

16. Line shapes

Remember that τ_σ (dimensionless) = S (cm) $\times N$ (cm⁻²) $\times l$ (cm); N = column density, l = line shape. The equivalent width $W \leq S \times N$.

Also, recall that the radiative transfer (excluding scattering, formally) is given by $I(\sigma) = I_0(\sigma)e^{-\tau(\sigma)} + B(\sigma, T)(1 - e^{-\tau(\sigma)})$, where I_0 is external and the blackbody function B is a property of the medium (its temperature).

Common $l(\sigma)$ functions are:

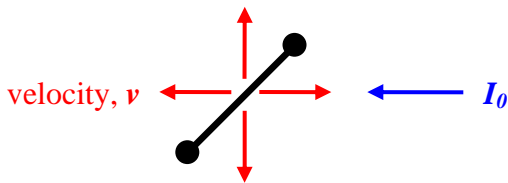
l_g (or l_d , Gaussian, from Doppler broadening)

l_l (Lorentzian, from lifetime or pressure broadening)

+ complications (outside of our scope):

- Speed dependence
- Dicke narrowing
- Galatry
- Sub/super Lorentzian
- Pressure shift
- Van Vleck-Weisskopf (zero frequency correction)

Doppler line broadening, line shape:



Molecules are moving in a Maxwell-Boltzmann distribution due to thermal motions:

$\rho_v dv = \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-(mv^2/kT)} dv$. An individual molecule sees $\sigma^* = \frac{\sigma_0}{1 \pm v/c}$. Doppler

broadening is *heterogeneous*, in that different molecules are affected differently.

Substituting for v ,

$$l_d = \frac{1}{\sigma_0} \left(\frac{mc^2}{2\pi kT} \right)^{1/2} \exp \left[\frac{-mc^2(\sigma - \sigma_0)^2}{2kT\sigma_0^2} \right] \text{ (cm)}.$$

In terms of b_e , (the half-width at 1/e intensity, or hw1e),

$$l_d = \frac{\pi^{-1/2}}{b_e} \exp \left[-\frac{(\sigma - \sigma_0)^2}{b_e^2} \right], \text{ where } b_e = \sigma_0 \left(\frac{2kT}{mc^2} \right)^{1/2}. \text{ This is normalized to } \int l_d d\sigma = 1.$$

Widths are also given as *half-width at half-maximum* (HWHM) and *full-width at half maximum* (FWHM). I prefer hw1e for Gaussians, because of the exponential form, and HWHM for Lorentzians (because of the physical form of the line shape, see below). For reference, for Gaussian line shapes, hw1e = HWHM / $\sqrt{\ln 2}$. In spectroscopic

applications, b_e is calculated as $b_e = 4.30140 \times 10^{-7} \sigma_0 \sqrt{\frac{T}{m(\text{amu})}}$, where T is the temperature ($^{\circ}\text{K}$) and m is the molecular mass in atomic mass units (e.g., $m(^{12}\text{C}) = 12$).

Example: what is b_e for a CO_2 line @ 667 cm^{-1} , and 300 K?

Doppler broadening has a strong σ dependence, and weak T , m dependence (since $\sqrt{T/m}$ doesn't vary as much over atmospheric temperatures and molecular weights).

Gaussian widths add in quadrature (from earlier noise discussion), although this doesn't come into play very often in atmospheric line widths.

Lorentzian line shapes: In general they come from anything that interrupts the lifetime of a state (e.g., collision or spontaneous emission).

Lifetime broadening (see Bernath for derivation: damped cosine, oscillating $\mu \Rightarrow$ Fourier transform).

$$l_l = \frac{b_l}{\pi (\sigma - \sigma_0)^2 + b_l^2}, \text{ normalized to } \int l_l d\sigma = 1, \text{ where } b_l = \text{HWHM}; b_l = \frac{1}{2\pi\tau} = \frac{A}{2\pi},$$

where A is the Einstein A coefficient for spontaneous emission. Remember,

$$A = \frac{64\pi^4 \sigma^3}{3h} |\mu_{u \rightarrow l}|^2. \text{ As an example, the far infrared rotational line of HCl (with a large}$$

μ) at 125 cm^{-1} has a (long) lifetime of $A = 0.35 \text{ s}^{-1}$. The σ^3 means shorter lifetimes and broader lines real quick as UV frequencies are approached. However, this is not usually so important for atmospheric spectroscopy purposes. Lifetimes are more important for reactions, since excited states (e.g. $\text{O } ^1D$) are an important energy source for atmospheric free radical chemistry. (Aside: actually $\text{O } ^1D$ has quite a long radiative lifetime despite large σ^3 since the transition moment is extremely small (the transition is *highly forbidden*. The lifetime in the troposphere through mesosphere is determined through *quenching* rather than spontaneous emission.)

Lorentzian lines add directly (as with Gaussians, easily confirmed using the convolution theorem).

Pressure (or collision) broadening

$$bl \approx \frac{1}{2\pi T_2}, T_2 = \text{the mean lifetime between collisions (which disrupt the coherence of the}$$

absorption or emission process). As before, $l_l = \frac{b_l}{\pi (\sigma - \sigma_0)^2 + b_l^2}$. Lorentzian broadening

is *homogeneous*, in that all molecules are affected the same. The reality for pressure broadening is much more complex than for pure lifetime or for Doppler broadening (see *complications*, above).

Pressure broadening dominates in the lower atmosphere and at lower frequencies (see shell figure).

Air broadening

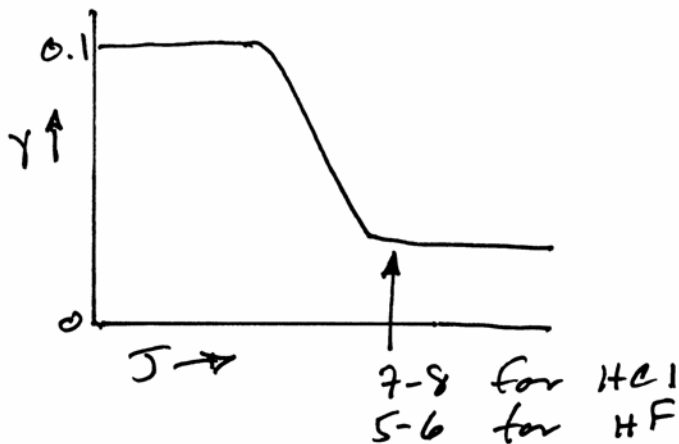
Pressure broadening is usually described as $b_l = \gamma P / P_0$, where γ is the *pressure broadening coefficient* (in $\text{cm}^{-1} \text{atm}^{-1}$) and P_0 is one atmosphere = 1013.25 millibars (*mbar*). For air,

$$\gamma \approx 0.79\gamma(\text{N}_2) + 0.21\gamma(\text{O}_2).$$

$\gamma(\text{O}_2)$ is usually slightly less than $\gamma(\text{N}_2)$.

Note that *bs* add directly: $b_{\text{total}} = b_{\text{lifetime}} + b_{\text{pressure}}$. A good average value for air is $0.05 \text{ cm}^{-1} \text{atm}^{-1}$, but:

Air broadening of polar molecules



The lower limit is $\sim 0.03 \text{ cm}^{-1} \text{atm}^{-1} = \text{hard sphere}$ or non-polar limit, which is about that given by the collision cross section at the van der Waals radii. Also note that $\gamma \approx T^{-(n+1)/2(n-1)}$ (see **Townes and Schawlow, Chapter 13**), where r^{-n} is the power of the dominant interaction between the colliding molecules (the most important term in the potential expansion). The n dependence also varies with rotational state.

Homework (due March 6)

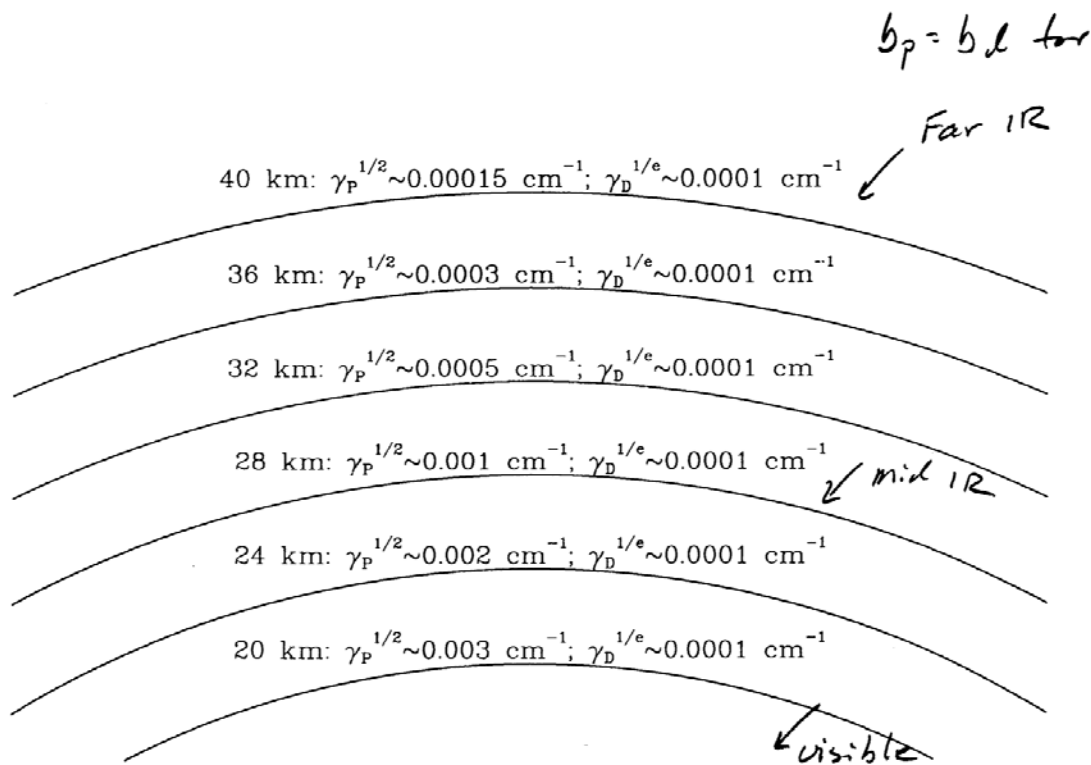
Calculate the Doppler hwl and pressure broadening HWHM for the following lines, using the temperature/pressure profile of the US1976 atmosphere:

Molecule	position	Pressure broadening coefficient ($\text{cm}^{-1} \text{atm}^{-1}$)
ClO	650 GHz	0.06
HCl	125 cm^{-1}	0.08

O ₃	9.6 μm	0.05
H ₂ O	1.02 μm	0.08
O ₂	762 nm	0.03

Calculate for sea level, tropopause, mid-stratosphere (25 km), and stratopause.

Where does which type of broadening dominate in the atmosphere and versus frequency? Values for a far infrared (100 cm⁻¹) line:



The Lorentzian line shape gets a lot of mileage. Many (although certainly not all) atmospheric conditions are well-approximated by it.

The strong and weak limits for Lorentzian absorption are

$$2\sqrt{S \times N \times b_l} \leq W \leq S \times N.$$

Saturated limit: $W = 2\sqrt{S \times N \times b_l}$. (Strong line, $\tau \gg 1$ for most of line, $e^{-\tau} \approx 0$.)

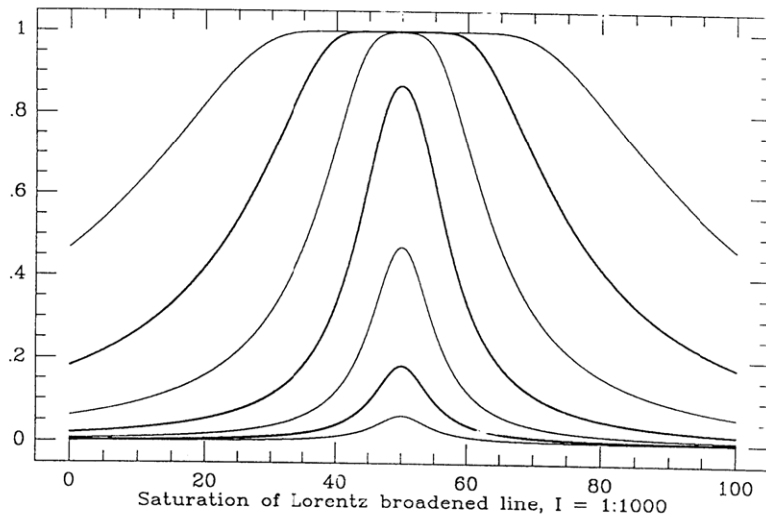
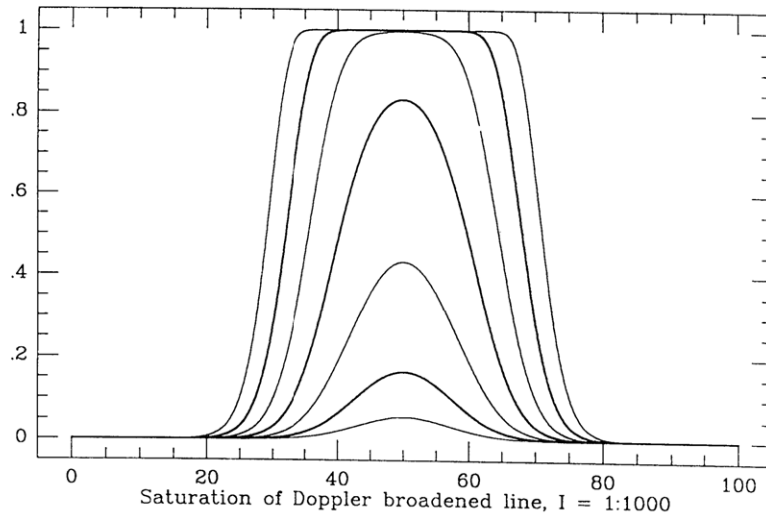
Unsaturated limit: $W = S \times N$. (weak line, $\tau \ll 1$ for most of line, $e^{-\tau} \approx 1 - \tau$.)

In between is the *curve of growth*, about which there are many approximations, nomographs, etc. (now mostly outdated since faster, cheaper computers make them less important).

One last factoid: For the same rotational transition, but different vibrational transitions, γ is about the same (although this is difficult to substantiate to better than 10-20%).

How lines saturate (examples):

Re-discuss differential and finite RT equation ($dI/d\tau = I - J$; $J = BB$) and definition of optical thickness $\tau = S$ (cm) $\times I$ (cm) $\times n$ (cm⁻²) = Σ (cm²) $\times \rho$ (cm⁻³) $\times d$ (cm).



The Voigt Function

This is the general line shape describing the case when both Lorentzian and Gaussian broadening is present, *e.g.*, pressure broadening and Doppler broadening. The Voigt function V is “simply” the convolution of the Lorentzian and Doppler functions:

$V = l_g \otimes l_l$, where \otimes denotes convolution:

$$V(\sigma - \sigma_0) = \int_{-\infty}^{\infty} l_g(\sigma' - \sigma_0) l_l(\sigma - \sigma') d\sigma'$$

The Voigt function is of great practical importance in radiative transfer and mathematical physics. Evaluating it quickly and accurately is the subject of a vast literature. For this purpose, the Voigt function is normally cast in terms of *reduced variables*, to give

$$V(\sigma - \sigma_0) = \frac{b_l}{\pi^{3/2} b_e^2} \int_{-\infty}^{\infty} \frac{e^{-x^2} dx}{a^2 + (\xi - x)^2}, \text{ where } x = \frac{\sigma' - \sigma_0}{b_e}; \quad \xi = \frac{\sigma - \sigma_0}{b_e}; \quad a = \frac{b_l}{b_e}.$$

Thus the *natural units* used in most Voigt formulations are

$$\text{Voigt } A = \frac{b_l}{b_e}; \text{ Voigt } X = \frac{\sigma - \sigma_0}{b_e} \text{ (i.e., calculate for } \sigma - \sigma_0 \text{ in units of } b_e\text{). With this}$$

$$\text{definition, } \int_{-\infty}^{\infty} V(X, A) dX = 1.$$

voigt363.f90 is a *very* accurate (but not particularly fast) Voigt subroutine (a function version is also available if you want values one at a time). Be careful of the normalization: It gives a Voigt profile normalized to area b_e (in the Doppler limit the line center is always $1/\sqrt{\pi}$). To get the Voigt line normalized to 1 you must divide by b_e !

For other options in the tradeoff between speed and accuracy, see the Schreier *et al.* *JQSRT* reference.

The Voigt function is closely related to the complex error function (see Schreier *et al.*); The Voigt function, V , and its first derivative, dV/dX , are related as the real and imaginary parts of a complex function. *All* higher derivatives may be obtained using a recursion formula which gives coefficients for expansion in V and dV/dX (**voigt363.f90** includes the first and second derivatives).

Homework (due March 8)

Select a combination of spectral line and atmospheric location from problem #9 where the Doppler and Lorentz widths are comparable. For a range of (line intensity, S) \times (column density, N), ranging from very small to quite large (optically thin to optically very thick), calculate the Voigt function, V , versus position and plot the results as either an emission line ($1 - e^{-SNV(\sigma)}$) or an absorption line ($e^{-SNV(\sigma)}$).

Extra (non-credit) homework problem

http://www.nasa.gov/mission_pages/LCROSS/main/

“LCROSS was launched June 18, 2009 as a companion mission to the Lunar Reconnaissance Orbiter, or LRO, from NASA’s Kennedy Space Center in Florida. After separating from LRO, the LCROSS spacecraft held onto the spent Centaur upper stage rocket of the launch vehicle, executed a lunar swingby and entered into a series of long looping orbits around the Earth.

“After traveling approximately 113 days and nearly 5.6 million miles (9 million km), the Centaur and LCROSS separated on final approach to the moon. Traveling as fast as a speeding bullet, the Centaur impacted the lunar surface shortly after 4:31 a.m. PDT Oct. 9 with LCROSS watching with its onboard instruments. Approximately four minutes of data was collected before the LCROSS itself impacted the lunar surface.”

The impact (from the 1980-kilogram lunar impactor) ejected about 10^6 Kg of material, some of which was water. It should (from pre-impact materials) “send up a plume of vapor and debris ... rising 30 to 40 miles above the surface.” For simplicity’s sake, assume the cloud is spherical and 25 km in diameter, and that it consists of x % H_2O and $(100 - x)$ % dust, by weight. Assume that the cloud is optically thin in dust and H_2O (then you only need to calculate the BB and H_2O spectra once).

There is a nice infrared band of water at $6.3 \mu m$ (actually centered at $1594.7498 \text{ cm}^{-1}$). Calculate the emission spectrum for this band, plus the dust. Assume spectra are taken when the cloud of gas and dust has cooled to the temperature where the Wien’s Law maximum in power is at the band center. Assume Doppler broadening only. I have put **01_hit04.4eps238.par** on the website. It contains the parameters for this band, $H_2^{16}O$ only, from $1300 - 1900 \text{ cm}^{-1}$, with many, many weak lines weeded out.

The lunar albedo is about 0.07 in the infrared: assume that the dust emission is 93% of blackbody. Assume the dust density is $2.5 \text{ grams cm}^{-3}$. Put the dust into $10 \mu m$ particles, to calculate emitting surface.

Assume the CMB is completely negligible (it is). I propose an instrument with 40 cm^{-1} hw1/e Gaussian line shape (although you may wish to try something else). Place a detector element to cover every 15 cm^{-1} .

Detectors and instrument: Rather than working out detector properties, instrument size, etc., assume that measurements can be made with signal-to-noise ratio (S/N) of 100 for 1 second of integration time, t (improving as \sqrt{t}) for the blackbody at the temperature determined above. Then you only need the column density through the cloud. **noise-for-extra-problem.dat** contains a 2000-point noise spectrum with RMS = 0.01 (*i.e.*, S/N=100). You can also calculate your own with **noise.f90**.

Set the problem up with 10% H_2O , plot the result, and see if you see anything. If not, what combination of H_2O fraction and integration time would give you a reasonable observation (say S/N = 5)? Do we need better detectors, or a larger instrument?

Introduction to Databases

HITRAN: <http://www.cfa.harvard.edu/hitran/>

GEISA: <http://ether.ipsl.jussieu.fr/etherTypo/?id=950>

JPL Molecular Spectroscopy <http://spec.jpl.nasa.gov/>

Cologne Database for Molecular Spectroscopy <http://www.astro.uni-koeln.de/cdms>