## §7.4. Doppler Linewidth and Lineshape

Generally the Lorentzian line profile with the natural linewidth $\delta\nu_n$, as discussed in the previous section, cannot be observed without special techniques, because it is completely concealed by other broadening effects. One of the major contributions to the spectral linewidth in gases at low pressures is the Doppler width, which is due to the thermal motion of the absorbing or emitting molecules.

Doppler effect is the phenomenon of frequency or wavelength shift when radiation source and receiver have relative motion. It was first described by Doppler. A typical example is the blown whistle of an approaching train: people feel the sound is "sharper" than it's at rest; while the whistle from a train leaving us sounds lower frequency than it's at rest. This means that when the radiation source (e.g., the train) moves towards the receiver (e.g., human's ears), the radiation (e.g., sound wave) frequency increases (i.e., wavelength becomes shorter — blue shift); when the radiation source moves away from the receiver, the radiation frequency decreases (i.e., wavelength becomes longer— red shift). The key point here is the relative motion between the emitter of the radiation (i.e., the source) and the receiver.

Consider an excited molecules with a velocity $\vec{v}$ relative to the rest frame of the observer. In the rest frame, an atom at rest emits a photon with frequency ω_0.
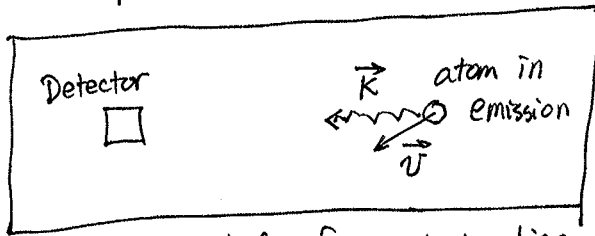
Doppler shift for emission line

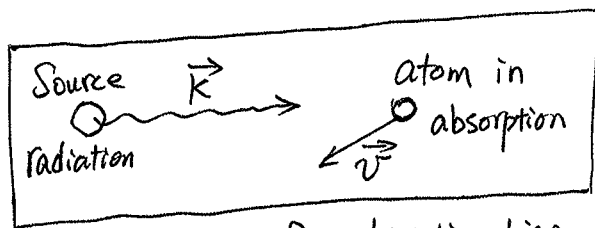When the atom moves relative to the detector with velocity $\vec{v}$, the frequency received by the detector becomes:

$$\omega_e = \omega_0 + \vec{k} \cdot \vec{v} \qquad (389)$$

When the atom moves towards the detector, $\vec{k} \cdot \vec{v} > 0$

$$\therefore \quad \omega_e > \omega_0 \quad \text{(blue shift)} \qquad (390)$$

When the atom moves away from the detector, $\vec{k} \cdot \vec{v} < 0$

$$\therefore \quad \omega_e < \omega_0 \quad \text{(red shift)} \qquad (391)$$

Doppler shift for absorption line

At rest, the resonance frequency for the atomic absorption is ω_0. If the atom moves relative to the detector with velocity $\vec{v}$, the apparent frequency of the radiation changes from its at rest frequency ω to a shifted frequency ω'

$$\omega' = \omega - \vec{k} \cdot \vec{v} \qquad (392)$$

When $\omega' = \omega_0$, the atom will have resonance absorption. Thus, the absorption frequency $\omega = \omega_a$ is given by

$$\omega_a = \omega_0 + \vec{k} \cdot \vec{v} \qquad (393)$$

Eqs. (389) and (393) are the expression of Doppler Shift in vector. The shift of absorption frequency is actually opposite to emission freq. When the atom moves towards the radiation source, $\vec{K} \cdot \vec{v} < 0$

$$\therefore \omega_a < \omega_0 \qquad \text{(red shift)}$$

When the atom moves away from the radiation source, $\vec{K} \cdot \vec{v} > 0$

$$\therefore \omega_a > \omega_0 \qquad \text{(blue Shift)}$$

But when expressed in vector, they have the same equation:

$$\omega_{e/a} = \omega_0 \pm \vec{K} \cdot \vec{v} \qquad (394)$$

If expressed in scalar, i.e., write out $\vec{K} \cdot \vec{v} = Kv\cos\theta$, where θ is the angle between $\vec{K}$ and $\vec{v}$. Then the sign (+ or −) will depends on $\cos\theta$. Usually, we define one direction as positive, e.g., when measuring vertical wind by lidar, define upward as $v_z = W > 0$. Laser pulse comes from ground, propagating upward, so $K_z = \dfrac{2\pi}{\lambda_0} = \dfrac{2\pi \nu_0}{c} = \dfrac{\omega_0}{c} > 0$.

Thus, the absorption frequency of the atom becomes

$$\omega_a = \omega_0 + K_z \cdot v_z = \omega_0 \left(1 + \frac{v_z}{c}\right) \qquad (395)$$

When the atom with upward velocity $v_z > 0$ emits a photon, the receiver is at ground, so the photon propagates downward, $K_z = -\dfrac{2\pi}{\lambda_0} = -\dfrac{\omega_0}{c} < 0$. Thus, the emission frequency
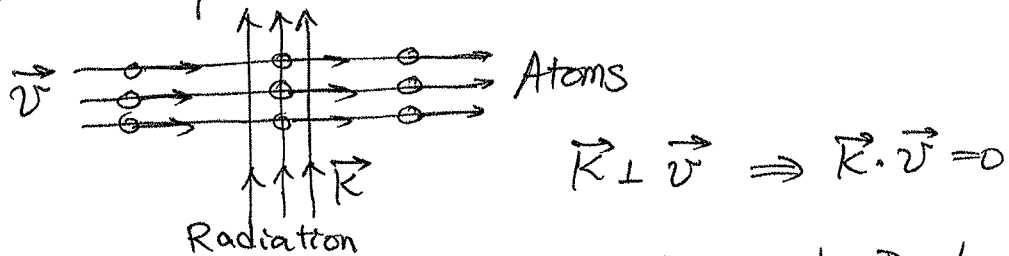
$$\omega_e = \omega_0 - \frac{\omega_0}{c} v_z = \omega_0 \left(1 - \frac{v_z}{c}\right) \qquad (396)$$

Thus, the frequency Shift between ω_a and ω_e is

$$\Delta\omega = \omega_a - \omega_e = 2\omega_0 \frac{v_z}{c} \qquad (397)$$

Above we discussed the linear Doppler shift $\vec{K} \cdot \vec{v} = K v \cos\theta$. Apparently, if $\theta = 90°$, i.e., $\vec{K} \perp \vec{v}$, then this shift is zero. In other words, we can avoid the first order Doppler shift by making the radiation field perpendicular to the velocity of atoms. This is why atomic beam or molecular beam is very useful:

$$\vec{K} \perp \vec{v} \implies \vec{K} \cdot \vec{v} = 0$$

Atomic/molecular beam to avoid 1st order Doppler shift.

Besides the 1st order, there are quadratic Doppler shift (2nd order) that is independent of velocity direction, but depends on the absolute value of $|\vec{v}|$. The minimization of 2nd order Doppler shift can only be done by laser cooling to decrease $|\vec{v}|$. This will be discussed in later laser spectroscopy.

For normal situation, atoms or molecules move randomly under thermal equilibrium (no fixed direction (like atomic beam). They follow a Maxwellian velocity distribution. At the temperature T, the number of molecules $n_i(v_z) dv_z$ in the level E_i per unit volume with a velocity component between v_z and $v_z + dv_z$ is

$$n_i(v_z) dv_z = \frac{N_i}{v_p \sqrt{\pi}} e^{-(v_z/v_p)^2} dv_z, \qquad (398)$$

where $N_i = \int n_i(v_z) dv_z$ is the total population density on level E_i, $v_p = \sqrt{2 k_B T / m}$ is the most probable velocity, m is the mass

of a molecule, and K_B is Boltzmann's constant.

From Eq.(395), $\qquad v_z = \dfrac{C(\omega - \omega_0)}{\omega_0}, \qquad dv_z = \dfrac{c}{\omega_0}d\omega$. $\qquad$ (399)

Inserting Eq.(399) into Eq.(398) gives the number of molecules with absorption frequencies shifted from ω_0 into the interval from ω to $\omega + d\omega$:

$$n_i(\omega)d\omega = N_i \frac{c}{\omega_0 v_p \sqrt{\pi}} e^{-\left[\frac{C(\omega - \omega_0)}{\omega_0 v_p}\right]^2} d\omega \qquad (400)$$

Substitute v_p equation into Eq.(400) and recall $\omega_0 = \dfrac{2\pi c}{\lambda_0}$, we get

$$n_i(\omega)d\omega = N_i \frac{1}{2\pi\sqrt{2\pi}\sqrt{\frac{K_B T}{m\lambda_0^2}}} \exp\left[-\frac{(\omega - \omega_0)^2}{(2\pi)^2 2 \cdot \frac{K_B T}{m\lambda_0^2}}\right] d\omega$$

Define the rms width for this Gaussian shape as

$$v_D = \sqrt{\frac{K_B T}{m\lambda_0^2}} \qquad (401)$$

$$\therefore \quad n_i(\omega)d\omega = \frac{N_i}{2\pi\cdot\sqrt{2\pi}\, v_D} \exp\left[-\frac{(\omega - \omega_0)^2}{(2\pi)^2 2 v_D^2}\right] \qquad (402)$$

Since the emitted or absorbed radiant power $P(\omega)d\omega$ is proportional to the density $n_i(\omega)d\omega$ of molecules emitting or absorbing in the interval $d\omega$, the intensity profile of a Doppler broadened spectral line becomes

$$I(\omega) = I_0 \exp\left[-\frac{(\omega - \omega_0)^2}{(2\pi)^2 2 v_D^2}\right] \qquad (403)$$

This is a Gaussian profile with a full width at half maximum (FWHM)

$$\delta\omega_D = \sqrt{8\ln 2}\cdot 2\pi\cdot v_D = 2\pi\sqrt{\frac{8\ln 2 \cdot K_B T}{m\lambda_0^2}} \qquad (404)$$

Using $\delta\omega_D$, Eq. (403) becomes

$$I(\omega) = I_o \exp\left[-\frac{(\omega-\omega_0)^2}{(\delta\omega_D)^2/(4\ln 2)}\right] = I_o \exp\left[-\frac{(\omega-\omega_0)^2}{0.36(\delta\omega_D)^2}\right] \quad (405)$$

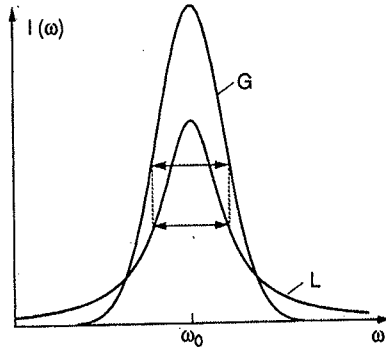Below is a comparison of Lorentzian and Gaussian line profiles with equal FWHM.

Fig. 3.7. Comparison between Lorentzian (L) and Gaussian (G) line profiles of equal halfwidths

The intensity I approaches zero for large arguments $(\nu-\nu_0)$ much faster for a Gaussian line profile than for a Lorentzian profile.

Define the normalized Gaussian line profile as

$$g_D(\omega) = \frac{1}{\sqrt{2\pi}\,(2\pi\sigma_D)} \exp\left[-\frac{(\omega-\omega_0)^2}{2\,(2\pi\sigma_D)^2}\right] \quad (406)$$

$$\therefore \int_0^\infty g_D(\omega)\,d\omega = \int_{-\infty}^{+\infty} g_D(\omega-\omega_0)\,d(\omega-\omega_0) = 1. \quad (407)$$

$$\therefore I(\omega) = I_o \cdot \sqrt{2\pi} \cdot (2\pi\sigma_D) \cdot g_D(\omega) \quad (408)$$

Total Energy $I_T = \int I(\omega)\,d\omega = I_o\,(2\pi\sigma_D)\sqrt{2\pi} \int g_D(\omega)\,d\omega = I_o\,(2\pi\sigma_D)\sqrt{2\pi}$

$$(409)$$

If we write in ν unit $(\nu = \omega/2\pi)$, then

$$g(\nu) = \frac{1}{\sqrt{2\pi}\,\sigma_D}\exp\left[-\frac{(\nu-\nu_0)^2}{2\sigma_D^2}\right] \quad (410)$$

$$\therefore I(\nu) = I_o' \cdot \sigma_D \cdot \sqrt{2\pi} \cdot g_D(\nu) = I_o' \exp\left[-\frac{(\nu-\nu_0)^2}{2\sigma_D^2}\right] \quad (411)$$

$$\because I_T = \int I(\nu)\,d\nu = I_o' \sigma_D \cdot \sqrt{2\pi} = I_o\,(2\pi\sigma_D)\sqrt{2\pi} \quad (412)$$

$$\therefore I_o' = 2\pi I_o \quad (413)$$

More detailed consideration shows that a Doppler-broadened spectral line cannot be strictly represented by a pure Gaussian profile, because of the natural linewidth caused by finite lifetime.
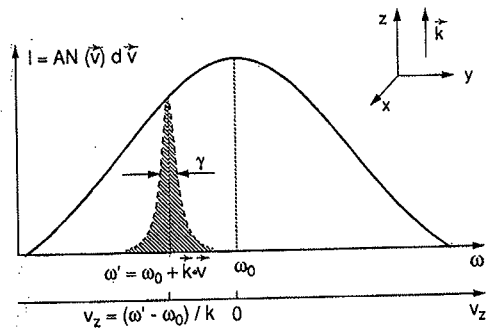

Fig. 3.8. Lorentzian profile centered at $\omega' = \omega_0 + k \cdot v = \omega_0(1 + v_z/c)$ for molecules with a definite velocity component v_z

Natural linewidth has a Lorentzian profile @ each $\omega' = \omega_0 + \vec{k} \cdot \vec{v}$

$$g_L(\omega) = \frac{\gamma/2\pi}{(\omega - \omega')^2 + (\gamma/2)^2} \qquad (4.14)$$

Thus, the spectral intensity distribution $I(\omega)$ of the total absorption or emission of all molecules at the transition $E_i \rightarrow E_k$ is the convolution of the Lorentzian profile with the Gaussian profile:

$$I(\omega) = I_0 \int n(\omega') \, g_L(\omega') \, d\omega'$$

$$= \frac{I_0 (\gamma/2\pi) N_i}{\sqrt{2\pi} \, (2\pi \sigma_D)} \int_0^\infty \frac{\exp\left[-\frac{(\omega' - \omega_0)^2}{2(2\pi \sigma_D)^2}\right]}{(\omega - \omega')^2 + (\gamma/2)^2} \, d\omega' \qquad (4.15)$$
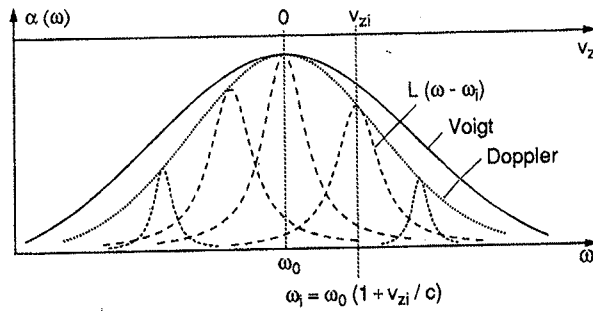
Fig. 3.9. Voigt profile as a convolution of Lorentzian line shapes $L(\omega_0 - \omega_i)$ with $\omega_i = \omega_0(1 + v_{zi}/c)$

This intensity profile, which is a convolution of Lorentzian and Gaussian profiles, is called a Voigt Profile.