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RADIATION FEATURES OF MOLECULAR GAS MIXTURES

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Abstract. The nature of thermal radiation from a layer of dense gas in local thermodynamic equilibrium with radiation is considered. The radiation spectrum of a gas layer containing a mixture of molecular gases and microparticles consists of a large number (hundreds and thousands) of peaks that rise above the pedestal corresponding to microparticle radiation. Changes in partial radiation fluxes with varying concentration of one of the active components are investigated. Information on molecular radiation parameters contained in the HITRAN database is of great importance for the analysis and calculations. It is shown that the model of a homogeneous atmosphere with spectrum averaging for one or all components is unreliable when analyzing radiation flux changes resulting from concentration changes of one of the radiating components. This model is only convenient for estimating integral parameters of gas radiation. The dense cloud model assumes that radiation in different directions of the layer is determined by different spatial regions that do not affect each other, and also assumes a sharp boundary for dispersed phase radiation. This model works better with increasing optical thickness of the layer relative to molecular components. The accuracy and capabilities of the dense cloud model are demonstrated by calculations of radiation fluxes generated by the standard atmosphere in the absorption bands of carbon dioxide molecules. A fundamental difference is shown between radiation flux changes from an optically dense gas layer with varying temperature when changing the concentration of an active component for single-component and multi-component systems. In a single-component gas, the change in partial radiation flux due to concentration changes of the radiating component is proportional to the temperature gradient, while in a multi-component gas, the change in partial radiation flux of a given component is almost compensated by reverse changes due to absorption by other components. A five-fold error in climate models for global temperature change due to changes in atmospheric carbon dioxide concentration is shown, as these models neglect the absorption of additional carbon dioxide radiation by water molecules and clouds. Additionally, the presented algorithms can serve as a basis for creating radiation amplifiers in the laser transition region for carbon dioxide with wavelengths near 9.5 μm and 10.6 μm. These amplifiers are suitable for monitoring combustion sources on Earth's surface from satellites, as well as engines and power plants using fuel combustion. The sensitivity of these laser amplifiers exceeds that of modern thermal imagers by orders of magnitude, and the specified spectral lines of laser transitions for amplification fall within the atmospheric transparency window.

Keywords: *thermal atmospheric radiation, radiation spectrum, greenhouse effect, HITRAN data bank*

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1. INTRODUCTION

The radiation of dense gas located above a hot surface manifests itself in various real situations where this radiation determines the energy balance of the surface and the gas above it. The most important example of this type is the Earth's atmospheric radiation, which is known as the greenhouse effect of the atmosphere. The role of Earth's greenhouse effect is not difficult to determine based on Earth's energy balance. Indeed, the average flow of solar radiation penetrating the atmosphere is 340W/m^2, and approximately half of this flow is absorbed by the Earth's surface. If we consider that the Earth's surface radiates as a black body and there is no atmosphere, then according to the Stefan-Boltzmann law, its surface temperature would be 234 K. In reality, the global temperature, i.e., the average surface temperature of the Earth, is 288 K [1].

Similarly, the radiation of other planets is another example of dense gas radiation, where local thermodynamic equilibrium is maintained between the radiation field and the gas comprising the planet's atmosphere. This range of problems also includes fires over large areas, particularly forest fires. In these cases, air of non-uniform temperature containing combustion products forms above the hot surface. The radiation of this air, absorbed by the hot surface, determines the surface temperature, which, in turn, affects the burning rate.

In the considered cases, the radiation of the gas layer, which includes molecular gases, belongs to the infrared spectrum and is accordingly created by gas molecules. Therefore, the emission spectrum of the gas layer is determined by vibrational-rotational and rotational radiative transitions between molecular states and consists of a large number of peaks, i.e., spectral lines broadened due to the interaction of radiating molecules with air molecules. Note the fundamental role of the HITRAN database in analyzing these problems, as this database provides extensive information on the parameters of radiative transitions in molecules [2–4]. In particular, the computer program used for the following analysis includes parameters of about ten thousand radiative transitions in molecules taken from the HITRAN database.

The nature of radiation from a gas layer determines its analysis method, using the "line by line" approach [5, 6], according to which the analysis is conducted for each frequency separately. Nevertheless, the emission problem of a flat gas layer itself is cumbersome [7–10], as it includes the gas emission spectrum, as well as spatial distributions of temperature and density of radiating components.

For simplification, certain models are used that make the problem under consideration transparent.

In this article, we rely on two models, whose comparison and combination allows us to understand their accuracy in describing atmospheric radiation. In the first one, the homogeneous atmosphere model [11], averaging is performed over the spectrum of radiating components of the layer or some of them. The other model, the dense cloud model, relates to the real atmosphere [12]. It assumes that dense clouds are concentrated at a certain distance from the layer boundary, limiting the emission region of molecular components. Comparing the results of these models allows us to estimate the accuracy with which we can calculate both the radiation fluxes created by different greenhouse components and the change in radiation flux when the concentration of one of the greenhouse components changes.

To demonstrate specific conclusions, we will focus on the air of the standard atmosphere as a radiating gas, which is a multicomponent system and includes three main greenhouse components – water and carbon dioxide molecules, as well as clouds consisting of water microdroplets or microparticles. Due to the peak structure of the emission spectrum, numerical computer methods are used to calculate radiation fluxes from the air layer. The calculations are based on the densities of molecular components and their spatial distributions according to the standard atmosphere model [1], and the cloud boundary follows from the data determining Earth's energy balance [12].

Further, for specific calculations of atmospheric radiation, we use a computer program [13] developed by one of the authors (D.A. Zhilyaev). It uses parameters of about 15,000 emission transitions in atmospheric molecules, taken from the HITRAN database. It incorporates a specific spatial distribution of greenhouse component density, as well as a spatial distribution of temperature. Along with the main greenhouse components (water molecules and carbon dioxide, as well as clouds), it accounts for the participation of trace components N_2O, CH_4, O_3 in the formation of layer radiation. This computer program was tested on the standard atmosphere model [1], which will also be used further.

2. DENSE CLOUD MODEL FOR MOLECULAR GAS LAYER RADIATION

Analysis of atmospheric emission shows that determining the radiation flux from an optically active molecular gas layer is a cumbersome task, as it requires initial information about both the spectral characteristics of the emitting gas and the spatial distribution of emitting components. The "line-by-line" model [5, 6], within which all emission parameters relate to a specific photon frequency ω, takes into account the emission spectrum of the gas layer, which combines with a specific spatial distribution of emitting components.

Due to the complexity of this problem, which requires the use of several parameters for analysis,

we will focus on Earth's atmosphere as one of the objects related to this problem. Earth's atmosphere contains three main greenhouse components, i.e., components that determine atmospheric emission. These components are water molecules, carbon dioxide molecules, and water microdroplets that form clouds. These greenhouse components are responsible for atmospheric radiation in the infrared spectrum region and provide approximately 99% of the atmospheric thermal radiation flux. The spatial distribution of carbon dioxide molecules coincides with the distribution of nitrogen and oxygen molecules due to the chemical passivity of these molecules. Water molecules in atmospheric air participate in condensation and evaporation processes, and therefore their spatial distribution in the atmosphere differs from the spatial distribution of nitrogen and oxygen molecules. On average, it can be determined from the analysis of water circulation passing through the atmosphere.

The most challenging task is determining the spatial distribution of clouds, consisting mainly of water microdroplets. The problem is that the average atmospheric humidity is less than 100% and decreases with increasing altitude. Therefore, on average, atmospheric water condensation is absent, but it actually occurs due to temperature fluctuations in atmospheric air in areas with lower temperatures. In reality, atmospheric water condensation occurs as a result of mixing streams of warm surface air penetrating into cold atmospheric layers [14]. However, when entering warm atmospheric regions, condensed water in moving air streams evaporates. This creates difficulties in determining the amount of condensed water and its distribution in the atmosphere. The problem of condensed water in the atmosphere is further complicated due to convective air movement [15].

Nevertheless, it is possible to determine one parameter related to clouds and characterizing cloud radiation on average. Indeed, on the one hand, based on the spatial distribution of water molecules and carbon dioxide, as well as temperature distribution, one can determine the radiation flux to the Earth's surface created by these molecules. On the other hand, the atmospheric radiation fluxes presented in the table are based on measurements and include the participation of clouds in the formation of atmospheric radiation. By comparing these fluxes, one can reconstruct the contribution of clouds to thermal radiation and determine the cloud parameter associated with this contribution.

The table shows statistically averaged values of infrared radiation fluxes taken from five sources [16]. The indicated radiation fluxes are the ratio of the total power of the radiation process for a given channel to the Earth's surface area. The given uncertainties follow from statistical averaging of fluxes obtained from different sources.

Further, we use a model of atmospheric radiation with one cloud parameter [12]. Specifically, we will assume that clouds are located at heights starting from a certain height h_{cl}, and then with increasing height, the optical density of clouds increases sharply. In this case, clouds radiate towards the Earth's surface as a black body with temperature $T(h_{cl})$, equal to the air temperature at the boundary height. Furthermore, the cloud separates the lower part of the atmosphere, so that processes in the atmosphere above the clouds do not affect the parameters of atmospheric radiation towards the Earth.

Thus, within the framework of the considered model, we have a radiating atmospheric layer between the Earth's surface and the lower edge of the cloud. This layer contains radiating molecules that create part of the atmospheric radiation flux directed towards the Earth's surface. Considering that the atmospheric temperature in the radiating layer changes weakly with height, we characterize this radiation with effective temperature T_ω for each radiation frequency. Radiation for a weakly inhomogeneous radiating flat gas layer, when temperature of air changes little in the space region, reduces to radiation of a gas layer with constant temperature.

Table. Average infrared radiation fluxes in Earth's energy balance [16]

Radiation channel	Energy flux, W/m^2
Atmospheric emission to Earth's surface	335 ± 7
Atmospheric emission to surrounding space	217 ± 8
Absorption by Earth's atmosphere	372 ± 6
Earth surface emission	393 ± 8
Transmission through atmosphere from Earth's surface	21 ± 1

Then the radiation flux J_ω for a given photon frequency within the presented model is determined by the relation

$$J_\omega = I_\omega(T_\omega)g(u_\omega) + I_\omega(T_{cl})[1 - g(u_\omega)], \quad (1)$$

where u_ω is the optical thickness of the atmospheric layer between Earth's surface and clouds, T_{cl} is the air temperature at the lower cloud edge, $g(u_\omega)$ is the layer opacity factor, $I_\omega(T_\omega)$ is the equilibrium radiation flux, which is determined by Planck's formula [17, 18]

$$I_\omega(T) = \frac{\hbar\omega^3}{4\pi^2c^2\left[\exp\left(\hbar\omega / T\right) - 1\right]}. \quad (2)$$

The layer opacity factor included in formula (1) $g(u_\omega)$in case of isotropic photon emission, as occurs in gas, is determined by expression [19]

$$g(u_\omega) = 2\int_0^1 \cos\theta\left[1 - \exp\left(-\frac{u_\omega}{\cos\theta}\right)\right]d\cos\theta \quad (3)$$

and represents the probability that a photon of given frequency ω, originating at one of the layer boundaries, moving at an angle θ to the surface does not reach the other layer boundary. In case of an optically thick layer for given frequency $g(u_\omega) = 1$. Based on these expressions for radiation flux from atmosphere to Earth's surface, we have

$$J_\downarrow = \int_0^\infty J_\omega d\omega. \quad (4)$$

The value of this quantity, obtained from measurements, is given in the Table.

As can be seen, along with the spectral parameters of the emitting components of the weakly inhomogeneous flat layer for the considered calculations of radiation fluxes of a gas layer containing a mixture of optically active molecules of different types and microparticles, information about their spatial distribution is required. The accuracy and reliability of the final result depend on the accuracy of this information. In particular, Fig. 1 shows the relationship between the radiation flux from the atmosphere to the Earth's surface $J_\downarrow$, which is a parameter of the Earth's and atmosphere's energy balance, and the cloud boundary h_{cl} in the range of radiation flux values from different sources used in the table. Based on this, the accuracy of partial parameters of atmospheric radiation can be determined.

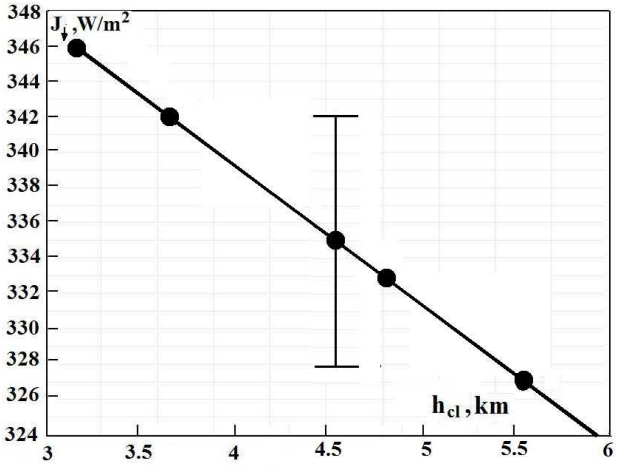

Fig. 1. Dependence of radiation flux from the atmosphere to the Earth's surface $J_\downarrow$ on the cloud boundary height h_{cl}. Circles correspond to five sources of the Earth's energy balance and its atmosphere

Note that to calculate radiation fluxes of a temperature-weakly inhomogeneous gas layer containing several emitting components, information about the spectrum of emitting molecules and particles, as well as their spatial distribution is necessary. The considered models allow to evaluate the sensitivity of the result to the nature of these distributions.

The above-mentioned computer program [13] allows determining various parameters of atmospheric radiation with given parameters and height distributions of atmospheric emitting components' density. The error of these parameters is determined by the range of values in which the cloud boundary is located. Fig. 2 shows the frequency dependence ω of optical thickness u_ω of atmospheric air for standard atmosphere parameters at limiting values of cloud boundary h_{cl} for the dense cloud model.

In addition, Fig. 3 shows the spectral dependence of the radiation flux J_ω of the standard atmosphere in the frequency range corresponding to the lower absorption band of carbon dioxide molecules using the dense cloud model. As can be seen, the dependence on the cloud boundary position is only manifested at the band edge with small optical thickness of the atmosphere as a radiating gas layer.

The assumption used in the dense cloud model is associated with neglecting the connection between the gas layer regions responsible for radiation escaping in different directions. This assumption holds for regions with large optical thickness of the gas layer. In the case of the atmosphere, radiation parameters weakly depend on the position of cloud boundaries. At the same time, the dense cloud model uses the real gas emission spectrum. Therefore, the dense cloud model provides higher accuracy in

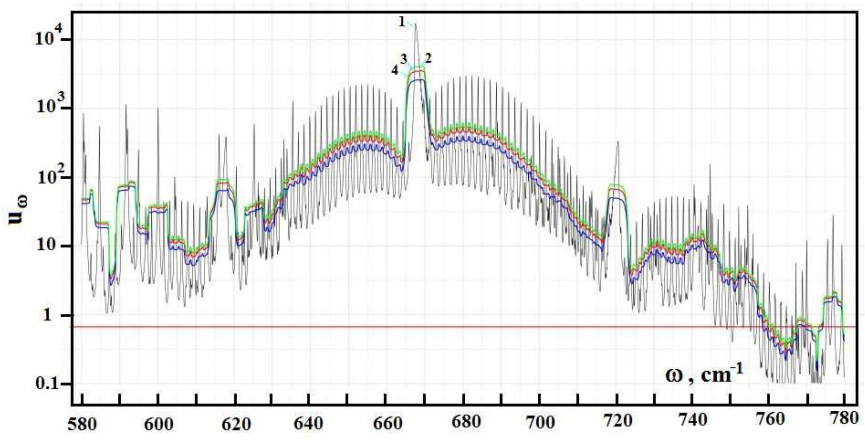

Fig. 2. Optical thickness u_ω of the atmosphere between the Earth's surface and cloud boundary within the dense cloud model in the lower absorption band of carbon dioxide molecules, $h_{cl} = 3.2$ km (1); curves 2, 3, 4 correspond to averaging over the frequency interval 5 cm^{-1} above and below the specified for cloud boundary heights of 3.2, 4.6, 5.6 km respectively

describing the radiative parameters of the gas layer the greater its optical thickness.

3. HOMOGENEOUS ATMOSPHERE MODEL

The homogeneous atmosphere model for thermal radiation of a plane layer of multicomponent gas [11] uses the absorption coefficient averaged over the spectrum of radiating components and exponential dependence on the distance to the lower boundary of the radiating layer h, so that the gas absorption coefficient is represented as

$$k_\omega(h) = k_0 \exp\left(-\frac{h}{\lambda}\right), \qquad (5)$$

where k_0, λ are parameters describing the radiation of the system under consideration. These parameters are determined by external conditions related to the distribution of radiating component densities by height, and radiation fluxes beyond the radiating gas layer. In the case of Earth's atmosphere, this uses parameters of the standard atmosphere [1] or local atmosphere. The atmospheric radiation fluxes toward Earth and into surrounding space are taken from the energy balance of Earth and its atmosphere, partially presented in the Table.

To determine the parameters of formula (5), only two flows from the table are used, namely, average radiation fluxes of the atmosphere to the Earth's surface ($J_\downarrow = 335 \pm 7$ W/m^2) and into surrounding space ($J_\uparrow = 217 \pm 8$ W/m^2). Let's present the algorithm for determining parameters of formula (5) within the framework of a homogeneous atmosphere model. We consider the radiating flat gas layer as weakly inhomogeneous, i.e., temperature changes slightly in the space region where radiation is formed. Thus, radiation of a weakly inhomogeneous layer is reduced to radiation of a gas layer with constant temperature. In the case of the standard atmosphere model, the radiation temperature is the same for all radiation frequencies, so in this case, it is convenient to introduce radiation temperatures in the direction of Earth ($T_\downarrow$) and into surrounding space $T_\uparrow$. These parameters are related to radiation fluxes by the relations

$$J_\downarrow = \sigma T_\downarrow^4, \; J_\uparrow = \sigma T_\uparrow^4, \qquad (6)$$

where $\sigma = 5.67 \cdot 10^{-8}$ W/m^2 is the Stefan—Boltzmann constant.

Moving to the parameters of the standard atmosphere [1], for the temperature of atmospheric layers responsible for radiation towards Earth and into surrounding space, we have

$$T_\downarrow = T_E - \frac{dT}{dh} h_\downarrow, \quad T_\uparrow = T_E - \frac{dT}{dh} h_\uparrow, \qquad (7)$$

where $T_E = 288$ K is the Earth's surface temperature, and $dT / dh = 6.5$ K/km is the temperature gradient for the standard atmosphere [1].

Let's introduce effective heights for layer radiation towards Earth ($h_\downarrow$) and into surrounding space ($h_\uparrow$) so that the radiation flux of a black body with temperature at a given height coincides with the corresponding radiation flux.

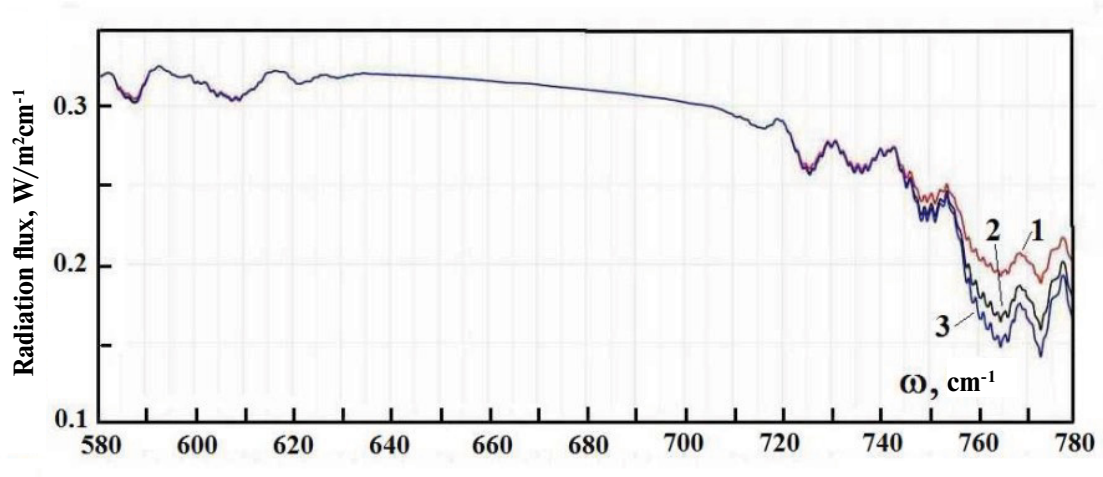

Fig. 3. Partial emission flux of the standard atmosphere to the Earth's surface, calculated within the dense cloud model and averaged over the nearest spectral lines. Averaging occurs in the interval including frequencies 5 cm^{-1} greater and less than the considered frequency. Cloud boundary h_{cl} = 3.2 (1), 4.5(2), 5.6 (3) km

In the case of Earth's standard atmosphere, this gives effective heights that determine atmospheric radiation towards Earth and into surrounding space of

$$h_{\downarrow} = 1.6 \pm 0.2, \quad h_{\uparrow} = 6.1 \pm 0.3\,\text{km}. \tag{8}$$

Within this model, there is a limiting value for the optical thickness of the layer. The values of distances from the boundary of the weakly inhomogeneous layer, responsible for radiation towards Earth and into surrounding space, follow from relation [20], so that the optical thickness to the corresponding boundary equals 2/3. From this, we obtain

$$k_0\lambda[1 - \exp(-h_{\downarrow} / \lambda)] = 2 / 3, k_0\lambda \exp(-h_{\uparrow} / \lambda) = 2 / 3.$$

Hence the equation for the parameter λ follows:

$$\exp(-h_{\downarrow} / \lambda) + \exp(-h_{\uparrow} / \lambda) = 1. \tag{9}$$

As a result of solving equation (9), we obtain numerical values of parameters for formula (5) for the standard atmosphere:

$$\begin{gathered} k_0 = 0.50 \pm 0.05\ \text{km}^{-1}, \\ \lambda = 4.8 \pm 0.4\ \text{km}, \\ u = k_0\lambda = 2.4 \pm 0.3. \end{gathered} \tag{10}$$

Note that the value $k_0\lambda$ is the optical thickness of the entire atmosphere.

From formula (10), it follows that the standard atmosphere can be conditionally considered an optically thick gas layer during thermal radiation emission in the infrared spectrum region. This allows using formulas (10) for the optical thickness of the layer, responsible for radiation. In particular, it follows that approximately $2 \pm 1\%$ of the radiation flux passes through the atmosphere if it is emitted isotropically, or $9 \pm 2\%$ of the radiation flux if only the portion of radiation propagating perpendicular to the surface is fixed. According to the table data, $5.3 \pm 0.3\%$ of the radiation flux created by Earth's surface passes through the atmosphere. Since the main contribution to the radiation flux passing through the atmosphere corresponds to frequencies with lower optical thickness of the layer, this indicates the inapplicability of the homogeneous atmosphere model for some radiation emission problems.

This discrepancy in atmospheric transparency, measured for the real atmosphere and calculated based on the homogeneous atmosphere model, indicates the crudeness of the considered model. Nevertheless, the homogeneous atmosphere model is a simple model for gas layer emission that allows separating the optical properties of the gas layer and spatial distribution of radiating components based on measured layer parameters.

However, the homogeneous atmosphere model inherently does not allow for changes in the concentration of its optically active components. Indeed, the total radiation flux of the atmosphere obtained from measurements can only be determined for the current atmospheric composition, but not for a modified atmosphere. To overcome this difficulty,

we will further modify the homogeneous atmosphere model. In this case, one of the greenhouse components is removed from the gas layer. This framework is analyzed within the homogeneous atmosphere model, and then the removed component is added back with its real spectrum. The parameters of the homogeneous atmosphere are selected so that the total spectral radiation fluxes in both directions from the gas layer coincide with their real values.

Further, we use the modified homogeneous atmosphere model for the standard atmosphere from which carbon dioxide has been removed. Within the framework of the considered model, the absorption coefficient k_ω of atmospheric air is given by the expression

$$k_\omega = k_0 \exp\left(-\frac{h}{\lambda}\right) + \kappa_\omega(h). \quad (11)$$

In the case of the atmosphere, parameters k_0, λ account for the absorption of water molecules and clouds, while κ_ω is the absorption coefficient due to carbon dioxide molecules.

Let's analyze the standard atmosphere [1] from the perspective of the modified homogeneous atmosphere model. Based on the table data, the radiation flux to the Earth's surface equals $J_\downarrow = 335$ W/m^2, and to the surrounding space is $J_\downarrow = 217$ W/m^2. Using spectral data for atmospheric molecules according to the HITRAN database and the dense cloud model, for the average total frequency radiation fluxes for the atmosphere without carbon dioxide, we have $J_\downarrow' = 324$ W/m^2 to the Earth's surface and $J_\uparrow' = 221$ W/m^2 to the surrounding space.

Performing operations for a homogeneous atmosphere model based on radiation flux values, we obtain respectively for effective radiation temperatures toward Earth's surface and into surrounding space $T_\downarrow' = 275$ K and $T_\uparrow' = 250$ K, and for the heights of the atmospheric layer responsible for radiation in the specified directions, $h_\downarrow' = 2.0$ km and $h_\uparrow' = 5.9$ km. Solving the equation with these parameters yields the following value for parameter in formula (11):

$$\lambda = 5.2 \text{ km}. \quad (12)$$

Furthermore, requiring that the total radiation fluxes of the atmosphere match the measured values, for the second parameter of formula (11) we obtain

$$k_0 = 0.60 \text{ km}^{-1}. \quad (13)$$

Fig. 4 shows the frequency dependence of the radiation flux from the standard atmosphere directed toward Earth's surface. Comparison of results from different models shows that the radiation flux depends on the emission spectrum for the considered model. Obviously, the partial radiation flux of the atmosphere to Earth's surface increases with the optical thickness of the atmosphere for a given frequency. In particular, in the atmospheric transparency window corresponding to the frequency range 800–1200 cm^{-1}, dense cloud models correspond to lower radiation fluxes than those following from the homogeneous cloud model. The opposite situation occurs at frequencies below 600 cm^{-1}.

4. CHANGES IN THE EMISSION OF A FLAT GAS LAYER

The models presented above aim to simplify the real situation, and our goal to understand how accurately the results obtained within these models correspond to real results. The most interesting aspect is the change in radiative parameters of the gas layer when the gas composition changes, i.e., how the radiative parameters of the gas layer depend on the concentration of greenhouse components. The most common problem of this type is calculating the modified parameters of the standard atmosphere, particularly the change in Earth's surface temperature, when the concentration of atmospheric carbon dioxide changes.

This problem was formulated by Arrhenius at the end of the 19th century and reflected in the title of his work [21] "Does the presence of heat-absorbing gases in the atmosphere affect Earth's temperature in any way?", although the work was devoted to analyzing experiments on the scattering of solar radiation by the Moon. During the Moon's movement, the angle at which reflected solar radiation enters Earth's atmosphere changes, which allows determining the optical thickness of the atmosphere for absorption in the spectrum associated with molecules CO_2 and H_2O. However, the spectral region responsible for this scattering corresponds to a different absorption band of the considered molecules.

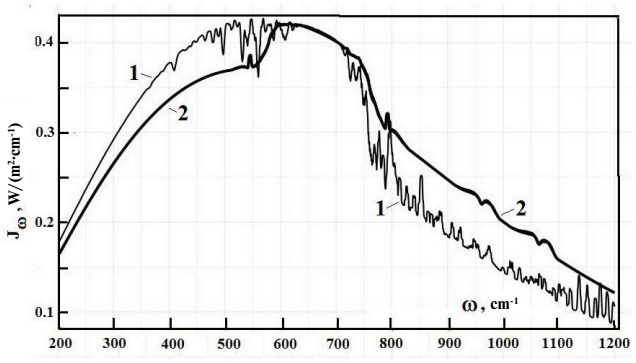

Fig. 4. Partial flux J_ω, emitted by the standard atmosphere in the lower absorption band of carbon dioxide molecules and incident on Earth's surface. This radiation flux is calculated within the dense cloud model with an average cloud boundary height of $h_{cl} = 4.6$ km (1), as well as the modified homogeneous atmosphere model (2)

Subsequent study of carbon dioxide's role in atmospheric radiation was initiated by new information on the spectral parameters of carbon dioxide molecules [22–24]. However, in these cases, due to limited information on the radiative parameters of water molecules and the role of condensed water in atmospheric emission, it was assumed that atmospheric radiation in the infrared spectrum region is determined only by molecules CO_2. This assumption is used in climate models [25], which leads to a large error in the total radiation flux of the atmospheric layer [26].

Currently, we have sufficient available information on the radiative parameters of greenhouse components, collected in the HITRAN database [2–4]. Based on the current state of atmospheric physics, it can be concluded that the assumption of a single-component radiating atmosphere violates Kirchhoff's law [27] for the real atmosphere. Indeed, according to Kirchhoff's law, changes in the concentration of one component of the radiating gas layer and the increase in radiation flux due to this component are partially compensated by absorption of other greenhouse components.

Essentially, the error in climate models is associated with replacing the change in total radiation flux ΔJ due to changes in the concentration of molecules CO_2 with an additional radiation flux $\Delta J(CO_2)$, created by molecules CO_2. The approximately five-fold difference [13, 28] between these radiation fluxes is determined by the overlap of greenhouse component spectra and follows from numerical calculations. Below, using a simple illustrative example, we will show that the reason for such a large error is related to the different nature of changes in fluxes ΔJ and $\Delta J(CO_2)$.

This effect is determined by the superposition of absorption spectra of molecules CO_2 on the spectra of atmospheric water molecules and water microdroplets. Such information is contained in the HITRAN database [2–4]. It allows reliable determination of changes in atmospheric radiation flux due to the introduction of additional carbon dioxide molecules into the atmosphere and reduction of radiation flux due to absorption of radiation flux by water molecules and clouds by the introduced molecules CO_2. The second effect is ignored in climate models [25], which leads to a five-fold overestimation of the total radiation flux change.

Although the reason for the error in climate models follows from numerical calculations [26], this work will present another transparent demonstration of this reason. Let's consider the case of an optically thick layer and calculate the ratio of the considered radiation fluxes, denoting the total absorption coefficient of the atmospheric layer as K_ω, the absorption coefficient created by carbon dioxide molecules as k_ω, and the absorption coefficient created by additional carbon dioxide introduced into the atmosphere as Δk_ω. For an optically thick gas layer, we use the relation [20], according to which the effective radiation temperature at a given frequency, T_ω, is the temperature at height h_ω, for which the optical thickness equals 2/3, i.e.

$$\int_0^{h_\omega} K_\omega d\omega = 2/3. \qquad (14)$$

In this case, the absorption coefficients for the flux ratio are taken at height h_ω, and the change in radiation flux $\Delta J_\omega(CO_2)$, created by added carbon dioxide molecules, equals

$$\Delta J_\omega(CO_2) = \frac{\Delta k_\omega k_\omega}{K_\omega^2} J_\omega(CO_2), \qquad (15)$$

where $J_\omega(CO_2)$ is the radiation flux created by molecules CO_2. Note that for the real atmosphere in the considered limiting case of an optically thick atmospheric layer, clouds do not contribute to the change in total radiation flux within the dense cloud model, and the absorption coefficients in formula (15) are taken at height h_ω.

On the other hand, the change in total radiation flux ΔJ_ω from the atmosphere at a given frequency ω is determined by the change in radiation temperature

ΔT_ω, which is related to the change in height Δh_ω, responsible for radiation at a given frequency according to equation (14). We have

$$\Delta T_\omega = -\frac{\partial T}{\partial h}\Delta h_\omega = \frac{\partial T}{\partial h}\frac{\Delta k_\omega}{k_\omega K_\omega}, \qquad (16)$$

where we assumed that the value Δk_ω does not depend on height. In particular, for the standard atmosphere, we have

$$\partial T / \partial h = 6.5 \text{ K/km}.$$

Based on formulas (1) and (16), for the change in total radiation flux ΔJ_ω we obtain

$$\Delta J_\omega = \frac{\partial J_\omega}{\partial T_\omega}\Delta T_\omega = $$

$$= J_\omega \frac{\hbar\omega}{T_\omega^2[1-\exp(-\hbar\omega / T_\omega)]}\left|\frac{\partial T}{\partial h}\right|\frac{\Delta k_\omega}{k_\omega K_\omega}. \quad (17)$$

From this, we find the ratio of the addition to the radiation flux $\Delta J_\omega(CO_2)$, created by carbon dioxide molecules, to the change in total radiation flux ΔJ_ω at a given frequency ω:

$$\eta_\omega = \frac{\Delta J_\omega(CO_2)}{\Delta J_\omega} = \frac{k_\omega^2}{K_\omega}\frac{T_\omega^2[1-\exp(-\hbar\omega / T_\omega)]}{\hbar\omega\,|\,\partial T / \partial h\,|}. \quad (18)$$

Let's perform an estimation based on formula (18), focusing on the frequency of the center of transition between the ground and lower vibrational states of the molecule CO_2, for which $\hbar\omega = 667$ cm^{-1}. For definiteness, let's assume $k_\omega = K_\omega / 2$, taking as a parameter of this formula $K_\omega = 1$ km^{-1}, which according to equation (14) corresponds to an effective radiation height $h_\omega = 2 / 3$ km and effective radiation temperature $T_\omega \approx 284$ K, and the optical thickness of the atmosphere between Earth's surface and clouds equals $u_\omega \approx 4$. Then based on formula (18), we obtain $\eta_\omega = 3.3$. If, maintaining the values of other parameters, we choose $K_\omega = 2$ km^{-1}, repeating the performed operations, we get $\eta_\omega = 6.8$. These values are of the same order of magnitude as the average value of this parameter $\eta_\omega = 5.2$ [13, 28]. Note that both examples correspond to a large optical thickness of the layer.

As can be seen, the change in radiation flux $\Delta J_\omega(CO_2)$, created by carbon dioxide molecules, and the change in total radiation flux ΔJ_ω are determined by different causes. The ratio of fluxes (18) is large when the temperature dependence on height is weak. The ratio η_ω becomes infinite if the atmospheric air temperature does not change with height. Furthermore, the greatest difference between the calculated changes in radiation fluxes due to changes in greenhouse component concentration in the atmosphere occurs in optically dense spectral regions, where an increase in the concentration of a given component causes partial absorption of radiation flux created by other components.

Fig. 5 shows the partial flux ratio η_ω in the absorption spectrum region of carbon dioxide molecules. The data in Fig. 5 confirm the above conclusion that the ratio in question increases with higher atmospheric optical thickness. Indeed, let's introduce the average ratio value η_ω for a given frequency interval according to the formula

$$\overline{\eta_\omega} = \frac{1}{\omega_2 - \omega_1}\int_{\omega_1}^{\omega_2}\eta_\omega d\omega, \qquad (19)$$

where ω_1, ω_2 are the boundary frequencies for the considered frequency interval. Returning to Fig. 5, we have for the average ratio $\eta_\omega = 5.6$ based on the data in Fig. 5 (upper panel), the value $\eta_\omega = 3.3$ according to the data in Fig. 5 (middle panel), and $\eta_\omega = 3.2$ using the data from Fig. 5 (lower panel).

The average value of the parameter under consideration dioxide lasers meter across the entire absorption region of carbon dioxide molecules is

$$\overline{\eta_\omega} = 5.0. \qquad (20)$$

These values coincide with the average value of this parameter, which is defined as [13, 28]

$$\overline{\eta_\omega}' = \frac{\overline{\Delta J_\omega}}{\Delta J_\omega(CO_2)} = 5.2 \pm 0.2.$$

Here, the change in total radiation flux is averaged over frequencies.

Thus, we have two models for analyzing radiation parameters of an active gas layer, including a mixture of molecular gases, specifically, which are tested on Earth's standard atmosphere. These include the dense cloud model and the modified homogeneous atmosphere model. Fig. 6 shows the change in partial radiation flux ΔJ_ω when doubling the concentration of carbon dioxide in the atmosphere, calculated based on these models. As can be seen, at certain frequencies, the atmospheric parameters under consideration significantly diverge, i.e., the partial radiative parameters of the atmosphere depend on the radiation spectrum.

It follows that the dense cloud model is preferable when analyzing the radiation of molecular gas mixtures including microparticles, since this model takes into account the real spectrum of molecular gases. In this case, we are primarily talking about a layer characterized by high optical density. To understand the dependence of radiation parameters on the used model parameters, Fig. 7 shows the change in the effective temperature of the standard atmosphere when doubling the concentration of carbon dioxide molecules for different cloud boundary positions.

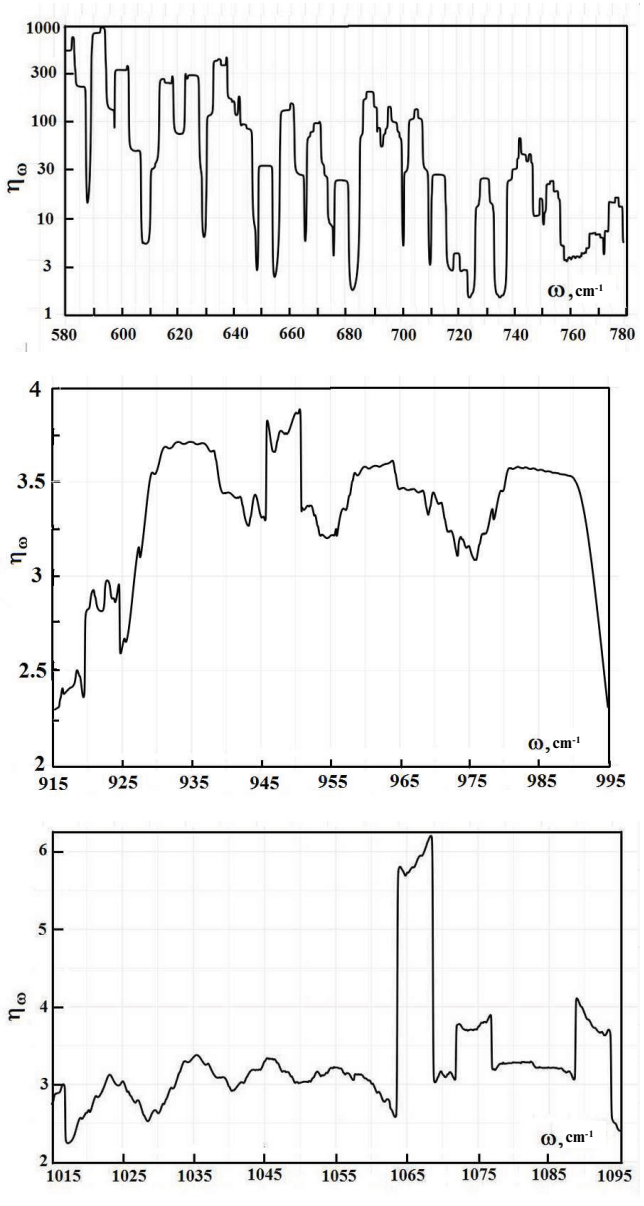

Fig. 5. The ratio of partial radiation fluxes $\eta_\omega = \Delta J_\omega(CO_2) / \Delta J_\omega$, created by carbon dioxide molecules, and the total radiation flux, which is calculated within the dense cloud model with cloud boundary at $h_{cl} = 4.6$ km: upper panel – the region of the lower absorption band of carbon dioxide molecules; middle and lower panels – absorption frequency bands used in carbon

In addition, Fig. 8 shows the partial changes in the radiation flux of the standard atmosphere ΔJ_ω when doubling the concentration of carbon dioxide molecules, as well as when removing carbon dioxide from the atmosphere for different cloud boundary positions within the dense cloud model. The used values of the cloud boundary correspond, according to the data in Fig. 1, to the radiation fluxes from the atmosphere to the Earth's surface, which are used in constructing the Earth's energy balance presented in the table. As follows from the data in this figure, the dependence of the result on the position of the cloud boundary becomes weaker as the optical thickness of the atmospheric layer between the Earth's surface and the clouds increases.

Fig. 9 shows the dependence of changes in the total radiation flux of the standard atmosphere on the cloud boundary position for a dense cloud model with doubled carbon dioxide concentration, as well as with carbon dioxide removal from the atmosphere.

For cloud boundary heights obtained for different variants of Earth's energy balance and its atmosphere, doubling the concentration of carbon dioxide leads to an increase in emission flux from the atmosphere, which ranges between 1.2 and 1.7 W/m^2. Removal of carbon dioxide from the atmosphere

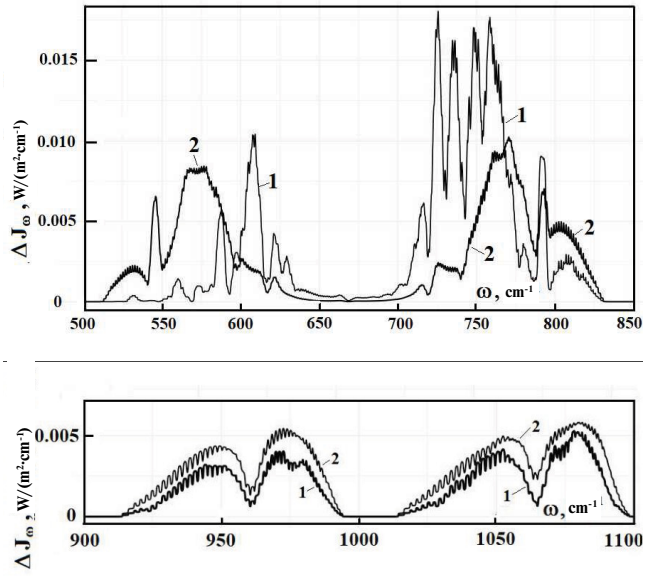

Fig. 6. Changes in partial radiation fluxes ΔJ_ω when doubling the concentration of carbon dioxide molecules in the standard atmosphere in absorption regions of carbon dioxide molecules: 1 – dense cloud model; 2 – modified model of homogeneous atmosphere

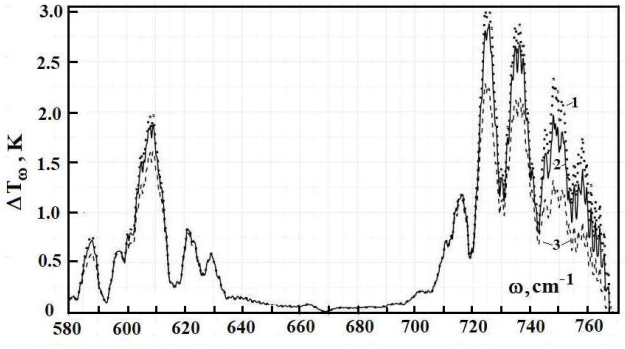

Fig. 7. Change in effective radiation temperature ΔT_ω when doubling the concentration of carbon dioxide molecules in the standard atmosphere in the lower absorption band of carbon dioxide molecules. Used dense cloud model with cloud boundary at h_{cl} = 3.2 (*1*), 4.6 (*2*), 5.6 (*3*) km

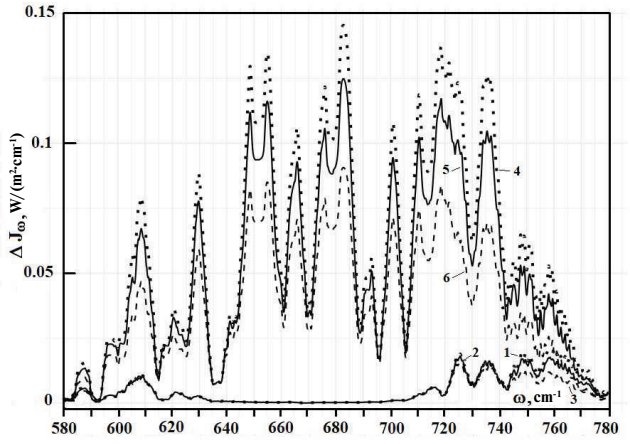

Fig. 8. Changes in partial radiation fluxes ΔJ_ω when doubling the concentration of carbon dioxide molecules (*1, 2, 3*) in standard atmosphere in the lower absorption band of carbon dioxide molecules, as well as when removing carbon dioxide from the atmosphere. A dense cloud model was used for cloud boundary h_{cl} = 3.2 (*1*), 4.6 (*2*), 5.6 (*3*) km, and in the case of carbon dioxide removal from the atmosphere at cloud height h_{cl} = 3.2 (*4*), 4.6 (*5*), 5.6 (*6*) km

leads to a decrease in atmospheric emission flux in the range between 8 and 13 W/m^2.

Change in atmospheric radiation flux to the Earth's surface $\Delta J_\downarrow$ due to changes in atmospheric gas concentration can be converted into change in Earth's surface temperature ΔT through climate sensitivity parameter S [29, 30]. This proportionality coefficient between global temperature change and change in radiation flux to Earth's surface based on conducted research we assume equals S = 0.5 m^2·K/W) [29–32], although this value is characterized by large uncertainty. As a result, for global temperature change following from doubling of atmospheric carbon dioxide concentration, we get

$$\Delta T = 0.6 \pm 0.1\text{K}, \qquad (21)$$

where the indicated uncertainty accounts only for difference between energy balance parameters derived from different sources. Uncertainty related to converting radiation flux change to Earth's surface into global temperature change is higher and, according to [12], equals 0.3 K. Meanwhile, climate models lead to the following value for this parameter:

$$\Delta T = 3.0 \pm 1.5\text{K}. \qquad (22)$$

Note that actual global temperature change over the past century and a half follows from averaging local temperatures obtained from measurements of approximately 6000 weather stations, as well as satellites in recent decades [33]. Global temperature increase has been observed since the eighties. If we compare global temperature change rate with carbon dioxide concentration growth rate, then according to measurements, for global temperature change with doubling of atmospheric carbon dioxide concentration [33–37] we get

$$\Delta T = 2.1 \pm 0.4\text{K}. \qquad (23)$$

As follows from comparing formulas (21) and (23), increase in atmospheric carbon dioxide concentration is a secondary factor in global

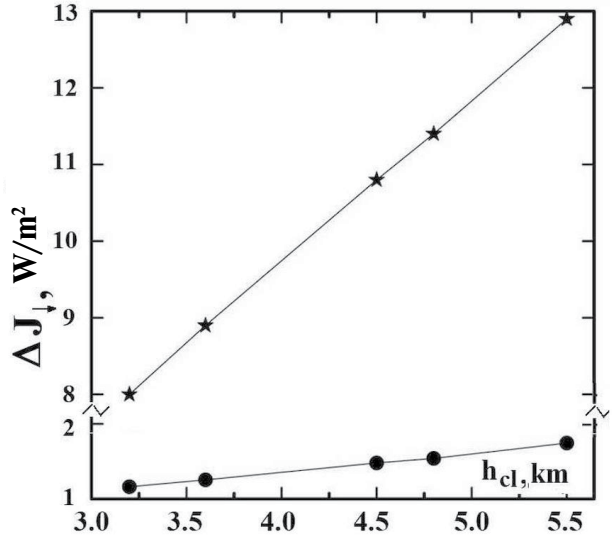

Fig. 9. Change in the frequency-summed increase of radiation flux from standard atmosphere to Earth's surface $\Delta J_\downarrow$ when doubling atmospheric carbon dioxide concentration (lower curve), as well as its decrease with complete removal of carbon dioxide from atmosphere (upper curve) depending on cloud boundary position

temperature rise, and climate models result several times exceeds observed value of this parameter.

5. CONCLUSION

The complexity of analyzing thermal radiation from a molecular gas layer with a dispersed phase at pressures around atmospheric is associated with the complex emission spectrum of the gas. At temperatures around room temperature, the radiation spectrum of this system includes hundreds and thousands of broadened spectral lines of molecules in the form of peaks that are above the continuous pedestal created by the dispersed phase, i.e., particles or droplets present in the gas. The conducted analysis showed that the spectrum-averaging model is not suitable when considering problems whose results depend on the spectral parameters of the gas. In particular, the model of a homogeneous atmosphere with averaging over molecular spectra is only suitable for estimating the integral radiative parameters of gas mixtures.

Let us consider physical objects for which the analysis presented above may be useful. First of all, this is Earth's atmosphere, used above to demonstrate and analyze certain aspects of the problem, as well as atmospheres of other planets. It is essential that in this case, reliable information about various radiation parameters of molecules in buffer gas at atmospheric pressure is available, which is collected in the HITRAN database [2–4] and accessible. Then, within the framework of the "line-by-line" method [5, 6], a connection can be established between the spectral parameters of local atmosphere radiation and the effective temperature of the space region determining emission at a given frequency, and the density of radiating molecules or particles in the given region.

Another type of physical objects where the considered spectral analysis is necessary relates to extensive forest and warehouse fires, where the thickness of the heated gas layer is significantly less than the extent of the air region heated by the fire. In this case, the nature of radiation transfer emitted by the heated region determines the vertical dimensions of this region, which in turn affects the burning rate.

The development of these methods allows for more precise measurements based on the spectroscopy of emitted molecular gas. Half a century ago, infrared diagnostics made it possible to solve special military tasks [38], in particular, during ocean monitoring from satellites, to identify jets of elevated temperature on the ocean surface formed by submarine movement, and to detect atmospheric pollutants. This diagnostics was also used in sensor systems for reconnaissance and surveillance. Modern thermal imagers with high resolution in the infrared spectrum region allow determining coordinates of individual engines and other sources of carbon dioxide emissions from satellites.

It should be noted that carbon dioxide is a convenient object for research. Carbon dioxide molecules are characterized by high stability and usually form gas, since phase transitions to other aggregate states occur at lower temperatures. The spectral line width corresponding to a specific vibrational-rotational transition at atmospheric pressure is approximately 0.1 cm^{-1}, while the distance between adjacent lines is approximately 1.5 cm^{-1}. Moreover, the ratio of radiation intensities at the center of the spectral line and between adjacent lines is 40. This indicates the possibility to separate adjacent lines and identify them.

Furthermore, the most convenient spectral region of carbon dioxide molecule absorption for satellite monitoring are bands with centers corresponding to laser transitions with wavelengths of 9.5 μm and 10.6 μm. These lines fall into the atmospheric transparency window in the wavelength range of 8–12 μm. According to Wien's law, these transitions occur most intensively at temperatures of 400–500 K. The special role of carbon dioxide in monitoring energy processes on Earth's surface and above was the reason why the spectral region of carbon dioxide molecule absorption was used to demonstrate the obtained results.

Let's consider one of the applications related to the problems under consideration. A major calamity of our time has become forest fires in dry weather, especially in hard-to-reach places like Siberia and the Far East. If we leave aside arson, ignition sources form over a long period underground at a depth of several meters, where organic remains are located and heat transfer is limited. Underground combustion is limited by oxygen penetration into the combustion zone, and therefore the formation of a combustion source takes several days. Then the burning emerges to the surface and spreads at high speed across the Earth's surface.

Monitoring of underground combustion sources can be carried out from satellites or drones in clear weather, when they mainly form, using thermal imaging devices. However, spectral instruments operating as radiation amplifiers in the region of laser transitions for carbon dioxide with wavelengths of 9.5 and 10.6 μm have sensitivity orders of magnitude higher, especially since these lines fall within the atmospheric transparency window.

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