

Global warming by thermal absorption of CO₂

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Abstract

The present study describes the absorption of thermal radiation from the earth's surface by CO₂ in the atmosphere. For this purpose the absorption spectrum for the vibrational-rotational structure of the CO₂ molecule is described. Only the vibration bands around 15, 5, and 4.3-micron wavelengths are important for the absorption spectrum. The vibration band around 15-micron wavelength has by far the largest absorption and is located almost at the top of the emission curve at an average earth temperature of 294 K. The individual rotational absorption lines of both the P- and Q- branches are 50 GHz apart. Due to pressure broadening, they overlap. The absorption of radiation from the earth's surface is for the present concentration CO₂ saturated. Absorbed radiation is converted into local heat via collisional relaxation and the radiation transport from the earth's surface to space is a process of absorption and re-emission. Half of the absorbed surface radiation will return and warm up the earth. In the case of only CO₂, increasing the present concentration of CO₂ will have a negligible effect on the global warming. In the presence of also water vapor the absorption will occur over almost the entire spectrum. In this case too, increasing CO₂ will practically not affect the global temperature.

Introduction

A climate catastrophe caused by CO₂ is nothing more than a hypothesis. The ideas of this hypothesis are based on unproven assumptions. The models derived from this hypothesis predict a catastrophic climate with higher temperatures that have so far proven to be inaccurate over the past decades. Climate is a very complex problem that unfortunately does not lend itself to experimental research. A better approach for research is found in extensive computer calculations of all relevant physical processes¹.

In the present study we describe the absorption of the thermal radiation of the earth's surface by the CO₂ content in the atmosphere. For the current concentration of CO₂, the absorption for thermal radiation is found to be saturated. This saturation also occur in the presence of water vapor.

The absorption causes local heating through molecular collisions. These “hot spots” become new radiation sources that subsequently emit photons. The radiation transport from the earth's surface is a process of absorption and re-emission. It will be discussed that half of the emitted surface radiation will return and warm up the earth. Because of saturation an increase of CO₂ will not enhance the greenhouse effect.

Vibrational- rotational structure of CO₂

The CO₂ molecule has strong infrared absorption bands that belong to the symmetric stretching vibration ν_1 , the degenerated bending vibration ν_2 and the asymmetric stretching vibration ν_3 . The vibrational states are usually indicated with the quantum numbers n_1, n_2 and n_3 of the respective vibrational modes. A vibrational transition during absorption may be accompanied with a rotational transition. For the electronic ground state the molecules with symmetric vibrations (ν_1, ν_2) have only even rotational J -numbers in the rotational spectrum, while the asymmetric vibration ν_3 has only odd J -numbers. According to the selection rule the transition of the absorbing molecule changes the rotational quantum number of the molecule with $\Delta j = \pm 1$, or 0. The P -branch transitions correspond to $\Delta j = -1$, the Q -branch to $\Delta j = 0$ and the R – branch to $\Delta j = +1$.

The bending mode is degenerated because there are two perpendicular vibrations. Quantum theory tells us that the degree of degeneracy if n_2 quanta are excited is equal to the number of different ways in which n_2 can be written as the sum of two integers which is equal to $n_2 + 1$. This degeneracy is indicated with the integer l . The vibrational state of CO₂ is described by the notation $(n_1 n_2^l n_3)$. For instance, for $n_2=2$ we have $l = 0, l = 2$ or $l = -2$. The value $l = 0$ is considered as a linear motion of the C-atom, whereas $l = 2$ and $l = -2$ are circular motions in opposite directions. During the circular motion the internuclear distances are unchanged and therefore they have no coupling with the ν_1 and ν_3 vibrations.

The rotational energy E_r of the molecule, according to quantum theory described by the integer j , is $(2j+1)$ -fold degenerated. Its energy is

$$E_r = B h c j (j + 1) \quad (1)$$

The constant $B = 0.42 \text{ cm}^{-1}$ depends slightly on the vibrational state. It is determined from the spectroscopy of the laser lines². Since depending on the vibrational state either odd or even j -numbers are missing, the rotational distribution is expressed by

$$n_{vj} = N_v \left(\frac{2hcB}{kT} \right) (2j + 1) e^{\left[-\frac{hc}{kT} j(j+1) \right]} \quad (2)$$

where n_{vj} is the number of molecules with rotational number j and vibrational state v . N_v is the total number of molecules in that vibrational state per unit volume. The value of j for which the maximum density is reached is found as

$$j_{max} \approx \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \quad (3)$$

For example, $j_{max} = 16$ for $T = 300\text{ K}$ and 14 for $T = 243\text{ K}$.

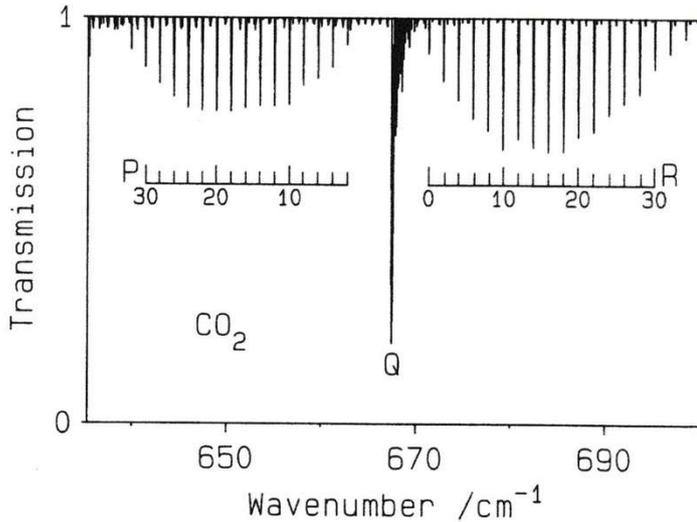


Fig. 1

For P -branch transitions the rotational energy is decreased by:

$$\Delta E_r = hcB[j(j+1) - (j-1)j] = 2hcBj$$

The frequency difference between two adjacent absorbing rotational lines in the P -spectrum is then:

$$\Delta \nu_r = 4cB = 5 \times 10^{10} \text{ Hz}$$

Similarly, we find the same difference in the R -branch. For the Q -branch all transitions coincide with the same absorbing wavelength. It should be noted that these frequency differences are independent on the rotational quantum number j . See fig.1.

At atmospheric pressure the line shape of the absorption is broadened by collisions where the kinetic energy of the colliding molecule takes care of the excess energy of the absorbing photon. The difference between the absorbed thermal photon and the molecular transition photon is exchanged with the kinetic energy of the colliding particles. The theory of this process turns out to be exceedingly complex, and is in many regards incomplete^{3,4}. In the limit that collisions have zero duration time it can be shown that the line shape is Lorentzian⁵. The normalized Lorentzian line shape function is then given by:

$$S(\nu, \nu_{12}) = \frac{\Delta \nu_p}{2\pi} \left[(\nu - \nu_{12})^2 + \left(\frac{\Delta \nu_p}{2}\right)^2 \right]^{-1} \quad (4)$$

where $\Delta \nu_p$ is the pressure dependent linewidth that corresponds to the frequency separation between the points where $S(\nu, \nu_{12})$ has half its

maximum value and ν_{12} is the center frequency of the transition. It is independent on the transition and can be measured as function of gas composition, pressure and temperature^{6,7}. Derived from CO₂ laser measurements the linewidth can be represented by the following formula:

$$\Delta\nu_p = 5.53 p \sqrt{\frac{300}{T}} \text{ MHz} \quad (5)$$

where p is the air pressure in torr.

At a pressure of 760 torr and a temperature of 273 K we find $\Delta\nu_p = 4.4 \times 10^9 \text{ Hz}$, at 500 torr and 243 K this quantity is $3 \times 10^9 \text{ Hz}$.

Since the collisions last for a short but finite duration the line shape leads to small but observable deviations from the ideal Lorentzian line shape. Far away from its center the Lorentzian line decays rather slowly whereas there are both theoretical and observational reasons to believe that the tails of the line die off faster than predicted by this Lorentzian profile⁴. Thus, although there is a strong decrease of absorption far away from the line center the satellite observations show (Fig.2) homogeneous absorption between the rotational lines indicating that deviations from the Lorentz profile are not significant in the frequency range of our interest. Those are the frequencies from the center of a line to half the frequency distance with its neighboring rotational line where the absorption cross section is at its minimum. It is about 5 times the linewidth.

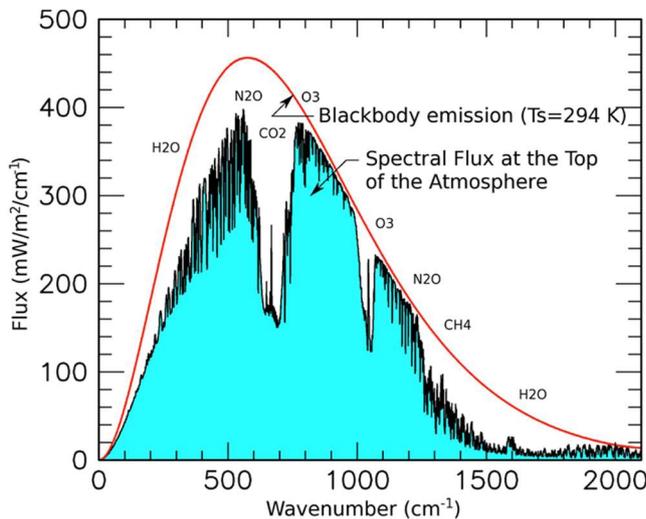


Fig.2

The absorption cross section for the simultaneous vibrational and rotational excitation from the initial state ν_{vr} to the final state ν_{vr}^* can be derived as²:

$$\sigma_{\nu_j \rightarrow \nu_j^*} = \frac{\lambda^2 (2j^* + 1)}{8\pi (2j + 1)} S(\nu, \nu_{12}) A_{\nu_j^* \rightarrow \nu_j} \quad (6)$$

where $A_{vj^* \rightarrow vj}$ is the transition rate for spontaneous emission from the initial rotational-vibrational state vj^* to the final state vj . Its value depends slightly on the rotational state².

Low-lying infrared absorption bands of CO₂

The population densities of the vibrational modes are conveniently described by the vibrational temperatures. They are 1800 K, 950 K and 3370 K for respectively the v_1 , v_2 and v_3 vibrations. Since these temperatures are much higher than the atmospheric temperatures only absorption from the ground and low-lying excited states are relevant to our purpose. The most intense ones involve excitations from the ground state to the lowest states of the bending and to the asymmetric vibrations (absorption involving the symmetric stretching vibration is not possible because of the absence of a dipole moment). Especially the absorbed radiation power by the ground state bending mode at about 15 microns is dominant. The absorbed radiation by the asymmetric vibration at about 4.3 micron is much less intense because the emitted radiation from the earth surface has its maximum at a wavelength of about 16-micron and drops fast for shorter wavelength. See fig.2. In the following table⁸ the low-lying infrared absorption bands of CO₂ are collected.

(cm^{-1})	(<i>micron</i>)	Lower state	Upper state
667	14.99	000	01 ¹ 0
2349	4.26	000	001
1932	5.17	000	03 ¹ 0
2076	4.82	000	11 ¹ 0
3609	2.77	000	02 ⁰ 1
3716	2.69	000	10 ⁰ 1
4860	2.06	000	04 ⁰ 1
4983	2.01	000	12 ⁰ 1
5109	1.96	000	20 ⁰ 1
618	16.18	01 ¹ 0	02 ⁰ 0
720	13.89	01 ¹ 0	10 ⁰ 0
1886	5.30	01 ¹ 0	04 ⁰ 0
2094	4.78	01 ¹ 0	12 ² 0
2137	4.68	01 ¹ 0	20 ⁰ 0

961	10.4	10 ⁰ 0	00 ⁰ 1
1063	9.4	02 ⁰ 0	00 ⁰ 1

The absorption of the individual bands

The (000 – 01¹0) band is by far the strongest absorber because its wavelength of 15 microns is near the top of the thermal emission curve. The absorption spectrum contains *P*-, *Q*- and *R*-branches⁹. See also fig.1.

The air density is about 2.78×10^{19} molecules per cm^3 . The present content of CO_2 is 400 ppm or 0.04% so that $N_{\text{CO}_2} = 1.1 \times 10^{16} \text{ cm}^{-3}$. At atmospheric temperatures practically all molecules are in the vibrational ground state. Although there is a decrease of density with height we consider it for our purpose as constant. For weak absorptions the effective absorption length will then be somewhat longer.

The line shape value S_c in the center of the line for an air pressure of 760 torr and a temperature of 273 K is according to eq. (4): $S_c = \frac{2}{\pi \Delta \nu_p} = 1.4 \times 10^{-10} \text{ sec}$.

The spontaneous emission rate A can be deduced from the data found in reference 9. These data are obtained with a completely enclosed spectrometer filled with CO_2 and using a grating of 1200 lines and a KBr prism. The slit included about 0.45 cm^{-1} . From these data we calculate for the present transition the value $A = 0.08 \text{ sec}^{-1}$. For $A = 0.08 \text{ sec}^{-1}$ we obtain by using eq. (6): $\sigma_{vj} = 10^{-18} \text{ cm}^2$.

Considering the zero or *Q*-branch the absorbed thermal flux density by the CO_2 molecules can be expressed according to the Lambert-Beer law as:

$$I_{\text{th}} = I_0 \exp[-\sigma_{vj} N_{\text{CO}_2} h] \quad (7)$$

where I_0 is the emitted flux from the earth surface and h the height from the surface in cm. Substituting the values for $\sigma_{vj} = 10^{-18} \text{ cm}^2$ and $N_{\text{CO}_2} = 1.1 \times 10^{16} \text{ cm}^{-3}$ we find the absorption at the line center as $I_{\text{th}} = I_0 \exp(-1.1 \times 10^{-2} h)$.

Thus, an absorption length $l_{\text{ab}} \sim 1\text{m}$.

For the *P*- and *R*-branch the situation is different because the absorption deals with the density of the involved rotational lines. Since for atmospheric temperatures practically all molecules are in the ground vibrational state the number of molecules with the rotational quantum number $j_{\text{max}} = 16$ is then obtained from eq. (2): $n_{j=16} = 0.078 N_{\text{CO}_2} = 8.6 \times 10^{14} \text{ cm}^{-3}$.

If we now substitute into eq. (7) the cross section $\sigma_{vj} = 10^{-18} \text{ cm}^2$ and the density $n_{vj} = 8.6 \times 10^{14} \text{ cm}^{-3}$ we obtain at the line center an absorption distance of 12m. The lowest absorption in the middle of two neighboring rotational lines at the frequency distance of $2.5 \times 10^{10} \text{ Hz}$ from the center we calculate by using eqs. (4) and (6) ; $\sigma_{vj}(2.5 \times 10^{10}) = 0.77 \times 10^{-20} \text{ cm}^2$. The molecular density in the middle is twice the above value or $17.2 \times 10^{14} \text{ cm}^{-3}$. The corresponding absorption distance becomes 750 m.

The fraction of the molecules for $j = 16$ is as indicated 0.078. This number decreases according to eq. (2) with increasing and decreasing j -values. For $j = 40$ this fraction is 0.012. This means that emitted infrared radiation that falls within the absorption region of the line $j = 40$ has at its center an absorption distance of 72m and in the middle of the lines an absorption distance of 4.5km. The fraction for $j = 2$ is 0.02 so that also these molecules saturate the thermal emission flux at a distance of about 50m and for the frequency in between the lines at 2.6km.

Considering the molecules from $j = 2$ to $j = 40$ we find that about 98% of all CO_2 molecules in the considered band completely saturates the emitted thermal radiation within a distance of about 4.5km. The same result will be obtained by considering the R - branch. Thus for the present concentration the thermal radiation is saturated and more CO_2 does not increase absorption.

The (000 - 001) band with a wavelength of about 4.3 microns is also considered as a strong absorber, although the thermal radiation intensity at this wavelength is according to fig.2 a very small fraction compared to that at 15-micron. For this band we are dealing with P - and R - transitions. The linewidths of the rotational transitions are again $\Delta\nu_p = 4.4 \times 10^9 \text{ Hz}$ and the line shape at the center is also $S_c = \frac{2}{\pi \Delta\nu_p} = 1.4 \times 10^{-10} \text{ sec}$. From reference 9 we derive for this band $A = 1.6 \text{ sec}^{-1}$. Using this value, the cross section for a vibrational-rotational transition is obtained from eq. (6): $\sigma_{vj} = 1.65 \times 10^{-18} \text{ cm}^2$. The molecular density for vibrational-rotational transition with $j = 16$ is the same as in the previous band: $n_{vj} = 8.6 \times 10^{14} \text{ (cm}^{-3})$. Using eq. (7) and the above values for n_{vj} and σ_{vj} we obtain the absorption distance from $\sigma_{vj} n_{vj} h = 1$ so that $h_{ab} \sim 7.5 \text{ m}$. Similar to the previous band we consider for the P - and R - branches also the frequency space between the line centers. We find that all thermal radiation is absorbed at the height of 2.7km.

The (000 – 03¹0) and (000 – 11¹0) bands with wavelengths of about 5 microns can be considered similar to the previous bands. The linewidths and line shapes are equal to those of the previous bands. This transition rate for spontaneous

emission can be obtained from reference 9. We use the value $A = 1.5$. We find $\sigma_{vj} = 2.1 \times 10^{-18} \text{ cm}^2$. For $j = 16$ we have again $n_{vj} = 8.6 \times 10^{14} \text{ cm}^{-3}$. Similar to the previous calculations, complete absorption over all frequencies of this band is reached at a height of 2.2km.

The absorption of the $(000 - 02^0_1)$, $(000 - 10^0_1)$, $(000 - 04^0_1)$, $(000 - 12^0_1)$ and $(000 - 20^0_1)$ bands occurs at wavelengths of about 2 microns. However, at 2-micron wavelength there is practically no emission at the considered temperature of 300 K.

The $(01^{10} - 02^0_0)$ and $(01^{10} - 10^0_0)$ bands are Fermi coupled at wavelength of about 15 microns. The wavelengths are close to those of the $(000 - 01^{10})$ band and the transitions of these three bands are always observed together in the absorption spectrum. However, the considered bands belong to the population density $N_1(\nu_2)$ of the first excited state of the bending mode. The density for $T = 273 \text{ K}$ can to a good approximation be given by $2N_{CO_2} e^{-\frac{T_2}{T}}$ where $T_2 = \frac{h\nu_2}{k}$. We find $N_1(\nu_2) = 0.06N_{CO_2} = 6.6 \times 10^{14} \text{ cm}^{-3}$. The linewidths and the line shapes are again the same as used above. For $j = 15$ we have then the density $5.2 \times 10^{13} \text{ cm}^{-3}$. This transition has according to reference 9 the value $A = 0.8 \text{ sec}^{-1}$. From eq. (6) we then find the absorption cross section equal to 10^{-17} cm^2 . We obtain for the line center of $j = 15$ an absorption height of 20 m. Similar to the previous calculations the absorption saturates over all frequencies at a distance of 7.5km.

The $(01^{10} - 04^0_0)$, $(01^{10} - 12^2_0)$ and $(01^{10} - 20^0_0)$ with wavelength of about 5 microns are very weak absorbers because of their multi-transitions and low density of the excited bending states which depend on the temperature of the environment. Low absorption means that the radiation within their bandwidths will reach high altitudes where the temperature is far below zero and consequently the population of the excited bending state decreases. These transitions, even with higher CO_2 concentration, are non-absorbers.

The $(10^0 - 00^0_1)$ and the $(02^0 - 00^0_1)$ bands at about 10-micron wavelength are Fermi coupled. Both bands have P - and R - branches. The linewidths and the line shapes are again the same as those used above. The transition rate A is obtained² from laser spectroscopy and is for both bands about 0.17 sec^{-1} . Using eq. (6) we obtain for the absorption cross section $9.5 \times 10^{-19} \text{ cm}^2$. Because the densities of the considered vibrational excited states are relatively low. The density of molecules in the (10^0_0) vibrational state can to a good approximation

be given by $N_1(\nu_1) = N_{CO_2} e^{-T_1/T}$ where $T_1 = \frac{h\nu_1}{k}$. Substituting $T_1 = 1900\text{ K}$ and $T = 273\text{ K}$ we find $N_1(\nu_1) = 9.5 \times 10^{-4} N_{CO_2} = 1.1 \times 10^{13}\text{ (cm}^{-3}\text{)}$. The number of these molecules with the rotational quantum $J = 16$ is then $8.5 \times 10^{11}\text{ (cm}^{-3}\text{)}$. We find the absorption distance for the strongest rotation line at 12.5 km. A comparable result is obtained for the absorption of molecules in the (02^0_0) vibrational state. Practically, both bands do not contribute to thermal absorption.

Transfer of absorbed infrared radiation

The two major greenhouse gases that control the thermal radiation flux from the earth's surface are CO_2 and water vapor. The thermal radiation excites vibrational-rotational transitions of these gases. Then, the excited molecules relax by molecular collisions, thereby heating the atmosphere.

Let us first consider the case that the only greenhouse gas is CO_2 . By far most of the thermal radiation has no interaction with the air molecules and radiates directly into space. Only radiation with frequencies that fit the absorption spectrum of CO_2 will be absorbed. It is not very likely that these excited molecules will lose their energy by radiation because the emission time is much larger than the relaxation time by molecular collisions. At atmospheric condition the relaxation processes^{11,12} are in the order of 10^{-6} sec, whereas the emission time may be of the order of 10^{-3} sec or larger. The transfer of the energy of the excited stretching vibrations with energy quanta $h\nu_1$ and $h\nu_3$ occurs at first internal via collisions with air molecules to the bending modes having the much smaller energy quanta $h\nu_2$. The excess quantum energy in this collision process is exchanged with the translational motion¹¹. Then, on its turn the bending modes having the smallest energy quanta will transfer during collisions their energy directly to translational motion of the air molecules. This means that the initially absorbed thermal emission results to local heating of the atmosphere. A part of the thermal radiation from this heating of the atmosphere will reach the earth's surface and increase its temperature in order to balance the incoming radiation from the sun. This is the greenhouse effect of CO_2 connected to global warming. As we have seen above, the absorption of thermal emission is practically saturated by the present concentration values of CO_2 . Thus, in case of increasing the atmospheric CO_2 concentration there will be a negligible increase of radiation absorption.

In the presence of both CO_2 and water vapor, thermal absorption is strongly enhanced. The absorption by water vapor is very strong. This is due to the strong permanent dipole moment of the asymmetric-top molecule, which also allows for pure rotational transitions in the long wavelength region. Absorption

therefore occurs over virtually the entire spectrum. The excited water vapor molecules relax also through molecular collisions, thereby similarly heating the atmosphere. A part of the resulting thermal radiation from this heated atmosphere will then again excite water vapor and CO₂. This process of excitation and heating will continue to occur over a part of the troposphere towards space as long as there is sufficient water vapor. Each time, a part of the produced radiation will go towards the earth's surface and another part towards space. With the current concentration of CO₂ there will always be saturation as we have discussed. More CO₂ will also in the presence of water vapor not enhance the absorption

Greenhouse effect limitation

The greenhouse effect is caused by photons that reach the earth's surface from the atmosphere. These photons originate because the earth's surface radiation is absorbed by atmospheric gases such as CO₂ and water vapor. This absorption causes, as we have discussed, local heating through molecular collisions. The locally heated atmosphere becomes a new radiation source that subsequently emits photons that are absorbed again. Thus, the radiation transport from the earth's surface is a process of absorption and re-emission. (If there were no absorbing gases, the surface radiation would directly reach space, and the atmosphere would not be heated.)

The direction of the emitted radiation in the atmosphere is random so that half goes toward the earth and the other half toward space. In every direction, photons are absorbed and subsequently new photons are emitted. The source of all these photons is the emitting earth's surface. From symmetry considerations, it follows that ultimately half of the emitted surface radiation that is absorbed by the greenhouse gases will return and warm up the earth.

As discussed before, the absorption of surface radiation by the current CO₂ concentration is practically saturated, so an increase in CO₂ can therefore not enhance the greenhouse effect.

Conclusions

The absorption of thermal emission from the earth by CO₂ occurs at wavelengths around 15, 5 and 4.3-microns. By far most absorption is around the 15-micron wavelength of the (000 – 0110) vibrational band. Within all

absorption bands, the central frequencies of the rotation lines are 50 GHz apart. However, satellite observations show that the absorption of individual rotation lines overlaps, so that in the frequency domain, the absorption width is determined by the width of the vibration band.

The global heating is caused by photons that reach the earth's surface from the atmosphere. It is argued that *half of the emitted radiation from the earth's surface that is absorbed by greenhouse gases will return and warm up the earth's surface.*

The main greenhouse gases are water vapor and CO₂. The absorption of surface radiation by the current CO₂ concentration is practically saturated, so *an increase in the CO₂ concentration cannot enhance the greenhouse effect.*

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