http://doi.org/10.35784/iapgos.2998 *received: 08.06.2022 | revised: 02.08.2022 | accepted: 15.09.2022 | available online: 30.09.2022*

ABSORPTION CHARACTERISTICS OF THERMAL RADIATION FOR CARBON DIOXIDE

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Abstract. *The article presents graphs of absorption of thermal radiation as a function of the mass of absorbing carbon dioxide per unit of illuminated area. Experimental research was preceded by an analysis of a simplified model of radiation absorption, paying attention to the phenomenon of saturation. The results of the experimental research were compared with the theoretical ones and the discrepancies were interpreted. Based on the conclusions, suggestions were made regarding the impact of further CO_2 emissions on climate change.*

Keywords: absorption characteristics, saturation of absorption, thermal radiation, Schwarzschild's equation

CHARAKTERYSTYKA ABSORPCJI PROMIENIOWANIA CIEPLNEGO DLA DWUTLENKU WĘGLA

Streszczenie. *W artykule przedstawiono wykresy absorpcji promieniowania cieplnego w funkcji masy absorbującego dwutlenku węgla na jednostkę oświetlanej powierzchni. Badania eksperymentalne poprzedzono analizą uproszczonego modelu absorpcji promieniowania, zwracając uwagę na zjawisko nasycenia. Wyniki badań eksperymentalnych porównano z teoretycznymi, a rozbieżności zinterpretowano. Na podstawie wniosków sformułowano sugestie dotyczące wpływu dalszej emisji CO2 na zmiany klimatyczne.*

Keywords: charakterystyka absorbcji, nasycenie absorbcji, promieniowanie cieplne, równanie Schwarzschilda

Introduction

The physical and chemical properties of carbon dioxide are well-known, and due to its frequent occurrence in chemical and biological processes, it is one of the most popular gases. In recent years, due to the coincidence of its absorption spectrum with a part of the thermal spectrum of the Earth's surface, carbon dioxide has gained much popularity as "a harmful gas, wreaking havoc on the climate and thus threatening the inhabitants of the planet". The absorption of thermal radiation in CO_2 has been given a lot of attention, among others, in such works as [7–10]. These works provide a valuable contribution to understanding the phenomenon of radiation absorption in the Earth's atmosphere, but they do not directly provide arguments for the apocalyptic vision related to CO_2 emissions. Such a vision is based on direct observation of nature, which shows that the rise of CO_2 concentration is accompanied by the rise of the temperature of the Earth's atmosphere. Apparently, it makes sense and therefore it is easily accepted by society. However, the fact that event A accompanies event B does not necessarily imply that the former is the cause of the latter. The events may be independent or vice versa, the second event may be the cause of the first. Therefore, it is worth getting acquainted with the results of the work [3], where, on the basis of the measurement results across the globe, it was shown that the cyclic peaks of temperature increase precede in time the corresponding peaks of CO_2 concentration. It follows unequivocally that it is not the increase in CO_2 concentration that causes the temperature increase, but conversely, the increase in temperature most likely causes the release of CO_2 from the oceans, leading to an increase in its concentration.

Another argument adopted by the society is the calculation results for the used computer models. However, as shown, among others, in [4], a relatively large number of input data should be used for these models. Of course, these data can only be obtained from the results of measurements carried out simultaneously at a very large number of measurement points around the globe and at different altitudes. One should also pay attention to the high dynamics of processes in the atmosphere. Moreover, it should be noted that the use of averaged quantities for nonlinear dependencies, such as the average temperature using the Stefan-Boltzmann law, can generate very large errors. So it seems that it is only possible to estimate the upper or lower limit of the possible value of the absorption of the Earth's thermal radiation in atmospheric carbon dioxide. The difference between these limits can be very large. In practice, it can be reduced by experimentally verifying the results of computer calculations at every stage of their implementation. Therefore, the experiment described in articles [5] and [6] was carried out, where it was shown that thermal radiation from the hot surface of the Moon, after passing through the Earth's atmosphere, is not absorbed in carbon dioxide. Thus, it was shown that for this radiation there is a complete saturation of the process. This may suggest that it may be similar in the case of the Earth's thermal radiation.

Therefore, in the present work, the research focused on the phenomenon of saturation of the absorption process of thermal radiation in a mixture of carbon dioxide and air.

1. A simplified description of the process of resonance absorption of radiation in gases

Illuminating a solution of an absorbing substance by a collimated beam of monochromatic radiation, one can obtain a decrease in the intensity of this radiation according to the Lambert-Beer's law:

$$I = I_0 e^{-\alpha \cdot l \cdot C} \qquad (1)$$

where:
I_0 – intensity of radiation penetrating the sample,
I – intensity of radiation after passing through the sample,
α – mass absorption coefficient [m^2 kg^{-1}],
l – thickness of the layer [m],
C – mass concentration [kg m^{-3}].

Absorption defined as the ratio of the energy of the absorbed radiation to the energy of the incident radiation at a given time can be described by the formula:

$$A = \frac{I_0 - I}{I_0} = 1 - e^{-\alpha \cdot l \cdot C} \qquad (2)$$

By introducing a new quantity called the absorbing mass per unit area defined as $m = l \cdot C$, equation (2) takes the form:

$$A = 1 - e^{-\alpha \cdot m} \qquad (3)$$

The graph of this function is shown in figure 1.

It can be seen that with the increase of m, the absorption will asymptotically approach the value 1 and for a sufficiently large value, we can assume that we are dealing with saturation.

It should be noted, however, that the absorbing substance not only absorbs the radiation but also emits it. However, while for monochromatic radiation, the resonance absorption occurs for a strictly defined wavelength (within the line width), then spontaneous emission is the result of all possible transitions and a small share for the wavelength corresponding to the absorbed radiation is neglected in the Lambert-Beer description. The situation is different with the absorption of thermal radiation. In this case, both absorption and emission take place for all possible transitions.

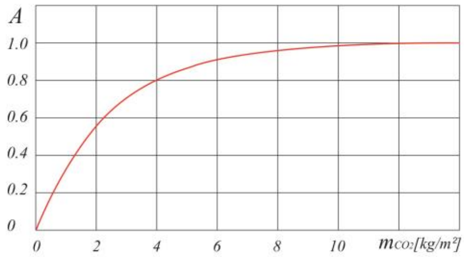

Fig. 1. Illustrative diagram of monochromatic radiation absorption as a function of the absorbing mass for α = 0.4 m^2/kg

Moreover, especially with low-temperature radiation sources, its intensity is relatively low. Thus, the thermal radiation emitted by the absorbing gas cannot then be neglected. The situation is further complicated by the fact that with a relatively large number of oscillatory-rotational lines and their overlapping at higher extinction values, the normalized line shape function $g(\nu)$ describing the frequency-dependent interaction of radiation with molecules becomes very complex. This phenomenon has been thoroughly analysed in [1]. It shows that the absorption of thermal radiation A in a gas is a corresponding function of the mass m of the absorbing substance and the pressure p of the gas in which this substance is dissolved. An arbitrary parameter A_0 related to the bandwidth was introduced and the absorption notation for $A \leq A_0$ was adopted in the form:

$$A = cm^d p^k \tag{4}$$

While for $A > A_0$

$$A = C + Dln(m) + Kln(p) \tag{5}$$

All quantities A_0, c, d, k, C, D i K are assumed to be empirically fitted quantities.

It should be noted, however, that the function $A(m)$, written by the formula (5) as a logarithmic function, is an increasing function for any large value of the argument m. Meanwhile, the absorption A, according to the definition, cannot exceed the value of 1. This clearly shows that formula (5) can describe the phenomenon relatively correctly only for a limited value of m.

The propagation of the Earth's thermal radiation in the atmosphere for various concentrations of CO_2 at a constant concentration of water vapor, as well as ozone and methane was described in the study cited in the introduction [2]. Performing the calculations for the adopted computer model, the author obtained the graph of the absorption of this radiation as a function of CO_2 concentration in the atmosphere presented in Fig. 2.

Taking into account that in a cylinder with a unit cross-sectional area (1m^2) and a height from the Earth's surface to the stratosphere, there is an air mass $m_{pow.} \cong 10^4$ kg, the mass of CO_2 in this cylinder can be determined for a given concentration according to the formula:

$$m_{CO_2}[kg/m^2] = m_{pow.}[kg/m^2] \cdot \frac{M_{CO_2}}{M_{pow}} \cdot \frac{C_{CO_2}[ppm]}{10^6} = 10^4 kg/m^2 \cdot \frac{44}{29} \cdot 10^{-6} \cdot C_{CO_2}[ppm] = 1{,}52 \cdot 10^{-2} kg/m^2 \cdot C_{CO_2}[ppm]$$

where:

M_{CO_2} – molar mass of carbon dioxide,

M_{pow} – molar mass of air,

$C_{CO_2}[ppm]$ – carbon dioxide concentration in the air.

Hence for the Earth's atmosphere:

$$C_{CO_2}[ppm] = 65{,}8 \cdot m_{CO_2}\ [kg/m^2].$$

Taking these dependencies into account, the graph in figure 2 can be replaced with the graph shown in figure 3. It can be seen that also this time the absorption function of A in the presented CO_2 mass range is increasing, especially for the value corresponding to the current CO_2 concentration in the atmosphere ~ 400 ppm ($m_{CO2} \approx 6$ kg/m^2) and the saturation should be expected only for higher m_{CO2} values. It should be noted, however, that these are the results of theoretical work with input data, the reliability of which may be questioned.

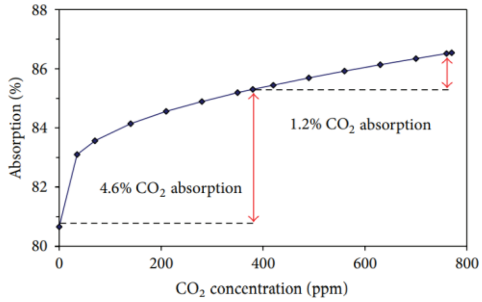

Fig. 2. Graph of the absorption of the Earth's thermal radiation as a function of CO_2 concentration in the atmosphere [2]

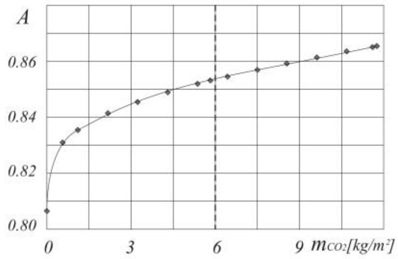

Fig. 3. Graph of the absorption of the Earth's thermal radiation as a function of the mass of CO_2 in the atmosphere per 1 m^2 of surface; the dashed line represents the mass of CO_2 for a concentration of 400 ppm

It should be noted, however, that these are the results of theoretical work with input data, the reliability of which may be questioned. Meanwhile, as mentioned in the introduction in [4] and [5], it has been experimentally demonstrated that there is a complete saturation of the process of absorption of thermal radiation from the moon in carbon dioxide in the Earth's atmosphere. Therefore, let us try to carry out the considerations once again, using the well-known Schwarzschild equation used, among others, in [6]:

$$\frac{dI_\lambda}{d\tau} = -I_\lambda + B_\lambda(T) \tag{6}$$

where: $d\tau = k_\lambda \rho ds$, τ – optical thickness measured rectilinearly (with neglecting refraction in the atmosphere), k_λ – mass absorption coefficient, ρ – density of the absorption medium, s – propagation path, $B_\lambda(T)$ – Kirchhoff-Planck's function.

Taking into account that the optical thickness is proportional to the mass of the absorbing substance m and assuming a constant temperature of the gas (omitting e.g. its heating by the absorption of radiation) after integration by frequency and neglecting the fact of widening of the oscillatory-rotational lines for large values of the absorbing mass, equation (6) can be written in the form:

$$\frac{dI}{dm} = -\alpha I + E \tag{7}$$

where α and E are constants.

The solution to equation (7) has the form:

$$I = \left(I_0 - \frac{E}{\alpha}\right) e^{-\alpha m} + \frac{E}{\alpha} \tag{8}$$

where I_0 is the intensity of the incident radiation.

Using equation (2), one can write:

$$A = \frac{I_0 - I}{I_0} = 1 - \left(1 - \frac{E}{\alpha I_0}\right) e^{-\kappa m} - \frac{E}{\alpha I_0} = \left(1 - \frac{E}{\alpha I_0}\right) - \left(1 - \frac{E}{\alpha I_0}\right) e^{-\alpha m} \tag{9}$$

By introducing the designation:

$$1 - \frac{E}{\alpha I_0} = \psi \tag{10}$$

formula (9) will take the form:

$$A = \psi(1 - e^{-\alpha m}) \tag{11}$$

Formula (11) is similar to formula (3) and shows that, analogically to monochromatic radiation, the absorption of thermal radiation have to saturate, reaching the value of ψ for a sufficiently large value of the absorbing mass m.

Of course, the presented considerations require experimental verification.

2. Experimental work

The aim of the experimental work was to measure the characteristics of the absorption of thermal radiation as a function of the mass of carbon dioxide absorbing this radiation. The scheme of the experiment is shown in figure 4.

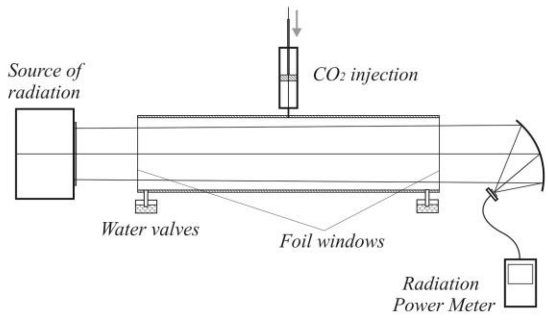

Fig. 4. Schematic diagram of a laboratory system for measuring the absorption of thermal radiation in carbon dioxide

It uses a source of thermal radiation analogous to that described in [5], introducing a graphite emissive surface applied to a copper plate adjacent to the flat surface of a glass vessel with heated oil. The absorption cuvette was made in the form of a horizontal PVC pipe, 1 m long and 150 mm in diameter, closed with removable windows made of polyethylene foil. A small closable opening was provided in the centre of the cuvette for introducing a defined volume of carbon dioxide. At the ends of the cuvette, there were two hoses with the ends immersed in water, constituting check valves, through which a part of the previous gas mixture was ejected from the cuvette, with a volume equal to the volume of introduced carbon dioxide. At the bottom of the cuvette there were two loosely connected panels with a thin rod led outside the cuvette through a suitable sealed passage. As a result, by pulling the rod out and inserting it, it was possible to mix the introduced portion of carbon dioxide with the previous mixture in the cuvette by the movements of the panels. Small portions of CO_2 were injected with a medical syringe, while larger portions were introduced using a graduated vessel filled with carbon dioxide closed with a water jacket at the bottom, which pushed the gas through the tap at the top into the cuvette. One hundred percent concentration of CO_2 in the cuvette was obtained by passing carbon dioxide from the vessel through it for 20 minutes, using a gas mixing device, and checking in the meantime whether the absorption increased further.

Table 1. Absorption of thermal radiation in carbon dioxide

T=78.6ºC			T=109.5ºC		
Measurement	m [kg/m^2]	A	Measurement	m [kg/m^2]	A
1	0	0	1	0	0
2	0.00561	0.0177	2	0.00561	0.0031
3	0.01101	0.0402	3	0.01101	0.0171
4	0.02202	0.0524	4	0.02202	0.0303
5	0.03303	0.0595	5	0.03303	0.0454
6	0.06213	0.0749	6	0.06213	0.055
7	0.09081	0.0848	7	0.09081	0.0676
8	0.11907	0.0853	8	0.13548	0.0761
9	0.16311	0.1014	9	0.17912	0.0863
10	0.20613	0.1046	10	0.22192	0.0913
11	0.24831	0.1083	11	0.26369	0.0903
12	0.28945	0.1117	12	2.078	0.12
13	2.078	0.13			

The tests were carried out for two temperatures of the radiation source: 78.6°C and 109.5°C, reading the radiation power on the meter. Using the formula (1) and taking I_0 as the radiation power for zero CO_2 concentration, the values of radiation absorption were calculated. The results are presented in table 1. On their basis, the graphs shown in Fig. 5 were made.

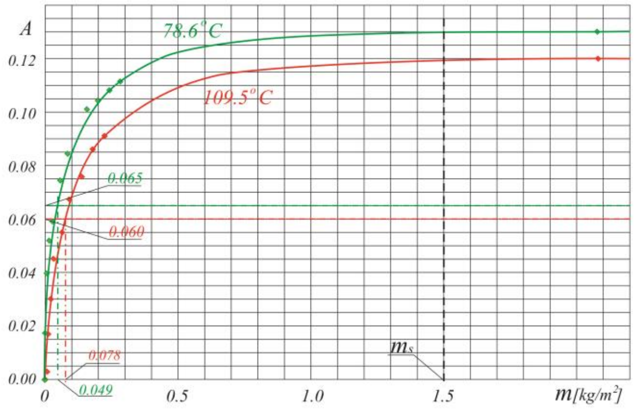

Fig. 5. Graph of absorption of thermal radiation as a function of absorbing mass of CO_2 for the source temperature of 78.6ºC and 109.5ºC, respectively

On the basis of the obtained graphs, it can be concluded that for the mass of carbon dioxide m_s = 1.5 kg/m^2, we are very close to the full saturation of absorption A_s, which for the source temperature of 78.6ºC corresponds to the absorption A_s = 0.13, while for the temperature of 109.5ºC A_s = 0.12. From the obtained graphs it is also possible to read the values of CO_2 mass for which the absorption value is equal to half of the maximum absorption. These readings show that for the source temperature of 78.6ºC $m_{1/2}$ = 0.049, while for 109.5ºC $m_{1/2}$ = 0.078. By introducing these values into the formula (11), for the temperature of 78.6ºC one can determine α_1 = 0.13, κ_1 = 14.1 m^2/kg and for the temperature of 109.5ºC α_2 = 0.12, κ_2 = 8,9 m^2/kg.

After inserting these values back into formula (11), the graphs were obtained, which are shown in the form of dashed lines in Fig. 6.

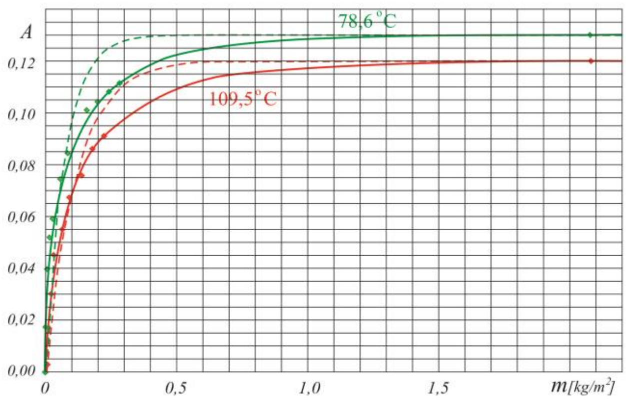

Fig. 6. Thermal radiation absorption charts: solid lines –experimental curves; dashed lines – curves made on the basis of formula (11)

The obtained graphs show that the actual saturation process is "slower" than the saturation process resulting from formula (11). However, as can be seen, the saturation process itself occurs and cannot be questioned.

3. Relating the results of experimental research to the Earth's atmosphere

As already mentioned in the first chapter, in the Earth's atmosphere in a cylinder with a diameter of 1 m^2 and an altitude from sea level to the stratosphere, there is a mass of carbon dioxide equal to:

$$m_{CO_2}[kg] = 1.52 \cdot 10^{-2} kg \cdot C_{CO_2}[ppm]$$

At a CO_2 concentration of 400 ppm, we get the value of the absorbing mass of carbon dioxide ~ 6 kg/m^2. Therefore, in Fig. 7, in order to better illustrate the phenomenon, the graph in Fig. 5 has been extended to this mass value.

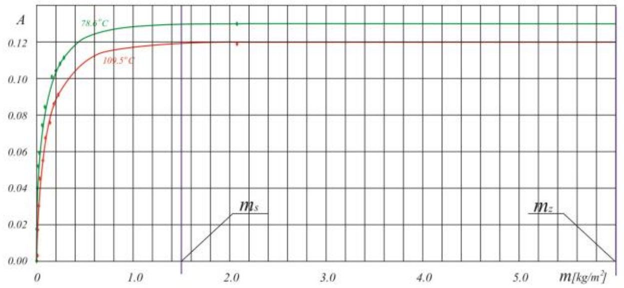

Fig. 7. Graph of absorption of thermal radiation in carbon dioxide, taking into account the mass of saturation m_s and the mass of CO_2 in the Earth's atmosphere m_z

It can be seen that practically with the mass of carbon dioxide of about 1.5 kg/m^2, the process of absorption of thermal radiation goes into saturation with a tendency to "faster" saturation at lower temperatures of the radiation source. So, for the current concentration of 400 ppm for which the mass of CO_2 in the atmosphere is ~ 6 kg/m^2, the limit is for times exceeded. Thus, it can be presumed that <u>the carbon dioxide additionally emitted into the atmosphere does not absorb thermal radiation and thus is not a greenhouse gas</u>.

4. Conclusions

The presented experimental work should be continued. Among other things, it would be necessary to carry out tests for a radiation source with a temperature close to the temperature of the Earth's surface and to measure the absorption of thermal radiation in a mixture of CO_2 with air for various temperatures and pressures. The obtained measurement results could then be used for appropriate computer models so that the final results could be compared with those adopted by the IPCC (Intergovernmental Panel on Climate Change).

Some of the works cited in the introduction and in chapter 1 and the results of the presented experiment, clearly suggest that there can be the saturation of the absorption of the Earth's thermal radiation in atmospheric carbon dioxide. If this was the case, the carbon dioxide additionally emitted into the atmosphere would not have to be the greenhouse gas. Therefore, taking into account the extremely high costs incurred as a result of reducing CO_2 emissions, more attention should be paid to the described experimental studies. However, hard coal and crude oil are valuable raw materials for the chemical industry, and burning them to produce energy is a sheer waste. The degradation of the natural environment is also associated with the extraction of coal. In addition, the often used old "soot" furnaces and primitive internal combustion engines emit a lot of harmful gases and dust. Therefore, it would be good to switch to energy from renewable sources and from nuclear reactors. However, when promoting climate projects, unproven hypotheses treated as a reliable source of information should not be used. It should be emphasized once again that the fact that two phenomena occur simultaneously does not imply that one is the cause of the other. All conditions and results of scientific research should be taken into account, especially the results of experimental work which are both a source of input data and a confirmation of the performed calculations.

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