Vertical Structure of the Atmosphere

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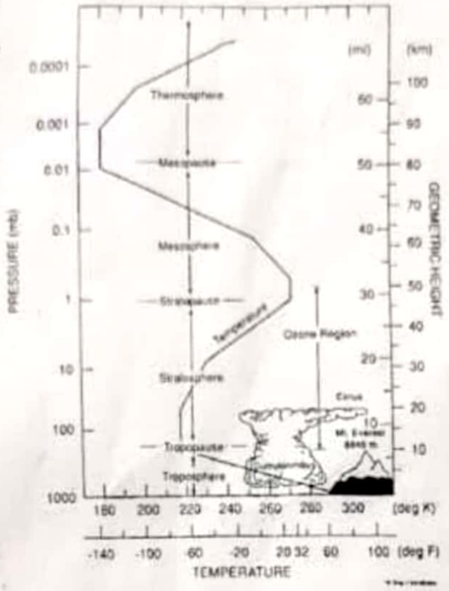

Figure 1.5. Vertical profile of the temperature between the surface and 100 km altitude as as defined in the U.S. Standard Atmosphere (1976) and related atmosphere layers. Note that the tropopause level is represented for midlatitude conditions. Cumulonimbus clouds in the tropics extend to the tropical tropopause located near 18 km altitude.

Reasons for the temperature profile:
- adiabatic vertical transport
- radiative cooling by water vapour
- absorption in the ozone layer
- oxygen absorption in the thermosphere

Consequences of the temperature profile:
- strong mixing in the troposphere
- low vertical mixing in the stratosphere
- very low humidity in the stratosphere (tropopause acts as a cooling trap)

Why should we care about Atmospheric Chemistry?

- scientific interest
- atmosphere is created / needed by life on earth
- humans breath air
- humans change the atmosphere by
    - air pollution
    - changes in land use
    - tropospheric oxidants
    - acid rain
    - climate changes
    - ozone depletion
    - ...
- atmospheric chemistry has an impact on atmospheric dynamics, meteorology, climate

The aim is

1. to understand the past and current atmospheric constitution
2. to predict future atmospheric constitution
3. to provide input for political decisions affecting atmospheric constitution

Solar Radiation

Solar Radiation in the earth's atmosphere has two main effects:

- heating
- energy input for deviations from equilibrium

Most chemical processes in the atmosphere are started by energy input from the sun; the consequences are determined by kinetics. الناتج

Energy of photons:

$$E = h\nu = hc/\lambda$$

h = Planck's constant, c = velocity of light
L=Lohschmidt's number

Convenient units:

$$E(\text{per mole}) = Lh\nu$$
$$= Lhc/\lambda$$
$$= \frac{119625}{\lambda}\frac{\text{KJ}}{\text{mol}}$$

$\Rightarrow$ extreme red (800nm) $\approx$ 150KJ/mol
extreme blue (400nm) $\approx$ 300 KJ/mol

$\Rightarrow$ visible light can produce electronic transitions up to photolysis of loosely bound chemical species

- scattering by air molecules (Rayleigh scattering)
- scattering by aerosols and clouds (Mie scattering)

⇒ The photon flux in the atmosphere is a strong function of wavelength, height, solar elevation and atmospheric constitution

Radiation in the Atmosphere

Source: sun, black body radiation of approx. 6000 K, cooler in the UV, warmer in the IR, strong absorptions in the solar atmosphere (Fraunhofer lines)

In the earth's atmosphere, there is مهم جدا

- strong absorption by O_2, O, N_2, and O_3 in the UV and many other absorbers in the IR (H_2O, CO_2, CH_4, ...)

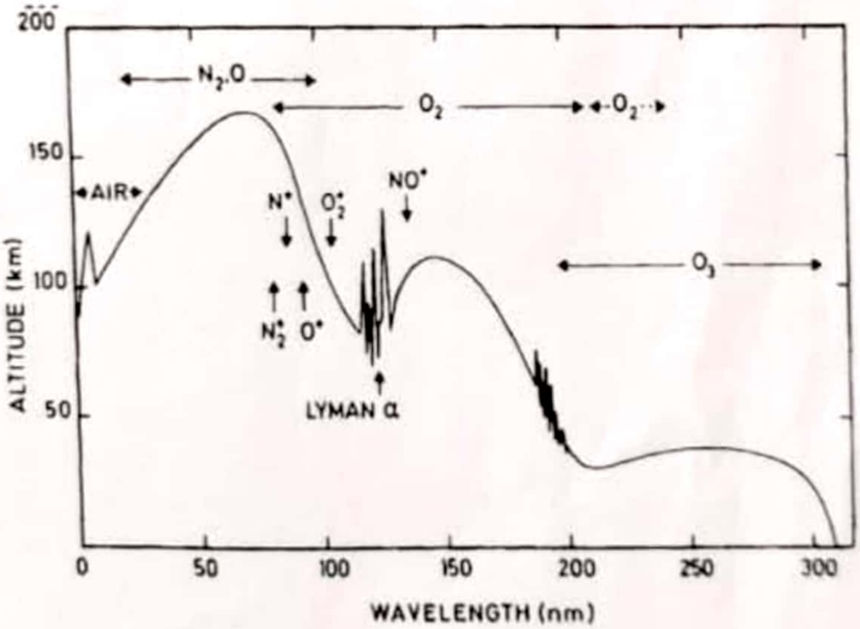

Fig. 4.3. Depth of penetration of solar radiation as a function of wavelength. Altitudes correspond to an attenuation of 1/e. The principle absorbers and ionization limits are indicated.

Absorption of Light

When photons are absorbed by a molecule, they change the energy states of

- the electrons
- the vibration
- the rotation

In general, energy levels of atoms or molecules are discrete, and the energy of the absorbed photon must fit the difference in energy

$$\nu = \Delta E / h$$

(**Resonance Condition**).

The **Intensity of a Transition** is determined by

- electronic transition moment, computed from the wavefunctions and transition dipole
- population of the upper and lower states

To avoid computation of the transition moment, often **Selection Rules** are given ($\Delta S=0$ or $\Delta L=\pm 1$ in atoms) to decide which transitions are allowed, and which forbidden.