Spectral Line Broadening

Introduction

No light source is truly monochromatic, each one emits light with a range of frequencies. Even a laser emits light with some range of frequencies, although that range can be very small. The causes of spectral line broadening are varied. We will look at some of the major sources for gases in a discharge tube.

Doppler Broadening

Within the discharge the atoms (or molecules) are constantly moving. Their speed and direction are random, and depend on the mass of the atom (or molecule) and the temperature of the gas. For example, the hydrogen atoms in a hydrogen discharge tube have an speed of about 3000 m/s at a temperature of 400 K.

As a result of this motion the light that is detected is Doppler shifted, and detected at a slightly different frequency that the light that would be emitted by an atom at rest. The Doppler shift is small, since the atomic speeds are quite small when compared to the speed of light ($v/c \sim 10^{-5}$), but this is enough to be detected. Since different atoms have different speeds the Doppler shift varies from atom to atom, and a range of frequencies is produced.

We can readily find an expression for the intensity of a line as a function of frequency for the case of Doppler broadening, using the Maxwell-Boltzmann distribution from statistical thermodynamics. The probability of finding an atom with components of velocity (v_x,v_y,v_z) is proportional to

$$f(v_x, v_y, v_z)\,dx\,dy\,dz = e^{-\frac{mv^2}{kT}} = e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{kT}}\,dx\,dy\,dz$$

If we let the direction of detection of the light the the x-direction, then the Doppler relationship becomes

$$\frac{\delta\lambda}{\lambda} = -\frac{\delta\nu}{\nu} = \frac{v_x}{c}$$

Any motion in the directions perpendicular to the x-direction does not produce a Doppler shift, and so does not contribute to line broadening. We can therefore average over all velocity components in these directions, and combine the result with the other constants in the equation. If we then write $\delta\lambda = \lambda - \lambda_o$ where λ_o is the wavelength that would be detected from a stationary atom, and eliminate v_x from the equations we have the expression

$$I = I_o e^{\frac{-mc^2(\nu-\nu_o)^2}{2kT\nu_o^2}} = I_o e^{\frac{-mc^2(\lambda-\lambda_o)^2}{2kT\lambda_o^2}}$$

The resultant curve is known as a Gaussian. The constant I_o is the u\intensity of the light at the wavelength of light emitted by a stationary atom. The width of the Gaussian (FWHM) can be

$$\frac{mc^2(\lambda-\lambda_o)^2}{2kT\lambda_o^2} = \ln 2$$

determined by finding the wavelengths at which the intensity drops to ½ I_o. That occurs when

$$\frac{\Delta\lambda}{\lambda_o} = \frac{\lambda-\lambda_o}{\lambda_o} = \sqrt{\frac{2\ln 2\, kT}{mc^2}}$$

that is

Substituting the known values for the constants, and converting the mass to atomic mass units yields the final result

$$\boxed{FWHM = 2\Delta\lambda = 7.2 \times 10^{-7} \lambda_o \sqrt{\frac{T}{m}}}$$

For example, the width of the 388.9 nm line of helium (atomic mass = 4) is

$$FWHM = 7.2 \times 10^{-7} * 388.9 * \sqrt{\frac{300}{4}} = 0.024 \text{ nm}$$

Pressure or Collision Broadening

Imagine that you have a single atom which stationary (so that we can ignore Doppler broadening for the time being). Furthermore, assume that it is emitting a monochromatic beam of wavelength λ_o. However, if another atom comes close to this (target) atom, then the it will perturb the energy levels of target atom, and the emitted wavelength will change, only to revert back to λ_o once the colliding atom has left again. After some (random) time another atom will come close to the target atom, and the emitted wavelength will change again. If we assume that the duration of any one collision is short in comparison to the time between collisions the emitted beam of light can be modeled as a series of sections (photons) each of wavelength λ_o, but of varying lengths.

Of course the time between these collisions is not constant, and so the photons don't have constant lengths. We need to know how many photons have length t, when the mean time between collisions is τ. To find that, consider the number of photons of length between T and T+dT, that is N(T). It must depend on the number that have already reached a duration t, multiplied by a constant

$$\frac{dN}{dT} = -AN$$

(The '-' sign indicates that if there are photons of length between T and dT, then N(T+dT) is less than N(T).) The solution of this equation is

$$N(T) = N_o\, e^{-AT}$$

If we use this expression to calculate the average length of a photon, and the average time between collisions

$$<T> = \frac{\int_0^\infty T\,N(T)\,dT}{\int_0^\infty N(T)\,dT} = \frac{\int_0^\infty T\,N_o e^{-AT}\,dT}{\int_0^\infty N_o e^{-AT}\,dT} = \frac{1}{A}$$

since this must equal τ we can write also that

$$N(T) = N_o\, e^{-T/\tau}$$

We now have an expression for the electric field in the photon

$$E = E_o\, e^{i(kx-\omega t)} \qquad (0 \geq t \geq T)$$

and an expression for the distribution of photon duration N(T). The last step is to take this time information and calculate the frequency distribution using Fourier Analysis

$$F(\omega) = \int_0^\infty N(t)\, e^{i(k_o x - \omega_o t)}\, e^{i\omega t}\, dt$$

in which $\omega_o = c/\lambda_o$ is the frequency of the light emitted by the atom between collisions, and $k_o = 2\pi/\lambda_o$ is its wavenumber.

At the position of the detector (x=L) the value of this integral is

$$F(\omega) = N_o e^{ik_o L}\left[\frac{-1}{i(\omega-\omega_o)+1/\tau}\right] = N_o e^{ik_o L}\frac{\tau}{1+(\omega-\omega_o)^2\tau^2}e^{i\phi}$$

In the final expression all terms are constant, except for the denominator. The maximum possible value of F(ω) occurs when $\omega=\omega_o$, that is at the frequency of the light emitted by the unperturbed atom, but with some light emitted at frequencies close to ω_o..

This form of this expression is called a Lorentz function. Its width (FWHM) is found from the condition $F(\omega) = ½\, F(\omega_o)$, that is when

$$(\omega - \omega_o)^2 \tau^2 = 1$$

or

$$\omega = \omega_o \pm 1/\tau$$

The FWHM is therefore $2/\tau$. As the number density of the atoms or molecules in the gas increases the time between collisions decreases, and the FWHM increases.

Natural Broadening

Experimentally it is possible to reduce the effects of both Doppler broadening and Collision broadening by reducing the temperature of the gas, and by reducing its pressure, respectively. By taking data at different temperatures and pressures they can both be effectively eliminated. However, even in the limit of low temperature and pressure the width of the spectral line is still not zero. There is a finite limit set not by the environment (ie temperature and pressure) but by the atoms themselves. This is referred to as the natural line width.

The wavelength of an emitted photon depends on the energies of the upper and lower levels

$$h\nu = \frac{hc}{\lambda} = E_U - E_L$$

However if some number of atoms are excited to the upper level, they will steadily drop down to the lower level, emitting photons as they do so. Any one atom can only “measure” the energy of the upper level for the time duration when it actually exists in that level. Using the Heisenberg Uncertainty Principle this finite time (δt) is associated with an uncertainty in the energy of the upper level (δE_u) according to

$$(\delta t)\,(\delta E_u) \sim \hbar$$

or in terms of frequency

$$(\delta t)\,(\delta \nu) \sim 1$$

The time any one atom stays in the upper level is variable. Different atoms will stay in the level for different times, which we can model as photons of different lengths. This model is very similar to that which was developed to understand collision broadening, and it should not be surprising that the result is the same, providing the average time between collisions (τ) is replaced with the average time an atom spends in the upper level, that is the radiative lifetime (τ_R). The spectral line is again represented by a Lorentz curve, with FWHM equal to $2/\tau_R$.

So far we have only considered the lifetime of the upper level. If the lower level is the ground state of the atom then the result is complete. However, when the lower level is also an excited level it has its own radiative lifetime, which adds another term to the above result

$$\mathrm{FWHM}=2\left[\frac{1}{\tau_{\mathrm{RU}}}+\frac{1}{\tau_{\mathrm{RL}}}\right]$$

Multiple Causes of Broadening

Although the above cases of line broadening have been considered separately, they can all occur at the same time. In many situations one dominates, but when two or more are of comparable width the overall profile has to be calculated as a convolution of two or more line shape functions.

Suppose that a line whose center frequency is ν_0, and which is subject to two separate mechanisms of line broadening. One of these produces a line shape described by the function $f(\nu)$. For example if this first mechanism were Doppler broadening then $f(\nu,\nu_o)$ would represent the Gaussian function above. The second mechanism is represented by a line shape function $g(\nu,\nu_o)$, which might be the Lorentz function above if the second mechanism were collisional broadening.

Of all the light arriving at the detector, consider only those photons which have the single frequency ν' as a result of the first broadening mechanism. The light from these photons has an intensity $I_\nu = I_o f(\nu',\nu_o)$. The second broadening mechanism will take these photons and produce a range of frequencies centered on the frequency ν', that is $I_\nu g(\nu,\nu')$. The total intensity is then the sum of all these terms, added over all possible frequencies ν'

$$I=\int_{\nu'=0}^{\infty} f(\nu',\nu_o)\,g(\nu,\nu')\,d\nu'$$

An integral of this forms is known as a convolution between the functions f and g.

Convolution of a Gaussian and a Lorentz function

In the case where one broadening mechanism is Doppler broadening and the other is either collisional or natural broadening, then the functions f and g are the Gaussian and Lorentz functions above

$$I=I_o\int_{\nu'=0}^{\infty} e^{\frac{-mc^2(\nu'-\nu_o)^2}{2kT\nu_o^2}}\,\frac{1}{1+4\pi^2(\nu-\nu')^2\tau^2}\,d\nu'$$

The result of this convolution is known as a Viogt line shape[1]. There is no easy expression for the result of the convolution, although it is related to the error function.

Convolution of two Lorentz functions

The convolution of two Lorentzians

$$I = I_o \int_{\nu'=0}^{\infty} \frac{1}{1+4\pi^2(\nu'-\nu_o)^2\tau_1^2} \frac{1}{1+4\pi^2(\nu-\nu')^2\tau_2^2} d\nu'$$

is also a Lorentzian, whose width is the sum of the individual widths[2]. This convolution corresponds to the line spectrum when the Doppler broadening is negligibly small, but both collisional and natural broadening are important.

Other causes of line broadening

1 http://en.wikipedia.org/wiki/Voigt_profile

2 http://books.google.com/books?id=KmwCsuvxClAC&pg=PA184&lpg=PA184&dq=convolution+lorentzian+and+lorentzian&source=bl&ots=0rfeQRhpR7&sig=5E3tJ6Vtny0OvsDaPMrxOQxfMYI&hl=en&ei=MX6jTZLeJZD2swO5seH5DA&sa=X&oi=book_result&ct=result&resnum=6&ved=0CDoQ6AEwBTgK#v=onepage&q=convolution%20lorentzian%20and%20lorentzian&f=false