Atmospheric Physics

Lecture 5

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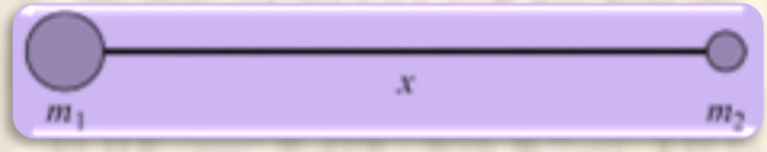
Basic spectroscopy of molecules

Vibrational and rotational states

As an illustration, we consider the vibrational and rotational states of a diatomic molecule, composed of an atom of mass m_1 and an atom of mass m_2



$$2\pi\nu_0 = \left(\frac{K}{m_r}\right)^{1/2}$$

$$m_r = \frac{m_1 m_2}{m_1 + m_2}$$

The reduced mass

The quantum-mechanical theory of the harmonic oscillator requires that we insert the potential function

$$V(x) = \frac{1}{2} K (x - x_0)^2$$

there results an infinite set of energy levels given by:

$$E_v = h\nu_0(v + \frac{1}{2}) \quad , \quad v = 0,1,2,...$$

Here *v* is the vibrational quantum number and takes integer values.

The levels are non-degenerate;
that is, there is only one state corresponding to each energy value E_v

For the strongest vibrational interactions this Hamiltonian takes

$$-\vec{p}.\vec{E}(t)$$

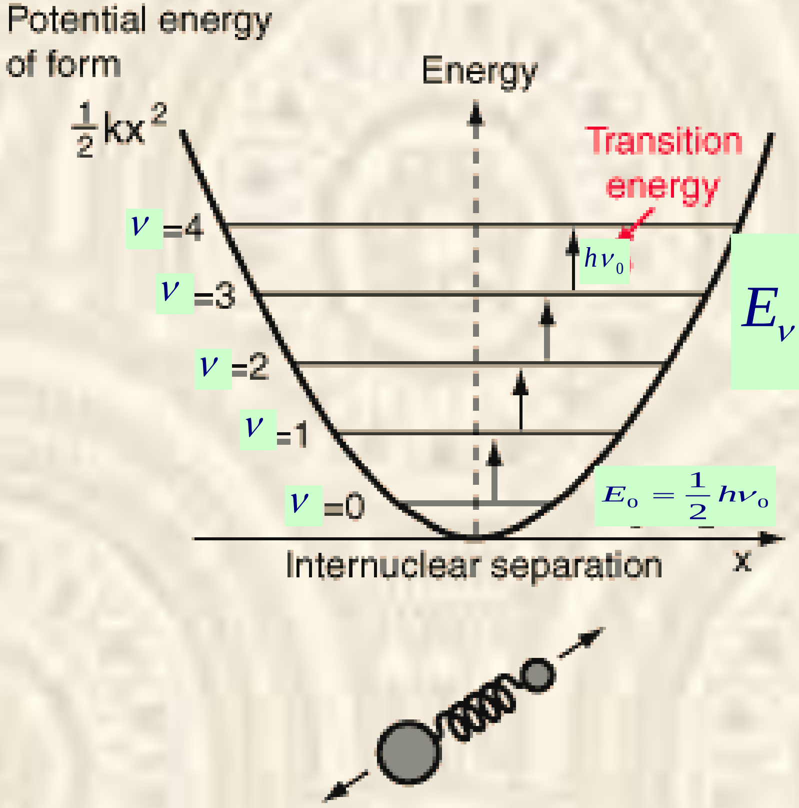
$\vec{p}$ the electric dipole moment of the molecule

$\vec{E}$ the electric field in the neighbourhood of the molecule.

For such a 'dipole transition' to occur, the dipole moment must change between the initial and final state.

Vibrational Spectra of Diatomic Molecules

The quantum-mechanical selection rule for a diatomic molecule states that in a dipole transition from one vibrational state to another, v can only increase or decrease by unity (Δv =±1), corresponding to an energy change $\Delta E = h\nu_0$



$$E_\nu = h\nu_0(\nu + \frac{1}{2})$$

x=0 represents the equilibrium separation between the nuclei.

We now consider the rotation of the same diatomic molecule, ignoring vibrations so that $x = x_0$

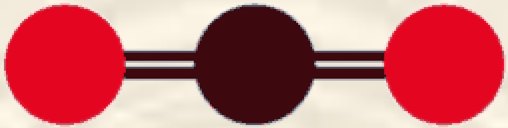
$I = m_r x_0^2$ $\hbar^2 J(J+1)$ $\hbar^2 = h/2\pi$

J is an integer, the rotational quantum number

$$E_j = \frac{1}{2I} J(J+1)\hbar^2 \quad , \quad J = 0,1,2,...$$

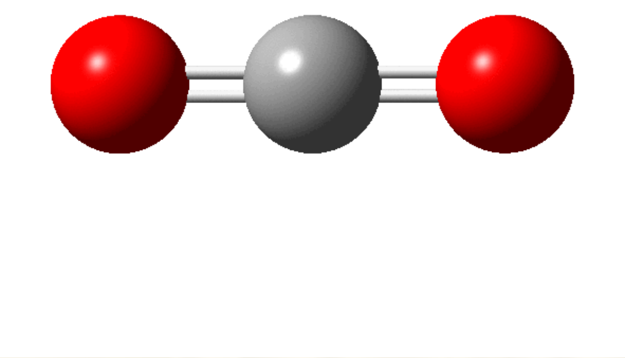
$$E_v = h\nu_0(v + \frac{1}{2}) \quad , \quad v = 0,1,2,...$$

The treatment of molecules with more than two atoms is more complex

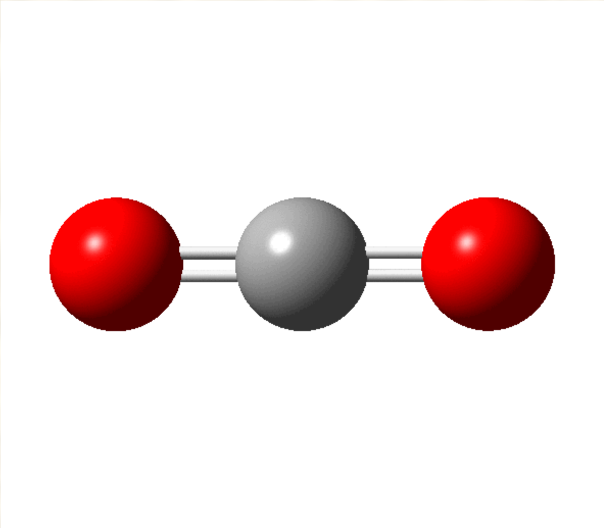


Carbon dioxide

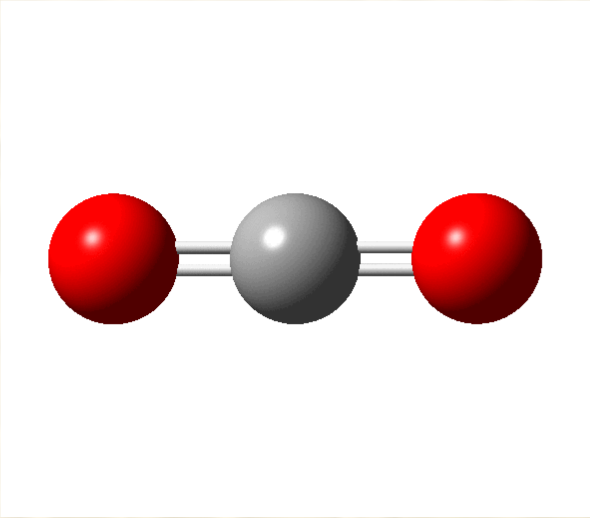
Vibrational modes of CO_2



$$\nu_1 = 1364 cm^{-1}$$

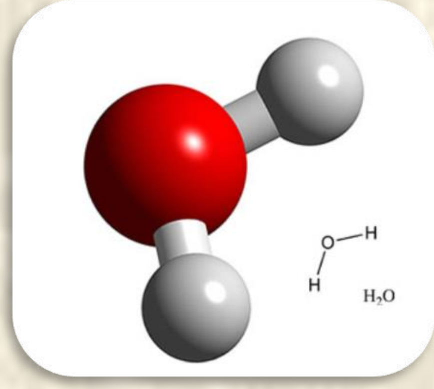


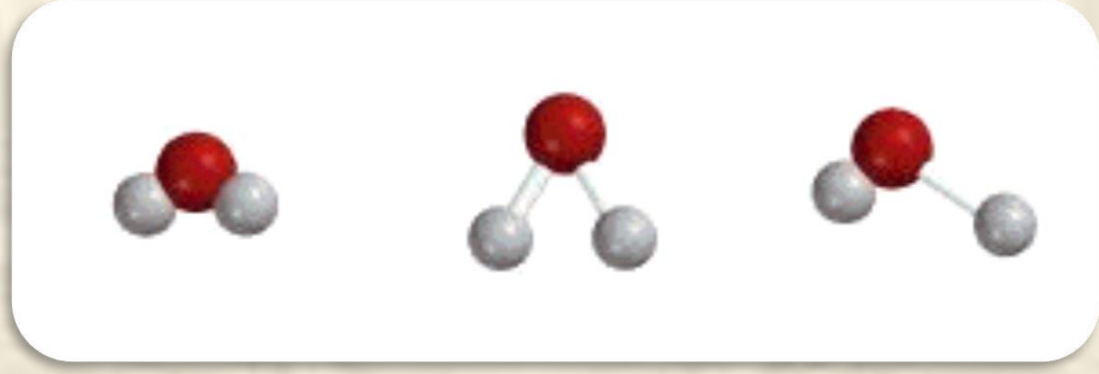
$$\nu_2 = 675 cm^{-1}$$

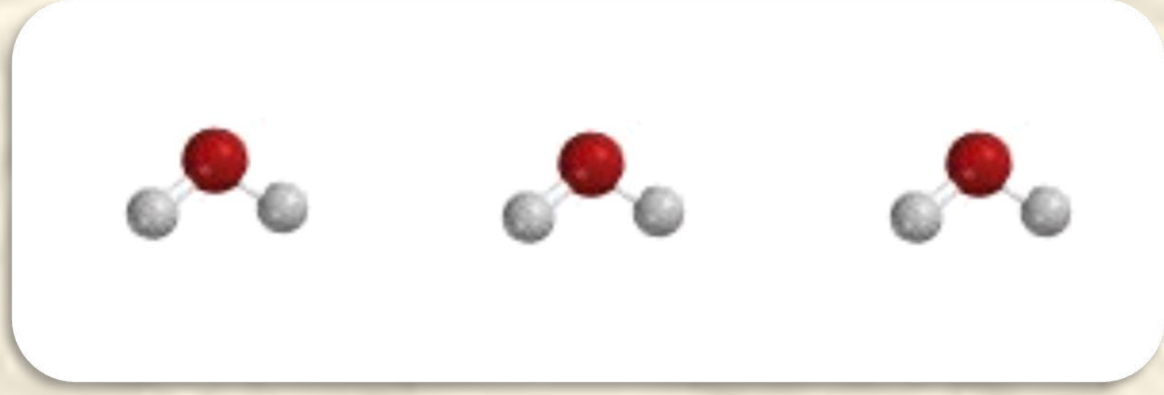


$$\nu_3 = 2399 cm^{-1}$$


O
O
O
Ozone = O_3


O—H
H
H_2O



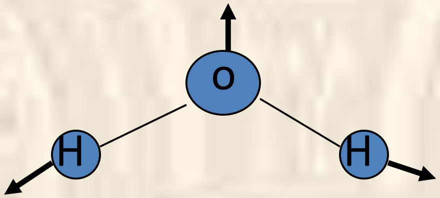


Water vapor (H_2O)

Most important IR absorber

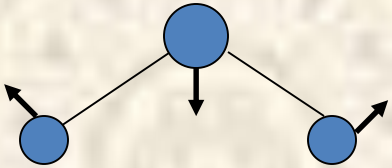
Asymmetric top → Nonlinear, triatomic molecule has complex line structure, no simple pattern

3 vibrational fundamental modes



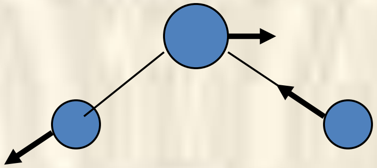
symmetric stretch

$v_1 = 2.74\ \mu m$



bend

$v_2 = 6.25\ \mu m$



asymmetric stretch

$v_3 = 2.66\ \mu m$

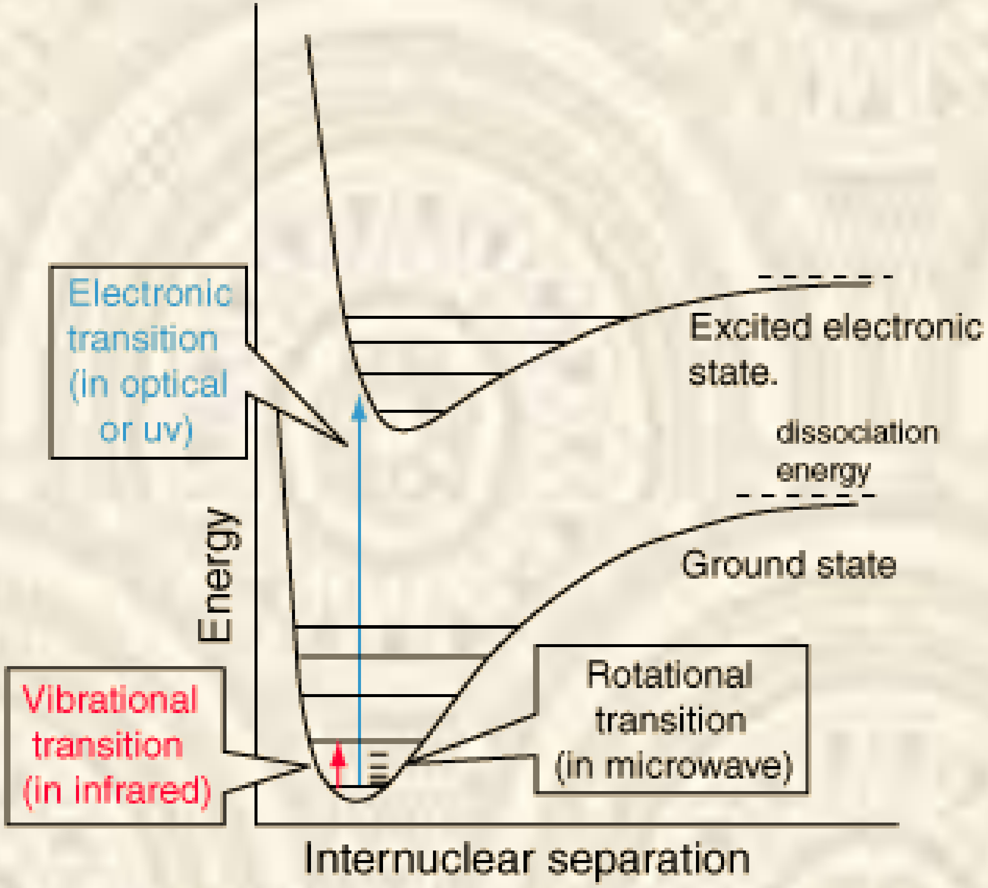
Higher order vibrational transitions ($\Delta v > 1$) give weak absorption bands at shorter wavelengths in the shortwave bands

^2H isotope (0.03% in atmosphere) and ^{18}O (0.2%) adds new (weak) lines to vibrational spectrum

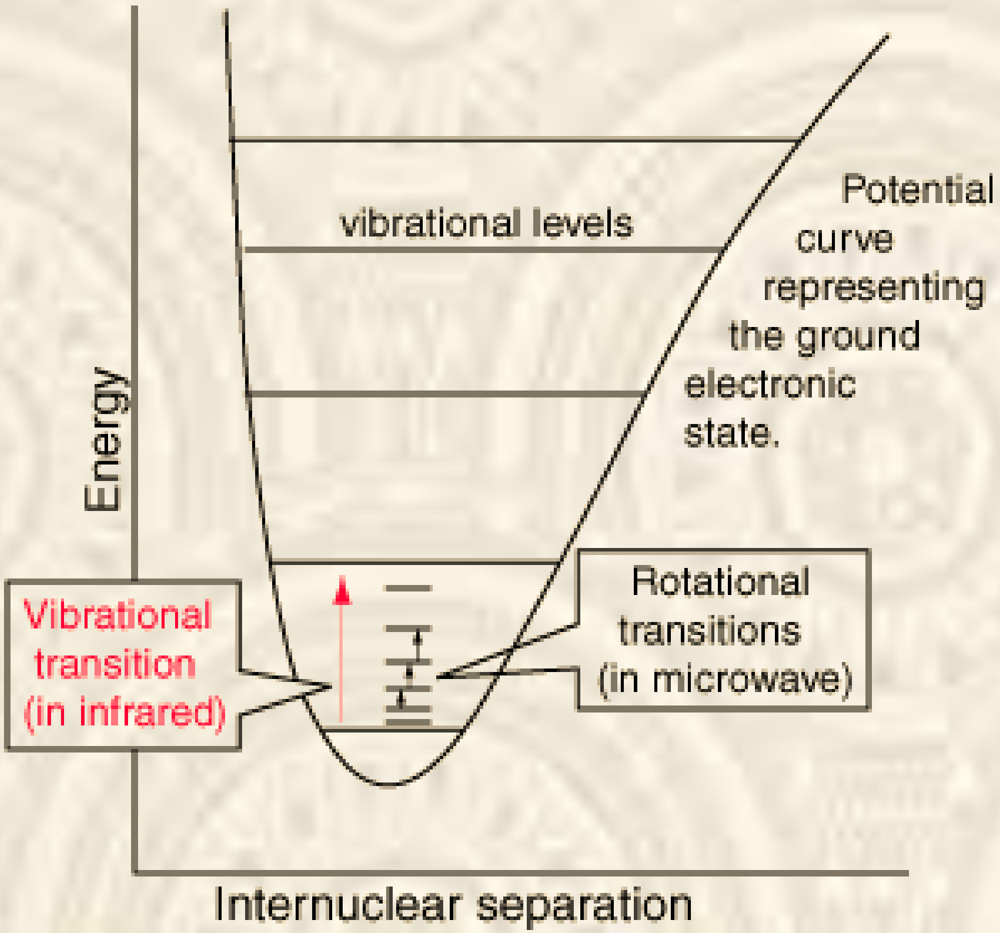
3 rotational modes (J_1, J_2, J_3)

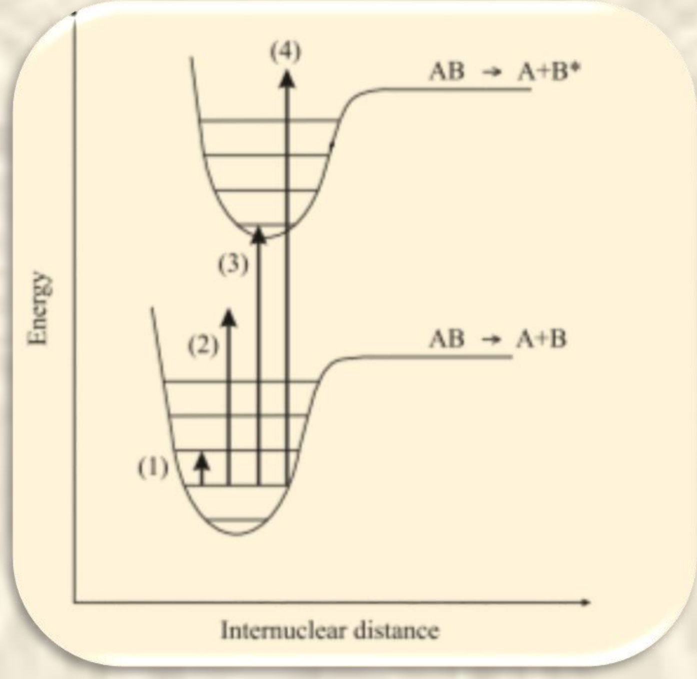
Overtones and combinations of rotational and vibrational transitions lead to several more weak absorption bands in the NIR

Molecular Spectra



Rotational Spectra





Molecular absorption processes

Electronic transitions

UV and visible wavelengths

Molecular vibrations

Thermal infrared wavelengths

Molecular rotations

Microwave and far-IR wavelengths

~10^{-18} J

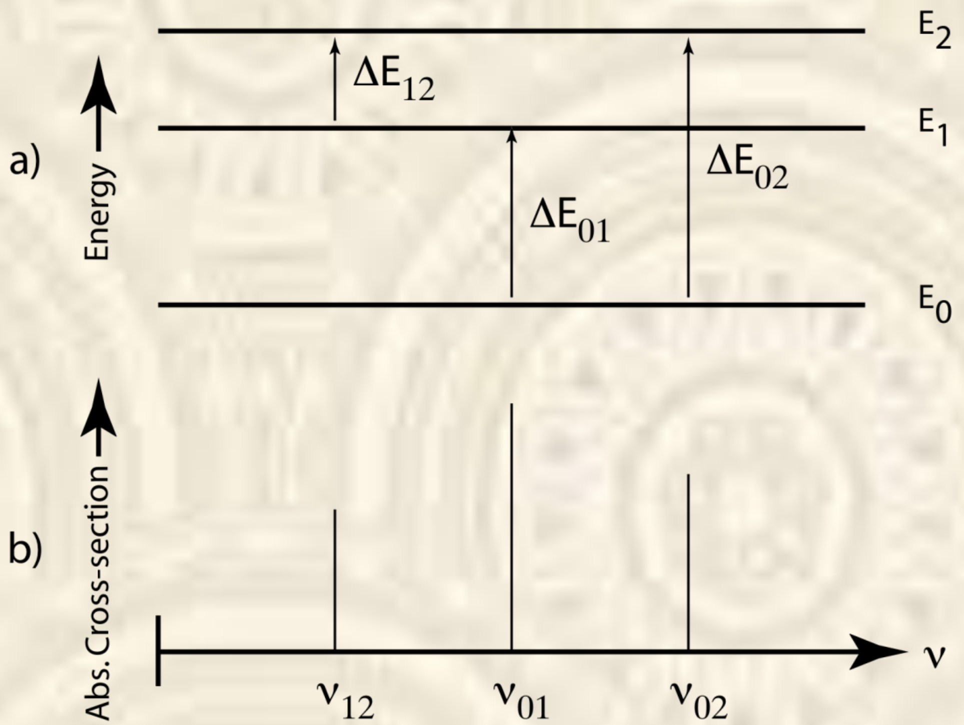
Increasing energy

~10^{-23} J

Each of these processes is quantized

Translational kinetic energy of molecules is unquantized

Absorption spectra of molecules



Hypothetical molecule with three allowed energy levels

Note relationship to emission!

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

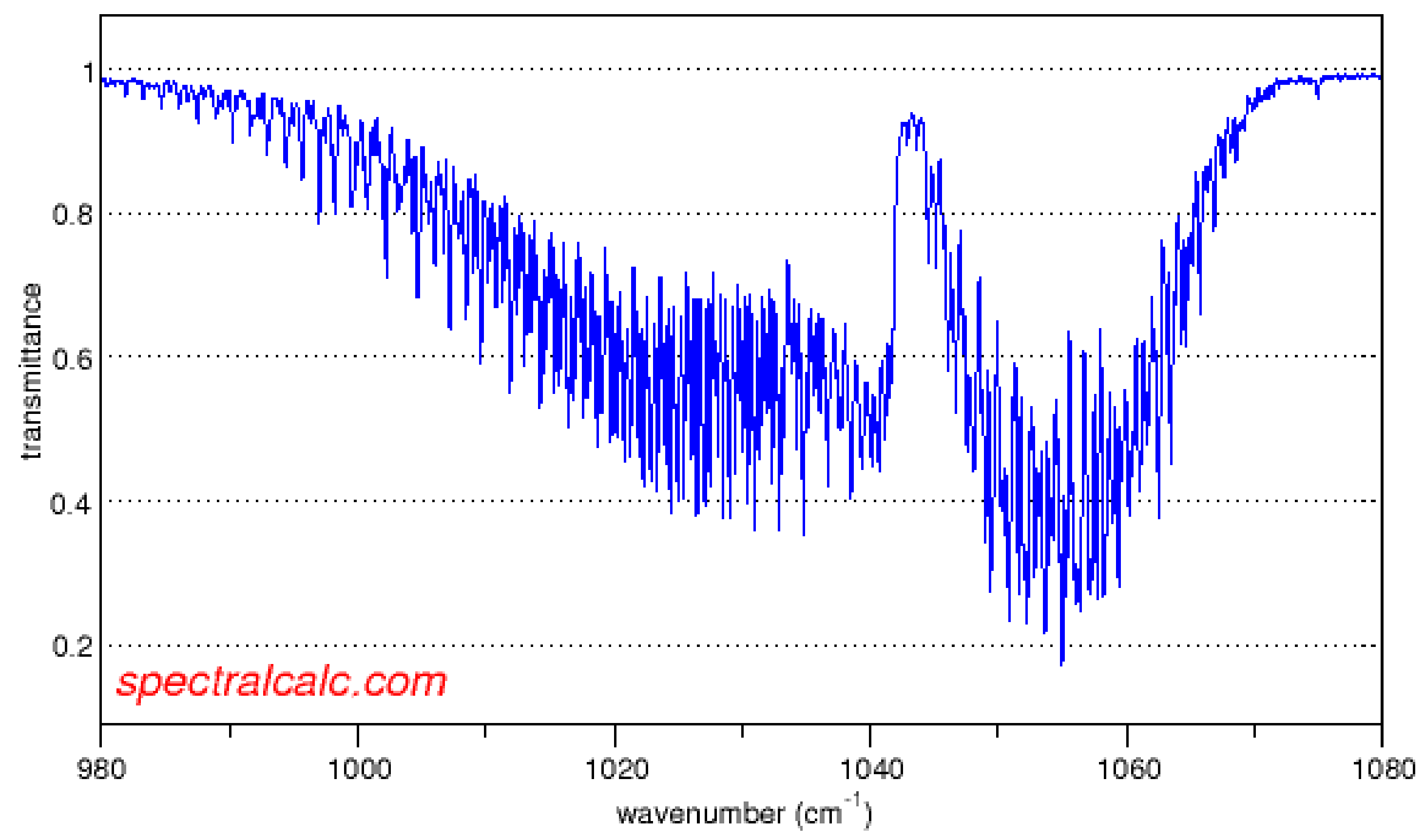
a) allowed transitions
b) positions of the absorption lines in the spectrum of the molecule

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

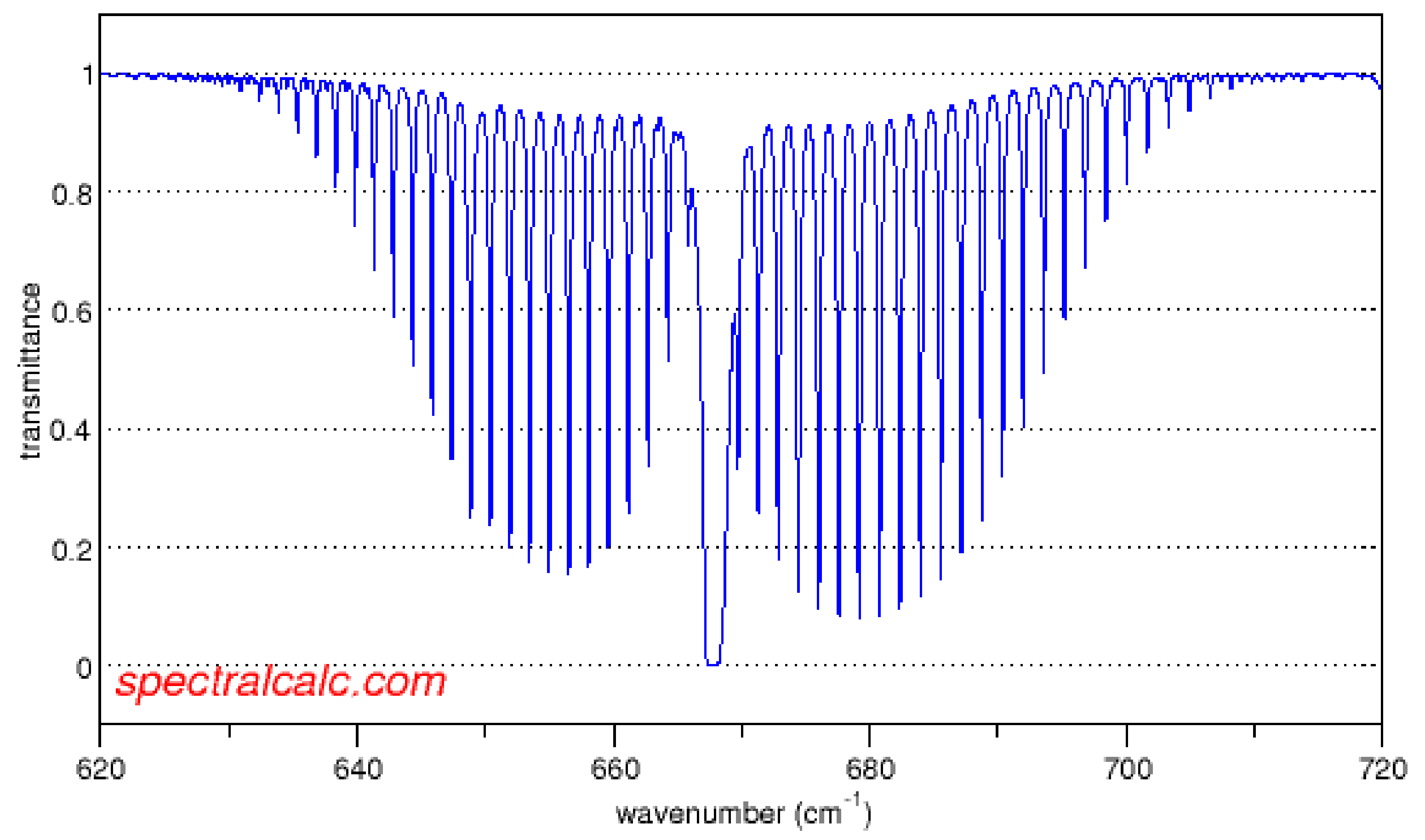
Transmittance spectrum for ozone (O_3)



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

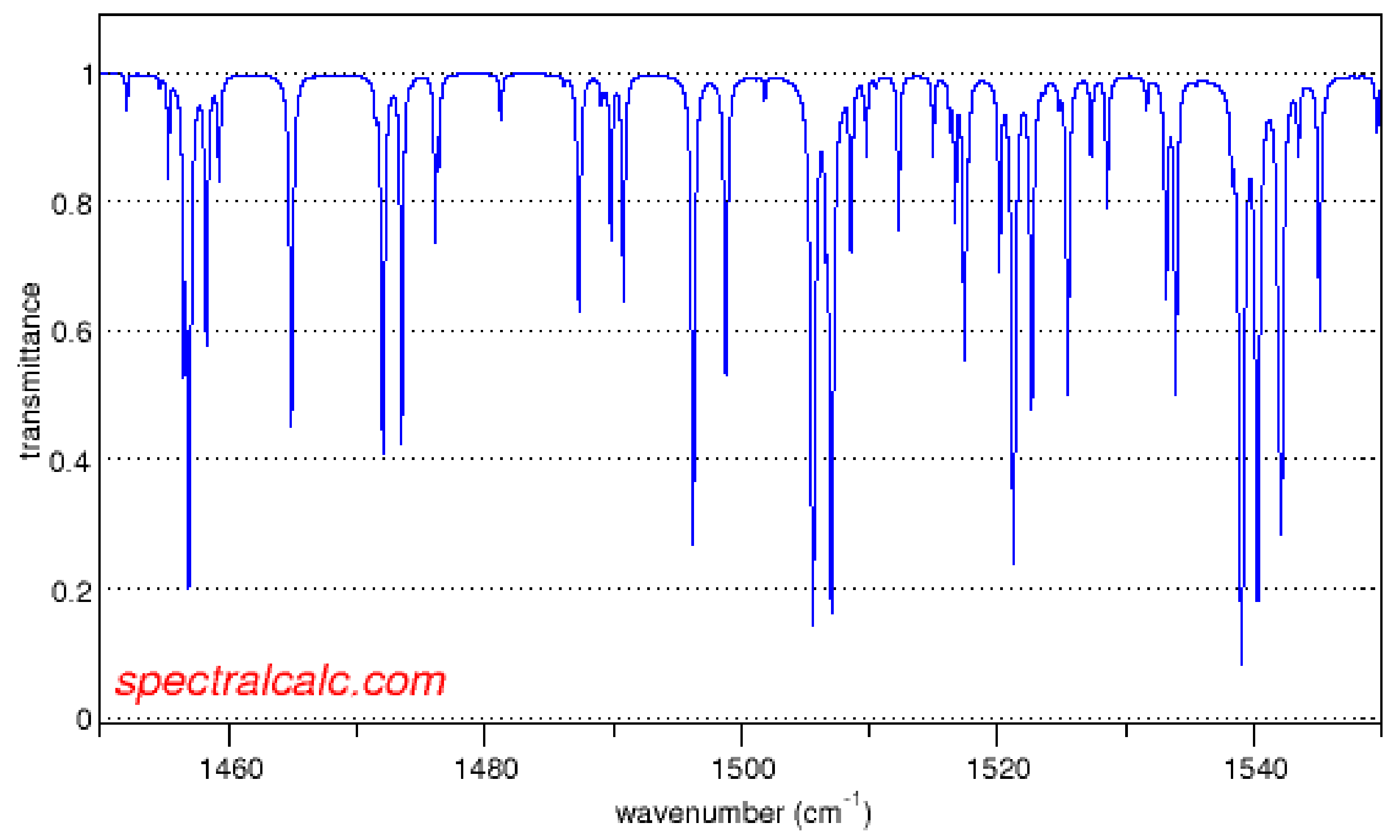
Transmittance spectrum for CO_2

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



Transmittance spectrum for H_2O

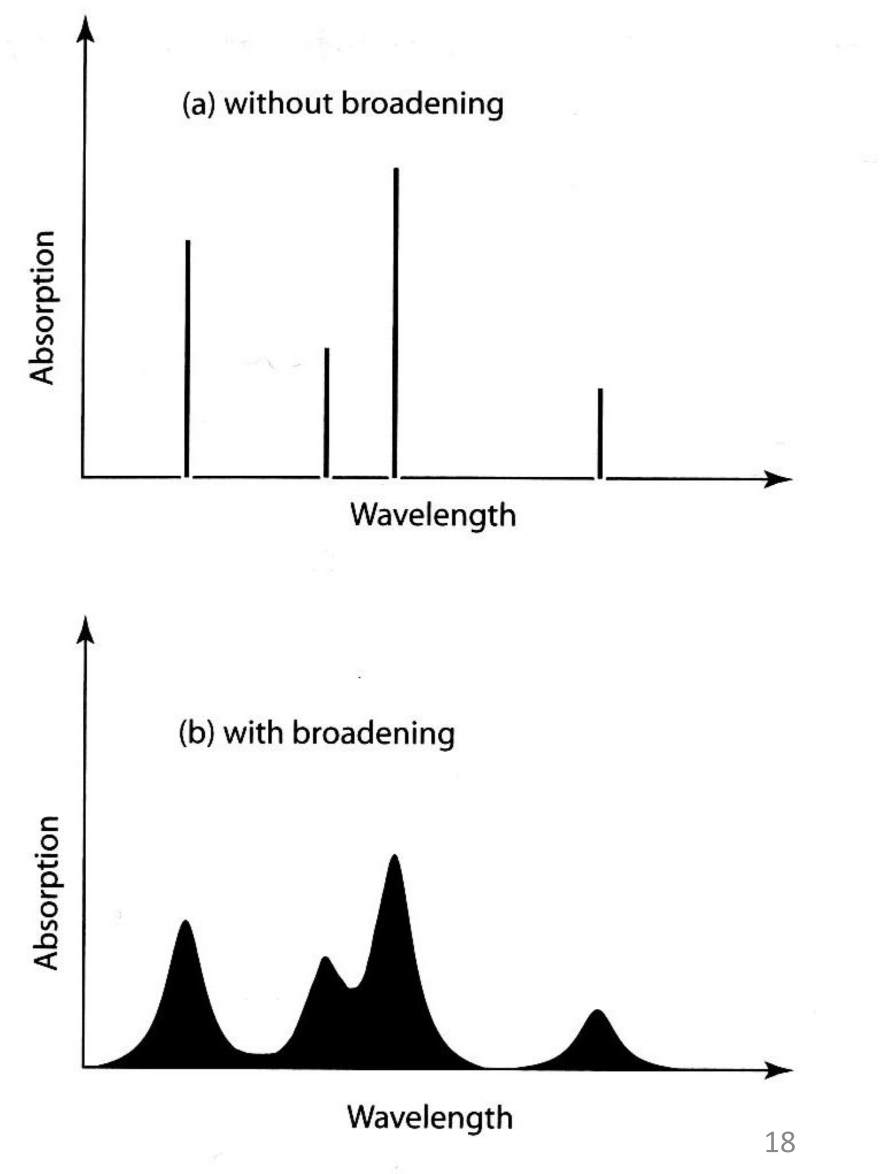
http://www.spectralcalc.com/calc/spectralcalc.php



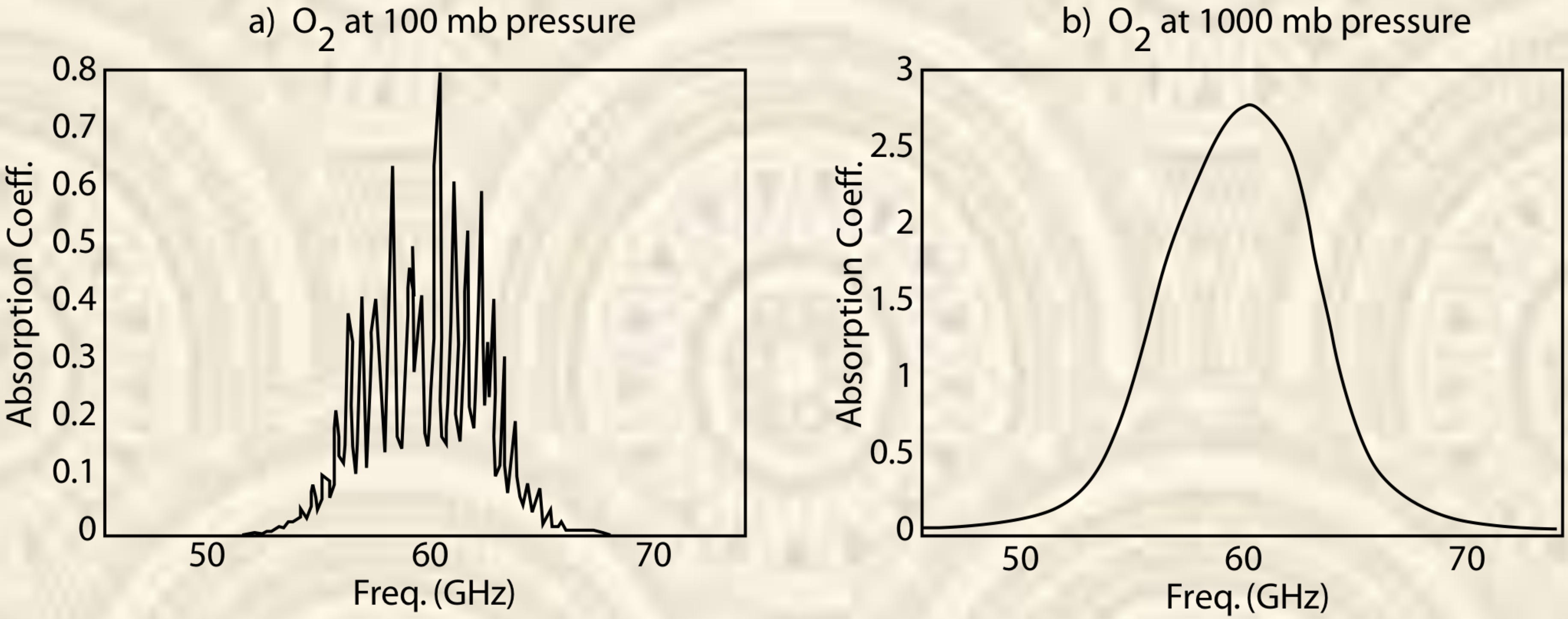
Absorption line shapes

- **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.

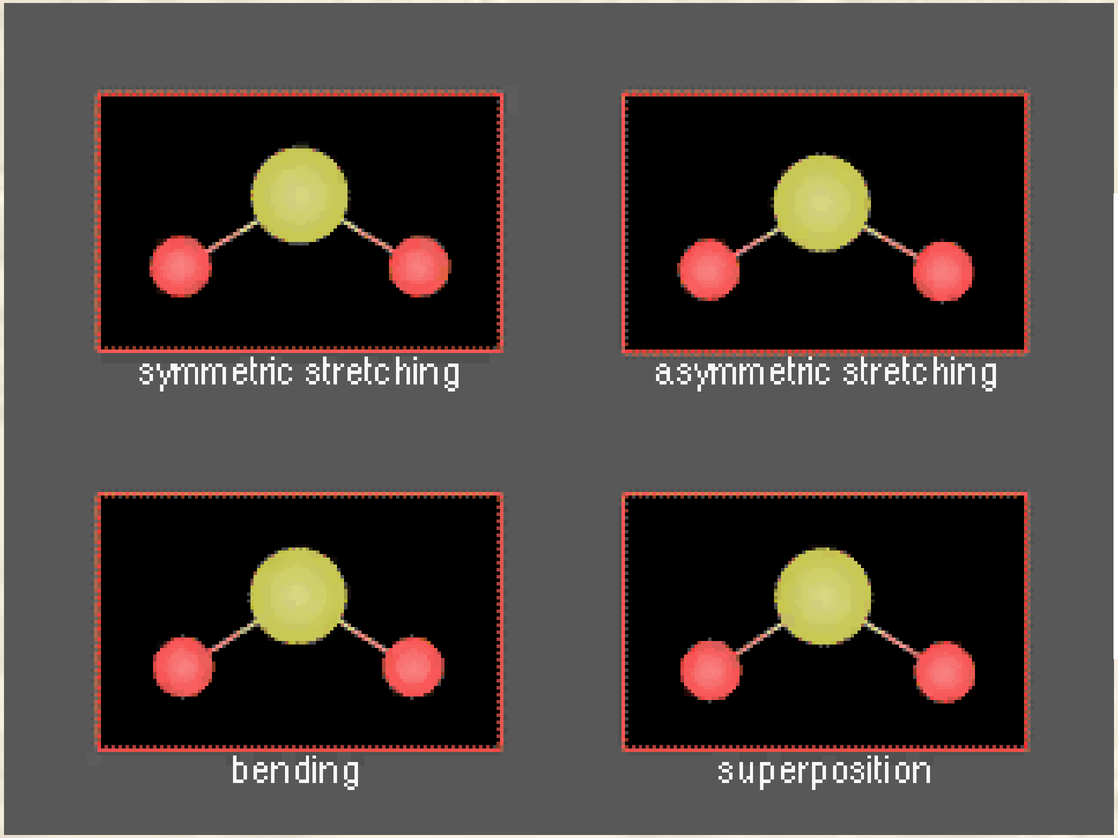


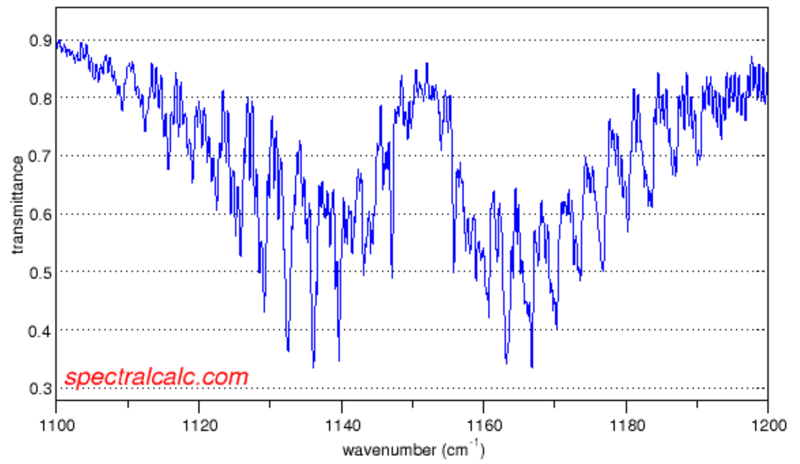
Pressure broadening



- 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.

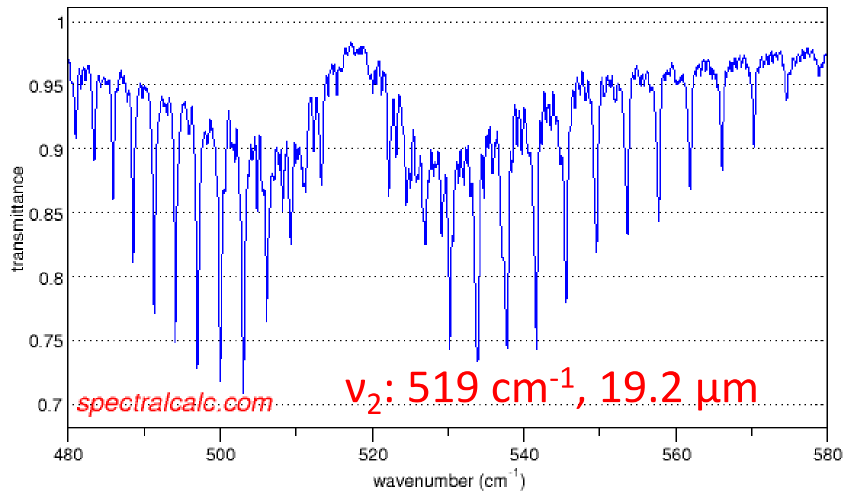
Sulfur dioxide (SO_2)



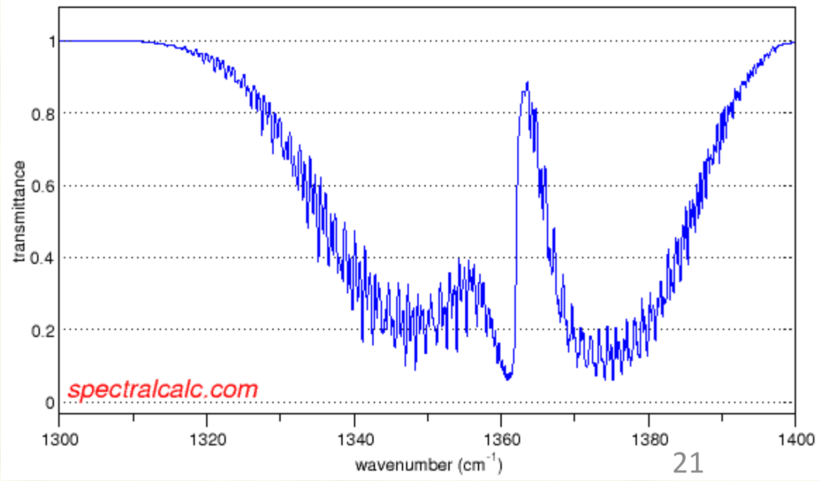


ν_1: 1151 cm^{-1}, 8.6 μm

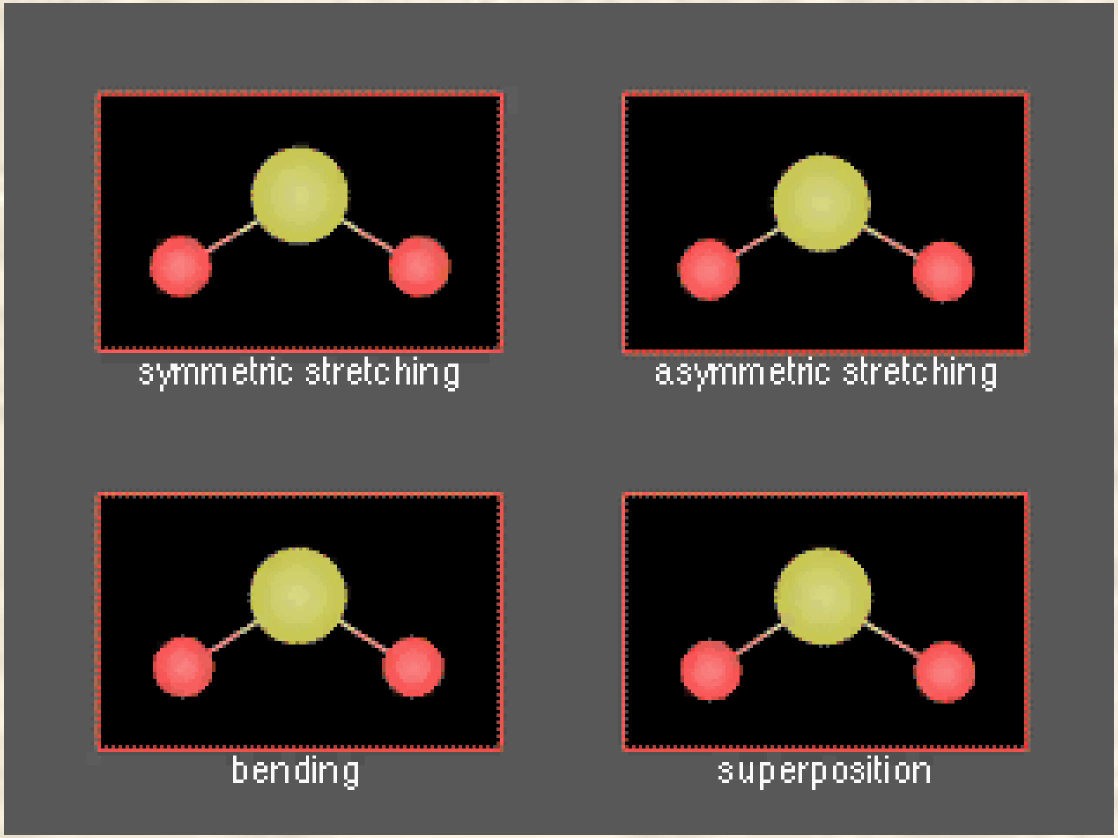
ν_3: 1361 cm^{-1}, 7.3 μm

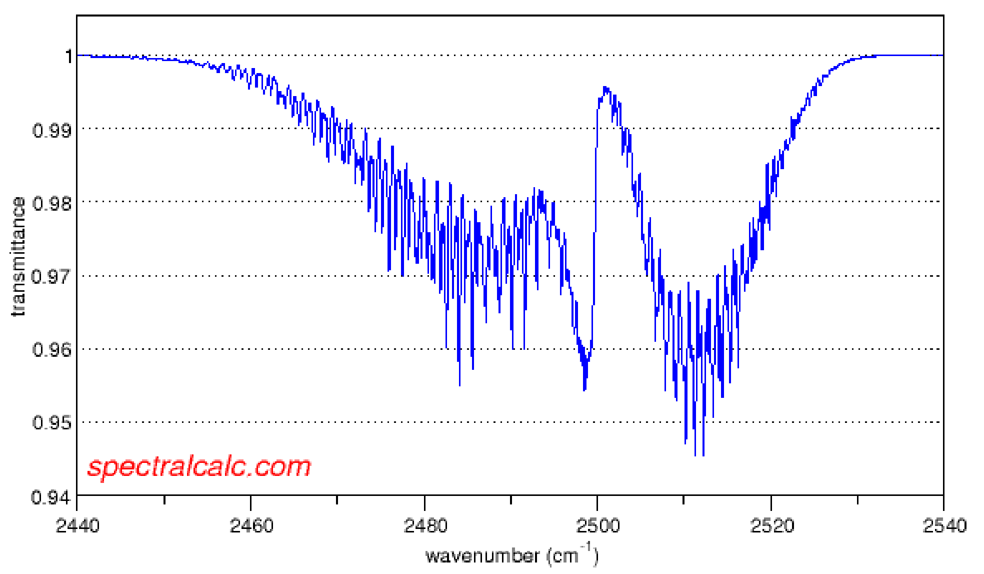


ν_2: 519 cm^{-1}, 19.2 μm



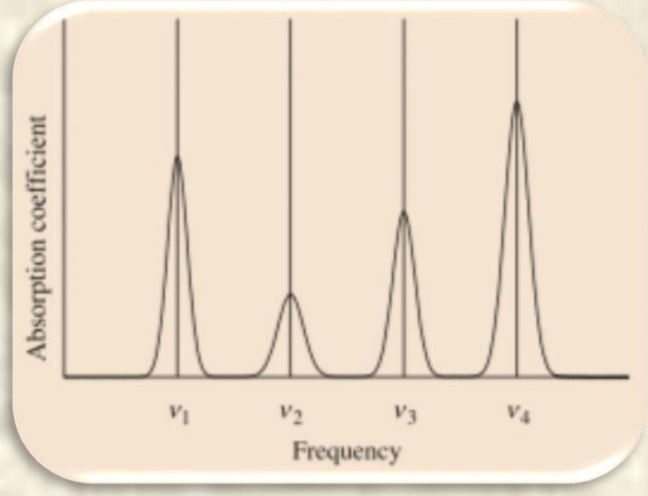
Sulfur dioxide (SO_2)





$\nu_1+\nu_3$: 2500 cm^{-1}, 4 µm

Line shapes



$$k_\nu = \sum_n S_n \delta(\nu - \nu_n)$$

$$k_\nu = \sum_n S_n f_n(\nu - \nu_n)$$

$$\int_{-\infty}^{\infty} f_n(\nu - \nu_n) d\nu = 1$$

$$f(\nu - \nu_n) = \left(\frac{\gamma_L}{\pi}\right) \frac{1}{(\nu - \nu_n)^2 + \gamma_L^2}$$

$$\gamma L = (2\pi\tau_c)^{-1}$$

$$\nu = \nu_0$$

$$\nu - \nu_0 = (u / c)\nu_0$$

$$u \ll c$$

$u+du$ $P(u)du$

$$P(u)=\left(\frac{m}{2\pi kT}\right)^{1/2}e^{-\frac{mu^2}{2k_BT}}$$

$$\int_{-\infty}^{\infty}P(u)\delta\left(\nu-\nu_0-\frac{u}{c}\nu_0\right)du\propto e^{-\frac{mc^2(\nu-\nu_0)^2}{2k_BT\nu_0^2}}$$

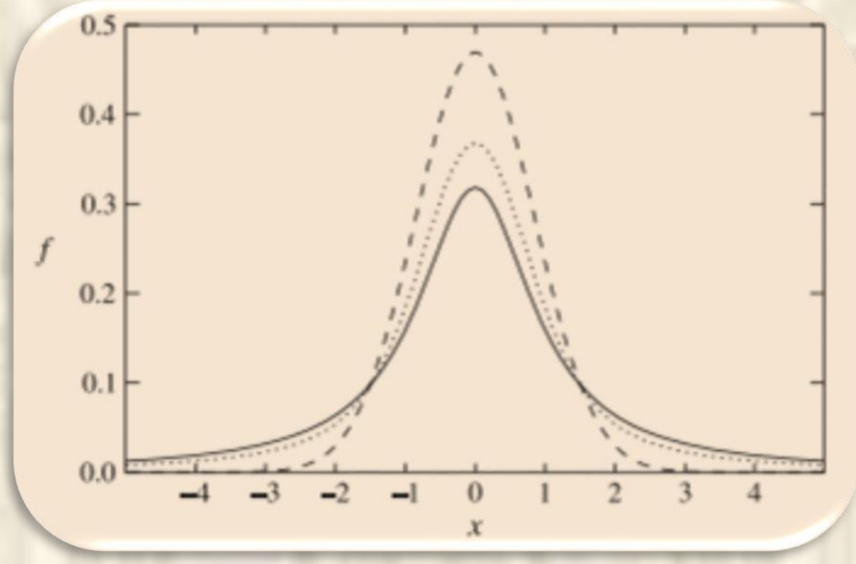
$$k_\nu=\frac{S}{\gamma D\sqrt{\pi}}e^{-\frac{(\nu-\nu_0)^2}{\gamma_D^2}}$$

$\gamma D(\ln 2)^{1/2}$

$$S=\int_{-\infty}^{\infty}k_\nu d\nu$$

$$\gamma D=\frac{\nu_0}{c}\left(\frac{2k_BT}{m}\right)^{1/2}$$

$T^{1/2}$



$$x = (\nu - \nu_n) / \alpha$$

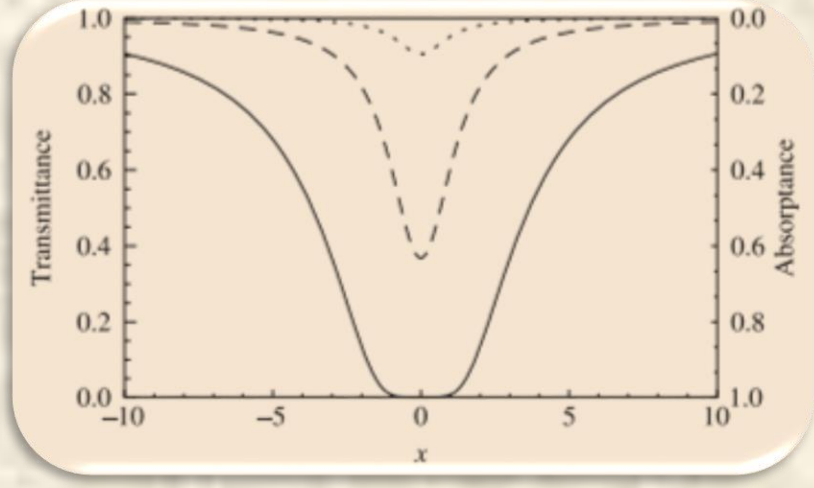
Transmittance

$$\tau_\nu(s_1,s_2)=\exp\left(-\left|\int_{-\infty}^{\infty}k_\nu(s)\rho_a(s)ds\right|\right)=\exp\left[-\left|\chi_\nu(s_2)-\chi_\nu(s_1)\right|\right]$$

$$\tau_\nu(s_1,s_2)=\exp\left[-k_\nu(p,T)u_a(s_1,s_2)\right]$$

$$u_a(s_1,s_2)=\left|\int_{s_1}^{s_2}\rho_a(s)ds\right|$$

$$u_a=\rho_a l$$



$q = u_a S / (\gamma L \pi)$ $q \gg 1$ $q \ll 1$

$A_\nu = 1 - \tau_\nu$

$$\bar{\tau}_r = \frac{1}{\Delta \nu_r} \int_{\Delta \nu_r} \tau_\nu d\nu$$

$\bar{A}_r = 1 - \bar{\tau}_r$

$$W_r = \int_{\Delta \nu_r} (1 - \tau_\nu) d\nu = \Delta \nu_r (1 - \bar{\tau}_r) = \Delta \nu_r \bar{A}_r$$

$\tau_r = e^{-k_\nu u_a} \approx 1 - k_\nu u_a$

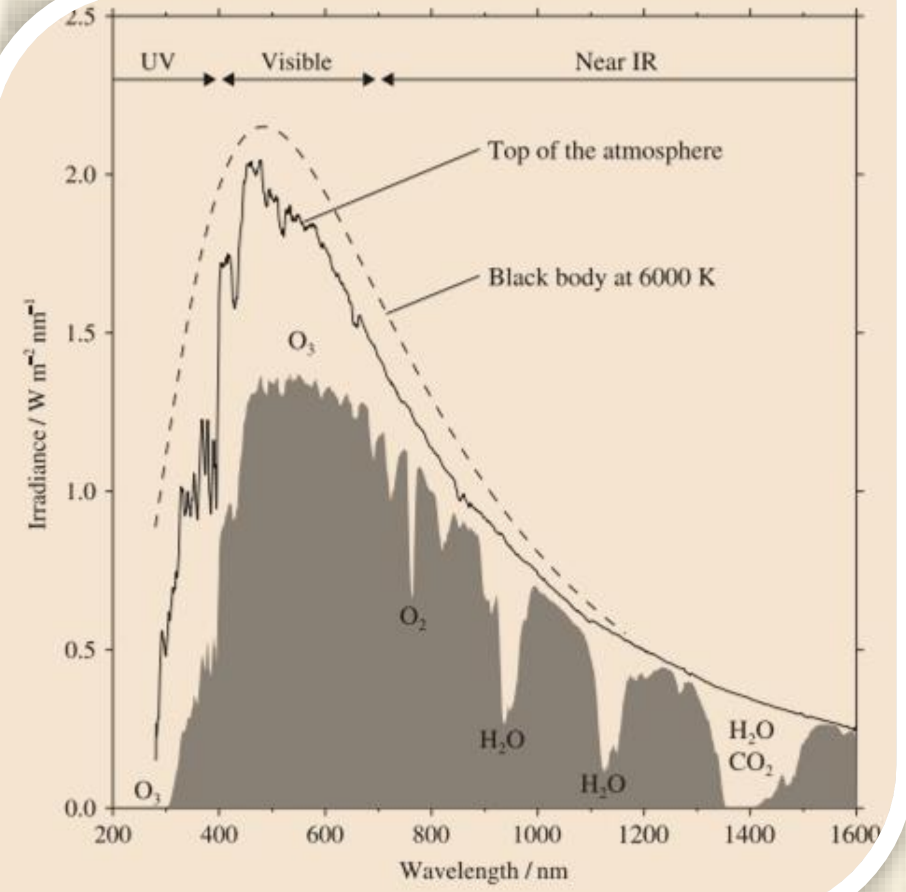
$$W_r \approx \int_{\Delta \nu_r} k_\nu u_a d\nu = S u_a$$ $$S = \int_{\Delta \nu_r} k_\nu d\nu$$

$$W \approx 2(Su_a \gamma L)^{1/2}$$

$$W \approx 2\gamma D \left\{ \ln \left[Su_a / (\gamma D \sqrt{\pi} \right] \right\}^{1/2}$$

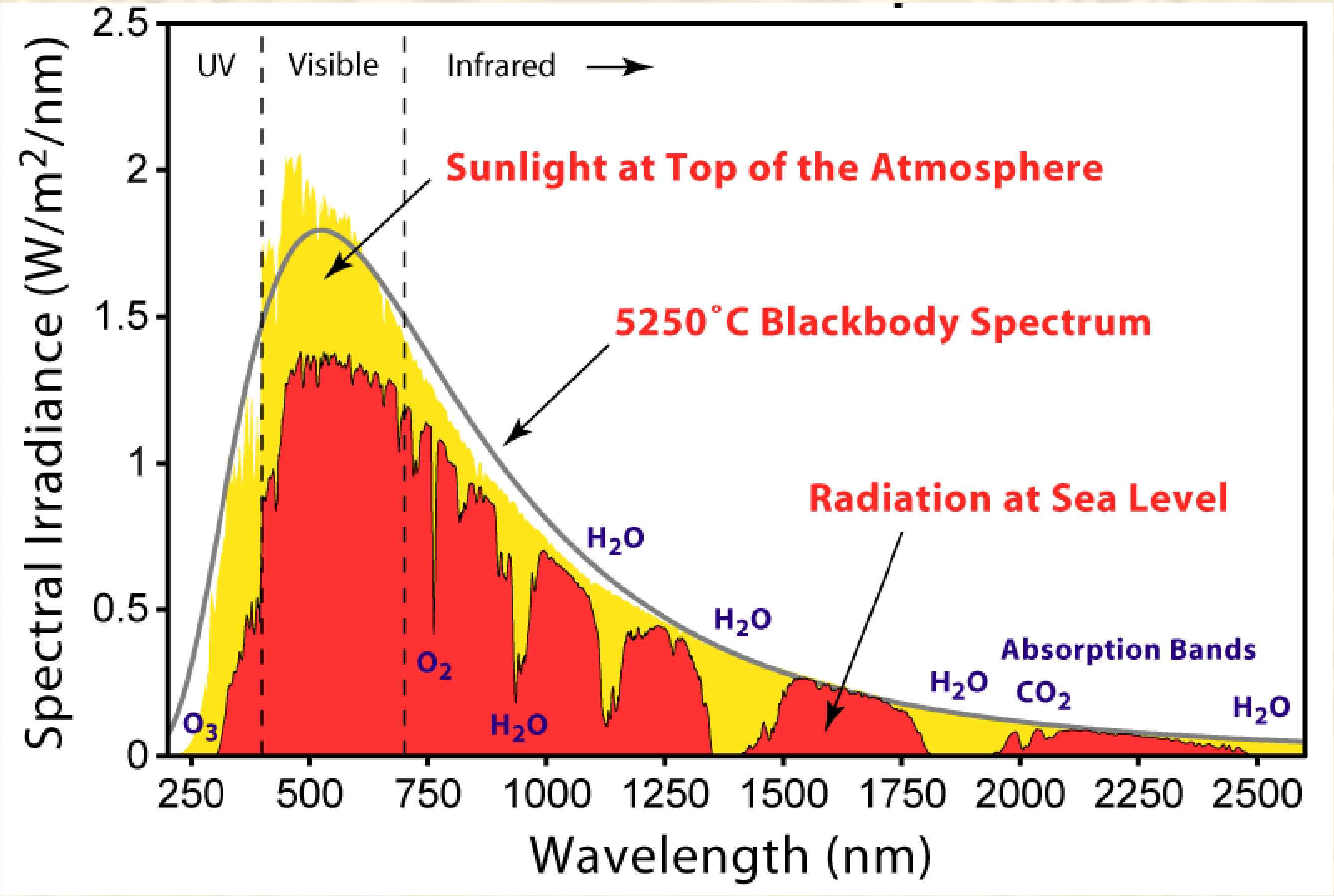
Absorption by atmospheric gases

The solar spectrum

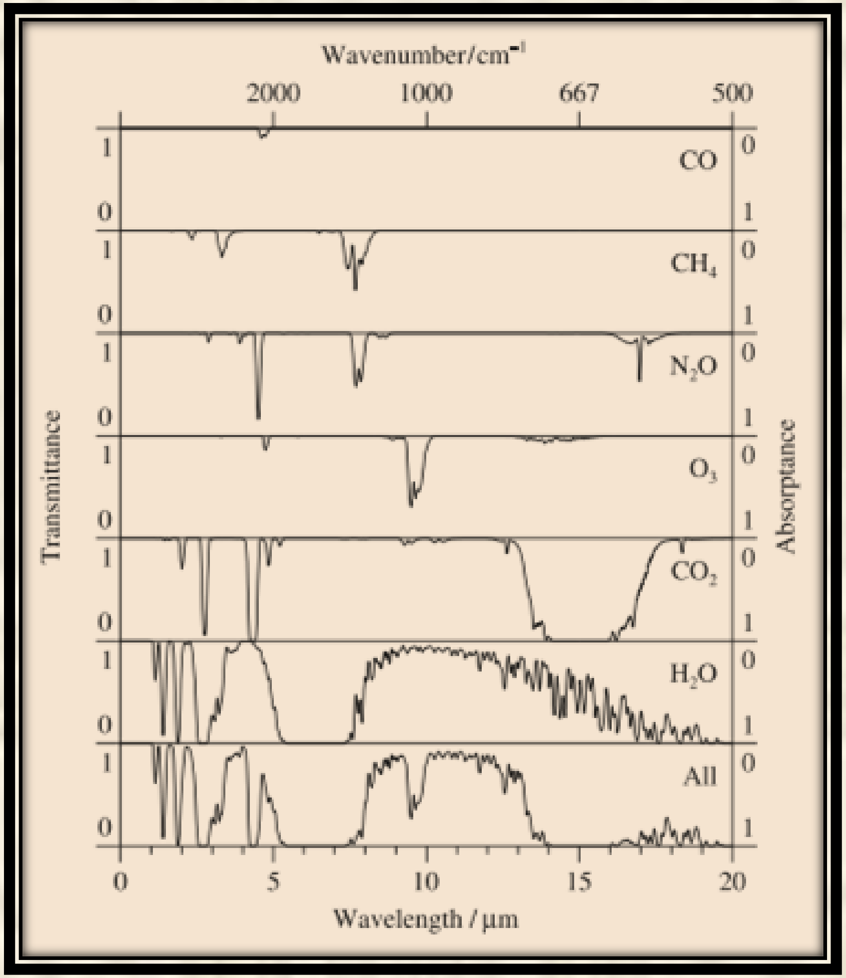


Radiation in the Atmosphere

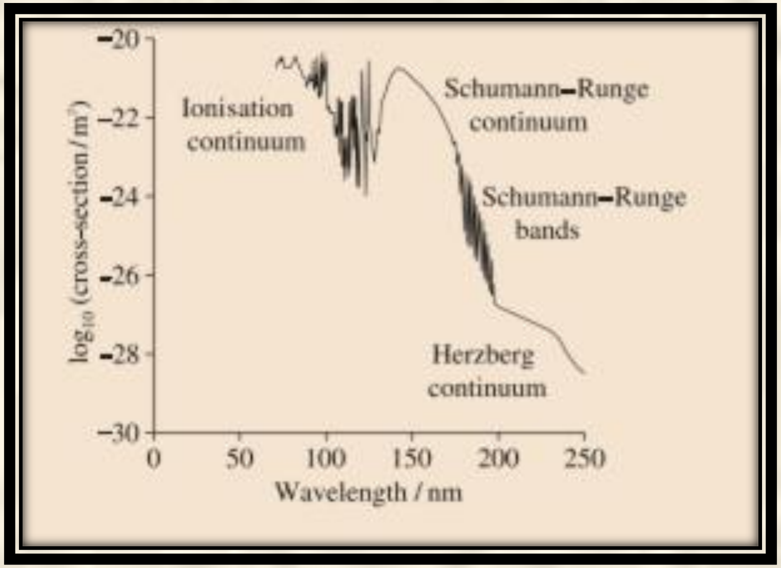
Deviations from blackbody due to absorption by the solar atmosphere, absorption and scattering by the earth's atmosphere (below).

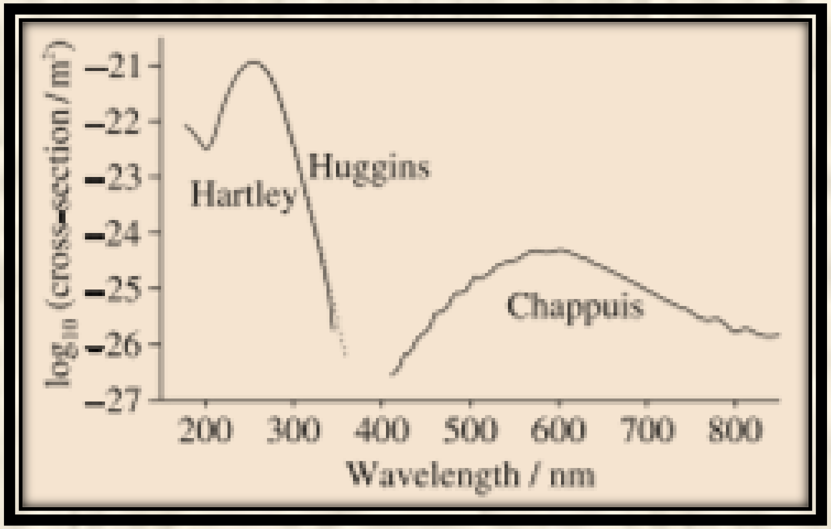


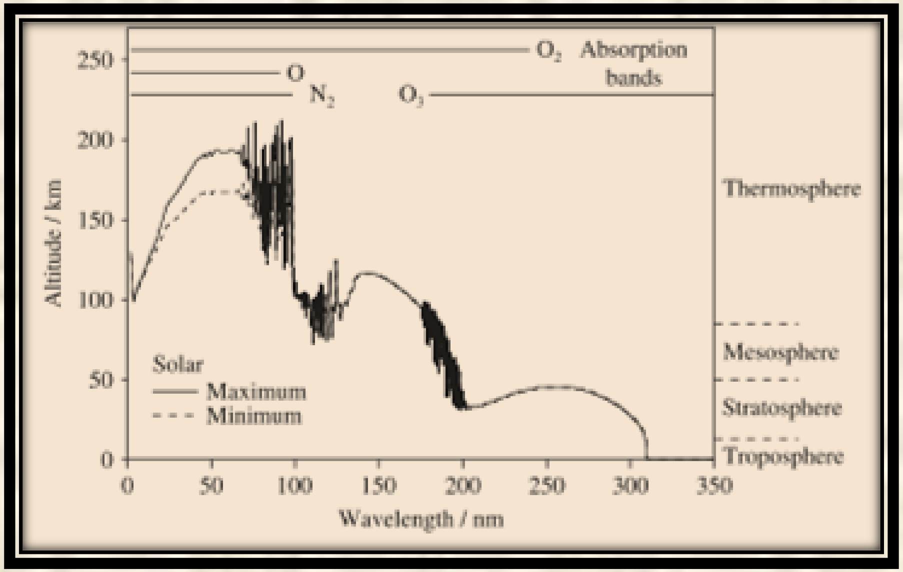
Infra-red absorption



Ultra-violet absorption




log10 (cross-section / m²)
−21
−22
−23
−24
−25
−26
−27
Hartley
Huggins
Chappuis
200
300
400
500
600
700
800
Wavelength / nm


Altitude / km
250
200
150
100
50
0
O₂ Absorption bands
O
N₂
O₃
Thermosphere
Mesosphere
Stratosphere
Troposphere
Solar
Maximum
Minimum
0
50
100
150
200
250
300
350
Wavelength / nm

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} $\rho_a z$

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

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

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

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

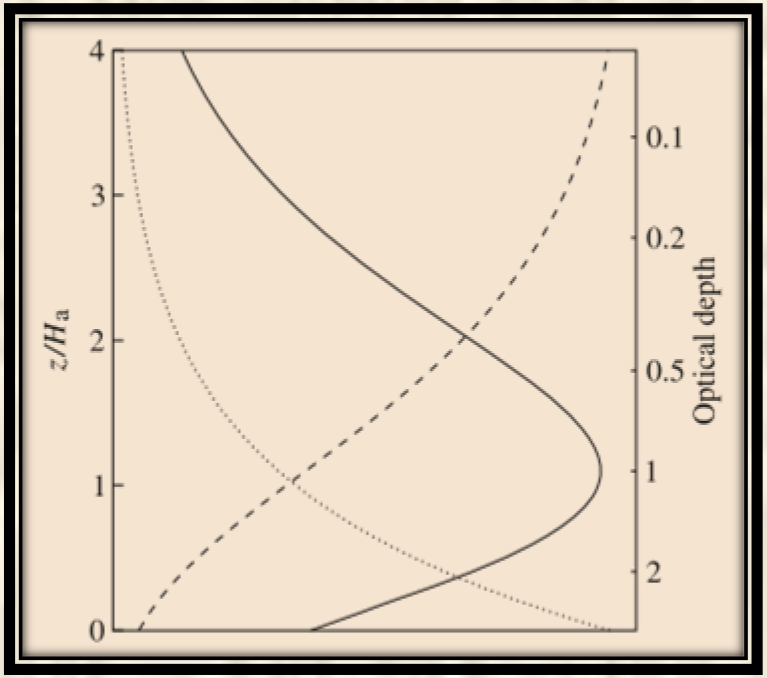
$$\rho Q_\nu^{sw} = \frac{d}{dz}\left(F_{\nu\infty}^{\downarrow} e^{-\chi_\nu(z)}\right) = F_{\nu\infty}^{\downarrow}\left(-\frac{d\chi_\nu}{dz}\right)e^{-\chi_\nu(z)}$$

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

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

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

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



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

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} $k_\nu \rho_a J_\nu A \Delta z$

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

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

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

τ_ν τ_ν^*

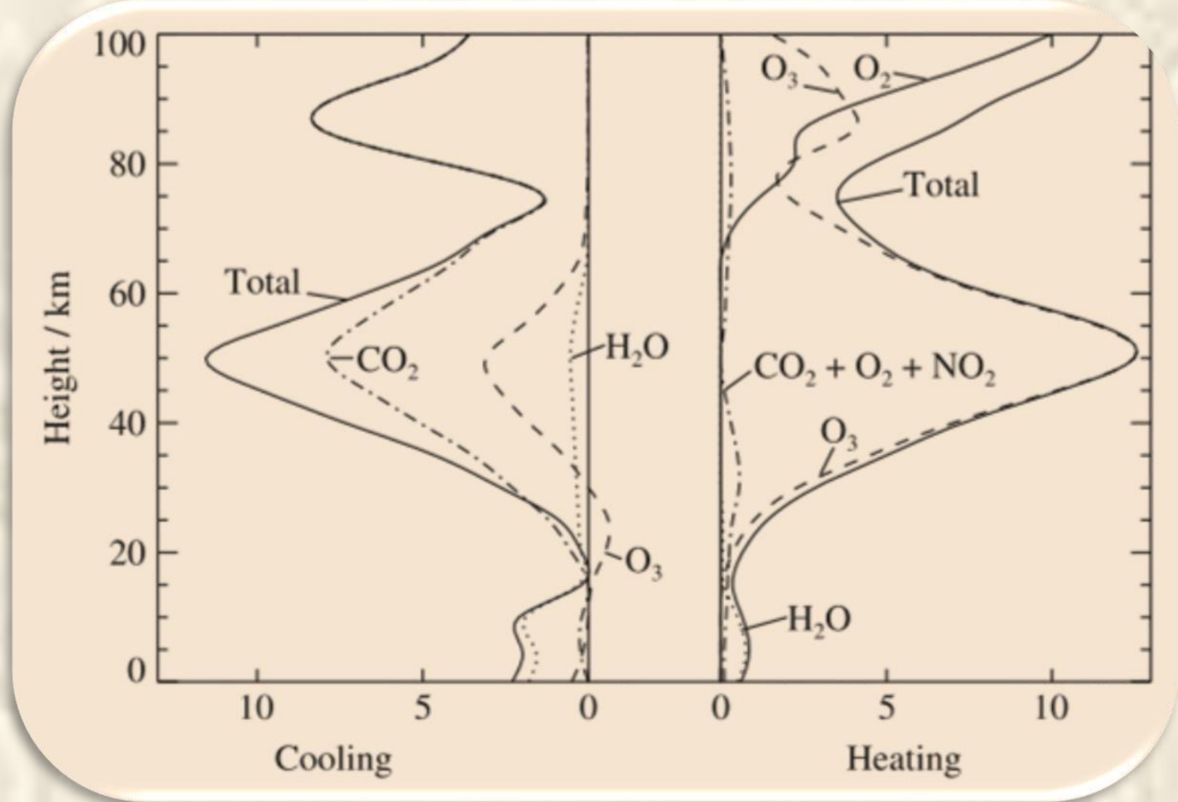
$$Q_\nu^{cts}(z) = \frac{\pi B_\nu(z)}{\rho(z)} \frac{\partial \tau_\nu^*(z,\infty)}{\partial z}$$

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

Net radiative heating rates

Q^{sw} / c_p

$-Q^{lw} / c_p$



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

$Q = 0$

$T_r(r)$

$Q(T_r(r)) = 0$ $T = T_r + \delta T$

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

$$Q(T_r) = 0$$

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

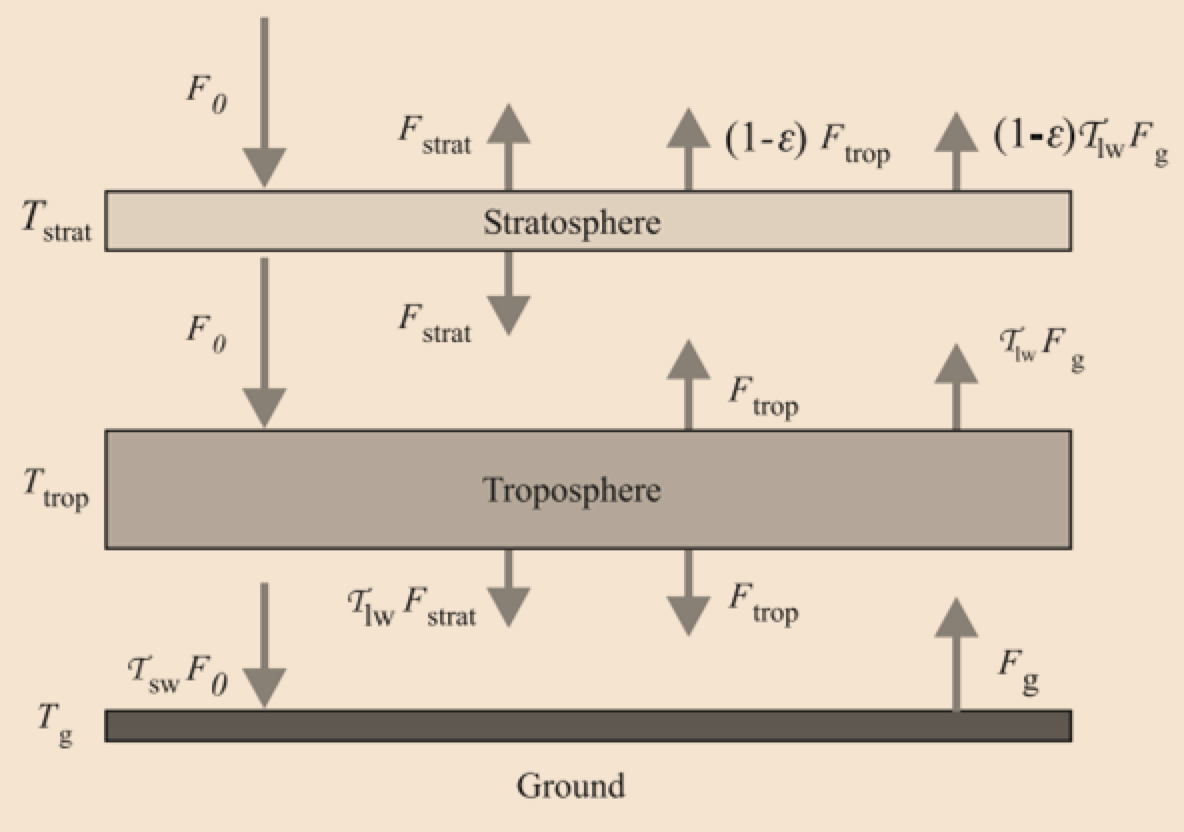
$$\tau_r = c_p \left(\partial Q / \partial T\Big|_{T=T_r}\right)^{-1}$$

The greenhouse effect revisited

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

T_{trop} τ_{sw} τ_{lw}

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



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

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

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

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

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

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

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

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

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

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

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

Continuously stratified atmosphere in radiative equilibrium

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$T_g > T_c$$

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

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

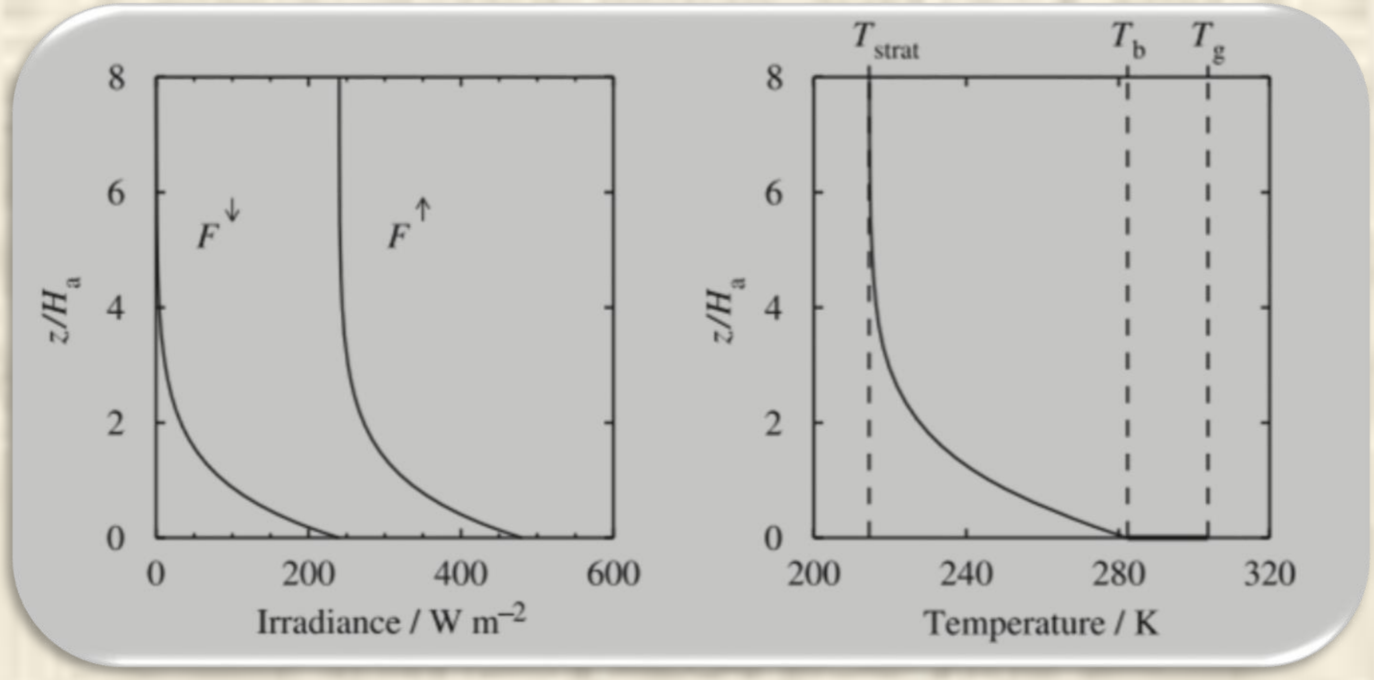
$$F^{\uparrow}(z) = \frac{1}{2}F_0(2+\chi_g^* e^{-z/H_a}) \qquad F^{\downarrow}(z) = \frac{1}{2}F_0\chi_g^* e^{-z/H_a}$$

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

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

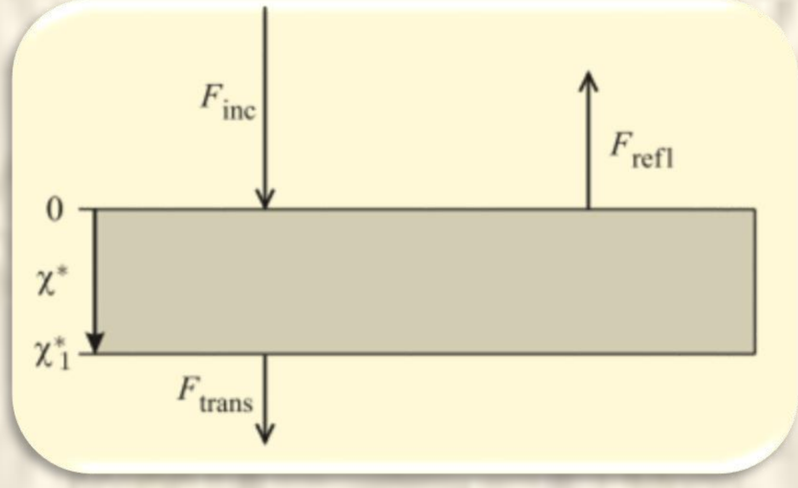
$$T \rightarrow \left(\frac{F}{2\sigma}\right)^{1/4} \text{ as } z \rightarrow \infty \qquad T_{strat} = 2^{-1/4} T_c$$

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



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

A simple model of scattering


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

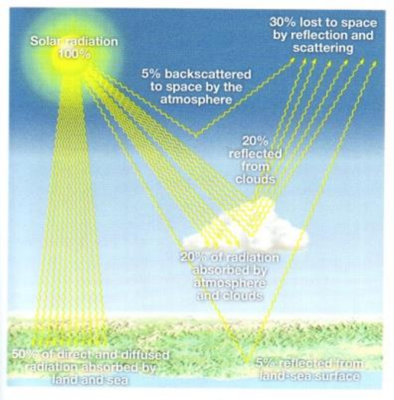
Shortwave Radiation

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, $20^4 = 160{,}000$