Doppler Broadening (continued)

In Lecture 9, we derived the Doppler lineshape function:

$$f_{\bar{\nu}}^{D} = \frac{1}{\alpha_D \sqrt{\pi}} \exp\left[-\left(\frac{\bar{\nu} - \bar{\nu}_0}{\alpha_D}\right)^2\right]$$

with Doppler HWHM $= \alpha_D \sqrt{\ln 2}$.

and $\alpha_D = \frac{\bar{\nu}_0}{c}\sqrt{\frac{2kT}{m}}$ Doppler width

e.g. HCl: for $\bar{\nu}_0 = 3000$ cm^{-1}
$\alpha_D = 3.7 \times 10^{-4}$ cm^{-1}

H_2O: for $\bar{\nu}_0 = 1600$ cm^{-1}
$\alpha_D = 2.8 \times 10^{-3}$ cm^{-1}

i.e. Doppler line widths are small but not negligible.

Four characteristics of Doppler lineshape:

1. Doppler width increases with the inverse of $\sqrt{m}$, so lighter molecules (H_2O) have wider lines than heavier molecules (CO_2).

(2) Doppler width increases with $\sqrt{T}$ (slowly).

(3) Doppler width increases with $\bar{\nu}_0$ so lines are wider in the visible than in the IR for a given molecule. Doppler broadening is more important at shorter wavelengths.

(4) Doppler lineshape decays exponentially i.e. very fast with $\bar{\nu}$, so lines are narrow and sharply defined.

Collision (Lorentz) Broadening

This is due to collisions between molecules which (in classical terms) cause random phase changes in the phase of the emitted wave. The emission therefore occurs in finite wavetrains whose length is determined by the time between collisions.

For the simplest theory of "billiard ball" molecules in a Boltzmann distribution, it can be shown that the lineshape is

$$f_{\bar{\nu}}^{L} = \frac{1}{\pi} \frac{\alpha_L}{(\bar{\nu} - \bar{\nu}_0)^2 + \alpha_L^2}$$ Lorentz lineshape

where $\alpha_L(p,T) = \alpha_L(p_0,T_0)\,\frac{p}{p_0}\sqrt{\frac{T_0}{T}}$

→ Lorentz half-width
α_L is the HWHM

$$\alpha_L(p_0,T_0) = \frac{1}{2\pi t(p_0,T_0)}$$

$t(p_0,T_0)$ = mean time between collisions
→ proportional to $\frac{1}{\text{bulk density}}$

so $\alpha_L \propto$ density

In theory, $\alpha_L(p_0,T_0)$ would be $0.07\ cm^{-1}$ for all cases.

However, in practice, $\alpha_L(p_0,T_0)$ varies from $\sim 0.01\ cm^{-1}$ to $\sim 0.5\ cm^{-1}$ depending on the state of the colliding molecule and the nature and state of the colliding partner.

Four characteristics of Lorentz lineshape:

① Lorentz width increases with pressure so collision broadening is more important in the lower atmosphere ($\lesssim 40$ km).

② Lorentz width is inversely proportional to $\sqrt{T}$ (weak dependence), although

T dependence can be more complicated than this.

3. Lorentz width is independent of $\bar{\nu}$, so collision broadening will be relatively more important at low $\bar{\nu}$ (longer λ).

4. The decay of the lineshape with $\bar{\nu}$ is very slow, inversely varying with $(\bar{\nu} - \bar{\nu}_0)^2$, so these lines have extensive wings.

Voigt Lineshape

Both Doppler and Lorentz broadening occur in the atmosphere, although collision effects dominate in the lower atmosphere.

In cases where both effects are important, the <u>Voigt profile</u> is used. This is a convolution of the Doppler and Lorentz effects. It does not have an analytic form and must be approximated numerically:

$$f_{\bar{\nu}}^{V}(\bar{\nu}-\bar{\nu}_0) = \int_{-\infty}^{\infty} f_{\bar{\nu}}^{L}(\bar{\nu}'-\nu_0)\, f_{\bar{\nu}}^{D}(\bar{\nu}-\bar{\nu}')\, d\bar{\nu}'$$

$$f_{\bar{\nu}}^{V} = \frac{1}{\alpha_D}\sqrt{\frac{\ln 2}{\pi}}\ \frac{1}{\pi}\ \frac{\alpha_L}{\alpha_D}\sqrt{\ln 2}\int_{-\infty}^{\infty} \frac{e^{-t^2}}{\left(\frac{\alpha_L}{\alpha_D}\right)^2 \ln 2 + (x-t)^2}\, dt$$

$$f_{\bar{\nu}}^{V} = \frac{1}{\alpha_D}\sqrt{\frac{\ln 2}{\pi}}\ \frac{y}{\pi}\int_{-\infty}^{\infty} \frac{e^{-t^2}}{y^2 + (x-t)^2}\, dt$$

where

$$y = \frac{\alpha_L}{\alpha_D}\sqrt{\ln 2} \quad \text{and} \quad x = \frac{\bar{\nu}-\bar{\nu}_0}{\alpha_D}\sqrt{\ln 2}$$

see slide 9 for plot of lineshapes.

Equivalent Width (slide 10)

The most important quantity to calculate in the radiative transfer equation is the energy absorbed along some path through a medium.

As a simple example, the energy absorbed by a line of strength S in a medium of density ρ is $\int_0^{\infty} (I_0 - I)\, d\bar{\nu}$

assuming the line is independent of other lines.

Using Schwarzchild's Equation, this becomes

$$\int_0^\infty I_0 \left[1 - \exp\left(- \int_0^x k_{\bar{\nu}}\, \rho\, dx \right) \right] d\bar{\nu}$$

If the intensity I_0 is independent of $\bar{\nu}$ (at least in the range of the spectral line) then we get

$$\text{absorbed energy} = I_0\, \Delta W$$

where

ΔW = equivalent width of the line

$$\Delta W = \int_0^\infty \left[1 - \exp\left(- \int_0^x k_{\bar{\nu}}\, \rho\, dx \right) \right] d\bar{\nu}$$

$$= \int_0^\infty \left[1 - \exp\left(- k_{\bar{\nu}}\, \rho\, x \right) \right] d\bar{\nu}$$

$$= \int_0^\infty \left[1 - \exp\left(- S f_{\bar{\nu}}\, \rho\, x \right) \right] d\bar{\nu}$$

using $k_{\bar{\nu}} = S f_{\bar{\nu}}$

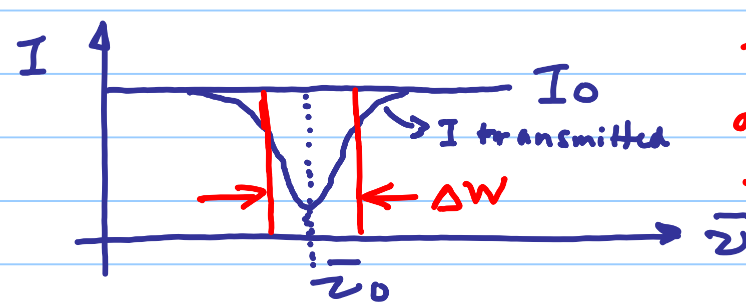
In the "weak limit" for which

$S f_{\bar{\nu}}\, \rho\, x \ll 1$,

the exponential can be expanded to get

$$\Delta W_{\substack{\text{weak}\\ \text{limit}}} = S \rho x$$

more useful in lab studies than the atmosphere



The integrated absorption is the same for the line and the rectangle.

Schwarzchild's Equation again:

Recall $\dfrac{dI}{d\chi} = I - J$ with $J = B$ valid for most atmospheric applications

To integrate this equation in its monochromatic form, scale by the integrating factor $e^{-\chi}$:

$$e^{-\chi} dI_{\tilde{\nu}} - e^{-\chi} I_{\tilde{\nu}}\, d\chi = -B_{\tilde{\nu}}\, e^{-\chi} d\chi$$

$$d\left(I_{\tilde{\nu}} e^{-\chi}\right) = -B_{\tilde{\nu}}\, e^{-\chi} d\chi$$

Integrate from $\chi = 0$ to χ:

$$I_{\tilde{\nu}} e^{-\chi} - I_{\tilde{\nu}_0} = -\int_0^{\chi} B_{\tilde{\nu}}(\chi')\, e^{-\chi'} d\chi'$$

(χ' = dummy variable)

Multiply by $e^{+\chi}$:

$$I_{\tilde{\nu}} = I_{\tilde{\nu}_0} e^{\chi} + \int_{\chi}^{0} B_{\tilde{\nu}}(\chi')\, e^{\chi - \chi'} d\chi'$$

Introduce transmission

$$\mathcal{T}_{\tilde{\nu}}(\chi - \chi') = e^{\chi - \chi'}$$

and

$$d\mathcal{T}_{\tilde{\nu}}(\chi - \chi') = -e^{\chi - \chi'} d\chi'$$

Note: χ is really $\chi_{\tilde{\nu}}$

So we now have

$$I_{\bar\nu} = I_{\bar\nu_0}\, \mathcal{T}_{\bar\nu}(\chi) + \int_{\tau(\chi)}^{\tau(0)} B_{\bar\nu}(\chi')\, d\mathcal{T}(\chi-\chi')$$

We can convert χ to geometric distance x:

$$I_{\bar\nu}(x) = I_{\bar\nu}(0)\, \mathcal{T}_{\bar\nu}(x,0) + \int_{\mathcal{T}_{\bar\nu}(x,0)}^{1} B_{\bar\nu}(x')\, d\mathcal{T}_{\bar\nu}(x,x')$$

where

$\mathcal{T}(x,y)$ = transmission from x to y (positive)

Now integrate over wavenumber.

$$\text{total energy} = \int_{\Delta\bar\nu} I_{\bar\nu}(x)\, d\bar\nu$$

$\Delta\bar\nu \rightarrow$ limited spectral interval

$$= \int_{\Delta\bar\nu} \left[I_{\bar\nu}(0)\, \mathcal{T}_{\bar\nu}(x,0) + \int_{\mathcal{T}_{\bar\nu}(x,0)}^{1} B_{\bar\nu}(x')\, d\mathcal{T}_{\bar\nu}(x,x') \right] d\bar\nu$$

On the scale of a vibration-rotation, B varies slowly with $\bar\nu$.

$\therefore$ The integral is over the monochromatic transmission $\mathcal{T}_{\bar\nu}$ and its differential.

Recall the equivalent width of a line:

$$\Delta W = \int (1-\mathcal{T}_{\bar\nu})\, d\bar\nu$$

Thus $\int_{\Delta\bar{\nu}} \tau_{\bar{\nu}} \, d\bar{\nu} = \Delta\bar{\nu} - \Delta W$

or the average transmission is

$\bar{\tau} = 1 - \frac{\Delta W}{\Delta \bar{\nu}}$ for a single line

Also the differential w.r.t. τ is $-d\,\Delta W$.

This means that (in principle), knowledge of ΔW allows Schwarzchild's Eqn. to be solved.

Two approaches:

① For flux density measurements, we can put the angular integration on the τ terms to obtain a "diffusivity factor" - type solution.

② For a spectral interval with many lines, the definition of equivalent width can be extended.

$\longrightarrow$ next section (Spectral Modelling)