

Lecture 6

Composition and structure of the atmosphere.

Basic properties of atmospheric gases.

Objectives:

1. Composition of the atmosphere:
 - Basic properties of atmospheric gases
 - Structure of molecules
2. Structure of the atmosphere:
 - Vertical structure of the atmosphere
 - Hydrostatic law

Required reading:

G: 1.3-1.5, 3.2.1

Additional/advanced reading

CNES online tutorial Session 1

<http://ceos.cnes.fr:8100/cdrom-00/ceos1/science/dg/dgcon.htm>

1. Composition of the atmosphere.

Atmosphere is composed of:

- Gases
- Aerosols (see Lecture 8)
- Water and ice cloud droplets (see Lecture 8)

➤ Atmospheric gases

Table 6.1 The gaseous composition of the atmosphere

Gases	% by volume	Comments
Constant gases		
Nitrogen, N ₂	78.08%	Photochemical dissociation high in the ionosphere; mixed at lower levels
Oxygen, O ₂	20.95%	Photochemical dissociation above 95 km; mixed at lower levels
Argon, Ar	0.93%	Mixed up to 110 km
Neon, Ne	0.0018%	Mixed in most of the middle atmosphere
Helium, He	0.0005%	
Krypton, Kr	0.00011%	
Xenon, Xe	0.000009%	
Variable gases		
Water vapor, H ₂ O	4.0% (maximum, in the tropics) 0.00001% (minimum, at the South Pole)	Highly variable; photodissociates above 80 km dissociation
Carbon dioxide, CO ₂	0.0365% (increasing ~0.4% per year)	Slightly variable; mixed up to 100 km; photodissociates above
Methane, CH ₄	~0.00018% (increases due to agriculture)	Mixed in troposphere; dissociates in mesosphere
Hydrogen, H ₂	~0.00006%	Variable photochemical product; decreases slightly with height in the middle atmosphere
Nitrous oxide, N ₂ O	~0.00003%	Slightly variable at surface; dissociates in stratosphere and mesosphere
Carbon monoxide, CO	~0.000009%	Variable
Ozone, O ₃	~0.000001% - 0.0004%	Highly variable; photochemical origin
Fluorocarbon 12, CF ₂ Cl ₂	~0.00000005%	Mixed in troposphere; dissociates in stratosphere

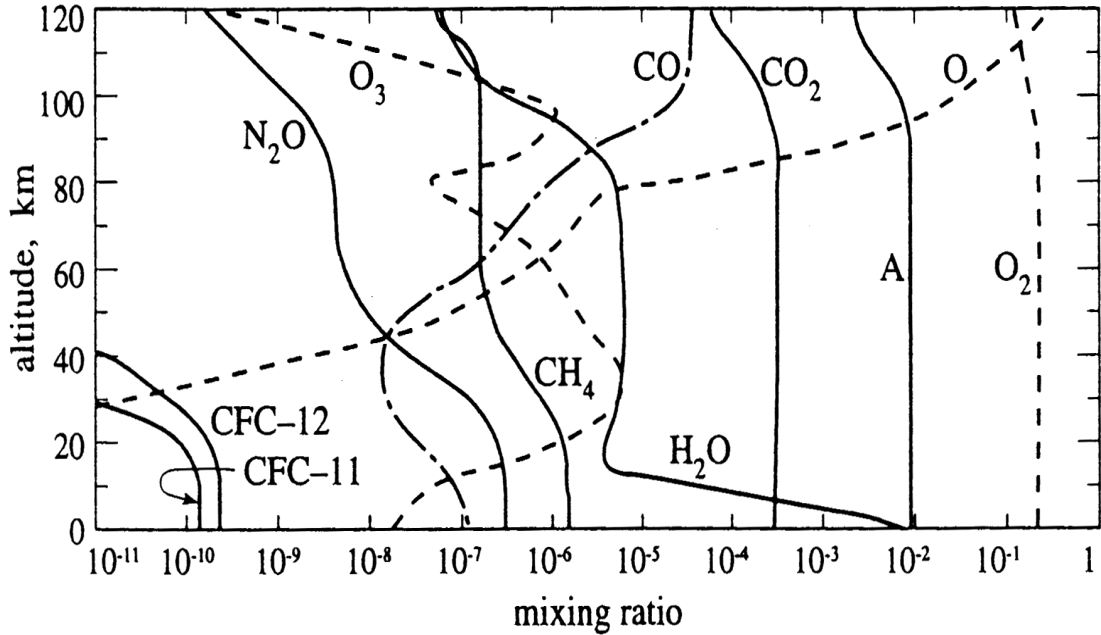


Figure 6.1 Vertical profiles of mixing ratios of some gases in the atmosphere.

Some important properties of atmospheric gases:

➤ *Obey the ideal gas laws:*

Boyle's law: $V \sim 1/P$ (at constant T and the number of gas moles μ)

Charles's law: $V \sim T$ (at constant P and μ)

Avogadro's law: $V \sim$ number of gas molecules (at constant P and T)

The equation of state: says that the pressure exerted by a gas is proportional to its temperature and inversely proportional to its volume:

$$P V = \mu R T$$

where R is the universal gas constant. If pressure P is in atmospheres (atm), volume V in liters (L) and temperature T in degrees Kelvin (K), thus R has value

$$R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

➤ The amount of the gas may be expressed in several ways:

i) **Molecular number density = molecular number concentration = molecules per unit volume of air;**

ii) **Density = molecular mass concentration = mass of gas molecules per unit volume of air;**

iii) **Mixing ratios:**

Volume mixing ratio is the number of gas molecules in a given volume to the total number of all gases in that volume (when multiplied by 10^6 , in ppmv (parts per million by volume))

Mass mixing ratio is the mass of gas molecules in a given volume to the total mass of all gases in that volume (when multiplied by 10^6 , in ppmm (parts per million by mass))

NOTE: Commonly used mixing fraction: one part per million 1 **ppm** (1×10^{-6}); one part per billion 1 **ppb** (1×10^{-9}); one part per trillion 1 **ppt** (1×10^{-12}).

iv) **Mole fraction** is the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture.

NOTE: mole fraction is equivalent to the volume fraction.

NOTE: The equation of state can be written in several forms:

using molar concentration of a gas, $c = \mu/v$: **$P = c T R$**

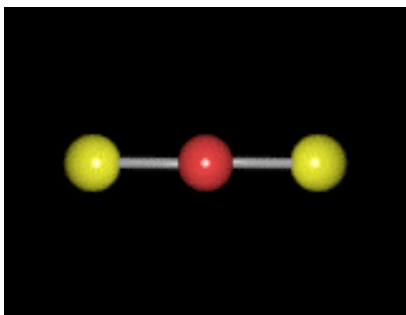
using number concentration of a gas, $N = c N_A$: **$P = N T R/N_A$ or $P = N T k_B$**

using mass concentration of a gas, $q = c m_g$: **$P = q T R / m_g$**

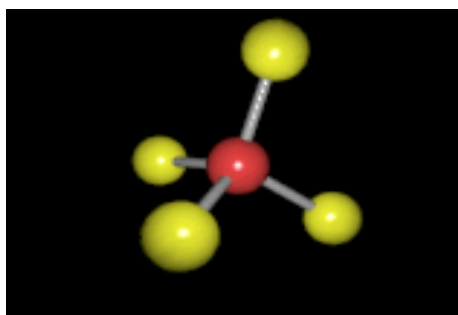
➤ Structure of molecules

Based on the geometric structure, molecules can be divided into four types

- **Linear molecules** (CO_2 , N_2O ; C_2H_2 , all diatomic molecules (e.g., O_2 , N_2 , etc))
- **Symmetric top molecules** (NH_3 , CH_3Cl)
- **Spherical symmetric top molecules** (CH_4)
- **Asymmetric top molecules** (H_2O , O_3):



CO₂



CH₄

Rotational and vibrational motions of the molecules:

- Molecules as a rigid quantized rotator:

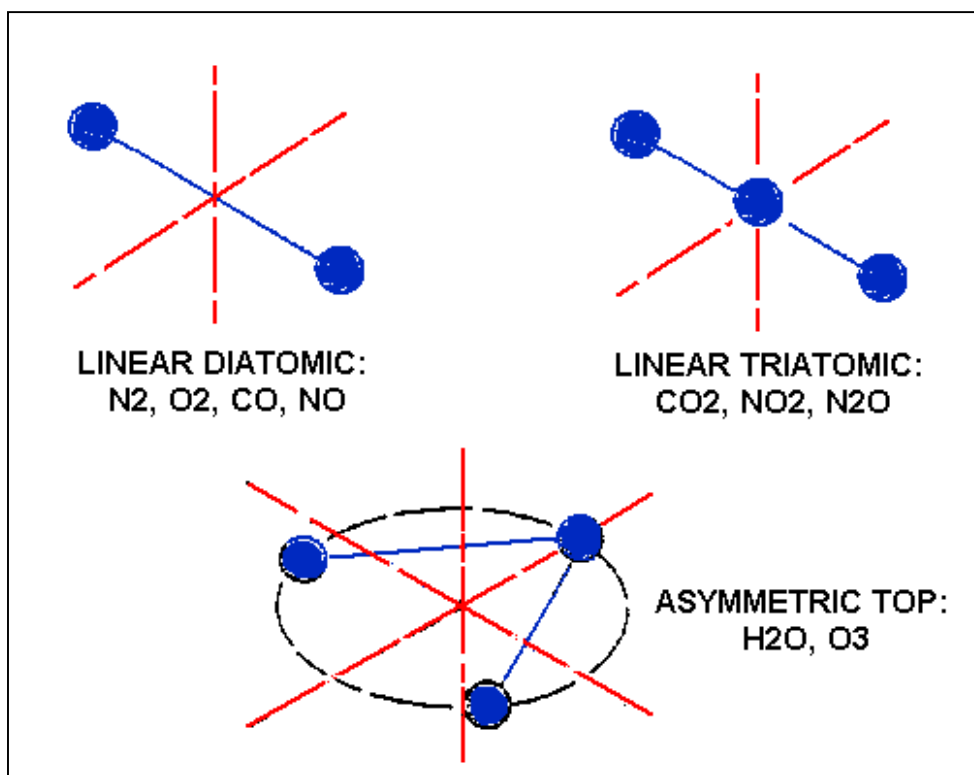


Figure 6.2 Axes (in red) of rotational freedom for linear and asymmetric top molecules.

- Molecules as a quantized vibrator:

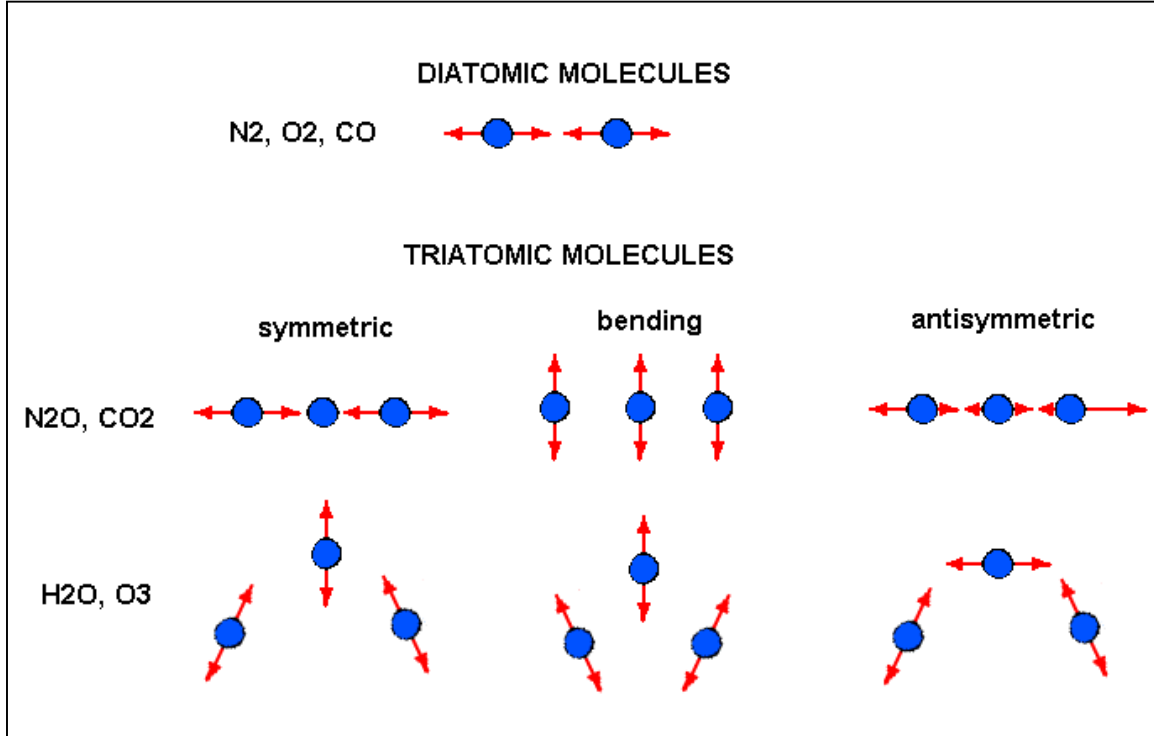


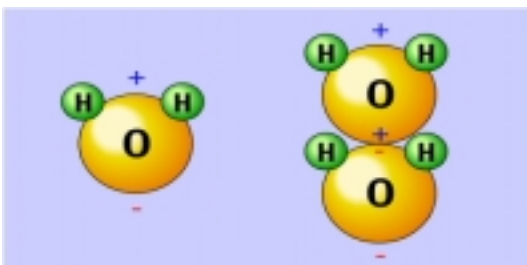
Figure 6.3 Vibrational modes of diatomic and triatomic atmospheric molecules.

NOTE: The number of independent vibrational modes (called **normal modes**) of a molecule with $N > 2$ atoms are $3N - 6$ for non-linear molecules and $3N - 5$ for a linear molecule.

- **The geometrical structure of a molecule determines its dipole.**

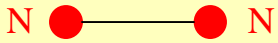
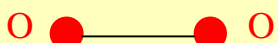
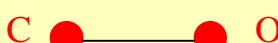
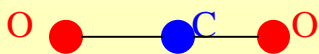
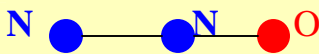
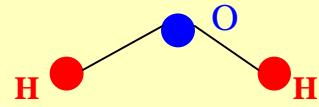
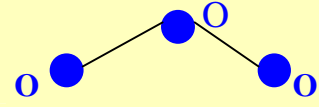
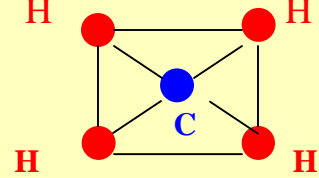
NOTE: A **dipole** is represented by centers of positive and negative charges Q separated by a distance d : **the dipole moment** = $Q d$

Example: water molecule



The unique way in which the hydrogen atoms are attached to the oxygen atom causes one side of the molecule to have a negative charge and the area in the opposite direction to have a positive charge. The resulting polarity of charge causes molecules of water to be attracted to each other forming strong molecular bonds.

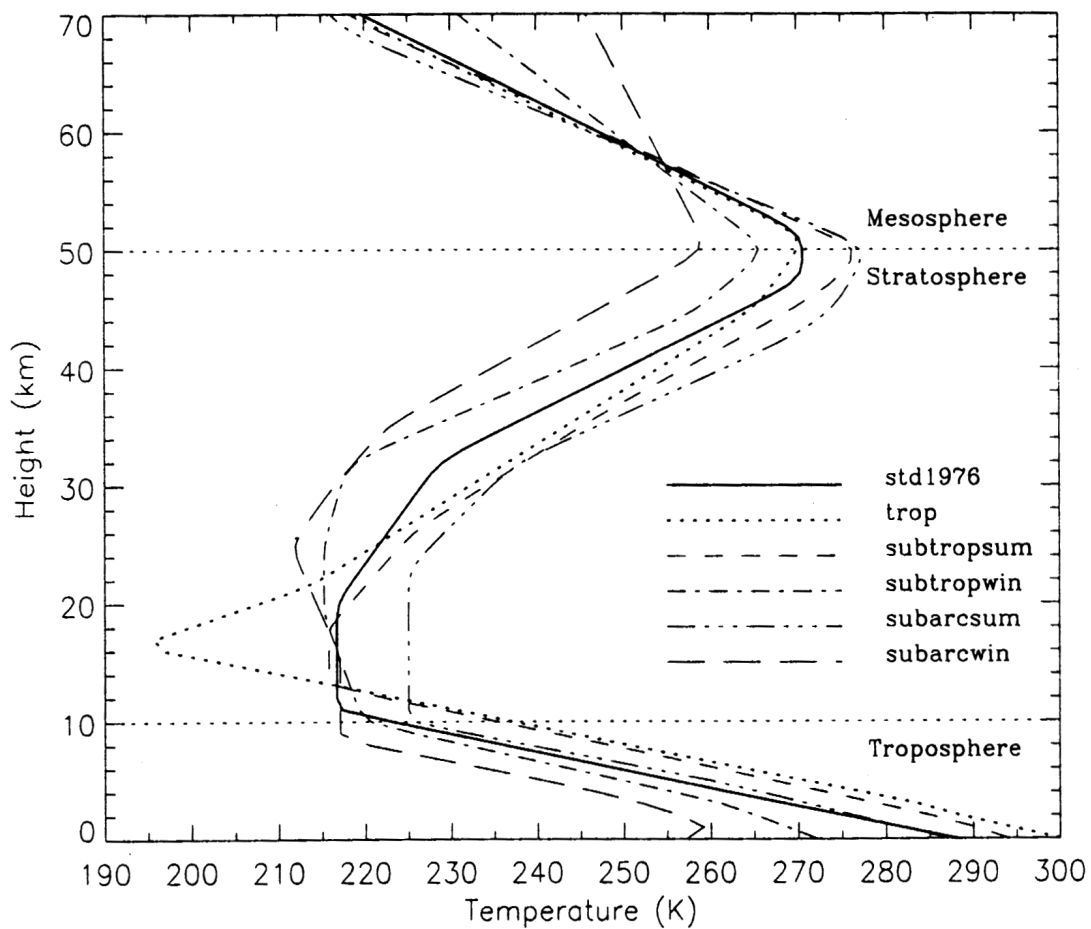
Table 6.2 Atmospheric molecule structure and dipole moment status.

Molecule	Structure	Permanent dipole moment	May acquire dipole moment
N ₂		No	No
O ₂		No	No
CO		Yes	Yes
CO ₂		No	Yes (in two vibrational modes)
N ₂ O		Yes	Yes
H ₂ O		Yes	Yes
O ₃		Yes	Yes
CH ₄		No	Yes (in two vibrational modes)

2. Structure of the atmosphere.

- Variations of temperature, pressure and density are much larger in vertical directions than in horizontal. This strong vertical variations result in the atmosphere being **stratified** in layers that have small horizontal variability compare to the variations in the vertical.

Figure 6.4 Temperature profiles of the standard atmospheric models often used in radiative transfer calculations. “Standard U.S. 1976 atmosphere” is representative of the global mean atmospheric conditions; “Tropical atmosphere” is for latitudes $< 30^{\circ}$; “Subtropical atmosphere” is for latitudes between 30° and 45° ; “Subarctic atmosphere” is for latitudes between 45° and 60° ; and “Arctic atmosphere” is for latitudes $> 60^{\circ}$.



- Except cases with temperature inversion, temperature always decreases in the lower troposphere.

Temperature lapse rate is the rate at which temperature decreases with increasing altitude.

$$\Gamma = - (T_2 - T_1) / (z_2 - z_1) = - \Delta T / \Delta z$$

where T is temperature and the height z.

- **Adiabatic process** is of special significance in the atmosphere because many of the temperature changes that take place in the atmosphere can be approximated as adiabatic.

For a parcel of dry air under adiabatic conditions it can be shown that

$$dT/dz = - g/c_p$$

where c_p is the heat capacity at constant pressure per unit mass of air and $c_p = c_v + R/m_a$ and m_a is the molecular weight of dry air. The quantity g/c_p is a constant for dry air equal to **9.76 C per km**. This constant is called **dry adiabatic lapse rate**.

- **The law of hydrostatic balance** states, that the pressure at any height in the atmosphere is equal to the total weight of the gas above that level.

The hydrostatic equation: $dP(z) / dz = - \rho(z) g$

where $\rho(z)$ is the mass density of air at height z, and $g = 9.81 \text{ m/s}^2$ is the acceleration of gravity.

- Integrating the hydrostatic equation at constant temperature as a function of z gives

$$P = P_0 \exp(-z / H)$$

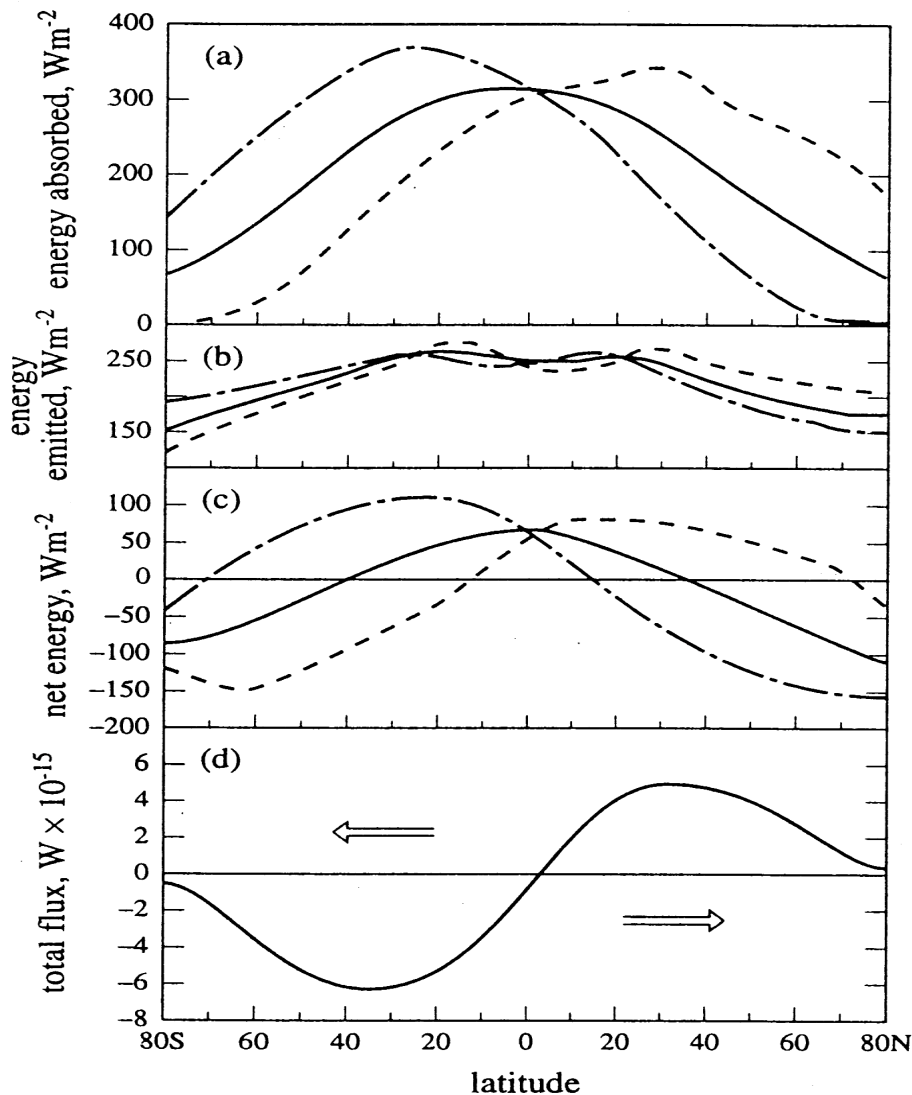
where H is **the scale height:** $H = k_B T / mg$; and m is the average mass of air molecule ($m = 4.8096 \times 10^{-26} \text{ kg/air molecule}$).

➤ **Air motion**

The key energy sources driving the wind systems on our planet:

- a) **Solar radiation** (energy emitted by Sun)
- b) Latent heat
- c) Thermal radiation (energy emitted by the surface of the Earth and the atmosphere)

Figure 4.4 Latitudinal distributions of radiative fluxes at TOA, except (d) which gives the horizontal flux that must be carried across latitudes. Solid curves are annual averages; dash-dot and dashed curves are averages over NH winter and summer months, respectively (from Goody, 1995).



NOTE:

- The uneven distribution of solar energy results from latitudinal variations in solar insolation (more in tropics, less at poles), and from differences in absorptivity of the Earth's surface. It creates the large-scale air motion to transport energy from the tropics toward the polar regions.
- This energy transport is affected by the rotation of Earth (the Coriolis effect). Thus, the general pattern of global air circulation is chiefly due to both solar radiation and Earth rotation.