

1. Line Broadening

1.1. Natural Broadening

Every excited quantum state has an intrinsic lifetime before it spontaneously decays to a lower energy state. (Note that because of this, non-LTE conditions depend on the excited states in question; i.e. different molecules become non-LTE at different pressures in the atmosphere.) At the most fundamental level, a transition between two states will not result in the absorption or emission of light of a single wavelength only. Instead a range of wavelengths can excite or de-excite quantum transitions. This *natural broadening* is a result of *Heisenberg's Uncertainty Principal* which indicates that there is an uncertainty in the energy state of a system, ΔE , due to an uncertainty in the lifetime of the state, Δt , such that $\Delta E \Delta t \approx h/2\pi$. Here $h = 6.626 \times 10^{-34} \text{ m}^2\text{kg/s}$ is the Planck's constant.

1.2. Pressure Broadening

In planetary tropospheres and lower stratospheres the perturbation of energy states by neighboring atoms plays a larger role in the formation of spectral lines giving rise to *Pressure Broadening*, which follows a Lorentz line shape:

$$f(\nu) = \frac{\alpha_L}{\pi[(\nu - \nu_0)^2 + \alpha_L^2]}, \quad (1)$$

where ν_0 is the wavelength of the transition in an unperturbed state and α is the line half width, i.e. the half width of the line at half maximum. At STP the line width is generally around 0.01-0.10 cm^{-1} . The width of the line, α_L , depends on temperature and pressure as

$$\alpha_L = \alpha_0 \frac{P}{P_0} \left(\frac{T_0}{T}\right)^n \quad (2)$$

where α_0 is the width determined at a temperature and pressure of T_0 and P_0 . The temperature dependence arises because the density (proportional to the inverse of T) and velocity (proportional to $T^{1/2}$). Thus the value of n is near 0.5. However n depends on the identity of the scattered and colliding molecules, and, like α_0 , must be determined from laboratory measurements. For molecules found in Earth's atmosphere, there are ample measurements of n and α_0 for *air broadening*, i.e. for molecules like submerged in a N_2 atmosphere, and for *self-broadening*, i.e. molecules colliding with like molecules. The

value of n is given in HITRAN only for air broadening conditions. Note that while air broadening values work well for Earth and Titan's atmospheres, both of which are N_2 based. They don't apply to any other atmosphere. For Venus the CO_2 molecules can be calculated with self-broadening values, since the atmosphere is largely composed of CO_2 , for other molecules, one must search the literature for measurements of the right values. In fact, there is a lack of information regarding these parameters.

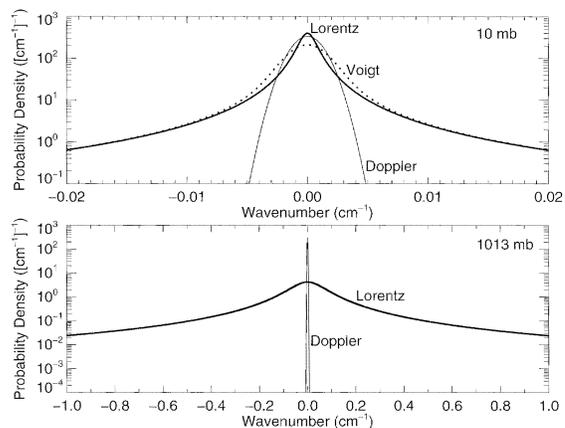


Fig. 1.— Examples of line profiles at two different pressures.

Another problem is the far wings of the lines, which do not follow the Lorentz line profile above. This is quite a big problem because at any given wavelength, and particularly those that represent windows in planetary atmospheres, generally there are more lines that are far away than nearby. The compounded effects of the addition of absorption from the far wings of lines can add up, and particularly affect the spectral regions where the atmosphere is most transparent, that is the *windows* from which radiation escapes to space.

1.3. Doppler Broadening

The thermal motion of molecules shifts the apparent frequency of the emitter as a result of the doppler effect. This effect depends on the mass of the emitter, the frequency of the line and the temperature. Doppler broadening largely determines the shape of lines in most stratospheres where the low pressure limits pressure broadening and the high temperatures

increase the effect of Doppler broadening.

The random motion of a bunch of molecules depends on the temperature, T , such that the mean speed of the velocity, v_0 , of the molecules velocity along the line of sight, v_s is :

$$\frac{1}{2}mv_0^2 = k_B T, \quad (3)$$

where m is the mass of the molecule. Note that the probability distribution of any particular component of the velocity follows the Maxwell-Boltzmann distribution. Therefore:

$$p(v_s) = \frac{1}{v_0\sqrt{\pi}} e^{-(v_s/v_0)^2}. \quad (4)$$

Now the expression for the Doppler shifted frequency for motions that are much smaller than the speed of light is:

$$\nu = \nu_0(1 - v_s/c), \quad (5)$$

where ν_0 is the frequency emitted in the molecule's rest frame and ν is that received by at a someone in a frame that is moving with a velocity v_s along the line of sight. That is:

$$v_s = c(\nu - \nu_0) \quad (6)$$

The line shape is governed by the probability that we measure a photon that is a distance $\Delta\nu = \nu - \nu_0$ from the center of the line. According to special relativity (Eq. 6) $\Delta\nu$ depends on the velocity along the line of sight v_s . Therefore the probability of finding the line shifted by $\Delta\nu$ is $p(v_s)$. The line shape is Gaussian, and, combining equations 4-6, is given by:

$$f_D(\nu - \nu_0) = \frac{1}{\alpha_D\sqrt{\pi}} \exp\left(-\frac{(\nu - \nu_0)^2}{\alpha_D^2}\right), \quad (7)$$

where

$$\alpha_D = \nu_0 \sqrt{\frac{2k_B T}{mc^2}}.$$

Note that the half width $\alpha_{1/2}$, where $f_D(\alpha_{1/2})/f_D(0) = 1/2$ is:

$$\alpha_{1/2} = \alpha_D \sqrt{\ln 2}.$$

1.4. Voigt Profile

Most of us who study both the stratospheres and tropospheres of planetary atmospheres use the *Voigt Profile*, which includes the effects of both pressure and doppler broadening. There is a good approximate expression for the Voigt profile in Liou's book, pg. 31.

2. Curve of Growth

Generally, the transmission, $T = I/I_0$, of light through a layer of atmosphere of optical depth τ decreases with the optical depth, following "Beers" law:

$$T = \frac{I}{I_0} = e^{-\tau},$$

where

$$\tau_\nu = kf(\nu)\rho\Delta s.$$

Here, k is the absorption coefficient and $f(\nu)$ is the line profile value at ν . We'll write the column abundance of our molecule as $N = \rho\Delta s$. Then:

$$\tau_\nu = kf(\nu)N.$$

The question that we ask is how does the transmission depend on the optical depth.

To approach this question, we define the *equivalent width*, W , of a line, as the width defined such that its total attenuation, summed over all frequencies, is equivalent to a total extinction over a wavelength region of width W . Therefore W has units of frequency, wavenumber or wavelength, and is:

$$W = \int (1 - T)d\nu = \int_0^\infty (1 - e^{-kf(\nu)N})d\nu$$

Now in the weak line limit, the optical depth in the center of the line τ_0 is smaller than 1:

$$\tau_0 = kf(\nu_0)N \ll 1,$$

we can expand the exponential and keep the first term, and:

$$W = \int_0^\infty (1 - e^{-kf(\nu)N})d\nu \sim \int_0^\infty kf(\nu)Nd\nu$$

and

$$W = kN \int_0^\infty f(\nu)d\nu = Nk.$$

Therefore, the equivalent width is line depends linearly on the optical depth for optically thin lines.

If the optical depth is high, say in the middle of the band, then the outgoing intensity can drop to zero. Essentially no additional attenuation occurs in the center of the band as the optical depth is increased. In this case we say that the line is *saturated* and additional attenuation occurs only in the line wings where

the optical depth is still low. In this case, the strong line limit, the optical depth at the line center τ_0 is greater than 1:

$$\tau_0 = kf(\nu_0)N \gg 1. \quad (8)$$

At some distance from the line center, say $\nu_0 \pm \Delta\nu$ then $\tau_\nu \sim 1$. We can approximate W as:

$$W = \int_0^{\nu-\Delta\nu} (1 - e^{-kf(\nu)N})d\nu + \int_{\nu-\Delta\nu}^{\nu+\Delta\nu} (1 - e^{-kf(\nu)N})d\nu + \int_{\nu+\Delta\nu}^{\infty} (1 - e^{-kf(\nu)N})d\nu.$$

The first and third terms are small in comparison to the middle term, and we neglect them. The middle term is just

$$W \sim \int_{\nu-\Delta\nu}^{\nu+\Delta\nu} d\nu \sim 2\Delta\nu$$

Now if we consider the Lorentz line shape, $\Delta\nu$ is defined (Eq. 8) and then from Eq. 1:

$$kf(\nu_0)N = \frac{kN\alpha}{\pi[(\Delta\nu)^2 + \alpha^2]} = 1.$$

Now $\alpha \sim \Delta\nu$ so:

$$\Delta\nu \sim \frac{\sqrt{Nk\alpha}}{2\pi}$$

and

$$W \sim 2\Delta\nu \sim \frac{\sqrt{Nk\alpha}}{\pi}.$$

Here we see that if a broadened spectral line is optically thick at the line center, then the equivalent width depends on the square root of the column abundance, i.e. optical depth.

This is an important point because it means that absorption due to saturated lines such as the important ν_2 vibration-rotation band of CO_2 at 664 cm^{-1} , is not as sensitive to an increase in the CO_2 abundance as is, for example, the CH_4 band at 1300 cm^{-1} which is optically thin. The CO_2 ν_2 absorption depends on the square root of the CO_2 abundance, whereas the CH_4 1300 cm^{-1} absorption depends linearly on the CH_4 abundance. For this reason, some people say that CH_4 is a more effective greenhouse gas.

Earlier than 2.7 billion years ago, Earth had less oxygen, and therefore the rate of methane destruction was lower. The methane abundance could have built up and possibly caused a significant greenhouse warming. The temperature however would have also depended on the water content of the atmosphere, because water has broad bands that absorb over large wavelength regions in the IR. It is water in fact that is by far the best greenhouse absorber. Its increase in the early and evaporating atmosphere of Venus caused the runaway greenhouse effect that we will talk about next.