Greenhouse Gases

Heat released from the Earth's surface can be absorbed by certain atmospheric molecules. These molecules later release the heat in all directions, effectively trapping some it. The concentration of heat-trapping gases in our atmosphere is increasing and the increase is the result of human activities. The burning of fossil fuels has increased the concentration of CO and CO_2. Nitrogen oxides and methane result from agricultural and industrial processes.

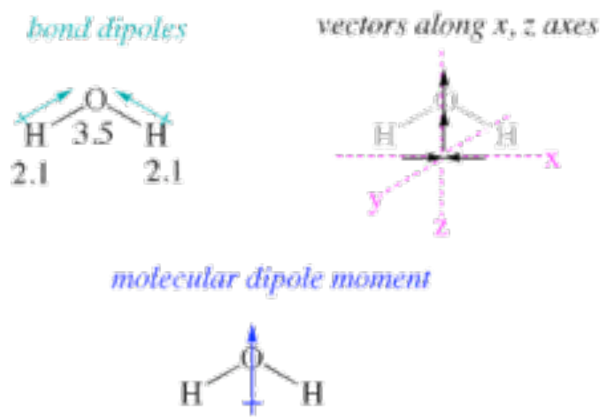
Today we will discuss the mechanism by which molecules absorb heat energy and the effect that these molecules have on atmospheric temperature and climate change.

Outline

Molecular Vibrations

Polar Bonds and the Dipole Moment

The electron density in covalent bonds depends on the electronegativity of the atoms in the bond. More electron density is closer to the more electronegative element of the pair. (Click here to see the electronegativity of elements in the periodic table.)



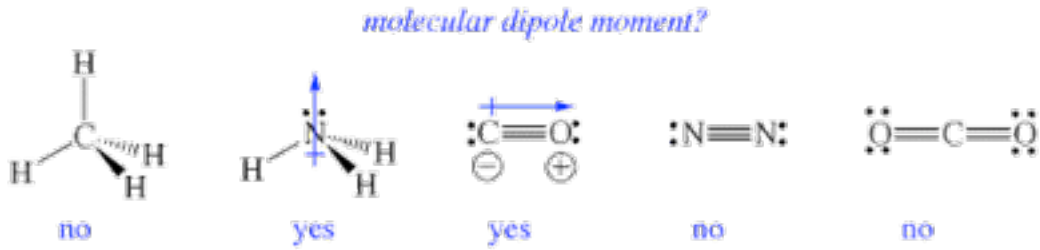
A **bond dipole** is a vector that represents the degree of charge separation in the bond. Here you can see the bond dipoles of each of the H-O bonds in water.

We can substitute the bond dipoles with vectors along the x and z axes, then sum these vectors.

The vector sum of of all of the bond vectors in a molecule is the **molecular dipole moment**. Water has a dipole moment as indicated here.

Some molecules with polar bonds have no dipole moment. The C-H bonds are only slightly polar but there is no overall dipole moment in CH_4 because the 4 bond dipoles cancel each other.

C-O bonds are polar and carbon monoxide has a molecular dipole. Carbon dioxide has no dipole moment because the the two bond dipoles cancel.

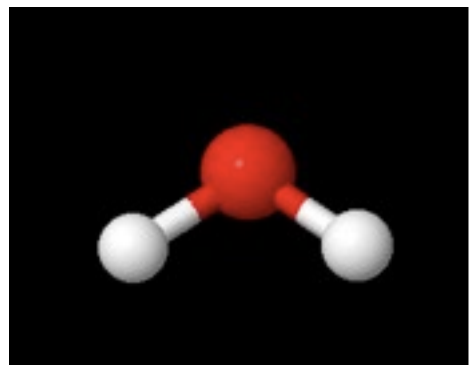


Vibrations

Monoatomic gases, such as helium, increase velocity as the temperature is increased. Polyatomic gases can vibrate as well as increase velocity when heat energy is added.

Lets examine the vibrations in water. Click on the picture at right to go to ChemTube3D by Nick Greeves at the University of Liverpool.

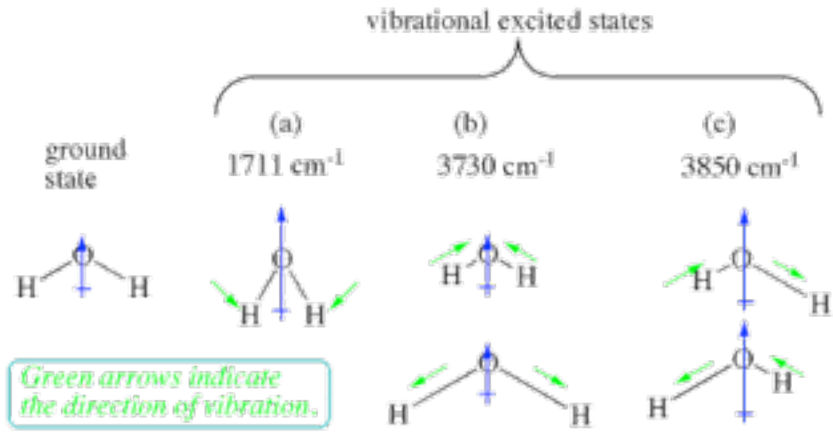
1. Click where indicated to show the frequency list.
2. Select, in turn, each of the 3 vibrations of the water molecule.
3. Does the dipole moment of water change when it vibrates?

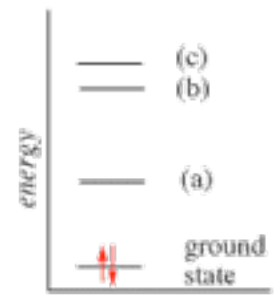


You can also examine the vibrations of hydrogen cyanide, carbon dioxide, ammonia, and methane.

Vibrational Energy States

When a molecule absorbs an amount of energy and vibrates, it has gone from its ground state to a vibrational excited state. Just like the transitions between electronic ground state and electronic excited states, only specific amounts of energy can be absorbed. Reciprocal wavelength, $1/\lambda$, is directly proportional to energy.





We can convert reciprocal centimeters to joules:

$E = hc/\lambda$

$E = (6.626 \times 10^{-37}\ \text{kJ s})(3.0 \times 10^{10}\ \text{cm s}^{-1})(1711\ \text{cm}^{-1}) = 3.4 \times 10^{-23}\ \text{kJ}$

$E = (6.626 \times 10^{-37}\ \text{kJ s})(3.0 \times 10^{10}\ \text{cm s}^{-1})(3730\ \text{cm}^{-1}) = 7.4 \times 10^{-23}\ \text{kJ}$

$E = (6.626 \times 10^{-37}\ \text{kJ s})(3.0 \times 10^{10}\ \text{cm s}^{-1})(3850\ \text{cm}^{-1}) = 7.7 \times 10^{-23}\ \text{kJ}$

Transitions between vibrational energy levels require much less energy than transitions between electronic energy levels. We can see this by the units that are used.

$$E = hc(\lambda)^{-1}$$

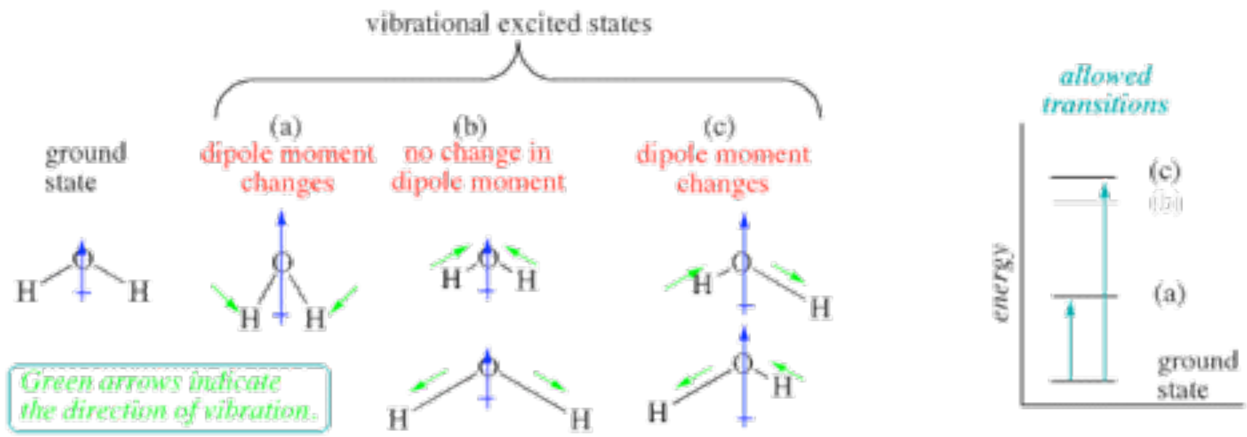
For electronic transitions, $(\lambda)^{-1}$ is in units of nm^{-1} and $hc = 2.0 \times \mathbf{10^{-19}}$ kJ nm

For vibrational transitions, $(\lambda)^{-1}$ is in units of cm^{-1} and $hc = 2.0 \times \mathbf{10^{-26}}$ kJ nm

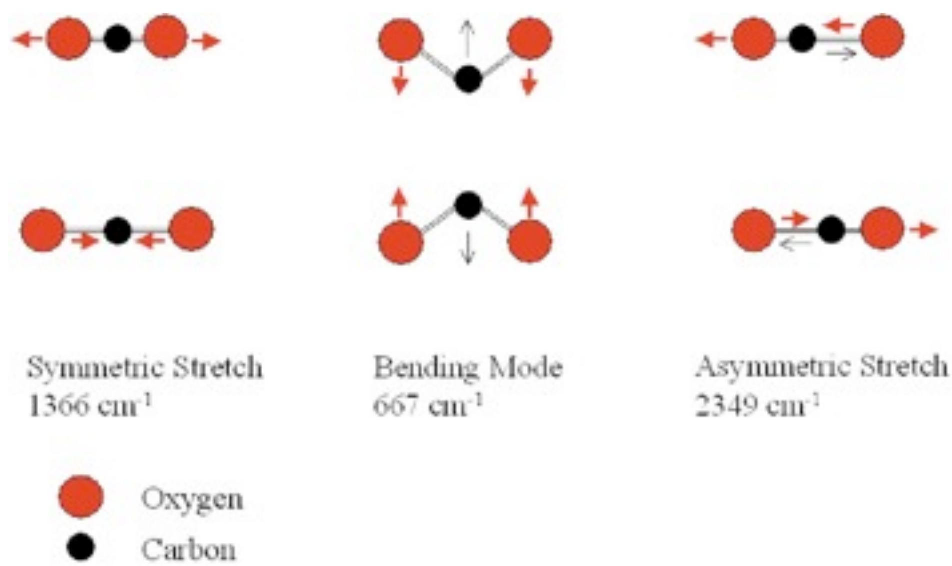
Heat Absorbing Gases

Selections Rules

Even though water has 3 vibrational modes, we observe that the molecule can absorb heat energy to access only two of them. ***Only vibrations where the dipole moment changes occur.*** This is a general rule, called a **selection rule**, that a change in molecular dipole must occur in the vibration for the transition to the vibrational level to be allowed.



Carbon dioxide doesn't have a molecular dipole in its ground state. However, some CO_2 vibrations produce a structure with a molecular dipole. Because of this, CO_2 strongly absorbs infrared radiation.

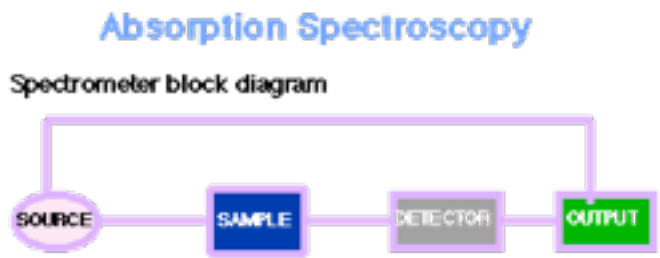


Can you find the vibrations of CO_2 that result in a change in the dipole moment?

IR Spectroscopy

Infrared (IR) electromagnetic radiation is in the range necessary to molecular vibrations.

Electronic spectroscopy uses visible or ultraviolet (UV) radiation to probe the absorption of energy by molecules between electronic energy levels. IR spectroscopy probes the absorption of energy by molecules between vibrational energy levels. The principle behind all forms of absorption spectroscopy is the same.



Electromagnetic radiation interacts with atoms or molecules within a sample. When radiation is absorbed, there is a transition from a low energy state to a higher energy state.

Some of this radiation is absorbed and the remainder passes through. A detector measures the radiation that passes through the sample. In a split-beam spectrometer, half of the radiation goes through the sample and the other half goes directly to the detector. The detector compares the intensity of the two signals.

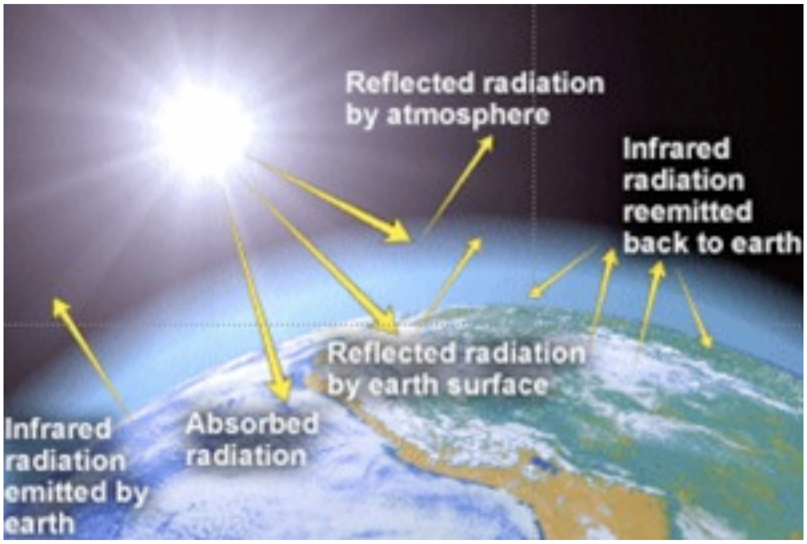
Wavelength	Radiation	Transition
10-50 nm	X-rays	core electron
50-1000 nm	UV-visible	valence electron
1000-20,000 nm	near infrared	vibrations
20,000-100,000 nm	far infrared	rotations
1-100 nm	microwaves	rotations
100-1000 nm	radio waves	nuclear spin

Green House Gases

The Earth absorbs solar energy and most of this energy is later released as heat, or IR radiation.

The most abundant gas molecules in the atmosphere, N_2 and O_2, are not able to absorb this energy and it passes through and out into space.

Carbon dioxide, methane, nitrous oxide, chlorofluorocarbons, and certain other gases absorb IR radiation from the Earth's surface and re-emit it in all directions. These gases act like the glass in a greenhouse to increase the temperature of the planet.



Water vapor is a significant greenhouse gas but its concentration in the air is regulated by the equilibrium between $H_2O(g)$ in the atmosphere and $H_2O(l)$ in surface bodies of water. The increases in other greenhouse gases is a direct result of human activity. Below is a table that shows the most important of these.

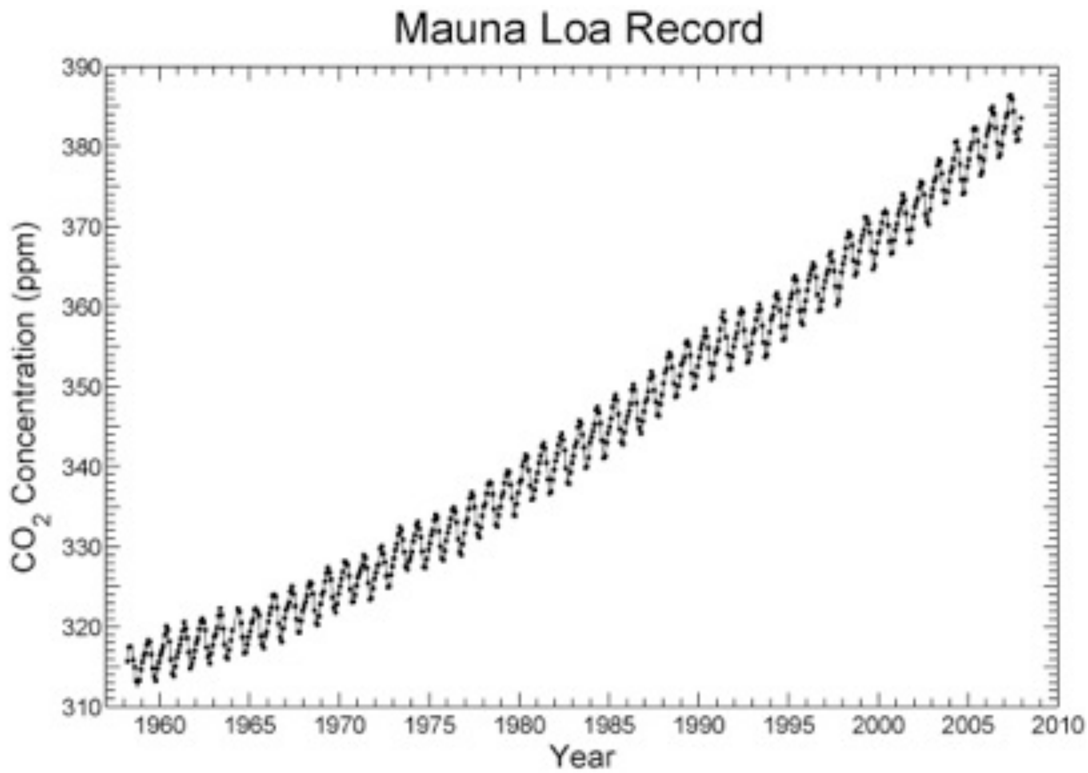
Gas	Current concentration	Residence time, in years	Relative global warming efficiency, 100-year horizon
CO_2	373 ppm	50–200	1
CH_4	1.77 ppm	12	23
N_2O	316 ppb	120	296
CFC-11	0.26 ppb	45	4600
HCFC-22	0.15 ppb	12	1700
HFC-134a	0.01 ppb	14	1300
Halon-1301	0.003 ppb	65	6900

Effect on Climate

Increasing Atmospheric Carbon Dioxide

The Intergovernmental Panel on Climate Change reported that the atmosphere is becoming warmer and that is is the result of human activity. Much of the data in this section is taken from their report on the physical science basis of climate change.

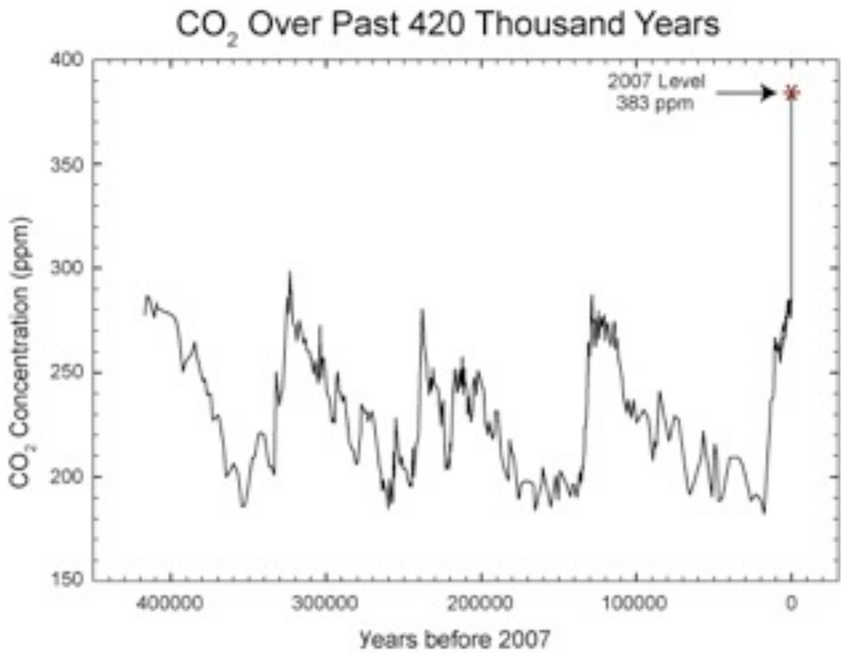
Careful, daily measurements of CO_2 content in the air have been taken by Charles Keeling and co-workers since 1957. There is a seasonal variation. Carbon dioxide is taken up by plants during the spring and summer months, then released through decomposition of plant material in the fall and winter. The concentration of carbon dioxide has been rising rapidly during this time.

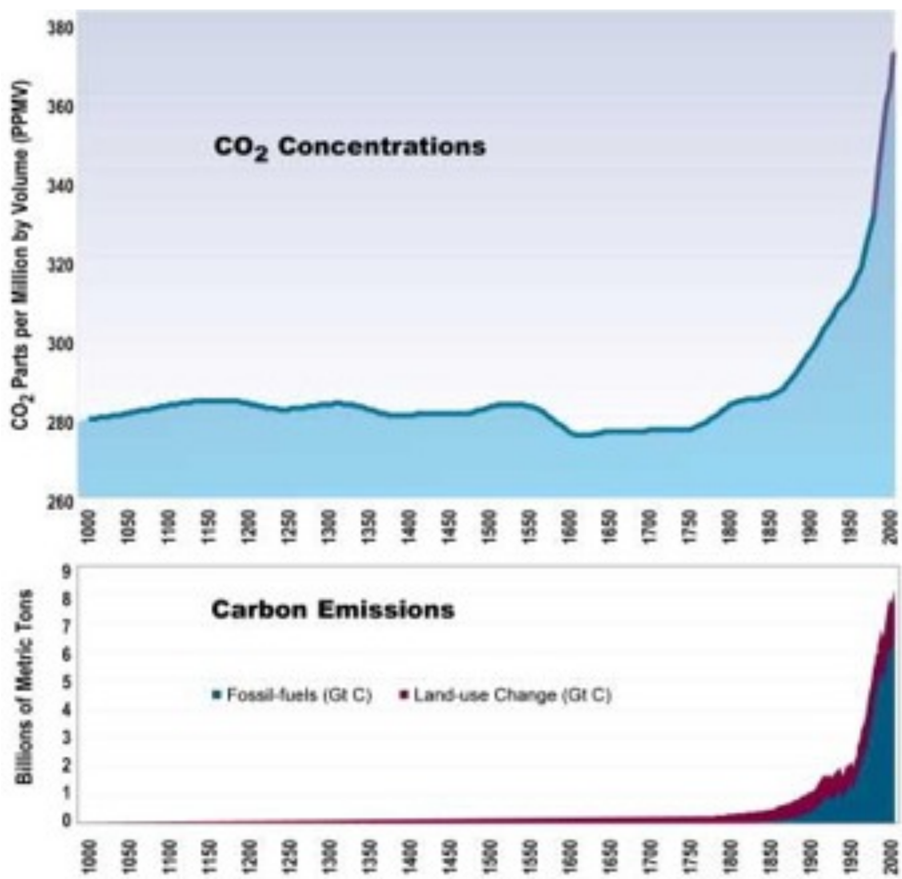


Yes, but couldn't this be one of the natural cycles of the Earth? The concentration of CO_2 in the atmosphere varies cyclicly but it hasn't been this high over that past 4 ice age cycles. *(Data before 1957 was obtained by a variety of methods including analysis of air in ice cores.)*

For the decade 1995-2005, the growth rate of CO_2 in the atmosphere was 1.9 ppm per yr and this is the largest change observed or inferred for any decade in at least the last 200 years.

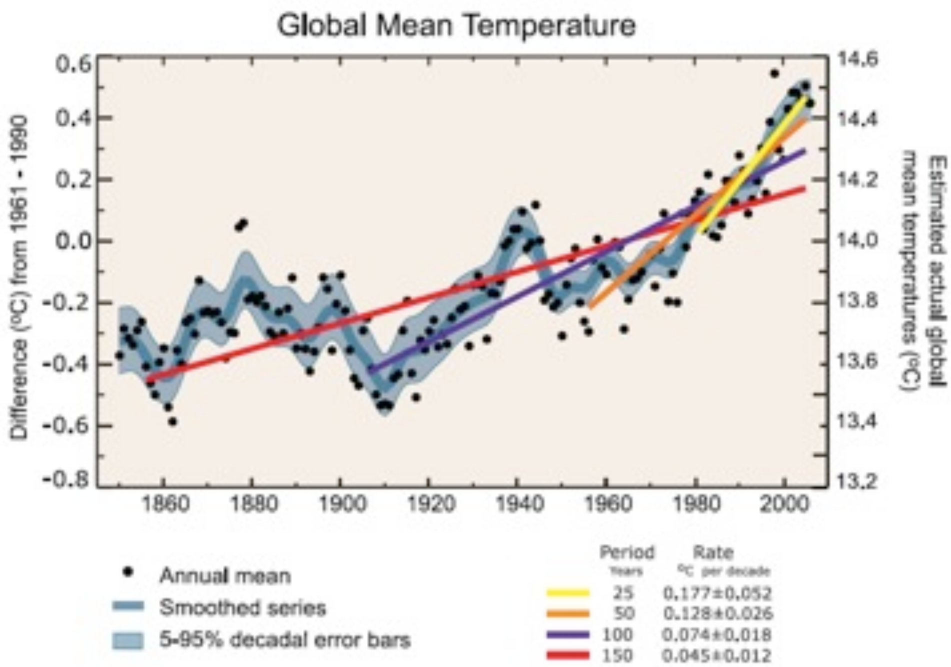
The increases in atmospheric CO_2 go along with increases in fossil fuel use.





Increasing Global Temperature

Accurate measurements exist since 1850 for global temperature. It is clear that that temperature of the planet is increasing and the rate of increase is becoming greater. Land is heating faster than the oceans but both are warming. The increasing of night time temperatures is greater than day time temperatures. The troposphere is becoming warmer as the stratosphere cools.



Effects on Climate

The ice in Greenland and at the poles is melting. As the ice melts, less of the solar radiation is reflected and the planet absorbs more heat. Click on the picture below to go to the New York Times site for more information.

As ice melts, it lubricates the area below a glacier. This accelerates glacier flow and "calving" where the glaciers more rapidly break and fall into the sea.

One potential consequence of climate warming is an intensification of the hydrological cycle, including more precipitation and more extreme precipitation events. The wet areas get wetter and the dry areas have more drought. Over the past 20 years there have been increases in precipitation in Europe, North America, and South America and decreases in Africa, Asia, and Australia. The total quantity of water vapor in the atmosphere has increased.

Sea Ice in Retreat

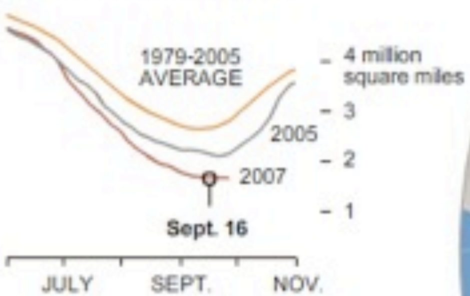
This summer saw a record-breaking loss of Arctic sea ice.

SUMMER SEA ICE | ATMOSPHERIC PRESSURE | AIR TEMPERATURE | CLOUD COVER | SOLAR HEATING

SUMMER SEA ICE

This summer saw a record-breaking loss of Arctic sea ice. Experts attribute the changes to the interaction of wind, weather, ice drift, ocean currents and greenhouse gases.

SUMMER SEA ICE EXTENT*



Sea ice extent is the area of ocean covered by at least 15 percent ice.

PERENNIAL SEA ICE

Ocean within this boundary had been covered with ice year-round since satellite records began in 1979. This summer was the first time that part of the perennial sea ice was open water.