Working with spectral lineshapes

- For atomic system, replace Dirac delta with transition lineshape

$$\int g\left(\nu-\nu_0\right)d\nu = 1$$

- Lorentzian lineshape (radiative, collisional broadening)

$$\delta\left(\nu-\nu_0\right)\rightarrow g_L\left(\nu-\nu_0\right)=\frac{2}{\pi\,\Delta\nu_0}\frac{1}{1+\left(\frac{2\left(\nu-\nu_0\right)}{\Delta\nu_0}\right)^2}$$

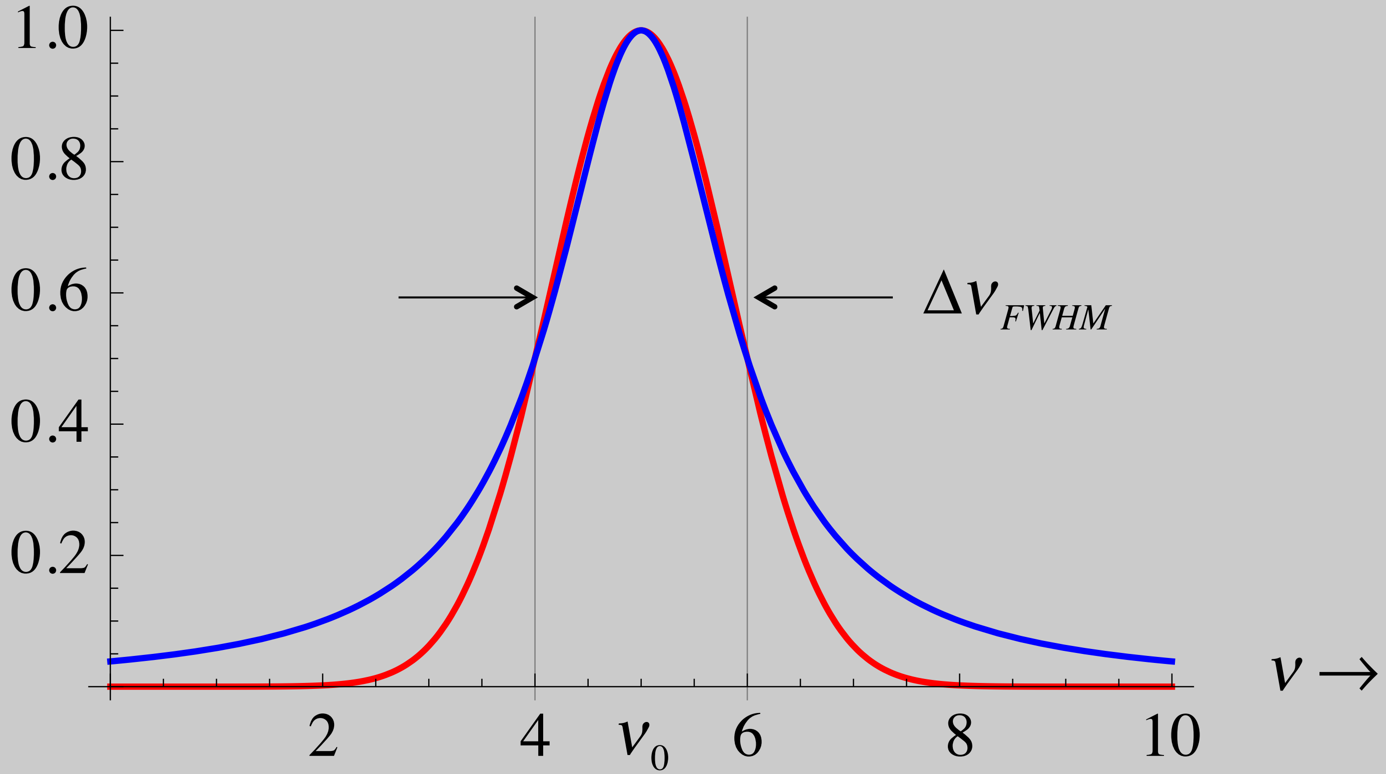
$\Delta\nu_0$ FWHM

- Doppler broadened (Gaussian) lineshape

$$\delta\left(\nu-\nu_0\right)\rightarrow g_G{}^*\left(\nu-\nu_0\right)=\frac{2}{\Delta\nu_0{}^*}\sqrt{\frac{\ln 2}{\pi}}\exp\left\{-4\ln 2\frac{\left(\nu-\nu_0\right)^2}{\Delta\nu_0{}^{*2}}\right\}$$

Lorentzian vs Gaussian lineshapes

- Lorentzian is much broader in spectral wings than Gaussian



Natural broadening

- Radiative broadening comes from the spontaneous emission lifetime of the state: energy-time uncertainty
- Fourier transforms
  - Forward: FT $$F(\omega) = \int_{-\infty}^{\infty} f(t) e^{i\omega t}\, dt$$
  - Inverse: FT^{-1} $$f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} F(\omega) e^{-i\omega t}\, d\omega$$
- Suppose exponential, oscillating decay in time domain

$$f(t) = \begin{matrix} e^{-\gamma t} e^{-i\omega_0 t} & \text{for } t \geq 0 \\ 0 & \text{for } t < 0 \end{matrix}$$

$$F(\omega) = \int_0^{\infty} e^{-\gamma t - i\omega_0 t} e^{i\omega t}\, dt = \left. \frac{e^{(-\gamma + i(\omega - \omega_0))t}}{-\gamma + i(\omega - \omega_0)} \right|_0^{\infty} = \frac{1}{\gamma - i(\omega - \omega_0)}$$

Complex Lorentzian

Lorentzian lineshape

- Complex Lorentzian separated into Re and Im

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

  - Real part corresponds to absorption effects
- Normalize

$$c\int \frac{\gamma}{\left(\omega - \omega_0\right)^2 + \gamma^2} d\omega = c\gamma\frac{\pi}{\gamma} = 1 \quad \rightarrow g_L\left(\omega - \omega_0\right) = \frac{\gamma / \pi}{\left(\omega - \omega_0\right)^2 + \gamma^2}$$

- Convert ω to v

$$c\int \frac{\gamma}{4\pi^2\left(\nu - \nu_0\right)^2 + \gamma^2} d\nu = c\gamma\frac{1}{2\gamma} = 1$$

$$\rightarrow g_L\left(\nu - \nu_0\right) = \frac{2}{\gamma}\left[1 + \left(\frac{2\left(\nu - \nu_0\right)}{\gamma / \pi}\right)^2\right]^{-1} = \frac{2}{\pi\,\Delta\nu_0}\left[1 + \left(\frac{2\left(\nu - \nu_0\right)}{\Delta\nu_0}\right)^2\right]^{-1}$$

Collisional broadening

- Elastic collisions don’t cause transition, but interrupt the phase
- Timescales:
  - Period of EM cycle much less than radiative lifetime $\frac{2\pi}{\omega_0} \ll \tau$
  - Avg time btw collisions < lifetime $\tau_c < \tau$
  - Duration of a collision << time btw coll, lifetime $\Delta\tau_c \ll \tau_c, \tau$
- Calculation:
  - FT over time 0 to τ_1 to get lineshape for a specific oscillation length
  - Average over probability of a given time between collisions:

$$P(\tau_1)d\tau_1 = \frac{1}{\tau_c} e^{-\tau_1/\tau_c} d\tau_1$$

Result:

Lorentzian shape with new width

$$\Delta\nu = \gamma / 2\pi + 1/\pi\,\tau_c$$

Doppler broadening

- From relative velocity of atom to input beam, Doppler shift:

$$\nu_0' = \frac{\nu_0}{1 - \mathrm{v}_z / c}$$

Beam propagating in *z* direction

  - Each atom in distribution is shifted according to its velocity

- Boltzmann distribution

$$P(\mathrm{v}_z) \sim \exp\left[-\tfrac{1}{2} M v_z^2 / k_B T\right]$$

- Average over distribution to get effective lineshape:

$$g^*(\nu - \nu_0) = \frac{1}{\nu_0}\left(\frac{Mc^2}{2\pi k_B T}\right)^{1/2} \exp\left\{\frac{Mc^2}{2k_B T}\frac{(\nu - \nu_0)^2}{\nu_0{}^2}\right\}$$

Gaussian lineshape

FWHM:

$$\Delta\nu_0{}^* = 2\nu_0\left[\frac{2k_B T \ln 2}{Mc^2}\right]^{1/2}$$

Doppler broadening in HeNe lasers

$$\Delta\nu_0{}^* = 2\nu_0\left[\frac{2k_BT\ln 2}{Mc^2}\right]^{1/2}$$

$$\lambda_0 = 632.8\text{nm}$$

$$\nu_0 = 4.74\times10^{14}\,\text{s}^{-1}$$

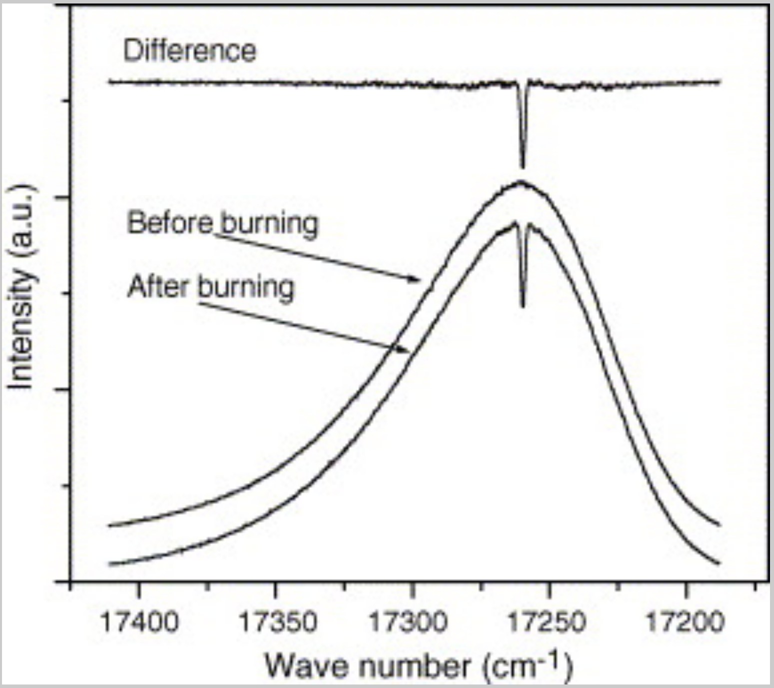
$$M = 20.12\ \text{amu}{=}3.34\times10^{-26}\text{kg}$$ For Neon

$$k_BT = 1/40eV = 4\times10^{-21}J$$

$$\Delta\nu_0{}^* = 1.55GHz$$

Inhomogeneous vs homogeneous broadening

- Homogeneous broadening: every atom is broadened by same shape
  - Radiative, collisional, phonon
  - All atoms participate in absorption or gain
- Inhomogeneous broadening:
  - Doppler broadening
  - Absorption or gain only by atoms in resonance
  - Leads to “spectral hole burning”



Fermi's golden rule generalized

- To account for the transition lineshape:

$$W_{12}(\nu) = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{12}|^2 \rho_\nu \,\delta(\nu - \nu_0) \rightarrow \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{21}|^2 \rho_\nu \, g(\nu - \nu_0)$$

- Example: narrow linewidth laser incident on atom

$$\rho_\nu = \frac{n}{c} I \,\delta(\nu - \nu_L)$$

- Total transition rate:

$$W_{12} = \int \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{12}|^2 \frac{n}{c} I \,\delta(\nu - \nu_L) g(\nu - \nu_0) d\nu$$

$$W_{12}(\nu_L) = \frac{2\pi^2}{3n\varepsilon_0 c h^2}|\mu_{12}|^2 I \, g(\nu_L - \nu_0)$$

Cross sections

- It is inconvenient to carry around all these constants and to use the dipole moments
  - Use values that connect to what we can measure
- Consider a beam passing through a gas of atoms with number density N_t (atoms/unit volume)
- Power absorbed/unit volume: $$\frac{dP_a}{dV} = W_{12} N_t h\nu$$
- Photon flux (photons/area/sec) $$F = \frac{I}{h\nu}$$
- Power in beam: $$P = I\,A = h\nu\,F\,A$$
- Evolution of flux: $$\frac{dF}{dz} = \frac{1}{h\nu}\frac{1}{A}\frac{dP}{dz} = -\frac{1}{h\nu}\frac{dP_a}{dV} = -W_{12} N_t$$

Cross sections

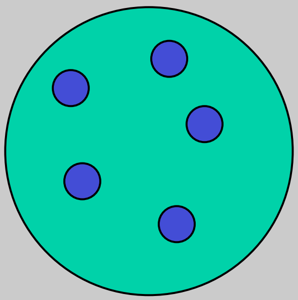
- Flux decreases as beam propagates in medium

$$\frac{dF}{dz} = -W_{12}N_t$$

- Define total absorption cross-section: $\sigma_{12} = \frac{W_{12}}{F}$

- So that: $\frac{dF}{dz} = -N_t\sigma_{12} \rightarrow F(z) = F_0 e^{-N_t\sigma_{12}z}$

- Physically, the cross-section is an effective area of the atom. In a low density gas, the beam of photons sees a collection of spheres:



$$\frac{dF}{F} = -N_t A dz \frac{\sigma_{12}}{A}$$

Frequency-dependent cross section

- Total cross section is obtained by integrating over lineshape (*h* for homogeneous):

$$\sigma_{12} = \int \sigma_h(\nu)\,d\nu$$

- Suppose we have a narrowband laser beam with a frequency that we can tune

$$W_{12}(\nu_L) = \frac{2\pi^2}{3n\varepsilon_0 ch^2}\left|\mu_{12}\right|^2 I\,g(\nu_L - \nu_0)$$

$$\sigma_h(\nu_L) = \frac{W_{12}(\nu_L)}{F} = \frac{W_{12}(\nu_L)}{I/h\nu_L} = \frac{h\nu_L}{I}\frac{2\pi^2}{3n\varepsilon_0 ch^2}\left|\mu_{12}\right|^2 I\,g(\nu_L - \nu_0)$$

$$\sigma_h(\nu_L) = \frac{2\pi^2}{3n\varepsilon_0 ch}\left|\mu_{12}\right|^2 \nu_L\,g(\nu_L - \nu_0)$$