The model of the earth appropriate to this power point is the earth averaged over its surface for a year. I will call this an earth-year, and henceforth "average" will mean an earth-year average. Geophysicists have determined that the earth, on this average, is radiating energy characteristic of 288K in good agreement with Planck's law for a blackbody. This average temperature is determined by the balance of the earth's Planck radiation, the solar radiation reaching the earth (and not reflected), and the greenhouse gas (henceforth GHG) radiation resulting in an average thermal steady-state. The result of the calculation to be presented pertains to the current year and the near future, and does not depend upon interpretations of the records of the earth's temperature history. The result is limited to the increase in average temperature expected as a direct result of increased CO_2 and does not pertain to the increases resulting from feed-back effects or deal with the distribution of the temperature increase over the earth.

There are two initial steps essential to the development of an understanding of what humans must do in order to halt and reverse the observed annual increases in the average temperature of the earth. The first is to become aware of the relative magnitudes of the rates at which we are introducing CO_2 into the atmosphere and at which it is being introduced by natural processes.The second is to become aware of the science describing the quantitative effect that this CO_2 has on the temperature of the surface of the earth. These are the topics of this power point.

The calculation of the effect of the observed increases in CO_2 concentration on the earth's average temperature that will be presented uses only spectroscopic data determined almost fifty years ago and established Physical Chemistry. It is the purpose of this power point to provide anyone with a knowledge of undergraduate Physics and Chemistry with the direct scientific demonstration that there is no doubt that at this point in time increases in CO_2 in the atmosphere have the direct result of increasing the earth's average temperature. The influence of water vapor in the atmosphere is not included in this calculation because its inclusion requires greatly increased computation. For consideration of the effect of water vapor, which enhances the GHG effect of CO_2 through what is called feedback, and decreases the effect of CO_2 through interference, see Schmidt, et. al., J. Geophys. Res., Vol. 115, D20106, (2110)
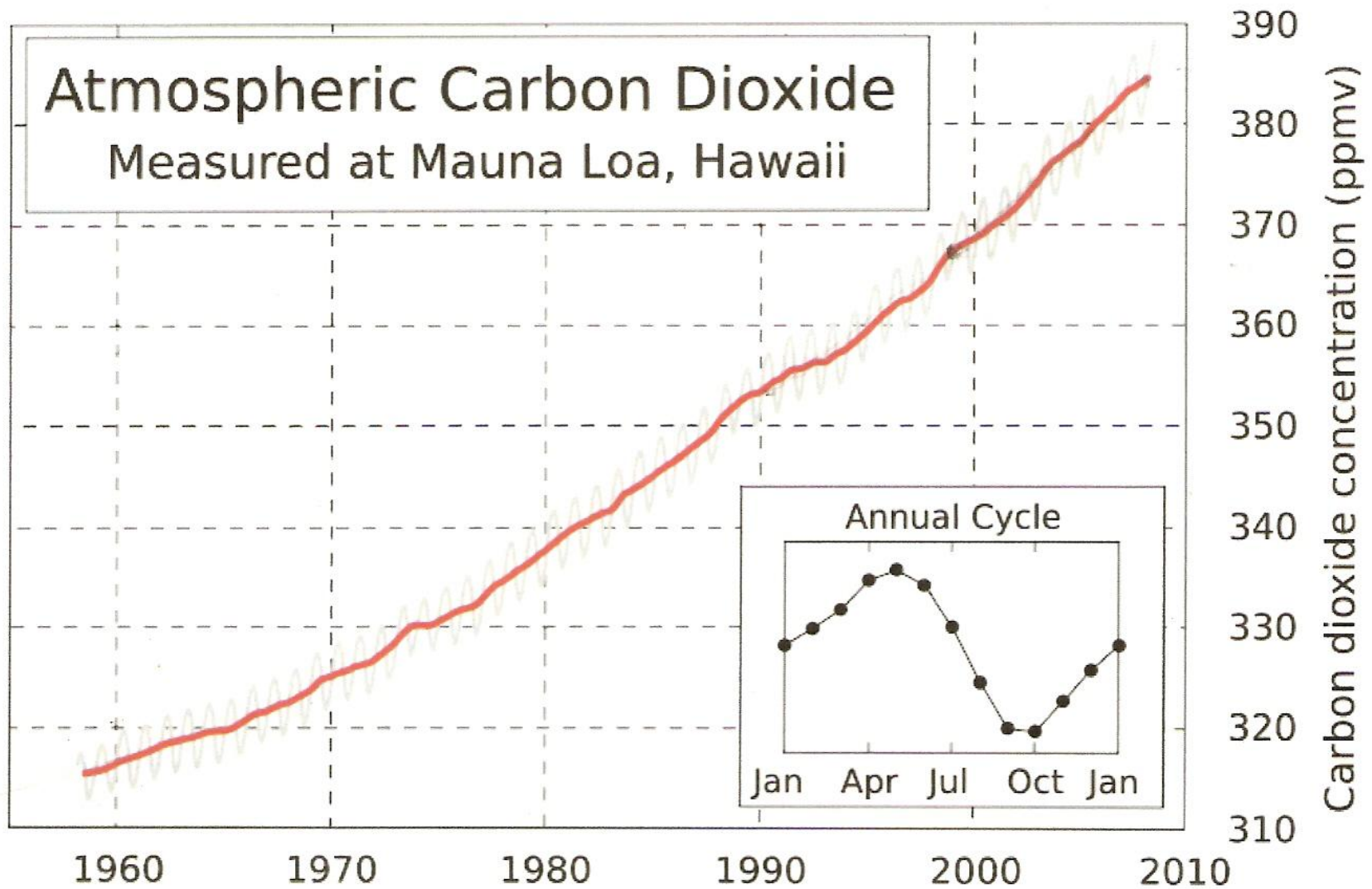
Current Consumption of Fossil Fuels

According to the U.S. DOE, in the year 2007 humans produced 29 billion metric tons of CO_2 through the combustion of fossil fuels. One metric ton = 2200 lbs

Production of Carbon Dioxide

Since the late 1950's spectroscopists at the Mauna Loa observatory have been collecting data on the concentration of CO_2 in the atmosphere. The plot of these data, as ppm vs. time in years, is known as the Keeling curve and is shown next.

The Keeling Curve

Atmospheric Carbon Dioxide
Measured at Mauna Loa, Hawaii

Carbon dioxide concentration (ppmv)

390, 380, 370, 360, 350, 340, 330, 320, 310

1960, 1970, 1980, 1990, 2000, 2010

Annual Cycle

Jan   Apr   Jul   Oct   Jan

Mauna_Loa_Carbon_Dioxide-en.svg (SVG file, nominally 850 × 547 pixels, file size: 16 KB)

6

This is a file from the Wikimedia Commons. The description on its **description page there** is shown

Polynomial Fit of the Keeling Curve

The Keeling curve fits a second-order polynomial:

$$\text{ppm} = [1.054 \times 10^{-2}]x^2 + [9.00 \times 10^{-1}]x + 315.5$$

where x = (yr − 1960). The fit yields an average deviation of ±0.2 ppm, which is the increase in 0.1 year. The data are given on slide #66 at the end of the presentation. The slope of this quadratic is 1.9 ppm/yr for 2007. In the next slide this slope is used to find the current rate of increase of CO_2 in the atmosphere in tons per year.

Conversion from ppm to Metric Tons

$$\text{dm}_{CO_2}^{atm}/\text{dt} = \text{ppm/yr} \times 10^{-6} \times \text{atmospheric pressure} \times g^{-1} \times 4\pi r_e^2$$

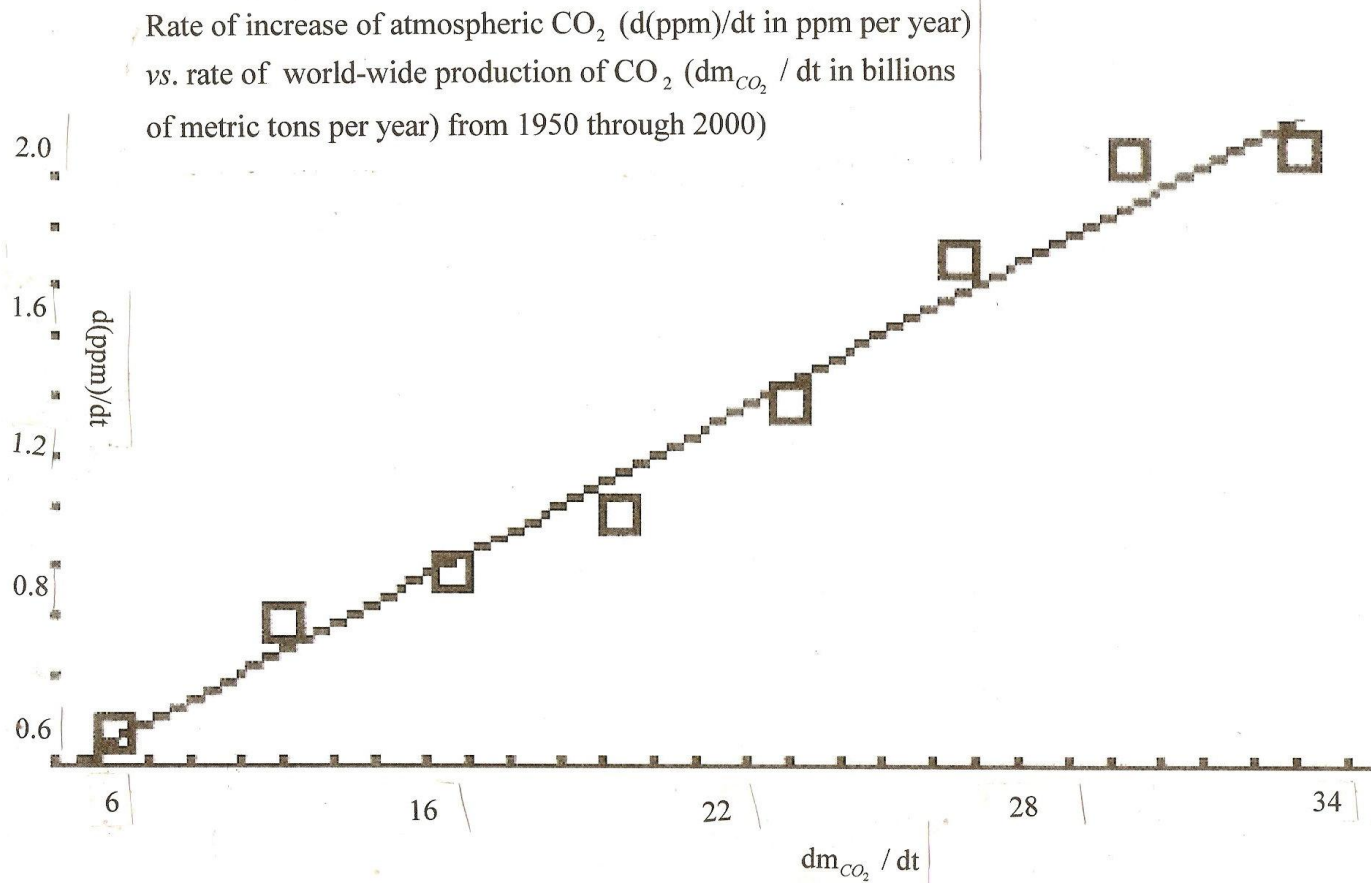$$\times \text{M}_{air}^{-1} \times M_{CO_2} = 15.7 \text{ billion metric tons per year}$$

Details

Combining Newton's law, F=ma, where $m = m_{atm}$ and $a = g = 9.8$ m s^{-2} with the definition of pressure, $P_{atm} = F_{atn} / a_e$, where a_e is the surface area of the earth, yields $m_{atm} = P_{atm} a_e / g$ which can be used to find the number of moles of air in the atmosphere as follows: The average P_{atm} is reported to be 101325 Nm^{-2} and $a_e = 4\pi r_e^2$ $= 4 \times 3.14159 \times (6.371 \times 10^6)^2 = 5.10 \times 10^{14}$ m^2, so $m_{atm} = 5.10 \times 10^{14} \times 1.013 \times 10^5 \times 9.8^{-1} = 5.27 \times 10^{18}$ kg, or, since the kg molecular weight of air is 0.028, $n_{atm} = 5.27 \times 10^{18} \times 0.028^{-1} = 1.88 \times 10^{20}$ moles. Thus the number of moles of CO_2 entering the atm per year is $1.9 \times 10^{-6} \times 1.88 \times 10^{20} = 3.58 \times 10^{14}$ and, multiplying by the molecular weight of CO_2, $dm_{CO_2} / d(yr) = 0.044 \times 3.58 \times 10^{14} = 1.57 \times 10^{13}$ kg/yr or 15.7 billion metric tons/yr in 2007.

Comparison of the Rates

There is a net addition to the atmosphere of 15.7 billion metric tons of CO_2 per earth-year as a result of all sources and sinks to be compared with the 29 billion metric tons produced by humans burning fossil fuels. Thus humans produce, through the combustion of fossil fuels, 13.3 metric tons of the CO_2 in excess of that entering the atmosphere. This excess CO_2, plus the quantity evolved during the production of CaO from $CaCO_3$, an essential step in the production of concrete, ends up somewhere other than in the atmosphere (probably mostly in the oceans, see Appendix A).

Furthermore, as the next graph shows, the rate at which carbon dioxide is entering the atmosphere is increasing linearly with the known rate of increase in the human combustion of fossil fuels.

Rate of increase of atmospheric CO_2 (d(ppm)/dt in ppm per year) vs. rate of world-wide production of CO_2 (dm_{CO_2} / dt in billions of metric tons per year) from 1950 through 2000)

Part I Conclusion

The only credible explanation for these rates is that humans are the principal source of the current increase of CO_2 in the atmosphere.

Part II. What is the contribution of greenhouse gases (GHG's: CO_2, H_2O, CH_4, O_3, etc) to the earth's energy balance?

Flux and Temperature

Flux, F, is the quantity of energy passing through a surface per unit area per unit time. The units of F are watts m^{-2}. According to the Stefan-Boltzmann Law the flux emitted by a body at thermal equilibrium at temperature T is given by:

$$F = \boldsymbol{\sigma} \times T^4.$$

where $\boldsymbol{\sigma} = 5.67 \times 10^{-8}\, \text{W} / \text{m}^2 \text{K}^4$. Note that to say "at temperature T" strictly means "at thermal equilibium". When we say something has a temperature we are, by the zeroth law of thermodynamics, saying that it is in thermal equilibium and, by Planck's Law, saying that it emits radiation according to the Stefan-Boltzmann Law. In reality no system is at equilibrium, so what is implied when it is said that a system has a temperature is that it is sufficiently close to equilibrium (to a Boltzmann distribution) that it is meaningful to speak of its temperature. This temperature (actually temperature approximation, but the distinction will be, as it always is, dropped in the remaining discussion) can be measured using any conventional thermometer. Such temperatures are measured at many different times and locations on the earth's surface and then averaged over space and time.

The Earth's Temperature With No GHG

Astrophysicists have determined that the average net (albedo subtracted) flux of energy arriving at the earth's surface from the sun is 239 W m^{-2} In the earth's current steady state the average energy coming to the earth from the sun equals the average energy emitted to the cosmos from the earth to far better than 1%. First consider what the average temperature would be in the absence of GHG fluxes. In this case, to a very good approximation, the only source of energy at the earth's surface is the sun, and the average would be given by the relation energy out = energy in, i.e.:

$$5.67 \times 10^{-8} \times T^4 = 239 \text{ W m}^{-2}$$

which yields T = 255 K. This is close to 0$^\text{o}$ Fahrenheit, and life on earth as we know it is impossible at this average temperature.
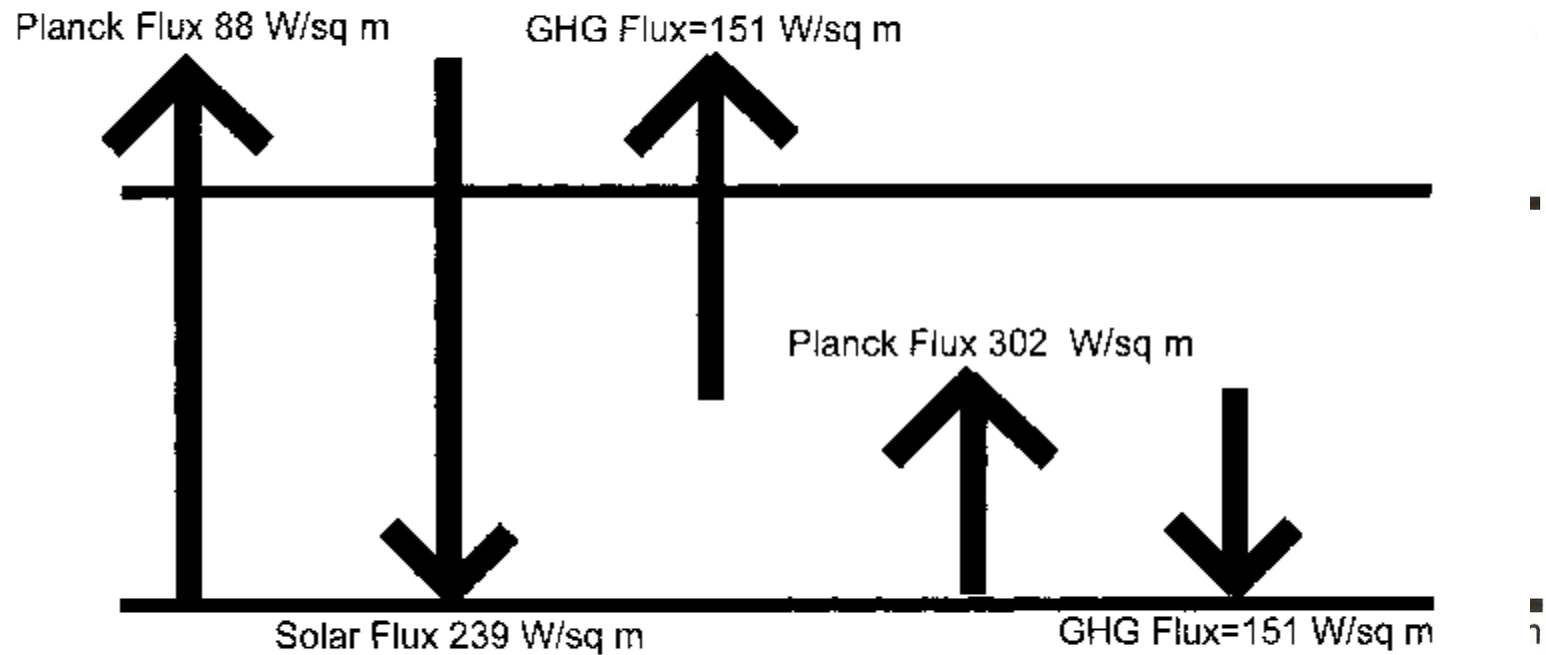
Energy Balance with GHG's

The average temperature is actually 288 K (59° F), not 255 K. The difference between these values results from absorption by the atmsophere of a fraction of the upward flux of radiation from the earth and the subsequent nondirectonal loss of the absorbed energy. In this fashion the atmosphere redirects some of the outgoing energy back to the earth's surface. The resultant average flux is $151 = \sigma \bullet [288^4 - 255^4]$ W m^{-2}. This power point uses standard Physical Chemistry to calculate the contribution made by CO_2 to this flux.

The surface area of a sphere with radius $r_e + h$ is $4\pi(r_e + h)^2$. Therefore the energy per unit time (power) passing through a surface at $r_e + h$ is $4\pi(r_e + h)^2 F_h$, where F_h is the flux at h. In order to compare powers passing through surfaces at different heights in terms of fluxes, as on the next slide (#19), it is convenient to define renormalized fluxes as the power passing through a surface at h but divided by the area of the surface at h=0. If the renormalized fluxes at two different values of h are equal the powers passing through the surfaces are equal as well. So far as the fluxes are of interest, taking the renormalized fluxes to be the same as the fluxes would amount to assuming that the curvature ofthe surfaces is negligible, an assumption which would, if the interest were in the fluxes rather than the power, introduce an error less than 1% for altitudes below 60 km .

Renormalized Flux Balance on the Earth

Planck Flux 88 W/sq m

GHG Flux=151 W/sq m

Planck Flux 302 W/sq m

Solar Flux 239 W/sq m

GHG Flux=151 W/sq m

Conclusion to Part II

The average renormalzed flux coming into the earth is 390 W m^{-2} and that from the GHG's is 151 W m^{-2}, i.e. 38.7 % of our incoming power is from absorption and redirection by GHG's

Henceforth :

F(p,q) means average flux to p from q

p or q=g means to or from the ground

p or q=a means to or from the atmosphere

p=TOA (defined on the next slide)

Example: F(g,a) is the average flux
to the ground from the atmosphere i.e.
is the GHG flux

The top of the atmosphere (TOA) is defined as infinite height. This infinity does not introduce a problem in the calculation because the necessary integral evaluated between the earth's surface and the TOA is:

$$\int_{g}^{TOA} \bar{N}dh = \int_{0}^{\infty} \bar{N}dh \ ,$$

where $\bar{N}$ is the concentration of a gas in moles per cubic meter. As will be shown, this integral has a value because $\bar{N}$ drops off exponentially with height.

Part III. What is the quantitive effect of the increasing CO_2 in the atmosphere upon the earth's average temperature?

Since the greenhouse effect of CO_2 results from the absorption and reemmission of radiation by CO_2 it is revealing to consider the physics of the absorption of radiation as it passes through an an atmosphere containing this gas.

Absorption and Emission of Photons

Infrared radiant energy emitted by the earth in an energy interval ($\Delta\lambda^{-1}$) interacts with CO_2 as it passes through the atmosphere. The most important interaction for the CO_2 GHG effect is the absorption during transition between the ground and first excited bending state of CO_2, for which the energy change is $\Delta\varepsilon = 1.32 \times 10^{-20}$ Joules and $\Delta\varepsilon/k = 960$ K when the molecule is in its rotational ground state. If the concentration of CO_2 in the ground state is symbolized $[CO_2]$ and $[CO_2^*]$ is the symbol for the concentration in the first vibrational excited state, then at equilibrium at a given T: $[CO_2^*]/[CO_2] = e^{-960/T}$. In the case that changes in rotational states are involved this takes the form $[CO_2^*]/[CO_2] = e^{-\Delta\varepsilon/kT}$ where $\Delta\varepsilon$ is the change in vibrational and rotational energy and $\Delta\varepsilon/k \cong 960$ K.

When CO_2 molecules at equilibrium pick up photons and go into an excited state: $CO_2 + photon \rightarrow CO_2^*$, then $[CO_2^*]/[CO_2] > e^{\Delta\varepsilon/kT}$ and equilibrium is reestablished either by isotropically emitting a photon or by some mechanism such as energy loss as a result of collisions. In the latter case $CO_2^* + M \rightarrow CO_2 + M^*$ where M and M^* are any molecule (e.g. N_2) and the kinetic energy of M^* is greater than that of M. In this case some molecules in the air are translationally excited and some of the infrared radiation that originated from the earth goes into raising the temperature of the air above the steady state value. This excess thermal energy is in turn lost isotropically through radiation. Since by either type of mechanism the radiation absorbed by CO_2 ends up being reemitted isotropically it leaves the atmosphere at the TOA and at the earth's surface in equal measure.

Consideration of CO_2 Rotational States

There are many rotational energy levels associated with the ground and first excited bending states of CO_2 , so there is a range of energies absorbed in the neighorhood of the $0 \rightarrow 1$ bending transition energy. The complexity of the absorption implied by the rotational states can be discerned from the GHG infrared spectrum placed on the web by astrophysicists at Ohio State University and shown on the next slide
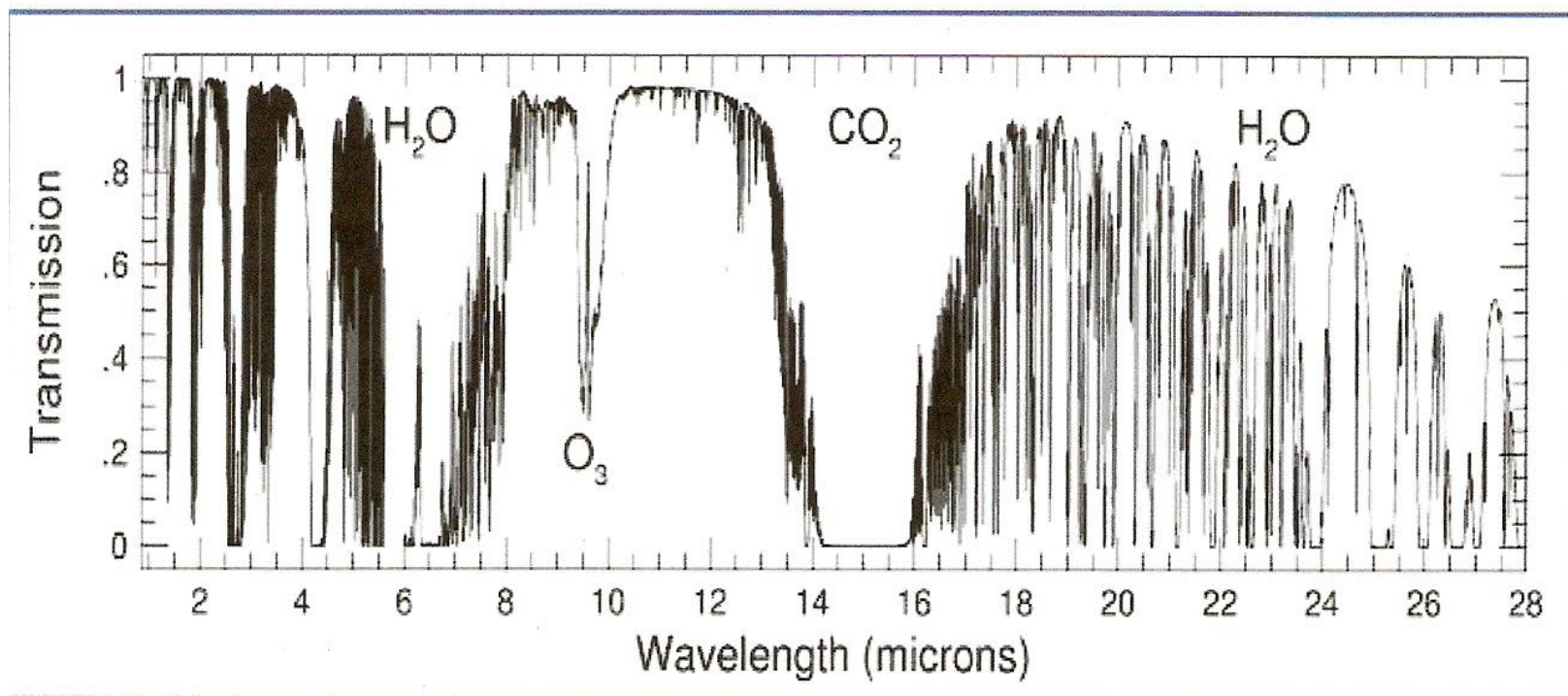
Infrared Absorption of the Atmosphere from 1-28 microns

Beer's Law

A generalization of Beer's Law is needed to determine the GHG effect of CO_2. As a first step the derivation of Beer's Law for absorption of intensity is recalled. The decrease in the intensity of a beam of monochromatic radiation as a result of absorption by CO_2 at any location along the line of propagation is given by:

$$dI = -k\bar{N}_{CO_2} Id\ell,$$

where I equals the intensity, $\bar{N}_{CO_2}$ equals the moles of CO_2 per unit volume, k is the molar concentration absorption coefficient (which is taken here to depend only upon the wavelength chosen) and $d\ell$ equals the change in path length. When integrated this gives Beer's Law:

$$\ln(I/I_o) = -k\int \bar{N}_{CO_2} d\ell$$

Definition of Linear Transmittance and Optical Thickness

Defining $\boldsymbol{\tau} = k \int \overline{N}_{CO_2} d\ell$ this can be written $T_\ell = e^{-\boldsymbol{\tau}}$ where $(T_\ell = I/I_o)$ is

called the linear transmittance and $\boldsymbol{\tau}$ is called the optical thickness.

$\int_0^L \overline{N}_{CO_2} d\ell$ defines $\tilde{N}$ (hence $T_\ell = e^{-k\tilde{N}}$) which is the number of moles of

absorbing gas in a volume 1 m^2 in cross section and L meters long. In

what follows k is taken to be constant for CO_2 at a given energy and

T_ℓ will depend only upon $\tilde{N}$ for a given transition.

CO$_2$ Absorption Data

The following figure shows a calculated and observed infrared spectrum for CO$_2$ in a $\Delta\lambda^{-1}$ interval from Stull, Wyatt, and Plass, Applied Optics, Vol. 3, No. 2, 250 (1964). This interval contains the wave numbers relevant to the interaction of CO$_2$ with the earth's Planck (thermal) radiation

# Theoretical and Calculated Absorption of CO_2 in the Infrared
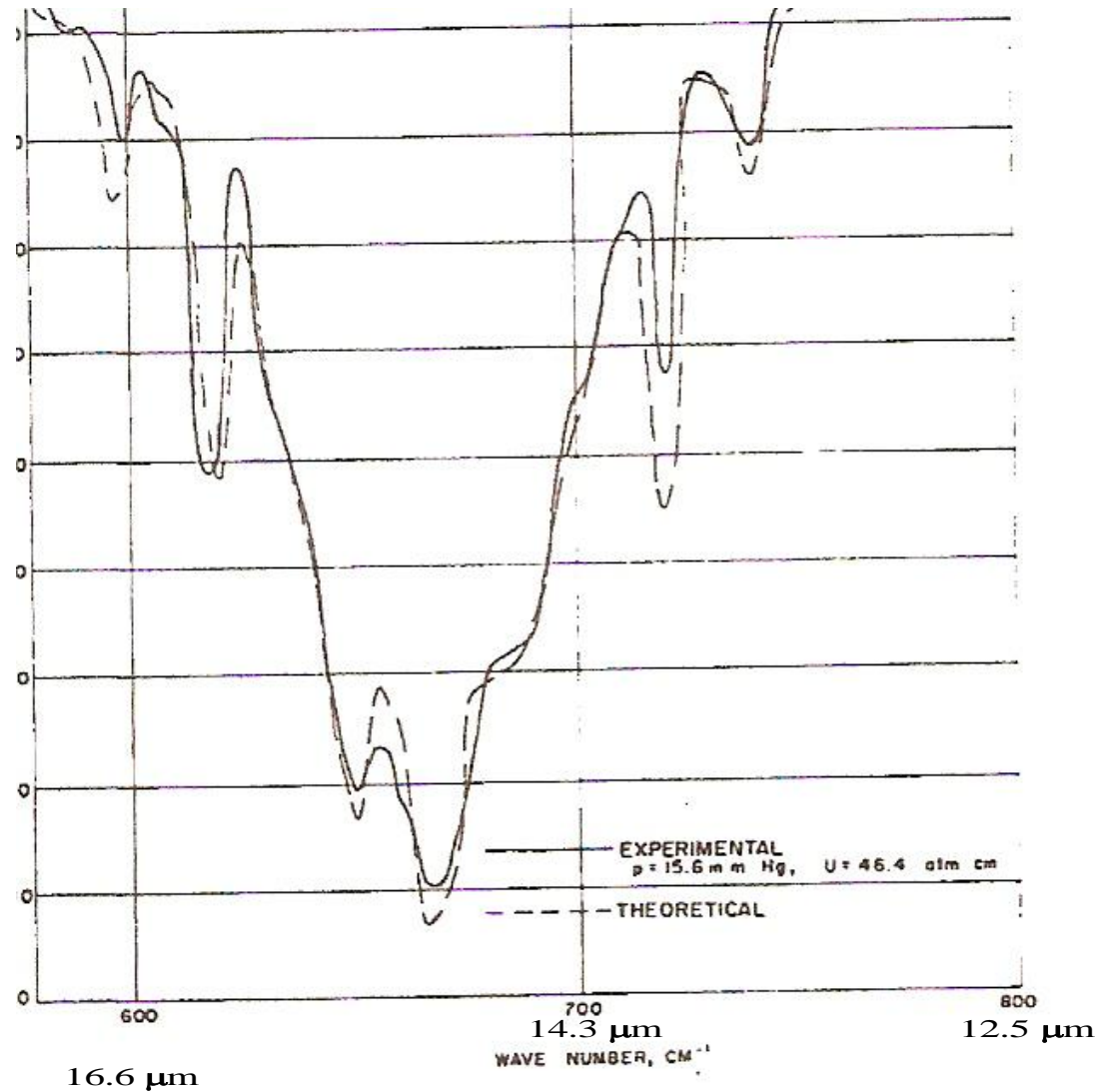
. 1.   A comparison of the theoretical calculations of the transtance with the experimental measurements of Burch *et al.*[6] for a pressure of 15.6 mm Hg and 46.4 atm-cm of CO_2.

The $\Delta\lambda^{-1}$ Interval and its Division into 11 Subintervals

The modes of CO_2 absorbing in this spectrum are the bending mode at λ=15 microns (or λ^{-1}=667 cm^{-1}) and the rotational modes (with wave numbers in multiples of about 0.35 cm$^{=1}$) associated with the bending mode. To include all the absorptions relevant to the greenhouse effect the region between 525 and 1075 cm^{-1} must be considered. This region (labeled $\Delta\lambda^{-1}$) will be divided into 11 subintervals labeled by i, each 50 cm^{-1}. wide. Even as early as the 1960's, when Stull et.al. did their work, computers were sufficiently fast that they were able to report absorption in $\delta\lambda^{-1}= 5$ cm^{-1} as well as in the 50 cm^{-1} intervals used here. However using the 5 cm^{-1} intervals would increase the work required to achieve the results obtained in this power point but would not yield results that differed significantly from those to be reported. It is my understanding that today climatologists do line by line calculations and the result is essentially unchanged from that obtained below. The fact that the 50 cm^{-1} intervals will result in a satisfactory fit with observation is apparent from the agreement between theory and observation previously shown on slide #32.. The next slide, #34, shows the 11 subintervals relative to the Planck envelope.

Planck Flux Showing the Chosen Wave Number Intervals
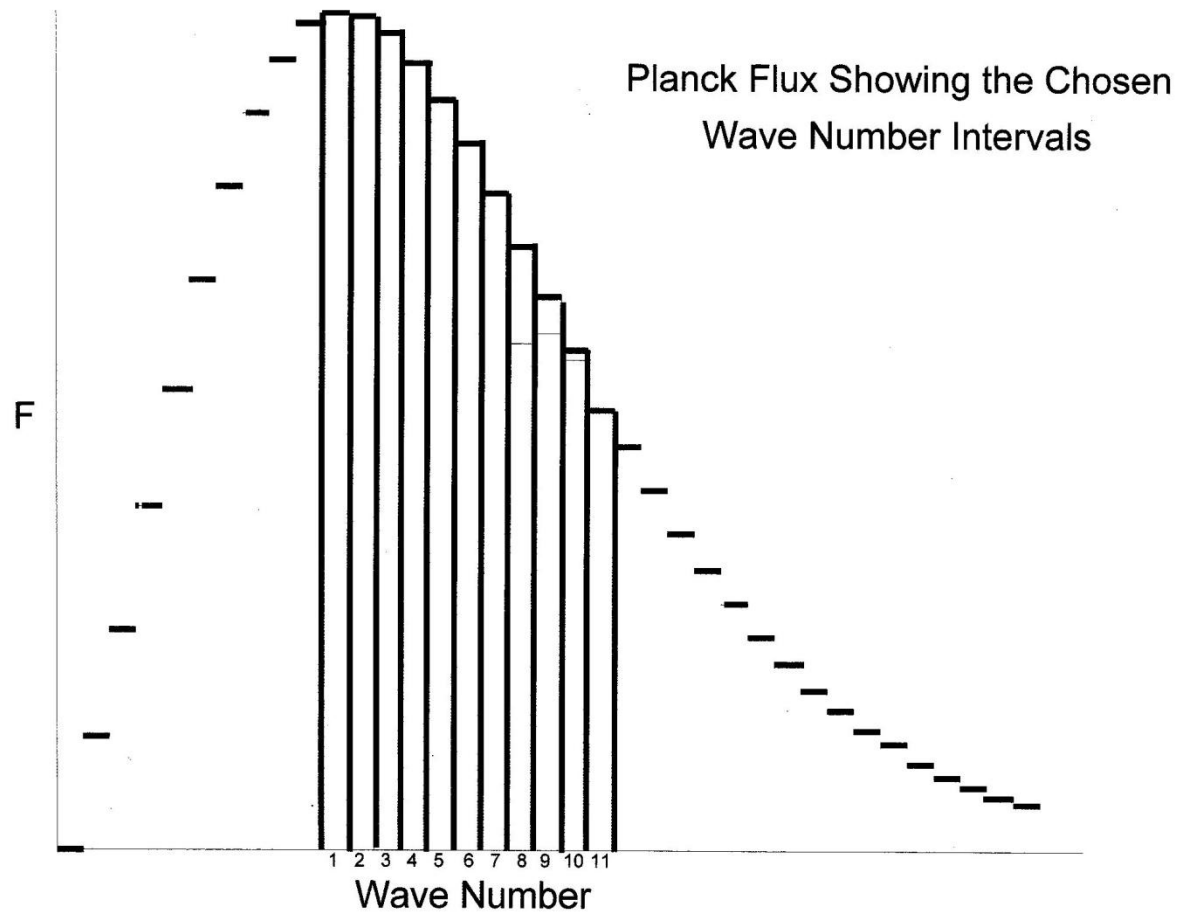
A Result We Will Need Later: Calculation of the Fraction of the Planck Flux in a $\Delta\lambda^{-1}$ Interval

The fraction of the Planck radiation in an interval between λ_1^{-1} and λ_2^{-1} is , using Planck's distribution law:

$$\int_{u(\lambda_1^{-1})}^{u(\lambda_2^{-1})} u^3 / (e^u - 1) du \, / \int_0^\infty u^3 / (e^u - 1) du$$

where $u = hc / \lambda k_B T$. This fraction for the $\Delta\lambda^{-1}$ region defined above is 0.489

Beer's Law for the Earth's Atmosphere

The case of absorption of Planck radiation in the atmosphere is more complicated than the monochromatic, linear Beer's Law $(\ln(I/I_o) = -\tau)$ case.

1. the source is a range of energies (not approximately monochromatic),

2. all directions (not just a single straight line) are of interest

3. the radiation that is reemitted is of interest (includes the greenhouse effect)

4. the absorption coefficient depends upon temperature and pressure (e.g. collisional broadening, thermal population). These effects are relatively small and will be ignored.

Statement of the Problem

The problem here is to find transmittances for $\Delta\lambda^{-1}$ for diffuse scattering by the vibrational-rotational frequencies of carbon dioxide. This is done by generalizing the absorption equation to the case of radiation in one of the 11 intervals and a given direction and then removing the angular dependence by integration to obtain Beer's law relating fluxes to the diffuse transmittance. Using the linear absorption coefficients given by Stull et. al. for the small intervals, the diffuse transmittances through the atmosphere will then be found for these small intervals. Beer's Law will then be further generalized to the case of a range of wave numbers ($\Delta\lambda^{-1}$) by using the fraction of the Planck radiation in each 50 cm^{-1} interval to compute the Planck averaged, diffuse transmittances for the $\Delta\lambda^{-1}$ interval

1. First the Case of a Line of Radiation

Let I_i be the intensity of radiation in the ith wave number interval originating from the earth's surface at an azimuthal angle ϕ and a zenithal angle θ. $\bar{N}_{CO_2} d\ell = \bar{N}_{CO_2} dz/\mu$ with $\mu = \cos\theta$ is the change in optical thickness and k_i is the linear absorption coefficient of CO_2, all at height z as the radiation passes through the atmosphere. The basic equation is Beer's Law for this case:

$$dI_i = -I_i k_i \bar{N}_{CO_2} dz / \mu$$

2. Change of Variable.

The optical depth for radiation with wave number in the ith interval traversing the vertical meters between a variable height z and fixed height x is defined:

$$\tau_i(z) = k_i \int_z^x \bar{N}_{CO_2}\, dh$$

so

$$d\tau_i = -k_i \bar{N}_{CO_2}\, dh$$

and the basic equation becomes, with the change of variable from height to optical depth:

$$\mu dI_i / d\tau_i = I_i.$$

When applied to the earth's total atmosphere $z = 0$ and $x \to \infty$.

3. Integration

.

At the basal surface: $z=0, \tau_i = \tau_i(g),\ I_i = I_i(a,g)$ and at $\lim_{x\to\infty} x = TOA, \tau_i = 0,$

and $I_i = I_i(TOA, g),$ so integration from g to TOA yields for the

angle θ $(\cos^{=1}\mu)$

$$I_i(TOA, g) = I_i(a, g) \lim_{x\to\infty} e^{-\tau_i(x,g)/\mu}$$

4. Calculation of Flux.

According to Gauss' Law, F is the vertical component of the intensity integrated over all values of θ and ϕ, so, if I_i were not dependent on angle, as at $z = 0$ (the Planck intensity is isotropic at the earth's surface):

$$F_i\,(a,g) = \int_0^{2\pi}\!\!\int_0^{\pi/2} I_i(a,g)\cos\theta\,\sin\theta\,d\theta\,d\phi = 2\pi \int_0^1 I_i(a,g)\,\mu\,d\mu = \pi\,I_i(a,g)$$

$$= \text{the earth's Planck flux}$$

According to Beer's Law, however, $I_i(\text{TOA}, g) = I_i(a, g) \lim\limits_{x \to \infty} e^{-\tau_{(i}(x,g)/\mu}$
(where $\mu = \cos\theta$), and thus $I_i(\text{TOA}, g)$ is dependent upon θ even if at the source at g it is isotropic. Thus the contribution to the flux at the TOA is:

$$F_i(\text{TOA}, g) = I_i(a, g) \int_0^{2\pi} \int_0^1 \lim_{x \to \infty} e^{-\tau_i(x,g))/\mu} \mu\, d\mu\, d\phi$$

$$= \pi\, I_i(a, g)\, 2 \int_0^1 \lim_{x \to \infty} e^{-\tau_i(x,g)/\mu} \mu\, d\mu$$

$$= F_i(a, g)\, 2 \int_0^1 \lim_{x \to \infty} e^{-\tau_i(x,g)/\mu} \mu\, d\mu$$

5. Definition of Diffuse Transmittance.

$$2\int_0^1 \lim_{x\to\infty} e^{-\tau_i(x,g)/\mu} \mu d\mu = T_{d.i}$$

defines the diffuse transmittance of radiation in the ith interval from g to TOA, so $F_i(TOA,g) = F_i(a,g) T_{d,i}$.

6. Review

The principal result is: of the flux of radiation in the ith interval that starts out from the earth's surface the diffuse transmittance is the fraction, $F_i(TOA,g)/F_i(a,g) = T_{d,i}$ that makes it through to TOA. That radiation which does not make it directly to TOA is redirected, half going up toward TOA and half going back toward g. In other words the difference between $F_i(a,g)$ and $T_{d,i}F_i(a,g)$ is twice the contribution to the GHG flux at either g or TOA

7. Generalization to a Broadband Source

The CO_2 GHG flux at the earth's surface arising from radiation in the ith small interval and between 0 and TOA is thus given by:

$$1/2(F_i\,(a,g) - T_{d.i}\,F_i\,(a.g))$$

Summing over i gives for the GHG flux:

$$1/2\sum_i [F_i\,(a,g) - T_{d,i}\,F_i\,(a,g)\,] = F_{tot}(g,a)$$

and recalling that for the earth's Planck radiation:

$$\sum_i F_i\,(a,g) = F_{\Delta\lambda^{-1}}(a,g) = 0.489 \times F_{tot}(a,g),$$

yields:

$$1/2\,(0.489 \times F_{tot}(a,g) - \sum_i F_i\,(a,g)T_{d,i} = F_{tot}(g,a)$$

in which $F_{tot}(a,g)$ is the Planck flux and $F_{tot}(g,a)$ is the CO_2 GHG flux.

8. Introduction of Absorption Data for CO_2

The linear transmittance data for the 11 intervals reported by Stull et. al. (and compared therein with experimental data as on #32) are presented on the the next slide in columns labeled by $\tilde{N}_{CO_2}$. ϑ_i is that fraction of the flux in the $\Delta\lambda^{-1}$ interval (between 525 and 1075 cm^{-1}) that falls in the ith small interval (see slide #34 for calculation of the ϑ_i 's). The ϑ_i 's are presented in the last column of the next table.

T$_\ell$ from Stull et. al.

i	409 moles m^{-2}	204.5 moles m^{-2}	81.8 moles m^{-2}	40.9 moles m^{-2}	ϑ_i
1	0.685	0.809	0.914	0.956	0.1117
2	0.023	0.063	0.165	0.282	0.1113
3	0	0	0	0.002	0.1090
4	0	0.003	0.013	0,038	0.1051
5	0.115	0.199	0.341	0.466	0.1000
6	0.705	0.824	0.929	0.959	0.0941
7	0.672	0.7775	0.875	0.927	0.0875
8	0.823	0.885	0.929	0.989	0.0807
9	0.909	0.949	0.978	0.994	0.0738
10	0.948	0.972	0.988	0.994	0.0669
11	0.775	0.856	0.927	0.960	0.0602

Calculation Of Broadband Diffuse Transmittance

As shown on #43 the values of the linear transmittance (the $T_{\ell,i}$'s given by Stull et.al. and on the previous slide) yield diffuse transmittance values according to:

$$T_{d,i} = 2 \times \int_0^1 e^{-\mu^{-1} \ln T_{\ell,i}} \, \mu d\mu.$$

The $T_{d,i}$'s, when multiplied by the corresponding ϑ_i 's, yield the Planck weighted values, $\vartheta_i T_{d,i}$, given on the slide #49. The sums of these for different $\tilde{N}_i$'s over the $\Delta\lambda^{-1}$ interval, $\displaystyle\sum_{i=1}^{11} \vartheta_i T_{d,i} = T_{d,\Delta\lambda^{-1}}$ are given at the bottoms of the columns labeled by the $\tilde{N}_i$'s. These are Planck weighted average, broadband, diffuse transmittances for CO_2 interacting with infrared radiation in the wave number region characteristic of the earth's Planck radiation.

$\vartheta_i T_{d,i}$

i	409 mole m^{-2}	204.5 mole m^{-2}	81.8 mole m^{-2}	40.9 mole m^{-2}
1	0.0595	0.0732	0.0947	0.1026
2	0.0008	0.0026	0.0086	0.0171
3	0	0	0	0
4	0	0	0.0004	0.0014
5	0.0050	0.0098	0.0198	0.0304
6	0.0523	0.0670	0.0821	0.0869
7	0.0451	0.0565	0.0686	0.0758
8	0.0573	0.0647	0.0704	0.0790
9	0.0619	0.0669	0.0708	0.0769
10	0.0603	0.0631	0.0651	0.0659
11	0.0388	0.0457	0.0523	0.0557
Σ	0.3810	0.4535	0.5328	0.5917

Note that:

$$F_{\Delta\lambda^{-1}}(TOA,g) = \sum_{i=1}^{11} F_i(TOA,g) = \sum_{i=1}^{11} F_i(a,g)T_{d,i}$$

$$= F_{\Delta\lambda^{-1}}(a,g) \sum_{i=1}^{11} [F_i(a,g)/F_{\Delta\lambda^{-1}}(a,g)]T_{d,i}$$

$$= F_{\Delta\lambda^{-1}}(a,g) \sum_{i=1}^{11} \vartheta_i T_{d,i}$$

$$= F_{\Delta\lambda^{-1}}(a,g)T_{d,\Delta\lambda^{-1}}$$

and thus the total GHG flux from CO_2 is

$$1/2F_{\Delta\lambda^{-1}}(a,g)(1-T_{d,\Delta\lambda^{-1}})$$

Hence, in order to calculate the CO_2 contribution to the greenhouse effect for the earth, a value for the total interval diffuse Planck averaged transmittance:

$$T_{d,\Delta\lambda^{-1}} = \sum_{i=1}^{11} \vartheta_i T_i^D$$

for the earth's atmosphere and Planck's law are all that is required.

Polynomial Fit of $T_{d,\Delta\lambda^{-1}}$ vs. $\tilde{N}_{CO_2}$

The $T_{d,\Delta\lambda^{-1}}$ values were interpolated to find $T_{d,\Delta\lambda^{-1}}$ for the total atmosphere

as follows: First the four values for $\sum\limits_{i=1}^{11} \vartheta_i T_{d,i} = T_{d,\Delta\lambda^{-1}}$ obtained above

from the data of Stull et.al. (slide #49) were fit to a polynomial:

$$T_{d,\Delta\lambda^{-1}} = 1.35\times10^{-6}(\tilde{N}_{CO_2})^2 - 1.16\times10^{-3}(\tilde{N}_{CO_2}) + 0.6254 \pm 0.004$$

Ñ for the Atmosphere Including Gravity

Assuming an isothermal atmosphere:

$$\tilde{N} = \int_0^\infty \bar{N}_{CO_2} dz = \bar{N}^o \times \int_0^\infty e^{-(Mg/RT)z} dz$$

$$= P^o/RT \times RT/Mg = (F_e/a_e)/(F_e/N_{CO_2}) = N_{CO_2}/a_e.$$

$\tilde{N}$ is the number of molecules in the path of a beam of photons 1 m^2 in area. At the constant k level of approximation neglect of the effect of changing temperature with altitude does not effect the calculated transmittance because it does not alter $\tilde{N}_{CO_2}$.

Using the N to Ñ conversion from the previous slide:

$$\tilde{N}_{CO_2}^{atm} = N_{CO_2}^{atm} / a_e = \text{ppm}_{CO_2} \times 1.88 \times 10^{14} / 5.10 \times 10^{14}$$

and the ppm vs. x (= year-1960)) polynomial from slide #7 to find Ñ in a given year, the polynomial on #51 can then be used to find $T_{d,\Delta\lambda^{-1}}$ for any year for which the Keeling curve remains accurate. The absorption using the value for 2007 (385 ppm) is shown on the next slide.

Carbon Dioxide Absorption
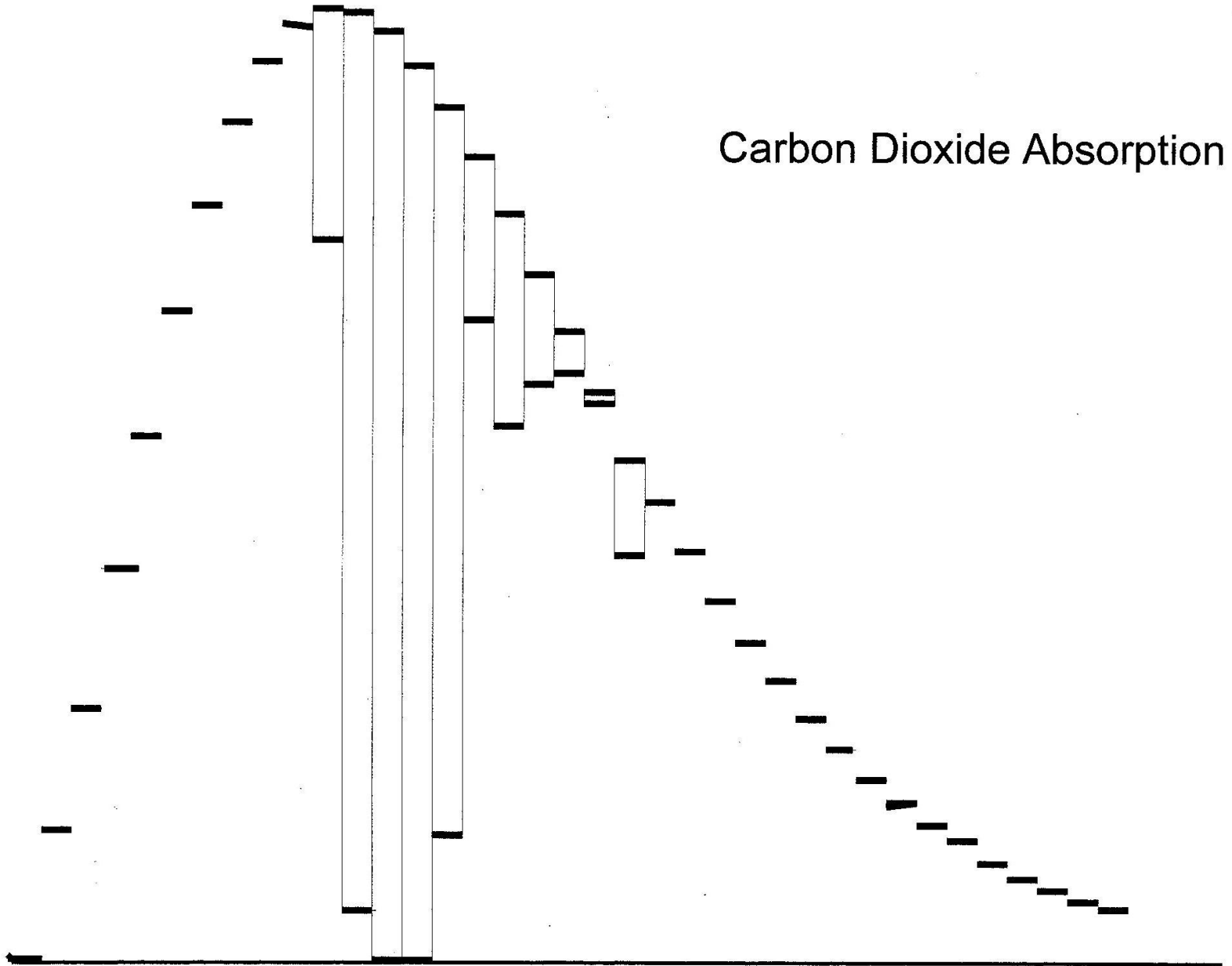
The Keeling curve was shown above to be fit by a polynomial $ax^2 + bx + c$ (x=year-1960). In what follows the contribution from CO_2 to the increase in the temperature earth will be calculated assuming that a,b, and c do not change with time. Thus, for the purpose of this calculation, it is assumed that the increase in the rate of production of CO_2 will continue as it is currently observed, i.e. the result obtained here corresponds to the current atmosphere and that currently anticipated by the Keeling curve.

Planck Fluxes at g and TOA

Recalling that:

$$F_{\Delta\lambda^{-1}}(a,g) = 0.489 \times F_{tot}(a,g), \text{ and}$$

$$F_{tot}(g,a) = 1/2\, F_{\Delta\lambda^{-1}}(a,g)(1 - T_{d,\Delta\lambda^{-1}}),$$

we have for the GHG effect of CO_2 :

$$F_{y_j}(g,a) = 0.2445 \times F_{y_j}(a,g)(1 - T_{d,y_j}),$$

where the F_{y_j}'s are the average fluxes for the year labeled by j and

T_{d,y_j} is the corresponding transmittance between g and TOA. Using T_{d,y_j}

obtained as above, the contribution of CO_2 to the GHG flux can be

calculated for any year from 1960 to the present and also any

future year for which the Keeling curve provides a good estimate

of ppm CO_2.

Taking the difference in fluxes between two years:

$$F_{y_2}(g,a) - F_{y_1}(g,a) = 0.2445 \times [F_{y_2}(a,g)\ (1 - T_{d,y_2}) - F_{y_1}(a,g)\ (1 - T^D_{d,y_1})]$$

Because the average earth is in a thermal steady-state the increase in the average GHG flux will be balanced by an equal increase in the average Planck flux from the earth:

$$F_{y_2}(g,a) - F_{y_1}(g,a) = F_{y_2}(a,g) - F_{y_1}(a,g)$$

Therefore, with F_{y_j} being the Planck flux for the jth year

$$F_{y_2} - F_{y_1} = 0.2445 \times [F_{y_2}(1 - T_{d,y_2}) - F_{y_1}(1 - T_{d,y_1})],$$

or:

$$F_{y_2}(1 - 0.2445(1 - T_{d,y_2})) = F_{y_1}(1 - 0.2445(1 - T_{d,y_1})),$$

and:

$$F_{y_1} / F_{y_2} = (1 - 0.2445(1 - T_{d,y_1})) / (1 - 0.2445(1 - T_{d,y_1}))$$

Substituting according to the Stefan-Boltzmann Law

(NOTE: T = temperature and T_d = transmissivity)

$$F_{y_2} / F_{y_1} = T_{y_2}^4 / T_{y_1}^4 = (1 - 0.2445(1 - T_{d,y_1})) / (1 - 0.2445(1 - T_{d,y_1}))$$

For example comparing 2107 (x=147) with 2007 (x=47):

$$(T_{2107}/T_{2007})^4 = (1 - 0.2445(1 - 0.4890))/(1 - 0.2445(1 - 0.4201))$$

which yields $(T_{2107} / T_{2007})^4 = 1.019$, and taking $T_{2007} = 288$ K,

$T_{2107} - T_{2007} = 288 \times 1.019^{1/4} - 288 = 1.4$ Kelvin degrees,

i.e. in the next 100 years the GHG effect of CO_2 will be to

increase the earth's average temperature by about 1.4 K^o. Calculation

of T between 2010 and 2110 gives the line shown on the next slide.
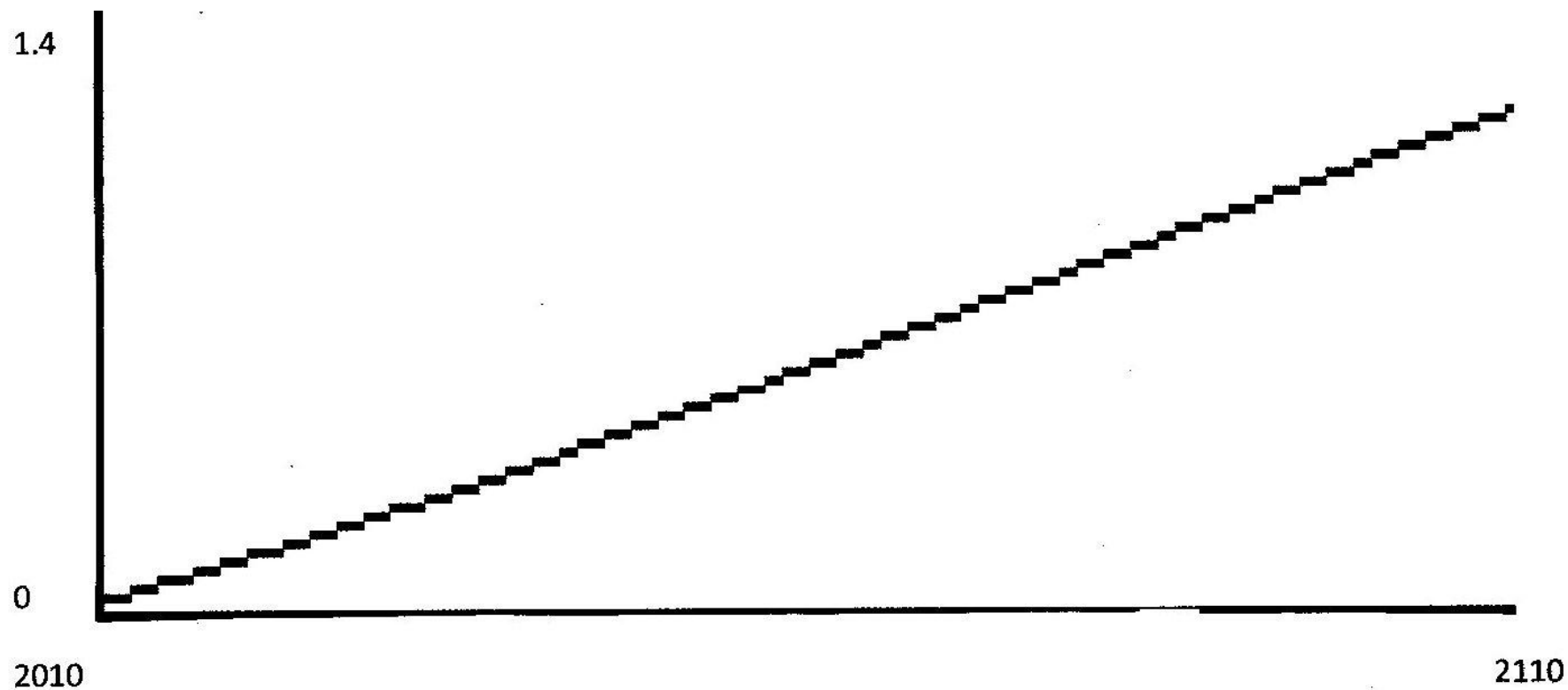
Carbon Dioxide GHG Forcing in Kelvin Degrees vs. Year

Summary

The science presented here demonstrates that the measured increase in quantity of atmospheric CO_2 that was shown by mass balance to be about 1/2 the increase from fossil fuel consumption, is sufficient to raise the earth's average temperature by about 1.4 K in the next 100 years This increase is larger than, but of the same order as, that believed to have occurred over the last 100 years. Therefore, to the extent that we are concerned about the current rate of increase, it is important to recognize that hard science shows that *the least* we can expect is a comparable contribution from CO_2 to the increase in the earth's average temperature for the next 100 years unless the Keeling curve is altered downward. Note that the alteration of the Keeling Curve will lag behind changes in human consumption because of the degassing of the seas that will occur when the partial pressure of CO_2 in the atmosphere is reduced (see the appendix for a brief treatment of dissolved CO_2).

Some Further Reasons For Serious Concern

The increase in temperature found here is almost certainly too low because:

1. The calculation is based upon the assumption that the Keeling curve will be as it has been, but this assumption ignores the expected large increases in fossil fuel consumption as the use of the fuels in the developing world , especially China and India, becomes more like it is in the U.S.

2. Feedbacks have been ignored e.g.

    i. melting of arctic ice (decrease in albido),

    ii. release of CO_2 from the earth and ocean due to increased temperature,

    iii. release of CH_4 from permafrost and ocean floor,

    iv. changes in the concentration of water in the atmosphere

Summary

$$\text{ppm}_{CO_2} = [1.054 \times 10^{-2}](yr - 1960)^2 + [9.00 \times 10^{-1}](yr - 1960) + 315.5$$

$$\tilde{N}^{atm}_{CO_2} = 0.369 \times \text{ppm}_{CO_2}$$

$$T^D_{\Delta\lambda^{-1}} = 1.35 \times 10^{-6}(\tilde{N}_{CO_2})^2 - 1.16 \times 10^{-3}(\tilde{N}_{CO_2}) + 0.6254 \pm 0.004$$

$$T_2^4 / T_1^4 = (1 - 0.2445(1 - T_1^D)) / (1 - 0.2445(1 - T_2^D))$$

APPENDIX A: SIMPLE P. CHEM,. OF CO_2 IN THE OCEANS.

Using the thermodynamic data available for $CO_2(g)$ and $CO_2(aq)$ yields the Henry's law constant for CO_2 in water, and for 385ppm $CO_2(g)$ at 288 K this yields (at saturation!) 9.86×10^{-6} molal $CO_2(aq)$. Similarly the equilibrium constants for the formation of $HCO_3^-(aq)$ from $CO_2(aq)$ and for its acid dissociation provide, together with the Debye-Hückel equation and the known average pH of the oceans (8.10), after some algebra, 5.86×10^{-4} molal $HCO_3^-(aq)$ and 4.2×10^{-6} molal $CO_3^-(aq)$. The rather large value for $HCO_3^-(aq)$ is perhaps the justication for the oft made claim that there is much more carbon dioxide dissolved in the ocean than there is in the atmosphere. However it should be noted that the carbon dioxide present as bicarbonate could neither have come from the atmosphere nor could it be outgassed into the atmosphere so long as the pH remains in the range of its historic values because it carries a negative charge and no reaction producing $CO_2(g)$ from $HCO_3^-(aq)$ not involving unbelievable changes in pH can be written. The bicarbonate certainly came in through the rivers of the world and is 99+% irrelevant to the exchange of carbon dioxide between the oceans and the atmosphere

Furthermore: Considering the ocean as a sink, even if the oceans were saturated to their depths, which is probably not the case, CO_2 would be entering the oceans from the atmosphere because of its increasing partial pressure. On the hand if, as seems likely, the deep ocean is not saturated, the deep ocean will act as a sink to which the surface CO_2 (aq) can diffue. . This is most probably the fate of most of the CO_2 produced by man and not ending up in the atmosphere. The idea that the oceans are a net source of the atmospheric CO_2 cannot be correct because this could be the case only if the oceans were net supersaturated with CO_2. If this were the case the oceans could not be a sink for the CO_2 produced in excess of that observed entering the atmosphere (14 billion of tons per year plus the additional human production while forming CaO from $CaCO_3$). That is, the oceans cannot be both a net sink and and a net source of atmospheric CO_2.

I fit the Keeling curve to a second-order polynomial:

$$ppm = 1.054 \times 10^{-2} x^2 + 9.00 \times 10^{-1} x + 315.8 \text{ where x=(yr-1960)}$$

ppm_{obs}	ppm_{fit}	$\sqrt{\Delta^2}$	yr
316.6	315.8	0.8	1960.0
320.0	320.0	0.0	1964.3
324.9	326.0	1.1	1970.0
330.0	330.4	0.4	1973.8
337.7	338.1	0.4	1980.0
340.0	339.9	0.1	1981.3
350.0	348.8	1.2	1987.6
353.3	352.4	0.9	1990.0
360.0	360.3	0.3	1995.0
368.2	368.8	0.6	2000.0
370.0	370.5	0.5	2001.0
380.0	379.3	0.7	2005.8
387.0	387.3	0.3	2010.0