

## Lecture 4.

### Composition and structure of the atmosphere.

#### Absorption and emission by atmospheric gases.

1. Structure and composition of the Earth's atmosphere.
2. Properties of atmospheric gases.
3. Basic principles of molecular emission/absorption.
4. Spectral line shapes: Lorentz, Doppler and Voigt profile.
5. Absorption spectra of main atmospheric gases. Summary of satellite sensors for measurements of atmospheric gases.

#### Required reading:

S: 1.3-1.5, 3.1-3.5; Petty: 9

### 1. Structure and composition of the Earth's atmosphere.

#### Temperature

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

$$\Gamma = - (T_2 - T_1) / (z_2 - z_1) = - \Delta T / \Delta z \quad [4.1]$$

where T is temperature and the height z.

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

$$dT/dz = - g/c_p \quad [4.2]$$

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**.

#### Pressure

- ✓ 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:**  $dP(z) / dz = - \rho(z) g \quad [4.3]$

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.

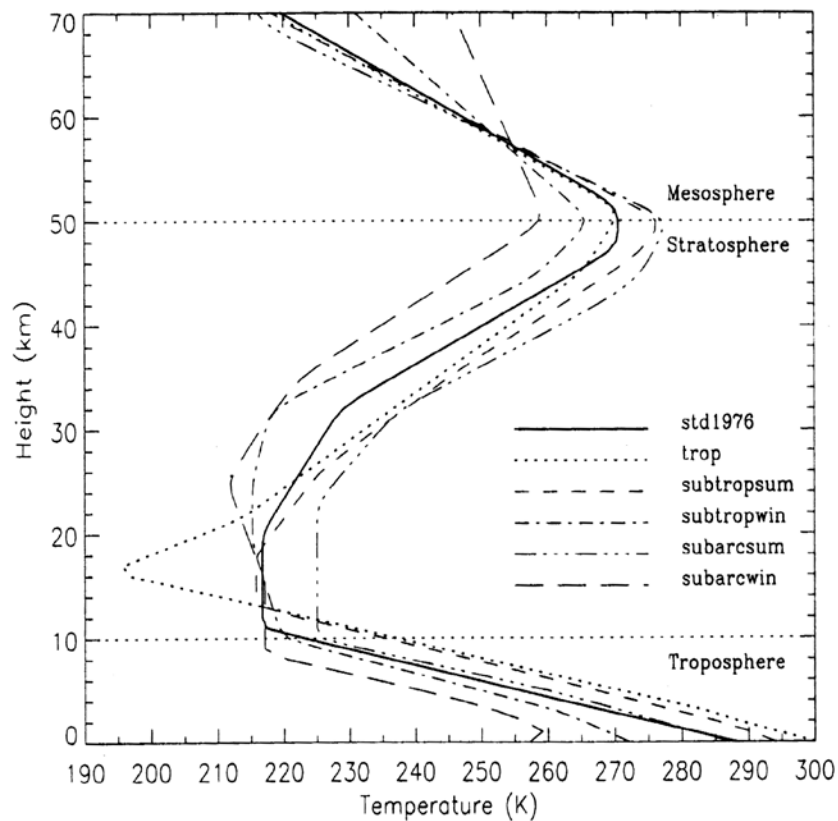
- Integrating the hydrostatic equation at constant temperature as a function of  $z$  gives

$$P = P_0 \exp(-z / H) \quad [4.4]$$

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

**Example:**  $T = 290$  K, gives  $H = 8500$  m ;  $T = 210$  K, gives  $H = 6000$  m

**Standard atmospheric models used in radiative transfer modeling:** each model includes profiles of  $T$ ,  $P$ , and concentration of main gases.



**Figure 4.1** Temperature profiles of the standard atmospheric models which are often used in radiative transfer calculations to represent different climatic zones. “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  $30^{\circ}$  and  $45^{\circ}$ ; “Subarctic atmosphere” is for latitudes between  $45^{\circ}$  and  $60^{\circ}$ ; and “Arctic atmosphere” is for latitudes  $> 60^{\circ}$ .

**Composition (gases)**

**Table 4.1** Three most abundant gases in planetary atmospheres (Yung and DeMore, 1999). Mixing ratios are given in parentheses. All compositions refer to the surface or 1 bar for the giant planets.

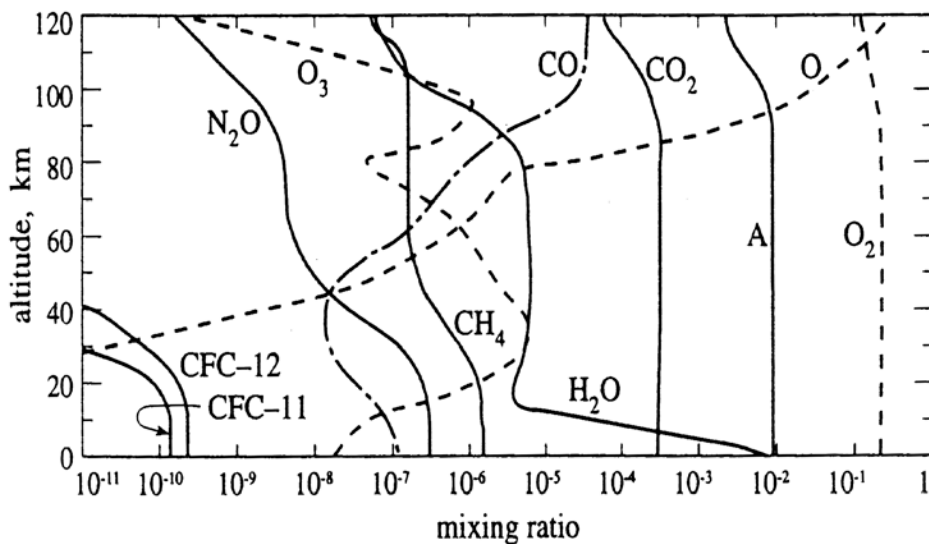
Jupiter	H <sub>2</sub> (0.93)	He (0.07)	CH <sub>4</sub> (3.0x10 <sup>-3</sup> )
Saturn	H <sub>2</sub> (0.96)	He (0.03)	CH <sub>4</sub> (4.5x10 <sup>-3</sup> )
Uranus	H <sub>2</sub> (0.82)	He (0.15)	CH <sub>4</sub> (1 –2 x10 <sup>-2</sup> )
Neptune	H <sub>2</sub> (0.80)	He (0.19)	CH <sub>4</sub> (2.0x10 <sup>-3</sup> )
Titan	N <sub>2</sub> (0.95-0.97)	CH <sub>4</sub> (3.0x10 <sup>-2</sup> )	H <sub>2</sub> (2.0x10 <sup>-3</sup> )
Triton	N <sub>2</sub> (0.99)	CH <sub>4</sub> (2.0x10 <sup>-2</sup> )	CO (<0.01)
Pluto	N <sub>2</sub> (?)	CH <sub>4</sub> (?)	CO (?)
Io	SO <sub>2</sub> (0.98)	SO (0.05)	O (0.01)
Mars	CO <sub>2</sub> (0.95)	N <sub>2</sub> (2.7x10 <sup>-2</sup> )	Ar (1.6x10 <sup>-2</sup> )
Venus	CO <sub>2</sub> (0.96)	N <sub>2</sub> (3.5x10 <sup>-2</sup> )	SO <sub>2</sub> (1.5x10 <sup>-4</sup> )
<b>Earth</b>	<b>N<sub>2</sub> (0.78)</b>	<b>O<sub>2</sub> (0.21)</b>	<b>Ar (9.3x10<sup>-3</sup>)</b>

**Table 4.2** The gaseous composition of the Earth's atmosphere

Gases	% by volume	Comments
<b>Constant gases</b>		
Nitrogen, N <sub>2</sub>	78.08%	Photochemical dissociation high in the ionosphere; mixed at lower levels
Oxygen, O <sub>2</sub>	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%	
<b>Variable gases</b>		
Water vapor, H <sub>2</sub> O	4.0% (maximum, in the tropics) 0.00001% (minimum, at the South Pole)	Highly variable; photodissociates above 80 km dissociation

Carbon dioxide, CO <sub>2</sub>	0.0365% (increasing ~0.4% per year)	Slightly variable; mixed up to 100 km; photodissociates above
Methane, CH <sub>4</sub>	~0.00018% (increases due to agriculture)	Mixed in troposphere; dissociates in mesosphere
Hydrogen, H <sub>2</sub>	~0.00006%	Variable photochemical product; decreases slightly with height in the middle atmosphere
Nitrous oxide, N <sub>2</sub> O	~0.00003%	Slightly variable at surface; dissociates in stratosphere and mesosphere
Carbon monoxide, CO	~0.000009%	Variable
Ozone, O <sub>3</sub>	~0.000001% - 0.0004%	Highly variable; photochemical origin
Fluorocarbon 12, CF <sub>2</sub> Cl <sub>2</sub>	~0.00000005%	Mixed in troposphere; dissociates in stratosphere

- ✓ 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. Therefore, a plane-parallel model of the atmosphere is often used in modeling the propagation of radiation through the atmosphere.



**Figure 4.2** Representative vertical profiles of mixing ratios of some gases in the Earth's atmosphere.

**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** ( $1 \times 10^{-6}$ ); one part per billion 1 **ppb** ( $1 \times 10^{-9}$ ); one part per trillion 1 **ppt** ( $1 \times 10^{-12}$ ).

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,  $q = c m_g$ :  **$P = q T R / m_g$**

Avogadro's number:  $N_A = 6.02212 \times 10^{23}$  molecules/mole

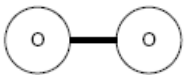
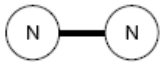
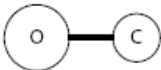
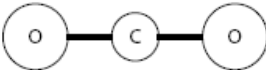


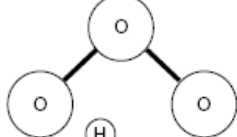
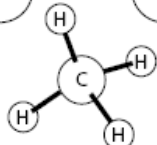
**2. Properties of atmospheric gases.**

- ✓ Atmospheric gases are highly selective in their ability to absorb and emit radiation. Each radiatively active gas has a specific absorption spectrum – its own signature.
- ✓ An atmosphere is the mixture of gases and thus the abundance of gases in the atmosphere controls the overall spectral absorption.
- ✓ Radiatively active gases in the Earth's atmosphere are highly variable in space and time.
- ✓ The ability of a molecule to absorb (emit) radiation is determined by its structure which controls whether the molecule has a dipole.

- **Structure of molecules:** is important for understanding energy forms and the ability of a molecule to absorb/emit radiation:

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

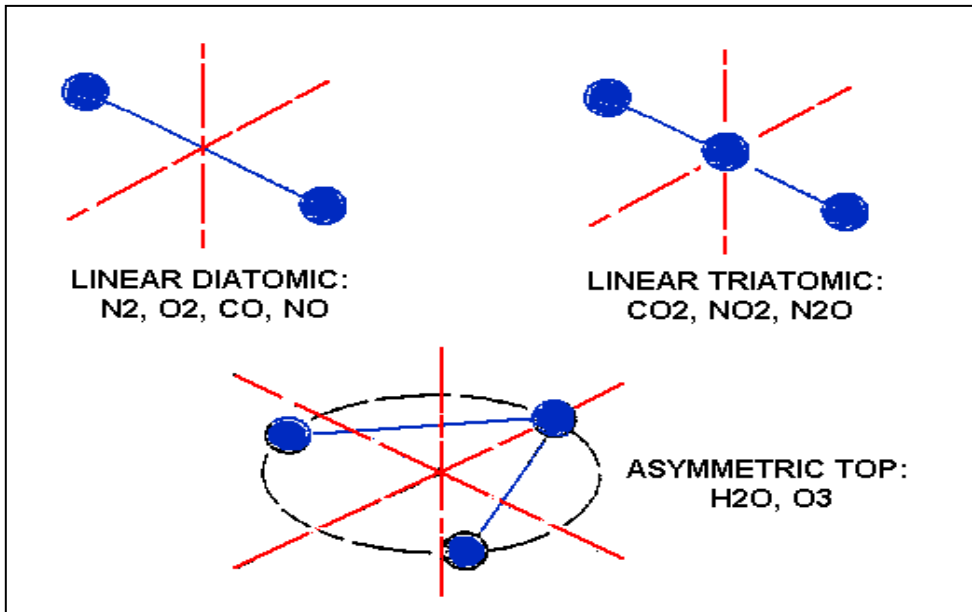
- Linear molecules ( $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ;  $\text{C}_2\text{H}_2$ , all diatomic molecules (e.g.,  $\text{O}_2$ ,  $\text{N}_2$ , etc))
- Symmetric top molecules ( $\text{NH}_3$ ,  $\text{CH}_3\text{Cl}$ )
- Spherical symmetric top molecules ( $\text{CH}_4$ )
- Asymmetric top molecules ( $\text{H}_2\text{O}$ ,  $\text{O}_3$ ):

Molecule	Structure		Permanent Electric Dipole Moment?	May acquire dipole moment
Oxygen		linear	No (magnetic dipole)	No
Nitrogen		linear	No	No
Carbon Monoxide		linear	Yes	Yes
Carbon Dioxide		linear	No	Yes
Nitrous Oxide		linear	Yes	Yes
Water		asymmetric top	Yes	Yes
Ozone		asymmetric top	Yes	Yes
Methane		spherical top	Yes	Yes

**Figure 4.3** Molecular structures of key atmospheric gases and the dipole moment status.

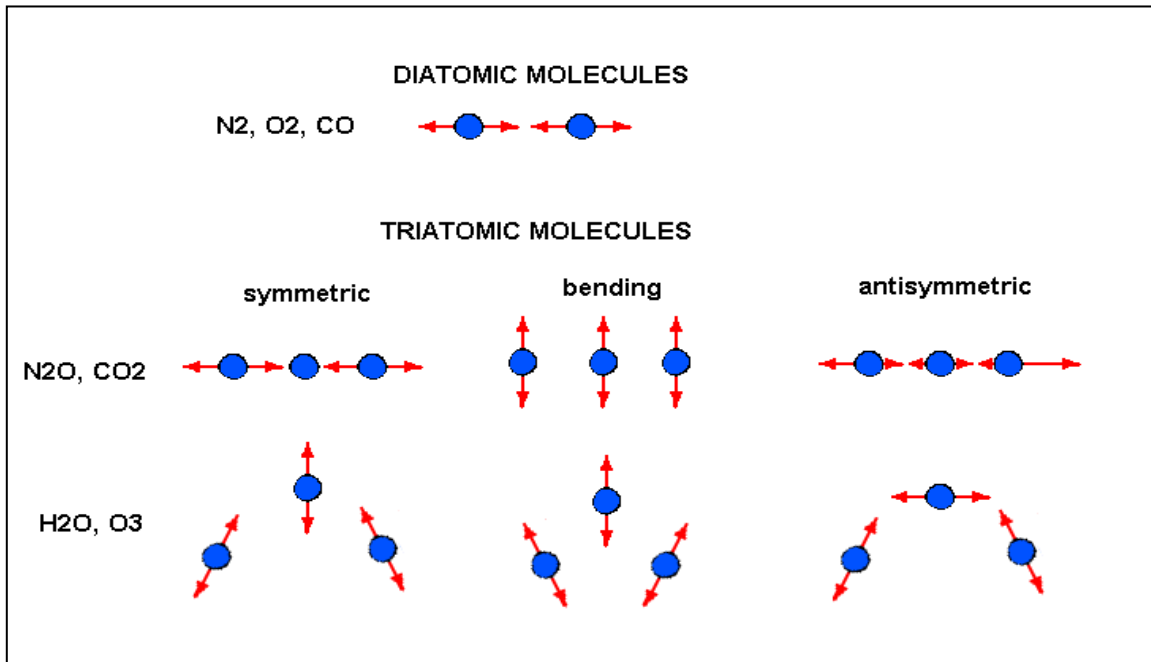
**Rotational and vibrational motions of the molecules:**

- *Molecules as a rigid quantized rotator:*



**Figure 4.4** Axes (in red) of rotational freedom for linear (2 degrees of rotational freedom and 2 equal moments of inertia) and asymmetric top molecules (3 degrees of rotational freedom and 3 unequal moments of inertia => H<sub>2</sub>O and O<sub>3</sub> have very complex spectra

- *Molecules as a quantized vibrator:*



**Figure 4.5** Vibrational modes of diatomic and triatomic atmospheric molecules.

### 3. Basic principles of molecular emission/absorption.

1) The origins of absorption/emission lie in exchanges of energy between gas molecules and electromagnetic field.

2) In general, total energy of a molecule can be represented as:

$$E = E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} + E_{\text{tr}}$$

$E_{\text{rot}}$  is the kinetic energy of rotation (energy of the rotation of a molecule as a unit body): about  $1\text{-}500\text{ cm}^{-1}$  (far-infrared to microwave region)

$E_{\text{vib}}$  is the kinetic energy of vibration: energy of vibrating atom about their equilibrium positions; about  $500\text{ to }10^4\text{ cm}^{-1}$  (near- to far-IR)

$E_{\text{el}}$  is the electronic energy: potential energy of electron arrangement; about  $10^4\text{-}10^5\text{ cm}^{-1}$  (UV and visible)

$E_{\text{tr}}$  is translation energy: exchange of kinetic energy between the molecules during collisions; about  $400\text{ cm}^{-1}$  for  $T = 300\text{ K}$

- From  $E_{\text{rot}} < E_{\text{tr}} < E_{\text{vib}} < E_{\text{el}}$  follows that:

i) Rotational energy change will accompany a vibrational transition. Therefore,

**vibration-rotation bands are often formed.**

ii) Kinetic collisions, by changing the translation energy, influence rotational levels strongly, vibrational levels slightly, and electronic levels scarcely at all.

- **Energy  $E_{\text{rot}}$ ,  $E_{\text{vib}}$ , and  $E_{\text{el}}$  are quantized** and have only discrete values specified by one or more **quantum numbers**. Not all transitions between quantized energy level are allowed - they are subject to selection rules.

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3) Radiative transitions of purely rotational energy require that a molecule possess a permanent electrical or magnetic dipole moment.

- If charges are distributed symmetrically => no permanent dipole moment => no radiative activity in the far-infrared (i.e., no transitions in rotational energy)

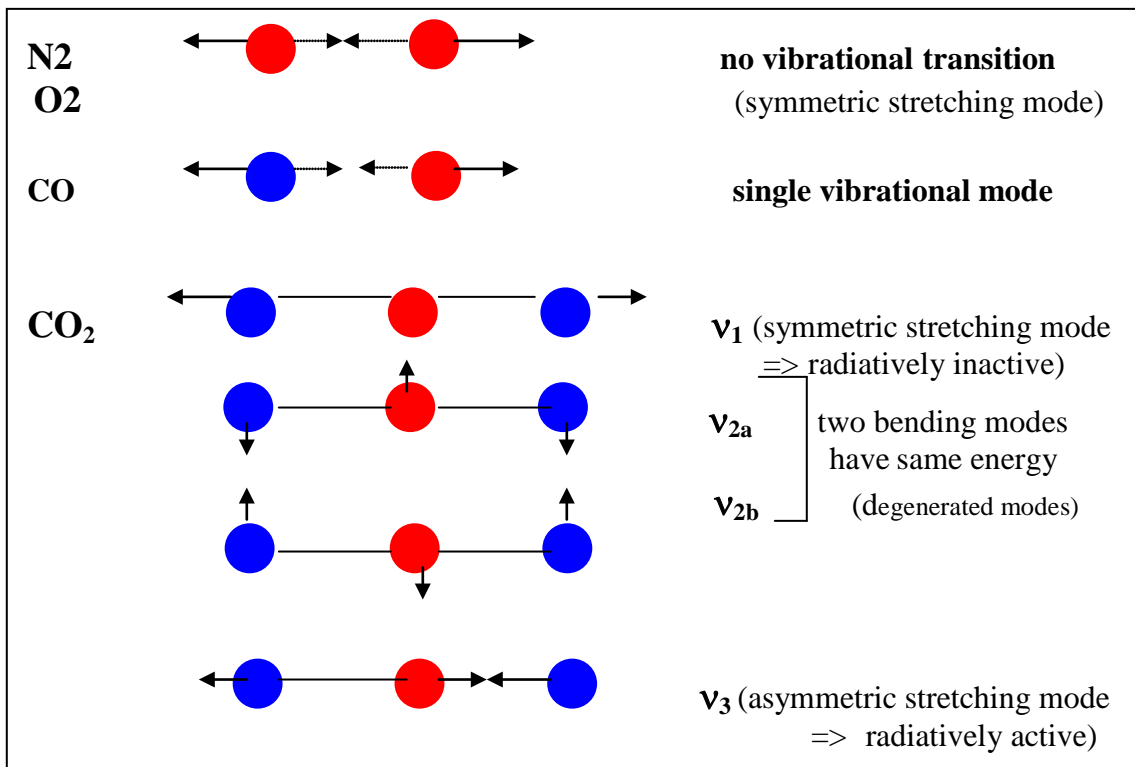
*Example:* homonuclear diatomic molecules ( $\text{N}_2$ ,  $\text{O}_2$ );

- $\text{O}_2$  has a weak permanent magnetic dipole and thus has a rotational transition in microwave.



- **CO, N<sub>2</sub>O, H<sub>2</sub>O** and **O<sub>3</sub>** exhibit pure rotational spectra because they all have the permanent dipoles.
- **CO<sub>2</sub>** and **CH<sub>4</sub>** don't have permanent dipole moment => no pure rotational transitions. But they can acquire the oscillating dipole moments in their vibrational modes => have vibration-rotation bands

**4) Radiative transitions of vibrational energy require a change in the dipole moment (i.e., oscillating moment)**



**Figure 4.6** Vibrational modes of diatomic and triatomic atmospheric molecules (see also Figure 4.5)

**NOTE:** Homonuclear diatomic molecules **N<sub>2</sub>** and **O<sub>2</sub>** don't have neither rotational nor vibrational transitions (because of their symmetrical structures) => no radiative activity in the infrared. But these molecules become radiatively active in UV.

**NOTE:** The number of independent vibrational modes of a molecule with  $N > 2$  atoms are  $3N - 6$  for non-linear molecules and  $3N - 5$  for a linear molecule. Both  $\text{H}_2\text{O}$  and  $\text{O}_3$  have three normal band  $\nu_1$ ,  $\nu_2$  and  $\nu_3$ : all are optically active.

$\text{CH}_4$  has nine normal modes but only  $\nu_3$  and  $\nu_4$  are active in IR.

### 5) Electronic transitions

- **Electrons on inner orbits** (close to the atomic nucleus) can be disturbed or dislodged only by photons having the large energies (short-wave UV and X-rays);
- **Electrons on the outermost orbits** can be disturbed by the photons having the energies of UV and visible radiation => these electrons are involved in absorption/emission in the UV and visible.
- Both an atom and a molecule can have the **electronic transitions**. Electronic transitions of a molecule are always accompanied by vibrational and rotational transitions and are governed by numerous selection rules.

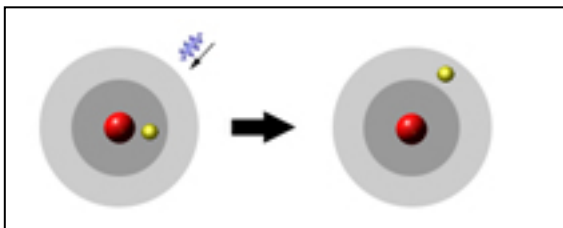
### 4. Spectral line shapes: Lorentz, Doppler and Voigt profile.

#### Atomic Absorption (Emission) Spectrum.

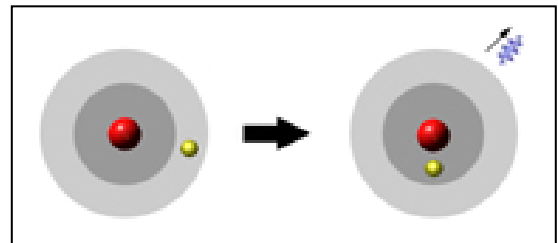
- Radiation emission (absorption) occurs only when an atom makes a transition from one state with energy  $E_k$  to a state with lower (higher) energy  $E_j$ :

$$\text{for emission: } E_k - E_j = h\nu$$

Absorption



Emission

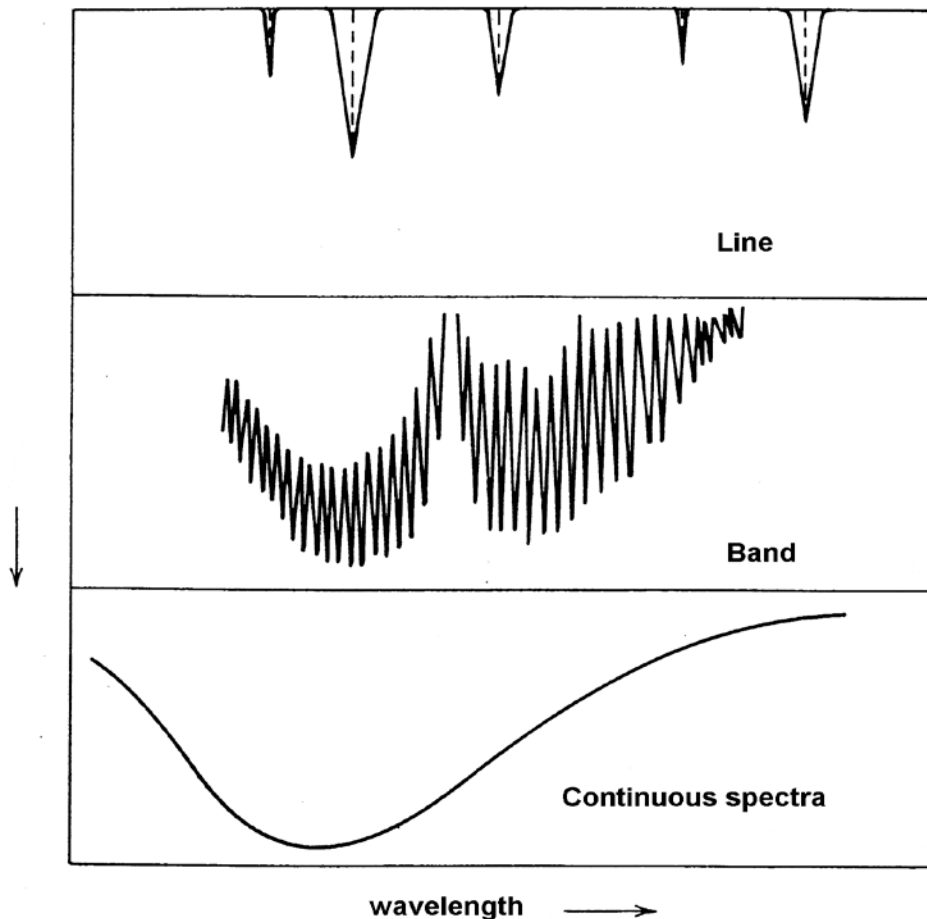


## Molecular Absorption/Emission Spectra

**Molecular absorption spectrum** is substantially more complicated than that of an atom because molecules have several forms of internal energy. This is the subject of **spectroscopy** and **quantum theory**.

### Three types of absorption/emission spectra:

- i) Sharp **lines** of finite widths
- ii) Aggregations (series) of lines called **bands**;
- iii) **Spectral continuum** extending over a broad range of wavelengths



**Figure 4.7** Concept of a line, band, and continuous spectra

**Three main properties that define an absorption line: central position of the line (e.g., the central frequency  $\tilde{\nu}_0$  or wavenumber  $\nu_0$ ), strength of the line (or intensity, S), and shape factor (or profile,  $f$ ) of the line.**

- Each absorption line has a width (referred to as **natural broadening of a spectral line**).
- In the atmosphere, several processes may result in an additional broadening of a spectral line of the molecules: 1) collisions between molecules (referred to as the **pressure broadening**); 2) due to the differences in the molecule thermal velocities (referred to as the **Doppler broadening**); and 3) the combination of the above processes.

**Lorentz profile** of a spectral line is used to characterize the **pressure broadening** and is defined as:

$$f_L(\nu - \nu_0) = \frac{\alpha / \pi}{(\nu - \nu_0)^2 + \alpha^2} \quad [4.5]$$

where  $f(\nu - \nu_0)$  is the shape factor of a spectral line;

$\nu_0$  is the wavenumber of a central position of a line;

$\alpha$  is the half-width of a line at the half maximum (in  $\text{cm}^{-1}$ ), (often referred as a **line width**)

- The **half-width** of the Lorentz line shape is a function of pressure P and temperature T and can be expressed as

$$\alpha(P, T) = \alpha_0 \frac{P}{P_0} \left( \frac{T_0}{T} \right)^n \quad [4.6]$$

where  $\alpha_0$  is the reference half-width for STP:  $T_0 = 273\text{K}$ ;  $P_0 = 1013 \text{ mb}$ .

$\alpha_0$  is in the range from **about 0.01 to 0.1  $\text{cm}^{-1}$**  for most atmospheric radiatively active gases. For most gases  $n=1/2$ .

**NOTE:** The above **dependence on pressure** is very important because atmospheric pressure varies by an order of 3 from the surface to about 40 km.

- The **Lorentz profile** is fundamental in the radiative transfer in the lower atmosphere where the pressure is high.
- The collisions between like molecules (**self-broadening**) produces the large line-widths than do collisions between unlike molecules (**foreign broadening**). Because radiatively active gases have low concentrations, the **foreign broadening** often dominates in infrared radiative transfer.

**Doppler profile** is defined in the absence of collision effects (i.e., pressure broadening) as:

$$f_D(\nu - \nu_0) = \frac{1}{\alpha_D \sqrt{\pi}} \exp \left[ - \left( \frac{\nu - \nu_0}{\alpha_D} \right)^2 \right] \quad [4.7]$$

$\alpha_D$  is the **Doppler line width**

$$\alpha_D = \frac{V_0}{c} (2k_B T / m)^{1/2} \quad [4.8]$$

where  $c$  is the speed of light;  $k_B$  is the Boltzmann's constant,  $m$  is the mass of the molecule (for air  $m = 4.8 \times 10^{-23}$  g).

- The Doppler broadening is important at the altitudes from about 20 to 50 km.

**Voigt profile** is the combination of the Lorentz and Doppler profiles to characterize broadening under the low-pressure conditions (above about 40 km in the atmosphere). (i.e., it is required because the collisions (pressure broadening) and Doppler effect can not be treated as completely independent processes:

$$f_{Voigt}(\nu - \nu_0) = \int_{-\infty}^{\infty} f_L(\nu' - \nu_0) f_D(\nu - \nu') d\nu' = \frac{\alpha}{\alpha_D \pi^{3/2}} \int_{-\infty}^{\infty} \frac{1}{(\nu' - \nu_0')^2 + \alpha^2} \exp \left[ - \left( \frac{\nu - \nu'}{\alpha_D} \right)^2 \right] d\nu' \quad [4.9]$$

**NOTE:** The Voigt profile requires numerical calculations.

**Nature of the Voigt profile:**

- At high pressure: the Doppler profile is narrow compare to the Lorentz profile so under these conditions the Voigt profile is the same as Lorentz profile.
- At low pressure: the behavior is more complicated – a kind of hybrid line with a Doppler center but with Lorentz wings.

**Absorption coefficient** of a gas is defined by the position, strength, and shape of a spectral line:

$$k_{a,\nu} = S f(\nu - \nu_0) \quad [4.10]$$

where **S** in the line intensity and **f** is the line profile:

$$S = \int k_{a,\nu} d\nu \quad \text{and} \quad \int f(\nu - \nu_0) d\nu = 1$$

***Dependencies:***

**S** depends on **T**;

**f(ν - ν<sub>0</sub>, α)** depends on the line halfwidth **α (p, T)**, which depends on pressure and temperature.

- ✓ **Optical depth due to gaseous absorption** is defined as a product of the absorption coefficient and the path length. Because the amount of an absorbing gas may be expressed in a number of possible ways ( e.g., molecules per unit volume, mass of molecules per unit volume, etc.), different kinds of absorption coefficient may be introduced is such a way that the optical depth remains unitless. Introducing a path length (or amount of gas), **u**, we have

$$\tau_\nu = \int_{u_1}^{u_2} k_{a,\nu} du \quad [4.11]$$

**Commonly used absorption coefficients:**

$k_{a,v}$  Volume absorption coefficient (in LENGTH<sup>-1</sup>)

$k_{m,a,v}$  Mass absorption coefficient (in LENGTH<sup>2</sup>/MASS)

$k_{cs,a,v}$  Absorption cross section (in LENGTH<sup>2</sup>) (cross section will also be denoted by  $\sigma$ )

Mass absorption coefficient = volume absorption coefficient/density

Absorption cross section = volume absorption coefficient/number concentration

Thus, optical depth can be expressed in several ways

$$\tau_v(s_1, s_2) = \int_{s_1}^{s_2} k_{a,v} ds = \int_{s_1}^{s_2} \rho k_{m,a,v} ds = \int_{s_1}^{s_2} N k_{cs,a,v} ds \quad [4.12]$$

**Table 3.3** Units used for path length, absorption coefficient, and line intensity

Absorbing gas (path length $u$ )	Absorption coefficient	Line intensity (S)
cm	cm <sup>-1</sup>	cm <sup>-2</sup>
g cm <sup>-2</sup>	cm <sup>2</sup> g <sup>-1</sup>	cm g <sup>-1</sup>
cm <sup>-2</sup>	cm <sup>2</sup>	cm
cm atm	(cm atm) <sup>-1</sup>	cm <sup>-2</sup> atm <sup>-1</sup>

*Units of the line profile,  $f$ :* LENGTH (often cm)

**Monochromatic transmittance  $T_v$  and absorbance** (or absorption)  $A_v$  of radiance along the path are defined as

$$T_v = \exp(-\tau_v) \quad A_v = 1 - T_v = 1 - \exp(-\tau_v) \quad [4.13]$$

**NOTE:** Same name: Transmission function = Transmittance

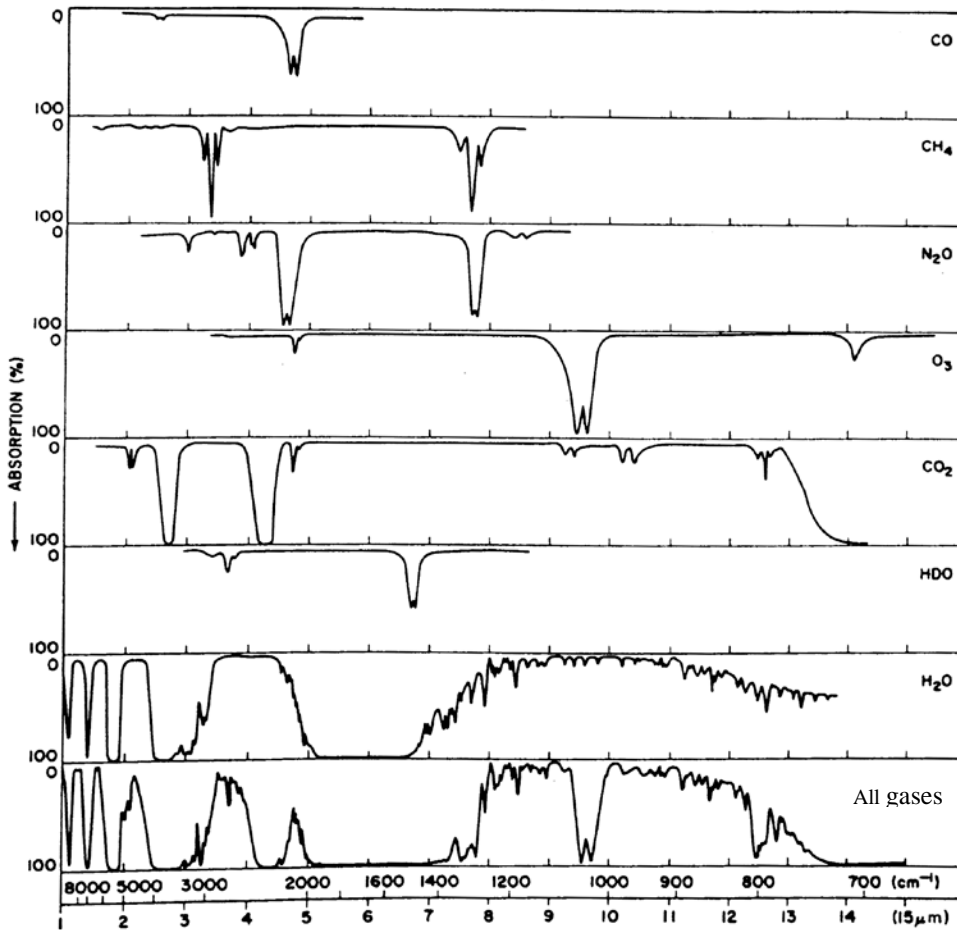
**5. Absorption spectra of main atmospheric gases (H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CFCs).**

- Each atmospheric gas has a specific absorption/emission spectrum – its own radiative signature.
- HITRAN is a main spectroscopic data base that contains information about 1,734,469 spectral lines for 37 different molecules (<http://www.hitran.com/>).

➤ **Microwave region:**

Molecule	Absorption line (Frequency, GHz)
H <sub>2</sub> O	22235; 183.3
O <sub>2</sub>	about 60; 118.75

➤ **Thermal IR region:**



**Figure 4.8** Low-resolution IR absorption spectra of the major atmospheric gases.



**Table 4.4** The most important vibrational and rotational transitions for H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and CFCs.

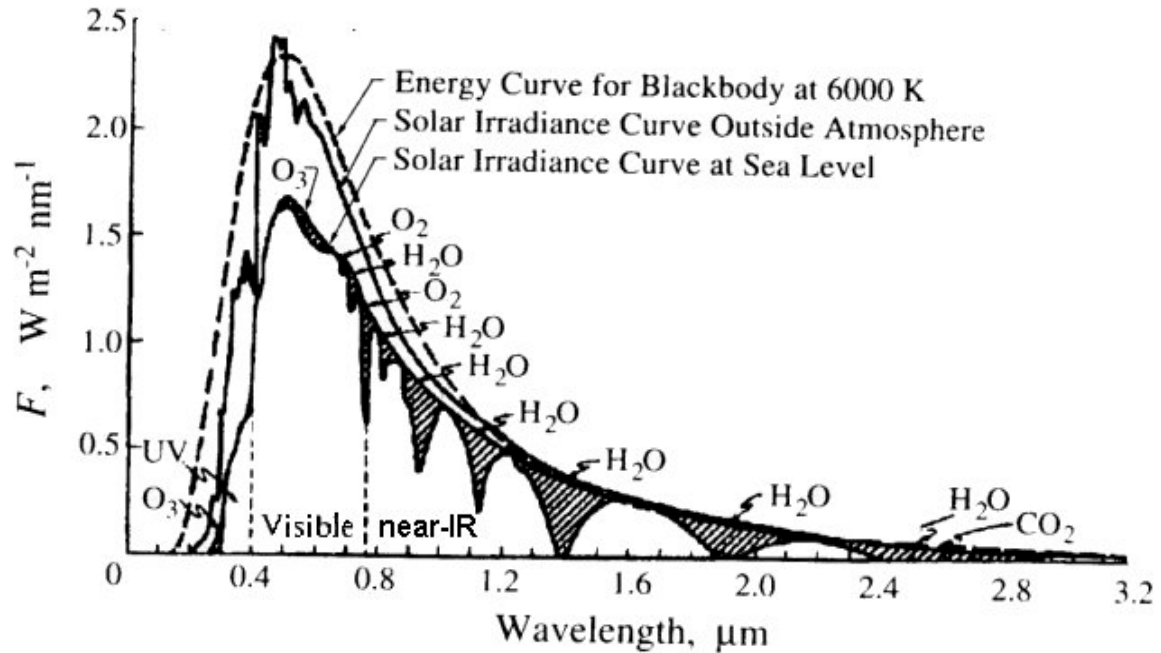
Gas	Center $\nu$ (cm <sup>-1</sup> ) ( $\lambda$ ( $\mu$ m))	Transition	Band interval (cm <sup>-1</sup> )
<b>H<sub>2</sub>O</b>	-	pure rotational	0-1000
	1594.8 (6.3)	$\nu_2$ ; P, R	640-2800
	continuum*	far wings of the strong lines; water vapor dimmers (H <sub>2</sub> O) <sub>2</sub>	200-1200
<b>CO<sub>2</sub></b>	667 (15)	$\nu_2$ ; P, R, Q	540-800
	961 (10.4)	] overtone and combination	850-1250
	1063.8 (9.4)		$\nu_3$ ; P, R
	2349 (4.3)	] overtone and combination	2100-2400
<b>O<sub>3</sub></b>	1110 (9.01)	$\nu_1$ ; P, R	950-1200
	1043 (9.59)	$\nu_3$ ; P, R	600-800
	705 (14.2)	$\nu_2$ ; P, R	600-800
<b>CH<sub>4</sub></b>	1306.2 (7.6)	$\nu_4$	950-1650
<b>N<sub>2</sub>O</b>	1285.6 (7.9)	$\nu_1$	1200-1350
	588.8 (17.0)	$\nu_2$	520-660
	2223.5 (4.5)	$\nu_3$	2120-2270
<b>CFCs</b>			700-1300

**NOTE:** Continuum absorption by water vapor in the region from 800-1200 cm<sup>-1</sup> remains unexplained. It has been suggested that it results from the accumulated absorption of the distant wings of lines in the far infrared. This absorption is caused by collision broadening between H<sub>2</sub>O molecules (called **self-broadening**) and between H<sub>2</sub>O and non-absorbing molecules (N<sub>2</sub>) (called **foreign broadening**).

➤ Near-IR and visible regions:

Absorption of visible and near-IR radiation in the gaseous atmosphere is primarily due to H<sub>2</sub>O, O<sub>3</sub>, and CO<sub>2</sub>.

**NOTE:** Atmospheric gases absorb only a small fraction of visible radiation.



**Figure 4.9** Solar spectral irradiance (flux) at the top of the atmosphere and at the surface.

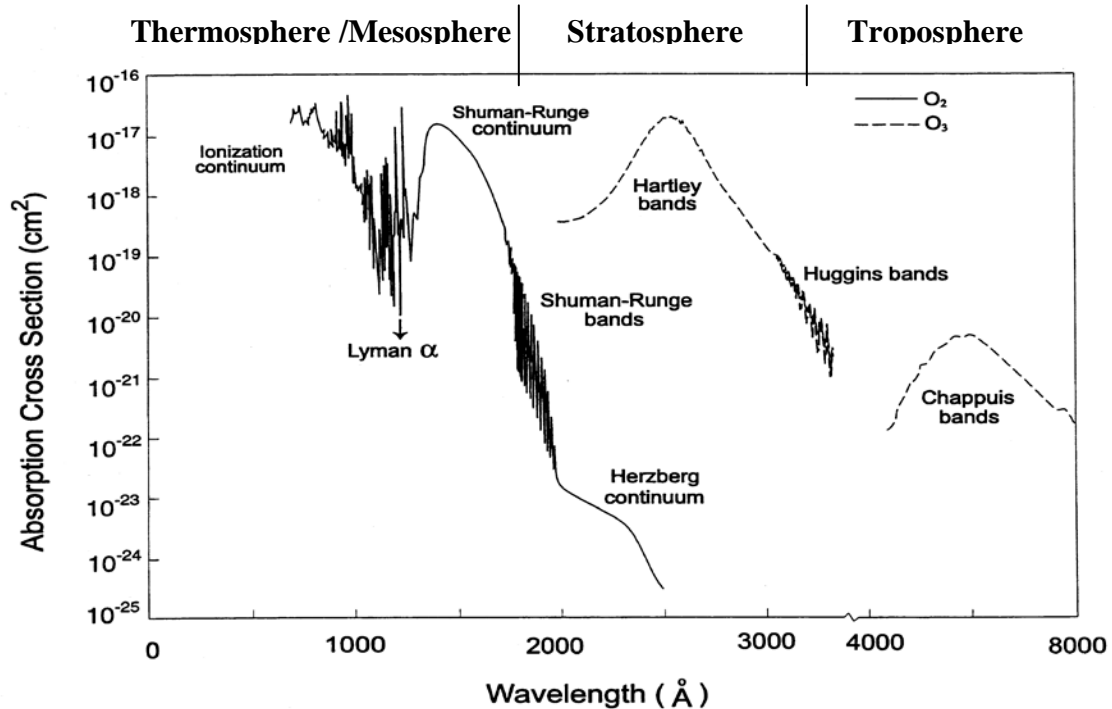
**Table 4.5** Wavelengths of absorption in the solar spectrum (UV + visible) by several atmospheric gases

<i>Gas</i>	<i>Absorption wavelengths (μm)</i>
N <sub>2</sub>	< 0.1
O <sub>2</sub>	< 0.245
O <sub>3</sub>	0.17-0.35
H <sub>2</sub> O	0.45-0.75
H <sub>2</sub> O <sub>2</sub> hydrogen peroxide	< 0.35
NO <sub>2</sub> nitrogen oxide	< 0.6*
N <sub>2</sub> O	< 0.24
NO <sub>3</sub> nitrate radical	0.41-0.67
HONO nitrous acid	< 0.4
HNO <sub>3</sub> nitric acid	< 0.33
CH <sub>3</sub> Br methyl bromide	< 0.26
CFC <sub>3</sub> (CFC11)	< 0.23
HCHO formaldehyde	0.25-0.36

**NOTE:** NO<sub>2</sub> absorb at  $\lambda < 0.6 \mu\text{m}$ , but photodissociate at  $\lambda < 0.4 \mu\text{m}$

➤ UV region:

Absorption of UV radiation in the gaseous atmosphere is primarily due molecular oxygen  $O_2$  and ozone  $O_3$ .



**Figure 4.10** Spectral absorption cross-sections of  $O_2$  and  $O_3$

**NOTE:**

- Bands of  $O_2$  and  $O_3$  at wavelengths  $< 1 \mu m$  are electronic transitions.
- These absorption bands are relatively uncomplicated continua because practically all absorption results in dissociation of the molecule (so the upper state is not quantized);
- Despite the small amount of  $O_3$ , no solar radiation penetrates to the lower atmosphere at wavelengths  $< 310 \text{ nm}$  (because of large absorption cross-sections of  $O_3$ );

- To avoid very complicated calculations of electronic transitions, numerous measurements of the **absorption cross-sections** of the atmospheric atoms and molecules absorbing in the UV and visible have been performed in laboratory experiments. In general, the absorption cross section varies with temperature.

**Satellite remote sensing of atmospheric gases (atmospheric chemistry, air pollution and other related applications)**

Instrument	Platform	Meas. Period	Typical Res. (km)	Global coverage (days) <sup>c</sup>	Spectral Range (µm)	Trop O <sub>3</sub>	SO <sub>2</sub>	Aer Ind	Trop NO <sub>2</sub>	HCHO	BrO	H <sub>2</sub> O	CO	CH <sub>4</sub>	HNO <sub>3</sub>	AOT	Aer prop.	CO <sub>2</sub>
TOMS	Nimbus 7, ADEOS, Earth Probe	1978-1992, 1996-1997, 1996-	38x38 nadir	~ 1	6 λ <sup>d</sup> 0.31-0.36	1 (low-lat)	1	1										
GOME	ERS-2	1995-2003	320x40 nadir	3	0.23-0.79	2-3	1	1	1	1	1	1						
IMG	ADEOS	1996-1997	8x8 nadir	variable	3.3-16.7	2-4							1.5-2.2	0.7-1.5	0.8-1.8			
MOPITT	Terra	2000-	22x22 nadir	3.5	4.7								1.5-2					
MISR	Terra	2000-	18x18e 9 angles	7	4 λ 0.45-0.87											1	1	
MODIS	Terra Aqua	2000- 2002-	10x10e nadir	2	36 λ 0.41-14.2											1	1	
SCIA-MACHY	Euvisat	2002-	60x30 nadir	6	0.23-2.3	2-3	1	1	1	1	1	1	1					1
ACE-FTS	SCISAT-1	2003-	4 limb	n/a	2-13	X			X			X	X	X	X			
MLS	Aura	2004-	3- 4.5 limb	n/a	Micro-wave	<150 hPa							<150 hPa		X			
OMI	Aura	2004-	13x24 nadir	1	0.27-0.50	2-3	1	1	1	1	1					1	1	
TES	Aura	2004-	5x8 nadir 2 limb	n/a	3.3-15.4	2						5	2					
PARASOL	PARASOL	2004-	16x18	1	9 λ 0.44-1.0											1	1	
CALIOP	CALIPSO	2006-	40x40	n/a	0.53, 1.06													
GOME-2	MetOp	2006-	80x40	1	0.24-0.79	2-3	1	1	1	1	1	1						
IASI	MetOp	2006-	12x12	0.5	3.6-15.5	2-3						10		1	1			1
OCO	OCO	2008?	5x5	1	0.76, 1.6, 2.1													1

**Table 4.6** Satellite instruments providing measurements of atmospheric composition (gases) [http://igac.jisao.washington.edu/newsletter/igac35/Mar\\_2007\\_IGAC\\_35.pdf](http://igac.jisao.washington.edu/newsletter/igac35/Mar_2007_IGAC_35.pdf)

<sup>a</sup>Some instruments measures aerosol and clouds also

<sup>b</sup>The number of independent degrees of freedom is given for each nadir measurement. A value of 1 indicates a tropospheric column and X denotes a partial tropospheric column.

<sup>c</sup>Value given for clear-sky conditions. Clouds impede the retrieval.

<sup>d</sup>Number of discrete wavelengths

<sup>e</sup>Radiances for MISR and MODIS are acquired at between 205 m and 1.1 km, depending on channel. Resolutions reported here are for the standard operational aerosol products.