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Collision and radiative processes in emission of atmospheric carbon dioxide

B M Smirnov

Joint Institute for High Temperatures, Izhorskaya 13/19, Moscow 125412, Russia

E-mail: bmsmirnov@gmail.com

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Abstract

The peculiarities of the spectroscopic properties of CO_2 molecules in air due to vibration-rotation radiative transitions are analyzed. The absorption coefficient due to atmospheric carbon dioxide and other atmospheric components is constructed within the framework of the standard atmosphere model, on the basis of classical molecular spectroscopy and the regular model for the spectroscopy absorption band. The radiative flux from the atmosphere toward the Earth is represented as that of a blackbody, and the radiative temperature for emission at a given frequency is determined with accounting for the local thermodynamic equilibrium, a small gradient of the tropospheric temperature and a high optical thickness of the troposphere for infrared radiation. The absorption band model with an absorption coefficient averaged over the frequency and line-by-line model are used for evaluating the radiative flux from the atmosphere to the Earth which values are nearby for these models and are equal $J_{\downarrow} = (64 \pm 3)$ W m^{-2} for the contemporary concentration of atmospheric CO_2 molecules and $J'_{\downarrow} = (70 \pm 2)$ W m^{-2} at its doubled value. The absorption band model is not suitable to calculate the radiative flux change at doubling of carbon dioxide concentration because averaging over oscillations decreases the range where the atmospheric optical thickness is of the order of one, and just this range determines this change. The line-by-line method gives the change of the global temperature (0.4 ± 0.1) K as a result of doubling the carbon dioxide concentration. The contribution to the global temperature change due to anthropogenic injection of carbon dioxide in the atmosphere, i.e. resulted from combustion of fossil fuels, is approximately 0.02 K now.

Keywords: collision processes, radiative processes, molecular spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

The goal of this paper is the analysis of radiative transitions involving carbon dioxide molecules and emissions of the Earth's atmosphere due to CO_2 molecules. This is an example of the problem of emission of a heated gas layer located over a flat surface, but the peculiarity of this problem is that infrared radiation is created by vibration-rotation transitions of molecules, and the width of a spectral line for an individual vibration-rotation transition is small compared to a frequency difference between neighboring spectral lines, so that broadening of the spectral lines is of importance for the emission process. In contrast to radiative transitions between electron states, where interaction potentials of radiating and perturbed gaseous molecules differ significantly for transition states, the interaction potentials are nearby for vibration states of transition. Therefore, the broadening cross section for radiative transitions between vibration states is small compared with the cross section of elastic molecule collisions. We below compare these cross sections for collisions with the participation of CO_2 molecules based on experimental data. This analysis allows us to understand peculiarities of the broadening theory of spectral lines for vibration transitions.

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Being guided by infrared emission of CO_2 molecules in atmospheric air, we have that collision processes of the CO_2 molecule with air molecules, mostly with nitrogen ones, allow one, on the one hand, to ascertain the character of equilibrium for vibrationally excited states of carbon dioxide molecules in atmospheric air and, on the other hand, to analyze the broadening of spectral lines for these transitions. Because of large radiative lifetimes for vibrationally excited molecules, they are found in thermodynamic equilibrium even at not very large pressures of a gas where radiative molecules are located. This simplifies the analysis of gas emission. First, reabsorption processes are unimportant under such conditions, and second, the radiative flux may be expressed through the absorption coefficient of this gas.

We below consider the elementary radiative processes involving CO_2 molecules and accompanied collision processes as a basis of the Earth's greenhouse effect involving carbon dioxide molecules. The absorption coefficient as a frequency function has the oscillating structure with local maxima at corresponding vibration-rotation transitions, and four vibration transitions are responsible for the emission of atmospheric CO_2 molecules in the infrared spectrum range. This allows one to determine the width of the absorption band for radiation towards the Earth's surface due to carbon dioxide molecules, and also the change of the global temperature through variation of the concentration of atmospheric CO_2 molecules. Analyzing this problem, we account for an altitude dependence for the atmosphere temperature along with the oscillation structure of the absorption coefficient due to CO_2 molecules in air. In this way, we combine this with important results obtained from the NASA organization during the last half-century that represent in a numerical form the evolution of some atmospheric parameters. These results include the energetic balance of the Earth and its atmosphere, monitoring of the concentration of atmospheric carbon dioxide at Mauna Loa observatory in Hawaii [1–4] and evolution of the global Earth's temperature during last 150 years on the basis of data of thousands meteorological stations over all the globe [5–8].

These data are analyzed within the framework of the standard atmosphere model [9], which averages atmospheric parameters over the globe, so that they depend on the altitude only. Finally, this allows one to determine the change of the global temperature only due to variations of the carbon dioxide concentration with an estimated accuracy. This gives additional information for the problem of the climate change [10–15].

In considering the radiation of atmospheric carbon dioxide, we restrict ourselves by emission of CO_2 molecules toward the Earth only. Along with evaluating the radiative flux created by CO_2 molecules, the change of this flux is analyzed as a result of the change of atmospheric carbon dioxide concentration. The presence of water vapor, water aerosols and other optically active components in the atmosphere which absorb in the spectrum range of CO_2 molecules is essential. These components change the character of emission of carbon dioxide molecules. First, these components absorb radiation emited by CO_2 molecules. This decreases both the radiative flux by CO_2 molecules, and its change due to variation of the atmospheric concentration of CO_2 molecules. Second, absorption of these components leads to an atmospheric optical thickness between 2 and 3 [16, 17]. This separates the atmosphere in two parts, so that the lower one, which determines the emission toward the Earth, is characterized by altitudes below 2 km.

Table 1. Radiative parameters of the CO_2 molecule: λ is the wavelength of vibration-vibration transition, E_* is the energy of the upper state, $\hbar\omega$ is the transition energy, τ is the radiative lifetime of the upper state for a given vibration transition.

Transition	λ, μm	, E_*, cm^{-1}	$\hbar\omega$, cm^{-1}	τ, s
$01^00 \longrightarrow 00^00$	14.9	667	667	0.64
$10^00 \longrightarrow 01^00$	13.9	1388	721	0.48
$02^00 \longrightarrow 01^00$	16.1	1285	618	0.83
$02^20 \longrightarrow 01^00$	15.0	1335	668	0.32

The classical approach to this problem is evaluation of the radiative flux due to CO_2 molecules or its additional value because of an increase of their concentration. The basis of this approach is the air absorption coefficient which may be evaluated on the basis of the regular or Elsasser model [18] or it may be taken from the data bank HITRAN [19] which contains parameters of radiative transitions with a high resolution. The absorption coefficient is a frequency oscillating function with maxima at centers of corresponding vibration-rotation transitions. Climatology usually deals with the absorption coefficient averaged over oscillations, whereas the method 'line-by-line' deals with the absorption coefficient at a given frequency and hence takes into account the oscillation structure of the absorption coefficient. Then the absorption band is extracted from the molecular spectrum, so that inside this band, the absorption of CO_2 dominates, while outside it, the absorption by CO_2 molecules is weak compared to that due to other components. Below, we analyze accurately the character of molecule interaction in the course of their radiation and evaluate the radiative fluxes by the 'line-by-line' method. This allows one to estimate the accuracy of the absorption band method that leads to an error of 20% for the total radiative flux of CO_2 molecules and the error is in several times more for evaluation of the derivative of this radiative flux over the carbon dioxide concentration.

2. Collision and radiative processes involving CO_2 molecule in air

Our final aim is to determine the radiative flux from the troposphere due to CO_2 molecules, and in the first stage of this analysis, we consider the behavior of an individual CO_2 molecule in atmospheric air. Table 1 contains radiative parameters of vibrationally excited states of CO_2 molecules [20–22]. There are three types of vibrations, symmetric, in the course which distances of oxygen atoms from the central carbon atom remain identical, while in antisymmetric vibration the distance between outermost oxygen atoms does not vary. During these vibrations three atoms of the CO_2 molecule are located in one line, while carbon atoms move perpendicular to the molecular axis in torsion vibrations. The first quantum number corresponds to symmetric vibrations, the second number refers to torsion vibrations, and the third number relates to antisymmetric vibrations.

One can find that the rate of quenching of vibrationally excited states in the troposphere is large compared to the radiative rate. Indeed, according to measurements [23] the rate constant of quenching of vibrationally excited state 01°0 is estimated as $k_{rel} = 5 \cdot 10^{-16}$ cm^3 s^{-1}. The criterion of the validity of the Boltzmann distribution for this excited state has the form

$$N_a k_{rel} \gg \frac{1}{\tau_r} \qquad (2.1)$$

where N_a is the number density of air molecules, and τ_r is the radiative lifetime for the upper state. This criterion is fulfilled under the condition $N_a \gg 3 \cdot 10^{15}$ cm^{-3}, while at the troposphere boundary at the altitude 10 km within the framework of the standard atmosphere [9], the number density of air molecules is $N_a = 7 \cdot 10^{18}$ cm^{-3}. Thus, the Boltzmann distribution over vibration states is realized in the troposphere.

We now analyze the peculiarity of radiative transitions for the CO$_2$ molecule. This linear symmetric molecule with a carbon atom in the center is characterized by the rotation constant $B = 0.39\,\mathrm{cm}^{-1}$, so that the energy of rotation excitation is $Bj(j+1)$, where j is the rotation momentum—a whole positive number. Using general concepts of molecular spectroscopy [24–27], we obtain from properties of the Clebsh–Gordan coefficients the selection rules for a radiative transition between an initial jm to a final state $j'm'$ (j is the rotation momentum of the molecule, m is the momentum projection onto the molecular axis) such that $j' - j = 0, \pm 1$, $m' - m = 0, \pm 1$, and the rotation energy in these transitions is small compared to the vibration one.

Thus, in accordance with the selection rules, we have three types of spectrum bands as a result of vibration-rotation transitions, so that the transition energy or the photon energy $\hbar\omega$ for the initial state with rotation momentum j is equal

$$\begin{gathered} \hbar\omega = \hbar\omega_o - 2Bj,\ j' = j-1 \longrightarrow P - band, \\ \hbar\omega = \hbar\omega_o, j' = j \ \longrightarrow Q - band, \\ \hbar\omega = \hbar\omega_o - 2B(j+1),\ j' = j+1 \longrightarrow R - band, \end{gathered} \qquad (2.2)$$

where $\hbar\omega_o$ is the energy of vibration transition without a change of the rotation momentum.

We have for probabilities W (the Hönl–London factors [28]) of spontaneous radiative transition from the state with the rotation momentum j in various final states after averaging over momentum projections

$$W_P = \frac{2j+3}{3(2j+1)},\ W_Q = \frac{1}{3},\ W_R = \frac{2j-1}{3(2j+1)} \qquad (2.3)$$

where indices indicate a branch of the rotation transition. As is seen, in the limit of large j, these probabilities become identical and are equal to 1/3. Being guided by large rotational momenta j, we below take the probability of each branch to be 1/3.

Thus, the indicated facts simplify a general character of the atmosphere emission [29–35]. Indeed, processes of reabsorption are absent under these conditions and the Boltzmann distribution over excited states results from collision processes. The radiation spectrum consists of a broaded line (Q-band) and two bands (P and R) in the form of a sum of broaded spectral lines with an identical distance between them.

3. Broadening of infrared spectral lines

The broadening of spectral lines due to vibration transitions of a CO$_2$ molecule under consideration results from collisions with air molecules that lead to the distribution function a_ω of photon emission over frequencies ω for a certain vibration-rotation transition in the Lorentz form

$$a_\omega = \frac{\nu}{2\pi\left[(\omega - \omega_o)^2 + (\frac{\nu}{2})^2\right]}, \qquad (3.1)$$

where ω_o is the central frequency, and this distribution function is normalized to one ($\int a_\omega d\omega = 1$); ν is the width of the spectral line, which is given by [36, 37]

$$\nu = N_a v \sigma_t. \qquad (3.2)$$

Here, N_a is the number density of air molecules, v is the relative velocity of colliding carbon dioxide and air molecules, and σ_t is the total cross section of this collision.

Let us make a simple estimation for the total cross section of collision of CO$_2$ and air molecules, assuming the dispersion interaction between radiating and gaseous molecules, where the interaction potential between them $U(R)$ at large distances R takes the form

$$U(R) = \frac{C_6}{R^6}. \qquad (3.3)$$

Then the total cross section of their collision is equal [38]

$$\sigma_t = 8.1 \left(\frac{C_6}{\hbar v}\right)^{2/5}. \qquad (3.4)$$

Averaging over collision velocities with the Maxwell distribution function, one can obtain for the specific width of the spectral line in accordance with the Lindholm–Foley theory [39, 40]

$$\frac{\nu}{N_a} = 7.2 \left(\frac{2T}{\mu}\right)^{3/10} \left(\frac{C_6}{\hbar}\right)^{2/5}, \qquad (3.5)$$

where T is the air temperature expressed in energetic units, and μ is the reduced mass of colliding molecules. Representing the parameter C_6 in atomic units and taking it for $CO_2 - N_2$ interaction to be $C_6 = 118$ [21], one can obtain at room temperature and atmospheric pressure $\nu = 0.32$ cm^{-1}, while according to measurements $\nu = 0.16$ cm^{-1} [41–44]. We will use below the latter value and the Lorentz character of broadening of spectral lines for vibration-rotation transitions according to formula (3.1).

Formula (3.5) is based on the assumption that the contribution to this cross section gives many collision momenta. In the same manner, the difference of the interaction potentials

$\Delta U(R)$ of the radiating molecule for transition vibration states between is expressed through the difference ΔC_6 for dispersion coefficients C_6 for these states as

$$\Delta U(R) = \frac{\Delta C_6}{R^6}, \tag{3.6}$$

where R is the distance between colliding molecules. Correspondingly, the specific width of the spectral line for the transition between vibration states for this interaction potential by analogy with formula (3.4) is given by

$$\frac{\nu}{N_a} = 7.2\left(\frac{2T}{\mu}\right)^{3/10}\left(\frac{\Delta C_6}{\hbar}\right)^{2/5}, \tag{3.7}$$

where T is the temperature expressed in energetic units, μ is the reduced mass of colliding particles. Taking at room temperature and atmospheric pressure $\nu = 0.16\ \mathrm{cm}^{-1}$ [41–44], one can obtain in atomic units $\Delta C_6 = 32$. As is seen, the difference of the interaction potentials of $CO_2 - N_2$ molecules for different vibration states is less in several times than the interaction potential for each vibration state.

Note one more important propery of broadening of spectral lines for transitions between vibration states. From formula (2.1), it follows the following asymptotic form for the frequency distribution function of emitting photons

$$a_\omega = \frac{\nu}{2\pi(\omega-\omega_o)^2},\ |\omega-\omega_o| \ll |\omega_b-\omega_o| \equiv \Delta\omega, \tag{3.8}$$

where ω_b is the boundary frequency, and beyond the bounds of this frequency, the distribution function a_ω is small compared to that given formula (3.8). We estimate the parameter $\tau_b = 1/\Delta\omega$ as a time of drift in the potential of interaction between a radiating and perturbed molecules. Let us take this interaction potential between colliding molecules in the Lennard-Jones form

$$U(R) = D\left[2\left(\frac{R_e}{R}\right)^6 - \left(\frac{R_e}{R}\right)^{12}\right], \tag{3.9}$$

where D is the depth of the potential well, and R_e is the equilibrium distance. We find the parameters of interaction between CO_2 molecules on the basis of the scaling law [45, 46] by comparing critical parameters of carbon dioxide and its parameters at the triple point with those for inert gases. This gives $D = (38 \pm 7)$ meV and $R_e = 0.32$ nm. Note that the interaction potential (3.9) correspond to the constant $C_6 = 2DR_e^6 \approx 140$ in atomic units, which exceeds the above value by 20%.

Let us determine a typical time of collision τ_b as a time of approach of slow molecules from the potential well bottom at the distance between particles R_e to its wall at the distance $R_e/2^{1/6}$ at zero orbital momentum. This gives

$$\frac{1}{\tau_b} \equiv \Delta\omega = \frac{10}{R_e}\cdot\sqrt{\frac{2D}{m}}, \tag{3.10}$$

where m is the mass of the carbon dioxide molecule. The above parameters give for CO_2 molecules in carbon dioxide $\Delta\omega \approx 100\ \mathrm{cm}^{-1}$ and for CO_2 molecules in air $\Delta\omega \approx 70\ \mathrm{cm}^{-1}$. These values characterize a range of frequencies for each vibration-vibration transition where this transition takes place. In particular, the total width of a spectral band for a given vibration-vibration transition of CO_2 molecules in air is below $100\,\mathrm{cm}^{-1}$ at any air pressure.

4. Absorption coefficient of atmospheric air with CO_2 molecules

The above parameters of interaction of radiating CO_2 molecules and perturbed air molecules allows one to determine the absorption coefficient of atmospheric air due to carbon dioxide molecules that gives a basis for determining the infrared radiation flux from the Earth's atmosphere. Let us fulfill this program. The absorption cross section σ_ω with radiative transition in a certain state is given by [36, 37]

$$\sigma_\omega = \frac{\pi^2 c^2}{\omega^2}\cdot\frac{a_\omega}{\tau}, \tag{4.1}$$

where a_ω is the distribution function of absorbed photons over frequencies, and we use for this function formula (3.1) under the considering conditions, and $1/\tau$ is the rate of this radiative transition. Correspondingly, the absorption coefficient k_ω at a given frequency ω is given by

$$k_\omega = N_v\sigma_\omega\left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right], \tag{4.2}$$

where N_v is the number density of absorbed molecules, and the last factor accounts for stimulated radiation.

From this, we have for the absorption coefficient k_ω^Q due to Q-absorption band with the rotation transition $j \to j$

$$k_\omega^Q = \frac{\pi c^2}{6\omega^2\tau_v}N_v\cdot\frac{\nu}{(\omega-\omega_o)^2+(\frac{\nu}{2})^2} \tag{4.3}$$

where ω_o is the central frequency for this transition, τ_v is the radiative lifetime for a given vibration state, and according to formula (3.8) the rate $1/\tau_Q$ of the radiative transition for Q-branch is $1/(3\tau_v)$, so that τ_v is the radiative lifetime of the upper vibration state in this transition.

In the same manner, one can represent the absorption coefficient k_ω^{PR} for P and R absorption bands

$$k_\omega^{PR} = \frac{\pi c^2}{6\omega^2\tau_v}\sum_j N_{vj}\cdot\frac{\nu}{(\omega-\omega_j)^2+(\frac{\nu}{2})^2}. \tag{4.4}$$

Here, $\hbar\omega_j$ is the transition energy in a given rotation state with the rotation momentum j, the number density N_{vj} of molecules in a given vibration and rotation states is determined by the Boltzmann formula that in the limit $T \gg B$ has the following form

$$N_{vj} = N_v\frac{B}{T}(2j+1)\exp\left[-\frac{Bj(j+1)}{T}\right],\ \sum_j N_{vj} = N_v. \tag{4.5}$$

From this, one can find the absorption coefficient at wings of the spectral bands

$$k_\omega^w = \frac{\pi c^2\nu}{6\omega^2\tau_v}N_v\left[\frac{1}{(\omega-\omega_o-\sqrt{2BT/\hbar})^2}+\frac{1}{(\omega-\omega_o+\sqrt{2BT/\hbar})^2}\right], \tag{4.6}$$

where in summation over j in the formula, we replace the transition frequency ω_j by its average value

$$\overline{\omega_j} = \omega_o \pm \sqrt{2BT}/\hbar \tag{4.7}$$

for P and R absorption branch correspondingly. Formula (4.6) holds true at wings of spectral bands according to the criterion

$$|\omega - \omega_o| \gg \sqrt{2BT}/\hbar. \tag{4.8}$$

We now represent the expression for k_ω^{PR} at a trunk of the absorption bands. We have for the transition energy $\hbar\omega$ if the initial rotation momentum is j for P and R absorption bands

$$\hbar\omega = \hbar\omega_o - B \pm B(2j+1). \tag{4.9}$$

As is seen, the transition energy for neighboring j is constant, which corresponds to the regular model or to the Elsasser model [18] for vibration-rotation absorption transitions. Accounting for $T \gg B$, one can use the following approximation in summarizing rotation momenta j

$$\sum_j \frac{N_{vj}}{(\omega-\omega_j)^2 + (\frac{\nu}{2})^2} \approx N_{vj} \sum_j \frac{1}{(\omega-\omega_j)^2 + (\frac{\nu}{2})^2}. \tag{4.10}$$

In summarizing rotation momenta j in this formula, we use the Mittag-Leffler theorem [47], which takes the form

$$\sum_{k=-\infty}^{\infty} \left[(x-k)^2 + y^2\right]^{-1} = \frac{\pi \sinh 2\pi y}{y(\cosh 2\pi y - \cos 2\pi x)}. \tag{4.11}$$

This exhibits the oscillation form of the absorption coefficient k_ω as a frequency function. Taking now $x = \hbar(\omega - \omega_i)/B$ and $y = \hbar\nu/4B$, one can represent the absorption coefficient k_ω due to a certain absorption band i in the form (for example, [14, 48, 49])

$$\begin{aligned} k_\omega^{PR} &= S(\omega)\varphi_i(\omega),\ \varphi_i(\omega) \\ &= \sinh \frac{\pi\hbar\nu}{2B}\left[\cosh \frac{\pi\hbar\nu}{2B} - \cos \frac{\pi\hbar(\omega-\omega_i)}{B}\right]^{-1}, \end{aligned} \tag{4.12}$$

where the transition intensity S_i for P and R absorption bands is given by formula

$$\begin{aligned} S(\omega) =& \frac{\pi^2 c^2}{3\omega^2} \frac{\hbar N_v}{2B\tau_v} \frac{\hbar|\omega-\omega_i|}{T} \\ &\times \exp\left[-\frac{\hbar^2(\omega-\omega_i)^2}{4BT}\right]\left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right]. \end{aligned} \tag{4.13}$$

Here, N_v is the number density of molecules for the lower vibration state of this transition, and τ_v is the radiative lifetime for an upper vibration state of this transition.

Let us apply these formulas to atmospheric carbon dioxide. The half-width of the spectral line equals to $\nu/2 \approx 0.08\ \mathrm{cm}^{-1}$ [41–44] for the strongest vibration transition of CO_2 molecule $\hbar\omega_i = 667\ \mathrm{cm}^{-1}$ in atmospheric air at the Earth's surface, and we use the same parameter for other vibration transitions. We take the contemporary concentration $c = 0.04\%$ of carbon dioxide molecules in atmospheric air that gives the number density of these molecules $N_v = 1 \cdot 10^{16}\ \mathrm{cm}^{-3}$ at the Earth's surface. We account for four vibration transitions given in table 1. The total absorption coefficient is the sum of these vibration transitions, and for a certain vibration transition the total absorption coefficient is

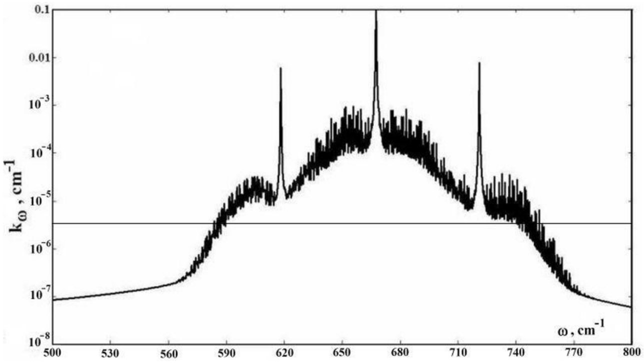

Figure 1. Total absorption coefficient k_ω at the Earth's surface due to atmospheric carbon dioxide molecules for the standard atmosphere model according to formulas (4.14) and (4.15).

$$k_\omega = k_\omega^Q + k_\omega^w + k_\omega^{PR}, \tag{4.14}$$

where partial absorption coefficients are given by formulas (4.3), (4.6), and (4.12). The absorption coefficient of atmospheric air near the Earth's surface is represented in figure 1.

One can find the Lorentz shape of spectral lines for CO_2 molecules located in air to be valid for the range $10^{17}\ \mathrm{cm}^{-3} \ll N_a \ll 10^{20}\ \mathrm{cm}^{-3}$ of the number density N_a of air molecules [48], i.e. it holds true in the troposphere and stratosphere. In addition, this mechanism of broadening of spectral lines is valid in the frequency range of figure 1. Note that according to the figure 1 data, the maximum absorption coefficient is equal to $\kappa_{max} = 0.06\ \mathrm{cm}^{-1}$ due to the Q absorption branch of the strongest vibration transition of CO_2 molecules in air. The absorption coefficient has an oscillation structure in the basic frequency range. In particular, near the Earth's surface, the ratio ξ of absorption coefficients at neighboring maximum k_{max} and minimum k_{min} according to formula (4.12) is equal

$$\xi = \frac{k_{max}}{k_{min}} = \left(\frac{4B}{\pi\hbar\nu}\right)^2. \tag{4.15}$$

This value near the Earth's surface equals to $\xi = 9$ and increases as the altitude grows. Below, we use the absorption coefficient given in figure 1 for evaluating the emission flux due to atmospheric carbon dioxide. In addition, our goal is to determine the change of the radiative flux as a result of the change in the concentration of CO_2 molecules. Evidently, the main contribution to this change follows from the spectrum range, where the optical thickness $u_\omega \sim 1$. The behavior of the absorption coefficient in this spectrum range at absorption boundaries is given in figure 2.

5. Model of atmospheric emission

In considering atmospheric emission, one can use as its basis the energetic balance of the Earth and its atmosphere. We take parameters of the Earth's energetic balance from the author's books [50–52] which used NASA data [53].

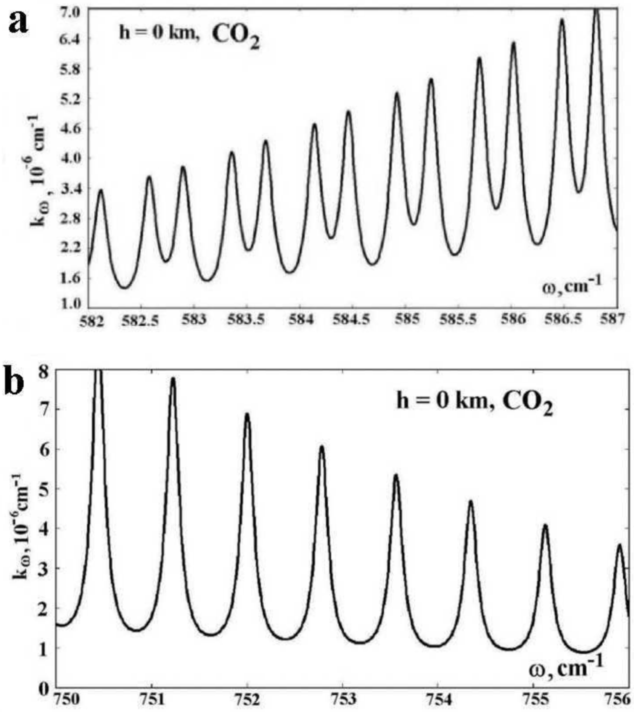

Figure 2. Absorption coefficient k_ω at the Earth's surface due to molecules of atmospheric carbon dioxide as a frequency function near boundaries of the absorption band at its left edge (a) and right one (b) in accordance with formula (4.15).

These data differ slightly from subsequent data for basic energetic channels (for example, [14, 15, 54–62]), so that the Earth's energetic balance varies slightly for the last half-century. In this consideration, we use values of the average radiative flux from the Earth's surface $J_E = 386\,\mathrm{W\ m^{-2}}$, the average radiative flux from the atmosphere toward the Earth $J_\downarrow = 327\ \mathrm{W\ m^{-2}}$, and the average heat flux $J_c = 47\,\mathrm{W\ m^{-2}}$ as a result of heat transfer by convection from the Earth to the atmosphere. These data will be inserted in models under consideration.

Our goal is to determine the emission flux of the Earth's atmosphere as a nonuniform flat gas layer located over the Earth's surface. This flux is created by CO_2 molecules. Using general physical principles in the solution of this problem for a given system—atmospheric air with CO_2 molecules, one can ascertain the validity of various models in the analysis of this problem. According to the above analysis, collision processes dominate in the course of propagation of infrared photons in the troposphere. This means that an excited molecule state resulted from absorption of a resonant photon is quenched in collisions with air molecules. Therefore, reabsorption of photons is not essential for atmosphere emission, and the rate of photon radiation at a given point is determined by the local gas temperature. Next, the troposphere thickness is small compared to the Earth's radius, and hence it may be considered as a flat layer of air. Assuming the temperature T of a layer which provides emission of photons at a given frequency to be constant, one can use Planck formula [63, 64] for the radiative flux at a given frequency j_ω through the flat boundary

$$j_\omega = \frac{\hbar\omega^3}{4\pi^2c^2}\left[\exp\left(\frac{\hbar\omega}{T}\right)-1\right]^{-1}, \tag{5.1}$$

where the second term in parenthesis accounts for stimulated radiation, and the thermodynamic equilibrium is supported between states of the transition.

The optical thickness of an atmospheric layer u_ω located between altitudes h_1 and h_2 above sea level for a given frequency ω is introduced as

$$u_\omega(h_1,h_2) = \int_{h_1}^{h_2} k_\omega dh, \tag{5.2}$$

and the total optical thickness of the atmosphere at a given frequency is given by

$$u(\omega) = u_\omega(0,\infty) = \int_0^\infty k_\omega dh, \tag{5.3}$$

where h is an altitude. The greenhouse effect acts if

$$u(\omega) \gg 1. \tag{5.4}$$

At frequencies for which this criterion holds true, the atmosphere emits in two sides, towards the Earth and outside it. We below analyze the radiative flux $J_\downarrow(\omega)$ towards the Earth since just this flux determines the energetic balance of the Earth.

Because the atmospheric temperature weakly varies with an altitude, one can reduce the radiative flux of a nonuniform atmosphere to that of the uniform one and the radiative temperature refers to a layer with the optical thickness from the surface $u(\omega) \sim 1$. A more accurate analysis [52, 65] allows one to represent this result in the form

$$J_\omega = j_\omega(1-\alpha),\ j_\omega = \frac{\hbar\omega^3}{4\pi^2c^2}\left[\exp\left(\frac{\hbar\omega}{T_\omega}\right)-1\right]^{-1} \tag{5.5}$$

where the effective radiative temperature T_ω is the temperature of a layer for which

$$u_\omega(T_\omega) = 2/3, \tag{5.6}$$

and a small parameter of this expansion is given by [52, 65]

$$\alpha = \frac{5}{18}\left(\frac{\hbar\omega}{T^2}\cdot\frac{dT}{du_\omega}\right)^2. \tag{5.7}$$

In particular, for atmospheric radiation toward the Earth under the assumption that the absorption coefficient is independent of the frequency, one can obtain for the radiative temperature $T_\downarrow$ and altitude h_ω that is responsible for atmospheric radiation [16, 17] within the framework of the standard atmosphere model [9]

$$T_\downarrow = 276\ \mathrm{K},\ h_\downarrow = 1.9\ \mathrm{km}. \tag{5.8}$$

Using the above assumption that the total absorption coefficient κ_o is independent of the frequency, one can find $\kappa_o = 2/3h_\downarrow = 0.35\ \mathrm{km^{-1}}$. We now check the validity of a small parameter (5.7) for the center of the main spectral line $\omega = 667\ \mathrm{cm^{-1}}$ with using the average absorption coefficient $\kappa_o = 0.35\ \mathrm{km^{-1}}$. Because $dT/dh = -6.5\ \mathrm{K\ km^{-1}}$ in the troposphere, we have $dT/du = dT/(\kappa_o dh)$, and substituting the

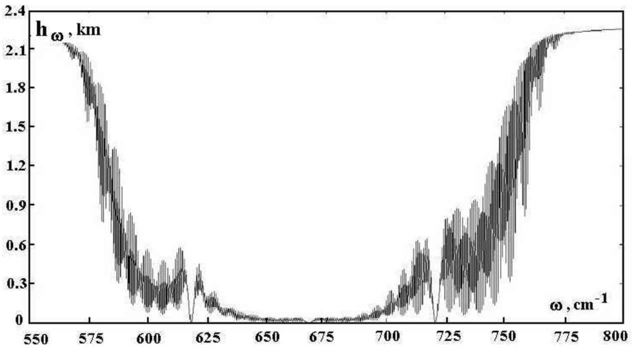

Figure 3. Atmospheric altitude $h_{\downarrow}(\omega)$ in accordance with formula (5.9) that is responsible for atmospheric radiation. The used absorption coefficient uses both atmospheric CO_2 molecules and other optically active components in this spectrum range.

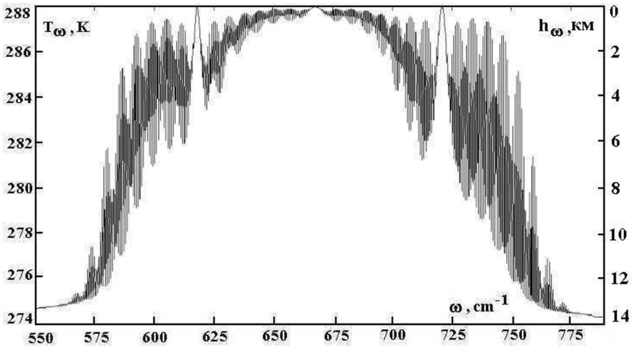

Figure 4. Atmospheric temperature T_ω according to formula (5.10) that is responsible for atmospheric radiation and includes both atmospheric CO_2 molecules and other optically active components in this spectrum range.

Earth's temperature $T = 288$ K in formula (5.7), we obtain a small parameter $\alpha = 0.01$ that allows us to reduce the problem with a varied atmospheric temperature to that with a constant temperature.

We now represent the atmospheric absorption coefficient as a sum of that k_ω due to CO_2 molecules and the absorption coefficient κ_ω due to other optically active components (mostly by water molecules and water aerosols). Taking the absorption coefficient due to CO_2 molecules according to formula (4.15) with accounting for four vibration transitions of table 1, one can obtain on the basis of formula (5.6) for the altitude h_ω which is responsible for atmospheric emission towards the Earth at a given frequency ω

$$h_{\downarrow}(\omega) = \frac{2}{3(k_\omega + \kappa_\omega)}, \tag{5.9}$$

and this dependence is represented in figure 3 in a spectral range of absorption of CO_2 molecules. From this, we have for the radiative temperature T_ω which is introduced as that of the atmosphere at the altitude h_ω

$$T_\omega = T_E - h_{\downarrow}\frac{dT}{dh} = T_E - \frac{2dT/dh}{3(\kappa_\omega + k_\omega)} \tag{5.10}$$

where $T_E = 288$ K is the Earth's temperature for the standard atmosphere model [9], and the temperature gradient is $dT/dh = 6.5$ K km^{-1}. Figure 4 contains the frequency dependence for the atmospheric temperature T_ω which characterizes emission at a given frequency ω.

6. Infrared emission of atmosphere due to CO_2 molecules

Let us determine the radiative flux from the atmosphere due to atmospheric carbon dioxide on the basis of the absorption coefficient given in figure 1 and by formula (4.14). Averaging the absorption coefficient over oscillations, one can introduce the absorption band for emission of air due to CO_2 molecules. Inside the absorption band, the optical thickness due to CO_2 molecules is large, and one can neglect by emission of other atmospheric components, whereas outside the absorption band, one can neglect by emission of CO_2 molecules. Formula (5.6) gives for boundaries frequencies

$$\omega_{1b} = 585\ \text{cm}^{-1},\ \omega_{2b} = 750\ \text{cm}^{-1}. \tag{6.1}$$

These values relate to the contemporary concentration of carbon dioxide. At the doubling value of this concentration, these boundary frequencies are equal to

$$\omega_{1b} = 581\ \text{cm}^{-1},\ \omega_{2b} = 755\ \text{cm}^{-1}. \tag{6.2}$$

From this, one can find the radiation flux due to atmospheric CO_2 molecules $J_{\downarrow}$, with the direction of the radiative flux towards the Earth's surface, according to formula

$$J_{\downarrow} = \int_{\omega_{1b}}^{\omega_{2b}} j_\omega d\omega = \int_{\omega_{1b}}^{\omega_{2b}} \frac{\hbar\omega^3 d\omega}{4\pi^2c^2}\left[\exp\left(\frac{\hbar\omega}{T_\omega}\right) - 1\right]^{-1}. \tag{6.3}$$

This gives the emission radiative flux $J_{\downarrow}$ towards the Earth's surface at the contemporary concentration of CO_2 molecules and that $J'_{\downarrow}$ at the doubled concentration

$$J_{\downarrow} = 67\ \text{W m}^{-2},\ J'_{\downarrow} = 71\ \text{W m}^{-2}. \tag{6.4}$$

The oscillation character of the frequency dependence for the absorption coefficient is of principle for infrared radiation resulted from vibration-rotation molecular transitions. In particular, in the case under consideration for radiation of atmospheric air with carbon dioxide molecules, the absorption band width is $\Delta\omega \sim 200$ cm^{-1}, and the distance between neighboring spectral lines is $2B \approx 0.8$ cm^{-1}, i.e. a number of spectral lines for vibration-rotation molecular transitions which partake in atmospheric emission exceeds 200. We above average these oscillations within the framework of the absorption band model, where CO_2 molecules dominate in atmospheric emission inside the absorption band with strict boundaries and do not partake in emissions outside the absorption band. One can check the validity of this model if the frequency oscillations of the absorption coefficient in the transition spectrum range are taken into account. This method is named 'line-by-line' analysis and the foundation of this method is described strictly in [19]. In the first turn, it is used for the analysis of atmospheric emission [66], so that this method is the basis for the evaluation of the molecule absorption coefficient in gases [67, 68]. These data may be used in diagnostics on the basis of infrared radiation [69].

In reality, using the line-by-line method does not complicate the evaluation of the radiative flux, because such a calculation consists in determining the emission flux J_ω at a given frequency with subsequent summation over frequencies. Within the framework of this method, we are based on the summarized absorption coefficient $k_\omega + \kappa$ of atmospheric CO_2 molecules and other atmospheric components. Then the partial flux due to CO_2 molecules is $k_\omega/(\kappa_o + k_\omega)$, and we obtain for the radiative flux towards the Earth due to carbon dioxide molecules

$$J_\downarrow = \int_{\omega_1}^{\omega_2} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2}\left[\exp\left(\frac{\hbar\omega}{T_\omega}\right) - 1\right]^{-1} \cdot \frac{k_\omega}{\kappa + k_\omega}, \tag{6.5}$$

where the frequencies ω_1 and ω_2 are chosen such that the absorption band for atmospheric carbon dioxide molecules is located between these frequencies. From this, one can obtain

$$J_\downarrow = 61 \text{ W m}^{-2},\ J'_\downarrow = 68 \text{ W m}^{-2}. \tag{6.6}$$

Accounting for the results of both models according to formulas (6.4) and (6.6), we have for the radiative fluxes towards the Earth due to CO_2 molecules for the contemporary and doubled concentrations of carbon dioxide molecules

$$J_\downarrow = (64 \pm 3) \text{ W m}^{-2},\ J'_\downarrow = (70 \pm 2) \text{ W m}^{-2}. \tag{6.7}$$

From this, one can estimate the accuracy of the absorption band concept. Indeed, emission fluxes within the framework of the absorption band concept exceed those with accounting for frequency oscillations of the absorption coefficient by approximately 20%. The equilibrium climate sensitivity (ECS) is the flux difference of these values at doubled and contemporary concentrations of CO_2 molecules and taking the difference from formulas (6.4) and (6.6) with an accepted value of 4 W m^{-2} [14, 15]. But this value differs from that evaluated with using the 'line-by-line' method in several times.

One can make the model more precise (5.8) by taking into account the fact that the radiative temperature of the atmosphere $T = T_\downarrow$ is frequency independent in the spectrum range outside the absorption band of CO_2 molecules, and inside the absorption band, it coincides with the radiative temperature T_E of the Earth. Then the atmospheric radiative temperature outside the range of absorption by CO_2 molecules is determined from the equation

$$\begin{aligned} J_\downarrow = &\int_0^{\omega_1} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2}\left[\exp\left(\frac{\hbar\omega}{T}\right) - 1\right]^{-1} \\ &+ J_\downarrow(CO_2) + \int_{\omega_2}^{\infty} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2}\left[\exp\left(\frac{\hbar\omega}{T}\right) - 1\right]^{-1} \\ &= 327 \text{ W m}^{-2}, \end{aligned} \tag{6.8}$$

where $J_\downarrow(CO_2)$ is given by formula (6.3) with accounting for absorption by CO_2 molecules. From this, we obtain instead of (5.8) the following parameters for a radiating atmosphere in a spectral range, where the radiation of CO_2 molecules is not essential

$$T_\downarrow = 274 \text{ K},\ h_\downarrow = 2.2 \text{ km}. \tag{6.9}$$

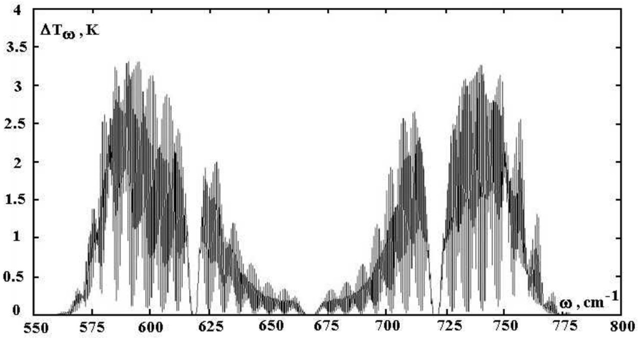

Figure 5. Increase of the radiative temperature for the flux towards the Earth resulting from doubling of the concentration of carbon dioxide molecules within the framework of the line-by-line model.

In addition, this gives the absorption coefficient $\kappa = 0.30$ cm^{-1} for components other than CO_2 and is less than that given by formula (6.3). We take above the frequency range from 550 cm^{-1} up to 800 cm^{-1} as a spectral range outside which emission CO_2 molecules is negligible.

From this, one can find the difference of radiative fluxes at the contemporary and doubled concentrations of atmospheric CO_2 molecules according to formula

$$\Delta J_\downarrow = \int\limits_{\omega_1}^{\omega_2} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2}\left\{\left[\exp\left(\frac{\hbar\omega}{T_\omega}\right) - 1\right]^{-1} - \left[\exp\left(\frac{\hbar\omega}{T'_\omega}\right) - 1\right]^{-1}\right\}, \tag{6.10}$$

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 determines an additional radiative flux towards the Earth due to this concentration change. Figure 5 represents the radiative temperature change depending on the photon frequency if the absorption coefficient other than carbon dioxide atmospheric components is $\kappa_o = 0.3$ km^{-1}.

One can explain why the absorption band model is not suitable for the change of the radiative flux due to doubling of the concentration of CO_2 molecules. This quantity is determined by spectral ranges where the atmospheric optical thickness is of the order of one. Because averaging over oscillations for the absorption band model removes such ranges from consideration, this model leads to a large error. Let us take the absorption coefficient for others rather than carbon dioxide atmospheric components in the form

$$\kappa = \kappa_o + a\cos[b(\omega - \omega_o)], ; \tag{6.11}$$

where $a < \kappa_o$, $b \sim 1$ cm^{-1}, and $\kappa_o = 0.3$ km^{-1}. Then formula (6.10) gives after averaging over the parameter b.

$$\Delta J_\downarrow = (1.0 \pm 0.2) \text{ W m}^{-2} \tag{6.12}$$

where with the radiative temperature, as is seen, this difference $\Delta J_\downarrow = J'_\downarrow - J_\downarrow$ according to the model of the frequency averaged absorption coefficient given in formulas (6.4) and

(6.6) exceeds by severals times its precise value obtained on the basis of the 'line-by-line' method.

Formulating the method to analyze the change of the global parameters which are responsible for the Earth's climate, Arrenius [70] considered atmospheric carbon dioxide as the basic greenhouse component. Then the ECS [71], the change of the global temperature at doubling of the atmospheric concentration of carbon dioxide is the parameter which characterizes the climate change due to variation of atmospheric composition. Above, we have evaluated the change of the radiative flux $\Delta J_\downarrow$ due to an increasing concentration of CO_2 molecules, and our subsequent task is to transfer the radiative flux change into the change of the global temperature ΔT. The ratio of these changes is named the climate sensitivity, i.e. it is defined as [14, 72]

$$S = \frac{\Delta T}{\Delta J_\downarrow}. \tag{6.13}$$

We now determine the reciprocal value $F = 1/S$ with taking into account the fact that the change of the global temperature causes the change of fluxes for various components, but the amount of these components in the atmosphere is unvaried.

In this consideration, we are based on the standard atmosphere model, so the Earth's temperature is $T_E = 288$ K, the temperature gradient $dT/dh = -6.5$ K km^{-1} is constant up to the tropopause at $h_o = 11$ km, where the atmospheric temperature equals $T_{min} = 217$ K, and the temperature difference between the Earth and tropopause is $\delta T = T_e - T_{min} = 61$ K. Let the temperature change at the Earth be ΔT, while the tropopause temperature is unvaried. We then determine the change of energy fluxes under the above conditions, where the water concentration is supported to be a constant.

We have for the temperature T_h at a given altitude h and its change ΔT_h under given conditions

$$T_h = T_E\left(1 - \frac{\delta h}{h_o}\right), \quad \Delta T_h = \Delta T\left(1 - \frac{h}{h_o}\right). \tag{6.14}$$

Correspondingly, a change ΔJ_h of the radiative flux, if it is created at the altitude h, is

$$\Delta J_h = 4\sigma T_h^3 \Delta T_h = \frac{4J_h \Delta T_h}{T_h}, \tag{6.15}$$

where σ is the Stephan–Boltzmann constant. In determining the convection flux change ΔJ_c, we assume the energy flux due to convection to be proportional to the temperature gradient, which gives

$$\Delta J_c = J_c \frac{\Delta T}{\delta T}. \tag{6.16}$$

Summarizing the flux changes, we have

$$\frac{1}{S} = \frac{4J_E}{T_E} - \frac{4[J_\downarrow - J(CO_2)]}{T_\downarrow}\left(1 - \frac{h_\downarrow}{h_o}\right) - \frac{J(CO_2)}{T(CO_2)}\left[1 - \frac{h(CO_2)}{h_o}\right] + \frac{J_c}{\delta T}, \tag{6.17}$$

where $J_E = 386$ W m^{-2}, $J_\downarrow = 327$ W m^{-2}, $J(CO_2) = 94$ W m^{-2}, $T_\downarrow = 274$ K, $h_\downarrow = 2.2$ km, $h_o = 11$ km, $h(CO_2) = 0.8$ km, $\delta T = 61$ K. From this, we have

$$S = 0.42 \text{ m}^2 \cdot \text{K W}^{-1}. \tag{6.18}$$

From this, it follows for the change of the global temperature as a result at doubling of the concentration of atmospheric CO_2 molecules.

$$\Delta T = (0.4 \pm 0.1) \text{ K}, \tag{6.19}$$

where the error accounts for the accuracy of used values, whereas the result depends on processes included in the above scheme. Indeed, we assume the atmospheric and Earth's albedo, as well as another interaction of solar radiation with the atmosphere and Earth, to be unvaried in the course of the change of the concentration of CO_2 molecules, and also the content of atmospheric water is conserved. Because anthropogenic fluxes of carbon dioxide in the atmosphere resulted from combustion of fossil fuels is about 5%, the contribution of the human activity to ECS (the temperature change as a result of doubling of the atmospheric carbon dioxide amount) is

$$\Delta T = 0.02 \text{ K}, \tag{6.20}$$

i.e. injections of carbon dioxide in the atmosphere as a result of combustion of fossil fuels is not important for the greenhouse effect. In addition, total removal of CO_2 from the atmosphere causes a decrease of the radiative flux towards the Earth by approximately 9 W m^{-2}. This corresponds to a decrease of the global temperature by approximately 4 K.

The value (6.19) may be compared with the ECS for a real atmosphere on the basis of data for evolution of the global temperature during past 150 years [7, 8] and the monitoring of atmospheric carbon dioxide [2, 3]. From this, it follows

$$\Delta T = (2.0 \pm 0.3) \text{ K}, \tag{6.21}$$

so that atmospheric carbon dioxide provides approximately 20% both the radiative flux towarsd the Earth and its change resulting from the change of the concentration of CO_2 molecules. The ECS which follows from treatment of data over the past 65 million years is [72–74]

$$\Delta T = (3.5 \pm 1.3) \text{ K}. \tag{6.22}$$

Evidently, a large error is determined by the change of conditions in different epochs.

Let us consider one more scenario of evolution of the global temperature if the equilibrium is supported between atmospheric carbon dioxide and oceanic $CaCO_3$ according to the scheme [75, 76]

$$CO_2 + CaO \leftrightarrow CaCO_3 \tag{6.23}$$

with the enthalpy $\Delta H = 178$ kJ mol^{-1} [77] for this process. If just this process provides the above equilibrium and the mass of atmospheric carbon dioxide is small compared to the oceanic one, the atmospheric CO_2 concentration c varies with the temperature T as

$$c \sim \exp\left(-\frac{\Delta H}{T}\right). \tag{6.24}$$

Hence, if the the carbon dioxide concentration and the global temperature are associated as a result of the chemical equilibrium (6.23), this connection is governed by the relation

$$\Delta T = \frac{\Delta H \ln(c_2/c_1)}{T^2}, \tag{6.25}$$

where T is the global temperature, c_1, c_2 are the initial and final concentrations of CO_2 molecules. This gives at doubling of carbon dioxide concentration ($c_2/c_1 = 2$)

$$\Delta T = 0.18\ \text{K}. \tag{6.26}$$

This exhibits that the feedback between the temperature change and that for concentrations of optically active atmospheric components may be of importance in the evolution of the global temperature.

7. Conclusion

Above, we connect the emission of a gaseous layer located over a hot surface with the greenhouse phenomenon in the Earth's atmosphere due to CO_2 molecules. This analysis exhibits the importance of interaction of a radiating molecule with surrounding air molecules that is essential both in broadening of spectral lines and for absorption of CO_2 molecules by other atmospheric components, as well as emission of these components. The evaluations fulfilled show that the contribution of emission of CO_2 molecules to the total radiative flux directed toward the Earth is approximately 20%, as well as this contribution to its derivation over the atmospheric carbon dioxide amount. Comparison of methods of the absorption band which uses the absorption coefficient averaged over its frequency oscillations and the 'line-by-line' method without this averaging exhibits the accordance of these methods for determination of the radiative fluxes and a strong difference in evaluation of its derivative. This shows the importance of the 'line-by-line' method for the analysis of climatic problems.

Note that above we give a simple algorithm to determine the total emission of the Earth's atmosphere due to CO_2 molecules with using the spectroscopic parameters of these molecules on the basis of classical molecular spectroscopy. We note the principal steps which allow us to obtain this algorithm in a simple form. First, there is a local thermodynamic equilibrium for vibrationally excited molecules. Therefore, radiation is created by vibrationally excited molecules which are formed in collisions with air molecules, and their number density is determined by the Boltzmann formula. Second, the atmospheric optical thickness exceeds one, i.e. radiation toward the Earth and outside are separated, and the radiative flux at a given frequency is the blackbody flux, so that the radiative temperature for this frequency is the temperature of an effective layer. Third, interaction between carbon dioxide molecules and other optically active atmospheric components is of importance. This means that a change of the concentration of CO_2 molecules leads simultaneously to a change of the radiative flux due to other components. Based on the total absorption coefficient, which is a sum of those due to CO_2 molecules and other atmospheric components, we take into account this effect. As a result, one can evaluate an additional radiative flux to the Earth's surface due to a change of the atmospheric carbon dioxide concentration, and the corresponding analysis convinces us that contemporary injection of carbon dioxide in the atmosphere as a result of combustion of fossil fuels is not important for the greenhouse effect.

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ORCID iDs

B M Smirnov https://orcid.org/0000-0002-8992-9814

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