow \quad \sigma = \frac{h\nu W}{I}$$



$$\therefore \alpha \equiv \sigma(N_1 - N_2) = \frac{h\nu W(N_1 - N_2)}{I}$$

$$\therefore \alpha = \frac{2\pi^2\nu}{3n\varepsilon_o c_0 h}|\mu|^2(N_1 - N_2)g(\Delta\nu)$$

And

$$\therefore \sigma \equiv absorption\ cross\text{-}section = \frac{\alpha}{(N_1 - N_2)}$$

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$$\therefore \sigma = \frac{2\pi^2}{3n\varepsilon_o c_0 h}|\mu|^2 \nu_0 g(\Delta\nu)$$

or in terms of A

$$\sigma = \frac{\lambda_o^2}{8\pi} Ag(\nu - \nu_o)$$

Life –time, Quantum Yield and Absorption Cross-section

Population decay processes for two level system

In the *absence* of electromagnetic radiation, the rate equation becomes

$$\frac{dN_2}{dt} = -\frac{N_2}{\tau} \qquad \tau \equiv \text{life time of this system}$$

which has solution:

$$N_2(t) = N_2(0)\, e^{-t/\tau}$$

However, not only spontaneous emissions are responsible for the decay of upper state population. Other processes such as collisions can also cause non-radiative decay. If we label the mean collision time as τ_{nr}, then the overall lifetime of state 2 is given by adding decay rates as follows:

$$\frac{1}{\tau}=\frac{1}{\tau_{sp}}+\frac{1}{\tau_{nr}}$$

The power emitted by spontaneous emission

$$P(t)=\frac{h\nu_0 N_2(t)V}{\tau_{sp}}=\frac{N_2(0)h\nu_0 V}{\tau_{sp}}e^{-t/\tau}$$

Notice; it decay by τ not by τ_{sp}

$$\phi \equiv \textit{flourescence quantum yield}=\frac{\textit{"photons" emitted by spontanous emission}}{\textit{atoms initially raised to level 2}}$$

$$=\frac{\int_0^\infty \frac{P(t)}{h\nu_0}dt}{N_2(0)V}=\frac{N_2(0)V\int_0^\infty e^{-t/\tau}dt}{N_2(0)V}=\frac{\tau}{\tau_{sp}}$$

$$\phi=\frac{\tau}{\tau_{sp}} \quad \textit{where} \quad \frac{1}{\tau}=\frac{1}{\tau_{sp}}+\frac{1}{\tau_{nr}}$$

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For more than two levels;

$$\frac{1}{\tau}=\left(\frac{1}{\tau_{21}}\right)_{sp}+\left(\frac{1}{\tau_{23}}\right)_{sp}+\ldots\ldots\ldots\ldots+\frac{1}{\tau_{nr}}\ , \quad \phi_{21}=\frac{\tau}{(\tau_{21})_{sp}} \quad (1)$$

By measuring both τ and ϕ, we can measure τ_{sp} .

Another quantity of interest is σ. We can determine it too

Recall;

$$\therefore \sigma=\frac{\alpha}{(N_1-N_2)}=\frac{2\pi^2}{3n\varepsilon_o c_0 h}|\mu|^2\nu_0 g(\Delta\nu) \quad (2)$$

And;

$$\frac{1}{\tau_{sp}}=\frac{16\pi^3\nu_o^{\,3}n|\mu|^2}{3h\varepsilon_o c^3}=\frac{\phi_{21}}{\tau} \quad (3)$$

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If all atoms are in ground state , $N_1=N_t$, $N_2=0$, then σ_{12} can be determine by measuring α

If the state of interest do not involve ground state, or if the population is unknown, we first determine τ_{sp} from which we obtain $|\mu|^2$ then we measure $g(\nu-\nu_0)$ by emission or absorption.

With $|\mu|^2$ and $g(\nu-\nu_0)$, we could calculate $\sigma(\nu)$

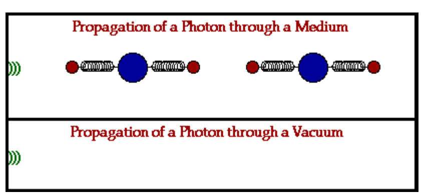
From (1) and (3) into (2), we get;

$$\sigma = \frac{c_0^2}{8\pi n^2 \nu_0^2}\frac{\phi_{21}}{\tau} g(\nu-\nu_0) = \frac{(\lambda/2)^2}{2\pi}\frac{\phi_{21}}{\tau} g(\nu-\nu_0) \quad , \quad \lambda = \lambda_0 / n$$

A simple model – classical electron oscillator

The interaction of light and matter is what makes life interesting. Everything we see is the result of this interaction. Why is light absorbed or transmitted by a particular medium? Light causes matter to vibrate. Matter in turn emits light, which interferes with the original light.

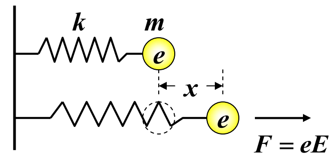
Destructive interference means absorption. Mere out-of-phase interference changes the phase velocity of light, or refractive index.



Consider an electron on a spring with position *xe*(*t*), and driven by a light wave, $E_0 \exp(-i\omega t)$:

Recall the electronic oscillator model at 1-D

Equation of motion:



$$\ddot{x}(t) + \gamma\,\dot{x}(t) + \omega_0^{\,2} x(t) = -\frac{e}{m} E_x(t)$$

Where $E_x(t)$ is an applied field and γ is damping rate

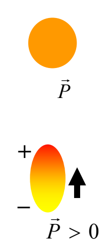
For steady-state solution, let

$$E_x(t) = \frac{1}{2}\left[E_x(\omega)e^{i\omega t} + c.c\right] \quad , \quad x(t) = \frac{1}{2}\left[X(\omega)e^{i\omega t} + c.c\right]$$

$$\therefore X(\omega) = \frac{(e/m)E_x(\omega)}{(\omega_0^2 - \omega^2) + i\gamma\omega}$$

The applied field induces a displacement which polarizes the medium

$$P = \varepsilon_0 \chi E \equiv N\mu = -NeX = \frac{-(Ne^2/m)E}{(\omega_0^2 - \omega^2) + i\gamma\omega}$$



Where N is number of atoms per unit volume

$$\Rightarrow \quad \chi(\omega) = \frac{-Ne^2}{m\varepsilon_0} \frac{1}{(\omega^2 - \omega_0^2) - i\gamma\omega}$$

Near resonance $\omega \approx \omega_0$ ➡ $\omega^2 - \omega_0^2 = (\omega - \omega_0)(\omega + \omega_0) \approx 2\omega_0(\omega - \omega_0)$

$$\therefore X(\omega) = \frac{e}{2m\omega_0} \frac{E_x(\omega)}{(\omega - \omega_0) + i\gamma/2}$$

This is called response function

$$|X(\omega)|^2 = \left(\frac{eE}{2m\omega_0}\right)^2 \frac{1}{(\omega - \omega_0)^2 + (\gamma/2)^2} \propto g(\omega - \omega_0)$$

We will see later WHY?

Because

$$g(\omega-\omega_0)=\frac{\gamma/2\pi}{(\omega-\omega_0)^2+(\gamma/2)^2}$$

Lorentzian line

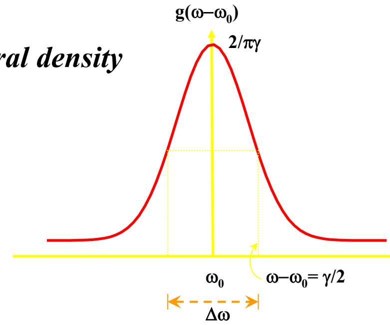
$$\int_{-\infty}^{\infty} g(\omega-\omega_0)\,d\omega=1 \quad , \quad NOTE\ ;\ 2\pi g(\omega-\omega_0)\,d\omega=g(\nu-\nu_0)\,d\nu$$

$$g(\omega-\omega_0)\equiv \text{Normalized power spectral density}$$

$$g(0)=\frac{\gamma/2\pi}{(\gamma/2)^2}=\frac{2}{\pi\gamma}$$

$\Delta\omega \equiv$ Full Width at Half Maxima

$\Delta\omega_{FWHM}=2\times(\gamma/2)=\gamma=1/\tau \quad , \quad \tau=$ life time



$$\Rightarrow \quad \chi_{res}(\omega)=-\frac{Ne^2}{2m\varepsilon_0\omega_0}\frac{1}{(\omega-\omega_0)-i\gamma/2}$$

$$=\frac{\pi Ne^2}{2m\varepsilon_0\omega_0}\left\{\frac{(\omega-\omega_0)/\pi}{(\omega-\omega_0)^2+(\gamma/2)^2}-i\frac{\gamma/2\pi}{(\omega-\omega_0)^2+(\gamma/2)^2}\right\}$$

$$=\chi'(\omega)-i\chi''(\omega)$$

$$\chi'(\omega)=\frac{Ne^2}{m\varepsilon_0\omega_0\gamma}\left(\frac{\pi\gamma}{2}\right)\frac{(\omega_0-\omega)/\pi}{(\omega-\omega_0)^2+(\gamma/2)^2}$$

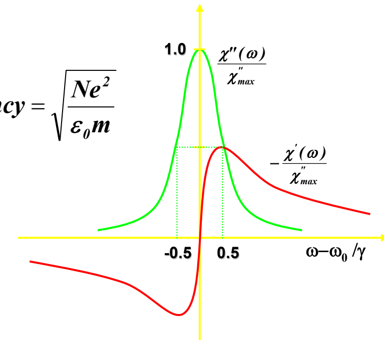
$$\chi''(\omega)=\frac{Ne^2}{m\varepsilon_0\omega_0\gamma}\left(\frac{\pi\gamma}{2}\right)\frac{\gamma/2\pi}{(\omega-\omega_0)^2+(\gamma/2)^2}$$

At $\omega=\omega_0$ $\quad \chi''(\omega=\omega_0)=\chi''_{max}=\dfrac{Ne^2}{m\varepsilon_0\omega_0\gamma}$

Recall;

$$\omega_p = plasma\ frequency = \sqrt{\frac{Ne^2}{\varepsilon_0 m}}$$

$$\therefore \chi''_{max} = \frac{\omega_p^2}{\omega_0 \gamma}$$



Wave propagation and $\chi(\omega)$

As the wave propagate through the medium, two modifications takes place. $\chi'(\omega)$ changes the refractive index (thus velocity) and $\chi''(\omega)$ absorbs optical energy.

$$\vec{D} \equiv Displacement\ vector = \varepsilon_o \vec{E} + \vec{P} = \varepsilon_o \vec{E} + \chi_{non\ res}\varepsilon_o \vec{E} + \chi_{res}\varepsilon_o \vec{E}$$

$$= \varepsilon\vec{E} + \chi_{res}\varepsilon_o \vec{E} = \varepsilon\left(1 + \frac{\varepsilon_o}{\varepsilon}\chi_{res}\right)\vec{E} \equiv \varepsilon'\vec{E}$$

$$E(z,t) = Re\left\{E_o e^{i\left(\omega t - k'z\right)}\right\}$$

where

$$k' = \omega\sqrt{\mu\varepsilon'} = \omega\sqrt{\mu\varepsilon}\left(1 + \frac{\varepsilon_o}{\varepsilon}\chi_{res}\right)^{1/2}$$

$$\approx k\left[1 + \frac{1}{2}\frac{\varepsilon_o}{\varepsilon}(\chi' - i\chi'')\right] = k\left[1 + \frac{\chi'}{2n^2}\right] - i\frac{k}{2n^2}\chi''$$

$$where \quad n^2 = \varepsilon / \varepsilon_0 = Re\ fractive\ index$$

For real part of k'

$$k' = k\left[1 + \frac{\chi'}{2n^2}\right] = \frac{\omega}{c_0} n(\omega)$$

$$for\ \omega < \omega_0\ ,\ \ \chi'\ \ is\ positive \Rightarrow\ k' > k\ \ or\ \ n$$

This is called normal dispersion

The imaginary part tells us;

$$E \propto e^{-i\left(k' z\right)} \propto e^{-i\left(-i\frac{k}{2n^2}\chi'' z\right)} \propto e^{-\frac{k}{2n^2}\chi'' z}$$

$$\because\ \ I \propto E^2$$

$$\therefore\ \ \ I(z) = I(0)\, e^{-\frac{k}{n^2}\chi'' z} = I(0)\, e^{-\alpha z}$$

$$\alpha \equiv Absorption\ coeffecient = \frac{k}{n^2}\chi'' = \frac{k}{n^2}\frac{\pi N e^2}{2m\varepsilon_0\omega_0} g(\Delta\omega)\ \ ,\ k = \omega/c$$

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$$\therefore \sigma = Absorption\ Cross\text{-}section = \frac{\alpha}{N} = \frac{\omega}{cn^2}\frac{\pi e^2}{2m\varepsilon_0\omega_0} g(\Delta\omega)$$

<u>**Transition dipole moment and Oscillator Strength**</u>

The concept of oscillator strength *f* has been developed to provide a theoretical reference for the intensity of a spectroscopic transition.

***f*= the ratio of the strength of a transition to the strength of a transition for an electron oscillating harmonically in 3 – dimension.**

$$f = Oscillator\ Strength = \frac{\sigma)_{atom}}{\sigma)_{osc.mod}}$$

$$\therefore\ \ f_{21} = \frac{4\pi}{3}\frac{m\omega_0}{e^2 h}|\mu_{21}|^2 = \frac{2}{3}\frac{m\omega_0}{e^2\hbar}|\mu_{21}|^2$$

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Example;

For $\mu = 1.6\times10^{-29}$ C.m, $\omega_0 = 3.77\times10^{15}\ s^{-1}$, $h = 6.6\times10^{-34}$, $e = 1.6\times10^{-19}$ C and $m=9\times10^{-31}$ kg ➡ $f= 0.215$

MORE ABOUT ELECTRON- OSCILLATOR MODEL AND ABSORPTION CROSS-SECTION

electron- oscillator model

$$\chi(\omega) = \frac{-Ne^2}{m\varepsilon_0}\frac{1}{(\omega^2-\omega_0^2)-i\gamma\omega}$$

$$D = \varepsilon_o E + \chi\varepsilon_o E \quad \Rightarrow \quad \varepsilon = \varepsilon_0(1+\chi)$$

$$Re\ fractive\ index = n = \sqrt{\frac{\varepsilon}{\varepsilon_0}} = (1+\chi)^{1/2} \approx 1+\frac{1}{2}\chi$$

$$\therefore n-1 = \frac{1}{2}\chi(\omega) = \frac{Ne^2}{2m\varepsilon_0}\frac{1}{(\omega_0^2-\omega^2)+i\gamma\omega}$$

In terms of classical electron radius r_e

$$\frac{e^2}{4\pi\varepsilon_0 r_e} = mc^2 \quad ➧ \quad r_e = \frac{e^2}{4\pi\varepsilon_0 mc^2} = 2.82\times10^{-15}\ m$$

$$\therefore n-1 = \frac{N}{2}4\pi\, r_e^2 c^2\, \frac{1}{(\omega_0^2-\omega^2)+i\gamma\omega}$$

$$\omega = 2\pi c/\lambda$$

$$\therefore\ n-1 = \frac{Nr_e}{2\pi}\frac{1}{\left(\frac{1}{\lambda_0}\right)^2+\left(\frac{1}{\lambda}\right)^2+i\left(\frac{\gamma}{\lambda\omega}\right)}$$

This is compares well with the quantum mechanical “Semier’s Eq”

$$n-1 = \frac{Nr_e}{2\pi}\sum_i \frac{f_i}{\left(\frac{1}{\lambda_i}\right)^2-\left(\frac{1}{\lambda}\right)^2} \quad , \qquad f_i = Oscillator\ strength$$

Absorption cross-section

$$\because \sigma_{2-level\ atom} = \frac{2\pi^2}{3n\varepsilon_o c_0 h}|\mu|^2 \nu_0 g(\Delta\nu)$$

$$and \qquad \frac{1}{\tau_{sp}} = \frac{16\pi^3 \nu_o{}^3 n|\mu|^2}{3h\varepsilon_o c^3} \quad , \; \lambda = \lambda_0 / n$$

$$\therefore \qquad \sigma_{2-level\ atom} = \frac{\lambda^2}{8\pi}\frac{g(\Delta\nu)}{\tau_{sp}}$$

At resonance; $\sigma(\nu_0) = \frac{\lambda^2}{8\pi}\frac{1}{\tau_{sp}}\frac{2}{\pi\gamma} = \frac{\lambda^2}{2\pi}$