

Spectral Lineshapes

We have been talking about the rotational and vibrational molecular energy transitions as though they are infinitely sharp. However they are not. They are blurred a bit in systematic ways.

The natural decay of molecules from a higher energy state to a lower energy state leads to a linewidth. The minimum linewidth is $1/(2\pi t)$ where t is the mean lifetime of the upper energy state. In practice one does not see this linewidth in atmospheric absorption lines because two other mechanisms produce broader line widths which are of primary relevance to the atmosphere. These are

- Doppler broadening \Rightarrow Doppler lineshape
- Collisional broadening \Rightarrow Lorentz lineshape

When the Doppler and Lorentz lineshapes have comparable widths, the actual lineshape is represented by the convolution of the two which yields the Voigt lineshape.

Line shapes

We define the lineshape as $f(\nu)$ where $f(\nu)$ is normalized such that

$$\int f(\nu) d\nu = 1 \quad (1)$$

We have introduced this to get the extinction coefficient

$$k(\nu) = S f(\nu) \quad (2)$$

where $k(\nu)$ is the extinction coefficient that tells us how much the signal is attenuated per unit path length, S is the line intensity or strength related to the Einstein coefficients. $f(\nu)$ is a probability distribution that defines how the line strength is spread in frequency. $k(\nu)$ has units of extinction coefficient times a wavelength, wavenumber or a frequency depending on how f is defined. f could be $f(\nu)$, $f(\omega)$ or $f(\lambda)$. We'll come back to the extinction coefficient shortly.

Doppler line shape

The Doppler lineshape is due to the random thermal motion of individual gas molecules. At any instant, some are moving towards the observer and some are moving away from the observer. The velocity of the molecules is tied closely to their temperature. The resulting random distribution of Doppler shifts is described by a Gaussian distribution:

$$f(\nu) = \frac{1}{\nu_D \sqrt{\pi}} \exp\left[-\left(\frac{\nu - \nu_0}{\nu_D}\right)^2\right] \quad (3)$$

where ν_0 is the center frequency of the absorption line and the Doppler line width, ν_D , is given as

$$\nu_D = \frac{\nu_0}{c} \sqrt{\frac{2\pi RT}{m}} \quad (4)$$

where R is the universal gas constant (8.31447215 J/K/mole. **Note error in EvZ on page 397**), T is temperature in K and m is the molecular mass per mole. Note that the square root term is

essentially the thermal velocity of the molecules of interest. The Doppler linewidth tends to be the dominant linewidth at higher altitudes where pressures are lower.

Collisional or Lorentz lineshape

Collisions between molecules cause the absorption line to broaden as well. Essentially the line width is the inverse of the mean time between collisions. The line shape is given as

$$f(\nu) = \frac{1}{\pi} \frac{\nu_L}{(\nu - \nu_0)^2 + \nu_L^2} \quad (5)$$

where ν_L is the Lorentz linewidth and ν_0 is the line center. It is related to the mean time between collisions, t_c , by

$$\nu_L = \frac{1}{2\pi t_c} \quad (6)$$

While ν_L depends on the particular molecules involved in the collisions, a good rule of thumb for estimating ν_L is to use 3 MHz/mbar times the atmospheric pressure in mbar.

To understand how the collisional broadening works, we can estimate the average time between collisions as the mean free path, L_c , between collisions of the molecules in the atmosphere divided by the thermal velocity of the molecules. Think of a molecule as having a collisional cross-sectional area, A_c , sweeping through the atmosphere as it moves. The average distance it will move before colliding with another molecule defines a volume, $L_c A_c$. For L_c to be the mean distance between collisions, this volume must be the average volume per molecule in the gas, that is, the inverse of the number density of the gas, n_g . So $L_c A_c = 1/n_g$ and

$$L_c = 1/(n_g A_c) = k_B T / (P A_c) \quad (7)$$

where k_B is Boltzmann's constant gas constant, T is the gas temperature and P is the gas pressure.

The thermal velocity, v_T , capturing the motion between the two molecules is

$$v_T = \sqrt{\frac{k_B T}{m}} \quad (8)$$

where m is the mass per molecule (not per mole). So the average time between collisions is

$$t_c = \frac{L_c}{v_T} = \frac{k_B T}{P A_c} \sqrt{\frac{m}{k_B T}} = \frac{1}{P A_c} \sqrt{m k_B T} \quad (9)$$

The collisional linewidth is then

$$\frac{1}{2\pi t_c} = \frac{P A_c}{\sqrt{m k_B T}} \quad (10)$$

Goody and Yung indicate the the Lorentz line width from a more complete accounting of kinetic theory is

$$\nu_c = \sum_i n_i A_{ci} \left[\frac{k_B T}{\pi} \left(\frac{1}{m} + \frac{1}{m_i} \right) \right]^{1/2} = \frac{P}{k_B T} \sum_i \frac{n_i}{n_{tot}} A_{ci} \left[\frac{k_B T}{\pi} \left(\frac{1}{m} + \frac{1}{m_i} \right) \right]^{1/2}$$

$$v_c = P \sum_i \frac{n_i}{n_{tot}} A_{ci} \left[\frac{1}{\pi k_B T} \left(\frac{1}{m} + \frac{1}{m_i} \right) \right]^{1/2} \quad (11)$$

where the i index indicates the i th species of molecule colliding with the radiating molecule.

$$\begin{aligned} \text{check units: } & \text{kg}^{-1} \text{ m}^{-1} \text{ s}^2 \text{ m}^2 \text{ m}^{-2} (\text{kg kg m}^2 \text{ s}^{-2} \text{ K}^{-1} \text{ K})^{1/2} \\ & = \text{kg}^{-1} \text{ kg m}^{-1} \text{ s}^2 \text{ m s}^{-1} = \text{s} \quad \text{OK} \end{aligned}$$

Note that the Lorentz or collisional linewidth scales linearly with pressure and inversely with the square root of temperature. The pressure dominates changes in linewidth with altitude since pressure changes exponentially with altitude. As a result, the collisional linewidth decreases exponentially with altitude. The temperature dependence must also be taken into account to estimate the correct linewidth. I note this because this type of broadening is often called *pressure* broadening but it really is *collisional* broadening (don't forget the temperature dependence).

Doppler vs. Collisional line widths vs. altitude

Note that the Doppler linewidth depends on the line frequency whereas the Lorentz width does not. Therefore at high pressures, the collisional width is wider while at low pressures the Doppler width is wider. The altitude and pressure of the transition depends on the center frequency, ν_0 . The higher ν_0 , the lower the altitude of the transition from collisional to Doppler broadening.

The collisional crosssection is the overlapping area between the radiating/absorbing molecule and the molecule it is colliding with. Note that the collisional crosssection, A_{ci} , has the index, i , because it depends on the two molecules involved. In Earth's atmosphere which is made up primarily of N_2 and O_2 , most of the collisions are with N_2 and O_2 molecules. So one has to find the collisional crosssection of H_2O for instance, with N_2 and O_2 molecules. In the Martian atmosphere, which is 95% CO_2 , one must obtain the cross section of the radiating molecule colliding with CO_2 . This is typically measured in a laboratory. In developing our proposal to remotely sense Mars, we discovered that the collisional broadening coefficient of H_2O with collisions with CO_2 is ~ 5 MHz/mb, not 3 MHz/mb.

Voigt lineshape

The Voigt lineshape captures the combined effects of the Doppler and Lorentz lineshapes via a convolution of the 2 lineshapes and is particularly important when the two line shapes are comparable in width. See for instance <http://scienceworld.wolfram.com/physics/VoigtLineshape.html>. There are software routines to calculate the Voigt lineshape. See note on page 83 in *Radiative Transfer in the Atmosphere and Ocean*, by Gary E. Thomas, Knut Stamnes about reviews of the Voigt lineshape.

Van Vleck - Weiskopf lineshape

As G&Y note, the van Vleck-Weiskopf line shape is a correction to the Lorentz line shape appropriate to the microwave portion of the spectrum. The form is

$$f(\nu) = \frac{1}{\pi} \left(\frac{\nu}{\nu_0} \right) v_L \left[\frac{1}{(\nu - \nu_0)^2 + v_L^2} + \frac{1}{(\nu + \nu_0)^2 + v_L^2} \right] \quad (12)$$

NOTE: this is an improvement to the Lorentz line only. It does not include the thermal Doppler line broadening and so is not a substitute for the Voigt profile as the Lorentz width becomes comparable to or less than the Doppler width or when probing near the line center where the thermal contribution may still be important. This distinction is important at higher altitudes and we ran into it while performing microwave sensitivity studies to the wind induced Doppler shift of microwave lines in the atmosphere of Mars.

Continuum

In the spectrum between lines, well beyond the linewidths, there is a continuum of absorption. This is not completely understood and there are various explanations. This may be due to the overlapping tails of many absorption lines. There is continuous absorption at higher pressures due for instance to N_2 - N_2 collisions for instance associated with induced (rather than permanent) electric dipoles created momentarily during the collisional process.