Absorption Line Shapes

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In the Earth's atmosphere, atomic and molecular absorption lines are dominated by two features: impact (or pressure) broadening and Doppler broadening. These lead to line widths much larger than the natural line width as given by the uncertainty principle ($\sim 1MHz$). The natural line width is much narrower than what is observed in the visible, infrared, sub millimetre, and even microwave regions. In general, we have N absorption lines for some gas, centred at absorption frequencies ν_i. Then the spectral density of the extinction $\kappa(\nu)$ multiplied by a frequency differential $d\nu$ along a path gives the extinction coefficient and we write

$$\kappa(\nu) = \rho_A \sum_{i=1}^{N} S_i f_i(\nu, \nu_{0\,i}). \tag{1}$$

Here, S_i are the line intensities (cm^2 per molecule), and the f_i are line shape functions. Also, $\nu_{0\,i}$ is the ith resonant frequency. We may imagine we have a uniform spectral irradiance I, in the form of plane parallel waves, shining straight along a path with a cross section of dA square centimetres and some length dL. The number of molecules per square centimetre along the path (ρ_A) is just the volumetric number density times the length dL. We may keep the concentration the same and double the length: this will have the same effect as doubling the concentration and keeping the length the same.

Note that we insist the line shape functions are normalised: this gives the quantities S_i the specific meaning that they are the total amount of light absorbed from the beam by the ith line. It is implied that the irradiance is low enough that linear approximations are good enough, and so the lines are additive.

It is quite common that the Lorentzian line shape is a good approximation, and the Lorentz line shape and width is arise from modelling collisions affecting the absorbing (or emitting) molecule. Then, in the absence of Doppler broadening, the Lorentz line shapes have the form

$$f_i(\nu, \nu_i) = \frac{\gamma_i/\pi}{\gamma_i^2 + \Delta\nu_i^2}, \tag{2}$$

where $\Delta\nu_i = (\nu - \nu_{0\,i})$. The line half - width gamma has units of frequency, and so the line shape function has dimensions of time. If we had a δ function absorption line for collisions

($\gamma \to 0$), Doppler broadening would lead to the following line shape once the spread of molecular velocities is taken into account.

$$f_i = \frac{1}{\sqrt{\pi}\gamma_{D_e}} \exp\left(-\frac{(\nu - \nu_{0i})^2}{\gamma_{D_e}^2}\right). \tag{3}$$

Here γ_{D_e} is the 1/e Doppler halfwidth. (The half width at half maximum is α_{D_e} multiplied by $\sqrt{\ln 2}$.)

There are temperature and pressure dependencies of course. The Lorentz half width is given by

$$\gamma_i = \gamma_{ref\,i} \frac{P}{P_{ref}} \left(\frac{T_{ref}}{T}\right)^n. \tag{4}$$

The reference pressure, at which the reference half width γ_{ref} is given, is usually one atmosphere, and the reference temperature for the HITRAN database [1] is 296K. The value for n is not an integer, and is obtained by experiment. It has a "classical value" of one half. We have left out the fact that the line centre also has a small pressure dependent shift from ν_0. The dependence of the Doppler width on temperature is given by

$$\gamma_{D_e} = \nu_0 \sqrt{\frac{2kT}{mc^2}}, \tag{5}$$

where m is the mass of the molecular species, and k is Boltzmann's constant.

There is a further complication to this picture. Often, our absorbing gas is a trace gas mixed in with air (which we suppose has no absorption lines in the part of the spectrum we examine). In this case the molecule of the trace gas shall nearly always collide with a Nitrogen or an Oxygen molecule. Sometimes however, there will be so much of the "trace" gas that collisions between two trace gas molecules are relevant. There need not be a great deal of the trace gas for this to happen, because the resonances between the trace molecules in these situations mean that such collisions can have a much larger broadening. In this situation we have both "foreign (or air) broadening" and "self broadening". Foreign broadening means line broadening due to trace gas molecules colliding with air molecules, and "self broadening" means line broadening due to collisions with like trace gas molecules. In HITRAN, the actual broadening is a pressure weighted combination of two widths, denoted γ_{air} and γ_{self}.

Of course, we have both Doppler and collision broadening happening at the same time, and the actual line shape is a convolution of the Doppler and Lorentzian line shapes with each other. This gives rise to the Voigt line shape, which in general is not trivial to calculate, especially as efficient as well as accuracy is required. A fairly recent method is given by Wells [2]. We shall not dwell on this matter here, and for the rest of this article, we shall ignore Doppler broadening. Any line shape that is discussed below can be convolved with the Doppler profile to take the Doppler effect into account.

1 The Van Vleck - Weisskopf and Van Vleck - Huber Line Shapes

So far so good, so what's wrong with it? For many purposes, the Lorentz line shape is a very good description of spectral lines. However, the Lorentz line shape is based on a physical model which makes many simplifying assumptions — as good models do. We need other line shapes wherever the assumptions leading to the Lorentzian line shape break down — and this breakdown shows up especially at low resonant frequencies. The Lorentz line shape wont work very well for resonances in the microwave region of the spectrum.

A trivial observation is that the Lorentz line gives non-zero absorption for the case of an electrostatic field! The Lorentzian line shape is unphysical in that it is not exactly zero for $\nu = 0$. Also, that the principle of detailed balance (microscopic reversibility) does not allow for a line shape which is perfectly symmetric about the resonant frequency, whereas the Lorentzian obviously is symmetric about ν_0.

Yet another physical objection is that causality is violated. The Kramers Kronig relations require that the imaginary part of the susceptibility χ, where $\chi = \chi_R + i\chi_I$, must be an odd function in ν. The mass absorption coefficient $\alpha(\nu)$ is related to χ_I via $\alpha = 2\pi\nu\chi_I c$.

Causality means that the mass absorption coefficient *must* be even in ν on the interval $(-\infty, \infty)$. This particular aspect can be remedied by putting (for a single line)

$$\alpha = S \times \left(\frac{\gamma/\pi}{\gamma^2 + (\nu - \nu_0)^2} + \frac{\gamma/\pi}{\gamma^2 + (\nu + \nu_0)^2} \right)$$

$$= S \times (f_L(\nu, \nu_0) + f_L(\nu, -\nu_0)) = S \times (f_L(\nu, \nu_0) + f_L(-\nu, \nu_0)) \,, \tag{6}$$

where f_L the Lorentzian function. Since this function is non zero for $\nu = 0$, we have an infinite imaginary part for the complex susceptibility at $\nu = 0$. (If we regard this as a function of positive ν only, we need not halve the line strength.)

An alternative to the Lorentzian is the Van Vleck-Weisskopf line shape [3]. This is valid at low frequencies. This line shape arises from a more sophisticated physical model. The discussion in a paper by Van Vleck and Huber [4] points out the physical distinction between the Lorentzian and the Van Vleck - Weisskopf line shapes. To paraphrase the latter paper, the Lorentzian is obtained by an impact model and assumes that the frequency of the radiation is so high that the Boltzmann distribution is unaffected by the radiation, and that the field does not do any work during a collision. During such a collision, an average of a large number of phases is taken and these cancel.

If it is assumed that the frequency is low enough so that the potential energy $(-exE)$ is included in the Boltzmann factor, which maintains Boltzmann equilibrium, the Van Vleck-Weisskopf line is arrived at instead of the Lorentzian. At any rate, the Van Vleck -

Weisskopf (VVW) line shape is

$$VVW(\nu) = \left(\frac{\nu}{\nu_0}\right)^2 \left(f_L(\nu, \nu_0) + f_L(-\nu, \nu_0)\right). \tag{7}$$

The Lorentzian and VVW lines shapes are discussed in the classical models section of [4], combined with the use of correlation functions and the Wiener-Kintchine theorem. Namely that the power spectral density of $x(t)$ is the Fourier transform of the autocorrelation of x.

Later in [4], when the Fluctuation-Dissipation theorem [5] is applied to a quantum analysis, the Van Vleck-Huber (VVH) line shape is arrived at. Namely

$$VVH(\nu) = \left(\frac{\nu \tanh(h\nu/2kT)}{\nu_0 \tanh(h\nu_0/2kT)}\right) \left(f_L(\nu, \nu_0) + f_L(-\nu, \nu_0)\right), \tag{8}$$

where h is Planck's constant, and k is Boltzmann's constant. In the quantum version of the fluctuation dissipation theorem, the quantity $2kT/(2\pi\nu)$ becomes $\hbar \coth(h\nu/2kT)$. Note that in the high temperature or low frequency limit, the VVH line shape tends to the VVW line shape. In the high frequency or low temperature limit, the hyperbolic tangent tends to unity.

In both the VVW and VVH line shapes, the theoretical model includes the effect of radiation field on the statistical thermodynamics of the gas. So the factors $\propto \nu^2$ or $\propto \nu \tanh(h\nu/2kT)$ are sometimes called "radiation terms", "radiation factors" and so on. In both cases, detailed balance is maintained so that absorption and emission are balanced at thermodynamic equilibrium. Also, if you see $\tanh(hc\tilde{\nu}/2kT)$ instead, then $\tilde{\nu}$ is a wave number rather than a frequency.

It is clear that, when the line width is narrow, and the resonant frequency is high, that the radiation factor is virtually constant across the absorption feature: in this case there is little difference in shape between either the VVW or the VVJ and the Lorentz line shape.

It is immediately obvious that the VVW line shape is *not* valid for $\nu >> \nu_0$, and that this line shape cannot be normalised. The absorption tends to a constant as $\nu \to \infty$. Though the VVH line does tend to zero (as $1/\nu$) in this limit, the integral over infinity still diverges. A baseline is sometimes subtracted and a cut-off introduced in the Lorentzians to avoid this problem. This *ad hoc* step is of practical use [6].

To be explicit, we suppose that for a single Lorentz line, we have some $\Delta\nu_c$ such that the function f is zero outside the interval $(\nu_0 - \Delta\nu_c, \nu_0 + \Delta\nu_c)$. Then we shall put $x = \nu - \nu_0$, and

$$f(x, \Delta\nu_c) = \begin{cases} \frac{\gamma/\pi}{\gamma^2+x^2} - \frac{\gamma/\pi}{\gamma^2+\Delta\nu_c^2} : & \text{if } -\Delta\nu_c < x < \Delta\nu_x \\ 0 : & \text{elsewhere.} \end{cases} \tag{9}$$

As it stands, the function f is not normalised.

$$\frac{\gamma}{\pi} \int_{-\Delta\nu_c}^{\Delta\nu_c} \frac{dx}{\gamma^2 + x^2} = \frac{1}{\pi} \int_{-\arctan(\Delta\nu_c)}^{\arctan(\Delta\nu_c)} d\theta. \tag{10}$$

So if we call our normalising factor N_f,

$$N_f = \frac{\pi/2}{\arctan(\Delta\nu_c) - \frac{\gamma\Delta\nu_c}{\gamma^2+\Delta\nu_c^2}}. \tag{11}$$

We can then define the function $\chi(x)$ as

$$\chi(x) = \begin{cases} N_f : & \text{if } -\Delta\nu_c < x < \Delta\nu_x \\ 0 : & \text{elsewhere} \end{cases} \tag{12}$$

We can re-write eqn.8 as

$$VVH(\nu) = \left(\frac{\nu \tanh(h\nu/2kT)}{\nu_0 \tanh(h\nu_0/2kT)}\right)^2 \left(f_L(\nu,\nu_0)\chi(\nu_0,\Delta\nu c) + f_L(-\nu,\nu_0)\chi(-\nu_0,\Delta\nu c)\right). \tag{13}$$

In fact, χ need not be a top hat function, and indeed different functions are used to fit the behaviour of absorption line "tails" better [7].

2 Epilogue

What is presented here is far from the end of the matter. Line shape and breadth theory is still a matter of current research and has moved far from early research mentioned here. Nevertheless, for many purposes the line shapes described here are adequate. The phenomenon of line mixing has not been mentioned, but when necessary it can be accounted for with a term proportional to $(\nu - \nu_0)$ being added to the numerator of the usual Lorentzian shape.

Another very general line shape is also used in the microwave region. This arose from an impact broadening model due to Ben-Reuven [8], also a line shape referred to as the "kinetic line shape" has been used [9] [10].

For the author's purposes, only the Lorentz, VVW, and VVH, lineshapes are required. Given the line centres, widths, and the parameters describing temperature variation and line shift, the spectral density function for the absorption coefficient can be determined. Whether or not the radiation factor needs to be included in this calculation can be determined from the source of the data.

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