

## Lecture 9.

### Absorption by atmospheric gases in UV and visible.

#### Objectives:

1. Electronic energy transitions.
2. Gaseous absorption in UV.
3. Gaseous absorption visible and near infrared (near-IR).
4. Some concepts of photochemistry of the atmosphere.

#### Required reading:

L80: 3.2-3.4

#### Additional/advanced reading

Le93: 17.1/G&Y89: 5.2-5.7

### 1. Electronic energy transitions.

**NOTE:** Various forms of internal energy of a molecule were defined and discussed in Lecture 5. Recall that  $E_{\text{rot}} < E_{\text{tr}} < E_{\text{vib}} < E_{\text{el}}$

**Electronic energy  $E_{\text{el}}$**  originates in the unstable configurations of electrons in atoms and molecules.

- **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.

- 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.

**NOTE:** Absorption cross-sections can be determined in the laboratory using the Beer-Bouguer-Lambert law (recall Lecture 2). In such an experiment, from a measure of the light intensity in the absence of sample ( $I_0$ ) and in the presence of a sample ( $I$ ) through a vessel of length  $l$  containing a known concentration ( $N$ ) of absorbing gas, one can obtain the absorption cross-sections from

$$\frac{I}{I_0} = \exp(-s_{a,l} N l)$$

**NOTE:** Recall Lecture 2: for a known absorption cross-section  $s_{a,l}$ , the absorption coefficient is calculated as  $b_{a,l} = s_{a,l} N$  where  $N$  is the number of molecules of a given gas per unit volume of air.

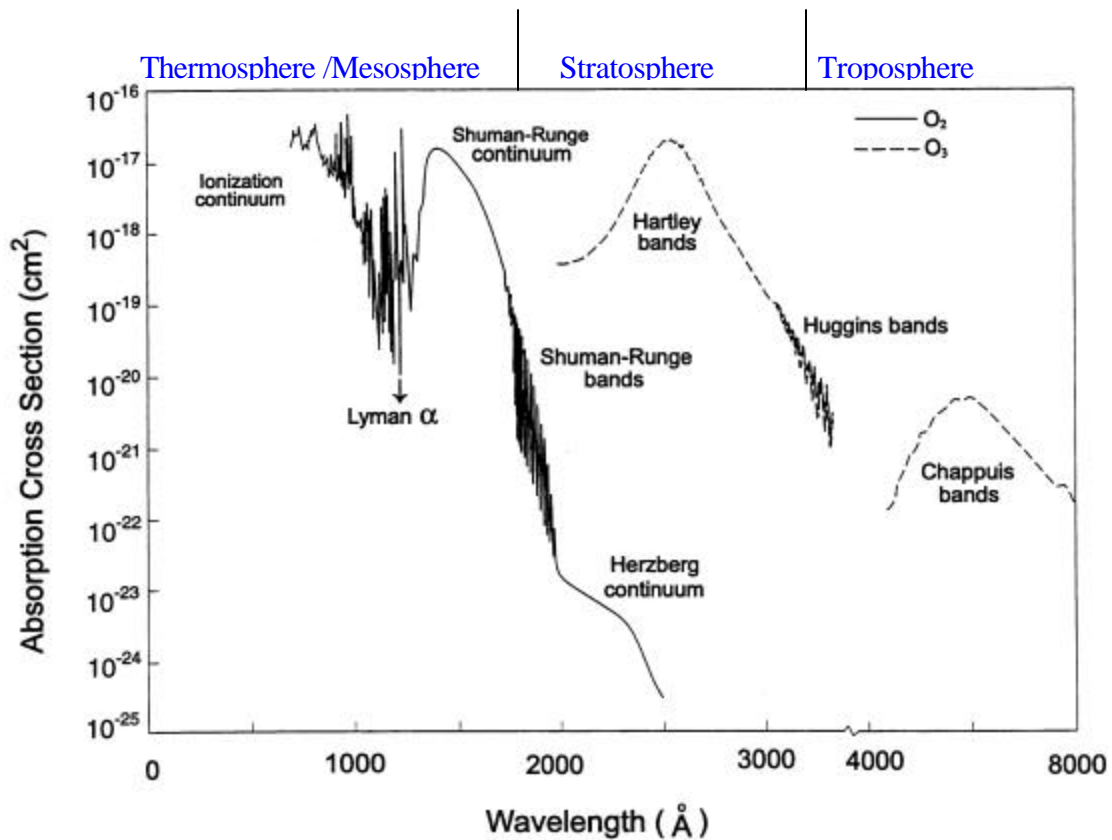
- Electronic transitions (i.e. high-energy UV photons) may cause various photochemical and photophysical processes.

Absorption of a high-energy photon ( $AB + h\nu \rightarrow AB^*$ ) may result in the following primary **photophysical** and **photochemical** processes:



## 2. Gaseous absorption in UV.

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



**Figure 1.** Spectral absorption cross-sections of  $O_2$  and  $O_3$

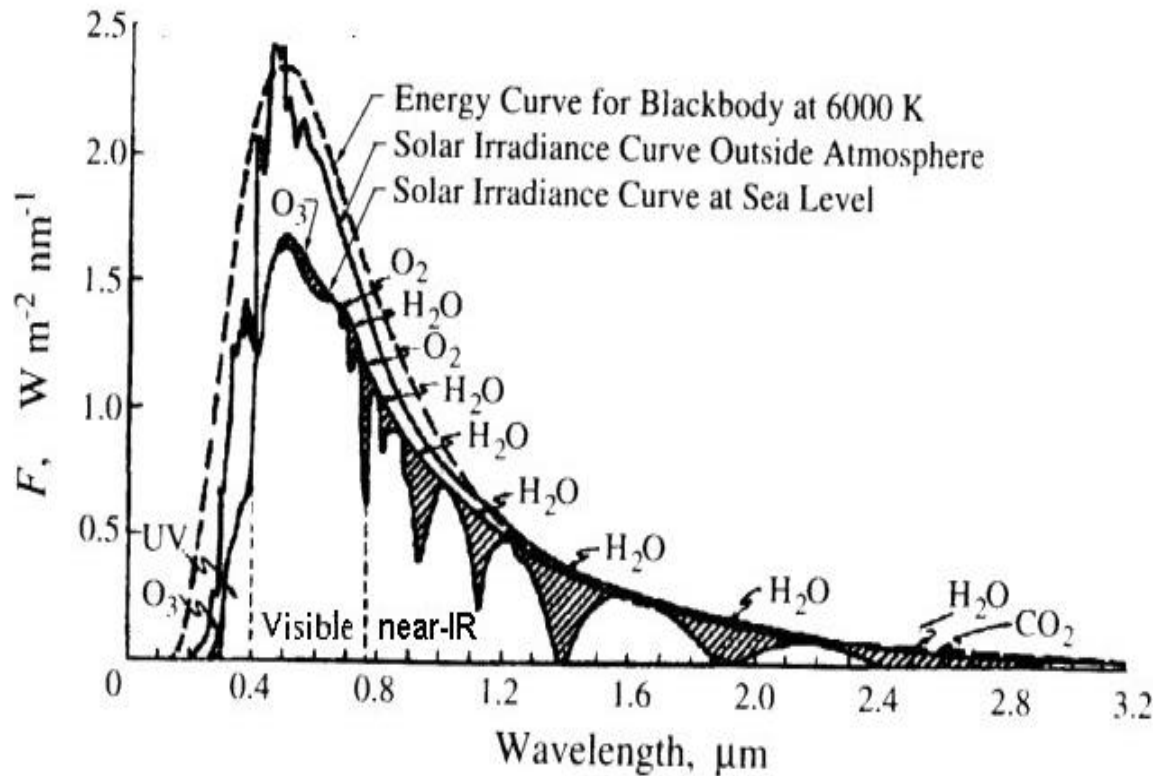
### **NOTE:**

- 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  $O_3$ );

### 3. Gaseous absorption in the visible and near IR.

- 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>.

**Figure 2.** Solar spectral irradiance (flux) at the top of the atmosphere and at the surface.



**NOTE:** Spectroscopic data for vibrational bands (for H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, etc.) in visible and near -IR are provided by HITRAN.

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

**Table 9.1** Wavelengths of absorption in the solar spectrum (UV + visible) by several atmospheric gases

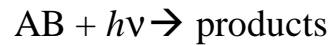
<b>Gas</b>	<b>Absorption wavelengths (mm)</b>
<b>N<sub>2</sub></b>	<b>&lt; 0.1</b>
<b>O<sub>2</sub></b>	<b>&lt; 0.245</b>
<b>O<sub>3</sub></b>	<b>0.17-0.35</b> <b>0.45-0.75</b>
<b>H<sub>2</sub>O</b>	<b>&lt; 0.21</b> <b>0.6-0.72</b>
<b>H<sub>2</sub>O<sub>2</sub></b> hydrogen peroxide	<b>&lt; 0.35</b>
<b>NO<sub>2</sub></b> nitrogen oxide	<b>&lt; 0.6*</b>
<b>N<sub>2</sub>O</b>	<b>&lt; 0.24</b>
<b>NO<sub>3</sub></b> nitrate radical	<b>0.41-0.67</b>
<b>HONO</b> nitrous acid	<b>&lt; 0.4</b>
<b>HNO<sub>3</sub></b> nitric acid	<b>&lt; 0.33</b>
<b>CH<sub>3</sub>Br</b> methyl bromide	<b>&lt; 0.26</b>
<b>CFC<sub>3</sub></b> (CFC11)	<b>&lt; 0.23</b>
<b>HCHO</b> formaldehyde	<b>0.25-0.36</b>

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

## 4. Some concepts of photochemistry of the atmosphere.

**Photochemistry** is the chemistry of atmosphere driven by sunlight.

**Photodissociation (or photolysis, or photolytic, or photochemical)** reactions are the cleavage of a molecule into two or more atomic or molecular fragments through the absorption of radiant energy.



with rate :

$$-\frac{d[AB]}{dt} = J[AB]$$

where **J** ( $s^{-1}$ ) is the **photolysis rate coefficient** for species AB.

**NOTE:** “same name”: **photolysis rate coefficient=photodissociation coefficient = photolysis frequency**

**Photolysis rate coefficient** is determined as

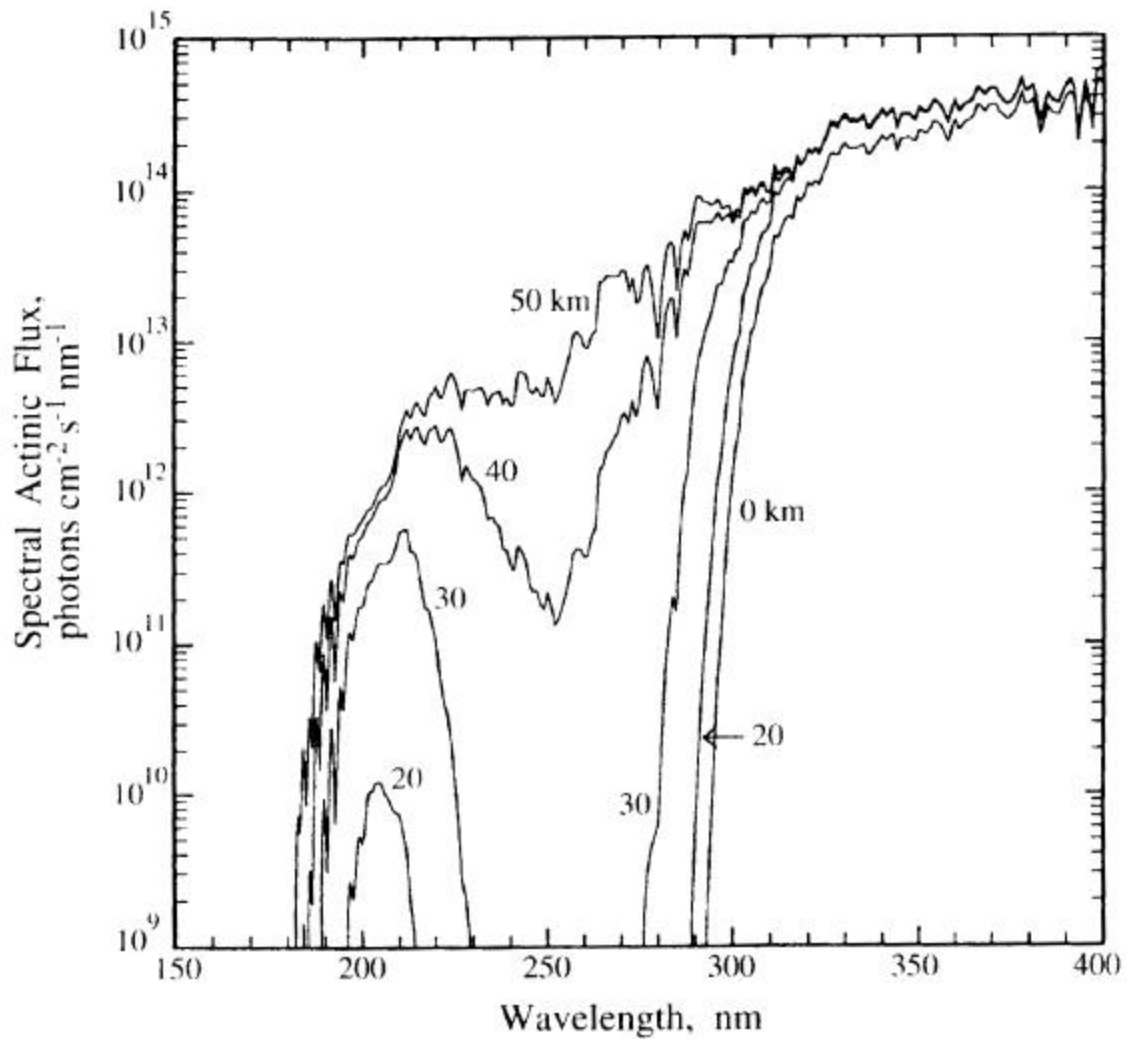
$$J(z) = \int_I \mathbf{s}_{a,I}(T(z)) \mathbf{f}_I(T(z)) F_{ac,I}(z) dI$$

where  $\mathbf{s}_{a,I}(T(z))$  is the temperature- and wavelength-dependent absorption cross section of a given species,  $\mathbf{f}_I(T(z))$  is the temperature- and wavelength-dependent **quantum yield**, and is  $F_{ac,I}$  is the wavelength-dependent **actinic flux**.

**Quantum yield** is the fraction of the number of photons striking a molecule that results in a dissociation of the molecule to specified products. It gives the efficiency of photolysis.

**Actinic flux** is the radiant flux from all directions on a volume of air (i.e. integrated over  $4\pi$  steradians). It is often expressed in units of  $[\text{photons cm}^{-2} \text{ s}^{-1} \mu\text{m}^{-1}]$ .

**Figure 9.3** Actinic flux at various altitudes in the atmosphere



NOTE: Photolysis rate for any molecules is determined by a combination of factors: absorption cross-section and actinic flux. Actinic flux depends on solar radiation at a given volume of air which depends on season, latitude, altitude, time of the day (or sun position), atmospheric composition (gases, aerosols, clouds). We will be modeling the actinic flux later in the course.

- Most molecules of atmospheric importance photolyze at ultraviolet (UV) wavelengths (such as: O<sub>3</sub>, O<sub>2</sub>, CFCs, N<sub>2</sub>O, HNO<sub>3</sub>), but some can be dissociated at visible wavelengths (such as, Cl<sub>2</sub>, NO<sub>3</sub>, NO<sub>2</sub>).

**Table 9.2** Rates and mechanism of some important photolysis processes in the atmosphere. (Rates are calculated for clear sky conditions (i.e. no aerosols, no clouds))

Process	Altitude range	Wavelength (μm)	Approximate Rate (s <sup>-1</sup> )
$O_2 + hv \rightarrow O(^1D) + O(^3P)$	> 50 km	< 0.174	10 <sup>-12</sup>
$O_2 + hv \rightarrow O(^3P) + O(^3P)$	stratosphere and above	< 0.246	10 <sup>-10</sup>
$O_2 + hv \rightarrow O(^1D) + O_2(^1\Delta)$	all	< 0.310	10 <sup>-5</sup> at 10 km 10 <sup>-3</sup> at 40 km
$NO_2 + hv \rightarrow NO + O(^3P)$	all	0.25 - 0.4	8x10 <sup>-3</sup> at surface 10 <sup>-2</sup> in stratosphere
$NO_3 + hv \rightarrow NO_2 + O(^3P)$	all	0.4 - 0.625	0.2 at surface 0.25 in stratosphere
$NO_3 + hv \rightarrow NO + O_2$	all	0.585-0.625	0.02
$N_2O_5 + hv \rightarrow NO_3 + NO_2$	stratosphere	< 0.32	2x10 <sup>-5</sup> at surface