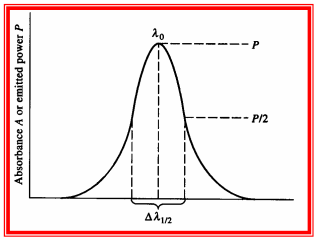
Atomic Line Widths

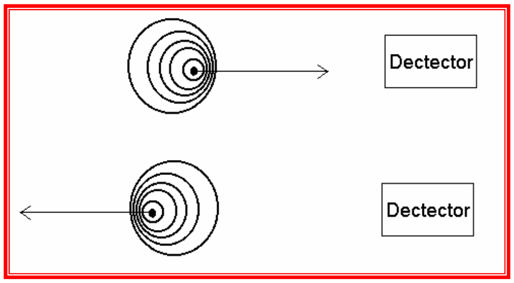
Theoretically, atomic lines will have 0 line width, but

Line broadening caused by

- uncertainty principle (10^{-4} Å)
  - natural line width - caused by finite lifetime of excited state
- pressure effects
  - collisions with other atoms cause changes in ground state energy
- electric and magnetic field effects



- Doppler broadening
  - if an atom emits radiation while moving toward the detector, the waves will be compressed, and the wavelength will be shorter
  - if an atom emits radiation while moving away from the detector, the waves will stretched out, and the wavelength will be longer
  - related effect for absorption



Line Broadening Mechanism

There are many reasons (mechanisms) which causes emission and absorption line to be broadening from the ideal $\delta(\Delta\omega)$ to realistic line shape $g(\Delta\omega)$.

HOMOGENEOUS BROADENING; The mechanism broadens the line of each individual atom. The line of the whole system is thus broadened in the same way.

INHOMOGENEOUS BROADENING; The total line of the system is broadened because the resonance frequencies of the atoms, for some reasons, are distributed over a band. The line of individual atoms are not necessarily broadens.

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Life-time Broadening (energy – decaying)

If the oscillation of classical oscillator decay with damping rate γ, the line-shape function is;

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

Lorentzian Line

The full radian-frequency linewidth is $\Delta\omega=\gamma$

Remember that the equation for the oscillator is;

$$\ddot{X}(t)+\gamma\,\dot{X}(t)+\omega_0{}^2X(t)=0$$

$$X(t)\sim e^{\left[-\frac{\gamma}{2}\pm\sqrt{\left(\frac{\gamma}{2}\right)^2-\omega_0^2}\right]t}$$

$$\approx e^{-\frac{\gamma}{2}t}\,e^{\pm i\omega_0 t}$$

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Thus, γ is the damping rate of X^2, *or oscillating energy*, the line-shape function $g(\Delta\omega)$ is also proportional to $|X(\omega)|^2$ and is some time called normalized power spectral density.

Near resonance; Let $X(t) \approx \frac{X(0)}{2} e^{-\frac{\gamma}{2}t} e^{\pm i\omega_0 t}, t > 0$

Fourier transformation $X(\omega) = \int_0^\infty X(t) e^{i\omega t} dt = \frac{X(0)}{2} \frac{-1}{\frac{-\gamma}{2} + i(\omega - \omega_0)}$

$$\therefore \quad |X(\omega)|^2 = \frac{X^2(0)}{4} \frac{1}{(\omega-\omega_0)^2 + (\gamma/2)^2} \propto g(\omega - \omega_0)$$

Spontaneous emission is an example of life-time broadening.
The energy of oscillator decays with rate γ=A; $\Delta\omega=\gamma=A=1/\tau_{sp}$

There are non-radiative process (not dephasing) which correspond to decaying of energy. In general $\frac{1}{\tau} = \frac{1}{\tau_{sp}} + \frac{1}{\tau_{nr}}$

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5

The linewidth broadening due to spontaneous emission may also interpreted by uncertainty principle.

If, $\Delta t \approx$life-time$=\gamma^{-1}=T_1$

$\Delta E\ \Delta t \approx \hbar/2$ ➡⇨ $\Delta E \sim \frac{\hbar}{2\Delta t} = \hbar(\frac{\gamma}{2}) = \frac{1}{2}\hbar\Delta\omega = half - width\ in\ energy$

Recall the electronic oscillator model at 1-D.
Equation of motion:

$$\ddot{x} + \gamma\dot{x} + \omega_a^2 x = -\frac{e}{m} E(t)$$ **where *E(t)* is an applied field**

Define electronic dipole moment $\mu = -ex$

With the equation of motion of μ

$$\ddot{\mu} + \gamma\dot{\mu} + \omega_a^2 \mu = \frac{e^2}{m} E(t)$$

A solution for $\mu(t)$ is

$$\mu(t) = \mu_o \exp\left[-\left(\frac{\gamma}{2}\right)(t - t_o) + i\omega_a(t - t_o) + i\phi_o\right]$$

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6

The decay time constant for $\mu(t)$ is $\gamma/2$.

Define the macroscopic polarization $\vec{P}$, where $\vec{P} = \frac{N\vec{\mu}}{V}$, and N: no. of dipoles , V: volume

Note $\vec{P}$ is in general a vector, it is the vector sum of N individual dipoles

The time behavior of $\vec{P}$ is different from μ . Before the decay of each individual dipole, $\vec{P}$ could decay by "DEPHASING"; the randomization of individual dipoles.

Generally, the equation of motion for $\vec{P}$ is

$$\ddot{P} + \left(\gamma + \frac{2}{T_2}\right)\dot{P} + \omega_a{}^2 P = \frac{Ne^2}{m}E(t)$$

T_2 is called the dephasing time.

The complete linewidth is given by more general expression for collision plus life-time broadening.

$$\boxed{\Delta\omega\Big|_{full\ width} = \gamma + \frac{2}{T_2}}$$

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7

Nature of Dephasing

Time behavior of individual dipole can be written as

$$\vec{\mu}_i(t) = \vec{\mu}_{io}\, exp\left[-\left(\frac{\gamma}{2}\right)(t - t_o) + i\omega_a(t - t_o) + i\phi_{oi}\right]$$

ϕ_{oi} is the phase angle for ith dipole

"Non-radiative" collisional processes could lead to randomization of phase angles between dipoles. The dephasing process is characterized by dephasing time T_2, which is often much shorter than $1/\gamma$. Examples of dephasing processes:

- Collisions between atoms. (mostly in gas phase)
- Phonon broadening: thermal agitation of the lattice that interact with the dipoles
- Dipolar coupling: Electrostatic field due to adjacent dipoles

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8

INHOMOGENEOUS BROADENING

Some line-broadening mechanism (e.g. Doppler effect) distributes the resonance frequencies of the atoms over a given band centered at ν_0

If $g^*(\nu_o' - \nu_o)$ represents the probability an atom has its resonance frequency between $\nu_o' - d\nu_o'$ and $\nu_o' + d\nu_o'$. Hence the total line shape (accounting for atoms at different resonance frequencies)

$$g_t(\nu_o, \nu) = \int_{-\infty}^{\infty} g^*(\nu_o' - \nu_o) \underbrace{g_L(\nu - \nu_o')}_{\text{Lorenzian line with a resonance frequency at } \nu_o} d\nu_o'$$

Let $x = \nu_o' - \nu_o$

$$g_t(\nu_o - \nu) = \int_{-\infty}^{\infty} g^*(x) g_L[(\nu - \nu_o) - x] dx$$

If $g_L[(\nu - \nu_o) - x] \cong \delta[(\nu - \nu_o) - x]$

$$g_t(\nu_o - \nu) = g^*(\nu_o' - \nu)$$

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For example, for atoms obeying Maxwell-Boltzmann distribution, the shift in resonance frequency is $\nu_o' = \dfrac{\nu_o}{\left(1 \pm \nu_x / c\right)}$.

The +,- sign apply to whether the velocity is in the same or opposite direction.

If the atoms follow the velocity distribution

$$P(v_x) dv_x = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{m v_x^2}{2kT}\right) dv_x$$

Then $$g^*(\nu_o' - \nu_o) = \frac{1}{\nu_o}\left(\frac{mc^2}{2\pi kT}\right)^{1/2} \exp\left[-\frac{mc^2}{2kT}\frac{(\nu_o' - \nu_o)^2}{\nu_o^2}\right]$$

When $g_L(\nu_o - \nu_o')$ is much narrower than g^*, $g_L(\nu_o - \nu_o')$ can be approximated as δ function and $g_t \approx g^*$.

$$\boxed{\begin{aligned} g_D(\nu) &= \sqrt{\frac{4 \ln 2}{\pi}} \frac{1}{\Delta\nu_D} \exp\left[-4 \ln 2\left(\frac{\nu - \nu_o}{\Delta\nu_D}\right)^2\right] \\ \Delta\nu_D &= \frac{2\nu_o}{c}\sqrt{\frac{2kT}{m}\ln 2} \end{aligned}}$$

Gaussian distribution

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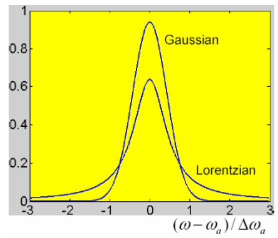
Lorenzian Line (homogeneous broadening)

$$\boxed{g_L(\nu) = \frac{\Delta\nu_L}{2\pi\left[(\nu_o-\nu)^2+\left(\frac{\Delta\nu_L}{2}\right)^2\right]} \qquad \Delta\nu_L = \frac{1}{2\pi}\left(A+2\nu_c\right)}$$

$$\textit{from} \quad \gamma \rightarrow \gamma + \frac{2}{T_2}$$



e.g. for light atoms emitting in the visible,

$$\Delta\nu_L \approx 100\,MHz \qquad \Delta\nu_D \approx a\ few\ GHz \qquad \Rightarrow \Delta\nu_D \cong 10^2\,\Delta\nu_L$$

Homogeneous Broadened Line width

$$\Delta\omega = \frac{1}{\tau_{sp}} + \frac{1}{\tau_{nr}} + \frac{2}{\tau_c} \quad , \qquad \tau_c = T_2$$

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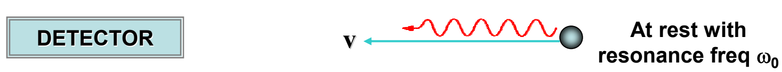
11

Notice that the process giving rise to τ_{nr} and τ_c are quite different. In gas, non-radiative decay τ_{nr} require an inelastic collision by delivering its energy to the sounding molecules. The dephasing collisions, which give rise to τ_c, are however elastic.

Relation between velocity (v) and observed frequency (ω_0').



The observed resonance frequency ω_0' by the detector is given by;

$$\omega_0' = \omega_0\left[1 \pm \frac{v}{c}\right] \quad , \qquad v << c$$

approaching

away

$$\boxed{\omega_0' - \omega_0 = \omega_0\frac{v}{c} \qquad or \qquad v = \frac{c\left(\omega_0'-\omega_0\right)}{\omega_0}}$$

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12