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Broadening of Spectral lines in Emission of Atomic and Molecular Gases

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ABSTRACT: An analogy is shown for broadening the spectral line of atoms in the case of competition between the short-range Doppler broadening mechanism and the long-range broadening mechanism, as well as for the absorption band of a molecular gas in the infrared (IR) spectral range, where a long-range part of the spectrum is also determined by the impact mechanism of the broadening, and the long-range part in the pedestal region the absorption band is associated with the distribution of molecules over the rotational states, and in the region of the wings of the absorption band, it is due to the finite time of collisions involving emitting molecules. The flux of resonance radiation produced by an excited atomic gas is estimated using the concepts of the spectral emission band of a high optical thickness of the gas. These concepts are used for a molecular gas where, in the framework of the regular model (the Elsasser model), expressions are obtained for the absorption coefficient related to a specific spectral absorption band, separately in the pedestal region and for the wings of the absorption band. As a demonstration of the possibilities of these concepts, based on them, the IR radiative flux was calculated on the surface of Venus from its atmosphere, which includes seven vibrational transitions of the carbon dioxide molecule and amounts to 26% of the total flux of IR radiation emitted by the surface of Venus. An analysis of the energy balance of Venus leads to the conclusion that the bulk of the IR radiation of the atmosphere of Venus falling on its surface is formed by microscopic dust in the atmosphere of Venus. This channel of the energy balance of Venus is realized if the mass of microscopic dust in the atmosphere of Venus is seven orders of magnitude less than the mass of atmospheric carbon dioxide. The absorption band model and the line-by-line model are compared in evaluation of the radiative flux toward the Earth's surface. This comparison exhibits that the absorption band model is suitable for evaluation of the radiative flux, but is characterized by a low accuracy in evaluation of its derivative over the concentration of emitting molecules.

1. INTRODUCTION

In the classical case, the Voigt profile for the spectral line is caused by the competition between the Doppler and Lorentz profiles of the spectral lines and is discussed for more than a hundred years [1]. This problem arises from the emission of resonantly excited atoms [2]. The tables of profiles of the spectral line [3] are created taking into account the competition of these spectral line broadening mechanisms at different ratios between line widths for the mechanisms under consideration.

The peculiarity of such competition is that the Lorentz broadening mechanism leads to a weak frequency dependence for the photon distribution function with respect to frequencies, whereas the Doppler broadening mechanism gives a sharp dependence on the frequency at the tail the photon distribution function. As a result, we find that the wing of the spectral line is determined by the Lorentz broadening mechanism, even in the limit of low number densities of a perturbed gas, when the Lorentz width of the spectral line is small in comparison with the Doppler width. In analyzing the competition between the Doppler and collisional mechanisms for broadening the spectral lines with different dependence of the photon distribution function on the frequency on the line wing, it is significant that the modified Voigt profile, taking into account the dependence of the collision rate on the emitted atom velocity, differs from the classical Voigt profile [4, 5, 6, 7].

The competition of different mechanisms of broadening of the spectral band takes place in molecular gases for the IR spectral range, created as a result of vibrational-rotational transitions of molecules. Then the emission or absorption spectrum of molecules results from individual vibrational-rotational transitions related to different values of the rotational molecular momenta. At high pressures of a perturbed gas, the neighboring broadened spectral lines are overlapped, so that the profile of the spectral absorption or emission band takes the form of the Voigt profile, which is confirmed by the rich information on spectral parameters of molecules in gases collected in the bank HITRAN [8] of spectral data for molecules. In this case, the Doppler part of the photon distribution function over frequencies for atoms is replaced by the distribution function over rotational states of molecules for transitions in molecules. Then the Voigt profile of the spectral band is realized at not low temperatures, when the spectral band is formed from many rotational transitions, and also at higher pressures than in the atomic case.

It is important that the spectral absorption band of molecular gases cannot be extended to band wings, whose frequency shift from the central part of the band exceeds an inverse collision time of emitted molecules with molecules of a perturbed gas. It is necessary to add to this that the difference in the interaction potentials of the emitted and perturbed molecules for the states of the radiative transition is small compared the interaction potentials for each of the transition states, that also restricts the limiting absorption band width for a given vibrational transition. Namely, the width of the absorption band determines the radiation flux created by these molecules due to vibrational transitions. The goal of this paper is to analyze the mechanisms of spectral lines broadening and their effect on the emission intensity of molecular gases.

2. VOIGT PROFILE OF SPECTRAL LINE IN ATOMIC GAS

We first estimate parameters of an atomic gas if the Doppler (or similar) broadening mechanism of spectral lines competes with the impact broadening resulted from collisions of an emitting atomic particle with perturbed particles in a gas. For definiteness, we will be guided by a simple atomic system, sodium vapor in the buffer gas, as well as carbon dioxide as a molecular system or its component. In this case, the distribution function of photons over frequencies a_ω due to a short-range broadening is described by the Lorentz distribution function

$$a_\omega = \frac{\nu}{2\pi[(\omega-\omega_o)^2+(\nu/2)^2]} \tag{1}$$

and the Doppler broadening in accordance with formula

$$b_\omega = \frac{2}{\Delta\omega\sqrt{\pi}}\exp\left[-\frac{(\omega-\omega_o)^2}{\Delta\omega^2}\right] \tag{2}$$

Here ν is the width of the spectral line for the short-range broadening mechanism, ω_o is the photon frequency at the line center, $\Delta\omega$ is the line width for the Doppler broadening, which in the case of the Maxwellian velocity distribution is given by formula

$$\Delta\omega = \omega_o\sqrt{\frac{2T}{mc^2}}, \tag{3}$$

where T is the gas temperature, c is the speed of light, and m is the atom mass. In the case of a sodium vapor at a typical temperature $T = 500K$ the line width is $\Delta\omega = 0.034cm^{-1}$. Combining the broadening mechanisms under consideration, we have, in accordance with the general principles of broadening of the spectral line [9, 10] for the photon distribution function f_ω with respect to frequencies

$$f_\omega = \int_{-\infty}^{\infty} a_{\omega'} b_{\omega'} d\omega' \tag{4}$$

The peculiarity of the Voigt profile is connected with its sharply varying pedestal in the frequency space, as well as the slowly varying function of the photon frequency distribution at the wings of the spectral line.

Let us consider this competition for the example of sodium vapor. The strong interaction of resonantly excited atoms with atoms in the ground state is determined by excitation transfer in the course of interaction between these atoms. The interaction potential between them has the dipole-dipole form. Collision of these atoms, along with elastic atom scattering, includes processes of excitation transfer and rotation of the angular momentum of the excited atom. The total collision cross section of these atoms σ_t is expressed in terms of the matrix element of the dipole moment operator **D** between the ground and excited states of the atom and is [11, 12]

$$\sigma_t = \frac{4.8\pi d^2}{\hbar v}, \tag{5}$$

where v is the relative collision velocity of atoms, and the square of the matrix element from the dipole moment operator between the ground state of the sodium atom with the moment 0 and its projection 0, and also the excited sodium atom with the moment 1 and its projection $M = 0, \pm 1$ is given by formula

$$d^2 = \frac{1}{3}\sum_M |\langle 00|\mathbf{D}|1M\rangle|^2 \tag{6}$$

and in the case of a sodium atom this value is equal $d^2 = 6.28e^2 a_o^2$. Accordingly, the width of the spectral absorption or emission line for the impact mechanism under consideration is [12, 13]

$$\nu = 4.8\pi d^2 N \tag{7}$$

where N is the number density of atoms in the vapor.

In the case of sodium, we have $\nu/N = 5.8\cdot 10^{-7}\ cm^3/s$. Because of the effective interaction for a resonantly excited atom with an atom in the ground state, the nature of the broadening can be dominant also in the case when these atoms are located in the buffer gas. In particular, we determine under what conditions the buffer gas makes a relatively small contribution to the broadening of the spectral line. The width of the spectral line ν due to the interaction with the atoms of a buffer gas is given by the formula [9, 10]

$$\nu = N v\sigma_t, \tag{8}$$

where N is the number density of buffer gas atoms or molecules, v is the relative collision velocity of a radiating atom with a buffer gas atom or molecule, σ_t is the total collision cross section of these atomic particles.

Let us determine the total cross section for the collision of atomic particles for the long-range interaction potential $U(R)$, which at large distances R between colliding atoms or molecules has the form

$$U(R) = -\frac{C_6}{R^6} \tag{9}$$

In this case, the total collision cross section for particles is [14]

$$\sigma_t = 8.1\left(\frac{C_6}{\hbar v}\right)^{2/5} \tag{10}$$

Assuming the Maxwellian distribution function of atoms over velocities and averaging over the velocities, we obtain on the basis of the formulas (8) and (10) for the specific width of the spectral line

$$\frac{\nu_b}{N_b} = 7.2\left(\frac{2T}{\mu}\right)^{3/10}\left(\frac{C_6}{\hbar}\right)^{2/5}, \tag{11}$$

where N_b is the number density of buffer gas atoms, T is the temperature of a buffer gas expressed in energy units, μ is the reduced mass of colliding particles.

As a demonstration of the effects under consideration, if emitted atoms are located in a buffer gas, let us consider sodium vapor in neon. In this case, the dispersion interaction constant equals $C_6 \approx 50e^2 a_o^5$ (e is the electron charge, a_o is the Bohr radius), so that formula (11) yields at the temperature $T = 500K$ for the specific width of the spectral line $\nu_b/N_b = 1.9 \cdot 10^{-9}\mathrm{cm}^3/\mathrm{s}$. Comparing with formula (7), which gives $\nu/N = 5.8 \cdot 10^{-7}\mathrm{cm}^{-3}/s$, we come to the conclusion that in the case under consideration, an identical contribution to the broadening under the action of the buffer gas-neon, and also as a result of the resonance interaction with sodium atoms occurs at the concentration of sodium atoms in neon 0.3%. Thereby, there is a wide range of sodium atom concentrations in neon, where the interaction with buffer gas atoms is insignificant.

Obviously, the Voigt profile of the spectral line, when the central part of the line is determined by the Doppler broadening mechanism, and the impact mechanism is realized at its wings, takes place in the range of atomic vapor densities

$$\Delta\omega > \nu, \tag{12}$$

where $\Delta\omega$ is given by the formula (3). This criterion has the form

$$N < N_o = \frac{\Delta\omega}{4.8\pi d^2}, \tag{13}$$

where $\Delta\omega$ is expressed in cm^{-1}. Formula (13) gives $N_o = 1.1 \cdot 10^{16} cm^{-3}$, and since the boundary between the impact and quasistatic broadening mechanisms of the spectral lines occurs at a density of sodium atoms $N \sim \sigma_t^{-3/2} \sim 2 \cdot 10^{16}\, cm^{-3}$, and the Voigt profile of the spectral line is realized for $N < N_o$, the transition to the spectral line wing with weakly varying function of the distribution of photons over frequencies occurs in the range of applicability of the short-range theory of the broadening of spectral lines. We note here that the quasistatic theory in participation of resonantly excited atoms leads to the same behavior of the spectral line profile at wings as the impact mechanism of broadening.

The analysis shows that the above system consisting of a buffer gas (neon) and a radiating impurity (sodium) exists at a buffer gas pressure of the order of 1 Torr, and the presence of a buffer gas does not affect the resonant radiation of the impurity. Now let us analyze the character of the radiation output from this system. We have the following expression for the absorption cross section of σ_ω at a given frequency [9, 10]

$$\sigma_\omega = \frac{\pi^2 c^2}{\omega^2} \frac{f_\omega}{\tau} \left[1 - \exp\left(-\frac{\hbar\omega}{T} \right) \right], \tag{14}$$

where f_ω is the photon frequency distribution function, τ is the radiative transition time, and the last factor takes into account the induced radiation. Being guided by the short- range mechanism of broadening of spectral lines, we therefore have for the absorption cross section σ_o and for the absorption coeficient $k_o = N\,\sigma_o$ at the center of the spectral line in neglection the induced emission

$$\sigma_o = \frac{\pi^2 c^2}{\omega^2} \frac{2}{\pi\nu\tau}, k_o = \frac{\lambda^2}{2\pi\tau\nu/N}, \tag{15}$$

where $\lambda = 2\pi c/\omega$ is the radiation wavelength. According to this formula, the absorption coeficient k_o at the center of the spectral line does not depend on the number density of emitting atoms or their mass. Next, since the specific width of the spectral line ν/N for the resonant transition according to the formula (7) is proportional to the square d^2 of the matrix element from the dipole moment between the states of the radiative transition, like to the radiative rate

$1/\tau$, the absorption coeficient k_o does not depend on this quantity. For a sodium vapor, where $\lambda = 589$ nm, $\tau = 1.6 \cdot 10^{-8}$s, $\nu/N = 5.8 \cdot 10^{-7}\, cm^3/s$, we obtain $k_o = 5.8 \cdot 10^4\, cm^{-1}$. Accordingly, the photon absorption coeficient k_ω at a frequency ω, related to wings of spectral lines, in accordance with the formula (1) is given by

$$k_\omega = k_o \frac{\nu^2}{4(\omega - \omega_o)^2} \tag{16}$$

Considering transfer of resonant radiation in a gas where the mean free path of a photon at the center of the line is small compared with the size of the system, we have that the character of this transfer is different from the transport of particles in a dense gas, where the transport of particles has the diffusion nature. In the case of diffusion transfer of particles, the particle displacement in one act of transfer occurs over a distance of the order of the particle mean free path in a gas, which is small in a dense gas compared to a size of the region occupied by it. Propagation of resonant radiation in a gas occurs in another manner and is described by the Biberman-Holstein equation [15, 16, 17]. As follows from this equation, displacement of a resonant photon over a large distance in a gas does not occur as a result of many reabsorptions near the spectral line center, but takes place due to emission at spectral line wings, and the probability of such an event is small. To analyze propagation of resonant radiation in a gas, it is convenient to use the Veklenko concept [18, 19], where an object of study is a separate excitation, and not a photon. Accordingly, the lifetime of an excited state τ_{ef}, i.e. the time of photon residence inside the gas volume, is estimated as $\tau_{ef} \sim \tau / P_*$, where τ is the radiative lifetime of an isolated atom, P_* is the probability of photon emission with a frequency ω^*, for which the mean free path of a photon is comparable to a size of the system L, i.e. $k(\omega_*)L \sim 1$. Since for $k_o L >> 1$, we have $P_* \sim \nu/|\omega_* - \omega_o|$ for the long-range broadening mechanism, and the effective lifetime of excitation residence inside the gas volume is estimated as

$$\tau_{ef} \sim \tau\sqrt{k_o L},\ k_o L \gg 1 \tag{17}$$

In particular, if this gas is located inside a cylindrical discharge tube of radius R, then for a homogeneous gas distribution in the tube, the effective excitation lifetime inside the gas volume is [20]

$$\tau_{ef} = 2.6\tau\sqrt{k_o R} \tag{18}$$

This time is taken into account in analyzing the kinetics of excited atoms in a gas. In addition, a width of the emission band $\Delta\omega$ under these conditions is

$$\Delta\omega \equiv |\omega_* - \omega_o| \sim v\sqrt{k_o L}, \tag{19}$$

i.e. a width of the emission band $\Delta\omega$ substantially exceeds the spectral line width ν for emission of an individual atom.

Let us consider these results from other positions, which will be used later for a molecular gas. We represent the volume of a gas containing resonantly excited atoms as a radiating system and determine the flux of resonance radiation that this system creates. Let a typical size of the system be L, and a typical number density of the excited atoms be N_*. Then a typical flux of photons j is estimated as

$$j \sim \frac{N_* L}{\tau_{ef}} \sim \frac{N_*}{\tau}\sqrt{\frac{L}{k_o}} \tag{20}$$

On the other hand, introducing the optical thickness u_ω (l) of the layer which depth is l, as

$$u_\omega(l) = \int_0^l k_\omega dz, \tag{21}$$

we have that photons of a given frequency attain the separation boundary, if they are emitted from regions with optical thickness $u_\omega \sim 1$. This gives for a partial flux of photons with a frequency from ω to ω + $d\omega$

$$j_\omega d\omega \sim \frac{N_*}{\tau}\frac{f_\omega d\omega}{k_\omega} = \frac{N_*}{\tau}\frac{d\omega}{k_o \nu} \tag{22}$$

As is seen, on the basis of formula (19) for the emission band width one can arrive at formula (20) for the total flux of photons passing through the interface.

Thus, considering the competition between the short-range and long-range broadening mechanisms of spectral lines, we find that for an optically dense system the resonant emission of an atomic gas is determined only by the long-range mechanism or by the impact broadening of spectral lines, which is realized at wings. This analysis allows us to formulate the concepts of the spectral emission band of photons on the basis of the system optical thickness for photons at a given frequency, which will be the basis for analyzing the radiation of a molecular gas.

3. ABSORPTION IN A MOLECULAR GAS

Analyzing the competition of different mechanisms of spectral line broadening for molecular gases, we are guided for simplicity by radiative properties of linear molecules of carbon dioxide. In investigating IR radiation of these molecules, we restrict ourselves to the vibrational-rotational radiative transitions of molecules, and because of a large set of rotational momenta of the molecule, the IR radiation of a molecular gas is determined by a large number of vibrational- rotational transitions. As a result, the emission or absorption spectrum of molecules contains a large number of broadened spectral lines, which are joined into a spectral absorption band.

Considering linear molecules of carbon dioxide, three atoms of which are on the same line, we first restrict ourselves by one vibrational transition. Because of a relatively high pressure, thermodynamic equilibrium is supported in a gas, so that the number density of molecules in a given vibrational-rotational state is given by formula

$$N_{v,j} = N_v \frac{B}{T}(2j+1)\exp\left(-\frac{\hbar\omega_o v}{T}\right)\exp\left[-\frac{Bj(j+1)}{T}\right] \tag{23}$$

Here j is the rotational number of the molecule, N_v is the total number density of molecules in the ground vibrational state, $\hbar\omega_o$ is the excitation energy of the vibrational level, v is the vibrational level number, B is the rotational constant, T is the temperature of the gas expressed in energy units, and further we shall assume that the criterion $B << T$ is fulfilled. We note that the thermodynamic equilibrium under consideration can be violated as a result of emission of excited molecules, so that in order to perform thermodynamic equilibrium, it is necessary that the destruction of excited molecules in collisions occurs more rapidly than that due to radiation. Accordingly, the criterion of thermodynamic equilibrium in the case of carbon dioxide for its pressure p has the form $p >> 0.1T\ orr$. Further we shall deal with much higher pressures, so that the thermodynamic equilibrium in a gas is certainly satisfied.

Let us consider the nature of vibrational-rotational transitions from the general positions of molecular spectroscopy [21, 22, 23, 24, 25]. The selection rules for radiative transitions in linear molecules with a change in the angular momentum j of the molecule follow from the properties of the Clebsch-Gordan coeficients, which connect the parameters of the rotational states of the initial and final transition states. These selection rules for CO_2 molecules correspond to the transitions $j \to j$ (Q-band), $j \to j - 1$ ((P -band) and $j \to j + 1$ (R-band). Since the energy of the rotational state of the molecule E_j is [14]

$$E_j = Bj(j + 1), \tag{24}$$

the energy of the rotational state does not change in the case of the Q-band. For P – band it is equal $\hbar\omega_j = \hbar\omega_o - 2B_j$, and for R- band, the energy of the transition $\hbar\omega_j$ is $\hbar\omega_j = \hbar\omega_o + B(j + 1)$, where $\hbar\omega_o$ is the energy of the vibrational transition.

Let us construct the absorption coefficient k_ω the gas, consisting of CO_2 molecules, as the sum of the absorption coeficients due to different vibrational transitions. We use the general expression (14) for the absorption cross section σ_ω at a given frequency. Separating the rotational transitions into Q, P and R - branches, we have that for large values of the rotational momenta j of the molecule, that the spontaneous radiative decay of the upper vibrational state with identical probability (1/3) for each of these branches, if a deformation vibration state partake in the radiative transition. Then for the collisional broadening of the spectral line (1), we have for the absorption coeficient pertaining to the given oscillatory transition

$$k_\omega = \frac{\pi^2 c^2}{3\tau_v \omega^2} \sum_j f_\omega N_{v,j} \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right] = \frac{\pi c^2}{6\tau_v \omega^2} \sum_j \frac{\nu N_{v,j}}{(\omega - \omega_j)^2 + (\nu/2)^2} \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right], \tag{25}$$

where τ_v is the radiative lifetime of the upper vibrational state for the considered vibrational transition, ν is the collisional width of the spectral line.

This formula gives for the absorption coeficient due to transitions for Q-band

$$k_\omega = \frac{\lambda^2}{24\pi\tau_v} \frac{\nu N_v}{(\omega - \omega_o)^2 + (\nu/2)^2} \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right], \tag{26}$$

since $\sum_j N_{v,j} = N_v$. Here $\lambda = 2\pi c/\omega$ is the radiation wavelength, N_v is the molecular density in the lower vibrational state of the transition, and $\hbar\omega_o$ is the energy of the vibrational transition. Accordingly, in the case of P and R bands, we have

$$k_\omega = \frac{\pi c^2}{6\tau_v \omega^2} a_\omega \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right],\; f_\omega = \sum_j \frac{\nu N_{v,j}}{(\omega - \omega_o \pm 2Bj/\hbar)^2 + (\nu/2)^2} \tag{27}$$

In this case, large angular momenta $j >> 1$ give the main contribution to the absorption coeficient.

Since the frequency difference for the neighboring transitions is independent of the rotational moment, the absorption coeficient for P and R branches is described by the regular model [26] "or the Elsasser model". In this case, the summation over the rotational momentum in the formula (27) is made for two cases. Namely, at frequencies related to the pedestal of the absorption band, we represent the sum in the form

$$\sum_j \frac{N_{v,j}}{(\omega - \omega_o \pm 2Bj/\hbar)^2 + (\nu/2)^2} = N_{v,j} \sum_j \frac{1}{(\omega - \omega_o \pm 2Bj/\hbar)^2 + (\nu/2)^2}, \tag{28}$$

assuming that the density of the molecules $N_{v,j}$ varies slightly in a convergence range of the sum, and using formula (23) for this quantity. We first determine the absorption coeficient averaged over the oscillations between neighboring spectral lines. Since $\overline{a_\omega} = 1/2B$, where $2B/\hbar$ is the distance between neighboring lines in the frequency space, we obtain [26, 27, 28]

$$\overline{k_\omega} \equiv g(\omega) = N_v \lambda^2 \frac{(\omega - \omega_o)}{6\tau_v \Delta\omega^2} \exp\left[-\frac{(\omega - \omega_o)^2}{\Delta\omega^2}\right]\left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right],\; \Delta\omega^2 = \frac{4BT}{\hbar^2}, \tag{29}$$

where N_v is the number density of perturbed molecules. Summing up the formula in the formula (28), taking into account the oscillating part of the absorption coeficient [29], we have, within the framework of the Elsasser model, the absorption coeficient [26, 27, 28, 30]

$$k_\omega = S(\omega)\varphi(\omega),\ \varphi(\omega) = \frac{\sinh\frac{\pi\hbar\nu}{2B}}{\left(\cosh\frac{\pi\hbar\nu}{2B} - \cos\frac{\pi\hbar|\omega-\omega_o|}{B}\right)}, \tag{30}$$

At the wing of the absorption band $j >> j_o (j_o \sim \sqrt{T/B})$ the sum (28) is reduced to the form

$$\sum_j \frac{N_{v,j}}{(\omega-\omega_o \pm 2Bj/\hbar)^2 + (\nu/2)^2} = \sum_j N_{v,j}\frac{1}{(\omega-\omega_o)^2} = \frac{N_v}{(\omega-\omega_o)^2}, \tag{31}$$

that gives the absorption coeficient at the wing of the *P* and *R*-branches of the absorption band

$$k_\omega = \frac{\pi c^2}{3\omega^2}\frac{\nu N_v}{\tau_v(\omega-\omega_o)^2}\left[1-\exp\left(-\frac{\hbar\omega}{T}\right)\right] \tag{32}$$

Summing the absorption coeficients (26) and (32) for *Q*, *P* and *R* branches of the absorption band and neglecting the shift relative to the transition center in the formula (32), we obtain for the total absorption coeficient at wings of the absorption band

$$k_\omega = \frac{\pi c^2}{3\omega^2}\frac{\nu N_v}{\tau_v(\omega-\omega_o)^2}\left[1-\exp\left(-\frac{\hbar\omega}{T}\right)\right] \tag{33}$$

It should be noted the peculiarity of a short-range broadening of spectral lines, which relates to radiation of molecules in the perturbed gas. The criterion for this broadening mechanism is the smallness of a typical collision time τ_c in comparison with a time characterized the spectral line broadening, i.e. with a time between neighboring collisions $1/\nu$ for the spectral line center or $1/|\omega - \omega_o|$ for its wings. It follows that at wings of the absorption band the absorption coeficient decreases sharply with removal from the transition center and, taking this fact into account, we transform the formula (33) for the absorption coefficient at wings of the absorption band to the form

$$k_\omega = \frac{\pi c^2}{3\omega^2}\frac{\nu N_v}{\tau_v(\omega-\omega_o)^2}\left[1-\exp\left(-\frac{\hbar\omega}{T}\right)\right]\cdot\exp\left[-\frac{(\omega-\omega_o)^2}{\Delta\omega^2}\right], \Delta\omega = 1/\tau_c \tag{34}$$

Let us estimate the limiting shift for the wing of the absorption band as $\Delta\omega = 1/\tau_c$ and connects this with the parameters of interaction between molecules of carbon dioxide. We approximate for simplicity the interaction potential of two molecules of carbon dioxide by the Lennard-Jones potential [31, 32]

$$U(R) = D\left[2\left(\frac{R_e}{R}\right)^6 - \left(\frac{R_e}{R}\right)^{12}\right], \tag{35}$$

where *D* is the depth of the potential well for the interaction of two molecules, R_e is the equilibrium distance between molecules, which corresponds to a minimum of the interaction potential. It is clear that the spherically symmetric interaction potential is a crude approximation for interaction of carbon dioxide molecules, but this allows us to determine the parameters of the interaction potential using similarity laws on the basis of comparison the interaction parameters of carbon dioxide molecules and inert gas atoms. Indeed, the scaling for inert gases [33, 34] allows one to connect critical parameters of inert gases and carbon dioxide, and also their parameters near the triple point. From this one can determine parameters of the pair interaction potential of molecules (35), which in the case of carbon dioxide molecules are D = (38 ± 7) meV and R_e = 0.32 nm. We also note that the inter-action potential (35) leads to the following value of the van der Waals interaction constant $C_6 = 2DR_e^6 \approx 140e^2 a_o^5$, which exceeds the calculated value [35] by 20%.

One can define a typical collision time for two molecules of carbon dioxide τ_c as a time of approach of slow molecules from the distance R_e at the minimum interaction potential of molecules to the distance $R_e/2^{1/6}$ that corresponds to the potential wall for slow molecules at zero orbital angular momentum, which is equal to

$$\frac{1}{\tau_c} \equiv \Delta\omega = \frac{10}{R_e}\cdot\sqrt{\frac{2D}{m}}, \tag{36}$$

where m is the mass of the carbon dioxide molecule. Hence we obtain the following estimate for the wing width of the absorption band of carbon dioxide molecules in carbon dioxide $\Delta\omega \approx 70cm^{-1}$. This fact restricts the flux of IR radiation emitted by carbon dioxide due to spectral line wings.

At this stage, we compare the profiles of the spectral lines for competition between the Doppler and long-range mechanisms of broadening of spectral lines in an atomic gas, as well as short-range and long-range mechanisms in a molecular gas. Despite the different nature of the broadening of the spectral lines in atomic and molecular gases, the analogy occurs for the photon frequency distribution function that contains short-range and long-range parts. In both cases a short-range mechanism of broadening has has the collision nature in both cases, whereas the character of the short-range part of the broadening is different. In a molecular gas, for the pedestal of the spectral band determined by formula (29), this part is related to the distribution over rotational states for radiating molecules, while the short-range part of the absorption band wing in accordance with the formula (34) arises in account of a finite time of collision between the radiating molecule and the perturbed gas molecule.

4. THE ENERGY BALANCE OF VENUS

It would seem that the analysis carried out is purely academic in nature, allowing a deeper understanding the character of interaction for different mechanisms of broadening of spectral lines. However, this understanding allows us to analyze the relevant problems related to natural processes and applied problems. Further, as one of such problems, we consider the energy balance of Venus near its surface, namely, IR radiation created by atmospheric carbon dioxide of Venus and directed to the surface. We consider a simplified scheme of the Venus energy balance, so that the generated power consists of the absorbed power of solar radiation and IR radiation created by the Venus atmosphere. Absorbed by the Venus surface, the total radiation power must be compensated by the power radiated by the Venus surface.

Let us give the parameters of Venus related to the problem under consideration. The atmosphere of Venus consists of carbon dioxide (96.5%) and nitrogen (3.5%) [36]. For simplicity, we assume carbon dioxide to be the only component of the Venus atmosphere. The gas pressure at the Venus surface is 92 atm, the temperature is $737K$ [36, 37], that corresponds to the number density of molecules of carbon dioxide near the Venus surface $N = 9.2 \cdot 10^{20}\ cm^{-3}$. The temperature gradient is about $-8K/km$ in the altitude range from 0 to 60km [37], and the scale of the change in the density of carbon dioxide molecules Λ in the Venus atmosphere, which is introduced on the basis of formula $\Lambda = d \ln N/d(1/h)$, where N is the number density of molecules in the atmosphere, h is the altitude above the Venus surface, and $\Lambda = 19km$.

Table 1

The spectroscopic parameters of the molecule CO_2 [40, 35, 41]: λ is the wavelength of the radiative transition for Q-branch, E_o and E_* are the energies of the lower and upper vibrational transition states, $\hbar\omega = E_* - E_o$ is the energy of the vibrational transition, τ_v is the radiative lifetime of the upper transition state with respect to the given transition. The adopted designations for the vibrational states of the carbon dioxide molecule are used, so that the first number corresponds to the symmetric vibration, the second corresponds to the torsional vibration, and the third to the antisymmetric vibration

Transition	λ, μm	E_*, cm^{-1}	E_o, cm^{-1}	$\hbar\omega$, cm^{-1}	τ_v, s
$01^{o}0 \to 00^{o}0$	14.9	667	0	667	0.33
$10^{o}0 \to 01^{o}0$	13.9	1388	667	721	0.56
$02^{o}0 \to 01^{o}0$	16.1	1285	667	618	0.79
$02^{2}0 \to 01^{o}0$	15.0	1335	667	668	0.37
$00^{o}1 \to 10^{o}1$	10.6	2349	1388	668	2.6
$00^{o}0 \to 02^{o}1$	9.4	2349	1285	1064	2.3
$00^{o}1 \to 00^{o}0$	4.26	2349	0	2349	0.0024

In constructing the energy balance of the surface of Venus and its atmosphere, we will model the Venus surface as a blackbody for IR radiation. We have that an absolutely black body with a temperature of $737K$ creates an IR radiative flux $J_o = 16.7kW/m^2$. On the other hand, the average flux of solar radiation per unit surface area of Venus $2.6kW/m^2$ [38]. The Venus albedo is 0.80 ± 0.02 according to [39] and 0.76 ± 0.01 according to [38]; we take it to be 0.78. It follows that the average flux of solar radiation absorbed by the atmosphere and surface of Venus is $0.5kW/m^2$. An additional contribution to the power absorbed by the surface of Venus is due to IR radiation produced by the molecules of carbon dioxide. To determine the radiative flux to the Venus surface, which contributes to the Venus energy balance, it is necessary to analyze the emission spectrum of carbon dioxide molecules in the IR spectral range, which is presented in Table 1. In addition, the diagram of Fig. 1 repeats this information.

The absorption coeficient of carbon dioxide for each of the branches is the sum of the absorption coefficients in the central part of the band (formula (29) for P and R-branches, and the formula (27) for Q-branch), and the absorption coefficient on a wing of the spectral band (formula (34)). As follows from the data in Table 1, there are seven absorption bands in the IR range of the spectrum of carbon dioxide molecules, with some neighboring absorption bands overlapping. The total absorption coefficient in the atmosphere of Venus near the surface of Venus is shown in Fig.2. As follows from Fig.2, the absorption of atmospheric carbon dioxide consists of four absorption bands, and two absorption bands are overlapped according to Table 1. Boundaries of absorption bands for the Venus atmosphere due to carbon dioxide molecules follow from the relation [42, 43]

$$k_\omega \Lambda = 2/3, \tag{37}$$

where Λ = 19 km is the scale of the change in the number density of molecules of carbon dioxide in the Venus atmosphere near its surface. On the basis of this formula, we have for the boundaries of the first two absorption bands $\omega_1 = 493cm^{-1}$ and $\omega_2 = 1174cm^{-1}$, which gives IR radiative flux to the Venus surface $J_1 = 3.5kW/m^2$. The third absorption band, which is created by the resonant radiation of the carbon dioxide molecule between the lower excited antisymmetric state and the ground vibrational state, has the boundaries $\omega_1 = 2258cm^{-1}$ and $\omega_2 = 2439cm^{-1}$ that leads to IR radiative flux to the Venus surface $J_3 = 0.9kW/m^2$. From this one can obtain the total radiative flux to the Venus surface, which consists of the absorbed flux of solar radiation and IR radiation generated by carbon dioxide molecules in the Venus atmosphere is $J = 4.9kW/m^2$.

As it follows from the data presented, solar radiation absorbed by the Venus surface contributes 3% to the total energy flux absorbed by the Venus surface. In this case, the contribution of IR radiation of the Venus atmosphere absorbed by its surface is 26% from the total flux of radiation absorbed or emitted by the Venus surface. Note that in the case of the Earth's energy balance, the last channel gives 20% [56, 58, 59]. Thus, we arrive at a contradiction

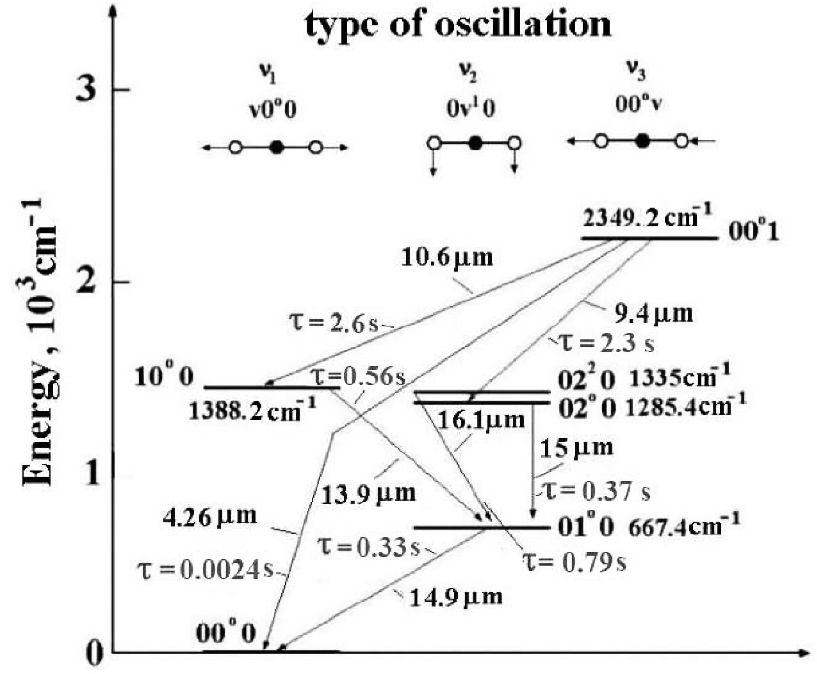

Figure 1: Spectrum of carbon dioxide molecule and its radiative parameters in IR spectral range, where they are determined by radiative vibration transitions, according to HITRAN data [40]

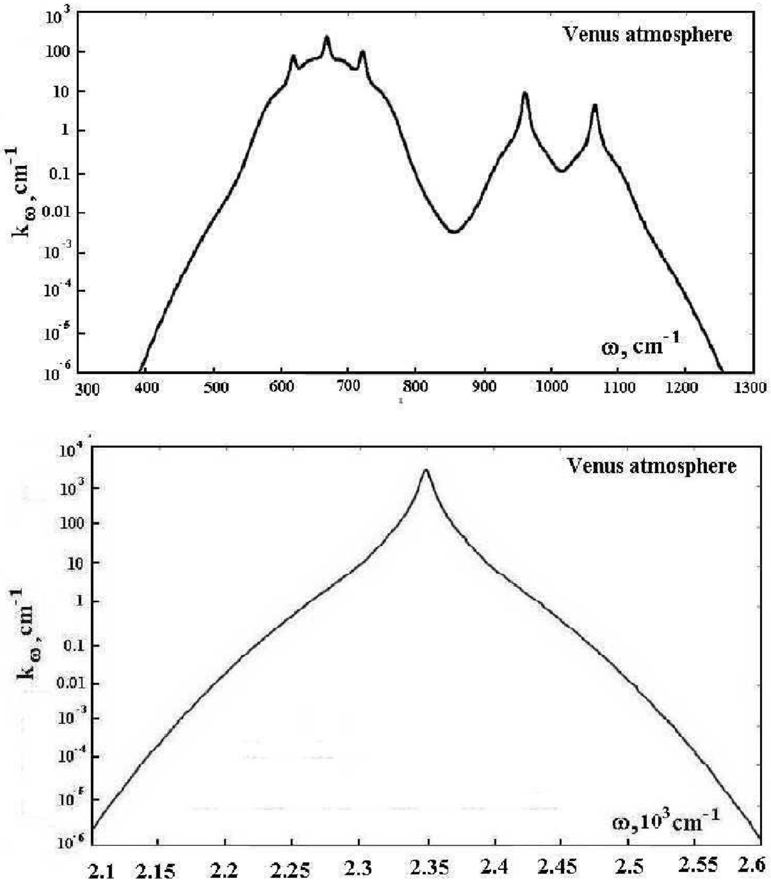

Figure 2: The absorption coefficient kù near the surface of Venus due to carbon dioxide molecules, calculated on the basis of the formulas (29) and (32)

according to which the power of radiation absorbed by the surface of Venus, is small extent (about one-third) compared to the power of IR radiation of its surface at the observed temperature. In searching the cause of the discrepancy between the indicated powers, we first analyze the accuracy of finding the above powers. For this purpose, we use the absorption band model [59] for carbon dioxide molecules, according to which radiation at frequencies inside this band is created by carbon dioxide molecules, whereas outside the absorption band, carbon dioxide molecules do not contribute to atmospheric emission. This requires a sharp change of the absorption coefficient kù near the boundary of the absorption band, which occurs in this case according to Fig.2. The accuracy of calculation the above radiation powers within the framework of the model used is better than 20%; the error in calculations also includes the fact that the radiative temperature of the Venus atmosphere near boundaries of the absorption bands is determined by the layers of the Venus atmosphere whose temperature differs from the temperature of its surface.

Let us ascertain which additional channels in the Venus energy balance can remove the contradiction obtained. Above we did not take into account the convective heat transfer from the Venus surface, associated with the vortex movement of carbon dioxide near its surface under the influence of the atmospheric temperature gradient. In the case of the Earth, the convective energy flux is about 10% of the total flux of solar radiation entering the Earth's atmosphere [56, 58, 59]. It can be expected that the relative contribution of convective transport in the energy balance of Venus does not exceed this value due to a high gas pressure in the atmosphere of Venus. Thus, convective transport in the atmosphere of Venus does not eliminate the above contradiction, especially since the convective transfer only increases the radiative energy flow to the Venus surface, which is necessary for the fulfillment of the Venus energy balance.

However, convective heat transfer in the Venus atmosphere causes the dust to move from the Venus surface to its atmosphere. In the case of micron-size dust particles, the action of gravity leads to their return to the Venus surface through years. The weighted dust is optically thick in the IR spectral range and even at a low dust concentration the IR radiative flux may be provided by dust particles. Note that in the case of the Earth's atmosphere, the role of dust does not be important, since atmospheric dust is washed out by atmospheric water for 8 – 9 days. At the same time, the energy balance of Venus and its atmosphere begins with absorption of solar radiation by the atmosphere [47], and then the absorbed energy is transferred to the Venus surface as a result of convection and radiative transfer. Here we do not consider the radiative transfer from upper layers of the Venus atmosphere to its surface, but we solve a simpler problem.

One can estimate a dust amount of the atmosphere from the condition that the dust optical thickness u with respect to IR radiation is of the order of one. This condition has the form

$$u_\omega = k_\omega L = \sigma_\omega N L \sim 1. \tag{38}$$

where σ_ω is the photon absorption cross section of a dust particle, N is the number density of particles in the atmosphere, L is the thickness of the atmosphere layer in which the dust is located. Assuming dust particles to be spherical, we assume a typical dust radius r to be small compared to the wavelength $\lambda \sim 10\mu m$, which leads to the following estimate for the photon absorption cross section of the dust particle [48]

$$\sigma_\omega \sim \pi r^2 \left(\frac{r}{\lambda}\right) \sim \left(\frac{V}{\lambda}\right), \tag{39}$$

where V is the average volume of dust particles. From this we obtain on the basis of formula (38)

$$\xi = \sigma_\omega N L \sim \lambda. \tag{40}$$

where ξ is a typical optical thickness of the dust layer, which ensures the absorption of IR radiation of the planet, if atmospheric dust is collected on the Venus surface.

Comparing this amount of dust with the amount of carbon dioxide in the atmosphere of Venus, we obtain that the concentration of dust molecules is $\sim 10^{-7}$ (the number of molecules of atmospheric dust to the number of molecules of carbon dioxide in the atmosphere) provides the effect under consideration when this dust consisting from solid particles of micron and submicron sizes, creates the IR radiative flux absorbed subsequently by the Venus surface. If this dust is collected at the Venus surface, it forms a layer of thickness of several tens of microns (several IR wavelengths). Note that the microscopic dust of the Venusian atmosphere is near its surface, in contrast to the clouds in the Venus atmosphere [49, 50, 51], which are located at an altitude of 60-70 km and provide IR radiation which goes outside this planet.

Let us note one more feature of this research. The performed calculations use information about spectroscopic parameters of carbon dioxide molecules taken from the HITRAN [40] data bank and including data for several hundred vibrational-rotational transitions of the carbon dioxide molecule. At present, this bank has information pertaining to hundreds of thousands of transitions involving carbon dioxide molecules [8], i.e. a small part of existed information related to this problem is sufficient for the calculations of the above parameters.

We also consider the peculiarity of spectroscopy of CO_2 molecules and its spectroscopic parameters which are taken on the basis of the HITRAN data bank [8,35,40]. Above we represent the general formulas (29) and (30) for the absorption coefficient due to linear triatomic molecules. The principal property of the carbon dioxide molecule is the symmetry of the electron wave function with respect to reflection respectively the plane which is perpendicular to the molecule axis and passes through the molecule center - the carbon nucleus. This leads to a certain symmetry of the rotation wave function which requires even values of the rotation momenta for even and zero values of the deformation (torsion) vibration and at odd values of the deformation vibration value only odd values of rotation momenta are realized [14].

Another peculiarity of the spectroscopy of the CO_2 molecule is such that states with forbidden values of rotation momenta exist as autodetachment ones. This means that the lifetime of these states is large compared to the radiative times of transitions. Therefore, these state partake in radiative transitions in accordance with the HITRAN data bank [8,35,40], and the change in the above general formulas consists in replacing B → 2B.

One can make the following step by using the HITRAN data directly [8,35,40]. Namely, we have the following connection between the average absorption coefficient $g(\omega)$ and the intensity of spectral lines S_i at corresponding frequencies according to the HITRAN data as

$$g(\omega) = N_v S_i \lambda_d \, , \tag{41}$$

where N_v is the number density of molecules in the initial vibration state, S_i is the intensity for i-th rotation state, λ_d is the wavelength for the energy difference d for neighboring spectral lines, and in this case this difference is d=4B. We use this approach in evaluation the emission of CO_2 molecules, though both cases lead to the

5. MODELS OF ABSORPTION IN MOLECULAR GASES

In analyzing emission and absorption of the Venus atmosphere near its surface in the IR spectrum range, we use the absorption coefficient as a sum of several vibration transitions. For the CO_2 molecule under consideration we use the regular model [26] for vibration- rotation transitions, and this absorption coefficient is contained in the data bank HITRAN [8] for a certain gas composition and certain temperature. Under real conditions, it is necessary to take into account that atmosphere temperature varies with an altitude. An important property of the absorption coefficient in the IR spectrum range, where it is determined by radiative transitions of molecules with different rotation momenta, is the oscillation structure of the absorption coefficient as a frequency function for the pedestal part according to formula (29). This property takes place at not high number densities of buffer gas molecules, and oscillations are absent for the Venus atmosphere, as it follows from Fig.2.

On contrary, in the Earth's atmosphere where the pressure is small compared to that of the Venus, these oscillation are significant not far from band centers. This is demonstrated in Fig. 3, where the absorption coeficient is given near the Earth's surface at the temperature $T = 288$K that corresponds to the standard atmosphere model [52], i.e.

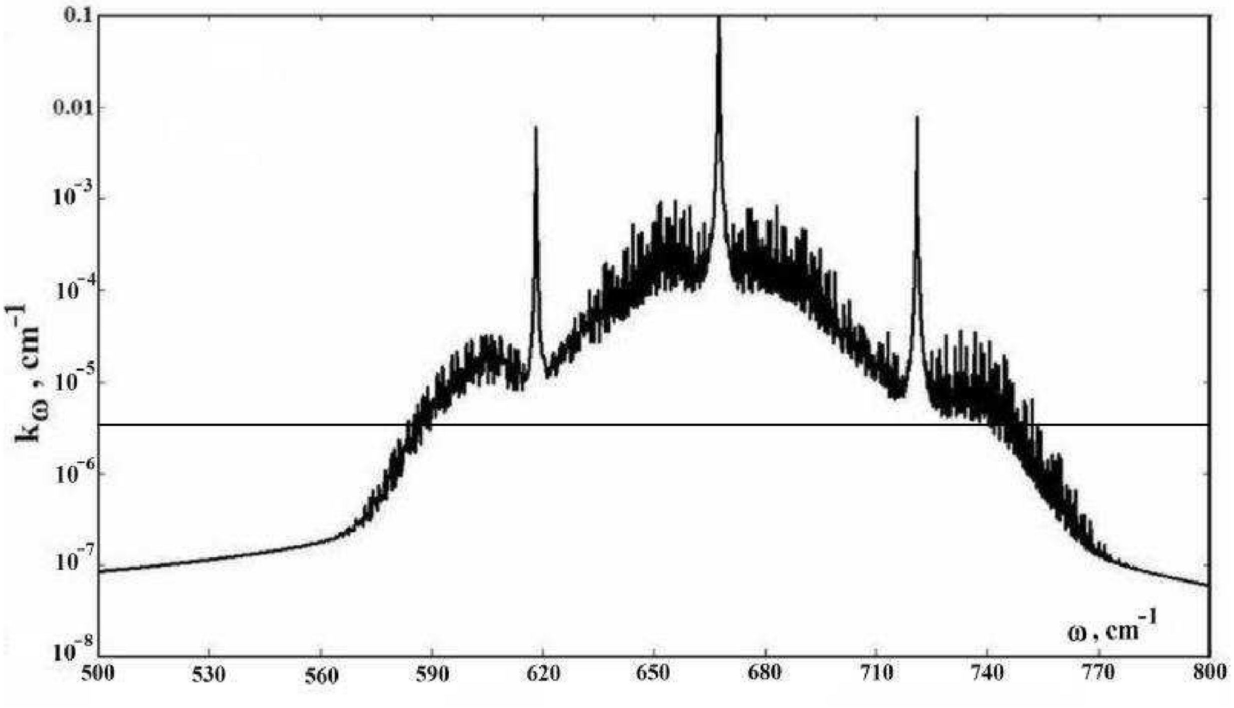

Figure 3: Total absorption coefficient k_ω at the Earth's surface due to atmospheric carbon dioxide molecules for the standard atmosphere model. The absorption coefficient is evaluated on the basis of formulas (29) and (34) for 4 vibration bands. A forward line shows the boundary of the absorption band

for the atmosphere with averaged parameters. In particular, Fig. 4 exhibits the oscillation structure of the absorption coefficient for the basic band of the main vibration transition of the CO_2 molecule at the wavelength of 15μm as a function of the rotation number j. The transition energy $\hbar\omega_j$ the variation energy for i-th vibration transition and the initial rotation momentum j of the molecule is given by

$$\hbar\omega_j = \hbar\omega_i - B \pm B(2j + 1), \tag{41}$$

where $\hbar\omega_i$ is the energy of the vibration transition, sign minus relates to P absorption branch, sign plus corresponds to R-branch. From this it follows for large $j >> 1$ $\hbar\omega_j = \hbar\omega_i - \mathrm{B} \pm 2\mathrm{B}j$ for P and R branches, and $\hbar\omega_j = \hbar\omega_j$ for Q-branch.

This information allows one to compare the absorption band model and the line-by- line one for evaluation the radiative flux emitted by an excited molecular gas. Indeed, the absorption band model, used above for evaluation the radiative flux from the Venus atmosphere to the Venus surface, is based on the assumption that inside the absorption band the radiative flux is created by CO_2 molecules, and outside the absorption band they do not give the contribution to the yield radiative flux. As is seen, it requires a narrow transiting range, where the optical thickness due to CO_2 molecules is of the order of one. This is fulfilled for conditions of the Venus atmosphere, given in Fig. 2. On contrary, under small number densities of a buffer gas, where neighboring vibration-rotation spectral lines are overlapped, a wide boundary of the absorption band occurs, as it follows from Fig. 5 for the absorption coefficient of the Earth's atmosphere near its surface due to CO_2 molecules.

It should be noted that in the case under consideration the absorption band width in atmospheric air due to carbon dioxide molecules is $\Delta\omega \sim 200 cm^{-1}$, and the distance between neighboring spectral lines is $4B \approx 1.56 cm^{-1}$, i.e. a number of spectral lines for vibration- rotation molecular transitions which partake in atmospheric emission exceeds 100. In the case of the Venus atmosphere, frequency oscillations of the absorption coefficient due to CO_2 molecules are absent and the absorption band has sharp boundaries with small contribution to the radiative flux. In

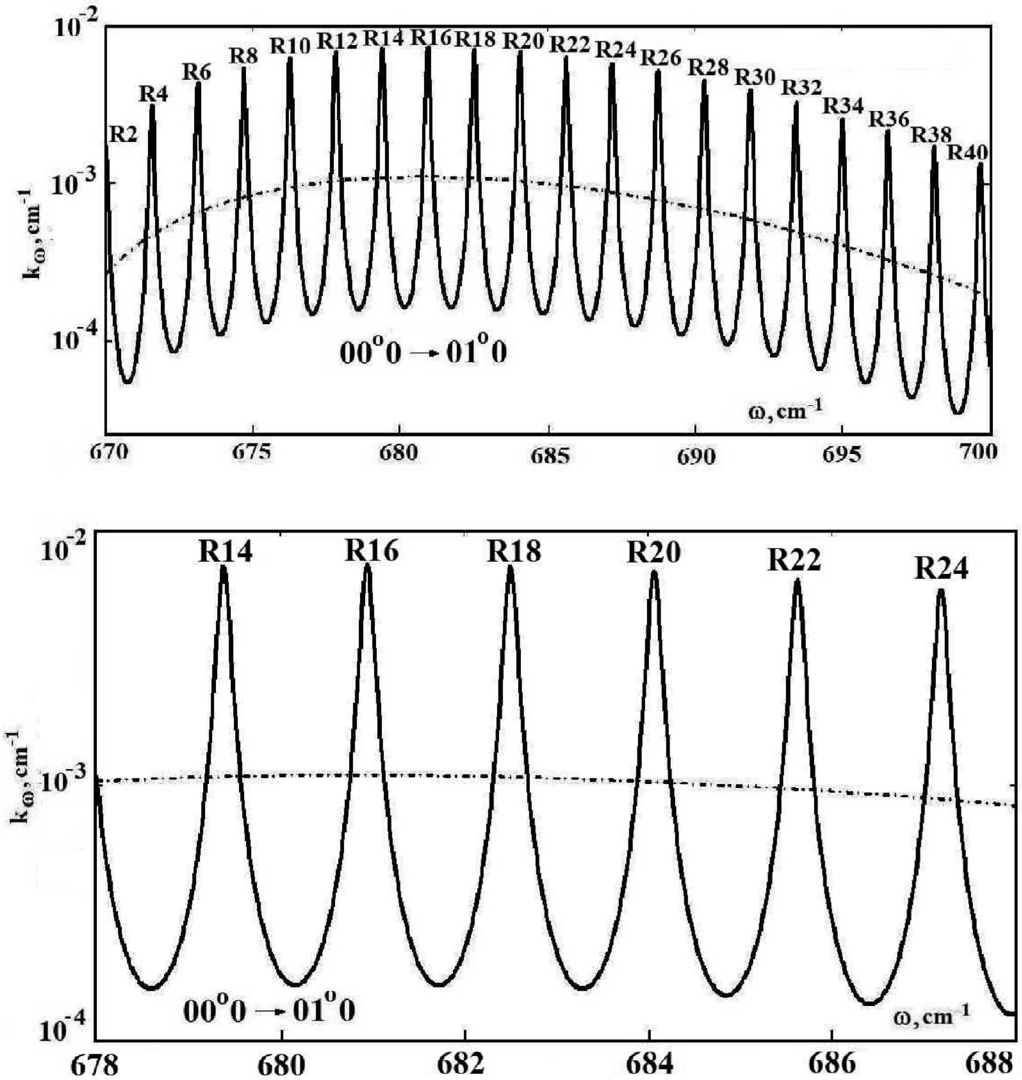

Figure 4: Absorption coefficient k_ω at the Earth's surface due to atmospheric carbon dioxide molecules as a reduced frequency function for the strongest vibration transition at 15μm. The reduced frequency coincides with the molecule rotation momentum at large momenta. The absorption coefficient relates to *R*-branch and is given in wide (a) and narrow (b) frequency ranges where transition lines are indicated. A dash-dotted line corresponds to the average absorption coefficient.

the case of oscillations, it is convenient to use the line-by-line method for evaluation the radiative flux, where the radiative flux is calculated separately for each frequency.

In this consideration it is necessary to take into account other than CO_2 molecules atmospheric radiators which absorb and emit in the spectral range of CO_2 molecules. A strong interaction between these radiators means that a change of the number density of CO_2 molecules causes a heightened absorption by other radiators, that complicates the determination of the change of the total atmospheric radiative flux. In order to account for this effect, it is convenient to introduce the total absorption coefficient K_ω as the sum of the absorption coefficient k_ω due to CO_2 molecules and that κ_ω due to other atmospheric radiators, mostly by water molecules, i.e.,

$$K_\omega = k_\omega + \kappa_\omega \tag{42}$$

Then in accordance with formula (37) the atmosphere altitude $h_\downarrow(\omega)$ which is responsible for emission at a given frequency ω, follows from the relation [42, 43]

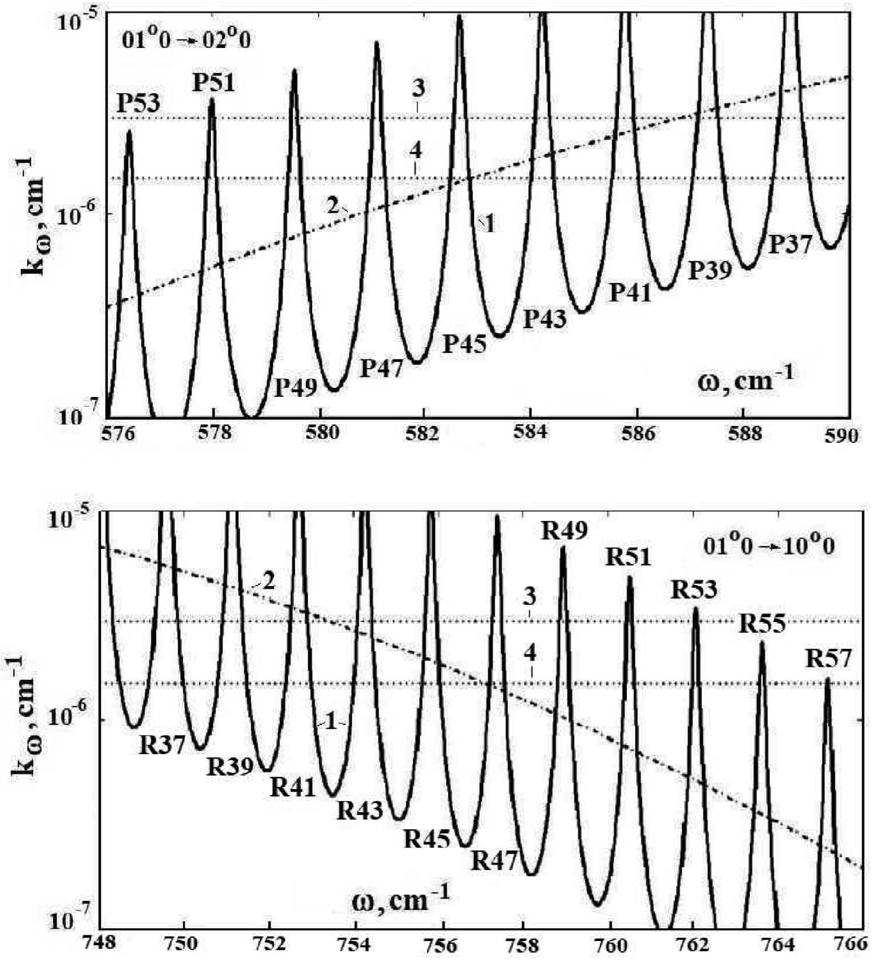

Figure 5: Absorption coefficient k_ω at the Earth's surface near the left (a) and right (b) boundaries for absorption by atmospheric CO_2 molecules a dash-dotted line corresponds to the average absorption coefficient, and dotted lines relate to boundary frequencies at the contemporary and doubled concentrations of atmospheric carbon dioxide molecules

$$h_{\downarrow}(\omega) = \frac{2}{3(k_\omega + \kappa_\omega)} \tag{43}$$

Correspondingly, the radiative temperature T_ω is the temperature of an effective layer which is responsible for emission at a given frequency, and this temperature is introduced for the total system consisting of CO_2 molecules and other optically active atmospheric components, according to the relation

$$T_\omega = T_E - h_{\downarrow}(\omega)\frac{dT}{dh} = T_E - \frac{2dT/dh}{3(\kappa_\omega + k_\omega)} \tag{44}$$

with the temperature gradient $dT/dh = 6.5K/km$. Here T_E is the Earth's temperature which is equal $T_E = 288$K for the standard atmosphere model [52]. The above expressions are valid for an optically dense atmosphere in the spectral range under consideration.

The absorption coefficient k_ω due to atmospheric CO_2 molecules in formulas (43) and (44) is given by formula (30). In order to determine the absorption coefficient κ_ω due to other atmospheric radiators, we use the energy balance for the Earth and its atmosphere that is represented in Fig. 6. The data of this Figure are taken from the

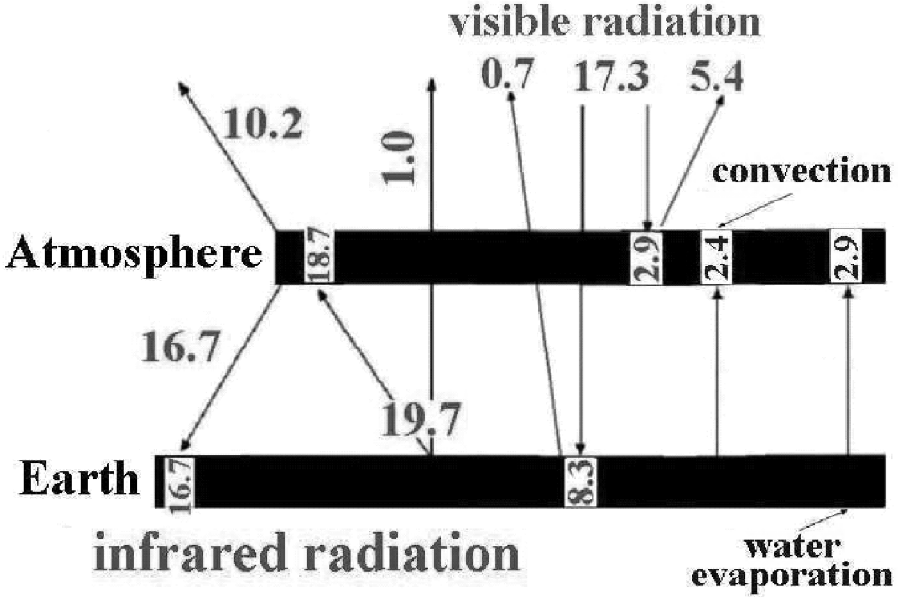

Figure 6: Expressed in $10^{16}W$ the powers of indicated processes which are obtained or lost by the Earth as a whole as well as by its atmosphere. Absorbed powers are given inside corresponding rectangulars, consumed powers are indicated near arrows

author's books [54, 55], which are the product of NASA investigations [53]. From this one can obtain the average energy fluxes which follow from the ratio of these powers to the area of the Earth's surface. All this are in accordance with subsequent data published both in original papers and also in books [56, 57, 58, 59, 60] within the limits of a few percent for basic channels. Evidently, the reason of this coincidence is that the data are taken from the same source - the data of NASA. In addition, because these data relate to various times within one half century, the rates of these energetic processes are natural and vary weakly during this time.

As it follows from Fig. 6, the basis of the Earth energetics is solar radiation which is converted partially into IR radiation as a result of the greenhouse effect, i.e. due to emission and absorption of IR radiation by the Earth and its atmosphere. Note that the Earth emits IR radiation almost as a blackbody. Indeed, if we apply the Stephan-Boltzmann law for radiation of the Earth's surface with the power given in Fig. 6, one can obtain the Earth temperature as $T = 287K$, whereas the standard atmosphere model gives the global Earth temperature $T_E = 288\text{K}$. We note also that the atmosphere removal leads to the global temperature $T = 278K$, if the Earth absorbs solar radiation completely and emits as a blackbody. Using data of Fig. 6, one can represent the radiative flux toward the Earth in the form

$$J_{\downarrow} = \int_0^\infty \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2}\left[\exp\left(\frac{\hbar\omega}{T_\omega}\right) - 1\right]^{-1} = 327W/m^2, \tag{45}$$

where the frequency temperature T_ω of radiation is given by formula (45).

Taking the absorption coefficient k_ω due to atmospheric CO_2 molecules on the basis of formula (30) and assuming the absorption coefficient κ_ω due to other atmospheric radiators to be independent of the frequency $\kappa_\omega = \kappa_o$, one can use formula (26) as an equation for κ_o. Solving this equation, we obtain $\kappa_o = 0.30km^{-1}$. On the basis of this solution, we give in Fig. 6 the frequency dependence for the atmospheric temperature T_ω which characterizes emission at a given frequency ω.

From this one can found the radiative flux toward the Earth due to atmospheric CO_2 molecules on the basis of the absorption band model according to formula

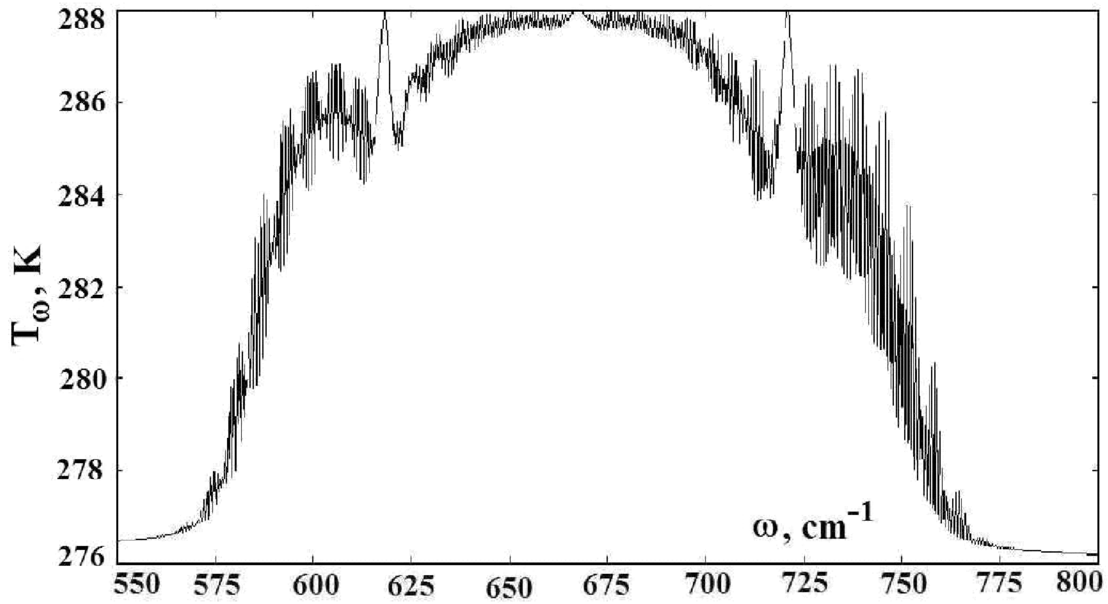

Figure 7: Atmospheric temperature T_ω according to formula (45) that is responsible for atmospheric radiation within the framework of the line-by-line model

$$J_\downarrow(CO_2) = \int_{\omega_1}^{\omega_2} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2}\left[\exp\left(\frac{\hbar\omega}{T_E}\right)-1\right]^{-1}, \tag{46}$$

and also within the framework of the line-by-line model, according to formula

$$J_\downarrow(CO_2) = \int_{0}^{\infty} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2}\left[\exp\left(\frac{\hbar\omega}{T_\omega}\right)-1\right]^{-1} \cdot \frac{k_\omega}{k_\omega + \kappa_\omega} \tag{47}$$

Here ω_1 and ω_2 are the boundaries of the absorption band by CO_2 molecules, and within the framework of the absorption band model inside this spectral range the radiative temperature T_ω coincides with the Earth's temperature because of layers, which are responsible for radiation at a given frequency, are located close to the Earth's surface. Both models give nearby values of the atmospheric radiative flux toward the Earth due to CO_2 molecules which at the contemporary concentration of atmospheric CO_2 molecules is approximately $67W/m^2$ with the accuracy of several percent. This is about 20% of the total radiative flux toward the Earth in the IR spectral range.

One more value under consideration is the diûerence $\Delta J_\downarrow(CO_2)$ of radiative fluxes toward the Earth's surface at doubling $J_\downarrow(CO_2)'$ and contemporary $J_\downarrow(CO_2)$ concentrations of atmospheric CO_2 molecules which is given by

$$\Delta J_\downarrow(CO_2) = J_\downarrow(CO_2)' - J_\downarrow(CO_2) \tag{48}$$

The absorption band model gives for the change of radiative fluxes under the above conditions

$$\Delta J_\downarrow(CO_2) = (3 \pm 2)W/m^2 \tag{49}$$

One can see a low accuracy according to this model, but this value coincides by the order of magnitude with that of $4W/m^2$ which is contained in books [56, 58].

A high error in this value follows from oscillations of the absorption coefficient that leads to an uncertainty in the boundaries of the absorption coefficient as a frequency function. In the case of the line-by-line method, one can find the difference of radiative fluxes at the contemporary and doubled concentrations of atmospheric CO_2 molecules according to formula

$$\Delta J_{\downarrow} = \int_{\omega_1}^{\omega_2} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2}\left\{\left[\exp\left(\frac{\hbar\omega}{T'_\omega}\right)-1\right]^{-1} - \left[\exp\left(\frac{\hbar\omega}{T_\omega}\right)-1\right]^{-1}\right\}, \qquad (50)$$

where T_ω and T'_ω are the radiative temperatures at the contemporary concentration of carbon dioxide molecules and its doubled value respectively, and just this difference is determined an additional radiative flux toward the Earth due to this concentration change. In reality, the absorption coefficient κ_ω due to other than carbon dioxide radiators has the oscillation structure also. Let us take it in the form

$$\kappa_\omega = \kappa_o + a\cos(\omega\tau + \tau_o), \qquad (51)$$

where $a < \kappa_o$. Changing values of parameters of formula (51) at $\kappa_o = 0.30 km^{-1}$, one can obtain

$$\Delta J_{\downarrow} = (1.0 \pm 0.2)\ W/m^2 \qquad (52)$$

As is seen, the absorption band model leads to a large error in this value. Hence, the absorption band model is not suitable in determination of the derivative of the radiative flux over the concentration of CO_2 molecules, but it is suitable for evaluation of the total radiative flux.

6. CONCLUSION

As it follows from the analysis carried out, in the case of competition between different mechanisms of broadening of spectral lines, short-range broadening influences weakly on the radiation flux produced by a gas with excited atoms or molecules. The calculations show that the radiative flux from an excited atomic or molecular gas is determined by the long- range part of the broadening or collisional broadening of spectral lines. Next, the concept of the absorption band (or emission) and the optical thickness of a gas system at a given radiation frequency can be used as the basis for analyzing the radiation of an excited gas, both atomic and molecular. These concepts allow us to calculate radiative fluxes under real conditions, that leaves the gas system, taking into account several overlapped absorption bands.

As a demonstration of application of these concepts, we consider IR radiation of the Venus atmosphere in the near-surface region, which is determined by molecules of carbon dioxide, the main component of the Venus atmosphere. Note the importance of the greenhouse effect for the Venus atmosphere. In particular, if we remove the Venus atmosphere and assume that its surface absorbs the Sun's radiation incident on it in the visible region of the spectrum, the surface Venus temperature becomes 463K, whereas in reality it is 737K. Evidently, IR radiation of the Venus surface is compensated, mainly, by the power of absorbed solar radiation in the visible spectral range, and also by the power of IR radiation from the near-surface layers of the Venus atmosphere. However, the total power of these radiative channels on the Venus surface does not exceed 30% from the radiative power of the Venus surface. Note that the accuracy of calculations for radiation fluxes due to atmospheric carbon dioxide is better than 20%, which confirms the reality of this contradiction and requires additional channels for energy fluxes to the Venus surface. Evidently, such a channel is determined by radiation of dust microparticles located in the Venus atmosphere.

In addition, the analysis of radiation of the Earth's atmosphere allows one to analyze the accuracy of the absorption band model and the line-by-line model for evaluation of the radiative flux toward the Earth's surface. In particular, one can convince that the absorption band model is valid for evaluation of the radiative flux, but this model is characterized by a low accuracy in evaluation of its derivative of the radiative flux over the concentration of emitting molecules.

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