Atmosphere Properties and Molecular Absorption Spectrum

Topics:
1. Atmospheric composition and structure
2. Molecular absorption line formation
3. Molecular absorption spectrum on Earth

Reading: Liou 1.3, 3.1, 3.2, 4.1, 4.2.1

Basic Properties of Terrestrial Planet Atmospheres

	Earth	Mars	Venus
mean distance from Sun ($\times 10^6$ km)	150	228	108
Eccentricity	0.017	0.093	0.007
Obliquity (tilt)	23.5	24	177
mean radius (km)	6371	3390	6052
length of solar day (days)	1	1	117
albedo	0.30	0.20	0.80
mean surface temperature (K)	288	215	730
mean surface pressure (bars)	1.01	~0.007	92
surface gravity g (m/s^2)	9.8	3.7	8.9
pressure scale height H (km)	8.5	10.5	15
dry adiabatic lapse rate (K/km)	9.8	4.5	10.5
mean lower atmos. lapse rate (K/km)	6.5	3	8
specific heat c_p (kJ kg^{-1} K^{-1})	1.004	0.83	0.85
gas law constant R_g (J kg^{-1} K^{-1})	287	189	189
mean molecular weight (g/mole)	29.0	43.2	43.5
cloud cover	60%	10%	100%

Ideal gas law is $p = \rho T R_g$; p is pressure, T is temperature, and ρ is density.
Hydrostatic relation is $dp/dz = -g\rho$.
Dry adiabatic lapse rate is $\Gamma_a = -dT/dz = g/c_p$.
Exponential scale height is $p \approx p_{sfc} \exp(-z/H)$ (H depends on T).

Composition of Atmospheres

Volume Fraction of Gases

	Earth	Mars	Venus	Absorbing
Nitrogen, N_2	0.781 (constant)	0.027	0.035	No
Oxygen, O_2	0.210 (constant)	0.0013	20 ppm	MW, visible
Argon, Ar	0.0093 (contant)	0.016	70 ppm	No
Water vapor, H_2O	5 ppm to 0.04	200 ppm	20 ppm	MW to near IR
Carbon Dioxide, CO_2	370 ppm (increasing) (slightly variable)	0.953	0.965	mid IR
Ozone, O_3	10 ppb to 15 ppm (peaks $\sim$35 km)			mid IR
Methane, CH_4	1.8 ppm (increasing)			mid IR
Nitrous oxide, N_2O	0.3 ppm			mid IR
Carbon Monoxide, CO	0.1 ppm (variable)	800 ppm	17 ppm	minor
Sulfur Dioxide, SO_2	1 ppb (variable)		150 ppm	on Venus
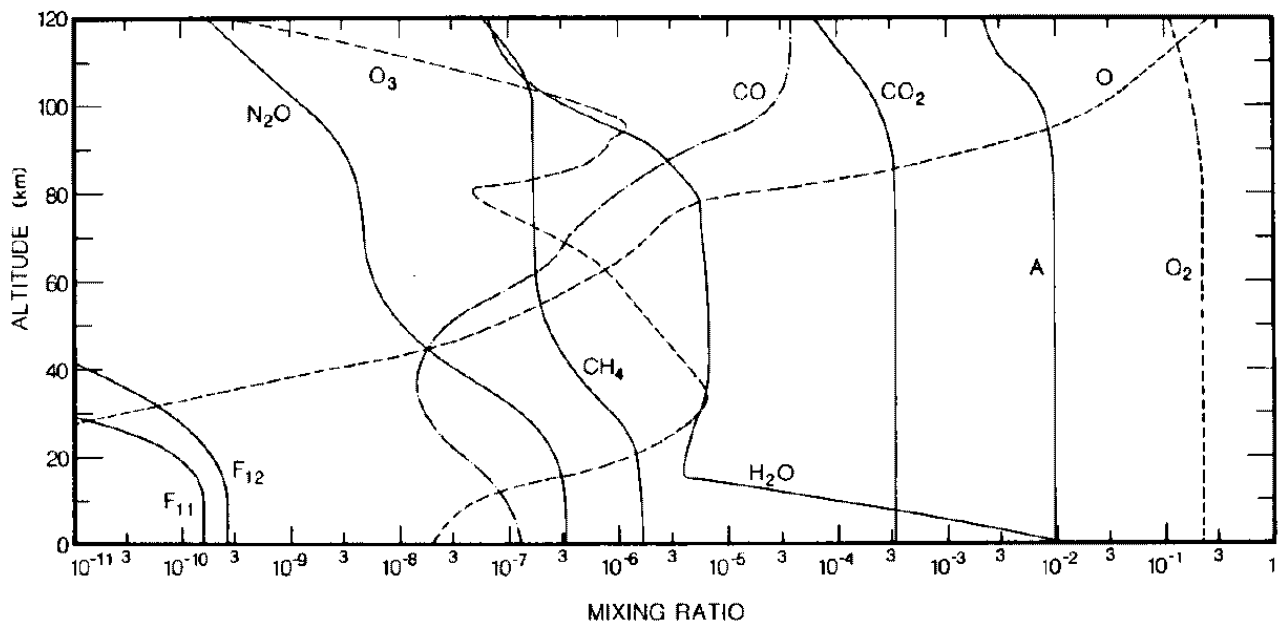
Vertical profiles of volume mixing ratio in the Earth's atmosphere at equinox. [Goody & Yung, Fig. 1.5]

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Aerosols

Aerosols are solid and/or liquid particles with diameters from 0.01 to 10 μm suspended in air.

Earth: Aerosols have minor, but important, radiative effect in Earth's atmosphere. Highest concentration is in the boundary layer ($<$2 km), decreasing with height in troposphere; also significant in stratosphere after large volcanic eruptions. Tropospheric aerosols are highly variable spatially depending on source regions, transport and mixing, and removal processes. Wide range of composition: e.g. sulfates from oceans and pollution, sea salt from ocean spray, mineral dust from soils, and organic compounds from fires.

Mars: Mineral dust in the atmosphere plays a major role in atmosphere radiation that determines temperature structure. Occasional very large dust storms have visible optical depth > 1.

Clouds

Clouds are suspended particles of condensed gases.

Earth: Water and ice clouds throughout troposphere. Location depends on dynamic circulation. Highly variable in structure and optical thickness. Density (water mass/air volume) decreases with temperature (height). Water droplets typically 4 to 25 μm radius; ice crystals 10 to 1000 μm in length.

Mars: Occasional water ice clouds form at low temperatures.

Venus: Dense uniform clouds of sulfuric acid droplet and crystals from 50 - 65 km. Optical depths typically 30; droplet radii from 1 to 10 μm. Thinner haze extends above cloud layer.

More on aerosol and cloud properties in a later section on particle scattering.

Atmospheric Structure

The Earth's atmosphere is divided into four general layers according to the temperature structure:

Region	Height range	Temperature trend
Troposphere	0 to 8 to 18 km	decreasing
Stratosphere	to ≈50 km	steady or increasing
Mesosphere	to ≈90 km	decreasing
Thermosphere	above 90 km	increasing

The temperature increases with height in Earth's stratosphere due to absorption of solar UV radiation by ozone. Venus and Mars do not have a stratosphere and mesosphere because they lack ozone (from oxygen).
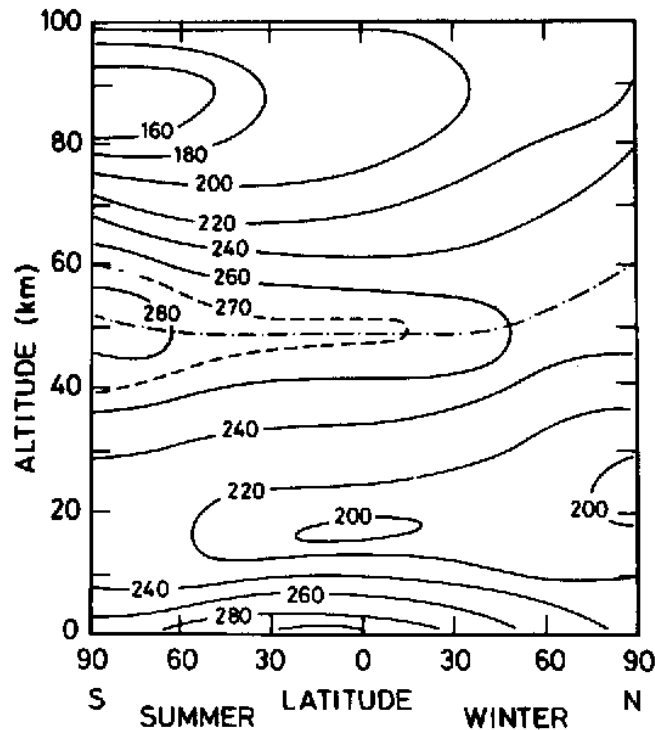
Temperature cross section of Earth's atmosphere at solstice. [Goody & Yung, Fig. 1.3]

The tropopause height is high in the tropics and low in the arctic.
The water vapor density is mainly a function of temperature in the troposphere due to the strong dependence of the saturation vapor density on temperature. Water vapor is a trace gas in the stratosphere.
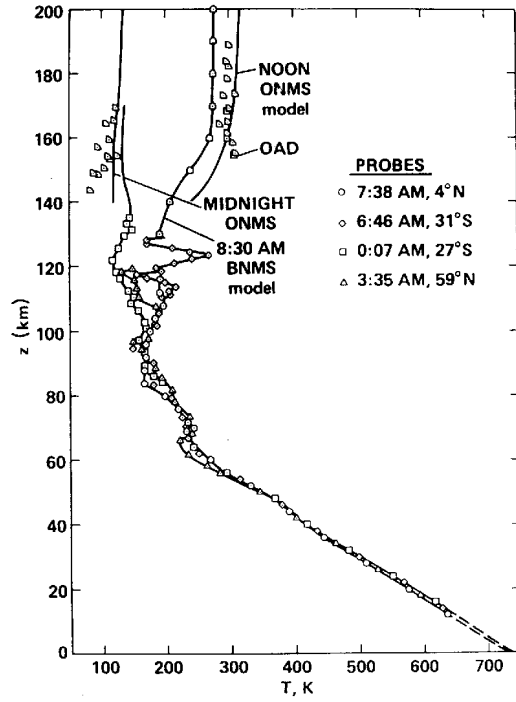The ozone amount is lowest in the tropics and highest in the subarctic winter due to the Brewer-Dobson circulation transport from equator to pole.
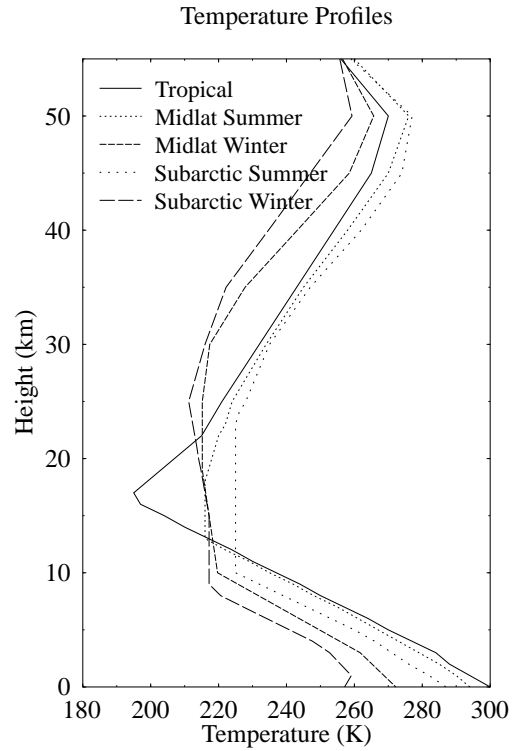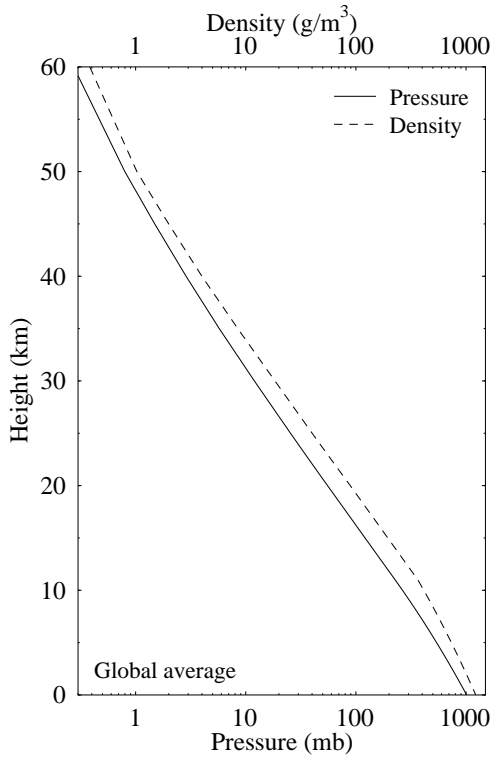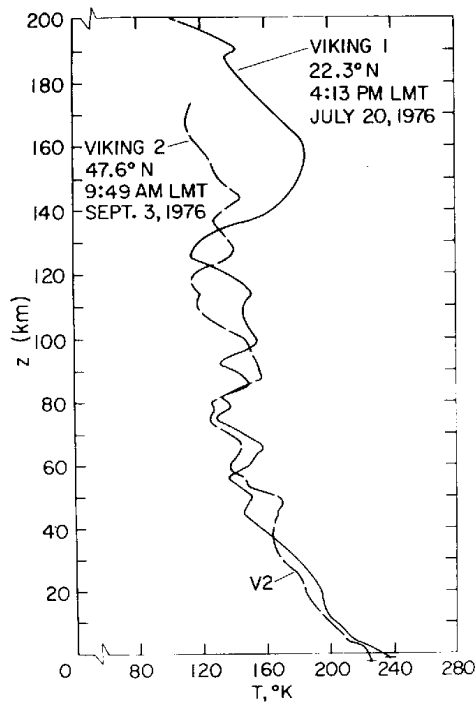
Pressure/density/temperature profiles of standard Earth atmospheres.
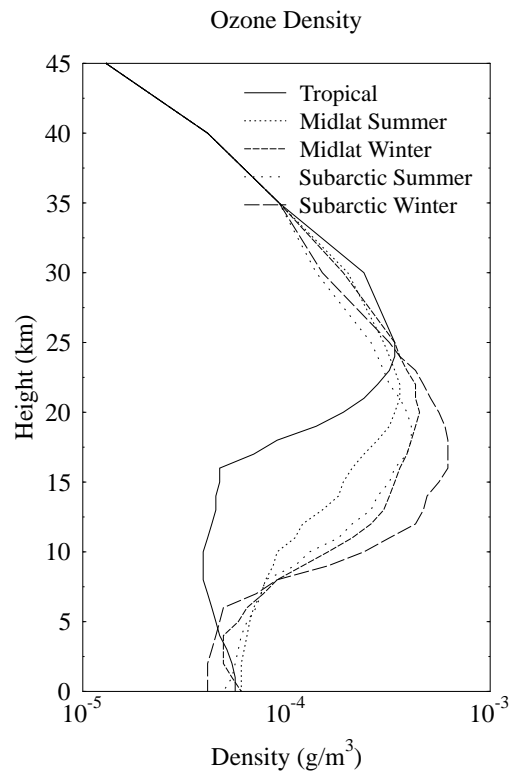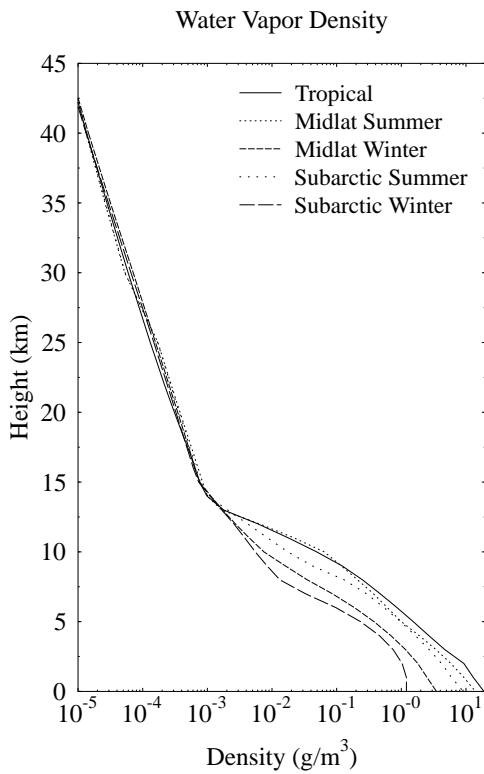
Water vapor and ozone density profiles of standard Earth atmospheres.

Venusian temperature profiles compiled by Seiff from Pioneer Venus observations. The acronyms refer to various experiments.

Martian temperature profiles from Viking entry data from Seiff and Kirk (1977).

Molecular Absorption

Quantum mechanics governs interaction of light and single molecules.
Absorption of a photon is due to a transition to a higher quantized energy level in an atom or molecule.
Frequency of a photon is proportional to energy of transition:

$$E_{\text{upper}} - E_{\text{lower}} = \Delta E = h\tilde{\nu} = hc\nu = hc/\lambda$$

where $h = 6.626 \times 10^{-34}$ J s is Planck's constant.
Electronic transitions cause absorption in visible and ultraviolet.
Absorption in the microwave and infrared is from two types of molecular transitions: rotational and vibrational.
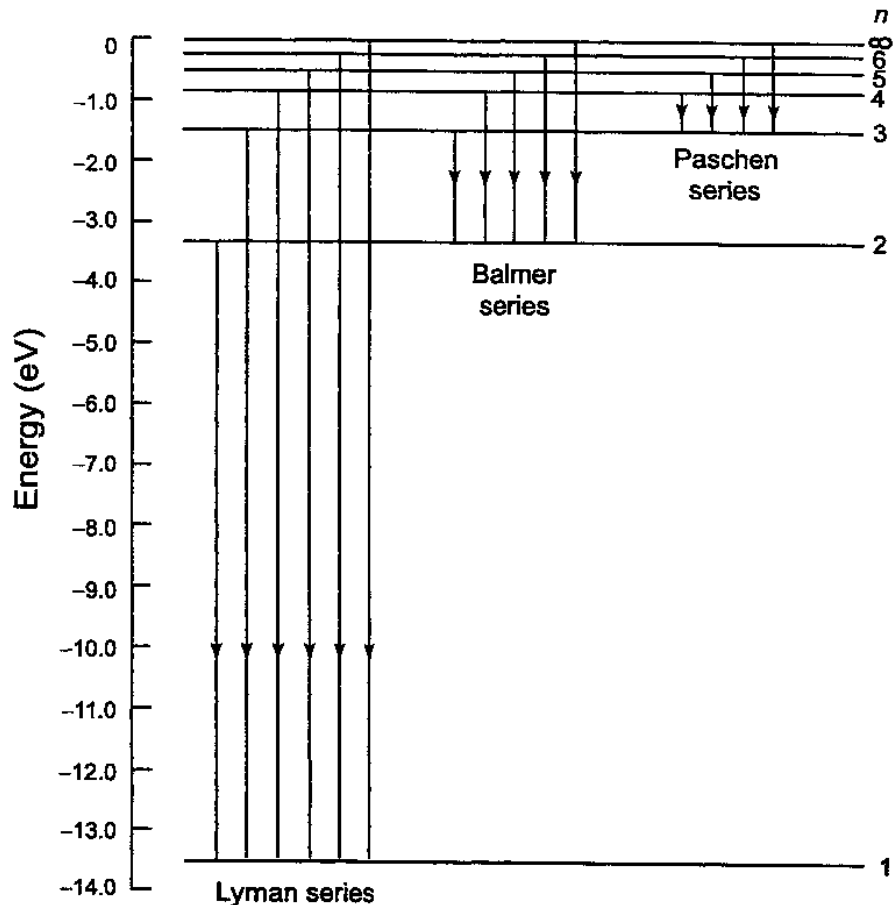
An energy level diagram for the hydrogen atom showing electronic transitions between different quantum numbers n. [Liou, 2001; Fig. 1.9]

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The energy of a molecule can be written as

$$E = E_{\mathrm{rot}} + E_{\mathrm{vib}} + E_{\mathrm{el}}$$

E_{rot} is the energy of rotation of molecule around center of mass; about 1-500 cm^{-1} (microwave to mid-infrared).

E_{vib} is the energy of vibration of atoms about their equilibrium positions; about 500-10^4 cm^{-1} (mid-infrared to near-IR).

E_{el} is the energy of the electron arrangement; about 10^4-10^5 cm^{-1} (visible and ultraviolet).

The different energies of a molecule, E_{rot}, E_{vib}, and E_{el} are quantized and can have only discrete vaues specified by one or more *quantum numbers*. Not all transitions between quantized energy levels are allowed; there are selection rules that specify which transitions are allowed.

Rotational Transitions

Rigid rotator model for linear molecules.   Rotational energy for molecule with moment of inertia I is $E = L^2/2I$. Moment of inertia is $I = \sum_i m_i r_i^2$.
Angular momentum L is *quantized*, so

$$E_J = \frac{J(J+1)(h/2\pi)^2}{2I}$$

where J is integer rotational quantum number.
Quantum mechanical selection rule (photon has angular momentum $h/2\pi$):
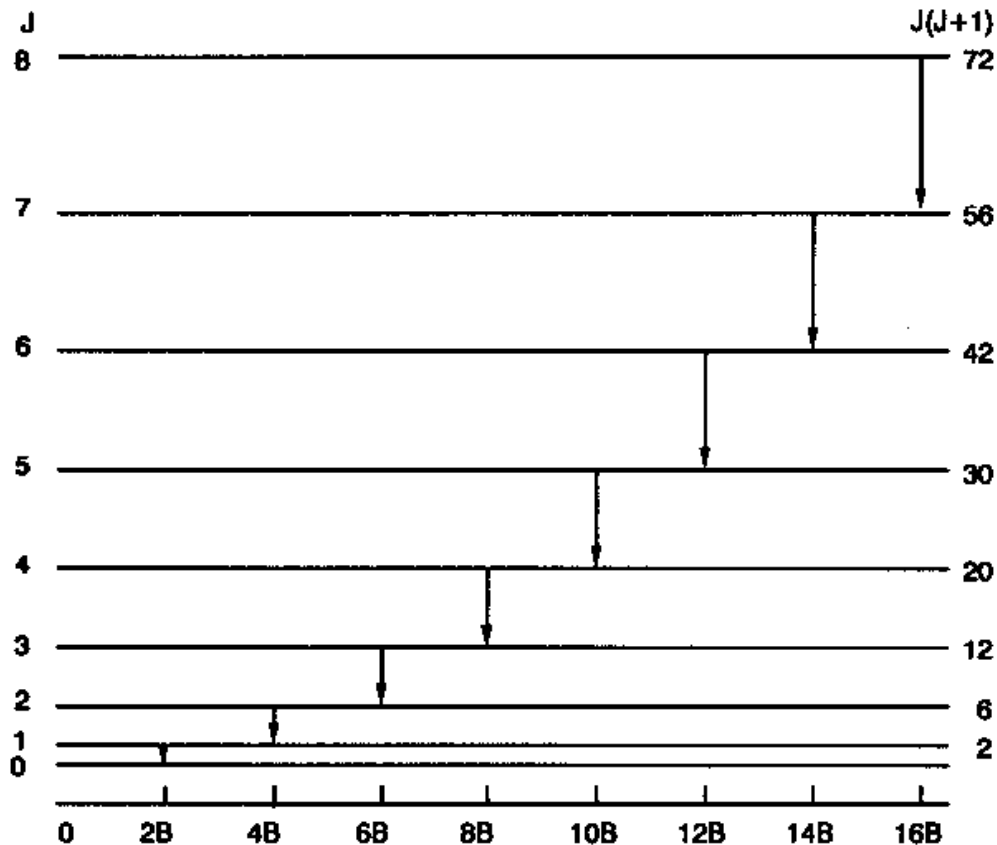
$$\Delta J = \pm 1$$

Therefore the wavenumber of a rotational transition is

$$\nu = \frac{1}{hc}(E_{J+1} - E_J) \; = 2B(J+1) \quad B = \frac{h}{8\pi^2 cI}$$

B is called the rotational constant (units: cm^{-1}).

Quadratic in J energy levels give linear in J transition energies or equally spaced absorption lines ($\Delta\nu = 2B$).

A rigid rotator has quadratically spaced energy levels that give evenly spaced absorption lines. Rotational forces distort the spacings in nonrigid rotators. [Kyle, Fig. 8.1]

Example: Assume a rotational constant of $B = 2.0\,\mathrm{cm^{-1}}$. Say a photon is absorbed in a rotational transition from $J = 7$ to $J = 8$. The rotational energy levels are $E_J = 56Bhc \rightarrow E_J = 72Bhc$ and the change in energy levels is $\Delta E = 16Bhc$ for a wavenumber of $\nu = 16B = 32\,\mathrm{cm^{-1}}$.

Nonlinear molecules: H_2O and O_3 are asymmetric tops with three moments of inertia; gives very complex spectra.

Permanent dipole moment needed for pure rotational lines:

Species	Pure rotation lines
H_2O, O_3	microwave and far IR
O_2	microwave (weak, from permanent magnetic dipole)
CO_2, N_2	none

Vibrational Transitions

Three vibrational modes of molecules:

ν_1 symmetric stretch (2.7 μm H_2O)

ν_2 bending mode (15.0 μm CO_2, 6.3 μm H_2O)

ν_3 asymmetric stretch (4.3 μm CO_2, 2.7 μm H_2O)

Vibrating molecule is like quantum mechanical harmonic oscillator:

$$E_n = h\nu = (n + 1/2)\frac{h}{2\pi}\sqrt{\frac{k_{bond}}{m_r}}$$

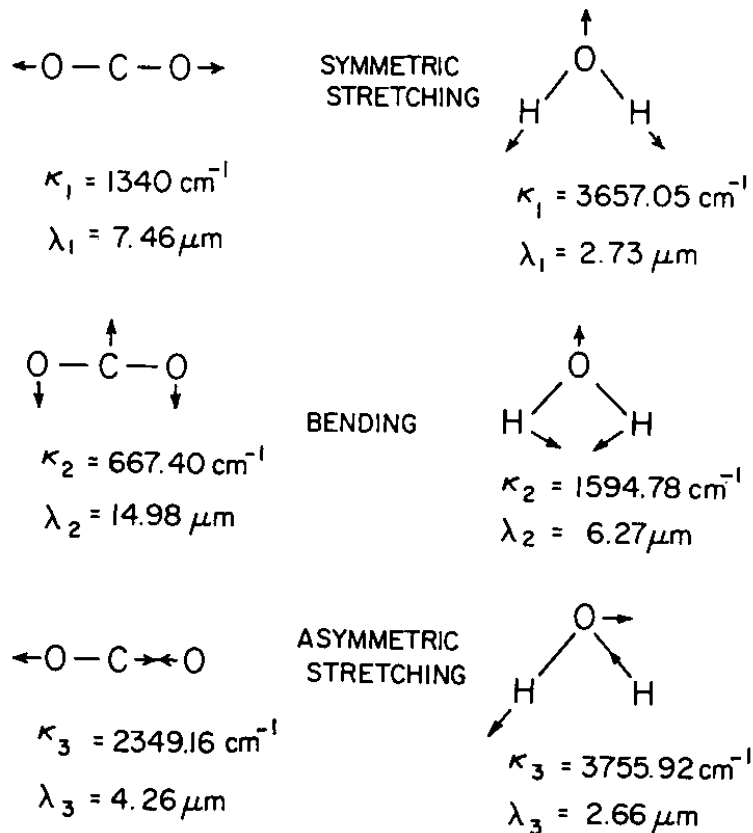k_{bond} = spring constant of bond, m_r = reduced mass,

n = vibrational quantum number.

Most infrared absorption bands from the fundamental transition: $n = 0 \rightarrow 1$.

Hot bands are from lower state $n > 0$.

Isotopic bands are from nonstandard isotopes in molecule.

Combination bands are from multiple vibrational mode changes.

Vibrational modes of carbon dioxide and water vapor. [Kidder and Vonder Haar, Fig. 3.15]

Vibrational-Rotational Transitions

Vibrational transitions include rotational transitions, giving a band of many absorption lines.

For a linear molecule: P branch ($\Delta J = -1$) is lines below band center (vibrational energy only), Q branch ($\Delta J = 0$) is near band center, R branch ($\Delta J = +1$) is above center.
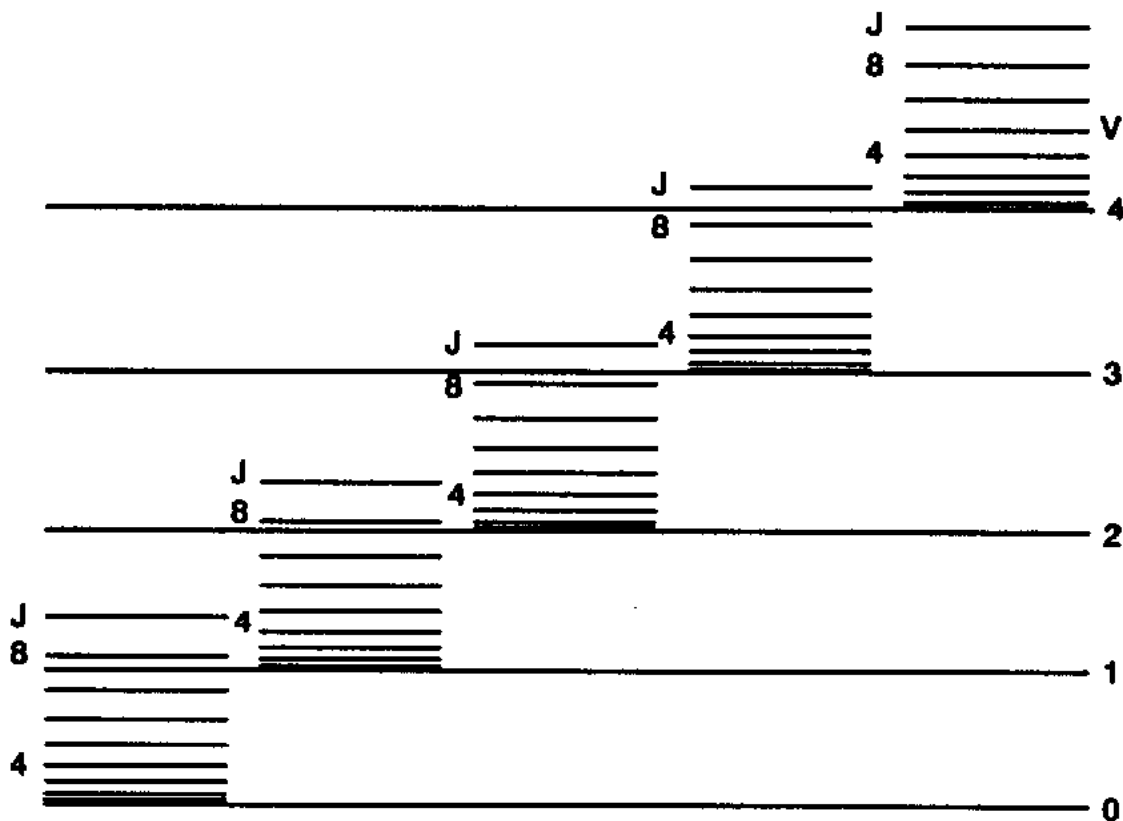
Compare rotational and vibrational transitions with thermal energy:
   Thermal ($k_B T$): $\nu = k_B T/hc = 250 \text{ K}/1.44 \text{ K cm} = 175 \text{ cm}^{-1}$
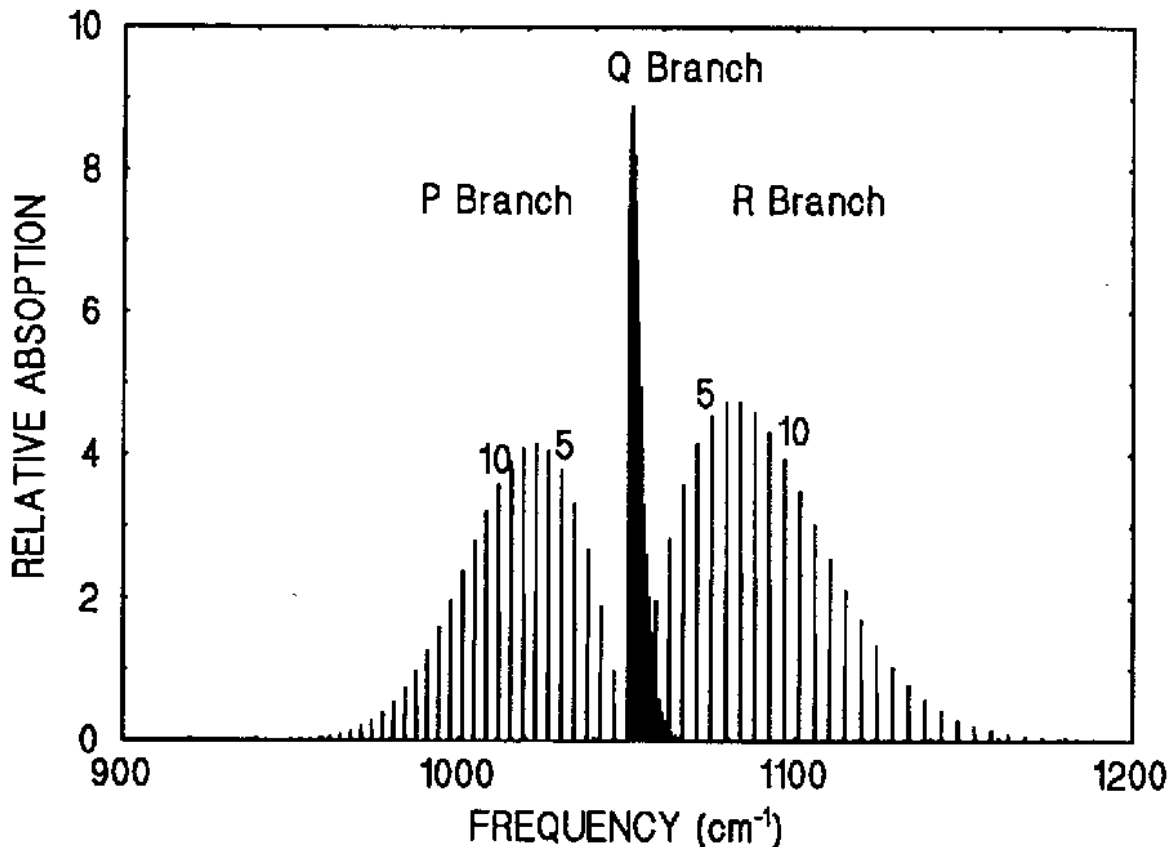   Vibrational transitions: $\sim 600 < \nu < 10000 \text{ cm}^{-1}$
   Rotational transitions: $\sim 1 < \nu < 500 \text{ cm}^{-1}$
Molecules in lowest vibrational state, but many rotational states occupied.

Each vibrational state has an associated set of rotational states. Each vibrational state has roughly the same set of rotational energies. [Kyle Fig. 8.5]

Simulated high resolution absorption spectrum of a linear molecule. The Q branch ($\Delta J = 0$) is sometimes allowed if there are more than two atoms in the molecule. [Kyle Fig. 9.2]

Absorption from a Line

Absorption spectrum of a single line is broken into two parts - shape and strength:

$$\tau = k_\nu u \quad k_\nu = S f(\nu - \nu_0) \quad \int f(\nu) d\nu = 1$$

τ is optical depth of layer, u is absorber amount, k_ν is absorption coefficient (e.g. g/cm^2), ν_0 is the line center frequency, $f(\nu)$ is the line shape function, and S is the line strength or intensity.

Units: $f(\nu)$ [cm] $\quad$ S [cm/g] or [cm/molec]

Dependencies: $S(T)$ depends on temperature; $f(\nu - \nu_0; \alpha)$ depends on line halfwidth $\alpha(p, T)$, which depends on pressure and temperature.

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Atmospheric Absorption Features

Water vapor H_2O asymmetric top
permanent dipole moment - strong pure rotational band ($< 600 \text{ cm}^{-1}$)
ν_2 - 6.3 um (1250 - 2200 cm^{-1}), ν_1, ν_3 close at 2.7 μm
Overtone and combination bands 3.2, 1.87, 1.38, 1.1, 0.94 μm

Water vapor continuum
Small but important absorption between lines not accounted for with standard line shape. From microwave to near infrared, especially important in atmospheric window 8 - 12 μm.
Form of absorption has self-broadening and foreign broadening terms:
$\quad k_\nu = \sigma_s e + \sigma_f (p - e)$ (e is vapor pressure)
$\sigma_f / \sigma_s \sim 0.002$ so in humid air, mainly is *e-type* absorption.
Simple, but dated, parameterization due to Roberts et al. (1976).
Clough et al developed a much more complicated semi-empirical parameterization called CKD (latest CKD_2.4 is in LBLRTM).

Carbon dioxide CO_2 linear
No permanent dipole moment $\rightarrow$ no pure rotational band.
Symmetry $\rightarrow$ no symmetric stretch (ν_1 band).
ν_2 - 15.0 μm band (550-750 cm^{-1}); ν_3 - 4.3 μm band
ν_1, ν_3 combination - 2.7 μm

Ozone O_3 asymmetric top
rotational band - but weak from low abundance
ν_1, ν_3 close - make 9.6 μm band (1000 - 1080 cm^{-1});
ν_2 - 14.3 μm (masked by CO_2 band)
Electronic transitions:
Chappuis, weak 0.5 to 0.7 μm
Huggins, 0.30 - 0.35 μm   Hartley, strong 0.20 to 0.30 μm

Nitrogen N_2
Nothing in IR. Electronic bands < 0.1 μm

Oxygen O_2

Permanent magnetic dipole $\rightarrow$ weak rotational band in microwave.

Microwave: band at 60 GHz, lines at higher frequencies

Weak bands in visible - "A" band 0.76 μm

Electronic bands < 0.2 μm

Methane CH_4 spherical top (no rotation band)

ν_3 at 3.3 μm, ν_4 at 7.66 μm
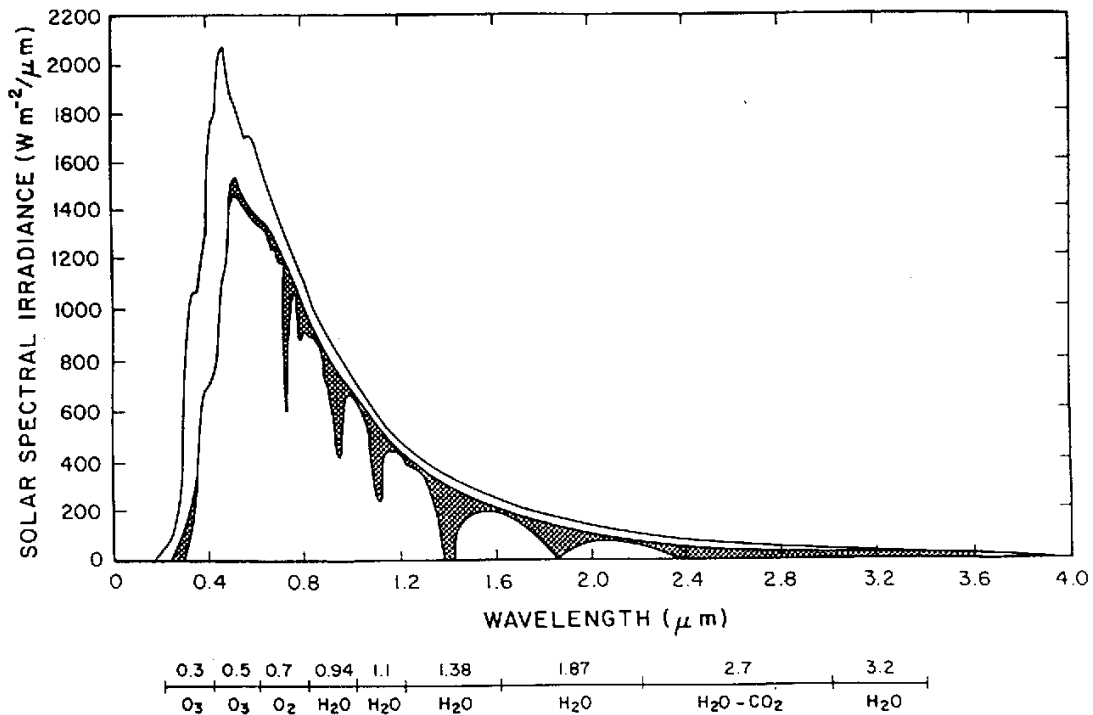

Nitrous oxide N_2O N-N-O linear (no rotation band)

ν_1 at 7.8 μm, ν_3 at 4.5 μm

Carbon monoxide   CO

ν at 4.65 μm

Sulfur dioxide SO_2 on Venus

ν_1 at 8.7 μm, ν_2 at 19.3 μm, ν_3 at 7.35 μm

Solar spectral irradiance at the top of the atmosphere and at sea level. The shaded ares represent absorption due to gases in the Earth's atmosphere. [Liou, 1980; Fig. 2.6]
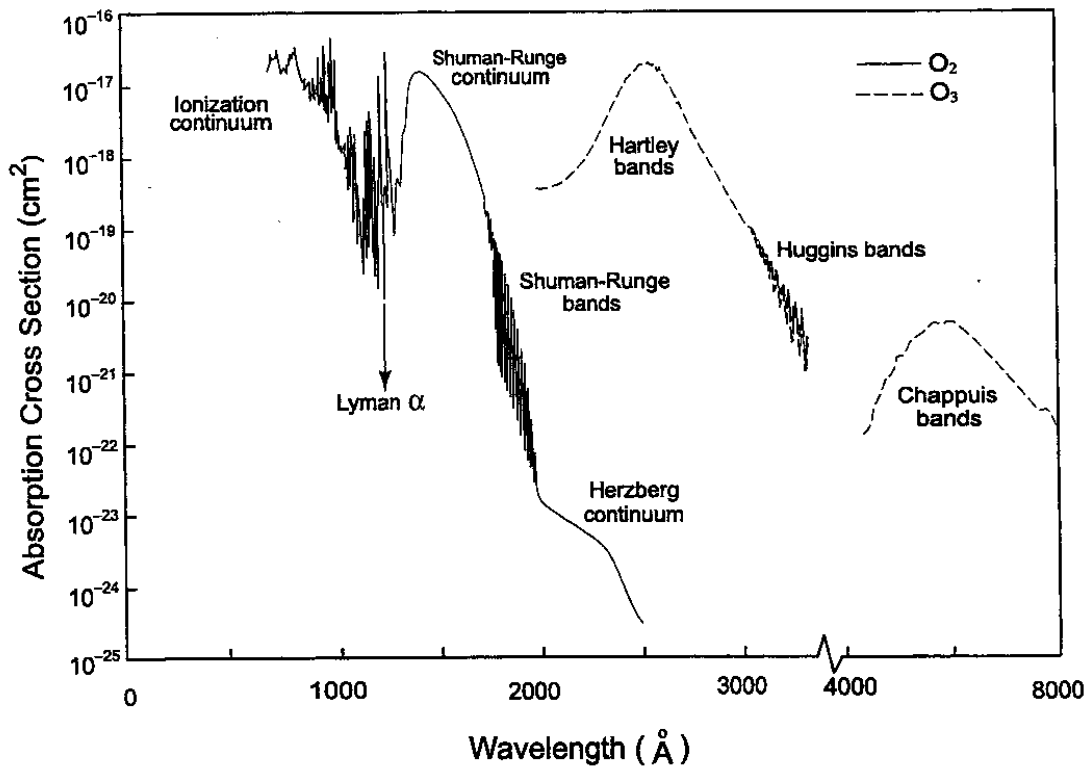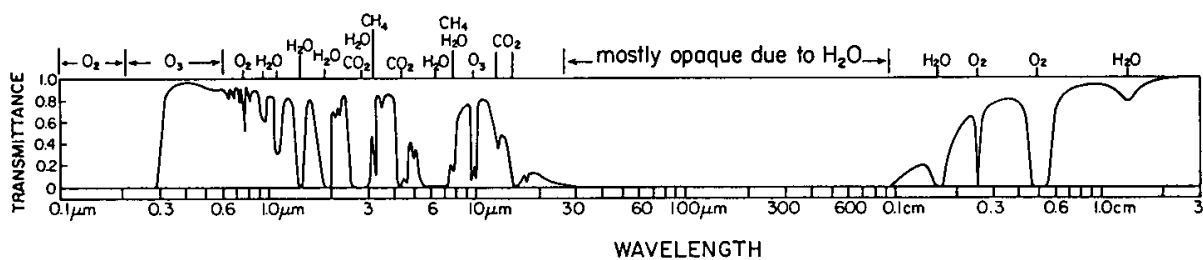
Absorption cross sections of ozone and molecular oxygen in the ultraviolet. [Liou, 2001; Fig. 3.5]
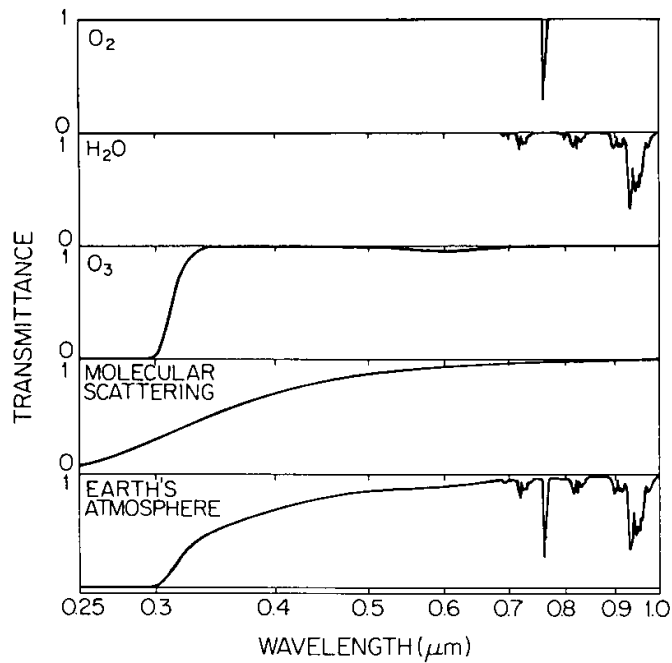
Vertical transmission in the Earth's atmosphere (molecules only) from 0.25 to 1.0 μm.[Kidder and Vonderhaar, Fig. 3.11]
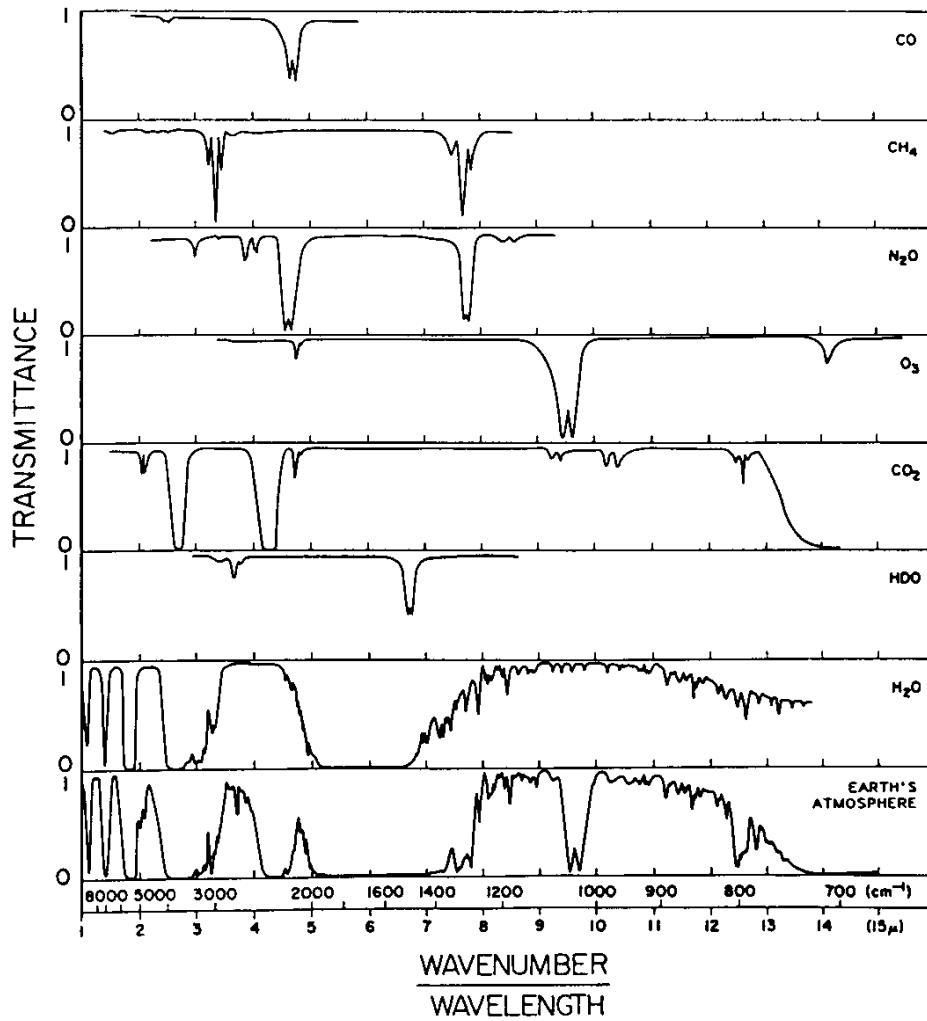
Infrared vertical transmission in the Earth's atmosphere (molecules only) [Kidder and Vonderhaar, Fig. 3.12]

Low resolution transmission modeled spectrum of the Earth's atmosphere showing molecular absorption bands at all wavelengths. [Kidder and Vonderhaar, Fig. 3.14]

Earth Transmission Spectra

US standard atmosphere
molecules only
MODTRAN3 model
10 cm^{-1} resolution

Space to 0 km

Space to 11 km
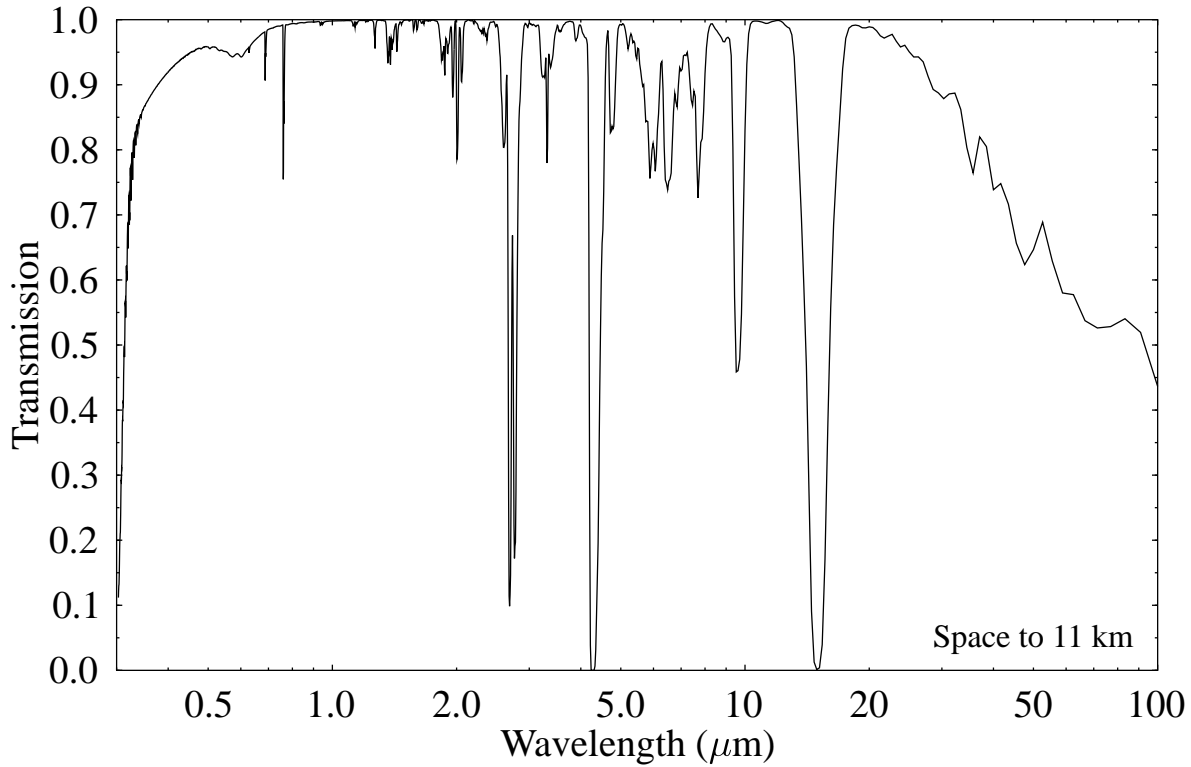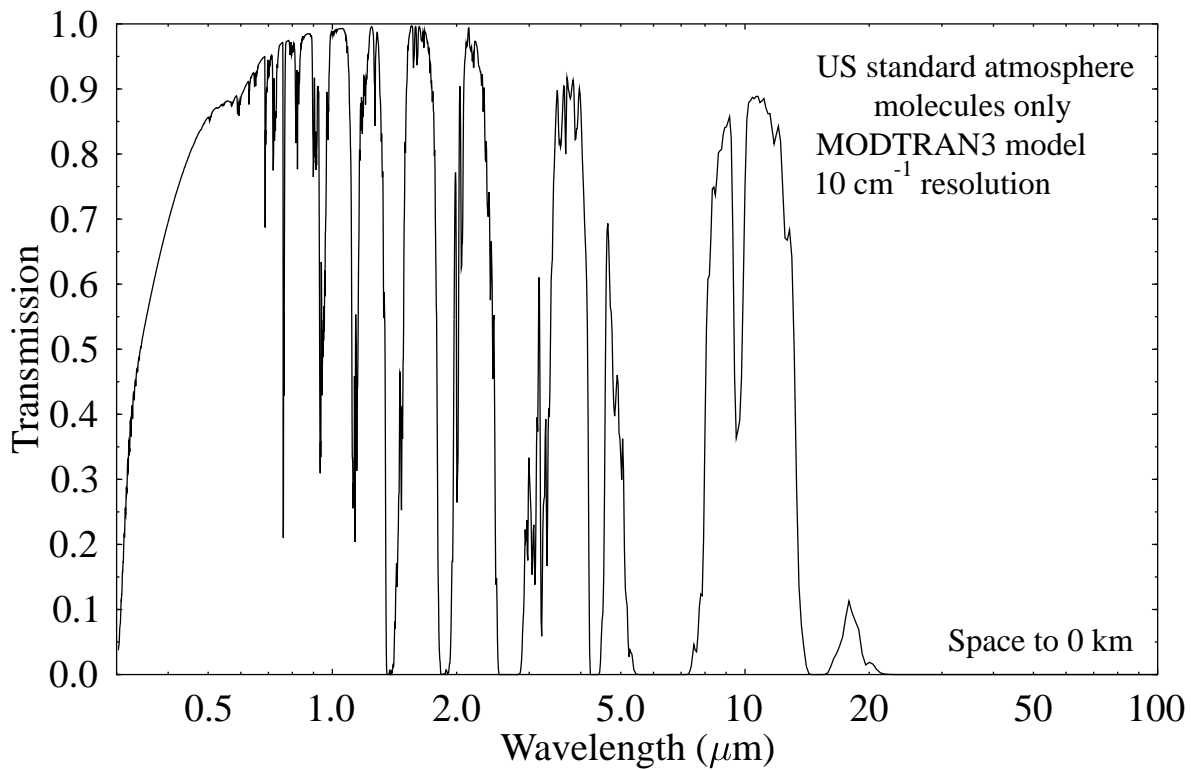
Low resolution transmission spectrum of the atmosphere down to the surface and to the tropopause.