

Global warming by thermal absorption of CO₂

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Abstract

The present study describes the absorption of thermal emission from the earth surface by CO₂ in the atmosphere. It is done on a fundamental physics base. In this way its “greenhouse effect” and its connection to global warming will be discussed. For this purpose, the vibrational-rotational structure of the CO₂ molecule is described. At atmospheric temperatures a few low-lying vibrational bands of CO₂ are relevant. It is found that independently from the vibrational state of the molecule the frequency separation between the rotational lines for both *P*- and *R*-transitions is constant and about 50 GHz. Furthermore, it is found that practically about 90% of the frequency space between the rotational lines of the absorbing vibrational bands around 15-, 5- and 4.3-micron wavelength contributes relatively little to the thermal absorption. Roughly, only 10% of its spectrum is active and the thermal radiation that falls within these regions is fully absorbed. This is not only the case for 400 ppm of CO₂ in the atmosphere but also for much smaller concentration values. Global warming depends on the thermal emission from the earth surface. It is practically not affected by the change of the CO₂ concentration.

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 CO_2 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 lines¹. Since depending on the vibrational state either odd or even j -numbers are missing, the rotational distribution is expressed by

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

where n_{vj} is the number of molecules with rotational number j and vibrational state ν . 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 $T = 243 \text{ K}$.

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 .

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^{2,3}. In the limit that collisions have zero duration time it can be shown that the line shape is Lorentzian⁴. 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^{5,6}. 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. According to observations this shape is correct roughly between its half maximum values. Further 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 much faster than predicted by this Lorentzian profile³. On the other hand, one might argue that for higher CO₂ content the tails of the absorption line will contribute additionally at high altitude. Because the air density falls exponentially with the altitude and so does the linewidth the relative increase of absorption of the tails at higher CO₂ content is negligible. For this reason, we consider in the following only transitions that falls within the linewidth $\Delta\nu_p$. Thus, we find that the rotational lines absorb radiation mainly within discrete narrow frequency regions with a bandwidth of about $4.4 \times 10^9 \text{ Hz}$. These narrow regions are separated by absorption-free regions between the rotational line distance of $5 \times 10^{10} \text{ Hz}$.

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 as¹:

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

where $A_{\nu j^* \rightarrow \nu j}$ is the transition rate for spontaneous emission from the initial rotational-vibrational state νj^* to the final state νj . Its value depends slightly on the rotational state¹.

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 ν_1 , ν_2 and ν_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 the asymmetric vibrations (absorption from 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. In the following table⁷ 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 a strong absorber because its wavelength of 15 microns is near the top of the thermal emission curve. The absorption spectrum contains *P*-, *Q*- and *R*-branches⁸.

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. 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 8. 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 as $I_{\text{th}} = I_0 \exp(-1.1 \times 10^{-2} h)$.

Substituting $h = 400 \text{ cm}$ all thermal radiation covered by the zero *Q*-branch is absorbed by CO_2 .

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): $n_{j=16} = 0.078 N_{\text{CO}_2} = 8.6 \times 10^{14} \text{ cm}^{-3}$.

Now we substitute into eq. (7) for the cross section $\sigma_{vj} = 10^{-18}$ and for the density $n_{vj} = 8.6 \times 10^{14}$. We obtain the absorption from $I_{\text{th}} = I_0 \exp(-8.6 \times 10^{-4} h)$. It is saturated after about 50 m. For a lower concentration of 200 ppm the radiation flux is absorbed at a height of 100 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 $j = 40$ is saturated over a distance that is about 6 times the absorption length for $j = 16$ i.e. about 300 m. The fraction for $j = 2$ is 0.02 so that also these molecules saturate the thermal emission flux within about 200 m. Thus, between $j = 2$ and $j = 40$ about 98% of all CO₂ molecules in the considered band absorb all the emitted infrared radiation that falls within their spectra within a distance of about 300 m and in the case of 200 ppm it is 600 m. The same result will be obtained by considering the *R*-branch.

The (000 - 001) band with a wavelength of about 4.3 microns is also considered as a strong absorber. 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 8 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: $n_{vj} = 8.6 \times 10^{14} \text{ (cm}^{-3}\text{)}$. Using eq. (7) and the above values for n_{vj} and σ_{vj} we consider again complete absorption for $\sigma_{vj} n_{vj} h = 4$. We find h less than 30 m. Similar to what found for the previous band all radiation that falls within the *P*- and *R*- branches is absorbed at the height of 180 m. Since the absorption depends on the product of density times height it is seen that for less CO₂ there is saturation at a higher level.

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 the *P*- and *R*- branches is reached at a height of 130 m.

The absorption of the (000 – 02⁰¹), (000 – 10⁰¹), (000 – 04⁰¹), (000 – 12⁰¹) and (000 – 20⁰¹) 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 (01¹⁰ – 02⁰⁰) and (01¹⁰ – 10⁰⁰) bands are Fermi coupled at wavelength of about 15 microns. The wavelengths are close to those of the (000 - 01¹⁰) 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 $j = 15$ an absorption height of 80 m and for the total absorption of all lines it will be about 480 m. Thus, these bands will also absorb all thermal radiation that falls within their bandwidths. In the case of 200 ppm the absorption height will be twice.

The $(01^{10} - 04^{00})$, $(01^{10} - 12^{20})$ and $(01^{10} - 20^{00})$ 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 $(10^0 - 00^0)$ and the $(02^0 - 00^0)$ 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 obtained¹ 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 other vibrational excited states are relatively low the density of molecules in the (10^0) 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 $N_1(\nu_1) = 9.5 \times 10^{-4} N_{CO_2} = 1.1 \times 10^{13}\text{ (cm}^{-3})$. The number of these molecules with the rotational quantum $J = 16$ is then $8.5 \times 10^{11}\text{ (cm}^{-3})$. Complete absorption for this strongest line would be reached with $\sigma_{vj} n_{vj} h = 4$ at an effective distance of 50 km. A comparable result is obtained for the absorption of molecules in the (02^0) vibrational state. Thus, since the density of air drops very fast at high levels both absorption bands are practically not contributing to the thermal absorption.

Transfer of absorbed infrared radiation

What happens with the absorbed energy? It is not very likely that the 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^{10,11} 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 motion¹⁰. 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. This heating of the atmosphere reduces the effective thermal emission from the earth surface. This is the greenhouse effect of CO_2 connected to global warming. As we have seen that the absorption of thermal emission is practical saturated by the present and also by much smaller concentration values of CO_2 . Thus, the variation of the CO_2 concentration in the atmosphere will have a negligible effect on global warming.

Conclusions

The absorption of thermal emission from the earth by CO_2 occurs at wavelengths around 15, 5 and 4.3 microns. The absorption is mainly limited to narrow frequency regions near the centers of the rotational lines. The frequency width of these absorbing regions is about 4 GHz whereas the frequency distance between the rotational lines for both *P*- and *R*- transitions for all absorbing bands is constant and about 50 GHz. Roughly about 10% of the infrared flux that falls within the absorption bands of CO_2 will be absorbed. The analysis is performed assuming 400 ppm CO_2 in the atmosphere for which we found saturation of absorption. This saturation occurs also for much smaller values of the CO_2 content, including 200 ppm. The greenhouse effect connected to global warming depends on the thermal emission or temperature of the earth surface and it is practically not affected by the change of the CO_2 concentration. *The observed increase of global warming cannot be related to the present increase of CO_2 .*

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