Calculation of Solar Absorption by Carbon Dioxide

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Abstract: The absorption of incoming solar radiation by atmospheric carbon dioxide was computed as a function of frequency and altitude. Atmospheric CO_2 at the 2017 level of 400 ppm absorbs less than 0.065 % of the incident solar flux on the earth. Doubling the CO_2 concentration changes this by a negligible amount. Hence, unlike the greenhouse effect, where CO_2 strongly absorbs infrared radiation emitted by the Earth, increasing carbon dioxide has a negligible effect on the absorption of Sunlight which is predominantly at visible wavelengths.

Keywords: carbon dioxide, solar radiation

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I – Black Body Radiation

Any object at a nonzero temperature emits radiation. The amount of power per unit area of a so called black body radiated into a unit solid angle from frequency ν to ν + dν is called the Brightness and is given by the following

$$B(\nu, T) = \frac{2\,h\,c^2\,\nu^3}{e^{\frac{\nu}{\theta}} - 1} \tag{1}$$

where T is the temperature in Kelvins, ν is the frequency in wavenumbers, h is Planck's constant, c is the speed of light, k is Boltzmann's constant and

$$\theta = \frac{k\,T}{h\,c} \tag{2}$$

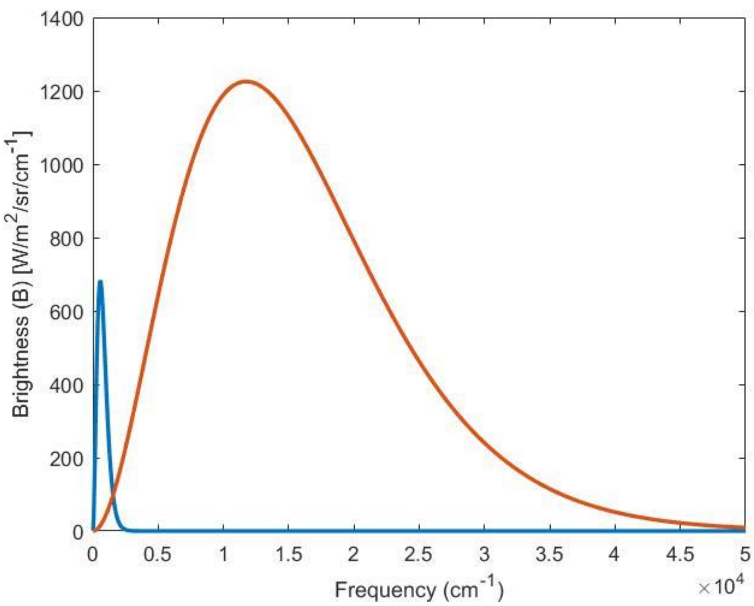


Fig. 1. Brightness Dependence on Frequency. The blue curve was computed for the Earth's average surface temperature of 288.7 K. It has a maximum brightness of 1.31×10^{-3} W/m^2/sr/cm^{-1} at 566 cm^{-1}. The red curve was computed for the Sun's surface temperature of 6000 K. It has a maximum brightness of 1.23 x 10^3 W/m^2/sr/cm^{-1} at 1.18 x 10^4 cm^{-1}. The blue curve has been multiplied by a factor of 5×10^3 to enhance its visibility.

The brightness maximum occurs at a frequency that satisfies

$$\frac{\partial B(\nu,T)}{\partial \nu} = 0 \tag{3}$$

Defining $x = \frac{\nu}{\theta}$, one finds the equation

$$0 = e^{x}(3 - x) - 3 \tag{4}$$

which has solution x = 2.8214. Hence, the frequency where the brightness is maximum is given by

$$\nu = 2.8214\ \theta \tag{5}$$

It is sometimes useful to measure the energy flux dependence on wavelength rather than frequency. The brightness given by equation (1) is the energy flux per unit solid angle from frequency ν to ν + dν can be equated to the energy flux per unit solid angle from wavelength λ to λ+ dλ as follows

$$B'(\lambda, T)\, d\lambda = B(\nu, T)\, d\nu \tag{6}$$

Using the speed of light c = ν λ and equation (1), one can find the following expression

$$B'(\lambda, T) = \frac{2\ h\ c^2}{\lambda^5 \left(e^{\frac{1}{\lambda\,\theta}} - 1\right)} \tag{7}$$

B' has units of $W/m^2/sr/\mu m$ and is plotted in Fig. 2. The wavelength where B' is a maximum is found by setting

$$\frac{\partial B'(\lambda,T)}{\partial \lambda} = 0 \tag{8}$$

which has solution

$$\lambda = \frac{4.965}{\theta} \tag{9}$$

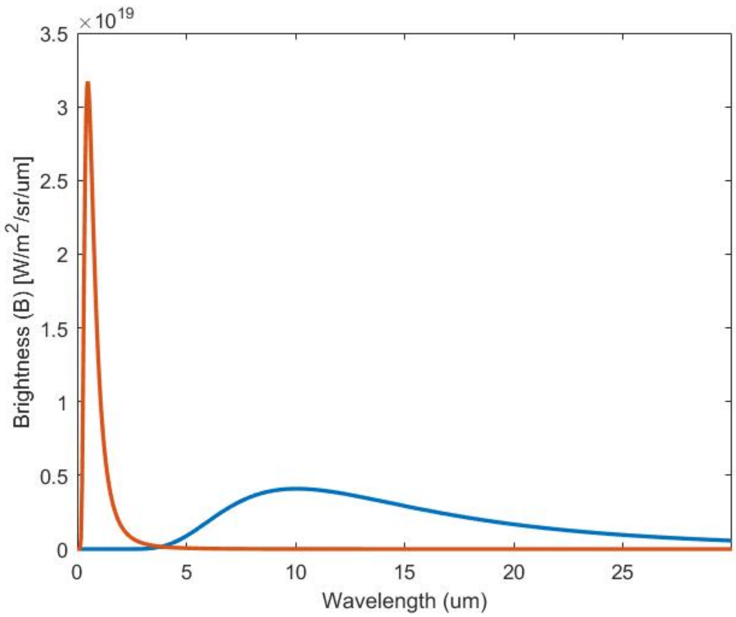


Fig. 2. Brightness dependence on Wavelength. The blue curve was computed for the Earth's average surface temperature of 288.7 K. It has a maximum brightness of 8.18×10^{12} W/m^2/sr/µm at 10.0 µm. The red curve was computed for the Sun's surface temperature of 6000 K. It has a maximum brightness of 3.16×10^{19} W/m^2/sr/µm at 0.483 µm. The blue curve has been multiplied by a factor of 5 x 10^5 to enhance its visibility.

The total energy flux F radiated by a body is found by integrating either equation (1) over all solid angles and frequencies or equation (7) over all solid angles and wavelengths giving the so-called Stefan Boltzmann equation

$$\mathrm{F} = \sigma T^4 \qquad (10)$$

where

$$\sigma = \frac{2\pi^5 k^4}{15\mathrm{c}^2\mathrm{h}^3} \approx 5.670\ x\ 10^{-8}\,\frac{\mathrm{W}}{\mathrm{m}^2\mathrm{K}^4} \qquad (11)$$

For the Earth this gives an energy flux of 393.9 $\frac{\mathrm{W}}{\mathrm{m}^2}$ and for the Sun $7.349 \times 10^7\ \frac{\mathrm{W}}{\mathrm{m}^2}$.

II – Atmospheric Pressure and Number Density

The atmosphere is divided into regions depending on altitude as given in Table 1.

Table 1. Range of altitudes for partitions of atmosphere.

Altitude Range (km)	**Name**
0 – 10	Troposphere
10	Tropopause
10 – 50	Stratosphere
50	Stratopause
50 – 100	Mesosphere

The pressure and number density strongly depend on the altitude z measured above the Earth's surface. To get an expression for the pressure dependence on altitude, consider a slab of atmosphere between altitudes z and z + dz having an area A. In equilibrium, the downward gravitational force is balanced by the difference in the pressures at the bottom and top of the slab.

$$\rho_a \, g \, A \, dz = [P(z) - P(z + dz)]A \tag{12}$$

Here, g is the acceleration due to gravity and the air density $\rho_a = \frac{P\,M_a}{R\,T}$ where $M_a = 29 \, \frac{g}{mol}$ is the average molar mass of air, $R = 8.314 \, \frac{J}{mol\,K}$ is the ideal gas constant and T is the air temperature. Equation (12) gives the following.

$$\frac{dP}{dz} = -\rho_a g \tag{13}$$

Integrating equation (13) gives

$$P(z) = P_0 e^{\frac{-z}{H}} \tag{14}$$

which is plotted in Fig. 3. Here, P_o is the pressure at the Earth's surface of 1×10^5 Pa and

$$H = \frac{RT}{M_a g} \tag{15}$$

is a characteristic height. Setting T equal to the average Earth surface temperature of 288.7 K gives a value of 8.45 km for H.

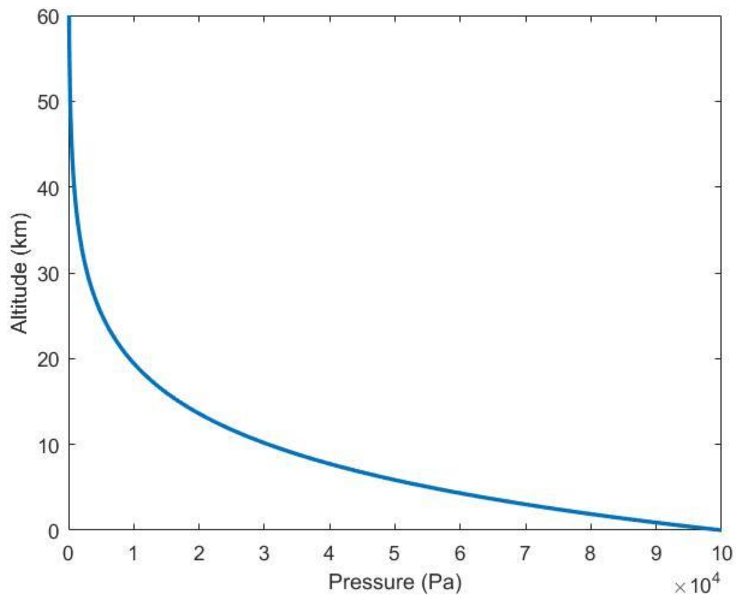


Fig. 3. Earth's atmospheric pressure dependence on altitude. The atmosphere was assumed to be at a constant temperature of 288.7 K.

The air density can be found using the ideal gas law

$$P\,V = N\,k\,T \tag{16}$$

where V is the volume occupied by the gas, k is Boltzmann's constant, N is the number of molecules, and T is the temperature in Kelvins. This can be solved to give the number density

$$n = \frac{N}{V} = \frac{P}{k\,T} \tag{17}$$

Substituting (14) into (17) gives

$$n(z) = n_o\, e^{\frac{-z}{H}} \tag{18}$$

where the air density at the Earth's surface $n_0 = \frac{P}{kT}$, has a value of $2.5 \times 10^{25}\ \frac{\text{molecules}}{\text{m}^3}$.

Equation (18) is plotted in Fig. 4.

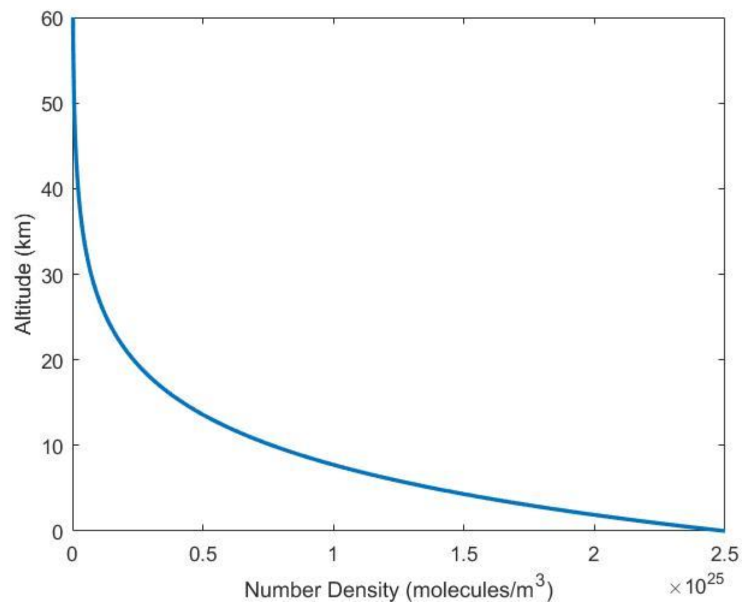


Fig. 4. Air Number density dependence on altitude.

The carbon dioxide number density is simply found by multiplying equation (18) by the CO_2 concentration of 400 ppm which is uniform throughout the atmosphere, giving $1 \times 10^{22}\ \frac{\text{CO}_2\text{molecules}}{\text{m}^3}$ at the Earth's surface.

III – Light Absorption of Cross Section of Carbon Dioxide

The two solar absorbing vibrational modes of carbon dioxide are shown in Fig. 5

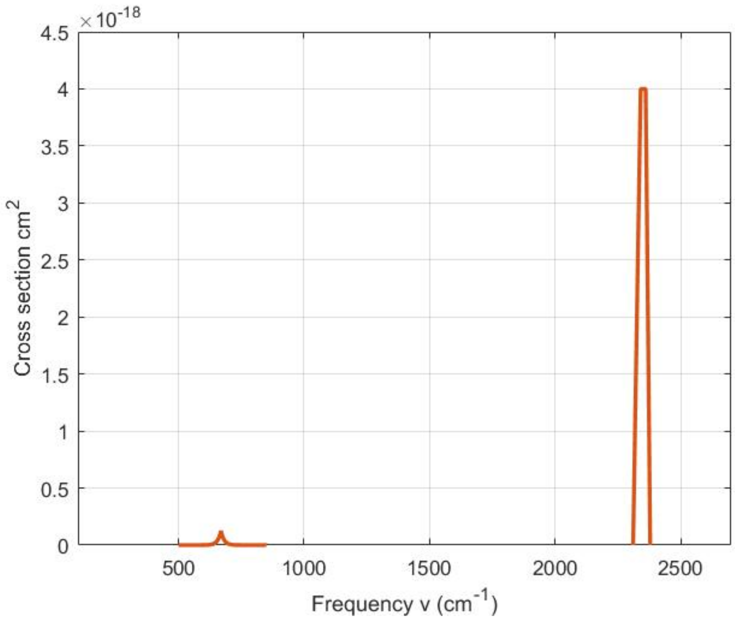


Fig. 5. The cross sections for carbon dioxide bending and asymmetric stretching modes with peaks at 669 cm^{-1} and 2340 cm^{-1} respectively.

The first peak shown in detail in Fig. 6 is known as the bending vibrational mode. Its cross section is well approximated by the following formula

$$\sigma = \sigma_e e^{-\lambda_e|\nu-\nu_e|} \tag{19}$$

where σ_e=1.26×10^{-19} cm^2 is the peak cross section at the frequency $\nu_e = 669$ cm^{-1} and $\lambda_e = 0.0812$ cm is the transition width parameter. The Earth black body radiation peaks at a frequency of 566 cm^{-1} as shown in Fig. 1 which is near the wavelength of the CO_2 bending mode resonance. This means carbon dioxide in the atmosphere acts as a blanket by absorbing Earth's radiation which is called the greenhouse effect.

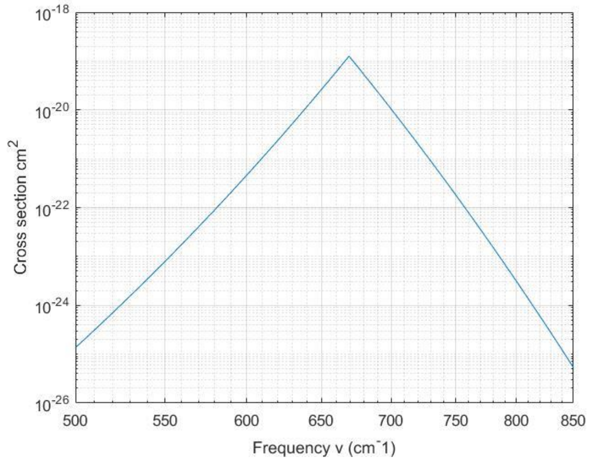


Fig. 6. Light absorption cross section of CO_2 bending vibrational mode.

The second peak in Fig. 5 is called the asymmetric stretching vibrational mode. Its cross section is approximated as shown in Fig. 7 by a series of straight line segments defined as follows

$$\sigma = \begin{cases} 1.33 \times 10^{-19}\nu - 3.08 \times 10^{-16} & 2310 \leq \nu < 2340 \\ 4.00 \times 10^{-18} & 2340 \leq \nu < 2360 \\ -2.22 \times 10^{-19}\nu + 5.28 \times 10^{-16} & 2360 \leq \nu \leq 2378 \end{cases} \quad (20)$$

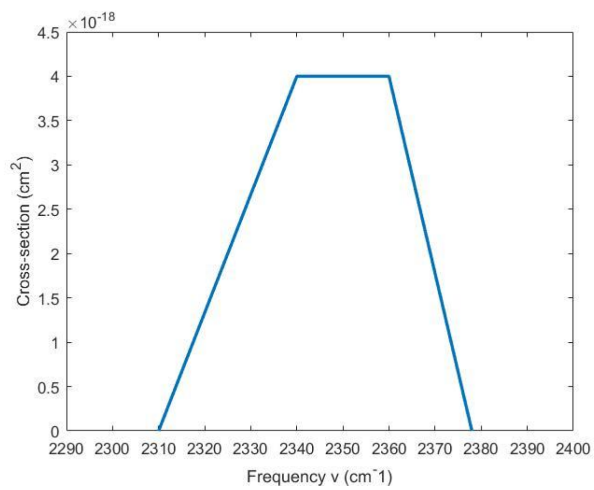


Fig.7. Light absorption cross section of CO_2 asymmetric vibrational mode.

IV – Solar Flux

The incoming solar flux per unit frequency at the top of the atmosphere is given by

$$\mathcal{F}_s(\nu) = \mathrm{f_{red}}\ \mathrm{B}(\nu, \mathrm{T_s}) \tag{21}$$

where B is the solar brightness evaluated at the Sun's surface temperature T_s and f_{red} is a reduction factor that depends on factors such as the distance of the Earth from the Sun. Integrating over frequency gives the incident solar flux

$$\begin{aligned} \mathrm{F_s} &= \int_0^\infty \mathcal{F}_s(\nu)\ d\nu \\ &= \mathrm{f_{red}} \int_0^\infty \mathrm{B}(\nu, \mathrm{T_s})\ d\nu \\ &= \mathrm{f_{red}}\ \pi\ \sigma\ \mathrm{T_s^4} \end{aligned} \tag{22}$$

The solar flux F_s incident on the top of the Earth's atmosphere has been measured to be 1370 W/m^2. Using the Sun's surface temperature T_s = 6000 K gives a value of $f_{red} = 5.93 \times 10^{-6}$ sr.

The solar flux per unit frequency transmitted through a vertical distance z measured from the top of the atmosphere is given by

$$\mathcal{F}(z, \nu) = \int_0^z \mathcal{F}_s(\nu) e^{\frac{-\kappa(\nu,z)\, z}{<\cos\theta_z>}}\ dz \tag{23}$$

where the absorption coefficient

$$\kappa(\nu, z) = \sigma_{CO_2}(\nu)\ \mathrm{n_{CO_2}}(z) \tag{24}$$

is the product of the absorption cross section $\sigma_{CO_2}(\nu)$ at frequency ν and the CO_2 number density $n_{CO_2}(z)$ at position z.

The exponent also contains a factor of $\cos\theta_z$ where the zenith angle θ_z is defined as shown in Fig. 8. It accounts for the different path lengths through the atmosphere of the solar rays incident on the Earth at different latitudes. The distance a solar ray passes through the

Earth's atmosphere before striking the surface is proportional to $1/\cos\theta_z$. The average of $\cos\theta_z$ is given by

$$< cos\theta_z > = \frac{\int_{Daylight} cos\theta_z \, d\Omega}{\int_{Daylight} d\Omega}$$

$$= \frac{\pi \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} cos\theta_z \, sin\theta_z \, d\theta_z}{2\pi} \tag{25}$$

$$= \frac{1}{2}$$

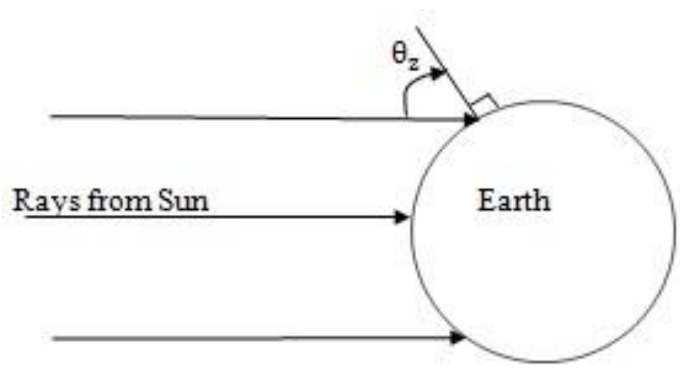
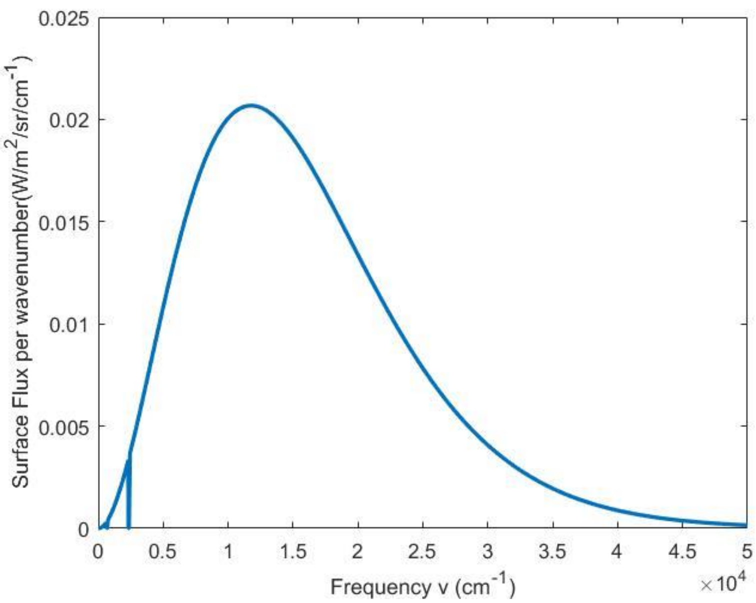


Fig. 8. Solar radiation incident on Earth. The angle that a solar ray makes relative to the direction perpendicular to the Earth's surface is called the zenith angle θ_z. It ranges from $-\pi/2$ at the South Pole, zero at the equator and $+\pi/2$ at the North pole.

The solar flux dependence on frequency was evaluated by the computer program given in the Appendix and is shown in Fig. 9. The integral in (23) is evaluated over the 100 km atmospheric thickness using a 0.1 km step size.

a)



b)

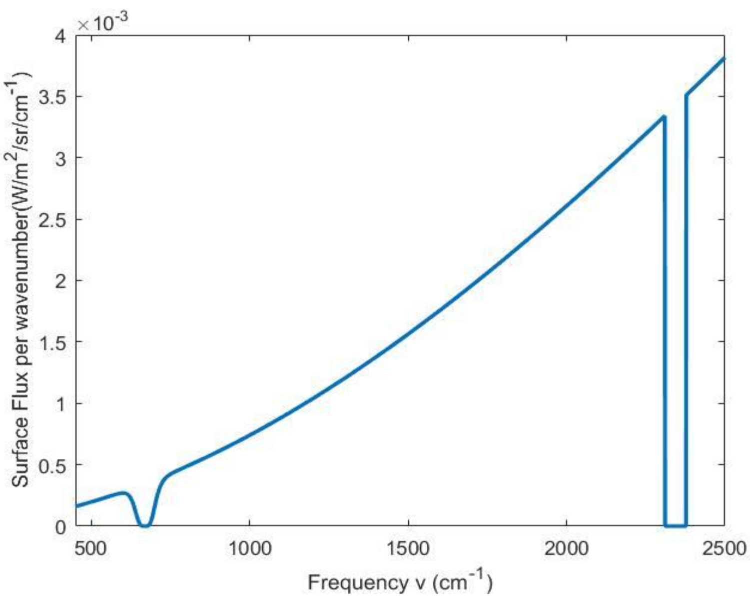


Fig. 9. Surface solar flux dependence on frequency. Fig. 9 (b) shows the absorption of the two CO_2 vibrations centered at 669 and 2340 cm^{-1}.

The total solar flux at position z is found by integrating equation (23) over all frequencies giving

$$F(z) = \int_0^\infty \mathcal{F}_z(z, \nu)\ d\nu \tag{26}$$

which is plotted in Fig. 10. The integral in equations (26) was done numerically by the computer program given in the Appendix using a frequency step size of 1 cm^{-1}.

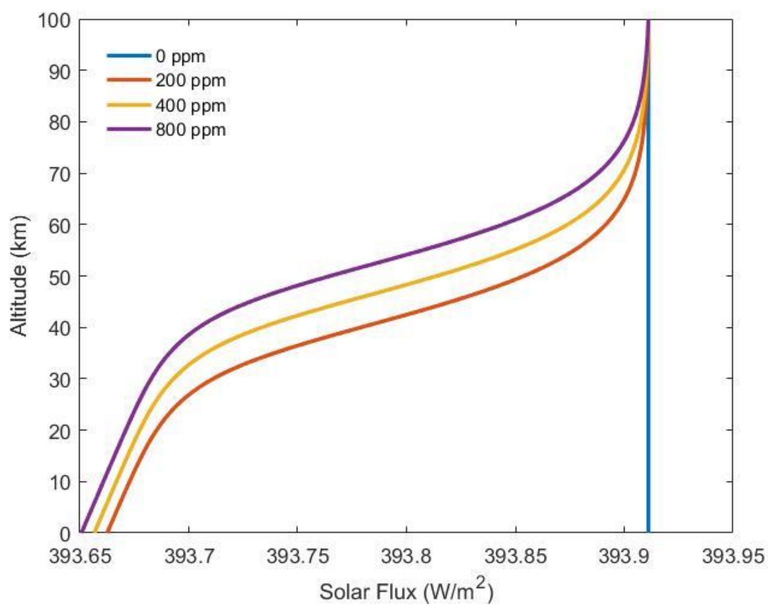


Fig. 10. Solar Flux dependence on Altitude. The blue curve shows the solar flux incident on the Earth's surface in the absence of CO_2 which equals 393.911 $\frac{W}{m^2}$ and is independent of altitude. The surface solar fluxes of 393.662, 393.656 and 393.650 $\frac{W}{m^2}$ correspond to the CO_2 concentrations of 200, 400 and 800 ppm, respectively.

V. Conclusion

Atmospheric carbon dioxide at the 2017 level of 400 ppm absorbs less than 0.065 % of the incident solar flux on the Earth. Doubling the carbon dioxide concentration changes the amount of absorbed solar radiation by less than 1.5×10^{-3} %. This small change occurs because the carbon dioxide absorption is already saturated at 400 ppm. Therefore, increasing carbon dioxide concentration has a negligible effect on absorption of the visible spectrum of solar radiation which is different than the greenhouse effect where carbon dioxide strongly absorbs infrared radiation emitted by the Earth.

VI – Appendix: Program for CO_2 Absorption of Solar Radiation

```
%% ALTITUDE VS TRANSMITTED SOLAR FLUX
% This code was written by Peter Gemayel on Tuesday May 15, 2018
% This script shows: 1) A graph of CO2 Number Density vs Altitude
%                    2) A graph of CO2 Cross sections vs Frequency
%                    3) A graph of Solar Flux vs Altitude
%                    4) A graph of the Surface Solar Flux vs Frequency

clear all
R = 8.314;                              %Gas Constant in J/(mol.K)
T = 288.7;                              %Average Earth temperature in Kelvin
Ma = 29e-3;                             %Average molar mass of air in kg
g = 9.81;                               %Gravitational acceleration in m/s^2
H=R*T/(Ma*g);                           %Characteristic Atmospheric Height in meters

%--------------------------------------------------------------------------
%Set boundaries for altitude
ztop = 100000;                          %top of atmosphere in meters
zsurface = 0;                           %Surface height of atmosphere in meters
Nalt = 1000;                            %Number of bins for integral of # density
dz=(ztop - zsurface)/Nalt;              %Height step size
z = linspace(1e5,0,Nalt);               %Height array in units of 100 m

%--------------------------------------------------------------------------
%Calculate CO2 number density vs height
%CO2 concentration is 400 ppm in 2017
CO2surf=400;                            %CO2 surface concentration in ppm
co2surface=(CO2surf/400)*1e16;          %CO2 density Earth surface molecules/cm^3
nco2_400 = co2surface*exp(-z./H);       %Number density function over altitudes
%Plot the Density Function vs altitude
figure(1)
plot(nco2_400,z)
set(findall(gca, 'Type', 'Line'),'LineWidth',2)
xlabel('Number Density (molecules/cm^3)')
ylabel('Altitude (km)')
yticklabels({'0','10','20','30','40','50','60','70','80','90','100'})
title('Altitude VS Number Density of CO2')
legend('400 ppm')
legend boxoff

%--------------------------------------------------------------------------
%Calculate frequency dependence of CO2 light absorption cross section
%First consider CO2 bending mode
v1=linspace(500,850,100);               %Frequency interval for CO2 bending
sigmab = 1.26e-19;                      %Cross-Section in cm^2
lambdab = 0.0812;                       %Wavelength in cm
vb = 669.2;                             %Peak requency for CO2 bending in cm^-1
sig1=sigmab*exp(-lambdab.*abs(v1 - vb)); %Cross-section in cm^2
%Next consider CO2 asymmetric stretching mode
v2=linspace(2300,2340,1000);            %Interval for first line
v3=linspace(2340,2360,1000);            %Interval for second line
v4=linspace(2360,2400,1000);            %Interval for third line
sig2=v2*1.3333e-19 -3.079923e-16;       %Equation for first line in cm^2
sig3(1,1:1000)=4e-18;                   %Equation for second line in cm^2
sig4=-v4*2.2222e-19+5.2843916e-16;      %Equation for third line in cm^2

vtot=[v1 v2 v3 v4];                     %Create array for all frequencies
sigtot=[sig1 sig2 sig3 sig4];           %Create array for all cross sections
```

```
%Plot the cross section of CO2 vs frequency
figure(2)
plot(vtot,sigtot)
grid on
xlabel('Frequency v (cm^{-1})')
xlim([100 2700])
ylabel('Cross section cm^2')
ylim([0 4.5e-18])
set(findall(gca, 'Type', 'Line'),'LineWidth',2)
text(600,2.5e-19,'CO_2 bending','fontSize',8)
text(1900,4.2e-18,'CO_2 asymmetric stretching','fontsize',8)
title('CO_2 cross section dependence on frequency')

%-----------------------------------------------------------------------
%Find solar flux at earth's surface
h=6.62607004e-27;                        %Planck's Constant in erg*sec
K=1.38064852e-16;                        %Boltzmann constant in erg/K
c=2.99792458e10;                         %Speed of light cm/s
TSOL=6000;                               %Temperature of the Sun in Kelvin
fred=pi*(288.7/TSOL)^4;                  %Reduction factor
nus1=0;                                  %Start frequency
nus2=100000;                             %Stop frequency
Delnu=1;                                 %Frequency step
nsloop=(nus2-nus1)/Delnu;                %Frequency intervals

for i=1:Nalt
    TOT1(i)=0;                           %Initialize total intensity for 0 ppm
    TOT2(i)=0;                           %Initialize total intensity for 200 ppm
    TOT3(i)=0;                           %Initialize total intensity for 400 ppm
    TOT4(i)=0;                           %Initialize total intensity for 800 ppm
end
%Loop for integrating over all frequencies and altitudes
for i1 = 1:nsloop
    nus=nus1+Delnu*i1;                   %Frequency value for every iteration
    SURFNU(i1)=nus;                      %Create array for all frequencies
    Sigma=0;                             %Initialize cross section
    if nus>=500 && nus<=850
        Sigma=sigmab*exp(-lambdab*abs(nus-vb));
    elseif nus>=2310 && nus<2340
        Sigma=nus*1.3333e-19 -3.079923e-16;
    elseif nus>=2340 && nus<2360
        Sigma=4e-18;
    elseif nus>=2360 && nus<=2378
        Sigma=-nus*2.2222e-19 +5.2843916e-16;
    end
    %calculate incident solar radiation at frequency nus
    ISOL= fred*(2*h*nus^3*c^2)/(exp((h*nus*c)/(K*TSOL))-1)/1000;%W/m^2/sr/cm^-1
    %Calculate solar intensity at frequency nus vs. altitude
    INU0(1)=ISOL;                        %Initialize the intensity for 0 ppm
    INU200(1)=ISOL;                      %Initialize the intensity for 200 ppm
    INU400(1)=ISOL;                      %Initialize the intensity for 400 ppm
    INU800(1)=ISOL;                      %Initialize the intensity for 800 ppm
    for i2 = 2:Nalt
        i3 = i2 - 1;
        INU0(i2) = ISOL;
        INU200(i2) = INU200(i3)*exp(-0.5*Sigma*nco2_400(i2)*dz);
        INU400(i2) = INU400(i3)*exp(-Sigma*nco2_400(i2)*dz);
        INU800(i2) = INU800(i3)*exp(-2*Sigma*nco2_400(i2)*dz);
    end
    SURFINT400(i1)=INU400(1000);  %Store surface solar flux for 400 ppm
    %Integrate solar flux over all intensities
    for i4=1:Nalt
        TOT1(i4)=TOT1(i4)+INU0(i4)*Delnu;
        TOT2(i4)=TOT2(i4)+INU200(i4)*Delnu;
        TOT3(i4)=TOT3(i4)+INU400(i4)*Delnu;
        TOT4(i4)=TOT4(i4)+INU800(i4)*Delnu;
    end
end
```

```
%Plot the solar flux vs altitude
figure(3)
plot(TOT1,z,TOT2,z,TOT3,z,TOT4,z)
set(findall(gca, 'Type', 'Line'),'LineWidth',2)
xlabel('Solar Flux (W/m^2)')
ylabel('Altitude (km)')
yticklabels({'0','10','20','30','40','50','60','70','80','90','100'})
title('Altitude VS Solar Flux')
legend('0 ppm','200 ppm','400 ppm','800 ppm','Location','northwest')
legend boxoff

%Plot the surface flux vs frequency
figure(4)
plot(SURFNU,SURFINT400)
xlim([0 5e4])
xlabel('Frequency v (cm^{-1})')
ylabel('Surface Flux per wavenumber(W/m^2/cm^{-1})')
title('Surface Solar Flux')
set(findall(gca,'Type','Line'),'LineWidth',2)

%Find the solar flux at earth's surface for CO2 = 0, 200, 400, 800 ppm
MIN0=min(TOT1);
MIN200=min(TOT2);
MIN400=min(TOT3);
MIN800=min(TOT4);
Table1 = table(MIN0,MIN200,MIN400,MIN800)
```