

The climate roles of H₂O and CO₂ from longwave absorption

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Abstract

In search for reproducibility of the results from sophisticated scientific research, the present work focuses on the longwave absorption in the atmosphere. It is found that the variability of Earth's surface temperature follows a near-proportional relationship between longwave absorption and the atmospheric trace gas concentrations of water vapor and CO₂. Furthermore, estimates are attempted on the CO₂ V/R-T (vibrational/rotational-to-translational) energy transfer as a dominant heating process.

Keywords: Climate Modelling, Atmospheric Longwave Absorption, Transient Climate, Ocean Heat Content, Translational Energy Transfer.

Introduction

A starting point of the present work has been the search for reproducibility on the statement that the longwave absorption by atmospheric CO₂ operates in saturation mode. The question has been how this can be reproduced by simple terms: If CO₂ is as important in the climate processes as commonly communicated, should the saturation effect leave its readily apparent footprint?

In earlier paleo-studies, a simple relationship has been revealed for the temperature effect (TCO_2 , surface temperature) of the atmospheric CO₂ concentration (pCO_2 , volume mixing ratio), termed the 'Eocene relationship': $TCO_2 = \ln(pCO_2/22) \cdot 6.68 \text{ }^\circ\text{C}$ [1]. It expresses the compound temperature contribution from CO₂ in equilibrium climate states, subsuming all related effects e.g. from water vapor. When complementing by further climate forces, these are treated as correction terms thus also reflecting the compound effect of all related processes. The simple Eocene relationship is consistent with paleo-measurements as well as simulation results. Furthermore, the frequently used Myhre formula [2] shows identical pattern when applying the factor $1.25 \text{ }^\circ\text{C}/(\text{W}/\text{m}^2)$ for the translation between radiative forcing and surface temperature [1].

The simple Eocene relationship provides a handy tool for further studies. It appears as a natural idea to explore the temperature-concentration dependency with help of the Eocene relationship. Additional analyses are described on the atmospheric V/R-T (vibrational/rotational-to-translational) energy transfer in view of its predominant role for the climate.

Equilibrium and transient climate driving forces

CO₂ By nature of its derivation, the Eocene relationship reflects equilibrium climate states. For the present atmospheric CO₂ lev-

el of about 400 ppmv, it points at a temperature increase of 2.3 °C in course of the industrial era.

Ice/snow albedo

From the Late Quaternary glacial-interglacial cycles, the entailed effect from ice/snow albedo is on average $\frac{2}{3}$ of the CO₂-determined temperature change and slightly lower for the present [1]. Throughout the present work, the ice/snow albedo contribution is approximated by 0.4 °C per 1 °C from CO₂.

Anthropogenic energy consumption

The anthropogenic energy consumption represents a radiation disturbance to the pre-industrial climate state. Applying a sensitivity of $0.75 \text{ }^\circ\text{C}/(\text{W}/\text{m}^2)$ on each year's disturbance difference relative to previous year's disturbance, the temperature contribution is estimated to less than 0.1 °C for year 2100 (projecting with an annual growth rate of 1.6 %/year from the present).

Ocean heat uptake

Of the precedingly expected temperature increase of 3.2 °C (2.3 °C from CO₂ plus $2.3 \cdot 0.4 \text{ }^\circ\text{C}$ from albedo), so far roughly $\frac{1}{3}$ have been experienced. According to fundamental natural processes, the difference may significantly be caused by the oceans taking up a substantial portion of energy from the atmosphere. To explore the trend with time for the industrial age, first the Eocene relationship is applied to determine the equilibrium temperatures associated with the measured CO₂ concentrations [3, 4]. Then, the resulting temperature changes are multiplied by a factor of 1.4 to account for the entailed albedo effects (for preciseness, the temperature-proportional effects). Year-on-year, the temperature differences are translated into radiation differences assuming ideal blackbody. An annual radiation increase (decrease with reversed signs) is then partly taken up by the oceans, the rest acting in the atmosphere to change its tempera-

ture. The corresponding radiation change is in turn taken up by the oceans in the subsequent year.

Figure 1 shows the resulting ocean heat content for the past decades with the ocean heat uptake ratio of 0.21 (dashed orange line), in comparison with observations for the upper 700 m in the 95 %-confidence level boundaries (solid blue lines) [5].

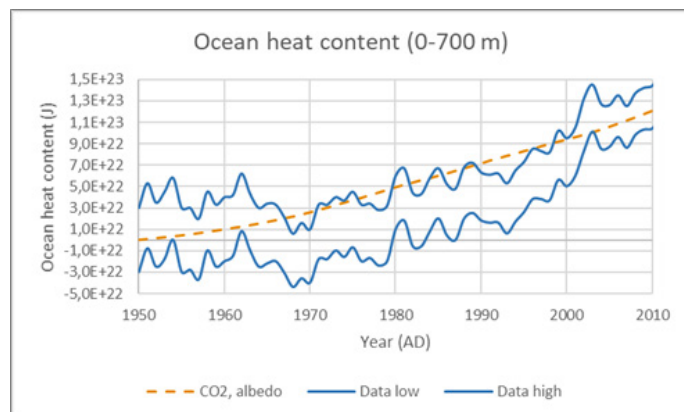


Figure 1: Annual mean globally integrated upper 700 m ocean heat content for the years 1950-2010 relative to 1950; solid blue lines: observations, upper and lower boundaries for the 95 % confidence level, reproduced from [5]; dashed orange line: results for the same period from computation (Eocene relationship-based) starting at year 1750, CO₂ and albedo considered (see text), subtracted by $3.1 \cdot 10^{22}$ J (value of 1950) for comparison purposes

Figure 2 presents the associated near-surface temperature trend: dashed orange line for the computed values according to the preceding description; solid blue lines for the 95 %-confidence envelope of the observed temperatures; dotted orange line for computed values according to the density proportionality scheme of the subsequent paragraph applied to the temperatures of the dashed orange line, with ocean heat uptake ratio 0.21 [6].

It is interesting that the applied model corresponds with the frequent communication that nearly the entire human-induced energy increase is being taken up by the oceans. Furthermore from the agreement between the dashed and dotted orange lines in Figure 2, the atmospheric temperature gain is interpreted to be attributed to rising longwave absorber concentrations, i.e. of CO₂ and water vapor, the latter via its characteristic temperature dependency (see below for further details).

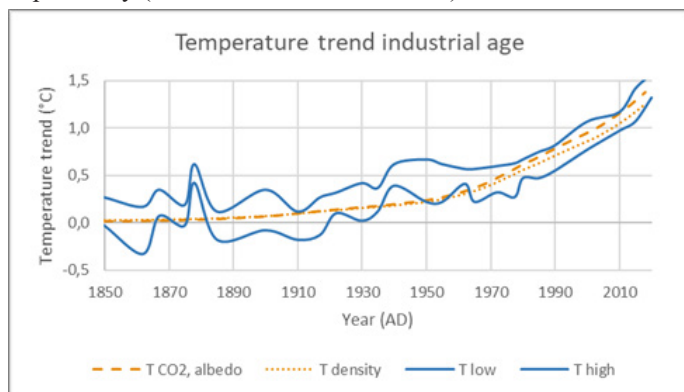


Figure 2: Average global near-surface atmospheric temperature trend during the industrial age; solid blue lines: observations in course envelope of 95 %-confidence intervals, arbitrary offset [6]; dashed orange line: computation results according to this

paragraph (Eocene relationship-based), corresponding to the dashed-orange ocean heat content line of Figure 1, temperature contributions from CO₂ and albedo; dotted orange line: density proportionality scheme of the subsequent paragraph applied to the temperatures of the dashed orange line, with ocean heat uptake ratio 0.21.

The agreement between the estimation and observations encourages the inference that the driving processes have correctly been identified and well described by simple means.

For completeness, it is noted that regular fluxes not explicitly mentioned in the present model are to be attributed to equilibrated conditions and therefore disregarded in the present context of transient-related ocean heat uptake. Besides, their sizes can be small. For instance, the geothermal surface flux amounts to a surface temperature contribution of less than 0.1 °C (details not described). Also, the submarine volcanic activity since 1750 is estimated with a cumulated ocean heat contribution by year 2010 of more than three orders of magnitude lower than the corresponding values of Figure 1 (details not shown).

Conclusion: So far during the industrial age, emerged temperatures are lower than expected for equilibrium climate states. The difference is interpreted to be predominantly caused by ocean heat uptake. Generally in equilibrium states, net ocean heat flow is zero; in contrast, relatively large at the onset of a disturbance to equilibrium; approaching zero again when settling towards a new equilibrium. A simple model based on equilibrium states can consistently reflect measurements on ocean heat content and temperature for the transient climate states of the recent past.

Eocene CO₂-temperature relationship and absorber molecule densities

From absorption characteristics and atmospheric mixing ratios, it is readily inferred that H₂O absorbs more longwave radiation than CO₂ and that both are the main absorbing media for Earth's radiation. To explore the interrelation between particle density and temperature, the working assumption is examined that absorption be proportional to the molecule (number) densities in the atmosphere.

The following model is applied. The number density (q) is set proportional to the volume mixing ratio (p), corrected by a small factor for the general density-temperature dependence. The starting point is at a surface temperature of 14 °C with 385.5 W/m² surface radiation (Q_{E0}), volume mixing ratios (p_0) of 0.4 % for H₂O and 280.3 ppmv for CO₂, and corresponding number densities (q_0). For H₂O, the volume mixing ratio is taken to linearly correlate with temperature by 7 %/°C (approximating the Clausius-Clapeyron Equation) and this multiplied by a fit factor (δ). For CO₂, the volume mixing ratio is multiplied by an attenuation fit factor (γ) to cater for absorption saturation effects. The starting point for the absorbed infrared radiation is a fit parameter (Q_{A0}). Absorption is scaled proportional to the summed number densities of H₂O and CO₂ ($\Delta Q_A = \Delta q / q_0 \cdot Q_{A0}$) and added to the radiation starting point ($Q = Q_{E0} + \Delta Q_A$), then transformed into temperature based on the ideal blackbody assumption.

An analysis has been performed for a temperature span of 13 °C. As first result, the equilibrium climate states according to the Eocene relationship are well reproduced (at deviations below 5 %) with (i) absorption at reference conditions (present) of $Q_{A0} = 57$ W/m², (ii) a linear H₂O concentration increase with temperature by 9.18 %/°C ($\delta = 1.311$, as approximation of the ex-

ponential 7 %/°C Clausius-Clapeyron relation and implicitly incorporating non-linear absorption-to-density dependencies), and (iii) a deviation of -4 % per 100 ppmv from direct proportionality in the CO₂-absorption relationship reflecting saturation effects ($\gamma = -4 \cdot 10^{-5} / \text{ppmv}$). If the radiation change from absorption (ΔQ_A) is subjected to the atmospheric window with 10 % direct transmittance, Q_{A0} shows as 63.4 W/m² with all other results retained. The present description will be continued for the above value $Q_{A0} = 57 \text{ W/m}^2$ (and no direct transmittance of ΔQ_A).

As second result, the industrial age is well reflected by the preceding density proportionality scheme, as shown by the dotted orange line of Figure 2 where ocean heat uptake is applied to the absorption change ΔQ_A with the ratio of 0.21.

In summary, the Eocene relationship reveals a near-proportional dependency of the absorbed radiation on the molecule densities of H₂O and CO₂ where the absorption is 57 W/m² at reference conditions (given by p_0 and Q_{E0}). In search for the interpretation, the absorption line intensities of HITRAN are divided into three groups. To the first group, the very strong absorption lines are assigned, where the temperature impact from absorption is assumed insensitive to density increases. The second group contains the medium-strong absorption lines, where the absorbed radiation may change with the number of molecules available for absorption. The third group contains the weak absorption lines which are interpreted to have a negligible share of the totally absorbed radiation at the given molecule densities [7].

With rectangular approximation of the absorption lines, the Planck distribution for the surface spectral radiance gives the following coverages by the line groups: Assigning line intensities $> 10^{-22}$ (line intensity in unit $\text{cm}^{-1}/(\text{molecule} \cdot \text{cm}^2)$) to the first group and intensities between 10^{-22} and 10^{-23} to the second group, the lines cover a radiance of 94 W/m² in the first (strong) group and of 61 W/m² in the second (medium-strong) group. This result supports the interpretation that the above 57 W/m² may be attributed to the medium-strong absorption lines where absorption is proportional to the number densities of the absorbing molecules. Also the 50 cm^{-1} -averaged representation of the absorption cross sections supports the possibility of a partial absorption-to-density proportionality [8].

Conclusion: The Eocene CO₂-temperature relationship is reproduced by a near-proportional dependency of absorbed radiation on the number densities of atmospheric H₂O and CO₂, wherein a CO₂ saturation effect showing as 4 % per 100 ppmv and the H₂O concentration approximated with a linear temperature dependency of 9.18 %/°C. The absorption-to-density proportionality acts on a defined portion of Earth's infrared radiation, i.e. on 57 W/m² at reference conditions. The proportionality scheme is consistent with energy budget considerations, there corresponding with the longwave radiation from the atmosphere to the surface. Furthermore, the proportionality scheme is consistent with simplified planetary emittance modelling over a wide range of climates and up to 4 billion years of history [9, 10].

Transient temperatures from absorbing-molecule densities

By nature of its derivation, the Eocene relationship reflects equilibrium climate states. Its usage is a consideration 'from the end': The eventually established temperature is pre-known from the CO₂ concentration. Also in the industrial-age calculation above, the water vapor concentration is determined from the pre-known temperature. Now, the consideration will be 'bottom

up', from the beginning of a disturbance to a given equilibrium state. Concentration and absorption are to determine the temperature from the disturbance itself without pre-knowledge of a 'to-be' temperature.

Model description

The above density proportionality scheme is adapted to the case of a gradual disturbance acting for some decades and then switched off. Two disturbance cases will be regarded: increase of radiation from the surface for 70 years and doubling/quadrupling of the CO₂ concentration in 70/140 years. To briefly summarize the adapted density scheme: With a year's disturbance, the longwave absorption in the atmosphere changes (effective after ocean heat uptake), in tail temperature changes (according to ideal blackbody), which in turn alters densities and thus absorption.

Model details: Starting point at year 0 is the same value set as in the previous paragraph: $p_0 \text{H}_2\text{O} = 0.4 \%$, $p_0 \text{CO}_2 = 280.3 \text{ ppmv}$ (p for volume mixing ratios, typically termed concentration within the present work), absorption $Q_{A0} = 57 \text{ W/m}^2$ at these concentrations, temperature 14 °C. Radiation contributions are translated into temperature contributions via the blackbody assumption. The absorption change (ΔQ_A) is taken proportional to the concentration change. The radiation at the end of a given year (Q) and the corresponding temperature (T) are

$$T = (Q/\sigma)^{1/4}, \quad Q(\text{year}) = Q(\text{year}-1) + \delta Q(\text{year}), \quad \delta Q = (1-u) \cdot \delta Q_A, \quad \delta Q_A = \Delta Q_A(\text{year}) - \Delta Q_A(\text{year}-1), \quad \Delta Q_A = (p - p_0) / p_0 \cdot Q_{A0}, \quad (1) \\ p \text{H}_2\text{O}(\text{year}) = p \text{H}_2\text{O}(T(\text{year}-1)), \quad p \text{CO}_2: \text{ see text}, \quad p = p \text{H}_2\text{O} + p \text{CO}_2,$$

in partly generic variable definitions, with u the ocean heat uptake ratio, σ the Stefan-Boltzmann constant, and starting at year=1 with $Q(0) = 385.5 \text{ W/m}^2$ and $\Delta Q_A(0) = 0$. (If δQ_A was subjected to the atmospheric window, all results were retained with $Q_{A0} = 63.4 \text{ W/m}^2$, compare remark in the previous paragraph).

Radiation increase

This density proportionality scheme (equation set 1) is applied to the scenario where the longwave radiation from the ground is steadily increasing within 70 years to an exemplary 3.2 W/m² stronger radiation, constant from year 71 onwards. The CO₂ concentration is set dependent on temperature via 20 ppmv/°C (from the Late Quaternary, cf. [1]) and the H₂O concentration as in the previous paragraph.

With an uptake ratio $u = 0.21$ on the yearly absorption change (δQ_A), the result for the atmospheric radiation change is obtained as 2.35 W/m² after the disturbance period, thus indicating the new equilibrium case.

This compares well with the 2.4 W/m² obtained for the same variability scenario in the energy budget studies, there also reflecting equilibrium conditions [9].

CO₂ increase

Next, the density scheme (equation set 1) is applied to doubling and quadrupling of the CO₂ concentration within 70 and 140 years, respectively, and the concentration kept constant afterwards. It turns out that the equilibrium temperatures as given by the Eocene relationship are only reached to 39 % and 25 % for the two scenarios. Something is different to the former disturbance of (direct) radiation change from the ground. Also, gradual dilution of ocean heat uptake alone does not lead to the equilibrium temperatures. Thus, absorption increase from increased CO₂

concentration appears too weak to drive temperatures to equilibrium (in the present proportionality scheme). There seems to be an additional process raising water vapor concentrations to the required equilibrium level. The impression is that such process is delayed to the original disturbance and vanishes with time (details not shown). The present scheme asymptotically delivers the Eocene equilibrium temperatures, if an additional radiation (to δQ) is introduced at 'ramp-up' termination (e.g. of 0.6 % in the doubling scenario) and afterwards, this additional radiation and the ocean heat uptake ratio are steadily decreasing by 6 %/100 years.

The results are summarized in Figure 3: the temperature change versus time in years from the starting point of quadrupling (upper red data set) and doubling (lower blue data set) of the CO₂ concentration, with quadrupling through the first 140 years and doubling through the first 70 years, both at constant annual rate, and the concentration kept constant afterwards. Results from previous sophisticated simulations are depicted by dashed lines, with the equilibrium temperatures – as established after 2000-3000 years – indicated on the right side by horizontal lines [11]. The single dots mark the corresponding temperatures according to the Eocene relationship. The dotted red and blue lines show the temperature results from the present model (equation set 1 with the precedingly described adaptation)

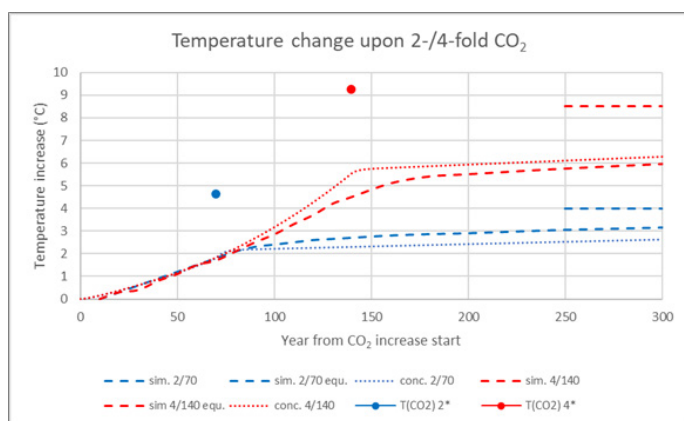


Figure 3: Temperature evolution with time upon quadrupling and doubling of the CO₂ concentration, quadrupling and doubling with constant annual rate through the first 140 and 70 years, respectively, and constant concentrations afterwards. Previous simulation results, reproduced from [11], from quadrupling (upper dashed red lines) and doubling (lower dashed blue lines), equilibrium temperatures after 2000-3000 years indicated by horizontal lines to the right. Temperature change according to the Eocene relationship by respective dots [1]. Temperatures from the concentration-proportionality of equation set (1) with amendment according to text: dotted red and blue lines.

The temperatures of the Eocene relationship and the previous equilibrium simulation results are in good agreement. In the 'ramp-up' period, the density proportionality scheme of equation set (1) is in good or fair agreement with the previous sophisticated simulations [11].

From the dotted blue line in Figure 3, i.e. for doubled CO₂ concentration, a rule of thumb may be extracted. Roughly 1/3 of the equilibrium temperature is rather contemporarily expected once the concentration increase ceases; 1/2, 2/3 and 80 % of the equilibrium temperature are reached about 70, 460 and 830 years from the beginning of the constant-concentration period.

Conclusion:

The longwave absorption-to-density proportionality – as revealed for equilibrium states from the Eocene relationship – also delivers convincing results in the transient climate regime. The results are consistent with energy budget considerations (scenario of surface radiation change) and with sophisticated simulations in the 'ramp-up' period of a continuous CO₂ change. In the latter case after disturbance switch-off, asymptotic approach towards equilibrium can be reproduced by a small extra-rise of the H₂O concentration via radiation increase in the order of 0.6 % upon disturbance switch-off, and by diluting of this increase and the ocean heat uptake ratio with 6 % / 100 years. As a rule of thumb, final equilibrium temperatures are anticipated on the millennium time scale about 3 times the contemporarily emerging temperatures at termination of the CO₂ concentration change.

Estimation on the atmospheric V/R-T (radiation-to-heat) transfer at CO₂

In the strong CO₂ absorption band at wavenumber 670 cm⁻¹, an absorbing CO₂ molecule close to the surface cannot de-excite via radiation to space for two major reasons. (A) An emitted photon is being re-absorbed by a nearby CO₂ molecule; only as the CO₂ density sufficiently decreases with the altitude gradient, an emitted photon has the chance to escape to space. (B) The average lifetime of an excited CO₂ molecule from spontaneous emission is of the order of several 100 ms, to about 50% between 300 and 800 ms [7]. On the contrary, the lifetime from relaxation via collisional V/R-T (vibrational and rotational to translational) energy transfer is orders of magnitude lower near Earth's surface.

The latter is estimated from previous research results related to the $\nu_2/667.5$ cm⁻¹ vibrational state of CO₂. With a volume mixing ratio for water vapor (H₂O) of 0.4 % near the surface and the given collisional transfer rates, H₂O plays the dominant role before N₂ as collision partner, the H₂O relaxation time being estimated to roughly 2 μ s. This is more than 5 orders of magnitude lower than the lifetime from spontaneous emission (see above) so that the latter has a negligible probability to occur [12-14].

At the altitude of 20 km, the situation changes. From mixing ratios and collisional transfer rates, N₂ is the dominant relaxation partner. With the temperature dependence of the collisional rate constant (roughly a decrease by a factor of 10 from the ground to 20 km altitude) and with the given densities at 20 km altitude, the lifetime from N₂ collision relaxation is estimated to 3 ms [12, 15]. From this – first order – consideration, emission to space from the given CO₂ band is not expected below 20 km altitude. This is consistent with simplified modelling results on the planetary emittance where emittance from CO₂ starts at about 20 km for cold, low-concentration conditions [10].

Conclusion: Absorption of Earth's infrared radiation by the strong lines of the atmospheric CO₂ is comprehended as being processed via translational energy transfer, which is equivalent to the transformation of radiation energy into heat. Starting at altitudes of the lower stratosphere, CO₂ can emit to space.

Discussion

The central aim of the present studies has been to search for reproducibility regarding the longwave absorption saturation of CO₂ in the atmosphere. A near-proportionality of absorption to the concentrations of CO₂ and water vapor has been found with its clear fingerprint in the surface temperature variability. The proportionality is supported by consistency throughout a variety of analyses. (i) The Eocene CO₂-temperature relationship

of equilibrium states is well reproduced. (ii) The measurements of ocean heat content and surface temperature are well reproduced for the transient states of the recent past. (iii) Proportionality-based results are conformant with energy budget considerations and planetary emittance modelling for a wide range of climates and up to 4 billion years of Earth's history. (iv) The proportionality is regarded conformant with line intensity-based absorption considerations. The significant heating process of the V/R-T transition upon longwave absorption on CO₂ is estimated to first order in its altitude dependency. In result, emittance to space from the strong CO₂ band can principally occur at altitudes higher than 20 km, consistent with simple modelling of the planetary emittance.

Supplementary Materials:

All data and code are available: <https://www.dropbox.com/scl/fi/8l7nzipdlbqv33rzatn2b/Longwave-absorption-data-and-code.xlsx?dl=0&rlkey=4h8ti7zym7r1716gx0mss05hh>

Conflicts of Interest:

No conflict of interest is to be declared.

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