

# Chapter 7

## Greenhouse Effect in Atmospheres of Earth and Venus



**Abstract** The greenhouse phenomenon in the atmosphere that results from emission of its molecules and particles in the infrared spectrum range is determined by atmospheric water in the form of molecules and microdrops and by carbon dioxide molecules for the Earth atmosphere and by carbon dioxide molecules and dust for the Venus atmosphere. The line-by-line method used the frequency dependent radiative temperature for atmospheric air with a large optical thickness in the infrared spectral range, allows one to separate emission of various components in atmospheric emission. This method demonstrates that the removal of carbon dioxide from the Earth's atmosphere leads to a decrease of the average temperature of the Earth's surface by 4 K; however, doubling of the carbon dioxide amount causes an increase of the Earth's temperature by 0.4 K from the total 2 K at CO<sub>2</sub> doubling in the real atmosphere, as it follows from the NASA measurements. The contribution to this temperature change due to injections of carbon dioxide in the atmosphere due to combustion of fossil fuel, and it is 0.02 K. The infrared radiative flux to the Venus surface due to CO<sub>2</sub> is about 30% of the total flux, and the other part is determined by a dust.

### 7.1 General Principles of Atmospheric Greenhouse Effect

#### 7.1.1 Nature of Atmospheric Greenhouse Effect

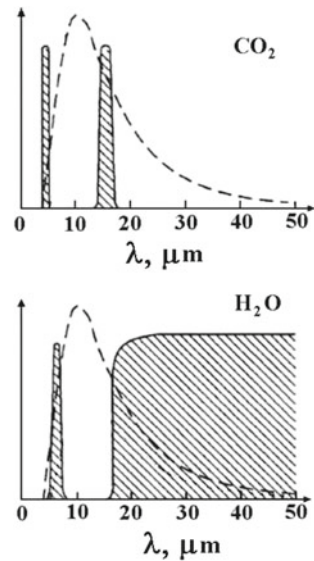
The nature of the greenhouse effect was understood almost two century ago [1, 2]; it is determined by a property of the matter over a surface. In a usual greenhouse, the Earth surface is heated as a result of absorption of solar radiation and it is cooled by emission of infrared radiation. This balance establishes the surface temperature. If place a partition over the surface which is transparent for visible radiation and returns to the surface partially infrared radiation, its heat balance changes and the surface temperature increases. In the Earth's atmosphere the role of this partition plays its atmosphere that must be transparent for visible solar radiation and it is not transparent for infrared radiation. As a result, the surface temperature increases compared with the case if the atmosphere is absent.

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**Fig. 7.1** Spectrum of emission of carbons dioxide molecules and water molecules located in atmospheric air and spectrum of equilibrium radiation at the temperature of 288 K [8, 9]

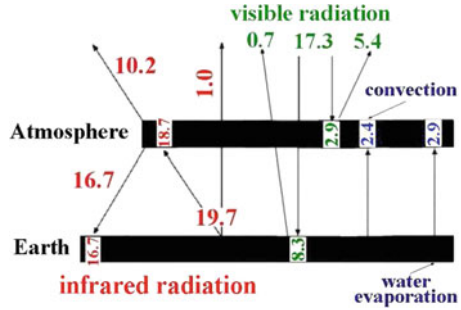


Infrared emission of the Earth's atmosphere is determined by vibration-rotation transitions of some atmospheric molecules, mostly  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , and also by radiation of aerosols and atmospheric particles [3]. As it was indicated above, Fourier [1, 2] describes the nature of the greenhouse effect in the Earth's atmosphere. The next step in understanding the greenhouse effect of the Earth atmosphere was made by Tyndall [4–6] who shown on the basis of his experiments with molecular gases [7] that greenhouse atmospheric properties are determined by molecular gases, such as a water vapor, carbon dioxide and methane.

It should be noted the peculiarity of the greenhouse effect which is demonstrated by Fig. 7.1 [8, 9]. This figure exhibits emission of atmospheric molecules of carbon dioxide or water in a restricted spectrum range, and radiation of water molecules is more important than that due to  $\text{CO}_2$  molecules for following reasons. First, water molecules have a dipole moment and hence they are more optically active objects. In atmospheric radiation it results in radiative rotation transitions without the change of a vibration molecular state. Rotation transitions determine a long-wave spectrum range. Second, the number density of water molecules in the atmosphere is higher than that for carbon dioxide molecules. In particular, the average number density of water molecules near the Earth's surface is  $4 \cdot 10^{17} \text{ cm}^{-3}$  compared to  $1 \cdot 10^{16} \text{ cm}^{-3}$  which we used above for the mean number density of atmospheric  $\text{CO}_2$  molecules. This shows an important role of aerosols in atmospheric emission.

Because the greenhouse phenomenon is connected with the atmosphere energetics involving solar radiation in the visible spectrum range as well as infrared radiation of the atmosphere, it is of importance for the energetic balance of the Earth and its atmosphere. These data represented in Fig. 7.2 are taken from books [10–13] of one of authors which in turn are based on the NASA data, in particular, on [14]. These

**Fig. 7.2** Expressed in  $10^{16}$  W the powers of indicated processes which lead to obtaining or loss of the energy by the Earth as a whole as well as by its atmosphere. Absorbed powers are given inside corresponding rectangulars, consumed powers are indicated near arrows



data are in accordance with those contained in books [15–20] and also with those of many papers, in particular, [21–26]. Evidently, the reason of this coincidence within the limits of a few percent for basic channels is that the data are taken from the same source—the data of NASA [14]. In addition, because these data relate to various times within one half century, one can conclude that the rates of these energetic processes have the natural character and vary weakly during this time range.

In evaluation some atmospheric parameters it is convenient to use the average energy fluxes. In consideration radiative processes in the atmosphere, it is convenient to operate with average radiative fluxes which result from dividing the total power of Fig. 7.2 to the area  $S = 5.1 \cdot 10^{14} \text{ m}^2$ , though the accuracy of these data is not enough. The average radiative flux of solar radiation in the visible spectrum range is  $340 \text{ W/m}^2$ , the average radiative flux of from the Earth’s surface in the infrared spectrum range is  $386 \text{ W/m}^2$ , the average radiative fluxes of from the atmosphere in the infrared spectrum range are  $327$  and  $200 \text{ W/m}^2$  towards the Earth and outside correspondingly. Additionally, the average radiative flux from the Earth’s surface that is not absorbed by the atmosphere and goes outside is  $20 \text{ W/m}^2$ . Note also that the average energy flux from the Earth to its atmosphere in accordance with data of Fig. 7.2 is equal  $57 \text{ W/m}^2$  due to water evaporation from the earth’s surface and  $47 \text{ W/m}^2$  due to convection.

From the energetic balance of the Earth and its atmosphere as a whole given in Fig. 7.2 it follows that the basis of this balance is solar radiation which is penetrated in the Earth’s atmosphere and it is converted partially in infrared radiation through emission and its absorption by the Earth and atmosphere. Note that the Earth emits infrared radiation almost as a black body. Since the grey coefficient of various objects on the Earth’s surface in the IR spectral range is close to one [27], the Earth’s surface may be considered as a black body for emission, that leads to the average Earth’s temperature to be  $T = 287 \text{ K}$ , whereas the standard atmosphere model [28] gives for the global Earth’s temperature  $T = 288 \text{ K}$ . We note also that the atmosphere removal leads to the global temperature  $T = 278 \text{ K}$ , if the Earth absorbs solar radiation completely and emits as a black body.

Let us represent the temperature  $T$  at a given point of the globe surface as  $T = T_g + \delta T$ , where  $T_g$  is the global temperature. Assuming that the Earth’s surface emits

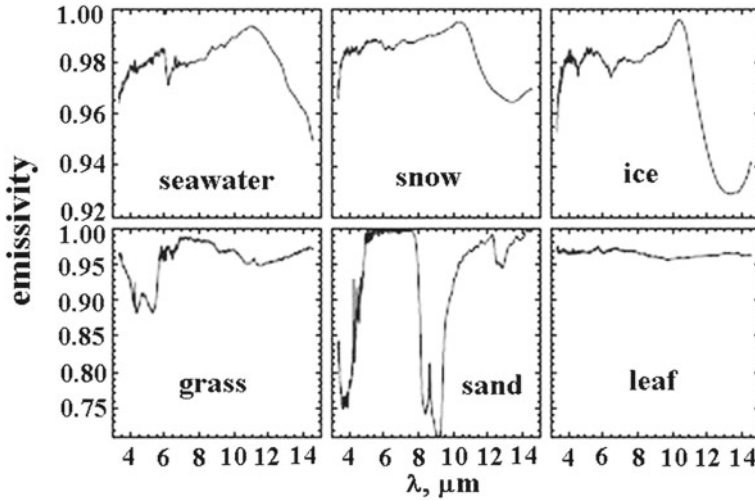


Fig. 7.3 Emissivity of various surfaces via the photon wavelength [27]

as a black body in the IR spectral range, one can obtain for the radiation power  $P_s$  of the Earth’s surfa0 parameter  $\delta T/T_g$

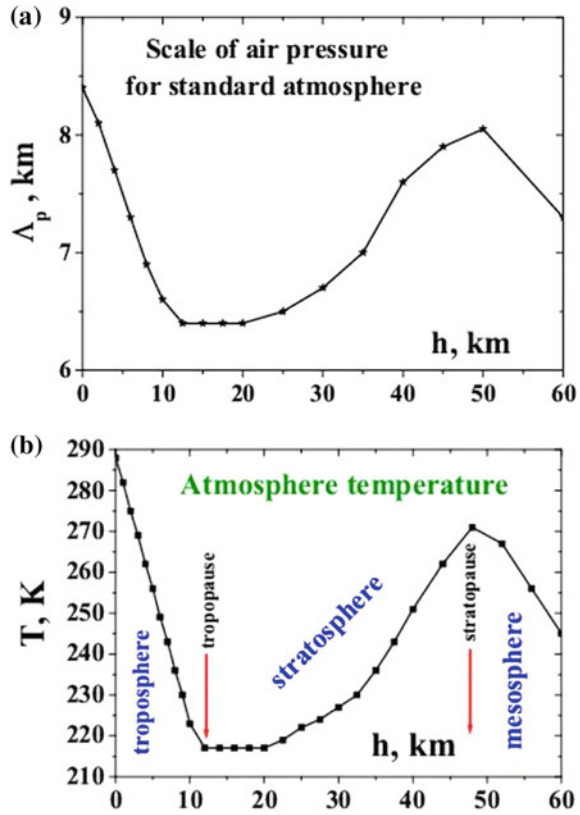
$$P_s = \sigma T_g^4 S \left[ 1 + 6 \left( \frac{\delta T}{T_g} \right)^2 \right], \tag{7.1.1}$$

where  $S = 5.1 \cdot 10^{14} \text{ m}^2$  is the area of the Earth’s surface. Because a typical values the temperature fluctuation  $\delta T$  are several Kelvin, the second term of formula (7.1.1) is small. Therefore, one can use the average surface temperature for its emission.

One can justify the black body model for the Earth’s surface by data of Fig. 7.3, where the grey coefficient or emissivity are given in the infrared spectrum range for objects which can determine the Earth’s emission. The grey coefficient is the ratio of the photon flux from the surface of a given object with a certain temperature to that of the black body surface with this temperature. This allows one to consider the Earth’s surface as a black body in evaluation of its emission, and the accuracy of this replace is about of several percents.

We now step aside from radiative processes and consider atmospheric phenomena which are important for the greenhouse effect in the atmosphere. Because this effect relates to the entire Earth, in its analysis it is convenient to deal with parameters averaged over the globe and time including a time of day and season. This leads to the model of standard atmosphere [28] which is characterized by average parameters and relates roughly to the USA atmosphere. Though atmospheric air consists of nitrogen (79%) and oxygen (20%), we below assume air molecules to be identical with the molecular weight  $m = 29 \text{ a.u.m}$ . The dependence on the altitude  $h$  for the

**Fig. 7.4** Scaling parameter of formula (7.1.2) (a) and the atmosphere temperature (b) as an altitude function for standard atmosphere



number density  $N_a(h)$  of air molecules, as well as other atmospheric molecules which are mixed with air ones, is given by formula

$$N(h) = N(0) \exp\left(-\frac{h}{\Lambda}\right) \tag{7.1.2}$$

The scaling parameter  $\Lambda$  follows from approximation the data of standard atmosphere by this formula, is represented in Fig. 7.4a. Figure 7.4b contains the altitude dependence of the atmosphere temperature and notations for atmospheric lower layers. Being guided by the greenhouse effect, we are restricted by the troposphere and lower stratosphere only, where the temperature gradient in the troposphere is close to  $dT/dh = -6.5 \text{ K/km}$ , as it follows from Fig. 7.4b.

In order to understand the character of atmospheric emission, one can introduce the effective temperature of an uniform atmosphere for each frequency. In other words, in the framework of the line-by-line model, we introduce the radiative temperature  $T_\omega$  which determines the emission flux at each frequency of atmospheric  $\text{CO}_2$  molecules in the total emission of the Earth’s atmosphere, we first use the radiative flux towards

the Earth's surface as the parameter which characterizes atmospheric radiators in accordance with equation

$$J_{\downarrow} = \int_0^{\infty} \frac{h\omega^3 d\omega}{4\pi^2 c^2} \left[ \exp\left(\frac{h\omega}{T_{\omega}}\right) - 1 \right]^{-1} = 327 \text{ W/m}^2, \quad J_{\uparrow} = \int_0^{\infty} \frac{h\omega^3 d\omega}{4\pi^2 c^2} \left[ \exp\left(\frac{h\omega}{T_{\omega}}\right) - 1 \right]^{-1} = 200 \text{ W/m}^2, \quad (7.1.3)$$

where  $J_{\downarrow}$ ,  $J_{\uparrow}$  are the radiative fluxes toward the Earth and outside it, and the radiative temperatures for radiation directed to the Earth and outgoing radiation are different. We below consider various models on the basis of formula (7.1.3). According to the simplest model, the atmospheric absorption coefficient is independent of frequency  $\omega$ , and then the radiative temperature towards the Earth  $T_{\downarrow}$  and outside it  $T_{\uparrow}$  follow from the Stephan-Boltzmann equation

$$J_{\downarrow} = \sigma T_{\downarrow}^4, \quad J_{\uparrow} = \sigma T_{\uparrow}^4,$$

These equations give for temperatures of layers which are responsible for atmospheric emission [19, 29]

$$T_{\downarrow} = 276 \text{ K}, \quad T_{\uparrow} = 244 \text{ K} \quad (7.1.4)$$

These temperatures follow from equations  $T_{\uparrow} = T([h_{\uparrow}])$  and radiation towards the Earth  $T_{\downarrow} = T([h_{\downarrow}])$ , where  $T(h)$  is the temperature at an altitude  $h$ . One can use the following connection between an appropriate of the atmospheric temperature and altitude for these temperatures

$$T_{\downarrow} = T_E - h_{\downarrow} \frac{dT}{dh}, \quad T_{\uparrow} = T_E - h_{\uparrow} \frac{dT}{dh}, \quad (7.1.5)$$

where within the framework the standard atmosphere model the average temperature gradient is  $dT/dh = 6.5 \text{ K/km}$ , and  $T_E = 288 \text{ K}$  is the temperature of the Earth's surface. From formulas (7.1.4) and (7.1.5) it follows for these altitudes

$$h_{\downarrow} = 1.9 \text{ km}, \quad h_{\uparrow} = 6.8 \text{ km} \quad (7.1.6)$$

It is of importance the local thermodynamic equilibrium for vibrationally excited molecules which accompanies the atmosphere greenhouse effect and requires large radiative times compared with collision times involving excited molecules in atmospheric air. Therefore radiative processes do not violate the Boltzmann distribution over excited vibrational and rotational states; the emission of this gas is determined by excited molecules which result from collisions of nonexcited molecules with gaseous ones, rather than from absorption of the radiation. From this consideration it follows that radiative transport does not give a contribution to the emission of this gas.

Indeed, the emission of photons created by vibrationally excited molecules does not violate this distribution if the rate of excitation of an excited state exceeds sig-

nificantly the rate of radiative decay of this state. In particular, for the basic radiative transition  $01^0_0 \rightarrow 00^0_0$  we have the rate constant of destruction of the upper state  $k_{\text{rel}} = 5 \cdot 10^{-16} \text{ cm}^3/\text{s}$  at room temperature [70]. Then we obtain the condition for the number density of air molecules  $N_a$  of the Boltzmann distribution

$$N_a \gg \frac{1}{k_{\text{rel}}\tau_r} \quad (7.1.7)$$

Taking the radiative lifetime  $\tau_r = 0.33 \text{ s}$  according to Fig. 4.3 data, we obtain the criterion (7.1.7) as  $N_a \gg 3 \cdot 10^{15} \text{ cm}^{-3}$ . This criterion is violated only outside the stratosphere.

We thus are based on the condition of local thermodynamic equilibrium in atmospheric air, and that the optical thickness of the atmosphere is large. Under these conditions, we reduce the atmosphere with an alternative temperature to that with a constant temperature. This is possible at a small temperature gradient that is a basis of expansion over a small parameter. Such an expansion allows us to find the radiative temperature  $T_\omega$  that characterizes the radiative flux at this frequency.

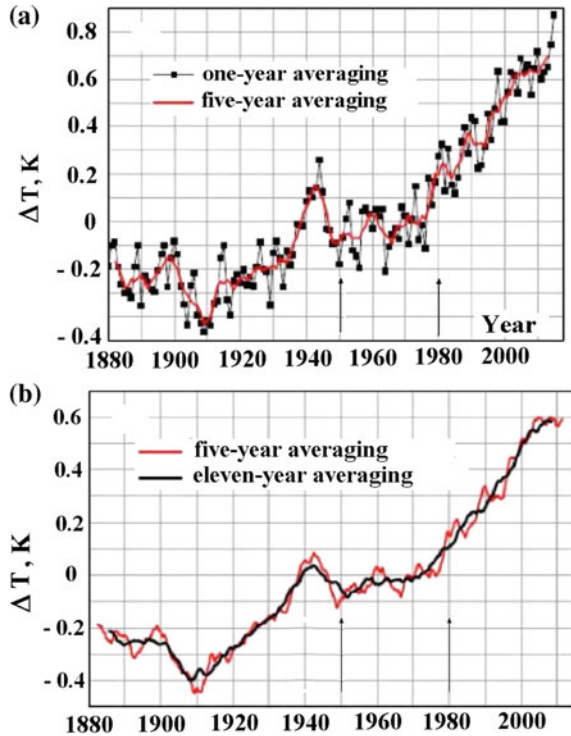
### 7.1.2 Global Properties of the Earth's Atmosphere

We below consider the atmospheric greenhouse effect in detail. The greenhouse effect is created by three atmospheric components, namely, by water vapor, carbon dioxide and water aerosols; though other greenhouse components gives a small contribution to this effect, their influence on the greenhouse effect will be considered also. Note that molecular greenhouse components, molecules of water and carbon dioxide located in atmospheric air, create infrared radiation as a result of vibrational-rotational or rotational transitions of molecules. Rates of such radiative transitions are relatively low, and hence they do not influence on thermodynamic equilibrium in air between vibrational and rotational states of greenhouse molecules. Hence, radiation emitted by the atmosphere is characterized by the air temperature.

Let us introduce the global Earth's temperature as the temperature of the Earth's surface averaged over all the globe surface and time. The global temperature is a parameter of the Earth's energetic balance. Variation of the global temperature in time characterizes the climate change, and our task is to determine the rate of change of the global temperature  $dT/dt$ , and the range of temporal variation which is measured in years. The problem is that chaotic variations of the global temperature, as well as the temperature at a given geographical point, in the course of a day and season reach tens degrees, so that the global temperatures averaged over year are of the order of 1 K. But variation of the global temperature for a century does not exceed 1 K.

The method [30] for variation of global temperature allows one to overcome the indicated problem and to decrease the fluctuations in determination of the global temperature by one order of magnitude. Within this method we compare temperatures at the same geographical point and time of day and season and construct the difference

**Fig. 7.5** Evolution of the global temperature with averaging for one and five years [31] (a), and for five and fifteen years [32, 33] (b). Arrows indicate years when the global temperature does not vary in average and is taken as a basic one



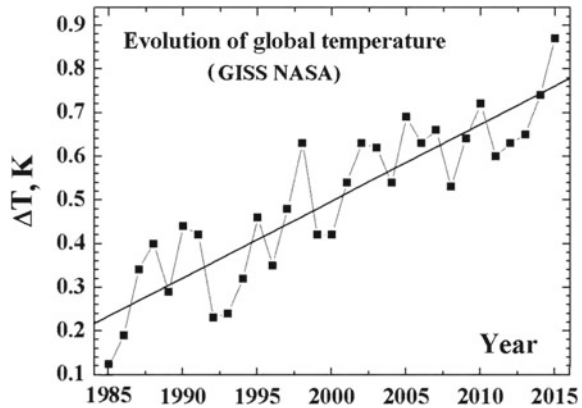
of these temperatures  $\Delta T$  at different years. Next this temperature difference is averaged over the Earth's surface and also over day and season time during the year. In this manner one can determine variation  $\Delta T$  of the global temperature in time and the rate  $d\Delta T/dt$  of its variation. Fluctuations of variation of the global temperature in this method are estimated as 0.1 K.

Realization of this method requires large information and a labor-intensive work. Nevertheless, this information follows from data of meteorological stations. A number of such meteorological stations was about 6 thousands in the second half of 19th century and now their number decreases in three times only, because the basic information follows from satellite measurements. Treatment of this information is made within the framework of NASA programs [Goddard Institute for Space Studies—GISS], and results of this treatment are given in [31–36]. Comparison of the global temperature change in summer and winter, as well as in daytime and night time or in North and South hemispheres gives that indicated values of  $\Delta T$  during a year does not exceed 0.2 K [32, 33].

Figure 7.5 give evolution of the global temperature with averaging over year, five years and fifteen years. One can see that the larger time of averaging, the smoother this dependence. From Fig. 7.5 it follows that year fluctuations of the global temperature are of the order of 0.1 K. One can see a non-monotonic evolution of the global temperature in time. Indeed, during 1880–1910 a weak cooling was observed that



**Fig. 7.6** Evolution of global temperature in last years [32]. The temperature variation is counted from the average global temperature in 1950–1980



was changed by a weak heating in 1910–1940 which was continued by cooling during 1940–1950. Next, during 1950–1980 the global temperature did not vary within the limit of its accuracy, and the Earth heating takes place after 1980. Basing on these data, we give in Fig. 7.6 evolution of the global temperature after 1985 when the global temperature was increased monotonically [37]. Approximation of these data by the linear time dependence gives for evolution of average change of the global temperature

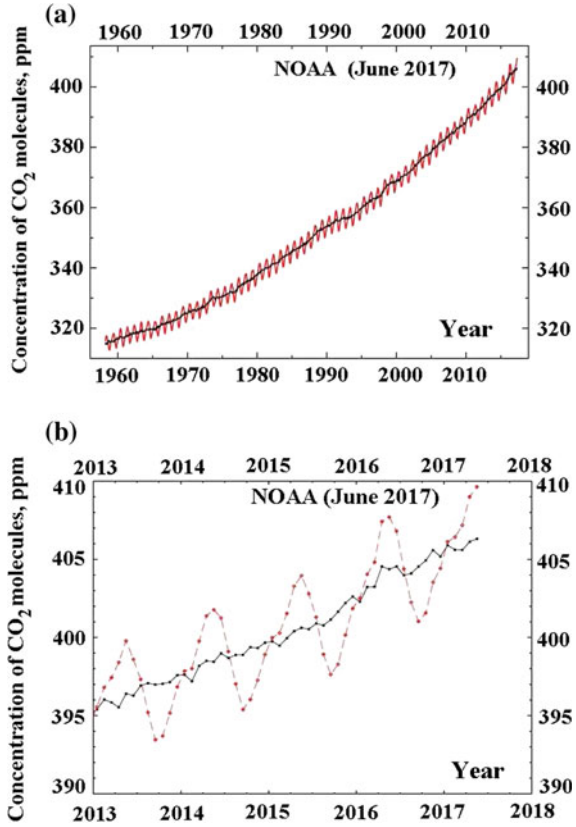
$$\frac{d\Delta T}{dt} = 0.018 \text{ K/yr}, \tag{7.1.8}$$

and the fluctuation (standard deviation) for data of Fig. 7.6 is equal  $\Delta = 0.09 \text{ K}$ . The latter means that a smooth (linear) time dependence for the global temperature change  $\Delta T$  is valid at time intervals above 5 years.

One of a greenhouse atmospheric component is carbon dioxide. The equilibrium of atmospheric carbon dioxide results from its conversion in a hard carbon in the photosynthesis processes, and the inverse process by processes of putrefaction and breathing of plants. As it follows from the carbon balance in the atmosphere [38–41], the rate of each process is approximately  $2 \cdot 10^9 \text{ ton/yr}$ , while the total carbon mass in atmospheric carbon dioxide is approximately  $2 \cdot 10^9 \text{ ton/yr}$ . This means that the average residence time of an atmospheric  $\text{CO}_2$  molecule is 4 years. In addition, the total carbon mass in fossil fuels, i.e. in coal, oil and methane, is  $1 \cdot 10^8 \text{ ton/yr}$ . This means that only 5% of the rate of carbon dioxide injections in the atmosphere corresponds to combustion of fossil fuels, i.e. the latter is not important for the balance of atmospheric carbon dioxide.

Detailed information about atmospheric carbon dioxide follows from monitoring of atmospheric  $\text{CO}_2$  that is made from 1959 in the Mauna Loa observatory (Hawaii, USA) [43–46]. This observatory is located at altitude 3400m above the sea level < that is far from sources or absorbers of carbon dioxide. Some results of this monitoring are given in Fig. 7.7. As is seen, the concentration of carbon dioxide

**Fig. 7.7** Concentration of CO<sub>2</sub> molecules in atmospheric air during the last half century (a) and for the last five years (b) according to [42, 43]; open circles corresponds to an average during a month, and filled squares relate to averaged data for year (one half year before and after an indicated data)



molecules in atmospheric air increases from 316 ppm in 1959 up to 409 ppm in 2017. In addition, the rate of an increase of the carbon dioxide concentration grows in time from 0.7 ppm/yr in 1959 up to approximately 2.1 ppm in 2017. The reason of season oscillations of the CO<sub>2</sub> concentration is explained that the photosynthesis process is stronger in the northern hemisphere, where it proceeds mostly in the period from May to September, and the photosynthesis is absent practically in the period from October to March. The data of Fig. 7.7a give the contemporary rate of variation of CO<sub>2</sub> concentration as

$$\frac{d \ln c}{dt} = 0.006 \text{ yr}^{-1}, \tag{7.1.9}$$

with an accuracy approximately 10%.

Within the framework of the Arrhenius concept [47], one can introduce the equilibrium climate sensitivity (ECS) [48] as a change of the global Earth temperature at the doubling of the atmospheric carbon dioxide concentration. This value is given by

$$\text{ECS} = \Delta T \frac{\ln 2}{\ln(c_2/c_1)}, \quad (7.1.10)$$

where  $c_1$  and  $c_2$  are concentration of  $\text{CO}_2$  molecules at the initial and final time, and  $\Delta T$  is the global temperature variation for this time interval. This value may be determine twofold. In the first case it follows from formulas (7.1.8) and (7.1.9). In the second case we take the concentration of  $\text{CO}_2$  molecules to be  $c_1 = 280$  ppm in a pre-industrial period, and  $c_2 = 410$  ppm at the present time, and the temperature change is  $\Delta = (0.8 \pm 0.1)$  K [49] for this time. As a result, we obtain

$$\text{ECS} = (2.0 \pm 0.3) \text{ }^\circ\text{C} \quad (7.1.11)$$

Note that this value follow from NASA measurements, rather than some evaluations.

The mean amount of atmospheric water is  $1.3 \cdot 10^{19}$  g [50–53] that corresponds to the mean water density in the atmosphere as  $3 \text{ g/m}^3$ . One can compare the water mass in the atmosphere with the atmosphere one  $5.1 \cdot 10^{21}$  g which relates to nitrogen and oxygen. This corresponds to the average concentration of water molecules in atmospheric air as approximately 0.4%, whereas near the Earth's surface the average concentration of water molecules in air is equal 1.7%. The total rate of water evaporation from the Earth's surface is  $3.9 \cdot 10^{20}$  g/yr [54–57] (only  $1.0 \cdot 10^{18}$  g in the form of snow), and the same rate relates to water returning to the Earth's surface. As it follows from this consideration, the power of the evaporation process is equal  $2.4 \cdot 10^{16}$  W (see Fig. 7.2) which is returned as a result of water condensation in the atmosphere. In this manner, the above power is transferred from the Earth to atmosphere.

From the amount of atmospheric water and the rate of its formation it follows that an average time of residence of water molecules in the atmosphere is approximately 9 days [57]. In the water balance between the land, ocean and atmosphere, precipitation of atmospheric water on the Earth's surface and uniform distribution over it gives a layer of liquid water of a thickness 2.5 cm [58]. The height of a precipitated layer may be used as a unit for amount of a water vapor in the atmosphere [59–63]. As it follows from data [59, 60], approximately 80% of atmospheric water is located at altitudes below 3 km. According to data [61–63], the rate of water precipitation on the Earth's surface is higher for oceans, whereas season variations of this rate are more for land.

Atmospheric water contains a small part of Earth's water with the mass of  $1.4 \cdot 10^{24}$  g. If this water would be distributed over the Earth's surface uniformly, the layer thickness will be 2.7 km. From this it follows that the most part of this water is located underground. Note that 96% of Earth's water is salty. In addition, open water located on the Earth surface is a source of atmospheric water and is found in equilibrium with it.

Near the Earth's surface the average partial pressure of water is about 2 Torr, whereas the saturated water pressure is 4.7 Torr at the temperature [64, 65]. Therefore atmospheric water is in the form of a vapor mostly, and a small part of water

exist in the form of aerosols, at least, at altitudes below 3 km. Because of the condensation process, the number density of water molecules decreases with an altitude  $h$  sharper than that in the case of air molecules. By analogy with formula (7.1.2), the dependence of the number density of water molecules  $N(\text{H}_2\text{O})$  on the altitude  $h$  may be approximated by

$$N(\text{H}_2\text{O}) = N_o \exp(-h/\lambda), \quad (7.1.12)$$

and the parameters of formula (7.2.27) are equal according to measurements [61–63] of the global atmospheric moisture at various altitudes

$$N_o = (4.2 \pm 0.2) \cdot 10^{17} \text{ cm}^{-3}, \quad \lambda = (2.0 \pm 0.2) \text{ km}, \quad (7.1.13)$$

Here the data of 1950–1960 and 2000–2010 are used, so that the values of these parameters vary during this time inside the indicated accuracy. In reality, the total amount of atmospheric water grows in time with the rate 0.07 g/kg per decade (1 g of water per 1 kg of air) [66–68], that corresponds to variation of the concentration of atmospheric water  $c$  as

$$\frac{d \ln c}{dt} = 7 \cdot 10^{-3} \text{ yr}^{-1} \quad (7.1.14)$$

From the end of 19th century an increase of the air moisture near the Earth's surface is equal approximately 4% [69].

### 7.1.3 *Models of Emission from Optically Dense Gaseous Layer*

We below represent the models for emission of the atmosphere considering it in average as a gaseous layer above the Earth's surface; its parameters depend on the altitude only because a typical thickness of the atmospheric layer which is responsible for its emission is small compared to the Earth's radius. But it is necessary to take into account a nonuniform distribution of the atmospheric temperature and number density of radiating and excited molecules. In this analysis it is of importance the local thermodynamic equilibrium for vibrationally excited atmospheric molecules because radiative times are large compared with collision times involving excited molecules in atmospheric air. Therefore radiative processes do not violate the Boltzmann distribution over excited vibrational and rotational states. From this it follows that radiation does not influences on the distribution, and radiative transport involving reabsorption processes is negligible. This fact decreases a number of models [70] which may be used in the analysis of atmospheric emission in the infrared spectrum range.

We now use a simple model on the basis of the assumption that the atmospheric absorption coefficient is independent of the frequency, and also it is a monotonous function of an altitude [19, 29]. Under these conditions one can determine the average optical thickness of the atmosphere. Let us approximate the altitude dependence of the absorption coefficient as

$$\kappa_{\omega} \equiv \frac{du_{\omega}}{dh} = A \exp\left(-\frac{h}{\lambda}\right), \quad (7.1.15)$$

In order to determine the parameters of this formula, we use formula (2.2.37) which allows one to find the altitude of the layers which are responsible for emission toward the Earth  $h_{\downarrow}$  and outside the atmosphere  $h_{\uparrow}$ . These altitudes satisfy to equations (2.2.31)

$$\int_{h_{\uparrow}}^{\infty} k_{\omega} dh = 2/3, \quad \int_0^{h_{\downarrow}} k_{\omega} dh = 2/3 \quad (7.1.16)$$

These equations allow one to determine the parameters of formula (7.1.15) [19, 29]

$$A = 0.35 \text{ km}^{-1}, \quad \lambda = 6.0 \text{ km}, \quad u = A\lambda = 2.1, \quad (7.1.17)$$

where  $u$  is the total optical thickness of the atmosphere. Thus, this model [19, 29] with the average absorption coefficient over the infrared spectrum range proves the validity of the model of a weakly varied optical thickness as an altitude function for optically thick layers under consideration.

Note that the used model for emission of a nonuniform gaseous layer is used a small parameter (2.2.37) which in the limit  $\hbar\omega > T$  has the form

$$\alpha = \frac{5}{18} \left( \frac{\hbar\omega}{T^2} \cdot \frac{dT}{du} \right)^2 \quad (7.1.18)$$

Let us determine altitudes which are responsible for emission toward the Earth and outside the atmosphere, the values of this small parameter are equal  $\alpha_{\downarrow} = 0.03$  and  $\alpha_{\uparrow} = 1/4$ .

We now extract one component from the absorbed gas and present the absorption coefficient of the entire gas  $K_{\omega}$  in the form

$$K_{\omega} = \kappa + k_{\omega}, \quad (7.1.19)$$

where  $k_{\omega}$  is the absorption coefficient of an extracted gaseous component and  $\kappa$  is that for other absorbed component. For example, if the standard atmosphere contains three main absorbed components: water molecules, water microdrops and carbon dioxide molecules, one can refer  $\kappa$  to water molecules and water microdrops, while  $k_{\omega}$  is the absorption coefficient of  $\text{CO}_2$  atmospheric molecules, and then one can find

the contribution of  $\text{CO}_2$  molecules to atmospheric absorption. In another example  $k_\omega$  refers to trace gases, and  $\kappa$  is the absorption coefficient of three basic absorbed components of the atmosphere. Below we focus on the first example because it is of the practical interest.

Let us formulate the algorithm to determine the contribution of a certain component of atmospheric air to its emission under given conditions. For obviousness, we will consider below as this example the emission of atmospheric carbon dioxide toward the Earth. One can use two models for determination the radiative flux  $j_\omega$  due to carbon dioxide, as well as the total radiative flux  $J_\omega$  to the Earth's surface due to all atmospheric components. According to formulas (7.1.15) and (7.1.16) one can characterize radiation at a frequency  $\omega$  by the radiative temperature  $T_\omega$  that is given by

$$T_\omega = T(h_\omega), \quad h_\omega = \frac{2}{3K_\omega} = \frac{2}{3(\kappa + k_\omega)} \quad (7.1.20)$$

This formula describes the emission towards the Earth and is based on the assumption  $h_\omega \ll \lambda$ . Next, the equality of the radiative temperature  $T_\omega$  for a given frequency and the temperature of an atmospheric layer located at an effective altitude  $h_\omega$  means local thermodynamic equilibrium for radiating molecules.

The radiative temperature  $T_\omega$  allows one to determine the radiative flux toward the Earth  $J_\omega$  at a given frequency  $\omega$  according to the Planck formula (2.2.37) [71, 72]

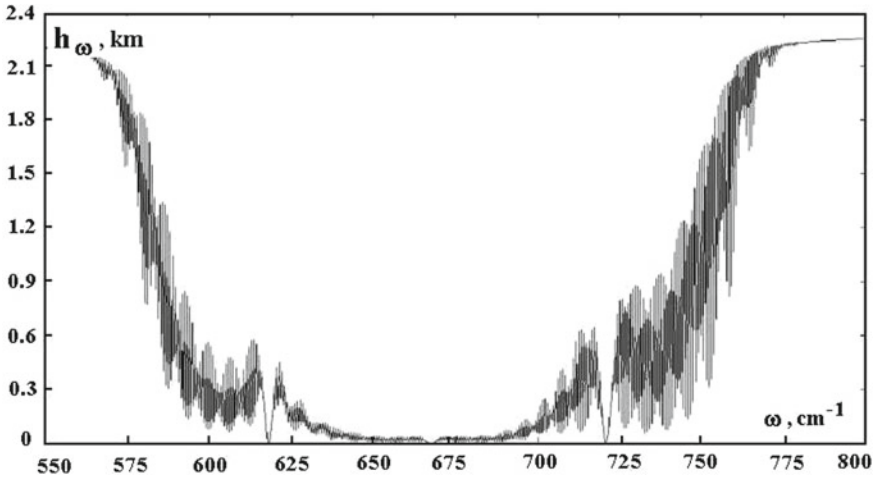
$$J_\omega = \frac{\omega^3}{4\pi^2 c^3 \{\exp [\hbar\omega/T_\omega] - 1\}}, \quad (7.1.21)$$

and this gives the total radiative flux as the integral of the partial ones (7.1.21). Using the partial radiative temperature  $T_\omega$  corresponds to the line-by-line model that means determination of partial radiative fluxes at each frequency and subsequent integration of these fluxes in the total radiative flux.

Another model, the absorption band model [19, 70, 73], is more rough and assumes that the emission takes place in a certain frequency range which is called the absorption band. This model holds true at high pressures where frequency oscillations of the absorption coefficient are absent, i.e. according to formula (4.2.16)  $k_\omega = \chi_\omega$ . In this case we are based on a sharp dependence  $\chi(\omega)$ , and one can introduce boundary frequencies  $\omega_1$  and  $\omega_2$  of the absorption band on the basis of the relations

$$k_{\omega_1} = k_{\omega_2} = \kappa \quad (7.1.22)$$

It is clear that this model does not work in a transient range of frequencies, whereas oscillations expand the transient range and hence decrease of the accuracy of this model. We below analyze the above models of atmosphere emission for main greenhouse



**Fig. 7.8** Effective altitude  $h_\omega$  which determines the radiative flux at a given frequency at the contemporary concentration of atmospheric carbon dioxide under the assumption that the absorption coefficient of atmospheric water is independent of the frequency [74]

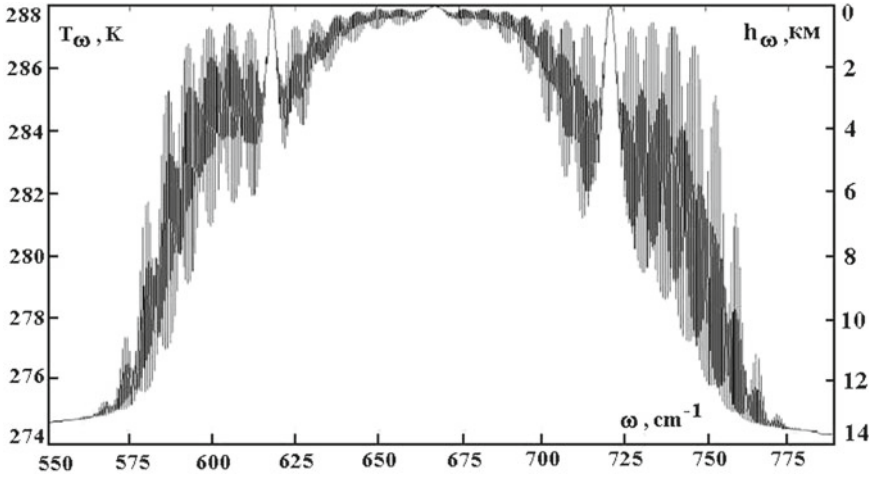
components of the atmosphere, namely, carbon dioxide molecules, water molecules and water microdrops—aerosols.

## 7.2 Greenhouse Effect in Atmospheres

### 7.2.1 Emission of Atmospheric $CO_2$ Molecules Towards the Earth

We now evaluate the radiative flux toward the Earth due to atmospheric molecules of carbon dioxide. For this it is necessary to take into account vibrational transitions in accordance with formula (4.2.27) which create the radiative flux towards the Earth. We use formulas (4.2.17), (4.2.18), and (4.2.21) for the absorption coefficient due to each vibrational transition, and also formula (4.2.25) for the absorption coefficient of  $P$  and  $R$  branches of atmospheric  $CO_2$  molecules, as well formulas (4.2.31) and (4.2.32) for  $Q$ -branch. All these evaluations relate for a high optical density of the atmosphere and the local thermodynamic equilibrium.

We first determine the radiative temperature  $T_\omega$  for atmospheric emission in the frequency range where it is created by atmospheric  $CO_2$  molecules. For the standard atmosphere model where the temperature gradient is  $dT/dh = 6.5 \text{ K/km}$ , formulas (7.1.5) and (7.1.18) give for the radiative temperature  $T_\omega$



**Fig. 7.9** Radiative temperature  $T_\omega$  at the contemporary concentration of atmospheric carbon dioxide for the line-by-line method under assumption that the absorption coefficient of atmospheric water is independent of the frequency [74]

$$T_{\omega_1} = T_E - h_\omega \frac{dT}{dh} = T_E - \frac{\alpha}{\kappa + k_\omega}, \quad (7.2.1)$$

where  $T_E = 288 \text{ K}$  is the Earth's temperature,  $h_\omega$  is the altitude which is responsible for radiation towards the Earth,  $\alpha = 4.3 \text{ K/km}$ . Figure 7.8 contains the effective altitude  $h_\omega$  which is responsible for radiation at a given frequency and is given by formula (7.1.20). Figure 7.9 gives the radiative temperature due to atmospheric carbon dioxide in accordance with formula (7.2.1). Roughly, this dependence may be approximated by a table-form that corresponds to the absorption band model. This means that inside the absorption band, the radiative temperature is equal to the Earth's temperature because of a high optical thickness of the atmosphere due to atmospheric  $\text{CO}_2$  molecules. Outside the absorption band  $\text{CO}_2$  molecules do not partake in origin of the radiative temperature, and within the framework of a constant temperature model the radiative temperature in this range is independent of the frequency.

Within the framework of the absorption model, we have on the basis of formula (7.1.22) for boundaries frequencies left  $\omega_{1b}$  and right  $\omega_{2b}$  from the absorption band at the contemporary amount of atmospheric carbon dioxide molecules

$$\omega_{1b} = 585 \text{ cm}^{-1}, \quad \omega_{2b} = 750 \text{ cm}^{-1} \quad (7.2.2)$$

Within the framework of the absorption band model, this gives the radiation flux  $J_\downarrow$  toward the Earth's surface due to atmospheric  $\text{CO}_2$  molecules



$$J_{\downarrow} = \int_{\omega_{1b}}^{\omega_{2b}} j_{\omega} d\omega = \int_{\omega_{1b}}^{\omega_{2b}} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2} \left[ \exp\left(\frac{\hbar\omega}{T_{\omega}}\right) - 1 \right]^{-1}, \quad (7.2.3)$$

where  $T$  is the atmosphere temperature near the Earth's surface. Using parameters of this formula for the standard atmosphere model, we obtain the value of the radiative flux at the contemporary number density of atmospheric  $\text{CO}_2$  molecules ( $N(\text{CO}_2) = 1 \cdot 10^{16} \text{ cm}^{-3}$ ) [74]

$$J_{\downarrow} = 67 \text{ W/m}^2 \quad (7.2.4)$$

One can fulfil the same operation at doubling number density of the amount of atmospheric carbon dioxide. Then instead of the values (7.2.2) we have the boundaries of the absorption band

$$\omega'_{1b} = 581 \text{ cm}^{-1}, \quad \omega'_{2b} = 755 \text{ cm}^{-1}, \quad (7.2.5)$$

that corresponds to the following radiative flux toward the Earth's surface [74]

$$J'_{\downarrow} = 71 \text{ W/m}^2 \quad (7.2.6)$$

On the basis of the line-by-line model, the radiative flux toward the Earth is given by

$$J_{\downarrow} = \int_{\omega_{1b}}^{\omega_{2b}} j_{\omega} d\omega = \int_{\omega_{1b}}^{\omega_{2b}} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2} \left[ \exp\left(\frac{\hbar\omega}{T_{\omega}}\right) - 1 \right]^{-1} \quad (7.2.7)$$

The emission radiative flux  $J_{\downarrow}$  toward the Earth's surface at the contemporary concentration of  $\text{CO}_2$  molecules and that  $J'_{\downarrow}$  at its doubled concentration are equal according to this formula [74]

$$J_{\downarrow} = 61 \text{ W/m}^2, \quad J'_{\downarrow} = 68 \text{ W/m}^2 \quad (7.2.8)$$

As a result, we have for the average radiative flux toward the Earth under these conditions [74]

$$J_{\downarrow} = (64 \pm 3) \text{ W/m}^2, \quad J'_{\downarrow} = (70 \pm 2) \text{ W/m}^2 \quad \Delta J_{\downarrow}(\text{CO}_2) = (5 \pm 2) \text{ W/m}^2, \quad (7.2.9)$$

where  $\Delta J_{\downarrow}(\text{CO}_2)$  is the difference of radiative fluxes toward the Earth due to atmospheric  $\text{CO}_2$  molecules as a result of doubling of the atmospheric concentration of  $\text{CO}_2$  molecules.

Let us assume that inside the absorption bands for atmospheric molecules of carbon dioxide which boundaries are given by formulas (7.2.2) and (7.2.5) the ra-

diative atmospheric temperature  $T_\omega$  coincides with the global Earth's temperature  $T = 288$  K. Then the atmospheric radiative flux is equal  $J = 67$  W/m<sup>2</sup> at the contemporary concentration of carbon dioxide molecules and  $J' = 71$  W/m<sup>2</sup> at the doubled concentration of carbon dioxide molecules. One can see that these values coincide within the accuracy limits with evaluations (7.2.9) on the basis of real radiative temperatures. The difference of these radiative fluxes coincides with the accepted flux difference 4 W/m<sup>2</sup> [16, 75], but this is not the change of the radiative flux toward the Earth due to doubling of the amount of atmospheric carbon dioxide because of a different spectral width of the absorption band. We below determine the change of the radiative flux toward the Earth due to doubling of the amount of atmospheric carbon dioxide. Next, from this it follows that the contribution of emission of CO<sub>2</sub> molecules to the total radiative flux toward the Earth is approximately 20%.

We now improve the model of frequency independent absorption coefficient which allowed one to determine the altitude  $h_\omega$  of an atmospheric layer which is responsible for emission toward the Earth's surface and the temperature of this layer  $T_\downarrow$  according to formula (7.1.6) and (7.1.4) as  $h_\downarrow = 1.9$  km,  $T_\downarrow = 276$  K. We now account for a heightened radiative flux  $J_\downarrow(\text{CO}_2)$  due to CO<sub>2</sub> molecules in their spectral range between  $\omega_1$  and  $\omega_2$ . Then we have the following equation for the radiative flux

$$J_\downarrow = \int_0^{\omega_1} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2} \left[ \exp\left(\frac{\hbar\omega}{T}\right) - 1 \right]^{-1} + J_\downarrow(\text{CO}_2) + \int_{\omega_2}^{\infty} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2} \left[ \exp\left(\frac{\hbar\omega}{T}\right) - 1 \right]^{-1} = 327 \text{ W/m}^2, \quad (7.2.10)$$

where  $T$  is the radiative temperature outside the absorption band by CO<sub>2</sub> molecules. As a result, we have for parameters of this range

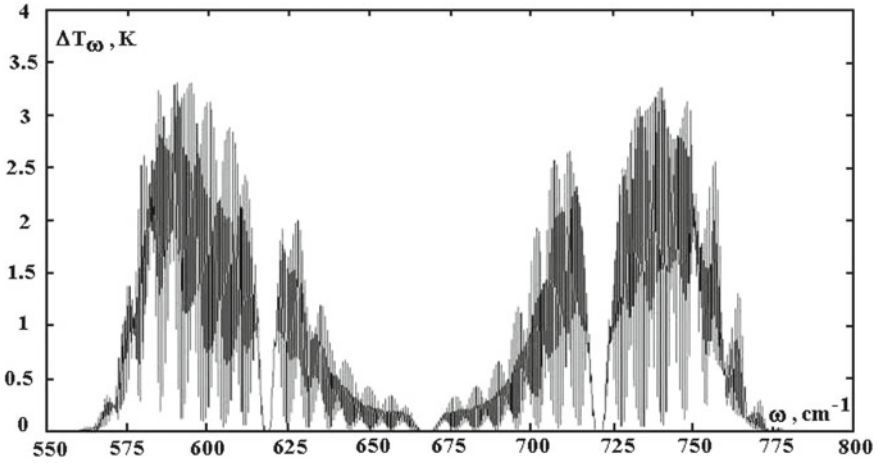
$$T_\downarrow = 274 \text{ K}, \quad h_\downarrow = 2.2 \text{ km} \quad \kappa = 0.30 \text{ km}^{-1} \quad (7.2.11)$$

We now check the validity of the method which allowed one to reduce the atmosphere with a varied temperature to the one where the temperature is independent of the altitude. It is based on a smallness of the parameter  $\alpha$  which is defined by formula (7.1.18). Outside the absorption band we have

$$\frac{dT}{du} = \frac{dT}{\kappa dh} = 22 \text{ K},$$

and formula (7.1.18) gives at boundaries (7.2.2) of the absorption band  $\alpha(\omega_{1b}) = 0.016$ ,  $\alpha(\omega_{2b}) = 0.026$  that confirms the validity of the method used.

Let us analyze the change of the radiative flux  $\Delta J_\downarrow$  toward the earth's surface as a result of doubling of the atmospheric carbon dioxide amount in order to determine the ECS (equilibrium climate sensitivity) subsequently. This increase leads to an increase of the radiative temperature for radiation directed toward the Earth, and this change is represented in Fig. 7.10 [74]. This allows one to determine an increase  $\Delta J_\downarrow$  of the radiative flux toward the Earth as a result of doubling of the concentration of atmospheric CO<sub>2</sub> molecules as



**Fig. 7.10** Increase of the radiative temperature for the flux toward the Earth resulted from doubling of the concentration of carbon dioxide molecules within the framework of the line-by-line model [74]

$$\Delta J_{\downarrow} = \int_{\omega_1}^{\omega_2} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2} \left\{ \left[ \exp\left(\frac{\hbar\omega}{T_{\omega}}\right) - 1 \right]^{-1} - \left[ \exp\left(\frac{\hbar\omega}{T'_{\omega}}\right) - 1 \right]^{-1} \right\}, \quad (7.2.12)$$

where  $T_{\omega}$  and  $T'_{\omega}$  are the radiative temperatures at the contemporary and doubled concentrations of atmospheric carbon dioxide molecules respectively. Note that this difference determines an additional radiative flux toward the Earth due to doubling of the concentration of atmospheric  $\text{CO}_2$  molecules, rather the value  $\Delta J_{\downarrow}(\text{CO}_2)$  in formula (7.2.9).

It is clear that the used model in which the frequency is independent of the absorption coefficient, is rough because the absorption coefficient as a frequency function oscillates strongly in reality. Therefore we take it in a more general form

$$\kappa = \kappa_o + a \cos[b(\omega - \omega_o)], ; \quad (7.2.13)$$

where  $a < \kappa_o$ ,  $b \sim 1 \text{ cm}^{-1}$ , and  $\kappa_o = 0.3 \text{ km}^{-1}$ , i.e. the average absorption coefficient in the range outside of the absorption band due to  $\text{CO}_2$  molecules is  $\kappa_o$  and (7.2.10) is fulfilled. Then formula (7.2.12) gives after averaging over the parameter  $b$ .

$$\Delta J_{\downarrow} = (1.0 \pm 0.2) \text{ W/m}^2 \quad (7.2.14)$$

As is seen, this difference  $\Delta J_{\downarrow} = J'_{\downarrow} - J_{\downarrow}$  is several times less than the that  $\Delta J_{\downarrow}(\text{CO}_2)$  defined by formula (7.2.9) as the difference of radiative fluxes toward the Earth which are created by  $\text{CO}_2$  molecules. This means that increase of the

flux due to  $\text{CO}_2$  molecules is accompanied by a more strong absorption of emitted radiation. It is convenient to represent formula (7.2.14) in the form

$$\frac{\Delta J_{\downarrow}(\text{CO}_2)}{d \ln c} = (1.4 \pm 0.3) \text{ W/m}^2 \quad (7.2.15)$$

In the same manner, one can determine the change of the radiative flux as a result of the change of the concentration of atmospheric water. Within the framework of the above model, the water contribution to the atmospheric radiative flux toward the Earth is characterized by the average absorption coefficient  $\kappa$  in formula (7.1.19). Indeed, increasing the average absorption coefficient  $\kappa$  by 10%, one can obtain an increase in the radiative flux to the Earth's surface by  $4.7 \text{ W/m}^2$ . Assuming the average absorption coefficient  $\kappa$  of atmospheric water to be proportional to the concentration of atmospheric water, one can obtain by analogy with formula (7.2.15)

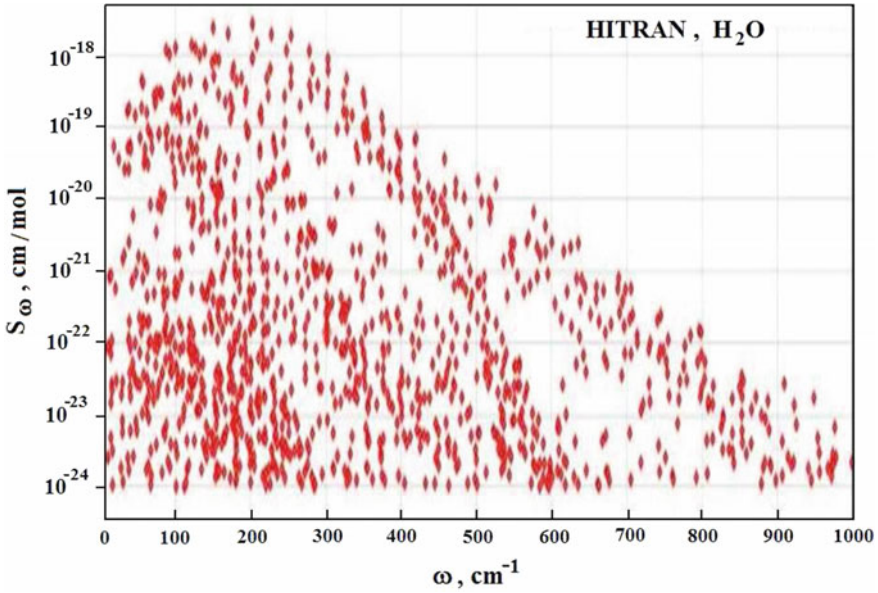
$$\frac{\Delta J_{\downarrow}(\text{H}_2\text{O})}{dc(\text{H}_2\text{O})} \approx 47 \text{ W/m}^2 \quad (7.2.16)$$

## 7.2.2 Water as Atmospheric Radiator

As we indicate above, basic atmospheric radiators are atmospheric carbon dioxide and water. From the above evaluations based on spectroscopic parameters of  $\text{CO}_2$  molecules it follows that carbon dioxide creates approximately 20% of the radiative flux in the infrared spectrum range that falls on the Earth. Hence atmospheric water in the form of  $\text{H}_2\text{O}$  molecules and water microdrops is responsible for approximately 80% of the radiative flux which is absorbed by the Earth in the infrared spectrum range.

Atmospheric water includes water molecules and water microdrops including those of clouds. One can evaluate the radiative flux due to atmospheric water molecules in the same matter as we done above in the case of  $\text{CO}_2$  molecules on the basis of spectroscopic parameters these molecules taken from the HITRAN data bank. But because of the complex character of the spectroscopy of water molecules, the visualization will be lost in this way; since our goal is to represent the physical picture of the greenhouse phenomenon and to show the role of spectroscopy in creation of this phenomenon, we use a more rough method for estimation of the role of water molecules.

In this consideration we return to the concept which is presented in Fig. 7.1. In spite of a low accuracy of spectra of this Figure compared to contemporary data, it demonstrates an important concept. Namely, molecules are optically active in a certain spectral range; continuous radiators, as water aerosols, are necessary to cover other spectral range. Basing of this concept, we divide the infrared spectrum which provides the atmospheric greenhouse effect in parts related to certain molecules; the rest spectrum part is covered by aerosols. Roughly, the absorption band due to carbon



**Fig. 7.11** Spectral intensity of atmospheric water molecules according to the HITRAN data bank at the temperature  $T = 296$  K [76]

dioxide molecules is restricted by the spectral range (7.2.2), and we below estimate boundaries of the absorption band for atmospheric water molecules..

Let us assume that the boundary frequencies of the absorption band for water molecules is created at altitudes  $h \sim 2$  km, as it takes place for CO<sub>2</sub> molecules. According to formula (2.2.38) this corresponds to the absorption coefficient  $k_\omega \sim 3 \cdot 10^{-6} \text{ cm}^{-1}$ . In order to reduce this estimation to data of Fig. 7.11, we express the absorption coefficient  $k_\omega$  averaged over oscillations through the spectral intensity  $S_\omega$  according to formula (4.2.16)

$$k_\omega = N(\text{H}_2\text{O})S_\omega\lambda_d,$$

where  $N(\text{H}_2\text{O}) \sim 10^{17} \text{ cm}^{-3}$  is the number density of water molecules; taking an average energy difference  $d \sim 0.1 \text{ cm}^{-1}$  for neighboring levels which is comparable with the line width, one can obtain  $\lambda_d \sim 10 \text{ cm}$  for the wavelength of photons which determine the radiative flux emitted by the atmosphere due to H<sub>2</sub>O molecules. Though the used formula (4.2.16) relates to molecules with a regular spectrum structure, it may be taken as an estimation.

From this one can obtain for boundary values of the spectral intensity  $S_\omega^* \sim 3 \cdot 10^{-24} \text{ cm/mol}$ . In addition it would be required the difference of energies for neighboring resonances  $d$  must be less than  $\nu \sim 0.1 \text{ cm}$ . If this relation is not fulfilled, a dip occurs in a dependence  $k_\omega$  between neighboring energy levels, and the absorption at indicated frequencies takes place if

$$S_\omega > \frac{\nu^2}{d^2} S_\omega^* \quad (7.2.17)$$

These estimations allows one to analyze the character of absorption of atmospheric water molecules on the basis of the HITRAN bank data given in Fig. 7.11. Roughly, the absorption band of water molecules is located from small frequencies up to absorption band of CO<sub>2</sub> molecules. The latter means that removing of carbon dioxide from the Earth's atmosphere conserves absorption inside its absorption band due to water molecules. At larger frequencies  $\omega > 800 \text{ cm}^{-1}$  absorption takes place only in narrow ranges due to some spectral lines.

Note that in contrast to atmospheric carbon dioxide, we are restricted by a rough consideration of atmospheric water because a real water amount in the atmosphere varies in wide ranges, whereas the concentration of atmospheric CO<sub>2</sub> molecules is more or less close to its average value because of a large residence time of these molecules in the atmosphere (approximately about of 4 years). For this reason, in analyzing the role of atmospheric water in the greenhouse effect we are based on the energetic balance of the Earth and its atmosphere.

Let us analyze the character of the atmospheric emission directed toward the Earth. We assume on the basis of Fig. 7.11 that atmospheric water molecules provides emission of the atmosphere at frequencies below  $800 \text{ cm}^{-1}$ . This range includes also the absorption band due to CO<sub>2</sub> molecules according to (7.2.2), i.e. the absorption bands due to atmospheric carbon dioxide and atmospheric water molecules are overlapped. Next, one can take the radiative temperature for atmospheric emission toward the Earth to be equal to the temperature of the Earth's surface, as we obtain above inside the absorption band due to CO<sub>2</sub> molecules. This gives the radiative flux toward the Earth  $J_\downarrow(\omega < 800 \text{ cm}^{-1}) = 233 \text{ W/m}^2$ , so that according to Fig. 7.2 data the total flux is  $J_\downarrow = 327 \text{ W/m}^2$ ; the other part of the flux is  $J_\downarrow(\omega > 800 \text{ cm}^{-1}) = 94 \text{ W/m}^2$ . Evidently, the latter is created by water microdrops since absorption by CO<sub>2</sub> and H<sub>2</sub>O molecules in this spectral range is weak. Accounting for also the radiative flux (7.2.9) that is determined by atmospheric carbon dioxide, one can obtain that the atmospheric radiative flux toward the Earth is created roughly in 20% by CO<sub>2</sub> molecules, in 50% by water molecules, and in 30% by water microdrops.

Water microdrops are of importance for atmospheric emission along with atmospheric water molecules and CO<sub>2</sub> molecules, in spite of a small amount of atmospheric water mass in the form of microdrops compared with that in the form of molecules. Because of a high optical thickness of the atmosphere at frequencies inside the absorption bands due to water and carbon dioxide molecules, the outgoing atmospheric radiation emitted by the Earth surface, is located in the spectrum range  $\omega > 800 \text{ cm}^{-1}$ . It is approximately  $J_p = 20 \text{ W/m}^2$  according to data of Fig. 7.2 or 5% of total emitted power from the Earth's surface.

Let us estimate the radiative temperature  $T_\omega$  and an effective altitude  $h_\omega$  for emission of aerosols in the range  $\omega > 800 \text{ cm}^{-1}$ . Above we found the radiative flux in this frequency range to be  $J_\downarrow(\omega > 800 \text{ cm}^{-1}) = 94 \text{ W/m}^2$ ; according to the Planck formula this corresponds to the radiative temperature  $T_\omega = 265 \text{ K}$ , that is realized at

the altitude  $h_\omega = 3.6$  km. The optical thickness  $u$  of the atmosphere in the spectral range where absorbers are water microdrops in accordance with the character of radiation propagation, follows from the equation

$$J_p = J'_E \int_0^\infty f(u) du \int_0^1 \exp\left(-\frac{u}{\cos\theta}\right) d \cos\theta, \quad (7.2.18)$$

where  $J'_E$  is the radiative flux from the Earth in this spectral range,  $f(u)$  is the distribution function over optical thicknesses,  $\theta$  is the angle between the normal to the Earth's surface and direction of photon motion. As a blackbody, the Earth emits the radiative flux  $J = 153 \text{ W/m}^2$  at frequencies above  $800 \text{ cm}^{-1}$ . Evidently, the flux  $J_t = 20 \text{ W/m}^2$  passes through the atmosphere in this spectral range, and the probability for a photon to pass through the atmosphere in the indicated spectral range is  $P = 0.13$ . On the other hand, taking for simplicity the distribution function in formula (6.3.2) as  $f(u) = \exp(-u/u_o)$ , we take for the probability of surviving of an emitted photon by the Earth

$$P = \int_0^1 \frac{\cos\theta}{u_o + \cos\theta} d \cos\theta = 0.13$$

Solution of this equation gives  $u_o = 3.2$ , i.e. microdrops form clouds with a large average optical thickness. It is clear that in reality the optical thickness of the atmosphere varies in time.

In addition, one can estimate the amount of the atmospheric water in microdrops, being guided by experiment [77]. According to this experiment, the average absorption cross section  $\sigma_{\text{abs}}$  of infrared radiation at the wavelength  $\lambda = (10 - 12) \mu\text{m}$  by water microdrops is  $\sigma_{\text{abs}} = (1.5 - 2.1) \cdot 10^{-6} \text{ cm}^2$ . The cross section of a typical microdrop which radius is  $r_o = 8 \mu\text{m}$  is  $\sigma = \pi r_o^2 = 2.0 \cdot 10^{-6} \text{ cm}^2$  corresponds to the measured value. On the other hand, the absorption cross section for a ball of a radius  $r_o$  with blackbody properties of its surface is given by [78]

$$\sigma_{\text{abs}} = \frac{\pi r_o^3}{r_o + C\lambda},$$

where  $\lambda$  is the wavelength, and the numerical coefficient  $C \sim 1$ . Let us denote the drop number density in clouds as  $N$ , and the average thickness of the layer as  $L$ . Then the optical thickness of this layer is

$$u = NL\sigma_{\text{abs}}$$

On the other hand, the water mass in microdrops per unit area of the Earth's surface under these conditions is

$$M = \frac{4}{3}\pi r_o^3 \rho N L,$$

where  $\rho = 1 \text{ g/cm}^3$  is the density of liquid water. From this we have

$$M = \frac{4\pi r_o^3}{3\sigma_{\text{abs}}}\rho u = \frac{4(r_o + C\lambda)}{3}\rho u \quad (7.2.19)$$

Under these conditions we obtain  $M \sim 10^{-2} \text{ g/cm}^2$ , i.e. of the order of 0.3% of the atmospheric water mass is contained in microdrops, i.e. this atmospheric water is found in clouds.

Basing on the observed data for evolution of global atmospheric parameters and the above spectroscopic analysis of the atmospheric greenhouse phenomenon, we below consider evolution of the global temperature as a result of an increase of the amount of atmospheric water and carbon dioxide separately. Let us represent the change of the global temperature  $T_g$ , if it is determined by variation of the concentrations  $c(\text{CO}_2)$  of atmospheric  $\text{CO}_2$  molecules and that  $c(\text{H}_2\text{O})$  of water molecules, in the form

$$dT_g = a \frac{dc(\text{CO}_2)}{c(\text{CO}_2)} + b \frac{dc(\text{H}_2\text{O})}{c(\text{H}_2\text{O})}, \quad (7.2.20)$$

where  $a = 0.7 \text{ K}$  according to (7.1.18). In order to determine the parameter  $b$ , we assume that the change (7.2.20) of the global temperature in a real atmosphere as a result of doubling of the concentration of  $\text{CO}_2$  molecules is determined by atmospheric carbon dioxide and water, and formula (7.1.18) gives that for  $\text{CO}_2$  molecules. In addition, we have that doubling of the concentration of  $\text{CO}_2$  molecules is caused by an increase of the radiative flux  $\Delta J = 1 \text{ W/m}^2$  due to these molecules and  $\Delta J_{\downarrow} = 4 \text{ W/m}^2$  due to other atmospheric radiators assuming those to be water molecules.

We above determine the average absorption coefficient  $\kappa_{\omega} = 0.33 \text{ km}^{-1}$  for the contemporary concentration of  $\text{CO}_2$  molecules from equation  $J_{\downarrow} = 327 \text{ W/m}^2$ . Correspondingly, doubling of the carbon dioxide concentration leads to equation  $J_{\downarrow} = 332 \text{ W/m}^2$  that gives  $\kappa_{\omega} = 0.35 \text{ km}^{-1}$ . Since the global temperature change due to atmospheric radiators other than  $\text{CO}_2$  molecules, is  $1.6 \text{ K}$  according to formulas (7.2.27) and (7.2.29), one can obtain from this that  $b = 25 \text{ K}$ . As it is seen,  $b \gg a$ , because on the one hand, the concentration of water molecules near the Earth surface is 40 times more than that of carbon dioxide molecules, and, on the other hand, a water molecule due to its dipole moment has a higher optical activity compared to the  $\text{CO}_2$  molecule. Note also that the correlation between evolution of the  $\text{CO}_2$  concentration and global temperature was used in this operation that exists only last 40 years.

In considering emission of atmospheric water in IR spectral range, we were based on simple models and measurements related to atmospheric water. One can expect a more fruitful method is to evaluate the absorption coefficient of atmospheric water on the basis of high-resolved spectroscopy of water molecules [79] in the same manner



as it is made for atmospheric carbon dioxide. But it is not reliable because of strong fluctuations in the concentration of water molecules and an important contribution of water microdrops which in spite a relatively small mass close the windows of transparency of water and carbon dioxide atmospheric molecules. Additional data for atmospheric carbon dioxide and water allow one to increase the reliability of parameters described the greenhouse atmospheric phenomenon.

In conclusion of the analysis of the greenhouse phenomenon in the Earth's atmosphere we note that atmospheric  $\text{CO}_2$  molecules give the contribution of approximately 20% both in the radiative flux of infrared radiation toward the Earth and the change of the global temperature due to growth of the amount of atmospheric carbon dioxide. The other part of these values relate to atmospheric water in the form of  $\text{H}_2\text{O}$  molecules and water microdrops. We determine the contribution from atmospheric carbon dioxide on the basis of the spectroscopy analysis because of a large residence time of  $\text{CO}_2$  molecules in the atmosphere that is approximately 4 years. The amount of atmospheric water varies in irregular manner depending on time and geographic point. Therefore we are based on the energetic balance of the Earth's atmosphere that is reliable. As a result, we obtain roughly that the contribution to the greenhouse effect due to  $\text{CO}_2$  molecules is 20%, due to water molecules is 50% and due to water microdrops is approximately 30%.

### 7.2.3 *Climate Sensitivity*

We above have determined the variation of the radiative flux toward the Earth due to a change of the concentration of atmospheric  $\text{CO}_2$  molecules. This causes a change of the Earth's temperature, and our task is to determine the connection between these values. The characteristic of this change is according to Arrenius [47] so called the equilibrium climate sensitivity [48] which is the change of the global temperature at doubling of the atmospheric concentration of  $\text{CO}_2$  molecules. But this problem may be formulated in a general form, as the global temperature change as a result of variation of the radiative flux  $\Delta J_{\downarrow}$  toward the Earth/s surface. Let us define the climate sensitivity [16, 80]  $S$  as the ratio of the global temperature variation  $\Delta T$  to the change  $\Delta J_{\downarrow}$  of the radiative flux toward the Earth, and this change causes the change of the global temperature  $\Delta T$ . We have

$$S = \frac{\Delta T}{\Delta J_{\downarrow}} \quad (7.2.21)$$

It is convenient to operate with a reciprocal value  $F = 1/S$ , which is called the radiative forcing, since the total radiative forcing is the sum of partial ones. In this consideration we assume the interaction of solar radiation with the atmosphere and Earth is not varied at a small Earth temperature change. This also takes into account that optical parameters of the atmosphere in the visible spectral range are not varied if these parameters in the infrared spectral range vary slightly, including the con-

servation of the Earth albedo. In this consideration, we are based on the standard atmosphere model, so that the Earth's temperature is  $T_E = 288\text{ K}$ , the temperature gradient  $dT/dh = -6.5\text{ K/km}$  is constant up to the tropopause at  $h_o = 11\text{ km}$ , where the atmospheric temperature equals  $T_{\min} = 217\text{ K}$ , and the temperature difference between the Earth and tropopause is  $\delta T = T_e - T_{\min} = 61\text{ K}$ . Let the temperature change at the Earth be  $\Delta T$ , 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.

One can obtain the temperature  $T_h$  at a given altitude  $h$  and its change  $\Delta T_h$  under given conditions

$$T_h = T_E \left( 1 - \frac{\delta h}{h_o} \right), \quad \Delta T_h = \Delta T \left( 1 - \frac{h}{h_o} \right) \quad (7.2.22)$$

Correspondingly, a change  $\Delta J_h$  of the radiative flux, if it is created at the altitude  $h$ , is

$$\Delta J_h = 4\sigma T_h^3 \Delta T_h = \frac{4J_h \Delta T_h}{T_h}, \quad (7.2.23)$$

where  $\sigma$  is the Stephan-Boltzmann constant. In determination of the convection flux change  $\Delta J_c$ , we assume the energy flux due to convection to be proportional to the temperature gradient, that gives

$$\Delta J_c = J_c \frac{\Delta T}{\delta T} \quad (7.2.24)$$

We use these relations below in determination the

The radiative flux from the Earth's surface  $J_E = 386\text{ W/m}^2$  is compensated partially by atmospheric emission through carbon dioxide and water molecules which equals approximately  $\Delta J_E = 216\text{ W/m}^2$  in the range  $\omega < 800\text{ cm}^{-1}$ . Assuming the radiative temperature for emission of atmospheric molecules to be equal to the Earth's temperature, one can find the radiative forcing  $F_E$  due to emission of the Earth and atmospheric molecules

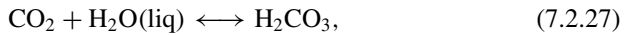
$$F_E = \frac{4\Delta J_E}{T_E} = 2.4\text{ W}/(\text{m}^2\text{ K}) \quad (7.2.25)$$

In accordance with the energetic balance of the Earth given in Fig. 7.2, we take the average energy flux due to water evaporation from Earth's surface to be  $J_{\text{ev}} = 57\text{ W/m}^2$  and due to atmospheric convection  $J_c = 47\text{ W/m}^2$ . The temperature dependence of the flux due to water evaporation is  $\sim \exp(-\Delta\varepsilon/T)$ , where  $\Delta\varepsilon = 0.43\text{ eV}$  is the binding of the water molecule for the liquid phase. The flux change  $\Delta J_c$  due to convection we assume to be proportional to the temperature change. As a result, we obtain for the change of the energy flux for these channels as

$$\Delta J_{\text{ev}} = J_{\text{ev}} \frac{\Delta \varepsilon \Delta T}{T_E^2}, \quad \Delta J_c = \frac{\Delta T}{T_E} J_c, \quad (7.2.26)$$

and these channels give  $F_{\text{ev}} = 3.4 \text{ W}/(\text{m}^2 \text{ K})$ ,  $F_c = 0.16 \text{ W}/(\text{m}^2 \text{ K})$ ,  $F_{\text{ev}} + F_c = 3.6 \text{ W}/(\text{m}^2 \text{ K})$ .

We determine also the feedback which takes into account the connection between an increase of the global temperature  $\Delta T$  and the concentration of optically active components. Let us use the Pauling concept [81, 82] according to which an increase of the carbon dioxide concentration in the atmosphere results from an increase of the global temperature, but not vice versa, as it is assumed in the standard consideration. In this case an atmospheric amount of carbon dioxide follows from equilibrium with ocean carbon dioxide which is dissolved in oceans and is located there in the form of  $\text{HCO}_3^-$  and other compounds. This equilibrium proceeds through the formation of



that means an equilibrium between free atmospheric  $\text{CO}_2$  molecules and bound ones in an indicated compound with liquid water, where the enthalpy of this transition is  $\Delta H = 178 \text{ kJ/mol}$  or  $1.8 \text{ eV}$  [83]. Because an amount of atmospheric carbon dioxide is less compared with bound carbon dioxide in this chemical compound, the concentration  $c(\text{CO}_2)$  depends on the temperature as

$$c(\text{CO}_2) \sim \exp\left(-\frac{\Delta H}{T}\right), \quad (7.2.28)$$

that leads to the following relation of a concentration change for atmospheric carbon dioxide and a temperature change  $\Delta T$  of the Earth's surface

$$\frac{\Delta \ln c(\text{CO}_2)}{d\Delta T} = \frac{\Delta H}{T^2} = 0.26 \text{ K}^{-1} \quad (7.2.29)$$

This gives for the radiative forcing  $F_f(\text{CO}_2) = 0.4 \text{ W}/(\text{m}^2 \text{ K})$  due to the feedback between the change of the atmospheric concentration of carbon dioxide and the temperature change  $\Delta T$  if we use formula (2.2.15).

By analogy with formula (7.2.22), we have for concentration of atmospheric water molecules

$$c(\text{H}_2\text{O}) \sim \exp\left(-\frac{\Delta \varepsilon_b}{T}\right), \quad (7.2.30)$$

where  $\varepsilon_b \approx 0.43 \text{ eV}$  is the binding energy of the water molecule on the surface of liquid water. This gives by analogy with formula (7.2.23)

$$\frac{d \ln c(\text{H}_2\text{O})}{d\Delta T} = \frac{\varepsilon_b}{T^2} = 0.06 \text{ K}^{-1} \quad (7.2.31)$$

From this on the basis of formula (2.2.15) we have

$$F_f(\text{H}_2\text{O}) = \frac{\Delta J_{\downarrow}(\text{H}_2\text{O})}{d \ln c} \frac{\Delta c(\text{H}_2\text{O})}{d\Delta T} = 2.8 \text{ W}/(\text{m}^2 \text{ K}), \quad F_f = F_f(\text{H}_2\text{O}) + F_f(\text{CO}_2) = 3.2 \text{ W}/(\text{m}^2 \text{ K}) \quad (7.2.32)$$

Because the radiative forcing due to an increase of the atmospheric concentration of water molecules due to an increase of the global temperature, we assume for simplicity, that the the radiative forcing as a result of the feedback due to the change of the atmospheric concentrations of carbon dioxide and water molecules to be equal. This gives for the radiative forcing due to this feedback  $F_f = 0.3 \text{ W}/(\text{m}^2 \text{ K})$ .

Summarizing the above values, one can obtain the total radiative forcing

$$F_t = F_E + F_{\text{ev}} + F_c - F_f \approx 2.8 \text{ W}/(\text{m}^2 \text{ K}), \quad S \approx 0.36 \text{ m}^2 \text{ K}/\text{W} \quad (7.2.33)$$

Note a low accuracy of the climate sensitivity since the radiative forcing is the difference of large values. The error increases also because atmospheric water molecules and water microdrops are not separated in this evaluation. In addition, according to evaluations [74] this value equals to  $S = 0.42 \text{ m}^2 \text{ K}/\text{W}$ .

It follows for the change of the global temperature as a result at doubling of the concentration of atmospheric  $\text{CO}_2$  molecules.

$$\Delta T = (0.4 \pm 0.2) \text{ K}, \quad (7.2.34)$$

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  $\text{CO}_2$  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

$$\Delta T = 0.02 \text{ K}, \quad (7.2.35)$$

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  $\text{CO}_2$  from the atmosphere causes a decrease of the radiative flux toward the Earth by approximately  $9 \text{ W}/\text{m}^2$ . This corresponds to a decrease of the global temperature by approximately 4 K.

The value (7.2.27) 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 [32, 33] and the monitoring of atmospheric carbon dioxide [43, 46]. This is given by formula (7.1.11)

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

so that atmospheric carbon dioxide provides approximately 20% both the radiative flux toward the Earth and its change resulted from the change of the concentration of CO<sub>2</sub> molecules. The ECS which follows from treatment of data over past 65 million years is [80, 84, 85]

$$\Delta T = (3.5 \pm 1.3) \text{ K}, \quad (7.2.36)$$

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

For determination of the absorption coefficient (7.1.15), the spectroscopy information about these molecules is required, and it is the content of the data bank [86] that may be used for such evaluations. In the case of CO<sub>2</sub> molecules an additional simplification of a simple structure of this molecule allows one to use the regular or Elsasser model [87] for its vibrational-rotational spectrum with spectroscopy parameters according to [88]. As a result, this allows one to determine ECS under conditions, that the concentrations of all the atmospheric radiators except CO<sub>2</sub> molecules are constant at doubling of the concentration of carbon dioxide molecules. As a result, under these conditions, the change of the global temperature within the framework of the absorption band and line-by line models is equal [19, 29, 74]

$$\text{ECS} = (0.4 \pm 0.1) \text{ K} \quad (7.2.37)$$

Comparing formula (7.2.37) with (7.1.11), one can conclude that approximately 20% of the change of the global temperature for a real atmosphere gives carbon dioxide, and then the contribution to the global temperature change from combustion of fossil fuels is approximately 1%.

In this consideration, we account for the total radiative flux toward the Earth equals  $J_{\downarrow} = 327 \text{ W/m}^2$  according to (7.1.12). Considering this as equation for the absorption coefficient of other atmospheric radiators than atmospheric carbon dioxide, one can obtain for the contemporary concentration of atmospheric CO<sub>2</sub> molecules  $\kappa_{\omega} = 0.33 \text{ km}^{-1}$ . This corresponds to the altitude  $h_{\downarrow} = 2 \text{ km}$  of a layer which is responsible for atmospheric emission, and its temperature  $T_{\downarrow} = 275 \text{ K}$  is the radiative temperature in spectral ranges outside absorption of CO<sub>2</sub> molecules. An indicated temperature differs slightly from (7.1.4) where the absorption coefficient for atmospheric carbon dioxide is averaged over frequencies. At the doubled concentration of CO<sub>2</sub> molecules this equation gives  $\kappa_{\omega} = 0.35 \text{ km}^{-1}$ .

According to the above mentioned NASA investigations, the concentration of atmospheric CO<sub>2</sub> molecules increases in time from 0.028% at the preindustrial period which finishes in 19th century, up to 0.041% now. The amount of atmospheric carbon dioxide results from the equilibrium between atmospheric and surface carbon [38–41] and consists mostly of the transition between atmospheric carbon dioxide and solid carbon in composition of plants. The carbon transition from the atmosphere to the Earth's surface proceeds in the photosynthesis process, whereas the opposite tran-

sition results from breathing and degradation of plants, as well as from combustion of fossil fuels. Roughly, the Earth atmosphere includes 800 billion tons of carbon in atmospheric carbon dioxide, and the residence time of an individual  $\text{CO}_2$  molecule in the atmosphere is approximately 4 years, i.e. an exchange between atmospheric and surface carbon is approximately  $2 \cdot 10^8$  ton/yr. The total carbon amount in coal, oil and methane which is extracted from the Earth's interior annually, is approximately 10 billion tons, i.e. the human activity gives the contribution of 5% to the carbon circulation. Hence, the contribution of the man activity in the equilibrium climate sensitivity (7.2.37) is

$$\Delta T = 0.02 \text{ K} \quad (7.2.38)$$

But a small contribution of injections of carbon dioxide in the atmosphere as a result of the combustion process does not mean that the influence of the man activity on global atmospheric parameters is absent practically at the contemporary level of the human activity. Indeed, from the preindustrial period up to now the concentration of atmospheric  $\text{CO}_2$  molecules increases by (40–50)%. This results from deforestation under the human activity. One can conclude from this analysis that contemporary using of fossil fuels which finally are injected in the atmosphere in the form of carbon dioxide and hence influence on the atmospheric spectroscopic properties; it gives the contribution to the global temperature change of approximately 1%.

### 7.2.4 Energy Balance of Venus and Its Atmosphere

We also apply the results of emission of a gas layer contained  $\text{CO}_2$  molecules for the analysis of the energetic balance of the Venus and its atmosphere. Figure 4.10 gives the frequency dependence of the Venus atmosphere near its surface due to atmospheric  $\text{CO}_2$  molecules, and below we use this to construct the energetic balance of the Venus and its atmosphere. Let us represent first parameters of the Venus atmosphere. The Venus atmosphere consists of carbon dioxide (96.5%) and nitrogen (3.5%) [89]. On the basis of this, for simplicity, we shall further assume that carbon dioxide is the only component of the Venusian atmosphere. The gas pressure at the surface of Venus is 92 atm, the temperature is 735 K [89, 90]. The temperature gradient is about  $-8 \text{ K/km}$  in the altitude range from 0 to 60 km and then decreases monotonically, as the altitude increases, to almost zero at an altitude of 100 km [90]. On the basis of measurements [90], the scale of the change in the number density of carbon dioxide molecules  $\Lambda$  in the Venus atmosphere, which is introduced on the basis of formula (7.1.2), varies from  $\Lambda = 19 \text{ km}$  at the surface Venus up to about 6 km at an altitude of 60 km, and 4 km at an altitude of 100 km. The number density of carbon dioxide molecules at the Venus surface is  $N = 9.2 \cdot 10^{20} \text{ cm}^{-3}$ , and also  $N = 6.6 \cdot 10^{18} \text{ cm}^{-3}$  and  $N = 1.2 \cdot 10^{15} \text{ cm}^{-3}$  at altitudes of 60 km and 100 km respectively.

Our task is to determine the contribution of carbon dioxide, located in the Venus atmosphere, the greenhouse effect. Indeed, the average flux of solar radiation per unit surface area of Venus is  $(2622 \pm 6) \text{ W/cm}^2$  [91] (for the Earth's surface this value is  $1365 \text{ W/cm}^2$ ). For the observed surface temperature  $735 \text{ K}$ , the flux of infrared radiation under these conditions is  $J_V = 1.7 \text{ W/cm}^2$ , i.e. heat fluxes are increased at approach to the planet surface. If the Venus absorbs all the solar radiation incident on it and then radiates as a black body, then its surface temperature will be  $463 \text{ K}$ .

In reality, most of the radiation penetrating into the Venus atmosphere is reflected, and the absorbed energy is consumed partially for creation of convective gas flow, while its main part is spent on atmosphere radiation. The Venus albedo is of  $0.80 \pm 0.02$  according to [92] and  $0.76 \pm 0.01$  according to [91]. As a result, the average radiative flux from the Venus atmosphere is  $(157 \pm 6) \text{ W/m}^2$  [93]. This corresponds to an average radiation temperature of about  $230 \text{ K}$ , which agrees with measurements [94, 95]. This temperature is realized at an altitude of  $70 \text{ km}$ , where the carbon dioxide pressure is  $28 \text{ Torr}$ .

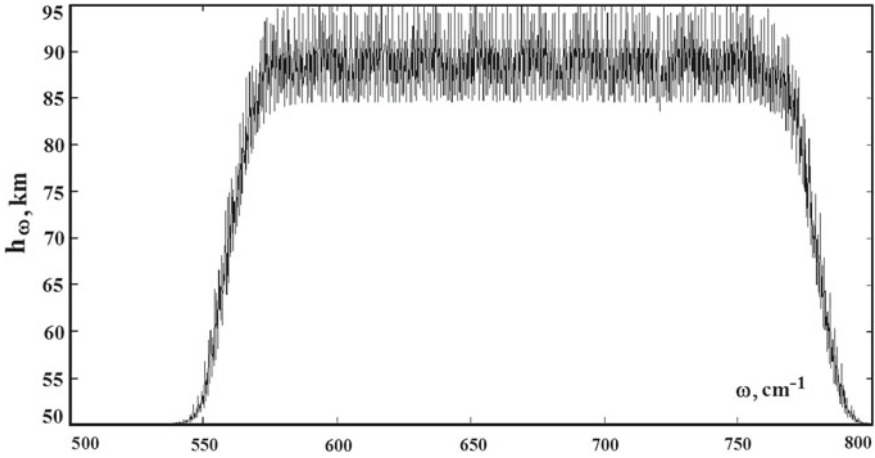
The analysis of the Venus energetic balance is beyond this work. Our task is to determine the role of carbon dioxide emission in the heat balance of the Venus. We will assume that the Venus atmosphere consists entirely of carbon dioxide and determine the radiative temperature in the spectrum range where carbon dioxide molecules emit. In the subsequent analysis, we use the representations of molecular spectroscopy (for example, [96–101]). Moreover, the  $\text{CO}_2$  molecule is a linear symmetric molecule, that simplifies the analysis of its oscillations.

We use formula (7.1.20) to find the radiative temperature  $T(\omega)$  of radiation leaving the Venus atmosphere in the range of the absorption spectrum of carbon dioxide molecules. Let us introduce the absorption band by molecules of carbon dioxide such, that the boundary frequencies for this band  $\omega_{1b}$  and  $\omega_{2b}$  in accordance with formula (7.1.22) are given by relations

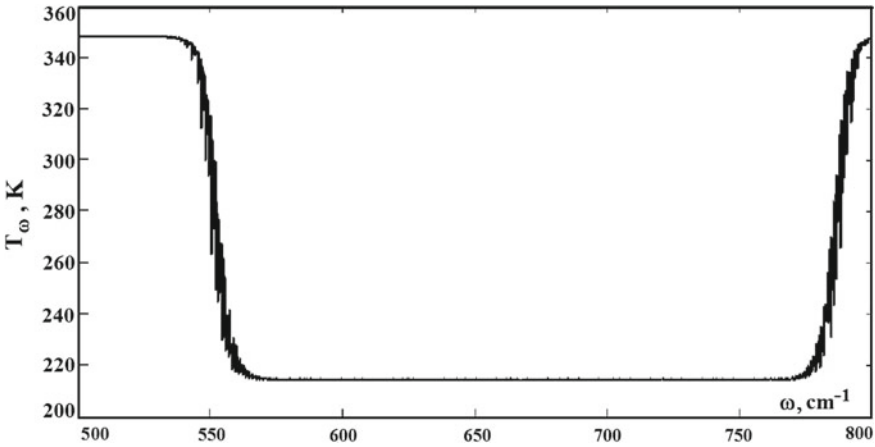
$$k_\omega(\omega_{1b})\Lambda = k_\omega(\omega_{2b})\Lambda = \frac{2}{3}, \quad (7.2.39)$$

where the scale for the change of the number density of radiating molecules is determined by formula (7.1.2).

If the width of the absorption band is determined by wings of spectral lines for individual vibrational-rotational transitions, it is convenient to average the absorption coefficient (4.2.25) for  $P$  and  $R$  branches over oscillations within one period, i.e. over the frequency range for transitions between neighboring rotational momenta. Next, on the basis of formula (7.1.20), we determine the altitude of an atmosphere layer  $h_\omega$  which is responsible for emission of photons at a given frequency, and the radiation temperature at a given frequency coincides with the temperature of this layer. Figure 7.12 contains the frequency dependence for this altitude. Correspondingly, the radiation temperature  $T(\omega)$  of photons, which are produced by emission of carbon dioxide molecules, is given in an indicated range of photon frequencies in Fig. 7.13 in accordance with formula (7.1.20).



**Fig. 7.12** Effective altitude of the Venus atmosphere which is responsible for creation of the radiative flux at a given frequency [102]



**Fig. 7.13** Effective temperature of the Venus atmosphere which is responsible for creation of the radiative flux due to emission of atmospheric  $\text{CO}_2$  molecules as a frequency function [102]

Let us determine the total outgoing radiation flux from the Venus atmosphere on the basis of formula (7.2.39) assuming that the radiative temperature for a part of the spectrum, which is not connected with carbon dioxide, is independent of the frequency. We have for the energy flux of radiation

$$J_\downarrow = \int_0^{\omega_1} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2 \left[ \exp\left(\frac{\hbar\omega}{T_o}\right) - 1 \right]} + \int_{\omega_1}^{\omega_2} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2 \left[ \exp\left(\frac{\hbar\omega}{T(\omega)}\right) - 1 \right]} + \int_{\omega_2}^{\infty} \frac{\hbar\omega^3 d\omega}{4\pi^2 c^2 \left[ \exp\left(\frac{\hbar\omega}{T_o}\right) - 1 \right]}, \tag{7.2.40}$$



and according to the measurements [93] this flux is  $J = (157 \pm 6) \text{ W/m}^2$ . Solving this equation, we find  $T_o = (249 \pm 3) \text{ K}$ , which corresponds to altitudes of 63–64 km. Note that clouds of the Venusian atmosphere, consisting of droplets of sulfuric acid, are concentrated in the altitude range of 60–70 km. Perhaps, these clouds are responsible for emission of thermal radiation in the range of the spectrum, not connected with molecules of carbon dioxide. We also note that at an altitude of 60 km the atmosphere temperature is 263 K, and the temperature gradient is  $dT/dh = 4 \text{ K/km}$ , and the scale of the change in the number density of  $\text{CO}_2$  molecules is  $\Lambda = 6 \text{ km}$ . This gives a small parameter (7.1.18)  $\alpha = 0.05$ , which characterizes the validity of the assumptions used.

Let us give the parameters of Venus related to the problem under consideration. The atmosphere of Venus consists of carbon dioxide (96.5%) and nitrogen (3.5%) [89]. For simplicity, we assume carbon dioxide to be the only component of the Venus atmosphere. The gas pressure at the Venus surface is 92 atm, the temperature is 737 K [89, 90], that corresponds to the number density of molecules of carbon dioxide near the Venus surface  $N = 9.2 \cdot 10^{20} \text{ cm}^{-3}$ . The temperature gradient is about  $-8 \text{ K/km}$  in the altitude range from 0 to 60 km [90], and the scale of the change in the density of carbon dioxide molecules  $\Lambda$  in the Venus atmosphere, which is introduced on the basis of formula  $\Lambda = d \ln N / d(1/h)$ , where  $N$  is the number density of molecules in the atmosphere,  $h$  is the altitude above the Venus surface, and  $\Lambda = 19 \text{ km}$ .

In constructing the energy balance of the surface of Venus and its atmosphere, we will model the Venus surface as a blackbody for IR radiation. We have that an absolutely black body with a temperature of 737 K creates an IR radiative flux  $J_o = 16.7 \text{ kW/m}^2$ . On the other hand, the average flux of solar radiation per unit surface area of Venus  $2.6 \text{ kW/m}^2$  [91]. The Venus albedo is  $0.80 \pm 0.02$  according to [92] and  $0.76 \pm 0.01$  according to [91]; we take it to be 0.78. It follows that the average flux of solar radiation absorbed by the atmosphere and surface of Venus is  $0.5 \text{ kW/m}^2$ . An additional contribution to the power absorbed by the surface of Venus is due to IR radiation produced by the molecules of carbon dioxide. To determine the radiative flux to the Venus surface, which contributes to the Venus energy balance, it is necessary to analyze the emission spectrum of carbon dioxide molecules in the infrared spectral range, which is presented in Fig. 4.3, so that the frequency dependence for the absorption coefficient is represented in Fig. 4.10.

The boundaries of absorption bands for the Venus atmosphere due to carbon dioxide molecules follow from the relation [13, 103]

$$k_\omega \Lambda = 2/3, \quad (7.2.41)$$

where  $\Lambda = 19 \text{ km}$  is the scale of the change in the number density of molecules of carbon dioxide in the Venus atmosphere near its surface in accordance with formula (7.1.2). On the basis of this formula, we have for the boundaries of the first two absorption bands  $\omega_1 = 493 \text{ cm}^{-1}$  and  $\omega_2 = 1174 \text{ cm}^{-1}$ , which gives IR radiative flux to the Venus surface  $J_1 = 3.5 \text{ kW/m}^2$ . The third absorption band, which is created by the resonant radiation of the carbon dioxide molecule between the lower excited antisymmetric state and the ground vibrational state, has the boundaries

$\omega_1 = 2258 \text{ cm}^{-1}$  and  $\omega_2 = 2439 \text{ cm}^{-1}$  that leads to IR radiative flux to the Venus surface  $J_3 = 0.9 \text{ kW/m}^2$ . From this one can obtain the total radiative flux to the Venus surface, which consists of the absorbed flux of solar radiation and IR radiation generated by carbon dioxide molecules in the Venus atmosphere is  $J = 4.9 \text{ kW/m}^2$ .

As it follows from the data presented, solar radiation absorbed by the Venus surface contributes 3% to the total energy flux absorbed by the Venus surface. In this case, the contribution of IR radiation of the Venus atmosphere absorbed by its surface is 26% from the total flux of radiation absorbed or emitted by the Venus surface. Note that in the case of the Earth's energy balance, the last channel gives 20% [16, 19, 75]. Thus, we arrive at a contradiction according to which the power of radiation absorbed by the surface of Venus, is small extent (about one-third) compared to the power of IR radiation from its surface at the observed temperature. In searching the cause of the discrepancy between the indicated powers, we first analyze the accuracy of finding the above powers. For this purpose, we use the absorption band model [19] for carbon dioxide molecules, according to which radiation at frequencies inside this band is created by carbon dioxide molecules, whereas outside the absorption band, carbon dioxide molecules do not contribute to atmospheric emission. This requires a sharp change of the absorption coefficient  $k_\omega$  near the boundary of the absorption band which is given in Fig. 4.9. The accuracy of calculation the above radiation powers within the framework of the model used is better than 20%; the error in calculations also includes the fact that the radiative temperature of the Venus atmosphere near boundaries of the absorption bands is determined by the layers of the Venus atmosphere whose temperature differs from the temperature of its surface.

Let us ascertain which additional channels in the Venus energy balance can remove the contradiction obtained. Above we did not take into account the convective heat transfer from the Venus surface, associated with the vortex movement of carbon dioxide near its surface under the influence of the atmospheric temperature gradient. In the case of the Earth, the convective energy flux is about 10% of the total flux of solar radiation entering the Earth's atmosphere [16, 19, 75]. It can be expected that the relative contribution of convective transport in the energy balance of Venus does not exceed this value due to a high gas pressure in the atmosphere of Venus. Thus, convective transport in the atmosphere of Venus does not eliminate the above contradiction, especially since the convective transfer only increases the missing energy flow to the Venus surface, which is necessary for the fulfillment of the Venus energy balance.

However, convective heat transfer in the Venus atmosphere causes the dust to move from the Venus surface to its atmosphere. In the case of micron-size dust particles, the action of gravity leads to their return to the Venus surface through years. The weighted dust is optically thick in the IR spectral range and even at a low dust concentration the IR radiative flux may be provided by dust particles. Note that in the case of the Earth's atmosphere, the role of dust does not be important, since atmospheric dust is washed out by atmospheric water for 8–9 days. At the same time, the energy balance of Venus and its atmosphere begins with absorption of solar radiation by the atmosphere [104], and then the absorbed energy is transferred to the Venus surface as a result of convection and radiative transfer. Here we do not consider

the radiative transfer from upper layers of the Venus atmosphere to its surface, but we solve a simpler problem.

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

$$u_\omega = k_\omega L = \sigma_\omega N L \sim 1, \quad (7.2.42)$$

where  $\sigma_\omega$  is the photon absorption cross section of a dust particle,  $N$  is the number density of particles in the atmosphere,  $L$  is the thickness of the atmosphere layer in which the dust is located. Assuming dust particles to be spherical, we assume a typical dust radius  $r$  to be small compared to the wavelength  $\lambda \sim 10 \mu\text{m}$ , which leads to the following estimate for the photon absorption cross section of the dust particle [78]

$$\sigma_\omega \sim \pi r^2 \cdot \frac{r}{\lambda} \sim \frac{V}{\lambda}, \quad (7.2.43)$$

where  $V$  is the average volume of dust particles. From this we obtain on the basis of formula (7.2.42)

$$\xi = V N L \sim \lambda u_\omega, \quad (7.2.44)$$

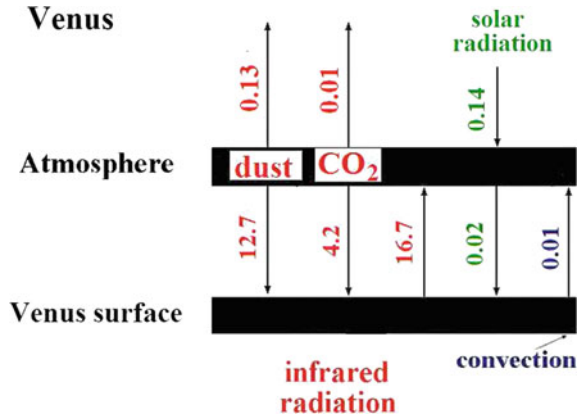
where  $\xi$  is a typical thickness of the dust layer, which ensures the absorption of infrared radiation of the planet, if atmospheric dust is collected near the Venus surface.

Comparing this amount of dust with the amount of carbon dioxide in the atmosphere of Venus, we obtain that the concentration of dust molecules is  $\sim 10^{-7}$  (the number of molecules of atmospheric dust to the number of molecules of carbon dioxide in the atmosphere) provides the effect under consideration when this dust consisting from solid particles of micron and submicron sizes, creates the IR radiative flux absorbed subsequently by the Venus surface. If this dust is collected at the Venus surface, it forms a layer of thickness of several tens of microns (several IR wavelengths). Note that the microscopic dust of the Venusian atmosphere is near its surface, in contrast to the clouds in the Venus atmosphere [95, 105, 106], which are located at an altitude of 60–70 km and provide IR radiation which goes outside this planet.

Let us note one more feature of the conducted research. The performed calculations use information about spectroscopic parameters of carbon dioxide molecules taken from the HITRAN data bank [79] and include data for several hundred vibrational-rotational transitions of the carbon dioxide molecule. At present, this bank has information pertaining to hundreds of thousands of transitions involving carbon dioxide molecules [79], i.e. a small part of existed information related to this problem is sufficient for the calculations of the above parameters.

As is seen, the disperse phase is the basic radiating component for outgoing radiation as well as for that directed to the Venus surface. In considering the radiative

**Fig. 7.14** Expressed in  $\text{kW/m}^2$  average energy fluxes of the Venus and its atmosphere [102]



flux toward the Venus surface, we assume that this radiation is created mostly by dust particles which arose in the atmosphere from the surface under the action of convective atmospheric motion. We considered sand particles as a more probable candidate for these particles which are a source of infrared radiation directed toward the Venus surface. In order to satisfy the energetic balance between the Venus surface and its atmosphere, it was required that the optical thickness due to sand particles corresponds to formula (4.1.17) for an atmospheric layer starting from the surface up to altitude  $h = 8$  km. From this one can find the total optical thickness of the Venus atmosphere due to sand particles as  $u = 1.8$  under the assumption that the concentration of sand particles is independent of the altitude up to high altitudes. Hence, the optical density of sand particles starting from the altitude  $h = 70$  km up to infinity is 0.002. Hence, sand particles cannot be responsible for outside radiation.

One can expect that radiators are aerosols which constitute clouds of the Venus atmosphere [95, 105, 106], are located at altitudes of 60–70 km and provide infrared outgoing radiation of this planet. The Venus is covered by a thick layer of clouds that extends between 55 and 70 km above the surface. These rapidly-moving clouds are mainly composed of micron-sized droplets of sulphuric acid and other aerosols. One can estimate a specific mass of aerosols  $\rho\xi$  which are responsible for emission of outgoing radiation of the Venus, where  $\rho$  is the mass density of aerosol material < and  $\xi$  is given by formula (7.2.44). One can find a specific mass  $m$  of these aerosols in analogy with that for dust particles created the radiation toward the Venus surface. Taking an identical mass density for dust particles near the Venus surface and aerosol particles in upper layers ( $\rho = 1.8 \text{ g/cm}^3$  for sulfur acid), one can obtain the same specific mass of particles  $M \approx 2 \text{ mg/cm}^2$  because of the identical optical thickness of comparable layers. The specific mass of carbon dioxide is  $50 \text{ g/cm}^2$  for the Venus atmosphere above 70 km, that gives for the aerosol mass concentration  $M/m \sim 4 \cdot 10^{-5}$ . As is seen, the mass concentration of aerosols which create the outgoing radiation of the Venus atmosphere is two orders of magnitude higher than that for dust particles which determine radiation toward the Venus surface.

Summarized the above data, one can construct the energetic balance of the Venus and its atmosphere which is presented in Fig. 7.14. Though the convection flux is included in this Figure, its value is less than the error for radiative fluxes, i.e. the contribution of the convection flux into the total one is negligible. Nevertheless, convection is of importance for Venus energetics because it lifts up dust particles from the Venus surface which provide its high temperature.

We above use the results for emission of carbon dioxide molecules in the infrared spectrum range for radiation of the Venus atmosphere, as a demonstration of the above methods for spectroscopy of molecules in gases. Note two peculiarities of this process. First, the temperature of the Venus surface is enough high, and the power of infrared radiation of the Venus atmosphere is two orders of magnitude larger than the power of solar radiation penetrated in the Venus atmosphere, but solar radiation is the basis of the energetic balance of the Venus. Second, under known parameters of the Venus atmosphere, one can evaluate precisely (with the accuracy better 20%) the power of emission due to atmospheric CO<sub>2</sub> molecules, and it is only one third from the power radiating by the Venus surface. This proves the presence of an atmospheric dust which amount is seven orders of magnitude less than the amount of atmospheric carbon dioxide, but this dust provides the atmosphere balance.

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