Atmospheric Physics

Lecture 7

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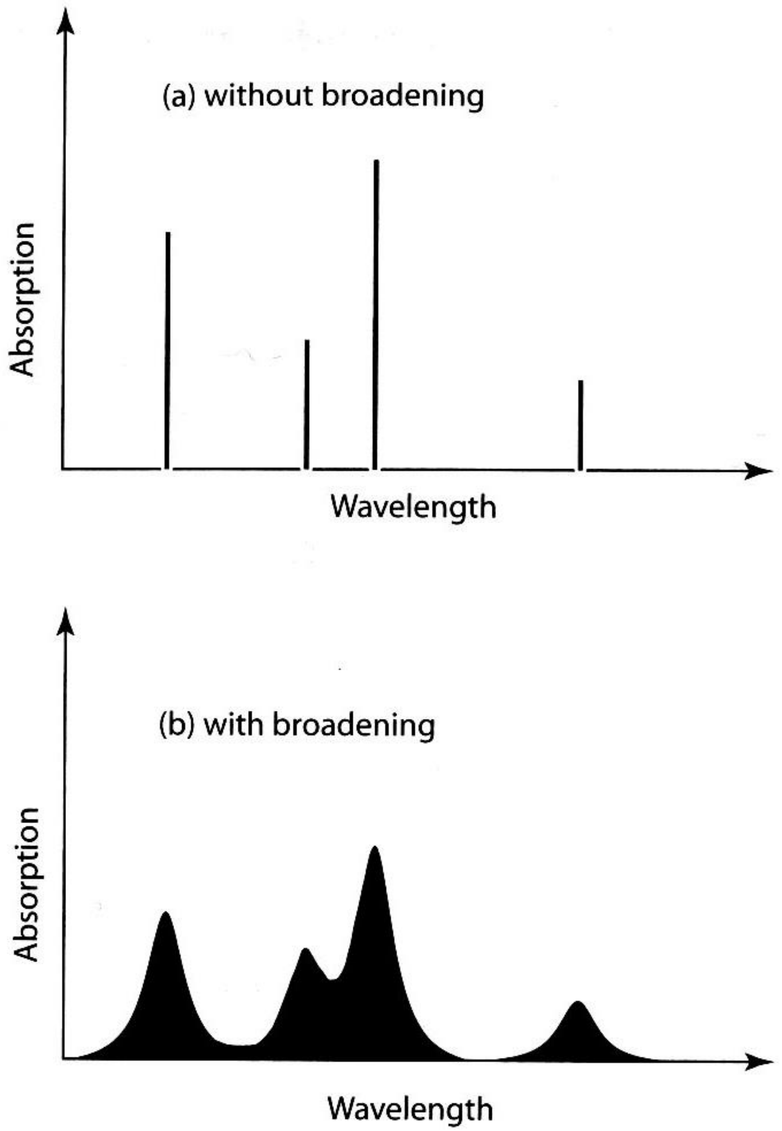
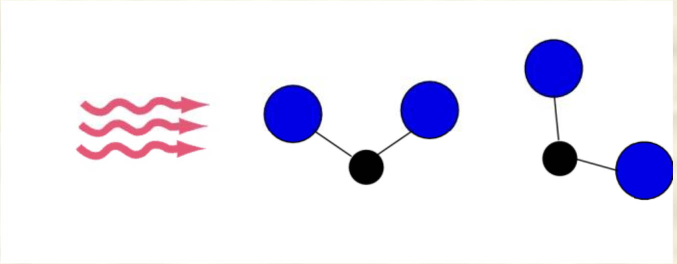
Absorption line shapes

Doppler broadening: random translational motions of individual molecules in any gas leads to Doppler shift of absorption and emission wavelengths (important in upper atmosphere)

Pressure broadening: collisions between molecules randomly disrupt natural transitions between energy states, so that absorption and emission occur at wavelengths that deviate from the natural line position (important in troposphere and lower stratosphere)





Molecules absorb radiation at particular wavelengths, depending on amount of energy required to cause vibration or rotation of atomic bond.

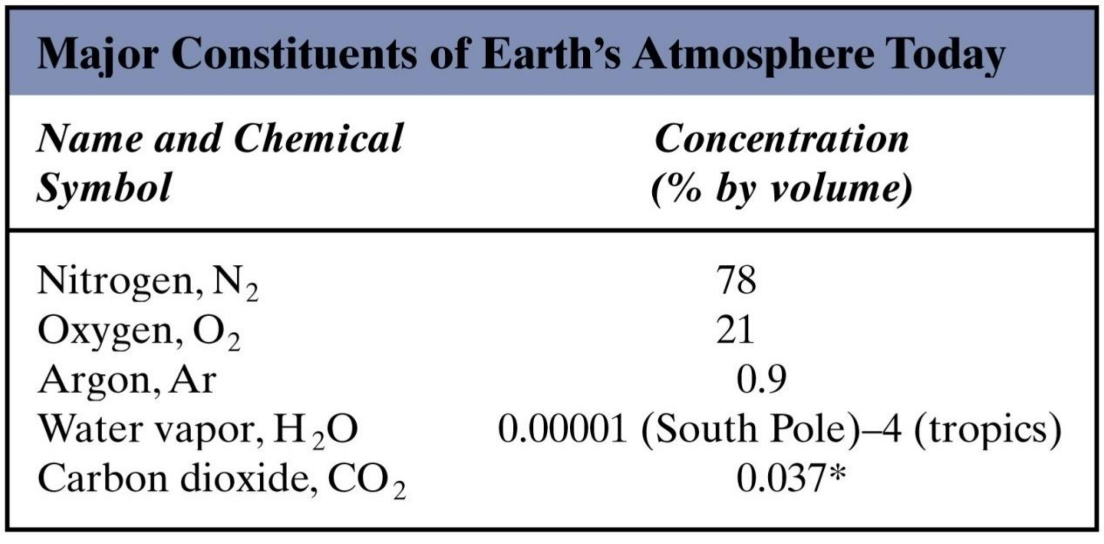
Two essential things for the greenhouse effect:

The Earth's atmosphere is mostly transparent to visible radiation (why not totally)

The Earth's atmosphere is mostly opaque to infrared radiation.

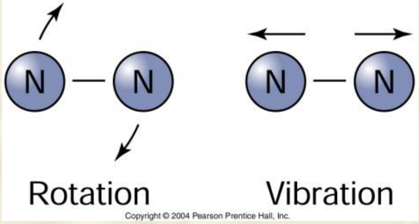
The composition of the Earth's atmosphere

(Plus other trace components, e.g. methane, CFCs, ozone)



Major Constituents of Earth's Atmosphere Today

Name and Chemical Symbol	*Concentration (% by volume)*
Nitrogen, N_2	78
Oxygen, O_2	21
Argon, Ar	0.9
Water vapor, H_2O	0.00001 (South Pole)–4 (tropics)
Carbon dioxide, CO_2	0.037*



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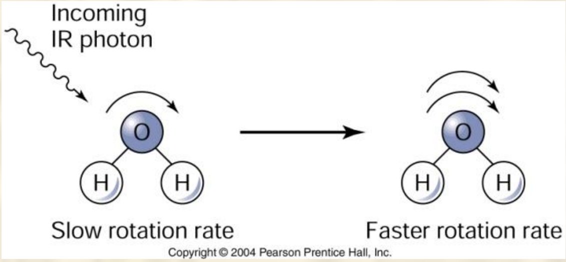
Bi-atomic molecules (O_2, N_2) can only absorb high energy photons, meaning ultraviolet wavelengths and shorter.



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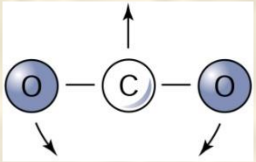
Tri-atomic molecules (H_2O, CO_2) can absorb lower energy photons, with wavelengths in the infrared



Radiation in the Atmosphere

Deviations from blackbody due to absorption by the solar atmosphere, absorption and scattering by the earth's atmosphere (below).

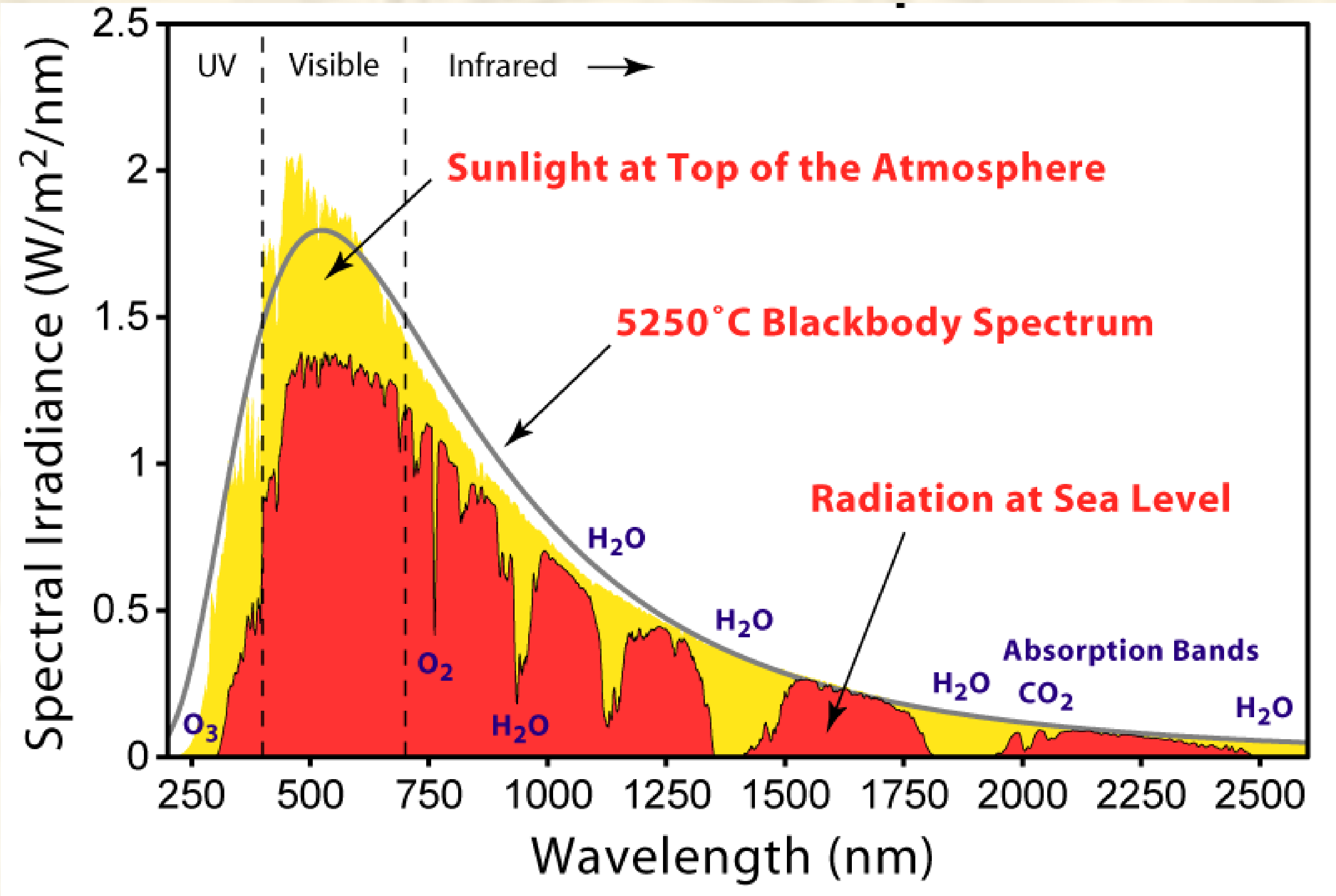
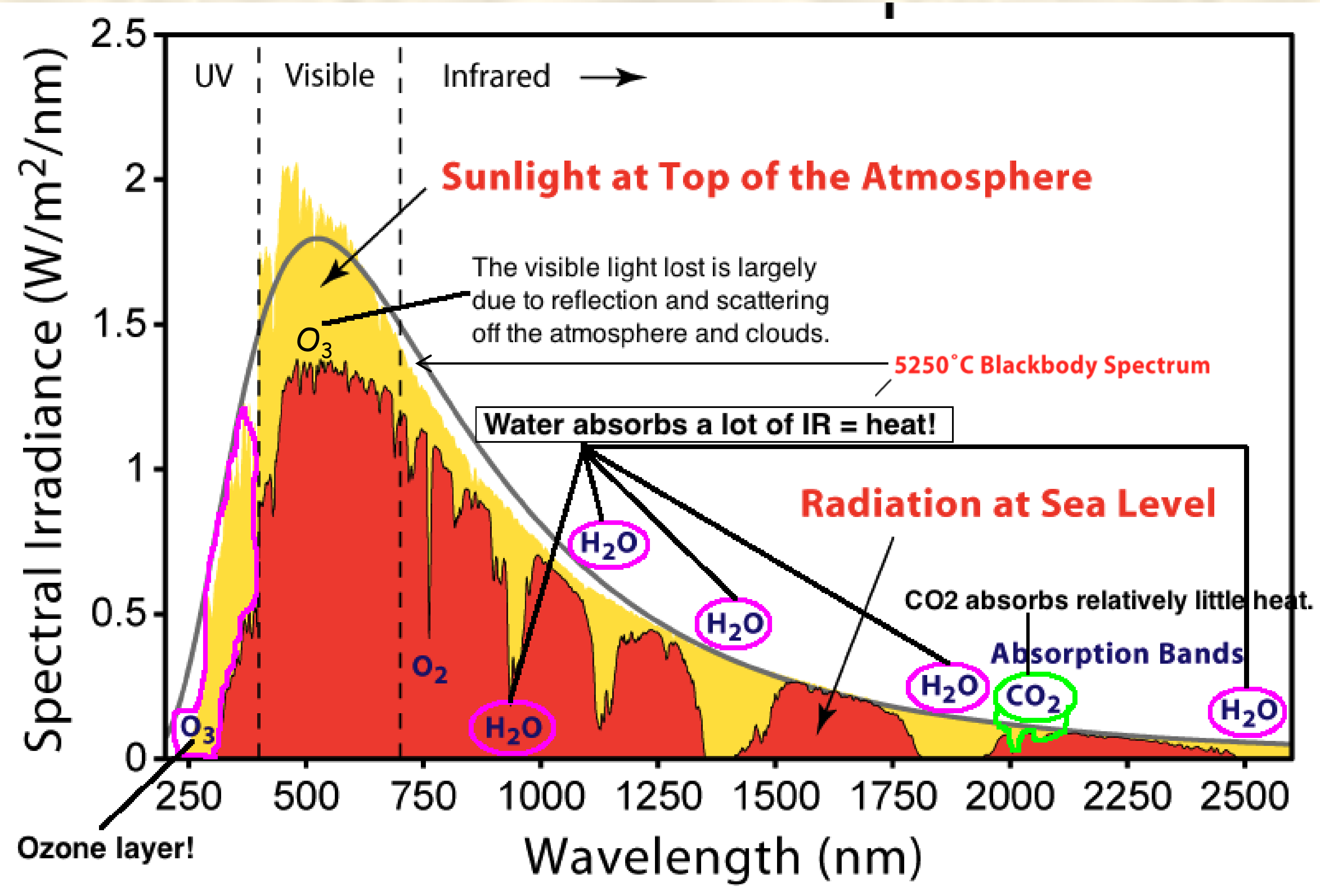


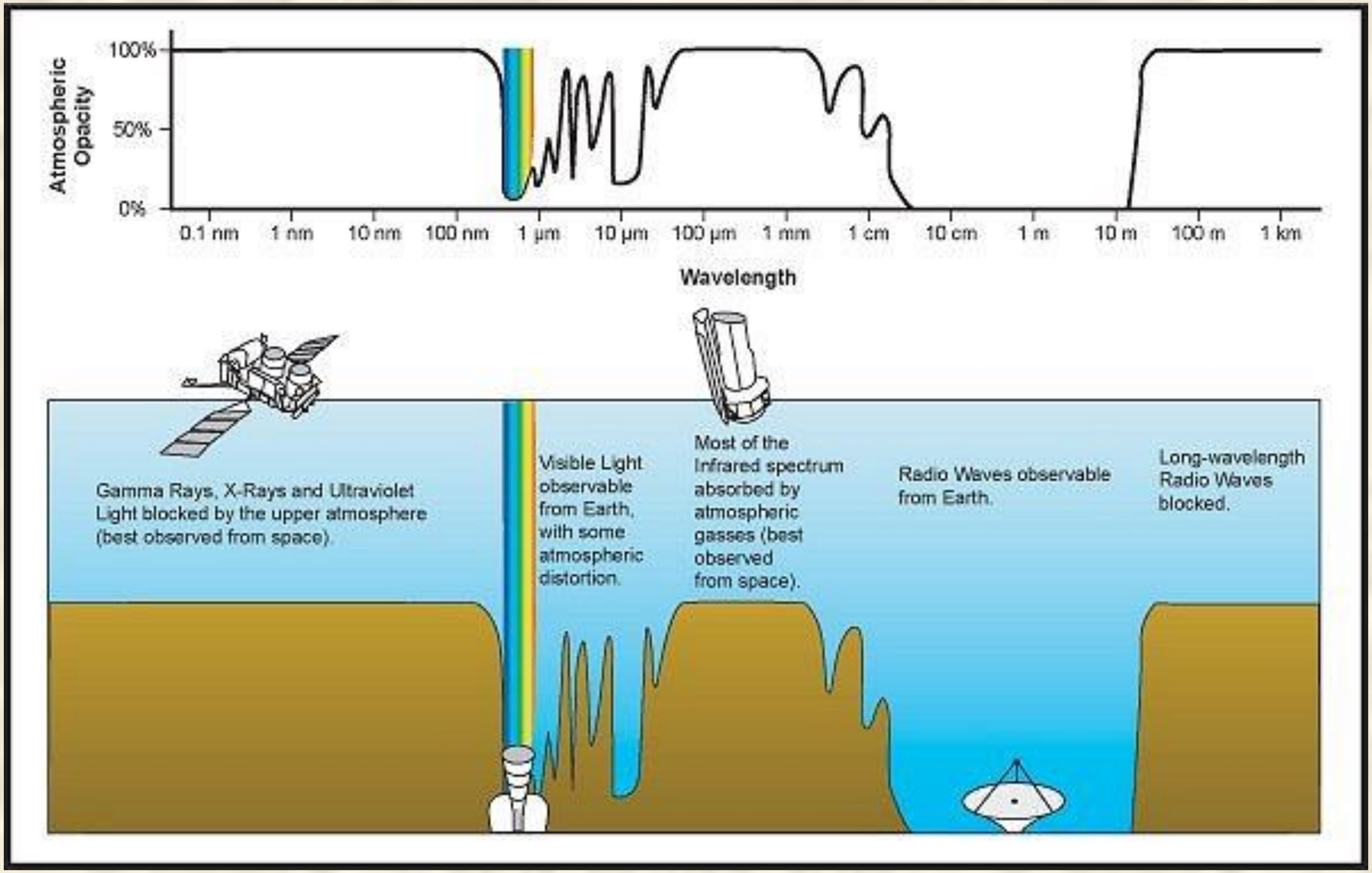
Fig. 3.13

Absorption by atmospheric gases

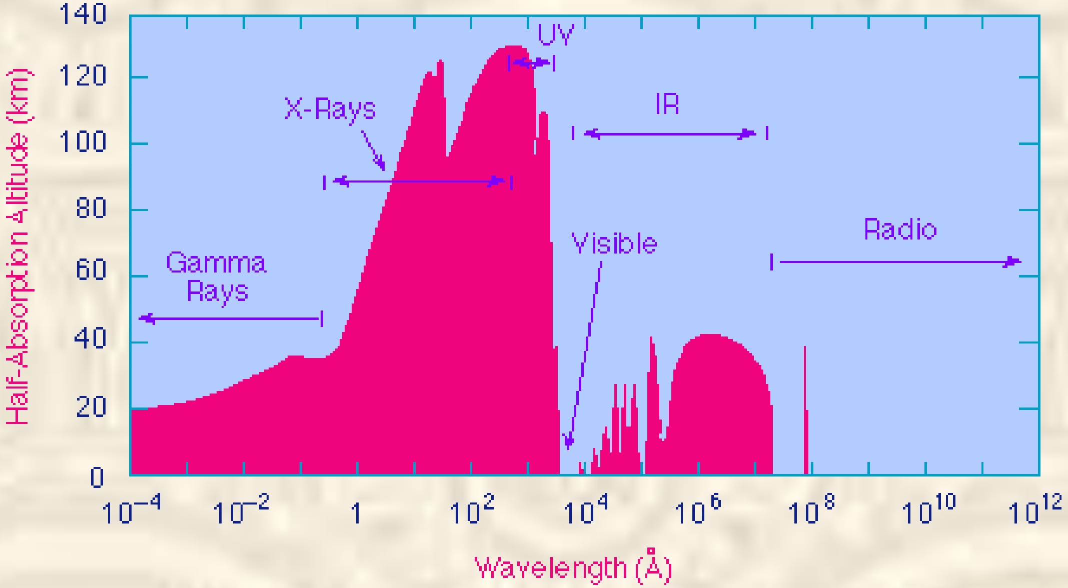
The solar spectrum



Atmospheric Windows



Atmospheric Windows



The dominant windows in the atmosphere are seen to be in the visible and radio frequency regions, while X-Rays and UV are seen to be very strongly absorbed and Gamma Rays and IR are somewhat less strongly absorbed.

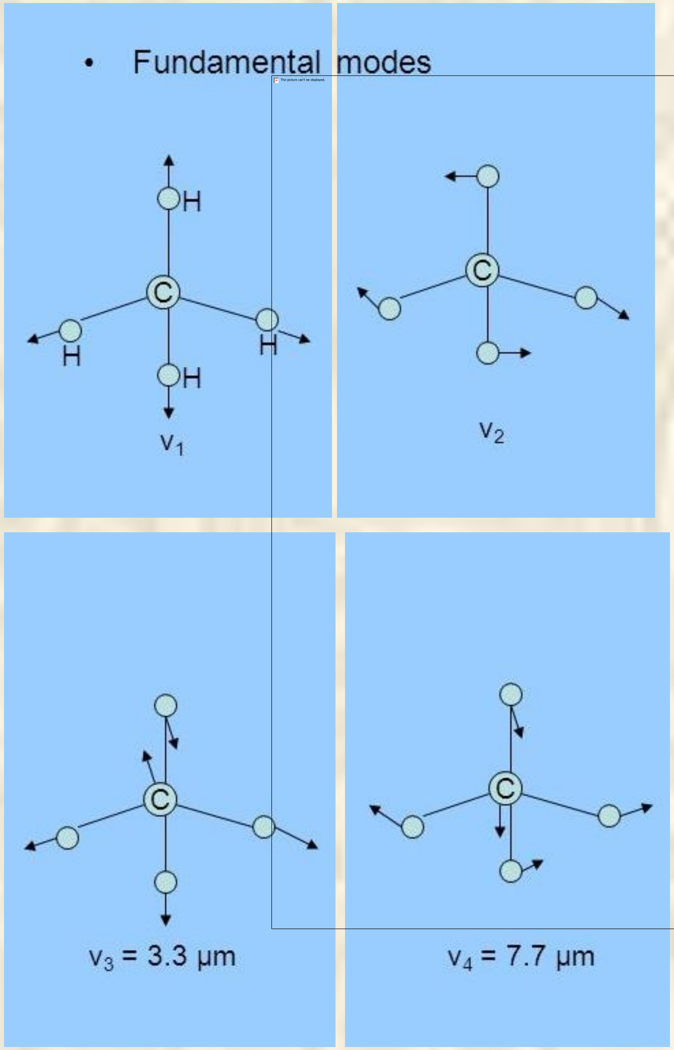
Infrared Windows in the Atmosphere

Wavelength Range	Sky Transparency	Sky Brightness
1.1 - 1.4 microns	high	low at night
1.5 - 1.8 microns	high	very low
2.0 - 2.4 microns	high	very low
3.0 - 4.0 microns	3.0 - 3.5 microns: fair 3.5 - 4.0 microns: high	low
4.6 - 5.0 microns	low	high
7.5 - 14.5 microns	8 - 9 microns and 10 - 12 microns: fair others: low	very high
17 - 40 microns	very low	very high
330 - 370 microns	very low	low

The Primary Greenhouse Gases

Infra-red absorption

CH_4



- Fundamental modes

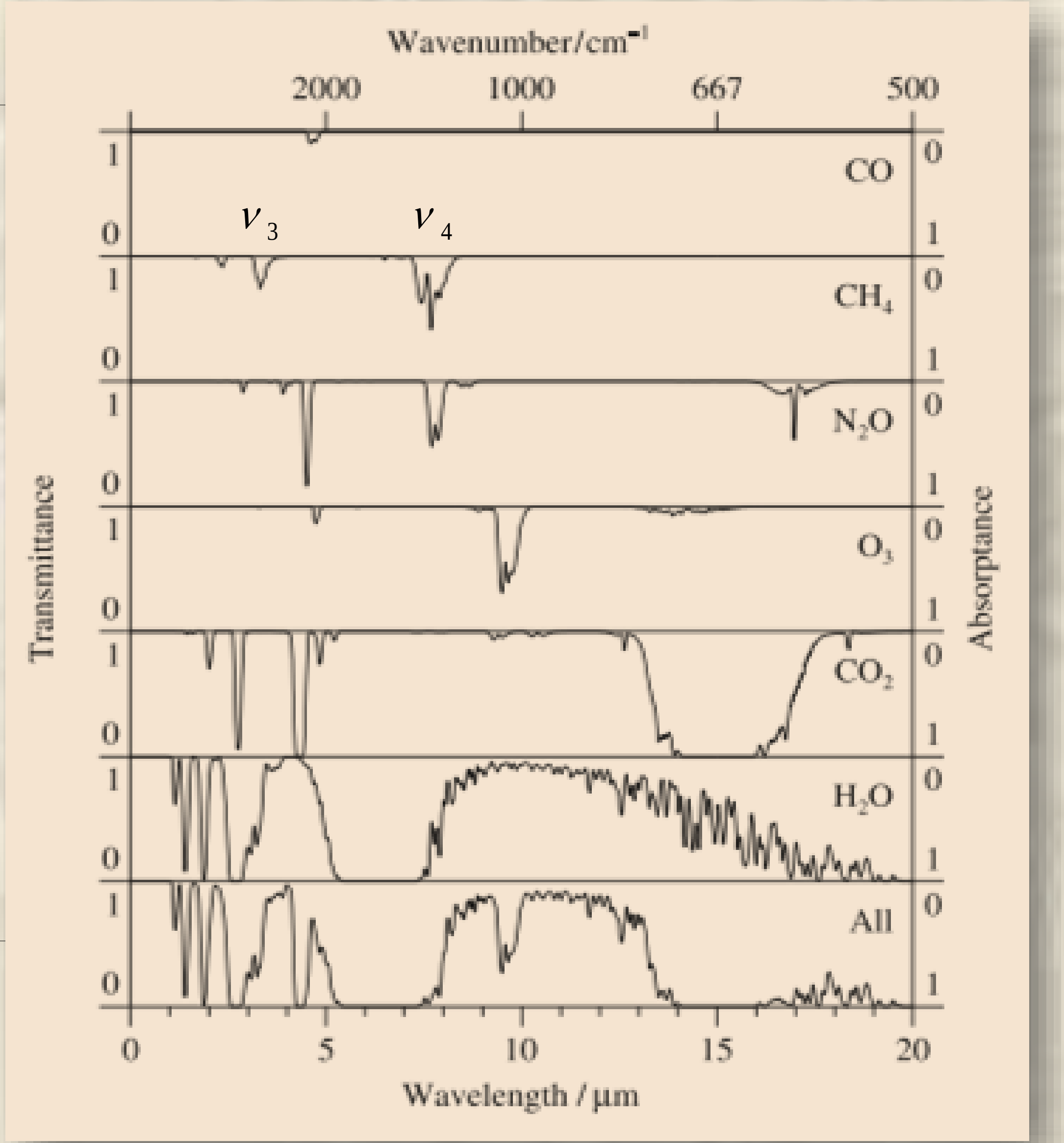


Fig. 3.14

Infra-red absorption

Nitrous oxide (N_2O)

Fundamental modes

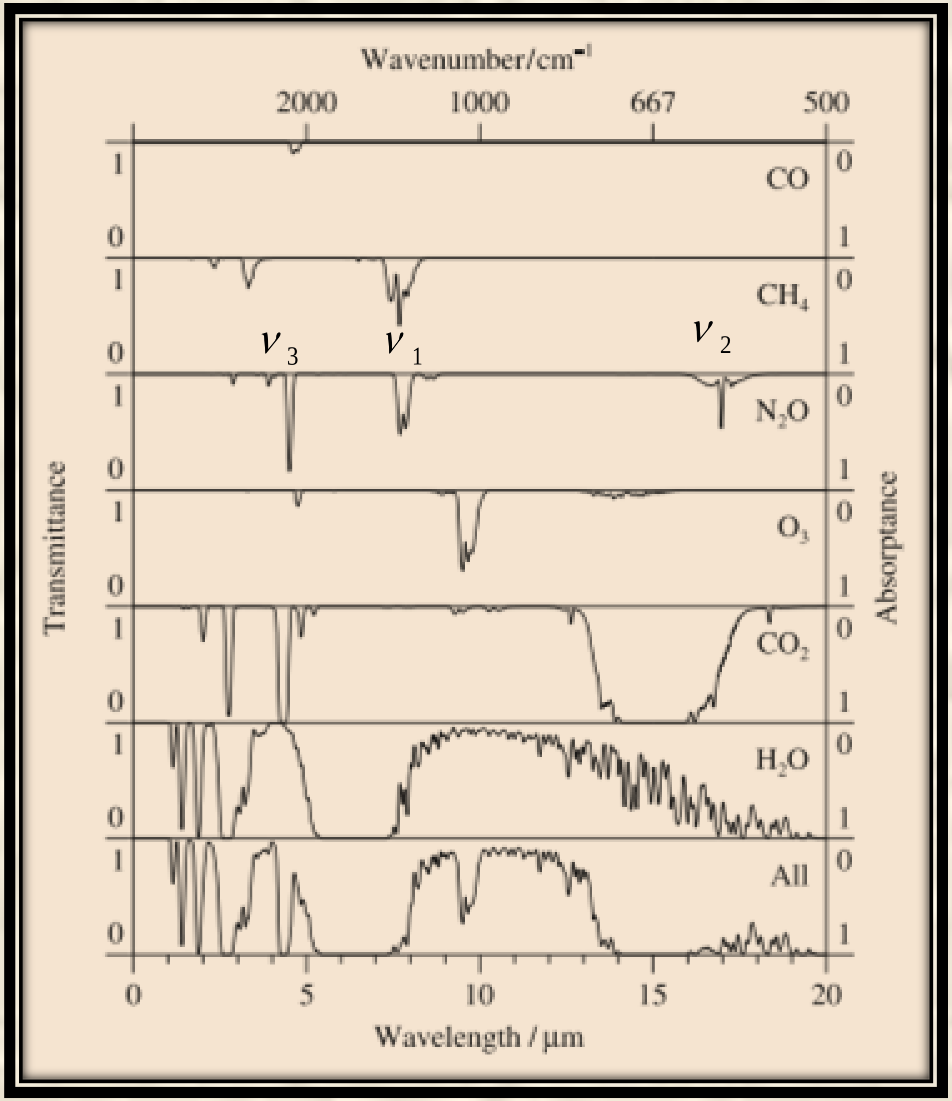
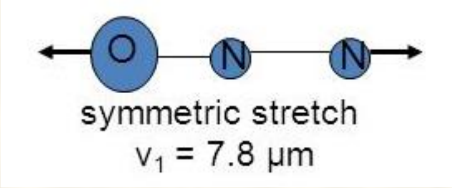
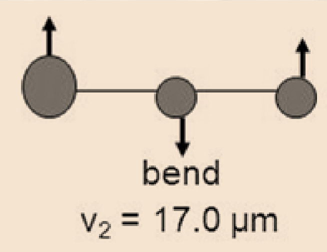


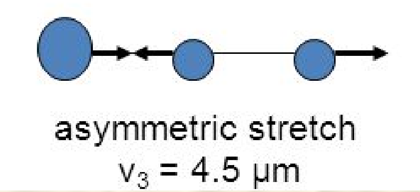
Fig. 3.14



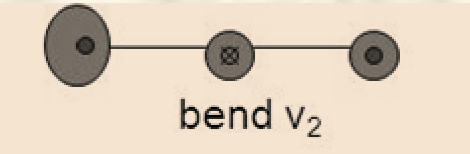
symmetric stretch
v_1 = 7.8 µm



bend
v_2 = 17.0 µm



asymmetric stretch
v_3 = 4.5 µm

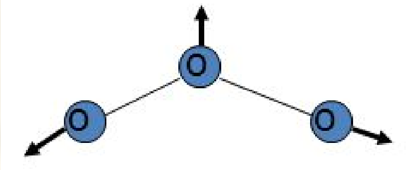


bend v_2

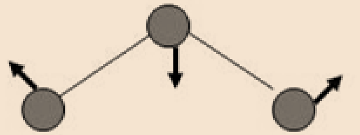
Infra-red absorption

Ozone (O_3)

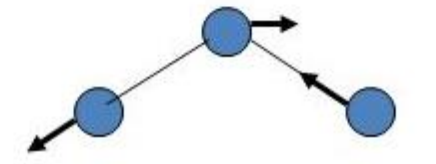
Fundamental vibrational modes



symmetric stretch
v_1 = 9.01 µm



bend
v_2 = 14.3 µm



asymmetric stretch
v_3 = 9.6 µm

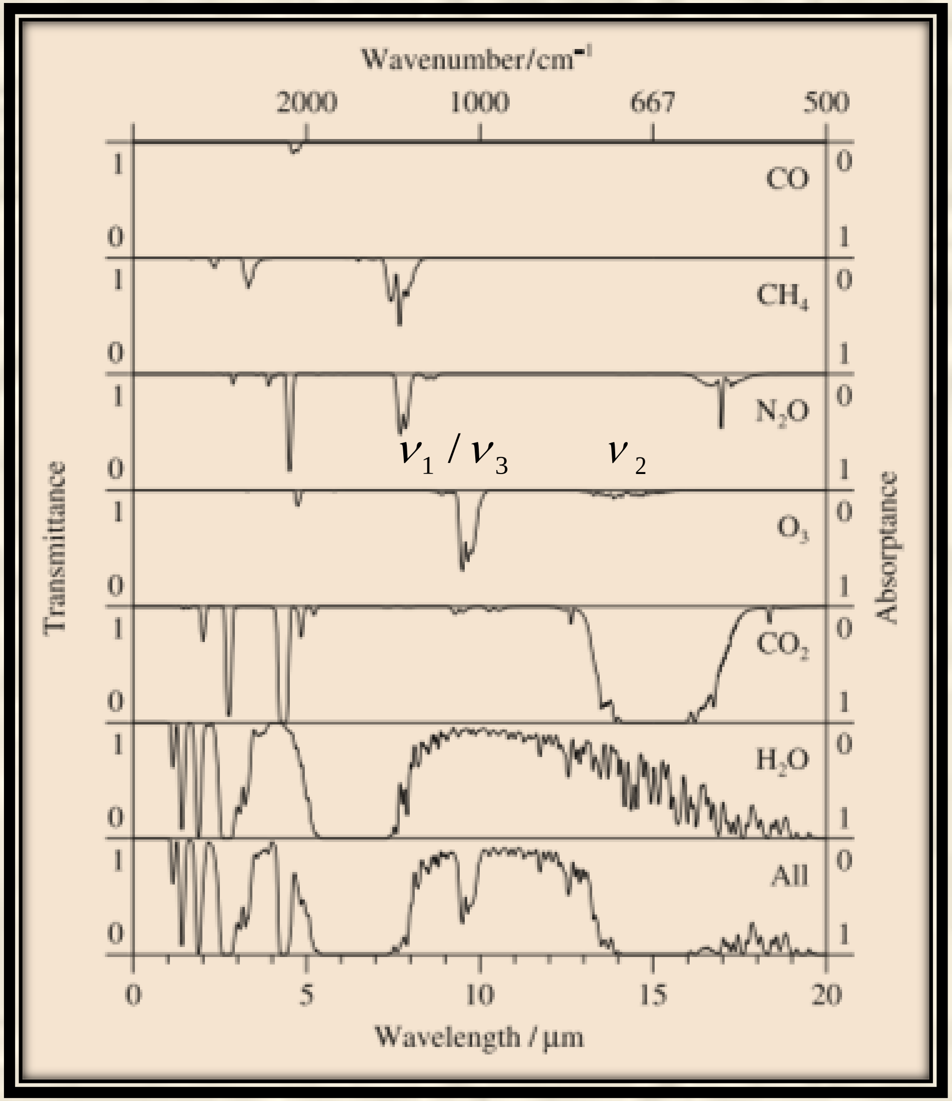
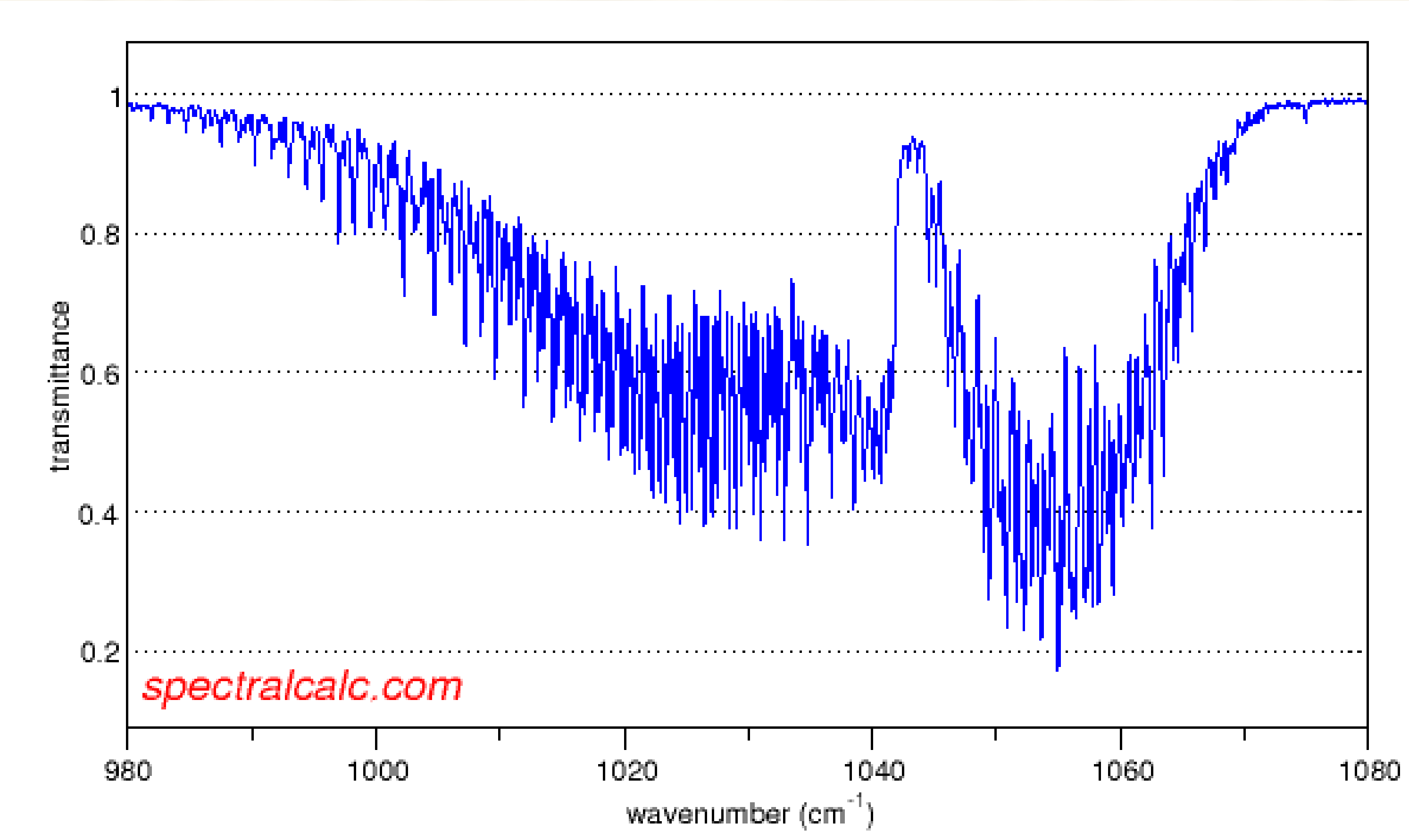


Fig. 3.14

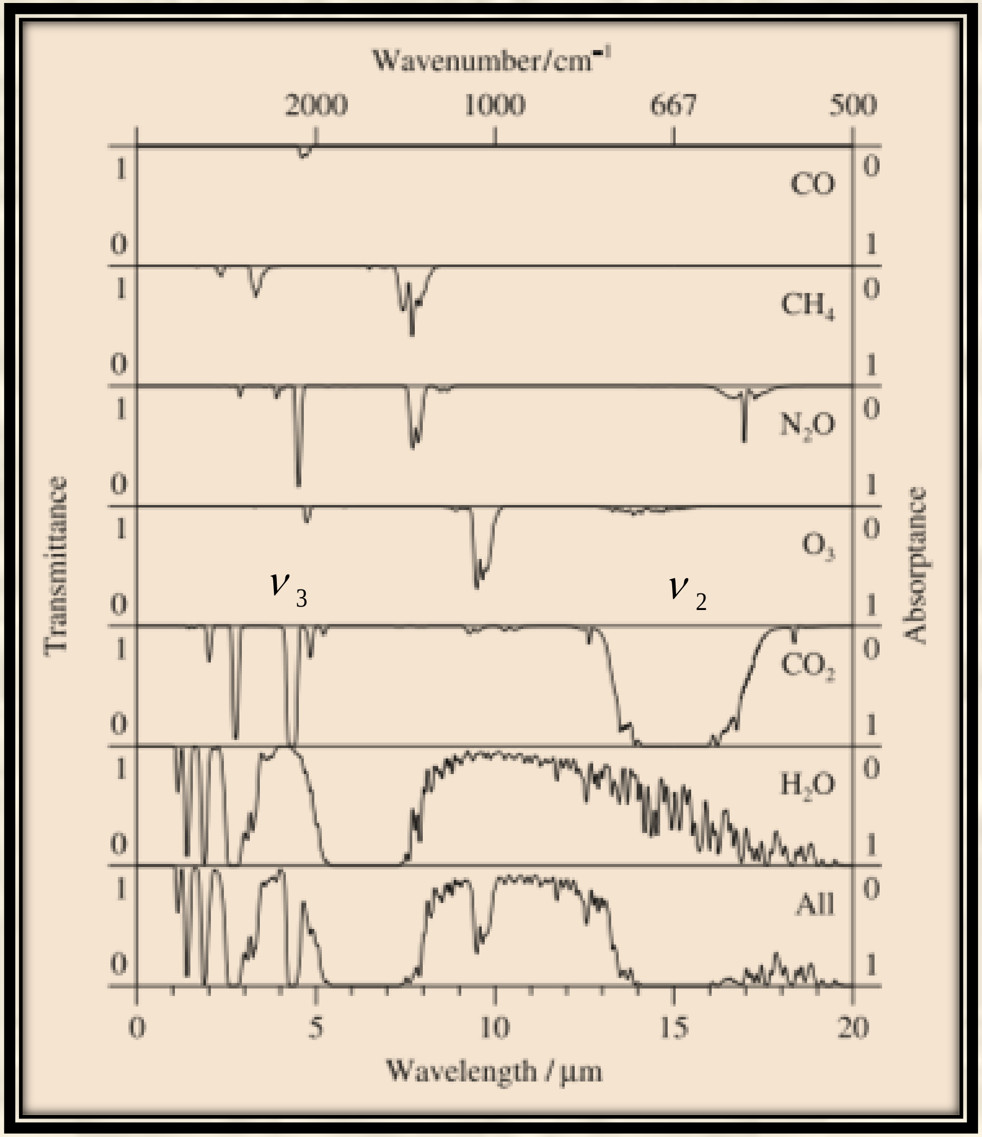
Transmittance spectrum for ozone (O_3)



http://www.spectralcalc.com/calc/spectralcalc.php

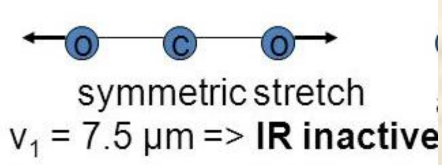
Infra-red absorption

Fig. 3.14

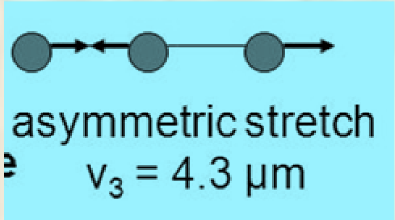


Carbon dioxide (CO_2)

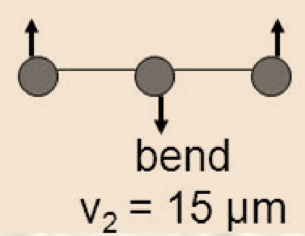
Fundamental modes:



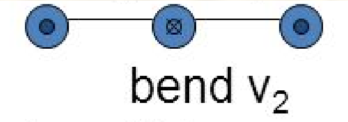
symmetric stretch
v_1 = 7.5 μm => **IR inactive**



asymmetric stretch
v_3 = 4.3 μm

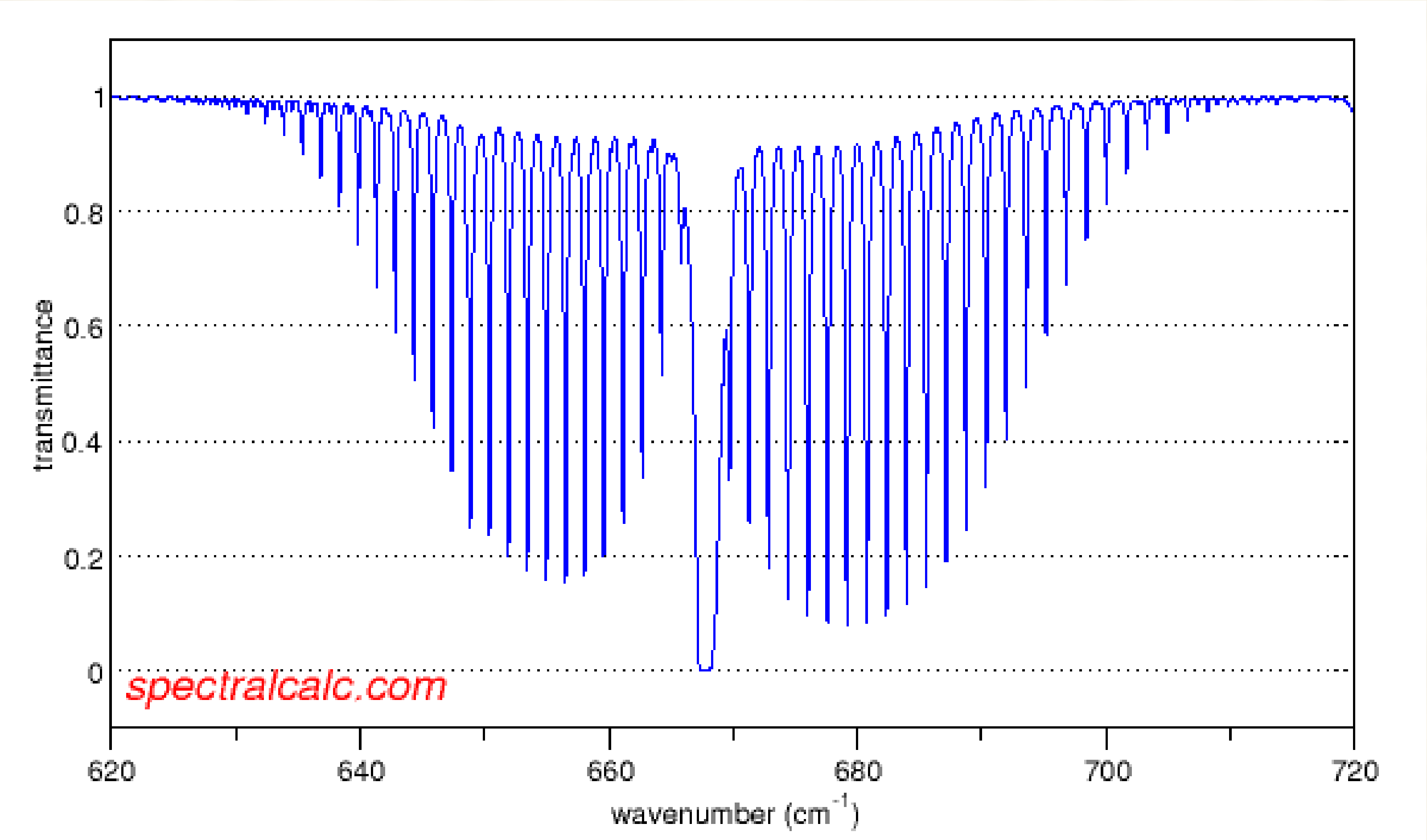


bend
v_2 = 15 μm



bend v_2

Transmittance spectrum for CO_2

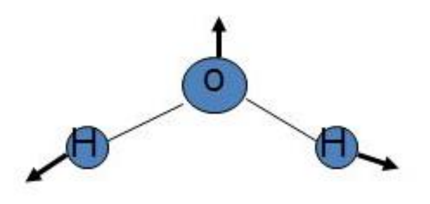


http://www.spectralcalc.com/calc/spectralcalc.php

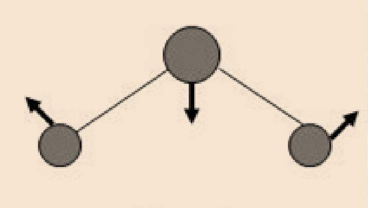
Infra-red absorption

Water vapor (H_2O)

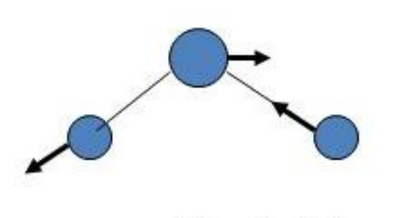
3 vibrational fundamental modes



symmetric stretch
$v_1 = 2.74$ µm



bend
$v_2 = 6.25$ µm



asymmetric stretch
$v_3 = 2.66$ µm

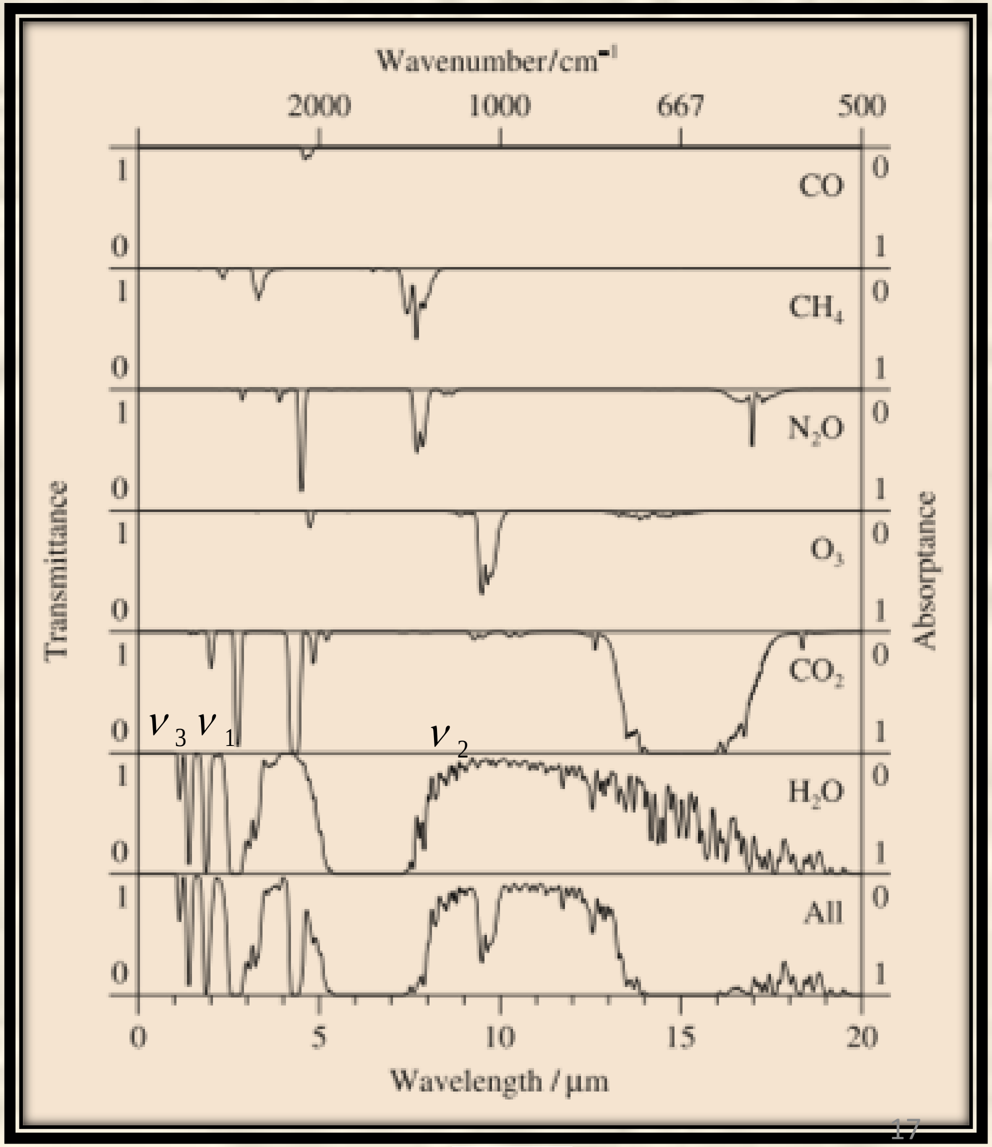
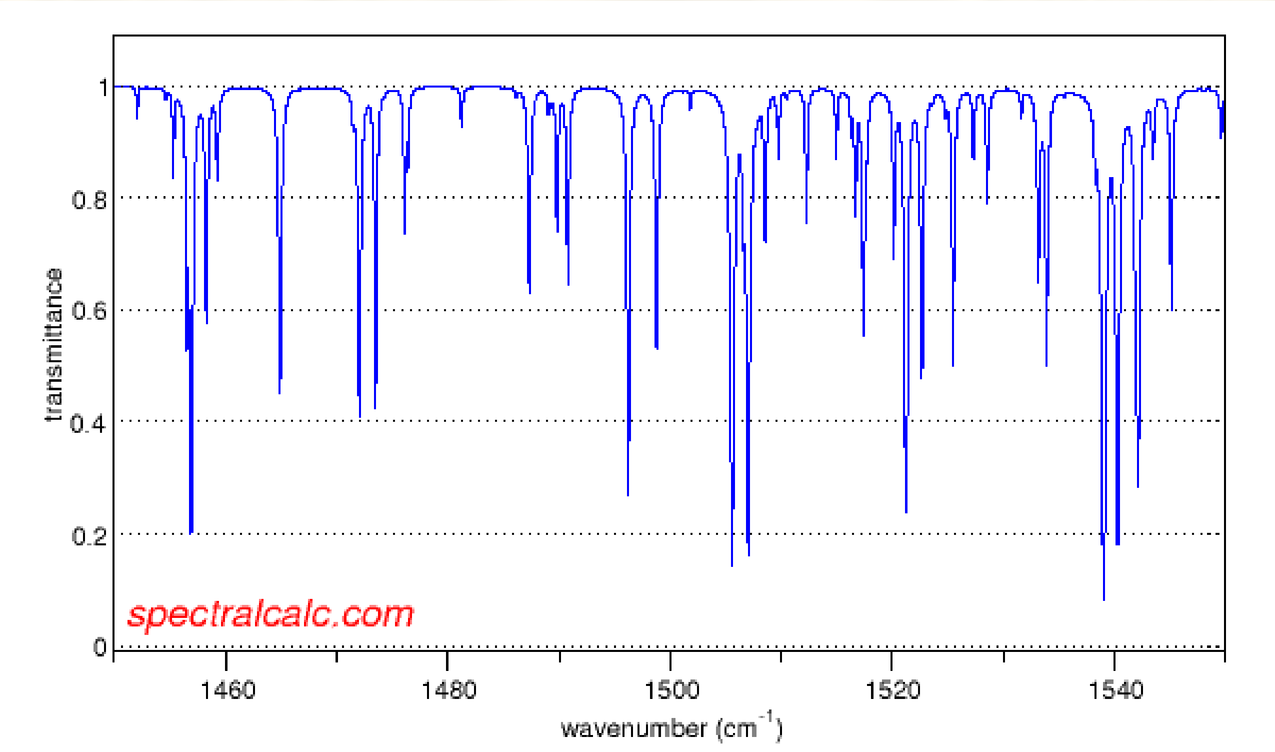


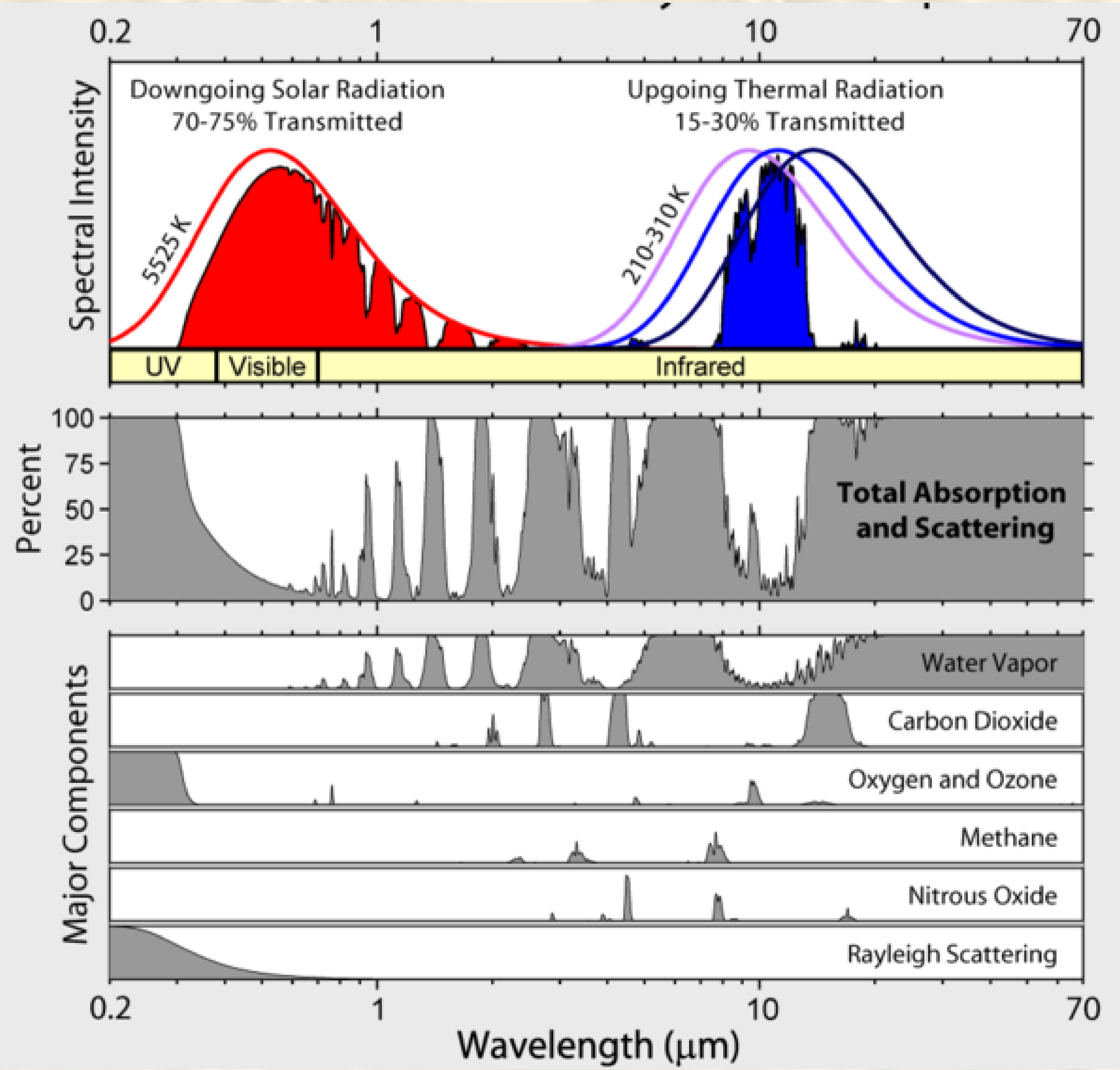
Fig. 3.14

Transmittance spectrum for H_2O



http://www.spectralcalc.com/calc/spectralcalc.php

Radiation Transmitted by the Atmosphere



Ultra-violet absorption

The absorption cross-section for O_2 has large values due to ionisation at Wavelengths below 100 nm in the range 100-300 nm there are irregular Bands of unknown origin.

$$O_2 \rightarrow O(^3P) + O(^1D)$$

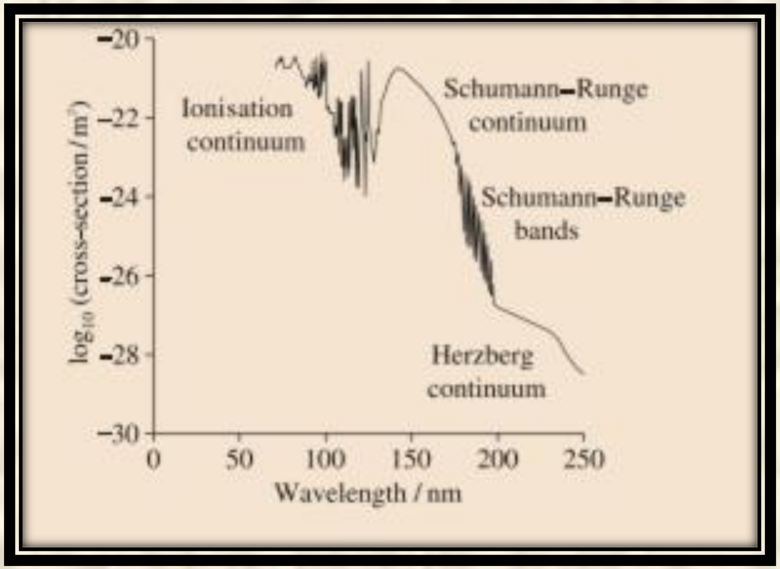
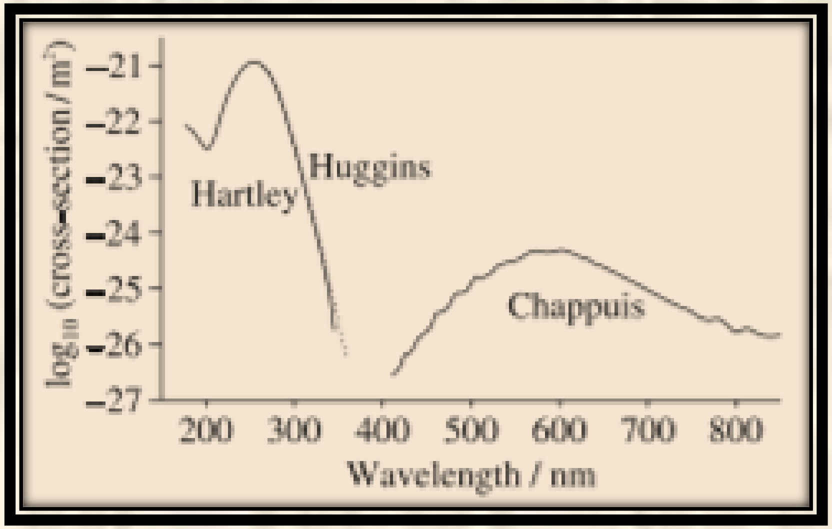
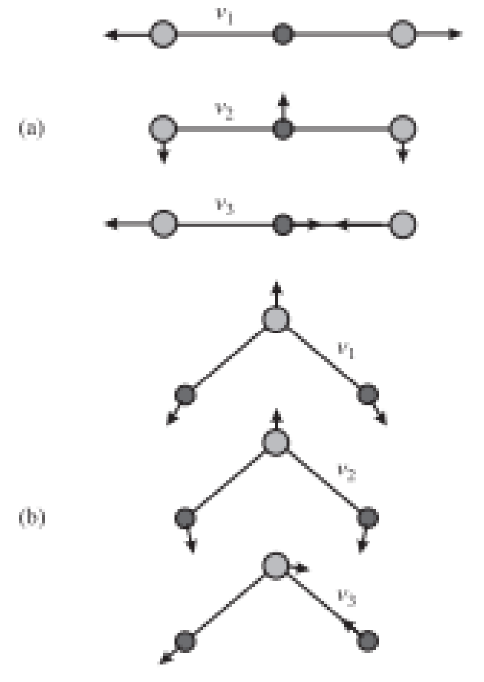


Fig. 3.15

General shape of the absorption cross-section as a function of wavelength for O2

Fig. 3.16 The absorption cross-section as a function of wavelength for O_3. Details of the fine structure of the Huggins band have been suppressed. In the Huggins band the solid line corresponds to a temperature of 203 K and the dashed line to a temperature of 273 K.





The altitude of unit optical depth for vertical solar radiation.

The principal absorption bands are shown

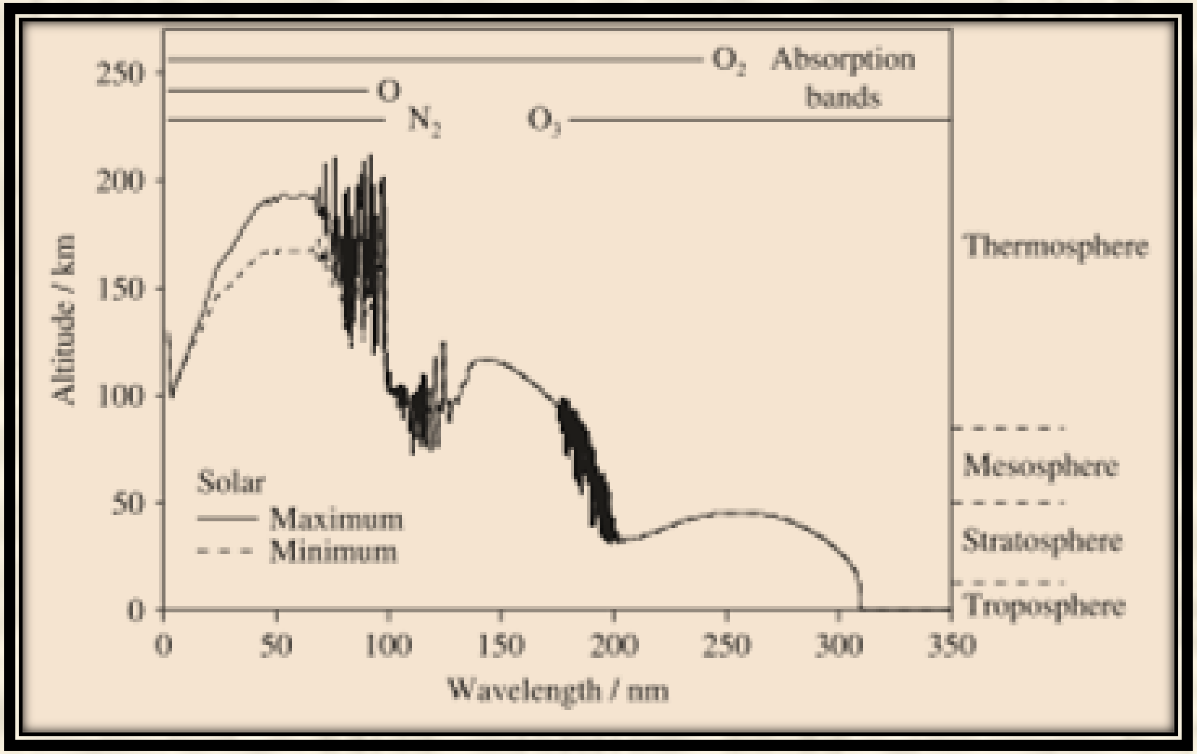


Fig. 3.17

Heating rates

Basic ideas

$AF_z(z)$

$A\Delta z$

$AF_z(z+\Delta z)$

$$A\left[F_z(z)-F_z(z+\Delta z)\right]\approx-(A\Delta z)dF_z/dz$$

$-dF_z/dz$

$$Q=-\frac{1}{\rho(z)}\frac{dF_z}{dz}$$

Q/c_p

$F_z(=F^{\uparrow}-F_{\downarrow})$

Short-wave heating

ρQ_{ν}^{sw} $\rho_a z$

$$\chi_\nu(z) = \int_z^\infty k_\nu(z')\rho_a(z')dz'$$

$$F_\nu^\downarrow(z) = F_{\nu\infty}^\downarrow e^{-\chi_\nu(z)}$$

$F_{\nu\infty}^\downarrow$ $e^{-\chi_\nu(z)}$ $\tau_\nu(z,\infty)$

$$F_{z\nu}(z) = -F_{\nu\infty}^\downarrow e^{-\chi_\nu(z)}$$

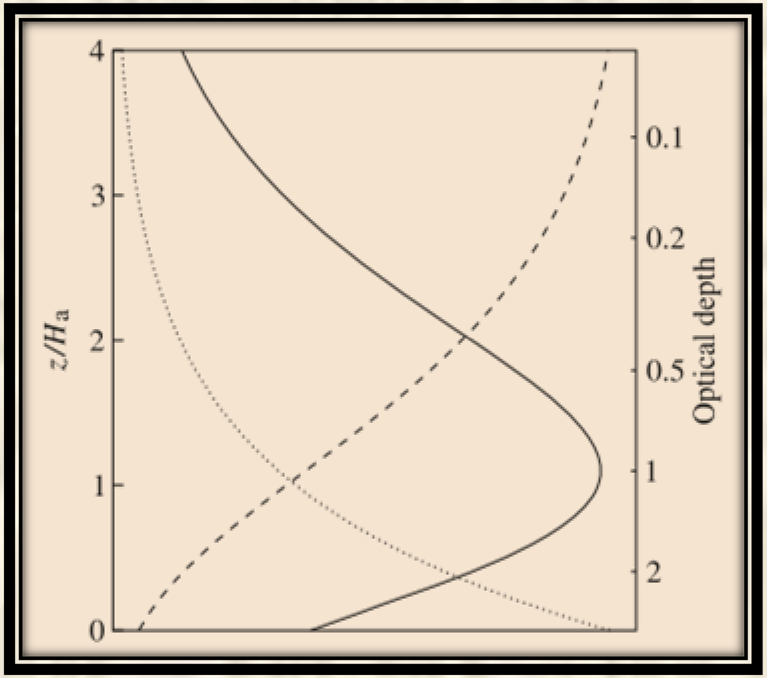
$$\rho Q_\nu^{sw} = \frac{d}{dz}(F_{\nu\infty}^{\downarrow} e^{-\chi_\nu(z)}) = F_{\nu\infty}^{\downarrow}(-\frac{d\chi_\nu}{dz})e^{-\chi_\nu(z)}$$

$$= F_{\nu\infty}^{\downarrow} k_\nu(z)\rho_a(z)e^{-\chi_\nu(z)}$$

$$\rho_a(z) = \rho_a(0)e^{-z/H_a}$$

$$\chi_\nu(z) = H_a k_\nu \rho_a(0)e^{-z/H_a} = \chi_\nu(0)e^{-z/H_a}$$

$$F_{z\nu} = -F_{\nu\infty}^{\downarrow} e^{-\chi_\nu(0)e^{-z/H_a}}$$



$$\rho Q_{\nu}^{sw}(z) = F_{\nu\infty}^{\downarrow} k_{\nu} \rho_{a}(0) e^{-z/H_a - \chi_{\nu}(0) e^{-z/H_a}}$$

Long-wave heating and cooling

$$F_\nu^{\uparrow}(z) = \pi \int_0^z B_\nu(z') \frac{\partial \tau_\nu^*(z', z)}{\partial z'} dz' + \pi B_\nu(0) \tau_\nu^*(0, z)$$

$\tau_\nu^*(z', z)$ $B_\nu(0)$ $J_\nu = B_\nu$

$$F_\nu^{\downarrow}(z) = -\pi \int_z^\infty B_\nu(z') \frac{\partial \tau_\nu^*(z', z)}{\partial z'} dz'$$

$$F_{z\nu}(z) = F_\nu^{\uparrow}(z) - F_\nu^{\downarrow}(z)$$

Q_ν^{lw} $k_\nu \rho_a J_\nu A \Delta z$

$$\tau_\nu(z,\infty) = \exp\left(-\int_z^\infty k_\nu \rho_a dz'\right)$$

$$\frac{\partial \tau_\nu(z,\infty)}{\partial z} = k_\nu(z)\rho_a(z)\tau_\nu(z,\infty)$$

$$B_\nu(z)\frac{\partial \tau_\nu(z,\infty)}{\partial z} A\Delta x$$

$$\tau_\nu \qquad \tau_\nu^*$$

$$Q_\nu^{cts}(z) = \frac{\pi B_\nu(z)}{\rho(z)}\frac{\partial \tau_\nu^*(z,\infty)}{\partial z}$$

$Q_\nu^{lw} \approx Q_\nu^{cts}$ $Q_\nu^{lw}(z)$ $Q^{lw}(z)$ τ_ν^*

Net radiative heating rates

Q^{sw} / c_p

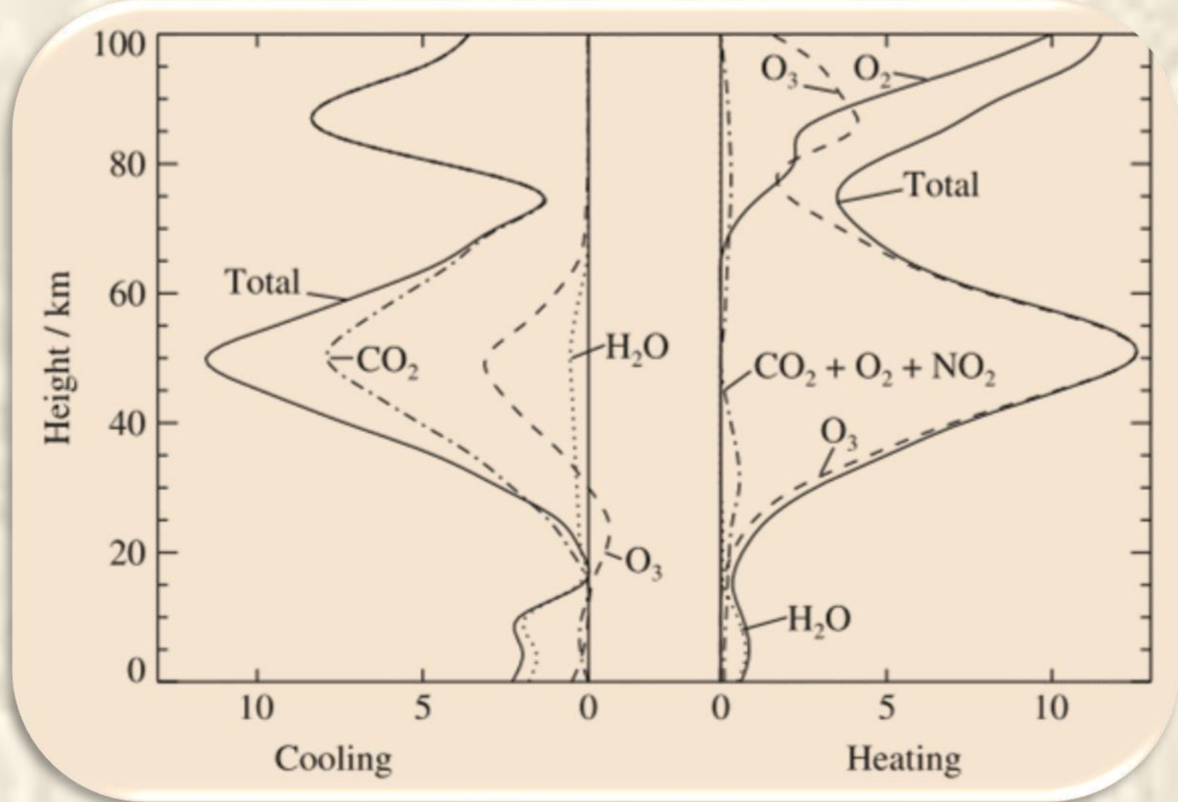
$-Q^{lw} / c_p$

$Q = Q^{sw} + Q^{lw}$

$Q = 0$

$T_r(r)$

$Q(T_r(r)) = 0$



$T = T_r + \delta T$

$$Q(T_r + \delta T) \approx Q(T_r) + \delta T \left.\frac{\partial Q}{\partial T}\right|_{T=T_r} = \delta T \left.\frac{\partial Q}{\partial T}\right|_{T=T_r}$$

$$Q(T_r) = 0$$

$$= -c_p \frac{\delta T}{\tau_r}$$

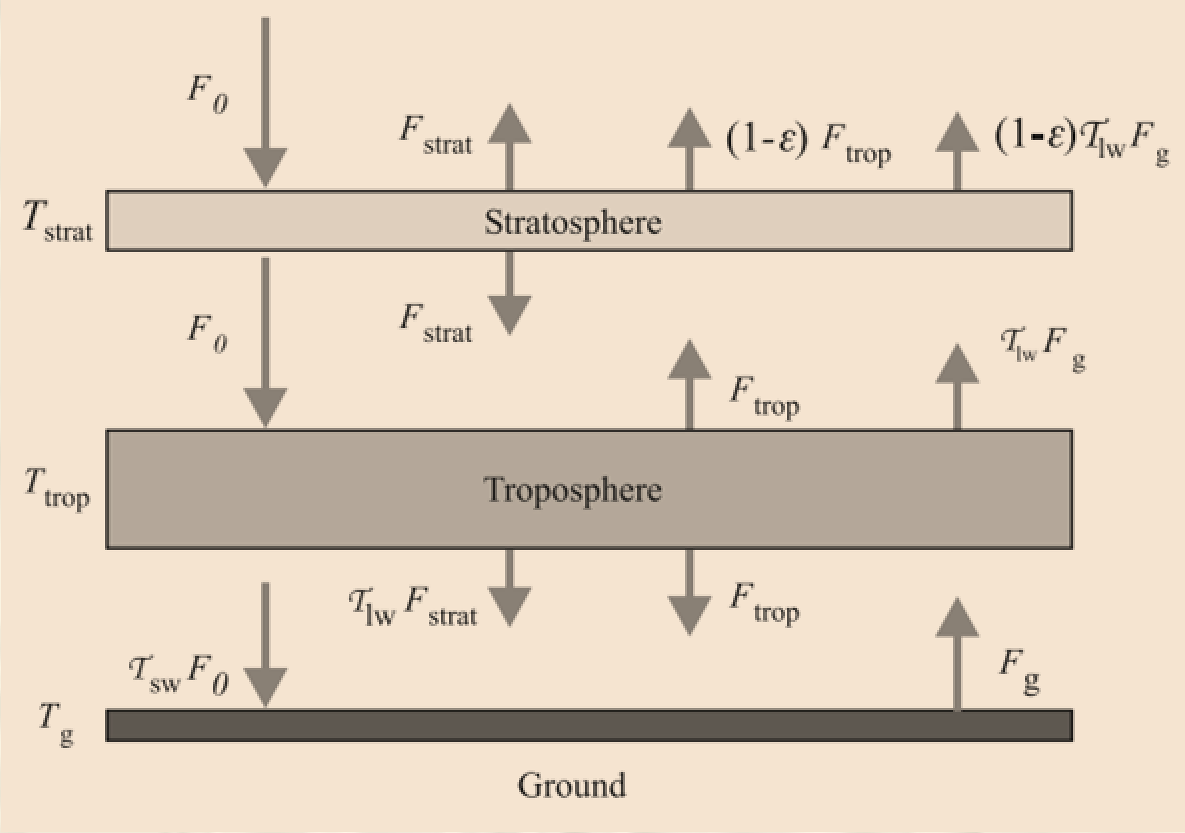
$$\tau_r = c_p(\partial Q / \partial T\big|_{T=T_r})^{-1}$$

The greenhouse effect revisited

Two-layer atmosphere in radiative equilibrium, including an optically thin stratosphere

T_{trop} τ_{sw} τ_{lw}

$$T_c \equiv \left(\frac{F_0}{\sigma}\right)^{1/4} \approx 255K$$



$$F_0 = F_{strat} + (1+\varepsilon)(F_{trop} + \tau_{lw}F_g)$$

$$F_{strat} = \sigma\varepsilon T_{strat}^4 \quad , \quad F_{trop} = \sigma(1-\tau_{lw})T_{trop}^4 \quad , \quad F_g = \sigma T_g^4$$

$$F_0 + F_{strat} = F_{trop} + \tau_{lw} F_g$$

$$2F_{strat} = \varepsilon (F_{trop} + \tau_{lw} F_g)$$

$$F_{trop} + \tau_{lw} F_g$$

$$F_0 + F_{strat} = (1 - \varepsilon)(F_0 + F_{strat})$$

$$\sigma \varepsilon T_{strat}^4 = F_{strat} = \frac{\varepsilon F_0}{2 - \varepsilon}$$

$\varepsilon \ll 1$ $\quad$ $\sigma T_{strat}^4 \approx \frac{F_0}{2}$ $\quad$ $T_{strat} \approx \frac{T_c}{2^{1/4}} = 214K$

$$F_{trop} + \tau_{lw} F_g$$

$$F_{trop} = \frac{2F_0}{2-\varepsilon} - \tau_{lw} F_g$$

$$\tau_{sw} F_0 + F_{lw} F_{strat} + F_{trop} = F_g$$

Continuously stratified atmosphere in radiative equilibrium

$$-\frac{dF^{\uparrow}}{d\chi^*} + F^{\uparrow} = \pi B(T)$$

$$\pi B(T) = \sigma T^4$$

$$\frac{dF^{\downarrow}}{d\chi^*} + F^{\downarrow} = \pi B(T)$$

$$Q^{sw} = 0 \qquad Q^{lw} = 0$$

$$F_z = F^{\uparrow} - F^{\downarrow} = \text{constant} \qquad F^{\downarrow}(0) = 0 \qquad F_z = F^{\uparrow}(0)$$

$$F_z = F^{\uparrow} - F^{\downarrow} = F_0$$

$$-\frac{d}{d\chi^*}(F^{\uparrow} - F^{\downarrow}) + F^{\uparrow} - F^{\downarrow} = 2\pi B(T)$$

$$\pi B(T) = \frac{1}{2}(F^{\uparrow} + F^{\downarrow})$$

$$\frac{d}{d\chi^*}(F^{\uparrow} + F^{\downarrow}) = F^{\uparrow} - F^{\downarrow} = F_0$$

$$F^{\uparrow} + F^{\downarrow} = F_0 \chi^* + \text{constant}$$

$$F^{\uparrow} + F^{\downarrow} = F_0 (1 + \chi^*)$$

$$F^{\uparrow} = \frac{1}{2} F_0 (2 + \chi^*)$$

$$F^{\downarrow} = \frac{1}{2} F_0 \chi^*$$

$$\pi B(T) = \sigma T^4 = \frac{1}{2} F_0 (1 + \chi^*)$$

$$F_0 (1 + \chi_g^*) / 2$$

$$\pi B(T_g) = \sigma T_g^4$$

$$\sigma T_g^4 = F_0(1+\frac{1}{2}\chi_g^*) = \sigma T_c^4(1+\frac{1}{2}\chi_g^*)$$

$$T_c \approx 255K \qquad \chi_g^* > 0$$

$$T_g > T_c$$

$$\rho_c(z) = \rho_a(0)e^{-z/H_a}$$

$$\chi^*(z) = \chi_g^* e^{-z/H_a}$$

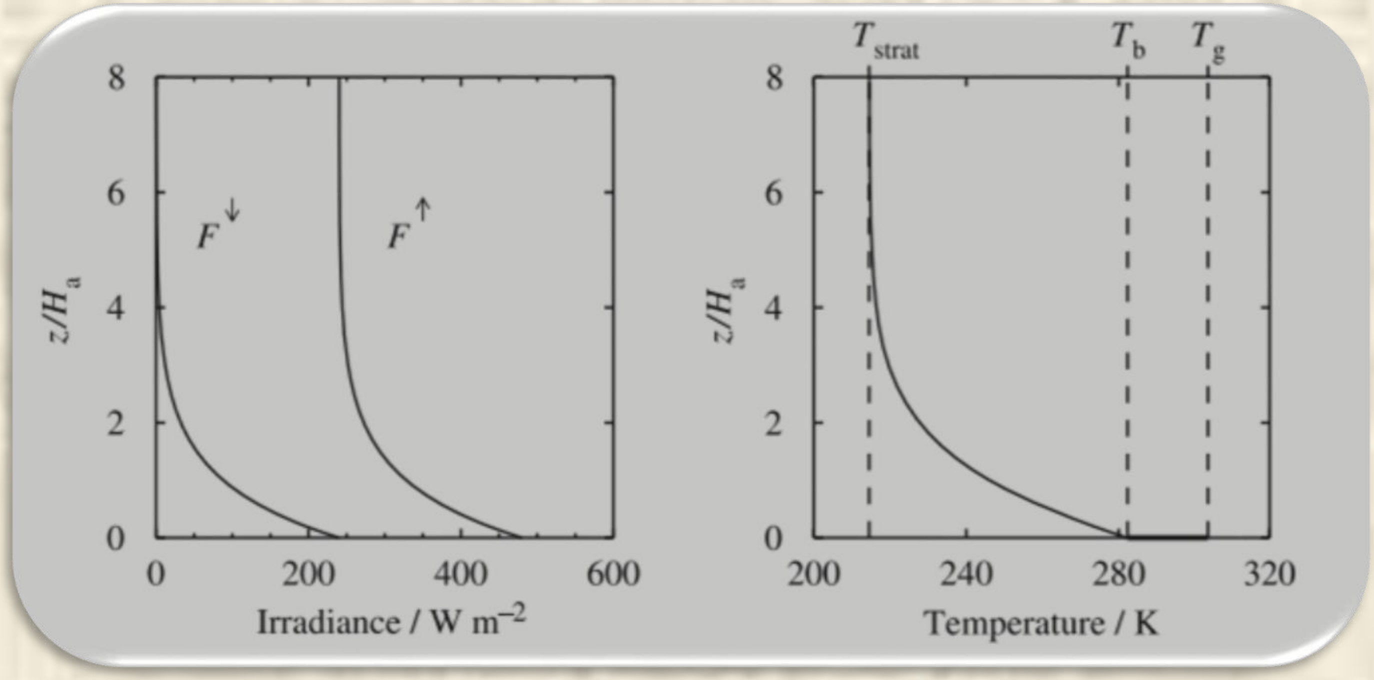
$$F^{\uparrow}(z) = \frac{1}{2}F_0(2+\chi_g^* e^{-z/H_a}) \qquad F^{\downarrow}(z) = \frac{1}{2}F_0\chi_g^* e^{-z/H_a}$$

$$T(z) = \left[\frac{F}{2\sigma_0}(1+\chi_g^* e^{-z/H_a})\right]^{1/4}$$

z / H_a $\qquad \chi_g^* = 2$ $\qquad F_0 = 240\ W / m^{\rightarrow 2}$

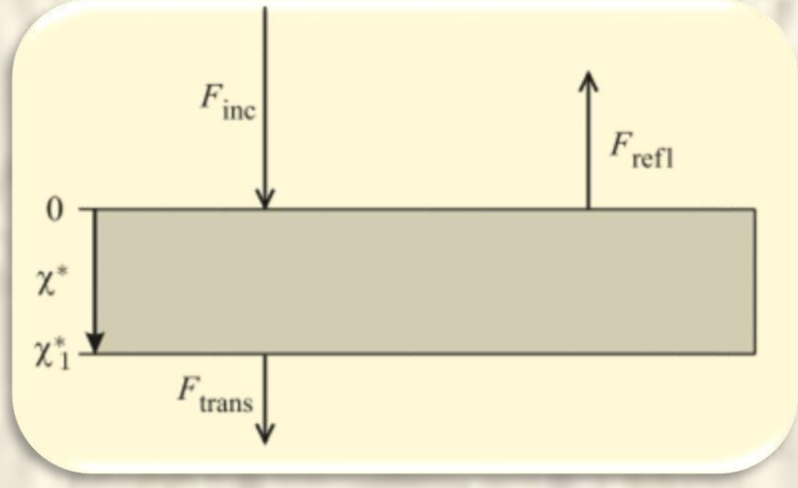
$$T \rightarrow \left(\frac{F}{2\sigma}\right)^{1/4} \text{ as } z \rightarrow \infty \qquad T_{strat} = 2^{-1/4} T_c$$

$$T(z) \rightarrow T_b \equiv T_c \left(\frac{1+\chi_g^*}{2}\right)^{1/4} \text{ as } z \downarrow 0$$



$$T_g \equiv T_c\left(\frac{2+\chi_g^*}{2}\right)^{1/4}$$

A simple model of scattering


F_{inc}
F_{refl}
0
χ^*
χ_1^*
F_{trans}

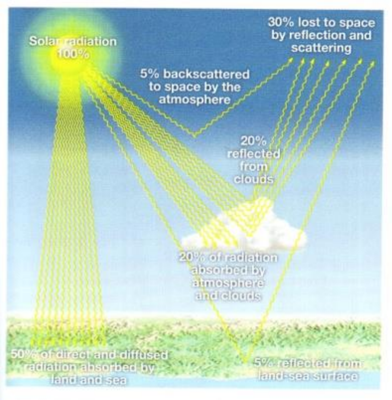
Shortwave Radiation

S_o = 1368 w m^{-2} is the **solar constant** for Earth

Insolation

$$R_0 = S_0 \left(\frac{d_m}{d} \right)^2 \cos \gamma$$

$$I_0 = \int_{t_1}^{t_2} R_0(t)\,dt$$



Stefan-Boltzmann Law

This law expresses the rate of radiation emission per unit area

$$R = \sigma T^4 \qquad \sigma = 5.67 \times 10^{-8}\, W / m^2 K^4$$

Compare the difference between the radiation emission from the sun and the Earth.

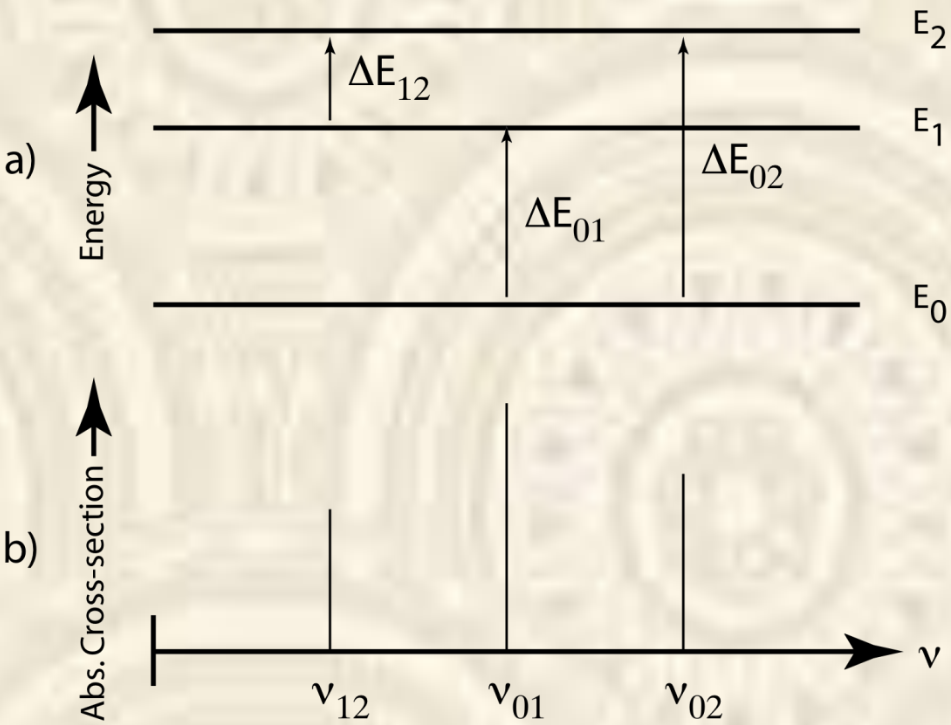
The sun with an average temperature of 6000 K emits 73,483,200 W/m^2

By contrast, Earth with an average temperature of 300 K emits 459 W/m^2

The sun has a temperature 20 times higher than Earth and thus emits about 160,000 times more radiation

This makes sense, $20^4 = 160{,}000$

Absorption spectra of molecules



Hypothetical molecule with three allowed energy levels

Note relationship to emission!

$\nu_{ij} = \Delta E_{ij}/h$

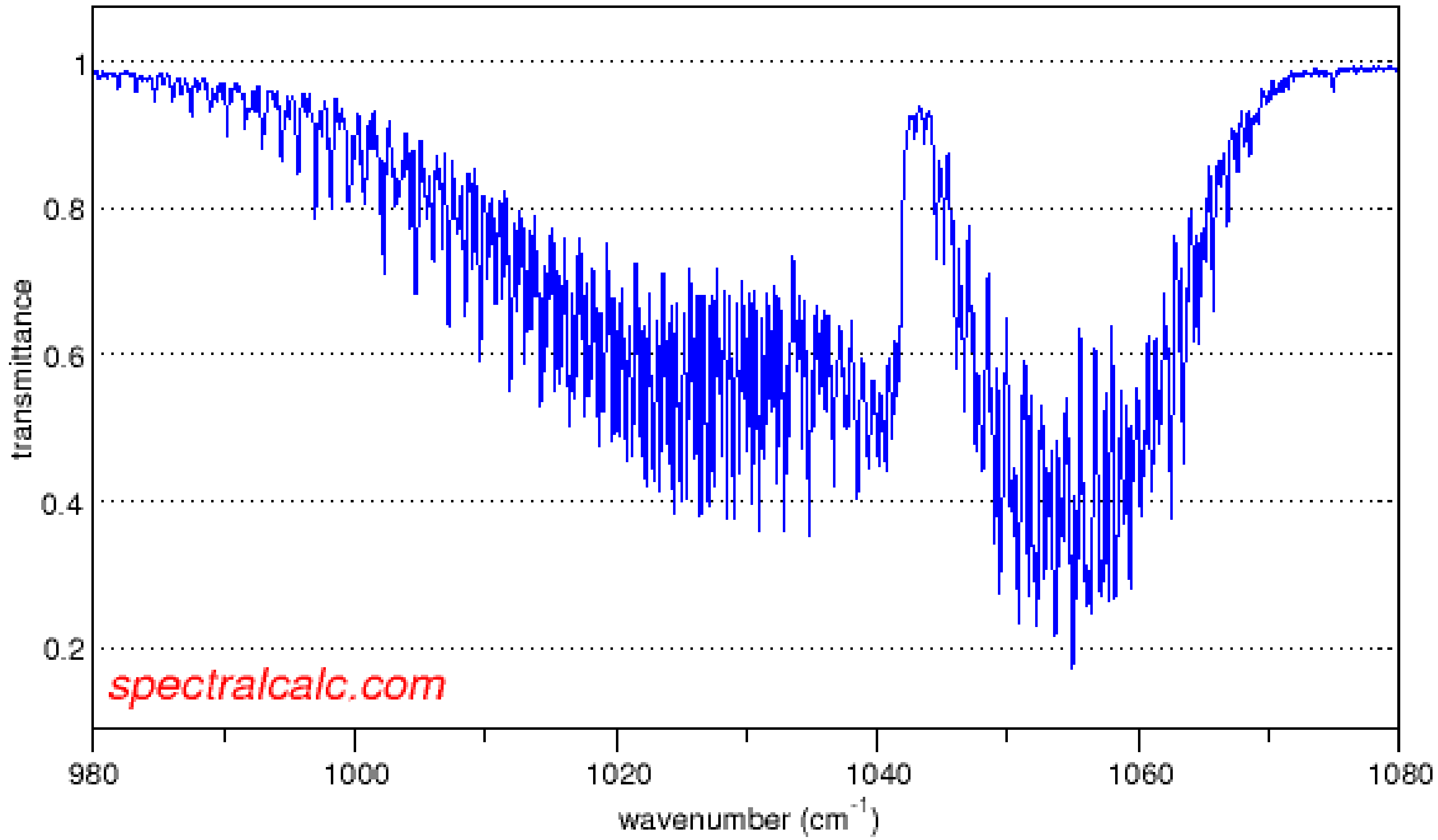
a) allowed transitions
b) positions of the absorption lines in the spectrum of the molecule

Line positions are determined by the energy changes of allowed transitions

Line strengths are determined by the fraction of molecules that are in a particular initial state required for a transition

Multiple degenerate transitions with the same energy may combine

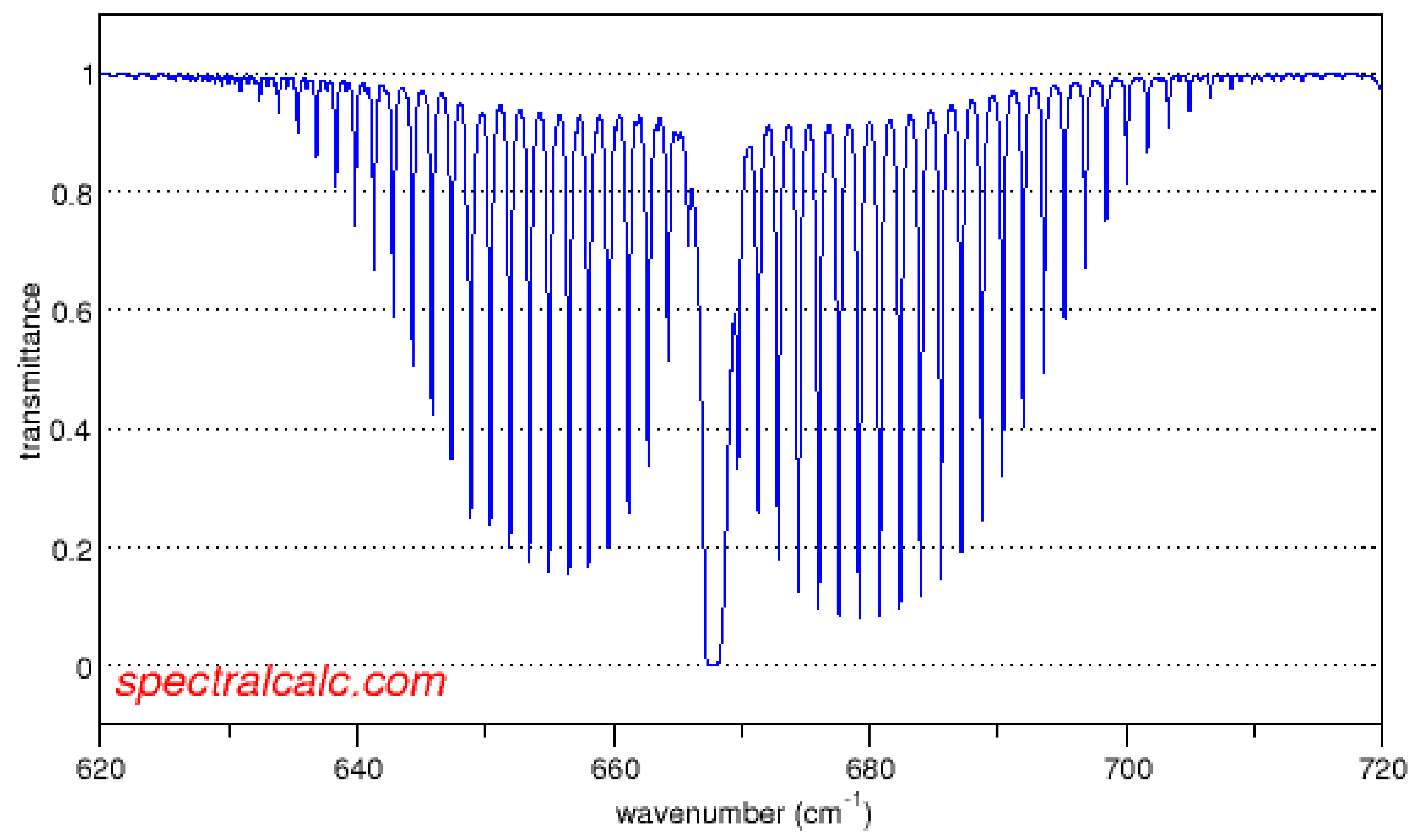
Transmittance spectrum for ozone (O_3)



http://www.spectralcalc.com/calc/spectralcalc.php

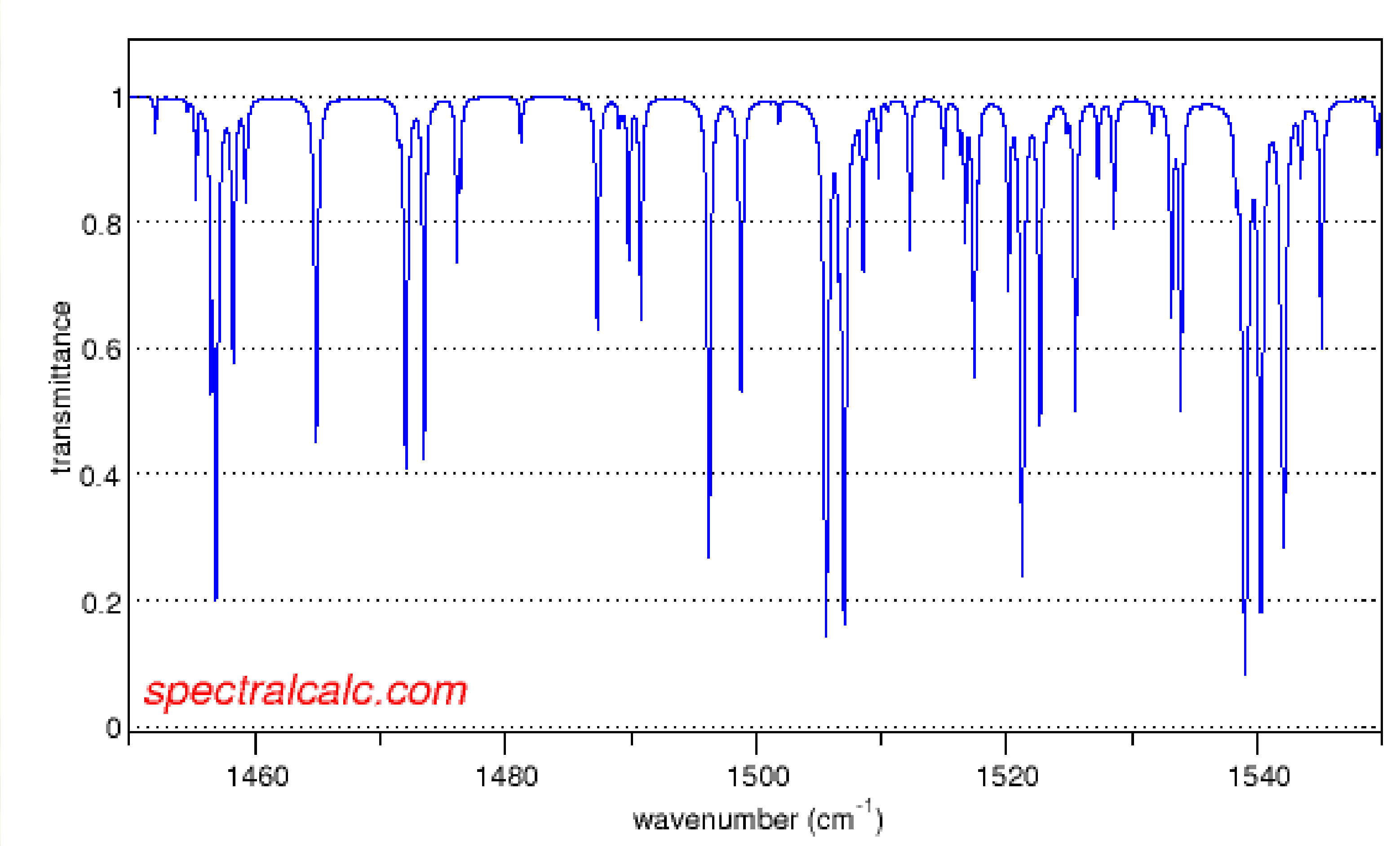
Transmittance spectrum for CO_2

http://www.spectralcalc.com/calc/spectralcalc.php



Transmittance spectrum for H_2O

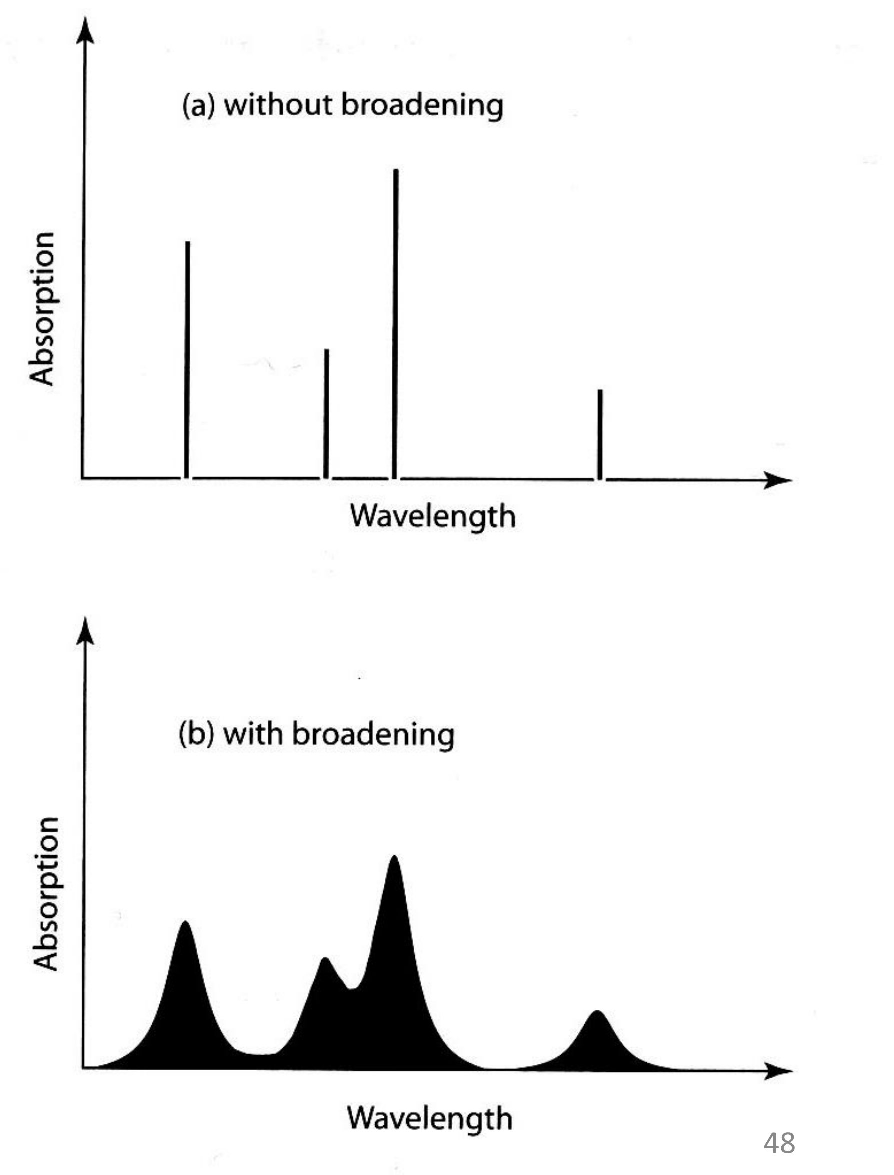
http://www.spectralcalc.com/calc/spectralcalc.php



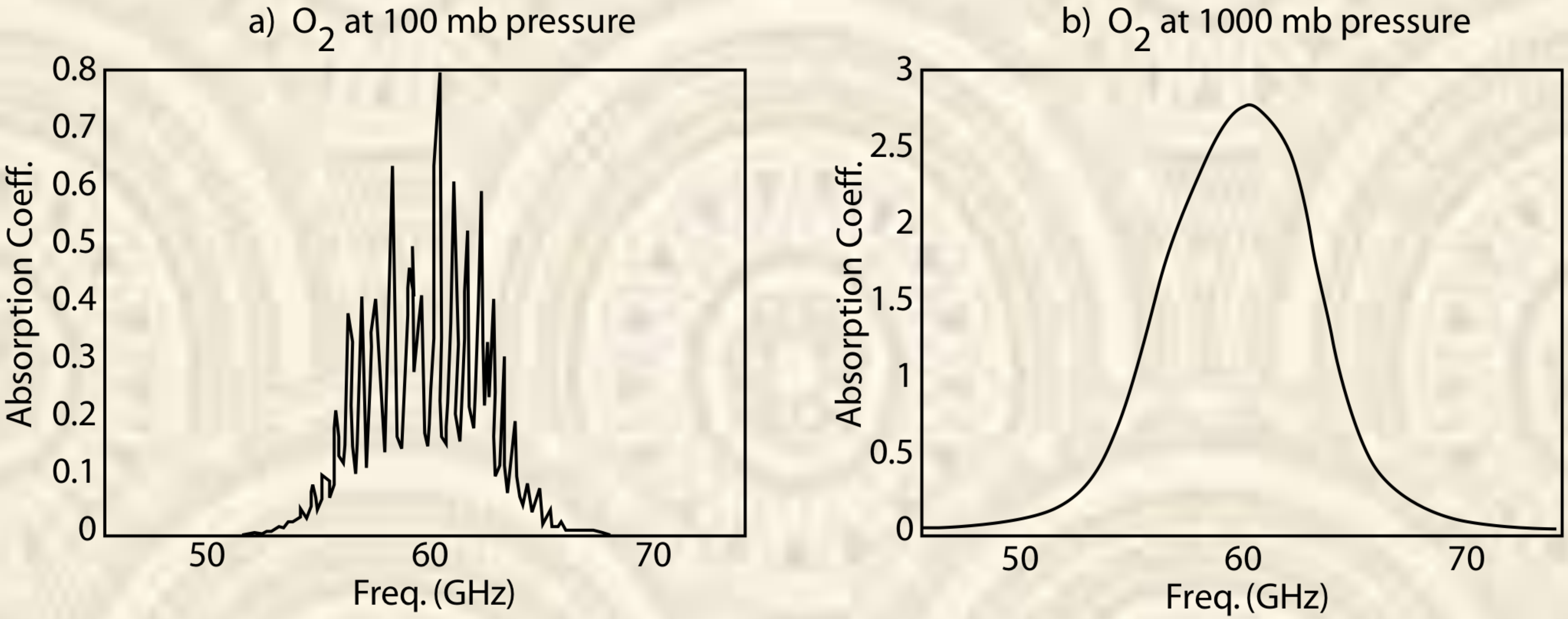
Absorption line shapes

- **Doppler broadening:** random translational motions of individual molecules in any gas leads to Doppler shift of absorption and emission wavelengths (important in upper atmosphere)
- **Pressure broadening:** collisions between molecules randomly disrupt natural transitions between energy states, so that absorption and emission occur at wavelengths that deviate from the natural line position (important in troposphere and lower stratosphere)

- Line broadening closes gaps between closely spaced absorption lines, so that the atmosphere becomes opaque over a continuous wavelength range.

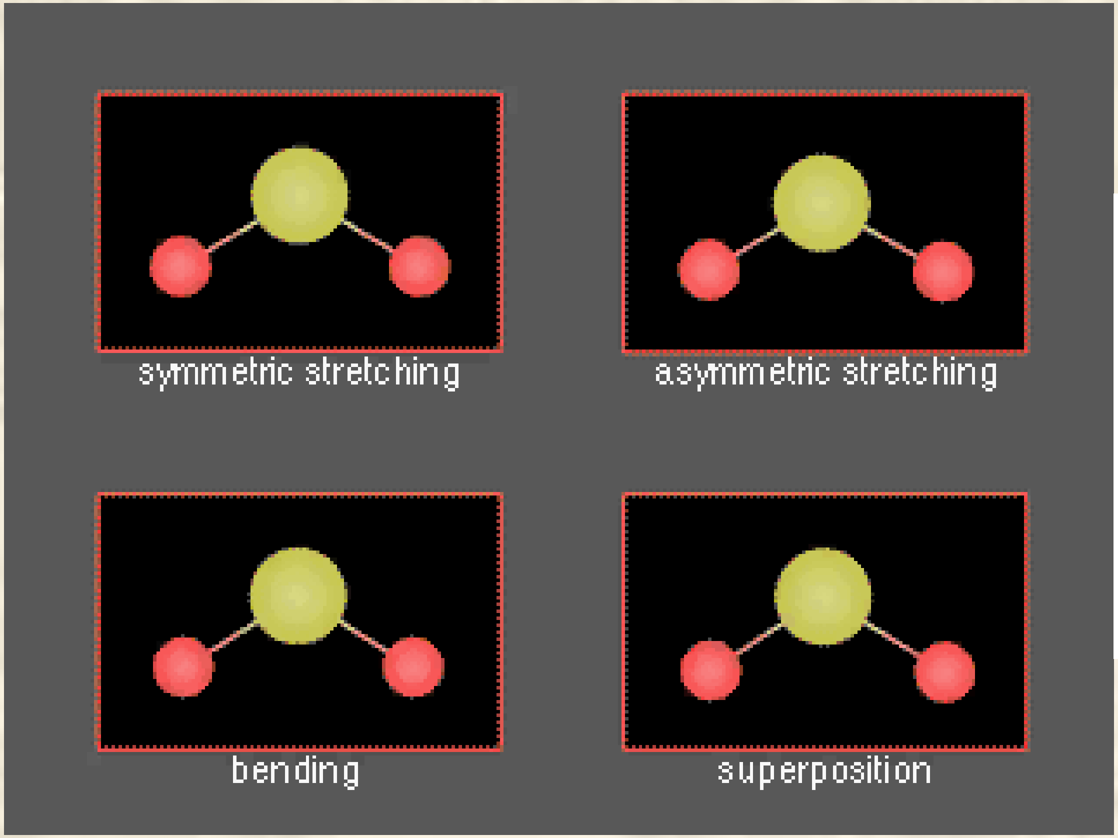


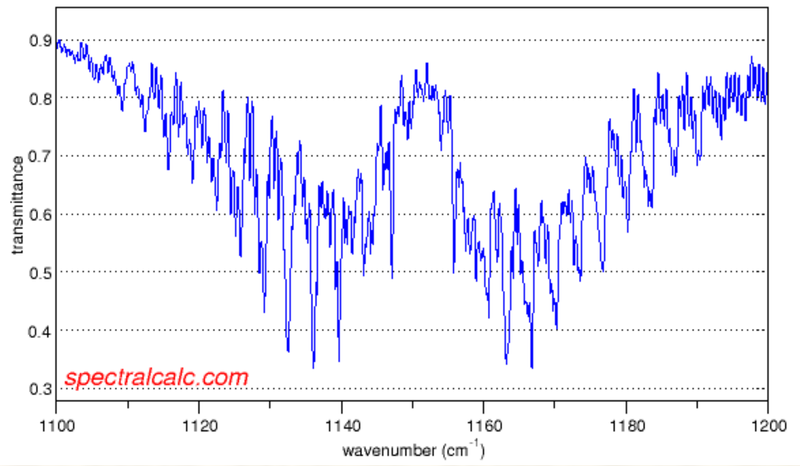
Pressure broadening



- Absorption coefficient of O_2 in the microwave band near 60 GHz at two different pressures. Pressure broadening at 1000 mb obliterates the absorption line structure.

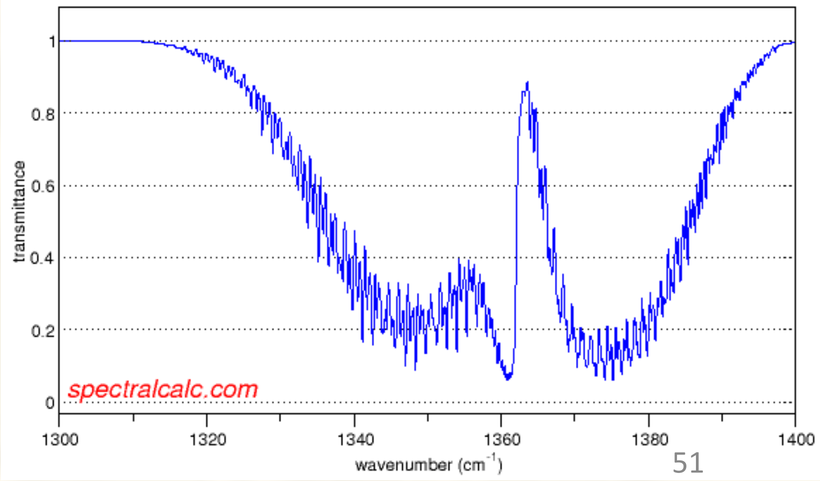
Sulfur dioxide (SO_2)

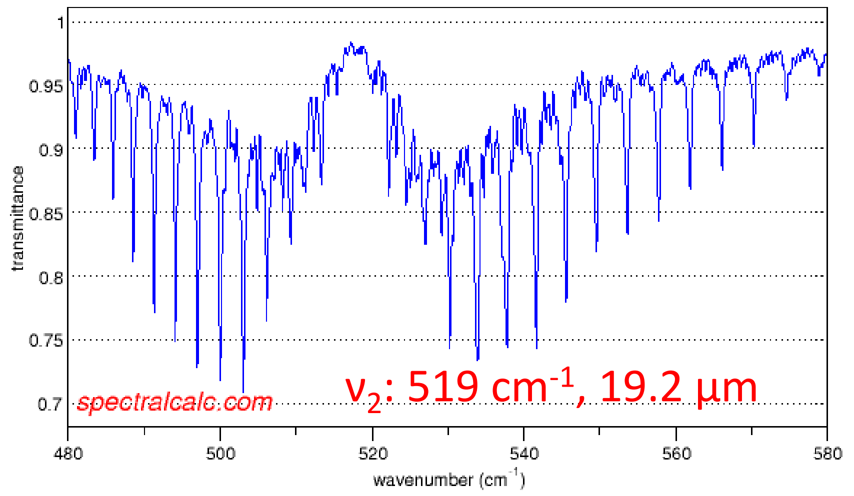




ν_1: 1151 cm^{-1}, 8.6 μm

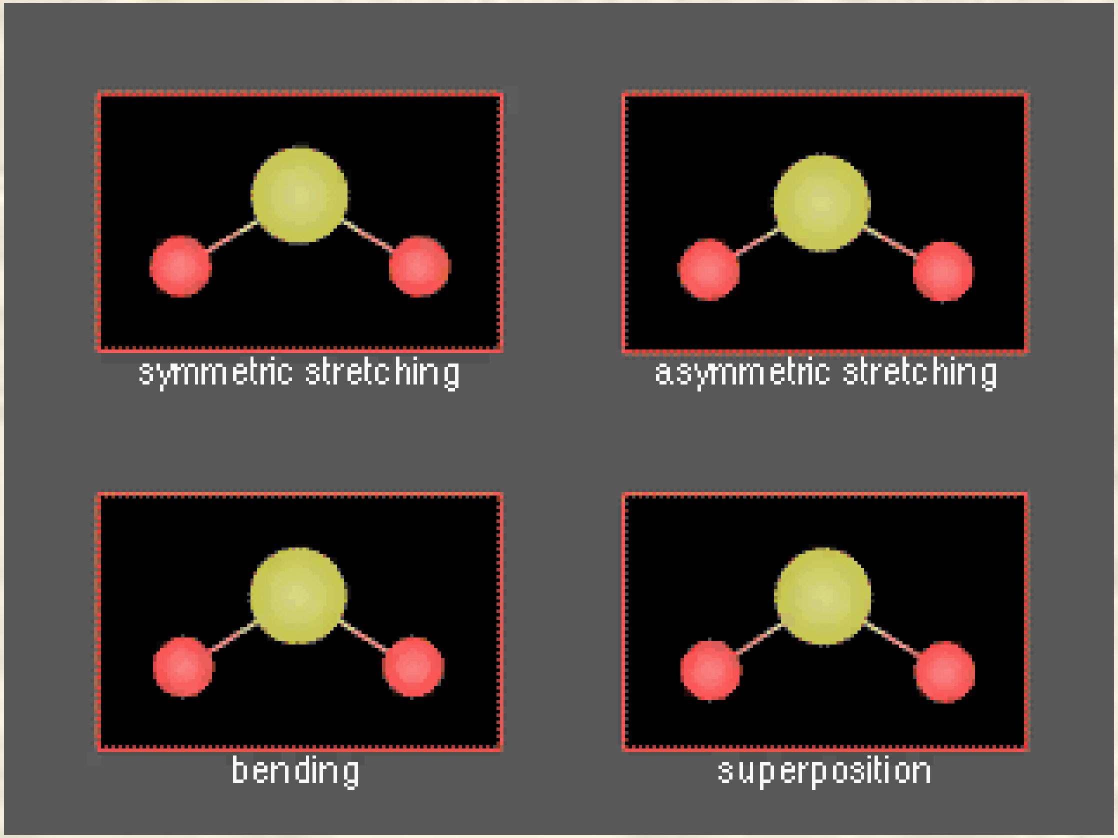
ν_3: 1361 cm^{-1}, 7.3 μm

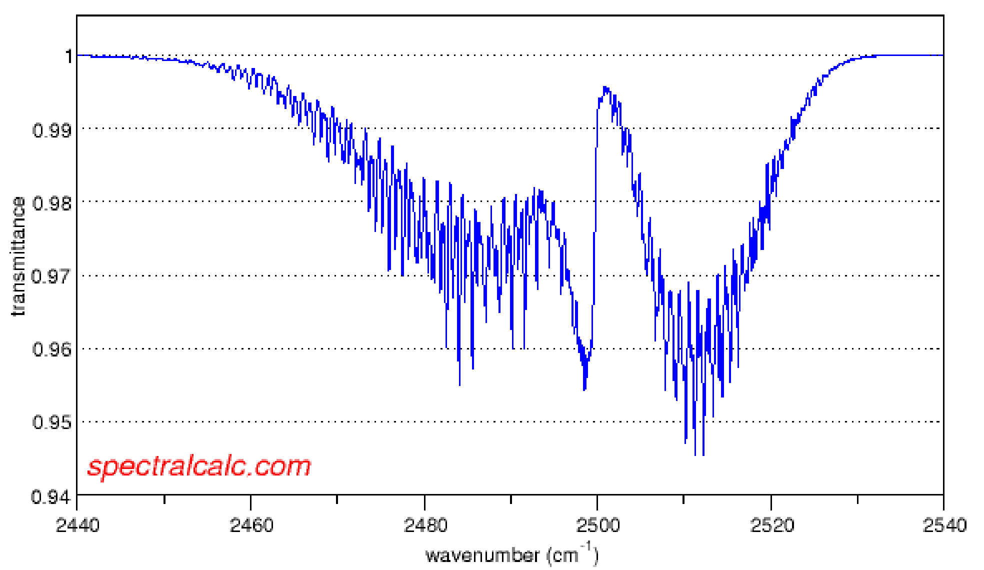




ν_2: 519 cm^{-1}, 19.2 μm

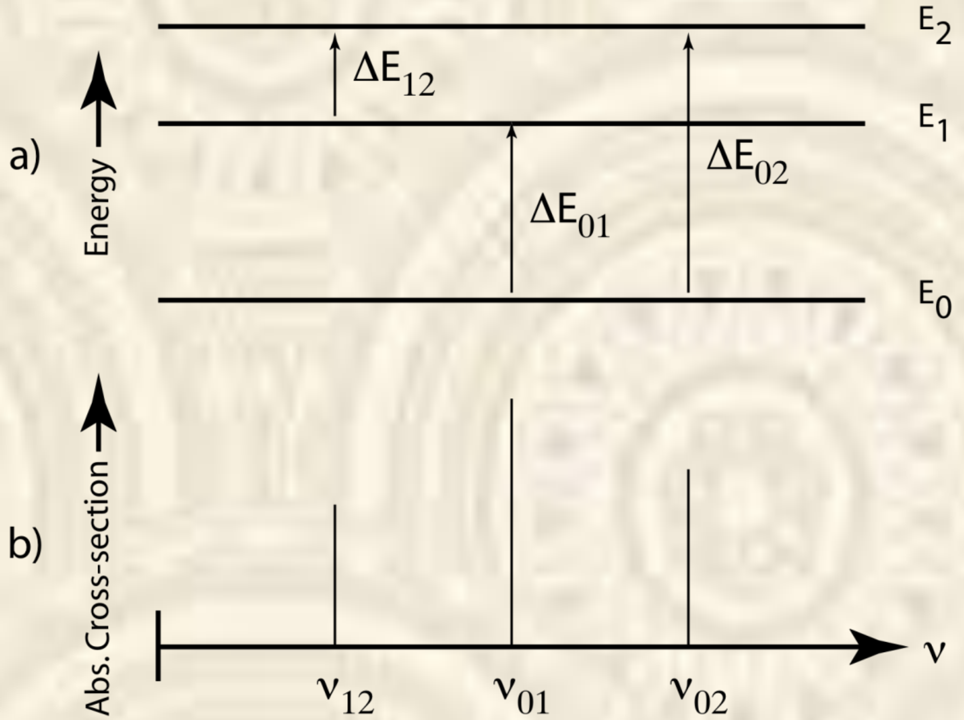
Sulfur dioxide (SO_2)





$\nu_1+\nu_3$: 2500 cm^{-1}, 4 µm

Absorption spectra of molecules



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