# **Fear No Carbon**

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Major Area of Study: Plasma Physics

Minor Area of Study: Atomic Physics and

Spectroscopy

### **Purpose**

To provide the intelligent layperson with a sufficient understanding of the scientific principles related to the current climate change issue to be able to confidently make informed decisions concerning where they stand in this matter.

# In the Beginning...

#### Greenhouse effect first discovered

• Discovery of the greenhouse effect is generally credited to Jean-Baptiste Fourier in 1824 when he calculated that a planetary object the size of the earth and at the same distance from the sun would be cooler than the earth at its surface. Concluded that the atmosphere has a blanket or insulating effect.

#### **Discovery of heat-trapping gases**

• In the mid 1800s, water vapor and carbonic acid gas (ie. CO<sub>2</sub>) were identified as gases that absorb and reradiate heat. This was in connection with Ice Age research at the time.

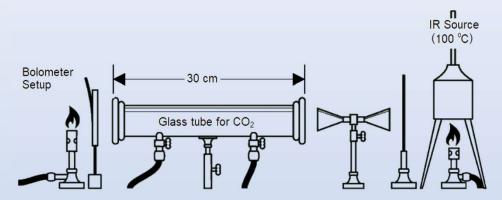
Eunice Foote, Circumstances Affecting the Heat of the Sun's Rays, American Journal of Science and Arts, 1856. Also, results announced at the 1856 meeting of the American Association for the Advancement of Science.

John Tyndall, On the Absorption and Radiation of Heat by Gases and Vapours, and on the Physical Connexion of Radiation, Absorption, and Conduction, Philosophical Transactions of the Royal Society of London,

• Tyndall also stated that small amounts of hydrocarbon vapors would produce great effects on the terrestrial rays and produce corresponding changes of climate.

#### Arrhenius vs. Ångström

- In 1896, Svante Arrhenius calculated that a doubling of CO<sub>2</sub> concentration would cause a 5-6°C increase in temperature. Unfortunately, however, his calculations involved use of the Stefan-Boltzmann law which assumes a blackbody spectral distribution at all altitudes, which is incorrect.
- A few years later (1900) Knut Ångström instructed his assistant J. Koch to devise and run tests to show the absorption of terrestrial (ie. upwelling IR) radiation by CO<sub>2</sub>. Below is a diagram of his setup.

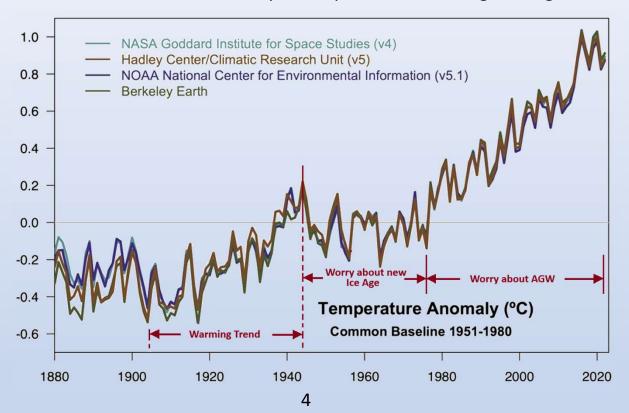


 In this setup, the 30 cm tube was first filled with pure CO<sub>2</sub> at atmospheric pressure and the amount of transmitted IR radiation measured with the bolometer. The tube was then filled with CO<sub>2</sub> at 2/3 atm pressure, and the transmitted IR dropped by only about 1 percent, indicating saturation of IR absorption by CO<sub>2</sub>. • In his paper titled About the Importance of Water Vapor and Carbon Dioxide During the Absorption of Earth's Atmosphere (Annalen der Physik, vol. 308(12): 720-732), Ångström concludes:

From these studies and calculations, it is clear, first, that no more that about 16 percent of Earth's radiation can be absorbed by atmospheric carbon dioxide, and secondly, that the total absorption is very little dependent on the changes in the atmospheric carbon dioxide content, as long as it is not smaller that 0.2 of the existing value.

- This paper contradicts and criticizes the results of Arrhenius who then strongly dismisses Ångström's claims in a paper titled *About the Heat Absorption through Carbon Dioxide* (Annalen der Physik, Vierte Folge(4): 690-705). His arguments, however, were not generally accepted for over fifty years.
- It should be noted that Arrhenius viewed the possibility of global warming from carbon dioxide (manmade or otherwise) as favorable since the climate threat that was generally perceived at the time was a new ice age. However, he far under-estimated the level of CO<sub>2</sub> emissions during the 20<sup>th</sup> century.

- Interest in Arrhenius and his work with greenhouse gases, especially CO<sub>2</sub>, was revived in the 1970s by people and organizations claiming that the increasing atmospheric CO<sub>2</sub> levels posed a warming threat to the global environment.
- Below is a plot showing mean temperature variations over the 20th century and up to 2020 from several different data sets. It indicates about when important perceived warming/cooling trends occurred.



### **Climate Modeling**

#### **General Circulation Models**

• General circulation models (GCM) are models in which a combined set of fluid equations, radiative transfer equations, thermodynamics, and possibly biological principles are solved in order to describe the circulation of the earth's atmosphere or oceans. Specific equations include:

Navier-Stokes Equation 
$$\rho \Big[ \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \Big] = \mu \nabla^2 \mathbf{v} - \nabla p + \rho \mathbf{g}(\mathbf{x}, t)$$
 Modified Stefan-Boltzmann Law 
$$L = \frac{\text{heat radiated}}{\text{area} \cdot \text{time}} = \epsilon \sigma T^4$$
 Clausius-Clapeyron Equation 
$$\ln \left( \frac{P_{\text{eq}}}{P_{\text{ref}}} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T_{\text{eq}}} \right)$$

• The first use of a GCM to predict the atmospheric effects of changing CO<sub>2</sub> levels is described in a paper by Manabe and Wetherald titled *Thermal Equilibrium of the Atmosphere with a Given Distribution of Relative Humidity* (Journal of the Atmospheric Sciences, Vol. 24, No. 3, May 1967). It was a 1D radiative-convective model that showed a "climate sensitivity" of 2.4°C. This is the temperature rise predicted with a doubling of CO<sub>2</sub> concentration.

- In 1975, Manabe and Wetherald considered this same problem but with a 3D model in a paper titled *The Effects of Doubling the CO2 Concentration on the climate of a General Circulation Model* (Journal of the Atmospheric Sciences). Showed a climate sensitivity of 2.4°C.
- Since that time, model capabilities have been expanded to include land surface, ocean, and sea ice as well as the atmosphere.
- Accuracy of the GCMs are tested and maintained through hind-casting techniques. This involves
  initializing the model to observed conditions at some point of time in the past. The model then runs
  and is updated at each time step with the recorded solar intensity, volcanic activity, and greenhouse gas
  levels. The model results are then compared with observed conditions to see how well they match.

#### **Climate Sensitivity Predictions**

- Climate sensitivity (ie. the effect on global temperature resulting from a doubling of CO<sub>2</sub>) is predicted from an idealized energy balance solution in which we first modify the Stefan-Boltzmann law to include an emissivity factor ε to account for all greenhouse absorption. This factor, in effect, becomes a "one size fits all" absorption factor for all frequencies in the EMR spectrum. *This is incorrect!* It ignores the absorption spectra for the individual GHGs and the fact that some may no longer be able to absorb at certain altitudes. This is an effect called *band saturation*.
- Unfortunately, however, this model is the basis upon which the IPCC and the climate change community in general advises us to reduce our "carbon footprints".

#### **The Charney Report**

- The report of an Ad-Hoc Study Group on Carbon Dioxide and Climate titled *Carbon Dioxide and Climate: A Scientific Assessment* came out in 1979. The study group was convened at the request of the Office of Science and Technology Policy under the auspices of the Climate Research Board of the National Research Council.
- The purpose of this study was to access the scientific basis for projection of possible future climate changes resulting from man-made releases of carbon dioxide into the atmosphere. A few results of the study are listed below.
  - Estimated the warming from a doubling of CO<sub>2</sub> to be near 3.0°C with a probable error of ±1.5°C.
  - Unable to find any overlooked or underestimated physical effect that could substantially reduce the currently estimated global warming due to a doubling of atmospheric CO<sub>2</sub>.
  - Capacity of the intermediate waters of the oceans to absorb heat could delay the estimated warming by several decades.
- It might also be noted that a warming trend in global temperatures, which started in the mid 1970s, continued after submission of this report until about the year 2000. During this time, climate worries from much of the population seemed to change from cooling to warming. This may have led to much credibility of the report and the general acceptance of the anthropogenic global warming (AGW) theory.

#### The 21<sup>st</sup> Century

- After reaching a peak temperature in 1998, global temperatures declined for a few years and then remained more or less level until about 2010, casting some doubt over the general population about the continuation or validity of global warming. During this time, there seemed to be a concerted effort among the climate-change advocates to keep the public convinced that global warming was real and caused by human CO<sub>2</sub> emissions.
- The DeSmog (www.desmog.com) website was founded in January 2006 to "clear the PR pollution that is clouding the science and solutions to climate change". The site also provides a Climate Disinformation Database where one can browse their "extensive research on the individuals and organizations that have helped to delay and distract the public and our elected leaders from taking needed action to reduce greenhouse gas pollution and fight global warming."
- The SkepticalScience (www.skepticalscience.com) website was opened in 2007 to "debunk misinformation that is harming our species' ability to deal with climate change caused by excessive anthropogenic greenhouse gas emissions". This site also accepts and posts comments from registered users on their various news articles and debunking of "climate myths". However, they only tolerate those comments that are not contrarian about climate change. Otherwise, the moderators will "correct" the individual commenting or delete the comment altogether if they can't do this. Interestingly, John Cook, the founder of this website, has a Ph.D. in cognitive science and not one of the physical sciences.

• At the time of the "Climategate" incident (2009), a Scientific American article indicated that recent polls showed that the number of Americans who believe that GHGs will cause average temperatures to increase had dropped from 71 percent to 51 percent. This article is at

www.scientificamerican.com/article/scientists-respond-to-climategate-controversy/

- In 2020, a paper titled *Dependence of Earth's Thermal Radiation on Five Most Abundant Greenhouse Gases* by W. A. van Wijngaarden and W. Happer appeared in the *arXiv* moderated archive. This paper provided a detailed analysis of the thermal effects of the greenhouse gases H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O, and CH<sub>4</sub> on the earth's atmosphere, properly taking band saturation into account. Calculations showed that a doubling of CO<sub>2</sub>, N<sub>2</sub>O, or CH<sub>4</sub> increases the forcings by a few percent.
- By contrast, the EPA claimed a 36% increase in radiative forcings by CO<sub>2</sub> alone since 1990. During this time, the CO<sub>2</sub> concentration went from about 350 ppm to 420 ppm *not even close to a doubling*.

References: EPA Environmental Topic titled Climate Change Indicators: Climate Forcing (www.epa.gov/climate-indicators/climate-change-indicators-climate-forcing)

NOAA Global Monitoring Laboratory, Trends in Atmospheric Carbon Dioxide (CO2) (gml.noaa.gov/ccgg/trends/mlo.html)

#### Use of "too hot" climate models

- This problem arose in 2019 from the Coupled Model Intercomparison Project (CMIP). This project combines the results of the world's climate models in preparation for the major IPCC reports which come out every 7 or 8 years.
- The CMIP results for 2019 indicated a "climate sensitivity" (ie. the warming expected when CO<sub>2</sub> concentrations are doubled over pre-industrial values) higher than 5°C in 10 out of 55 models. Previous CMIP runs, however, indicated sensitivities between 2°C and 4.5°C.
- Also, the CMIP 2019 results were inconsistent with a landmark study that relied on paleoclimate and observational records instead of global modeling to assess the earth's climate sensitivity. This study found that the value sits somewhere between 2.6°C and 3.9°C.
- The divergence in sensitivity estimates is a "sobering example of the complexity of the climate system," says Christopher Field, a Stanford University climate scientist who focuses on impacts.
- Dozens of published studies have used projections based on the raw average of all CMIP6 models, which now runs "hotter" than IPCC projections. Zeke Hausfather, climate research lead at Stripe (payment services company) and IPCC co-author states "We must move away from the naïve idea of model democracy."

Reference: Paul Voosen, "Use of 'too hot' climate models exaggerates impacts of global warming", ScienceInsider, 4 May 2022

## **Energy Conservation**

**Kinetic Energy --** Energy of motion



Flying baseball



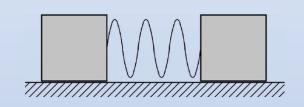
Swinging hammer



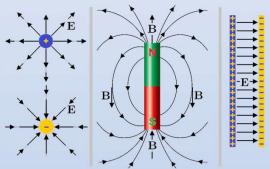
**Potential Energy** -- Energy that is stored in the system with the "potential" of taking some other form such as kinetic or thermal energy.



Object elevated in gravity



Stretched/compressed spring



Electric and magnetic fields

**Thermal Energy** -- Energy involving the motion of microscopic particles which form the macroscopic bodies on the system. Results only in temperature changes and not observable motion.

- In a system without dissipative or frictional forces, the sum of the kinetic and potential energies (ie. the total energy) must remain constant. For example, a rock falling over a cliff loses potential energy (from gravity) since its height above the ground is decreasing. At the same time, however, it gains an equal amount of kinetic energy since gravity is accelerating it downward.
- For a system with friction, a portion of the kinetic energy is converted to thermal energy. This means that the sum of the potential energy and the (macroscopically observable) kinetic energy decreases. However, the total energy, which now includes thermal energy, still remains constant.

**Therefore**, the total energy contained in an isolated system is conserved (ie. remains constant) under any physical process. While this energy may assume different forms, the sum-total of all such energies must remain unchanged.

### **Wave Motion**

Energy can also be transmitted in the form of waves. Familiar examples include acoustic (or sound) waves, water surface waves, string vibrations, and electromagnetic waves.

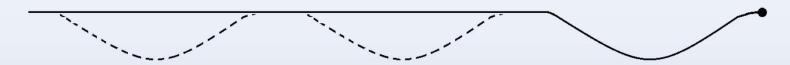
#### **Traveling Pulse Waves**

• Consider first a long string where we maintain a tension from one end. We give it a quick shake from this end, and a pulse or disturbance propagates down the string as shown below.



- This pulse carries energy from the initial shake along the string, although each point on the string is displaced only a small distance.
- Since each point on the string is displaced perpendicular to the string, this is a *transverse* wave.

• If the other end of the string is clamped in place, the pulse will reflect from this end point, switch polarity, and propagate in the opposite direction.



#### **Traveling Periodic Waves**

• Suppose now we generate smooth, periodic motion to the left end of the string, and let *T* and *c* be the time period of this motion and the wave-speed respectively. The profile of such a traveling wave would be similar to the one shown below.



In studying periodic, waves this profile is generally taken as a mathematical sine-wave since the outputs of generators and most electronics are of this type.

#### Some wave-related definitions

Amplitude A = Maximum displacement of points on wave from their unperturbed values

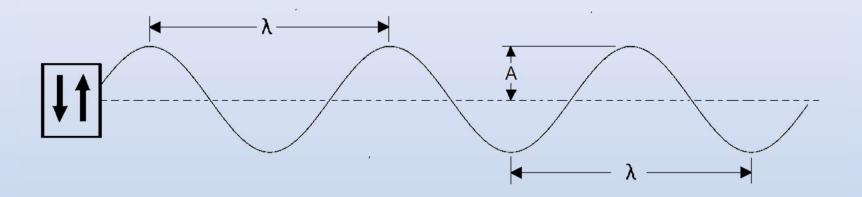
Speed of Propagation c = Speed at which wave profile advances

Wave Period T = Time it takes wave to complete a single oscillation

Wave-Length  $\lambda$  = Distance between two successive crests or troughs as shown below

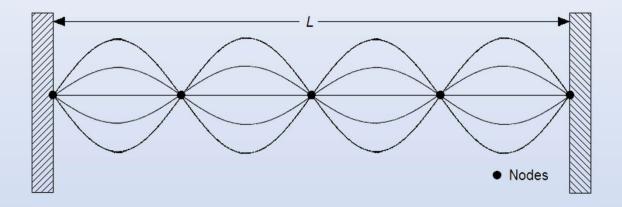
= Distance wave profile advances in one wave period = cT

Frequency  $v = Number of wave oscillations per second = <math>1/T = c/\lambda$ 

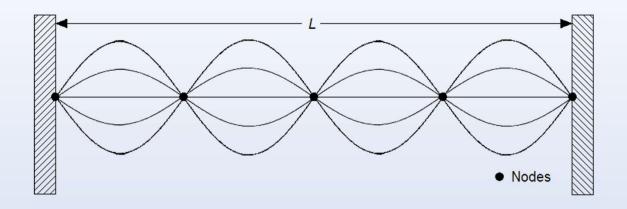


#### **Standing Waves**

• We now consider wave motion in a string of finite length *L* that is rigidly clamped to zero displacement at both ends. In this case, we have equal amplitude waves traveling in each direction as they reflect from the endpoints. These waves superimpose on each other to form a standing wave pattern as shown below.



• Note that this spatial profile has *nodes* (ie. points on the string where the displacement is a constant zero) that are evenly spaced with a separation distance of  $\lambda/2$  between successive nodes. Also, the boundary condition that the string is clamped at both ends requires that both endpoints be nodes.



- This means that the length L must be an integer multiple of  $\lambda/2$ . Expressing this as an equation, we write  $L = n \ (\lambda/2)$  or equivalently  $\lambda = 2L/n$ . But since the frequency  $v = c/\lambda$ , we then have v = nc/(2L).
- The equation v = nc/(2L) implies that the wave frequency v is *quantized*. That is, it is restricted to certain discrete values instead of the continuum of values allowed for traveling waves. This concept is critical for understanding the quantization of energy in atoms and molecules which also have a wave character.
- Also, as a side topic, the quantization of frequency in vibrating strings is what makes string musical instruments possible. In this case the fundamental frequency v (when n = 1) sets the note for that string, and the higher harmonics (when n > 1) correspond to the higher octaves of that note. The combination of these higher harmonics is what determines the tone quality of the instrument.

# **Electromagnetic Radiation**

And God Said ...

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0}$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

... and there was light

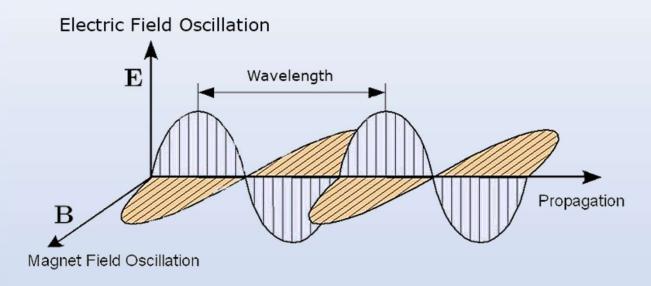
- These equations, known as *Maxwell's Equations*, along with the *Lorentz Force Law* form the foundation of classical electromagnetic theory. James Clerk Maxwell first published this set of equations in 1861 and 1862 after pulling together the works of Gauss, Ampère, and Faraday into a more unified theory of electricity, magnetism, light, and other forms of radiation which were previously regarded as separate phenomenon.
- Maxwell first used the equations to put forth the theory that light is an electromagnetic phenomenon. In free space where the charge and current densities are both zero, the set of equations reduces to

$$\nabla \cdot \mathbf{E} = 0 \qquad \nabla \times \mathbf{B} = \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \qquad \nabla \cdot \mathbf{B} = 0$$

- Using vector calculus, it can be shown that wave-like solutions for both the electric and magnetic fields exist to this set of equations.
- The wave-speed associated with these solutions is shown to be  $c=\frac{1}{\sqrt{\mu_0\epsilon_0}}=2.998\times 10^8~\mathrm{m/sec}$

• The spatial dependence of a plane-wave solution to the given set of equations is shown below. These are considered to be transverse waves since the electric and magnetic fields, equivalent to the string displacement in our previous examples, are perpendicular to the direction of propagation.



• The specific directions of the electric and magnetic fields is what defines the polarization of the wave.

### **Blackbody Radiation**

- A blackbody, by definition, is a body (or object) that absorbs all electromagnetic radiation (EMR) incident
  upon its surface, and all of this energy is subsequently re-radiated after reaching thermal equilibrium inside
  the body. While somewhat idealized since no such material exists, this concept can work well if the
  spectrum of the source radiation is within the absorption range of the body.
- Blackbody radiation is the EMR emitted by such a body when it is in thermal equilibrium with its surroundings at some given temperature. This spectrum depends only on temperature and not composition of the body. Therefore, it is sometimes called *thermal radiation*.
- A few commonly observed examples of near blackbody spectra are listed below in their order of temperature.



Electric stove unit 505°K



Heat treated steel 1644°K



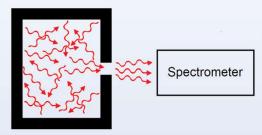
Light bulb filament 2800°K



Electric arc welding 7300°K

• Note that the wavelengths of these spectra tend to decrease with increasing temperature.

 Measurements of this type of radiation in the laboratory are generally done with cavity radiators as shown below.



- In this setup, the cavity walls are held at a constant temperature and only a small fraction of the radiation propagating inside the cavity exits through the small hole toward the detector. Therefore, the cavity radiation is in near thermal equilibrium.
- For more common occurrences of near blackbody radiation such as heating solid materials, the atoms and molecules within the sample tend to re-direct exiting radiation, thereby acting similarly to the cavity walls.
- In 1900, Lord Rayleigh derived the following (Rayleigh–Jeans) law for calculating the spectral radiance of a blackbody based on classical statistical mechanics

$$B_{\nu}(\nu,T) = \frac{2\nu^2k_BT}{c^2}$$
  $k_B$  = Boltzmann's Constant = 1.381 × 10<sup>-23</sup> joule K<sup>-1</sup>

• While this formula works well for low frequencies (or long wavelengths), it predicts what has been called the "ultra-violet catastrophe" at higher frequencies.

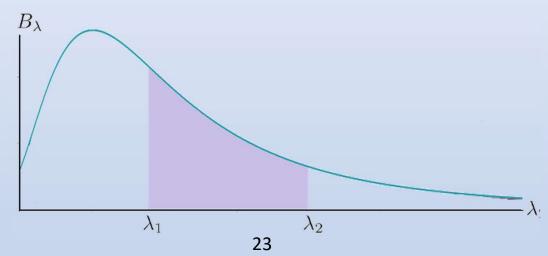
• In 1901, Max Planck obtained the following formula for the (frequency based) spectral density of a blackbody, which is now called Planck's Radiation Law.

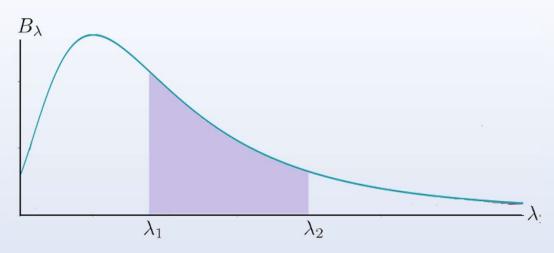
$$B_{
u}(
u,T) \,=\, rac{2h
u^3}{c^2} rac{1}{e^{h
u/(k_BT)-1}}$$
  $k_B$  = Boltzmann's Constant = 1.381 × 10<sup>-23</sup> joule K<sup>-1</sup>  $h$  = Planck's Constant = 6.626 × 10<sup>-34</sup> joule sec

• This same law can also be expressed as a wavelength based spectral density as follows:

$$B_{\lambda}(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/(\lambda k_B T)} - 1}$$

• The total radiance (ie. energy per unit area per unit time) emanating from the surface of a blackbody within a finite wavelength interval  $\lambda_1 \le \lambda \le \lambda_2$  is given by the area under the  $B_{\lambda}(\lambda,T)$  curve between  $\lambda_1$  and  $\lambda_2$  as shown in the figure below.





• From calculus, the value of the above-shown area is referred to as an integral, and is generally expressed as

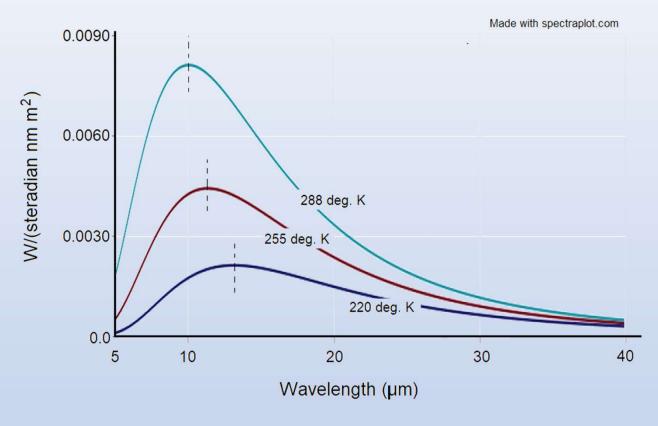
$$L(\lambda_1, \lambda_2, T) = \int_{\lambda_1}^{\lambda_2} B_{\lambda}(\lambda, T) d\lambda$$

 $\bullet$  If we carry out this integral over all values of  $\lambda$  , we have

$$L(T) = L(0, \infty, T) = \int_0^\infty B_\lambda(\lambda, T) \, d\lambda = \frac{2\pi^5 k_B^4}{15c^2 h^3} \, T^4 = \sigma T^4$$

where  $\sigma$  is the Stefan-Boltzmann constant which consists only of other known physical constants. This is known as the *Stefan-Boltzmann Law*. It is a very simple, compact expression of the total EMR radiance (ie. energy per unit area per unit time) emanating from a blackbody.

• Below are plots showing spectral radiance of blackbodies at a few different temperatures using Planck's Radiation Law.



• Suppose now that we start with a blackbody held at some temperature T, and then make it transparent over some range of frequency v. Any EMR within that transparent band would, of course, exit the body. Radiation within the still-absorbed band, however, would remain unaffected since radiation of different frequencies act independently of each other. Layers of the atmosphere generally act as a blackbody over some spectral bands but not others.

#### Fundamental physical implications of the blackbody spectrum

- While Planck's Radiation Law "hit the nail on the head" in regard to explaining the cavity radiation results, he made an interesting assumption in its derivation. He assumed that electromagnetic waves of frequency v could carry energy only in integer multiples of hv.
- This was the birth of quantum physics. For the first time, a physical quantity, energy in this case, was *quantized*. That is, it was not allowed a continuum of values as in classical physics, but instead restricted to certain *discrete* values.
- Further evidence of the quantization of electromagnetic energy is provided in the *photo-electric effect* discovered by Albert Einstein in 1915.
- Therefore, we have seen that electromagnetic energy, predicted classically as a wave, also has a particle character. This leads to the concept of "particles of light" called photons, each carrying energy E = hv.

## **Spectral Lines and Bands**

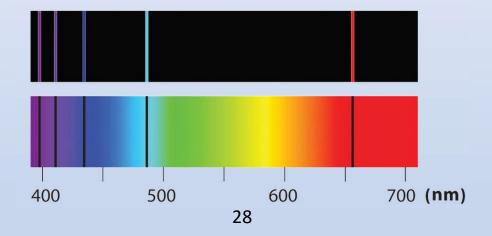
#### **Line Spectra**

- In the previous section, we saw that EMR, classically regarded a wave, also has a particle character. Well -- with a touch of irony -- entities such as electrons, atoms, and molecules that we have generally regarded as particles also have a wave character.
- This being the case, the energy (and other *dynamic variables* from classical physics) of a system of particles in bound motion, such as a molecule, is *quantized* analogous to the vibrational frequencies of a string held at both ends. That is, the energy is restricted to certain discrete values instead of allowed an entire continuum as in classical physics.
- Therefore, the interaction of EMR with atoms and molecules must be handled in the realm of quantum physics. So, if we have a molecule that includes states n and m with energies  $E_n$  and  $E_m$  (where  $E_n > E_m$ ) and a transition  $n \to m$  occurs, a photon with frequency v would be released such that

$$E_{\mathrm{photon}} = h\nu = E_n - E_m$$
 or  $\nu = \frac{E_n - E_m}{h}$ 

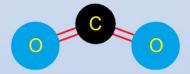
• The set of all such frequencies v for allowed downward transitions is referred to as the *emission spectrum* of the atom or molecule.

- For upward transitions, an *absorption spectrum* can be observed where the sample is illuminated with a source that is sufficiently broadband to include all wavelengths of interest. The spectral output then appears as a bright continuum of wavelengths from the source with dark lines at the absorption wavelengths.
- Since a single isolated atom/molecule has such discretely defined allowed energy levels, the spectra observed in the laboratory of a low-pressure gas sample consists of sharp lines at the allowed photon frequencies  $v = (E_n E_m)/h$ .
- It should be noted, however, that some *natural line broadening* does occur as the result of uncertainty of energy during the transition.
- Below are shown the emission (top) and absorption (bottom) line spectra of H<sub>2</sub> in the visible range.

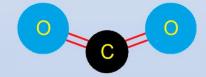


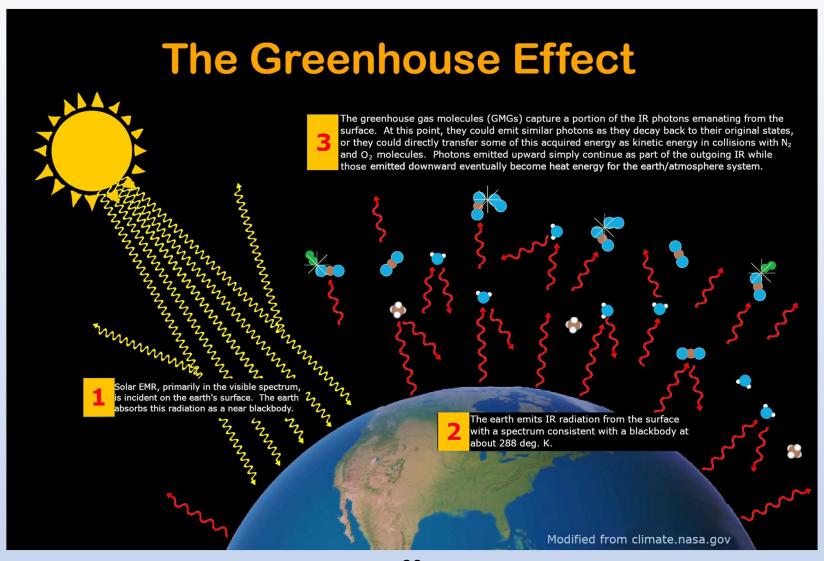
#### **Band Spectra**

- In most cases of practical interest, such as atmospheric physics, we are not working with isolated atoms or molecules, but with gases at higher pressures. Therefore, the molecules undergo collisions which can perturb their energy levels and interrupt transitions, resulting in spectral line broadening. This is generally called *pressure* or *collision* broadening.
- Another type of line broadening is *Döppler* broadening. This occurs when the emitting molecule is moving relative to the receiving molecule, giving a shift in frequency as observed by the receiving molecule, analogous to the shift in frequency of a high-speed train whistle as it passes an observer on the ground.
- In cases of extreme line broadening such as solids or high-pressure gases, the atoms/molecules lose spectral identity and the spectrum approaches that of a blackbody.
- Also, in greenhouse gases (which are at least tri-atomic), IR absorption/emission occurs in transitions between vibrational *bending* modes of the molecule. This results in several closely spaced spectral lines that are mostly "washed over" by pressure broadening.
- Below are illustrations showing the atomic motions of a CO<sub>2</sub> molecule corresponding to its IR absorbing bending mode transitions.









#### A relatively simple but adequate model for atmospheric greenhouse warming

• In this (one-dimensional) model, we consider a vertical column of air with cross-sectional area A as shown in the figure to the right. Let z denote the altitude coordinate.

A

 $\Delta z$ 

- At zero altitude (z=0), we assume a given upwelling irradiance of  $I_{\nu 0}$  which would most likely correspond to a blackbody of temperature 288°K. This irradiance is at least partially absorbed by the GHGs as it rises, and converted into heat energy for the greenhouse effect.
- Consider a thin slice of this column at altitude z and thickness  $\Delta z$ . Suppose that in 1 second,  $P_{\nu}(z)$  photons of frequency  $\nu$  from the upwelling radiation (inside the column) pass altitude z. Let us determine how many of these are absorbed.
- We first note that since these photons are identical and passing through the same space, they all have the same probability of being absorbed. Therefore, we can express the number of photons (at frequency v) that are absorbed between z and  $z + \Delta z$  as

$$\Delta P_{\rm abs}(z,\Delta z) = (\text{single - photon absorption probability between } z \text{ and } z + \Delta z) \times P_{\nu}(z)$$

• Also, for small values of  $\Delta z$ , we expect the probability of single photon absorption to be proportional to the number of greenhouse gas molecules in the slice. Therefore, we write

$$\Delta P_{\rm abs}(z, \Delta z) \approx \text{(some factor)} \times N(A \Delta z) \times P_{\nu}(z)$$

where N is the GHG density (molecules/meter<sup>3</sup>). This approximation becomes exact as  $\Delta z \rightarrow 0$ .

• The "some factor" quantity in the last expression actually has a name – the absorption cross-section  $\sigma_{v}$ , and is stored as the absorption spectra in databases such as HITRAN for numerous molecules and frequencies. Therefore, the last statement can be written as

$$\Delta P_{\rm abs}(z, \Delta z) \approx \sigma_{\nu} P_{\nu}(z) N(A \Delta z)$$

• Now, in going from z to  $z + \Delta z$ ,  $P_v$  must decrease by the amount  $\Delta P_{abs}(z, \Delta z)$ . Therefore, we have

$$\Delta P_{\nu}(z) = P_{\nu}(z + \Delta z) - P_{\nu}(z) \approx -\sigma_{\nu} P_{\nu}(z) N(A \Delta z)$$

ullet Then, since the irradiance  $I_{\nu}(z)$  is proportional to  $P_{\nu}/A$ , this statement implies that

$$\Delta I_{\nu}(z) = I_{\nu}(z + \Delta z) - I_{\nu}(z) \approx -\sigma_{\nu}I_{\nu}(z) N \Delta z$$

• Dividing both sides of this approximation by  $\Delta z$  then gives us

$$\frac{\Delta I_{\nu}(z)}{\Delta z} \, \approxeq \, -\sigma_{\nu} N \, I_{\nu}(z)$$

• At this point, we use the fact that this approximation becomes exact as  $\Delta z \rightarrow 0$  to obtain the equation governing the attenuation of the upwelling IR with increasing altitude. Using notation from calculus, we obtain

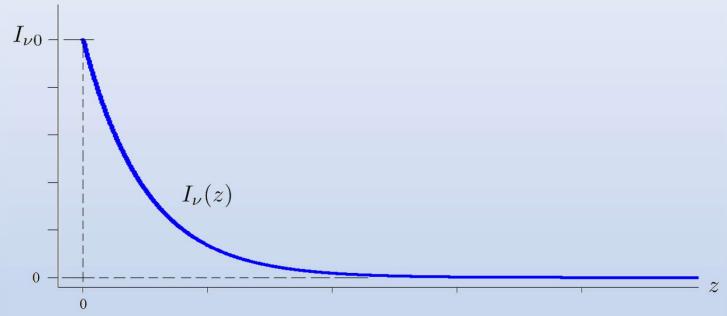
$$\lim_{\Delta z \to 0} \frac{\Delta I_{\nu}(z)}{\Delta z} = \frac{dI_{\nu}}{dz}(z) = -\sigma_{\nu} N I_{\nu}(z)$$

$$ullet$$
 This equation is known as the Beer-Lambert Law.  $\qquad rac{dI_{
u}}{dz}(z) \, = \, -\sigma_{
u} N \, I_{
u}(z)$ 

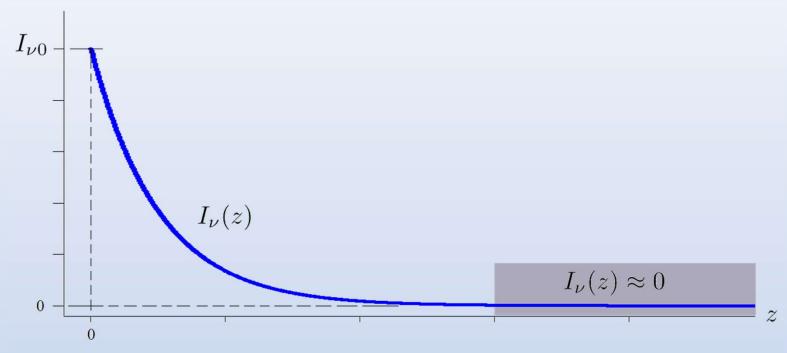
• It is a differential equation that expresses the rate of change of the irradiance  $I_v$  with respect to z in terms of itself. Assuming that N is constant, the solution of this equation is the exponential function

$$I_{\nu}(z) = I_{\nu 0} \exp(-\sigma_{\nu} N z) = I_{\nu 0} e^{-\sigma_{\nu} N z}$$

where  $I_{v0}$  is the (given) zero altitude value of  $I_v$ . Below is a sample plot of such a function.



ullet From this graph, we see that the irradiance  $I_{v}$ , which is the source of energy for greenhouse warming, approaches zero at higher altitudes.

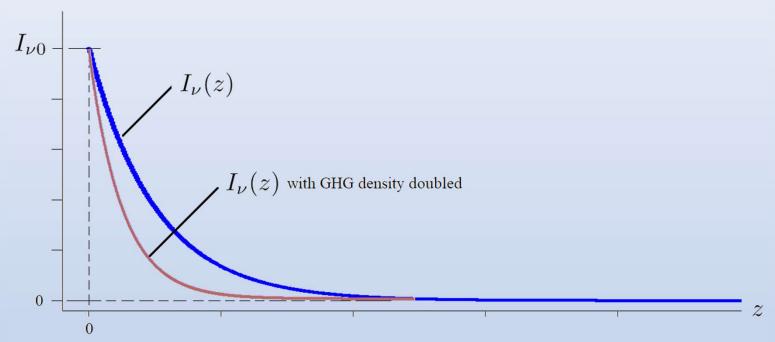


• Now if  $I_v$  decays to negligible values below the tropopause, then the upwelling IR radiation at frequency v is completely absorbed, and increasing the GHG concentration will not cause more warming at this frequency. This effect is generally called *band saturation*.

ullet In fact, from the solution  $I_{\nu}(z)$  shown below, we see that the exponential factor approaches zero faster with larger values of the GHG density N.

$$I_{\nu}(z) = I_{\nu 0} \exp(-\sigma_{\nu} N z) = I_{\nu 0} e^{-\sigma_{\nu} N z}$$

ullet Below is a graph showing the original solution  $I_{\nu}(z)$ , and the resulting solution if we double the density N.



ullet At this point, it probably should be noted that references may use decadic extinction cross-sections  $\delta_v$  instead of those based on the natural exponential system. In this case, the irradiance is expressed as

$$I_{\nu}(z) = I_{\nu 0} \, e^{-\sigma_{\nu} N z} = I_{\nu 0} \, 10^{-\delta_{\nu} n z}$$
 where 
$$\delta_{\nu} = \frac{N_A \sigma_{\nu}}{\ln(10)}$$
 
$$n = \frac{N}{N_A} = \text{density of GHG in moles/m}^3 \quad N_A = \text{Avagadro's number}$$
 
$$= 6.023 \times 10^{23}$$

- Therefore, we see from our model that IR radiation rising from the surface can be absorbed by the GHGs and converted into heat energy which warms the atmosphere and the surface in what is generally called the *greenhouse effect*. GHGs with high absorption at one or more frequency bands, however, can absorb all (or at least most) upwelling irradiance in those bands, resulting in *band saturation*. In this case, **no** further energy for warming can be absorbed from the saturated bands.
- The *radiative forcing* from  $CO_2$  in our model is given simply by  $I_{v0}$ . This is a measure of the drop in radiative flux leaving the atmosphere that occurs by adding  $CO_2$  to the atmosphere. Since this radiant energy is now *not* leaving the climate system, it generally takes the form of thermal energy, thereby raising temperatures.
- According to the IPCC, the technical definition of a radiative forcing is the change in the net, downward minus upward, radiative flux (expressed in  $W/m^2$ ) due to a change in an external driver of climate change.

#### Measurements of absorption cross-sections by Heinz Hug

- In 1998, Dr. Heinz Hug, a German Chemist, conducted his own measurements of the decadic extinction cross-sections  $\delta_{\nu}$  for both the 15 µm and 4.2 µm CO<sub>2</sub> bands
- In his setup, he started with synthetic  $CO_2$ -free air and added  $CO_2$  with a microliter syringe so that the concentration was 357 ppm (concentration in 1993). After obtaining the 15  $\mu$ m and 4.2  $\mu$ m  $CO_2$  band spectra at this concentration, he increased it to 714 ppm and re-ran the procedure.
- For more information on his procedure and the equipment used, check out his online paper titled *The Climate Catastrophe A Spectroscopic Artifact?*, and can be accessed at www.john-daly.com/artifact.htm
- The values of the cross-sections  $\delta_{\nu}$  he obtained were 20.2 m³/mole for the 15  $\mu$ m band, and 29.9 m³/mole for the 4.2  $\mu$ m band.
- Assuming a CO<sub>2</sub> concentration of 357 ppm and an altitude of 10 m, we obtain

$$\delta_{\nu} nz \,=\, 20.2 \, \frac{\mathrm{m}^2}{\mathrm{mole}} \, *\, 0.0159 \, \frac{\mathrm{moles}}{\mathrm{m}^3} \, *\, 10 \, \mathrm{m} \,=\, 3.212$$
 which gives us a transmission factor of  $\, T \,=\, \frac{I_{\nu}(z)}{I_{\nu 0}} \,=\, 10^{-\delta_{\nu} nz} \,=\, 10^{-3.212} \,=\, 0.000612$ 

Equivalently, this corresponds to an absorption of over 99.9 percent in just 10 meters. Therefore, it would be unreasonable to expect that doubling the amount of CO<sub>2</sub> would result in any further greenhouse warming.

• Dr. Hug also refuted a statement in the IPCC First Assessment Report (1990) that

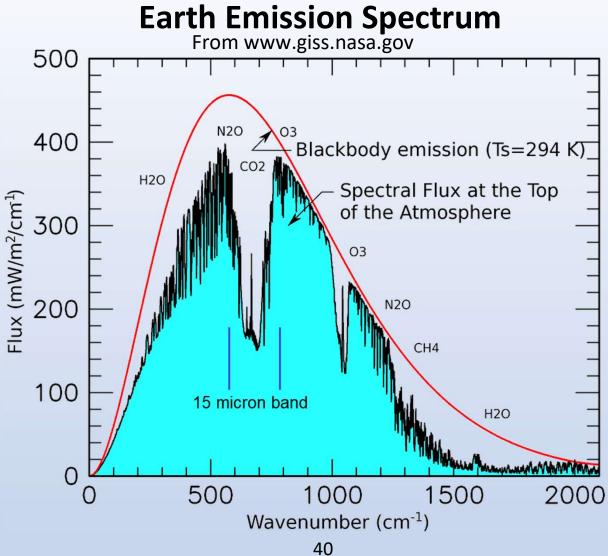
The effect of added carbon dioxide molecules is, however, significant at the edges of the 15  $\mu$ m band, and in particular around 13.7 and 16  $\mu$ m

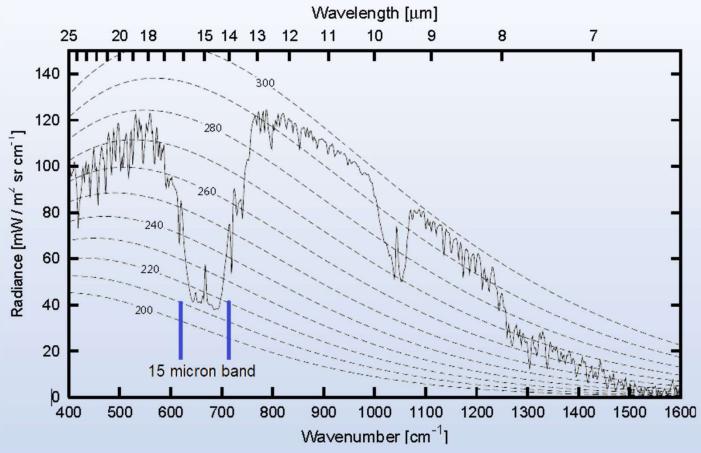
From the absorption data gathered, he was able to show that the increase in absorptivity resulting from doubling the  $CO_2$  concentration was about 0.17% – or about 1/80 of the value predicted by the IPCC.

- On 11 October 2001, Heinz Hug and Jack Barrett presented papers at the DECHEMA Colloquium (Frankfurt, Germany) expressing doubts about the manner in which spectroscopic principles had been applied by members of the IPCC in coming to their conclusions about future climate change.
- Specifically, Hug and Barrett were concerned about the fact that the IPCC claims that the air is warmed only by contact with the warmed soil/ocean surfaces, and that CO<sub>2</sub> merely recycles the upward IR photons and returns 90% of the absorbed radiation to the surface. The IPCC disregards the possibility of IR energy being converted to translational kinetic energy through collisions of vibrationally excited CO<sub>2</sub> molecules with N<sub>2</sub> and O<sub>2</sub>.
- However, carbon dioxide has been historically known as a heat absorbing gas. It can be readily shown that exposing a vessel containing CO<sub>2</sub> to IR radiation results in an almost immediate temperature increase without any contact with the earth. This can happen only if IR energy is being converted to kinetic energy of the molecules within the vessel.

- After direct warming of the lower layers of the atmosphere in this manner, heat could then be carried upward through convection, a much more efficient process of heat transfer. This, however, is also not included in the IPCC arguments.
- Additionally, it might be indicated here that human-built glass greenhouses for growing plants are designed to impede *convection* and not conduction or radiation. Glass is a poor insulator and radiative transfer is slow.
  - Reference: Heinz Hug and Jack Barrett, *Hug and Barrett versus IPCC*, available only online at <a href="https://www.john-daly.com/forcing/hug-barrett.htm">www.john-daly.com/forcing/hug-barrett.htm</a>
- In the paper titled *Dependence of Earth's Thermal Radiation on Five Most Abundant Greenhouse Gases* by W. A. van Wijngaarden and W. Happer, the authors make a similar but more indepth analysis of the thermal effects of the greenhouse gases H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O, and CH<sub>4</sub> using absorption cross-section values from the HITRAN database. Calculations showed a high degree of saturation in all five of the GHGs considered, and that a doubling of CO<sub>2</sub>, N<sub>2</sub>O, or CH<sub>4</sub> increases the forcings by a few percent.
- While the results of van Wijngaarden and Happer were not identical to those of Hug and Barrett, both showed values of CO<sub>2</sub> radiative forcings that were orders of magnitude less than the corresponding EPA values.







Note that at frequencies within the 15  $\mu$ m band, the radiance corresponds to a blackbody at 210-220  $^{\circ}$ K, which is consistent with temperatures in the upper layers of the atmosphere. This means that in this band, the orbital sensor is receiving thermal emissions from this layer only, and any upwelling radiance within this band at lower altitudes is extinct.

#### False rebuttals to CO<sub>2</sub> band saturation

- Climate change "experts" often use the fact that the total spectral intensity never reaches zero in the absorption band to argue that there will be  $15\mu m$  radiation available for absorption at all altitudes, and therefore there is no extinction of this absorption band. The fallacy of this argument is that the total spectral intensity that is recorded consists of a thermal radiation term along with the attenuated upwelling radiation  $I_v$  (from the surface). For our arguments, however, it is only the  $I_v$  intensity that is used. Once the thermal radiation term is subtracted from the total intensity, the remaining value  $I_v$  is at or near zero within the  $15\mu m$  absorption band.
- Probably the most used claim is what some call the "surface budget fallacy" which states that we need to consider energy exchanges near the TOA rather than the surface, without giving clear justification for doing so. In fact, this method isn't even applicable to our model since it is *at the surface* where the upwelling radiation is given.
- As mentioned earlier, it was claimed in the *IPCC First Assessment Report* (1990) that the effect of added CO<sub>2</sub> was "significant" at the edges of the 15μm band without clear justification of their results. Dr. Hug obtained a value for this effect that is about 1/80 of the value obtained by the IPCC.

### **Conclusion**

 Carbon dioxide (CO<sub>2</sub>) has two important properties that make it an excellent greenhouse gas for atmospheric warming

Strong absorption band at wavelength 15  $\mu$ m near the peak of the earth's upward IR thermal spectrum Bending vibrational mode of the CO<sub>2</sub> molecule allows direct transfer of thermal energy from an excited CO<sub>2</sub> molecule to the atmosphere through collisions with N<sub>2</sub> and O<sub>2</sub> molecules.

- However, strong absorption at a particular wavelength of the upward IR radiation also means depletion of that wavelength at lower altitudes, thereby resulting in *band saturation* where it takes larger increases in CO<sub>2</sub> concentration to attain the same increase in heat absorption.
- In the case of CO<sub>2</sub>, band saturation is so high that even a doubling of its concentration would have miniscule effect on the upward IR radiation it absorbs and converts into heat.
- Thus, it seems that we need *fear no carbon*, contrary to the views of the Climate Science Community.