Lecture 7.

Composition and structure of the atmosphere.

Absorption and emission by atmospheric gases.

1. Spectral line shapes: Lorentz, Doppler and Voigt profile

2. Absorption spectra of main atmospheric gases.

3. Summary of satellite sensors for measurements of atmospheric gases

Required reading:

S: 3.3-3.5;

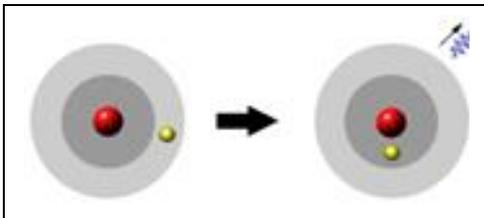*Suggested reading*:

Liou 1.3.2, 3.2

1. Spectral line shapes: Lorentz, Doppler and Voigt profile
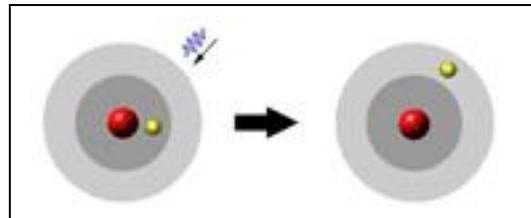
Atomic Absorption (Emission) Spectrum.

- 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:

$$for\ emission: \quad E_k - E_j = h\nu$$

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:

1)   Sharp **lines** of finite widths

2)   Aggregations (series) of lines called **bands**

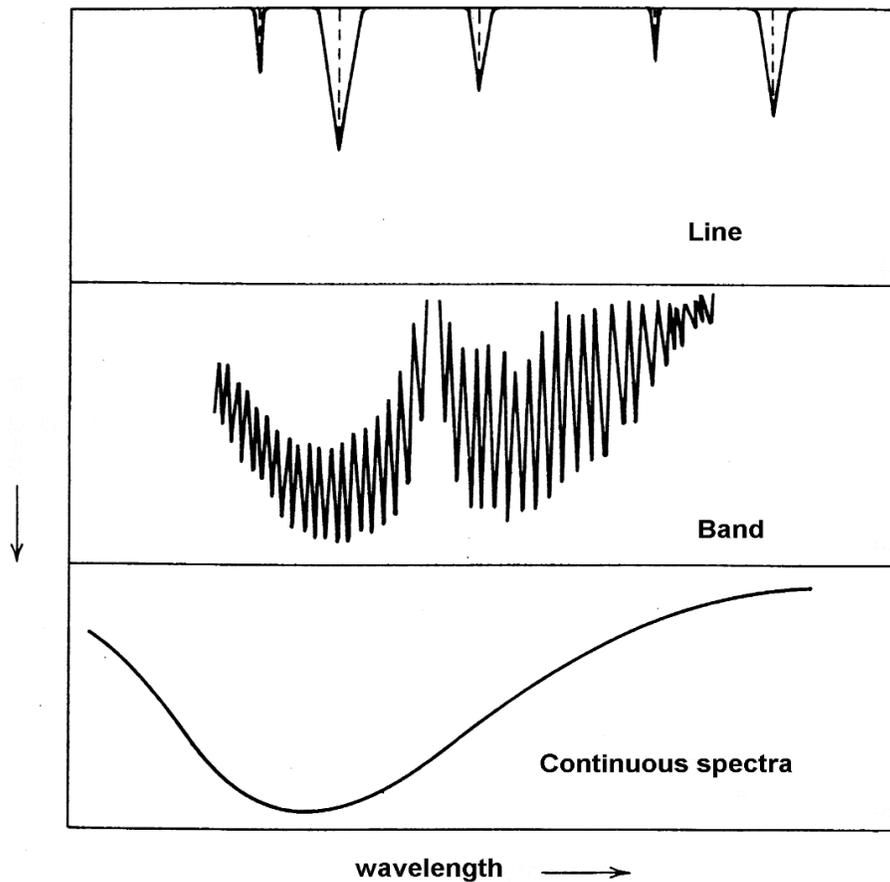3)   **Spectral continuum** extending over a broad range of wavelengths

Figure 7.1 Concept of a line, band, and continuous spectra

Three main properties that define an absorption line:

1) **Central position of the line** (e.g., the central frequency ν_0 or wavenumber $\tilde{\nu_0}$)

2) **Strength of the line** (or intensity, S)

3) **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:

    i) collisions between molecules (referred to as the **pressure broadening**)

    ii) due to the differences in the molecule thermal velocities (referred to as the **Doppler broadening**)

    iii) the combination of the above processes.

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

$$f_L(\nu - \nu_0) = \frac{\alpha / \pi}{(\nu - \nu_0)^2 + \alpha^2}$$ [7.1]

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

ν_0 is the wavenumber of a central position of a line;

α is the half-width of a line at the half maximum (in 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

$$\alpha(P,T) = \alpha_0 \frac{P}{P_0} \left(\frac{T_0}{T} \right)^n$$ [7.2]

  where α_0 is the reference half-width for STP: $T_0 = 273K$; $P_0 = 1013$ mb. α_0 is in the range from **about 0.01 to 0.1 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:

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

[7.3]

α_D is the **Doppler line width**

$$\alpha_D = \frac{\nu_0}{c}(2k_B T / m)^{1/2}$$

[7.4]

where **c** is the speed of light; k_B is the Boltzmann's constant, **m** is the mass of the molecule (for air m = 4.8x10^{-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:

$$f_{Voigt}(\nu - \nu_0) = \int_{-\infty}^{\infty} f_L(\nu' - \nu_0) f_D(\nu - \nu') d\nu' =$$

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

[7.5]

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:

$$k_{a,\nu} = S f(\nu - \nu_0)$$ [7.6]

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

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

Dependencies:

- **S** depends on **T**

- $f(\nu - \nu_0, \alpha)$ 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

$$\tau_\nu = \int_{u_1}^{u_2} k_{a,\nu} du$$ [7.7]

Commonly used absorption coefficients:

$k_{a,\nu}$ Volume absorption coefficient (in LENGTH^{-1})

$k_{m,a,\nu}$ Mass absorption coefficient (in LENGTH^2/MASS)

$k_{cs,a,\nu}$ Absorption cross section (in LENGTH^2) (cross section will also be denoted by σ)

Mass absorption coefficient = volume absorption coefficient/density

Absorption cross section = volume absorption coefficient/number concentration

Thus, optical depth can be expressed in several ways

$$\tau_\nu(s_1, s_2) = \int_{s_1}^{s_2} k_{a,\nu} ds = \int_{s_1}^{s_2} \rho k_{m,a,\nu} ds = \int_{s_1}^{s_2} N k_{cs,a,\nu} ds$$ [7.8]

Table 7.1 Units used for path length, absorption coefficient, and line intensity

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

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

Monochromatic transmittance T_ν and absorbance (or absorption) **A_ν** of radiance along the path are defined as

$$T_\nu = \exp(-\tau_\nu) \qquad A_\nu = 1 - T_\nu = 1 - \exp(-\tau_\nu)$$

[7.9]

NOTE: Same name: Transmission function = Transmittance

2. Absorption spectra of main atmospheric gases (H_2O, CO_2, O_3, CH_4, N_2O, 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:**

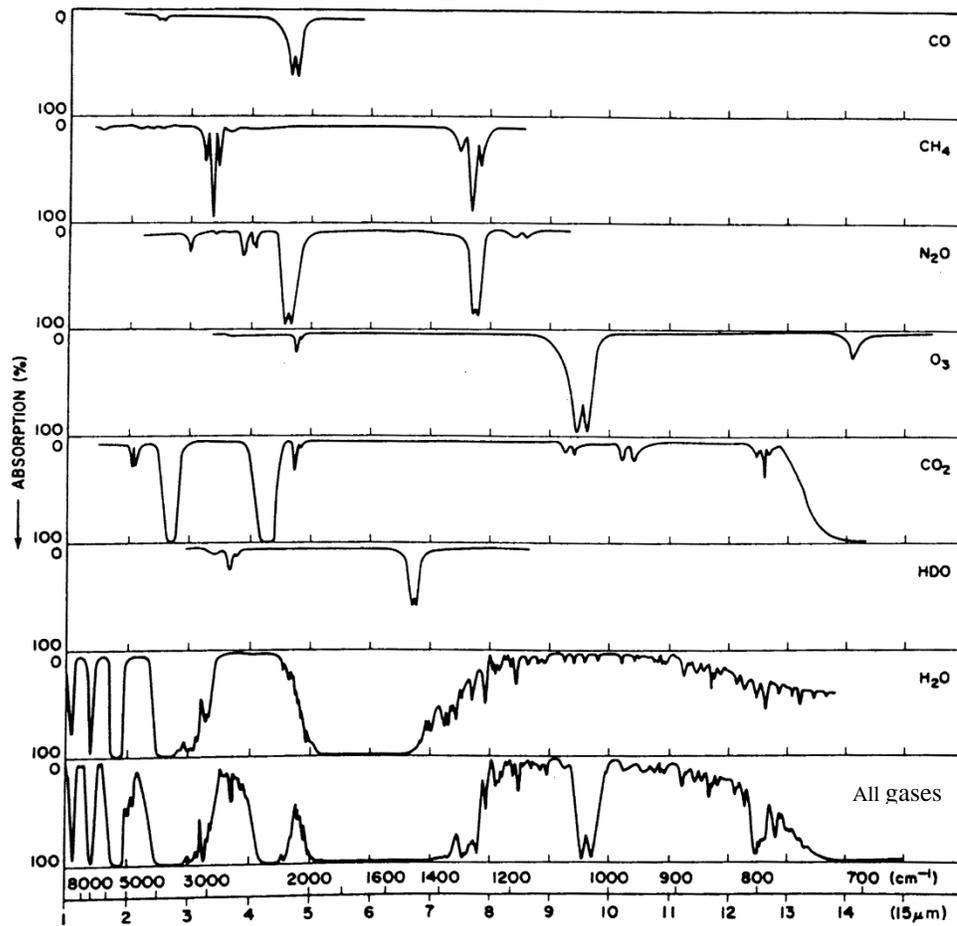| Molecule	Absorption line (Frequency, GHz)
H_2O	22235; 183.3
O_2	about 60; 118.75

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

Table 7.2 The most important vibrational and rotational transitions for H_2O, CO_2, O_3, CH_4, N_2O, and CFCs.

Gas	Center ν (cm^{-1}) (λ(μm))	Transition	Band interval (cm^{-1})
H₂O	-	pure rotational	0-1000
	1594.8 (6.3)	ν_2; P, R	640-2800
	continuum*	far wings of the strong lines; water vapor dimmers $(H_2O)_2$	200-1200
CO₂	667 (15)	ν_2; P, R, Q	540-800
	961 (10.4)	overtone and combination	850-1250
	1063.8 (9.4)	ν_3; P, R overtone and combination	
	2349 (4.3)		2100-2400
O₃	1110 (9.01)	ν_1; P, R	950-1200
	1043 (9.59)	ν_3; P, R	600-800
	705 (14.2)	ν_2; P, R	600-800
CH₄	1306.2 (7.6)	ν_4	950-1650
N₂O	1285.6 (7.9)	ν_1	1200-1350
	588.8 (17.0)	ν_2	520-660
	2223.5 (4.5)	ν_3	2120-2270
CFCs			700-1300

NOTE: Continuum absorption by water vapor in the region from 800-1200 cm^{-1} 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_2O molecules (called **self-broadening**) and between H_2O and non-absorbing molecules (N2) (called **foreign broadening**).

> **Near-IR and visible regions:**

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

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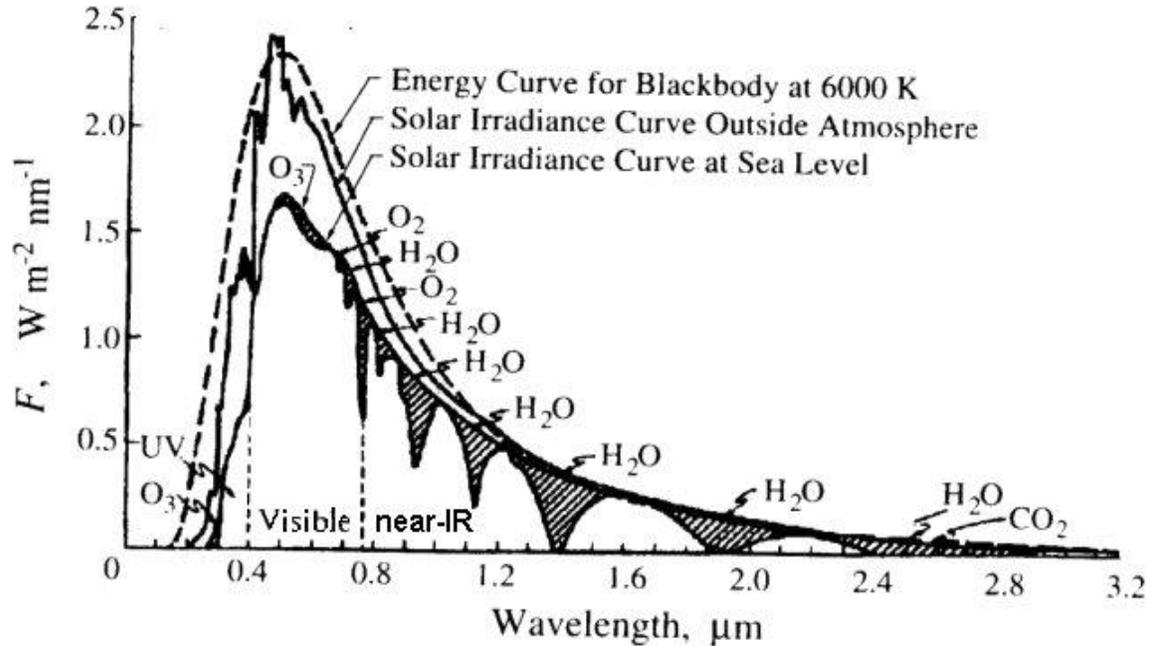

Figure 7.3 Solar spectral irradiance (flux) at the top of the atmosphere and at the surface.

Table 7.3 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

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

> ## UV region:
>
> Absorption of UV radiation in the gaseous atmosphere is primarily due molecular oxygen O_2 and ozone O_3.
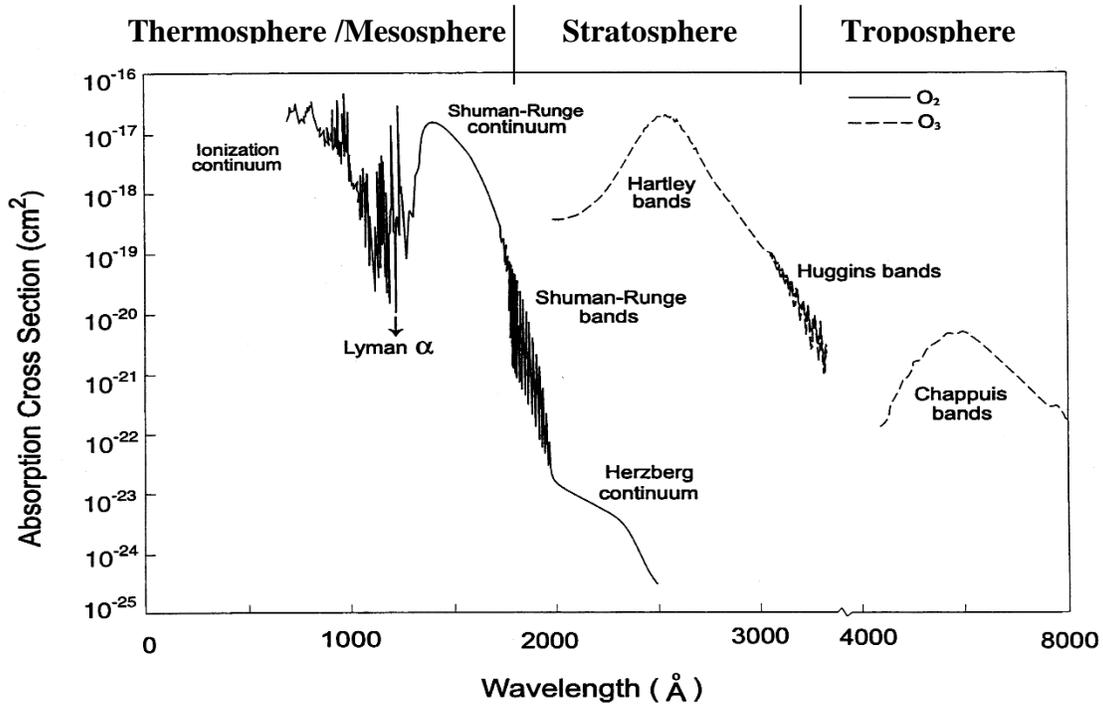

Figure 7.4 Spectral absorption cross-sections of O_2 and O_3

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);

- 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.

3. Summary of satellite sensors for measurements of atmospheric gases

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

Instrument	Platform	Meas. Period	Typical Res. (km)	Global coverage (days)[e]	Spectral Range (μm)	Trop O_3	SO_2	Aer Ind	Trop NO_2	HCHO	BrO	H_2O	CO	CH_4	HNO_3	AOT	Aer prop.	CO_2
TOMS	Nimbus 7, ADEOS, Earth Probe	1978-1992 1996-1997 1996-	38x38 nadir	~1	6λ[d] 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	4λ 0.45-0.87											1	1	
MODIS	Terra Aqua	2000- 2002-	10x10e nadir	2	36λ 0.41-14.2											1	1	
SCIA-MACHY	Envisat	2002-	60x30 nadir	6	0.23-2.3	2-3	1	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	9λ 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 7.4 Satellite instruments providing measurements of atmospheric composition

(gases) https://igacproject.org/sites/default/files/2016-07/Issue_35_Mar_2007.pdf

[a]Some instruments measures aerosol and clouds also
[b]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.
[c]Value given for clear-sky conditions. Clouds impede the retrieval.
[d]Number of discrete wavelengths
[e]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.