



**Fig. 9.9:** Approximate linewidth as a function of altitude for three prominent absorption bands.

more absorption out in the far wings of the line.

Both Doppler and pressure broadening occur at all levels of the atmosphere. However, if the degree of broadening by one mechanism is substantially greater than that due to the other, then the latter may be neglected. The relative importance of each may therefore be assessed by way of the ratio of  $\alpha_D$  to  $\alpha_L$ , using (9.30) and (9.35):

$$\frac{\alpha_D}{\alpha_L} \approx \left[ \frac{p_0}{\alpha_0 c} \sqrt{\frac{2k_B}{T_0}} \right] \frac{T\nu_0}{p\sqrt{m}} \sim [5 \times 10^{-13} \text{ mb Hz}^{-1}] \left( \frac{\nu_0}{p} \right), \quad (9.37)$$

where we have assumed that  $n \approx 1/2$  and, in the far righthand terms, used “typical” values for  $m$ ,  $T$ ,  $\alpha_0$ . Because pressure varies by several orders of magnitude through the atmosphere, whereas all other variables (except  $\nu_0$ ) typically vary by less than a factor of two, we conclude that  $p$  is the principal factor determining whether Doppler broadening or pressure broadening prevails in any given case. If we choose  $\nu_0 = 2 \times 10^{13} \text{ Hz}$ , corresponding to a wavelength

of 15  $\mu\text{m}$ , we find that  $\alpha_D \approx \alpha_L$  at  $p \sim 10$  mb. At this altitude, the two broadening processes are of roughly equal importance. For lines in the microwave band, we have  $\nu_0 \sim 10^{11}$  Hz, so that the pressure level at which parity occurs is in the vicinity of 0.1 mb or less. Fig. 9.9 depicts the transition from predominantly pressure broadening at low altitudes to primarily Doppler broadening at higher altitudes for the two cases discussed above.

When  $\alpha_D$  is of the same order of magnitude as  $\alpha_L$ , both Doppler and pressure broadening must be considered simultaneously. In this case, it is necessary to use the hybrid *Voigt* line shape, which accounts for both mechanisms. Near the center of the line, it behaves like a Doppler profile; in the wings, it has the characteristics of the Lorentz profile. The interested student should consult p. 112 of GY89 for further details.

## 9.4 Continuum Absorption

The most important absorption features in the IR and microwave bands are due to bands of discrete absorption lines, as discussed above. However, outside the major resonant absorption bands, one generally finds some level of atmospheric absorption that does not exhibit line-like structure. This is known as *continuum* (or *nonresonant*) absorption, because it tends to vary smoothly with frequency.

There are at least three causes of continuum absorption, two of which, *photoionization* and *photodissociation* are well-understood and affect primarily the very short wavelength end of the solar spectrum. The third, affecting spectral windows throughout the infrared and microwave bands, is significant both for remote sensing and for thermal radiative transfer in the atmosphere but is, unfortunately, less well understood.

### 9.4.1 Photoionization

Photoionization occurs when a photon has enough energy not only to excite an electron in an atom to a higher level but to actually strip it completely from the atom, creating a positively charged ion and a free electron. We saw earlier that ordinary electron excitation was constrained to discrete energy levels, leading to absorp-

tion/emission lines in the visible and UV bands. A fixed amount of energy is also required to ionize an atom. However, any photon *exceeding* that ionization energy can be absorbed in the course of an ionization event; the excess energy appears in the form of kinetic energy of the ion and/or the free electron. Recall that translational kinetic energy is not quantized; hence there is no constraint on the exact energy level of the photon.

The ionization of atoms requires very energetic photons. It is observed primarily in connection with X-ray and gamma radiation from extraterrestrial sources. It is therefore a phenomenon that is of relatively little interest from an atmospheric radiation point of view. However, it is responsible for the existence of the *ionosphere*, a highly conductive region of the atmosphere that has important implications for the propagation of radio waves.

## 9.4.2 Photodissociation

A second cause of continuum absorption is photodissociation. Just as photoionization is electronic excitation carried to the extreme that the electron completely separates from the atom, photodissociation is molecular vibration carried to the extreme that the molecule breaks into two pieces. Thus, any photon whose energy  $E$  exceeds the chemical binding energy  $E_{\text{bond}}$  between two components of a molecule can induce photodissociation, with the excess energy  $\Delta E = E - E_{\text{bond}}$  appearing as unquantized kinetic (thermal) energy.<sup>5</sup> At the molecular level, of course, a gain in kinetic energy is synonymous with an increase in temperature.

The binding energies in the diatomic molecules of gases like  $\text{O}_2$ ,  $\text{N}_2$ , etc., tend to be large. Therefore, only very short wavelengths can dissociate them (see Section 3.4.1).

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<sup>5</sup>Again, to return to the refrigerator magnet analogy: imagine that only 0.01 J of energy is necessary to separate a 20 g magnet from the door, but that, by whatever means, you supply 1 J of mechanical energy to the magnet (e.g., by snapping a wet dish towel at it). The magnet will acquire 0.99 J of kinetic energy, corresponding to a speed of almost 10 m/sec.