

Lecture 7.

Absorption spectra of atmospheric gases in the IR, visible and UV regions.

1. Absorption coefficient and transition function.
2. Gaseous absorption in the IR.
3. Gaseous absorption in the visible and near infrared.
4. Gaseous absorption in the UV.
5. Spectroscopic databases: HITRAN

Required reading:

L02: 3.2, 4.2.1

Additional reading:

Rothman L.S. et al., The HITRAN 2008 molecular spectroscopic database. Journal of Quantitative Spectroscopy and Radiative Transfer, V100, 533-572, 2009.
<http://www.cfa.harvard.edu/hitran/>

1. Absorption coefficient and transmission function.

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

$$k_{a,\nu} = S f(\nu - \nu_0) \quad [7.1]$$

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

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

Line intensity (or line strength) gives total absorption associated with the line.

Line shape (or line profile) gives the distribution of absorption about the center of the line (see Lecture 6:).

Units of the line profile, f: LENGTH (often cm); **Units of absorption coefficient and intensity** – see Table 7.1 (below)

Dependencies:

S depends on **T**;

$f(\nu - \nu_0, \alpha)$ depends on the line halfwidth $\alpha(\mathbf{p}, \mathbf{T})$, which depends on pressure and temperature.

✓ **Path length** (or **path**) is defined as the amount of an absorber along the path.

Since the amount of the absorbing gas can be expressed in different ways (see Lecture 5) the different measures of path length are used.

For instance, if the amount of an absorber is given in terms of mass density, then **mass path length** (also called **optical mass**) is

$$u = \int_{s_1}^{s_2} \rho(s) ds$$

Homogeneous absorption path:

$k_{a\nu}$ does not vary along the path \Rightarrow optical depth is $\tau = k_{a\nu}u$

Inhomogeneous absorption path: when $k_{a\nu}$ varies along the path, then

$$\tau = \int_{u_1}^{u_2} k_{a,\nu} du$$

NOTE: In general, τ_ν depends on both the wavenumber and path length.

NOTE: The product of the absorption coefficients and path length (=optical depth) should be unitless.

Table 7.1 Units used for the path length (or amount of absorbing gases); absorption coefficient, and line intensity.

Absorbing gas (path length u)	Absorption coefficient	Line intensity (S)
cm	cm^{-1}	cm^{-2}
g cm^{-2}	$\text{cm}^2 \text{g}^{-1}$	cm g^{-1}
molecule cm^{-2}	$\text{cm}^2/\text{molecule}$	cm/molecule
cm atm	$(\text{cm atm})^{-1}$	$\text{cm}^{-2} \text{atm}^{-1}$

Monochromatic transmittance T_v and absorbance A_v of radiance along the path are defined as

$$T_v = \exp(-\tau_v) \quad A_v = 1 - T_v = 1 - \exp(-\tau_v) \quad [7.2]$$

NOTE: same name: Transmission function = Transmittance

NOTE: A_v is also called absorption or absorption function or absorptivity.

2. Gaseous absorption in the IR

Main atmospheric gases absorbing/emitting in the IR: CO₂, H₂O, O₃, CH₄, N₂O, CFCs.

- ✓ Each atmospheric gas has a specific absorption/emission spectrum – its own signature.
- ✓ *Continuum absorption by water vapor* is defined as any observed absorption by water vapor not attributable to the Lorentz line contribution within 25 cm⁻¹ of each line. 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 H₂O molecules (called **self-broadening**) and between H₂O and non-absorbing molecules (N₂) (called **foreign broadening**). The most recent work suggested that the large portion of the continuum might be due to collision-induced transitions and does not relate to the line wings.
- ✓ Position of absorption line centers differs for isotopes of the same molecule.

Table 7.2 Main vibrational transition of water vapor isotopes.

Gas	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}
H ₂ ¹⁶ O	3657.05	1594.75	3755.93
H ₂ ¹⁷ O	3653.15	1591.32	3748.32
H ₂ ¹⁸ O	3649.69	1588.26	3741.57
HD ¹⁶ O	2723.68	1403.48	3707.47
D ₂ ¹⁶ O	2669.40	1178.38	2787.92

- ✓ Atmospheric pressure strongly affects the absorption spectra of gases (through pressure broadening). This poses a major problem in computing the transfer of IR radiation through the atmosphere with varying pressure, temperature, and amount of gases.

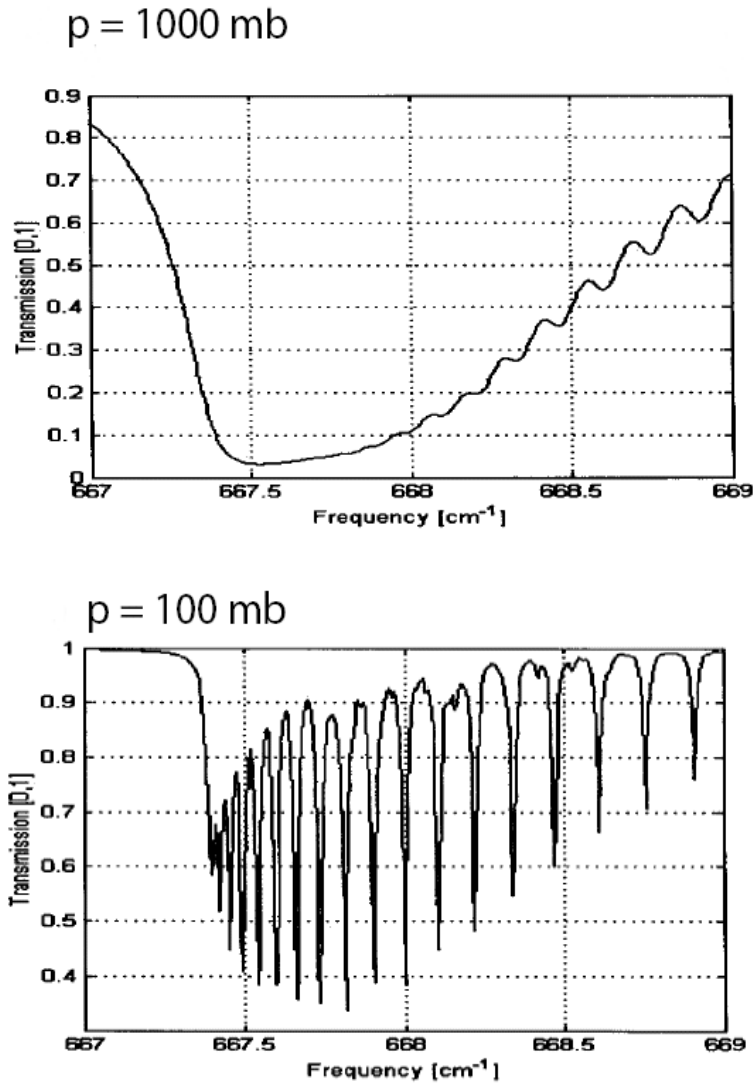


Figure 7.1 Example of *high spectral* resolution transmission spectra of a one-meter path with typical CO₂ concentration at 1000 mb and 100 mb.

Table 7.3 The most important vibrational and rotational transitions for H₂O, CO₂, O₃, CH₄, N₂O, and CFCs.

Gas	Center ν (cm⁻¹) (λ(μm))	Transition	Band interval (cm⁻¹)
H₂O	- 1594.8 (6.3) continuum*	pure rotational ν ₂ ; P, R far wings of the strong lines; water vapor dimers (H ₂ O) ₂	0-1000 640-2800 200-1200
CO₂	667 (15) 961 (10.4) 1063.8 (9.4) 2349 (4.3)	ν ₂ ; P, R, Q] overtone and combination ν ₃ ; P, R overtone and combination	540-800 850-1250 2100-2400
O₃	1110 (9.01) 1043 (9.59) 705 (14.2)	ν ₁ ; P, R ν ₃ ; P, R ν ₂ ; P, R	950-1200 600-800 600-800
CH₄	1306.2 (7.6)	ν ₄	950-1650
N₂O	1285.6 (7.9) 588.8 (17.0) 2223.5 (4.5)	ν ₁ ν ₂ ν ₃	1200-1350 520-660 2120-2270
CFCs			700-1300

NOTE: Chlorofluorocarbons (CFCs) are a family of chemical compounds.

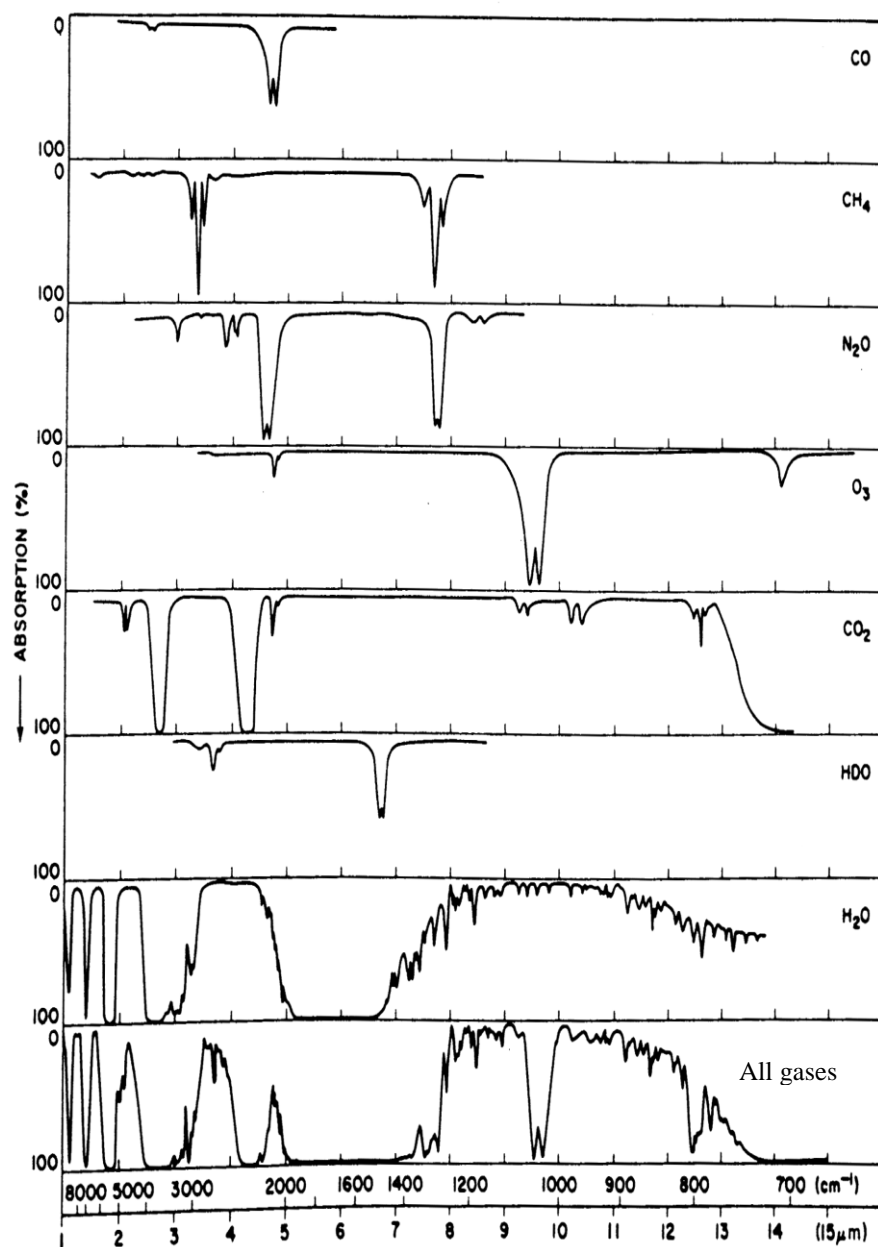
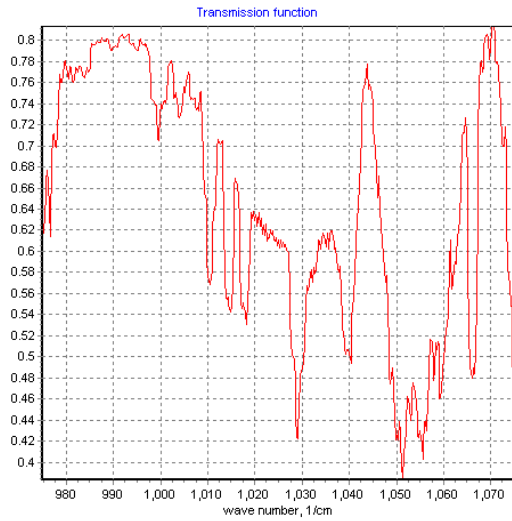


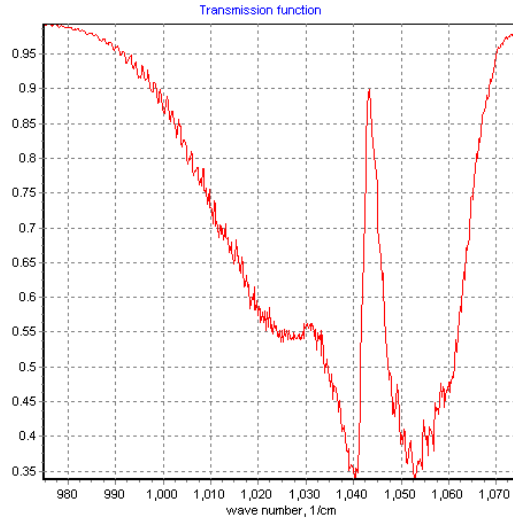
Figure 7.2 *Low-resolution* infrared absorption spectra of the major atmospheric gases.

Resolution $\Delta\nu = 1 \text{ cm}^{-1}$

Atmospheric layer 0-13 km

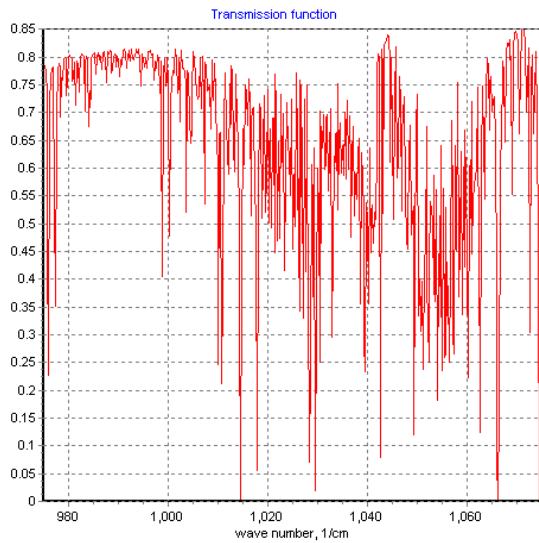


Atmospheric layer 13-50 km



Resolution $\Delta\nu = 0.001 \text{ cm}^{-1}$

Atmospheric layer 0-13 km



Atmospheric layer 13-50 km

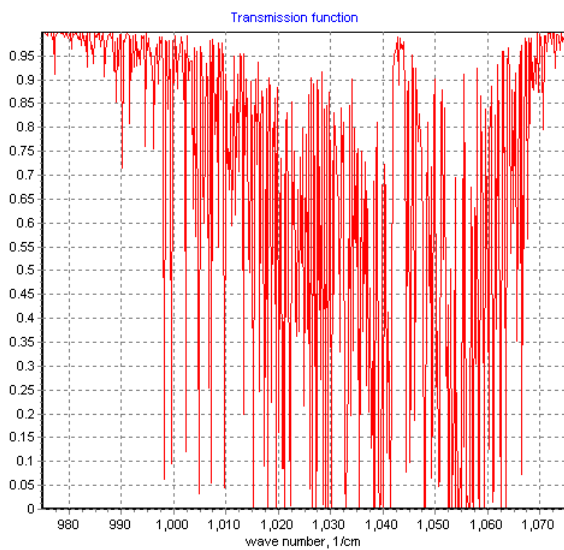


Figure 7.3 Examples of *high-resolution* absorption function computed with the LBL radiative transfer code (see Lecture 8).

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

- ✓ Absorption of visible and near IR radiation in the gaseous atmosphere is primarily due to **H₂O**, **O₃**, and **CO₂**.

Table 7.4 Main Visible and near-IR absorption bands of atmospheric gases

Gas	Center ν (cm ⁻¹) (λ (μ m))	Band interval (cm ⁻¹)
H₂O	3703 (2.7)	2500-4500
	5348 (1.87)	4800-6200
	7246 (1.38)	6400-7600
	9090 (1.1)	8200-9400
	10638 (0.94)	10100-11300
	12195 (0.82)	11700-12700
	13888 (0.72)	13400-14600
	visible	15000-22600
CO₂	2526 (4.3)	2000-2400
	3703 (2.7)	3400-3850
	5000 (2.0)	4700-5200
	6250 (1.6)	6100-6450
	7143 (1.4)	6850-7000
O₃	2110 (4.74)	2000-2300
	3030 (3.3)	3000-3100
	visible	10600-22600
O₂	6329 (1.58)	6300-6350
	7874 (1.27)	7700-8050
	9433 (1.06)	9350-9400
	13158 (0.76)	12850-13200
	14493 (0.69)	14300-14600
	15873 (0.63)	14750-15900
N₂O	2222 (4.5)	2100-2300
	2463 (4.06)	2100-2800
	3484 (2.87)	3300-3500
CH₄	3030 (3.3)	2500-3200
	4420 (2.20)	4000-4600
	6005 (1.66)	5850-6100
CO	2141 (4.67)	2000-2300
	4273 (2.34)	4150-4350
NO₂	visible	14400-50000

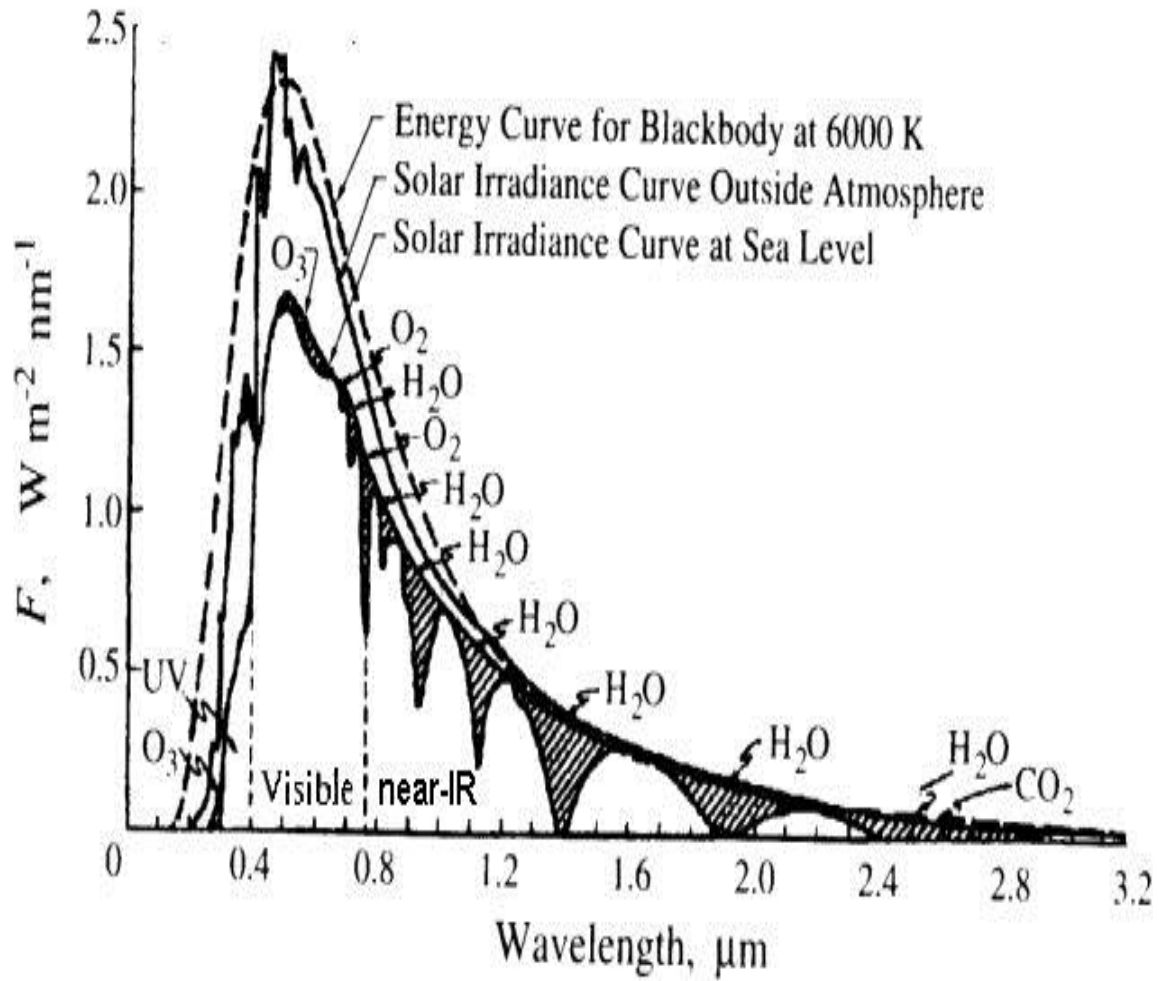


Figure 7.4 Solar spectral irradiance (flux) at the top of the atmosphere and at the surface.

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

4. Gaseous absorption in the UV.

Table 7.5 Wavelengths of absorption in the solar spectrum (UV + visible) by several atmospheric gases

Gas	Absorption wavelengths (μm)
N₂	< 0.1
O₂	< 0.245
O₃	0.17-0.35 0.45-0.75
H₂O	< 0.21 0.6-0.72
H₂O₂ hydrogen peroxide	< 0.35
NO₂ nitrogen oxide	< 0.6*
N₂O	< 0.24
NO₃ nitrate radical	0.41-0.67
HONO nitrous acid	< 0.4
HNO₃ nitric acid	< 0.33
CH₃Br methyl bromide	< 0.26
CFCl₃ (CFC11)	< 0.23
HCHO formaldehyde	0.25-0.36

* **NO₂** absorb at $\lambda < 0.6 \mu\text{m}$, but photodissociate at $\lambda < 0.4 \mu\text{m}$

NOTE: 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.

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

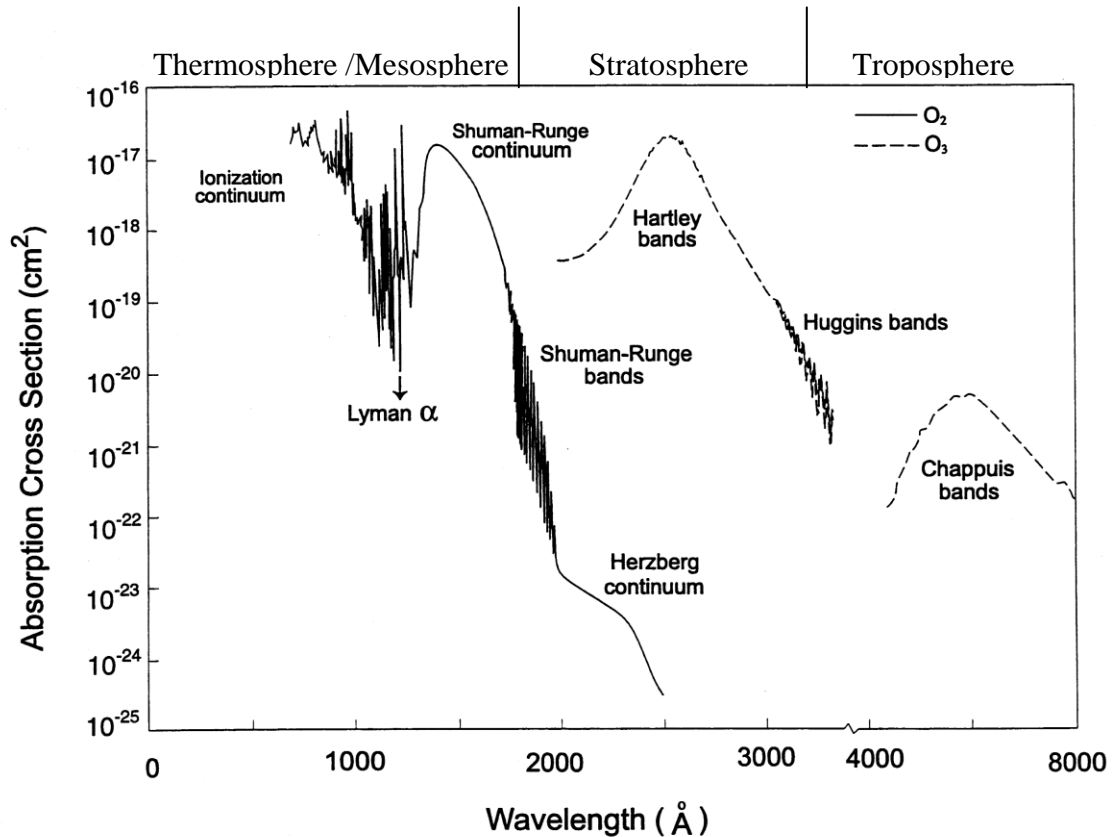


Figure 7.5 Spectral absorption cross-sections of O_2 and O_3

NOTE:

- Bands of O_2 and O_3 at wavelengths $< 1 \mu\text{m}$ 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);

5. Spectroscopic database HITRAN

(High-resolution TRANsmission molecular absorption database)

<http://cfa-www.harvard.edu/hitran/>

- ✓ The database is a long-running project started by the Air Force Cambridge Research Laboratories (AFCRL) in the late 1960's in response to the need for detailed knowledge of the infrared properties of the atmosphere.
- ✓ The HITRAN'2008 Database (Version 13.0) contains 2,713,968 spectral lines for 39 different molecules, including the atom O (singlet) and the ion NO+. Files for three more molecules, ClONO₂, SF₆, and CF₄ are stored separately in the /HITRAN2008/Supplemental/ folder.
- ✓ In addition to the Mega-line HITRAN2008 database, there are directories containing files of aerosol indices of refraction, UV line-by-line and absorption cross-section parameters, and more extensive IR absorption cross-sections.

NOTE: Information (and links) about other databases –

see under “Other Lists” at **<http://cfa-www.harvard.edu/hitran/>**