Course Name: An Introduction to Climate Dynamics, Variability and Monitoring

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ATMOSPHERIC ABSORPTION AND RADIATIVE TRANSFER

Good morning class and welcome to our continuing coverage on climate dynamics, climate variability and climate monitoring. We have seen in the previous class, we started our discussion on why atmospheric gases interact with electromagnetic waves and absorb certain wavelengths of electromagnetic radiation. We saw that different molecules that are present in the atmospheric gas have different modes of translation, rotation and vibration which are associated with different frequencies. And when the electromagnetic wave frequency matches with these vibrational frequency or rotational frequency of dipole moments then and only then the photons corresponding to this electromagnetic radiation get absorbed by the gases activating that vibrational or that rotational dipole moment activity. So, if a molecule has a dipole moment, then its rotation causes fluctuation in electrical and magnetic field that can resonate with certain frequency bands of EM radiation. Hence, molecules with dipole moments like H_2O, N_2O etc. can absorb EM radiation over certain frequency ranges which energizes the molecular dipole moment oscillations. That's one way that electromagnetic wavelengths get absorbed. Water vapor particularly is a very strong absorbent of this type. Furthermore, the molecules tend to vibrate at certain specific frequencies which are called harmonic frequencies.

When the electromagnetic radiation at frequencies close to these vibrational harmonic frequencies are incident on the molecule, then the resonance occurs and the corresponding vibrational mode is activated by absorption of that electromagnetic wave. That is absorption happens when the vibrational frequency is equal to the electromagnetic wave frequency. So that's the general idea. Now at what vibrational modes do the various atmospheric gases absorb radiation? The largest constituents of the atmosphere are of course nitrogen and oxygen. These are symmetric homonuclear molecules with no dipole moments.

So rotational frequency based activation is off the table. Furthermore, because they are homonuclear molecules, their bonds are extremely stiff and hence their vibrational frequency modes are also at extremely high values of frequency. So, if the bonds are extremely strong, the vibrational mode corresponding to those bonds have very high activation frequencies. And the usual electromagnetic waves that are present from the sun cannot provide them with enough energy to activate their vibrational modes. As a result, oxygen and nitrogen do not absorb much of EM radiation either emitted by the sun or the earth's surface.

So, the two most common gas molecules in our atmosphere oxygen and nitrogen have such stiff vibrational such stiff bond that their vibrational modes are not activated by solar or terrestrial radiation and hence they are they do not interact with the radiation passing through our atmosphere. Hence, the selective absorption that happens, happens for the other trace molecules that are present in our atmosphere which are the heteroatomic molecules. Molecules made up of more than two atoms and non-linear molecules having lower bond stiffness. And these have several different types of vibrational modes whose harmonic frequencies are within the range of the electromagnetic radiation emitted by the sun and the earth surface. So, molecules like ozone, carbon dioxide, water vapor, carbon monoxide, methane, nitrous oxide.

So, these molecules are strong absorbers of various bands of solar and terrestrial electromagnetic radiation. Because most of these are heteroatomic molecules and the interatomic bonds are not as stiff, others like ozone are nonlinear that is planar molecules and hence different vibrational modes are there, some of which are less stiff which makes it possible for these molecules to absorb electromagnetic radiation. Since, these are minor constituents of the Earth's atmosphere, so their absorption efficacy depend upon their concentration in the atmosphere. And this is the reason why anthropogenic activity can significantly perturb their concentration and affects Earth's energy balance. Nitrogen and oxygen are transparent.

These are the major constituents. If these were absorbing the radiation, then no amount of emissions would have had any effect. But since these are transparent, it's the trace gases which are absorbing and the amount by which they are absorbing depends strongly on the concentration of these trace gases. Which is why emission of these trace molecules through anthropogenic activity can significantly part of their absorption efficacy, both in the solar range and in the terrestrial range, changing the heat budget of the Earth. Some of the major vibrational modes of the various trace species are shown here. Some of these are from the, so remember the terrestrial emission band is 5 to 100 micrometers with the peak at around 15 micrometers. The solar band is 0.2 to 4 micrometers with the peak at around 0.5 to 0.6 micrometers.

Now here, for example, if you look at CO_2, it has a vibrational mode at 15, which is the peak of the terrestrial emission range. Hence, CO_2 is a very strong absorber of terrestrial thermal radiation, which is why emission of CO_2 has such an impact on the energy budget of the earth. N_2O also has a value at 17 micrometers which is close to the peak terrestrial emission band and hence N_2O is also a strong greenhouse gas. It has another mode at 7.78 which also is in the terrestrial range and hence there also N_2O can absorb a significant fraction of the terrestrial emissions.

Water vapour, for when it comes to vibrational modes, the water vapor vibrational modes are at lower frequencies 2.7, 6.2, 2.65. Lower wavelengths. So, these are all wavelengths sorry not frequencies. So, these are the 6.27 is just at the beginning of the terrestrial emissions and 2.73 and 2.65 are in the solar infrared region.

So, water vapor plays a significant part in absorbing the solar short infrared band of radiation. We will also see that water vapour has a significant dipole moment and hence the rotational absorption of electromagnetic waves through the activation of the dipole moment based rotation is an important aspect of why water vapour is such an effective absorption of radiation. So, there are two ways by which ozone impact the heat budget of the earth. Firstly, ozone is formed in the stratosphere by absorbing UV radiation. So, it is a strong absorber of UV radiation through photoresorciation process between oxygen and ozone, which we will discuss separately just now, just a little bit later.

But also, it has a set of vibrational frequencies at 9 micrometers, 14 micrometers and 9.5 micrometers, all of which are present within the terrestrial emission band. So ozone is also a strong absorber of terrestrial radiation. Similarly, NO2 is also present in the within the terrestrial radiation emission band. Methane has also a strong presence here as well as it has a strong rotational dipole moment as well which absorbs a lot of the radiation emissions for methane.

So, these molecules play an important role in absorbing both terrestrial thermal emission as well as the infrared region of the solar radiation. One issue here is these are extremely sharp frequencies.

So, 4.67, 7.78, 6.27, etc. and this is true for isolated molecules. So in extremely dilute gas, when the molecules are not colliding with other molecules, there the absorption modes are extremely sharp and is at a specific frequency only. So for isolated molecules one would need photons of exact frequency as the vibrational mode frequency for absorption to occur. The exact EM frequency should match the vibrational frequency.

However, in the atmosphere especially at the lower ranges, troposphere, stratosphere, etcetera, the gas molecules are colliding continuously with each other which is adding or removing small amounts of energy from these molecules. So, in the presence of other molecules especially at high enough pressures the gas molecules collide frequently with other gas molecules around it and through these collisions can exchange energy with the other gas molecules. And this exchange of energy means that the gas molecules can get some energy or give some energy to neighboring gas molecules through these collisional processes. These collisional energy contributions can allow radiative activation of vibrational modes to occur over a broader range of photon frequencies. So what is happening is, suppose you have a photon whose frequency is close to but not exactly the same as a vibrational frequency for a gas molecule.

But because the gas molecule is colliding with other gas molecules frequently, that energy difference between the photons energy and the vibration energy can be compensated by energy transfer from a neighboring molecule with which it is colliding at that given instant. So, this small delta E differences can be taken up from the collision processes with other neighboring molecules. Making it possible for that gas molecule to absorb the photon even though the photon's frequency is somewhat different from the resonant vibrational frequency or resonant rotational frequency for that gas molecule. This allows the absorption lines to broaden into absorption bands with a peak shaped distribution. So when for an isolated atom you have very sharp absorption lines whereas when the atoms are present with neighboring atoms with significant enough pressure then because of the collision processes the absorption lines broaden into absorption peaks because there is remains a finite probability that photons with frequency somewhat different from the resonant frequency can also get absorbed due to the compensation energy transfer effects of the collisions.

So photons with frequencies slightly larger or smaller than the harmonic frequency will also have a finite probability of getting absorbed as collisions can add or subtract the requisite energy mismatch during the absorption process. The collision induced broadening of absorption lines is called pressure broadening and is a dominant phenomenon in the troposphere and the stratosphere where the pressure is high enough such that molecular collisions are frequent. So, this makes it possible this pressure broadening effect makes it possible for the atmospheric gases to absorb over a reasonably large band of frequencies from the electromagnetic wave range that is incident on it either from the solar source or terrestrial sources. So, given this theory, what is the absorption bands for the various molecules present in the atmosphere? So, here we look at 1 to 15 micrometers. So, 1 to 3 is the short infrared range, the solar infrared region, 5 to 15 is the initial section of the far infrared radiation at which terrestrial emission is taking place.

So, if you see carbon monoxide, it is absorbed. So, 0% is that complete transmission is occurring. 100% is complete absorption is happening. So, carbon monoxide absorbs at around 4.5 micrometers. You see a pressure broadened peak of carbon monoxide at 4.5 micrometers. Methane has two distinct pressure broadened peaks, one at around 3.5 micrometers and the other, so this is 2.5 micrometers, 3, 4, 5, 6, 7 and this is at 7.5 micrometers. So, methane has two absorption peaks or valleys at 3.5 and 7.5 micrometers. Nitrous oxide also has two absorption peaks or valleys at 3.5 and 6.5 micrometers. Ozone has a major absorption peak at 8.5 and 8.6 or 8.8 micrometers. So, this you can see here. This corresponding this 9 and 9.59, these are the ozone absorption peaks here ok. This is 9, so this is ozone 9.5 ok. CO2, if you remember, CO2 has one strong absorption peak at 15.

So, here you are going to 0 at around 14. So, this is a strong absorption peak of CO2 and also in the short wave region it has an absorption peak at 2.8 and around 4.3 or 4.4.

Water vapour is a very interesting molecule. So, it has a set of short absorption peaks just before 2 and between 2.8 and then a very broad peak between 5 and 7 micrometers, which is associated with the dipole moment of water vapor. And later also it will have a very broad absorption peak beyond 15 micrometers which is again associated with the rotational dipole moment based absorption of water. So, water vapor specifically is a very strong absorber not because of its vibrational absorption but because of its dipole moment based rotational absorption. Now the rotational modes of a molecule are much closely spaced compared to the vibrational resonant frequencies of a molecule.

Hence, because water vapor is such a strong dipolar molecule, its rotational modes of activation form a near continuous region over large ranges of the IR spectrum. One such continuous region is between 5 to 7 micrometers. Another continuous region is far broader, anything above 15 micrometers. So 15 to 100 micrometers, water is a very, very strong absorber of infrared radiation. And if you combine all of these molecules, you get the aggregate absorption.

And here you can see that apart from certain specific windows between 8 to 9.5 micrometers and 10 to 12.5 micrometers, most of the terrestrial emission is getting blocked by various atmospheric gases. This is the combined effect of CO2 and water vapor combining together to create a strong absorption value beyond 14 micrometers. There is strong absorption due to ozone at around 9.5 micrometers. Between 5 to 7 micrometers, water vapor essentially eliminates all types of transmission processes. And other cases are combined to have also in the short wave region of the solar spectra there are certain regions where also you are getting strong absorption. So, what is left is certain transparent regions within 8 and 9.5 and 10 and 12.5 micrometers in which terrestrial emission can get out into space.

Apart from the above absorption bands, water molecule has a permanent dipole moment and hence its rotational modes also absorb EM radiation. The rotational modes of water molecule activate over a broad EM wavelength above 12 micrometers. It's not exactly 12, it's around 14 micrometers. So, water molecules also absorb IR radiation strongly for wavelengths longer than 12 micrometers. The absorption band of water including the rotational absorption is shown here.

So, here the absorption percentage is 100 at the top and 0 at the bottom. So, all the gray zones are where water vapor is able to absorb, and you can see it's the kind of the opposite of this region here. So from 12 onwards the absorption ability of water continues to increase and by around 16 it's around 100%. From 16 micrometers to 100 micrometers, water absorbs everything. So, what we see here is the majority of the outgoing terrestrial emissions is blocked by water vapor and also CO2 in the 14 to 15 band.

So, water vapor and CO2 are the two strongest greenhouse gases followed by ozone, N2O, methane, etc. Much of the incoming solar radiation is not absorbed by the atmospheric gases. So here we see some absorption in the near infrared spectra, but in the visible spectra, atmosphere is more or less transparent to radiation.

However, UV radiation in the range of 0.2 to 0.3 micrometers interacts with ozone in the stratosphere, breaking it down to ozone and oxygen radical, which is called a photodissociation reaction. So, UV radiation is absorbed by ozone which actually breaks the third OO bond to create oxygen and O radical. And this is a photodissociation reaction which absorbs the UV radiation. Thus ozone absorbs much of the UV radiation coming from the sun. Water vapor absorbs part of the near solar IR radiation that you can see here, so all these regions, here, here, here, here are absorbed by water vapor.

A significant fraction of the visible radiation is also reflected and scattered by aerosols and clouds. So, even though it is not absorbed, it can be, it is reflected or scattered. So, it is part of the albedo effect and hence does not reach the surface directly. So, the figure below shows the solar irradiance. Irradiance is solar flux density at the top of the atmosphere and the part that is directly incident on the surface.

So, the yellow region is the solar irradiance at the top of the atmosphere before the atmospheric effect comes into play and the red region is that which is directly hitting the surface. So, the yellow sunlight without atmospheric absorption and then red is sunlight at the sea level. The visible range is around this region here. So between around 350 micrometers to around 700 micrometers, and here, this region is not actually absorbed, but it is reflected back by clouds, aerosols, snow, etc. This region here is basically ozone-based absorption of UV radiation.

Then beyond this is the near-infrared region, 750 nanometers which is 0.75 micrometers to 2.5 micrometer and here all of these regions are basically H_2O and partly CO_2 based absorption of the near infrared radiation. But we can see that a significant fraction of the sunlight especially the visible part does get is incident on the surface whereas certain parts of the IR radiation is also incident on the surface.

For terrestrial radiation the situation is different. Most of the radiation is absorbed by the gases except for small windows between 8 to 9.5 micrometers and 10 to 12 micrometers. Thus the atmosphere is an excellent absorption of terrestrial radiation which then re-radiates both towards the space and to the ground as we saw in our simplified greenhouse gas model. So here, is the absorption percentage and this is the wavelength in micrometers and you can see here this 0.3 micrometers is the UV region. This is getting absorbed. So, 0.4 to around 0.7 is the visible region where most of the radiation is getting transmitted to the surface. So, this is neglecting all the albedo based reflection effects. So, this is just absorption with transmission.

So, most of the visible spectrum is getting transmitted. Then 0.7 to around 3 is the near infrared region. Here there is significant absorption by water vapor as you can see. Then the terrestrial band starts from 5 micrometers. Here most of it is getting absorbed by ozone, water vapor, N_2O etc.

There are only two small windows at around those two bands 8 to 9.5 and 10 to 12 micrometers. Where, the atmosphere is transparent to the terrestrial infrared radiation after which once a, so CO_2 absorption happens strongly in this region after which water vapor starts absorbing everything through its rotational mode of activation, okay, 200 micrometers. And you can see the effect of water vapor if you go 11 kilometers above the surface where water vapor is much lower. Remember as you increase in altitude, the concentration of water vapor decreases dramatically because of the decrease in the temperature in the corresponding saturation pressure. So, at 11 kilometers above so near the top of the troposphere there is very little water vapor and you see this entire region solar energy is penetrating, so most of the absorption between 15 micrometer, so here the CO_2 peak is very clearly visible so this is the CO_2 peak here okay because CO_2 is a well mixed gas CO_2 concentration remains relatively stable as does methane N_2O concentration.

So, this region helps us to see the other greenhouse gases much more clearly. If you measure the absorption spectra at 11 kilometers at the top of the atmosphere, then you get clearly the CO_2 spectra, the CH_4 spectra, the CO spectra, other CH_4 and N_2O spectra. The water vapor concentration is lower, but it still absorbs significantly even at this trace amounts here. So, this entire plateau is water vapor mediated, this region is water vapor mediated, these broader regions are also mostly water vapor mediated.

But CH_4, CO, N_2O are responsible for these peaks here. So, what we see therefore is that the overall message is atmosphere is transparent in the visible spectra, water vapor absorbs part of the near infrared spectra of sun, ozone absorbs the most of the UV radiation coming from the sun. The far infrared region where earth is emitting there are only two small windows. namely 8 to 9.5 micrometers and 10 to 12 micrometers which is transparent. Rest of the region is absorbed primarily due to the presence of water vapor and rotational activation modes as well as due to contributions of methane, N_2O and CO_2 based absorption spectrum, ok.

So, this kind of gives us the overall idea. In the next class, we will start to create the model of, how we can take into account this absorption rate of radiation, both the solar radiation and the terrestrial radiation and how it impacts the heat budget of the earth. So, thank you for listening and see you in the next lecture.