in the υ' and υ'' levels, the Q-branch may be seen as a group of very closely spaced lines.

The vibrational and rotational transitions discussed above are for the harmonic-oscillator rigid rotator in which the selection rules are given by $\Delta J = \pm 1$ and $\Delta \upsilon = \pm 1$. Because of the anharmonicity of the oscillator, the transition $\upsilon = 1 \leftarrow 0$ differs from the transition $\upsilon = 2 \leftarrow 1$. The upper-state band $2 \leftarrow 1$ does not have the same frequency as the ground-state band $1 \leftarrow 0$. Moreover, anharmonicity also changes the selection rules from those for a harmonic oscillator in which all integral changes of the quantum numbers are allowed. For example, $\Delta \upsilon = 2$ gives the first *overtone band* with twice the frequency of the normal (fundamental) mode. Simultaneous changes in two different vibrational quantum numbers give rise to *combination* and *difference bands* with frequencies that are the sum or difference of the normal-mode frequencies. They normally have smaller transition probabilities than fundamentals.

1.3.2 Line Broadening

Monochromatic emission is practically never observed. Energy levels during energy transitions are normally changed slightly due to both external influences on atoms and molecules, and the loss of energy in emission. As a consequence, radiation emitted during repeated energy transitions is nonmonochromatic, and spectral lines of finite widths are observed. The broadening of spectral lines is caused by: (1) the damping of oscillator vibrations resulting from the loss of energy in emission (the broadening of lines in this case is considered to be normal); (2) the perturbations due to reciprocal collisions between the absorbing molecules and between the absorbing and nonabsorbing molecules; and (3) the *Doppler effect* resulting from the difference in thermal velocities of atoms and molecules. The broadening of lines due to the loss of energy in emission (natural broadening) is practically negligible as compared to that caused by collisions and the Doppler effect. In the upper atmosphere, we find a combination of collision and Doppler broadenings, whereas in the lower atmosphere, below about 20 km, collision broadening prevails because of the pressure effect.

1.3.2.1 PRESSURE BROADENING

The shape of spectral lines due to collisions, referred to as *pressure broadening,* is given by the *Lorentz profile* (Lorentz, 1906). It is expressed by the formula

$$k_\nu = \frac{S}{\pi} \frac{\alpha}{(\nu - \nu_0)^2 + \alpha^2} = S f(\nu - \nu_0), \tag{1.3.10}$$

where k_ν denotes the absorption coefficient, ν_0 is the wavenumber of an ideal, monochromatic line, α is the half-width of the line at the half-maximum and is a function of pressure and to a lesser degree of the temperature, $f(\nu - \nu_0)$ represents the shape factor of a spectral line, and the line strength or line intensity S is defined by

$$\int_{-\infty}^{\infty} k_\nu d\nu = S. \tag{1.3.11}$$

In this case, we say the absorption coefficient is normalized. Figure 1.11 illustrates the Lorentz profile.

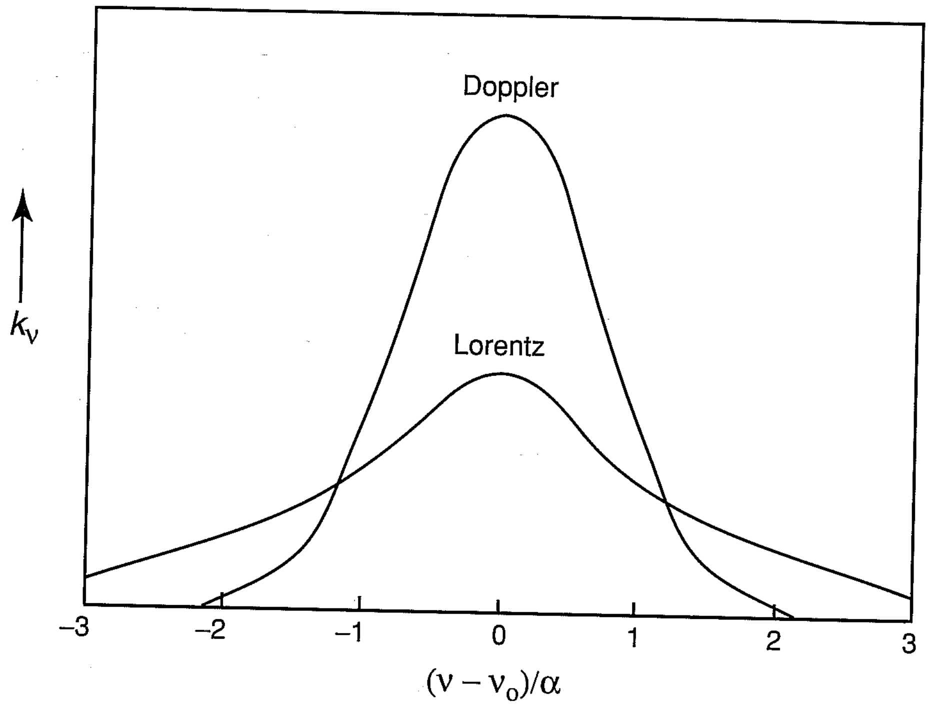

Figure 1.11 Demonstrative Lorentz and Doppler line shapes for the same intensities and line widths.

The Lorentz shape of absorption lines is fundamental to the theory of infrared radiative transfer in the atmosphere and thus, we should give a brief explanation of how the formula denoted in Eq. (1.3.10) is derived. An isolated molecule emits or absorbs an almost purely harmonic wave given by

$$f(t) = A \cos 2\pi \nu_0 ct, \tag{1.3.12a}$$

where c is the velocity of light and A is an arbitrary amplitude. During the period $-t/2$ to $t/2$, the distribution of amplitude $g(\nu)$ of the wave in the discrete wavenumber domain may be obtained from the Fourier cosine transform as follows:

$$\begin{aligned} g(\nu) &= \sqrt{\frac{2}{\pi}} \int_0^t (A \cos 2\pi \nu_0 ct') \cos 2\pi \nu ct' dt' \\ &= \frac{A}{(2\pi)^{3/2} c} \left[\frac{\sin \pi(\nu_0 + \nu)ct}{\nu_0 + \nu} + \frac{\sin \pi(\nu_0 - \nu)ct}{\nu_0 - \nu} \right]. \end{aligned} \tag{1.3.12b}$$

Generally, the widths of absorption lines are much smaller than ν_0, so that the first term in Eq. (1.3.12b) may be neglected when it is compared to the second.

The only deviation from purely harmonic behavior would be produced by the damping due to the loss of energy in emission. In the infrared, the spectroscopic effect of this damping is extremely small. However, if a radiating molecule collides with another molecule, it alters the radiating harmonic wave train due to the intermolecular forces, and the frequency of the emitting molecules would be temporarily shifted by an appreciable amount. Since the collision may be considered to be instantaneous, we may assume that the principal effect of the collision is to destroy the phase coherence of the emitted wave train. That is to say, after the collision the molecule starts emitting at another phase and these new phases are now randomly distributed. From general statistical principles, the time between collisions is distributed according to Poisson's law that the probability a collision occurs between t and $t + dt$ is e^{-t/t_0}, where t_0 is the mean time between collisions. All the initial phases of the wave trains must be averaged. Thus, the absorption coefficient will be given by

$$k_\nu = A' \int_0^\infty [g(\nu)]^2 e^{-t/t_0}\, dt, \tag{1.3.13}$$

where $[g(\nu)]^2$ is the distribution of intensity, and A' is a certain constant. Further, by letting $1/t_0 = 2\pi\alpha c$(α in cm^{-1}) and using Eq. (1.3.11), we find that Eq. (1.3.13) becomes equivalent to Eq. (1.3.10). Here, $2\pi\alpha c$ is the number of collisions per molecule per unit time. [Exercise 1.14 requires the derivation of Eq. (1.3.10) from Eq. (1.3.13).] The Lorentz line shape also can be derived from the classical theory of absorption and dispersion as shown in Appendix D.

From the kinetic theory of gases, the dependence of the half-width α on pressure and temperature is given by

$$\alpha = \alpha_0 (p/p_0)(T_0/T)^n, \tag{1.3.14}$$

where α_0 is the width at the standard pressure, p_0(1013mb), and temperature, T_0(273K). The index n ranges from $1/2$ to 1, depending on the type of molecule. When $n = 1/2$, it is known as the classical value. Under the reference condition, α_0 ranges from about 0.01 to 0.1 cm^{-1} for most radiatively active gases in the earth's atmosphere and depends on the spectral line. For the CO_2 molecule, it is fairly constant with a value of about 0.07 cm^{-1} (see Section 4.2.1 for further discussion).

1.3.2.2 DOPPLER BROADENING

Assuming that there is no collision broadening in a highly rarefied gas, a molecule in a given quantum state radiates at wavenumber ν_0. If this molecule has a velocity component in the line of sight (the line joining the molecule and the observer), and if $v \ll c$, the velocity of light, the wavenumber

$$\nu = \nu_0 (1 \pm v/c). \tag{1.3.15}$$

Note that because of the conventional use of notation the wavenumber ν and the velocity v appear indistinguishable. Let the probability that the velocity component lies between v and $v + dv$ be $p(v)\, dv$. From the kinetic theory, if the translational states are in thermodynamic equilibrium, $p(v)$ is given by the Maxwell–Boltzmann distribution so that

$$p(v)\, dv = (m/2\pi KT)^{1/2} \exp(-mv^2/2KT)\, dv, \tag{1.3.16}$$

where m is the mass of the molecule, K is the Boltzmann constant, and T is the absolute temperature.

To obtain the Doppler distribution, we insert the expression of ν in Eq. (1.3.15) into Eq. (1.3.16), and perform normalization to an integrated line intensity S defined in Eq. (1.3.11). After these operations, we find the absorption coefficient in the form

$$k_\nu = \frac{S}{\alpha_D\sqrt{\pi}} \exp\left[-\left(\frac{\nu-\nu_0}{\alpha_D}\right)^2\right], \tag{1.3.17}$$

where

$$\alpha_D = \nu_0(2KT/mc^2)^{1/2}, \tag{1.3.18}$$

is a measure of the Doppler width of the line. The half-width at the half-maximum is $\alpha_D\sqrt{\ln 2}$. The Doppler half-width is proportional to the square root of the temperature.

A graphical representation of the Doppler line shape is also shown in Fig. 1.11. Since the absorption coefficient of a Doppler line is dependent on $\exp[-(\nu-\nu_0)^2]$, it is more intense at the line center and much weaker in the wings than the Lorentz shape. This implies that when a line is fully absorbed at the center, any addition of absorption will occur in the wings and will be caused by collision effects rather than Doppler effects.

1.3.2.3 VOIGT PROFILE

In the altitude region extending from about 20 to 50 km, effective line shapes are determined by both collision- and Doppler-broadening processes. We must add the Doppler shift component to the pressure-broadened lines at wavenumbers $\nu' - \nu_0$ in order to combine the two effects. The Doppler line redistributes the Lorentz line at wavenumber ν' to ν. The line shapes for pressure and Doppler broadening may then be expressed by $f(\nu'-\nu_0)$ and $f_D(\nu-\nu')$, respectively. To account for all possible thermal velocities, a convolution of the Lorentz and Doppler line shapes can be performed to obtain

$$\begin{aligned} f_v(\nu-\nu_0) &= \int_{-\infty}^{\infty} f(\nu'-\nu_0) f_D(\nu-\nu')\, d\nu' \\ &= \frac{1}{\pi^{3/2}}\frac{\alpha}{\alpha_D}\int_{-\infty}^{\infty} \frac{1}{(\nu'-\nu_0)^2+\alpha^2} \exp\left[\frac{-(\nu-\nu')^2}{\alpha_D^2}\right] d\nu'. \end{aligned} \tag{1.3.19a}$$

This line shape is referred to as the *Voigt profile*.

To simplify the representation of the Voigt profile, we let $t = (\nu-\nu')/\alpha_D$, $y = \alpha/\alpha_D$, and $x = (\nu-\nu_0)/\alpha_D$. Thus, we have

$$f_v(\nu-\nu_0) = \frac{1}{\alpha_D\sqrt{\pi}} K(x, y), \tag{1.3.19b}$$

where the Voigt function is defined by

$$K(x, y) = \frac{y}{\pi}\int_{-\infty}^{\infty} \frac{1}{y^2+(x-t)^2} e^{-t^2}\, dt. \tag{1.3.20}$$

Many attempts have been made to simplify the computation of the Voigt function. Closed-form approximations can be developed. The Voigt profile satisfies the requirement of normalization such that

$$\int_{-\infty}^{\infty} f_v(\nu - \nu_0) d(\nu - \nu_0) = 1. \tag{1.3.21}$$

Exercise 1.17 requires the derivation of Eq. (1.3.19b) and the proofs that in the limits of $\alpha \to 0$ and $\alpha_D \to 0$, the Voigt profile reduces to the Doppler and Lorentz shapes, respectively.

One final note is in order. The line strength of a specific molecule that undergoes a transition from an upper energy state i to a lower energy state j is proportional to the square of the transition probability defined by

Physics "of S" →

$$\mathbf{R}_{ij} = \int \psi_i^* \mathbf{M} \psi_j \, dV, \tag{1.3.22}$$

where **M** is the matrix of the dipole moment related to the time-dependent Hamiltonian, V is the volume, $\psi_{i,j}$ are wave functions of the upper and lower energy states that can be determined from Schrödinger's equation, and ψ^* is the conjugate of ψ. The line strength for absorption also depends on the ratio of the population, n_j, of the lower energy state of the transition to the total population of the absorbing gas, n. At thermodynamic equilibrium, this ratio is defined by the Boltzmann factor in the form

$$n_j/n = g_j e^{-E_j/KT} \Big/ \sum_i g_i e^{-E_i/KT}, \tag{1.3.23}$$

where the integer g_j is called degenerate or statistical weight, which is the number of distinct states having energy E_j. The denominator on the right side of Eq. (1.3.23) is the *partition function*, which can be determined for both vibrational and rotational states.

1.3.3 Breakdown of Thermodynamic Equilibrium

In Section 1.2.4, we pointed out that in thermodynamic equilibrium, the source function is given by the Planck function, which depends only on temperature, frequency, and the velocity of light, and that within a small constant-temperature enclosure in which nothing changes, an element of matter absorbs and emits according to Planck's and Kirchhoff's laws. However, as was first pointed out by Einstein, emission is also affected by the incident radiation field, referred to as *induced emission*. In the following, we wish to address the extent to which the source function and absorption coefficient can be changed from their equilibrium values by the action of incident radiation. Since the discussion now involves departure from the equilibrium state, the thermodynamic arguments cannot be followed. We must now use a microscopic statistical model to understand the condition under which Kirchhoff's law cannot be applied.

Thermodynamic equilibrium can be defined in terms of Boltzmann's law for the distribution of molecules between two states. Consider a simple case where emission

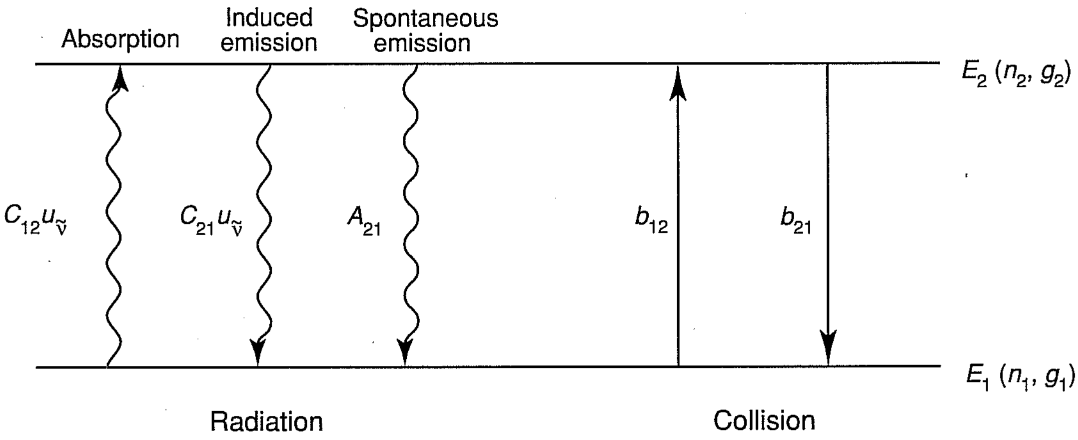

Figure 1.12 Radiative and collisional transitions connecting two energy states E_1 and E_2 where n_i are the numbers of molecules at the level E_i per unit volume; g_i are the statistical weights; b_{21} denotes the probability of transition by collisions per unit of time from the upper level E_2 to the lower level E_1 and b_{12} from E_1 to E_2; C_{12}, C_{21}, and A_{21} are the Einstein coefficients associated with emission and absorption; and $u_{\tilde{\nu}}$ denotes the radiant energy density.

(or absorption) occurs through transitions between the energy levels E_1 and E_2 of a two-level energy system, as shown in Fig. 1.12. Let n_1 and n_2 be the numbers of molecules at these levels per unit volume; and g_1 and g_2 denote the statistical weights, defined in Eq. (1.3.23). In accordance with Boltzmann's law, the distribution of molecules between two states is defined by

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \exp\left(-\frac{E_2 - E_1}{KT}\right) = \frac{g_2}{g_1} e^{-h\tilde{\nu}/KT}, \qquad (1.3.24)$$

where $\tilde{\nu}$ is the emitting frequency from Planck's relation denoted in Eq. (1.3.1). Under complete equilibrium, Eq. (1.3.24) is obeyed for all energy states throughout the medium. It is known that collisions acting alone will bring about a Boltzmann distribution and consequently a Planck source function. However, in a collisionless medium, radiation can bring about almost any population of energy levels through absorption and induced emission involving a radiating molecule and a photon (C coefficients), as shown in Fig. 1.12. Radiative transitions can also take place spontaneously without the presence of a photon or a colliding molecule (A coefficients). This occurs from the upper level to the lower level. Including both collision and radiation processes, one can show from the balance of transitions between two energy levels that the state population ratio is given by

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \frac{\eta + u_{\tilde{\nu}}}{\eta \exp(h\tilde{\nu}/KT) + 8\pi h\tilde{\nu}^3/c^3 + u_{\tilde{\nu}}}, \qquad (1.3.25)$$

where $u_{\tilde{\nu}}$ is the energy density and the coefficient that governs the relative importance of collision and radiation is defined by

$$\eta = \frac{b_{12}\,(\text{collision})}{C_{12}\,(\text{radiation})}. \qquad (1.3.26)$$

Exercise 1.18 requires the derivation of Eq. (1.3.25). The population of energy levels and the resulting source functions will be governed by the conflict between radiative and collisional effects. The rate of collisional adjustment of state populations is determined by a relaxation time proportional to the pressure. Radiative adjustment is determined by the natural lifetime of the excited states with respect to radiative transitions and is dependent on specific molecules but independent of the state of the medium. When the collision events are much larger than the radiative transitions, then $\eta \gg 1$ and Eq. (1.3.25) reduces to Eq. (1.3.24). In this case, LTE should occur and Planck's law will be valid. On the other hand, if $\eta \ll 1$, then a different source function would be required. In the earth's atmosphere, pressure varies rapidly with height and since collisional processes are dependent on pressure, there will be a sharply defined relaxation level below which Planck's law (LTE) is valid for transitions between energy levels but above which a different source function will be required (non-LTE). This level occurs at about 60–70 km in the earth's atmosphere.

1.4 Introduction to Radiative Transfer

1.4.1 The Equation of Radiative Transfer

A pencil of radiation traversing a medium will be weakened by its interaction with matter. If the intensity of radiation I_λ becomes $I_\lambda + dI_\lambda$ after traversing a thickness ds in the direction of its propagation, then

$$dI_\lambda = -k_\lambda \rho I_\lambda \, ds, \tag{1.4.1}$$

where ρ is the density of the material, and k_λ denotes the mass extinction cross section (in units of area per mass) for radiation of wavelength λ. As discussed in Section 1.1.4, the mass extinction cross section is the sum of the mass absorption and scattering cross sections. Thus, the reduction in intensity is due to absorption by the material as well as to scattering by the material.

On the other hand, the radiation's intensity may be strengthened by emission from the material plus multiple scattering from all other directions into the pencil under consideration at the same wavelength (see Fig. 1.13). We define the source function coefficient j_λ such that the increase in intensity due to emission and multiple scattering is given by

$$dI_\lambda = j_\lambda \rho \, ds, \tag{1.4.2}$$

where the source function coefficient j_λ has the same physical meaning as the mass extinction cross section. Upon combining Eqs. (1.4.1) and (1.4.2), we obtain

$$dI_\lambda = -k_\lambda \rho I_\lambda \, ds + j_\lambda \rho \, ds. \tag{1.4.3}$$

Moreover, it is convenient to define the source function J_λ such that

$$J_\lambda \equiv j_\lambda / k_\lambda. \tag{1.4.4}$$