Chapter 4. Greenhouse Gases

Abstract

The layer model assumes that the atmosphere acts as a blackbody in the infrared, absorbing and emitting all frequencies of IR light. In reality, gases absorb IR light selectively, and most of the gas in the atmosphere doesn't interact with IR light at all. The difference can be understood in terms of the effect of molecular vibration on the electromagnetic field. Because gases absorb IR selectively, there are some radiation bands that are completely absorbed (the gases are saturated), and others such as the atmospheric window, where no gases absorb. This leads to much higher greenhouse forcing per molecule from some trace gases, such as freons, SF_6, or to a lesser extent methane, than from more abundant gases such as CO_2. Some absorption bands fall in the middle of the IR emission spectrum of the earth's surface, while other bands fall outside this spectrum and are therefore irrelevant to the heat budget.

About Gases

The layer model is what we call an idealization of the real world. Now that we understand the core mechanism of the greenhouse effect, by understanding the layer model, we can add things one at a time from the real world, and see how they affect the way that earth's temperature is controlled. The first modification we have to make to the layer model is to think more about real gases in the atmosphere.

Let's begin by defining different ways of describing the amounts of gases in the atmosphere. The word **concentration** means number of molecules within some volume. The difficulty this raises for gases in the atmosphere is that there are fewer molecules per volume overall as you go up in the atmosphere. The major gases in the atmosphere are pretty well mixed, so that the concentrations of these gases go down proportionally with altitude. This is why it's hard to breath oxygen quickly enough on Mount Everest. It is often more convenient to talk about proportions of gases, like oxygen is about 20% of the molecules of gas in the atmosphere, and nitrogen almost 80%. The proportion of CO_2 is currently 0.037%. We can express that in a more convenient way by saying 370 parts per million or **ppm**. This number is called a **mixing ratio**. The mixing ratio of a gas is numerically equal to the pressure exerted by the gas, denoted for CO_2 as **pCO_2**. In 2005 as I write this the pCO_2 of the atmosphere is reaching 380 μatm. It is rising by about 1.5 ppm per year, which is the same as saying 1.5 μatm per year.

Gases, Vibrations, and Light

Most of the mass of an atom is in its nucleus, which resembles the massive sun at the center of the solar system. Electrons float in ghostly quantum mechanical probability clouds, called **orbitals**, around the nucleus. Two nuclei of two different atoms always repel each other, because of their positive charges. The orbitals for the electrons fit together better, however, with certain numbers of orbitals than with others. Electrons from two different atoms may be able to combine their orbitals in such a way that they are lower energy, as if happier, when they share, a **chemical bond**. A chemical bond is like a spring in that the two nuclei on either end of the bond have some freedom to move closer or farther apart. There is an optimum distance for the nuclei to be from each other. Closer, and the positive nuclei will start to repel each other. Farther, and you get less energy gain from sharing the electrons. A bond vibrates when the distance between the nuclei oscillates between the nuclei being too close together, then too far apart.

Gases are the simplest type of molecule, and they only vibrate in very particular ways. Vibrations in a gas molecule are like vibrations of a piano string in that they are fussy about frequency. This is because, like a piano string, a gas molecule will only vibrate at its "ringing" frequency. The ringing frequency of an oscillator made of weights and springs depends on two things: the amount of weight on the ends and the strength of the spring holding them together. Heavy weights will have enough inertia to keep a bond growing in the wrong direction for longer than will a pair of light weights, so the frequency of the vibration will be slower. If the spring is very strong, it will reverse the velocity of a vibration more quickly, and the frequency of the oscillation will be higher. Vibrations in chemical bonds depend on the mass of the nuclei and on the energy penalty for having the nuclei too close or too far apart: the springiness of the chemical bond.

However, the vibrations of many gas molecules, such as the major gases in the atmosphere oxygen and nitrogen, are invisible to the electromagnetic field. They don't shine light or absorb infrared light; we say they are not **infrared active**. Oxygen and nitrogen are not greenhouse gases, because they are transparent to infrared light. These molecules are invisible because when you stretch one, it doesn't change the electric field. These are symmetric molecules, made of two identical atoms whose electric fields just cancel each other out. Neither atom can hold the electrons any more tightly than the other. In general, symmetrical molecules with only two atoms are not greenhouse gases.

We can break the symmetry, making a molecule of NO for example. This is a very reactive molecule, an ingredient for producing urban smog, but that's another story. NO has one atom of each element, and as a result has a slight imbalance in its distribution of electrons. One side of the molecule will have a slight positive charge, and the other will be slightly negative. We could oscillate the electric field simply by rotating an NO molecule. Also, if we vibrate an NO molecule, the steepness of the transition from slightly positive to slightly negative will oscillate with time. By these mechanisms, NO could be a greenhouse gas, but it turns out not to be a very important one because there is not very much of it.

Molecules with more than two atoms have more than one chemical bond. All of their bonds ring together rather than each bond ringing with its own characteristic frequency. Water, H_2O, is a molecule that is bent in its lowest energy state (Figure 4-1). This is because several of the electron orbitals stick off in the direction that appears in my diagram to be empty space. Hydrogen atoms hold their electrons more loosely than oxygen atoms, and so each hydrogen has a slightly positive charge (marked in Figure 4-1 using the lowercase greek letter delta, as $\delta+$). The oxygen end of the molecule has a slight negative charge. Just as for the NO molecule, rotating an H_2O molecule would oscillate the electric field and generate light. Because the arrangement of the nuclei in H_2O are more complex than for NO, there are several modes of vibration of the water molecule, including a symmetric stretch and a bend. These modes are also infrared active.

The CO_2 molecule is shaped in a straight line with carbon in the middle (Figure 4-2). It is a symmetric molecule; the oxygen atom on one end pulls the electrons just as tightly as the other oxygen on the other end. Therefore rotating the molecule at rest has no effect on the electric field. Nor does a symmetric stretch. However, there are two modes of vibration which do generate an asymmetry in the electric field. One is an asymmetric stretch, and the other is a bend. The bend is the most climatically important one, as we shall see next.

How a Greenhouse Gas Interacts with Earth-Light

We have seen that gases are terrible blackbodies, because they are very choosy about which frequencies they absorb and emit. What we will now see is that some frequency bands are more important to the climate of the earth than others. There are two factors to consider. One is the concentration of the gas, which we will discuss in a bit. The other is the frequency of the absorption band relative to the blackbody spectrum for the earth.

Figure 4-3 shows blackbody spectra again for temperatures ranging from 300 K, a hot summer day, down to 220 K, which is about the coldest it gets in the atmosphere, up near the troposphere at about 10 km altitude. There is also a jagged-looking curve. This is the intensity of light that an infrared spectrometer would see if it were in orbit over the earth, looking down. Figure 4-3 is not data, but rather a model simulation from one of our on-line models. You can point a web browser at http://forecast.uchicago.edu/models/radiation.html to run this model yourself. We will do so in the exercises.

The spectrum of the light leaving the earth going into space ranges between two different blackbody spectra, a warmer one of about 270 K, and a colder one from about 220 K.

The parts of the spectra that seem to follow the colder blackbody curve come from greenhouse gases in the upper atmosphere. They follow the colder blackbody curve because it is cold in the upper atmosphere. The most pronounced of these absorption bands, centered on a wave number of about 700 cycles/cm, comes from the bending vibration of CO_2. Light of this intensity that shines from the surface of the earth is absorbed by the CO_2 in the atmosphere (Figure 4-4). The CO_2 in the atmosphere then radiates its own light at this frequency. Remember from Chapter 1 that light emission and absorption is a two-way street.

Other parts of the spectrum, most notably the broad smooth part around 1000 cycles/cm, follow a warmer blackbody spectrum. These come directly from the ground.

The atmosphere is transparent to infrared light in these frequencies. This band is called the **atmospheric window**.

The situation is analogous to standing on a pier and looking down into a pond of water. If the water were very clear, you could see light coming from the bottom; you would see rocks or old tires or whatever in the reflected light. If the water were murky, the light you would see would be scattered light coming from perhaps just a few inches down into the water. The old tires would be invisible, alas.

Remember we said that the total energy flux from one of these spectra can be "eyeballed" as the total area under the curve. The areas of the pure blackbody curves are going up proportionally to the temperature raised to the fourth power, because of the Stefan-Boltzmann equation (our equation 2-1 in Chapter 2). The area trick works with our new jagged spectrum as well. The effect of an atmospheric absorbtion band is to take a bite out of the blackbody spectrum from the earth's surface, decreasing the area and therefore decreasing the outgoing energy flux.

Compare the CO_2 absorption band at 700 cycles/cm with the absorption band of methane at around 1300 cycles/cm. The CO_2 band has a lot more room to change the outgoing infrared energy flux than does the methane band, simply because the earth and the atmosphere radiate a lot more energy near 700 cycle/cm than near 1300 cycles/cm. Both blackbody spectra are pretty low intensity in the methane band.

Band Saturation

The core of the CO_2 bend absorption band, between 600 and 800 cycles/cm, looks smooth rather than jagged and it follows a blackbody spectrum from about 220 K. This is about as cold as the atmosphere gets, and if we change the amount of CO_2 in the atmosphere, the intensity of light in this range does not get any lower (Figure 4-5). We call this phenomenon **band saturation**. You can see it in a series of model runs in which the CO_2 concentration of the atmosphere goes up from zero to 1000 ppm. The current concentration of CO_2 in the atmosphere is about 370 ppm, as we will learn more in Section II. If there were no CO_2 in the atmosphere, the atmosphere would be transparent to light of around 700 cycles/cm, as it is in the atmospheric window. Adding the first 10 ppm of CO_2 has a fairly noticeable impact on the shape of the outgoing light spectrum, but increasing CO_2 from say 100 to 1000 has a somewhat subtler effect.

I have plotted the total energy intensity I_{out} in W/m^2 as a function of the concentration of CO_2 in the atmosphere in Figure 4-6. Changes in CO_2 concentration have the greatest effect if we were starting out from no CO_2 and adding just a bit. The first 10 ppm of added CO_2 changes I_{out} by as much as going from 10 to 100, or 100 to 1000 ppm. We can understand why by analogy to our murky pond or by looking back at Figure 4-4. As we increase the murkiness of the water, we decrease the distance that a photon of light can travel before it is absorbed. It doesn't take much murk in the water to obscure the old tire on the bottom, shifting the depth to which we can see from the bottom at say 3 meters to maybe only one meter. If we make the pond a lot murkier we will only be able to see a few cm down into the water. Making it murkier still will limit our view to only one cm.

The change in depth is getting less sensitive to the murkiness of the pond. In the same way, the changes in the temperature at which the atmosphere radiates to space get smaller as the CO_2 concentration of the air gets higher. You just see the coldest light that you can get.

The band saturation for CO_2 makes CO_2 a less potent greenhouse gas than it would be if we had no CO_2 in the air to start with. Let's revisit our comparison of the CO_2 and methane as greenhouse gases. Methane had a disadvantage because its absorption band sort of fell in the suburbs of the earth-light spectrum whereas CO_2 fell right downtown. Now we see the advantage shifting the other way. Methane has a much lower concentration in the atmosphere. You can see from the jagged edges of the methane peak in Figure 4-3 that the methane absorption band is not saturated. For this reason, in spite of the suburban location of the methane band, a **molecule of methane** added to the atmosphere is **20 times more powerful than is a molecule of CO_2**.

If the edges of the absorption bands were completely abrupt, as if CO_2 absorbed 600 cycles/cm light completely and 599 cycles/cm light not at all, then once an absorption band from a gas was saturated, that would be it. Further increases in the concentration of the gas would have no impact on the radiation energy budget for the earth. CO_2, the most saturated of the greenhouse gases, would stop changing climate after it exceeded some concentration. It turns out that this is not how it works. Even though the core of the CO_2 band is saturated, the edges of the band are not saturated. When we increase the CO_2 concentration, the bite that CO_2 takes out of the spectrum doesn't get deeper, but it gets a bit broader.

The bottom line is that the energy intensity I_{out} in units of W/m^2 goes up proportionally to the log of the CO_2 concentration, rather than proportionally to the CO_2 concentration itself (we would say linear in CO_2 concentration). The logarithmic dependence means that you get the same I_{out} change in W/m^2 from any doubling of the CO_2 concentration. The radiative effect of going from 10 to 20 μatm pCO_2 is the same as going from 100 to 200 μatm, or 1000 to 2000 μatm.

The sensitivities of climate models are often compared as the average equilibrium temperature change from doubling CO_2, a diagnostic number that is called $\mathbf{\Delta T_{2x}}$. Most models have ΔT_{2x} between 2 and 5 K, which is the same as 2 to 5°C. You can use ΔT_{2x} to estimate a temperature change resulting from some change in CO_2. Note that this is the ultimate temperature change, after hundreds or even thousands of years have passed (see Chapters 7 and 12). The equation is

$$\Delta T = \Delta T_{2x} \times \frac{\ln\left({new\ pCO_2}/{orig.pCO_2} \right)}{\ln(2)} \tag{4.1}$$

where ln is the natural log, the reverse operation of the exponential function e^x, The symbol e denotes a number which has no name other than simply e. We will meet e again in Chapter 5. The exponential function is to raise e to a power of x. If

$$e^x = y$$

then

$$y = \ln(x)$$

Equilibrium temperature changes from changes in CO_2, assuming various ΔT_{2x} values, are shown in Figure 4-7.

What happens to the energy balance of the earth if we add a greenhouse gas to its atmosphere? If the energy budget was in equilibrium before, it isn't any more, because the greenhouse gas has decreased the amount of energy leaving the earth to space. We can see this visually as the big bite out of the spectrum going from the top to the middle diagram in Figure 4-8. The decrease in energy flux is proportional to the area of that bite, the difference between the top and middle figures. Remember back to chapter 2, the premise of the layer model is that the energy coming into and going out of the planet must balance, and the planet accomplishes this feat by adjusting its temperature. If we want to re-balance the energy flux after kicking it by adding CO_2, we do that by increasing the temperature of the ground. Using the on-line model, we find that a temperature change of 8.5 K brings us back to the same energy output I_{out} as we had before. Looking at the bottom result in Figure 3-8, we see that the new, warmer output spectrum has risen everywhere compared to the middle figure. Visually, we have cut some area out of the CO_2 absorption band, and added it in the atmospheric window and other parts of the spectrum, until the overall area under the curve is the same as it was initially. Adding the CO_2 caused the planet to warm.

Take-Home Points

Gases absorb / emit infrared light if they vibrate at the frequency of the light, and if its vibration has a dipole moment that affects the electric field. O_2 and N_2 are not greenhouse gases. All molecules of three or more atoms are infrared active.

A greenhouse gas has a stronger impact on the radiative balance of the earth if it interacts with light in the middle of the earth-light spectrum.

Band saturation: A greenhouse gas at relatively high concentration like CO_2 will be less effective, molecule per molecule, than a dilute gas like methane.

Further Reading

The Discovery of Global Warming (2003) by Spencer Weart. This is a historical account of the science and the scientists who discovered global warming including my favorite, Svante Arrehnius, who used the infrared spectrum of moonlight, in 1896, to predict that doubling CO_2 would raise global temperature by 3-6° C (whereas the modern prediction is 2-5°C). There is a good discussion of piecing together the band saturation effect in this book.

IPCC Scientific Assessment 2001, from Cambridge University Press or downloadable from http://www.grida.no/climate/ipcc_tar/. Chapter 6 **Radiative Forcing of Climate Change**.

Figure Captions

1. Vibrational modes of a water molecule that interact with infrared light in the atmosphere.

2. Vibrational modes of a CO_2 molecule that interact with infrared light in the atmosphere.

3. The solid line is a model-generated spectrum of the infrared light escaping to space at the top of the atmosphere. For comparison, the broken lines are blackbody spectra at different temperatures. If the earth had no atmosphere, the outgoing spectrum would look like a blackbody spectrum for 270 K, between the 260 K and 280 K spectra shown. The atmospheric window is between about 900 - 1000 cm^{-1}, where no gases absorb or emit infrared light. CO_2, water vapor, ozone, and methane absorb infrared light emitted from the ground, and emit lower-intensity infrared from high altitudes where the air is colder than at the surface.

4. A comparison of the fate of infrared light in the optically thick CO_2 bend frequency (left) versus the optically thin atmospheric window (right).

5. A demonstration of band saturation by CO_2. The addition of 10 ppm CO_2 (upper right) makes a huge difference to the outgoing infrared light spectrum relative to an atmosphere that has no CO_2 (upper left). Increasing CO_2 to 100 and 1000 ppm (lower panels) continues to affect the spectrum, but you get less bang for your CO_2 buck as CO_2 concentration gets higher.

6. Band saturation viewed in a different way from Figure 4-5. This is a plot of the total energy flux carried by all infrared light, which is proportional to the area under the spectrum curves in Figure 4-5. The outgoing energy flux is less sensitive to CO_2 when CO_2 concentration is high.

7. The average temperature of the earth as a function of atmospheric CO_2 concentration and the climate sensitivity parameter, ΔT_{2x}.

8. A demonstration of the greenhouse effect of CO_2. In the top panel, we begin with no CO_2. Let's assume that the energy budget of the earth was in balance at a ground temperature of 270 K. In the middle panel, we add 1000 ppm CO_2, decreasing the outgoing energy flux. The ground and the atmosphere above it respond by warming up 8.5 K. The total outgoing energy flux is restored to its initial value. The total energy flux is proportional to the area under the curves. CO_2 takes a bite out of the top curve to generate the middle curve, but then the bottom curve bulks up everywhere to compensate.

Projects

Answer these questions using the on-line model at http://forecast.uchicago.edu/Projects/radiation.html . The model takes CO_2 concentration and other environmental variables as input, and calculates the outgoing IR light spectrum to space, similarly to Figures 3-3, 3-5, and 3-7. The total energy flux from all IR light is listed as part of the model output, and was used to construct Figure 3-6.

1. Methane. Methane has a current concentration of 1.7 ppm in the atmosphere, and it's doubling at a faster rate than is CO_2.

a) Is ten additional ppm of methane in the atmosphere more or less important than ten additional ppm of CO_2 in the atmosphere at current concentrations?

b) Where in the spectrum does methane absorb? What concentration would it take to begin to saturate the absorption in this band? (How do you identify saturation of a band, on a spectrum plot?)

c) Would a doubling of methane have as great an impact on the heat balance as a doubling of CO_2?

d) What is the "equivalent CO_2" of doubling atmospheric methane? That is to say, how many ppm of CO_2 would lead to the same change in outgoing IR radiation energy flux as doubling methane? What is the ratio of ppm CO_2 change to ppm methane change?

2. CO_2.

a) Is the direct effect of increasing CO_2 on the energy output at the top of the atmosphere larger in high latitudes or in the tropics?

b) Set pCO_2 to an absurdly high value of 10,000 ppm. You will see a spike in the CO2 absorption band. What temperature is this light coming from? Where in the atmosphere do you think this comes from?

3. Earth Temperature. Our theory of climate presumes that an increase in the temperature at ground level will lead to an increase in the outgoing IR energy flux at the top of the atmosphere.

a) How much extra outgoing IR would you get by raising the temperature of the ground by one degree? What effect does the ground temperature have on the shape of the outgoing IR spectrum and why?

b) More water can evaporate into warm air than cool air. By setting the model to hold the water vapor at constant relative humidity rather than constant vapor pressure (the default) calculate again the change in outgoing IR energy flux that accompanies a 1 degree temperature increase. Is it higher or lower? Does this make the earth more sensitive to CO_2 increases or less sensitive?

c) Now see this effect in another way. Starting from a base case, record the total outgoing IR flux. Now increase pCO_2 by some significant amount, say 30 ppm. The IR flux goes down. Now, using the constant vapor pressure of water option, increase the Temperature Offset until you get the original IR flux back again. What is the change in T required? Now repeat the calculation but at constant relative humidity. Does the increase in CO_2 drive a bigger or smaller temperature change? This is the water vapor feedback.

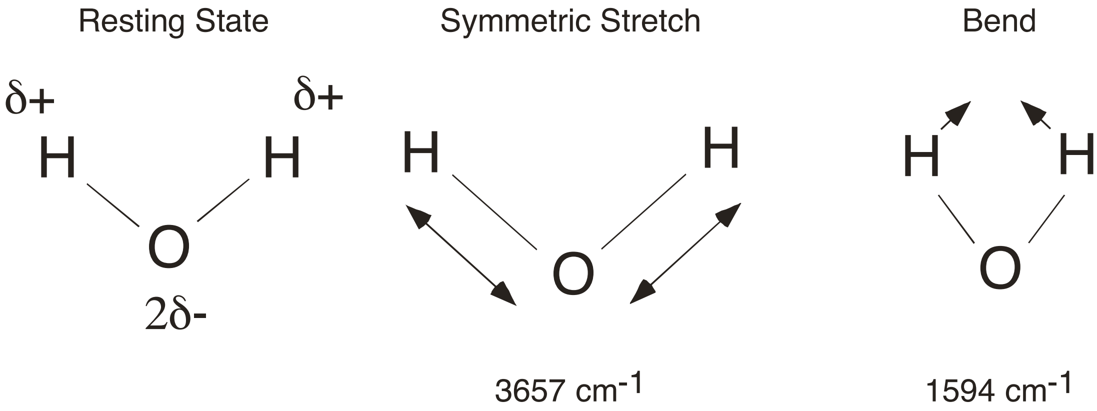
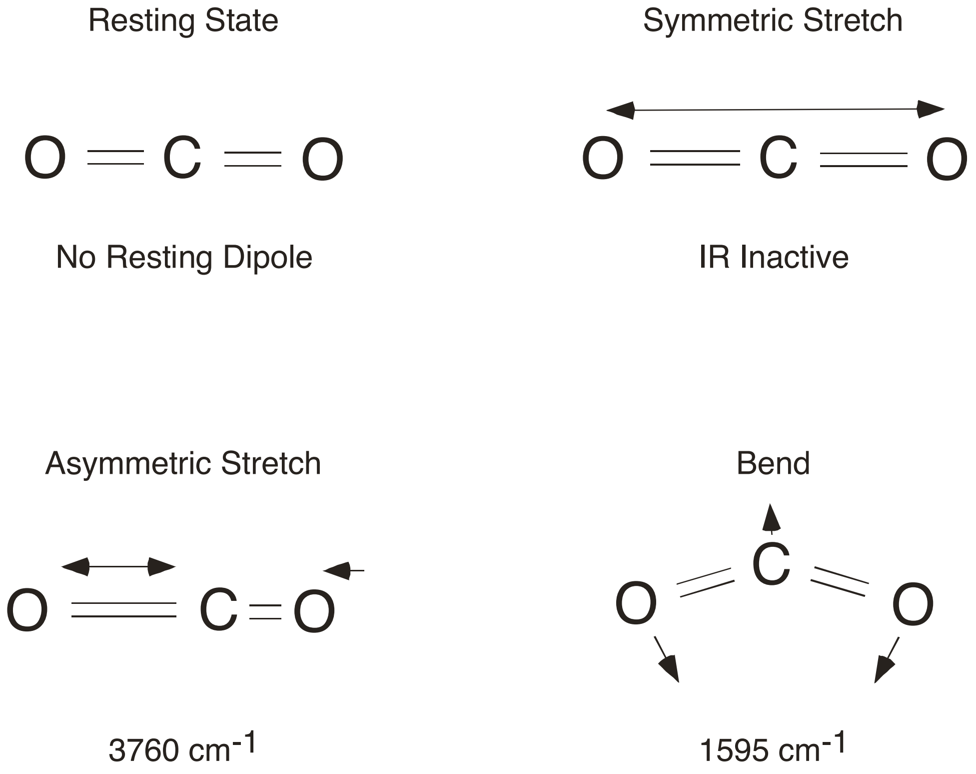

Resting State
Symmetric Stretch
Bend
δ+
δ+
H
H
O
2δ-
H
H
O
3657 cm-1
H
H
O
1594 cm-1

Figure 4-1


Resting State

No Resting Dipole

Symmetric Stretch

IR Inactive

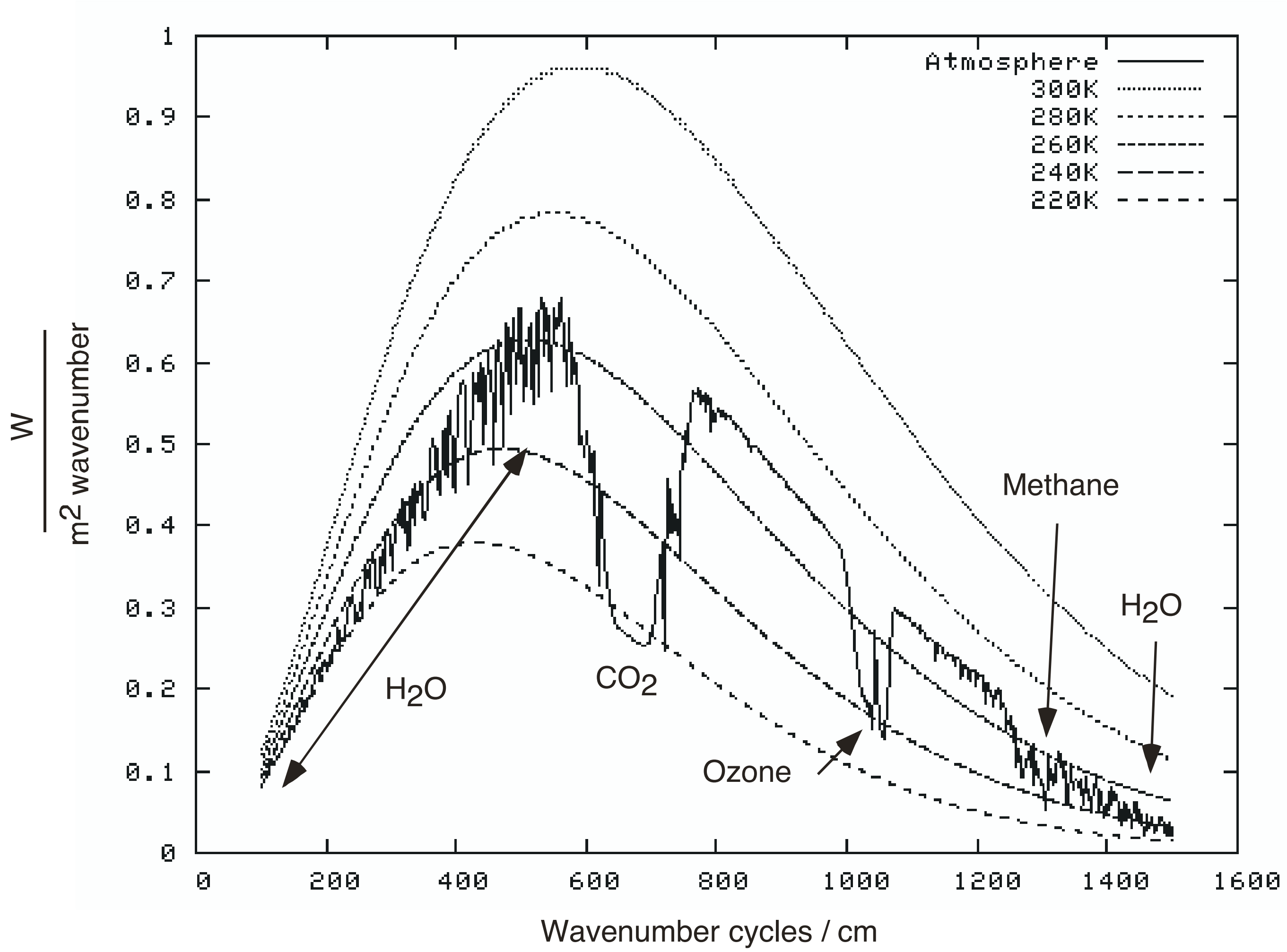
Asymmetric Stretch

3760 cm^{-1}

Bend

1595 cm^{-1}

Figure 4.2



1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000
1200
1400
1600
W / m^2 wavenumber
Wavenumber cycles / cm
Atmosphere
300K
280K
260K
240K
220K
H2O
CO2
Ozone
Methane
H2O

Figure 4-3

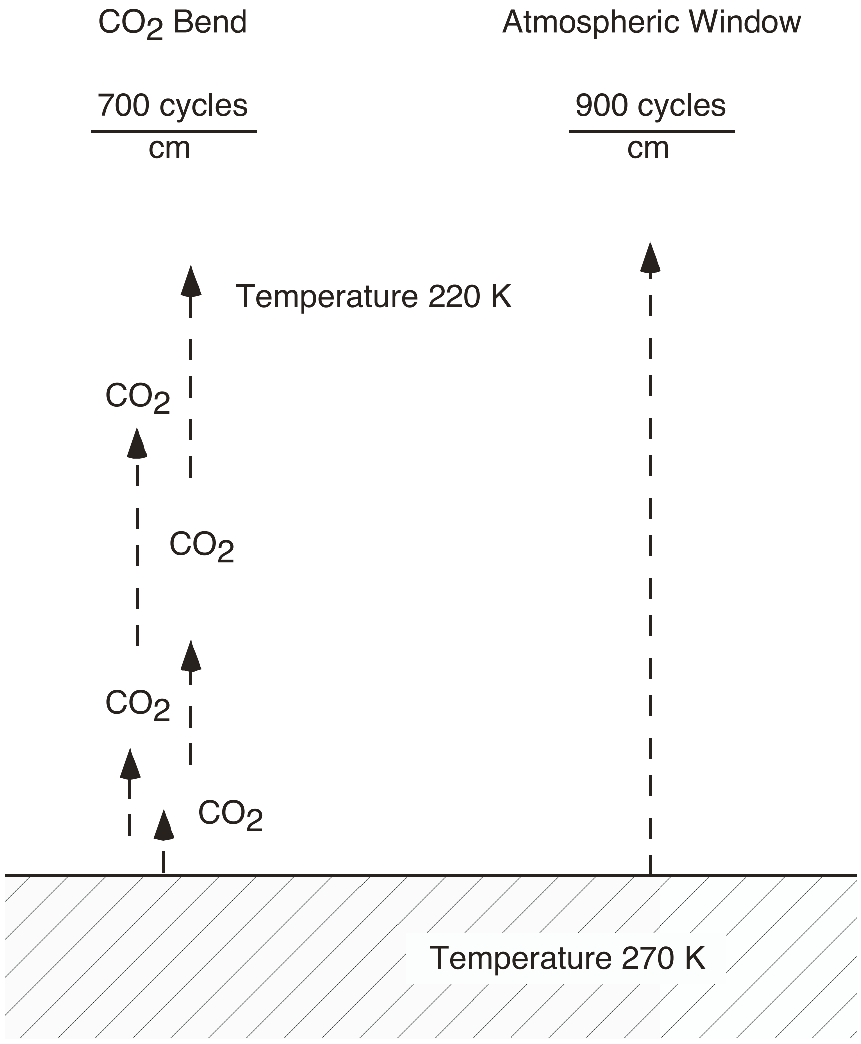

CO_2 Bend
$\frac{700 \text{ cycles}}{\text{cm}}$
Atmospheric Window
$\frac{900 \text{ cycles}}{\text{cm}}$
Temperature 220 K
CO_2
CO_2
CO_2
CO_2
Temperature 270 K

Figure 4-4

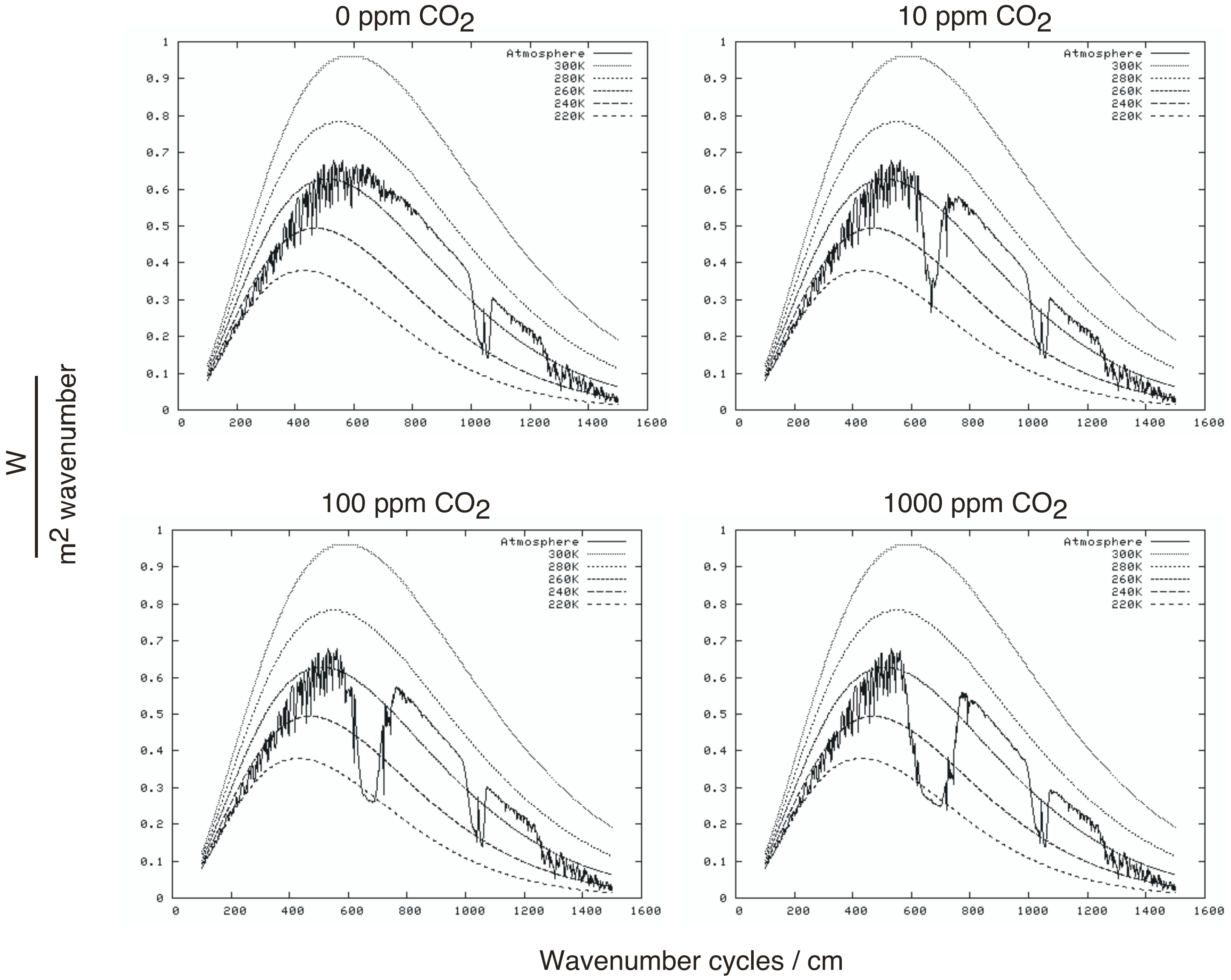

0 ppm CO$_2$
10 ppm CO$_2$
100 ppm CO$_2$
1000 ppm CO$_2$
Atmosphere
300K
280K
260K
240K
220K
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
200
400
600
800
1000
1200
1400
1600
W / m^2 wavenumber
Wavenumber cycles / cm

Figure 4-5

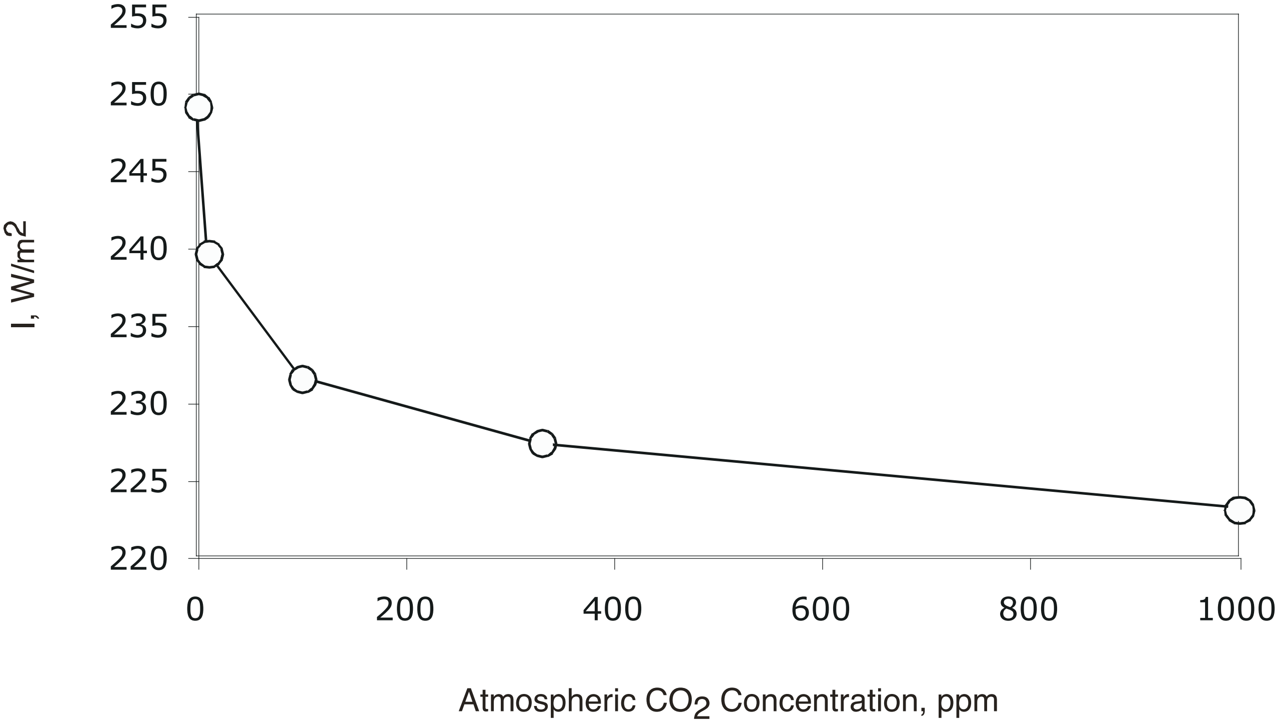

255
250
245
240
235
230
225
220
0
200
400
600
800
1000
I, W/m2
Atmospheric CO2 Concentration, ppm

Figure 4-6

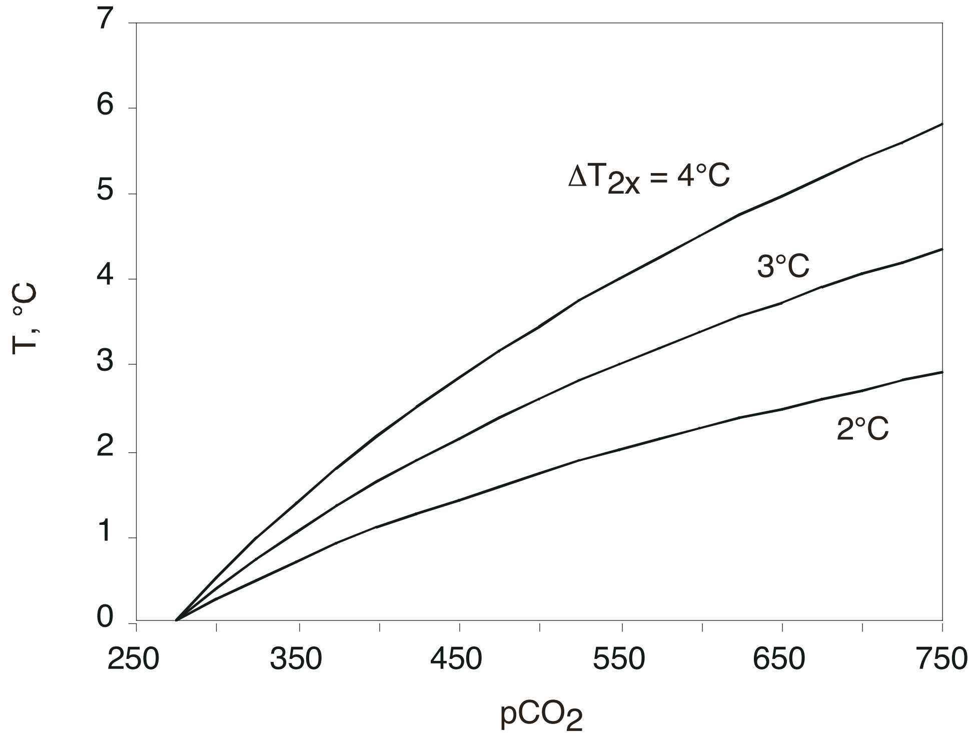
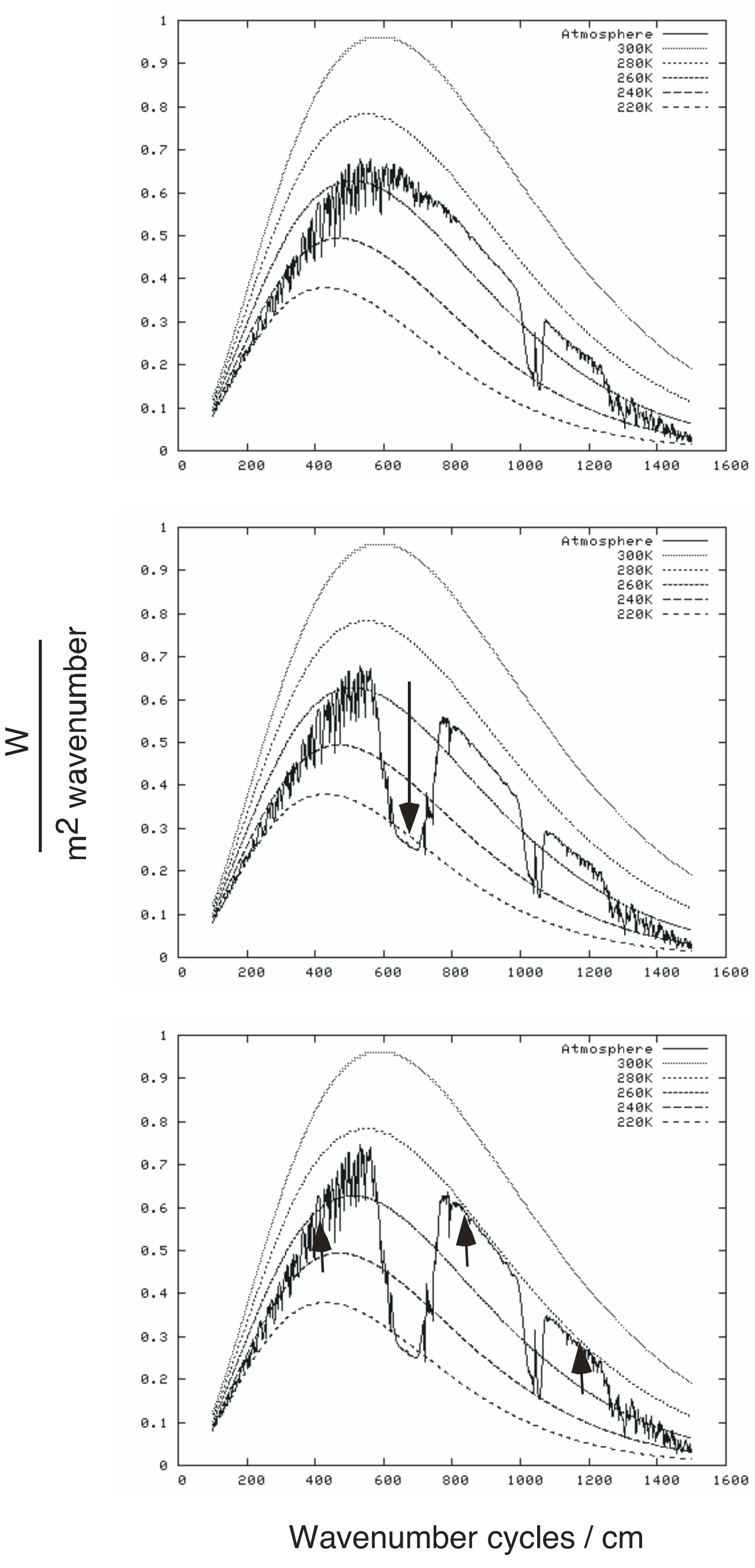


Figure 4-7



No CO_2

I_{out} = 249 W/m^2

1000 ppm CO_2

I_{out} = 223 W/m^2

1000 ppm CO_2

8.5 K warmer

I_{out} = 249 W/m^2

Figure 4-8