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Qualitative Considerations on the Influence of the Gases Water Vapor and Carbon Dioxide on the Global Environmental Temperature from the Point of View of Textbook Knowledge

Wolfram Vogelsberger

Institute of Physical Chemistry, Chemistry and Earth Science Faculty, Friedrich-Schiller-University, Jena, Germany
Email: wolfram.vogelsberger@uni-jena.de

Abstract

The solar radiation that hits the Earth conditions the dynamic equilibrium that prevails on our planet. Consideration of basic physical-chemical knowledge shows that this equilibrium can be changed only by additional energy input or prolongation of the interaction time solar radiation—Earth matter. The contribution of $H_2O(g)$ and CO_2 to the protection of the earth against excessive warming is experimentally and by basic laws of nature secured. For a greenhouse effect, a part of the earth radiation must be radiated back to the earth and then into space. If one understands the earth radiation as radiation of a black body with the average global environmental temperature, from all vibrations normal modes of the gases $H_2O(g)$ and CO_2 only the bending mode of CO_2 with 4% of the solar constant can contribute beside the rotational modes of the water to the greenhouse effect. The contributions of the normal modes of $H_2O(g)$ and CO_2 to the heat capacity of the atmosphere are negligible. Therefore, in agreement with studies by K. Ångström, CO_2 contributes only to the stabilization of the global environmental temperature. Whether the use of renewable energies can actually at least mitigate the increase of the environmental temperature is by no means certain but must be examined for each individual case. With certainty, this goal can only be achieved by reducing the energy consumption of mankind.

Keywords

Global Temperature, Irradiation, Dynamic Equilibrium, Heat Capacity, Greenhouse Effect

1. Introduction

The influence of water vapor, $H_2O(g)$ and CO_2 on the global environmental temperature is extensively discussed also in the daily press. The great interest in this problematic is understandable since an increase of the global temperature of the atmosphere changes the living conditions for plants and animals drastically in part, so that species may die out. In particular, a currently observed increase in mean environmental temperature is attributed to human activities and attributed to the influence of CO_2 in the atmosphere [1] [2], while water receives little mention. The temperature rise is mainly attributed to a greenhouse effect caused by an increased concentration of greenhouse gases in the atmosphere. Among these gases, CO_2 is attributed a major role. The rise in temperature is manmade and could be prevented if processes that generate CO_2 were largely avoided. CO_2 is declared a climate killer.

Extreme weather phenomena, which of course have always existed in the history of the earth, are attributed to the increased CO_2 content in the atmosphere. However, it is obvious that weather is caused by air movements and changes in the aggregate state of water. Thereby the influence of clouds (water vapor) is known to everyone from own experience. These changes of the aggregate states regulate the temperature since they are connected with phase transition enthalpies. Details can be found in reference [3] and references therein. Therefore, at this point of the discussion this cloud—effect is not considered, although it is crucial for our weather as stated.

We want to examine here the influence of the two gases $H_2O(g)$ and CO_2 somewhat more near. A suggestion for this work is given by measurements of K. Ångström [4]. He investigated the solar radiation at an altitude of 3200 m with an apparatus consisting of two tubes, one filled with air and the other with CO_2 at atmospheric pressure. He found no significant difference in the passage of sunlight through the two tubes. From this fact he concluded that the frequencies of sunlight relevant to CO_2 had already been screened by the atmosphere. He wrote: "*Nach dieser Untersuchung scheint es also hervorzugehen, dass das Absorptionsvermögen der Kohlensäure in dem Bande Y so kräftig ist, dass die bezügliche Absorption schon vollendet ist, bevor die Strahlung zu uns anlangt,*" ("According to this investigation, it appears that the absorption capacity of carbonic acid in band Y is so strong that the relevant absorption is already completed before the radiation reaches us,") This statement is particularly remarkable, since he compared volumes without CO_2 with an atmosphere consisting entirely of CO_2. The CO_2-portion in his experiment was 100% compared to 0.4‰ in today's atmosphere. Almost every interested citizen believes to have a well-founded opinion on this problem and relies on supposedly generally accepted views for his considerations. Since a very large number of results are available, which reported especially on investigations with electromagnetic radiation, it is not difficult to find works, which support also in the result opposite opinions. In view of this fact, it seems superfluous to waste any more thoughts on this prob-

lem area, especially since these considerations, as stated in the title, are based on textbook knowledge and contain only qualitative statements. However, it must be taken into account that these statements are based on widely accepted basic knowledge and do not require any new assumptions. The qualitative character of the statements is understandable in view of the complexity of the numerous influences on the temperature of our environment and does not only apply to the facts presented here. That textbook knowledge of all things should provide a new perspective on the problem seems at least very surprising, considering the almost endless variety of statements on this problem. In order to be understood by as many readers as possible, we choose as starting point of our considerations the status report of the German Bundestag Carbon Dioxide [5]. Some of the connections and facts presented in this paper may seem superfluous to a scientifically educated reader. However, since the essay is intended to address as many interested people as possible, a somewhat more comprehensive form of presentation has been chosen. Our main focus is on the vibrational motion of the molecules, since the corresponding excitation energies are in the range of thermal radiation. Further problems, such as the combination of fundamental vibrations or changes of the molecular geometry, are not treated in order to keep the focus on the essential facts. In the first place it is reminded that without water and without carbon dioxide on the earth no aerobic life is possible, therefore it is meaningful with the evaluation of both gases to do without inappropriate drastic statements. Necessarily for both gases also natural regulation mechanisms exist like the change of the aggregate state with water and the interaction of assimilation and dissimilation with carbon dioxide, which control the appropriate processes and prevent undesirable developments. This essay is an attempt to present the role of CO_2 in our environment in a reasonable way and without polemics, using scientific facts that are already presented in textbooks. In the bibliography [6] [7] [8] [9] [10] a number of textbooks are given, in which the scientific connections discussed here can be read. The facts used here are treated in all books, of course also in newer editions, relevant quotations point to particularly suitable representations and are provided with an appropriate reference and the page number. Surprisingly, a picture will emerge which deviates from the usual representations and opinions, and which shows that the greatest care is required, especially in such an existential question as the assessment of the influence of humans on the global environmental temperature. It is certainly superfluous at this point to point out once again that mankind can only change the influences on the global temperature that it has caused itself.

2. The Possibilities of Energy Storage of Molecules

The differential temperature change, dT, in the transfer of thermal energy, dQ, to a body is described by Kirchhoff's law [6]

$$dQ = C dT . \tag{1}$$

C is the heat capacity of the body. The difference between processes occurring at constant volume or constant pressure will be pointed out at the appropriate places, if necessary. In order to understand energetic effects and transformations in our living space it is necessary to get an overview of the ways in which molecules and atoms can absorb energy. In the following we will only speak of molecules, atoms are included if necessary. In the order of decreasing energy these are 1) the electron—excitation (changes in the electron shell of the molecules). We do not consider this form of energy storage for the moment. The possibilities 2 - 4 are movements of the molecules as a whole or the change of the distances of their single components to each other, 2) excitation of molecular vibrations (change of distances to each other in molecules), 3) rotational movements of molecules (rotation of molecules around a rotation axis), 4) movement of molecules as a whole in space. Each of these forms of motion involves several possibilities. As an example, we consider the motion in space (translation), it assumes excitation in three independent spatial directions. Each of these possibilities is called a mode of motion of the molecule, which can absorb energy. This energy depends on the temperature, T, at which the molecules are located. It has been shown that at moderate temperatures, such as those encountered in our environment, the same energy $E_M = 1/2\ kT$ is absorbed by each mode (k = Boltzmann constant). This is the equipartition theorem of energy [7]. (vibratioal modes count twice because potential and kinetic energy can be energetically excited independently). The concentration in the atmosphere of the gases we consider, $H_2O(g)$ and CO_2, depends on the prevailing temperature and pressure. Furthermore, the concentration in the case of water vapor is influenced by possible changes of state of aggregation and in the case of CO_2 assimilation and dissimilation of living organisms, which illustrates the complexity of the situation. In this consideration, we restrict ourselves to a gas volume of $V = 1$ m³ a total pressure $p = 1 \times 10^5$ Pa and the constant CO_2 amount of substance $n_{CO_2} = 0.0167$ mol (Corresponds to 400 ppm, taken from the Keeling—curve [11] [12] at the temperature = 14.5˚C) as well as the H_2O—partial pressure, p_{H_2O}, in the temperature range $0˚C < \vartheta < 40˚C$ [13]. The partial pressure ratio, p_{H_2O}/p_{CO_2}, for both gases under the indicated conditions is shown Figure 1. It can be seen that in the range of standard temperature $\vartheta = 25˚C$, the pressure ratio for saturation $p_{H_2O}/p_{CO_2} = 79$ and for 75% saturation $p_{H_2O}/p_{CO_2} = 31$ and 50% saturation $p_{H_2O}/p_{CO_2} = 21$. The concentration of water vapor considerably exceeds that of CO_2 at the indicated humidity. In addition to its concentration in the atmosphere, two energetic effects based on molecular properties are relevant. The one effect to be considered with influence on ambient temperature is thermal degradation. It takes into account that in electronically excited states all the other molecular modes are also excited and can give off some of their energy to the surrounding by radiative or nonradiative decay. The second effect of the molecules is that they absorb the heat radiation coming from a source and then radiate it in all spatial directions.
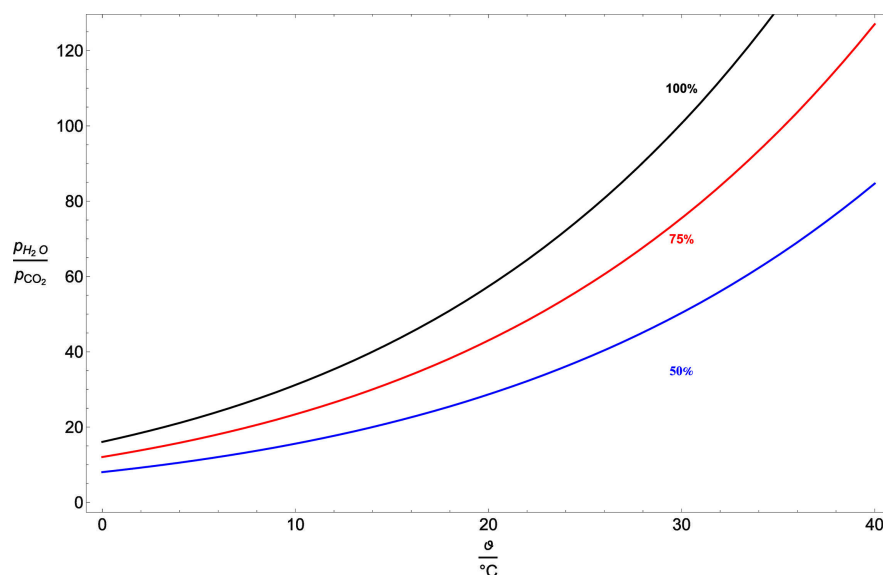
Figure 1. Ratio of the partial pressures p_{H_2O}/p_{CO_2} at different moistures as function of temperature.

Applied to the sun-earth system with its atmosphere, this means that molecules in the atmosphere can reflect solar energy back towards space, thus reducing this contribution of solar energy to global warming (protection against excessive temperature rise). The reverse case, that molecules in the atmosphere absorb heat energy radiated from the Earth and radiated some back toward the Earth, can also occur, of course. This heat energy radiated back to the earth has again the possibility to interact with other partners and contribute to the increase of the environmental temperature. This mechanism is called the greenhouse effect. Since thermal radiation is preferentially in the infrared spectral region, where molecular vibrations can also interact with energy, this region of the electromagnetic spectrum is particularly relevant to our considerations. In the following discussion we limit ourselves to this range, since we want to investigate the influence of the gases $H_2O(g)$ and CO_2 on the environmental temperature.

3. The Dynamic Equilibrium: Solar Energy, Global Warming, Energy Radiation

All forms of energy and storage occurring on earth originate from the sun. There is a dynamic equilibrium. The essence of this dynamic thermal equilibrium is that energy is radiated onto a body, E_S, until the energy radiated from the body, E_L, has the same value, $E_L = E_S$. This irradiation causes the temperature of the body to change until this condition is met. The temperature of the body is the driving force for the radiation. The temperature of the body can be changed in several ways. 1) One way is to change the amount of energy supplied, ΔE. In this case, the temperature of the body changes until $E_S + \Delta E = E_L + \Delta E$ again is valid. The additional energy can come from another energy source or be stored in

some form in the body. 2) Another possibility is that the contact time between the body and the energy supply is changed. A change of the interaction time energy—molecules from which the body is built up changes the temperature of the body until again $E_S = E_L$ is fulfilled. The intensity of the solar radiation arriving above the earth at the end of the atmosphere is given by the solar constant, $E_0 = 1367$ W·m^{-2}. This value is an average value that has been set as a standard by the World Meteorological Organization. It is set as 100%. The energetic situation in a near-surface volume, whose boundaries can be arbitrary (system) is shown in Scheme 1.

The scheme is highly simplified and the power data essential for our considerations are taken from the Sachstandsbericht of the German government [5] and given in the scheme as % of E_0. Only the energy components essential for our considerations are shown. These are: 1) the radiated energy, the solar constant, E_0, and the energy arriving and absorbed on the earth's surface, E_A (yellow color), 2) the energy radiated back to space unchanged by the atmosphere, E_R^0, and by the Earth's surface, E_R, respectively (gray color), 3) the energy radiated from the Earth or atmosphere after absorption, E_E and E_E^0 (red color) 4) the energy radiated after interaction with the molecules of the atmosphere, E_T (greenhouse effect, green color) 5) additional energy possibly added to the system and reflected after the interaction, E_F (magenta color). All these energies are related as usual to an area, $F = 1$ m^2 and an exposure time of t s (powers with $t = 1$ s unit W·m^{-2}). In the dynamic equilibrium, the energy supplied and the energy radiated are equal in magnitude, the energy of the system is constant.

$$E_0 - E_R - E_R^0 = E_A = E_E^0 + E_T = \text{constant} \qquad (2)$$

A peculiarity is observed for the energy, E_T, which causes the greenhouse effect. Due to absorption emission and reflection, its residence time in the system is tripled compared to the part E_A^0. This is indicated in the scheme by the two additional arrows with dashed border. The interaction time with the molecules of the system is prolonged, thus the heat transfer to the system increases, its temperature is in this way slightly increased compared to the case without additional absorption emission and reflection. Before determining how the temperature in the system can be changed, the basic course of changes in the system is summarized. The system is initially in dynamic equilibrium. The temperature of the system increases due to the energy supply. A new dynamic equilibrium state is established. The same reasoning applies, of course, to a withdrawal of energy from the system and the associated decrease in temperature. Now some possibilities for the temperature change of the system shall be considered. 1) The energy $Q_F = F·t·E_F$ is supplied to the system, see Scheme 1. The energy supply takes place over the area, F, in the time, t. Thus, the corresponding power E_F, which must be considered in our energetic considerations, depends on both quantities and consequently they must be known. It is valid

$$\Delta T = \frac{Q_F}{C} = \frac{F \cdot t \cdot E_F}{C} \qquad (3)$$

Energetic Balanceof a Volumeof the Atmosphere Near to the Surface
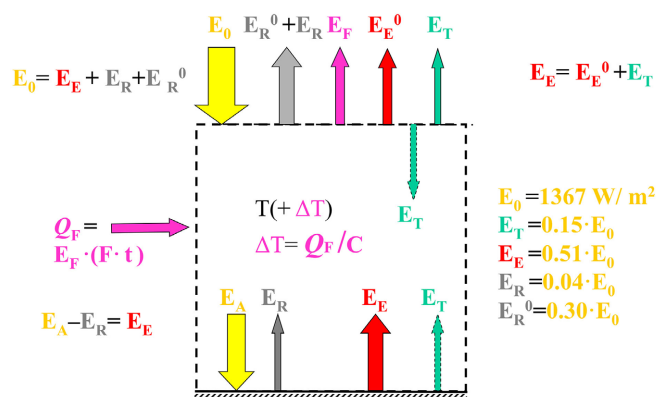
Scheme 1. Symbolic representation of the energetic balance in the atmosphere.

Since the area of 1 m² is considered, it is evident from Equation (3) that the temperature change increases with the exposure time. After setting the increased temperature, $T + \Delta T$ (enhanced driving force), E_F is naturally released by the system, because there is a somewhat changed equilibrium compared to the initial equilibrium ($E_A + E_F = E_E + E_F$). 2) The additional energy can of course also come from an energy depot that was created at an earlier time (fossil energy sources).

3) The energy is taken from the reflected energy E_R^0 or E_R *i.e.* these proportions become smaller. Because of the constancy of E_0, E_A increases and the temperature in the system increases according to Equation (3). 4) Another case is the use of a part of the energy E_A for work output. In this case, there should be no influence on the system temperature because the energy remains in the system and is radiated as heat at the end of the process. However, if the energy is stored before it is used, it will be missing in the dynamic equilibrium, an intermediate cooling will occur, which will be compensated when it is used. If, however, the missing energy in the dynamic equilibrium is compensated in the meantime by the abundant solar energy, a temperature increase results during use. 5) The following considerations are intended to contribute to an influence of the environmental temperature by gaseous components of the atmosphere, a possible greenhouse effect.

4. The Spectrum of Solar Radiation and Its Interaction with the Vibrational Normal Modes of Gaseous Water and Carbon Dioxide

The frequency—or wavelength—distribution, $E_\nu d\nu = E_\lambda d\lambda$, of solar radiation on the Earth is very well described by Planck's radiation law, Equation (4) [8]. In the following consideration, the wavelength representation is used.

$$E = \frac{2 \cdot \pi \cdot h \cdot c^2 \cdot K_\lambda}{\lambda^5} \left\{ \frac{1}{\exp\left[\dfrac{h \cdot c}{k \cdot \lambda \cdot T}\right] - 1} \right\} \tag{4}$$

h = Planck's constant, c = speed of light, k = Boltzmann constant, λ = wavelength of radiation (to be used in units of m), T = absolute temperature, and K_λ = 2.13×10^{-11} m/µm is a constant to be determined so that the integral over all wavelengths of the solar spectrum at the solar temperature of T = 5800 K used in this paper, gives the solar constant, E_0. The solar temperature given is in good agreement with measured data.

In Figure 2 the intensity of solar radiation is plotted as a function of the wavelength of the solar spectrum according to Planck's formula (The abscissa is scaled logarithmically). All curves are shown as interpolation formulas and thus can be easily integrated [14]. The black continuous curve, A, corresponds to a solar temperature of 5800 K. The black jagged curve, B, indicates the power actually arriving on Earth. It depends on the angle of incidence sun—observer and is given as "air-mass", AM (perpendicular incidence: AM = 1). A corresponding representation used as reference for the radiation arriving on earth, AM = 1.5, is to be found in numerous places also in the Internet e.g. [5] [15] [16]. Furthermore, the energy radiated back from the Earth into space is also plotted in Figure 2, and this will be discussed later. (The black and the red jagged curve are interpolation functions, which were created by taking over some points from the indicated representations, they reflect the ratios qualitatively).

Comparing the integration result over both curves A and B in the wavelength range 0.3 µm < λ < 100.0 µm, we find that the atmosphere protects the Earth's surface from about one-third (ΔE = 36.2%) of the solar irradiance. Considering our qualitative considerations, this quantity is in good agreement with the data in ref, [5], $E_R^0 + E_R = 34\%$. In the part of the infrared spectral range, 0.8 µm < λ < 20.0 µm, by integrating both curves, we find that the difference between them is also about one third (36.1%). In this wavelength range and even further into the infrared region, the vibrations of H_2O and CO_2 also lie, see Table 1 (The normal modes can combine additively or subtractively). All listed vibration modes of H_2O and CO_2, contribute to the shielding in the infrared spectral region. Both gases have therefore protected the Earth's surface in this wavelength range from about one third of the thermal radiation sent to Earth by the Sun, thus preventing excessive heating of the atmosphere. For excitation of each vibrational mode of the molecules H_2O and CO_2, the energy $E_\nu = kT = h\nu = hc\tilde{\nu}$ is available at complete excitation. The corresponding molar energy values and the associated wavenumbers are given for the various normal vibrations in Table 1.

Table 1. Spectroscopic quantities of $H_2O(g)$ and CO_2.

Molekule	$\tilde{\nu}/cm^{-1}$	$\lambda/µm$	ν/PHz	$E/kJmol^{-1}$	Θ/K	$C_V^{\,\vartheta}/J \cdot K^{-1} \cdot m^{-3}$
H_2O Normal-modes	$\tilde{\nu}_1 = 3656.7$	$\lambda_1 = 2.73$	$\nu_1 = 0.11$	$E_1 = 43.74$	$\Theta_1 = 5261.22$	2.2×10^{-5}
	$\tilde{\nu}_2 = 1594.8$	$\lambda_2 = 6.27$	$\nu_2 = 0.05$	$E_2 = 19.08$	$\Theta_2 = 2294.58$	0.13
	$\tilde{\nu}_3 = 3755.8$	$\lambda_3 = 2.66$	$\nu_3 = 0.11$	$E_3 = 44.93$	$\Theta_3 = 5403.81$	1.4×10^{-5}
CO_2 Normal-modes	$\tilde{\nu}_1 = 1388$	$\lambda_1 = 7.20$	$\nu_1 = 0.04$	$E_1 = 16.60$	$\Theta_1 = 1997.04$	6.5×10^{-3}
	$\tilde{\nu}_2 = 667.4$	$\lambda_2 = 14.98$	$\nu_2 = 0.02$	$E_2 = 7.984$	$\Theta_2 = 960.248$	5.9×10^{-2}
	$\tilde{\nu}_3 = 2349$	$\lambda_3 = 4.257$	$\nu_3 = 0.07$	$E_3 = 28.10$	$\Theta_3 = 3379.72$	1.5×10^{-4}
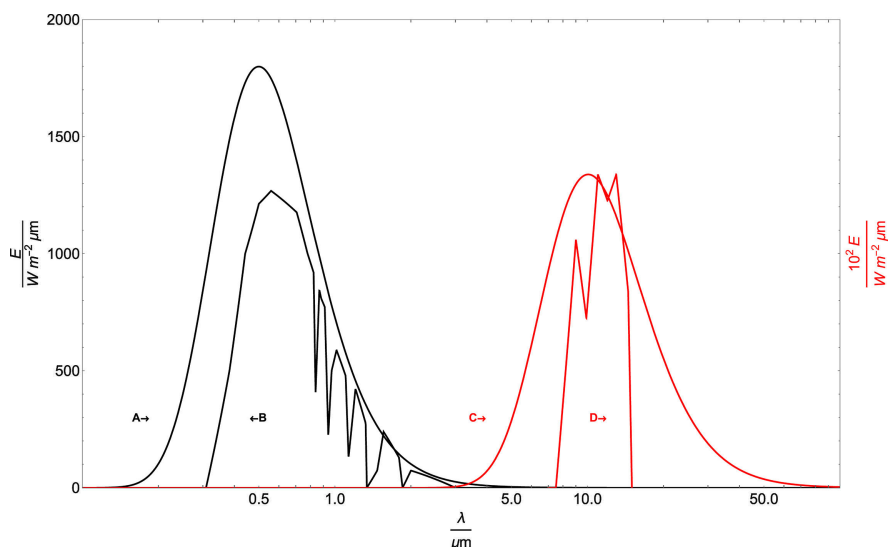
Figure 2. Irradiance spectra for different cases.

In the penultimate column of **Table 1**, the critical temperatures, $\Theta_i = hc\tilde{v}_i/k$, for the various vibrations of the molecules are given. These critical temperatures must be exceeded for a mode to be fully excited and contribute to the full extent, *i.e.*, with $E_v = kT$, to the thermal energy of a molecule. Since a temperature of 5800°C has been assumed for solar radiation, all normal vibrations can be excited and contribute to the shielding effect. In order to explain the greenhouse effect, it is common to take the thermal energy radiated from the Earth as radiation from a black body with temperature $T = 287.65$ K in the Planck sense [5]. The radiation of the black body is characterized by the fact that thermal equilibrium exists between the radiation in the body and the temperature prevailing in the body [8]. This condition must be fulfilled for the following discussion.

The corresponding curve for radiation from a black body with a temperature of $T = 287.65$ K is also shown for $E_E = 697$ W·m⁻² (51% of E^0 [5]) in **Figure 2** (red continuous curve, C). The jagged red curve, D, qualitatively reflects the radiation emanating from the earth [5]. The axis labels on the two energy axes differ by a factor of one hundred, which means that the energy radiation per square meter and second from the Earth is much smaller than the radiation from the Sun. According to Wien's displacement law, Equation (5) [9], the radiation from the Earth has a maximum at a wavelength $\lambda_{max} = 10.07$ μm or a wavenumber $\nu = 992.65$ cm⁻¹ [9], see **Figure 2**.

$$\lambda_{max} = \frac{h \cdot c}{4.965 \cdot k \cdot T} \tag{5}$$

For this reason, especially the bending mode of carbon dioxide, see **Table 1**, can be excited by the Earth radiation. This is not true for the other vibrations of CO_2 and H_2O. **Figure 2** shows that radiation is emitted from the earth in this wavelength range [5]. Integration over the interpolation function (7 μm λ 15 μm) yields 4.83% of E_0. However, no statement is made as to whether excitation

of the molecules CO_2 and H_2O actually occurs. Since the excitation of the molecules may also have occurred by direct solar radiation, excited molecules cannot be distinguished according to the source of their excitation. A statement on this is possible by considering the contribution of normal modes to the heat capacity of our model system. The relationship between the contribution of a vibration mode to the heat capacity at constant volume, C_V, and temperature is given by Equation (6) ([10] p. 552). n is the amount of substance of the gas in the volume $V = 1$ m³ and R_G is the universal gas constant.

$$C_V = n \cdot R_G \left\{ \frac{(\Theta_{schw}/T) e^{-(\Theta_{schw}/2T)}}{1 - e^{-(\Theta_{schw}/T)}} \right\}^2 \tag{6}$$

For the wavenumber of the heat energy radiated from the Earth, at 287.65 K, $\tilde{v}$ = kT/hc = 199.92 cm⁻¹. The heat energy radiated from the Earth is therefore E_{RE} = 2.292 kJ·mol⁻¹. The critical temperatures Θ_i listed in Table 1, which must be reached to excite the molecules as completely as possible, exceed this quantity by far. In other words heat would have to pass from the temperature $T = 287.65$ K to the values given in the table. Such a process is forbidden by the second law of thermodynamics. The total heat capacity of the gas mixture in the volume $V = 1$ m³ is obtained as the sum of the contributions of the gases to the mixture. The calculations are made according to the above statements ($V = 1$ m³, $p = 1 \times 10^5$ Pa, $n_{CO_2} = 0.0167$ mol, $n_{H_2O} = 0.690$ mol). In accordance with our objective, we consider only the vibrational contributions of CO_2 and H_2O. The vibrational contribution to the heat capacity, C_V as a function of temperature is calculated according to Equation (6). It is shown for the different vibration modes of CO_2 and H_2O in Figure 3 for our model volume. At high temperatures, as expected, the value $E_v = kT$ is obtained for each molecular vibration. In the last column of the table, the C_v-values for $T = 287.65$ K, with the relevant amounts of substances of the gases at this temperature, $n_{CO_2} = 0.0167$ mol and, $n_{H_2O} = 0.690$ mol, calculated according to Equation (6), are given for all vibrations C_V^ϑ.

Consequently, none of the vibration modes listed in Table 1, can be involved in the greenhouse effect to any significant extent in the classical picture. The largest contribution to C_V is provided by the bending mode of water (0.1‰ of the total heat capacity). The contributions of the symmetric and the antisymmetric stretching modes of H_2O as well as the modes of CO_2 are insignificant. Since there is a strong temperature dependence of the vapor pressure especially for, H_2O(g) as described above, the question can also be asked about how a change in the amount of substance affects the result of the calculation. In the relevant temperature range 0˚C < ϑ < 40˚C, the relationship of the heat capacity with temperature-dependent amounts of substance, $n(\vartheta)$ at complete saturation, to the calculations with invariant amounts of substance, n = const. shown in Figure 3, is shown in Figure 4. It can be seen that there is hardly any influence for CO_2 while for H_2O a tripling of the value given in the table for $\vartheta = 14.5$˚C can be obtained. However, it should be noted that even with this somewhat extended calculation, there is no significant contribution of the normal vibrations to the heat
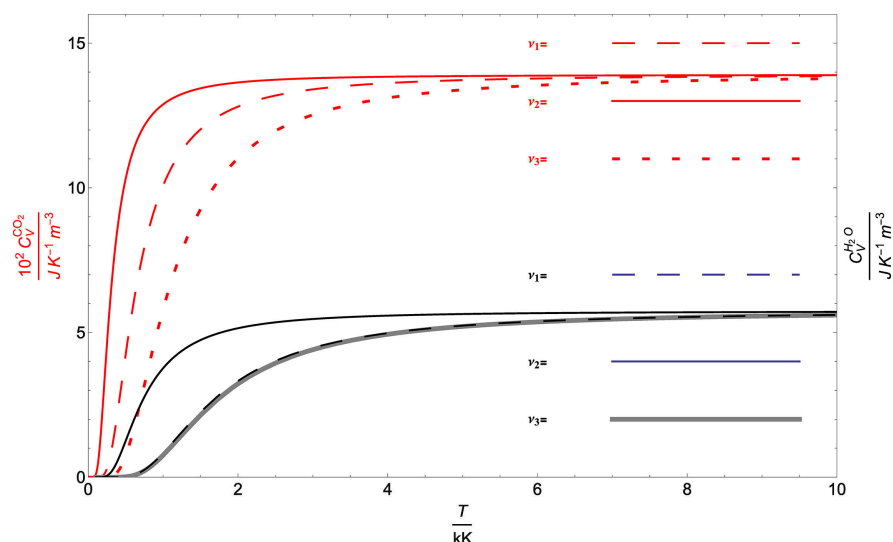
Figure 3. Heat capacity, C_V, of modes of $H_2O(g)$ and CO_2 as function of temperature calculated by use of constant amount of substance $n(\vartheta = 14.5°C)$.
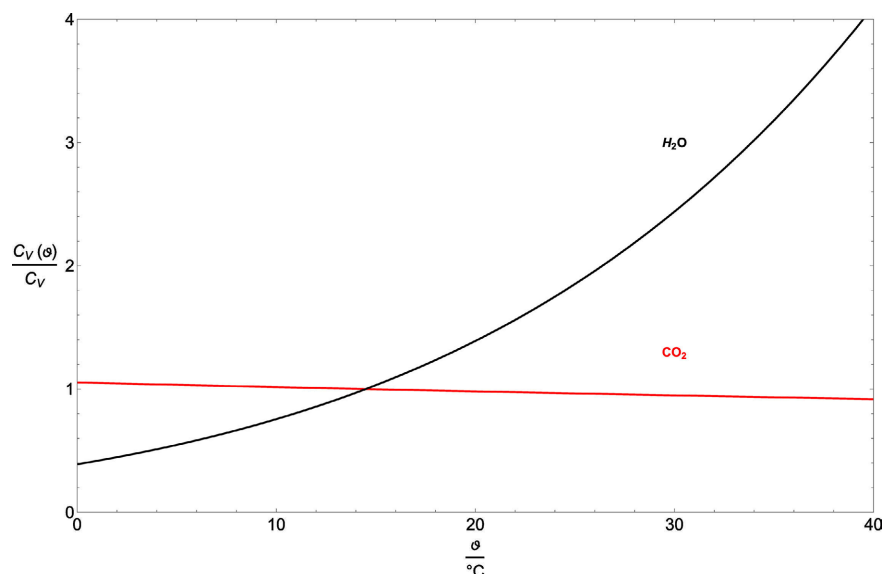
Figure 4. Heat capacity of modes of $H_2O(g)$ and CO_2 calculated by use of temperature dependent amount of substance, $n(\vartheta)$, $C_V(\vartheta)$, compared to heat capacity C_V at $\vartheta = 14.5°C$ as function of temperature.

capacity. Since CO_2 has no dipole moment, its rotational motion cannot be excited. Consequently, only the rotational degrees of freedom of H_2O can be involved in the greenhouse effect. The characteristic rotational temperatures of the asymmetric rotor water are $\Theta_1 = 40$ K, $\Theta_2 = 21$ K and $\Theta_3 = 13$ K ([10] p. 553). They are all excited at $T = 287.65$ K and consequently contribute to the greenhouse effect. For completeness, we also mention that all translational degrees of freedom of the molecules in our model system are excited with energy $\varepsilon_{Trans} = 1/2$ kT. Because the excitation of the molecules may also have been due to direct solar radiation, excited molecules cannot be distinguished according to the source of their excitation. The small contribution of the normal vibrations of CO_2 and

H_2O to the heat capacity of the system we are considering does not support a significant excitation by terrestrial radiation.

Such a statement is possible only by an appropriate laboratory experiment. Ångström states in the cited work as a result of laboratory measurements: "*Aus diesen Untersuchungen und Berechnungen geht klar hervor: erstens, dass höchstens ca.* 16 *Proc. von der Erdstrahlung durch die atmosphärische Kohlensäure absorbirt werden, und zweitens, dass die Gesamtabsorption sehr wenig von den Veränderungen in dem atmosphärischen Kohlensäuregehalt abhängig ist,*" "From these investigations and calculations it is clear: first, that at most about 16 perc. of the terrestrial radiation is absorbed by the atmospheric carbonic acid, and second, that the total absorption depends very little on the changes in the atmospheric carbonic acid content," (applies to the "radiation of a black body of 100˚C"). Consequently, the considerations presented here are qualitatively in agreement with the results measured by Ångström. The correctness of the conclusions, which resulted from the considerations to the heat capacity, is confirmed. One must also take into account that for the above presented relations to the effect of CO_2 as a greenhouse gas, this excitation is a prerequisite, and no additional conditions must be fulfilled.

5. The Role of Humans in the Change of the Global Temperature

Since an increased rise in global temperature was observed with the onset of the industrial era, *i.e.*, about 200 years ago, it is reasonable to assume that human activities are responsible for this increase. In fact, there is a very good correlation between the increase in the world population and the increase in the concentration of CO_2 in the atmosphere [12], confirming the human influence on the global properties of the atmosphere. However, the above considerations suggest that an increase in the concentration of CO_2 does not have a decisive influence on the increase in global environmental temperature and confirms the measurements of K. Ångström [4]. It is shown, as already stated, that the annual energy consumption of mankind can increase the temperature of the atmosphere up to a height of 1 km by 0.8˚C/a [12]. If for this estimation only nearer to earth layers of the atmosphere are included, one finds out that a 100 m thick layer experiences a temperature increase of 8˚C/a, while a layer thickness of 10 m, in which the measurement of the surface temperature takes place, would increase the temperature even by 109˚C/a. It does not seem appropriate to neglect this contribution with the reference to the large energy input of the sun. This energy input has caused the increase of the global temperature from −18˚C to 14.5˚C. At 14.5˚C the dynamic equilibrium is reached, for which $E_A = E_E$. The intensity of solar radiation is balanced, only its increase, ΔE_A, would cause an increase in temperature. Therefore, two aspects should be considered when assessing the impact of renewable energy use on global temperature. One is that the renewable energy, ΔE_N, may come from the fraction of solar energy that is

otherwise reflected unimpeded into space, $E_{RE}^T = E_{RE}^0 + E_R - \Delta E_N$, thus acting in addition and reducing the total reflected energy, E_{RE}^T. And on the other hand, that energy stored after generation, ΔE_N^S, is absent in the dynamic equilibrium during the storage period and can be replaced by abundant solar energy, while acting as an additional source during later use. Therefore, both influences cause a temperature increase in the atmosphere. In the greenhouse effect, which is based on the extension of the contact time between energy and matter, at best only one normal mode of CO_2 can be involved to a small extent, in addition to the other possibilities. Undisputed is the participation of CO_2 in the protection of the earth's atmosphere from excessive warming. The designation of a gas indispensable for aerobic life processes as a climate killer is nonsensical. Two aspects must also be considered in connection with the influence of humans on a change in temperature in the atmosphere. These are that, first, an increase in world population increases this influence. And second, that to reduce this influence, energy consumption must be kept as low as possible through economical use of energy and sustainability. Thus, it is clear that a reasonable way to avoid the further increase of the world population is also a contribution to prevent or limit the further increase of the global environmental temperature.

6. Summary

In summary, it is concluded that both gases CO_2 and H_2O cause the shielding of the earth's surface against about one third of the infrared part of the solar radiation. On the other hand, it is only certain that water molecules in particular can contribute to the greenhouse effect to a considerable extent by exciting their rotational modes. The undoubted effect of clouds has not been treated in this paper. If one takes the earth as a black-body with a temperature of 287.65 K, an excitation of the bending mode of CO_2 is possible according to its wavelength distribution and it can be involved in the greenhouse effect as well as the rotational modes of $H_2O(g)$. Whether and to what extent the excitation of the vibration occurs cannot be determined by measurements in the atmosphere. However, it follows from the considerations of heat capacity presented here that no significant effect can be expected. This result supports the experimental results found by Ångström. The power radiated to the earth by the sun is completely re-radiated. It serves only to maintain the global temperature, which acts as a driving force for the radiation. The additional energy input from the use of fossil fuels can therefore cause an increase in global temperature. The use of renewable energy is not necessarily suitable and sufficient for preventing the increase in global temperature. The influence of application of renewable energies to the global temperature must be investigated thoroughly for any special case. There is no general answer possible. Some special cases are discussed in reference [12]. When evaluating the effect of renewable energy on global environmental temperature, it must also be taken into account that in the case of renewable energy storage, a deficit in the global dynamic equilibrium of our environment is created, which

can be immediately compensated by the large irradiated energy output of the sun. With the facts stated here, which are described in textbooks of physical chemistry, the opinion must be contradicted that CO_2—molecules are mainly responsible for the increase of the global environmental temperature. Effective ways to prevent the increase of the global temperature are only possible by changes of live conditions of humans, sparingly use of all forms of energy, reuse of materials whose production was particularly energy-intensive, and sustainability of economic processes this is the economical use of energy and all measures to preserve and restore our natural environment.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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