11

Selective radiation

This chapter considers the basic energy concepts, including the detailed equilibrium principle, and the basic mechanisms of selective radiations underlying the quantum model of radiative transfer theory (RTT). The chapter presents the analysis of basic equations and fundamental concepts required for studying radiative transfer in gas media. The total solution of the equation of radiative transfer, given in the present chapter, has been widely used in considering radiative transfer in the terrestrial atmosphere. The main attention is given to the analysis of solutions of radiative transfer theory intended for studying radiative transfer processes in the microwave band.

11.1 MECHANISMS OF SELECTIVE RADIATION

The direct use of results of a macroscopic version of radiative transfer theory, investigated in Chapters 9 and 10 for quantum systems, cannot apparently give satisfactory results by virtue of the physical character of the methodological approach itself. Whereas researchers understood this circumstance for the optical and IR bands at the beginning of the twentieth century, for the microwave band the features of transmission in gas media became topical only at the end of the 1940. This has been associated with intensive exploration of the short-centimetre and millimetre bands for the tasks of meteorology, radar, radio-astronomy and, a bit later, for remote sensing of the terrestrial atmosphere (Zhevakin and Naumov, 1967; Kislyakov and Stankevich, 1967; Tseitlin, 1966; Staelin, 1969; Kondratyev and Timofeev, 1970; Malkevich, 1973; Rosenkranz, 1975; Skolnik, 1980; Brown, 1999). A significant step in this direction was made in 1945 by R. Dicke, who discovered the microwave (in the centimetre band) radiation of the properly terrestrial atmosphere using the modulation method of noise radiation reception proposed by himself (see Chapter 2).

Unlike in the macroscopic systems, radiation processes in quantum systems should be investigated from a different viewpoint, namely, using the photon model of radiative transfer, as well as quantum notions on some atomic and molecular processes. The emission of radiation is a process of emitting the photons, and the absorption of radiation is the capture of photons by a quantum particle. Selective radiation arises in atoms and molecules at energy transitions from the upper levels downward, and selective absorption is the reverse process. According to quantum mechanics, the energy transition in transferring between energy levels ($E_2 > E_1$) is related to the frequency of emitted or absorbed radiation as follows: $E_2 - E_1 = h\nu = \hbar\omega$, where h is the Planck constant and $\hbar = h/2\pi$. In other words, a strictly fixed frequency corresponds to the transition between particular energy levels. Therefore, in the absence of any external phenomena the emission (and, accordingly, the absorption) spectrum of a quantum system will have the form of a delta-shaped line, which cannot be recorded by spectroscopic instruments. In reality, however, under real physical conditions the spectral lines of gases have a quite finite width and shape in the form of narrow lines and frequency bands. These types of radiation, caused by features of the internal structure and the internal dynamics of a quantum system, can be reliably recorded by spectroscopic instruments. We shall note here that it is the shape of radiation lines (or bands) that bears the basic information load on the physical state of gases.

Such a process, in which the atom or molecule absorbs or emits a photon, but neither ionization nor recombination of ions and electrons takes place, is called the bound-bound absorption or emission. The atom or molecule transfers from one quantified energy state to another. This can be rotational, vibrational or electronic states in molecules and electronic states in atoms. Since the bound–bound transitions correspond to particular discrete energy levels, the absorption and emission coefficients will have sharp peaks in frequency dependence in the form of a series of spectral lines. Usually, the molecule has a 'grid' of electronic levels (and, accordingly, frequency peaks), which are spaced both far from each other and close to each other. These levels represent, basically, rotation–vibration levels of energies. Since these selective lines have a finite width owing to various broadening factors, in some cases (as, for example, for oxygen emission lines in the terrestrial atmosphere) separate lines 'merge' into the frequency bands and sometimes have a very complicated shape.

If the atom (or molecule) absorbs an external photon, whose energy is sufficient to cause ionization, a generated ion and free electron can have arbitrary kinetic energy. Therefore, the coefficient of bound–free absorption represents a continuous function of frequency, until the energy of an external photon is sufficient for atom ionization. The reverse process is called free–bound emission (recombination). In this case the ion and free electron recombine, releasing a photon, and the energy of the generated atom corresponds to that of discrete bound states. The free emission forms a continuous spectrum, since the recombining particles can have arbitrary kinetic energy. The recombination of quantum systems into electronic levels with high values of the principal quantum number and subsequent cascade processes to underlying levels result in the formation of lines, which are called recombination lines. This type of microwave line plays a major part in radio-astronomy when studying the interstellar medium structure (Sunyaev, 1986). It is virtually impossible to realize the conditions for generating recombination radio lines under terrestrial conditions directly.

The full picture of radiation (and, accordingly, absorption) spectra of quantum systems can be very complicated – it can either include separate lines, or form bands, or possess a continuous spectrum. So, the electronic spectra, caused by changing electronic motion, cover the ultraviolet and visible regions, the vibration spectra – near- and medium-infrared regions, and the rotational spectra – the far infrared and the microwave parts of spectrum. Some part of these lines can be 'immersed' in a continuous spectrum. The theory of molecular and atomic spectra and the experimental spectroscopic results are outlined in a series of monographs (see, for instance, Penner, 1959; Chandrasekhar, 1960; Sobolev, 1963; Basharinov *et al.*, 1968; Siegel and Howell, 1972).

The selective radiations of elementary quantum oscillators (atoms and molecules) in the microwave band are related to the presence of discrete energy levels having rather small differences of levels, of the order of some hundredth or thousandth fractions of an electronvolt. So, the quantum with frequency of 2.4×10^{14} Hz will correspond to an energy drop of 1 eV (see Appendix A, Table A.6). And, accordingly, the quantum of centimetre-band radiation with frequency of 24 GHz (a wavelength of 1.25 cm) will possess energy of 10^{-4} eV. It is important to note also that the energy of a quantum can also be presented in the temperature scale; that is to say, when quantity kT is expressed in eV, then the temperature $T = 11\,600$ K corresponds to the value of $kT = 1$ eV. And then the absolute temperature of $\sim$1.2 K can be put in correspondence with the quantum of centimetre-band radiation with a frequency of 24 GHz.

Responsible for radiation in the microwave band are quite specific energy transitions, namely:

- electronic atomic transitions between close levels with high quantum numbers;
- transitions between molecular rotational levels and rotation–vibration levels;
- transitions between atomic and molecular levels of fine and superfine structure.

The intensity of spontaneous radiation of a set of oscillators is determined by the intensity of transition (the force of an oscillator) and the population of emitting levels. The form of radiation lines depends on the temperature of oscillators and on their interaction with an ambient medium. Under equilibrium conditions the population of energy levels is determined by the Boltzmann distribution, and only under this condition, according to the Kirchhoff law (recall that this is a direct consequence of the fluctuation–dissipation theory, FDT), there exists an unambiguous relation between the emissivity and absorptivity of a quantum system. For a set of quantum particles at the equilibrium state, the detailed equilibrium principle proposed in 1916 by A. Einstein is valid. Using these backgrounds and supplementing them with a photon model, we can proceed now to the microscopic formulation of the equation of radiative transfer for quantum systems.

11.2 THE DETAILED EQUILIBRIUM PRINCIPLE

Consider the bound–bound transitions in an absorbing medium subjected to the effect of incident radiation with spectral intensity $I(\Omega)$. For the sake of simplicity we shall consider the medium to consist of atoms not interacting between each other and having two energy levels ($E_j > E_i$). Assume also the medium to be enclosed inside a black envelope at constant temperature – this is the equilibrium radiation condition (see section 4.4). The atom in a medium can absorb the energy of incident radiation and, as a consequence of this, it can execute transition from energy state i to state j. Therefore, the state j will possess a greater energy than the state i, or, in other words, the state j is 'excited' with respect to i. The number of transitions per time unit from the level i to j depends on the incident radiation intensity and on the population of the state i. Let n_i be the number of atoms in a unit volume at state i. We introduce now the Einstein coefficient B_{ij}, which is determined as the probability of transition per unit of time in a unit volume from state i into state j under an effect of the incident radiation flux in a unit of solid angle, and is a function of the considered set of atoms only. Thus, with regard to the radiation flux, falling from all directions, the number of transitions per unit of time will be equal to

$$\left(\frac{\mathrm{d}n_i}{\mathrm{d}t}\right)_{i\to j} = B_{ij} n_i \int_{\Omega=4\pi} I(\Omega)\,\mathrm{d}\Omega \tag{11.1}$$

Since the Einstein coefficients depend only on states i and j of a particular set of atoms, they can be taken out of the sign of the integral over a solid angle.

The number of transitions from the excited state j to the initial state i depends on two factors. These factors are: spontaneous radiation, which depends on population n_j at the excited state, and induced (stimulated) radiation, which depends on population n_j and on the radiation field strength. So, we introduce A_{ji} as the probability of transitions by spontaneous radiation in a unit of solid angle, and we shall consider B_{ji} to be the probability of transitions at induced radiation. Then the number of transitions from state j to state i will be equal to

$$\left(\frac{\mathrm{d}n_j}{\mathrm{d}t}\right)_{j\to i} = 4\pi n_j A_{ji} + n_j B_{ji} \int_{\Omega=4\pi} I(\Omega)\,\mathrm{d}\Omega \tag{11.2}$$

Since for a set of randomly oriented, emitting atoms, at the equilibrium state, the spontaneous radiation is isotropic on the average, then $4\pi A_{ji}$ is the probability of transition from state j to state i by spontaneous radiation of energy over all directions.

For a set of atoms, at the equilibrium state, the detailed equilibrium principle proposed by A. Einstein is valid. The essence of this principle consists in the fact that at the equilibrium state the rates of direct and reverse transitions between any two states should be equal, if all transition processes are taken into account. Therefore, quantities $\mathrm{d}n/\mathrm{d}t$ in equations (11.1) and (11.2) are equal, i.e.

$$B_{ij} n_i \int_{\Omega=4\pi} I(\Omega)\,\mathrm{d}\Omega = 4\pi n_j A_{ji} + n_j B_{ji} \int_{\Omega=4\pi} I(\Omega)\,\mathrm{d}\Omega \tag{11.3}$$

and in this case, under equilibrium conditions, in a supposed isothermal ideally black envelope, the radiation intensity is equal to the radiation intensity of an ideally black body $I_{\mathrm{B}}(\nu, T)$ (see Chapter 6). For the equilibrium black-body radiation the intensity of an incident flux is also isotropic; therefore,

$$\int_{\Omega=4\pi} I_{\mathrm{B}}(\nu, T)\,\mathrm{d}\Omega = 4\pi I_{\mathrm{B}}(\nu, T) \tag{11.4}$$

Solving equation (11.3) with respect to $I_{\mathrm{B}}(\nu, T)$, we obtain

$$I_{\mathrm{B}}(\nu, T) = \frac{A_{ji}}{(n_i/n_j)B_{ij} - B_{ji}} \tag{11.5}$$

Under thermal equilibrium conditions the populations of energy levels are related to each other according to the Boltzmann distribution law. If E_i and E_j are the energy states, then, according to the Boltzmann distribution law,

$$\frac{n_i}{n_j} = \exp\left[-\frac{E_i - E_j}{kT}\right], \tag{11.6}$$

where k is the Boltzmann constant. Since the difference of energies $E_j - E_i$ is equal to the photon energy, which is either absorbed or emitted, and, in accordance with this phenomenon, the transition from E_i to E_j or backwards takes place. Then, with regard to this circumstance, expression (11.5) can be rewritten as:

$$I_{\mathrm{B}}(\nu, T) = \frac{A_{ji}}{B_{ij}\left(\exp\left(h\nu/kT\right) - \dfrac{B_{ji}}{B_{ij}}\right)}. \tag{11.7}$$

Comparing this expression with the expression for Planck's spectral black-body radiation intensity (6.2), we obtain the following relations between the Einstein coefficients:

$$B_{ij} = B_{ji}, \tag{11.8}$$

$$\frac{A_{ji}}{B_{ij}} = \frac{\mathrm{h}\nu}{2\pi^2 c_0^2} = I_{\mathrm{B}}(\nu, T)(\exp\left(h\nu/kT\right) - 1). \tag{11.9}$$

Although up to the time of the derivation of these relations induced radiation has not been found experimentally, the analysis based on equations (11.2) and (11.3) convincingly indicates that it does really exist. If we discard the term that takes into account the induced radiation in equation (11.3), and then carry out the analysis in the same order, then, according to Einstein's derivation, the final equation will be as follows:

$$I_\nu(\nu, T) = \frac{2h\nu}{c_0^2 \exp\left(h\nu/kT\right.}. \tag{11.10}$$

It can be shown by simple comparison, that the relation obtained is none other than the Wien radiation law (see relation (6.9)). Thus, it is the comparison of Einstein's derivation with Planck's formula that was a decisive theoretical factor for the assertion of the existence of induced radiation. But only in 1954 did the special experiments on the amplification and generation of microwave electromagnetic radiation at the wavelength of 1.24 cm, using beams of ammonia (NH_3) molecules and a specially produced population inversion, make it possible to finally prove the existence of induced radiation (Prochorov, 1984).

11.3 THE PHOTON MODEL AND THE TRANSFER EQUATION FOR QUANTUM SYSTEMS

The radiation field and radiative transfer for quantum systems can be sequentially described by means of the photon model. It is useful both in studying the physics of radiative transfer in quantum systems, and in using numerical calculation schemes, for example, the Monte Carlo method (Marchuk, 1976).

11.3.1 Photon model

In considering radiation as a set of photons, the conditions at any point of a medium are specified by means of the function f of the distribution of photons.

Let

$$f(\nu, \mathbf{r}, S)\, \mathrm{d}\nu\, \mathrm{d}V\, \mathrm{d}\Omega \tag{11.11}$$

be the number of photons moving in the direction S in the volume $\mathrm{d}V$ with coordinate $\mathbf{r}$ in the frequency range $\mathrm{d}\nu$, that includes frequency ν, inside the solid angle $\mathrm{d}\Omega$, whose axis coincides with the direction S. Each photon possesses energy $h\nu$. Then the radiation energy in a unit volume and in a unit of frequency range is equal to the integral from quantity $\mathrm{h}\nu f(\nu, \mathbf{r}, S)\, \mathrm{d}\Omega$ over all solid angles. It is called the volume density of monochromatic radiation energy and is written in the form:

$$U_\nu(\nu, \mathbf{r}) = \mathrm{h}\nu \int_{4\pi} f(\nu, \mathbf{r}, S)\, \mathrm{d}\Omega \tag{11.12}$$

To determine the radiation intensity it is necessary to know the radiation flux in the direction S that intersects the site $\mathrm{d}A$ perpendicular to the direction S. The velocity of photons is equal to c, and the density of a flux of photons that intersects the site $\mathrm{d}A$ in the direction normal to it, equals $f\, \mathrm{d}\nu\, \mathrm{d}\Omega$. Then the number of photons, intersecting the site $\mathrm{d}A$ in the direction S per unit time, is equal to $cf\, \mathrm{d}\nu\, \mathrm{d}\Omega\, \mathrm{d}A$. The energy, transferred by these photons, will be equal to $\mathrm{h}\nu cf\, \mathrm{d}\nu\, \mathrm{d}\Omega\, \mathrm{d}A$. By the spectral intensity of radiation we mean the energy of radiation, transferred in the given direction per unit of time through the unit site perpendicular this direction, in a unit of a solid angle and in a unit of frequency range. Then the radiation intensity at point r in the direction S is written in the form:

$$I_\nu(\nu, \mathbf{r}, S) = \mathrm{h}\nu cf(\nu, \mathbf{r}, S)\, \mathrm{d}\Omega. \tag{11.13}$$

Excluding f from (11.12) by means of (11.13), we shall find the relation between the volume density of radiation energy and radiation intensity:

$$U_\nu(\nu, \mathbf{r}) = \frac{1}{c}\int I_\nu(\nu, \mathbf{r}, S)\,\mathrm{d}\Omega \tag{11.14}$$

This integral is often used in studying the density of the integral radiation flux.

11.3.2 Transfer equation

The transfer equation for macroscopic systems was derived in section 9.3. Now we shall consider it from the microscopic point of view, using the physical concepts on a detailed equilibrium and a photon model. The pencil of beams with intensity $I_\nu(\nu, \mathbf{r}, S)$ passes through a gas along the path S. Let the atoms (or molecules) of gas be at one of two energy states i or j, where j is the excited state with respect to i, so that $E_j > E_i$. The volume densities of atoms at these states are equal to n_i and n_j, respectively. On the section dS of the path the losses or increments of energy determine the change of intensity on this section. If we neglect the scattering, then, in accordance with the Einstein model, the variations of intensity of the external flux will be conditioned by spontaneous radiation, absorption and induced radiation. In this case it can easily be thought that spontaneous and induced radiation will make a positive contribution to the change of a current intensity of the electromagnetic radiation flux. And, in its turn, the induced absorption will provide a negative contribution, or, in other words, the extraction of energy from the external flux. Applying the photon model and taking into consideration only transitions between two energy levels, we obtain the increment (per unit of path) of the beam intensity owing to spontaneous radiation, as a product of three quantities: a number of transitions per unit of time (or the probability of spontaneous transition A_{ji}), a number of particles n_i in a unit volume and the transition energy $h\nu$. Thus, we can write:

$$\frac{\mathrm{d}I_\nu(\nu, \mathbf{r}, S)}{\mathrm{d}s} = A_{ji} n_j \mathrm{h}\nu. \tag{11.15}$$

Similar relations can be derived for induced radiation and absorption taking into account the circumstance that the flux is recorded in one direction only. Then the transfer equation will be as follows:

$$\frac{\mathrm{d}I_\nu(\nu, \mathbf{r}, S)}{\mathrm{d}s} = A_{ji} n_j \mathrm{h}\nu + B_{ji} n_j I_\nu \mathrm{h}\nu - B_{ij} n_i I_\nu \mathrm{h}\nu. \tag{11.16}$$

Though, strictly speaking, the radiation of a considered system is not fully equilibrium, nevertheless, the Einstein coefficients obtained above can still be used, since they depend only on the energy states and on the considered set of atoms (rather than on the external radiation). Using relations (11.8) and (11.9), we obtain the final expression for the equation of radiative transfer in quantum systems:

$$\frac{1}{a_\nu}\frac{\mathrm{d}I_\nu(\nu, \mathbf{r}, S)}{\mathrm{d}s} = I_{\nu\mathrm{B}}(\nu, T) - I_\nu(\nu, \mathbf{r}, S), \tag{11.17}$$

where

$$a_\nu = B_{ij} n_i \mathrm{h}\nu (1 - \exp(-h\nu/kT)). \tag{11.18}$$

From comparison of the obtained equation with the equation for a macroscopic version of the transfer theory (9.22) it follow that the quantum version of the transfer equation fully corresponds to the transfer equation for absorbing and emitting macroscopic media (see relation (9.28)), and coefficient a_j is similar to the absorption coefficient in the macroscopic equation. If we discard the induced radiation in the Einstein approach (as was done in deriving relation (11.10)), then coefficient a_ν will contain only the terms in front of the brackets, and in this case it is called the true absorption coefficient a_ν^+. It can be seen from (11.18) that the true absorption coefficient is directly proportional to two quantities, namely, the population of initial states of absorbing components n_i and coefficient B_{ji}, which determines the probability of transitions per unit of time from state i to state j. The calculation of population n_i, at least in the case of local thermodynamic equilibrium, is a problem of statistical mechanics.

The Einstein coefficients for many electronic transitions can be calculated by means of quantum mechanics, and, therefore, coefficient a_ν can be found on the basis of the microscopic approach. In determining the spectral absorption coefficient by the methods of statistical and quantum mechanics it is necessary to know the transition processes which can take place. As we have noted, in atoms and molecules of complicated structure such a great number of transitions is possible that researchers either restrict themselves to calculation of the most important transitions only, or try to apply the statistical or simplified model (Penner, 1959; Zhevakin and Naumov, 1967; Loudon, 1973).

11.4 MECHANISMS OF BROADENING OF SPECTRAL LINES

If a gas is non-dissociated and non-ionized, the internal energy of the gas (disregarding the energy of translational motion) is presented by discrete vibration, rotational and electronic energy states of atoms or molecules. The absorption of a photon can cause transition from one energy state of an atom or molecule into a state with higher energy. Since only discrete energy states participate in these transitions, only those photons with a strictly definite amount of energy can be absorbed. Therefore, the discrete transitions result in the absorption of the photons of strictly definite frequency, causing the appearance of dark lines in the transmission spectrum, i.e. the radiation transmitted through a layer of the investigated gas. For this reason such a process is called absorption in lines. According to the Kirchhoff law, the radiation of the same system will represent a linear radiation in the form of spectral lines. From the spectral approach viewpoint, such a type of absorption and emission can be presented in the form of a delta-shaped function (see Chapter 2). However, many physical conditions in which gases exist result in broadening the lines, which therefore have a finite frequency range with the centre at the frequency of basic transition. The value of this range and the change of absorptivity (emissivity) within its limits (in other words, the shape of a line) depend on the physical process that causes spectral line broadening. For these reasons, the parameters of lines (or bands) of radiation contain valuable information on the physical state of gases. This information includes, for example, the physicochemical structure of a gas; the temperature and pressure in a gas medium; the relative velocity of motion of an object; the degree of deviation of gas medium conditions from the equilibrium (the degree of nonequilibrium); the possible actuation of other physical mechanisms; the inhomogeneity of distribution of parameters in a gas medium; and other features. Therefore, the shape of a line is the chief factor of interest for radio-astronomy and remote sensing tasks. Some of the important broadening mechanisms are called natural broadening, Doppler broadening and collisional broadening (the broadening due to collisions).

11.4.1 The line shape

The variation of the absorption (emission) coefficient depending on frequency within the limits of a broadened single spectral line is called the line shape. The shape of a typical spectral line is presented in Figure 11.1. The central part of a line is sometimes called the line nosing, and the descending branches of a curve, which are far from the central frequency, are called the line wings. Because of the great physical importance of the line shape it was accepted as being expedient to introduce the integrated absorption coefficient S_{ij} for a single line, which presents the integral over the total frequency band (here the integration is possible both over the circular frequency $\omega = 2\pi\nu$ and over the frequency ν):

$$S_{ij} = \int_0^\infty a_\omega(\omega)\,\mathrm{d}\omega = \int_0^\infty a_\nu(\nu)\,\mathrm{d}\nu \tag{11.19}$$

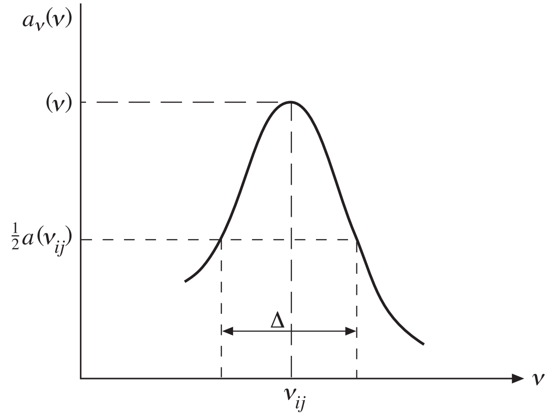

Figure 11.1. Schematic sketch of single spectral line shape. Notation is explained in the text.

and the line-shape parameter with a natural normalization:

$$b_{ij}(\omega) = \frac{a_\omega(\omega)}{S_{ij}}; \int_0^\infty b_{ij}(\omega)\,\mathrm{d}\omega = 1. \tag{11.20}$$

Often for the line-shape parameter the normalization is carried out for the value of $b_{ij}(\omega_{ij})$ at the central transition frequency.

Note that these definitions result in the simple relation:

$$\frac{b_{ij}(\omega)}{b_{ij}(\omega_{ij})} = \frac{a_\omega(\omega)}{a_\omega(\omega_{ij})}, \tag{11.21}$$

which means saving the line shape at its normalization.

One of the important quantitative characteristics of the line shape is the 'full' half-width of the line, designated by Δ. This parameter represents the line width (in the units of frequency in the given consideration) at the middle of a maximum height of the line (Figure 11.1). Such an approach ensures the unambiguous choice of a definite line width required for describing its properties. Since quantity $a_\omega(\omega)$ asymptotically tends to zero with increasing difference $|\omega - \omega_{ij}|$, it is rather difficult (and sometimes impossible) to define the line width in terms of frequencies, at which quantity $a_\omega(\omega)$ becomes close to zero. Since different terminology can be used in various literature sources, particular care should be exercised in applying the line width notion. So, the line-shape parameter is sometimes defined in the system of 'true' (noncircular) frequencies, and by the line width is meant the 'full' half-width of the line with the numerical factor of one half (Zhevakin and Naumov, 1967). From the normalization condition (11.20) it follows that $b_\nu(\nu) = 2\pi b_\omega(2\pi\nu)$, and also $a_\nu(\nu) = 2\pi a_\omega(2\pi\nu)$.

Generally speaking, the contours of spectral lines are determined by many perturbation influences, which have an effect on the magnitudes of the energy levels of an emitting quantum system (atom or molecule). Below we shall consider three basic and most physically clear broadening mechanisms, as well as the line shapes stipulated by them.

11.4.2 Natural broadening

The natural broadening of a line is closely associated with Heisenberg's uncertainty principle, according to which:

$$\Delta E_j\,\Delta t_j \sim \frac{h}{2\pi}, \tag{11.22}$$

where ΔE_j and Δt_j imply, respectively, the indeterminacy in energy of the upper level, from which the transition occurs, and the indeterminacy in time, during which the quantum system exists at this (excited) level. In the absence of the external field of radiation Δt_j can be identified with the variations of an emissive (fluorescent) lifetime of the considered transition. The physical sense of this parameter is as follows: if the external flux saturating a quantum system is 'switched off', then excited atoms (molecules) will return into the basic state, and the stored energy will be scintillated in the form of a flux of quanta. The number of atoms at excited state N_j and, therefore, the intensity of an emitted flux, will decrease as

$$N_j = N_j^0 \exp(-A_{ji}t) \tag{11.23}$$

In this case $\tau_R = (1/A_{ji})$ and is called the emissive (fluorescent) lifetime. The observation of this fluorescent radiation is just the experimental method of measuring the Einstein coefficient A_{ji}.

The relationship, similar to (11.22), takes place for the lower energy state as well. Therefore, the indeterminacy in the transition frequency will be equal to

$$\Delta\nu = \frac{1}{h}(\Delta E_j + \Delta E_i) = \frac{1}{2\pi}(\gamma_j + \gamma_i), \tag{11.24}$$

where γ_j and γ_i designate the reverse lifetimes of levels. It follows from this relation that the indeterminacies in an emitted frequency and, accordingly, the width of a spectral line, will be related to indeterminacies of energy levels, and also they will be inversely proportional to lifetimes at two energy states. As follows from the quantum mechanics (Penner, 1959), the density function (the probability) of the fact that the energy of a system at any 'blurred' m-state lies between E and $E + \Delta E$, is equal to:

$$W(E)\,\mathrm{d}E = \frac{\gamma_m}{h}\frac{\mathrm{d}E}{\left(\dfrac{2\pi}{h}\right)^2 (E - E_m)^2 + \left(\dfrac{\gamma_m}{2}\right)^2}. \tag{11.25}$$

If we designate by $J(\nu)$ the probability of observation of the radiation frequency lying between ν and $\nu + \mathrm{d}\nu$, and integrate (11.25) over all possible values of E, then we obtain the following expression for $J(\nu)$:

$$I(\nu)\,\mathrm{d}\nu = \frac{\gamma_i + \gamma_j}{4\pi^2(\nu - \nu_{ij})^2 + \frac{1}{4}(\gamma_i + \gamma_j)^2}. \tag{11.26}$$

The physical sense of the obtained expression consists in the fact, that it describes the shape of a line of emission (absorption) for the transition under the natural broadening conditions. From this expression it is possible to obtain the line-shape parameter (11.20) in the form of the so-called Lorentz shape (or resonance) line (in circular frequencies):

$$b_{ij}(\omega) = \frac{\Delta_n/(2\pi)}{\Delta_n^2/4 + (\omega - \omega_{ij})^2}. \tag{11.27}$$

It can easily be seen from this expression, that the line shape is symmetrical with respect to ω_{ij} in the units of frequency and depends on the line half-width Δ_n and on the transition frequency ω_{ij}. The maximum value of the line shape at the transition frequency will be

$$b_{ij}(\omega_{ij}) = \frac{2}{\pi}\Delta_n, \tag{11.28}$$

and the integral is

$$2\int_{\omega_{ij}}^{\infty} \frac{\Delta_n/2\pi}{\Delta_n^2/4 + (\omega - \omega_{ij})^2}\, \mathrm{d}\omega = 1, \tag{11.29}$$

which corresponds to the normalization condition for the line shape (see expression (11.20)).

The physical sense of a half-width of the line under natural broadening can be understood by comparing expressions (11.27) and (11.26). The value of the half-width of a line (in circular frequency units) is determined by the finite lifetime of an excited state: $\Delta_n = \gamma_j = 1/\tau_{\mathrm{R}}$. The numerical values of lifetimes of atoms and molecules lie in a very wide band – for electronic transitions they lie between 10^{-9} and 10^{-6} s, and in vibrational transitions they have the order from 10^{-3} to 10^{-1} s. And, accordingly, for lifetimes of the order of 10^{-8} s the half-width of a line (in frequency units) will be lower than 10 MHz.

11.4.3 Doppler broadening

The atoms or molecules of absorbing or emitting gas are not at the stationary state, but have some definite distribution of velocities related to the energy of their thermal motion. If for a motionless atom or molecule the frequency of light, emitted or absorbed in the given transition, is equal to ω_{ij}, then the frequency of electromagnetic radiation, absorbed or emitted by a molecule moving at velocity v_x in the direction of a line of sight, is equal, according to the Doppler principle, to

$$\omega = \omega_{ij}\left(1 - \frac{v_x}{c}\right). \tag{11.30}$$

It is known from statistical mechanics that at the thermal equilibrium state and in the absence of an external field of force the distribution of velocities of a homogeneous ideal gas obeys the Maxwell distribution law. The latter can be written both for velocity vector magnitudes (in three-dimensional space), and for projections of a vector of velocities on selected directions (on the one-dimensional axis x, for example). Note also that the Maxwellian distribution of molecules over velocities can also be established as a result of mutual collisions between molecules in their chaotic thermal motion. Various forms of this distribution are used in various physical investigations. So, in the case of remote sensing we have a situation where the observer perceives radiation propagating along a single coordinate axis. In this case the velocities of interest are directed along this axis, either towards the observer, or away from him (i.e. along the velocity vector projection on the observation axis).

According to the classical Maxwell model, the number of particles dn, having velocity magnitude in the range from v up to $v + \mathrm{d}v$, is determined by the expression:

$$\frac{\mathrm{d}n}{n} = \left(\frac{m}{2\pi \mathrm{k}T}\right)^{3/2} \exp(-(mv^2/2kT))4\pi v^2\, \mathrm{d}v. \tag{11.31}$$

Here ν is the magnitude of a particle's velocity, m is the particle mass, k is the

Boltzmann constant, T is the absolute temperature of a thermostat where the particles in the total quantity of n are enclosed. It can easily be seen that the distribution is valid for $v \geq 0$ and belongs to the gamma distribution type. However, the distribution for the velocity vector projection on the chosen direction has an essentially different character and can be obtained using the well-known transformation in probability theory (Feller, 1971) that forms an analytical relationship between the density function p_v of the length of a random vector in three-dimensional space and the density p_x of the length of its projection in a fixed direction:

$$p_x(t) = \int_t^{\infty} p_v(y) \frac{\mathrm{d}y}{y}. \tag{11.32}$$

The reverse transformation can also be obtained:

$$p_v(t) = -tp_x'(t), t > 0. \tag{11.33}$$

Applying the first transformation for distribution (11.31), it can be shown that the projections of random vectors in space on any axis of any Cartesian system have a normal density with zero expectation. Thus, at the thermal equilibrium state the fraction $\mathrm{d}n/n$ of molecules whose velocity projections in the given direction (the observation direction is axis x) lie between v_x and $v_x + \mathrm{d}v_x$, is equal to

$$\frac{\mathrm{d}n}{n} = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2kT}\right) \mathrm{d}v_x, \tag{11.34}$$

which corresponds to the normal distribution with zero expectation. It is interesting to note that in his study of the velocity distribution of molecules in three-dimensional space Maxwell has proceeded from the opposite approach. That is to say, he supposed that in any Cartesian coordinate system three velocity components represent independent random variables with zero expectation. And this circumstance entails the Maxwell distribution over velocities (11.31) by means of transformation (11.33).

Using (11.30) and (11.31), we eliminate v_x and determine the numerical value of a fraction of molecules emitting in each elementary increment of the frequency range owing to the Doppler broadening. As a result, we obtain the formula of a spectral line corresponding to the Gaussian shape of distribution, i.e.

$$b_{ij}(\omega) = \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta_{\mathrm{D}}} \exp\left[-4(\omega - \omega_{ij})^2 \frac{\ln 2}{\Delta_{\mathrm{D}}^2}\right], \tag{11.35}$$

where Δ_{D} is the 'full' half-width of the line at the Doppler broadening. The shape parameter $b_{ij}(\omega)$ depends only on Δ_{D} and the transition frequency ω_{ij}, where

$$\Delta_{\mathrm{D}} = \frac{2\omega_{ij}}{c} \left(\frac{2kT}{m} \ln 2\right)^{1/2} \tag{11.36}$$

that is, Δ_{D} depends on ω_{ij}, T and m. The dependence of Δ_{D} on $T^{1/2}$ indicates that the Doppler broadening is essential at high temperatures.

The relations obtained above have been derived under the assumption of the absence of relative velocities between the observer's coordinate system and the emitting gas medium. If, however, such velocities do take place (as, for example, for space objects observed from the Earth), then the Doppler shift will be observed as the change of the basic transition frequency and, therefore, of the frequency shift of the whole line.

11.4.4 Collisional broadening

The classical theory of collisional broadening rises from electronic theory, developed by H. Lorentz in 1905–1906. This theory, in describing an absorbing system, uses the notion of attenuating oscillations of a linear oscillator with a finite attenuation coefficient.

Collisions between the atoms (or molecules) in a gas medium can be an important source of broadening of the line of emission (absorption). A comprehensive analysis of collisional broadening is fairly complicated (Penner, 1959; Loudon, 1973). Here we shall consider only those details of the physical process of collisional broadening which are necessary for illustrating the nature of this mechanism. The main attention will be given to the same pair of energy states, which has been used previously. In the present case, however, we shall disregard the Doppler and natural (emissive) contributions to the line width; therefore, the quantum particles emit the wave at a fixed frequency. Disregarding an emissive line width is equivalent to the supposition that the emissive lifetime is high as compared to the mean time between collisions of quantum particles. Let us consider a single excited atom that emits light at frequency ν_{ij}. One can imagine that the wave train of electromagnetic radiation is continuously emitted by the atom so long as it undergoes collision. During collision the energy levels of an emitting atom are shifted by the effect of forces of interaction between two colliding atoms. Therefore, during collision the emitted wave train is interrupted. When the wave with frequency ν_{ij} is restored after collision, all its characteristics coincide with the characteristics of this wave before collision, except the phase, which is not bound to the wave phase before collision. If the duration of collision is fairly short, then any radiation emitted during collision can be neglected, whereas the frequency of light is shifted relative to ν_{ij}. In this case the collisional broadening effect can be adequately described on the basis of a model in which each excited atom always emits at frequency ν_{ij}. However, during each collision the phase of an emitted wave randomly changes. The observed scattering of emitted frequencies is stipulated by the fact that the wave breaks into finite trains, whose Fourier components contain, among others, the frequencies which differ from the true value of ν_{ij}. The wave train, emitted by a single atom, is depicted schematically in Figure 11.2, which shows the time dependence of the electric field amplitude $E(t)$ at a fixed observation point. The collision time is designated by the vertical line, which is followed by the random change of the wave phase. According to the kinetic theory of gases (see Loudon, 1973; Prochorov, 1984), the probability $p(\tau)\,\mathrm{d}\tau$ of the fact that the time of free path of an atom (molecule) lies in the interval from τ to

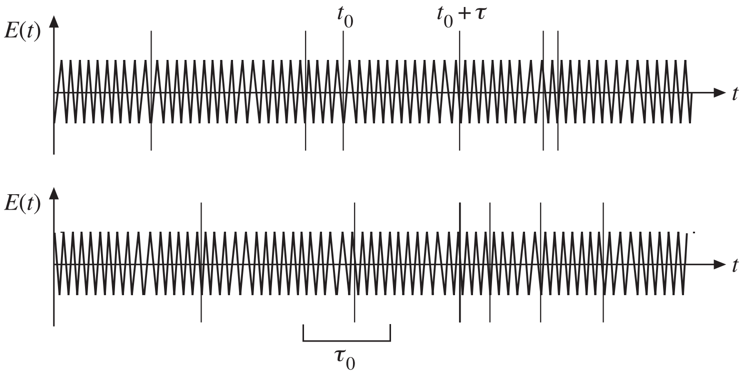

Figure 11.2. Schematic presentation of an electrical field amplitude in the form of oscillation intervals, emitted by a single atom. Vertical lines denote collisions, separated by free run times, the average time of which is shown as τ_0.

$t + \mathrm{d}t$, is determined by the expression

$$p(\tau)\,\mathrm{d}\tau = \left(\frac{1}{\tau_0}\right)\exp\left(-\frac{\tau}{\tau_0}\right)\mathrm{d}\tau, \tag{11.37}$$

where the mean free path time τ_0 (s) can be written as

$$\tau_0 = 3 \times 10^{-10}\frac{P_0}{P}. \tag{11.38}$$

Here P and P_0 are the values of pressure at the studied altitude and on the ground, respectively. Free path times in Figure 11.2 are chosen in accordance with the probability distribution presented in (11.37). Let us consider a period of the free path time of an atom beginning at time t_0 and with duration τ. From the Maxwellian electrodynamics point of view, the complex amplitude of the radiation field can be written as follows:

$$E(t) = E_0\,\exp[-\mathrm{j}\omega_{ij}t + \varphi], t_0 < t < t_0 + \tau, \tag{11.39}$$

where φ is the wave phase for the given free path, and E_0 and ω_{ij} are the same for any free path. The field $E(t)$ in (11.39) can be presented in the form of spectral presentation as the Fourier integral (see Chapter 2). Then the amplitude of a complex spectrum at arbitrary frequency ω is determined as:

$$\dot{S}(\omega) = \frac{1}{2\pi}\int_{t_0}^{t_0+\tau} E(t)\exp(\mathrm{j}\omega t)\,\mathrm{d}t = \frac{E_0}{2\pi}\exp[\mathrm{j}(\omega - \omega_{ij})t_0 + \varphi]\frac{\exp[\mathrm{j}(\omega - \omega_{ij})\tau]}{\mathrm{j}(\omega - \omega_{ij})}. \tag{11.40}$$

It follows from this relation, that the Wiener spectrum (the spectral intensity) of radiation of a train of oscillations can be written as

$$G_\tau(\omega) \cong |\dot{S}(\omega)|^2 = \left(\frac{E_0}{\pi}\right)^2 \frac{\sin^2[(\omega - \omega_{ij})\tau]}{(\omega - \omega_{ij})^2}. \tag{11.41}$$

The frequency dependence of a train of oscillations with the limited generation time is proportional to the well-known dependence $(\sin x/x)^2$. However, at any time the total intensity of radiation of a gas medium consists of the contributions from a great number of excited atoms (molecules). The free path times of different atoms are distributed according to the expression for the probability (11.37). As a consequence, for finding the total intensity of radiation of a medium the value of intensity of radiation of a train of oscillations should be multiplied by the probability (11.37) and integrate the result over all values of τ:

$$G(\omega) = \int_0^\infty G_\tau(\omega)p(\tau)\,\mathrm{d}\tau \cong \frac{1}{2}\frac{1}{(\omega - \omega_{ij})^2 + (1/\tau_0)^2}. \tag{11.42}$$

Therefore, the frequency distribution of the emission line with collisional broadening has the Lorentz shape characterized by the width of $2/\tau_0$. Now we estimate the length of a train of oscillations for microwave radiation under terrestrial atmospheric conditions. So, for the gas density, corresponding to the pressure of 10^5 Pa (the sea surface level) at a temperature of 20°C the mean value of time of collisions is 3×10^{-10} s. For radiation with the wavelength of 1 cm (30 GHz) the wave period will be 3×10^{-11} s, and, thus, the train of oscillations for a collisional mechanism will be generated by ten oscillations of the electromagnetic wave only. At the same time, for natural broadening the train of oscillations will be equal to 1000 and more wave periods and, accordingly, the line stipulated by this type of broadening will be at least 100 times narrower than the line of collisional broadening.

A more detailed study results in the following expression for the line shape parameter:

$$b_{ij}(\omega) = \frac{\Delta_C/2\pi}{\Delta_C^2/4 + (\omega - \omega_{ij})^2}, \tag{11.43}$$

i.e. it has the same shape as at natural broadening.

The 'full' half-width Δ_C is determined by the frequency of collisions (or by the mean free path time), and its approximate value can be found from the kinetic theory of gases

$$\Delta_C = 8\sqrt{\pi}D^2 P(MkT)^{-1/2}, \tag{11.44}$$

where D is the diameter of atoms or molecules, P is the pressure of one gas component. Note that the half-width value for the collisional mechanism (unlike the Doppler one) is proportional to the gas pressure and inversely proportional to $T^{1/2}$. Thus, the broadening due to collisions becomes a key mechanism at high pressures and low temperatures.

It is of interest to note that the subsequent detailed quantum-mechanical analysis of the collisional broadening mechanism has resulted in comparatively small variations (and only on the wings) of the line shape, which was obtained as

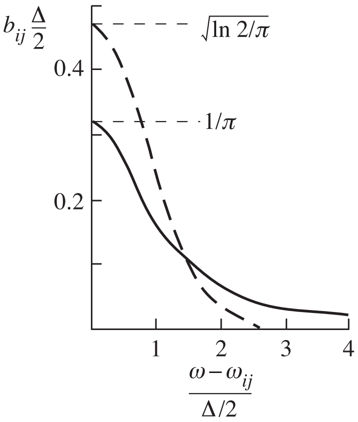

Figure 11.3. A line shape for Doppler (broken line) and Lorentzian (solid line) broadenings. Areas, bordered by each curve and coordinates axes, are equal.

early as at the beginning of the twentieth century by H. Lorentz proceeding from the classical concepts of the kinetic theory of gases (Penner, 1959; Zhevakin and Naumov, 1967).

The collisional broadening often represents a key mechanism in application problems of microwave radiation transmission through the terrestrial atmosphere; so, the other broadening mechanisms can be neglected in these cases. Figure 11.3 gives the comparison of the Doppler and Lorentz line shapes for the same values of their half-widths and the area restricted by the curves. As compared to the Doppler shape, the Lorentz shape has a smaller height at the line centre, but a greater height near the line wings. Even if the Doppler broadening is determining near the line centre, the collisional broadening is often an important mechanism in forming the line far from the line centre (on the line wings).

11.4.5 Compound shape of the line

The expressions for the widths of lines, excited by various mechanisms, indicate that, depending on the physical conditions in a gas medium (temperature, pressure), the widths of lines can vary within very wide limits. So, for example, under terrestrial atmospheric conditions up to the altitudes of the order of 50 km the mean value of the interval of Doppler broadening is essentially smaller than the lifetime at an excited state – on one hand. But, on the other hand, the relationship between the temperature and pressure are such that the collisions become a key factor in forming the width and shape of lines of emitting gases. At altitudes higher than 50 km the situation is just the opposite: the line shape is almost completely determined by the Doppler broadening mechanism. A similar situation takes place in the open space as well.

However, when the contributions of the Doppler, collisional and, probably, emissive broadening are comparable in magnitude, it is necessary to determine the compound shape of a line, stipulated by these three simultaneously acting processes. Let us consider, first, the combination of mechanisms resulting in a line broadening which separately determine the line shape described by functions $F_1(\omega)$ and $F_2(\omega)$. The corresponding compound shape of a line is described by the function

$$F(\omega) = \int_{-\infty}^{\infty} F_1(x) F_2(\omega + \omega_0 - x)\,\mathrm{d}x \tag{11.45}$$

Here ω_0 is the common central frequency for two distributions. The integral relation, presented above is none other than the convolution integral. Proceeding from physical considerations, one can say that the integration in (11.45) relates each frequency component of distribution F_1 with the broadened distribution that corresponds to the mechanism resulting in distribution F_2. Obviously, by repeated applications of equation (11.45) it is possible to associate any number of mechanisms resulting in line broadening. Note also, that the final shape of a line does not depend on the order of associating the contributions, so that the value of the integral in (11.45) is invariant with respect to exchanging the places of functions F_1 and F_2.

Now we carry out two curious examples. If two sources of broadening (for example, collisions between the molecules of various components of a gas medium) result in the Lorentz shapes of a line with widths Δ_{L_1} and Δ_{L_2}, then it can easily be seen, that the total line is also Lorentz one and has the width

$$\Delta_{\mathrm{L}} = \Delta_{\mathrm{L}_1} + \Delta_{\mathrm{L}_2}. \tag{11.46}$$

However, if the broadening mechanisms result in the Gaussian shapes of lines with differing widths, Δ_{D_1} and Δ_{D_2} (for example, two identical gas components with different temperatures), then the compound line will also be Gaussian with the width determined, however, by the absolutely different relation:

$$\Delta_{\mathrm{D}}^2 = \Delta_{\mathrm{D}_1}^2 + \Delta_{\mathrm{D}_2}^2. \tag{11.47}$$

11.4.6 Voigt line

Let us consider the important type of a symmetrical line contour, which arises as a result of simultaneous action of the Doppler and collisional mechanisms with the same central frequency. The analysis of a compound line indicates, that it is impossible to obtain the analytical expression for the line shape in this case. As usual, the form of this line is kept in the normalized integrated shape with a precision of constant coefficients (Penner, 1959):

$$F(\xi, a) = \int_{-\infty}^{\infty} \frac{\exp(-y)^2}{a^2 + (\xi - y)^2}\,\mathrm{d}y, \tag{11.48}$$

where

$$a = \frac{\Delta_{\mathrm{C}}}{\Delta_{\mathrm{D}}} (\ln 2)^{1/2}; \xi = \frac{\omega - \omega_{ij}}{\Delta_{\mathrm{D}}} (\ln 2)^{1/2}. \tag{11.49}$$

For the purposes of the practical use of this type of line detailed numerical tables were compiled. The corresponding line shape was called the Voigt line. It has a shape intermediate shape between the Lorentz and the Gaussian.

11.4.7 Model of bands

The gases usually dealt with in remote sensing tasks are either diatomic or polyatomic and, consequently, possess vibrational and rotational energy states, which are not peculiar to monoatomic gases. At moderate temperatures the transitions between vibrational and rotational states usually make the main contribution to the absorption coefficient in the most important regions of the thermal radiation spectrum.

With increasing temperature of gaseous systems (at burning of gases) the processes of dissociation, ionization and electronic transitions become more noticeable. So, the contribution of these processes into the absorption coefficient should also be taken into account. If the gas absorption coefficient is determined experimentally, the contributions from radiation in the lines and continuous radiation are summed. In calculating these coefficients it is necessary to analyse each absorption process separately and then to calculate the total coefficient by summing up the contributions from various processes as independent processes. As a rule, the rotational–vibrational bands of spectral absorption consist of a group of closely situated spectral lines appearing owing to transitions between vibrational and rotational energy states. The absorption lines in some parts of the spectrum are situated so close together, that in the majority of cases the single lines cannot be isolated by spectroscopic instruments. Owing to broadening, the lines either seem to be overlapping (because of the finite value of instrument's spectral resolution), or are overlapping in reality – the lines, while merging, generate the so-called absorption bands. The great number of possible energy transitions, which can result in the appearance of a set of spectral lines, is explained by the presence of a set of energy levels and transitions whose radiation frequencies can fall in quite different spectral intervals. The transitions between rotational levels of the same vibrational state correspond to small values of the difference in energies. Therefore, these transitions correspond to the lines within the limits of bands situated in the far-infrared and microwave regions. A principal feature of the microwave band is the presence of single absorption lines of major components of the terrestrial atmosphere – water vapour and oxygen. If the transitions from the rotational level in one electronic and vibrational state to the rotational level in the other electronic and vibrational state take place, then high values of the difference in energies are obtained, and the system of bands is formed in the high-frequency visible and ultraviolet regions of spectrum. The radiation bands are usually separated by the sections of the spectrum of relatively weak absorption. These sections of the spectrum are called the transparency windows.

A possible approach to the description of gas properties consists in studying the absorptivity of bands and lines separately and in deriving empirical relations describing the characteristic of each band. So, two models are widely used which represent two extreme cases of the disposition of single lines and the intensity of emission in them.

In the Elsasser model all lines have identical Lorentz shape (equation (11.43)), as well as identical height and distance between the lines (and, therefore, an identical value of integrated absorption coefficient S_C for all lines). In this case quantity a_ω becomes a periodic function of frequency. This function depends on parameters determining the contour of the Lorentz lines, as well as on the distance, δ, between them. The absorption coefficient for any particular value of frequency is determined by summing the contributions from all adjacent lines. Summing all contributions with allowance for relation (11.43) that describes the Lorentz contour of a line, we obtain

$$a_\omega(\omega) = \frac{S_C}{2\pi} \sum_{n=-\infty}^{\infty} \frac{\Delta_C}{\Delta_C/4 + (\omega - n\delta)^2}. \tag{11.50}$$

According to the other model (the Mayer–Goody model), the vibrational–rotational band consists of a great number of non-uniformly (randomly) disposed lines having arbitrary distribution of intensity. According to this model, the position of lines and their intensity do not depend on each other.

Many additional difficulties arise in considering gaseous mixtures. For example, the partial pressure, p, of absorbing gas in a multi-component mixture varies depending on T and P; the population of energy levels depends on temperature T, and the overlapping of spectral lines varies depending on pressure P. It is fairly difficult to formulate the analytical dependence of the line shape on T, p and P for the mixture of real gases. The getting of practically useful results largely depends on experimental investigations, and the theory is used as an indicator in this respect.

11.5 RADIATION TRANSMISSION THROUGH A GAS LAYER

We shall consider the problem of electromagnetic radiation transmission through a layer of gas having selective frequency properties. Earlier we obtained the basic equation of transfer theory for quantum systems (11.17). Here we shall present this equation for consideration (for the sake of simplicity and clarity) in the one-dimensional case, where the external radiation, possessing its specific (arbitrary, generally speaking) spectral characteristics $I_{\nu O}(\nu)$, passes through a layer of absorbing and emitting gas. This equation is as follows:

$$\frac{\mathrm{d}I_\nu(\nu, s)}{\mathrm{d}s} = a_\nu(\nu, s) I_{\nu B}[\nu, T(s)] - a_\nu(\nu, s) I_\nu(\nu, s). \tag{11.51}$$

The boundary condition in this case can be written as $I_\nu(\nu, 0) = I_{\nu O}(\nu)$. Dependencies $a_\nu(\nu, s)$ and $I_{\nu B}[\nu, T(s)]$ characterize the electrodynamical and thermal spatial features of the medium studied. Solving equation (11.51), for example, by the well-known integrating multiplier method, for the given boundary condition, we obtain the following solution:

$$I_\nu(\nu,s) = I_{\nu\mathrm{O}}\ \exp\left[-\int_0^s a_\nu(\nu,s')\,\mathrm{d}s'\right] + \int_0^s a_\nu(\nu,s') I_{\nu\mathrm{B}}[\nu,T(s')]\ \exp\left[-\int_{s'}^s a_\nu(\nu,s'')\,\mathrm{d}s''\right]\mathrm{d}s'. \tag{11.52}$$

If we suppose that the pressure, temperature and structure of gas are constant in a medium, then $a_\nu(\nu)$ and $I_{\nu\mathrm{B}}[\nu,T]$ do not depend on the coordinate, and equation (11.52) can be presented in the following, widely used, form:

$$I_\nu(\nu,s) = I_{\nu\mathrm{O}}\ \exp(-a_\nu(\nu)s) + I_{\nu\mathrm{B}}(\nu,T)(1-\exp(-a_\nu(\nu)s)). \tag{11.53}$$

The multipliers of the values of intensities play an important part in remote sensing practice. For this reason they received their characteristic names. So, the spectral transmissivity factor $\Gamma(\nu)$ of homogeneous absorbing gas of thickness s, measured in the radiation transmission direction, is determined in the form of

$$\Gamma_\nu(\nu) = \exp(-a_\nu(\nu)s), \tag{11.54}$$

and the spectral absorptivity α_ν in the form of

$$\alpha_\nu(\nu) = 1-\exp(-a_\nu(\nu)s) = 1-\Gamma(\nu). \tag{11.55}$$

If we use the Kirchhoff law (Chapter 4) in the form of equality of the spectral absorptivity and spectral emissivity, then formula (11.55) will also characterize the spectral emissivity of a gas layer of thickness s.

In a number of cases (in the infrared and optical bands especially) the spectral properties of instruments are insufficient for separating the spectral absorption lines of gases. In this case it becomes necessary to consider the integral characteristics of intensity I in the finite band $\Delta\nu$ of an instrument:

$$I = \int_{\Delta\nu} I_\nu(\nu)\,\mathrm{d}\nu = \int_{\Delta\nu} I_{\nu\mathrm{O}}\ \exp(-a_\nu s)\,\mathrm{d}\nu + \int_{\Delta\nu} I_{\nu\mathrm{B}}(\nu,T)(1-\exp(-a_\nu s))\,\mathrm{d}\nu. \tag{11.56}$$

If the frequency band $\Delta\nu$ contains a sufficient number of narrow lines and, at the same time, it is sufficiently small, so that it is possible to replace $I_{\nu\mathrm{O}}(\nu)$ and $I_{\nu\mathrm{B}}[\nu,T]$ in this frequency band by their average values $I_{\nu\mathrm{O}}$ and $I_{\nu\mathrm{B}}(T)$, respectively, then $I_{\nu\mathrm{O}}(\nu)$ and $I_{\nu\mathrm{B}}(T)$ can be taken out of the sign of integral, and equation (11.56) will take the form of

$$I = \overline{I_{\nu\mathrm{O}}}\int_{\Delta\nu}\Gamma_\nu(\nu)\,\mathrm{d}\nu + \overline{I_{\nu\mathrm{B}}(T)}\int_{\Delta\nu}\alpha_\nu(\nu)\,\mathrm{d}\nu. \tag{11.57}$$

The strict calculation of integrals in expression (11.57) is rather difficult even for simple types of lines, as, for example, for the Lorentz-type line. Special methods of calculating these integrals have been developed and improved, both for single lines and for Elsasser's, Mayer–Goody's and other types of models.

The analysis of expression (11.53) indicates that there exist two radically different forms of exhibiting spectral lines – in the form of so-called 'absorption' lines and 'straight' lines, depending on the type and conditions of the experiment.

11.5.1 The 'cold' layer approximation

This approximation is characterized (see section 9.3) by the fact that the external (with respect to the gas layer) radiation essentially exceeds the thermal radiation of a gas layer. In this case the radiation intensity at the gas layer exit can be presented as

$$I_\nu = I_{\nu \mathrm{O}} \exp[-a_\nu(\nu)s]. \tag{11.58}$$

If the layer has small optical thickness $\tau_\nu = a_\nu(\nu)s \ll 1$, then the expression obtained is simplified

$$I_\nu = I_{\nu \mathrm{O}}(1 - a_\nu(\nu)s). \tag{11.59}$$

It directly follows from this relation that, if the input electromagnetic signal possesses a broadband (and planar) spectrum, then the output signal will appear as an 'inverted' line (or absorption line) (Figure 11.4(a)). The 'dark' Fraunhofer lines in the optical bright spectrum of the Sun are an example of such lines.

If the layer is not semi-transparent and the optical path value exceeds the value of unity, then the form of the absorption line will be essentially distorted (Figure 11.4(a)). And, in its turn, the informative saturation of such a type of measurement will sharply decrease.

11.5.2 Thermal radiation approximation

In its turn, in the aforementioned approximation, only that component in expression (11.53) is considered, which is bound to thermal radiation. And, thus, we have the following expression for thermal radiation of a gas layer:

$$I_\nu = I_{\nu \mathrm{B}}(\nu, T)[1 - \exp(-a_\nu(\nu)s)]. \tag{11.60}$$

In the case of a semi-transparent gas layer with a small optical thickness value the expression is simplified:

$$I_\nu = I_{\nu \mathrm{B}}(\nu, T)a_\nu(\nu)s. \tag{11.61}$$

It follows from this expression that for a semi-transparent gas layer its spectral properties will be determined by multiplying the straight radiation line and the spectral form of an ideal black body (see Chapter 6). If the line is narrowband enough, then the $I_{\nu \mathrm{B}}(\nu, T)$ value in the spectral range of the line can be presented by the average (constant) value, and then the radiation spectrum of gas will exactly correspond to the radiation line.

If the gas layer is not semi-transparent and the optical path value exceeds the value of unity, then the form of the straight line will be distorted, but in a

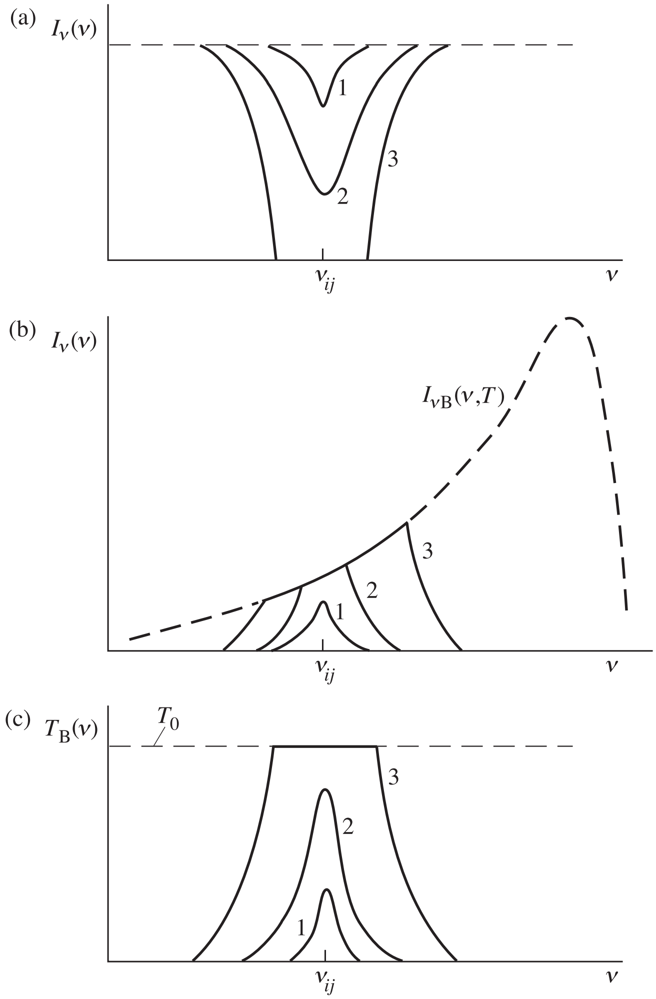

Figure 11.4. Schematic sketches of spectral intensity transfer by way of a gas layer: (a) intensity transmission through a gas layer (in cold layer approximation); (b) the spectral emission of a gas layer (in the form of an intensity); (c) the spectral radiobrightness temperature of a gas layer. Figures show gas layers with increased values of optical paths ($\tau_1 < \tau_2 < \tau_3$). $I_{\nu B}(\nu, T)$ is the Planck function.

completely different manner than in the case of absorption line distortion. That is to say, the straight line of gas radiation will seem to gradually fill in the spectral form of an ideal black body (Planck's function), until it is completely filled for $\tau \to \infty$ (Figure 11.4(b)). Thus, the radiation of any gas at very high optical thickness values corresponds to the black-body radiation, and the measurements carried out under such conditions will not yield any information on the physicochemical properties of the gas.

11.5.3 The Rayleigh–Jeans approximation

As we have already noted, in the microwave band the Rayleigh–Jeans approximation for spectral black-body radiation (Chapter 6) can be applied, and the brightness temperature notion can be used. Using these approaches for expression (11.53), we obtain the solution of the basic equation (11.51) in terms of brightness temperatures:

$$T_{\mathrm{B}}(\nu) = T_{\mathrm{BS}}(\nu)\exp[-a_{\nu}(\nu)s] + T_0[1 - \exp[-a_{\nu}(\nu)s]], \qquad (11.62)$$

where by T_0 is meant the thermodynamic temperature of a gas layer and by $T_{\mathrm{BS}}(\nu)$ the brightness temperature of external radiation. Note that the introduction of this term for external radiation is rather formal, because the physical nature of radiation from this source can be arbitrary and should not obligatorily have the character of thermal radiation.

As in the case of a gas layer with a small optical path value in terms of thermal intensity, the radiation of a gas layer in the 'brightness temperature – frequency' coordinate system will represent a straight line. However, as the optical path value grows, the shape of the line will be distorted, but in a completely different manner as in the case of intensity – the line will form a kind of small house with a flat top to the roof (Figure 11.4(c)). A representative example of this situation can be, as we shall see below, the radiation of a set of lines of emission of oxygen in the terrestrial atmosphere close to the wavelength of 5 mm.

11.5.4 Two-layer approximation

In the cases where the spatial density of the gas or its composition varies the shape of the line of absorption and emission will essentially differ from the shape of the profile of a homogeneous layer line. And it will also depend on the distribution of a spatial density of quantum oscillators (atoms and molecules) and admixtures causing collisions, as well as on the thermodynamic properties of a system. Total absorption in a medium with a variable density is presented in the form of an integral along the direction of sighting

$$\tau_{\nu}(\nu) = \int_0^L a_{\nu}(\nu, s)\,\mathrm{d}s. \qquad (11.63)$$

Consider now the simplified hypothetical model: the two-layer homogeneous gas ($L = L_1 + L_2$), but with different broadening mechanisms related to the same frequency of central transition ν_{ij}. So, we suppose that in the first layer collisional broadening predominates, and in the second layer the broadening is determined by Doppler thermal scattering. Then the full optical path of a system will be equal to the sum of the optical paths in layers:

$$\tau(\nu) = \tau_1 + \tau_2 = S_{\mathrm{C}} b_{ij\mathrm{C}} L_1 + S_{\mathrm{D}} b_{ij\mathrm{D}} L_2. \qquad (11.64)$$

Depending on the position of observation frequency with respect to the central transition frequency, the contribution of various mechanisms will be different and,

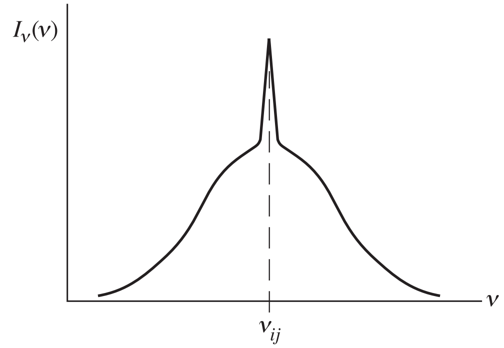

Figure 11.5. Schematic presentation of a total profile for the compound emission line of a non-homogeneous structure.

therefore, the total profile of a line will have a fairly complicated shape. So, for $|\nu - \nu_{ij}| \gg \Delta_D$, i.e. on the far line wings, the collisional mechanism $\tau_1 > \tau_2$ will predominate:

$$\tau \cong \tau_1 = S_C \frac{\Delta_C}{4\pi^2(\nu - \nu_{ij})^2} L_1. \tag{11.65}$$

In the resonance region of a line for $|\nu - \nu_{ij}| \ll \Delta_C$ the Doppler broadening mechanism will predominate, i.e. $\tau_1 > \tau_2$:

$$\tau \cong \tau_2 = S_D \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta_D} \exp\left[-16\pi^2(\nu - \nu_{ij})^2 \frac{\ln 2}{\Delta_D^2}\right] L_2. \tag{11.66}$$

The schematic shape of the total profile of the integral absorption (emission) line of a two-layer system is shown in Figure 11.5. If in the gas medium the additional complicated thermal picture is present, then the total profile shape will be even more complicated. Even in this simplifying example there is the necessity for careful analysis of the shape of the line, both in the resonance region (near the central transition) and in the peripheral region or line wings.

11.6 MICROWAVE RADIATIVE TRANSFER IN THE TERRESTRIAL ATMOSPHERE

Microwave radiative transfer in the free terrestrial atmosphere is determined, first of all, by the molecular oxygen and atmospheric water vapour content, as well as by the altitude distribution of basic meteorological elements (including altitude dependencies of pressure, temperature, humidity and other parameters). The contribution of other gaseous components (such as hydroxyl, ozone, nitrogen oxide) to microwave transfer is essentially lower, so the contribution of minor gaseous components will not be considered in the present book. Certainly, this does not deny at all the importance of their contribution to the total energy balance of the terrestrial atmosphere.

11.6.1 Atmospheric models

A variety of atmospheric models are used to study in detail the microwave radiation of the atmosphere, chosen according to the physical problem addressed. Since in the given formulation we need the qualitative formulation of the problem, we shall make use of the so-called exponential model. In this atmospheric model the altitude profiles of temperature $T(H)$ are described by a linear function, and the pressure and humidity profiles are approximated by exponential functions, that is,

$$\left.\begin{aligned} T(H) &= T_0 - kH, \; H < 11\,\text{km} \\ T(H) &= T_{11}, \qquad H > 11\,\text{km} \end{aligned}\right\}, \tag{11.67}$$

$$p = p_0 \exp(-\alpha_p H), \tag{11.68}$$

$$\rho = \rho_0 \exp(-H/H_V), \tag{11.69}$$

where $k = 6.5°\text{C/km}$ is the altitude gradient of temperature, H_V is the characteristic height of water vapours, ρ is the absolute humidity (g/m^3) that determines the quantity of water vapour (g) contained in 1 m^3 of humid air (g/m^3). The altitude profile of specific humidity, q, that determines the quantity of water vapour (g) contained in 1 m^3 of humid air (g/kg), can be described under normal conditions by the exponential function up to altitudes of the order of 16 km, that is,

$$q(H) = \begin{cases} q_0 \exp(-\alpha_0 H), & 0 \le H \le 16\,\text{km}, \\ q_1, & 16 < H < 75\,\text{km}, \end{cases} \tag{11.70}$$

where $\alpha_0 = 0.48\,\text{km}^{-1}$; $q_1 = 0.461\,97 \times 10^{-3}$.

Under anomalous humidity distributions it can occur that layers arise which contain either greater or lower moisture content as compared to (11.69).

The special atmospheric models take into account both seasonal and latitudinal characteristics and determine the altitude profiles of temperature, air density and humidity for latitudinal belts of the terrestrial globe, as well as for separate regions of dry land and sea water areas under typical seasonal conditions (Kondratyev and Timofeev, 1970; Sakerin and Kabanov, 1997; Zuev and Komarov, 1987; Randel *et al.*, 1996; Trenberth, 1997; Pokrovskaya and Sharkov, 1997; Sharkov, 1998).

11.6.2 Stratified atmosphere radiation

The radiobrightness temperature of thermal radiation of a stratified atmosphere under the local thermodynamic equilibrium conditions can be written, according to (11.52), in the conventional form as

$$T_\text{B}(\nu) = \int_0^\infty \gamma(H) T(H) \exp\left[-\int_0^H \gamma(z)\,\text{d}z\right] \text{d}H, \tag{11.71}$$

where $\gamma(\nu, H) = a_\nu(\nu, H)$ is the spectral absorptivity of all gaseous components of the atmosphere, which depends both on frequency and on the height over the earth's surface. Note that in the given formula the dimension of this quantity is neper/m, and in measurement practice the dimension of dB/m is used (see relations (1.33) and (1.34) of Chapter 1). This relation does not include the contribution from the boundary surface medium.

To make clearer physical aspects of the contribution into radiation of gaseous components, the notion of the mean temperature $T_{\mathrm{AV}}(\nu)$ is usually introduced. This quantity is equal to the isothermal atmosphere temperature with the radiobrightness equivalent to (11.71). Thus, relation (11.71) can be presented in the form:

$$T_{\mathrm{B}}(\nu) = T_{\mathrm{AV}}(\nu)\int_0^\infty \gamma(H)\,\exp\left[-\int_0^H \gamma(z)\,\mathrm{d}z\right]\mathrm{d}H = T_{\mathrm{AV}}(\nu)[1-\exp(-\tau(\nu))], \tag{11.72}$$

where $\tau(\nu)$ is the total absorption of all gaseous components of the atmosphere at the given frequency in the beam propagation direction. With account taken of the vertical profile of temperature distribution in the troposphere, the mean temperature of the atmosphere can be written in the form:

$$T_{\mathrm{AV}}(\nu) = \frac{\displaystyle\int_0^\infty \gamma(H)T(H)\,\exp\left[-\int_0^H \gamma(z)\,\mathrm{d}z\right]\mathrm{d}H}{\displaystyle\int_0 \gamma(H)\,\exp\left[-\int_0^H \gamma(z)\,\mathrm{d}z\right]\mathrm{d}H} = T_0 - \Delta T(\nu), \tag{11.73}$$

where $T_0(0)$ is the temperature near the Earth surface, $\Delta T(\nu) = 10$–$30\,\mathrm{K}$, depending on the state of the atmosphere and absorption intensity.

Since in the free atmosphere for wavelengths greater than 8 mm and for observation angles lower than 80° the total absorption value $\tau \ll 1$, then relation (11.71) is approximated by the linear dependence with respect to the total absorption and cosecant of observation angle θ:

$$T_{\mathrm{B}}(\nu) \cong [T_0 - \Delta T(\nu)]\tau(\nu)\,\mathrm{cosec}\,\theta. \tag{11.74}$$

It can easily be seen from this relation that the emissive characteristics of the atmosphere will be presented in the form of radiation straight lines.

Absorption in the free atmosphere is mainly determined by selective absorptions in oxygen and water vapour. The character of processes responsible for radiation and the line shape essentially depend on the emitting layer height. At altitudes lower than 70 km the average interval between collisions of molecules constitutes only a small part of the lifetime of excited states. This corresponds to fulfilment of local thermodynamic equilibrium conditions and allows collisions to be considered as a factor determining the spectral line shape. At these altitudes the pressure exceeds units of millibars; the broadening of the absorption line of water vapour due to collisions, evaluated by the relation $\Delta\nu(\mathrm{Hz}) \sim 3\times 10^9 p/p_0$, equals units of megahertz (and greater) and considerably exceeds the values of Doppler broadening, which equals fractions of megahertz. Relaxation times, having the order of fractions of a microsecond, under these conditions exceed the values of an interval between collisions estimated by the relation

$$t(s) \sim 3 \times 10^{-10} p/p_0. \tag{11.75}$$

At altitudes exceeding 50 km the radiation equilibrium takes place, and the line shape assumes the character of a mixed Voigt line and then, as the altitude increases, it is conditioned by purely Doppler broadening.

11.6.3 Molecular oxygen

This gas is of undoubted interest for remote investigations, since its abundance in the Earth's atmosphere up to altitudes of the order of 100 km (the so-called homosphere) represents a nearly constant quantity which does not depend on seasonal conditions. In addition, the oxygen absorption bands in the microwave region possess some certain and universal specificity, which makes it possible to use them for studying temperature profiles, both in the surface layer of the atmosphere (at altitudes up to 0.5 km), in the troposphere (at altitudes of 0.5–7 km), and in the stratosphere and lower mesosphere (35–55 km) (Zhevakin and Naumov, 1967; Rosenkranz, 1975; Naumov *et al.*, 1999).

The microwave spectrum of the oxygen molecule O has some specific features. The oxygen molecule does not have any electrical dipole moment, but, owing to the presence of an unpaired electron, it has a considerable magnetic moment. At ground level the structure of terms of an oxygen molecule is triplet one. The microwave spectrum arises from transitions between triplet levels of a fine structure formed by the coupling of a rotational angular momentum (the quantum number N) and electronic spin (the quantum number s). The quantum number of the total angular momentum will be $J = N + s$. The selection rules ($\Delta J = \pm 1, \Delta N = 0$) allow for two types of transition of a magnetic dipole – the transitions arise between the state $J = N$ and the state $J = N \pm 1$ in the form of two series of transition lines of various intensity, grouped in a rather narrow range of the order of 15 GHz near the frequency 60 GHz, and contain a single and prominent line at the frequency of 118.74 GHz (the wavelength of 2.53 mm). The line broadening is determined by the mechanism of collisions of oxygen molecules between each other and with the molecules of nitrogen.

The spectra of absorption in atmospheric oxygen have been first calculated by J. Van-Vleck, then updated by Zhevakin and Naumov (1967) and then considered by Rosenkranz (1975) as applied to microwave sensing.

The coefficient of absorption in atmospheric oxygen $\gamma_0(\nu)$ can be presented as

$$\gamma_0(\nu) = CP\left(\frac{\nu}{T}\right)^2 F(\nu), \tag{11.76}$$

where T is expressed in K, pressure P in millibars, frequency in GHz, and C is 1.434 for $\gamma_0(\nu)$ in dB/km. For the expression of F the first order of approximation of the theory of overlapping lines results in the following expression (Rosenkranz, 1975):

$$F = P\left\{\sum_N \Phi_N[f_N^+(\nu) + f_N^+(-\nu) + f_N^-(\nu) + f_N^-(-\nu)]\right\} + \frac{0.70w_b}{\nu^2 + (Pw_b)^2}, \tag{11.77}$$

where

$$f_N^{\pm} = \frac{w_N(d_N^{\pm})^2 + (\nu - \nu_N^{\pm})y_N^{\pm}}{(\nu - \nu_N^{\pm})^2 + (Pw_N)^2} \tag{11.78}$$

and d_k is the amplitude of the kth line, ν_k are their frequencies, Φ_k is the population of a primary level bound with this transition, $y_N^{\pm}$ is the interference factor (mbar); the resonance half-width w_N (GHz/mbar) equals

$$w_N = 1.16 \times 10^{-3}\left(\frac{300}{T}\right)^{0.85} \tag{11.79}$$

and the half-width of a non-resonant component w_b (GHz/mbar) is equal to

$$w_b = 0.48 \times 10^{-3}\left(\frac{300}{T}\right)^{0.89}. \tag{11.80}$$

The detailed values of diagonal matrix elements, populations of levels, interference factors can be obtained from the paper by Rosenkranz (1975).

For a single and very strong line at the wavelength of 2.53 mm the expression for $\gamma_0(\nu)$ can be presented in the simpler form (Kotlyar and Novak, 1987):

$$\gamma(H,\nu) = 1.2305\frac{P(H)\nu^2}{[T(H)]^3}\exp\left\{-\frac{4.14}{T(H)}\right\}\frac{4\nu^2\,\Delta\nu(H)}{(\nu_0^2 - \nu^2)^2 + 4\mu^2[\Delta\nu(H)]^2}, \tag{11.81}$$

where $\nu_0 = 118.750\,343$ GHz, $P(H)$ and $T(H)$ are pressure and temperature profiles, $\Delta\nu$ is the half-width of this line:

$$\Delta\nu(H) = [(\Delta\nu_C(H))^2 + (\Delta\nu_D(H))^2]^{1/2}. \tag{11.82}$$

Here $\Delta\nu_C$ and $\Delta\nu_D$ correspond to impact and Doppler mechanisms:

$$\Delta\nu_D = 7.52 \times 10^{-6}\sqrt{T(H)};\ \Delta\nu_C(H) = \alpha P(H)(0.21 + 0.78\beta)\left[\frac{300}{T(H)}\right]^n, \tag{11.83}$$

where $\beta = 0.75$, $n = 0.9$, $\alpha = 2.131 \times 10^{-3}$ GHz/mbar.

Of great scientific and practical interest is the oxygen absorption band centred with respect to the wavelength of 5 mm and composed of 49 fairly intensive spin-rotational lines with the azimuthal quantum number $K < 49$ (Staelin, 1969; Rosenkranz, 1975; Troitsky *et al.*, 1993; Naumov *et al.*, 1999). The widths of these spectral lines near the earth's surface are $\sim$1 GHz, whereas the mean distance between the centres of lines is $\sim$0.5 GHz. The consequence of this circumstance is the overlapping of spectral lines in low layers of the atmosphere. It is these overlapped lines which form the absorption band considered. The oxygen lines are distinguished at altitudes $h > 20$ km, where the atmospheric pressure decreases down to values of $\sim$40 mbar. The majority of lines (about 20) are concentrated in the range of frequencies of 55–65 GHz, and 14–15 spectral lines fall on each of the

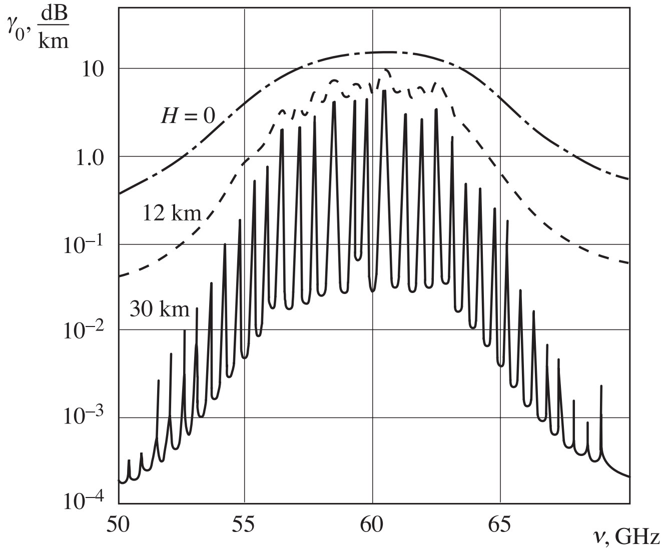

Figure 11.6. Frequency characteristics of the one-way attenuation in terrestrial oxygen in the 5-millimetre range at various altitudes (H, km) above the ground.

ranges 45–55 GHz and 65–75 GHz. The optical thickness of the atmosphere increases in the long-wavelength section of the band – from values of ~0.3 at the frequency of 50 GHz up to values of ~3 at the frequency of 55 GHz. At the centre of the 5-mm band the values essentially exceed unity: $\tau \approx 10$–45. At the short-wavelength wing of the band the optical thickness decreases from the indicated values and becomes of the order of 0.3. The qualitative picture of the absorption spectrum in atmospheric oxygen for various altitudes over the earth's surface is demonstrated in Figure 11.6. It can easily be seen that the electromagnetic signal transmission at wavelengths close to 5 mm at the earth's surface level is virtually impossible, since even at the distance of 10 km the attenuation of a signal can exceed 10^{20} times. Note that all these events take place under conditions of an optically transparent atmosphere.

The monotonous character of optical thickness variation on the band wings is violated by its increasing at the centres of some lines located here. The character of spectral dependence of the optical thickness in the 5-mm band determines also the spectral dependence of radiobrightness temperature in this band at zenithal observation from the earth's surface (see relation (11.71) and Figure 11.7). At the centre of the 5-mm band of the contribution of separate lines to radiobrightness temperature of the atmosphere is screened by their high absorption in lower layers of the atmosphere, and distinguishing resonances in radio-emission are revealed only on wings of the 5-mm band. It can easily be seen from relation (11.71), that the maximum value of a spectral curve will just be equal to the value of the weighted mean temperature of the atmosphere (which equals 285 K in the given case).

The altitude dependence of the oxygen absorption coefficient has a fairly complicated character, strictly speaking (see relations (11.76), (11.81) and (11.83)).

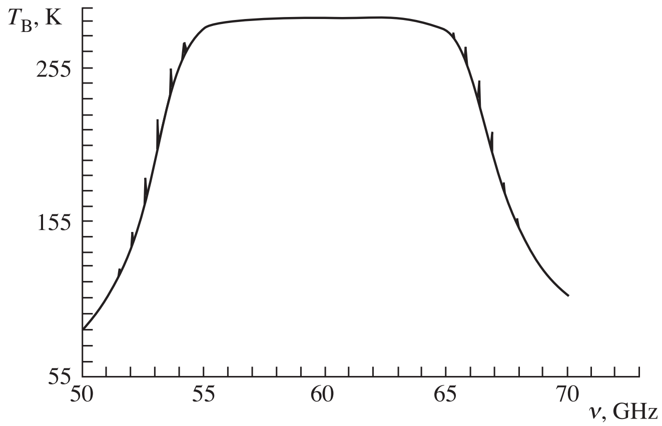

Figure 11.7. Frequency characteristics of the brightness temperature with zenithal observation in the 5-millimetre range at sea level condition.

However, observational experiments have shown that exponential (or linearly exponential) dependence can be quite satisfactory for remote sensing purposes. It has the form:

$$\gamma_0(\nu, H) = \gamma_0(\nu, O)\, \exp\left(-\frac{H}{H_0}\right), \tag{11.84}$$

where quantity H_0 characterizes the effective height of the oxygen layer that absorbs microwave radiation. This quantity strongly depends on the region where the sensing frequency is selected. So, for regions lying outside the resonance frequencies, quantity H_0 equals about 5.1–5.3 km. At the same time, near the resonance transition points the effective path length can increase 2–5 times owing to absorption in the high layers of the atmosphere and equals, for example, $H_0 = 21$ km for $\nu = 63$ GHz.

According to (11.84), the total absorption of oxygen at zenithal observation will be

$$\tau_0(\nu) = \int_0^\infty \gamma_0(\nu, H)\, \mathrm{d}H \cong \gamma_0(\nu, O) H_0. \tag{11.85}$$

When the outgoing radiation flux is observed in the frequency range where the molecular oxygen transition lines (the 5-mm band and the 2.53-mm line) are situated, the shape of the radiobrightness temperature spectrum of the atmosphere depends on the vertical temperature distribution and on the altitude profile of the absorption coefficient (11.70). The stability of the altitude distribution of oxygen and the features of absorption lines allow one to use the information on the shape of the outgoing radiation spectrum across a wide range of microwave remote sensing problems. They include the detailed investigations of temperature profiles in the boundary layer of the atmosphere (Troitsky *et al.*, 1993; Naumov *et al.*, 1999), in the troposphere (Rosenkranz *et al.*, 1972; Kapitza, 1983; Kotlyar and Novak, 1987; Kotlyar and Khapin, 1990; Gasiewski and Johnson, 1993), as well as in the stratosphere and mesosphere (Kondratyev, 1997; Naumov *et al.*, 1999).

11.6.4 Atmospheric water vapour

The remote investigation of the spatial distribution of water vapour on various spatial and temporal scales is of principal significance in studying the thermal and hydrodynamic state of the troposphere and stratosphere (Kondratyev and Timofeev, 1970; Mitnik, 1972; Kramer, 1996; ESA, 1996b; English *et al.*, 1999; Hartmann *et al.*, 1996; Holton *et al.*, 1995; WMO, 1990a,b; Randel *et al.*, 1996). This is, first of all, due to the huge stores of heat hidden in spatial fields of water vapour. Note here that in the optical band water vapour represents a transparent medium and cannot be recorded by optical instruments directly.

Unlike the oxygen molecules, the physical nature of absorption spectra of water vapour is caused by completely different factors, namely, by the volume structure of a vapour molecule. So, the rotational spectra of molecules of a volume structure of symmetrical and asymmetrical top type are directly related either to the molecule structure symmetry or, on the contrary, with its asymmetry. The rotational spectrum of molecules of symmetrical top type can be presented (similarly to the rotational spectrum of linear molecules) in the form of a set of equispaced lines (the so-called equidistant spectrum). The energy levels of molecules having asymmetrical top structure (as, for example, the molecules of water vapour or triatomic oxygen (ozone)) do not have any simple analytical presentation. Even in the presence of slight asymmetry the absorption spectrum of a molecule drastically differs from a set of equispaced lines, thus forming a sharply non-equidistant spectrum. The detailed calculation of energy transitions, beginning with the long-wavelength extremity, gives the following values of wavelengths of most intensive microwave lines in the band of $\lambda > 300$ micrometres: 1.35 cm; 0.164; 0.093; 0.079; 0.054; 0.04 and 0.034.

The calculations of microwave absorption spectra of monomeric molecules of water vapour in the terrestrial atmosphere, carried out by Van-Fleck, have been essentially updated later by S. A. Zhevakin and L. P. Naumov. They have described the absorption line shape by solving the kinetic equation and by taking into account the contribution of absorption from ‘wings’ over all rotational transitions of the microwave band (Zhevakin and Naumov, 1967). The features of microwave lines are under detailed study at present (Bhattacharya *et al.*, 1983; Bauer *et al.*, 1986).

The absorption coefficient of water vapour $\gamma_{\mathrm{WV}}(\nu, H)$ for the first and most informative line of 1.35 cm can be presented in the following semi-empirical form:

$$\gamma_{\mathrm{WV}}(\nu, H) = \gamma_{\mathrm{WVR}}(\nu, H) + \gamma_{\mathrm{WVNR}}(\nu, H), \tag{11.86}$$

where the ‘resonance’ term $\gamma_{\mathrm{WVR}}(\nu, H)$ is described by the relation

$$\begin{aligned}\gamma_{\mathrm{WVR}}(\nu, H) = {} & \frac{343\nu^2\,\Delta\nu\, a(H)}{[T(H)]^{5/2}}\exp\left(-\frac{644}{T(H)}\right) \\ & \times\left[\frac{1}{(\nu-\nu_0)^2+[\Delta\nu(H)]^2}+\frac{1}{(\nu+\nu_0)^2+[\Delta\nu(H)]^2}\right].\end{aligned} \tag{11.87}$$

Here $\nu_0 = 22.235\,\text{GHz}$. The 'non-resonance' term is

$$\gamma_{\text{WVNR}}(\nu, H) = 2.55 \times 10^{-3} \frac{\nu^2 a(H)\,\Delta\nu(H)}{[T(H)]^{3/2}}. \tag{11.88}$$

In this case the line half-width is determined as

$$\Delta\nu(H) = \frac{0.126P(H)\left[1 + 0.11\dfrac{a(H)T(H)}{P(H)}\right]}{[T(H)]^{0.626}}, \tag{11.89}$$

where $P(H)$ there is the pressure profile.

The width of spectral lines at altitudes of up to 50 km is determined by collisions of water vapour molecules with nitrogen molecules.

The altitude dependence of the absorption coefficient is determined by the altitude distribution of meteorological elements. Because of the high sensitivity of water vapour content to thermohydrodynamical processes in the atmosphere (and, especially, in the troposphere), the altitude dependence of water vapour can be very complicated and represents, in itself, a subject of special investigations (Rosenkranz *et al.*, 1982; Zuev and Komarov, 1987; Sakerin and Kabanov, 1997; Pokrovskaya and Sharkov, 1997). Since the altitude dependencies of humidity and pressure at the ground state have predominantly exponential character, the exponential (or linearly exponential) altitude dependence of absorption can be assumed to be quite satisfactory for sensing purposes. It has the following form:

$$\gamma_{\text{WV}}(\nu, H) = \gamma_{\text{WV}}(\nu, O)\,\exp\left[-\frac{H}{H_{\text{W}}}\right], \tag{11.90}$$

where H_{W} characterizes the effective height of a water vapour layer.

It follows from this relation, that the total absorption of the atmosphere will be

$$\tau_{\text{WV}}(\nu) = \int_0^\infty \gamma_{\text{WV}}(\nu, H)\,\mathrm{d}H \cong \gamma_{\text{WV}}(\nu, O)H_{\text{W}}. \tag{11.91}$$

For the non-resonance region the effective height of a layer equals 2.1 km. For the resonance region (near the absorption maximum) the effective height two to three times exceeds the HW value in the non-resonance region. Thus, the variation of the total absorption and, accordingly, the spectral variations of brightness temperature are sensitive to variations of water vapour distribution at low values of pressure, i.e. in the region of fairly high altitudes. Figure 11.8 presents the spectrum of brightness temperature at zenithal observation of the atmosphere in the 1.35-cm absorption line under the condition of exponential profile of humidity and for a profile with anomalous distribution in the high-altitude layers of the atmosphere. This indicates that in sufficiently selective microwave observations the anomalous distributions of water vapour in the atmosphere can be estimated by means of radiospectrometers.

Of special interest are microwave investigations of the water vapour content in the stratosphere and mesosphere, which are being carried out at present. Water

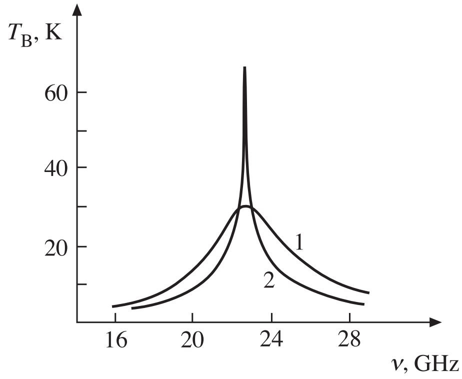

Figure 11.8. The effect of vertical humidity profile on water vapour emission line shape at 22.2 GHz frequency: (1) for exponential profile; (2) for the profile with irregular distribution.

vapour (along with ozone) plays an important part in physicochemical processes in the middle atmosphere (Rosenlof *et al.*, 1997; Holton *et al.*, 1995). Since the amount of water vapour in the middle atmosphere is very low, the investigations are carried out using the strong absorption lines of 183 and 325 GHz. And these investigations are carried out using the special limb observation technique in order to maximally increase the optical path in the sighting direction (Weinstock *et al.*, 1995; Abbas *et al.*, 1996; Hartmann *et al.*, 1996; Bevilacqua *et al.*, 1996).

11.6.5 Absorption of microwaves in the terrestrial atmosphere

Let us consider the general character of spectral absorption in the terrestrial atmosphere, taking into account two basic gases and making allowance for disperse media (primarily, rain precipitation). As we have already noted, from the viewpoint of electromagnetic interactions, the gaseous and disperse media of the terrestrial atmosphere are independent processes. Therefore, their energy contributions (the absorption of electromagnetic waves) can be summed up. It is just this basis on which complex semi-empirical models are usually constructed for calculating the characteristics of electromagnetic wave propagation in the atmosphere with different meteorological states. So, in particular, H. J. Liebe (1989) constructed the atmospheric millimetre-wavelength propagation model, which is specially intended for practical calculations in observational remote sensing problems.

The millimetre-wavelength absorption spectrum of the terrestrial atmosphere with allowance for two basic gases (water vapour and oxygen) and in the presence of rain precipitation of various intensities is shown in Figure 11.9. Under clear atmosphere conditions, except for a fairly weak line of water vapour absorption at the frequency of 22.2 GHz, four basic absorption bands dominate in the spectrum, namely: (a) a complex of rotational lines of oxygen at the frequency of 60 GHz; (b) a single strong oxygen absorption line at the frequency of 118 GHz; (c) two strong water vapour absorption lines at the frequencies of 183 and 325 GHz. Along with the

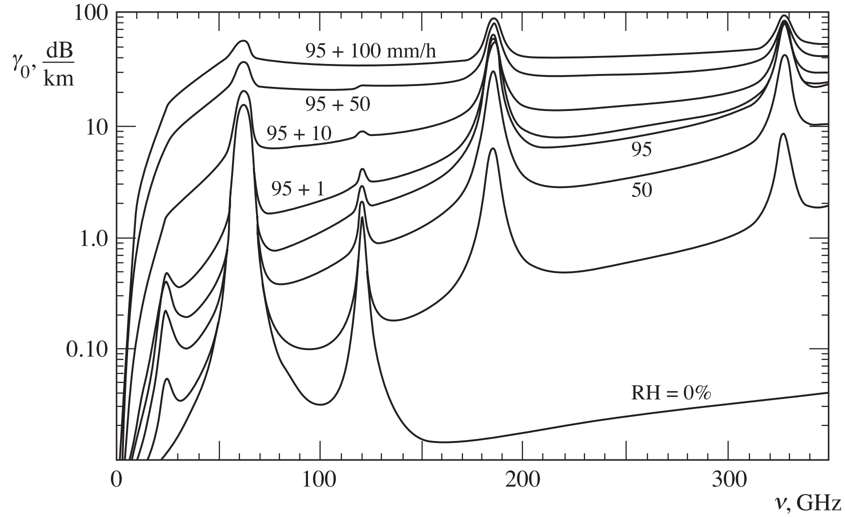

Figure 11.9. One-way attenuation in the terrestrial atmosphere over the frequency range from 0 to 350 GHz for four rain cases ($R = 1, 10, 50, 100$mm/h) added to a sea level condition (P, T, RH = 95%). Also shown are dry (RH = 0%) and moist (RH = 10%, 50%). RH is relative humidity. RH magnitudes 10, 50, 95 and 100% correspond to 2, 10, 17 and 20 g/m^3 for absolute humidity (Liebe, 1989).

strong absorption lines mentioned, there exist some very weak absorption lines in the oxygen and water vapour spectra (Liebe, 1989) which cannot be represented in the scale of Figure 11.9. By virtue of their 'weakness', they are not usually utilized in remote sensing applications. The contribution of other atmospheric gases (such as ozone) to the total absorption is also rather weak. The spectral windows, where the local minimum of atmospheric absorption is achieved (the transparency windows), are centred on frequencies of 36, 90–100, 150 and 210–300 GHz. The values of absorption in transparency windows are mainly determined by the presence of water vapour and systematically increase as the frequency grows. It is important to note that, whereas in oxygen absorption bands (of 60 and 118 GHz) the presence of water vapour has virtually no effect, in all other frequency bands the influence of water vapour dominates.

The presence of disperse structures (such as fogs, precipitation of various types) in the atmosphere drastically changes the spectral picture of absorption in the millimetre wavelength band. So, a quite weak rain precipitation with intensity of 10 mm/hour virtually completely 'blocks' not only transparency windows but even oxygen absorption bands themselves (Figure 11.9). Such a high sensitivity of short-centimetre and millimetre wavelength bands to the state of gaseous and disperse media of the atmosphere made it possible to produce, even at the earliest stage of development of microwave remote sensing methods (in the 1960s), effectively operating radiothermal ground-, space- and aircraft-based complexes (Haroules and Brown, 1968; Rabinovich *et al.*, 1968, 1970; Basharinov *et al.*, 1968, 1969, 1971, 1974; Staelin, 1969, 1981; Akvilonova *et al.*, 1971, 1973; Kondratyev *et al.*, 1975; Amirkhanyn *et al.*, 1975; Kakar and Lambrigtsen, 1984). Multifrequency radiothermal techniques for investigating gaseous components and disperse structures in the terrestrial atmosphere and appropriate microwave instrumentation are being actively developed now as well (English, 1995; Bruzzi, 1995; Ferraro *et al.*, 1996; Weinstock *et al.*, 1995; Wang *et al.*, 1997a,b,c; Kondratyev, 1997; Wang *et al.*, 1998a,b; English, 1999; Matzler, 2000; Konig *et al.*, 2000; Bizzari and Spera, 2000; Bizzari *et al.*, 2000; IPCC, 2001).