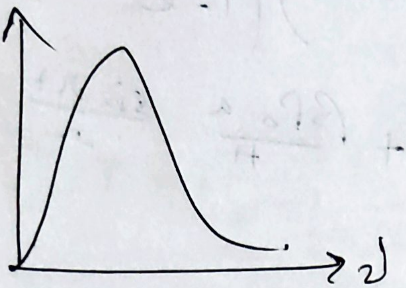
Spectral Line Shape



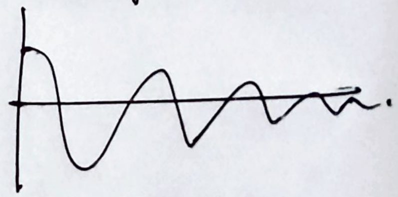
Natural Line broadening. → particular state has life time. and depending on that it has a natural width.

$\Delta E \, \Delta\tau \sim \hbar$

$\Delta E \sim \frac{\hbar}{\Delta\tau}$ $\Delta\tau$ = life time.

Oscillator Model

damped oscillator.



$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = 0$

damping.

$I = \frac{1}{(\omega-\omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$ (Lorentzian fn)

Energy response $= E = \frac{1}{2}\tilde{x}^*\tilde{x}$

for visible light ~~x~~ $\Delta\tau_{vib} \approx 0.1$ sec

$\Delta E \, \Delta\tau = \hbar$

$h\Delta\nu = \frac{\hbar}{\Delta\tau} \Rightarrow \Delta\nu = \frac{\hbar}{h\,\Delta\tau} = \frac{1}{2\pi\,\Delta\tau}$

$= \frac{1}{2\pi \times 0.1}$ sec^{-1}

Line shape of Absorption Spectra :-

Now, we have external force, forced oscillation.

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = \frac{qE_0 e^{i\omega t}}{m}$$

$$x = x_0 e^{i\omega t}$$

$$(i\omega)^2 x_0 \cancel{e^{i\omega t}} + \gamma i\omega x_0 \cancel{e^{i\omega t}} + \omega_0^2 x_0 \cancel{e^{i\omega t}} = \frac{qE_0}{m} \cancel{e^{i\omega t}}$$

$$-\omega^2 x_0 + i\gamma\omega x_0 + \omega_0^2 x_0 = \frac{qE_0}{m}$$

$$x_0 = \frac{qE_0}{m(\omega_0^2 - \omega^2 + i\gamma\omega)}.$$

Dipole moment $\vec{P} = qx = q \cdot \dfrac{q\vec{E}}{m(\omega_0^2 - \omega^2 + i\gamma\omega)}$.

polarizibility : $\vec{P} = \dfrac{\text{dipole moment}}{\text{volume}}$.

N = density of oscillator → electron.

$$\vec{P} = \frac{Nq^2\vec{E}}{m(\omega_0^2 - \omega^2 + i\gamma\omega)} = \underbrace{\chi}_{\text{susceptibility}} E \varepsilon_0 \quad \text{——— (1)}$$

~~Direct~~ Dielectric constant $\varepsilon = (1+\chi)\varepsilon_0$.

$$\chi = \varepsilon_r - 1 = \frac{\varepsilon}{\varepsilon_0} - 1 = \underbrace{n}_{\text{refractive index}}{}^2 - 1$$

for $n \approx 1$ $\quad \chi = 2(n-1)$. ——— (2)

from ① we can write

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

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

$$n = n' - ik = 1 + \frac{Nq^2}{2m\varepsilon_0}\frac{(\omega_0^2-\omega^2-i\gamma\omega)}{[(\omega_0^2-\omega^2)^2+(\gamma^2\omega^2)]}$$

$$\boxed{n' = 1 + \frac{Nq^2}{2m\varepsilon_0}\frac{(\omega_0^2-\omega^2)}{[(\omega_0^2-\omega^2)^2+(\gamma\omega)^2]}} \longrightarrow ⓐ$$

Electric field of EM radn in vac.

$$\vec{E} = E_0 e^{i(\omega t - k_0 z)}.$$

Electric field in medium:

$$\vec{E} = E_0 e^{i(\omega t - nk_0 z)}.$$

$$= E_0 e^{i(\omega t - (n'-ik)k_0 z)}$$

$$= E_0 e^{-kk_0 z} e^{i(\omega t - n'k_0 z)}.$$

Lambert Beers Law

$I = I_0 e^{-\alpha z}$ α = abs. coefficient

$(Amp)^2$ — Intensity.

$$I = E_0^2 \, e^{-2Kk_0 z} \, e^{2i(\omega t - n' k_0 z)}.$$

$$I = I_0 e^{-\alpha z}$$

$$\alpha = 2Kk_0 .$$

$$\boxed{\alpha = 2k_0 \cdot \frac{Nq^2 \gamma\omega}{2m\varepsilon\left[(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2\right]}} \longrightarrow (b)$$

$$\omega = ck \longrightarrow k_0 = \frac{\omega_0}{c}$$

Kramer's-Kronig Eqn. (a), (b).
Relation.

gives real part of RI and absorption coefficient of light following this oscillator model.

$$n' = 1 + \frac{Nq^2(\omega_0^2 - \omega^2)}{2m\varepsilon_0\left[(\omega_0^2 - \omega^2) + (\gamma\omega)^2\right]}$$

$$\alpha = 2k_0 \frac{Nq^2 \gamma\omega}{2m\varepsilon_0\left[(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2\right]}$$

Close to Resonance $\omega_0 \approx \omega$

$$n' = 1 + \frac{Nq^2(\omega_0 + \omega)(\omega_0 - \omega)}{2m\varepsilon\left[(\omega_0 + \omega)^2(\omega_0 - \omega)^2 + (\gamma\omega)^2\right]} \approx 1 + \frac{Nq^2 \, 2\omega_0(\omega_0 - \omega)}{2m\varepsilon\left[4\omega_0^2(\omega_0 - \omega)^2 + (\gamma\omega)^2\right]}$$

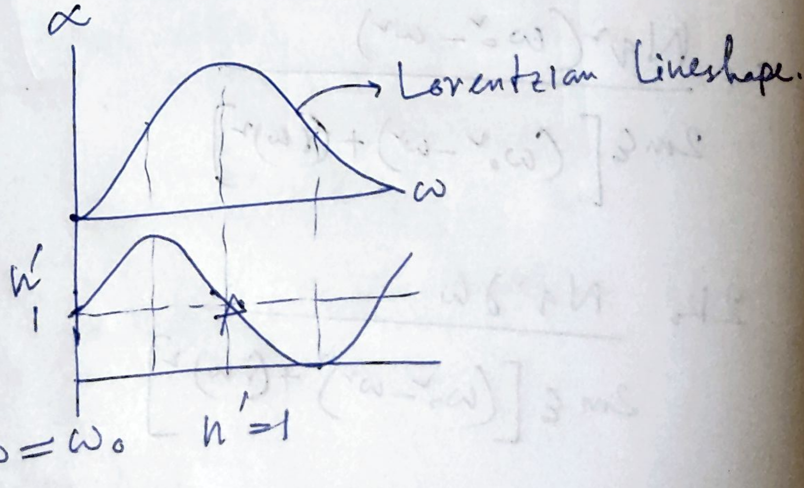
$$n' = 1 + \frac{Nq^2(\omega_0-\omega)}{4m\varepsilon\{\omega_0\left[(\omega_0-\omega)^2+\left(\frac{\gamma}{2}\right)^2\right]}$$

$$\alpha = 2k_0 \frac{Nq^2\,\omega\gamma}{2m\varepsilon\left[4\omega_0^2(\omega_0-\omega)^2+(\gamma\omega)^2\right]}$$

$$= \frac{\cancel{2}k_0}{\cancel{2}m\varepsilon_0}\,\frac{Nq^2\cancel{\omega_0}\gamma}{4\omega_0^{\cancel{2}}\left[(\omega_0-\omega)^2+\left(\frac{\gamma}{2}\right)^2\right]}$$

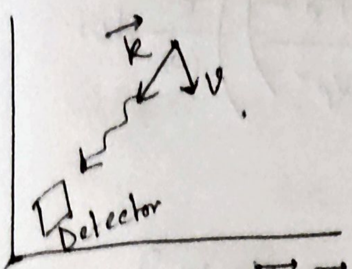
$$= \frac{Nk_0 q^2\gamma}{4m\varepsilon_0 c\cancel{\omega_0}\left[(\omega_0-\omega)^2+\left(\frac{\gamma}{2}\right)^2\right]}$$

$$= \frac{Nq^2\gamma}{4m\varepsilon_0 c\left[(\omega_0-\omega)^2+\left(\frac{\gamma}{2}\right)^2\right]}$$



at $\omega=\omega_0$ $n'=1$

Doppler Broadening :-



Natural line broadening is for static atom.

$$\omega = \omega_0 \pm \vec{k}\cdot\vec{v}$$

+ : source is moving towards detector

− : source is moving away from the detector.

Assume $k \to k_z$ $(0,0,k_z)$ $\qquad k = \frac{\omega}{c}$

$v \to v_z$

$(0,0,v_z)$ $\qquad \omega = \omega_0\left(1+\frac{v_z}{c}\right)$ — ①

E_i: energy of atom per unit volm in the i th state

No. of molecules having energy E_i moving with velocity v_z and $v_z + dv_z$

$$n_i(v_z)\,dv_z = \frac{N_i}{\sqrt{\pi}\,v_p}\exp\left(-\left(\frac{v_z}{v_p}\right)^2\right)dv_z \quad \text{— ②}$$

v_p = most probable speed. $= \sqrt{\frac{2kT}{m}}$

Total no. of atom in the ith state $N_i = \int n(v_z)\,dv_z$

From ① $\longrightarrow d\omega = \omega_0 \frac{dv_z}{c}$

$$\longrightarrow v_z = \left(\frac{\omega}{\omega_0} - 1\right)c = \frac{(\omega-\omega_0)c}{\omega_0}$$

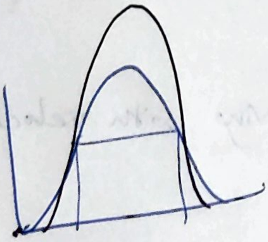
From (2)

$$n(\omega)\,d\omega = \frac{N_i}{\sqrt{\pi}\,V_p} \exp\left(-\left(\frac{(\omega-\omega_0)^2 c^2}{\omega_0^2 V_p^2}\right)\right)\frac{c}{\omega_0}\,d\omega$$

$$= \frac{N_i c}{\sqrt{\pi}\,V_p\,\omega_0} \exp\left[-\frac{(\omega-\omega_0)^2 c^2}{\omega_0^2 V_p^2}\right] d\omega$$

Intensity $I = I_0 \exp\left[-\frac{(\omega-\omega_0)^2 c^2}{\omega_0^2 V_p^2}\right]$ (gaussian fn)

intensity of the atoms in the frequency range ω and $\omega + d\omega$ or in energy range E and $E + dE$ following Maxwell - Boltzmann distribution.



FWHM

$$\exp\left[-\frac{(x-x_0)^2}{\sigma^2}\right] \qquad \exp\left[-\frac{(\omega-\omega_0)^2}{\omega_0^2 V_p^2}\right]$$

$\sigma = \frac{\omega_0 V_p}{c}$

FWHM $= 2\sqrt{\ln 2}\,\sigma$

$$\delta\omega_D = 2\sqrt{\ln 2}\,\frac{\omega_0 V_p}{c}$$

$$= 2\sqrt{\ln 2}\,\frac{\omega_0}{c}\sqrt{\frac{2kT}{m}}$$

$$= \frac{\omega_0}{c}\sqrt{\frac{8kT\ln 2}{m}} = \frac{\omega_0}{c}\sqrt{\frac{8T N_A k \ln 2}{N_A m}}$$

$$= \frac{\omega_0}{c}\sqrt{\frac{8RT\ln 2}{M}}$$

$$\boxed{\delta\nu_D = 7.16\times10^{-7}\,\nu_0\sqrt{\frac{T}{M}}}$$

M = Molar mass.

~~Q~~ for Na D line $\tau = 16\,ns$

$\delta\nu_N = 10\,MHz$

$\Delta E \Delta t = \hbar$

$$\Delta E = \frac{\hbar}{\Delta t}$$

$$\hbar\omega = \frac{\hbar}{\Delta t} \Rightarrow \Delta\nu = \frac{\hbar}{h\,\Delta t} = \frac{1}{\Delta\tau \times 2\pi}$$

$\delta\nu_D$ at $500K$ $M = 23$

$$\lambda_0 = 589\,nm \qquad \nu = \frac{c}{\lambda} = \frac{3\times10^{8}\,m/s}{589\times10^{-9}\,m}$$

$$= 0.00509\times10^{17}\,s^{-1}$$

$$= 0.509\times10^{15}\,s^{-1}$$

$\omega = 2\pi\nu$

$\delta\omega = 2\pi\,\delta\nu$ $= 5\times10^{14}\,s^{-1}$

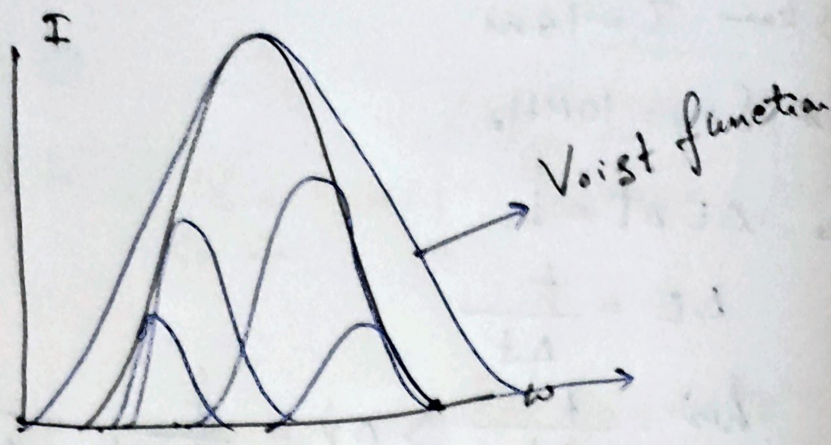
$\cancel{\delta\nu = \frac{1}{2\pi}\delta\omega = \frac{1}{2\pi}\left[7.16\times10^{-7}\right]}$

$$\delta\nu_D = 7.16\times10^{-7}\,\nu_0\sqrt{\frac{T}{M}}$$

$$= 7.16\times10^{-7} \times 0.509\times10^{15}\sqrt{\frac{500}{23}}$$

$$= 7.16\times 0.509\times10^{8}\times 4.66$$

$$= 16.98\times10^{8} = 1.6\times10^{9}\,Hz$$



for ~~Eac~~ each ω you'll have a Lorentzian broadening, you get gaussian fn for doppler broadening.

for natural broadening you get Lorentzian fn

~~B~~. Combining both we get Voigt fn.

$$I = C\int \exp\left[-\frac{(\omega_0-\omega')^2 c^2}{\omega_0^2 v_p^2}\right]\frac{1}{(\omega-\omega')^2+(\gamma/2)^2}\,d\omega'$$

~~\$~~ In instrument we get