A physical demonstration of the increase in global surface energy due to increasing P_{CO_2}

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Abstract

Although study of the effect of energy-absorbing gases in our atmosphere has a two-hundred year history and an unequivocal explanation based on scientific observation and theory, a significant fraction of the public and even a few scientists doubt the correlation between the increasing the partial pressure of atmospheric carbon dioxide (P_{CO_2}) and the observed increase in terrestrial temperature over the past 120 years. Although the basic science showing that CO_2 would absorb the infrared radiation emitted by the earth produce a surface-warming effect was first calculated by Arrhenius in 1896, the issue was neglected by the scientific community for decades. Today there are ample climate models of the climactic effects arising from the forcing term of increasing P_{CO_2}. In this paper we follow Arrhenius' concept, although we use the HITRAN database as the input to prove the connection between earth's surface temperature and atmospheric absorption of terrestrial radiation in a direct manner that the reader can also implement. The spectra of CO_2 are enormously complicated, broadened by Fermi Resonance, and intense because of the quantum coupling of the rotation of CO_2 to its bending. Using an on-line database for the transitions of CO_2 the reader will easily be able to show that CO_2 reduces the transmittance of the Earth's thermal radiation through the atmosphere, which in turn results in heating of the surface. The model does not make any predictions other than that the global temperature will increase as a function of P_{CO_2}. The result is at the intersection of Physics, Atmospheric Science, and Psychology since the demonstration is a powerful tool that will give scientists the impetus to reach out to the public with lucid explanations based on physical principles.

Introduction

There is a need for a clear statement of the quantitative connection between increasing atmospheric carbon dioxide (CO_2) levels and changes in the global energy balance. While this connection is widely accepted among scientists, the economic implications of the problem have resulted in widespread denial elsewhere in society. Recent events, such as the cataclysmic fires in Australia, Amazonia[1] and California,[2] the hot spot in the Pacific Ocean responsible for killing millions of fish[3] and the accelerated pace of arctic and Antarctic melting[4] highlight the urgency of the problem. These changes are predicted to become the new normal, but the larger danger arises as the earth approaches tipping points, such as the conversion of northern boreal forests from net carbon uptake to sources of carbon emission[5] or the drying out of the Amazon basin.[6] These events put a spotlight on the need for increased understanding of the earth's energy balance. In spite of overwhelming evidence, denial is as active as at any time in the past century by those who fear that change will result in economic dislocation In fact, the imposition of political considerations on science has increased in recent years.[7] This situation calls for a first-principles approach that gives scientists the tools to address an issue that may be outside their specialized field of study.

There is an enormous body of work by climatologists that substantiates the connection between a warming trend and the dramatic rise in CO_2 ppm over the past 120 years. Although skeptics have questioned the significance and magnitude of the trend toward increasing global average temperature, recent record temperatures, and melting of polar ice at an accelerated pace have all but obliterated the argument that temperature rise is not a concern. Moreover, there is no question that the increase in CO_2 partial pressure is a consequence of human activity, principally the combustion of fossil fuels. Therefore, the last bastion of the critics is to question the link between the temperature rise and the increase in P_{CO_2}. That link is considered a result of the *greenhouse gas* effect, which is specifically caused by the strong absorption of the earth's thermal radiation by carbon dioxide in the range 9-17 μ.

The physics of *thermal radiation* is taught as the initial motivation for Quantum Mechanics in most Physical Chemistry curricula.[8] Textbooks refer to Blackbody Radiation but the name blackbody can be confusing. We prefer the term *thermal radiation* since it describes how the radiation emitted stars and planets permits each to have a different temperature at equilibrium. Because the subject is introduced with a focus on Planck's justification for quantized radiation, the other aspects of the theory are often omitted in Chemistry curricula, despite their importance. For example, Kirchoff's law of absorption states that perfect absorbers are black in color because all wavelengths are absorbed, hence the name blackbody. In Kirchoff's model, emission depends on wavelength and is a function of temperature only. These laws are statements about ideal spheres used to explain how the planets, stars and other celestial bodies can exist in thermal equilibrium at different temperatures. In the 1860s scientists were trying for the first time to reconcile thermodynamics and radiation physics. The question was: how can two objects be at equilibrium, yet be at different temperatures? The answer was: thermal radiation is a universal phenomenon, and it means that every object in the universe radiates at a wavelength that is inversely proportional to its temperature. Stars provide visual examples of thermal radiation. Stars would be blackbodies if it were not for the fact that atoms are an ionized plasma so there are many thousands of absorption lines. The emission of stars is far from perfect because of the absorption by hydrogen, helium, and a surprising range of other elements that form as the stars age. The circa 25,000 intense narrow bandwidth absorption bands of atomic transitions in our Sun are known as Frauenhofer lines.

The empirical relationships that describe the radiation and temperature of stars and planets have been known since the 1880's and are given the names, the Stefan-Boltzmann law[9] and the Wien displacement law.[10] The Stefan-Boltzmann law states that

$$F = \sigma T^4 \tag{1}$$

Where F is the radiation flux from the surface in W/m^2, T is absolute temperature and $\sigma = 5.678\ x\ 10^{-8}$ W/m^2/K is known as the Stefan-Boltzmann constant. Using only the above law, the radius of the sun, the radius of the earth's orbit and the temperature of the sun, one can calculate an accurate temperature of the surface of a bare earth (without an atmosphere). To obtain an accurate result we must include albedo, A, which is the reflection of some of the radiation by the earth. If one uses the values $A = 0.3$, $R_{sun} = 7\ x\ 10^8$ m, $R_{orbit} = 1.5\ x\ 10^{11}$ m and T_{sun}= 5780 K, one obtains $T_{bare\ earth}$ = 255 K. These parameters are quite reliable. The albedo is the most difficult to measure, hence it is a parameter the could change somewhat depending on the composition of the atmosphere we call attention to it as an assumption of our model.

$$T_{bare\ earth} = \sqrt{\frac{\sqrt{(1-A)}R_{sun}}{2R_{orbit}}} T_{sun} \tag{2}$$

This formula works well for planets that have little or no atmosphere, such as Mars or Neptune. This application assumes that the planet rotates about an axis with an azimuthal angle close enough to perpendicular to the plane of the orbit that the energy is equally distributed over the surface. It is not appropriate for Mercury, which does not rotate about a planetary axis. It also fails for the surface of Earth, which is more than 30 ^{o}C warmer because of its absorbing atmosphere. The earth would be a giant snowball if it lacked a CO_2 atmosphere.

The emission wavelength of thermal radiation by celestial bodies is inversely proportional to the steady-state temperature. This inverse proportionality was observed empirically using a platinum filament in the 1860s and later called the Wien displacement law,

$$\lambda_{max}T = 2.88\ x\ 10^{6}\ nm - K \tag{3}$$

From this equation we can calculate that the maximum emission wavelength of the sun and earth are 524 nm and 11,300 nm, respectively.

It has been recognized for well over 150 years that the surface temperature of a planet will be strongly affected by the presence of an atmosphere. The delay in recognition of the importance of energy-absorbing gases in Earth's atmosphere by the scientific community is a discouraging fact that exemplifies how self-deception can impede the progress of the search for the truth.[11] The concern raised by Svante Arrhenius in an article published in 1896[12] has stood the test of time.[13] Although Arrhenius had a limited data set, obtained mainly from Langley's observations of infrared radiation from the moon,[14] he was able to use those data and Stefan-Boltzmann law to estimate the increase in temperature at the surface of the earth that would be caused by an increase in CO_2 partial pressure. Today the International Panel on Climate Change (IPCC) and hundreds of research groups publish both measurements and simulations that document the correlation with great accuracy. Of course, instead of a few points of lunar radiation scribbled in a notebook, modern atmospheric science is based on satellite data and quantum theory of transitions.

It is interesting from the point of view of the history of science that Svante Arrhenius' result was disputed from the very beginning by Knut Ångström, the son of the famous Jonas Ångström for whom the unit of atomic length was named.[15] In an ostentatious experiment Knut Ångström traveled to the island of Tenerife in 1900 and climbed Pico de Teide to test whether pure

CO_2 would absorb more incident solar radiation than air at the same pressure. The study describes how tubes containing pure CO_2 gas and air, both at atmospheric pressure, were compared by detecting the transmittance of the sun's radiation through the tube on the mountain top. However, the great expense to reach high elevation, where the equatorial sun's radiation would be relatively intense, was unnecessary. The heating of the earth's surface by CO_2 absorption does not depend on incident solar radiation. CO_2 absorbs the long-wavelength emission from the earth, and very little of the short wavelength emission from the sun. In that paper, Ångström did briefly describe an experiment by his *colleague* Koch to measure the absorption of infrared thermal radiation emitted at 373 K passing through a CO_2 atmosphere. There is an apparent discrepancy by a factor of 15 in both the cross-sectional number density and the magnitude of the change in absorbance when the CO_2 pressure was reduced in the result attributed to Koch. The publication did not mention that Mr. Koch was an undergraduate student. There was no follow-up or validation of Mr. Koch's claim by experienced researchers. Despite the apparent flaws and second-hand reporting, Ångström's article appears to have ended any debate for decades afterwards. In 1938 there were discoveries in atmospheric monitoring[16] and an increasing understanding of CO_2 absorption of infrared light[17,18] both of which showed a glimmer of interest for the deeper problem posed. However, the consequences of absorption of energy by the atmosphere were ignored until Keeling began measuring the P_{CO_2}in the atmosphere in 1958.[19] By that time, there was a measurable and significant annual increase in CO_2 pressure in the atmosphere. By the 1960s, there was a growing consensus that the increase in P_{CO_2}in the atmosphere was correlated with a temperature increase at the earth's surface. Although the great majority of scientists agree that there is a correlation between P_{CO_2} and the documented temperature increase, there is financial and political support for a small minority of scientists who argue against such a correlation. To be generous in our interpretation Ångström was deceiving himself by means of his poorly conceived experiment. It is evident that self-deception exists in science, and it is particularly prevalent in areas of great current interest. Consequently, there is a need for physical science to provide a basic understanding of the issue that can be spread to the widest possible audience.

An enormous amount of work and thought that has gone into climate science including long-term implications based on studies of geology, paleogeology and oceanography.[20] The scientific objections to the link between anthropogenic CO_2 on the increasingly indisputable rising temperature of the earth's surface have been disproven.[21-26] However, the question remains: how can the scientific community disseminate an understanding of the alarming trends in a clear and understandable fashion? Computer simulations have great value for understanding marine and atmospheric cycles involved in the redistribution of energy throughout the geosphere, both in terms of chemical cycles, heat transfer and radiation balance. These methods have been applied to the effects of forcings and feedback loops on the energy balance in the atmosphere The collective efforts of many scientists have contributed to resources such as the Community Atmospheric Model (CAM3.0).[27-30] A second major initiative is the Coupled Model Intercomparison Project (CMIP).[31-34] These are open source computational models that include the oceans, ice, land and their interaction with the atmosphere useful for climate scientists.[35] A complete model of the effects of changes in any gas added to the atmosphere progresses from energy balance methods to complete global descriptions using finite difference methods on a grid.[36] These models include the full range atmospheric phenomena included in the water cycle, all relevant gases and the role of oceans and land, to describe the radiation balance. The great majority of scientists agree with the fundamental conclusion that increasing CO_2 in the atmosphere is a forcing term that is correlated with the temperature increase at the earth's surface.[27-29,37-42]The treatment presented here provides an appreciation of the starting point for such simulations and would permit a scientist with any related background to defend the basic ideas without necessarily understanding the details of a complex computer simulation. It certainly helps that the result of the simple model presented here is in reasonable agreement with the models.

Our approach is to employ a simple radiation equilibrium model that explains the greenhouse gas effect. The application includes a static model that properly calculates the surface temperature of the earth at a given fixed pressure of CO_2. The entire calculation is given in the Supporting Information, along with an Excel and python script showing the step-by-step calculation of temperature from an input CO_2 absorption spectrum from HITRAN and P_{CO_2}. In the Supporting Information we also present an analytic differential model that explains how continually emitting CO_2 leads to an imbalance in the radiation flux at the top of the atmosphere, which in turn causes the earth to heat continuously in the presence of constant incident solar radiation. We neglect scattering and reflection within the atmosphere, which greatly simplifies the treatment of radiation fluxes. The sole external variables are albedo and water vapor.

A reduction in transmittance due to an increase in energy-absorbing gas concentration will require an increase in the earth's surface temperature to compensate. The small net decrease in emission of ~0.85 W/m^2 in the spectral regions where earth emits radiation are caused by mainly by CO_2 absorption that creates a radiative forcing.[42,43] A great deal of effort has gone into measuring and modeling radiative forcings as a function of CO_2 concentration and distribution in the atmosphere.[44-49] Rather than calculating the CO_2 spectrum from first principles. To demonstrate this in a simple model we will use a publicly available database to obtain absorption transitions and their intensities. Computer codes such as MODTRAN also use the *hi*gh-resolution *tran*smission molecular absorption database (HITRAN) database to calculate radiation transfer in the atmosphere using either line-by-line or band models, respectively.[50] Comprehensive simulations are usually implemented in a layer-by-layer approach to account for all terms, absorption, emission and scattering in each layer. Non-specialists can learn to access the database and determine the spectrum of CO_2 from the tabulated values for a much simpler calculation that we have implemented in an Excel spreadsheet, an IgorPro spreadsheet, or using python scripts where we use only the output absorption intensities that are available in HITRAN. These are freely available in the Supporting Information.

Experimental evidence for increase in the concentration of atmospheric CO_2

The Keeling Curve shown in Figure 1 consists of observations of the measured ppm of CO_2 in the atmosphere at Moana Loa, Hawaii versus time in years.[51] The data for CO_2 ppm since 1958 have been summarized in ongoing web publications maintained by Scripps Institute. There are two easily discernable temporal variations of the CO_2 ppm level. There is a periodic annual variation (shown in the inset) superimposed on a super-linear increase. The fluctuations about the global average are due to local sources and sinks of CO_2 resulting from seasonal variation in plant growth and decay, industry, heating of buildings in the winter other aspects of the carbon cycle. These are continually measured by the GLOBALVIEW network of total carbon measurement spectroscopy centers.[52] The available data, taken over a large number of altitudes at different latitudes by NOAA, lead us to conclude that mixing is rapid in the atmosphere, which means that the Keeling curve is an accurate representation of global trends in atmospheric CO_2 concentration. [19]

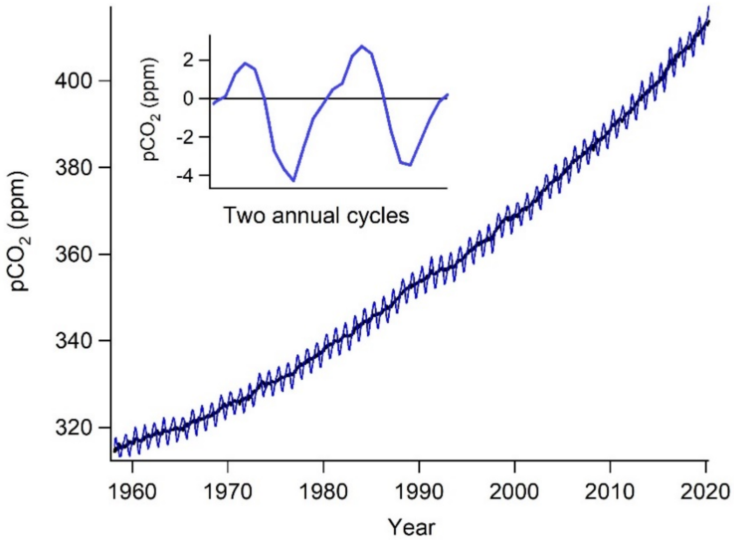

Figure 1. The Keeling Curve. The Moana Loa data are compared with data collected at latitudes between the Antarctic and the arctic and at high altitudes. These data demonstrate that the long term global increase in CO_2 ppm is accurately measured at Moana Loa.[19]

The underlying long-term increase shown in black in Figure 1 is super-linear, but not exponential. When fit to a quadratic polynomial in units of months, m:

$$\delta P_{CO_2}(m) = 2.601\,(\pm 0.244) + 0.06372\,(\pm 0.00152)\mathrm{m} + 9.029 \times 10^{-5} - 5\,(\pm 1.98 \times 10^{-6})\,\mathrm{m}^2$$

From the linear term, we can estimate:

$$\frac{\delta P_{CO_2}(m)}{\delta m} = 0.0637 \tag{4}$$

The periodic component is quite smooth, which implies that the mixing time of carbon dioxide in the atmosphere is short relative to the time of seasonal change. The Keeling Curve data collected in the last decade are essentially linear with a slope of 2.1 ppm per year. This corresponds to a global atmospheric increase of about 16 billion tons per year whereas economic data demonstrate that the worldwide annual combustion of fossil fuels produces more than twice that amount. It is apparent that approximately 50% of the CO_2 produced from combustion sources is taken up by the world's oceans. Far from helping to solve any problems caused by the atmospheric effects, the ocean uptake of CO_2 contributes to acidification, which may have future adverse consequences for phytoplankton and global O_2 levels if current trends continue.

Experimental evidence for absorption by atmospheric CO_2

Between 1970 and 1980 the NASA Nimbus IV satellite circled the earth at about 1100 km above the surface to collect atmospheric data. The principal absorbing and emitting species in the spectrum at the top of the atmosphere are water vapor (spread over most of the spectrum), carbon dioxide (between 590 and 790 cm^{-1}), ozone (between 1000 and 1100 cm^{-1}), and methane (between 1250 and 1450 cm^{-1}). A calculated spectrum for the earth's atmosphere matches the experiment extremely well.[53] Zhong and Haigh calculated the outgoing radiation at the top of the atmosphere including both infrared absorption and emission, using a layer-by-layer approach. Although it is great simplification, we show that a simple absorption model can also describe the forcing by CO_2 that results from the reduction in transmittance as P_{CO_2} increases. Across the range from 0 – 2,400 cm^{-1} the absorption spectrum consists primarily of absorption by CO_2 and H_2O vapor.[53] We show further that it is a good approximation to treat different absorbing species as additive constituents in a gas mixture. This approach is similar to that employed by Arrhenius, but with much better data thanks to HITRAN and the hindsight of more than 120 years that justifies the Planck theory and the integral of the Planck distribution known as the Stefan-Boltzmann law (Eqn. 1). Given the complexity of many models, a convincing physical demonstration must be feasible for even a non-specialist to implement a calculation to prove the validity of the correlation. We use a spreadsheet implementation of the calculation of the surface temperature of the earth, which is complemented by visualization and computation tools.

In solution chemistry absorption is calculated using the Beer-Lambert Law in the form $\ln(I/I_0) = -kc\ell$, where variables are the intensity, I, the molar absorptivity, k, the path length, ℓ, and concentration, c. In fact, since $I/I_0 = \rho/\rho_0$, radiation fluxes are affected by the same law. Both ratios are equal to the transmittance, τ. The concentration, c, is not constant in an atmospheric column. Calculation of intensity involves an integral over the variable c as a function altitude. The value of this integral is the number of moles of absorber in the column length, called the cross-sectional number density, u, given here in units of moles of absorbing gas per m^2. The quantity u for the earth's atmosphere is related to the atmospheric pressure, P, and the molecular weight of absorbing gas, M_{m,CO_2}, by u = P_{CO_2}/gM_{m,CO_2} where g is the acceleration of gravity. The mass of CO_2 in the atmosphere is

$$m_{CO_2} = \frac{P_{atm}A}{g} x_{CO_2} \quad (5)$$

where, $A = 1\ m^2$, $g = 9.8\ m/s^{-2}$, $P_{atm} = 1.013\ x\ 10^5\ N/m^2$, and $x_{CO_2} = 4.2\ x\ 10^{-4}$. This mass is converted to moles using the molar mass of CO_2 ($M_{m,CO_2} =$ 0.044 kg/mol). Using these quantities, we can calculate the limiting cross-sectional number density for CO_2 per m^2 for absorption up to the top of the atmosphere as

$$u_{TOA,CO_2} = \frac{m_{CO_2}}{M_{m,CO_2}A} \quad (6a)$$

The cross-section number density is $u_{TOA,CO_2} =$ 98.7 moles per square meter. We can also use Eqn. 5 to write this cross-sectional density as a proportionality to x_{CO_2}.

$$u_{TOA,CO_2} = \frac{P_{atm}}{M_{m,CO_2}g} x_{CO_2} \quad (6b)$$

Computation of CO_2 spectra

To calculate the rate of global energy change due to increasing CO_2 pressure we need to integrate the transmittance of all CO_2 transitions that absorb a fraction of the earth's emission. Infrared absorption by molecules in the gas phase results from simultaneous vibrational and rotational transitions, so-called rovibrational transitions. Figure 2 shows that CO_2 has three infrared-active vibrational modes, the asymmetric stretch, ν_3 at 2,349 cm^{-1} and two orthogonal bending modes, ν_2, each at 667 cm^{-1}.[54] The asymmetric stretch is far removed from the peak of the Planck emission of the earth at 288 K, which is approximately at 11,000 nm or 900 cm^{-1}. Since it absorbs in region very weak region of the earth's thermal flux the absorption has little effect on temperature. The symmetric stretch, ν_1, is not observed in the infrared spectrum, but is Raman active. Both ν_1 and $2\nu_2$ have an expected transition energy of 1334 cm^{-1}. This coincidence of two modes that have the same symmetry leads to a phenomenon known as Fermi resonance, which splits the band energy to give two observed Raman bands at 1285 cm^{-1} and 1388 cm^{-1}. As a consequence, there are two additional bands in the ν_2 infrared spectrum with origins at 667 ± 50 cm^{-1} or ~620 cm^{-1} and ~720 cm^{-1} as shown in Figure 2A. Because the CO_2 bending mode involves angular momentum from the bending vibration, all three branches of rotational-vibrational spectrum, P, Q, and R are infrared active.

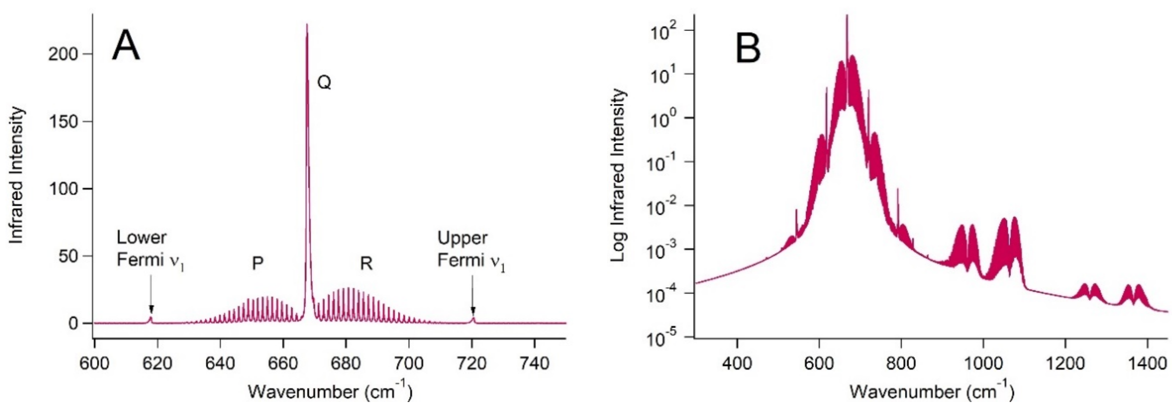

Figure 2. A. Infrared absorption spectrum of the bending mode of CO_2 obtained from data in the HITRAN database, including the Fermi splitting, which is indicated as the upper and lower Fermi levels. [55] B. The CO_2 absorption spectrum from 300-1450 cm^{-1} shown on a logarithmic scale. The lines obtained from the HITRAN database were dressed with Gaussian lineshapes that included a collisional broadening of 0.13 cm^{-1}.[56]

The two bending modes of CO_2 have additional infrared absorptions owing to Fermi resonance, which are also indicated in Figure 2. A Fermi resonance is a quantum mechanical result of the interaction of a two-quantum transition in the bending mode with the symmetric stretching mode. The two-quantum transition is totally symmetric because the square of any spectroscopic term is totally symmetric. The interaction gives rise to a splitting resulting from the sum and difference interaction energy between these two transitions. The splitting was first observed in the Raman spectrum of the symmetric stretching band of CO_2 in 1930 by Enrico Fermi.[57] Because the coupling is a mutual effect, the splitting is observed in the infrared transition of the bending mode as well. The Fermi resonance splitting energy is ~100 cm^{-1} so that the consequence of Fermi resonance in the infrared spectrum is a new set of absorptions with the entire set of rovibrational transitions located at 618 cm^{-1} and 720 cm^{-1} on either side of the main Q-band at 667 cm^{-1} (see Figure 2A).

It is convenient to obtain spectral intensities for CO_2 from the HITRAN database. There are approximately 67,700 transitions between 150 and 2400 cm^{-1} for natural abundance CO_2. Many of the absorption bands are very weak. Precisely because they are weak, these absorption bands are far from saturated. The CO_2-only model calculation quantitatively confirms that many weak lines give rise to increasing absorption throughout the entire range of CO_2 partial pressure. Given the Gaussian line width of γ = 0.13 cm^{-1} the spacing of these transitions is so dense that there is a continuous region of absorption extending from 400 – 1000 cm^{-1}, which includes the peak region for the earth's thermal radiation. Only the central region is saturated. The wings of the rotational branches and Fermi resonance associated rotational lines are far from saturated at the current concentration of 410 ppm obtained from the Keeling curve in Figure 1.[51] These features are evident in Figure 2A, which shows the progression of rovibrational bands in both the high and low energy directions and the Fermi-resonance origins. In the following we calculate the transmittance of these bands under atmospheric conditions as a function of CO_2 ppm. The skeptic's *saturation hypothesis*, which states that increasing CO_2 will not affect the absorption of energy from the earth has been addressed by Schildknecht in a recent article describing a spectroscopic and radiation model for the energy-absorbing gas effect.[57] We build on this work by providing a quantitative calculation of the transmittance of the atmosphere under terrestrial conditions. The intense central Q-band is saturated but large spectral flanking regions of the P- and R-band are not near saturation. The overall effect is nearly a linear dependence on CO_2 ppm up to P_{CO_2}~ 0.0006. There is some curvature by P_{CO_2}~ 0.001 atm, i.e. 1,000 ppm, but the saturation region begins at several thousand ppm of CO_2.

Methods

Assuming emission of a point source on the surface of the earth into a vertical column of the atmosphere with an area of 1 meter squared, the magnitude of the flux, $F_o(T)$, can be compared to the flux of thermal radiation in the presence of the angle dependence of CO_2 absorption,

$$F_{TOA}(T) = 2\pi hc^2 \int_0^1 \int_0^\infty \frac{\tilde{\nu}^3 e^{-k_{CO_2}(\tilde{\nu})u_{CO_2/\mu}}}{e^{hc\tilde{\nu}/kT} - 1} d\tilde{\nu}\, \mu d\mu \tag{7}$$

where $\mu = \cos\theta$. Combining the above results, the calculated flux transmittance at τ_{atm} is

$$\tau_{atm} = \frac{F_{TOA}(T)}{F_0(T)} \tag{8}$$

To calculate F_0 one assumes that $e^{-k_{CO_2}(\tilde{\nu})u_{CO_2}} = 1$. The transmittance is a function of the CO_2 ppm because u_{CO_2}depends on the concentration of CO_2 in Eqn. 7.

We can obtain the molar absorptivity of the CO_2 transitions from spectral measurements of infrared absorption bands of CO_2, which have been tabulated in the HITRAN database.[58] Similar calculations are possible for other energy-absorbing gases such as H_2O and CH_4. Methane is an increasing concern because of the large amount of this gas trapped in permafrost that will be released as warming continues creating a greater forcing. However, methane plays a relatively minor role today, compared to CO_2. We will include H_2O as a constant because it plays a major role in feedback processes and is important to any approximate model of atmospheric transmittance.

Results

Calculation of the effect of an energy absorbing gas on the transmittance of surface radiation

In order to implement the CO_2-only model as a predictive broadband steady-state model for absorption by the atmosphere, we can use the transmittance in the range 250 – 1990 cm^{-1}. The Planck curve initially has the following appearance, i.e. when P_{CO_2}= 420 ppm.

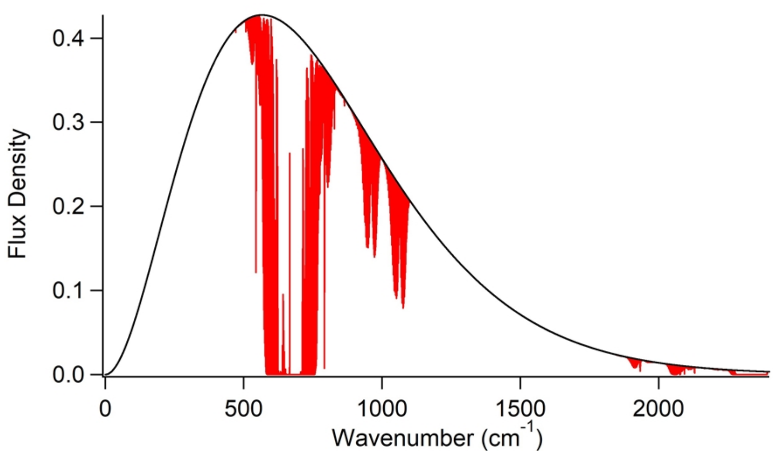

Figure 3. Planck thermal emission of the earth (black) assuming a surface temperature of 288 K compared to the emission combined with the transmission spectrum of CO_2 obtained from the HITRAN database (red).

The region between 250 – 1990 cm^{-1} has been plotted as transmittance at 410 and 1000 ppm for comparison in Figure 4.

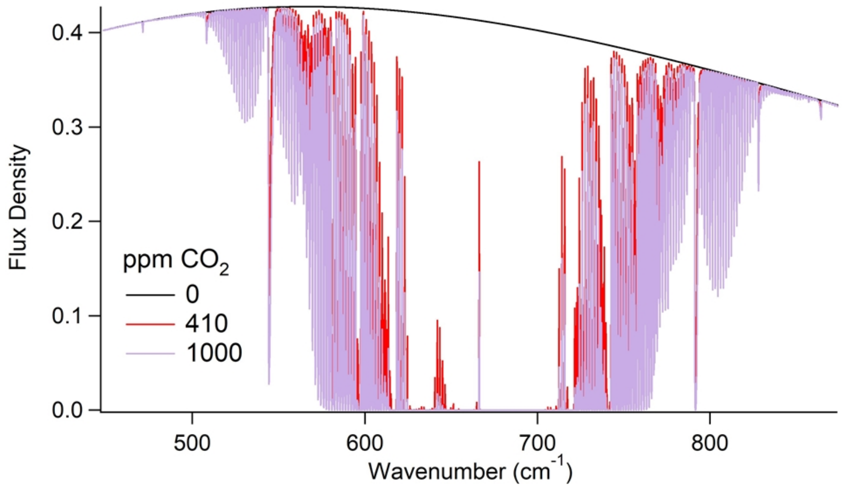

Figure 4. Comparison of the transition spectrum of CO_2 at 410 and 1000 ppm.

The average transmittance in the entire region shown in Figure 3 was used to estimate the change in transmittance across the Planck curve. We assumed that there is no significant change below 250 cm^{-1} or above 1990 cm^{-1} for this CO_2-only model. The Planck curve and each modified Planck curve with CO_2 transmittance included were integrated numerically. Then the ratio of the integrated flux is taken to obtain the transmittance at a given value of CO_2 ppm (see Supporting Information).

Consideration of the transmittance of water vapor

In order to approximate the effect of H_2O vapor on the CO_2 absorption, we use the fact that transmittances are multiplicative.

$$\tau_{atm} = \tau_{H_20}\tau_{CO_2} \tag{9}$$

For relatively small changes in the of ppm of CO_2 we can treat the H_2O transmittance as a constant and estimate that the decrease in total transmitted intensity as

$$\frac{\delta\tau_{atm}}{\delta ppm} \cong \tau_{H_2O}\frac{\delta\tau_{CO_2}}{\delta ppm} \tag{10}$$

The H_2O transmittance is a constant multiplicative factor because H_2O is relatively constant in the atmosphere (although it has cyclic variation in feedback loops), while CO_2 transmittance decreases as can be seen graphically in Figures 3 and 4.

The relative change due to CO_2 obtained from the calculated transition of HITRAN data was multiplied by an assumed $\tau_{H_2O} = 0.80$ in order to include the effect of H_2O and all other gases that absorb the earth's thermal emission to create the line shown in Figure 5. According to this model, CO_2 by itself accounts for ~20 % of the reduction in transmittance of the atmosphere at present.

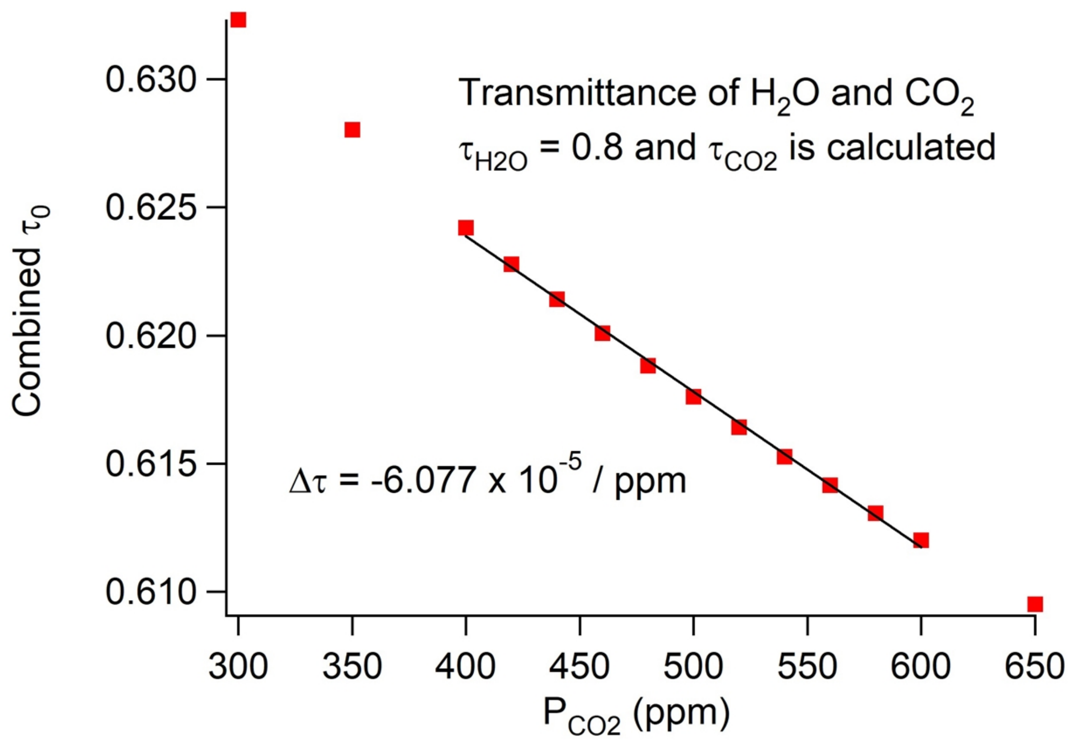

Figure 5. Global average transmittance of energy-absorbing gases. It was assumed that the transmittance due to all gases other than CO_2 was 0.80 and the differential effect and slope of the line is due only to CO_2. The model separates the effects of CO_2 from those other gases.

The change in the transmittance as a function of CO_2 ppm obtained from the regression line in Figure 5 is given by

$$\tau_{atm} = 0.648 - 6.077 \times 10^{-5}\, ppm \qquad (11)$$

The role of transmittance in the radiation equilibrium model

The model treats the earth's surface with no distinction between land, ocean or atmosphere, except that the atmosphere is an energy-absorbing layer that reduces the flux that escapes to space. The basis of the model used to calculate the temperature of the earth is that the incident radiation flux from the sun equals the flux from the earth. [59]

$$F_{solar} = F_{bare\ earth} \qquad (12a)$$

When the atmosphere is included it must still be true that the radiation leaving the earth at the TOA is equal to the solar flux.

$$F_{solar} = F_{TOA} \qquad (12b)$$

In order to maintain radiation equilibrium between the sun and earth, the radiation emitted from the TOA must be the same as the radiation emitted by the surface of the bare earth, i.e. the earth without the atmosphere. This also follows from Eqns. 12a and b.

$$F_{TOA} = F_{bare\ earth} \qquad (12c)$$

Next, we assume that the flux at the top of the atmosphere is reduced by the transmittance of the atmosphere that we calculated above.

$$F_{TOA} = F_{atm} \qquad (13)$$

Since we can calculate $F_{bare\ earth}$ we can solve for the flux at the surface of the earth surrounded by an absorbing atmosphere, F_{atm}. Since $\tau_{TOA} < 1$, the requirement for radiation balance at the top of the atmosphere at equilibrium requires the flux at the earth's surface to be larger than the flux of at top of the atmosphere. At equilibrium with a fixed amount of energy absorbing gas we have

$$F_{atm} = \frac{F_{bare\ earth}}{\tau_{TOA}} \tag{14}$$

Therefore, when the Stefan-Boltzmann law is applied $\sigma T_{atm}^4 \tau_{TOA} = \sigma T_{bare\ earth}^4$, and

$$T_{atm} = \frac{T_{bare\ earth}}{\sqrt[4]{\tau_{TOA}}} \tag{15}$$

Figure 6 shows the result of this calculation. Since $T_{bare\ earth} =$ 255 K, the equilibrated surface temperature of the earth surrounded by an atmosphere of CO_2 at 410 ppm is $T_{atm} =$ 285.4 K. According to NOAA the average temperature over the past 10 years has been 13.9 ^oC or 288.9 K. Clearly, using only natural abundance CO_2 and neglecting all other greenhouse gases will give a lower bound. However, the main point of this calculation is to estimate the rate of change of transmittance and temperature as the CO_2 partial pressure increases.

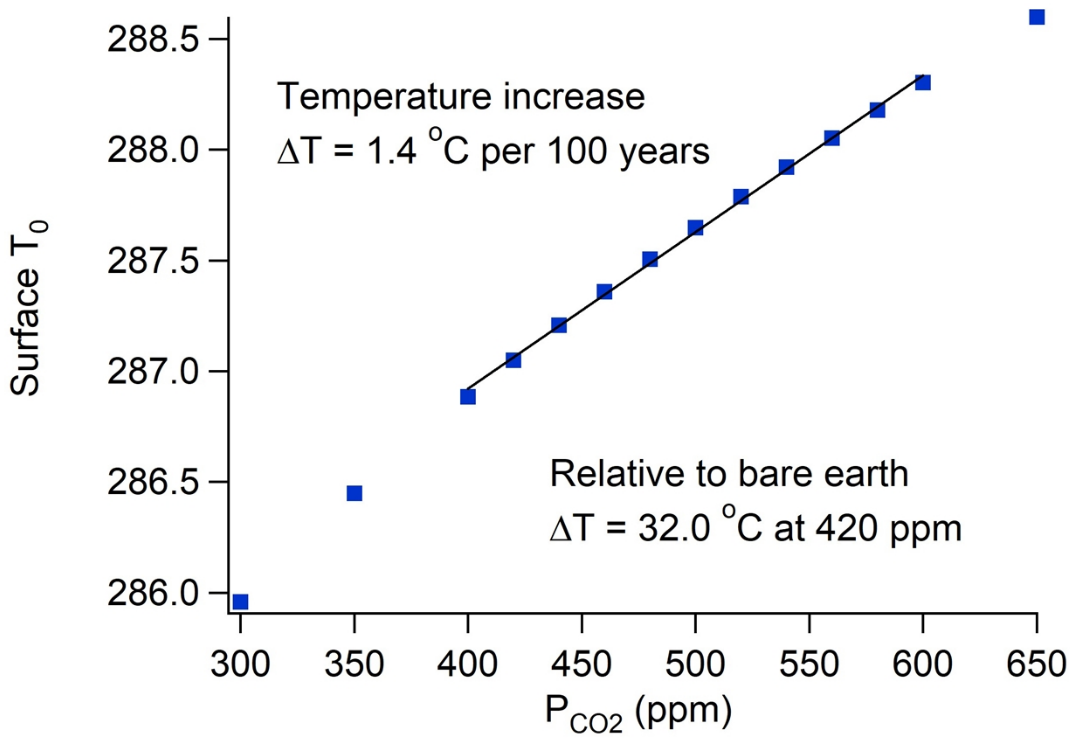

Figure 6. The correlation between the partial pressure of CO_2 in the atmosphere and the surface temperature calculated using radiation equilibrium while also accounting for the transmittance of the atmosphere.

The temperature increase compared to bare earth is 32.0 ^oC because of the greenhouse effect. The calculated warming since the earliest tabulated values in P_{CO_2} to the present is 1.1 ^oC. Current estimates of the warming in the atmosphere and ocean since the beginning of the industrial revolution are 1.0 ^oC and 0.8 ^oC, respectively. The ocean is the long-term heat sink because of its larger mass and much higher heat capacity. Thus, the calculated value compares well with either atmospheric or oceanic temperature changes. The model predicts that the surface temperature will have increased on average by an additional 1.4 ^oC when 600 ppm is reached. This would occur in the early 22nd century at the current rate of emission of CO_2. The model predicts an annual increase of 0.014 ^oC, which agrees with sophisticated climate models.

Discussion

There are many details that have been neglected in the radiation model described above. A detailed treatment of the energy balance by radiative transfer in the atmosphere would include reflection, transmission, and absorption of layers of atmosphere to account for changing pressures, temperature, and composition with altitude. Computer simulations are based on the above factors combined with the effects of radiative transfer, convection, and Coriolis forces as well as ocean currents, gas exchange and convection, but also absorption by other gases such as CH_4, O_3 and N_2O, H_2O feedback and scattering by aerosols. Although these are all important aspects, we only need the Planck radiation law and data for CO_2 absorption to obtain the fundamental result from the most important forcing term, P_{CO_2}. We have chosen the HITRAN database to calculate the transmittance in Eqn. (8) because it is the most complete and accessible to the public. Since the concentration of H_2O is variable in the atmosphere, we have assumed a cross-sectional number density that gave a reasonable agreement with the temperature trend. These parameters were used in an Excel spreadsheet provided in the Supporting Information. The HITRAN data for CO_2 were processed by summing Gaussian peaks with a linewidth of 0.13 cm^{-1}. Circa 67,700 transitions were used as input and the processed spectral data file consisted of 240,000 evenly spaced points from 0.01 to 2,400 cm^{-1}. Excel and IgorPro can easily manage these arrays. These materials are available in the Supporting Information. The Excel spreadsheet contains the spectra data in column B (Figure 2), the transmittance data in column I, the Planck distribution in column K and the product of the transmittance with the Planck distribution in column L (Figure 3). The spreadsheet allows calculation atmospheric transmittance and temperature for an input P_{CO_2}. In the final column (M) the integrated flux distributions with and without CO_2 are compared, the total transmittance of the atmosphere is calculated (with H_2O transmittance as a constant multiplier) and the temperature of the earth for a given CO_2 ppm is calculated according to Eqn. (15). Changes to the CO_2 linewidth and H_2O cross-sectional number density cannot alter the inescapable conclusion that increasing P_{CO_2} results in an increase in the temperature of the earth's surface.

Scientists have previously attempted to calculate the forcing term due to CO_2 with similar motivation, namely to illustrate the energy-absorbing effect of CO_2. In the 1960s, Stull, Wyatt and Plass used the data available at that time to estimate the absorbance using a statistical approach to determining the absorbance of segments of the CO_2 spectrum that had a width of 10 cm^{-1} or 50 cm^{-1}.[56] A statistical method was used because only the most intense CO_2 bands had been tabulated and the researchers were aware that there were numerous isotopologues and the Fermi resonance effect that created a congested spectrum.[56] Today, There is no longer a need for the complications of a statistical model since the CO_2 absorption lines are available from the HITRAN database. The HITRAN database also permits calculations that include isotopes of CO_2 and consideration of other greenhouse gases such as CH_4 and O_3. These are easy to implement by the methods used here, merely by selecting the spectral intensities corresponding to those species in the output from the HITRAN database, which has more than one million entries for CO_2 and its isotopologues.

There are three mechanisms by which the excited CO_2 can lose its absorbed energy: collisional deactivation, spontaneous emission, and stimulated emission. We can ignore spontaneous emission. In the text, "Atmospheric Radiation"[60] by Goody and Yung, the collisional lifetime of excited carbon dioxide is estimated to be 25 microseconds when the pressure is 1 bar and the temperature is 180 K. Even where the pressure of the atmosphere is 0.008 bar, near its lowest point, at 32 km and at 217 K, the collisional lifetime is 2 milliseconds while the spontaneous decay half-life of carbon dioxide in the first bending mode excited state is estimated to be about 0.75 seconds.[60] Thus, even at 32 km, where the ratio has its minimum value, there are about 375 collisional deactivations for every spontaneous emission. Stimulated emission makes a small contribution given that the equilibrium constant for population of the vibrational excited state of the CO_2 bending mode is relatively small and only ~ 3.7 % is populated a 298 K. Collisional deactivation dominates leading to dissipation of absorbed radiation as heat. Collectively, the molecules of the atmosphere also radiate as a thermal body, which should be considered in a detailed radiation equilibrium model.[61,62] We include the thermal radiation by the atmosphere itself as part of the total radiation from the earth's surface. This is clearly an enormous simplification.

The transmittance model based on the best available spectroscopic data show that CO_2 absorption in the atmosphere is saturated in the central region of the spectrum, but not in the flanking regions. Indeed, we can estimate that CO_2 will approach total saturation only when the partial pressure reaches many thousands of ppm, although it begins to depart from linearity at less than 600 ppm. There are many CO_2 bands, including the rovibrational progression and Fermi resonance bands, which are thermally populated to different extent. While the center of the transition, the Q-branch and most intense portions of the P and R branches are saturated, there are thousands of absorption bands that have sufficient concentration-dependent absorption intensity to act as a significant radiative forcing that increases the internal energy of atmosphere. Increasing P_{CO_2} results in decreasing transmittance which in turn increases the temperature at the surface of the earth. Despite its simplicity the radiation equilibrium model is quite accurate regarding the change in temperature, which is of greatest interest. The Keeling curve shows that P_{CO_2} increases at a rate of 2.1 ppm/year. At this rate, global P_{CO_2} will increase from its current value of 410 ppm to 600 ppm in 90 years. According to the radiation calculations using either method developed here, the temperature is predicted to increase by approximately 1.4 ^{o}C over this time. This is an entirely reasonable estimate when compared to more sophisticated models. The methods given here can be implemented by non-specialists to help them understand the imbalances in the system caused by a forcing, which is one of the foundations for climate system modeling.

The method implemented here provides a simple way to compare the energy-absorbing gas effect and its consequences with studies by critics of climate sciences.[63] The work by Schmidt and co-workers suggests that H_2O absorption swamps out CO_2 and that doubling the current P_{CO_2} would have little effect on the temperature. Using data from the HITRAN database processed by either an Excel spreadsheet or python code those claims could be put to the test. Based on evidence we can establish a correlation between P_{CO_2} increase and temperature rise. The data are the Keeling curve, the mass of the atmosphere, the earth's radius, the solar radius, and the temperature of the sun.

The issue we have addressed in this paper is the fact that chemists, physicists, and other non-climatologists are at a disadvantage in invoking climate-science computer models as evidence of changes in the energy balance of the earth and its atmosphere. The intent of the analytical approach to the energy-absorbing gas phenomenon is not to replace these detailed studies, but rather to make non-specialists aware of fundamental reasoning associated with interpretation of climate science that are often poorly understood by the public. The Excel spreadsheet is entirely based spectroscopy, geometry, and radiation physics that is taught at the undergraduate level in several disciplines. It is rarely taught in a cohesive manner that covers all aspects in each discipline because of crowded curricula. The model and calculation are a proposed remedy for those who feel that the subject of climate change deserves more attention in teaching and research.

Conclusion

We believe that the approach shown here and in the spreadsheet tool will be of value because many scientists have a reluctance to base a statement on a "black box" argument. It is not because of mistrust in the results, but rather that non-specialists do not feel sufficiently well versed in the methods to explain or defend the predictions of modeling or simulations that they have not conducted themselves. The model presented here provides chemists, physicists, and other interested scientists a demonstration of the effect of atmospheric absorbance on the surface temperature based on the fundamentals of spectroscopy and the theory of thermal radiation in its most elementary form, the Stefan-Boltzmann law. While the general concept of a *greenhouse gas* is widely understood, the correlation of CO_2 as an energy-absorbing gas with an increase in terrestrial temperature is best described using a quantitative model. It is gratifying that this model has stood the test of time since Arrhenius published a version of it in 1896, albeit with much more limited data.

Availability of Data and Materials Declaration

All materials will be made available on request. At present they are posted on a website located at: http://stemed.site/NCSU/Research/atm/index.html.

Funding Declaration

The authors did not receive support from any organization for the submitted work.

Ethics Approval

We understand and abide by the ethical guidelines of the journal.

Consent to Participate

Both authors consented to collaborate on this work in advance of the writing of the manuscript.

Consent for Publication

Both authors are aware of and support publication of this manuscript.

Competing Interest Declaration

The authors declare no competing interests.

Author Contributions

The authors contributed equally to this manuscript. Both were involved in the writing. Hugo. Franzen provided the radiation equilibrium methods, geometrical, and physical chemistry, aspects. Stefan Franzen provided spectroscopic applications, developed tools to use spectroscopic data, wrote all codes and made the figures.

Supporting Information

The supporting information consists of a differential flux method for determining the surface temperature of the Earth and the increase proportional to the CO_2 ppm increase in both an Excel and IgorPro spreadsheet. A parallel approach to the same data processing is provided in Python scripts. These are all given on the website: http://stemed.site/NCSU/Research/atm/index.html. The topics are numbered.

1. Theoretical intensities of CO_2 transitions
3. Methods for spectral calculations, flux, and effect of linewidth
3. Fortran programs for calculating the geometrically averaged line shapes
4. Atmospheric temperature increase as result of CO_2 increase (differential flux method)
5. Earth_Temperature Spreadsheet, Earth_Temperature_Spreadsheet.pdf and Python scripts that demonstrate the columns of the spreadsheet graphically and follow each step of the derivation from HITRAN CO_2 absorption bands to CO_2 transmittance and finally surface temperature of the Earth.

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