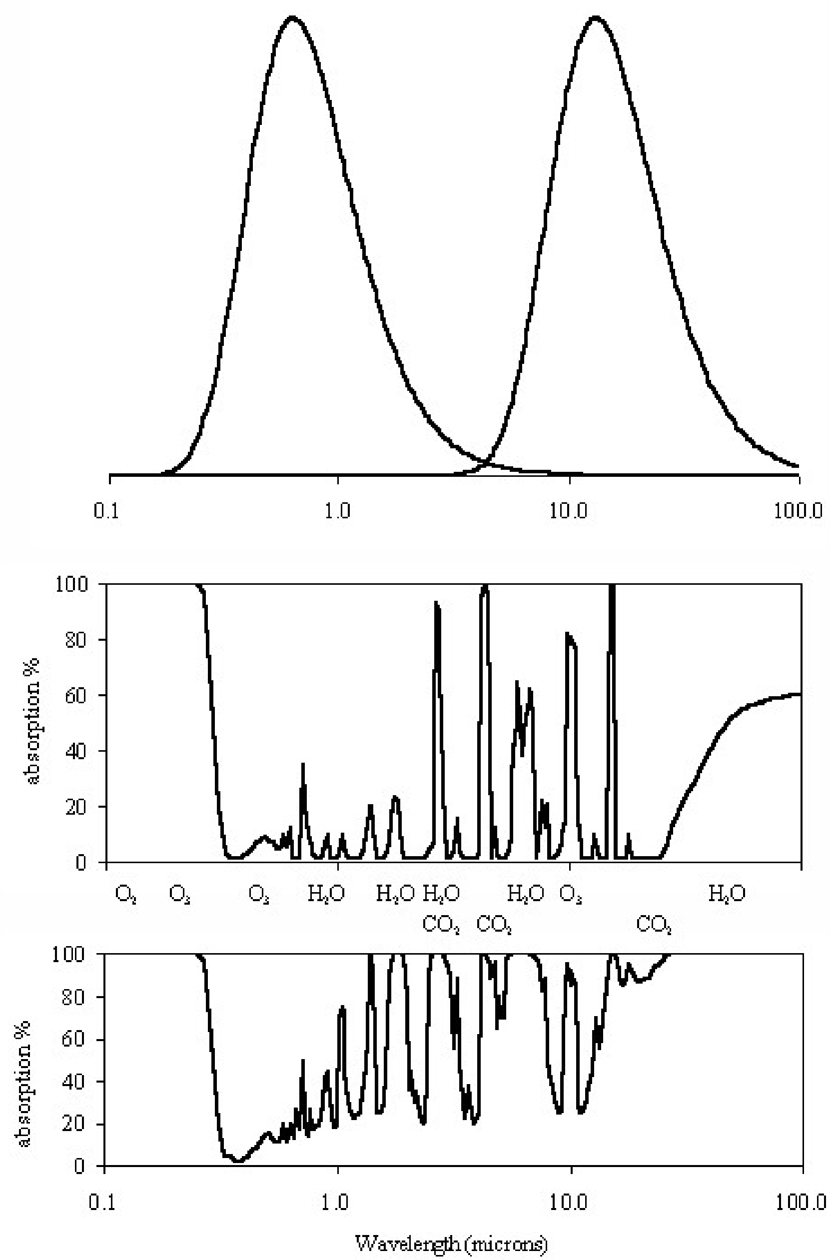
Absorption of Radiation by Trace Gases

So far we have assumed that the atmosphere acts simply to scatter and reflect incoming shortwave radiation and does not absorb light.

However this is not the case.

The atmosphere interacts with both incoming solar radiation and outgoing terrestrial radiation.

The strength of the interaction as a function of wavelength is responsible for the heating of the lower atmosphere.



SHORTWAVE RADIATION

Blackbody curves for emitters at 5777 K and 280 K are shown in the previous figure

Also shown is the fraction of light entering the top of the earth's atmosphere that is absorbed before reaching 10 km (middle panel) and sea level (bottom panel) as a function of wavelength.

At 10 km (top of the troposphere) virtually all radiation below 290 nm has been absorbed. All radiation below 100 nm is absorbed in the thermosphere above 100 km. O_2 absorbs strongly at wavelengths between 100 and 200 nm and also in a weaker band between 200 and 245 nm.

O_2 absorptions attenuate incoming UV radiation of less than 200 nm above an altitude of 50 km. Light of wavelengths of between 200 and 300 nm is strongly absorbed in the stratosphere by ozone (O_3) and transmission of radiation of wavelengths less than 290 nm is negligible below 10 km.

Between 300 and 800 nm the stratosphere is only weakly absorbing and most of the solar radiation at these wavelengths is transmitted into the troposphere.

There is little tropospheric absorption below 600 nm but H_2O and CO_2, at high tropospheric concentrations, deplete the near IR part of the incoming solar flux appreciably. Hence, surface solar irradiance is dominated by visible wavelengths.

LONGWAVE RADIATION

Much of the outgoing radiation is absorbed in the lowest 10 km where several different molecules are efficient absorbers of upwelling IR radiation

Much of the outgoing radiation of wavelengths less than 7 μm is absorbed by water vapour, with some contribution from methane and nitrous oxide, N_2O.

Light of wavelengths longer than 13 μm is efficiently absorbed by CO_2. This band, centred at 15 μm, is important as it lies close to the maximum of the longwave irradiance spectrum.

At longer wavelengths water vapour is excited into many rotational states that effectively form an absorption continuum beyond 25 μm.

Minor absorbers between the CO_2 and water bands are mainly N_2O and CH_4. The only fraction of the outgoing radiation that is transmitted through the troposphere without undergoing appreciable absorption lies in the so-called atmospheric window between 7 and 13 μm.

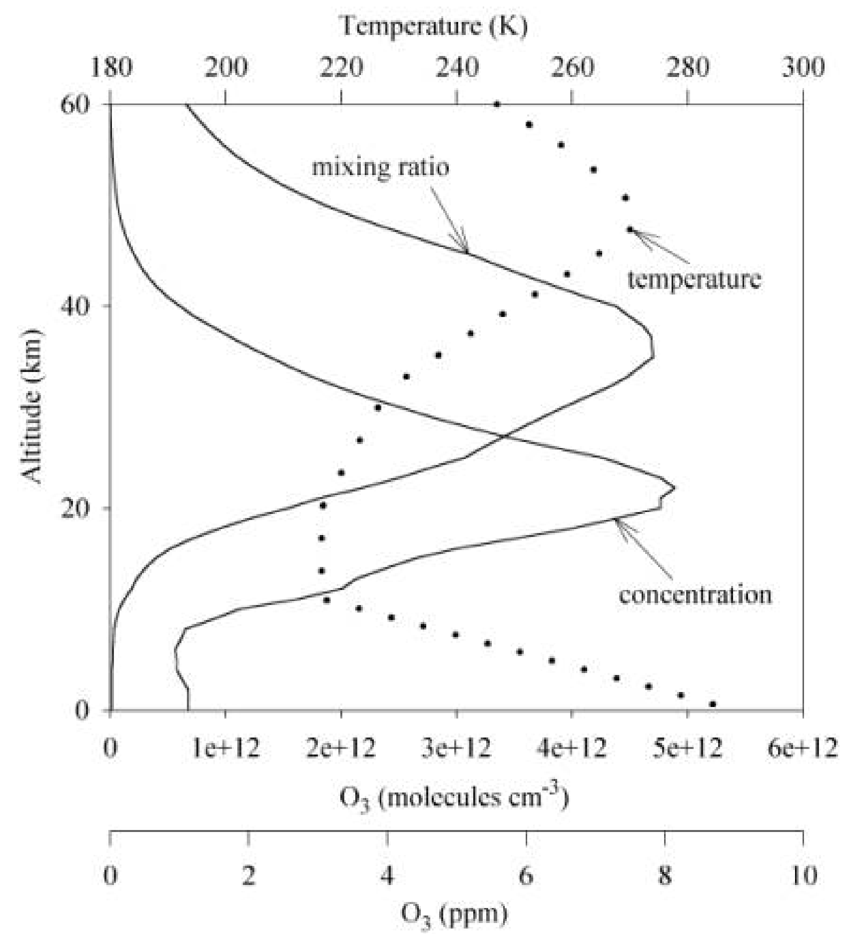
The only significant absorptions of infra-red radiation in the stratosphere are due to ozone. The 9.6 μm band of ozone happens to lie in the middle of the atmospheric window and as a result means that stratospheric ozone plays a significant role in the outgoing longwave radiation budget of the Earth.

Solar Radiation, Ozone and Stratospheric Temperature

We have already seen that ozone is a very efficient absorber of solar radiation between 200 and 300 nm.

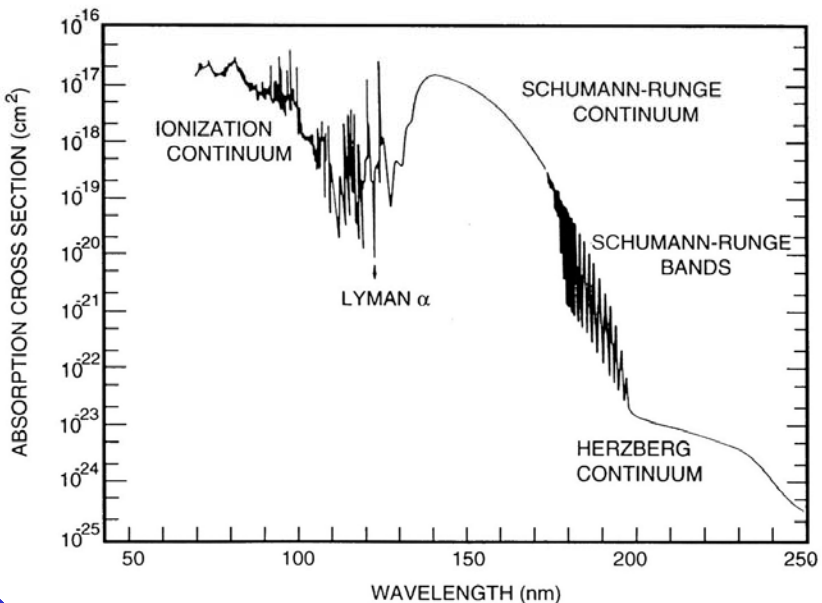
The main layer of ozone in the atmosphere is situated between 15 and 30 km and reaches a maximum concentration of around 5 x 10^{12} molecules cm^{-3} at 22 km.

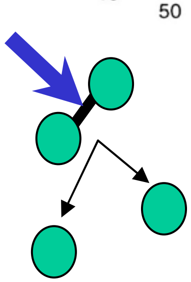
The maximum temperature at the top of the stratosphere occurs at around 50 km, well above the main ozone layer. To understand the effect of stratospheric ozone on the temperature profile we need to understand the way ozone is created and destroyed in the mesosphere and stratosphere.



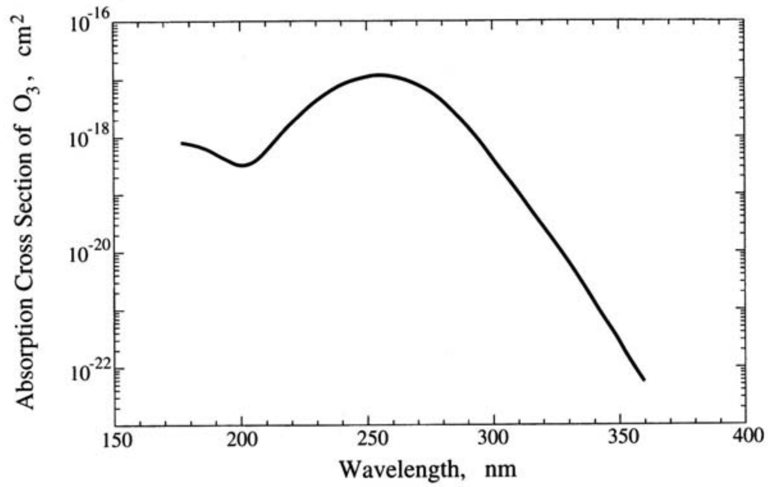
Ozone Photolysis

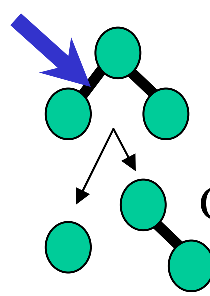
Ozone is formed from the photo-dissociation of molecular oxygen but is itself removed by photo-dissociation. Photo-dissociation is the fragmentation of a molecule as a result of its absorption of a photon that is energetic enough to break its molecular bonds. Both O_2 and O_3 absorb ultra-violet (UV) light very strongly and prevent highly energetic radiation penetrating to lower altitudes.





O_2 absorption cross section

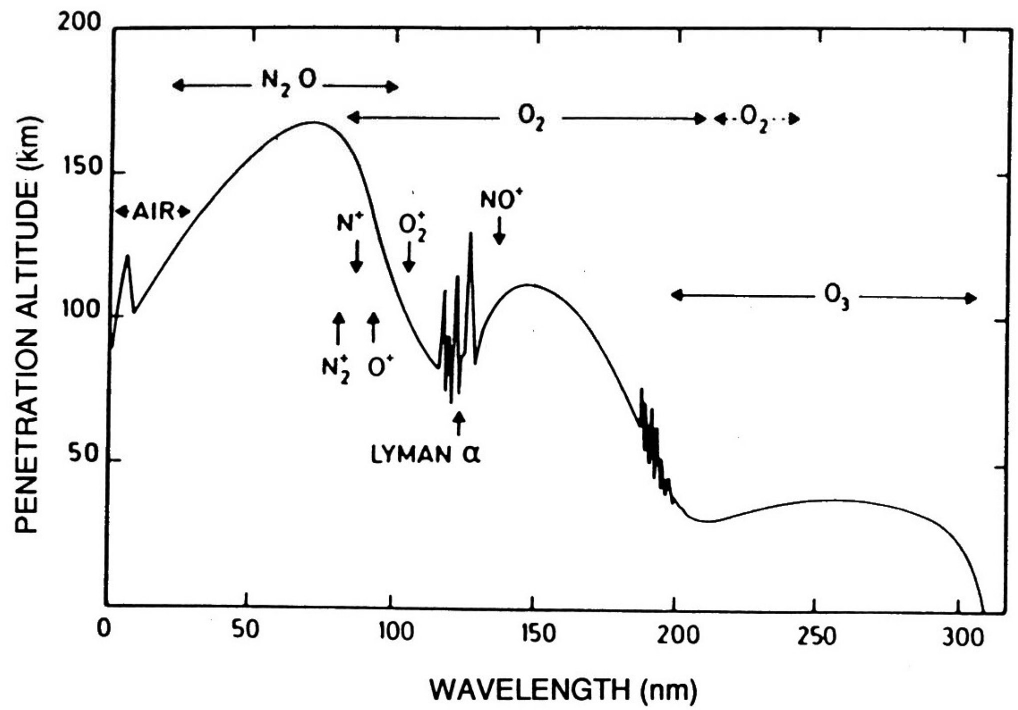




O_3 absorption cross section

The penetration of UV light

The extent to which UV light penetrates the Earth's atmosphere as a function of wavelength
Also shown are the gas species responsible for its absorption



UV Photo-Dissociation of O_2 and O_3 and Stratospheric Temperature 1

Ozone is formed from the photo-dissociation of molecular oxygen but is itself removed by photo-dissociation. Photo-dissociation is the fragmentation of a molecule as a result of its absorption of a photon that is energetic enough to break its molecular bonds. Both O_2 and O_3 absorb ultra-violet (UV) light very strongly and prevent highly energetic radiation penetrating to lower altitudes.

The peak in the absorption cross section of O_2 occurs in the Schumann-Runge continuum at around 145 nm. For wavelengths less than 175 nm O_2 is dissociated into two oxygen atoms, one of which is electronically excited. This strong absorption prevents sunlight of wavelengths below 175 nm from penetrating below around 70 km. The oxygen atoms formed as a result of O_2 photolysis react with other molecules of O_2 to form ozone.

Strong absorption cross sections of ozone occurring between 240 and 300 nm with a maximum value of 1.1×10^{-17} cm^2 at 255 nm. As a result, above 60 km ozone is photolysed very efficiently back to O_2 and atomic oxygen, reducing its concentration and favouring the existence of atomic oxygen.

UV Photo-Dissociation of O_2 and O_3 and Stratospheric Temperature 2

The Herzberg continuum between 200 and 240 nm is responsible for photolysis of O_2 below 60 km because the shorter wavelengths have already been removed while radiation of these wavelengths penetrates down to around 20 km.

High up in the atmosphere little O_3 is produced as the air density is low and there is little O_2 to be photolysed or to subsequently react with the atomic oxygen formed by its photolysis.

As we descend through the atmosphere the density increases, favouring ozone formation via the combination of atomic and molecular oxygen and the concentration of ozone increases.

A maximum concentration in O_3 is observed at around 20 to 25 km. Lower in the stratosphere the overhead ozone column is now significant and absorbs much of the radiation between 200 and 290 nm, thus limiting photolysis of oxygen and slowing the rate of ozone formation. The concentration of ozone reduces and reaches a minimum by the tropopause where radiation of less than 290 nm is almost completely removed.

UV Photo-Dissociation of O_2 and O_3 and Stratospheric Temperature

The absorption of UV radiation by both oxygen and ozone leads to their photolysis and the energy involved in these sunlight-induced reactions produces local warming. The temperature at a particular altitude will then be a combination of the rates of photolysis of the two oxygen species, in particular ozone, and the air density.

The rates of photolysis will depend on the local incidence of radiation and thus on the optical density of the atmosphere in the column above at a given wavelength. This in turn will be dependent on the overhead concentration profile of O_2 and O_3 themselves.

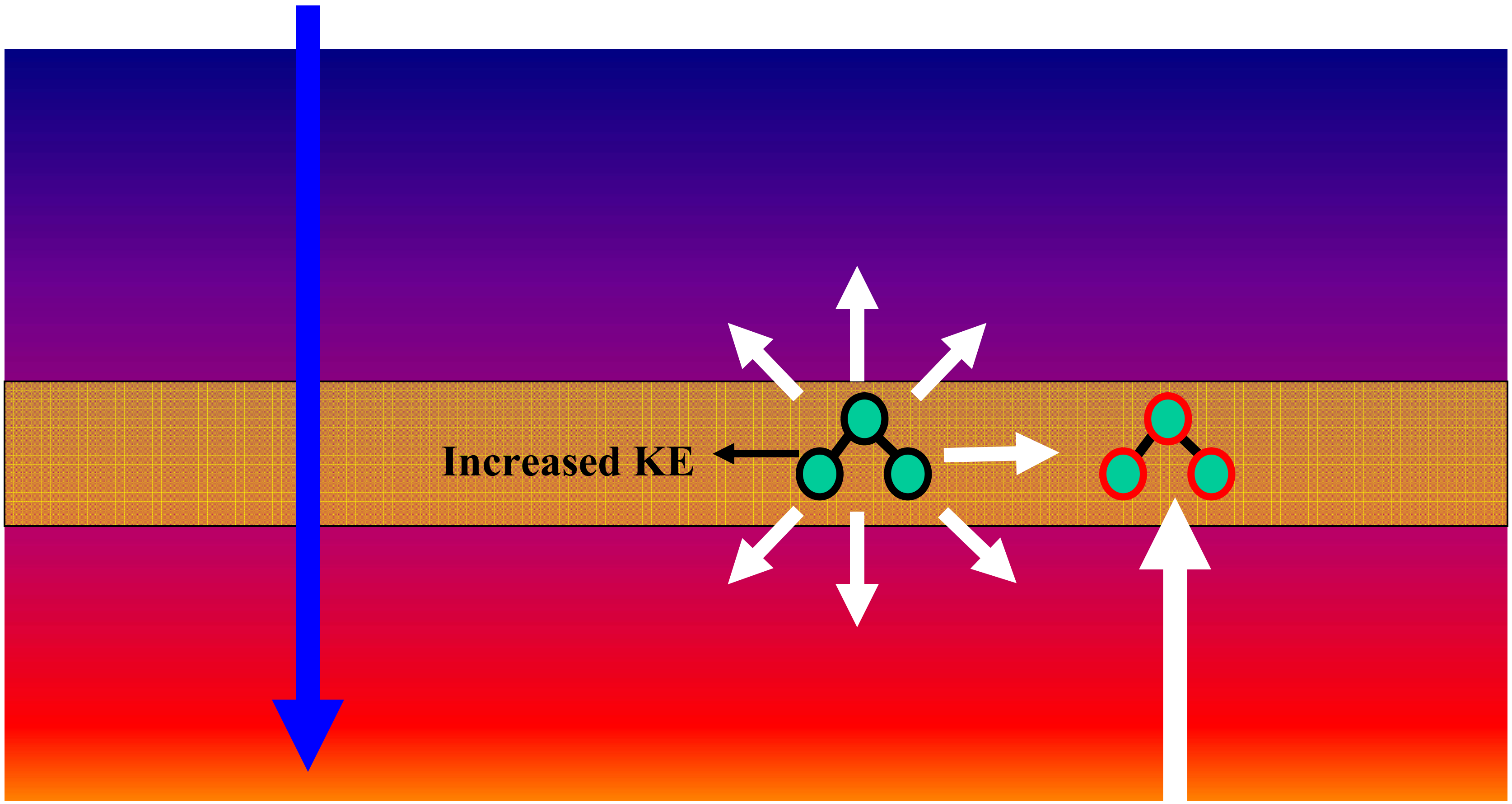
As the air density increases any products of photo-chemical processes that remain energetically excited are deactivated more rapidly via an increased chance of collisions, leading to an increase in temperature.

Although the temperature profile is strongly linked to that of ozone its maximum occurs not at the maximum ozone concentration, but above it and close to the region where the photolytic formation and loss processes of ozone are most rapid.

Trapping of Longwave Radiation 1

Incoming Visible no absorption

Upwelling IR absorbed by CO_2, H_2O, N_2O, CH_4, CFCs etc and re-radiated in all directions



Trapping of Longwave Radiation 2

Photons in the IR region are less energetic and induce vibrational and rotational excitations of molecules. These excitations do not cause chemical changes in the absorbing molecule, instead the excited molecule, below 100 km at least, is rapidly deactivated by collisions and the energy absorbed from the original photon is distributed thermally.

We can imagine the effect on a layer of atmosphere as a result of these interactions. Some fraction of the outgoing longwave radiation entering the base of the layer is absorbed by molecules such as CO_2, H_2O and CH_4 in the layer.

The absorbed energy is transferred to kinetic energy by collisions between the absorbing molecules and others in the layer. The layer will itself act as a blackbody and re-radiate infra-red radiation, however the layer will radiate uniformly in all directions and so acts to increase the longwave flux through the lower layers of the atmosphere.

This process raises the local temperature in the lower layers of the atmosphere above that predicted from a straightforward equilibrium calculation performed earlier.