

## Interaction of radiative molecules in gas emission.

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**ABSTRACT:** Thermal emission of a gas system is considered in the infrared spectrum range if the radiative flux is created by several components. Interaction between these components results from radiative processes of absorption and emission through them. This interaction is analyzed on the basis of the example, where greenhouse components, H<sub>2</sub>O and CO<sub>2</sub> molecules, as well as clouds, partake in atmospheric emission. In this case an increasing concentration of one component causes an increase of the radiative flux due to this component and leads to a decrease of the radiative flux due to other components. The total change of the radiative flux is a sum of changes due to all the greenhouse components. In particular, doubling of the concentration of atmospheric CO<sub>2</sub> molecules leads to an increase of the radiative flux creating by CO<sub>2</sub> molecules which is larger in six times compared to the change of the total radiative flux. This result is based on HITRAN bank data for spectroscopic parameters of CO<sub>2</sub> and H<sub>2</sub>O molecules. But in contemporary computer climate models this interaction between atmospheric carbon dioxide and water is neglected. This mistake starts from evaluations by Plass in 1956 who has not enough spectroscopic information for this, and subsequently this was transferred in contemporary climatological models mechanically.

### 1. INTRODUCTION

We below consider infrared emission of a weakly nonuniform gaseous layer which radiation is created by a mixture of molecular gases and spectra of radiation of these gases are overlapped. In addition, this gas is dense that provides the thermodynamic equilibrium between the states of gaseous molecules, as well as between molecules and photons [1, 2, 3, 4]. Under conditions of local thermodynamic equilibrium, an upper state of the radiative transition between molecular states is formed as a result of molecular collisions, whereas molecular excited states resulted from photon absorption are quenched by gaseous molecules. Being guided by thermal emission of the Earth's atmosphere, we aim to show that the spectrum overlapping may be considered as an interaction of optically active components. Indeed, an increase of amount of one component causes an increasing radiative flux due to this component and leads simultaneously to a decreasing radiative flux owing to another components. Unfortunately, this fact was ignored in evaluation of an increase of the Earth's global temperature due to an increase of the concentration of atmospheric carbon dioxide molecules. Because this mistake was included in climatological computer models, it leads to a large error in predictions of the climate change due to variations of atmospheric carbon dioxide. We below consider this problem in detail.

### 2. RADIATION OF GASEOUS FLAT LAYER

In considering the emission from a gaseous layer, we are based on the "line-by-line" model [5, 6]. This means that some radiating parameters are functions of a frequency and then they are averaged or summarized over frequencies. In addition, we use the Kirchhoff law [7] or the principle of detailed balance that establishes the connection between direct and inverse processes, i.e. between absorption and emission processes in this case. This allows us to use the absorption coefficient as a parameter of the absorption process as a characteristic of the emission process. Next, being guided by the Earth's atmosphere, we take a radiating gas to be located inside a flat layer where radiating parameters depend only on a distance from its boundary. The total absorption coefficient  $k_{\infty}$  is the first such a parameter, and the optical thickness of the layer  $u_{\infty}$  is introduced as

$$u_{\omega} = \int_0^L k_{\omega}(h) dh, \tag{2.1}$$

where L is the layer thickness, and h is a distance from the boundary.

In case of the local thermodynamic equilibrium for each layer of a temperature T (h), one can represent the total radiative flux  $J_{\omega}$  of noncoherent radiation as a sum of fluxes from each layer in the form [10]

$$J_{\omega} = \int_0^1 d\cos\theta \int_0^{u_{\omega}} du \exp\left(-\frac{u}{\cos\theta}\right) \cdot \frac{\hbar\omega^3}{4\pi^2c^2} \left[ \exp\left(\frac{\hbar\omega}{T(h)}\right) - 1 \right]^{-1} \tag{2.2}$$

Here  $\hbar$  is the Planck constant, c is the light velocity, and T is the gas temperature.

If the gas temperature inside the gaseous volume is independent of the temperature (T(h)=const), the radiative flux intersected the layer boundary is given by

$$J_{\omega} = I_{\omega}g(u_{\omega}), \tag{2.3}$$

Here  $I_{\omega}$  is the equilibrium radiative flux that is given by the Planck formula [8, 9]

$$I_{\omega} = \frac{\hbar\omega^3}{4\pi^2c^2 \left[ \exp\left(\frac{\hbar\omega}{T}\right) - 1 \right]}, \tag{2.4}$$

The quantity  $g(u_{\omega})$  is the opaque factor which in the case of the flat layer geometry is given by [10]

$$g(u_{\omega}) = \int_0^1 d\cos\theta \int_0^{u_{\omega}} du_L \exp\left(-\frac{u_L}{\cos\theta}\right) = 2 \int_0^1 \cos\theta \cdot d\cos\theta \left[ 1 - \exp\left(-\frac{u_{\omega}}{\cos\theta}\right) \right], \tag{2.5}$$

In the limit of a large optical layer  $u_{\omega} \gg 1$ , the opaque factor is  $g(u_{\omega}) = 1$ , and the radiative flux from the gaseous layer is equal  $J_{\omega} = I_{\omega}$ .

Let us determine the radiative flux from a weakly nonuniform gaseous layer, where the temperature dependence from a distance from the boundary T (h) is weak as it takes place for the Earth's atmosphere. Then one can expand the expression (2.2) over a small parameter which contains the temperature gradient. In this way one can reduce the radiative flux of a nonequilibrium gaseous layer to that with a constant temperature. In this operation we introduce the effective radiative flux at a distance  $h_{\omega}$  from the boundary, which is responsible for emission at a given frequency, and the radiative temperature  $T_{\omega}$ , so that

$$T_{\omega} = T(h_{\omega}), J_{\omega} = \frac{\hbar\omega^3}{4\pi^2c^2} \cdot \left[ \exp\left(\frac{\hbar\omega}{T_{\omega}}\right) - 1 \right]^{-1} \cdot (1 - \alpha), \tag{2.6}$$

where a small parameter  $\alpha$  is given by [11, 12]

$$\alpha = \frac{5}{18} \left( \frac{\hbar\omega}{T^2k_{\omega}} \cdot \frac{dT}{dh} \right)^2 \tag{2.7}$$

In the case of the Earth's atmosphere at frequencies which corresponds to the maximum of the radiative flux from the Earth's surface this small parameter is  $\alpha \sim 0.01$ .

In particular, in the case of a large optical thickness of the layer  $u_\omega \gg 1$  we have [11, 12]

$$u(h_\omega) = \int_0^{h_\omega} k_\omega(h) dh = \frac{2}{3} \quad (2.8)$$

Evidently, at a low optical thickness an effective layer is located at the layer middle distance. Combining the limiting cases, one can obtain for the position  $h_w$  of an effective layer [13]

$$u(h_\omega) = \frac{u_\omega}{2 \exp(-u_\omega) + 1.5u_\omega} \quad (2.9)$$

We below use these relations for the analysis of emission of a gaseous layer contained a mixture of molecules.

### 3. ATMOSPHERIC EMISSION TOWARD THE EARTH

Starting from general principles of radiative transfer in a gaseous matter, we simplify the problem considering this process under thermodynamic equilibrium between radiation and gaseous system. Next, we consider this problem for the Earth's atmosphere that allows us to extract some peculiarities of interaction between radiation and atomic system which are lost in a general case. There are three greenhouse atmospheric components which determine infrared emission of the atmosphere and include along with H<sub>2</sub>O and CO<sub>2</sub> molecules the water microdrops which form clouds. Indeed, according to the Twomey concept [14, 15], each molecule absorbs in a certain spectral band, and remained spectral gap is covered due to particles. Water microdrops or clouds consisting of them are such absorbed particles for the Earth's atmosphere.

Separating emission of molecular components from that of water microdrops spatially, we use the model [13], where clouds consisting of water microdrops are not located at low atmospheric altitudes, whereas at high altitudes they are optically thick for infrared radiation. We introduce the altitude  $L$ , so that optically active molecules gives the contribution to the Earth's emission below this altitude only, while clouds emit as a blackbody with the boundary at this altitude. Then the partial radiative flux  $J_\omega$  from the atmosphere toward the Earth in accordance with formula (2.3) is given by [13]

$$J_\omega = I_\omega(T_\omega)g(u_\omega) + I_\omega(T_{cl})(1 - g(u_\omega)), \quad (3.1)$$

where  $u_\omega$  is the optical thickness of the atmospheric layer from the Earth's surface up to the altitude  $L$ , and this quantity is determined by atmospheric molecules only,  $T_{cl}$  is the atmospheric temperature at the altitude  $L$  or the cloud temperature. Evidently, the cloud altitude  $L$  is determined by the atmospheric mass of condensed water and its distribution over altitude. Because we have not this information, the parameter  $L$  we find from the condition that the average radiative flux from the atmosphere to the Earth is equal 327W/m<sup>2</sup>, as it follows from the energetic balance of the Earth and its atmosphere. We also assume clouds to be dense near its boundary.

The absorption coefficient  $k_\omega$  at a frequency  $\omega$  due to optically active molecules of a certain type may be represented in the form [16]

$$k_\omega = N \sum_j S_j(T) a_{\omega-\omega_j}, \quad (3.2)$$

where  $N$  is the total number density of molecules of this type,  $\omega_j$  is the frequency of the spectral line center,  $S_j(T)$  is the intensity of  $j$ -th transition at the gas temperature  $T$ ,  $a_{\omega-\omega_j}$  is the frequency distribution function for emitted photons. We here consider noncoherent radiation and therefore summarize the radiative intensities from individual molecules and spectral lines. Taking into account the impact mechanism of broadening of spectral lines that has the form

$$a_{\omega-\omega_j} = \frac{\nu_j}{2\pi[(\omega - \omega_j)^2 + (\nu_j/2)^2]},$$

where  $\nu_j$  is the width of j-spectral line. In addition, the basic temperature dependence of the transition intensity  $S_j(T)$  is the exponential one, i.e.

$$S_j(T) = S_j(T_o) \exp\left(\frac{\varepsilon_j}{T_o} - \frac{\varepsilon_j}{T}\right)$$

As a result, formula (3.2) takes the form

$$k_\omega = N \sum_j \frac{S_j(T_o)\nu_j}{2\pi[(\omega - \omega_j)^2 + (\nu_j/2)^2]} \cdot \exp\left(\frac{\varepsilon_i}{T_o} - \frac{\varepsilon_i}{T}\right) \quad (2.3)$$

According to this formula, the absorption coefficient includes four parameters for each radiative transition, namely, the central frequency  $\omega_j$  of this transition, its width  $\nu_j$ , the intensity  $S_j(T_o)$  of this transition at the indicated temperature  $T_o$ , and the excitation energy  $\varepsilon_j$  of the lower state of this radiative transition.

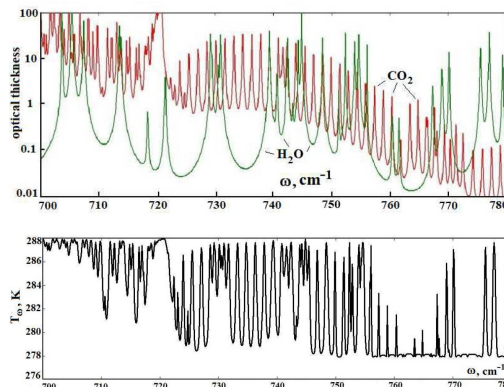
These parameters are contained in the HITRAN (High resolution TRANsmision) database. Information of this database which use both theoretical and experimental data is increased and improved in time [17, 18]. In addition, this information is available in the form “on line”[19, 20]. On the basis of this information, one can evaluate the parameters of radiative transitions, as well as partial fluxes at a given frequency and the total radiative fluxes due to a given greenhouse components.

Some evaluations [13] within the framework of this scheme for the model of standard atmosphere [21], i.e. for average atmospheric parameters, are given in Fig.1c. As it follows from this Figure, the standard atmosphere is opaque with respect to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules for frequencies below  $800\text{cm}^{-1}$ , whereas it is transparent with respect of these molecules at frequencies above  $800\text{cm}^{-1}$ . In addition, as it follows from the energetic balance of the Earth and its atmosphere the cloud parameters are  $L = 3.5 \text{ km}$  and  $T_{cl} = 266\text{K}$ .

One can use the above scheme to analyze the interaction of gaseous components in the yield emission if spectra of these components are overlapped. Fig.1d presents the changes of the radiative fluxes to the Earth as a result of doubling of atmospheric carbon dioxide. We define the change of radiative fluxes up to a given frequency  $\omega$  as

$$\Delta J(\omega) = \int_0^\omega \Delta j_\omega,$$

where  $\Delta j_\omega$  is the change of the radiative flux per unit frequency.



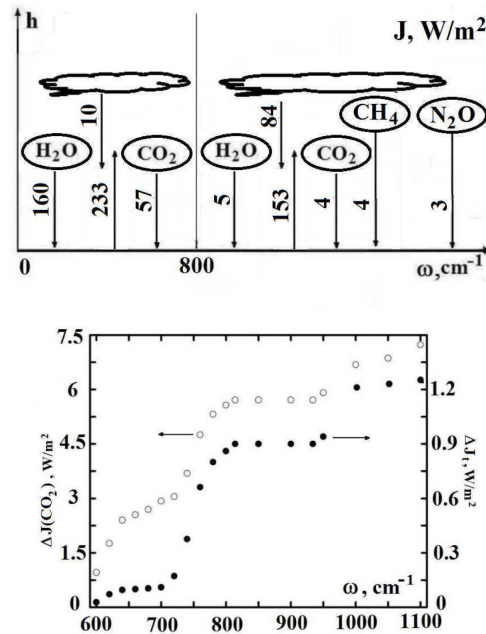


Fig. 1: Optical thickness of the atmosphere in the gap between the Earth and clouds gap due to  $CO_2$  molecules (in red) and  $H_2O$  ones (in green) in the frequency range (700 -780) $cm^{-1}$  (a), the radiative temperature for emission of the atmospheric gap between the Earth's surface and clouds due to  $CO_2$  and  $H_2O$  molecules in this frequency range (b), average radiative fluxes between the Earth and clouds due to indicated atmospheric components are given in  $W/m^2$  (c), and changes of radiative fluxes toward the Earth as a result of doubling of the carbon dioxide concentration due to carbon dioxide molecules  $\Delta J(CO_2)$  and the total one  $\Delta J_t$  (d) [13].

In addition, we give in Table 1 the flux changes due to components of standard atmosphere as a result of the concentration doubling for carbon dioxide molecules. Note the connection between changes of fluxes

$$\Delta J_t = \Delta J(CO_2) + \Delta J(H_2O) + \Delta J_{cl}, \quad (3.4)$$

where  $\Delta J_t$  is the change of the total radiative flux from the atmosphere to the Earth, and  $\Delta J(CO_2)$ ,  $\Delta J(H_2O)$ ,  $\Delta J_{cl}$  are changes of the radiative fluxes to the Earth due to  $CO_2$  molecules,  $H_2O$  molecules, and water microdrops of clouds correspondingly. This relation holds true for any frequency range. The results represented are the basis of the analysis of interaction between optically active components through their radiation.

Table 1. Changes of radiative fluxes from the standard atmosphere to the Earth as a result of doubling of the concentration of  $CO_2$  molecules in the infrared spectrum range [13]. Here  $\Delta J_t$  is the change of the total radiative flux from the atmosphere to the Earth,  $\Delta J(CO_2)$ ,  $\Delta J(H_2O)$ ,  $\Delta J_{cl}$  are the changes of the radiative fluxes to the Earth due to  $CO_2$  molecules,  $H_2O$  molecules, and water microdrops of clouds correspondingly in an indicated frequency range. The frequency ranges are given in  $cm^{-1}$ , and changes of radiative fluxes are expressed in  $W/m^2$ .

Frequency range, $\Delta\omega$	$\Delta J(CO_2)$	$\Delta J(H_2O)$	$\Delta J_{cl}$	$\Delta J_t$
580 – 600	0.96	-0.89	-0.04	0.03
600 – 620	0.81	-0.74	-0.03	0.04
620 – 640	0.63	-0.61	0	0.02
640 – 660	0.15	-0.14	0	0.01
660 – 680	0.18	-0.18	0	0
680 – 700	0.21	-0.20	0	0.01
700 – 720	0.12	-0.03	-0.03	0.06
720 – 740	0.64	-0.05	-0.39	0.20
740 – 760	1.07	-0.10	-0.68	0.29
760 – 780	0.56	-0.02	-0.40	0.14
780 – 800	0.25	-0.02	-0.17	0.06
800 – 850	0.15	-0.03	-0.08	0.04
900 – 950	0.20	0	-0.16	0.04
950 – 1000	0.76	-0.01	-0.53	0.22
1000 – 1050	0.18	0	-0.13	0.05
1050 – 1100	0.37	0	-0.26	0.11
total	7.24	-3.02	-2.90	1.32

We now analyze the change of radiative fluxes to the Earth given in Table 1. Fig.2 contains the vibration spectrum of the CO<sub>2</sub> molecule. There are three types of vibrations, namely, symmetric, antisymmetric and torsion ones, and Fig.2 gives above the character of motion of molecule atoms in corresponding oscillations. The absorption band for thermal emission of the atmosphere includes four lower transitions with the change of the torsion quantum number by one, and the absorption band of atmospheric carbon dioxide ranges approximately from 580cm<sup>-1</sup> up to 750cm<sup>-1</sup>. Fig.1d shows that the increase of radiative fluxes  $\Delta J(\text{CO}_2)$  and  $\Delta J_t$  are collected at boundaries of this absorption band, mostly, at the violet boundary where the absorption coefficient due to water molecules is lower than that at another boundary of the absorption band.

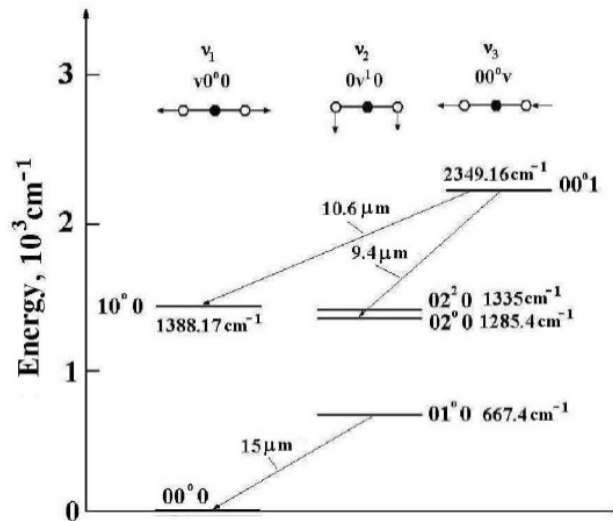


Fig. 2: Types of the lowest vibration states of the CO<sub>2</sub> molecules, energies of the lowest vibration levels, and parameters of radiative transitions.

In addition, according to Table 1 data the contribution of about 30% follows from laser transitions of wavelengths of 9.4 $\mu\text{m}$  and 10.6 $\mu\text{m}$  at which the atmosphere is transparent. This spectrum range gives the contribution of 2% to the total radiative flux due to CO<sub>2</sub> molecules. Thus, on the basis of Table.1 and Fig.1d data, approximately 40% of the radiative flux change due to CO<sub>2</sub> molecules  $\Delta J(\text{CO}_2)$  as a result of doubling of the carbon dioxide amount in the atmosphere is formed in the frequency range between 700cm<sup>-1</sup> and 850cm<sup>-1</sup> that corresponds to the violet boundary of the absorption band of CO<sub>2</sub> molecules. In this spectral range approximately 60% of the change of the total radiative flux  $\Delta J_t$  is created.

Thus, on the basis of the scheme (3.1) one can determine the atmospheric radiative flux to the Earth for a given concentration of greenhouse components. Along with this, one can determine a change of the radiative flux  $\Delta J_t$  as a result of variation of the concentration of greenhouse components. But it is convenient to characterize such variations through the change of the global temperature  $\Delta T$ , i.e. the change of the average Earth's temperature. One can transit to the global temperature change through the climate sensitivity  $S$  [22, 23] by the relation

$$S = \frac{\Delta T}{\Delta J_{\downarrow}} \quad (3.5)$$

The climate sensitivity describes the reaction of the system Earth-atmosphere to an additional energy flux to the Earth's surface. This quantity is sensitive to parameters of this system and therefore the accuracy of this value is low. For example, this value according to data in past for some geographical points lies within the limits between 0.3 and 1.9(m<sup>2</sup> K/W ) according to [23]. The same study for other data in past [24] gives for the corridor of this value from 0.25 up to 0.79(m<sup>2</sup> K/W ). This exhibits a low accuracy of the climate sensitivity that depends on the character of their determination.

In spite of the low accuracy of this quantity, the difference of evaluations is not so large. In particular, the climate sensitivity is 0.55(m<sup>2</sup> K/W ) according to [22], 0.64(m<sup>2</sup> K/W ) according to [25], 0.49(m<sup>2</sup> K/W ) according to [26], and

0.42(m<sup>2</sup> K/W ) according to [27]. Without going into details of these evaluations, one can take the climate sensitivity on the basis of statistical average of these data as [13]

$$S \approx (0.5 \pm 0.1) \frac{m^2 \cdot K}{W} \quad (3.6)$$

On the basis of this analysis, we estimate the accuracy of evaluations of radiative fluxes as several percent, and the accuracy of the global temperature change as 50%.

#### 4. CHANGE TO ATMOSPHERIC CARBON DIOXIDE IN GLOBAL TEMPERATURE

Along with the atmospheric radiative flux toward the Earth the above analysis allows one to determine the flux dependence on the concentration of greenhouse components. We below consider this problem in the standard method by introduction Equilibrium Climate Sensitivity (ECS) [28] that is the global temperature change as a result of the doubling of the concentration of CO<sub>2</sub> molecules. It should be noted that according to definition of ECS, other conditions remain unvaried in the course of doubling of the carbon dioxide concentration. This quantity characterizes the connection between the change of atmospheric composition and the global temperature change. The analysis exhibits the role of interaction between greenhouse components due to overlapping of their spectra. This means the competition for radiation of components with overlapped spectra, i.e. an increase of the atmospheric radiative flux as a result of doubling of the carbon dioxide amount leads to an increasing flux due to carbon dioxide molecules and a decreasing flux due to water molecules and water microdrops. Our task is to prove that this interaction is important for a real atmosphere.

Our position is that the standpoint which is used in contemporary computer codes with absence of this interaction is not correct and leads to a remarkable error in an evaluated effect followed from the change of atmospheric composition. We analyze also why this standpoint was accepted, and therefore below we study the history of this standpoint. In this analysis we start from the classical paper by S.Arrenius [33]. He was the first who opens this problem in 1896 in the following form “Is the temperature of the ground in any way influenced by the presence of heat-absorbing gases in the atmosphere?”. It should be noted that possibilities in that time were restricted. In reality, in this paper the Langley experiments were analyzed for scattering of solar radiation reflected from the moon which allows one to evaluate absorption in the spectrum range related to CO<sub>2</sub> and H<sub>2</sub>O molecules. But these spectral ranges correspond to strong resonant radiative transitions which are not important for thermal emission of the atmosphere because of small wavelengths.

Analyzing the Arrhenius paper [33], it is necessary to take into account the science state in that time, because it was before the Wien law [34]. Nevertheless, just Arrhenius set the problem under consideration. In addition, he taken carbon and water molecules as basic greenhouse components. As a result, the radiative flux due to atmospheric components is a sum of those due to carbon dioxide and water molecules. Because of that understanding the problem, these radiative fluxes were taken independently.

The most contemporary computer codes which are used in the climatology are based on the assumption of the independence for atmospheric radiative fluxes due to CO<sub>2</sub> and H<sub>2</sub>O molecules. Probably, it follows from research of G.N.Plass [35, 36] in fifties. These studies taken into account the influence of H<sub>2</sub>O molecules on emission of CO<sub>2</sub> molecules. It was used the regular (Elsasser) model with a random distribution of spectral lines in the frequency space. According to this analysis, the presence of H<sub>2</sub>O molecules in the atmosphere causes a decrease of the radiative flux change due to variation of the carbon dioxide amount which does not exceed 20%. Since evaluations are restricted by the spectrum range (12-18)μm which includes basic emission of CO<sub>2</sub> molecules in the real atmosphere, G.N.Plass assumes that an increase of the thermal emission of CO<sub>2</sub> molecules outside this spectral range is compensated by a decrease due to H<sub>2</sub>O molecules.

This conclusion contradicts to evaluations used contemporary values of rates of radiative transitions from the HITRAN database [19, 20]. Moreover, from Table 1 it follows that the radiative flux change due to carbon dioxide molecules is compensated by the change of that due to water molecules which was taken into account in the above

studies and approximately the same contribution follows from emission of water microdrops. But in contrast to the conclusion of Plass [35], where the contribution of water is small, our analysis [13] on the basis of contemporary information for rates of radiative transitions leads to another conclusion, namely, water molecules and microdrops compensate to a noticeable extent the change of the radiative flux due to carbon dioxide molecules.

Let us consider the smallness of the change of the total radiative flux with respect to that due to  $\text{CO}_2$  molecules from the standpoint of the scheme (3.1) where interaction between radiation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules with air takes place. Their emission is restricted by the altitude of  $L = 3.5\text{km}$ , where the air temperature is  $T = 266\text{K}$ . From this it follows that the minimum radiative temperature which corresponds to the middle of the radiation region and is realized at low optical thicknesses, is equal  $277\text{K}$ . Thus the range of radiative temperature of air located in a gap between the Earth's surface and clouds, ranges between  $277\text{K}$  and  $288\text{K}$ , i.e. this temperature range is small.

Basing on this, we consider the model for optically dense mixture that the air temperature between the Earth and clouds is independent of an altitude. Then the yield radiative flux at a given frequency is determined by the Planck formula (2.4). Let us change the concentration of  $\text{CO}_2$  molecules at an unvaried constant temperature of air in a gap. Evidently, it leads to the change of the radiative flux  $\Delta J(\text{CO}_2)$  due to  $\text{CO}_2$  molecules, while because the air temperature is conserved, the change of the total radiative flux is zero  $\Delta J_t = 0$ . Again we have that the changes of the total radiative flux and that due to  $\text{CO}_2$  molecules are different.

The above analysis based on contemporary information about radiative transitions in atmospheric air gives that the change of the total radiative flux as a result of an increase of the concentration of  $\text{CO}_2$  molecules in atmospheric air is (5-6) times lower than the change of the radiative flux created by  $\text{CO}_2$  molecules. This contradicts to old evaluations [35, 36] which became the basis of contemporary climatological models. Note that radiative fluxes and their changes are evaluated with a high accuracy. For example, in old evaluations by G.N.Plass [35] which are represented above this accuracy for the radiative flux due to atmospheric  $\text{CO}_2$  molecules is estimated as 4%.

Considering methods of ECS evaluation with and without interaction of greenhouse components, we first represent the author models. In these models the absorption coefficient  $K_w$  for greenhouse components of the atmosphere is taken as

$$K_w = k_w + \kappa_w, \quad (4.1)$$

where  $K_w$  is the absorption coefficient due to  $\text{CO}_2$  molecules, and  $\kappa_w$  is that due to water molecules or water molecules and water microdrops.

Note that the form (4.1) of the absorption coefficient together with the model "line- by-line"[5] includes interaction between greenhouse components. Within the framework of formula (4.1) as the basis of evaluation, the author gone from a simple model to more complex and more real models in description of the spectrum of greenhouse components. The results are given in Table 2, and we below analyze it.

**Table 2. Values of ECS or the global temperature change at doubling of the concentration of  $\text{CO}_2$  molecules under various assumptions in formula (4.1).**

Model	$\Delta T, ^\circ C$	Reference
1	0.5	[29, 30]
2	0.4	[27]
3	0.5	[31, 32]
4	0.6	[13]

The model 1 [29, 30] of Table 2 uses the absorption coefficient  $k_w$  of formula (4.1) which is averaged over frequency oscillations between neighboring spectral lines and a frequency average atmospheric absorption coefficient  $\kappa_w$ . The model 2 [27] of Table 2 uses the absorption coefficient  $\kappa_w$  of formula (4.1) accounts for frequency oscillations between neighboring spectral lines and a frequency average atmospheric absorption coefficient  $\kappa_w$ . The



model 3 [31, 32] uses the HITRAN data for spectral parameters of CO<sub>2</sub> and H<sub>2</sub>O molecules, whereas water microdrops are distributed over altitudes in the same manner as water molecules, and the fourth model [13] accounts for spatial separation atmospheric water molecules and microdrops or clouds in accordance with formula (3.1).

For data of Table 2 we used the climate sensitivity value  $S = 0.5(\text{m}^2 \text{K/W})$ . In addition, the first three models of Table 2 do not account for laser transitions of Fig.2, and we add their contribution to ECS increasing it by 30%. As it follows from Table 2 data, values of ECS for various models under consideration varies between 0.4°C and 0.6°C. Estimating the accuracy of data of Table 2 as 50%, one can conclude a small sensitivity of this value to model assumptions. Then based on the scheme (3.1), one can obtain [13]

$$ECS = (0.5 \pm 0.2)^\circ C \quad (4.2)$$

In contrast to evaluations of ECS on the basis of the above models which take into account overlapping of absorption spectra for greenhouse atmospheric components, results of calculations with using some climatological models are grouped around  $ECS = 3^\circ C$ . Indeed, according to the Intergovernmental Panel on Climate Change [37] the ECS ranges from 1.5°C up to 4.5°C. Next, the statistical average of calculated ECS in papers [35, 38, 39, 40, 41, 42, 43, 44] gives the same result

$$\Delta T = (3.0 \pm 1.5)^\circ C \quad (4.3)$$

Thus, evaluation of ECS on the basis of the assumption that spectra of atmospheric greenhouse components are not overlapped which was suggested by G.N.Plass [35], leads to values which exceed those with accounting for overlapping of spectral lines in several times. This difference allows one to see the importance of this assumption.

## 5. CONCLUSION

There are two types of evaluation of the global temperature change as a result of variation of the carbon dioxide concentration with accounting for interaction between greenhouse components and without it. This means that overlapping of spectra of greenhouse components, atmospheric carbon dioxide and water, leads to different values of change of the global temperature as a result of variation of the carbon dioxide concentration. This difference is approximately six times that exceeds remarkably the uncertainty due to different methods and conditions of evaluations. From this one can conclude that used climatology models ignore interaction between greenhouse components and therefore the results of such calculations are not correct.

In this paper we try to find the root of this discrepancy. As a result, it was in Plass evaluations [35]. In that time the problem of atmospheric carbon dioxide was set strictly. As an example, we give the title of the Calendar paper in 1949 [45] "Can carbon dioxide influence climate?". Fulfilling a series of calculations, G.N.Plass and his collaborations understand the possibility of interaction between emission from atmospheric carbon dioxide and water. But information about radiative parameters for CO<sub>2</sub> and H<sub>2</sub>O molecules was restricted in that time. Basing on spectroscopic data of that time, Plass [35] estimated that the presence of water molecules in the atmosphere decreases the atmospheric radiative flux by 20%.

Contemporary data for radiative parameters of CO<sub>2</sub> and H<sub>2</sub>O molecules in the infrared spectrum range from the HITRAN data base [18] leads to another result. Namely, the presence of atmospheric water causes a decrease of the radiative flux from the atmosphere in six times, rather 20%. Unfortunately, a wrong Plass conclusion about a low role of atmospheric water was included mechanically in climatological codes which lead to incorrect results and require the revision.

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