Greenhouse Gases

Why some gases are greenhouse gases, but most aren't, and some are stronger than others

About Gases

The layer model is what is called an **idealization** of the real world. It has the essential ingredient of the greenhouse effect, but it is missing numerous things that are important in the real atmosphere. Starting from the Layer Model, the next few chapters add things one at a time, assembling the rest of the ingredients that control the temperature of the real Earth. The first task is to understand how real gases interact with infrared (IR) light in the real atmosphere.

Let us begin by defining different ways of describing the amounts of gases in the atmosphere. The word **concentration** means the number of molecules within some volume. The difficulty this raises for gases in the atmosphere is that the concentration, defined in this way, changes as the gas expands or contracts. It is often more convenient to talk about proportions of gases; for example, oxygen is about 20% of the molecules of gas in the atmosphere, and nitrogen is almost 80%. The proportion of CO_2 is currently 0.039%. We can express that in a more mnemonic way by saying 390 parts per million, or **ppm**. This number is called a **mixing ratio**.

A gas exerts pressure, a pushing force, on itself or on the surface of anything in contact with it. The force comes from deflected momentum of gas molecules bouncing off the surface. The pressure of a mixture of gases can be taken apart into what are called **partial pressures** arising from each type of molecule in the gas, which add up to the total pressure. The partial pressure of CO_2, for example, is written as **pCO_2**.

One might expect heavier gases to contribute disproportionately to the pressure because they seem like they would hit the walls harder. It works out, however, that heavier gas molecules are moving more slowly than the light ones are, just enough so that the pushing force, proportional to the mass times the velocity, is the same on average with every type of molecule regardless of how heavy it is. It is as if a bunch of ping-pong balls and bowling balls rolled against the wall all pushed equally on the wall. They are equal because you have to roll the bowling balls more slowly. At a given temperature, each molecule has the same amount of energy on average invested in motion, what is called **kinetic energy**. A heavy molecule will move more slowly with its allotment of kinetic energy.

> A gas pressure, in units of microatmospheres (μatm), is numerically nearly equal to its mixing ratio in parts per million (ppm).

The bottom line is that the partial pressure from a gas is more or less proportional to the mixing ratio, the numerical proportion of the gas. If you think in pressure units of atmospheres, the actual numbers are the same for the partial pressure and the mixing ratio. For CO_2, for example, the mixing ratio is currently about 390 ppm, and its pCO_2 is about 390 μatm.

Gases, Vibrations, and Light

Most of the mass of an atom is in its nucleus, which resembles conceptually a massive sun at the center of a solar system. Two nuclei of two different atoms always repel each other because of their positive charges. Electrons float in ghostly quantum mechanical probability clouds, called **orbitals**, around the nucleus. For some combinations of atoms, the electrons fall into orbitals that are shared between the two nuclei. These electrons are the glue that holds together a **chemical bond** between the atoms.

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, lowest-energy distance for the nuclei to be from each other. If they are any closer, the positive nuclei will start to repel each other. Farther from each other, 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. This is called a **stretching vibration**.

An atom may participate in more than one chemical bond. The bonds, and extra electrons that the central atom holds on to, arrange themselves around the atom to find their positions and angles of least energy. Here again there is some flexibility in the angle of the bond, which leads to a **bending vibration**.

> Chemical bonds vibrate at particular frequencies.

Molecular vibrations in gas molecules are like vibrations of a piano string in that they tend to be at specific "ringing" frequencies. For weights and springs, the vibrational frequencies depend on two things: the mass of the weights and the springiness of the spring holding them together. Imagine the weights moving together, nearing the optimal distance but with enough momentum to carry them closer than they would like to be, continuing the oscillation. Heavier weights would have enough inertia to keep moving closer for a longer time than would a lighter pair of weights, so the frequency of the vibration will be slower with heavy weights. If the spring is very stiff, 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 stretching or bending the bond, which determines the springiness of the chemical bond.

Most forms of liquid and solid molecules are not so "choosy" about frequency of IR light that they can absorb or emit, because the molecules interact with each other so much that more or less all frequencies of IR light can be absorbed and emitted. Liquids and solids are pretty good blackbodies, in other words. Gases however only absorb and emit specific frequencies of IR light, meaning that they are generally not very good blackbodies.

In fact, most of the gases in the atmosphere do not absorb or emit IR light at all, because vibrations in their bonds do not create an imbalance in the electrical field. Both O_2 and N_2, the most abundant gases in the atmosphere, 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, so there is no difference between the electrical field on one side of the molecule versus the other. The symmetry is unbroken when you stretch or compress the bond. Symmetrical molecules with only two atoms are never greenhouse gases.

> To create or absorb infrared light, the molecule must be electrically lopsided, at least in passing.

If the symmetry is broken by having different types of atoms on each side, like carbon monoxide (CO) or nitrogen oxide (NO), the molecules begin to have some greenhouse properties. Both these types of molecules are very reactive and are not found in enough abundance in the atmosphere to lead to much greenhouse effect, but these are good stepping-stone molecules to think about before moving to more complicated atoms like CO_2. Because the atoms have different charges in their nuclei, their chemistry is different, including how hard they pull on those electrons in their shared chemical bond. One side of the molecule will probably have a slight positive charge, and the other will be slightly negative. This charge imbalance is called a **dipole moment**. When the bond vibrates, it changes the steepness of the transition from positive to negative, which drives the electric field. Changing the electric field is how greenhouse gases interact with IR light. One could even oscillate the electric field by simply rotating the molecule.

Molecules with three or more atoms must have more than one chemical bond because a single bond never connects more or less than two atoms. Imagine a set of three weights connected in a line with two springs. When this contraption is jiggled, its bonds bend and stretch together, as an integrated system, rather than each bond simply vibrating according to its own springiness and weight, independent of the other. The whole thing rings like a bell, and like a complex bell with a rich tone, there are multiple oscillations with different frequencies all going on at once.

The CO_2 molecule is shaped in a straight line with carbon in the middle (Figure 4-1). Oxygen tends to pull on electrons more tightly than carbon does, but the oxygen atom on one side pulls the electrons just as tightly as the other oxygen on the other side. The molecule has no permanent electrical field asymmetry (dipole moment). If all you do to the molecule is rotate or stretch it, you have not broken the symmetry and you will have no effect on the electric field.

> The CO_2 bending vibration mode is the important one for climate.

However, two modes of vibration do generate an asymmetry in the electric field. The most important CO_2 vibrational mode for climate is the **bending vibration**. When the CO_2 molecule is bent, the oxygens, carrying slight negative charges, swing from one side of the molecule to the other. The CO_2 bending vibration absorbs and emits IR light; it is said to be **infrared active**. The next section shows that the bending vibration absorbs IR light in the heart of Earth's emission spectrum, giving it strong leverage over Earth's climate.
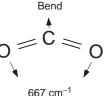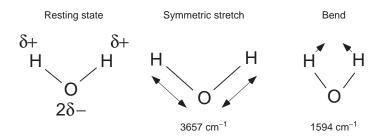

Figure 4-1 Vibrational modes of a CO_2 molecule that interact with infrared light in the atmosphere.

Resting state   Symmetric stretch   Bend

$\delta+$ $\delta+$

H   H   H   H   H   H

O   O   O

$2\delta-$ 3657 cm^{-1} 1594 cm^{-1}

Figure 4-2 Vibrational modes of a water molecule that interact with infrared light in the atmosphere.

The other vibrational mode is an **asymmetric stretch**, in which one bond is growing longer as the other gets shorter, back and forth. There is less IR light of this frequency to absorb in the atmosphere, so this mode has less impact on the Earth's radiation budget than the bend does.

Water, H_2O, is a molecule that is bent in its lowest energy state (Figure 4-2). This is because the oxygen has two pairs of electrons hanging off it, which push the hydrogens toward the other side. Hydrogen atoms hold their electrons more loosely than oxygen atoms in chemical bonds, so each hydrogen has a slightly positive charge (denoted in Figure 4-2 as the lowercase Greek letter delta $\delta+$). The oxygen end of the molecule has a slight negative charge. In contrast to CO_2, water has a dipole moment built into its resting structure. 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 is more complex than for NO, there are many modes of vibration of the water molecule, including a symmetric stretch and a bend. These modes are also IR active.
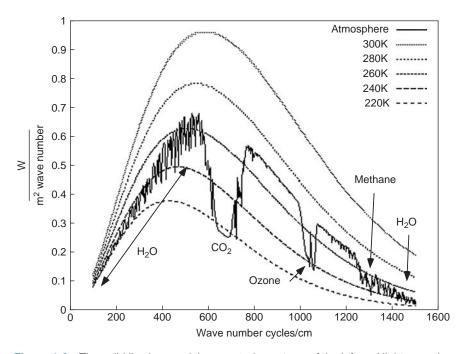
> Water vapor is very electrically lopsided and can absorb and emit lots of frequencies of infrared light.

How a Greenhouse Gas Interacts with Earthlight

Figure 4-3 shows blackbody spectra for temperatures ranging from 300 K, surface temperature on 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 moving among the smooth ones. This is the intensity of light that an IR 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 online models that will be used in the Exercises. The Web address is http://understandingtheforecast.org/projects/infrared_spectrum.html.

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. Parts of the spectrum, most notably the broad, smooth part around 1,000 cycles/cm, follow the warmer blackbody spectrum. There do not happen to be any gases in the atmosphere that absorb or emit at this frequency, so this IR light is coming directly from the ground. Because the greenhouse gases in the atmosphere are transparent to IR light in this band of frequencies, it is called the **atmospheric window**.

> The blackbody curves are like the temperature scale on a thermometer. You can read the temperature of the infrared source as its intensity against this scale.
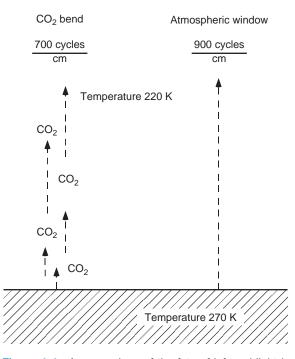
Figure 4-3 The *solid line* is a model-generated spectrum of the infrared light escaping to space at the top of the atmosphere. For comparison, the *broken lines* are blackbody spectra at different temperatures. If the Earth had no atmosphere, the outgoing spectrum would look like a blackbody spectrum for 270 K, between the 260 K and 280 K spectra shown. The atmospheric window is between about 900–1,000 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.

Other parts of the spectrum seem to follow the colder blackbody curve, like, for example, at around 700 cycles/cm. This IR light is coming from greenhouse gases in the cold upper atmosphere. The big dip in the spectrum at about 700 cycles/cm is from the bending vibration of CO_2. IR light emission and absorption are a two-way street (Chapter 1), so CO_2 absorbs the intense, "warm" IR from the ground at this frequency and re-emits the same frequency but at a lower intensity, because of its colder temperature (Figure 4-4). The atmosphere is called **optically thick** in the CO_2 bend frequency range and **optically thin** in 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 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. The muddy lake is optically thick, so the light you see comes from near the top.

Figure 4-3 is constructed so that the area under a curve of a spectrum is proportional to the total energy flux. You can eyeball the energy change as the area change. The areas of the pure blackbody curves go up proportionally to the temperature raised to the fourth power because of the Stefan-Boltzmann equation (Equation 2-1 in Chapter 2). The area trick works with the jagged spectrum as well, representing the total energy loss of the planet to space. The effect of an atmospheric absorption 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.
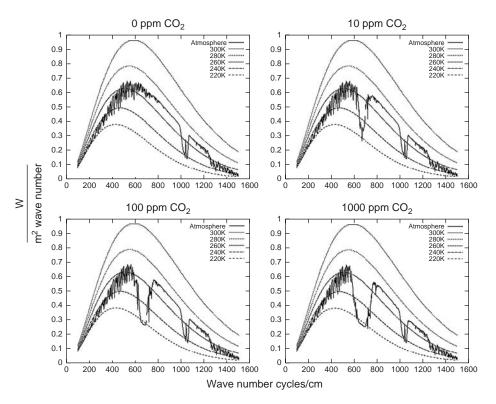
CO$_2$ bend

Atmospheric window

$\dfrac{700 \text{ cycles}}{\text{cm}}$

$\dfrac{900 \text{ cycles}}{\text{cm}}$

Temperature 220 K

CO$_2$

CO$_2$

CO$_2$

CO$_2$

Temperature 270 K

Figure 4-4 A comparison of the fate of infrared light in the optically thick CO$_2$ bend frequency (*left*) versus the optically thin atmospheric window (*right*).

Methane absorbs IR light at around 1300 cycles/cm. Whereas the CO$_2$ bending vibration absorbs right at the peak of the blackbody spectrum of the Earth, methane absorbs in one of the tails of the spectrum. In a competition between CO$_2$ and methane for which is the stronger greenhouse gas, the advantage here goes to CO$_2$. However, the next section introduces another difference between the gases, which more than makes up for this, so that methane winds up as the more powerful greenhouse gas of the two.

The Band Saturation Effect

Figure 4-5 shows the results from a series of model runs for different atmospheric CO$_2$ concentrations, ranging from 0 to 1000 ppm. For reference, the atmosphere in 2010 contains about 390 ppm. With no CO$_2$, the atmosphere would be transparent to light of around 700 cycles/cm, like 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, a sharp V-shaped slice out of the spectrum. As the CO$_2$ concentration is increased to 100 ppm, the center of the peak runs into the blackbody curve from just a bit colder than 220 K, and it does not get any deeper as the CO$_2$ concentration is raised to 1000 ppm. This is the **band saturation effect**, the band referring to the range of frequencies, and saturation meaning "used up," all absorbed by the CO$_2$.

The reason for the saturation effect can be understood by analogy to the murky pond. As the water gets murkier, it decreases the distance that a photon of light can travel before it is absorbed. It does not take much mud in the water to obscure the old tire on the bottom, shifting the visible depth from the bottom at say 3 m to maybe only 1 m. If the pond gets a lot murkier, you will be able to see only a few centimeters down into the water. Making it murkier still will limit the view to only 1 cm. The change in depth is getting less sensitive to the murkiness of
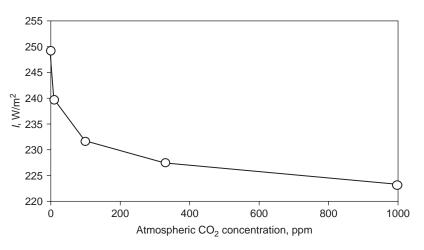
Figure 4-5 A demonstration of band saturation by CO_2. The addition of 10 ppm CO_2 (*upper right*) makes a huge difference to the outgoing infrared light spectrum relative to an atmosphere that has no CO_2 (*upper left*). Increasing CO_2 to 100 and 1,000 ppm (*lower panels*) continues to affect the spectrum, but you get less bang for your CO_2 buck as CO_2 concentration gets higher.

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 center of an absorption band gets saturated as the gas gets more concentrated, but the band gets fatter.

    Each model run returns a value for the total IR energy flux leaving the location, called I_{out} on the webpage and in units of W/m^2. These values are plotted in Figure 4-6. There is a huge change in the outgoing energy flux between the runs with 0 ppm and 10 ppm because you go from having no absorption to having a quite noticeable peak by adding a relatively small amount of CO_2, just 10 ppm. Then, as you go up to 100 and 1,000 ppm, the change in energy balance for each new molecule of CO_2, or each new ppm of CO_2, gets weaker.

    The energy balance never becomes totally insensitive to further additions of CO_2, however. More CO_2 will always make it warmer, even up to the 70 atm of CO_2 in the atmosphere of Venus. In part, this is because as the CO_2 concentration increases, the absorption peak in Figure 4-5 gets fatter, even if it cannot get much deeper. The middle of the absorption band is saturated, but the edges are unsaturated.

Figure 4-6   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 the CO_2 concentration is high.

> Even though the center of the CO_2 bend frequency is saturated, more CO_2 would still affect Earth's infrared energy output.

Given that the absorption bands are determined by vibrational frequencies of the molecule, one might have expected that the edges of the bands would be quite sharp, as if CO_2 absorbed 600 cycles/cm light completely and 599 cycles/cm light not at all. There are several reasons for the fuzziness in the peaks. One is **Doppler shifting**. Like a train whistle, which sounds a higher pitch as the train approaches, then lower after it passes and is moving away, the frequency of light that the molecule "sees" depends on the speed of the molecule, toward or away from the IR light source. If the molecule is moving away from the light source, it will absorb a slightly longer wavelength of light.

The absorption bands are also "smeared out" when gas molecules interact with each other, a phenomenon called **pressure broadening**. Liquids and solids are often fairly good blackbodies because the molecules are so close to each other that they share energy. Even if the frequency of the light is different from the frequency of the vibration, if the molecule is bathed in other molecules, it may be possible to take up the "slop" and absorb the light anyway. Gas molecules are generally too far apart from each other to act in this way, but they still do it to some extent, more so if the pressure is higher. The CO_2 on Venus, for example, is at such high pressure that its absorption bands are extremely broadened.

Even if the saturation effect were complete, so that the peaks did not get fatter with high concentration, adding more of the greenhouse gas would still increase the temperature of the Earth, for the same reason that adding layers to the layer model also increases the ground temperature. The layers in the layer model are by definition completely saturated in that they absorb all the incoming IR, re-radiating at all frequencies. Adding a second pane of glass to the layer model increases the ground temperature (this is the answer to one of the Exercises). On Venus, even though the absorption of IR by the 70 atm of CO_2 is completely saturated, adding more CO_2 would still increase its temperature further.

> The most dilute gases have awesome climate-changing power.

The bottom line is that the more abundant the greenhouse gas is, the less powerful each molecule is in warming the climate. The band saturation for CO_2 makes CO_2 a less potent greenhouse gas, per molecule, than it would be if we had no CO_2 in the air to start with. Revisiting the comparison between CO_2 and methane as greenhouse gases, methane had a disadvantage because its absorption band fell in the suburbs of the Earth-light spectrum, whereas CO_2 fell right downtown. Now, considering the band saturation effect, the advantage shifts to methane because it has much lower concentration. 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 off-peak location of the methane absorption band, a molecule of methane added to the atmosphere is about 40 times more powerful than is a molecule of CO_2.

For CO_2, 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 (which would be linear in CO_2 concentration). The logarithmic dependence means that you get about 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 ppm pCO_2 is about the same as going from 100 to 200 ppm or 1,000 to 2,000 ppm.

> Earth's temperature rises in proportion to the number of CO_2 doublings.
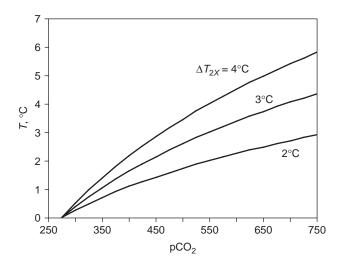
The sensitivities of climate models are often compared as the average equilibrium temperature change from doubling CO_2, a diagnostic that is called the **climate sensitivity** and abbreviated as ΔT_{2x}. It takes several centuries for climate models to respond fully to a change in CO_2, reaching the equilibrium. Most models have ΔT_{2x} between $2°$ and $5°C$, and past climate changes in the real world indicate that the real climate sensitivity of the Earth is probably in this range (Chapter 11).

If you subjected the planet to higher CO_2 concentrations for a few thousand years, there might be changes to the huge ice sheets in Greenland and Antarctica that could lead to even higher global temperatures, so the **Earth-system climate sensitivity** is probably higher than the model ΔT_{2x} values, which do not include such long-term effects. CO_2 emission from fossil fuel combustion will elevate the CO_2 concentration of the atmosphere for hundreds of thousands of years (Chapters 7 and 12), giving plenty of time for the full climate sensitivity of the Earth to express itself.

> The climate sensitivity to doubling CO_2 is the first benchmark that climate scientists compare between models.

One can use ΔT_{2x} to calculate the temperature change after a few centuries in response to changing CO_2 using an equation:

$$\Delta T = \Delta T_{2x} \times \frac{\ln\left(\text{new pCO}_2 \Big/ \text{original pCO}_2\right)}{\ln(2)} \qquad (4\text{-}1)$$

Figure 4-7 The average temperature of the Earth as a function of atmospheric CO_2 concentration and the climate sensitivity parameter, ΔT_{2x}.

where "ln" is the natural logarithm function, the reverse operation of the exponential function e^x. The symbol e denotes a number that 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
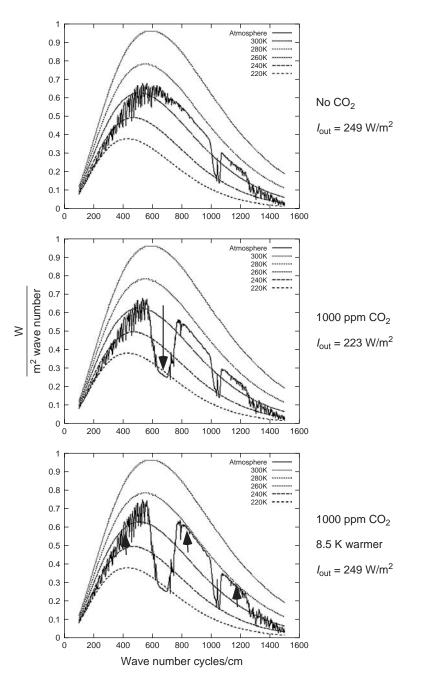
$$e^x = y$$

then

$$x = \ln(y)$$

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

The Greenhouse Effect of Gases

The basic idea of the greenhouse effect still works the way it did in the Layer Model (Chapter 3). Figure 4-8 shows the outgoing IR spectrum of an Earth with no CO_2 in the atmosphere. Let us say that this outgoing energy flux is just in balance with incoming sunlight energy.

Now add 1,000 ppm CO_2 to the atmosphere (middle panel), a huge change, so that the effect in the spectra will be easy to see. The energy fluxes in these plots are proportional to the area under the curves. The CO_2 absorption band is like a bite taken out of the curve, decreasing its area, therefore also decreasing the outgoing energy flux. The model reports that I_{out} decreases from 249 W/m^2 without CO_2 to 223 W/m^2 with CO_2.

The greenhouse effect drives the surface temperature to balance the energy budget. The online model allows you to change the surface temperature, and by trial and error you can find that warming the Earth up by 8.5°C brings I_{out} back up to about what it was before adding the CO_2. In the bottom panel in Figure 4-8, the effect of the warming can be seen as a shift upward where the arrows are pointing. Especially in the atmospheric window, the intensity of the IR energy flux increases as the Earth warms. Visually, if the spectrum were a pile of ice cream and you wanted to make a volcano, you could scoop out some ice cream from the summit, making the hole where the CO_2 absorption band is, and then spread it back in on the sides of the pile where the atmospheric window is and other parts of the spectrum, so that in the end the overall size of the ice cream pile is the same as it was initially. Adding the CO_2 caused the planet to warm, intensifying the IR energy flux, especially in the atmospheric window, to balance its energy budget.

Figure 4-8   A demonstration of the greenhouse effect of CO_2. In the *top panel*, begin with no CO_2. Assume that the energy budget of the Earth was in balance at a ground temperature of 270 K. In the *middle panel*, add 1,000 ppm CO_2, decreasing the outgoing energy flux. The ground and the atmosphere above it respond by warming up 8.5 K in the *bottom panel*. 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.

TAKE-HOME POINTS

■ Gases absorb or emit IR 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, including CO_2, water vapor, and methane, are greenhouse gases.

■ A greenhouse gas has a stronger impact on the radiative balance of the Earth if it interacts with light in the middle of the Earthlight 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.

STUDY QUESTIONS

1. Why don't most of the gases in the Earth's atmosphere contribute to the greenhouse effect?

2. Does the band saturation effect prevent global warming from CO_2? If not, what effect does it have?

3. Compare and contrast CO_2 and CH_4 as greenhouse gases. Which factor tends to make CO_2 stronger, and which factor tends to make methane stronger? Which gas is stronger overall?

FURTHER READING

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

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."

Exercises

Answer these questions using the on-line model at http://understandingtheforecast.org/Projects/infrared_spectrum.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 4-3, 4-5 and 4-7. The total energy flux from all IR light is listed as part of the model output and was used to construct Figure 4-6.

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

    a) Would an additional 10 ppm of methane in the atmosphere have a larger or smaller impact on the outgoing IR flux than an additional 10 ppm of CO_2 at current concentrations?

    b) Where in the spectrum does methane absorb? What concentration does it take to begin to saturate the absorption in this band? Explain what you are looking at to judge when the gas is saturated.

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 CO_2 absorption band. What temperature is this light coming from? Where in the atmosphere do you think this comes from?

Now turn on clouds and run the model again. Explain what you see. Why, at night, is it warmer when there are clouds?

3. **Water vapor.** 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 5°C? 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 into 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 5°C temperature increase. Is it higher or lower? Does water vapor 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 to 550 ppm. The temperature in the model stays the same (it's just how the model is written), so 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?