Infrared absorption capability of atmospheric carbon dioxide

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Abstract

The well-known absorption properties of CO_2 and the physics of thermal radiation permit to estimate the infrared absorption of the atmospheric CO_2. The earth is considered as a homogeneous spherical infrared emitter with a temperature of 288 K. An idealized atmosphere, the CO_2 content of which is the only infrared absorber, surrounds the emitter. Over 200'000 discrete absorption lines of CO_2 are taken into account for the numerical calculations. By assuming that the absorbed energy is converted entirely into heat, we deliberately overestimate the heat retention capability of CO_2. The thermal occupation statistics of the CO_2 energy states plays a key role in these calculations. The calculated heat retention is converted into a temperature increase, ΔT. Doubling the present CO_2 concentration only results in $\Delta T < 0.24$ K. At the present rate of CO_2 concentration increase of 1.2% per year, it will take almost two hundred years to reach ten times the present concentration resulting in $\Delta T < 0.80$ K. By neglecting the thermal statistics, we obtain similar but incorrect results propagated by the International Panel on Climate Change.

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I. Introduction

The earthly climate is the consequence of a very complex thermodynamic system the details of which cannot be understood even with the most complex models and computer simulations. It is of great importance to realize that the weather is a chaotic phenomenon that is primarily characterized by duration of sunshine, temperature, wind, cloud coverage, fog and all forms of precipitation. These elements are interdependent in a non-linear fashion, and can change dramatically over very short time and distance scales. The climate is definable as an ensemble of recurrent similar weather patterns for a specific region. Therefore, it also represents a chaotic entity. The fluctuations of the characteristic weather elements tend to be very large, if compared on a daily scale. The characteristic climate elements fluctuate less, because averages are made over longer time spans i.e. many years. But the fluctuations on a yearly base remain very important, and they make it very difficult to discern a clear trend. Even box averaging over several years does not necessarily reveal a valid trend. Analyzing such data by correlations may be helpful to establish a physical model [1]. However, the resulting model can only be valid, if it is consistent with solid physical and chemical principles.

The correlation between temperature measurements and the anthropogenic increase of the CO_2 concentration is interpreted to be the cause of the apparent climate change. Since the inception of the Intergovernmental Panel on Climate Change, IPCC, in 1988, all their reports maintain that the observed temperature increase is proportional to the logarithmic CO_2 concentration [2-5]. But over the years, the proportionality constant has been systematically reduced to damp the original catastrophic predictions.

Rather than trying to match climate observations by complicated and questionable models, we are focusing at the essential and well-established laws of physics to calculate the heat retention capability of the CO_2 in the atmosphere. This problem is still very complicated to solve correctly. In view of the dire predictions of the IPCC, we are establishing a solid upper limit of the green house effect as a function of the CO_2 concentration. We are considering a quasi equilibrium state and are not interested to make a prediction how it is attained. Fortunately, the CO_2 in the atmosphere is chemically quite stable and does not aggregate to become liquid or solid. Its rotational-vibrational absorption properties play a crucial role in quantifying its effectiveness as a greenhouse gas. Critics of the IPCC reports often overlook this fact, as they tend to argue on the basis of few dominant absorption lines.

We also do not consider different greenhouse gases such as water vapor or possible interactions with it. The case of water vapor is far more complex, because it also involves phase transitions and even chemical reactions. In addition, CO_2 reacts with water droplets to form H_2CO_3, $(HCO_3)^-$, etc. possessing very different infrared (IR) absorption bands

than H_2O vapor or CO_2. These chemical interactions are important in the oceans but not in the atmosphere, because the reactivity in the latter is quite low.

To reduce the calculation effort, we make the following principal assumptions. Firstly, we consider the earth as a homogeneous black body emitter of T = 288 K corresponding to the yearly mean temperature. This temperature is based on satellite observations. Secondly, the atmosphere can absorb IR radiation only thanks to CO_2. We do not consider any albedo effect. Thirdly, the CO_2 concentration follows the barometric pressure of the atmosphere thanks to atmospheric turbulences. Fourthly, we neglect all possible chemical reactions of CO_2.

We briefly review in Section II Planck's radiation and the related Stefan-Boltzmann law. We discuss the main features of the IR absorption in Section III and crudely model the CO_2 concentration of the actual atmosphere. From this model, we calculate the highest possible absorption of the IR radiation by the CO_2. We present the results together with a discussion in Section IV. The conclusions are drawn in the final section V.

II. Planck's radiation and the Stefan-Boltzmann law

At the absolute temperature, T, of a black body, its radiation density per steradian within a small reduced energy interval, du, is given by

$$dS = \sigma_S T^4 f(u)\, du, \tag{1}$$

where u is defined as

$$u = h\nu / k_B T, \tag{2}$$

with

$$f(u) = (15 / \pi^4)\, u^3 / (e^u - 1). \tag{3}$$

The symbols have the following meaning: The Stefan-Boltzmann constant, σ_S; Planck's constant, h; Boltzmann's constant, k_B; and the frequency of the light ν. The integral of the distribution function, f(u), over du from 0 to ∞ is unity. This yields the Stefan-Boltzmann law; the total radiation intensity per steradian of a black body is equal to $S_0 = \sigma_S T^4$. The maximum of f(u) for T = 288 K occurs at $u = u_{max} = 2.8214$ with $f(u_{max}) = 0.2189$. A small temperature increment, ΔT, necessitates a radiative intensity increase, F, given by

$$F \approx 4\, \sigma_S T^3\, \Delta T = 4\, S_0\, (\Delta T / T). \tag{4}$$

Conversely, if we calculate the absorption of the green house gas CO_2 as a function of its concentration, c_{co2}, and assume that all its absorbed energy is converted into heat, we can

use Eq. (4) to establish an upper limit of the temperature increase, ΔT_{max}. Accordingly, we only need precise information of the CO_2 absorption in the spectral IR region.

III. Absorption of radiation by CO_2

An individual CO_2 molecule displays an absorption spectrum consisting only of discrete lines that are broadened by the Doppler effect and collisions with the dominant atmospheric gases N_2, O_2, Ar. The simple linear arrangement of its atoms indicated by O-C-O allows only for 2 principal bond stretching, 1 bending, and 1 rotational modes that lead to infrared absorption. Combinations of the natural isotopes of C and O yield a sizeable number of absorption lines. In addition, the superposition involving rotational states results in a huge number of lines that are distributed over the entire infrared spectrum. The strongest lines occur near the wavelengths, $\lambda = 15$ μm and $\lambda = 4.25$ μm. We note that the 15 μm lines with $u \approx 3.33$ are sufficiently close to $u_{max} = 2.8214$ to provide a good overlap with the black body radiation. The even stronger lines at $\lambda = 4.25$ μm, $u = 11.75$, experience a 100 times smaller overlap with the black body radiation than the lines near 15 μm. Accordingly, this band can only contribute little to the absorbed energy. The huge numbers of very weak lines distributed over the whole IR spectrum nevertheless contribute to the absorption in a non-negligible fashion. We note that many weak lines near 10 μm make the CO_2 laser possible. The HITRAN data [6] comprehensively list more than 400'000 discrete lines distributed over the whole IR spectrum. We label them with an arbitrary number j. For the absorption calculations, we include all lines within $2.9\ \mu m < \lambda(j) < 29\ \mu m$ roughly corresponding to $1.7 < u(j) < 17$. According to the HITRAN data, this involves over 200'000 lines that we have taken into account for our calculations. These transitions are subject to the selection rules of the quantum mechanics. We emphasize, the lines can only contribute to the absorption, if their corresponding ground state, $E_v(j)$, is occupied and their corresponding upper state $E_c(j)$ is empty with $u(j) = [E_c(j) - E_v(j)] / k_B T$. The Boltzmann statistics governs the probability of occupation [7], $p_{v,\,c}(j) = \exp(-E_{v,\,c}(j)/ k_B T)$. The absorption likelihood and thus the absorbance of a specific line is proportional to the product $p_v(j)\,(1 - p_c(j))$. The HITRAN data provides all the necessary data to correctly calculate the IR absorption including $E_v(j)$. In the following, we represent the normalized frequency and the full width at halfwidth maximum u_j and Δu_j respectively.

After an absorption event, the CO_2 molecule is in an excited state with an estimated lifetime, $\tau_{rad} = (u_j / \Delta u_j)^2 / \nu \approx 6$ μs for the 15 μm lines. This corresponds to the spontaneous radiative decay rate, $R_{rad} = 1.7 \times 10^5\ s^{-1}$. Collisions with the dominant gases of the atmosphere lead to a non-radiative decay. At sea level and T = 288 K, the collision rate of all gas molecules is approximately the inverse of the mean free time between collision. Its value is $7 \times 10^9\ s^{-1}$. The present CO_2 concentration amounts to $c_{co2} = 400$ ppm. This leads to a non-radiative collision rate with the CO_2 $R_{non} = 28 \times 10^5\ s^{-1}$. The chances of radiative emission in this situation is given by $R_{rad} / (R_{rad} + R_{non}) \approx 0.06$. In the troposphere, where most of the absorption takes place, most of the absorbed energy by the CO_2 heats the dominant atmospheric gases. This is, however, no longer the case in the stratosphere and even higher levels, where the collision rate is dramatically decreased.

The atmosphere exhibits a strong pressure and temperature dependence with the height above sea level, x. The absorption strength strongly depends on the resulting large CO_2 concentration variation. To keep the calculation manageable, we make a number of additional simplifying assumptions. Firstly, we consider an isothermal atmosphere of T = 288 K with an exponential barometric pressure dependence. The characteristic barometric height at which the pressure falls to 1 / e compared to that at sea level is $x_0 = 7996$ m [8]. The constant temperature assumption is contrary to experience. It tends to overestimate the absorption, because the temperature decreases for all x < 12 km. Reduced temperatures imply decreased ground state probabilities and reduced absorption. Secondly, the half widths of the absorption lines include collision and Doppler broadening. These values are also reduced at high atmospheric levels. This fact again leads to a slight overestimation of the absorption. We approximate the CO_2 absorption for a given line by

$$\alpha(x, u_j) = \alpha_0(u_j) \exp(- x / x_0), \tag{5}$$

where $\alpha_0(u_j)$ represents the absorbance of the line j at sea level.

To calculate the absorption of our atmosphere, we use Fig. 1 that describes the geometry and the variables. The radius of the earth is R = 6371 km. The elementary surface element, dA, is situated at an arbitrary point, P_0, and has the value $dA = R^2 \sin\varphi \, d\varphi \, d\phi$. It radiates into 2π steradian. The angle, ϕ, is in the plane perpendicular to the axe OP. We want to calculate the elementary excitation at the point P. To do so, we need to consider an arbitrary intermediate point Q at the distance ρ from P_0. The intensity of the elementary radiation, $\delta I(\rho, u)$, propagating in a lossy medium represented by a variable absorption, $\alpha(\rho, u_j)$, follows the differential expression

$$d\delta I(\rho, u_j) + (2 / \rho + \alpha(\rho, u_j)) \, \delta I(\rho,u_j) \, d\rho = 0. \tag{6}$$

The position of the wave front is at ρ, and $d\rho$ is a small distance perpendicular to it. The product of absorbance and intensity represents the locally absorbed energy per second and per unit volume. To calculate the elementary excitation at the point P we have to integrate Eq. (6) over the distance, r, given by P_0P. We arbitrarily choose P to be situated at $x_h \gg R$ above sea level to ascertain that $\alpha(x, u_j)$ of Eq. (5) becomes negligibly small. The running height above sea level is $x = \rho \cos\theta$. The intensity of the elementary excitation at the point P becomes with the aid of Eq. (1) and Eqs. (5 and 6)

$$dI (x_h, u_j) = (1 + x_h / R)^2 \, (S_0 / 2\pi) \cos\theta \, f(u_j) \, \Delta u_j \, r^{-2} \, \exp[-\int_0^r \alpha(\rho, u_j) \, d\rho] dA. \tag{7}$$

The first factor is necessary to normalize the radiation intensity to the surface of the earth. The product $(S_0 / 2\pi) \cos\theta \, f(u_j) \, \Delta u_j$ represents the elementary radiation within the bandwidth Δu_j. The $\cos\theta$ factor is necessary, because the unit vector of the surface element makes an angle, θ, to the direction of ρ. None of the variables depend on ϕ. Its trivial integration yields 2π. We can simplify Eq. (7) considerably by putting P at infinity

that yields $\cos\theta = \cos\varphi$, and $(R / r)^2 (1 + x_h / R)^2 = 1$. The absorbed power $I_a(u_j)$ for a given line j due to the elementary excitation at P_0 after integration over $d\phi$ becomes

$$dI_a(u_j) = S_0 f(u_j) \Delta u_j \cos\varphi \{1 - \exp[-\int_0^r \alpha(\rho, u_j) d\rho]\} \sin\varphi \, d\varphi. \quad (8)$$

The total absorbed energy, F, is given by integrating over $d\varphi$ from 0 to $\varphi = \pi/2$ and by summing over all absorption lines. Details of this elementary calculation are given in Appendix I.

$$F = \sum_j I_a(u_j). \quad (9)$$

In Eq. (9), we have neglected the possible IR absorption and re-radiation effect known as photon recycling. Close to sea level this effect is small because of the highly non-radiative collision processes described above. In the lower stratosphere ($x > 24$ km), collisions events become significantly reduced and photon recycling more important. This effect also tends to reduce F. As a consequence, the value obtained from Eq. (9) represents definitely an upper limit of the heat retention. At the present T = 288 K, F is already included for $c_{co2} = 400$ ppm. Accordingly, we have to reduce it to $\Delta F = F(c_{co2}) - F(400\ ppm)$. The concomitant temperature increase is obtained from ΔF with Eq. (4). Since all values of F represent upper limits, we call them from now on F_{max} and ΔF_{max}. It also is justified to call the calculated temperature increase ΔT_{max}. From now on, we refer to the calculated values only as ΔF_{max} and ΔT_{max}. Realistic estimates of ΔF and ΔT can be obtained by introducing a reduction factor, $f < 1$. Satellite observations of IR radiation permit a rough estimate [9], $f \approx 0.7$.

IV. Results and Discussion

We have calculated ΔF_{max} and ΔT_{max} for four concentrations namely 400 ppm, 800 ppm, 2000 ppm and 4000 ppm. The results are listed in Table I. They can be quite accurately fitted with logarithmic concentration dependence. We get the following expressions for $\Delta F_{max} / Wm^{-2}$ and $\Delta T_{max} / K$, if we measure c_{co2} in ppm and normalize it to 400 ppm.

$$\Delta F_{max} = 1.881 \log_e (c_{co2} / 400), \quad (10)$$

and

$$\Delta T_{max} = 0.347 \log_e (c_{co2} / 400). \quad (11)$$

The maximum deviation from the values given in Table I. by using Eq. (11) is 0.02 K. It is noteworthy that the logarithmic concentration dependence of Eqs. (10 and 11) is contrary to the assertion of some IPCC critics that claim a saturation of both ΔF and ΔT with increased CO_2 concentration [9, 10]. Their argument would only be acceptable, if the number of absorption lines would be limited to a small number of weak absorption lines.

This unfortunately is not the case as clearly shown by the HITRAN data. Furthermore, we also notice in Table I that the band B2 slightly increases its contribution relative to that of B1; a clear signature of the role of the weak bands.

A doubling of the present level of c_{co2} results in $\Delta T < 0.24$ K. The tenfold value of c_{co2} yields $\Delta T < 0.80$ K. These moderate temperature increases are not critical at all. If we maintain an annual c_{co2} increase of 1.2%, it takes almost two centuries to reach this tenfold value. Therefore, mankind has plenty time to adapt. At pre-industrial times, we had $c_{co2} = 285$ ppm. The resulting temperature increase according to Eq. (11) only amounts to $\Delta T < 0.12$ K. This value shows clearly that the observed increase, $\Delta T_{obs} \approx 1$ K, is much larger than that attributable to CO_2. We notice that the yearly fluctuations are generally much greater than ΔT obtained over this long time interval. Lu[1] establishes a correlation of ΔT with solar activity, cosmic rays and ozone reactions with fluorocarbons in the stratosphere. According to his result, CO_2 only plays a minor role in the temperature evolution since pre-industrial times. Our calculation is compatible with his finding. His thesis about fluorocarbon-ozone reactions being dominant for the warming is very interesting. We note that photonic solar radiation fluctuations [11] are near 1 Wm^{-2}, but the particle flux variations, only a small fraction of the total energy flux, are far more important for chemistry and water vapor condensation.

Based on all these facts, we assert that CO_2 is a very weak and innocent green house gas. We emphasize that our simplifying assumptions are by no means trying to minimize the absorption potential of CO_2. To the contrary, they lead to overestimating the limiting values. The assumption of a constant temperature and black body radiation definitely violates reality and even the principles of thermodynamics. But this is not of great importance, because we are only interested in an upper limit. Furthermore, the calculations are based on integration yielding a smoothing effect. The uncertainty of T = 288 K of a few degrees slightly affects S_0 and the results. A 3 K uncertainty yields $\Delta S_0/S_0 \sim 4.2\%$.

Our upper limit of the temperature increase is considerably lower than even the lowest one given by the recent IPCC report of 2014. We agree with their functional form, but strongly disagree with their magnitude. In a test calculation, we use the identical HITRAN data without taking the occupation probabilities of the CO_2 energy states into account. In this fashion, we get ΔF_{max} and ΔT_{max} close to six times higher than the ones given in Table I, thereby approaching the ones of the IPCC reports [2-5]. Also the contribution by the Band B2 becomes over 3 times that shown in Table I. We also suspect that the omission of the cos φ factor in Eq. (8) contributes to overestimating by at least another factor of two. The catastrophic temperature increases predicted by the IPCC, therefore, have no scientific justifications and are simply based on false premises. The principal error is probably caused by the lack of considering the occupation probabilities of the energy levels by the IPCC.

There remains the question of the existence of feedback. This effect is thought to amplify or attenuate a small temperature change. Such mechanisms are easy to imagine, but they are extremely difficult to quantify and to observe. Lindzen [12] has tried to observe

feedback by complicated correlation studies. He found a tendency to negative feedback that attenuates induced temperature changes. This is quite comforting, because the weak CO_2 concentration effect is, therefore, not magnified.

V. Conclusion

Our results clearly demonstrate that CO_2 is a very weak green house gas and cannot be brought into connection with the anthropogenic climate change. The observed temperature increase since pre-industrial times is close to an order of magnitude higher than that attributable to CO_2. We find that the increase of CO_2 only might become dangerous, if the concentrations are considerably greater than 4000 ppm. At present rates of increase this would take more than 200 years. Accordingly, demands for sequestering CO_2 are completely unjustified and the issue and trading of CO_2 certificates is an economic absurdity. The apparent climate change must have a very different origin and the scientific community would be well advised to look for causes of climate change that can be solidly based on physics and chemistry.

This paper must not, however, become a pretext for unlimited burning of fossil fuels. Incomplete oxidization together with heavy metal, aerosol and radioactivity emissions could be harmful to the health and the environment.

Acknowledgements

It is a great pleasure to acknowledge H. Baumann , J. Lüthi, H. R. Müller, and H. van den Bergh for stimulating discussions. In addition, I want to especially thank my colleagues, P. Jacquot, T. Lasser, and R. P. Salathé for also critical reading this manuscript.

Appendix I

The integral over the running distance, ρ, in Eqs. (7 and 8) is readily evaluated by replacing x with ρ cos θ yielding

$$\alpha(\rho, uj) = \alpha_0(u_j) \exp(- \rho \cos \theta / x_0). \quad \text{(A1)}$$

The integral becomes

$$\exp[-\int_0^r \alpha(\rho, u_j)\, d\rho] = \exp\{- x_0\, \alpha_0(u_j)[1 - \exp(- r \cos \theta / x_0)] / \cos \theta \} \equiv I_e(r, \theta, u_j). \quad \text{(A2)}$$

For $r = \infty$, we get with $\theta = \varphi < \pi/2$

$$I_e(\varphi, u_j) = \exp[- x_0\, \alpha_0(u_j) / \cos \varphi]. \quad \text{(A3)}$$

With Eq. (A3), we have to integrate the differential expression of Eq. (8) over dφ from 0 to π/2. We obtain

$$I_a(u_j) = S_0\, f(u_j)\, \Delta u_j \int_0^{\pi/2} [\, 1 - I_e(\varphi, u_j)\,] \cos \varphi \sin \varphi \, d\varphi. \quad \text{(A4)}$$

References

1. Q.-B. Lu, Int. J.Mod. Phys. **B27**, No. 17, (2013) 1350073

2. A. Lacis, J. Hansen, P. Lee, T. Mitchell, and S. Lebedeff, Geophys. Res. Lett. **8,** 1035-1038 (1981)

3. J. Hansen, I. Fung, A. Lacis, D.Rind, S. Lebedeff, R. Ruedy, G. Russell, and P. Stone, J. Geophys. Res. **93**, 9341-9364 (1988)

4. First Assessment Report 1990, Chapter 2, Radiative Forcing of Climate by K.P.Shine et al.

5. IPCC 2013 Working Group II report

6. http://www.cfa.harvard.edu/hitran/ and L.S. Rothman et al. J. Quant. Spect. and Rad. Transfer **110**, 533-572 (2009). We use the CDSD-296 databank. The 2012 HITRAN version complements the near infrared data that is of no concern for this study

7. Gerhard Herzberg, ‘‘Molecular Spectra and Molecular Structure: II, Infrared and Raman Spectra of Polyatomic Molecules’’, Van Nostrand Reinhold, New York, 1945

8. F. K. Reinhart, unpublished

9. N. Kalmanovitch: 58_GEOCANADA_2010_ABSTRACT_Norm_Kalmanovitch.pdf

10. H. Hug, A spectroscopic artifact: www.john-daly.com/**artifact**.htm

11. C. Fröhlich, Space Sci. Rev. **176**, 237-252, (2013)

12. R. S. Lindzen and Y.-S. Choi, Geophys. Res. Letters, **36**, L16705, (2009), doi: 10.1029/2009GL039628

Table Caption

Table I: Upper limit for infrared radiation retention and corresponding temperature increases for four different CO_2 concentrations. B1 and B2 stand for the percentage contribution of the absorption bands within the limits $1.72 < u < 3.62$ and $3.62 < u < 17.2$ respectively. The corresponding wavelength limits are $29\ \mu m > \lambda > 13.8\ \mu m$ and $13.8\ \mu m > \lambda > 2.9\ \mu m$.

Figure Caption

Fig. 1. The geometry considered for the integration and the identification of the variables. The radius of the earth is R = 6371 km. The surface element is at the point P_0. The distances P_0P and P_0Q are r and ρ respectively. The angles are shown with greek letters. The angular variable, ϕ, around the axe OP is not shown. Θ approaches φ for P going towards infinity.

Table I

c_{CO2} / ppm	400	800	2000	4000
F_{max} / Wm^{-2}	5.600	6.900	8.595	9.943
ΔF_{max} / Wm^{-2}	0	1.300	2.995	4.342
ΔT_{max} / K	0	0.240	0.553	0.802
B1 %	97.61	97.17	96.73	96.49
B2 %	2.39	2.83	3.27	3.51

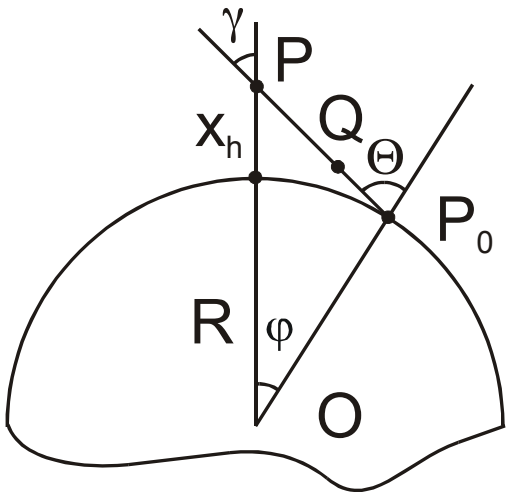

Fig. 1