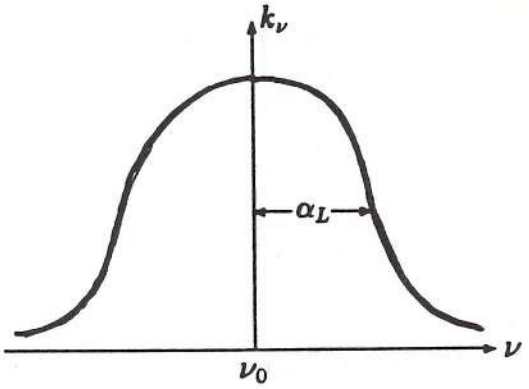
4.2 Line Shapes

In the theoretical development we showed that spectral absorption occured at discrete frequencies. In practice we observe a distribution of absorption about a central frequency. We will consider two main mechanisms which are important for pure rotational and vibrational-rotational bands.

4.2.1 Collision or Pressure Broadening



The energies of molecules are slightly disturbed during collisions, enabling the molecule to absorb (emit) at frequencies close to the unperturbed frequency. This gives rise to a Lorentz line shape for which the absorption coefficient k_ν is given by the expression

$$k_\nu = \frac{S}{\pi} \frac{\alpha_L}{\alpha_L^2 + (\nu - \nu_0)^2}$$

where α_L is the Lorentz half-width, i.e half the width at half the maximum of k_ν, and S is the line intensity, or line strength.

Consider the total area under the curve:

$$\int_{-\infty}^{+\infty} k_\nu d\nu = \int_{-\infty}^{\infty} \frac{S}{\pi} \frac{\alpha_L}{\alpha_L^2 + (\nu - \nu_0)^2} d\nu$$

$$= \frac{S}{\pi} \int_{-\infty}^{\infty} \frac{\alpha_L}{\alpha_L^2 + (\nu - \nu_0)} d\nu = \frac{S}{\pi} \tan^{-1}\left(\frac{\nu - \nu_0}{\alpha_L}\right)\Bigg|_{-\infty}^{\infty}$$

$$= \frac{S}{\pi} \pi = S$$

the total number which is to be absorbed or emitted is constant.

Question: Why did we integrate from $-\infty$ to $+\infty$?

To be precise the limits should have been 0 to ∞. However the contribution to the integral from $-\infty$ to 0 is very small and hence very little contribution to total. For example if $\nu_0 = 1000\ cm^{-1}$, $\alpha_L = 0.1\ cm^{-1}$

$$\int_{-\infty}^{0} = \tan^{-1}\left(\frac{\nu-\nu_0}{\alpha_L}\right)\Big|_{-\infty}^{0} = -\tan^{-1}(-10^4) + \pi/2 \approx 10^{-4}$$

The line intensity S is not constant but varies with temperature in a complicated manner. Many line intensities increase with increasing temperature corresponding to an increase in the number of molecules in excited energy states, but some with small lower state energies may decrease slightly in intensity as the gas becomes warmer.

α_L is directly proportional to pressure and also varies with temperature approximately proportional to $T^{1/2}$. (*) As the pressure decreases the lines become narrower and the maximum value of k_ν becomes greater. If we took the limit as the pressure tended to zero we would get a delta function. In fact this limit is never reached as other broadening mechanisms take over.

(*) $T^{-1/2}$

Typical values of α_L at STP are 0.05 cm^{-1} to 0.1 cm^{-1}. Pressure broadening is the most important mechanism throughout the troposphere and sometimes well above the tropopause. At higher altitudes the low pressure makes it less important.

4.2.2 Doppler Broadening

The thermal motion of the molecules gives a Doppler shift in the frequency of absorption (emission) of radiation. For example the emission from a molecule moving towards an observer is shifted upwards in frequency, downwards for a molecule moving away. The result is a distribution of frequencies about the central frequency ν_0, with the absorption coefficient given by:

$$k_\nu = \frac{S}{\alpha_D}\left(\frac{ln2}{\pi}\right)^{1/2} \exp\left(-ln2\left(\frac{\nu-\nu_0}{\alpha_D}\right)^2\right)$$

Unlike the collisional broadening we have an analytic expression for the Doppler half-width α_D:

$$\alpha_D = \frac{\nu_0}{c}\left(\frac{2kT\,ln2}{m}\right)^{1/2}$$

Here T is the temperature in Kelvin and m is the mass of the molecule. It is easy to verify that we again have

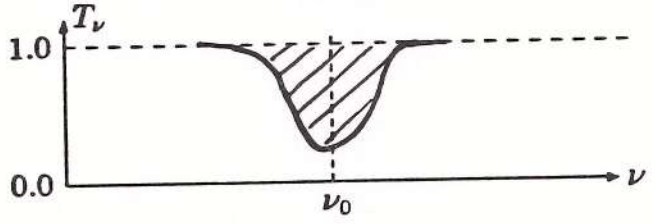
$$\int_{-\infty}^{+\infty} k_\nu = S$$

In the troposphere we usually have $\alpha_L \gg \alpha_D$, but as we go up in the atmosphere α_L decreases and we eventually get to an altitude at which $\alpha_D > \alpha_L$. When the two half-widths are comparable in size we must consider the two broadening mechanisms simultaneously and the absorption coefficient is given by the convolution of the two line shapes, an integral that can be evaluated on a computer. The resulting line shape is called the Voigt profile.

4.3 Mean Transmittances for a Homogeneous Path

Our eventual aim is to be able to calculate fluxes of radiant energy, which, we recall, involves integration of the specific intensity over frequency. In this section we will consider the calculation of transmittance over a finite frequency interval for a homogeneous path. Using a few hand-waving arguments we will later show how to extend this to non-homogeneous paths by defining an "equivalent" homogeneous path, i.e. we will be able to extend our methods to to an atmosphere in which the temperature, pressure and absorber concentration vary along the path of the radiation.

4.3.1 Isolated Lorentz line



The simplest case that we can consider is that of an isolated Lorentz line. The transmittance is $\exp(-k_\nu u)$
The absorbtance = 1 - transmittance = $1 - \exp(-k_\nu u)$

The shaded area under the curve is defined to be the **equivalent width** A of the spectral absorption line

$$A = \int_{-\infty}^{+\infty} (1 - \exp(-k_\nu u)) d\nu$$

For the Lorentz profile this can be shown to be

$$A = 2\pi\alpha_L \, x \exp(-x)[I_0(x) + I_1(x)]$$

where $x = Su/(2\pi\alpha_L)$ is the optical thickness one half-width α_L away from the line center.

The expression $x \exp(-x)[I_0(x) + I_1(x)]$ is called the Ladenberg-Reiche function. I_0 and I_1 are Bessel functions of imaginary argument whose values are given in tables or can be evaluated in computer routines. In one of your problem sets you will use a computer program to calculate the values that you need.

There are two important limiting cases in which the expression for the equivalent width simplifies to more manageable forms:

Weak line approximation

If $k_\nu u$ is small for all ν, even at the line center, we have

$$1 - \exp(-k_\nu u) \approx k_\nu u$$

and we can integrate the expression for the equivalent width A

$$A = \int_{-\infty}^{+\infty} k_\nu u \, d\nu = Su$$

The error in A will be less than 10% for $x < 0.2$.

The same argument holds for any line shape, and we get $A = Su$, although the error estimate given above will not be the same for non-Lorentz lines.

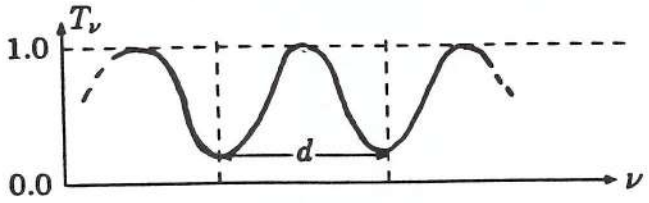
Strong line approximation

For a very strong line the center becomes opaque and the absorption depends only on the shape in the wings of the line. It can be shown that for large x

$$A = 2\sqrt{Su\alpha_L}$$

The error is less than 10% for $x > 1.63$. The region of validity is refered to as the square root region. We must have 4 times the absorber amount to double the absorption. Note that the result is valid only for Lorentz lines, not for Doppler or other line shapes. However it can often be used for the mixed Doppler-Lorentz line shape since the absorption in the wings is determined largely by the Lorentz component.

Set of isolated Lorentz lines



Consider a set of isolated Lorentz lines of equal intensity S and half-width α_L uniformly spaced frequency d apart.

The average transmittance $\overline{T}$ is:

$$\begin{aligned}\overline{T} &= \frac{d-A}{d} \\ &= 1 - A/d \\ &= 1 - (2\pi\alpha_L/d)\; x\exp(-x)[I_0(x) + I_1(x)]\end{aligned}$$

For weak lines this becomes

$$\overline{T} = 1 - (Su/d)$$

For strong lines

$$\overline{T} = 1 - (2/d)\sqrt{Su\alpha_L}$$

4.3.2 The Elsasser band model

So far we have considered isolated lines, i.e. lines for which the contribution of neighboring lines is so small that it can be neglected. Under typical conditions we find that individual lines overlap and at most frequencies the contributions of several lines are important, in which case we must sum the absorption coefficients of all the individual lines. We can generalize the

result that we have just obtained above, to find the average transmittance of equally spaced lines of equal intensity and equal Lorentz half-width with the non-overlapping restriction removed.

Suppose that the center of one line is at frequency ν_0. The lines will be centered at $\nu_0 + nd, \quad n = 0, \pm 1, \pm 2, \ldots$. The absorption coefficient at frequency ν is

$$k_\nu = \sum_{n=-\infty}^{\infty} \frac{S}{\pi} \frac{\alpha_L}{\alpha_L^2 + (\nu - \nu_0 - nd)^2}$$

To find the mean transmittance of the band we integrate over any frequency interval of length d, since the transmittance is periodic with period d.

$$\overline{T} = \frac{1}{d} \int_{\nu_0}^{\nu_0 + d} \exp(-k_\nu u) d\nu$$

This can be shown to reduce to (believe it or not!)

$$\overline{T} = \frac{1}{2\pi} \int_{-\pi}^{\pi} \exp\left(\frac{-\beta x \sinh \beta}{\cosh \beta - \cos z} \right) dz$$

where

$$\beta = \frac{2\pi \alpha_L}{d}$$

This messy integral has been evaluated numerically and tabulated for selected values of the parameters x and β.

The Elsasser or regular band model is a reasonably good approximation for some bands of diatomic molecules and linear triatomic molecules. It can be extended to line shapes other than the Lorentz, in which case the expression for $\overline{T}$ is different and usually more complicated, but can still be evaluated numerically.

4.3.3 The Random or Statistical model

In this model the lines are not equally spaced but are distributed at random within a spectral interval. The lines may be of equal intensity or, more generally, given by a probability function $P(S)$ such that the probability of finding a line with intensity in the interval $(S, S + dS)$ is $P(S)dS$. If the lines are equally intense the probability function $P(S)$ is a delta function.

For the statistical model the average transmittance $\overline{T}$ is given by

$$\overline{T} = (1 - \overline{A}/D)^n$$

where n is the number of lines in the spectral interval
D is the width of the spectral interval
$\overline{A} = \int_0^\infty A(S)P(S)dS$
and $A(S)$ is the equivalent width of a line of intensity S.

We can interpret $\overline{A}$ as the "mean" equivalent width of the lines in the interval, weighted by their intensity probability. If all of the lines have equal intensity S then $\overline{A} = A(S)$, i.e. $\overline{A}$ is just the equivalent width of a single line, and the mean transmittance $\overline{T}$ is the product of the average transmittances of each of the lines in the interval.

When n becomes large the expression for $\overline{T}$ tends to an exponential expression:

$$\overline{T} = (1 - \overline{A}/D)^n \rightarrow \exp(-n\overline{A}/D) = \exp(-\overline{A}/d)$$

where $d = D/n$ is the average spacing between the lines.

A frequently used probability distribution function is an exponential form

$$P(S) = \frac{1}{S_0} exp(-\frac{S}{S_0})$$

giving

$$\overline{A} = \frac{2\pi\alpha_L x_0}{(1 + 2x_0)^{1/2}}$$

where

$$x_0 = S_0 u/(2\pi\alpha_L)$$

This corresponds to a situation in which there are very few strong lines but many weak lines, often observed with such gases as water vapor. The average transmittance for Lorentz lines is then

$$\begin{aligned} \overline{T} &= \left(1 - \frac{\beta x_0/n}{(1 + 2x_0)^{1/2}}\right)^n \\ &\rightarrow \exp\left(\frac{-\beta x_0}{(1 + 2x_0)^{1/2}}\right) \qquad \text{for large } n \end{aligned}$$

Other probability functions can be, and have been, used. We have to find one that fits reasonably well our observed distribution of spectral lines and which yields an expression for $\overline{A}$ that can be integrated easily. Values for A

transparent.

$$\begin{aligned} k_\nu &= \frac{S}{\pi}\frac{\alpha_L}{\alpha_L^2 + (\nu-\nu_0)^2} \\ &\approx \frac{S}{\pi}\frac{\alpha_L}{(\nu-\nu_0)^2} \qquad \text{since } (\nu-\nu_0)^2 \gg \alpha_L^2 \end{aligned}$$

The transmittance T_ν at frequency ν is

$$\begin{aligned} T_\nu &= \exp\left(-\int k_\nu du\right) \\ &= \exp\left(-\int \frac{S\alpha_L}{\pi(\nu-\nu_0)^2} du\right) \end{aligned}$$

Now if the temperature is constant we can write $\alpha_L = \alpha_0 p$, where α_0 is constant, and we get

$$\begin{aligned} T_\nu &= \exp\left(-\frac{S\alpha_0}{\pi(\nu-\nu_0)^2}\int p du\right) \\ &= \exp\left(-\frac{S\alpha_0}{\pi(\nu-\nu_0)^2}\overline{p}\,\overline{u}\right) \\ &= \exp\left(-\frac{S\overline{\alpha}_L}{\pi(\nu-\nu_0)^2}\overline{u}\right) \end{aligned}$$

i.e., the transmittance is the same as that of a homogeneous path with pressure $\overline{p}$ and optical path $\overline{u}$, so that the result is exact in the strong line limit.

The treatment for temperature variations along the path is not simple since both the line intensity and the half-widths are temperature dependent, the former in a complicated manner. The easiest recourse is to define the equivalent temperature

$$\overline{T} = \left(\int T du\right)/\left(\int du\right) = \frac{1}{\overline{u}}\int T du$$

Other more complicated expressions are sometimes used.

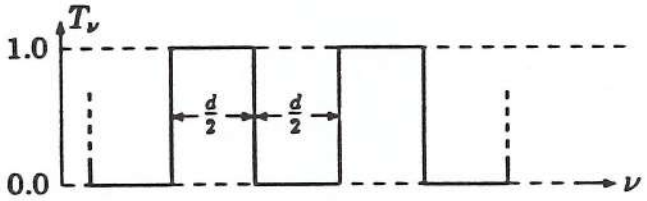
The reduction to an equivalent homogeneous path with pressure $\overline{p}$, temperature $\overline{T}$ and optical path $\overline{u}$ is known as the **Curtis-Godson Approximation**. It introduces some error into the transmittance calculations,

may be obtained from tables, or the weak and strong line approximations may be used if appropriate.

The random model works best for non-linear molecules like ozone and water vapor. The spectral intervals chosen must be made large enough so that the distribution of line intensities obeys the probability distribution for the intensities and the lines are spectrally distributed in a random fashion.

The regular (Elsasser) and random models are in some senses opposite extremes from complete orderliness to absolute chaos. There are many models that attempt to bridge this gap but none will be considered in these notes.

CAUTION. Mean transmittances cannot be multiplied in the same way that monochromatic transmittances can. For example, consider the case in which the mean transmittance is 0.5, illustrated on below. If the radiation passes through second exactly similar path, the transmittance for the two paths is exactly the same and the mean transmittance is still 0.5. If the radiation were passed a path which was similar except that the frequency was shifted up or down by $d/2$, then the combined paths would absorb all the radiation and the mean transmittance would be 0.0. The result from multiplying mean transmittances is 0.25. In a real atmosphere the conditions are more like the first case considered.



4.4 Extension to non-homogeneous paths

The results obtained for homogeneous paths are comparatively simple, but the mathematics becomes much more complicated if we allow the pressure and temperature to vary along the path. For this reason we usually attempt to reduce the non-homogeneous case to an "equivalent" homogeneous path. Consider first the special case in which temperature is constant, but pressure is allowed to vary along the path. We define the equivalent optical

path $\bar{u}$ and equivalent pressure $\bar{p}$ by the expressions

$$\bar{u} = \int du$$

$$\bar{p} = \frac{\int p du}{\int du}$$

$$= \frac{1}{\bar{u}} \int p du$$

The integrals are taken along the path of the radiation.

These expressions for $\bar{u}$ and $\bar{p}$ were chosen to give exact results in two limiting cases of absorption by isolated pressure broadened lines, the weak line and strong line approximations. In practice we find that many atmospheric absorption lines fit into one of the two categories and the approximation is not too bad in the intermediate region.

Consider first the weak line region.

$$A = \int_{-\infty}^{+\infty} \left(1 - \exp(-\int_u k_\nu du)\right) d\nu$$

For the weak line we have $\int k_\nu du << 1$ for all ν and, as before, we expand the exponential function in a series, dropping terms of order 2 or higher.

$$A = \int_{-\infty}^{+\infty} \int_u k_\nu \, du \, d\nu$$

Changing the order of integration we get

$$A = \int_u \int_{-\infty}^{+\infty} k_\nu \, d\nu \, du$$

$$= \int_u S \, du$$

$$= S \int_u du$$

$$= S\bar{u}$$

i.e. the expression is exact for the weak line limit.

Now look at the strong line case. Here the absorption is complete near the line center and it is only in the wings of the line that the line is partially

generally a few percent or less, but enormously simplifies the computation. This, or some other similar type of approximation, is nearly always used in flux calculations and does not lead to serious errors in the evaluations of fluxes and flux divergences. Uncertainties in spectral line parameters are often a larger source of error than the Curtis-Godson approximation.

4.5 Angular Integration

Flux computations require integration over all angle or, with the assumptions that we made earlier, over zenith angle θ. For each angle the mass path will be different and hence the transmittance will vary. To avoid lengthy and repeated calculations a mean zenith angle is often used. From equation 2.2

$$F_\nu = 2\pi \int I_\nu \cos\theta \sin\theta d\theta = 2\pi \int I_\nu \mu d\mu$$

The limits of integration depend on whether we are computing the upward or downward hemispheric fluxes.

In this equation I_ν is a function of μ, i.e. it depends on the zenith angle θ. What we would like to do is to replace the integral by something simpler, to avoid angular integration. The mean value theorem tells us that there exists some value $\overline{\mu}$ of μ such that

$$2\pi \int I_\nu(\mu)\mu d\mu = 2\pi \int I_\nu(\overline{\mu})\mu d\mu = \pi I_\nu(\overline{\mu})$$

We generally consider the upward and downward components of F_ν separately. When we do this we find that the "average" value μ is not the same under all conditions, but depends on the radiation field. However the value $1/\overline{\mu} = \sec\overline{\theta} = 1.66$ is generally a fairly good approximation to the true value for upward directed radiation,while $1/\overline{\mu} = \sec\overline{\theta} = -1.66$ works well for the downward component. This approximation leads to errors of a few percent, acceptable for many applications. Its use means that the transmittance calculation does not have to be repeated for a large number of zenith angles.

This approximation was designed to be used with long-wave radiation. For solar radiation we do not have to go through the angular integration since the solar radiation comes from only one angle, at least in the case in which scattering is neglected.

4.6 Line-by-line methods

The use of band models introduces errors because the models merely approximate the true spectrum since lines are never exactly evenly spaced with equal intensities, nor are they ever randomly distributed, only approximately so. Q-branches are notorious, they are neither random nor regular but have their own peculiar distribution. If highly accurate transmittances are needed, band models are just not good enough. An example of an application that requires high accuracy is the remote sounding of the atmosphere to determine its temperature structure. A satellite measures the specific intensity in selected spectral regions and the temperature of the atmosphere may be deduced provided that the atmospheric transmittances are known.

With a fast computer available a direct approach to determining average transmittances can be employed. The intergration of the transmittance T_ν over frequency may be performed directly by numerical methods (quadrature) using the Trapezoidal Rule, Simpson's Rule or more complicated schemes.

$$\overline{T} = \int T_\nu d\nu \approx \sum_i w_i T_i$$

where T_i is the transmittance at frequency ν_i within the interval of integration and the w_i are weights of the quadrature formula. The individual T_i are found from the absorption coefficient at frequency ν_i, which is the sum of the absorption coefficients of each of the individual spectral lines.

Non-homogeneous paths may be treated as follows. The path followed by the radiation may be approximated by a number of successive homogeneous layers. At frequency ν_i the transmittance is found by multiplying the transmittances of each individual layer before averaging over frequency. This largely removes the necessity of the Curtis-Godson approximation. Integration over angle to give fluxes can also be done accurately, if fluxes are required.

The numerical errors in the line-by-line method can be made as small as we please. All we need is a fast computer of the sort commonly available in a large installation today. At the present time it is extensively used for remote soundings, but is too slow to be used directly in flux calculations. We modestly add that the author of these notes was one of the first investigators to use the line-by-line method for transmittances calculations.