The Effect of Collisions upon the Doppler Width of Spectral Lines

R. H. DICKE
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey
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Quantum mechanically the Doppler effect results from the recoil momentum changing the translational energy of the radiating atom. The assumption that the recoil momentum is given to the radiating atom is shown to be incorrect if collisions are taking place. If the collisions do not cause broadening by affecting the internal state of the radiator, they result in a substantial narrowing of the Doppler broadened line.

QUANTUM mechanically, the Doppler effect results from the recoil momentum given to the radiating system by the emitted photon.[1] This recoil momentum implies a change in the kinetic energy of the radiating atom which is in turn mirrored by a corresponding change in the photon's energy. This change in the photon's energy is proportional to the component of the atom's velocity in the direction of emission of the photon and leads to the normal expression for the Doppler effect. Since for gas pressures commonly encountered the fraction of the time that an atom is in collision is negligibly small, it might seem reasonable to assume that the recoil momentum is absorbed by the single radiating atom or molecule rather than by an atomic aggregate. In this case the Doppler breadth would, within limits, be pressure-independent. Actually, under certain circumstances, this assumption is far from correct. Collisions which do not affect the internal state of the radiating system have a large effect upon the Doppler breadth.

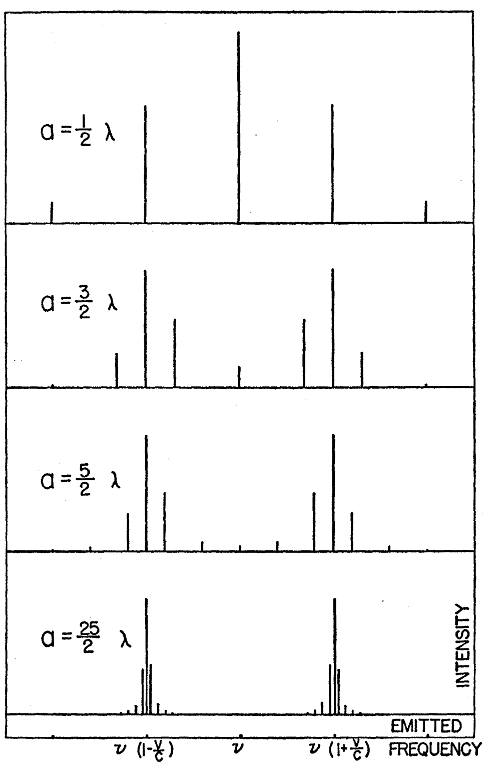

FIG. 1. Spectral distribution of radiation emitted by an atom confined to a one-dimensional box of width a.

The effect of collisions upon the Doppler effect is best illustrated with a simple example treated first classically and then quantum mechanically. Assume that the radiating atom, but not the radiation, is confined to a one-dimensional well of width a, and that it moves back and forth between the two walls with a speed v. The wave emitted by the atom is frequency modulated with the various harmonics of the oscillation frequency of the atom in the square well. For negligible collision and radiation damping, the spectral distribution of the emitted radiation is obtained from a Fourier series. A set of equally spaced sharp lines is obtained. They occur at the non-Doppler shifted frequency plus-or minus-integral multiples of the oscillation frequency of the atom in the square well. The intensity distribution of these lines is shown for several values of a/λ in Fig. 1.

In the quantum-mechanical description of this example, the radiating system possesses two types of energy, internal and external. The external energy is the quantized energy of the atomic center-of-mass moving in the one-dimensional square well. In a transition in which a photon is absorbed or emitted, both the internal and external quantum numbers may change. The frequency of the emitted photon is

$$\nu_{nm}=\nu+(h/8Ma^2)(n^2-m^2).$$

Here ν is the frequency of the non-Doppler shifted line, M is the mass of the radiator, and n, m are integers. A calculation of the transition probabilities gives results for the intensities which are for large n and m essentially the same as the classical results (Fig. 1).

The introduction of a Maxwellian distribution in v in the case of the classical calculation leads to a continuous distribution very similar to a normal Doppler distribution plus a sharp non-Doppler broadened line (see Fig. 2). The fraction of the energy radiated in the sharp line is

$$\frac{\sin^2(\pi a/\lambda)}{(\pi a/\lambda)^2}.$$

[1] E. Fermi, Revs. Modern Phys. 4, 105 (1932).

The sharp line has its origin in the fact that, for a nonintegral value of $\pi a/\lambda$, the normal unshifted frequency is emitted by all atoms independent of their speed. Since for $a \geq \frac{1}{2}\lambda$ the dominant noncentral lines in Fig. 1 are always close to the normal Doppler shifted frequencies, the broad distribution has a line contour nearly identical with the normal Doppler line. For $a < \frac{1}{2}\lambda$, the distribution increases in breadth but becomes much weaker.

For the quantum-mechanical treatment, a Maxwell-Boltzmann distribution among the various energy levels leads to a fine complex of lines having frequencies ν_{nm}. If the zero-point energy of oscillation of the atom in the well is very small compared with kT, the degenerate frequency $\nu = \nu_{nn}$ is usually the most intense single frequency emitted. For a small amount of collision or natural broadening, the complex of lines becomes a continuous distribution (Fig. 2) essentially identical with that given by the classical calculation. Note that although the atom is in contact with the walls of the cavity only an infinitesimal part of the time, the probability of the photon's momentum being given to the walls rather than to the atom is finite, being

$$\frac{\sin^2(\pi a/\lambda)}{(\pi a/\lambda)^2}.$$

For a gas confined to a large volume but with a mean free path small compared with a wavelength, the shape of a Doppler broadened line has been calculated treating the radiation classically and using a statistical procedure. In this treatment the phase of the radiation emitted as a function of the time is given by the position of the radiator as a function of the time. The probability distribution of position given by diffusion theory is used to calculate the mean intensity as a function of frequency. Substantially the same result is obtained also quantum mechanically, using a method similar to Foley's.[2] This quantum-mechanical calculation is valid only if the recoil energy of the radiator is small compared with kT. Assuming that the Doppler

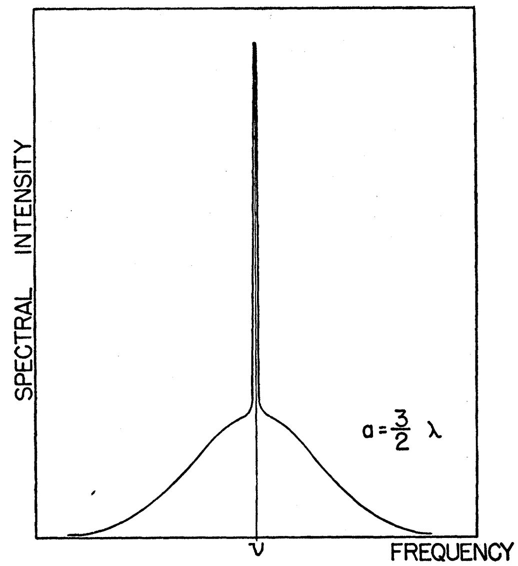

FIG. 2. Doppler broadened line of a gas in a one-dimensional box.

effect is the only appreciable source of the line breadth, it is found that the line has a Lorentz rather than Gaussian shape. The line contour is given by

$$I(\alpha) = I_0 \frac{2\pi D/\lambda^2}{(\alpha - \nu)^2 + (2\pi D/\lambda^2)^2}.$$

The width of the line at half-intensity is, in cycles per second, $4\pi D/\lambda^2$. Here D is the self-diffusion constant of the gas. This line width is roughly $2.8L/\lambda$ times that of a normal Doppler broadened line (L is the mean free path). Therefore, under those conditions for which the calculation is valid, the line breadth which is wholly Doppler is greatly reduced.

Because of the requirement that the gas collisions should not influence the internal state of the radiator, the above results are ordinarily valid only for certain magnetic dipole transitions. Nuclear magnetic resonance absorption, paramagnetic resonance absorption, and S-state hyperfine transitions are examples of transitions which are but weakly affected by collisions.

[2] H. M. Foley, Phys. Rev. 69, 616 (1946).