

Let talk in more detail about how radiation is absorbed and emitted by a gas. One of the most elementary ways that radiation can interact with matter is when photons interact with isolated atoms. Here is a sketch of a Bohr atom, with a nucleus in green here, comprised, generally, of a collection of protons and neutrons, and electrons orbiting in discrete shells numbered here n equals 1, n equals 2, and n equals 3, et cetera.

The electrons orbiting in the outer shells have more energy than electrons orbiting in the inner shells. According to the rules of quantum mechanics, only discrete transitions are allowed between these shells. So if a photon of the right frequency comes in, of exactly the right frequency, then it can excite a transition of the electron orbits from the shell that they're in to a higher shell.

Likewise, that electron orbit can spontaneously decay back, as shown by this yellow curve, to a lower shell, which corresponds to the emission of a photon in a discrete wavelength. These electronic transitions are part of the way that radiation interacts with gases and the atmosphere. But generally speaking, in our atmosphere, these are only active for very, very highly energetic photons in the ultraviolet part of the spectrum and don't have a lot to do with absorption and emission of infrared radiation in our atmosphere.

If we look at the rules by which these electronic transitions occur, we have a photon energy, which is given by Planck's constant h times the frequency of radiation corresponding to that photon. The atomic energy levels are likewise discretized. According to n times $h \nu$ where n is an integer starting with zero and going up. As we just stated, an isolated atom can absorb only those photons whose energy is equal to the difference between two atomic energy levels. As I've mentioned before, this involves really just the ultraviolet visible parts of the solar spectrum.

Now, if we have radiation interacting with molecules, they have additional energy levels. Molecules have potential rotational and vibrational transitions. We'll begin with something called the simple homonuclear diatomic molecule, that is, a molecule composed of two atoms that are identical. Nitrogen N_2 and molecular oxygen in our atmosphere are good examples of homonuclear diatomic molecules. Because they are symmetric, there is no electric dipole moment-- that is a difference between the center of charge and the center of mass in a molecule-- and for that reason, these molecules really cannot

interact with electromagnetic radiation. This is the reason why the primary constituents of our atmosphere are almost completely transparent both to solar and to terrestrial radiation.

A more interesting case is that of a heteronuclear diatomic molecule, for example, carbon dioxide. Because of the asymmetry of these molecules, they can have electric dipole moments and rotational modes as well. Even such a simple atom as carbon monoxide, CO, can have many different rotational vibrational transitions, as given by this diagram, which shows for two different vibrational frequencies, 0 and 1, different rotational modes. So there are all kinds of energy transitions possible, giving rise to a much richer line absorption and emission spectra.

Polyatomic molecules can interact with radiation in many more ways even than that. So let's talk about an atom made of three molecules. It can be shown that there are three times $n-6$ vibrational modes, where n is the number of atoms in a molecule, and numerous rotational and rotational-vibrational modes in such a molecule. So the molecules could rotate around a common axis, they can vibrate, there are dipole moments, which are permanent and or temporary.

Let's talk about the three fundamental vibrational modes of a water molecule as an example, water being a fairly plentiful greenhouse gas in our atmosphere. So here we have a animation of a water molecule consisting of an atom of oxygen, given by yellow here, and two atoms of hydrogen. And here we're illustrating something called the OH-symmetric stretching mode, where the two hydrogen atoms vibrate back and forth in sync.

Here's another of the three principal modes or fundamental modes of a water molecule. This is the HOH-bending, where the two hydrogen atoms bend back and forth. And here is an asymmetric stretching mode of the water molecule. So there are all kinds of different vibrational modes. They are also rotational modes, which are not shown here in combinations of those, giving water vapor a very rich emission absorption spectra. Water vapor being relatively plentiful in our atmosphere is a principal greenhouse gas, you can think of these animations here as illustrating that the water molecule is, in many ways, the cheerleader for our greenhouse effect.

Here, in fact, is an example of infrared absorption coefficients for water vapor as a function of wavelength given here. So this is an infrared part of the spectrum, or terrestrial part, going from 1 to 100 microns logarithmically; and the green curve you see here shows the absorption coefficient as a function of wavelength for water vapor. You can see these rich bands of water vapor absorption, many,

many emission absorption bands.

The red curve at the top shows the absorption coefficient of liquid water, which is somewhat more continuous. This is important, because, of course, we do have liquid water in the atmosphere in the form of cloud droplets and raindrops. And ice, once again, cloud water and precipitation in frozen form has a rich continuous spectrum.

Now, an important feature of radiative transfer is Kirchoff's law. There's actually various forms of Kirchoff's law, but the most important form that we'll emphasize here is that the coefficient of black-body radiation, or the fraction of black-body radiation absorbed by a particular object or a particular molecule, is equal to the fraction of radiant energy emitted at the same wavelength in black-body radiation. This is important, so absorption spectra and emission spectra of a gas will be the same if the gas is of the same temperature.

So we can put it all together and talk about the total energy of molecules in a gas. We call that E_{total} and it's comprised of energy locked up in the Bohr atom. This can change by electronic transitions, vibrational modes of molecules, rotational modes of molecules-- we should, perhaps, add to that combinations of vibrational-rotational modes-- but in any case, the sum of the energies is the sum of the two components. And this part, which is translational, the kinetic energy of molecule, of course, is related to its temperature.

So translational energy is kinetic energy of molecular motions of a gas, proportional to the temperature. It's not quantized. Molecules in a gas can absorb more frequencies than isolated atoms because of the greater number of degrees of freedom of molecules. Collisions between molecules can carry away energy or supply energy to interactions between matter and photons.

And this brings us to the subject of various ways by which the theoretically infinitesimal lines of emission and absorption spectra actually turn out to have finite width. The most fundamental part of this is called natural broadening. This is a direct consequence of Heisenberg's uncertainty principle and places a lower bound on actual line width.

Another means by which the actual spectra are broader than infinitesimal lines is Doppler broadening, caused by the fact that the velocity of atoms or molecules relative to the observer follows a Maxwell distribution. And therefore, the radiation is slightly Doppler shifted, with respect to the molecule causing

a shift in the absorption or emission of radiation. This produces, it turns out, a Gaussian line shape, rather than a delta function.

There is another effect called pressure broadening-- collisions between molecules affect the absorption and emission of radiation. This effect depends mostly on pressure, which is proportional to the rate of collisions. And the broadening effect is more nearly described by a Lorentzian profile in those cases. And we'll compare in the next slide Gaussian and Lorentzian profiles.

There are other broadening mechanisms besides these three, but they are less important in our atmosphere.

This compares the Lorentzian profile, which is associated with pressure broadening to the Gaussian profile, associated with Doppler broadening. You can see that the Gaussian profile falls off much more steeply from the central wavelength than does the Lorentzian profile.