APPENDIX VIII: Line broadening mechanisms in gases

The high resolution experiments, particularly with the Fabry-Perot interferometers, provide the opportunity to measure the line shapes of emission lines in gases. In fact, observing the modes of the HeNe laser drift through the (Gaussian) line profile of the 632.8 nm Ne transition provides an example of the possibility of doing "sub-Doppler" spectroscopy.

There are two principal types of line broadening mechanisms in gases-Doppler and lifetime broadening. Doppler is inhomogeneous and lifetime broadening is homogeneous. There origins are sketched below.

Doppler broadening originates from the Doppler shift of the moving atoms:

$$\nu = \nu_o(1 \pm v_x/c) \text{ or } \qquad \Delta\nu = \nu_o(v_x/c).$$

The velocity distribution is assumed Maxwellian:

$$\text{Prob}(v_x) \sim \exp[-E/2kT] \sim \exp[-mv_x^2/2kT].$$

Note that there is a direct proportion between the number of atoms with velocity v_x and the probability that a photon will be emitted having the Doppler shift $\Delta\nu$. Thus,

$$I(\Delta\nu) = I_o \exp[-(\Delta\nu/\nu_o)^2/(kT/2mc^2)].$$

You may readily show that the <u>full</u> width at half maximum of this lineshape is

$$\Delta\nu_{FWHM} = 2\nu_o\,[2\ln 2\; kT/(mc^2)]^{1/2} \qquad = \nu_o(1.24 \text{ x } 10^{-5})(T/300)^{1/2}(m_p/M)^{1/2}.$$

Thus Doppler broadening leads to Gaussian lineshapes. Note carefully its dependence on atomic mass and temperature!

Lifetime broadening is Lorentzian as the following argument shows. Consider a sinusoidal wave packet with a decaying amplitude:

$$E(t) = E_o \exp[-(\Gamma/2)t - i\omega_o t],$$

[note the irradiance is just the Poynting vector of E & M:

$$I(t) = \varepsilon_o c\, E^*(t)E(t) = \varepsilon_o c\, E_o^2\, e^{-\Gamma t},$$

so that Γ is the usual decay constant $\Gamma = \tau^{-1}$].

Its Fourier transform is:

$$E(\omega) = E_o \; \exp[-(\Gamma/2)t-i\omega t] \exp[i\omega t] \, dt,$$

$$= E_o [i(\omega-\omega_o) + (\Gamma/2)]^{-1}.$$

Now the irradiance (intensity) as a function of frequency is

$$I(\omega) = \varepsilon_o c \, E(\omega)^* E(\omega) = I_o/[(\omega-\omega_o)^2 - (\Gamma/2)^2].$$

Thus, the full width at half maximum for this Lorentzian line shape is readily shown to be

$$\Delta\nu_{FWHM} = \Delta\omega/2\pi = \Gamma/2\pi = 1/(2\pi\tau),$$

where τ is the lifetime associated with the radiation process.

It should be noted that the lifetime broadening discussed may be the "natural" lifetime (i.e., the radiative decay lifetime) or also, if collisions are frequent enough, this may be the mean lifetime between collisions. In this case is is possible to estimate a collision rate Γ as

$$\Gamma = n\sigma v$$

where n is the number density of the gas atoms, σ is a collision cross section, and v is the mean velocity of approach. Of course, $n = P/kT$; to a first-order approximation,

$\sigma = \pi(r_1 + r_2)^2$; and the relative speed of approach is $v = (v_1^2 + v_2^2)^{1/2}$,

where r_1 and r_2 are effective collision radii, and v_1 and v_2 are mean thermal velocities [$v \cong (3kT/m)^{1/2}$]. For most neutral atoms (in the ground state) the collision radii are of the order of 1.5 to 3 Å.

For example: $r_{He} = 1.09$ Å
$r_{Ne} = 1.30$ Å
$r_{Ar} = 1.82$ Å
$r_{N2} = 1.88$ Å
and $r_{CO2} = 2.30$ Å.