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Methane in greenhouse effect of the Earth's atmosphere

B.M.SMIRNOV, D.A.ZHILYAEV

Joint Institute for High Temperatures of Russian Academy Sciences, Izhorskaya 13/19, Moscow, 127412, Russia

ABSTRACT: The "line-by-line" method together with the energetic balance of the Earth are used for evaluation of thermal emission of the standard and dry atmosphere toward the Earth due to methane molecules. From this analysis it follows that the contribution of emission of methane molecules to the radiative flux from the atmosphere is small as well as the contribution from emission of N_2O molecules. Correspondingly, the contribution of other trace gases in atmospheric emission toward the Earth is negligible. The methane case allows one to demonstrate the interaction of radiating components through the radiation field owing to the Kirchhoff law. As a result, the radiative fluxes from the atmosphere to the Earth are different for the real and dry atmosphere.

1. INTRODUCTION

Methane is one of atmospheric components of low concentrations which partake in the greenhouse effect. The concentration of atmospheric methane molecules increases by 2.5 times from 1750 up to now [1, 2, 3, 4]. In addition, contemporary heating of the Earth's may lead to thawing of permafrost that leads to extraction of methane from swamps. This gives various speculations and discussions about the methane role in the climate change. Therefore below we evaluate the greenhouse effect due to emission of atmospheric methane for various scenaria of its evolution in the atmosphere.

2. METHANE IN THE EARTH'S ATMOSPHERE

We first consider the amount of methane in the Earth's atmosphere. Atmospheric methane is a greenhouse component. The concentration of atmospheric methane molecules varies from 0.72ppm in the pre-industrial epoch to 1.9ppm now [1], and we give in Fig.1 evolution of the concentration of atmospheric methane [1, 2, 3, 4]. Because the residence time of methane molecules in the Earth's atmosphere is 8 years [5], these molecules are mixed with air molecules uniformly as a result of air convection. It should be noted the contribution of the human activity to the contemporary amount of atmospheric methane, that is (50-65)% [6].

According to data of Fig.1, the contemporary atmospheric concentration of methane molecules is approximately 1.9ppm that corresponds to the number density of methane molecules $N_m = 5.10^{13}cm^{-3}$ near the Earth's surface. The absorption band of the methane molecule is centered at the frequency $\omega = 1306\ cm^{-1}$. On the basis of data of data of Fig.1 one can account for the number density of methane molecules per unit area of the vertical atmospheric column that is responsible for emission of methane molecules and is equal approximately $4.10^{19}cm^{-2}$. In addition, the radiative lifetime of a triply degenerate

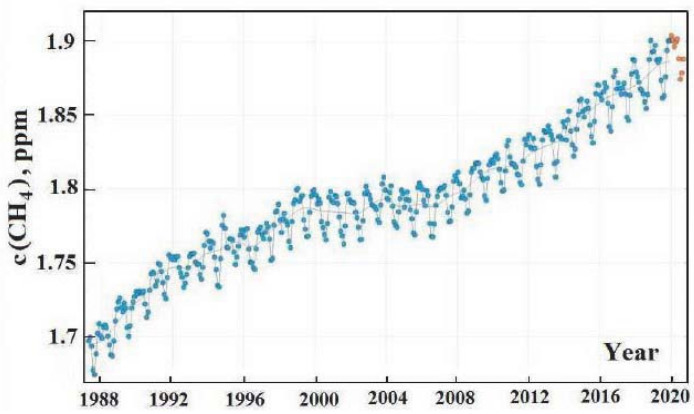

Figure 1: Evolution of the global concentration of methane molecules in the atmosphere last time [3, 4].

deformation vibration states is τ_v= 0.4s, the rotation constant for the methane molecule is B = 5.2cm^{-1} [7, 8, 9, 10].

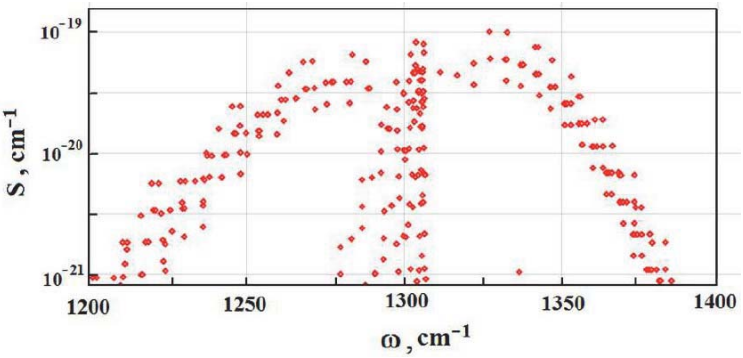

Figure 2: Intensities of spectral iine of the methane molecule located in atmospheric air [13].

In consideration emission of methane molecules in the atmosphere, we use parameters of radiative transitions for methane molecules taken from the HITRAN data bank [11, 12, 13]. Fig.2 contains HITRAN bank data for the intensities of spectral lines of methane molecules located in atmospheric air. As is seen, the absorption band of methane molecules lies in the frequency range approximately from 1200cm^{-1} up to 1350cm^{-1}. We below evaluate radiative parameters of the Earth's atmosphere due to atmospheric methane being guided by this frequency range.

3. EMISSION MODEL FOR ATMOSPHERE TOWARD THE EARTH

According to various versions of the energetic balance of the Earth and its atmosphere, atmospheric regions, where its emissions is created to the Earth's surface and outside, are separated. Therefore a small part (approximately 5%) of the radiative flux emitted by the Earth's surface comes outside the atmosphere. This means that outgoing radiation of the atmosphere does not influence on that directed to the Earth's surface.

In evaluation the radiative fluxes due to various greenhouse components of the atmosphere we are based on the model which formulated in [14] and the algorithm for their calculation is characterized by following features.

1. We use parameters of the model of standard atmosphere [15]. Within the framework of this model, the number density of air molecules N(air), water molecules N(H_2O), methane molecules N(CH_4), and molecules of nitrogen dioxide N(N_2O) depending on the altitude h over the Earth's surface are determined by formulas

$$N(air) = N_a \exp\left(-\frac{h}{\Lambda}\right),\ N(H_2O) = N_w \exp\left(-\frac{h}{\lambda}\right),\ N(CH_4) = N_m \exp\left(-\frac{h}{\Lambda}\right),\ N(N_2O) = N_n \exp\left(-\frac{h}{\Lambda}\right), \tag{3.1}$$

The scale parameters in these formulas are equal Λ = 10km, λ = 2.0km, and the number densities of atmospheric molecules near the Earth's surface are

$$N_a = 2.55 \cdot 10^{19} cm^{-3}, N_w = 3.4 \cdot 10^{17} cm^{-3},\ N_m = 5 \cdot 10^{13} cm^{-3},\ N_n = 7.6 \cdot 10^{12} cm^{-3} \tag{3.2}$$

We take here the water moisture of the real atmosphere near the Earth to be η = 80%. In addition, the temperature T_E near the Earth's surface, and the temperature gradient dT/dh are equal

$$T_E = 288K,\ \frac{dT}{dh} = -6.5K/km \tag{3.3}$$

2. Under pressures of the order of atmospheric one, the width of spectral lines $\Delta\nu$ is small compared to the difference of frequencies $\Delta\omega$ for neighboring spectral lines

$$\Delta\nu \ll \Delta\omega \tag{3.4}$$

This leads to the line structures of the spectrum of atmospheric molecules, i.e. the radiative spectrum consists of broaden spectral lines of radiating atmospheric molecules. Hence, the "line-by-line" model [16, 17] is the basis of these evaluations and integral radiative fluxes follow from these partial fluxes.

3. The emitting atmosphere model includes three basic greenhouse components, namely, H_2O molecules, CO_2 molecules and liquid water microdroplets as the basic condensed phase in the atmosphere. In addition, trace greenhouse components of the atmosphere, as CH_4 molecules and N_2O molecules, give a small contribution to the resulting radiative fluxes.

4. Along with the local thermodynamic equilibrium for atmospheric components, the equilibrium takes place between the radiation field and atmospheric air. For the model of standard atmosphere, the atmosphere temperature is independent of a geographic coordinate and depends weakly on the altitude h over the Earth's surface. This allows one to reduce the radiation of optically active molecules of a weakly nonuniform layer to that of a layer of a constant temperature T_ω [18, 19] that is the radiative temperature at a given frequency.

5. Parameters of radiative transitions of greenhouse molecules are taken from the HITRAN data bank [11, 12, 13] and, therefore, we use the formalism for rates of molecular radiative processes of this data bank [20].

6. The energetic balance of the Earth and its atmosphere is taken into account. According to this balance, radiative fluxes toward the Earth and outside are determined by different atmospheric regions and are separated, i.e. the radiative fluxes to the Earth which are connected with its temperatures do not depend on processes in high layers of the troposphere.

7. Basic greenhouse components are separated, so that clouds are located starting from at a certain altitude, and they are characterized by a sharp boundary. Radiation from greenhouse molecules is created in a gap between the Earth's surface and clouds.

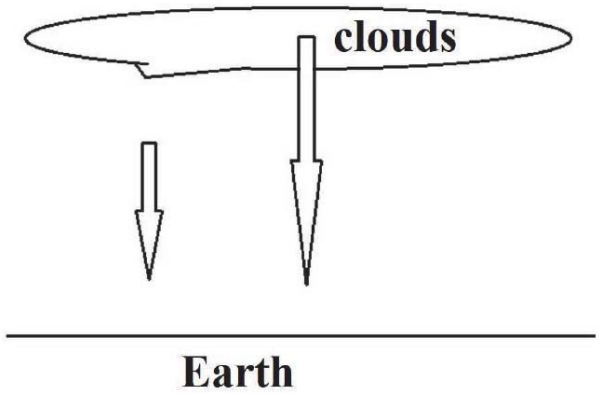

Figure 3: Character of emission of the atmosphere toward the Earth according to which the radiative flux consists of those from clouds and atmospheric molecules located in the gap between the Earth and clouds.

We also include in this analysis the contemporary understanding of atmospheric physics and processes in the atmosphere [16, 17, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34].

4. PARAMETERS OF ATMOSPHERIC EMISSION TO THE EARTH DUE TO METHANE MOLECULES

We first present the parameters which characterize the parameters of emission of the atmosphere. We are based on the Kirchhoff law [35] according to which radiators of the gas are simultaneously the absorbers. Hence parameters of elementary processes of absorption and emission of an electromagnetic wave are connected by the principle of detailed balance. This allows us to use the absorption coefficient k_ω for a given atmosphere point in the analysis of atmospheric emission. Another radiative parameter of the atmosphere, its optical thickness u_ω is expressed through the absorption coefficient k_ω by the expression

$$u_\omega = \int_0^{h_{cl}} k_\omega dh, \tag{4.1}$$

where h is the altitude over the Earth's surface, h_{cl} is the cloud altitude.

The optical thickness of the atmosphere inside the absorption band of methane molecules is given in Fig.4

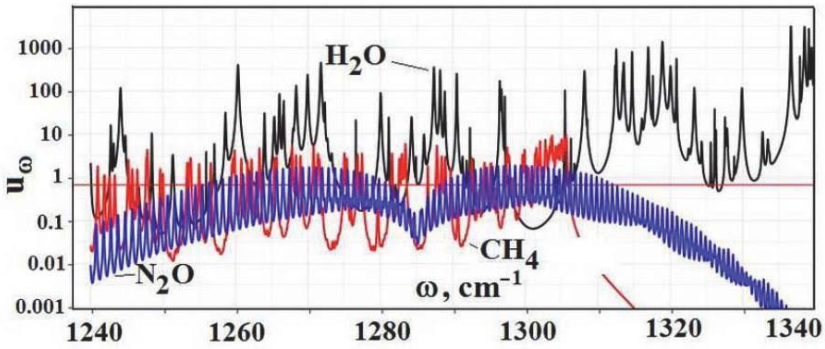

Figure 4: Optical thickness u_ω of the atmospheric gap between the Earth and clouds due to optically active atmospheric molecules CH_4, N_2O and H_2O in the absorption bands of trace gases. The couud altitude is h_{cl} = 4.6km.

In considering the emission of methane molecules of the atmosphere, we are based on the above model. Within the framework of this model, the radiative flux J_ω at a given frequency ω which is emitted by the atmosphere and is absorbed by the Earth, is given by [14]

$$J_\omega = I_\omega(T_\omega)g(u_\omega) + I_\omega(T_{cl})[1 - g(u_\omega)] \tag{4.2}$$

Here T_ω is the radiative temperature for atmospheric molecules, T_{cl} is the temperature of the cloud boundary, I_ω(T) is the radiative flux of a blackbody with a temperature T at this frequency that is given by the Planck formula [36, 37]

$$I_\omega(T) = \frac{\hbar\omega^3}{4\pi^2c^2\left[\exp\left(\frac{\hbar\omega}{T}\right) - 1\right]}, \tag{4.3}$$

and the opaque factor $g(u_\omega)$ of a uniform gaseous layer is given by [38, 39]

$$g(u_\omega) = 2\int_0^1 \cos\theta d\cos\theta \left[1 - \exp\left(-\frac{u_\omega}{cos\theta}\right)\right] \tag{4.4}$$

Formula takes into account the thermodynamic equilibrium of air molecules of the atmosphere with the radiation field through optically active molecules of air and water microdroplets of clouds.

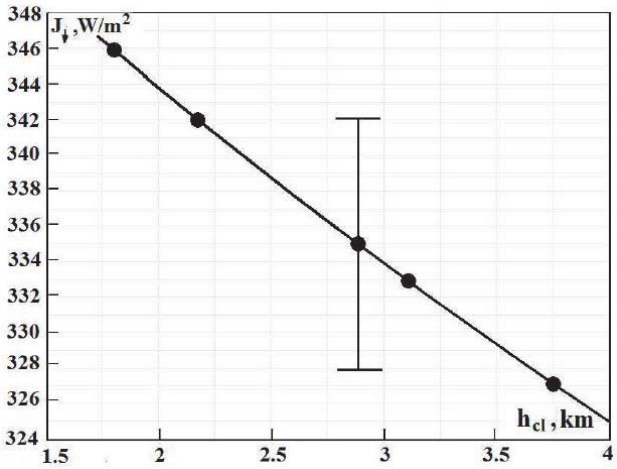

Figure 5: Dependence of the total radiative flux $J_{\downarrow}$ from the atmosphere to the Earth on the altitude of the cloud boundary h_{cl}.

The altitude h_{cl} of the cloud boundary follows from the energetic balance of the Earth and its atmosphere. This parameter can be determined from the the total radiative flux $J_{\downarrow}$ of the atmosphere toward the Earth's surface. Then the cloud altitude h_{cl} follows from the expression for the total radiative flux

$$J_{\downarrow} = \int J_{\omega} d\omega \tag{4.5}$$

One can note different values of the cloud altitude hcl which follows from different versions of the energetic balance of the Earth. These data are given in Fig.5 and Table 1. Within the framework of the model of standard atmosphere, the radiative temperature T_{cl} for a given frequency follows from the relation

$$T_{cl} = T_E - h_{cl} \frac{dT}{dh}, \tag{4.6}$$

where the global temperature equals T_E = 288K for the contemporary standard atmosphere, and its gradient is dT/dh = 6.5K/km. In subsequent evaluations we use average values of cloud parameters h_{cl} and T_{cl} in accordance with data of Table 1.

Table 1. Values of the total radiative flux from the atmosphere to the Earth, as it follows from different versions of the energetic balance. The references give sources of various versions. The altitude h_{cl} of the cloud boundary and the temperature T_{cl} of cloud emission relate to the corresponding version of the Earth's energetic balance.

Number	1	2	3	4	5	average
$J_{\downarrow}$, W/m^2	327	327	333	346	342	335 ± 7
Reference	[33, 40, 41, 42]	[30]	[43, 44, 45, 46]	[47]	[48]	-
h_{cl}, km	5.6	5.6	4.8	3.2	3.7	4.6 ± 0.7
T_{cl}, K	252	252	257	267	264	258 ± 6

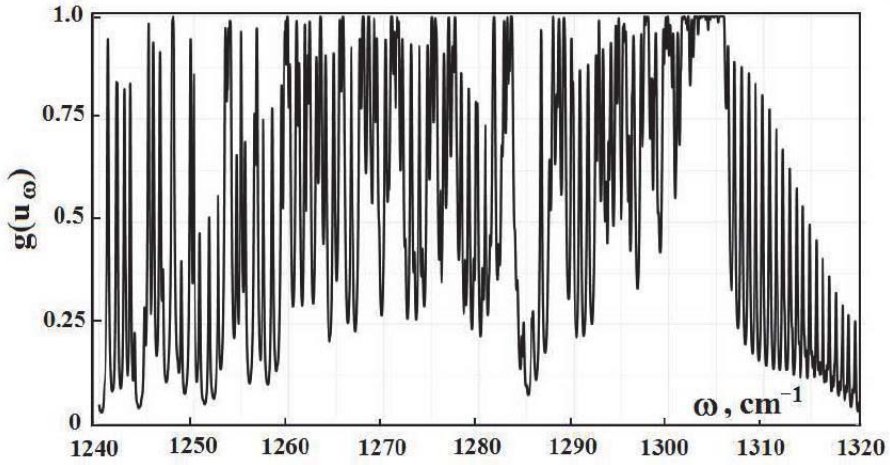

Figure 6: Opaque factor $g(u_\omega)$ for the standard atmosphere in the range of absorption of methane molecules.

In using the above model, we give in Fig.6 the opaque factor of the atmosphere inside the absorption band of methane molecules for parameters of the model of standard atmosphere with an average moisture η = 80%. Fig.7 represents the frequency dependence of the average opaque factor inside the absorption band for the real and dry atmosphere, and Fig.8 gives the radiative temperature in this frequency range.

In accordance with formula (4.2), the partial radiative flux $J_\omega(CH_4)$ due to methane molecules is determined by formula

$$J_\omega(CH_4) = \frac{k_\omega(CH_4)}{\kappa_\omega} I_\omega(T_\omega) g(u_\omega), \tag{4.7}$$

where $k_\omega(CH_4)$ is the absorption coefficient at an altitude h_ω due to methane molecules, κ_ω is the total absorption coefficient at this altitude, and the radiative temperature T_ω at this altitude h! for the model of standard atmosphere is given by

$$T_\omega = T_E - h_\omega \frac{dT}{dh}, \tag{4.8}$$

We give in Fig.9 and Fig.10 the partial radiative fluxes J_ω created by methane molecules at a given frequency. Data of Fig.9 relate to standard atmosphere of the moisture of η = 80%, whereas the averaged values of the radiative fluxes due to methane molecules are given in Fig.10.

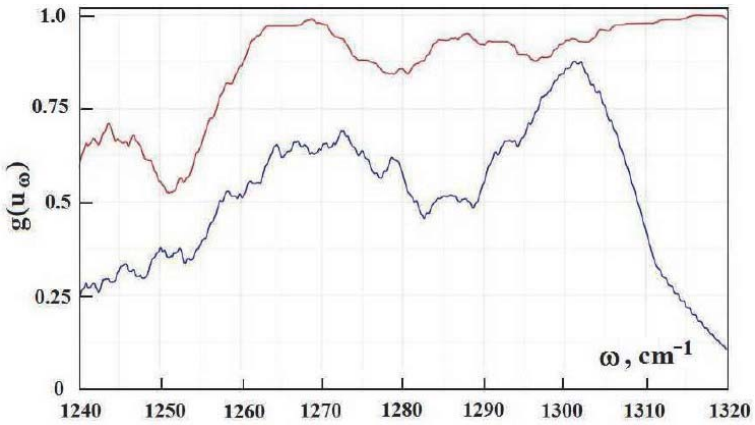

Figure 7: Opaque factor $g(u_\omega)$ of the atmosphere in the frequency range of absorption of methane molecules averaged over a frequency range of 5cm^{-1} (2.5cm^{-1} below a given frequency and above it) for the standard atmosphere of a moisture of η = 80% (red) and for a dry atmosphere, where the moisture is η = 0% (blue).

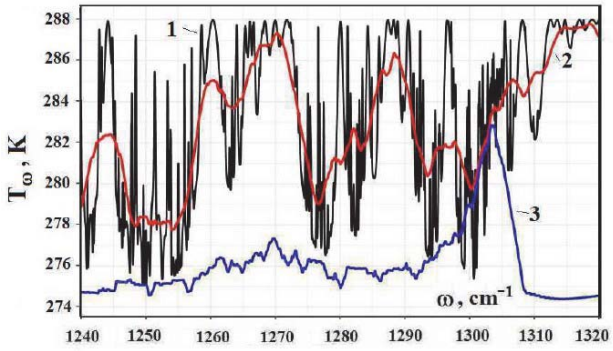

Figure 8: Radiative temperature T_ω of the standard atmosphere (black) in the range of absorption of methane molecules (1). The radiative temperature averaged over a frequency range of 5cm^{-1} (2.5cm^{-1} below a given frequency and above it). These data relate to for the standard atmosphere (2) of a moisture of η = 80% (2) which is given in red and that for a dry atmosphere (3) given in blue (the moisture is η = 0%).

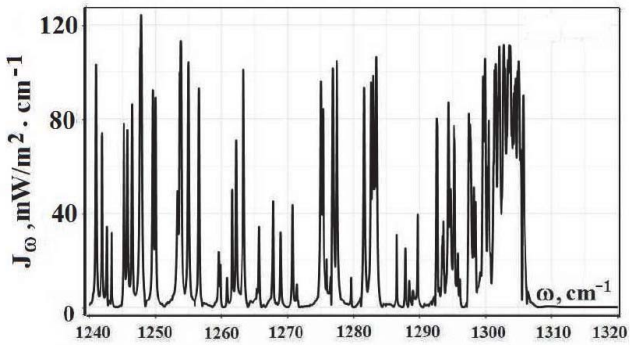

Figure 9: Partial radiative flux J_ω(CH$_4$) created by methane molecules of the standard atmosphere.

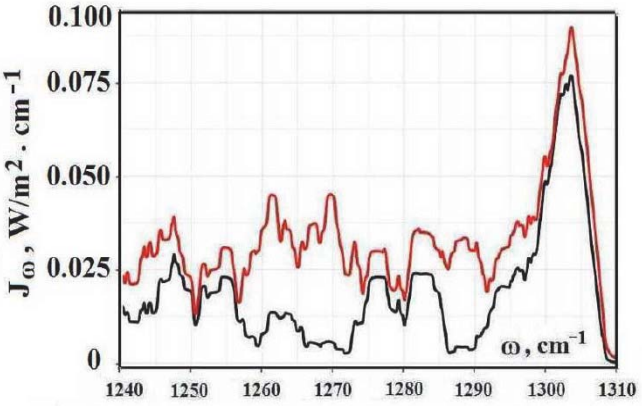

Figure 10: Partial radiative flux J_ω(CH$_4$) created by methane molecules averaged over a frequency range of 5cm^{-1} (2.5cm^{-1} below a given frequency and above it) for the standard atmosphere (black) and for a dry atmosphere (red).

4.1 Character of emission of CH4 molecules in the atmosphere

We now analyze the character of atmospheric emission which parameters are presented in the above Figures. The absorption band for methane molecules ranges from 1240cm^{-1} up to 1320cm^{-1}, so that in this analysis we restrict ourselves by only this frequency range. We give in Table 2 the radiative fluxes from the atmosphere to the Earth's surface inside the absorption of methane molecules under various conditions. As it follows from data of this Table, molecules H_2O, CH_4 and N_2O compete through the radiation field due to the Kirchhoff law [35]. According to this law these molecules are simultaneously radiators and absorbers. For this reason, removal of H_2O molecules or CH_4 molecules from the atmosphere leads to an increase of the radiative flux from the atmosphere due to other greenhouse components.

Table 2. Expressed in W/m^2 the values of the radiative fluxes from the atmosphere to the Earth in the frequency range from 1240cm^{-1} to 1320cm^{-1}, i.e. at frequencies of the absorption band of methane molecules, for different atmosphere compositions. The radiative fluxes for all frequencies are given in parentheses.

	CH_4	H_2O	N_2O	total
dry atmosphere	2.3 (2.8)	0	1.9	8.2
standard atmosphere	1.3 (1.6)	6.2	0.8	4.2
atm. without methane	0	6.5	0.9	7.4

From Table 2 data it follows also that though the frequency range between 1240cm^{-1} and 1320cm^{-1} is the absorption band for methane molecules, the frequency range outside this one gives an additional small contribution to the total radiative flux created by methane molecules.

One more greenhouse component of atmospheric air as a trace gas is nitrous dioxide (N_2O). Though the concentration of N_2O molecules in the atmosphere is less by an order of magnitude compared to that for methane molecules, more favorable spectroscopic parameters may provide the existence of an absorption band even at such concentration. We take the concentration of atmospheric N_2O molecules to be 0.3ppm according to measurements [49, 50], and this concentration grows slightly in time being 0.27ppm in 18 century, 0.28ppm in 19 century, and 0.29ppm in 20 century [51]. We also use below spectroscopic parameters of N_2O molecule [7, 8, 9, 10, 52, 53] which include the rotation constant of this linear molecule B_o = 0.419cm^{-1}. The radiative time τ_r = 5ms corresponds to the vibration frequency 1 = 2224cm^{-1}, and the radiative time τ_r = 80ms relates to the vibration frequency 3 = 1285cm^{-1}.

It should be noted that the contribution of other trace gases into the greenhouse effect is negligible due to their low concentration. In particular, the contribution of ozone molecules of the troposphere to the radiative flux from the atmosphere to the Earth's surface may be ignored because of a small concentration. Though absorption due to stratospheric ozone is observed with satellites, this absorption is not of interest for the thermal balance of the Earth.

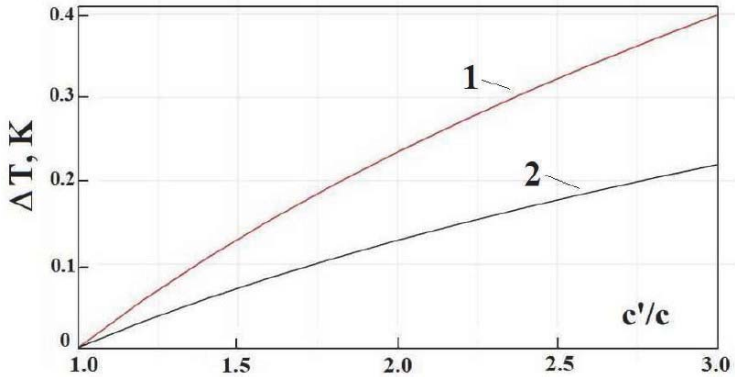

Figure 11: Change of the global temperature as a result of variation for the concentration of methane molecules from c that corresponds to the real atmosphere to c'. 1 respects to the dry atmosphere, 2 relates to the real atmosphere.

Competition of greenhouse components through their interaction with the radiation field becomes apparent if the concentration of this greenhouse component changes. As a result of variation of its concentration, the radiative flux varies due to this component. Change of the radiative flux absorbed by the Earth's surface causes an increase of the global temperature. The characteristic of this effect is the proportionality coefficient between these values, that is the climate sensitivity S [30, 54]. In order to demonstrate the role of atmospheric methane in the establishment of the global temperature, we leave aside details of determination of the climate sensitivity which accuracy is worse. We are based on an average value of the climate sensitivity S = 0.5m^2/(W · K) [14] that is an average value over several papers. Then the change of the global temperature ΔT as a result of the change of the radiative flux ΔJ from the atmosphere to the Earth's surface is given by

$$\Delta T = S\Delta J \tag{4.9}$$

Fig.11 gives the change of the global temperature ΔT as a result of transition from the concentration of methane molecules c in the real atmosphere to this value c'. One can see that water removal from the atmosphere increases

the change of the atmospheric radiative flux due to methane molecules as a result of an increasing concentration of methane molecules. This leads also to an increase of the global temperature.

5. CONCLUSION

Because of a large residence time of methane molecules in the Earth's atmosphere that equals to 8 years [5], these molecules are distributed uniformly over the atmosphere owing to convective motion of air. Then the standard atmosphere model describes the methane behavior in the atmosphere. Within the framework of the model of standard atmosphere and "line-by-line" method, accounting for properties of the real atmosphere and the energetic balance of the Earth, we analyze carefully radiative processes in the atmosphere with participation of methane molecules. As a result, one can conclude that methane molecules give a low contribution to an observed increase of the global temperature of our planet. The contribution of other trace gases is also negligible.

In addition, this analysis demonstrates an interaction of greenhouse components through the radiation field. This follows from the Kirchhoff law [35] according to which radiators of the atmosphere are simultaneously the absorbers. As it follows from data of Table 2 and Figures according to which radiative parameters of the atmosphere are different for a real and dry atmosphere. In the same manner, removal of methane molecules from the atmosphere changes the radiative fluxes due to other components.

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