Lecture 6.

Absorption by atmospheric gases in the IR, visible and UV spectral regions.

Objectives:

1. Gaseous absorption in thermal IR.
2. Gaseous absorption in the visible and near infrared.
3. Gaseous absorption in UV.
4. 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://cfa-www.harvard.edu/hitran//

High resolution spectral modeling **http://spectralcalc.com/**

1. Gaseous absorption in the thermal IR.

Main atmospheric gases absorbing/emitting in the IR: CO_2, H_2O, O_3, CH_4, N_2O, CFCs.

- ✓ Each atmospheric gas has a specific absorption/emission spectrum – its own spectral signature.

- ✓ Position of absorption line centers differs for isotopes of the same molecule.

Table 6.1 Main vibrational transition of water vapor isotopes.

Gas	v_1, cm^{-1}	v_2, cm^{-1}	v_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

- ***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 H_2O molecules (called **self-broadening**) and between H_2O and non-absorbing molecules (N_2) (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.

- 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.

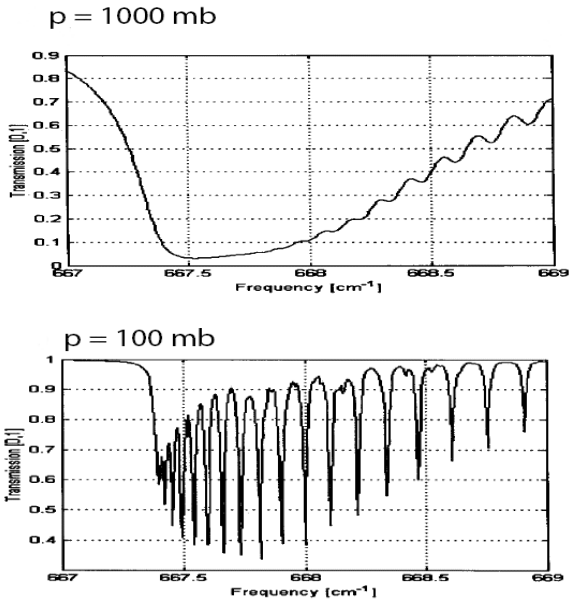

Figure 6.1 Example of ***high spectral*** resolution transmission spectra of a one-meter path with typical CO2 concentration at 1000 mb and 100 mb.

Table 6.2 The most important vibrational and rotational transitions for H_20, CO_2, O_3, CH_4, N_2O, and CFCs.

Gas	Center ν (cm^{-1}) ($\lambda(\mu m)$)	Transition	Band interval (cm^{-1})
H_2O	- 1594.8 (6.3) continuum*	pure rotational ν_2; P, R far wings of the strong lines; water vapor dimmers $(H_2O)_2$	0-1000 640-2800 200-1200
CO_2	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
O_3	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
CH_4	1306.2 (7.6)	ν_4	950-1650
N_2O	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.

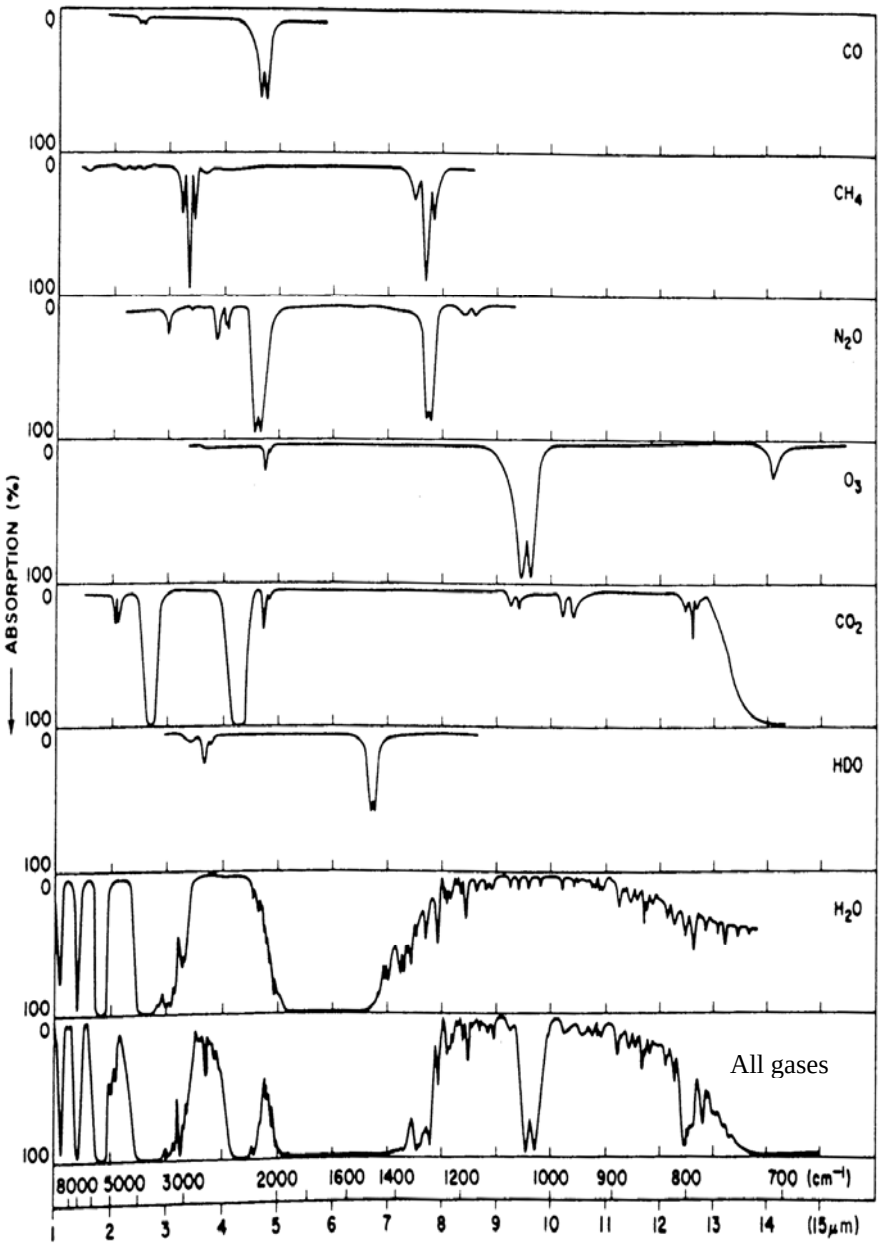

Figure 6.2 ***Low-resolution*** infrared absorption spectra of the major atmospheric gases. (compare to Figure 6.3 that shows transmission with higher spectral resolution)

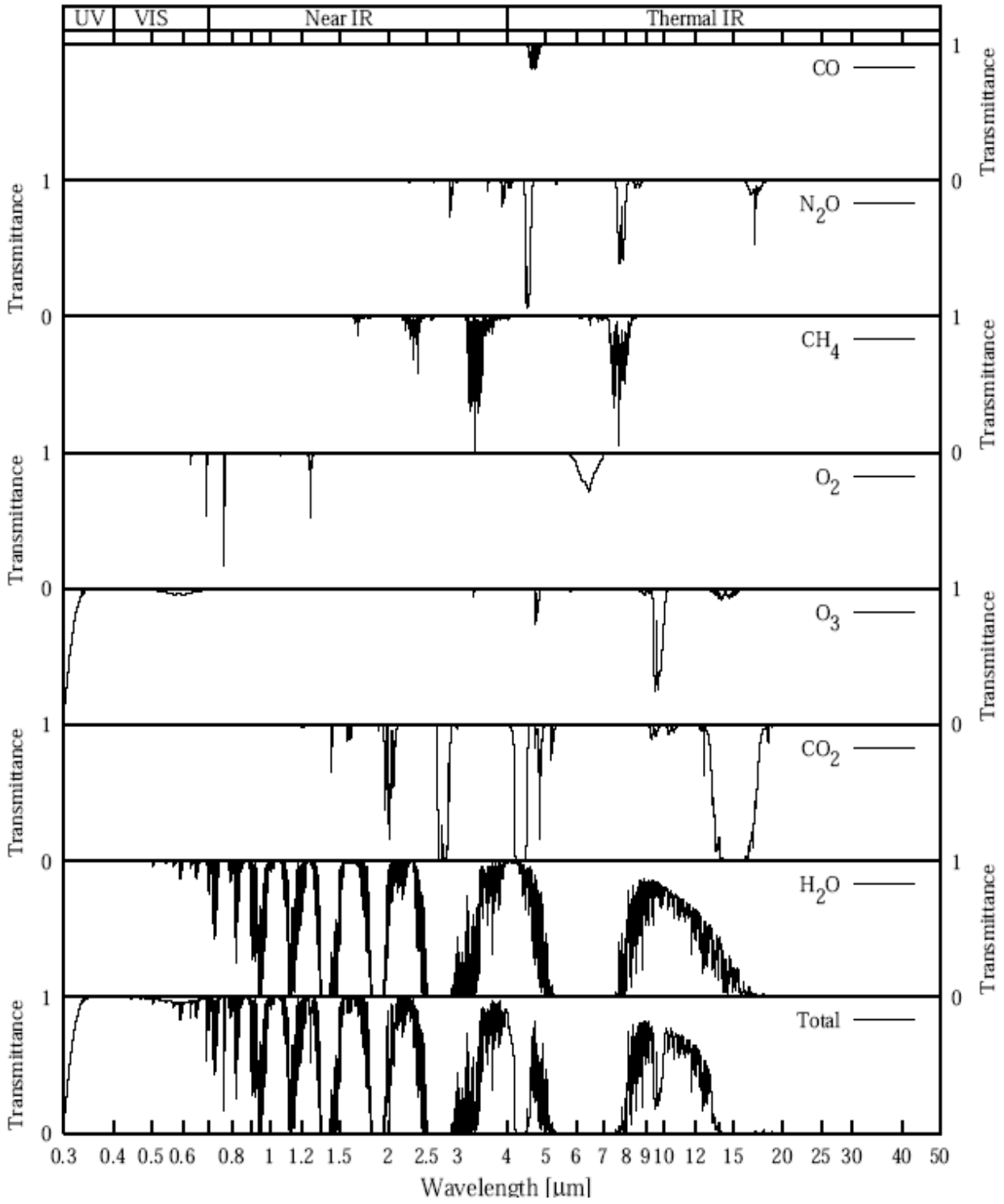

Figure 6.3 Transmission spectra of the major atmospheric gases.

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

- ✓ Absorption of visible and near IR radiation in the gaseous atmosphere is primarily due to **H_2O, O_3, and CO_2.**

Table 6.3 Main Visible and near-IR absorption bands of atmospheric gases

Gas	Center ν (cm^{-1}) ($\lambda(\mu m)$)	Band interval (cm^{-1})
H_2O	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
CO_2	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
O_3	2110 (4.74)	2000-2300
	3030 (3.3)	3000-3100
	visible	10600-22600
O_2	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
N_2O	2222 (4.5)	2100-2300
	2463 (4.06)	2100-2800
	3484 (2.87)	3300-3500
CH_4	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
NO_2	visible	14400-50000

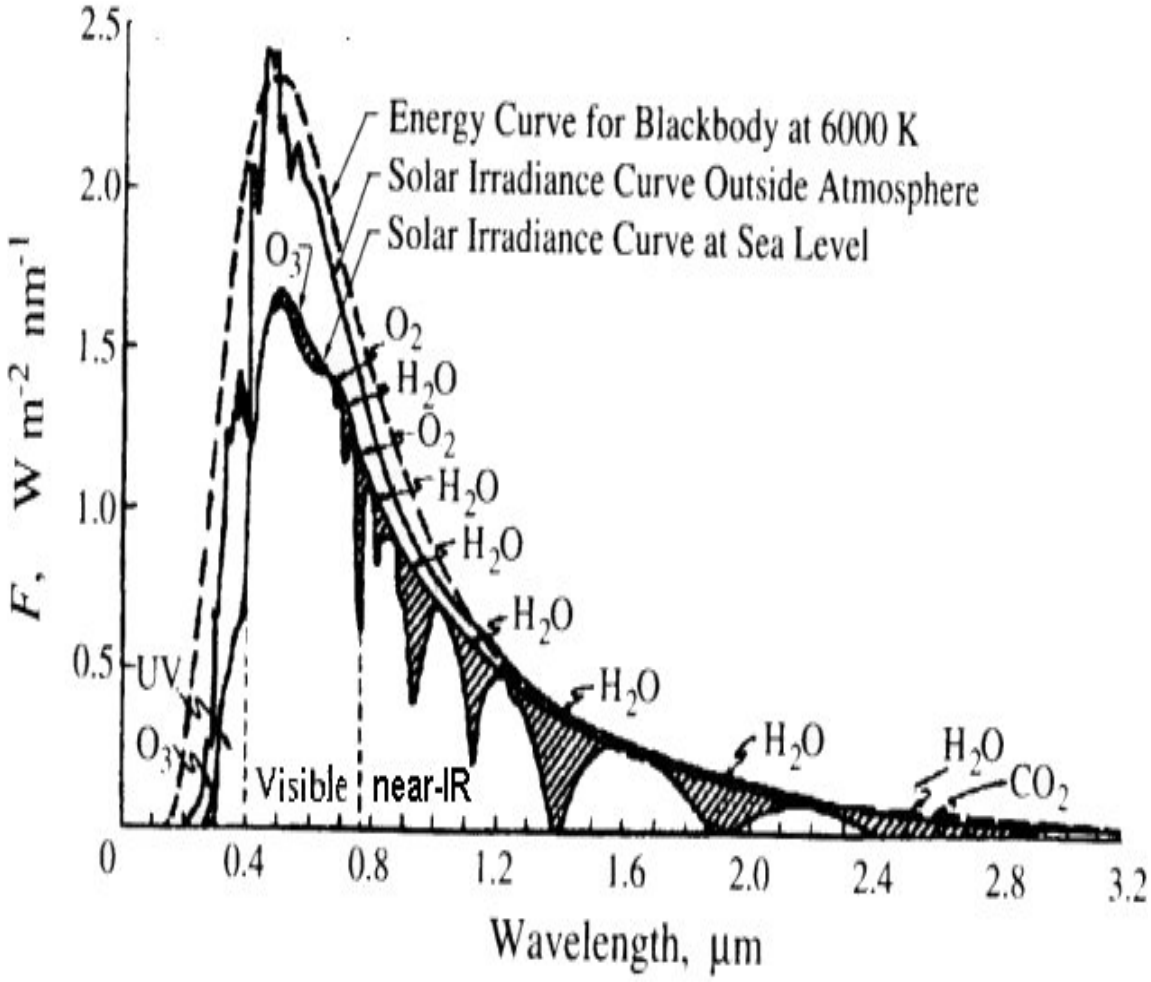

Figure 6.4 Solar spectral irradiance (flux) at the top of the atmosphere and at the surface.

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

3. Gaseous absorption in the UV.

Table 6.4 Wavelengths of absorption in the solar spectrum (UV + visible) by several atmospheric gases

Gas	Absorption wavelengths (μm)
N_2	**< 0.1**
O_2	**< 0.245**
O_3	**0.17-0.35** **0.45-0.75**
H_2O	**< 0.21** **0.6-0.72**
H_2O_2 hydrogen peroxide	**< 0.35**
NO_2 nitrogen oxide	**< 0.6***
N_2O	**< 0.24**
NO_3 nitrate radical	**0.41-0.67**
HONO nitrous acid	**< 0.4**
HNO_3 nitric acid	**< 0.33**
CH_3Br methyl bromide	**< 0.26**
$CFCl_3$ (CFC11)	**< 0.23**
HCHO formaldehyde	**0.25-0.36**

* **NO_2** absorb at $\lambda < 0.6$ μm, but photodissociate at $\lambda < 0.4$ μm

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.

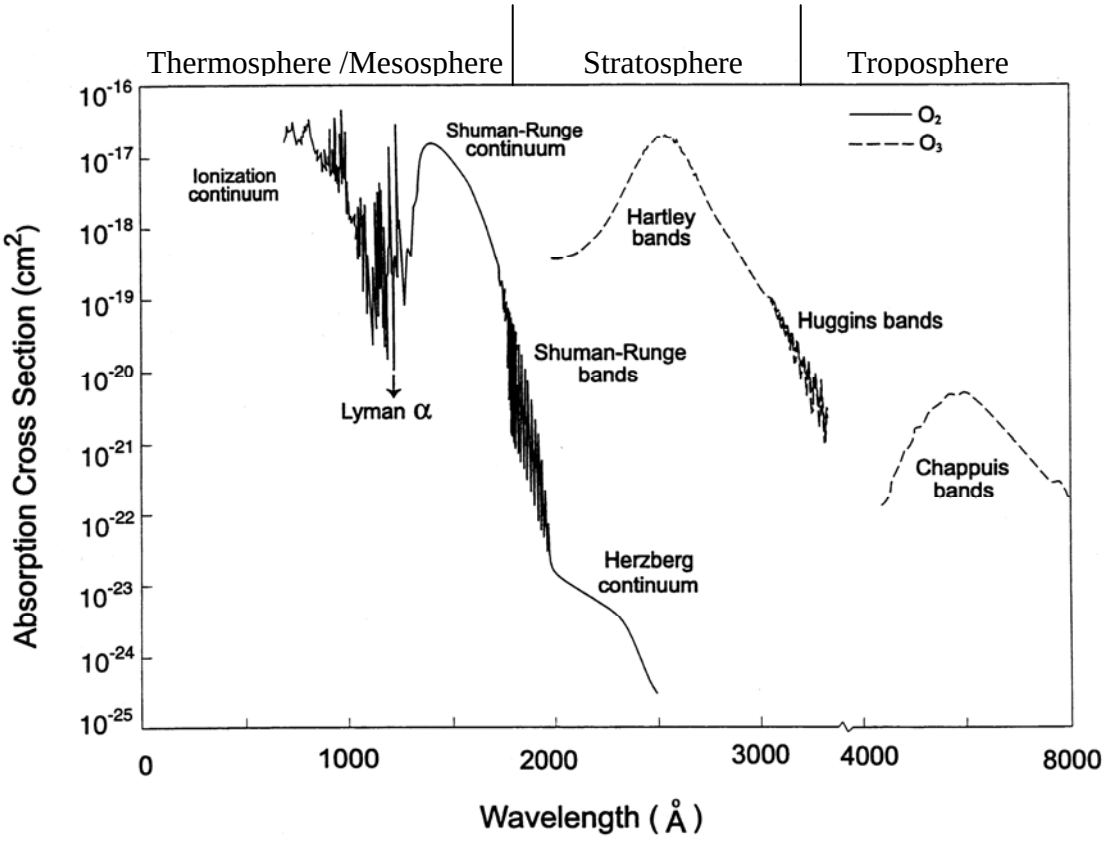

Figure 6.5 Spectral absorption cross-sections of O_2 and O_3

NOTE:

a) Bands of O_2 and O_3 at wavelengths < 1 μm are electronic transitions.

b) These absorption bands are relatively uncomplicated continua because practically all absorption results in dissociation of the molecule (so the upper state is not quantized);

c) Despite the small amount of O_3, no solar radiation penetrates to the lower atmosphere at wavelengths < 310 nm (because of large absorption cross-sections of O_3);

4. 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.
- ✓ Free to users, need to order and install a free software package HAWKS (**H**ITRAN **A**tmospheric **W**or**ks**tation)
- ✓ The current HITRAN'2008 Database (Version 13.0) contains 2,713,968 spectral lines for 39 different molecules.
- ✓ In addition to the 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

HITRAN Tree structure