

# Infrared radiation transfer in molecular gases

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Physical models of the theory of infrared radiation transfer in molecular gases are reviewed and their usefulness in the solution of particular problems is demonstrated. Theoretical predictions are compared with experimental data. Particular attention is devoted to analytic methods capable of providing (1) clear descriptions of the physics of the phenomenon, (2) a better understanding of the dependence of the final result on the parameters of the problem, and (3) a reasonably reliable final result that is valid over a broad range of variation of the parameters of the gaseous medium. The radiation transfer process is examined both for equilibrium and nonequilibrium gaseous media. The final section deals with the analysis of certain processes occurring in the Earth's atmosphere.

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## 1. INTRODUCTION

The particular feature of infrared radiation transfer in a molecular gas is that it involves the participation of a large number of vibration-rotation states of the molecule. The absorption and emission spectrum consists of a set of individual lines corresponding to particular vibration-rotation transitions. Moreover, the mutual disposition and the intensities of the individual lines are related to the structure of the gas molecules. These lines are broadened and suffer partial overlap in the case of a gas. The nature of this broadening and the degree of overlap of individual lines depend on the physical conditions obtaining in the gas, but mainly on its composition, density, and temperature. This is why the absorption coefficient of a molecular gas is usually a highly oscillating function of the wavelength of the infrared radiation, and this, in fact, determines the nature of the radiation transfer process in such media.

The problem of radiative heat transfer in a molecular gas arises in connection with attempts to determine the optimum operation of high-temperature equipment and in the study of processes occurring in the Earth's atmosphere and in the atmospheres of other planets. Traditional approaches to this question have evolved in a number of different directions. One of them relies on modern computer technology and very complete data on the absorption spectra of the molecules forming the gas.

For example, modern programs developed for the emission spectrum of carbon dioxide contain data on the position and intensity of thousands of lines associated with particular vibration-rotation transitions. This approach yields the most accurate results in simple physical situations, and the precision is determined by the precision with which the parameters introduced into the program are known.

For all their advantages, however, computerized methods cannot be used to elucidate the dependence of the results on the leading parameters of the problem or to estimate the precision of these results. Moreover, the results obtained in this way are relatively expensive, and the time required to obtain them is quite long. The other traditional method, namely, the semiempirical approach, is free from these disadvantages. It is based on simple models of absorption bands of molecular components, which include basic data on the distribution, intensity, and shape of individual lines, and relies on experimental data. In the final analysis, the semiempirical method provides us with simple working formulas capable of describing the transfer of infrared radiation in a certain (relatively narrow) range of parameter values, so that the final results can be obtained rapidly and reliably. This approach has deservedly become very popular in the solution of radiation transfer problems for the real atmosphere,<sup>1-4</sup> when the atmospheric parameter values lie in a narrow range and ex-

perimental data are available.

Models of molecular bands on which the semiempirical method is based originate in the work of Elsasser and Goody, who were concerned with regular and random models. The application of analytic methods to these models, in turn, leads to rapid solutions of particular problems in the theory of infrared radiation transfer in molecular gases. However, the precision of analytic methods is lower than that of the semiempirical approach within the range of applicability of the latter. It is also lower than the precision of the numerical calculations if the physical parameters fed into the computer are known with sufficient precision. However, analytic methods result in a better understanding of the dependence of the final result on the parameters of the problem and provide a clear physical description as well as a relatively reliable result over a broad range of parameter values of the gaseous medium. This is particularly important in connection with the emergence of an increasing number of problems in which the range of variation of the physical parameters of the medium is quite large. Examples of this include the evolution of planetary atmospheres in the past, the determination of their composition in the near future, and the question of the effects of appreciable changes in the amount of different molecular components of the Earth's atmosphere on its heat balance and on global climate. In addition, there are the problems of infrared radiation transfer under completely new physical conditions. For example, in connection with the study of the upper atmospheres of planets, there is considerable interest in the transfer of infrared radiation in a molecular gas in the absence of local thermodynamic equilibrium.

The aim of this review is to survey modern analytic methods for the investigation of radiative transfer in molecular gases. These methods are based on asymptotic techniques which, in turn, rely on the fact that the number of lines in the absorption and emission spectra of the molecules is large, and on certain other relationships that lead to the emergence of a small parameter in the theory.

## 2. CHARACTERISTICS OF RADIATION TRANSFER IN A GASEOUS MEDIUM

### A. Basic parameters of the radiation transfer process in a gas

We must first introduce the various quantities that determine the radiation transfer process in a gaseous medium.<sup>1-11</sup> We shall begin by assuming that the propagation of radiation has no effect on the density of excited and unexcited particles. This occurs, in particular, when the rate of radiative decay of excited particles is much smaller than the rate of quenching of excitation by collisions (a more precise definition of this will be given below). We shall use the following terminology. The energy carried by radiation of frequency  $\omega$  in a given direction per unit area per unit time will be called the spectral power flux density. The same quantity averaged over all directions of propagation will be referred to simply as the spectral power density. If a given layer of gas transmits radiation with spec-

tral power flux density  $I_\omega$ , the equation satisfied by  $I_\omega$  in the interior of the gas layer is

$$\frac{dI_\omega}{dx} = -k_\omega I_\omega, \quad (2.1)$$

where  $k_\omega$  is the absorption coefficient of the gas at frequency  $\omega$ , and  $x$  is the distance measured in the direction of propagation. If  $x=0$  and  $x=L$  characterize the boundaries of the gas layer, the spectral power flux density leaving the layer is given by

$$I_\omega(L) = I_\omega(0) \exp\left(-\int_0^L k_\omega(x) dx\right). \quad (2.2)$$

The quantity

$$u(\omega) = \int_0^L k_\omega(x) dx$$

is called the optical thickness of the layer and is an important parameter governing the transmission of radiation by the layer. When  $u(\omega) \gg 1$ , the mean free path of a photon of a given frequency is small in comparison with the linear dimensions of the layer. The opposite relationship obtains when  $u(\omega) \ll 1$ .

The absorption function is a useful quantity and is defined as follows. The absorption function for a frequency interval  $\Delta\omega$  is given by

$$A = \frac{1}{\Delta\omega} \int_{\omega_0 - \frac{\Delta\omega}{2}}^{\omega_0 + \frac{\Delta\omega}{2}} [1 - \exp(-u(\omega))] d\omega \quad (2.3)$$

and is the average probability that the gas layer will absorb radiation of any frequency within the range  $\Delta\omega$ .

We must now determine the resultant spectral power flux density leaving a planar layer of gas at constant temperature, whose parameters are functions of only one variable,  $x$ , measured at right-angles to its boundary. The equation for the spectral power flux density propagating at an angle  $\theta$  to the layer boundary, which is usually referred to as the transfer equation, is

$$\frac{dI_\omega}{dx} = -\frac{k_\omega}{\cos\theta} (I_\omega(\theta, x) - 2e_\omega). \quad (2.4)$$

The solution of this equation, subject to the boundary condition  $I_\omega(\theta, 0) = 0$  is

$$I_\omega(\theta, L) = 2e_\omega [1 - \exp\left(-\frac{u(\omega)}{\cos\theta}\right)].$$

Since the resultant power flux density is perpendicular to the layer boundary, we can substitute  $\cos\theta = 1/t$  and find that its spectral density is

$$J_\omega(L) = \int_0^1 I_\omega(\theta, L) \cos\theta d\cos\theta = 2e_\omega \int_1^\infty t^{-3} [1 - \exp(-u(\omega)t)] dt. \quad (2.5)$$

If the optical thickness  $u(\omega)$  is large, then, under the conditions of thermodynamic equilibrium,  $J_\omega(L) = e_\omega$  and is equal to the spectral density near a perfect black body of given temperature. Hence, we have

$$e_\omega(T) = \frac{h\omega^3}{4\pi^2c^2} \left[ \exp\left(\frac{h\omega}{T}\right) - 1 \right]^{-1}, \quad (2.6)$$

where  $T$  is equal to the temperature of the gas.

In the case of a molecular gas, the set of vibration-rotation transitions between two vibrational states will be referred to as a vibrational transition, and the corresponding set of spectral lines will be referred to as

the molecular band corresponding to the given vibrational transition. Usually, the band of frequencies within which the molecular gas radiates and absorbs appreciably though the particular vibrational transition is small in comparison with the frequency  $\omega_0$  at the center of the band. Moreover, at temperatures greater than, or of the order of, room temperature, the width of this region is much less than  $T/\hbar$ . It is convenient to introduce the function

$$W(t) = \int_{-\infty}^{+\infty} [1 - \exp(-t\nu(\omega))] d(\omega - \omega_0), \quad (2.7)$$

which, for  $t=1$ , is called the equivalent width of the molecular band. The total power flux density is then given by

$$J = \int J_\omega d\omega = 2e_0(T) \int_0^\infty W(t) t^{-3} dt = e_0(T) \bar{W}, \quad (2.8)$$

where  $e_0 \equiv e_{\omega_0}$ . The power flux density emitted by the gas at angle  $\theta$  to its boundary can also be expressed in terms of the equivalent width of the band:

$$I(\theta) = 2e_\omega(T) W\left(\frac{1}{\cos\theta}\right). \quad (2.9)$$

The equivalent width of a molecular band is the effective width of the range of frequencies in which the gas radiates as a perfect black body. It is readily seen that it is directly related to the absorption function defined by (2.3). If the intensity of the spectral lines is a relatively slow function of frequency, then

$$W = \int_{-\infty}^{+\infty} A(\omega) d(\omega - \omega_0), \quad (2.10)$$

where  $W \equiv W(1)$  and the absorption function  $A$  is defined on a frequency interval containing a large number of lines with very similar intensities. It is clear from (2.8) and (2.9) that the distribution of the integrated parameters of molecular radiation can be readily determined if we know the equivalent width of a molecular band. When we examine the various methods of the theory of infrared radiation transfer, we shall therefore frequently reduce the final result to the evaluation of the equivalent width of the band, which directly determines the power flux density from a plane layer of gas, emitted at right-angles to its surface. This enables us, on the one hand, to avoid excessive mathematical manipulation and, on the other hand, to devote more attention to the dependence of the integrated parameters of molecular radiation on the intensity, shape, and relative disposition of the individual spectral lines. If the gas layer is temperature-inhomogeneous, and if it departs from thermodynamic equilibrium in its distribution over the vibrational states of the molecules, both the integrated parameters of the molecular radiation and the equivalent width of the band are determined by the temperature distribution within the gas and the rates of collisional and radiative quenching of the vibrational excitation of the molecules. These two cases will be examined in detail in Sec. 4.

## B. Structure of vibration-rotation spectra of molecules

The integrated parameters of infrared radiation propagating in a gas are largely determined by the struc-

ture of the vibration-rotation spectrum of the gas molecules. In the case of thermodynamic equilibrium, the structure of the spectrum, i.e., the relative disposition of the lines and the distribution of line intensities over the spectrum, are determined by the symmetry of the radiating molecules. We begin by considering the structure of an individual vibration-rotation band, i.e. a band corresponding to transitions between two vibrational states (Fig. 1).

The rotational level energy of a linear molecule is determined by a single quantum number, namely, the angular momentum  $j$ , and is given by

$$E_j = B j(j+1), \quad (2.11)$$

where  $B = \hbar^2/2I$  is the rotational constant of the molecule and  $I$  is its moment of inertia. In the dipole approximation, radiative transitions are allowed between states whose angular momenta differ by not more than unity.<sup>12-14</sup> Hence, we find that the rotation-vibration transition frequencies, i.e., the frequencies corresponding to the centers of the spectral lines, are given by

$$\left. \begin{aligned} \omega_0 - \frac{2Bj}{\hbar}, & \quad j' = j-1, & \text{P-branch,} \\ \omega_0, & \quad j' = j, & \text{Q-branch,} \\ \omega_0 + \frac{2B(j+1)}{\hbar}, & \quad j' = j+1, & \text{R-branch;} \end{aligned} \right\} \quad (2.12)$$

where  $j, j'$  are the angular momentum quantum numbers of the molecule in its lower and upper states, respectively, and  $\hbar\omega_0$  is the energy of the vibrational transition. Lines in the *P* and *R* branches are equidistant and separated by  $2B/\hbar$ . The line intensity falls slowly with distance from the band center. The dependence of intensity on the rotational quantum number, i.e., on the frequency of the emitted radiation, is determined by the Boltzmann distribution over the vibrational states:

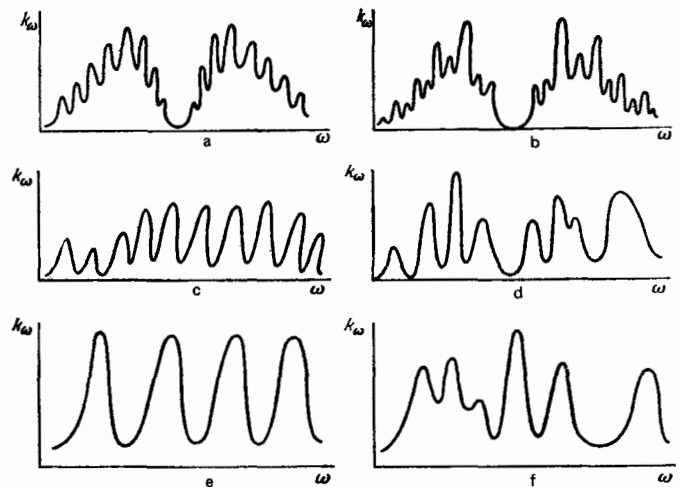


FIG. 1. Absorption coefficient as a function of frequency in the case of molecular vibration-rotation spectra:  $\omega$ —frequency,  $k_\omega$ —gas absorption coefficient. (a) Spectrum of linear molecules in the absence of intensity alternation. (b) Spectrum of linear molecules in the presence of intensity alternation. (c) Spectrum of molecules of a spherical top type (R branch). (d) Spectrum of molecules of an asymmetric top type. (e) Elsasser regular model. (f) Goody random model.

$$f(j) = \frac{B}{T} (2j+1) \exp \left[ -\frac{Bj(j+1)}{T} \right], \quad (2.13)$$

where  $T$  is the temperature. It is assumed that  $B \ll T$ .

The equidistant distribution of lines in the spectra of linear molecules is violated by the dependence of the rotational constant on the vibrational quantum number. The rotational constant, in fact, decreases with increasing energy of vibrational excitation of the molecule.<sup>12</sup> This ensures that the line separation in the  $P$  branch increases, whereas that in the  $R$  branch decreases, by the amount  $\Delta B j / \hbar$  with increasing distance from the band center ( $\Delta B$  is the difference between the rotational constants in the lower and upper vibrational states, respectively). Thus, the separation between the center of a given line in the  $Q$  branch and the band center increases with increasing  $j$  in accordance with the quadratic law  $\omega_0 - \omega_{jj} = (\Delta B / \hbar) j(j+1)$ . The ratio of the characteristic separation between neighboring  $Q$ -branch lines to their width is determined by  $(\Delta B / \gamma) \sqrt{T/B}$ , where  $\gamma$  is the width of a spectral line. The value of the difference  $\Delta B$  between rotational constants is smaller by two or three orders than the rotational constant  $B$  itself. When the gas density exceeds about  $10^{18} \text{ cm}^{-3}$ , it is found that  $(\Delta B / \gamma) \sqrt{T/B} \ll 1$ , and the  $Q$ -branch lines merge together.

It is important to note that the  $Q$ -branch appears as a result of vibrational transitions only when the component of the electron angular momentum along the axis of the molecule or the vibrational angular momentum is nonzero in the initial or final states. Unless this is so, the symmetry of the rotational wave functions of the two states participating in the transition is the same, the associated dipole moment is zero, and there is no  $Q$ -branch. The other interesting feature of the vibration-rotation spectra of molecules is the alternation of intensity.<sup>12-14</sup> This phenomenon occurs in molecules incorporating nuclei of the same isotope. The rotational levels of the molecules then have a definite symmetry with respect to the interchange of such nuclei, and their population is determined by the total nuclear spin. The formula given by (2.13) is then modified by the inclusion of the statistical weights of rotational levels, which represent the influence of nuclear spin. Since radiative transitions between molecular states with different symmetry with respect to the interchange of nuclei are forbidden, the intensities of neighboring spectral lines corresponding to transitions between symmetric and antisymmetric states are then appreciably different. The ratio of their intensities is  $(i+1)/i$  when the nuclear spin  $i$  is an integer, and  $i/(i+1)$  when it is a half-integer. This effect ensures that molecules containing identical nuclei with zero spin have some of the rotational states "removed." For example, in the case of the  $\text{CO}_2$  molecule, only rotational states with even  $j$  are populated in the ground vibrational state, whereas only rotational levels with odd  $j$  are populated in the case of excitation of an antisymmetric vibration. This ensures that the intensities of neighboring lines in the vibration-rotation spectrum of  $\text{CO}_2$  are practically the same, and the separation between the lines is  $4B/\hbar$ .

The rotational levels of a molecule in the form of a

spherical top are, just as for a linear molecule, characterized by the rotational angular momentum  $j$ , and the energies are again given by (2.11). The vibration-rotation spectra of such molecules have, therefore, equidistant lines with line separation  $2B/\hbar$ . The degree of degeneracy of the rotational levels is  $g(2j+1)^2$ , where  $g$  is a factor representing the influence of nuclear spin. For small values of  $j$ , this factor depends on  $j$ . When  $B \ll T$ , the distribution of the molecules over the rotational levels ( $j \gg 1$ ) in the case of spherical top molecules is

$$f(j) = \frac{1}{\sqrt{\pi}} \left( \frac{B}{T} \right)^{3/2} (2j+1)^2 \exp \left[ -\frac{Bj(j+1)}{T} \right]. \quad (2.14)$$

Moreover,  $\int_0^\infty f(j) dj = 1$  and, since  $B \ll T$ , the maximum of the distribution function corresponds to angular momenta  $j \sim \sqrt{T/B} \gg 1$ .

Since both the linear and the spherical-top molecules have relatively simple spectra that are easily interpreted, we shall use these spectra to demonstrate the scope of the theory of radiation transfer. The spectra of molecules in the form of symmetric and asymmetric tops are more complicated.<sup>12</sup> However, the basic parameters of the spectra can even then be estimated. Thus, suppose that the characteristic value of the rotational constants of such molecules is  $\sim B$ . In the case of the asymmetric top, there are three nondegenerate rotational degrees of freedom. The number of strong spectral lines corresponding to each of them is  $\sim \sqrt{T/B}$ , more or less as in the case of linear and spherical top molecules. The total number of strong lines in the spectrum is, therefore,  $\sim (T/B)^{3/2}$ , and the average separation between neighboring lines is  $\sim B^2/\hbar T$ . Similarly, one can readily show that, in the case of the symmetric top, the number of strong lines is  $\sim T/B$  and the average separation between them is  $\sim (B/\hbar)(B/T)^{1/2}$ .

### C. Intensity and shape of spectral lines due to vibration-rotation transitions in molecules

The quantitative characteristics of radiation transfer in gases are largely determined by the intensities and shapes of spectral lines. In this section, we shall briefly summarize our information on the intensities and shapes of lines associated with vibration-rotation transitions in molecules. The absorption coefficient of a molecular gas due to radiative transitions between rotational sublevels of two vibrational states of a molecule is given by

$$k_\omega = \sum_{if} S_{if} a(\omega_{if} - \omega), \quad (2.15)$$

where  $i, f$  represent the upper and lower vibrational states involved in the transition and  $\hbar\omega_{if}$  is the transition energy. The function  $a(\omega_{if} - \omega)$  characterizes the frequency distribution of photons emitted as a result of the transition, i.e.,  $a(\omega_{if} - \omega)d\omega$  is the probability that the frequency of the emitted photon lies in the range between  $\omega$  and  $\omega + d\omega$ . This function is normalized so that  $\int_{-\infty}^{\infty} a(\omega_{if} - \omega)d\omega = 1$ . The intensity of the spectral line emitted as a result of the transition is given by

$$S_{if} = \frac{\pi^2 c^2}{\omega^3 \tau_{if}} \left( N_f - \frac{g_f}{g_i} N_i \right), \quad (2.16)$$

where  $N_i, N_f$  are the concentrations of molecules in the upper and lower vibration-rotation states,  $g_i, g_f$  are the statistical weights of these levels, and  $1/\tau_{if}$  is the probability of spontaneous emission due to the  $i \rightarrow f$  transition per unit time. The radiative lifetime of the excited molecule with respect to the particular vibrational transition is  $\tau = \left(\sum_f \frac{1}{\tau_{if}}\right)^{-1}$  and is a slowly varying function of its rotational state.

The lifetime  $\tau$  is very sensitive to the electron density distribution in the molecule which, as a rule, is not known with the required precision. It must therefore be determined experimentally. Table I summarizes some experimental data on the lifetimes of certain vibrationally excited molecules. More complete data can be found in Refs. 15 and 16.

Without going into the selection rules for vibration-rotation transitions in molecules, which are described in some detail in Refs. 12 and 15, we shall concentrate our attention on the shape of spectral lines due to vibration-rotation transitions. The line broadening as a function of gas pressure is known to be determined by the Doppler, collisional, or quasistatic mechanisms.<sup>16-20</sup>

Doppler broadening is connected with the random motion of radiating particles, and occurs at sufficiently low pressures. The corresponding frequency distribution is

$$a(\omega - \omega_0) = \frac{1}{\omega_0} \sqrt{\frac{Mc^2}{2\pi T}} \exp\left[-\frac{Mc^2}{2T} \frac{(\omega - \omega_0)^2}{\omega_0^2}\right]; \quad (2.17)$$

where  $\omega_0$  is the frequency corresponding to the line center,  $M$  is the particle mass, and  $T$  is the gas temperature. The characteristic Doppler linewidth is  $\sim \omega_0 \langle v \rangle / c$ , where  $\langle v \rangle$  is the average thermal velocity of the particles. At higher pressures, broadening is de-

termined by the collisional mechanism, i.e., it is produced by collisions between radiating and surrounding particles, which result in a change in the phase of the radiated electromagnetic waves. In this case,

$$a(\omega - \omega_0) = \frac{\gamma}{2\pi} \frac{1}{(\omega - \omega_0 - \Delta)^2 + (\gamma/2)^2}, \quad (2.18)$$

where  $\Delta$  is the line shift,  $\gamma = N\langle\sigma v\rangle$  is the collisional width,  $N$  is the density of the perturbing particles,  $\sigma$  is the total collision cross section of the particles, and  $v$  is the relative collision velocity. The angle brackets represent averaging over particle velocities. The total scattering cross section  $\sigma$  corresponds to a potential equal to the difference between two interaction potentials. The first of them corresponds to the interaction between the perturbing particle and the radiating particle in the upper state involved in the transition, and the second corresponds to its interaction with the radiating particle in its lower state. We shall not reproduce the complete expression for the line shift because the magnitude of this shift is much smaller than the linewidth and has practically no effect on radiation transfer characteristics. Collisional broadening exceeds Doppler broadening when the gas density satisfies the condition

$$N \gg N_1 = \frac{\omega_0 \langle v \rangle}{c \langle \sigma v \rangle}. \quad (2.19)$$

We must now determine the limiting gas density for which most of the line profile is described by collisional broadening theory. The dominant contribution to broadening is due to collisions with impact parameter  $\sim \sqrt{\sigma}$ . Collisional theory is valid for most of the line if the characteristic time  $1/\gamma$  corresponding to a frequency shift of the order of the linewidth is much greater than the duration of such collisions. Hence, we find that collisional broadening theory is valid for

$$N \ll N_2 = \frac{1}{\sigma^{3/2}}. \quad (2.20)$$

The quasistatic (statistical) broadening theory is valid when the reverse inequality is satisfied. This theory is based on the assumption that the radiating particle is located in an external quasistatic field due to fixed surrounding particles. This field produces a shift of the energy states of the radiating particle. It is clear that the assumptions underlying the quasistatic approximation are opposite to those upon which collisional broadening theory is founded.

Spectral line wings are described by the quasistatic theory even when most of the line is governed by the collisional mechanism. It is readily shown that the collisional theory of broadening is valid only for frequency shifts less than  $\langle v \rangle / \sqrt{\sigma}$ . For lines corresponding to vibration-rotation transitions in molecules, this quantity is of the order of  $1-10 \text{ cm}^{-1}$ .

Table II summarizes the orders of magnitude of the densities  $N_1, N_2$ , given by (2.19) and (2.20) in the case of vibration-rotation transitions in carbon dioxide in a nitrogen atmosphere. The formula also gives the values of  $N_3$ , for which the collisional linewidth is equal to the separation between neighboring lines, and the absorption coefficient becomes a smooth function of frequency.

TABLE I. Radiative lifetime of vibrationally excited molecules.\*)

Molecule	Vibrational transition	Energy of vibrational transition	Radiative lifetime for given transition, sec	Molecule	Vibrational transition	Energy of vibrational transition	Radiative lifetime for given transition, sec
CO	1-0	2443.1	0.031	NH <sub>3</sub>	4(E)	3443.6	0.5
HCl	1-0	2886	0.092			3449.6	
HF	1-0	3962	0.0091		2(A <sub>1</sub> )	3337.2	0.15
OH	1-0	3584.6	0.062			3336.2	
NO	1-0	1904	0.061	NH <sub>3</sub>	4(E)	1626.1	0.23
CO <sub>2</sub>	00 <sup>0</sup> 1-00 <sup>0</sup> 0	2349	0.0023			1621.4	
	01 <sup>0</sup> 0-00 <sup>0</sup> 0	667.4	0.66		2(A <sub>1</sub> )	968.3	0.060
	00 <sup>0</sup> 1-02 <sup>0</sup> 0	1064	2			932.5	
	00 <sup>0</sup> 1-10 <sup>0</sup> 0	961	1.2	C <sub>2</sub> H <sub>2</sub>	3(Σ <sub>g</sub> <sup>+</sup> )	3287	0.011
CS <sub>2</sub>	3(Σ <sub>g</sub> <sup>+</sup> )	1532.5	0.0062		5(Π <sub>u</sub> )	722.1	0.19
	2(Π <sub>u</sub> )	396.8	20	CCl <sub>4</sub>	3(F <sub>2</sub> )	795	0.09
HCN	3(E)	712	0.67		4(F <sub>2</sub> )	310	1500
	1(A)	3312	0.014	CCl <sub>3</sub> F	1(A <sub>1</sub> )	1085	0.061
H <sub>2</sub> O	2(A <sub>1</sub> )	1595	0.064		4(E)	846	0.072
	3(B <sub>1</sub> )	3756	0.015	CH <sub>4</sub>	3(F <sub>2</sub> )	3018.9	0.032
H <sub>2</sub> S	1(A <sub>1</sub> )	2614.6	10		4(F <sub>2</sub> )	1305.9	0.42
	2(A <sub>1</sub> )	1182.7	12.5	CH <sub>3</sub> Cl	4(E)	3041.8	0.18
N <sub>2</sub> O	1(A)	1299.8	0.080		1(A <sub>1</sub> )	2966.2	0.045
	3(E)	596.4	6.6		5(E)	1454.6	0.59
	2(A)	2276.5	0.0048	CF <sub>2</sub> Cl <sub>2</sub>	1(A <sub>1</sub> )	1095	0.036
NO <sub>2</sub>	2(A <sub>1</sub> )	1621	0.0067		6(B <sub>1</sub> )	1152	0.05
O <sub>3</sub>	3(B <sub>1</sub> )	1042	0.125		8(B <sub>2</sub> )	915	0.039
SO <sub>2</sub>	3(B <sub>1</sub> )	1361.8	0.024	SF <sub>6</sub>	3(F <sub>1u</sub> )	932	0.026
	1(A <sub>1</sub> )	1151.4	0.29		2(F <sub>1u</sub> )	613	1
	2(A <sub>1</sub> )	517.7	1.1				

\*)If the lower level corresponds to the ground state, then column 2 indicates the number of the vibration in the upper state and its symmetry.

TABLE II. Collisional broadening of lines due to vibration-rotation transitions in CO<sub>2</sub>.\*)

$\omega_0$ , cm <sup>-1</sup>	Vibrational transition	$N_1$ , cm <sup>-3</sup>	$N_2$ , cm <sup>-3</sup>	$N_3$ , cm <sup>-3</sup>
667.4	0110—0090	10 <sup>17</sup>	2·10 <sup>20</sup>	3·10 <sup>20</sup>
961	0091—1090	10 <sup>17</sup>	10 <sup>20</sup>	2·10 <sup>20</sup>
1063.8	0091—0290	2·10 <sup>17</sup>	2·10 <sup>20</sup>	3·10 <sup>20</sup>
2349.2	0091—0090	4·10 <sup>17</sup>	2·10 <sup>20</sup>	3·10 <sup>20</sup>

\*)  $\omega_0$  is the frequency of the vibrational transition, i.e., the frequency corresponding to the center of the band. The gas temperature is assumed to be 300°K.

It is clear from Table II that the collisional theory of broadening is valid over a broad range of gas densities, much greater than the corresponding range for the atomic resonance lines. This is characteristic for most vibration-rotation transitions of molecules. Gas densities of the order of 10<sup>17</sup> – 10<sup>20</sup> cm<sup>-3</sup> are realized, on the one hand, in planetary atmospheres and, on the other, in many laboratory experiments. This has stimulated the development of experimental studies of collisional line profiles in the infrared molecular spectrum. The most important experimental procedures rely on measurements of integrated absorption in a particular spectral line, and on direct measurements of the line profile at high pressures, or with the aid of laser beams. Table III lists collisional linewidths for vibration-rotation transitions in a number of molecules with linear or spherical structure.<sup>21-34</sup> Most of these are of the same order of magnitude, so that reliable estimates can be performed even where direct measurements are not available.

### 3. MODELS OF MOLECULAR BANDS

To analyze the properties of infrared radiation transfer that are connected with the rapidly oscillating structure of the absorption coefficient of a molecular gas, we must have an analytic representation of the absorption coefficient in a certain frequency band. This can be based on band models that lead to analytic expressions for the absorption coefficient as a function of frequency. Two models of bands are used in practice. The first, the regular or Elsasser model, as-

TABLE III. Collisional half-width of spectral lines corresponding to vibration-rotation transitions in a number of molecules at room temperature and atmospheric pressure ( $j \sim 10$ – $20^*$ ).

Emitting molecule	Energy of vibrational transitions, cm <sup>-1</sup>	Perturbing particle	Half-width $\gamma/2$ , cm <sup>-1</sup>	Emitting molecule	Energy of vibrational transitions, cm <sup>-1</sup>	Perturbing particle	Half-width $\gamma/2$ , cm <sup>-1</sup>
CO	2143.1	He	0.05	N <sub>2</sub> O	2223	N <sub>2</sub>	0.08
		Ne	0.04			N <sub>2</sub> O	0.10
		Ar	0.04			Ar	0.03
		Kr	0.04			Xe	0.04
		Xe	0.04			Ar	0.02
		H <sub>2</sub>	0.07			Kr	0.04
		N <sub>2</sub>	0.05			Xe	0.06
		CO	0.05			He	0.05
		CO <sub>2</sub>	0.05			H <sub>2</sub>	0.07
		N <sub>2</sub>	0.08			N <sub>2</sub>	0.05
CO <sub>2</sub>	667.4 961	He	0.07	CH <sub>4</sub>	3018.9	O <sub>2</sub>	0.04
		N <sub>2</sub>	0.08			CH <sub>4</sub>	0.07
		CO <sub>2</sub>	0.12				
		N <sub>2</sub>	0.07				
		CO <sub>2</sub>	0.10				
	1064	N <sub>2</sub>	0.07				
		CO <sub>2</sub>	0.10				

\*) These figures are averages over the rotational states in the indicated range. The data are accurate to within ~20%.

sumes that neighboring spectral lines have constant separation and equal intensity. In the other model, which is referred to as the random or Goody model, it is assumed that the separation between neighboring lines varies in a random fashion and is governed by a statistical law. It is further assumed that the line-intensity distribution follows some particular law.

The regular and random models correspond to the two limiting cases of molecular spectrum. Thus, in the first case, the disposition of the lines and their intensity distribution follows some order whereas, in the second case, there is no order. These two band models will be taken as a basis for our study of infrared radiation transfer in molecular media.

#### A. Regular model

The regular model was first put forward by Elsasser in 1938,<sup>35</sup> and is often referred to in the literature as the Elsasser model. It is clear from Fig. 1 that this model works best for the vibration-rotation spectra of linear molecules. In its simplest form, it assumes that the spectral lines have identical intensities and shapes. The absorption coefficient of the gas is then given by

$$k_\omega = S \sum_n a(\omega_0 + nd), \quad (3.1)$$

where  $S$  is the line intensity,  $d$  is the frequency difference between neighboring lines,  $\omega_0$  is the frequency at the band center, and  $n$  is the line number. This formula shows that the absorption coefficient is a periodic function of frequency and that the period is  $d$ . If the width of an individual spectral line is large in comparison with line separation, the absorption coefficient involves contributions of many lines and the summation sign in (3.1) can be replaced by integration. Since  $\int a(\omega)d\omega = 1$ , we have

$$k_\omega = \frac{S}{d}.$$

The regular model is particularly convenient in the case of the Lorentz line shape of an individual line. In this case, the sum in (3.1) can be evaluated on the basis of the Mittag-Leffler theorem.<sup>36</sup> This results in an analytic expression for the absorption coefficient at a given frequency:

$$k_\omega = \frac{S\gamma}{2\pi} \sum_n \frac{1}{(\omega - \omega_0 - nd)^2 + (\gamma/2)^2} = \frac{S}{d} \frac{\text{sh}(\pi\gamma/d)}{\text{ch}(\pi\gamma/d) - \cos[2\pi(\omega - \omega_0)/d]}. \quad (3.2)$$

According to this formula, the absorption coefficient has an oscillatory structure. The maxima lie at the centers of the corresponding spectral lines, and the minima lie half-way between neighboring maxima. The ratio of maximum to minimum values of the absorption coefficient is

$$\frac{\text{ch}(\pi\gamma/d) + 1}{\text{ch}(\pi\gamma/d) - 1} = \text{cth}^2 \frac{\pi\gamma}{2d}.$$

This ratio is large when the width of the individual spectral lines is small, i.e.,  $\gamma \ll d$ , and its value then is  $(2d/\pi\gamma)^2$ .

The regular model is capable of describing the real situation as well.<sup>37</sup> Suppose we have a gas consisting of linear or spherically symmetric molecules, and that the spectral line band corresponding to a particular vibra-

tional transition does not overlap other bands. The absorption spectrum of the gas then consists of equidistant lines (Fig. 1) and, if the intensities of lines determining the absorption coefficients at a given frequency in (3.1) are not too different, the radiation transfer process in a layer of the gas is satisfactorily described by the regular model.

Henceforth, our description of the regular model will be concentrated on the Lorentz profile since this case is the most important in practice. For the Lorentz line shape, the regular model is valid if

$$\frac{d \ln S(\omega)}{d\omega} \max(\gamma, d) \ll 1. \quad (3.3)$$

We shall now demonstrate the possibility of using the regular model to determine the characteristics of infrared radiation transfer in an isothermal planar gas layer consisting of linear molecules. The optical thickness of the gas layer, which can subsequently be used to determine all the characteristics of infrared radiation transfer, is then given in accordance with (3.2) by:

$$u(\omega) = \int_0^L k_\omega dx = \frac{S(\omega)L}{d} \frac{\text{sh}(\pi\gamma/d)}{ch(\pi\gamma/d) - \cos[2\pi(\omega - \omega_n)/d]}, \quad (3.4)$$

where  $L$  is the linear dimension of the layer (we assume, for simplicity, that the density of the molecules does not depend on position). It is clear that the optical thickness is an oscillating function of frequency and has two envelopes,  $u_{\max}(\omega)$  and  $u_{\min}(\omega)$ , which pass through the maxima and minima of this function:

$$u_{\max}(\omega) = \frac{S(\omega)L}{d} \text{cth} \frac{\pi\gamma}{2d}, \quad u_{\min}(\omega) = \frac{S(\omega)L}{d} \text{th} \frac{\pi\gamma}{2d}. \quad (3.5)$$

These envelopes are the characteristics that can be used as a basis for describing the transfer of infrared radiation in the gas layer. Let  $\omega_{\max}$  be the frequency at which  $S(\omega)$  has a maximum. The parameters enabling us to subdivide the overall transfer process into individual limiting cases are then the quantities  $u_{\min}(\omega_{\max})$  and  $u_{\max}(\omega_{\max})$ . The characteristic values of the densities  $N_4$  and  $N_5$ , for which  $u_{\min}(\omega_{\max}) = 1$  and  $u_{\max}(\omega_{\max}) = 1$  in the  $P$ - and  $R$ -branches of  $\text{CO}_2$  and  $\text{CH}_4$  molecules in the Earth's atmosphere are listed in Table IV.

When  $u_{\max}(\omega_{\max}) \ll 1$ , the gas layer is optically transparent at all frequencies. This case is relatively simple because  $u(\omega) \ll 1$  in all the formulas, and all the problems can readily be solved in this case. The equation given by (2.7) yields for the equivalent width of the molecular band

$$W = S_0 L, \quad (3.6)$$

where  $S_0$  is the integrated intensity of the molecular band, which is equal to the sum of all the spectral-line intensities. This expression retains its form for molecules of any structure if the optical thickness of the

TABLE IV. Characteristic values of the densities of molecular components corresponding to different limiting cases of radiation transfer in the Earth's atmosphere.

Vibrational transition	$\text{CO}_2$ $\omega_0 = 667.4 \text{ cm}^{-1}$	$\text{CO}_2$ $\omega_0 = 2349.6 \text{ cm}^{-1}$	$\text{CH}_4$ $\omega_0 = 1305.9 \text{ cm}^{-1}$	$\text{CH}_4$ $\omega_0 = 3089 \text{ cm}^{-1}$
$N_4, \text{ cm}^{-3}$	$1.5 \cdot 10^{14}$	$4 \cdot 10^{13}$	$6 \cdot 10^{15}$	$3 \cdot 10^{15}$
$N_5, \text{ cm}^{-3}$	$4 \cdot 10^{18}$	$2.5 \cdot 10^{10}$	$1.5 \cdot 10^{11}$	$7 \cdot 10^{10}$

layer of gas is much less than unity at the centers of the strongest lines.

We shall now concentrate our attention on the opposite limiting case  $u_{\max}(\omega_{\max}) \gg 1$ , for which all photons are absorbed in the gas layer in a certain frequency band. We then consider the situation where the width of individual spectral lines is much less than the separation between neighboring lines ( $\gamma \ll d$ ), and the optical thickness of the layer is a rapidly oscillating function of frequency. This is the most interesting case.<sup>1)</sup> The range of parameter values that we are considering can be divided into two parts, depending on the magnitude of  $u_{\min}(\omega_{\max}) \ll 1$ , strong absorption occurs only near the maxima of individual lines, for which the optical thickness of the layer is found from (3.2) to be

$$u(\omega) = \frac{u_{\max}(\omega)}{1 + [2(\omega - \omega_n)/d]^2}, \quad (3.7)$$

where  $\omega_n$  is the frequency corresponding to the center of the  $n$ -th line. Hence, using (2.3), we find that the absorption function for the given frequency interval is

$$A(\omega) = \frac{\gamma}{d} \sqrt{\pi u_{\max}(\omega)} \approx 2 \sqrt{\frac{u_{\min}(\omega)}{\pi}}. \quad (3.8)$$

This formula can be simply derived. Photons are absorbed in a narrow frequency interval in which  $u(\omega) \approx 1$ . The width of this interval in the neighborhood of the absorption line maximum is given by (2.4) and is  $\Delta\omega \sim \gamma \sqrt{u_{\max}(\omega)}$ . Since the separation between neighboring lines is equal to  $d$ , the absorption function for a photon, i.e., the probability that it will fall into the frequency interval  $\Delta\omega$ , is of the order of  $A \sim \Delta\omega/d \sim (\gamma/d) \sqrt{u_{\max}(\omega)}$ , which confirms (3.8).

To find the equivalent width of bands in this limiting case, we must combine the widths of the individual absorption intervals near each maximum. The result is

$$W = \sum_n \Delta\omega_n = \int \Delta\omega_n \frac{d\omega}{d} \sim \int \sqrt{u_{\min}(\omega)} d\omega.$$

The quantity  $\Delta\omega_n$  is the equivalent width of an individual line. It is readily seen that, in this case, and if  $u_{\min}(\omega_{\max}) \ll 1$ , the difference  $\Delta\omega_n$  is much less than  $d$ . More rigorous calculations show that the band width  $W$  in the case of linear and spherically symmetric molecules is given by

$$\frac{AW}{2\sqrt{BT}} = C_W \sqrt{u_{\min}(\omega_{\max})}. \quad (3.9)$$

This formula is valid also for the equivalent band width  $\bar{W}$  averaged over all the angles of escape of photons from the gas layer, and thus determining the resultant power flux density of the radiation from it. The values of the coefficient  $C$  are listed in Table V. It is clear that the equivalent band width depends on the parameters of the problem, as indicated by the above estimate. We note that the equivalent width  $\bar{W}$  of the emission band is greater than the equivalent width  $W$  of the absorption band because the absorption process which we are considering corresponds to the propagation of photons at right-angles to the gas layer, whereas the

<sup>1)</sup>We shall confine our attention to the  $P$  and  $R$  branches because, as was shown in Ref. 38, the  $Q$  branch affects the equivalent width of the band only when  $u_{\max}(\omega_{\max}) \lesssim 1$ .

TABLE V. Values of the coefficient  $C$  in (3.9).

	Linear molecules	Spherically symmetric molecules
$C_W$	3.55	3.72
$C_{\bar{W}}$	4.73	4.96

radiation is in fact emitted at different angles, so that the effective thickness of the layer is greater.

The above case, corresponding to  $u_{\min}(\omega_{\max}) \ll 1$ , is known as the isolated-line model because, in this case, absorption and emission by the gas layer are concentrated in individual nonoverlapping frequency intervals near the centers of the corresponding spectral lines. The isolated-line model can also be used for arbitrary molecules if the equivalent linewidth is much less than the mean separation between lines. The equivalent band width is then given by

$$W = \sum_n \Delta\omega_n. \quad (3.10)$$

In the case of collisional and Doppler broadening, the equivalent width is given by<sup>5</sup>

$$\Delta\omega_n = \begin{cases} \gamma \sqrt{\pi u_{\max}}, & \text{collision broadening,} \\ \gamma_D \sqrt{\frac{\ln u_{n \max}}{\ln 2}}, & \text{Doppler broadening,} \end{cases} \quad (3.11)$$

where  $\gamma_D$  is the Doppler linewidth and  $u_{n \max} \gg 1$  is the optical thickness of the gas layer at the line center.

We now return to linear molecules and analyze the other limiting case, i.e.,  $u_{\min}(\omega_{\max}) \gg 1$ . Here, the absorption function is given by

$$A(\omega) = \operatorname{erf} \sqrt{u_{\min}(\omega)}, \quad u_{\max}(\omega) \gg 1, \quad (3.12)$$

where  $\operatorname{erf}(x) = (2/\sqrt{\pi}) \int_0^x e^{-t^2} dt$ . As can be seen, for frequencies for which  $u_{\min}(\omega) \gg 1$ , the absorption function is equal to unity. For frequencies for which  $u_{\min}(\omega) \ll 1$ ,  $u_{\max}(\omega) \gg 1$ , the absorption function is given by (3.8) and is determined by absorption near the center of the corresponding transition.

The equivalent band width can be estimated in this case as before, i.e., by adding the width of individual intervals for which  $u(\omega) \geq 1$ . The equivalent band width then consists of a segment for which  $u_{\min}(\omega) \geq 1$ , and individual frequency intervals in the neighborhood of the corresponding transitions for which  $u_{\min}(\omega) \ll 1$ ,  $u_{\max}(\omega) \gg 1$ . Analysis shows that, when  $u_{\min}(\omega_{\max}) \gg 1$ , the main contribution to the equivalent band width is provided by the first region. The latter is thus the width of the interval whose limits can be found from

$$u_{\min}(\omega_{\lim}) \sim 1. \quad (3.13)$$

A simple result is obtained when the line intensity is a rapidly varying function of frequency near the edges of the absorption region, i.e.,

$$\left. \frac{d \ln S(\omega)}{d \ln \omega} \right|_{\omega=\omega_{\lim}} \gg 1. \quad (3.14)$$

We can then use the asymptotic expression for  $u_{\min}(\omega)$  which gives the following result for the limiting frequency in the band:

$$u_{\min}(\omega_{\lim}) = 0.14, \quad \text{where } W = 2\omega_{\lim}. \quad (3.15)$$

Similarly,

$$\bar{W} = 2\omega_{\lim}, \quad \text{where } u_{\min}(\omega_{\lim}) = 0.085. \quad (3.16)$$

We note that, in the case of emission and absorption by linear molecules, the rotational levels of which are populated in accordance with the Boltzmann distribution, the condition given by (3.14) assumes the form

$$hW \gg 2\sqrt{BT}, \quad (3.17)$$

so that the limit of the emission and absorption band is determined by the tail of the distribution of the molecules over the rotational states. When  $B \ll T$ , the condition given by (3.17) is also valid for spherical top molecules. In this case, the equivalent bandwidth is also given by (3.15) and (3.16).

Figure 2 shows a comparison between theory and experiment<sup>39,40</sup> for the equivalent width of the fundamental vibration-rotation band of CO at  $T = 300^\circ\text{K}$  [in these experiments,  $u_{\max}(\omega_{\max}) \gg 1$ , so that  $W$  depends only on  $u_{\min}(\omega_{\max})$ ]. The maximum discrepancy between experiment and calculations is about 10% and can be ascribed to both experimental uncertainties and theoretical errors connected, above all, with the uncertainty in the collisional linewidth  $\gamma$ . In this particular calculation,  $\gamma$  was assumed to be the same for all the lines, and equal to  $0.16 \text{ cm}^{-1}$  at atmospheric pressure. In point of fact, it is a function of  $j$  and varies between  $0.20$  and  $0.10 \text{ cm}^{-1}$ . This restricts the precision of the calculations to 5–10%. When the dependence of the rotational constant on the vibrational state is taken into account, the uncertainty becomes smaller still.

## B. Random model

The other popular model of a band of spectral lines is the random or statistical model, put forward by Goody.<sup>41</sup> It is based on the assumption that the lines are distributed randomly in a certain frequency interval. Physically, this model is suitable for describing molecular spectra with complex irregular structure, for example, the spectra of molecules in the form of an

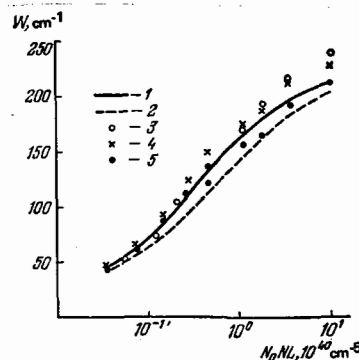


FIG. 2. Equivalent width of the fundamental vibration-rotation band of CO at  $T = 300^\circ\text{K}$  in a nitrogen atmosphere:  $N_0$ —density of CO molecules,  $N$ —density of nitrogen molecules,  $L$ —path traversed by radiation. 1—regular model, 2—random model, 3—calculations by Edwards and Maynard,<sup>55</sup> 4—experimental data,<sup>40</sup> 5—experiment.<sup>39</sup>



asymmetric top. Moreover, the random model provides a basis for approximate (but relatively accurate) calculations of the characteristics of molecular radiation in certain other cases, for example, in the case of overlap of several regular bands.

We shall consider two approaches to the random model. The first, developed by Goody himself,<sup>3,41</sup> consists of the following. Let us suppose that the position of an individual line in a given frequency band is independent of the position of the other lines, and that the shapes and widths of all the lines are the same. If there are  $n$  lines within the frequency band  $\Delta\omega$ , the absorption function is given by

$$A = 1 - \frac{\int_{-\frac{\Delta\omega}{2}}^{\frac{\Delta\omega}{2}} \dots \int_{-\frac{\Delta\omega}{2}}^{\frac{\Delta\omega}{2}} d\omega_1 \dots d\omega_n \int_0^\infty \dots \int_0^\infty \prod_i P(S_i) e^{-S_i L a(\omega_i)} dS_i}{\int_{-\frac{\Delta\omega}{2}}^{\frac{\Delta\omega}{2}} \dots \int_{-\frac{\Delta\omega}{2}}^{\frac{\Delta\omega}{2}} d\omega_1 \dots d\omega_n \int_0^\infty \dots \int_0^\infty \prod_i P(S_i) dS_i}; \quad (3.18)$$

where  $a(\omega_i)$  is the line shape and  $P(S_i)$  is the function describing the line intensity distribution, i.e.,  $P(S_i)dS_i$  is the probability that the intensity of the  $i$ -th line will lie between  $S_i$  and  $S_i + dS_i$ . It is also assumed that the center of the first line lies in the interval between  $\omega_1$  and  $\omega_1 + d\omega_1$ , whereas the center of the second line lies in the interval between  $\omega_2$  and  $\omega_2 + d\omega_2$ , and so on, for the  $n$  lines. Since  $\int_0^\infty P(S_i)dS_i = 1$ , and the  $n$  integrals in the numerator of (3.18) are all equal, we may transform (3.18), so that it reads

$$A = 1 - \left[ \frac{1}{\Delta\omega} \int_{-\frac{\Delta\omega}{2}}^{\frac{\Delta\omega}{2}} d\omega \int_0^\infty dS P(S) \exp(-SLa(\omega)) \right]^n. \quad (3.19)$$

Since the width of the frequency interval that we are considering is much greater than the linewidth, we can change the order of integration in (3.19) and, if we pass to the limit as  $n \rightarrow \infty$ , we obtain

$$A = 1 - \exp \left[ -\frac{1}{d} \int_0^\infty P(S) W(S) dS \right], \quad (3.20)$$

where  $W(S) = \int_{-\infty}^{+\infty} [1 - \exp(-Sa(\omega)L)] d(\omega - \omega_0)$  is the equivalent linewidth,  $\omega_0$  is the frequency corresponding to the center of the line, and  $d$  is the average separation between the lines. For a band consisting of lines of equal intensity and having the Lorentz shape, the absorption function corresponding to  $u_{\max} = 2SL/\pi\gamma > 1$ , i.e., large optical thickness of the layer at the line centers, is equal to

$$A = 1 - \exp \left( -2 \sqrt{\frac{u_{\min}}{\pi}} \right). \quad (3.21)$$

If, in addition,  $u_{\min} = (\pi\gamma/2d)^2 u_{\max} \ll 1$ , we have  $A = 2\sqrt{u_{\min}/\pi}$ , which is exactly the same as the result predicted by the regular Elsasser model (3.8), obtained under similar assumptions. This agreement was to be expected because, when  $u_{\max} \gg 1, u_{\min} \ll 1$ , absorption in the band consists of absorption in the individual non-overlapping lines. The result is, therefore, independent of the model used. The parameter  $u_{\min}$  which, in the regular model, is the optical thickness of the gas layer at the minima of  $k\omega$ , has a different interpretation here, namely, it is the average effective optical

thickness of the layer in the intervals between spectral lines.

The advantage of the random model is that it can be used to express the integrated characteristics of molecular radiation in the band in terms of the equivalent width of an individual spectral line. The random model is, therefore, convenient in studying the transport of radiation in molecular bands with non-Lorentzian profiles, and when several molecular bands superimpose so that other methods are very laborious.

We shall use a different approach to this range of problems and, in particular, to the random model. First, we must translate the entire problem to a different language by introducing the distribution function  $f(u)$  for the optical thickness of the gas layer under investigation.<sup>42-45</sup> The quantity  $f(u)du$  is the probability that the optical thickness of the layer lies between  $u$  and  $u + du$ .

To demonstrate the possibilities of this method, we begin by returning to the previously considered case of the regular model and the Lorentz line profile. The optical thickness of the layer as a function of frequency will be taken in the form

$$u(\omega) = u_{\max} \frac{\text{ch}(\pi\gamma/d) - 1}{\text{ch}(\pi\gamma/d) - \cos[2\pi(\omega - \omega_0)/d]}.$$

We then have

$$f_{\text{reg}}(u) du = \frac{2d\omega}{d}, \quad 0 \leq \omega - \omega_0 - nd \leq \frac{d}{2}.$$

We have used the fact that the probability of randomly falling into a particular frequency interval is proportional to the size of this interval. The last two expressions can be used to find the formula for  $f_{\text{reg}}$  in this case:<sup>43</sup>

$$f_{\text{reg}}(u) = \frac{1}{\pi u} \sqrt{\frac{u_{\min} u_{\max}}{(u_{\max} - u)(u - u_{\min})}}, \quad (3.22)$$

where  $u_{\min} \leq u \leq u_{\max}$ . For all other values of  $u$ , we have  $f_{\text{reg}}(u) = 0$ .

This approach will not, of course, yield anything at all when the regular model is valid and the problem can be solved exactly. However, it is convenient for obtaining approximate results when the distribution of the line centers and the alternation of their intensity are both relatively complicated. Within the framework of the random model, the distribution function  $f_{\text{rand}}(u)$  can be found<sup>44,45</sup> with the aid of the method developed in the quasistatic theory of broadening of spectral lines.<sup>46</sup> The expression for  $f_{\text{rand}}(u)$  is derived in the Appendix. Here, we reproduce the final results for a set of lines of equal intensity and the same shape, which we shall use below:

$$f_{\text{rand}}(u) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp \left\{ -itu - \frac{1}{d} \int_{-\infty}^{+\infty} [1 - \exp(itSLa(\omega))] d(\omega - \omega_0) \right\} dt. \quad (3.23)$$

The absorption function for a molecular band is then given by

$$A = \int_0^\infty [1 - \exp(-u)] f_{\text{rand}}(u) du. \quad (3.24)$$

Integrating with respect to  $u$  in (3.24) and expressing

the integral with respect to  $t$  in terms of the residue at  $t=i$ , we obtain the formula given by (3.21). The two approaches to the random model are thus seen to yield the same result. This was to be expected because both approaches rely on the same physical assumptions.

The parameter ranges defined by  $u_{\max} = 2SL/\pi\gamma \gg 1$ ,  $\gamma \ll d$  are the most interesting for a molecular gas. Here, the function  $u_{\min} f(u, u_{\min})$  depends on the single parameter  $u/u_{\min}$ . When  $u_{\min} \ll 1$ , absorption is largely confined to the frequency interval in which the optical thickness is much greater than  $u_{\min}$ . In this interval, the distribution function is the same for both models and is given by

$$f(u) = \frac{u_{\min}^{1/2}}{\pi u^{3/2}} \quad (3.25)$$

For other values of the parameters, we have  $f_{\text{rand}}(u) < f_{\text{reg}}(u)$ .

Comparison of the absorption functions corresponding to the regular and random models (Fig. 3)<sup>5</sup> shows that the two are not very different. For  $u_{\max} \gg 1$  and  $\gamma/d \ll 1$ , this comparison is particularly useful because the absorption functions depend on the single parameter  $u_{\min}$ . When  $u_{\min} \ll 1$  and  $u_{\min} \gg 1$ , we have  $A_{\text{reg}} = A_{\text{rand}}$ , whereas  $A_{\text{rand}}$  is somewhat smaller than  $A_{\text{reg}}$  for intermediate values of  $u_{\min}$ . The maximum difference occurs for  $u_{\min} = 1.27$ , for which  $A_{\text{reg}} = 0.9$  and  $A_{\text{rand}} = 0.72$ . The fact that the absorption function in the regular model is greater than the absorption function in the random model can be readily explained as follows. When the distribution of spectral lines within a band is random, there is a definite probability that the separation between neighboring lines in some particular interval of frequency will be greater than the average separation between them throughout the frequency interval under consideration. At the same time, the separation between neighboring lines will be smaller in some other interval. Thus, when  $u_{\min}$  is of the order of unity throughout the bands, the absorption function in the first of these intervals will be much smaller, whereas, in the second interval, it will be much greater as compared with the situation where the separation between the lines in each of these intervals is equal to the average separation for the entire band. This ensures that the absorption function obtained for the random distribution of lines in the band is somewhat lower than the absorption function for an ordered distribution of lines.

The fact that the results obtained for the regular and random models are not very different indicates that the

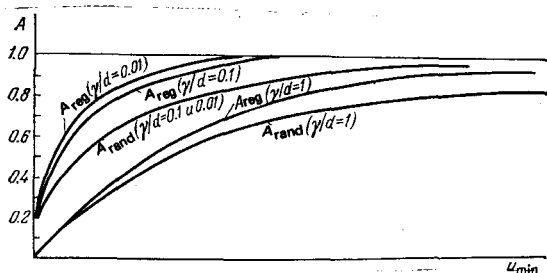


FIG. 3. Dependence of the absorption function in the case of the regular and random models on the parameter  $u_{\min}$  for different values of the ratio  $\gamma/d$ .

latter model can be used even for investigating radiation transfer processes in molecular bands with regular structure. Thus, for example, in the case of linear molecules, it may be considered that the lines are distributed randomly in a frequency interval containing a large number of lines of roughly the same intensity. On the other hand, the line intensity is then a slowly varying function of frequency, in accordance with (3.3).

In our view, the random model is convenient in connection with various problems in the theory of infrared radiation transfer, e.g., in the case of molecular bands with non-Lorentz line profiles and when several regular bands overlap. This enables us, at the cost of some loss of accuracy, to solve relatively laborious problems by using analytic methods and simple computation techniques, which is particularly convenient when a semiquantitative answer to a particular question is required. Above, we estimated the error associated with using the random model to determine the absorption function. It did not exceed 20%. The same conclusion follows from comparison of the equivalent width of an individual vibration-rotation band calculated on the basis of the random and regular models when the conditions for the validity of the latter are satisfied (Fig. 4).<sup>44,45</sup> Since the regular and random models reflect the two limiting cases, namely, order and disorder in the spectrum of molecules, respectively, the discrepancy between these two models should be greater than the discrepancy between either of them and the observed result. This means that the error incurred through the systematic use of the random model in the solution of real problems should not exceed 20%. We note that the accuracy of the parameters characterizing the width and shape of spectral lines, which are used in these calculations, may well be of the same order. As an example, Fig. 2 shows the results obtained with the random model for the equivalent width of the ground-state vibration-rotation band of the CO molecule. As can be seen, these data are close to the results obtained with the regular model and to the experimental data.

We shall use the random model to determine the equivalent width of a set of intersecting vibration-rotation bands of linear molecules, consisting of lines with Lorentz profiles. As before, we shall assume that the lines are distributed randomly in a sufficiently narrow frequency interval within each band, and that the average separation between lines is greater than their width, whilst the optical thickness of the gas layer at the line centers is large.<sup>44,45</sup> Within the framework of the random model, the equivalent width of a set of such bands can be determined in the same way as for an individual band. In fact, using Eq. (4) of the Appendix for the function  $f_{\text{rand}}(u)$ , and assuming that the line intensity distribution is

$$P(S) = \sum_k \frac{d_k}{d_k} \delta(S - S_k),$$

where  $S_k$  and  $d_k$  are the line intensity and average line separation in the  $k$ -th band, respectively, we find from (3.24) that the absorption function is

$$A(\omega) = 1 - \exp \left[ -2 \sum_k \sqrt{\frac{u_k \min(\omega)}{\pi}} \right],$$

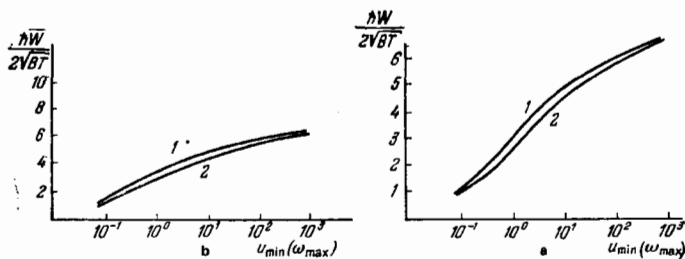


FIG. 4. Equivalent width of an individual vibration-rotation band due to linear molecules: 1—regular model, 2—random model.  $W$ —equivalent width of band (Fig. a),  $\bar{W}$ —equivalent width of band averaged over the angle of emission of photons from the gas layer (Fig. b).

where  $u_{k \text{ min}}$  is the parameter  $u_{\text{min}}$  corresponding to the  $k$ -th band. All the expressions resulting from the random model for the average spectral characteristics of an individual band are thus seen to retain their form under the substitution

$$\sqrt{u_{\text{min}}(\omega)} \rightarrow \sum_k \sqrt{u_{k \text{ min}}(\omega)}.$$

If the maximum value of the parameter  $u_{\text{min}}$  for each band is much less than unity, the required equivalent width is equal to the sum of widths of all the bands, each of which is given by (3.9). Conversely, if there are frequencies for which  $u_{\text{min}}(\omega) \gg 1$ , we can use the asymptotic expression to obtain the result. The equivalent width  $W$  of a band is then equal to the width of the frequency interval in which

$$\sum_k \sqrt{u_{k \text{ min}}(\omega)} \geq 0.50. \quad (3.26)$$

Similar results are obtained for the width  $\bar{W}$  of an emission band except that, in the latter case, the numerical coefficient on the right-hand side of (3.26) is equal to 0.39.

We note that, when the power flux is calculated in the case where there are several overlapping bands, the concept of the equivalent band width  $W$  may lose its practical significance. We have introduced it to define the radiant flux emitted by a gas layer, assuming that the width of the band is small in comparison with the transition frequency and the ratio  $T/\hbar$ . This may not be so when several bands are found to overlap. The resultant power flux of infrared radiation emitted by a gas layer is then given by

$$J = \int e_\omega d\omega; \quad (3.27)$$

where  $e_\omega$  is, as before, the spectral powerflux density emitted by the surface of a perfect black body with given temperature, and the integral is evaluated over the

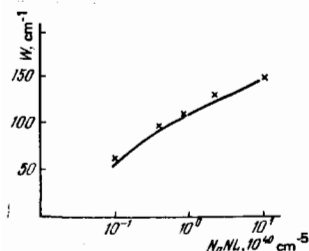


FIG. 5. Equivalent width of the 15- $\mu$  absorption band of  $\text{CO}_2$  at  $T = 300^\circ\text{K}$  in a nitrogen atmosphere.  $N_0$  and  $N$  are the densities of  $\text{CO}_2$  and  $\text{N}_2$  molecules,  $L$  is the path length traversed by the radiation,  $\times$ —experimental data.<sup>47</sup>

frequency band in which  $\sum_k \sqrt{u_{k \text{ min}}(\omega)} \geq 0.39$ .

Figure 5 shows the experimental data<sup>47</sup> and the results obtained from the random model for the equivalent width of the 15- $\mu$  band of the  $\text{CO}_2$  molecule at  $T = 300^\circ\text{K}$ . Bands associated with the eight vibrational transitions 667.4, 618, 721, 741.7, 587.3, 791.5, 667.7, and 647  $\text{cm}^{-1}$  were taken into account in the calculations. The spontaneous emission times for these transitions were taken from Ref. 48.

The desire to achieve maximum agreement between the regular and random models, on the one hand, and experimental data, on the other, and to use these models for practical calculations, has led to a large number of published modifications of both models. Many of these modifications (see, for example, Refs. 49–51) form the basis for semiempirical methods. They are described in some detail in monographs and reviews (see, for example, Refs. 3 and 10), and will not be considered here. We merely note that the above method of determining the equivalent width of bands is, in principle, similar to the method described in Refs. 52–55. The latter is based on the assumption that the lines are distributed randomly in a sufficiently narrow frequency interval, and that their intensity distribution is exponential. The absorption function found in this way is then integrated with respect to frequency, using the true or empirical values of  $u_{\text{min}}(\omega)$  and  $u_{\text{max}}(\omega)$ . Although the Edwards-Maynard method does not reflect the actual situation in the spectra of linear molecules, it does lead to results that are in fairly good agreement with experiment (Fig. 2). Its main disadvantage is that, when one deals with relatively complicated situations (for example, in the case of several overlapping bands), it involves a number of empirical parameters that can be obtained only by comparing calculations with experiment.

#### 4. MODELS OF BANDS IN INFRARED RADIATION TRANSFER

In practice, one is frequently concerned with a temperature-inhomogeneous molecular gas, or a molecular gas in which there is no thermodynamic equilibrium with respect to the vibrational degrees of freedom. The physical picture of this process is then, of course, much more complicated, and the regular and random models of line bands become even more valuable as ways of analyzing this picture. If the problem involves small characteristic parameters, these methods often

yield a reliable quantitative result in analytic or semi-analytic form. For example, the relative variation in temperature of the gas layer, or the ratio of the rates of quenching of vibrational and rotational excitation of molecules, can serve as parameters of this kind.

Temperature inhomogeneity or the absence of local thermodynamic equilibrium is characteristic for the Earth's atmosphere and other planetary atmospheres. We shall therefore conclude this review by analyzing some of the problems in the physics of the atmosphere. This will demonstrate the possibilities of analytic methods using band models for the solution of particular problems.

#### A. Radiation emitted by a temperature-inhomogeneous molecular gas

We shall now consider the radiation emitted by a plane layer of gas which is in thermodynamic equilibrium. We shall assume that its parameters depend only on the coordinates measured at right-angles to the surface. We shall also suppose that the temperature is given as a function of this coordinate and is independent of time. The characteristic variation of temperature within the layer will be taken to be much smaller than the temperature itself. If absorption by the gas is due to vibration-rotation transitions from the ground vibrational state of the molecules, the temperature inhomogeneity within the gas layer has practically no effect on the equivalent width  $W$  of the band responsible for the absorption of external radiation. Temperature changes then lead only to small changes in the optical thickness of the gas layer. On the other hand, the dependence of the equivalent width of the band on the optical thickness is a relatively smooth function. If a large number of vibration-rotation states of the molecules participate in the radiation transfer process, the absorption coefficient of the gas has an appreciable dependence on the coordinate. The effect of temperature inhomogeneity in the gas on the equivalent width of the band can then be very considerable.

A number of approximate methods for the determination of absorption by an inhomogeneous gas medium is discussed in the literature.<sup>3,9,10</sup> One of the most successful methods is the Curtis-Godson approximation,<sup>56</sup> which describes an inhomogeneous optical path with the aid of two parameters, namely, the average pressure and the average number of absorbing molecules. This means that absorption in an individual line in an inhomogeneous medium is replaced by absorption in a homogeneous medium. The average width and intensity of lines are chosen by comparing the approximate results with the exact results in the limits of large and small optical thicknesses of the gas layer at the line center.

We shall now illustrate the Curtis-Godson method by considering an individual line with a Lorentz profile. The equivalent linewidth in this case is given by

$$W_L = \int_{-\infty}^{+\infty} \left[ 1 - \exp \left( - \int_0^L \frac{S(x) \gamma(x) dx}{(\omega - \omega_0)^2 + (\gamma(x)/2)^2} \cdot \frac{1}{2\pi} \right) \right] d(\omega - \omega_0), \quad (4.1)$$

where the dependence of intensity and linewidth on the coordinate,  $S(x)$  and  $\gamma(x)$ , is connected with the variation of temperature and density of the absorbing molecules within the gas layer in the direction of propagation of radiation, and  $L$  is the path length traversed by radiation in the gas. In the limiting cases of large and small optical thickness of the layer at the center of the spectral line, the equivalent linewidth  $W_L$  is equal to  $\sqrt{2} \int_0^L S(x) \nu(x) dx$  and  $\int_0^L S(x) dx$ , respectively. Replacing the functions  $S(x)$  and  $\gamma(x)$  in (4.1) by certain average values  $\bar{S}$  and  $\bar{\gamma}$ , we obtain the usual formula for  $W_L$  (see, for examples, Refs. 3 and 5). If we then compare it with the exact expressions for the limiting cases, we obtain the required average values of the intensity and linewidth:

$$\begin{aligned} \bar{S} &= \frac{1}{L} \int_0^L S(x) dx, \\ \bar{\gamma} &= \frac{\int_0^L S(x) \gamma(x) dx}{\int_0^L S(x) dx}. \end{aligned} \quad (4.2)$$

Similarly, we can examine the absorption of radiation in an inhomogeneous gaseous medium in the case of a non-Lorentz profile and molecular bands of regular or random structure. In addition to the Curtis-Godson method, there are also a number of multiparameter approximations. Moreover, there are several semi-empirical methods for examining radiation transfer in an inhomogeneous atmosphere. They are discussed in some detail in Goody's monograph<sup>3</sup> and we shall not pause to consider them here.

The influence of temperature inhomogeneity on the intensity of radiation emitted by a molecular gas is also important when the emitted radiation is due to transitions between the ground and first excited vibrational states of the molecules. The power flux of radiation from any particular isothermal volume of the gas is then proportional to the spectral density of the radiation emitted by a perfect black body,  $e_\omega(T)$ , which is given by  $e_\omega \sim \exp(-\hbar\omega/T)$  when  $\hbar\omega \geq T$ , so that even small changes in temperature within the gas layer have an appreciable effect on its radiation characteristics.

Semiempirical modifications suffer from the disadvantage that any complication of the problem deprives us of the ability to estimate the precision of the final result. The above method, which is based on the comparison of the results obtained from the two physically opposite models, namely, the regular and the random models, is convenient in this respect. We shall demonstrate this by determining the average spectral power flux density from a plane layer of a molecular gas at a given frequency at right-angles to its boundary. We take the spectral density in the form

$$I_\omega = 2 \int_0^\infty f(u) du \int_0^u e_\omega[T(x)] \exp(-u'(x)) du'(x), \quad (4.3)$$

where  $f(u)$  is the appropriate distribution function and  $u'(x)$  is the optical thickness of the gas layer between the point  $x$  and the boundary through which the radiation escapes. This formula follows from the definition of the power flux emitted at right-angles to the surface. The inner integral is the required spectral density corresponding to optical thickness  $u$ . The second integral

gives the average over the optical thickness. When the gas temperature is constant, we have  $I_\omega = 2e_\omega A(\omega)$ , where  $A(\omega) = \int_0^\infty (1 - e^{-u})f(u)du$  is the absorption function [see (3.24)]. This follows from the physical meaning of the spectral power flux density.

We now introduce  $z(x) = [u'(x)/u](0 \leq z \leq 1)$  and rewrite (4.3) for the Lorentz profile of a spectral line in the case where the average separation between neighboring lines is much greater than their width and the optical thickness of the line center is large ( $u_{\max} \gg 1$ ). If we use (3.22) for the distribution function within the framework of the regular model, we obtain

$$I_\omega = 2 \int_0^1 e_\omega [T(z)] \sqrt{\frac{u_{\min}(\omega)}{\pi z(x)}} \exp(-u_{\min}(\omega)z(x)) dz, \quad (4.4)$$

where  $u_{\min} = (\pi/2d^2) \int_0^L S(x)\gamma(x)dx$  is the generalization of the parameter  $u_{\min}$  to the case of an inhomogeneous medium.

In the case of the random model, substitution of (3.23) in (4.3) yields

$$I_\omega = 2 \int_0^1 e_\omega [T(z(x))] \sqrt{\frac{u_{\min}(\omega)}{\pi z(x)}} \exp[-2\sqrt{\frac{u_{\min}(\omega)z(x)}{\pi}}] dx. \quad (4.5)$$

In the limit  $u_{\min} \ll 1$ , when the regular and random models go over into the isolated-line model, we can set the exponentials in (4.4) and (4.5) equal to unity and obtain the same result, namely,

$$I_\omega = \int_0^1 e_\omega [T(z)] \sqrt{\frac{u_{\min}(\omega)}{\pi z}} dz. \quad (4.6)$$

This formula corresponds to  $u_{\max} \gg 1$ , i.e., the case where the molecular gas layer is opaque at the centers of the strongest lines. In the other limiting case ( $u_{\max} \ll 1$ ) when the gas layer is optically transparent throughout the frequency range, we can use (2.15), (2.16), and (4.3) and obtain the following simple expression for the radiant flux emitted at right-angles to the layer boundary:

$$I = \int I_\omega d\omega = \frac{\hbar\omega_0}{4\tau} \int N^*(x) dx; \quad (4.7)$$

where  $N^*(x)$  is the density of vibrationally excited molecules, which depends on the coordinate  $x$ ,  $\tau$  is the radiative lifetime of the excited molecule for the particular vibrational transitions, and  $\omega_0$  is the zeroth frequency of this transition.

If the temperature is constant throughout the layer, we find that, in the case of the regular model, Eq. (4.4) yields

$$I_\omega = 2e_\omega A(\omega), \quad A(\omega) = \text{erf} \sqrt{u_{\min}(\omega)}, \quad (4.8a)$$

whereas the random model gives [see (4.5)]

$$I_\omega = 2e_\omega A(\omega), \quad A(\omega) = 1 - \exp\left(-2\sqrt{\frac{u_{\min}(\omega)}{\pi}}\right). \quad (4.8b)$$

The maximum difference between these formulas is 20% and occurs for  $u_{\min} = 1.27$ . The formulas given by (4.8a) and (4.8b) are generalizations of (3.11) and (3.20) to the case where the line intensity  $S$  and linewidth  $\gamma$  are functions of height of the layer.

If we know the function  $T(x)$ , we can calculate the "perpendicular" intensity emitted by the layer using

(4.3) and, in the case of the Lorentz profile, using directly (4.4) and (4.5). There is, however, another method, namely, the asymptotic method based on the slow variation of temperature within the gas layer.<sup>37,44,45</sup> Its principle is as follows. The radiation escaping through the boundaries of the layer originates mainly from a certain region within the layer. We shall suppose that the gas temperature in this region and, consequently, the spectral density  $e_\omega[T(x)]$  vary relatively slowly in that region. This corresponds to

$$\frac{\hbar\omega\delta T}{T^2} \ll 1, \quad (4.9)$$

where  $\delta T$  can be interpreted as the characteristic change in temperature within the region responsible for the escaping radiation. We now expand  $e_\omega[T(x)]$  in (4.3) into a series in powers of  $z$  around a certain point  $z(x_\omega)$ . The value of  $z(x_\omega)$  will be determined from the condition that the integral of the linear term of the expansion must be zero. Retaining only the first two terms in the expansion in terms of the small parameter given by (4.9), we obtain the following expression for the required spectral power flux density:

$$I_\omega = 2e_\omega [T_\omega] A(u_{\min}(\omega)), \quad (4.10)$$

where  $T_\omega \equiv T(x_\omega)$ . We have thus reduced the problem to that of the emission of radiation by an isothermal gas layer held at some effective temperature  $T_\omega$ . The accuracy of this method depends on the sum of terms of the series that have been neglected.<sup>57</sup>

We shall illustrate the asymptotic method by evaluating the intensity  $I_\omega$  for  $u_{\min}(\omega) \gg 1$  and  $u_{\min}(\omega) \ll 1$ . We shall assume, for simplicity, that the vibrational transition energy  $\hbar\omega_0$  is large in comparison with the temperature, so that  $e_\omega(T) \sim \exp(-\hbar\omega/T)$ . Let us take  $u_{\min}(\omega) \gg 1$  first. The main contribution to the final result is due to  $z \sim 1/[u_{\min}(\omega)]$ . In the neighborhood of this point, we have

$$e_\omega [T(z(x))] = e_\omega [T(z_0)] \exp\left[-\frac{\hbar\omega}{T^2} T'(z_0)(z-z_0)\right], \quad z_0 = z(x_\omega). \quad (4.11)$$

Hence, for the regular model (we take the line profile to be of the Lorentz shape), we have

$$I_\omega = e_\omega [T(z_0)] \int_0^1 \exp\left[-\frac{\hbar\omega}{T^2} T'(z_0)(z-z_0)\right] \sqrt{\frac{u_{\min}(\omega)}{\pi z}} \times \exp(-u_{\min}(\omega)z) dz = e_\omega [T(z_0)], \quad (4.12)$$

where  $z_0$  is determined by demanding that the integral must be equal to unity:

$$z_0 = \frac{1}{2u_{\min}(\omega)}. \quad (4.13)$$

For the random model, (4.5) gives

$$I_\omega = e_\omega [T(z_0)] \int_0^1 \exp\left[-\frac{\hbar\omega}{T^2} T'(z_0)(z-z_0)\right] \times \sqrt{\frac{u_{\min}(\omega)}{\pi z}} \exp\left[-2\sqrt{\frac{u_{\min}(\omega)z}{\pi}}\right] dz = e_\omega [T(z_0)], \quad (4.14)$$

$$z_0 = \frac{\pi}{2u_{\min}(\omega)}. \quad (4.15)$$

In both cases, condition (4.9) now takes the form

$$\frac{\hbar\omega}{u_{\min}(\omega)T^2} |T'(z_0)| \ll 1. \quad (4.16)$$

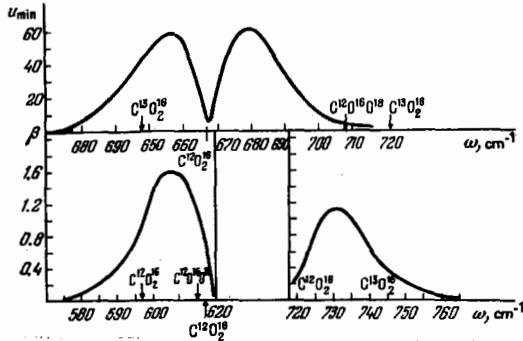


FIG. 6. The function  $u_{\min}(\omega)$  for carbon dioxide in the terrestrial atmosphere. Vertical lines show zeroth frequencies of fundamental vibrational transitions in carbon dioxide molecules and their isotopes.

When  $u_{\min}(\omega) \ll 1$ , Eqs. (4.4) and (4.5) give

$$I_{\omega} = e_{\omega} [T(z_0)] \cdot 2 \sqrt{\pi u_{\min}(\omega)}, \quad (4.17)$$

$$z_0 = \frac{f}{3}, \quad (4.18)$$

and (4.3) assumes the form

$$\frac{h\omega\Delta T}{T^3} \ll 1, \quad (4.19)$$

where  $\Delta T$  is the temperature drop across the entire gas layer.

The convenience of the above method in the case of the random model lies in that it does not become more complicated when several bands are found to overlap. This is not unexpected because, in the random model, the overlapping of several bands is equivalent to the presence of one band with intensity distribution  $P(S) = \sum_k (d/a_k) \delta(S - S_k)$  (see Sec. 3). If we use the distribution function  $f_{\text{rand}}(u)$  given by Eq. (A4) in the Appendix, we find from (4.3) that the spectral power flux density from a plane layer, emitted at right-angles to its surface, is

$$I_{\omega} = 2 \int_0^1 e_{\omega} [T(z(x))] \sum_k \sqrt{\frac{u_{k \min}(\omega)}{\pi x(x)}} \times \exp\left(-2 \sum_k \sqrt{\frac{u_{k \min}(\omega) z(x)}{\pi}}\right) dx. \quad (4.20)$$

Comparison of (4.20) with (4.5) will readily show that, in an inhomogeneous gas medium (just as in the uniform isothermal gas), the transition from an individual vibration-rotation band to a set of overlapping bands is equivalent to the replacement

$$\sqrt{u_{\min}(\omega)} \rightarrow \sum_k \sqrt{u_{k \min}(\omega)}$$

in the formulas for the average spectral characteristics of the emitted radiation.

Thus, the combination of the random model and the

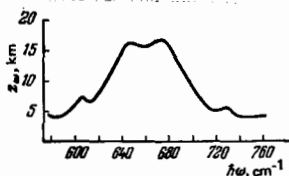


FIG. 7. Height of the layer of Earth's atmosphere in which radiant flux of frequency  $\omega$ , which escapes into the surrounding space, originates [the temperature of this layer appears in (4.10)].

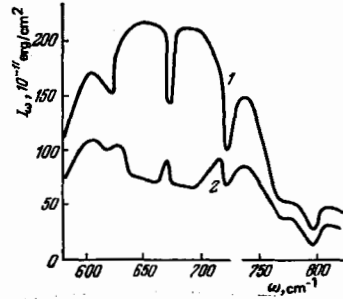


FIG. 8. Average spectral powerflux density due to atmospheric carbon dioxide plotted against frequency:<sup>67</sup> 1—radiant flux incident on the Earth's surface, 2—radiant flux escaping from the atmosphere into surrounding space.

asymptotic method can be used to determine the characteristics of infrared radiation transfer in a molecular gas layer when several bands are found to overlap. Figures 6–8 demonstrate this in the case of radiation emitted by carbon dioxide gas in the real atmosphere. This radiation is produced by eight overlapping bands. The most important are those corresponding to the vibrational transitions  $00^0 - 01^0$ ,  $01^10 - 02^00$ ,  $01^10 - 10^00$  with frequencies  $\omega_0$  respectively equal to 667.4, 617, and 721  $\text{cm}^{-1}$ . Figure 6 shows the minimum optical thickness  $u_{\min}(\omega)$  at a given frequency, and Fig. 7 shows the height of the layer responsible for the atmospheric emission at a given frequency [the temperature of this layer appears in (4.10) which gives the spectral power flux density escaping into surrounding space]. Figure 8 shows the radiation fluxes produced by the carbon dioxide gas that fall on the Earth's surface and escape beyond the limits of the atmosphere.<sup>2)</sup> These calculations were based on the parameters of the standard atmosphere.<sup>3)</sup>

One of the important aspects of this problem is the accuracy of the calculations. This is determined by two factors, namely, the uncertainty introduced by the use of the random model of a band and the uncertainty due to the use of the asymptotic theory. The former has already been examined, whereas the latter is connected with the use of the small parameter defined by (4.9) and can be estimated by examining the neglected terms. In particular, in the above example of atmospheric carbon dioxide, the error introduced by using the asymptotic method to obtain the resultant radiant flux escaping beyond the limits of the atmosphere turns out to be 4%, whereas the error in the flux falling on the Earth's surface is 2%. For the radiant flux emitted at right-angles to the Earth's surface, the error is 4% and 7%, respectively. It is clear that the uncertainty introduced by using the asymptotic method for the temperature-inhomogeneous gas layer does not exceed, in this case, the error due to the use of the random model.

## B. Transfer of infrared radiation in a nonequilibrium molecular gas

A new situation arises when radiation upsets thermodynamic equilibrium. If the time necessary for a ra-

<sup>2)</sup>For brevity, we shall henceforth refer to the radiation power flux simply as the radiant flux.

diative transition is less than the time for quenching a vibration-rotation state of a molecule by collision, the distribution of the molecules over the vibrational states is different from the Boltzmann distribution, and the propagation of radiation through the medium affects the population of vibration-rotation states. This has been examined in some detail in the case of atomic gases with one emission line (see, for example, Refs. 18 and 58). The population of excited states is then given by the Biberman-Holstein equation,<sup>59,60</sup> and can frequently be found from the formula

$$N^*(\mathbf{r}) = N_B^* \frac{k_{rel} \tau N}{k_{rel} \tau N + D(\mathbf{r})}; \quad (4.21)$$

where  $N_B^*$  is the density of excited particles in thermodynamic equilibrium, described by the Boltzmann distribution, and  $k_{rel}$  is the rate constant for the quenching of excited states by collision with gas particles;  $N$  is the density of these particles,  $\tau$  is the radiative transition time, and  $D(\mathbf{r})$  is the probability that a photon emitted at point  $\mathbf{r}$  succeeds in leaving the system without absorption. This formula has a simple physical interpretation (see Refs. 61 and 62 for the range of its validity). If the collisional relaxation time of the excited states,  $(Nk_{rel})^{-1}$ , is much less than the radiative lifetime  $\tau$ , the Boltzmann distribution over the excited states follows from (4.21) (since  $D \leq 1$ ). Next, if radiation is trapped within the volume, so that  $D \ll Nk_{rel}\tau$ , thermodynamic equilibrium is not upset either, because the characteristic time for the escape of a photon from the volume is long in comparison with the excited-state relaxation time due to collisions.

It is clear that, when the isolated-line model is valid, the theory of resonance-radiation transfer within individual lines can be extended to the case of infrared radiation transfer in a molecular gas. However, in the case of molecular gases, the distribution over vibrational and rotational states is important. The most interesting case from this point of view is that where the distribution over the rotational states corresponds to thermodynamic equilibrium whereas the distribution over the vibrational states departs from equilibrium. There is a relatively broad range of gas densities for which these conditions are satisfied. The gas densities must then lie within the range

$$\frac{1}{k_r \tau} = N_r \ll N \ll N_v = \frac{1}{k_v \tau}, \quad (4.22)$$

where  $k_v$  and  $k_r$  are the vibrational and rotational relaxation constants, and  $k_v \ll k_r$ . One can verify that this range is broad enough by examining Table VI which lists the values of the densities  $N_r$  and  $N_v$  for a number of vibrational transitions in  $\text{CO}_2$  in terrestrial, Martian, and Venusian atmospheres.<sup>63</sup> The rate constants

TABLE VI. Values of  $N_r$  and  $N_v$  for vibrational transitions in  $\text{CO}_2$  in terrestrial, martian, and venusian atmospheres.

Vibrational transition	Earth		Mars		Venus	
	0001 - 0000	0110 - 0000	0001 - 0000	0110 - 0000	0001 - 0000	0110 - 0000
$N_r$ , $\text{cm}^{-3}$	$10^{12}$	$10^{10}$	$10^{12}$	$10^{10}$	$10^{12}$	$10^{10}$
$N_v$ , $\text{cm}^{-3}$	$3 \cdot 10^{17}$	$10^{15}$	$6 \cdot 10^{16}$	$3 \cdot 10^{14}$	$6 \cdot 10^{16}$	$3 \cdot 10^{14}$

for the processes are taken for the temperature of the layer at the height at which the atmospheric density is  $N_v$ .

In the case of the equilibrium distribution of molecules over the vibrational states, the physical picture of infrared radiation transfer (we are considering an individual vibration-rotation band) is similar to the transfer of resonance radiation even when there is considerable overlap between the spectral lines in the band.<sup>64</sup> However, in this case, the profile of the molecular band plays the role of the resonance line profile and, in many cases, the former is the product of a smooth and a rapidly oscillating function of frequency. The form of the smooth function, which represents the variation in the amplitude of the oscillations with frequency, is determined by the Boltzmann distribution of the molecules over the vibrational states. The rapidly oscillating function, on the other hand, is determined by the shape of the spectral lines associated with vibration-rotation transitions and the separation between neighboring lines. The concentration of the vibrationally excited molecules can be found from the Biberman-Holstein formula:

$$\int G(\mathbf{r}, \mathbf{r}') y(\mathbf{r}') d\mathbf{r}' + \beta - (1 + \beta) y(\mathbf{r}) = 0, \quad (4.23)$$

where  $y(\mathbf{r}) = N^*(\mathbf{r})/N_B^*$ , and  $\beta = k_v N \tau$  is the number of events of quenching of vibrational excitation during the spontaneous emission time. The Green's function can, in general, be written in terms of the distribution over the optical thickness.<sup>64</sup>

The question of thermodynamic equilibrium in a layer of a molecular gas of characteristic linear dimensions  $L$  can be readily resolved if we find the quantity

$$D(L) = \int_{-\infty}^{+\infty} b(\omega - \omega_0) \exp[-Sb(\omega - \omega_0)L] d(\omega - \omega_0), \quad (4.24)$$

i.e., the probability that a photon will traverse a path  $L$  without absorption. In (4.24)  $S$  is the integrated band intensity and  $b(\omega - \omega_0)$  is the frequency distribution function characterizing the shape of the molecular band profile ( $\int_{-\infty}^{+\infty} b(\omega - \omega_0) d(\omega - \omega_0)$ ). When  $D(L) \ll \beta$ , and  $k_{rel} = k_v$ , it is clear from (4.21) that thermodynamic equilibrium occurs in the interior of the gas layer (it may be upset near the boundaries of the layer).

We must now find the probability  $D(L)$  in the case when the function  $b(\omega - \omega_0)$  corresponds to an individual vibration-rotation band of a linear molecule. Comparison of (4.24) with (2.7) will readily show that

$$D(L) = \frac{dW(SL)}{d(SL)}. \quad (4.25)$$

In the limit  $u_{\min}(\omega_{\max}) \ll 1$ , when the overlap of individual lines can be neglected, we can use (3.9) and show that for a Lorentz line profile ( $\gamma \ll 2B/\hbar$ ):

$$D(L) = 0.76 \frac{1}{V u_{\max}(\omega_{\max})}. \quad (4.26)$$

In deriving this expression, we used the fact that

$$u_{\min}(\omega_{\max}) = \left(\frac{\pi \hbar \gamma}{4B}\right)^2 u_{\max}(\omega_{\max}) = \frac{2SL}{\pi \gamma} \left(\frac{\pi \hbar \gamma}{4B}\right)^2 \sqrt{\frac{B}{2\epsilon T}}.$$

We recall that (4.26) is practically the same as the result for an individual Lorentz line if the optical thick-

ness of the gas layer at the line center is  $u_{\max} \gg 1$ . The reason for this agreement is that the main contribution to  $D(L)$  in the case of the molecular band is provided by strong lines for which  $u_{\max} \gg 1$ . A different situation occurs in the case of Doppler broadening. Here it follows from (3.11) that the equivalent width of the Doppler line is a logarithmic function of  $u_{\max}$  for  $u_{\max} \gg 1$ . The main contribution to  $D(L)$  in the molecular band is therefore provided by lines for which  $u_{\max} \sim 1$ . Direct calculation based on (4.24) yields<sup>64</sup>

$$D(L) = \frac{\sqrt{\pi}}{2u_{\max}(\omega_{\max})} \quad (4.27)$$

The probability  $D(L)$  given by (4.27) is in this case much greater than the analogous probability in the case of an individual Doppler line.

In the other limiting case, when  $u_{\min}(\omega_{\max}) \gg 1$ , the integrated characteristics of infrared radiation are largely determined by the shape of the envelopes  $u_{\min}(\omega)$  and  $u_{\max}(\omega)$ . If we use (3.15) and (4.25), we find that, for the Lorentz profile,

$$D(L) \sim \sqrt{\frac{T}{B}} \frac{\gamma}{W u_{\min}(\omega_{\max})} \quad (4.28)$$

The above results can be generalized to the case of an inhomogeneous gaseous medium if the characteristic variation in the temperature of the gas layer is small in comparison with the temperature itself. This enables us to consider the transfer of infrared radiation in the absence of thermodynamic equilibrium in the real atmosphere. As an example, Fig. 9 shows the concentration of  $\text{CO}_2$  molecules in the  $01^1_0$  state as a function of height in the terrestrial atmosphere. These data are not very different from numerical calculations (see, for example, Ref. 65).

### C. Transfer of infrared radiation and thermal balance of planets

The propagation of infrared radiation in planetary atmospheres has an important effect on thermal balance. This is why the above model can be used to perform numerical estimates of the contribution of individual components of the atmosphere to its thermal state. When taken together with the physicochemical processes occurring in the atmosphere, this enables us to reconstruct the evolution of planetary atmospheres in the past, and to establish the tendencies which they are likely to follow in the future. Let us consider some problems of this kind in relation to the Earth's atmosphere.

According to contemporary ideas about the history of our planet,<sup>66-69</sup> the Earth's atmosphere was initially very tenuous. It did not contribute to the thermal balance of the Earth, and the Earth's surface temperature was low. However, the surface temperature rose as more carbon dioxide was released into the atmosphere from the Earth. This was due to the infrared radiation flux arriving from the atmosphere onto the Earth's surface and originating from carbon dioxide molecules in the atmosphere. The increased temperature of the surface gave rise to an increase in the amount of water vapor in the atmosphere, which enhanced still further

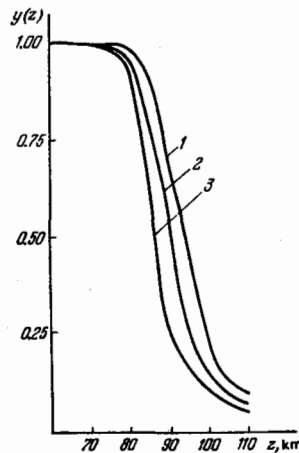


FIG. 9. Concentration of vibrationally excited  $\text{CO}_2$  molecules in the  $01^1_0$  state as a function of height in the Earth's atmosphere: curves 1-3 correspond to vibrational relaxation constants of  $2 \times 10^{-14}$ ,  $7.5 \times 10^{-25}$ , and  $3 \times 10^{-45}$   $\text{cm}^3/\text{sec}$  for  $T = 300$  K with a corresponding extrapolation into the region of lower temperatures;  $z$ —height of the atmosphere,  $y(z)$ —ratio of true concentration to its Boltzman value at the temperature corresponding to the height  $z$ .

the greenhouse effect. The eventual result of all these processes was that the temperature of the Earth rose until all the ice on the Earth's surface melted. Under these conditions, carbon dioxide, which was partially dissolved in water, could enter chemical reactions with silicates to form carbonates in sedimentary rocks. This led to a reduction in the amount of carbon dioxide in the atmosphere and to a stabilization of the thermal parameters of our planet. Figure 10 shows the variation in the composition of the atmosphere and the surface temperature of the Earth according to one version of these calculations.<sup>69</sup> It is clear that calculations concerned with the evolution of our atmosphere must include the formation and decomposition of the gaseous components of the atmosphere as well as the emission and absorption of photons by the atmosphere at each stage. At the same time, the theory of radiation transfer need not be too precise because many of the other parameters are uncertain and it is desirable to have the final relationships in a simple and readily interpretable form. All this is assured by the analytic approaches described above. We also note that the availability of a physical picture of the evolution of the Earth's atmosphere is quite important and valuable be-

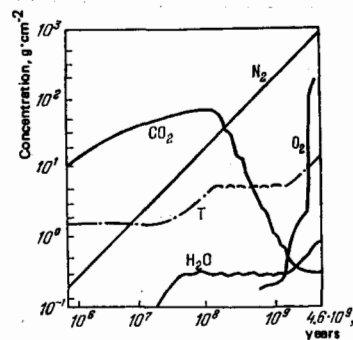


FIG. 10. Variation in the composition of the atmosphere and temperature of the Earth's surface during the evolution of the planet.



cause the history of the atmosphere determines much that is of value in the organic and inorganic world that is now available to mankind.

The other range of problems in the physics of the Earth's atmosphere is concerned with the influence of individual molecular components on the heat balance and climate of the Earth. An increase in the concentration of an individual molecular component in the atmosphere produces an increase in the flux of infrared radiation onto the Earth's surface due to the molecules of this component. Thus, an increase in the concentration of molecules of a particular species in the atmosphere gives rise to an increase in the temperature of the Earth's surface.

The rise in the surface temperature of the Earth due to the accumulation of carbon dioxide in the atmosphere has been examined in considerable detail.<sup>44,70-72</sup> Atmospheric carbon dioxide plays an important role in the heat balance of the Earth. The Earth's surface temperature would fall by 10-12° if carbon dioxide were to be removed from the atmosphere. An increase in the amount of carbon dioxide in the atmosphere by a factor of two, on the assumption that the atmosphere is transparent in the region of absorption by carbon dioxide molecules, would produce a rise of 1.5-3 degrees in surface temperature. The discrepancy between different published calculations<sup>70-79</sup> is due to the different way in which the spectrum of carbon dioxide was represented, to the different distribution of temperature with height in this atmosphere, and to the different way of separating the additional flux of radiation falling on the Earth's surface along different channels of the Earth's heat balance.

An increase in the concentration of carbon dioxide in the terrestrial atmosphere has, in fact, been observed and is connected with the most intensive activity of Man, namely, the combustion of fossil fuels (oil, coal, and gas). This is why the problem of changes in the thermal balance of the Earth due to the accumulation in the atmosphere of carbon dioxide of anthropogenic origin is very important. Figure 11 shows the change in the surface temperature of the Earth as a function of the concentration of carbon dioxide in the atmosphere for different atmospheric humidities.<sup>79 3)</sup> The absorption spectrum of water molecules overlaps the absorption spectrum of carbon dioxide, so that water vapor in the atmosphere provides the strongest masking of changes in the optical properties of the atmosphere in the infrared due to the increase in carbon dioxide concentration.

The accumulation of atmospheric carbon dioxide is the most dramatic consequence of the influence of Man on the composition of the terrestrial atmosphere. However, there are less intensive effects of this kind which can occur with or without the participation of Man and affect the heat balance of the Earth. For example, Fig. 12 shows the variation in the surface tem-

<sup>3)</sup>The average humidity in the atmosphere was taken as 60%, in accordance with the parameters of the standard atmosphere.<sup>80</sup>

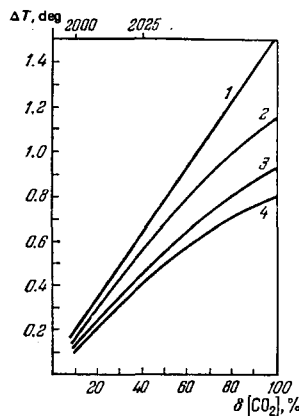


FIG. 11. Temperature variation of the Earth's surface plotted against the concentration of atmospheric carbon dioxide: curves 1-4 correspond to atmospheric humidities of 0%, 20%, 70%, and 100%,<sup>79</sup>  $\delta[\text{CO}_2]$ —increase in the concentration of  $\text{CO}_2$  from the present value ( $3.26 \times 10^{-4}$ ). The dates shown along the upper horizontal axis are given in accordance with the forecasts reported in Refs.<sup>81,82</sup> for the amounts of carbon dioxide in the atmosphere. The change  $\Delta T$  was calculated on the assumption that, according to published data,<sup>83,84</sup> 79% of energy dissipated by the Earth's surface is emitted in the form of thermal radiation. It was assumed that also the same fraction of the additional radiated flux  $\Delta I$  will be radiated, i.e.,  $\Delta T = 0.195 \Delta I / \sigma T^3$ , where  $\sigma$  is the Stefan-Boltzmann constant, and  $T$  is the Earth's surface temperature.

perature as a function of variation in the concentration of atmospheric methane.<sup>85</sup> Only that part of the emission of methane molecules that is not masked by water vapor was taken into account. The average concentration of methane near the Earth's surface is  $1.5 \times 10^{-6}$  and the average flux of methane molecules from the Earth's surface into the atmosphere (due to the decomposition of organic material in the soil) is  $2 \times 10^{11} - 3 \times 10^{11} \text{ cm}^{-2}$ .<sup>86</sup> The decomposition of methane in the atmosphere is connected with chemical reactions in which it participates, so that its lifetime in the atmosphere is roughly three years. It is clear from the figure that natural variations in atmospheric methane correspond to changes in the Earth's temperature by hundredths of a degree.

Several questions have arisen in recent years in relation to the effect of small atmospheric impurities on the Earth's heat balance (see, for example, Refs. 87-89). Semiempirical methods and approaches based on computer technology are unsuitable for this type of estimate. On the other hand, from the point of view of analytic approaches, this case is the most convenient because low density provides us with a small param-

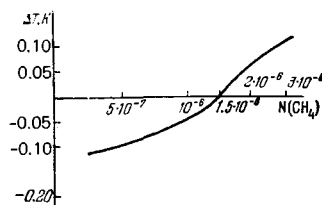


FIG. 12. Change in Earth's temperature as a function of the concentration of atmospheric methane. It was assumed that  $\Delta T = 0$  for average methane concentration of  $1.5 \times 10^{-6}$  (Ref. 85).

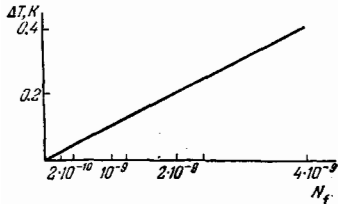


FIG. 13. Change in Earth's temperature as a function of the concentration of freons in the atmosphere ( $N_f$  is the total concentration of freons).

eter of the theory, and lines corresponding to individual transitions do not overlap. The situation is particularly simple when the optical thickness of the atmosphere at the line center of the strongest transition is small in comparison with unity. The radiation flux due to the small molecular impurity is then given by (4.7) and is independent of the line-broadening parameters.

Figure 13 shows the temperature of the Earth's surface as a function of the concentration of freons ( $\text{CCl}_2\text{F}_2$  and  $\text{CCl}_3\text{F}$ ) in the atmosphere. It was assumed that the atmosphere was optically transparent for photons emitted by freon molecules in the band  $800\text{--}1200\text{ cm}^{-1}$ . The additional flux of radiation falling from the atmosphere onto the Earth's surface as a result of the emission of radiation by atmospheric freons is calculated from (4.7). The present concentration of freons in the atmosphere is  $2 \times 10^{-10}$ , but an increase in this concentration by an order of magnitude would produce an increase of 0.2 degrees in the Earth's temperature, which is in agreement with Refs. 88–89. With the modern level of industrial activity, this increase in the concentration of freons may occur over a period of a few decades, since the lifetime of freons in the atmosphere is also of the order of a few decades.<sup>90–93</sup>

We note one further feature of the effect of molecular components on the heat balance of the Earth. According to (3.10) and (3.11), the equivalent width  $W$  of an absorption band in the isolated-line model (large optical thickness at the line centers) with collision broadening is proportional to  $\sqrt{N_1 N}$ , where  $N_1$  is the density of molecules of the particular component and  $N$  is the total density of the atmosphere. If, on the other hand, the optical thickness of the atmosphere at the line centers is small, then  $W \sim N_1$ . Hence, it follows that the surface layer of the atmosphere plays the dominant role in molecular infrared emission by low-concentration impurities. For example, the density of ozone near the Earth's surface is, on the average, about  $10^{12}\text{ cm}^{-3}$ , whereas, at heights of 30–40 km, the concentration is  $4 \times 10^{12} - 0.5 \times 10^{12}\text{ cm}^{-3}$ .<sup>94,95</sup> Thereafter, the ozone concentration declines rapidly. The product of ozone density by the density of air molecules near the Earth's surface is about  $2 \times 10^{31}\text{ cm}^{-6}$ . At 20 km, this quantity is just under  $10^{31}\text{ cm}^{-6}$ , whereas, at 30 km, it is equal to  $10^{30}\text{ cm}^{-6}$ . The effect of variations in ozone density in the stratosphere on the thermal balance of the Earth is therefore quite small. The total contribution of ozone to the thermal balance of the Earth, expressed in units of  $\Delta T$ , is 0.4 degrees.<sup>4)</sup> (This means

<sup>4)</sup>The flux of radiation onto the Earth's surface due to atmo-

that, if all ozone were to be removed from the Earth's atmosphere and the atmosphere were to become transparent near the center of the ozone absorption spectrum, the temperature of the Earth would fall by 0.4 degrees.) Hence, we may also conclude that the effect of infrared emission by molecular impurities in the stratosphere and in the upper layers of the atmosphere on the thermal balance of the Earth is not smaller than the influence of molecular impurities near the Earth's surface.

## 5. CONCLUSIONS

We have described the asymptotic methods of the theory of infrared radiation transfer in molecular gases. They are based on models of vibration-rotation bands. Particular attention was devoted to the simplest approaches leading to output data whose precision can be estimated. Such approaches are interesting in two respects. On the one hand, they readily yield semiquantitative solutions of problems connected with the influence of radiation transfer processes on different phenomena and on the characteristics of the gas as functions of its parameters. We gave a number of examples of this kind which were connected with the elucidation of the effects of individual molecular components of the atmosphere on the thermal balance of the Earth. The number of such problems is continuously increasing in the context of studies of the ecology of the atmosphere and of the properties of other planets. Asymptotic methods are particularly convenient when qualitative solutions are sufficient.

On the other hand, the methods that we have reviewed are also convenient in the mathematical solution of global problems on the transport of gas layers in the atmosphere and in laboratory systems. They enable us to set up simple algorithms that take into account infrared radiation transfer during complicated processes. This means that mathematical models providing satisfactory descriptions of complicated real phenomena (e.g., in weather forecasting) can be developed with the aid of modern computers.

## APPENDIX

### Derivation of the expression for $f_{\text{rand}}(u)$

We shall begin by assuming that all the lines in the band have the same intensity. We introduce the char-

spheric ozone was estimated within the framework of the isolated-line model, assuming atmospheric lack of transparency at frequencies corresponding to the centers of the strongest lines. The radiant flux due to an individual line is given by<sup>8,20</sup> (see Sec. 4, subsec. A for notation):

$$J = 2 \int d\omega \int_0^1 ds e_{\omega} [T(z)] \int_0^{\infty} dt e^{-z u n(\omega) t} u_n(\omega) t^{-2},$$

and, in the case of the Lorentz profile, this becomes

$$J = \frac{2}{3} \int_0^1 \frac{e_{\omega} [T(z)]}{\sqrt{z}} \sqrt{2} \int S_n(x) \gamma(x) dx dz.$$

The intensity of an individual line was estimated from the known integrated intensity within the band and the fact that the number of strong lines in the band is  $\sim (T/B)^{3/2}$  (see Sec. 3).

acteristic function

$$\chi(t) = \int_0^{\infty} e^{itu} f(u) du = \prod_h \int_0^{\infty} e^{itu_n} p(u_n) du_n = \prod_n \chi_n(t), \quad (\text{A.1})$$

where  $\chi_n(t)$  is the characteristic function for optical thickness  $u_n$  due to the  $n$ -th line and  $p(u_n)du_n$  is the probability that  $u_n$  will lie between  $u_n$  and  $u_n + du_n$ . We have used the fact that the total optical thickness of the layer is given by

$$u = \sum_n u_n, \quad f(u) = \int_0^{\infty} \dots \int_0^{\infty} p(u_n) \delta(u - \sum_n u_n) du_n.$$

Inverting (A.1), we obtain for the probability of having a given value

$$f(u) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \chi(t) \exp(-itu) dt. \quad (\text{A.2})$$

Let us now consider a large number of lines in a frequency interval  $\Delta\omega$ . In the random model, the probability that the center of the  $n$ -th line will lie at a distance between  $\omega_n$  and  $\omega_n + d\omega_n$  from the frequency interval  $d\omega_n$  is  $d\omega_n/\Delta\omega$ . Hence we find that the characteristic function for  $u_n$  is:

$$\chi_n(t) = \frac{1}{\Delta\omega} \int \exp(itu_n(\omega)) d\omega_n = 1 + \frac{1}{\Delta\omega} \int [\exp(itu_n(\omega) - 1)] d\omega_n.$$

Since, as  $\Delta\omega \rightarrow \infty$  the function  $\chi_n(t) \rightarrow 1$ , we have in this limiting case

$$\ln \chi_n(t) = \int \frac{1}{\Delta\omega} [\exp(itu_n(\omega)) - 1] d\omega_n.$$

Hence

$$\ln \chi(t) = \sum_n \ln \chi_n(t) = \frac{\Delta\omega}{d} \ln \chi_n(t), \quad (\text{A.3})$$

where  $d$  is the average line spacing. In deriving (A.3), we assumed that  $\chi_n(t)$  was the same for all lines. From (A.2) and (A.3), we then have the required distribution function:

$$f(u) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp\left\{-itu - \frac{1}{d} \int_{-\infty}^{+\infty} [1 - \exp(itSLa(\omega))] d(\omega - \omega_0)\right\} dt,$$

where  $a(\omega)$  is the shape of the spectral line and  $SLa(\omega)$  determines the optical thickness  $u_n$  due to an individual line. For simplicity, it was assumed here that the intensities and line shapes were the same at all points of the gas. If the lines have a certain intensity distribution  $P(S) \int_0^{\infty} P(S) dS = 1$ , then (A.3) must be augmented by integration with respect to  $dS$  with the weight  $P(S)$ , and the formula for  $f(u)$  becomes

$$f(u) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp\left[-itu - \frac{1}{d} \int_0^{\infty} P(S) dS \int_{-\infty}^{+\infty} [1 - \exp(itSLa(\omega))] d(\omega - \omega_0)\right] dt. \quad (\text{A.4})$$

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