10 Radiatively active gases

In this lecture we want to look at radiatively active gases in the atmosphere. Radiatively active gases are gases which absorb or emit radiation in some relevant wavelength and therefore influence the radiation budget in the atmosphere.

10.1 Spectral quantities

We have used different quantities in relation to radiation (radiance, irradiance, transmission etc.). To investigate the spectral structure, we have to use corresponding spectral quantities, e.g. “Spectral radiance”, “Spectral irradiance”, “Spectral transmission”. These quantities can be defined in different ways:

- per unit wavelength /m (or more conveniently /µm)
- per wave number (cm$^{-1}$)$^{-1}$
- or per unit frequency Hz$^{-1}$

For example the differential form of the Swartzschild equation for the radiance goes from

$$\frac{dL}{dz} = -\sigma_a (L - B)$$

in the grey case to

$$\frac{dL_\lambda}{dz} = -\sigma_\lambda (L_\lambda - B_\lambda)$$

in the spectral case. Here, $L_\lambda$ is the spectral radiance (per unit wavelength) and $B_\lambda$ is the Planck function.

10.2 Spectral radiance - thermal emission

In the grey case, the thermal emission is $B(T) = \sigma T^4$. In the spectral case it is given by the Planck function. In terms of wavelength, this is:

$$B_\lambda(T) = \frac{2hc}{\lambda^5 \left( e^{hc/\lambda kT} - 1 \right)}$$

and in terms of frequency it is:

$$B_\nu(T) = \frac{2h\nu^3}{c^3 \left( e^{h\nu/kT} - 1 \right)}$$

where

Planck constant: $h = 6.63 \times 10^{-34}$ Js

Boltzmann constant: $k = 1.38 \times 10^{-23}$ JK$^{-1}$

The units of $B_\lambda$ are Wm$^{-2}$sr$^{-1}$m$^{-1}$ while the units of $B_\nu$ are Wm$^{-2}$sr$^{-1}$Hz$^{-1}$. The function $B_\lambda$ is shown for different temperatures in figure 1. Note the following features:

- For every wavelength, the radiance increases with temperature.
- The maximum of this function moves towards shorter wavelengths with temperature (this is called the Wien displacement law)
- The spectral exitance of a black body is given by $E_\lambda = \pi B_\lambda$. 
10.3 Spectral emissivity and transmittance

The spectral emissivity equals the spectral absorptivity at every wavelength (Kirchhoff’s law). In lecture 6 we saw that the total transmittances of several stacked layers multiply. The same is true for spectral transmittances:

$$\tau_\lambda(a, c) = \tau_\lambda(a, b) \cdot \tau_\lambda(b, c)$$ (1)

But note: The band-integrated transmittances do not multiply. You can easily see that when you consider two layers of different composition, one of which absorbs at one wavelength and the other at a different wavelength.

10.4 Molecular spectra

The spectra come from absorption and emission due to several quantum physical processes

- electronic excitation
- rotation
- vibration (for complex molecules many different possibilities)

All these are quantized. The energy of the rotational states is typically an order of magnitude less than the vibrational states, and the electronic transitions have even higher energies. Rotational transitions occur in the far infra-red and microwave regions and vibrational transitions in the near infra-red, so these transitions have strong effects on the solar and terrestrial radiation.

10.4.1 Rotational Transitions

- Linear Molecule: energy levels are $$E = \frac{\hbar}{4\pi I} J(J+1)$$, $$J = 0, 1, 2, 3 \cdots$$, where $$I$$ is the moment of inertia of the molecule.
- A photon carries one quantum of angular momentum, so a transition between states must be such that $$\Delta J = \pm 1$$ ...
- ...so frequencies of absorption/emission are: $$f_{J, J+1} = \frac{\hbar}{2\pi I} (J + 1)$$ — evenly spaced at $$f_0$$, $$2f_0$$, $$3f_0$$ ...
- Absorption/emission can only take place if the molecule has a dipole moment: HCl and HCN have this sort of spectrum but N₂ does not.
- Nonlinear molecules (e.g. O₃, H₂O) also have rotational spectra (if they have a dipole moment) but the lines are not evenly spaced.
10.4.2 Vibrational Transitions
- Single bond considered as a Quantum simple harmonic oscillator. Energy levels are \( E_n = (n + \frac{1}{2})h\nu \) \( n = 0, 1, 2, \ldots \) where \( \nu \) is the classical frequency of the harmonic oscillator.
- Selection rule says that \( \Delta n = \pm 1 \) so absorption/emission frequency is \( \nu \) for any \( n \).
- A pure vibration spectrum would be a single line, but a quantum transition must cause the rotational quantum number \( J \) to change by 1, so we get a band of lines with the same \( \Delta n \) but different \( J \)s
- A molecule with \( > 2 \) atoms will have several vibrational modes, each causing a separate band.
- For absorption/emission to occur, the bond must have a dipole moment. The molecule as a whole might not have one (e.g. \( \text{CH}_4 \)).

10.4.3 Some radiatively active molecules
Remember that emission/absorption due to rotation and vibration can only occur in molecules that can change their dipole moment when vibrating or rotating. The most abundant gases in the atmosphere, Oxygen and Nitrogen, however, are symmetric linear molecules with zero dipole moment. The dipole moment remains zero when they rotate or when they vibrate. This is why absorption/emission in the atmosphere is mostly due to the less common molecules.
- Carbon dioxide is a linear molecule O-C-O and has no rotational lines, but it changes its dipole moment when the two arms stretch asymmetrically or bend, so there are vibrational bands.
- Methane (\( \text{CH}_4 \)) is a symmetrical molecule and it too has no pure rotational transitions, but has vibrational ones.
- Water (\( \text{H}_2\text{O} \)) and Ozone (\( \text{O}_3 \)) are non-linear molecules with a dipole moment, so they have both vibrational bands and pure rotational lines.

10.5 Line Width
The spectral lines have a certain line width related to the life time of the excited state by the Heisenberg uncertainty principle. The natural lifetime is usually very long and the linewidth related to it is therefore very narrow. The lines are further broadened through the following processes:
- Doppler: because the molecules move, the observed energy from the emission/absorption of a particular molecule is Doppler shifted. In total, this leads to a line broadening proportional to the square root of the temperature (velocity distribution!).
- Collision (Lorentz) broadening occurs when the molecules have a high probability to change state when they collide with other molecules. This influences the lifetime and therefore the line width. This is \( \propto p \) and has a dependence on \( T \) as well.

10.5.1 Doppler Broadening
The component of molecular velocity in the direction towards the observer is given by a Boltzmann distribution:
\[
P(u_x) = \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left( -\frac{mu_x^2}{2kT} \right)
\]
If a molecule is moving towards (or away) from you as it emits, the observed frequency will be higher (or lower) than that in the molecule’s frame of reference. This is called the Doppler shift, and is given by:

\[ \nu - \nu_0 = \frac{\nu_0 v}{c} \]

so the line shape is given by:

\[ F(\nu) \propto \exp \left( - \frac{m(\nu - \nu_0)^2 c^2}{2kT \nu_0^2} \right) \]

a Gaussian shape with a width\(^1\) of

\[ \Delta \nu = \sqrt{\frac{2kT \nu_0^2}{mc^2}} \]

### 10.5.2 Collision (pressure) broadening

Collision broadening gives a Loren(t)z line shape:

\[ F(\nu) \propto \frac{1}{\gamma^2 + (\nu - \nu_0)^2} \]

This is an approximation, but is a good one except for very large values of \((\nu - \nu_0)^2\). The broadening parameter \(\gamma\) is given by

\[ \gamma = \gamma_0 p \left( \frac{T_0}{T} \right)^\beta \]

where the parameters \(\gamma_0\) and \(\beta\) must be obtained by experiment or by detailed quantum-mechanical calculations. Typical values are \(\gamma_0 = 300\, \text{MHz/mb}\) and \(\beta = 0.7\) for \(T_0 = 300\, \text{K}\).

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\(^1\)There is an extra numerical factor required to convert this to a half-width. The important thing is the \(\sqrt{T}\) dependence.
10.5.3 Combined broadening

Real spectral lines are affected by both Doppler and collision broadening and have a line shape that is a convolution of the two shapes. This is called the “Voigt” lineshape. Figure 2 shows all three shapes. In many cases, one effect predominates over the other so that either the Doppler or collision line can be used. Collision is the dominant effect in the atmosphere below 30 km (for infra-red – in the microwave region, collision broadening dominates up to 60 km). Above that the density is too low and Doppler broadening becomes important.

10.6 Recipe for radiance calculation

So in total when one wants to calculate the radiative transfer in the atmosphere, the process is quite messy and computationally intensive:

- Specify composition, pressure and temperature at each level
- For each species:
  - identify lines near the required wavelength
  - look up spectroscopic data
  - calculate the line shape function
  - sum to get the mass absorption coefficient
- weighted sum of mass absorption coefficients for all species to get volume absorption coefficient
- repeat for every level of atmosphere
- numerically integrate Schwarzschid’s equation

This is computationally expensive:

- Number of lines could be 1000s
- Not a trivial computation

But various fast methods exist that use approximations.

10.7 Radiatively active Gases

Radiatively active gases are atmospheric gases which absorb/emit in some relevant wavelength in the atmosphere and therefore influence the radiation budget. The following are most relevant. Their vertical distribution is shown in lecture 9, and their spectra in Figure 3. Generally, the distribution of these gases is determined by the sources and sinks, and their life time (i.e. how much they can be transported to different levels before they are destroyed).

- Water vapour: Mainly in the troposphere. It enters the atmosphere at ground level (evaporation) and is removed through precipitation, so in the troposphere the amount decreases with height. In the stratosphere there are no sinks, so it has a long lifetime and is well distributed, i.e. constant volume mixing ratio (VMR).
  
  Water vapour is the most important radiatively active gas, absorbs in wide bands, particularly in the infrared (outgoing terrestrial radiation!).

- Carbon dioxide: It has a constant vertical distribution, because it does not take part in chemical processes in the atmosphere (no sources and sinks, long lifetime), so that it’s well mixed throughout the atmosphere. (To be precise: there are sources and sinks at the surface, but they are small compared to the actual concentration, so that it’s generally well mixed)
Figure 3: The top panel shows the black body curves for solar radiation and terrestrial radiation. At the very low end of the solar spectrum (wavelengths less than 300 nm) the atmosphere becomes opaque due to the electronic spectrum of oxygen. The figure also shows the absorption at ground level (i.e. the combined effect of all gases) and at 11 km (i.e. only stratosphere). The main difference is the effect of water vapour in the troposphere.

- Ozone: Ozone is produced by chemical processes involving hard solar radiation and three body collisions. The radiation increases with height, but the probability for three-body-collisions decreases with height, so that the maximum VMR is somewhere in between at ca 35 km. As ozone reacts easily, the VMR decreases both above and below this level.
- Methane is produced at the surface (decomposition of organic matter). It is slowly destroyed by oxidation in the atmosphere (lifetime ca 15 years), so it is well mixed with almost constant distribution in the troposphere, but the concentration decreases with height in the stratosphere where it is transported only by slower diffusion processes.
- Nitrogen oxides: Qualitatively, the same Nitrogen oxides show the same distribution as Methane, for similar reasons (produced at surface, lifetime 100 years).
- CFC, halocarbons, organics: Produced at the surface (anthropogenic). Different life times (some organics quite short, halocarbons several centuries). Concentration decreases in the stratosphere.