Line Broadening Mechanisms

1) Doppler Broadening

The thermal motion of absorbing atoms leads to small variations in the absorbed frequency ν due to the Doppler effect. If ν_0 is the centroid frequency of the absorption line, then the Doppler effect will shift the frequency toward

$$\nu = \nu_0 \left(1 + \frac{v_r}{c}\right), \tag{1}$$

where v_r is the component of the velocity of the absorbing atom along the line of sight. Thus, the Doppler shift has an amplitude

$$\Delta\nu = \nu_0 \frac{v_r}{c}. \tag{2}$$

To quantify the magnitude of this effect, remember that the distribution of particle speeds in LTE is a Maxwellian. Since we are only interested in the velocity distribution along our line of sight, this is just

$$\frac{dn(v_r)}{n_{tot}} = \sqrt{\frac{m}{2\pi\, k\, T}} \exp\left(-\frac{m\, v_r^2}{2\, k\, T}\right) dv_r. \tag{3}$$

Now use the fact that

$$v_r = \frac{c\,(\nu - \nu_0)}{\nu_0} \quad , \qquad dv_r = \frac{c\, d\nu}{\nu_0}, \tag{4}$$

so that

$$\frac{dn(\nu)}{n_{tot}} = \frac{c}{\nu_0} \sqrt{\frac{m}{2\pi\, k\, T}} \exp\left(-\frac{m\, c^2\,(\nu-\nu_0)^2}{2\,\nu_0^2\, k\, T}\right) d\nu, \tag{5}$$

where the distribution function now refers to the number of particles capable of intercepting photons of frequency ν due to their velocity offset. Note further that the optical depth scales such that $\tau(\nu) \propto n(\nu)$. We define the absorption line profile $\phi(\nu)$ such that

$$\tau(\nu) = \tau_0\, \phi(\nu) \tag{6}$$

where τ_0 is the total absorption depth, and the profile function $\phi(\nu)$ is normalized so that $\int_0^\infty \phi(\nu)\, d\nu = 1$. Further, we define the **Doppler width**,

$$\Delta\nu_D \equiv \frac{\nu_0}{c} \sqrt{\frac{2\, k\, T}{m}}. \tag{7}$$

With these definitions, Eq. (5) yields the absorption line profile function due to Doppler broadening:

$$\phi(\nu) = \frac{1}{\Delta\nu_D \sqrt{\pi}} \exp\left(-\frac{(\nu-\nu_0)^2}{\Delta\nu_D^2}\right). \tag{8}$$

This is a Gaussian with full width at half maximum

$$(\Delta\lambda)_{1/2} = \frac{2\,\lambda_0}{c}\sqrt{\frac{2\,kT\,\ln 2}{m}}. \tag{9}$$

In some physical situations we may also have to take into account not only thermal motion of the atoms, but also bulk motions, which may be due to, for example, turbulent motion in the gas. This can be accomplished by adding a velocity term $v_{\rm turb}$ to the thermal velocity, and we can define an **effetive Doppler width**

$$\Delta\nu_D^{\rm eff} \equiv \frac{\nu_0}{c}\sqrt{\frac{2\,k\,T}{m} + v_{\rm turb}^2}. \tag{10}$$

2) Natural Broadening

As a consequence of the Heisenberg uncertainty principle,

$$\Delta E\,\Delta t \sim \hbar, \tag{11}$$

the energy level of an excited state of an atom or ion can never be determined precisely because its life time Δt is finite. Thus, the line profile is broadened over a natural line width of $(\Delta\lambda)_{1/2} = (\lambda_0^2/[2\pi\,c])\,(1/\Delta t_i + 1/\Delta t_f)$, where Δt_i and Δt_f are the life times of the initial and the final state, respectively. This effect leads to a Lorentz profile function,

$$\phi(\nu) = \frac{\gamma}{4\pi^2}\,\frac{1}{(\nu-\nu_0)^2 + (\gamma/4\pi)^2}, \tag{12}$$

where the width γ is related to the spotaneous decay rates A_{kl} of the excited state k into all lower states l through

$$\gamma = \sum_l A_{kl}. \tag{13}$$

The decay rates A_{kl} result from the quantum-mechanical treatment of the respective transitions, and can be found in standard tables.

3) Collisional Broadening

If the absorbing atom or ion responsible for an absorption line is suffering frequent collisions with other atoms or ions, the electron energy levels will be distorted. This is another mechanism leading to broadening of emission and absorption lines, called **collisional broadening** or **pressure broadening**. The magnitude of this effect depends on the frequency $\nu_{\rm col}$ at which such collisions occur. This frequency can be estimated as

$$\nu_{\rm col} = v_{\rm th}\,n\,\sigma_{\rm col}, \tag{14}$$

where $v_{\rm th} = \sqrt{2\,kT/m}$ is the thermal speed of the atoms or ions, n is their density, and $\sigma_{\rm col}$ is their cross section for collisions. The line profile resulting from collisions is a Lorentzian, just like the case of natural broadening (see Eq. 12). Moreover, the effects natural and collisional broadening can be combined by using an effective width

$$\Gamma = \gamma + 2\nu_{\rm col} \tag{15}$$

and the natural + collisional broadening line profile

$$\phi(\nu) = \frac{\Gamma}{4\pi^2}\,\frac{1}{(\nu-\nu_0)^2 + (\Gamma/4\pi)^2}. \tag{16}$$

4) Combined Doppler, Natural, and Collisional Broadening

All three broadening mechanisms affect the line profiles. The profiles are thus a combination:

$$\phi(\nu) = \frac{\Gamma}{4\pi^2}\sqrt{\frac{m}{2\pi\,kT}}\int_{-\infty}^{\infty}\frac{e^{-mv_r^2/(2kT)}}{(\nu-\nu_0-\nu_0 v_r/c)^2 + (\Gamma/4\pi)^2}\,dv_r, \tag{17}$$

which can be expressed in terms of the Voigt function:

$$\phi(\nu) = \frac{1}{\Delta\nu_D\sqrt{\pi}}\,H(a,u), \tag{18}$$

where

$$H(a,u) \equiv \frac{a}{\pi}\int_{-\infty}^{\infty}\frac{e^{-y^2}}{a^2+(u-y)^2}\,dy \tag{19}$$

is called the Hjerting function, and

$$a \equiv \frac{\Gamma}{4\pi\,\Delta\nu_D} \quad , \qquad u \equiv \frac{\nu-\nu_0}{\Delta\nu_D}. \tag{20}$$

In a typical situation, the quantity a defined in equation (20) is small, which leads to a profile in which the center is dominated by the Doppler profile and the wings are dominated by the Lorentzian component.