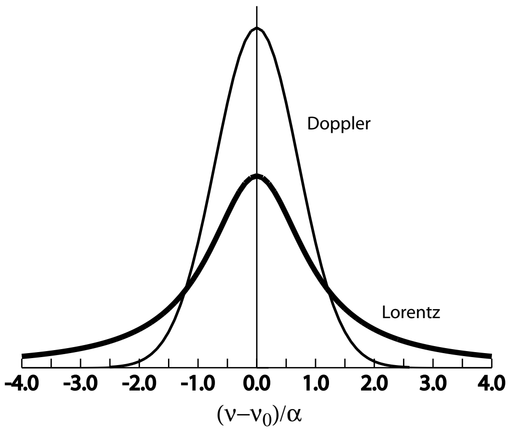

Fig. 9.7: Comparison of the Doppler and Lorentz line shapes for equal widths and strengths.

Although the shape of $f(\nu - \nu_0)$ depends on the broadening mechanism, one feature common to all shape functions is that the maximum occurs at the line center $\nu = \nu_0$, and the function falls sharply and monotonically with increasing $|\nu - \nu_0|$. Moreover, the line shape is usually symmetric about ν_0 (except in the microwave band); therefore it is common to succinctly characterize the overall width of the line via a parameter $\alpha_{1/2}$ known as the *half width at half-maximum*. That is to say, $\alpha_{1/2}$ represents the value of $|\nu - \nu_0|$ for which the absorption cross-section falls to half of its maximum value at the line center; i.e. $f(\alpha_{1/2}) = f(0)/2$.

Let us now consider the two major line broadening mechanisms and their implications for the shape function $f(\nu - \nu_0)$.

9.3.2 Doppler Broadening

In any gas, individual molecules are in constant motion, following random ballistic trajectories interrupted only by collisions with other molecules. The average kinetic energy of all of the molecules is proportional to the temperature. From the perspective of a stationary observer, each molecule has a random velocity component v_s toward or away from the observer. The statistical probability of any particular velocity component v_s along the line-of-sight s is given by the Maxwell-Boltzmann distribution

$$p(v_s) = \frac{1}{v_0\sqrt{\pi}} e^{-(v_s/v_0)^2} , \tag{9.27}$$

where $v_0 = \sqrt{2k_B T/m}$ represents the standard deviation (or root-mean-squared value) of v_s, m is the mass per molecule ($= M/N_0$, where M is the molar mass and $N_0 = 6.02 \times 10^{23}$), T is the temperature, and k_B is the Boltzmann constant.

The motion of each molecule along a particular line-of-sight introduces a Doppler shift into the frequency of the photons it emits and absorbs, as measured from the perspective of a stationary observer. In Problem 2.2, you were asked to show that, in the case of an EM wave traveling at the speed of light c, the Doppler-shifted frequency is given by

$$\nu' = \nu(1 - v/c) , \tag{9.28}$$

where ν is the frequency as measured by an observer who is stationary relative to the source, and ν' is the frequency measured by an observer moving with a velocity component v *away* from the source.

Because of the Doppler effect, EM frequencies that would appear not to coincide with the nominal position ν_0 of an absorption line can be absorbed, nevertheless, by any molecule having the right relative velocity. Conversely, radiation whose frequency *is* equal to ν_0 can only be absorbed by those relatively few molecules whose relative velocity is close to zero. The net effect, therefore, is a decrease in the likelihood of absorption by a molecule at ν_0 and an increase at nearby frequencies.

Combining (9.27) with (9.28) yields the line shape for Doppler broadening:

$$f_D(\nu - \nu_0) = \frac{1}{\alpha_D\sqrt{\pi}} \exp\left[-\frac{(\nu - \nu_0)^2}{\alpha_D^2}\right] , \tag{9.29}$$

where

$$\alpha_D = \nu_0\sqrt{\frac{2k_B T}{mc^2}} . \tag{9.30}$$

We can find the line halfwidth at half max $\alpha_{1/2}$ by setting

$$\frac{f_D(\alpha_{1/2})}{f_D(0)} = \frac{1}{2} \tag{9.31}$$

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and solving for $\alpha_{1/2}$. We find that

$$\alpha_{1/2} = \alpha_D \sqrt{\ln 2}\,. \tag{9.32}$$

The interpretation of (9.29) is straightforward. This Maxwell-Boltzmann distribution of line-of-sight velocities (9.27) is Gaussian; therefore the Doppler-broadened shape of an initially narrow line is also Gaussian. The mean speed of the molecules, and therefore the line width, increases with temperature and decreases with molecular mass. The shape of the Doppler profile is depicted in Fig. 9.7.

9.3.3 Pressure Broadening

In Section 9.2, the occurrence and position of absorption lines was justified under the implicit assumption that molecules were free to make transitions between their various energy states without external interference. For gases in the tenuous upper atmosphere, this is a reasonable assumption. In the denser portions of the atmosphere (i.e., in the stratosphere and troposphere), collisions occur between molecules with very high frequency. The effect of a collision is to "shock" the molecule at a time when it might just be in the process of emitting or absorbing a photon. Not surprisingly, this adds a significant new level of complexity to the problem of predicting which wavelengths might be most readily absorbed or emitted during a particular transition. In fact, no exact theory has yet been developed to describe the so-called *pressure broadening* of absorption / emission lines that results.

It is beyond the scope of this book to go through the heuristic arguments that have been used to derive an approximate expression for the shape of pressure broadened lines. Suffice it to say that one common model invokes collision-induced random phase shifts imposed on an otherwise "pure" sinusoidal oscillation to explain the resulting "smearing" of emitted (and absorbed) frequencies about the nominal frequency ν_0. The interested student is referred to Section 3.3.1 of S94 and Section 3.3 of GY89 for details.

The bottom line, for our purposes, is that pressure broadening is usually described adequately, though by no means perfectly, by the

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