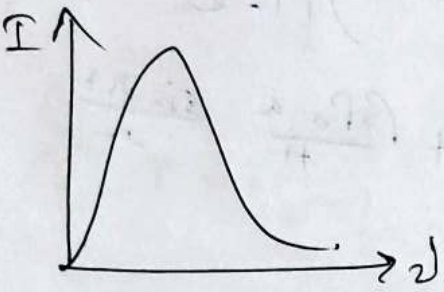
Spectral Line Shape



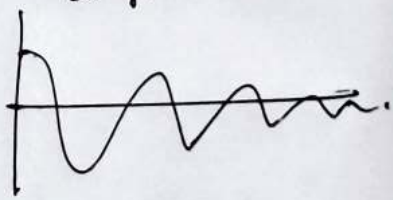
Natural Line broadening. → particular state has life time. and depending on that it has a natural width.

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

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

Oscillator Model

damped oscillation.



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

(γ: 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 ✱ $\Delta \tau_{vib} \approx 0.1$ sec

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

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

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

Line shape of Absorption Spectra :-

Now, we have external force, forced oscillation.

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

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

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

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

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

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

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

N = density of oscillator → electron.

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

↓ susceptibility.

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

$$\chi = \varepsilon_r - 1 = \frac{\varepsilon}{\varepsilon_0} - 1 = n^2 - 1$$

↓ refractive index.

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

from ① we can write

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

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

$$\downarrow$$

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

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

Electric field of EM rad^n 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 Beer's Law

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

$(Amp)^2$ - Intensity.

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

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

$$\alpha = 2K k_0.$$

$$\alpha = 2k_0 \frac{N q^2 \gamma \omega}{2m\varepsilon \left[(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2\right]} \longrightarrow (L)$$

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

Kramer's-Kronig Relation. @, (b).

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

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

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

Close to Resonance $\omega_0 \approx \omega$

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

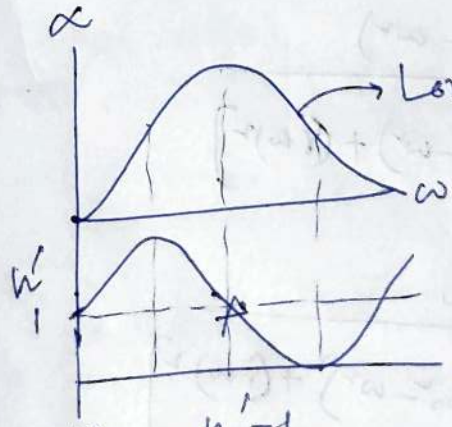
$$n' = 1 + \frac{Nq^2(\omega_0 - \omega)}{4m\varepsilon_0\omega_0\left[(\omega_0-\omega)^2 + \left(\frac{\gamma}{2}\right)^2\right]}$$

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

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

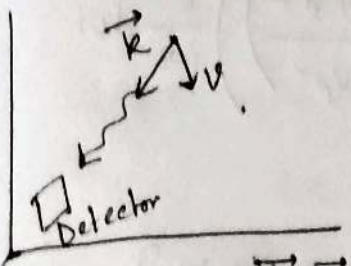
$$= \frac{Nk_0q^2\gamma}{4m\varepsilon_0 c\omega_0\left[(\omega_0-\omega)^2 + \left(\frac{\gamma}{2}\right)^2\right]}$$

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



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 $k \to k_z$ $(0, 0, k_z)$ $\quad k = \frac{\omega}{c}$.

$v \to v_z$

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

E_i : energy of atom per unit volm in the ith 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) $\longrightarrow d\omega = \omega_0 \frac{dv_z}{c}$

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

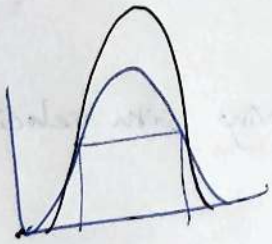
From (2)

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

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

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

$$\exp\left[-\frac{(x-x_0)^2}{\sigma^2}\right] \Bigg| \quad \exp\left[-\frac{(\omega-\omega_0)^2}{\omega_0^2 v_p^2}\right]$$

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

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

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

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

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

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

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

$M = m_0 N_A$ mass.

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

$\delta\nu_N = 10\,MHz$

$\Delta E \Delta t = \hbar$

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

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

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

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

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

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

$\omega = 2\pi\nu$

$\delta\omega = 2\pi\delta\nu$

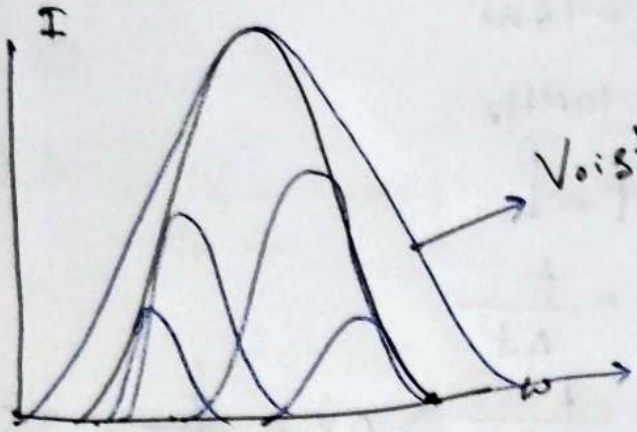
$\delta\nu = \frac{1}{2\pi}\delta\omega = \frac{1}{2\pi} 7.16\times10^{-7} = 5\times10^{14}\,s^{-1}$

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

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

$= 7.16\times0.509\times10^8 \times 4.66$

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



for 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.

$$I = C \int \exp\left[-\frac{(\omega_0 - \omega')^2 C^2}{\omega_1^2 v_p^2}\right] \frac{1}{(\omega - \omega')^2 + (\gamma/2)^2} d\omega'$$

In instrument we get