HOW CO2 Causes Warming & the Log Effect

Donald Bogard,   Sept. 2018

General Considerations.

   This commentary gives a broad and moderately detailed summary of exactly how CO2 and increasing atmospheric CO2 can produce warming. I am not aware of a summary that covers the subject broadly but simply. This explanation was compiled in bits and pieces from various locations. Here I cover several topics conceptually (not mathematically), including the nature of IR radiation and it's absorption by CO2; the concept of emission height for IR loss to space; and how increasing CO2 concentration influences IR absorption producing a log-like relation between increasing CO2 and temperature. I assume that the reader has some basic familiarity with the structure of molecules and the nature of radiation and its interaction with matter. Please comment on anything you may disagree with.

   Radiation from the Sun arrives at Earth spread across a wide range of energies (wavelengths), but predominately in the visible region. Much of this radiation is absorbed by Earth's surface and a smaller part by the atmosphere. Because Earth's temperature is much lower than the Sun's, Earth radiates away that absorbed energy mainly in the IR (infra-red). For Earth to maintain a constant temperature proportional to the solar energy it receives, it must immediately radiate that energy as IR back to space. If there occurs any delay in radiating that energy away, the Earth's surface will warm in proportion to the amount of the delay. A portion of the IR radiation emitted by Earth's surface does pass directly to space. However, so-called greenhouse gases (CO2, H2O, CH4, etc.) absorb part of that emitted IR at specific wavelengths. These molecules then emit a new IR photon of the same wavelength. Such IR absorption and emission can and typically does occur over and over in the atmosphere. It is the details of that IR absorption that produces warming.

Basic IR Absorption, Emission, & Energy Transfer.

   Most IR absorption by CO2 occurs at wavelengths of ~15 μm (micrometers), with a smaller amount absorbed at ~4.3 μm. Although both CO2 and H2O absorb at ~15 μm, but mainly CO2 at ~4.3 μm, the surface IR emission is usually much greater at ~15 μm (see Fig. 1). When an IR photon is absorbed by a specific C=O molecular bond, the energy level of that bond is increased. Because the C=O bond has many possible modes of vibration and rotation (discussed later), each with a different energy level, when a C=O bond absorbs energy it can be left in one of many distinct energy levels. Each of these energy levels and the specific energy absorbed in getting there
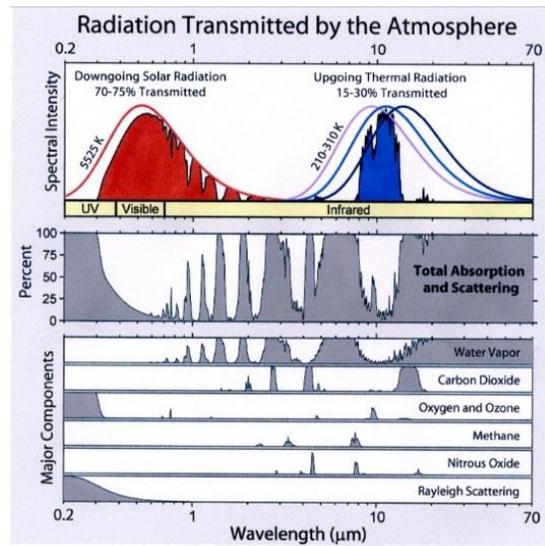

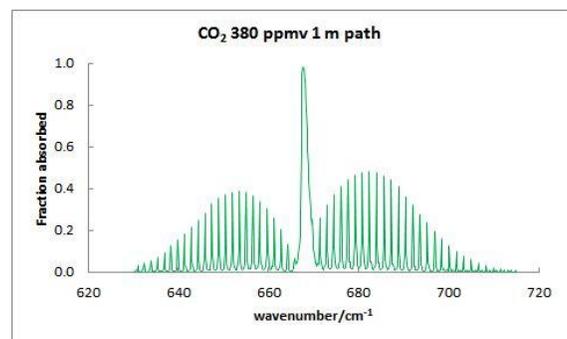Fig. 1. Some radiation characteristics.

Fig. 2. The v=0 to v=1 vibration-rotation transition.

is fixed and must obey quantum rules. Although the average wavelength of the IR photon absorbed is 15 microns, the range of wavelengths for various absorbed photons is much wider and can absorb IR across ~13-17 μm.

   Figure 2 shows the range of quantized wavelengths the lowest vibration energy state of the

C=O bond can absorb for 330 ppm atmospheric CO2 at sea level. There are many more possible quantum energy states than represented by the vertical "spikes" in the figure. Here each quantum level represents some combination of vibrational and rotational energy modes. (Fig. 2 and similar graphs often use wave number rather than wavelength, where wave number is simply the inverse of wavelength in cm.) At 330 ppm atmospheric CO2, only the major vibrational energy level at a wavenumber of 666 is saturated, where saturation implies that all IR photons of that wavelength emitted by Earth's surface would be absorbed before reaching space. By contrast, the many rotational energy states to either side of this central peak are not saturated and at 330 ppm absorb less than 40% of the relevant IR wavelengths emitted from the surface. These smaller energy levels play an important role when CO2 is increased, as I discuss later.

Atmospheric gases are in rapid, constant motion due to their kinetic energy and thus experience continual collisions. These collisions readily transfer energy from one molecule to another. For atmospheric gases near standard temperature and pressure (STP, i.e., summer and near sea level), molecular collisions occur on a time scale of nano-seconds, but less frequently at higher altitudes and low temperatures. For all molecules in a gas, transfer of kinetic energy often occurs through the kinetic energy of motion and via energy contained in specific bonds. Thus, when a CO2 molecule absorbs an IR photon and gains increased vibrational energy in a specific C=O bond, that extra energy can be transferred to another molecule that collides with that bond. That is, transfer of kinetic energy between molecules often occurs through their bonds. In this manner, absorption of IR radiation by molecular bonds of specific molecules (e.g., CO2) in a mixed gas (e.g., air) transfers that energy into increased kinetic motion and temperature of the whole gas mixture. That is how IR absorption by greenhouse gases warms the atmosphere. Because near STP atmospheric molecules collide every few nano-seconds, such energy transfer into the gas is very rapid.

When a CO2 molecule absorbs an IR photon, an alternate consequence is to radiate away an IR photon of the same wavelength. Or, a CO2 molecule whose kinetic energy and bond energy levels are too low to radiate an IR photon may at some point gain additional C=O bond energy from a molecular collision and then radiate away an IR photon. However, after gaining sufficient C=O bond energy to permit IR emission, that C=O bond cannot emit an IR photon immediately. Rather, there exists a bond relaxation time defined by the vibrational frequency, and this relaxation time restricts how quickly the bond may lose energy through IR photon emission. For CO2 emitting a 15 µm IR photon, this relaxation time is one to ten microseconds.
https://noconsensus.wordpress.com/2010/08/17/molecular-radiation-and-collisional-lifetime/

Because the time constant for a CO2 molecule to transfer extra energy to another molecule via molecular collision is much faster than the time constant to lose that energy via IR emission, a CO2 molecule is much more likely to transfer newly gained bond energy as kinetic energy into the gas mixture than to emit an IR photon. If it were otherwise, heating of the atmosphere by IR absorption would not be an efficient process. Because of the very short times involved in IR emission, it is quite unlikely that the overall time delay, even considering possibly scores of individual IR absorptions and emissions before photon escape to space, is sufficient to produce measurable atmospheric warming.

Emission Height & Atmospheric Warming.

To aid examination of the question of how CO2 produces warming, Fig. 3 shows satellite data for the intensity of upwelling IR radiation (in mw/m^2) as a function of wave number (wave length above graph). The measurements were made over the hot Sahara desert, where absorption by H2O is minimized. The major CO2 absorption band around 666 cm^{-1} (15 µm) is labeled; H2O absorbs below ~550 cm^{-1}; there are no significant absorbers over ~800-950 cm^{-1}. The dashed lines represent various IR emission temperatures calculated from the basic relation that equates the IR emission rate of a material to the Stefan-Boltzmann constant multiplied by temperature raised to the fourth power ($E=\sigma T^4$). The measured data across wave numbers thus reveal the temperature of the atmosphere where that IR was emitted. Across ~800-950 cm^{-1}, the IR flux is consistent with emission at a temperature of ~318K (~45C) and thus identifies part of the near-continuous IR emission from the hot Sahara desert surface. In

contrast, the central part of the CO2 emission around 15 µm is consistent with a temperature of ~215K (~ minus 58C) and thus defines emission from very high in the atmosphere. (The atmosphere cools with increasing height at an average rate of ~6.5K/km called the lapse rate.) Because the upper atmospheric temperature is much lower, the emission rate is also lower (~40 mw/m^2 versus ~160 mw/m^2 from the surface). The atmospheric height at which this IR emitted by CO2 was detected was the CO2 *Emission Height* for this measured IR at this location and that particular time and temperature profile. This concept of emission height is not a specific altitude, but a vertical region of the atmosphere, and it simply represents the approximate altitude where a ~15 µm photon emitted by a C=O bond was more likely to escape into space than be absorbed. Thus, an emission height depends on several variable factors, including the specific species and IR wavelength, the location, and the atmospheric temperature profile.

Figure 3 reveals one fundamental method by which greenhouse gases like CO2 produce atmospheric warming. If an atmosphere contained no IR absorbers, then all IR emission to space would occur from the warmer surface. Because greenhouse gases like CO2 do absorb and emit IR, and because that absorption-emission process occurs many times as the energy migrates upward in the atmosphere, then the final IR emission to space occurs from the colder higher atmosphere. Consequently, because temperature is lower there, the emission rate is slower and the atmosphere beneath must warm to re-establish an energy equilibrium. This process by which solar radiation mainly is deposited at the surface, but is lost as IR from the high atmosphere underlies the atmospheric temperature profile (lapse rate).

To better understand how an incremental increase in atmospheric CO2 can produce an incremental increase in temperature requires that we go into more detail concerning the data in Fig. 3 and the atmospheric temperature profile. Fig. 4 shows typical schematics of atmospheric temperature up to 30 km for three latitudes – equator, polar, and
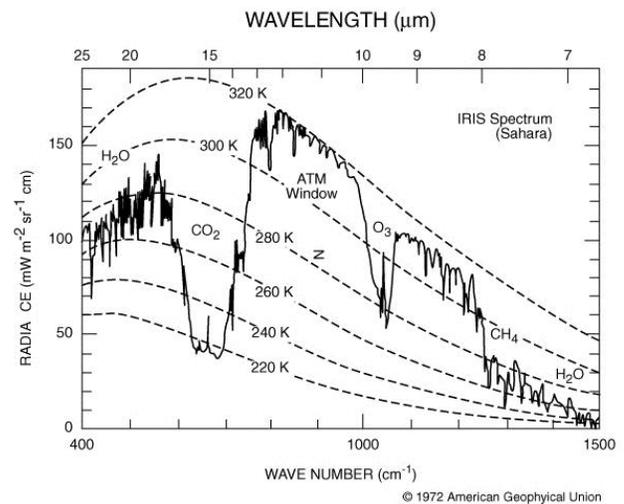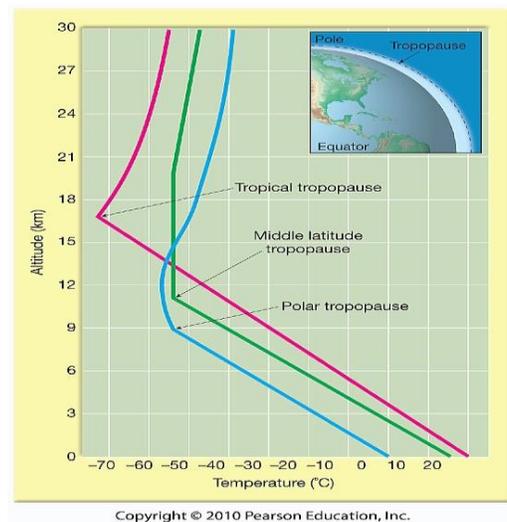

Fig. 3. Satellite measure IR spectrum.

Figure 4. Typical atmospheric temperature profiles.

mid-latitude. The tropopause, defined as the boundary between the troposphere and the stratosphere, is the altitude where temperature stops decreasing with altitude and eventually begins to increase. Sometimes this change in lapse rate occurs relatively quickly, and sometimes temperature only slows and remains relatively constant over a significant range of altitudes. The tropopause commonly occurs between ~9 km and ~18 km, and the temperature at the tropopause commonly lies between -50 and -70C. The deepest part of the CO2 absorption band in Fig. 3, with an indicated temperature of ~-58C, indicates that emission occurred around the tropopause.

If additional CO2 is added to the atmosphere, its concentration at the old emission height goes up, and the probability that an emitted IR photon will escape Earth goes down. The actual emission height thus increases. However, because of the temperature lapse rate (Fig. 4) this new emission height is in a colder part of the atmosphere and the IR emission rate decreases. Because less energy is now escaping Earth, it warms until the temperature at the new emission height is sufficiently high to bring energy gain and loss back into balance. This is the basic mechanism by which additional CO2 increases warming.

Details of the Warming Mechanism.

To interpret details of Fig. 3 and atmospheric warming when more CO2 is added, we need a greater understanding of how the C=O bond absorbs across wavelength and with increasing CO2 concentration. Fig. 5 shows the ~15 μm absorption band where relative absorption is plotted on a log scale covering 12 orders of magnitude, rather than the linear scale of Fig. 2. In detail, IR absorption by the C=O bond spreads across a very wide wavelength range, but absorption intensity decreases dramatically with increasing distance from the ~15 μm center of the absorption. (The ~4 μm CO2 absorption overlaps on the left of the graph.) In addition, the individual absorption lines become broader as the absorption intensity increases near the ~15 μm band center, as indicated by comparing Fig. 6 with Fig. 3. (Fig. 6 doubles the IR path length for the same CO2 concentration, and is equivalent to doubling CO2 concentration over the same path length.) Line broadening, in part, is produced by increased molecular collisions and doppler effects. This characteristic of IR absorption explains why the C=O band width representing ~-58C emission spreads across a wider wavelength in Fig. 3 than might be predicted from Fig. 2. An IR photon near the ~15 μm peak is more likely to be absorbed than one at 14 or 16 μm, and photons at 13 or 17 μm are even less likely to be absorbed. A lower probability of being absorbed implies a long path length between absorptions. This means that the emission height for IR emission varies with the emitted photon
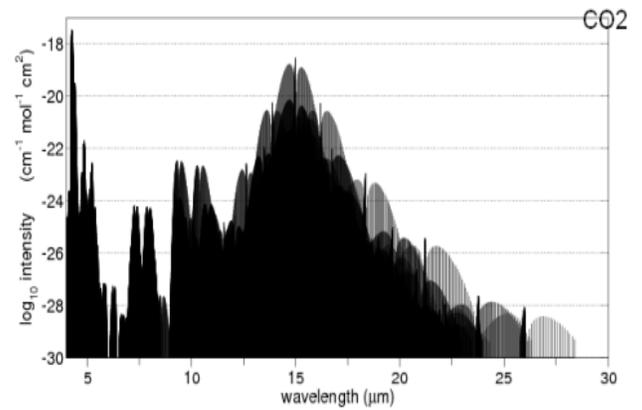

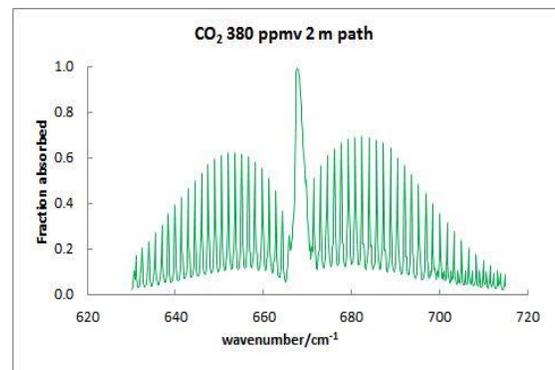Fig. 5. All IR emissions in the 15 μm CO2 band. Calculated from HITRAN data base.

Fig. 6. IR absorption for 2x the CO2 amount as Fig. 2.

wavelength, and thus reflects a different atmospheric temperature and altitude. This is apparent in Fig. 3, where, as emitted photons have increasingly different wavelengths from 15 μm, the IR intensity and the emission temperature both increase because their emission height is lower in the atmosphere. Weather satellites take advantage of this characteristic to measure different atmospheric depths of an IR emission band.
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Details About CO2 IR Energy Transitions.
(Read or skip to next section.)

Some people seem to think of the quantum limitations on IR absorption and emission as arising from the radiation itself. However, the quantum limitations derive from the specific molecular bond. Many different energy transitions are possible with the C=O bond, but also many rules and forbidden transitions exist. Vibrations (bond bending and stretching) are the most energetic and are given the designation of v=0 for the lowest energy level, v=1 for

the next energy level, and so on. Rotation about the bond have lower energy than vibration. For the ~15 µm C=O bond, there are 13 permitted vibrational energy transitions spanning 544-1064 cm^{-1}, the most important being from the ground state (where most atmospheric CO2 molecules reside). Some of these transitions have similar energy of ~667 cm^{-1} and produce the large central peak in Figs. 2 & 5. Other vibrational transitions are less prominent, but two at 618 cm^{-1} and 721 cm^{-1} are obvious in CO2 spectra. (These last two are not shown in Fig. 2 because it only shows transitions between v=0 and v=1, but they are apparent in Fig. 5.)

There are many transitions involving changes in bond rotation levels. These produce the many smaller IR absorption peaks to either side of each center vibrational peak (Fig. 2). Other vibrational energy changes produce similar associated distributions of rotational energy changes (Fig. 5). For CO2, a change in rotational level (absorption or emission) cannot be produced by photon interaction alone unless a vibrational change also occurs. However, changes in rotational energy levels can and do occur through molecular collisions.
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Saturation and the Log Effect of CO2 Warming.
Some claim that adding more CO2 to the atmosphere cannot produce more warming because the relevant absorption wavelengths are already saturated. Saturation is commonly defined as the amount of CO2 required to decrease the IR flux by a factor of 1/e. But this definition applies to the IR source being in one location, e.g. the Earth's surface. Every CO2 molecule residing above Earth's surface is not only an absorber of ~15 µm IR, but also an emitter. This is how IR energy moves upward, by repeated absorption and emission at all altitudes. It is not absorption of various wavelengths that directly contributes to warming, but at what rate each IR photon is emitted at its emission height. If all photons in the ~15 µm band were absorbed and not later emitted, what would stop increasing atmospheric warming?

To better understand this process, it is useful to examine how warming would progress as CO2 is increasingly added, beginning at a very low level.

Determination of such details of CO2 warming are typically done by using the HITRAN spectral data base, which is a large compilation of very-high resolution spectral data and model calculations used to predict and simulate the transmission and emission of light in the atmosphere. Figure 7 shows one result of such calculations across 500-750 µm for incremental additions of atmospheric CO2 of 1, 10, 100, 300, and 1,000 ppm (beginning at zero -- different colored lines). Each absorption spectrum is vertically offset (downward) by 5 mmW/m^2sr-1cm^{-1} to enable comparison. At 1 ppm CO2, very little IR absorption results because the absorption is very narrow (only showing the v=0 to v=1 vibration transition), and because IR emission would occur from very low in the atmosphere, where temperature is warm. At 10, 100, and 300 ppm CO2, the central vibration peak becomes larger, the lesser vibration peaks at 618 and 721 µm appear, and associated rotation bands appear and grow. Adding increasing CO2 to the atmosphere does three things. It increases the amount of absorption in the most sensitive part of the ~15 m absorption spectrum; it broadens the effectiveness of IR absorption across a wider wavelength range; and, because increasing CO2 raises the emission height for all wavelengths, it causes an increasing proportion of the IR emission to occur from colder regions of the atmosphere. This third point is important because as an increasing
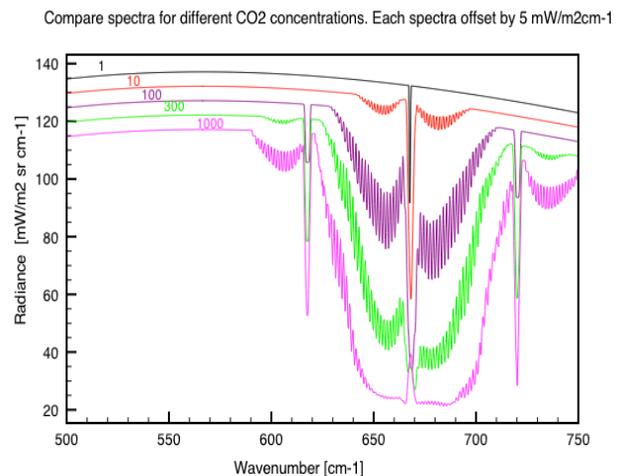

Compare spectra for different CO2 concentrations. Each spectra offset by 5 mW/m2cm-1

Fig. 7. How increasing CO2 widens and deepens the ~15 m absorption band from 1 to 1,000 ppm.

<u>fraction of IR emission occurs from colder regions, the addition of more CO2 becomes less effective at warming</u>.

At 1,000 ppm CO2 in Fig. 7, the central vibrational peak reverses direction and increases IR radiance. This likely occurs because the assumed temperature profile used in the calculations defined a reversal in lapse rate at this height; i.e., temperature began increasing (see Fig. 4). Often actual satellite IR spectra show a similar IR emission reversal; see Fig. 3. Although such reversals in IR emission of the major vibration peak would tend to produce atmospheric cooling at that height, the effect would be dominated by the lower temperature and IR emission from the increasing width of the overall ~15 μm band.

The consequence of the underlined text above is in principle revealed by Fig. 8, which plots outgoing 13-17 μm IR against increasing atmospheric CO2, assuming a constant surface temperature of 288K (15C) and dividing the atmosphere into 100 meter vertical layers. (The assumed lapse rate for the calculations are not stated.) The curve labeled "surface" refers to the lowest layer or two and defines that ~15 μm IR emitted from this layer directly to space. High initially because the emission height is in lower, warmer atmosphere, this component rapidly decreases toward zero as the emission band spreads (Fig. 7) and emission occurs from higher, colder atmosphere. By contrast, that ~15 μm IR emitted from the higher atmosphere increases because growing CO2 increases the absorption band width (Fig. 7). The cross-over point is ~100 ppm CO2. The total ~15 μm absorption defines a log-like descending curve for absorption as CO2 increases above ~300 ppm.

The conclusion that increasing atmospheric CO2 produces a log-like decrease in the rate of is confirmed by several independent calculations (Fig. 9). Here the amount of warming is expressed in radiative forcing (w/m^2), where ~3.7 w/m^2 of such forcing would increase atmospheric temperature by about 1.1 deg-C for each doubling of CO2 concentration. This curve suggests that starting from today's 400 ppm CO2 and ~2 w/m^2 of radiative forcing, doubling CO2 to 800 ppm would increase that forcing to almost 6 w/m^2. In principle, any
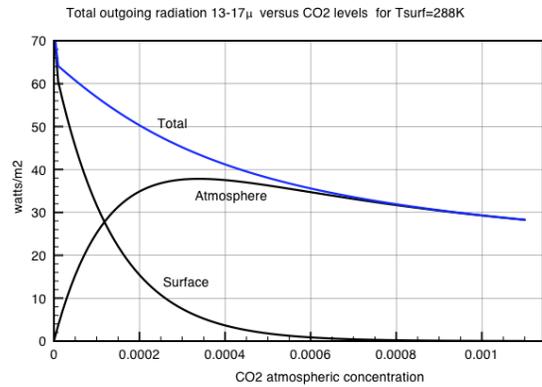

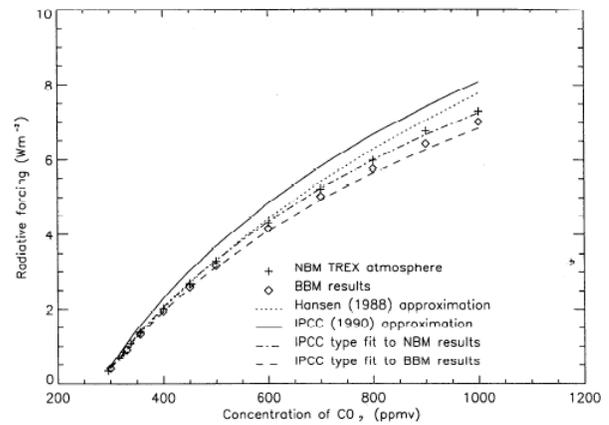Fig. 8. Relative effects of CO2 IR emission from near surface & high in atmosphere.

Fig. 9. Calculation results of radiative energy with increasing CO2.

decrease in IR emission with growing CO2 caused only by a decrease in emission height temperature should be a linear effect, given the atmosphere lapse rate is typically linear, as shown by Fig. 4. Therefore, the log-like character of the total IR absorption by CO2 demonstrates the dominance of increasing IR emission from the growing width of the band as CO2 increases (Fig. 7). The measured IR spectrum in Fig. 3 suggests that of the revealed CO2 emission across ~600-800 um, at least half occurred from the sides of the absorption band at lower altitude and higher temperature, where the rate of IR emission is enhanced compared to the band center.

Figure 10 documents an intriguing feature of the effect of IR emission by CO2 as its concentration increases. That is each doubling of atmospheric CO2 concentration produces a smaller relative temperature increase. This is illustrated by Fig. 10, where the log curve has been normalized relative to

measured temperature and CO2 concentration. From 200 ppm CO2 to 400 ppm CO2, temperature increases by 1.5C; from 400 ppm to 800 ppm CO2, temperature only increases by 1C. Note that Fig. 10 only applies to direct warming produced by CO2 alone, without any effects from warming feedbacks.

Fig. 10. Log relation between increasing CO2 and temperature.

I recommend the 8-part series on effects of CO2 on climate by Science of Doom; on line.

Sources of Figures.
Fig. 1.
https://commons.wikimedia.org/wiki/File:Atmospheric_Transmission.png
Figs. 2 & 6.
http://www.barrettbellamyclimate.com/page15.htm
Fig. 3. American Geophysical Union, 1972.
Fig. 4. Lutgens and Tarbuck's *The Atmosphere*, 2001.
Fig. 5. https://scienceofdoom.com/2009/11/28/co2-an-insignificant-trace-gas-part-one/ calculated from
http://www.spectralcalc.com/spectral_browser/db_intensity.php
Fig. 7. http://clivebest.com/blog/?p=1169
Fig. 8. http://clivebest.com/blog/?p=1169
Fig. 9. Myhre et al, *Geophysical Research Letters* (1998).
Fig. 10.
https://agupubs.onlinelibrary.wiley.com/doi/epdf/10.1029/98GL01908