

Atmospheric Physics

Lecture 6

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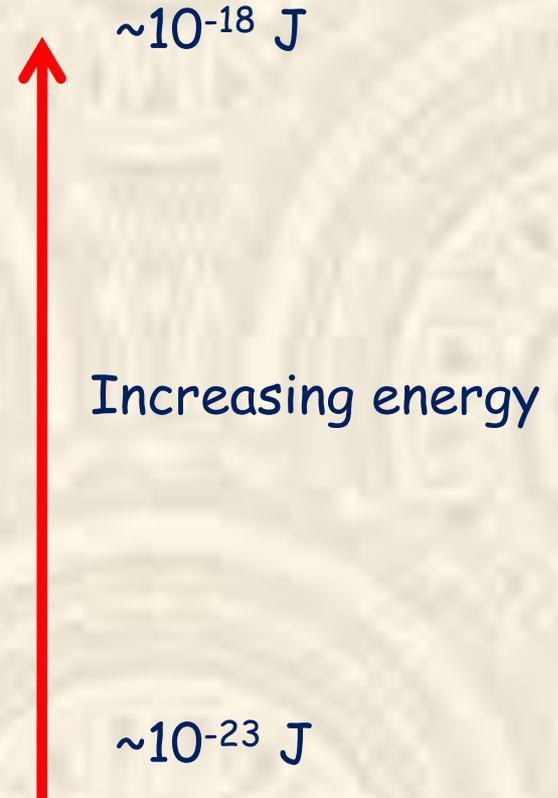
Molecular absorption processes

Electronic transitions
UV and visible wavelengths

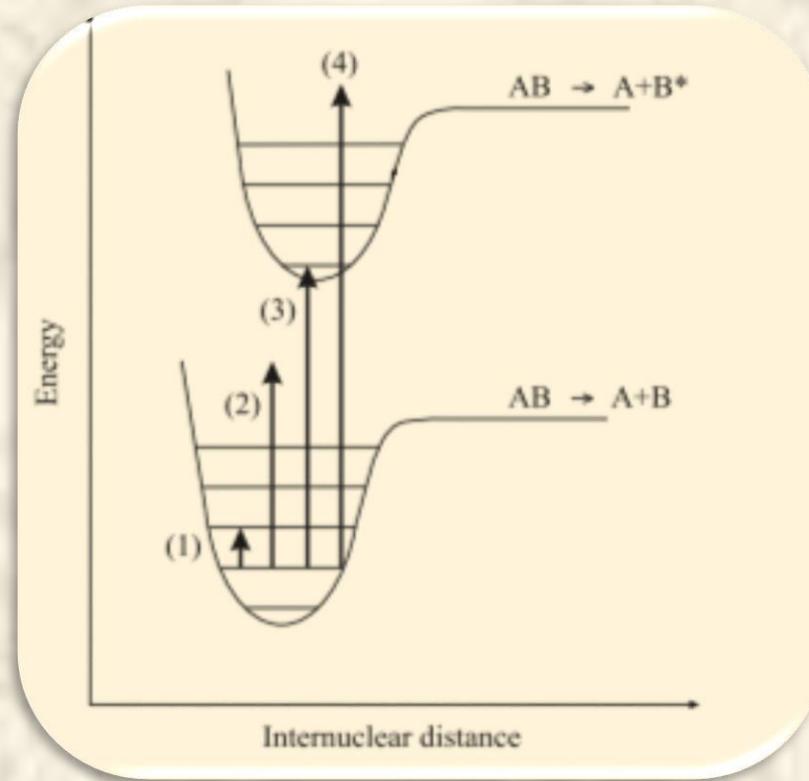
Molecular vibrations
Thermal infrared wavelengths

Molecular rotations
Microwave and far-IR wavelengths

Each of these processes is quantized
Translational kinetic energy of molecules is unquantized



Schematic energy diagram for a diatomic molecule



$$E_\nu = h\nu_0\left(\nu + \frac{1}{2}\right) \quad , \quad \nu = 0,1,2,\dots$$

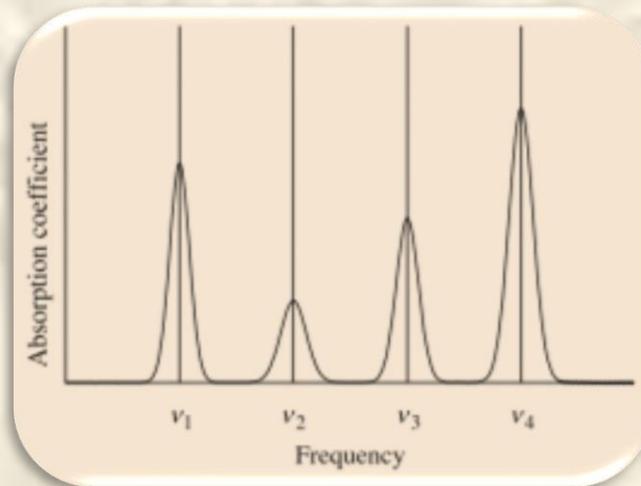
Line shapes

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

where the S_n are constants, called the line strengths

$\delta(\nu - \nu_n)$ is the Dirac delta function.

However, this model of sharp, delta-function, peaks in the extinction coefficient is an idealisation. In practice several physical effects lead to a broadening of the sharp peaks



$$k_\nu = \sum_n S_n \delta(\nu - \nu_n) \quad \text{Is replaced by} \quad k_\nu = \sum_n S_n f_n(\nu - \nu_n)$$

f_n are line-shape functions, each normalised such that

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

There are two main cases

(a) Collisional or natural broadening

The energy levels have finite lifetimes for one of two reasons

1) there is a collisional lifetime τ_c

2) excited states have a natural lifetime τ_n with respect to spontaneous decay.

In the case of collisional broadening we obtain the Lorentz line shape, of the form

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

$$\gamma_L = (2\pi\tau_c)^{-1} \quad \text{the half-width at half maximum of the line}$$

We can get τ_c and hence γ_L from kinetic theory, in terms of the mean molecular velocity (which is proportional to $T^{1/2}$), number density (proportional to p/T) and collision cross section, giving the following temperature and pressure dependence of γ_L

$$\gamma_L = pT^{-1/2}$$

A similar calculation applies to natural broadening, but in this case

$$\gamma_L = (2\pi\tau_n)^{-1}$$

In the infra-red, the corresponding line width is much less than that due to collisional broadening and than that due to the Doppler broadening discussed below, so natural broadening can usually be neglected. However, natural broadening can be important in the ultra-violet.

$$\tau_n \ll \tau_c$$

b) Doppler broadening

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

assuming that $u \ll c$ $u, u+du$ $P(u)du$

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

m is the molecular mass. The spectral line shape, rather than being a delta function, becomes the convolution of P(u) with a delta function:

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

We then get the Doppler line shape $k_\nu = \frac{S}{\gamma_D \sqrt{\pi}} e^{-\frac{(\nu - \nu_0)^2}{\gamma_D^2}}$

on normalising such that $S = \int_{-\infty}^{\infty} k_\nu d\nu$

where, $\gamma_D = \frac{\nu_0}{c} \left(\frac{2k_B T}{m}\right)^{1/2}$

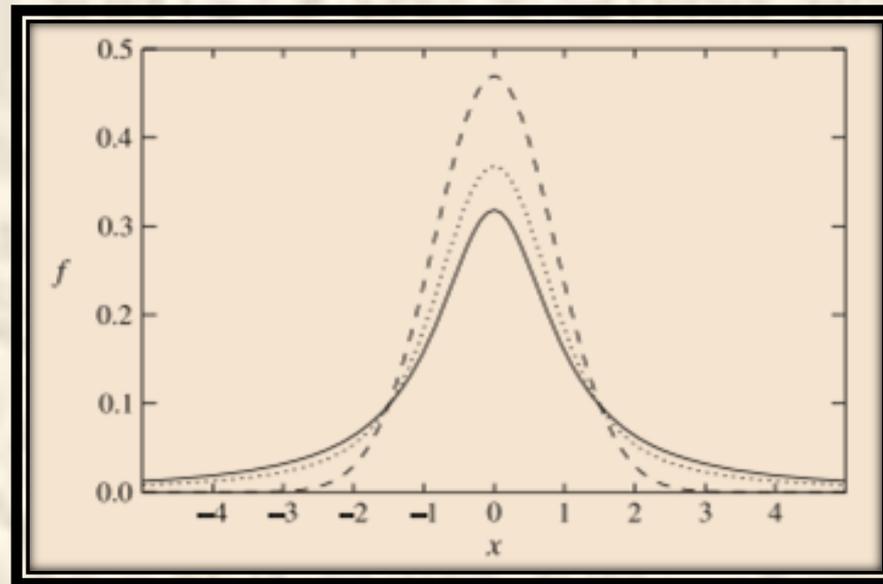
The half-width at half maximum is $\gamma_D (\ln 2)^{1/2}$

and is proportional to $T^{1/2}$

but independent of p

The Lorentz and Doppler line shapes are shown in Figure; also shown is the Voigt line shape, which applies when both collisional and Doppler broadening are important.

The fact that γ_L is proportional to pressure (see equation $\gamma_L = pT^{-1/2}$) means that collisional broadening dominates at low altitudes (<30 km), in the infra-red. Higher up, Doppler broadening becomes significant in the visible and ultra-violet.



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

Transmittance

the spectral transmittance

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

$$\chi_\nu(s) = \int_{s_0}^s k_\nu(s')\rho_a(s')ds' \quad \text{the optical path}$$

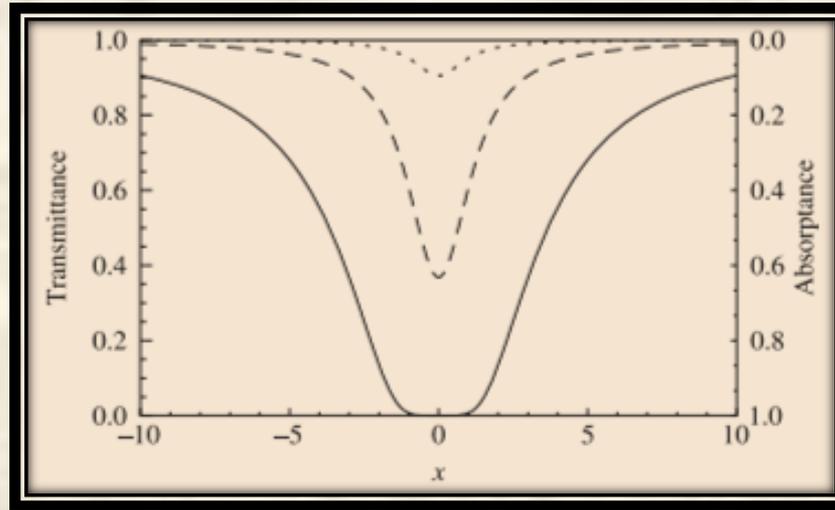
$$L_\nu(s) = \int_0^{\chi_\nu} J_\nu(\chi')e^{-(\chi_\nu - \chi')}d\chi' + L_{\nu 0}e^{-\chi_\nu}$$

for measurements under laboratory conditions at fixed p and T , above Eq.

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

$$u_a(s_1, s_2) = \left|\int_{s_1}^{s_2} \rho_a(s)ds\right| \quad \begin{array}{l} \text{the mass of absorber gas, per unit} \\ \text{transverse cross-sectional area, in the path} \end{array}$$

If the absorber density is also constant along the path, then $u_a = \rho_a l$ where l is the length of the path.



$$x = (\nu - \nu_0) / \gamma_L$$

$$q = u_a S / (\gamma_L \pi)$$

$$A_\nu = 1 - \tau_\nu \quad \text{the absorptance}$$

($q \gg 1$, solid curve)

($q \ll 1$, dotted curve)

band transmittance

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

Two other useful quantities are the **band absorptance**

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

and the **equivalent width or integrated absorptance**

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

Note that for small amounts of absorber (again at fixed p and T along the path), we have

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

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

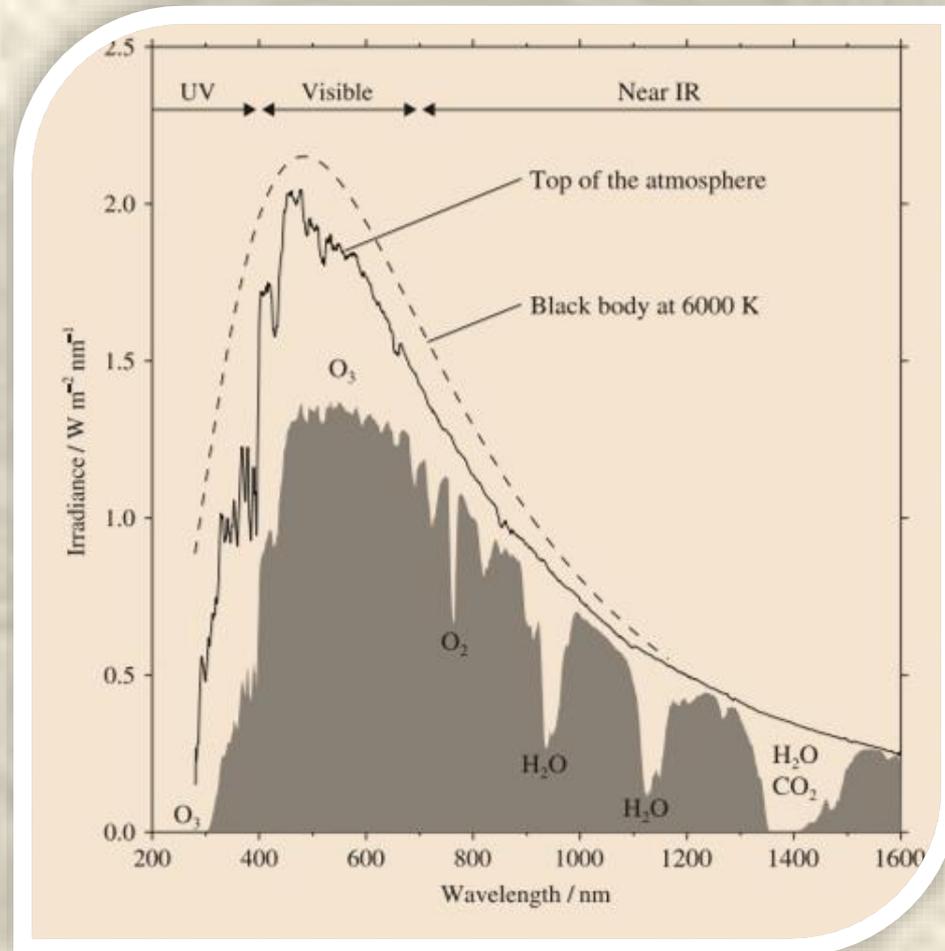
using
$$S = \int_{\Delta\nu_r} k_\nu d\nu$$

to obtain the strong-line approximations $W \approx 2(Su_a \gamma_L)^{1/2}$
for a Lorentz line and

$$W \approx 2\gamma_D \left\{ \ln \left[Su_a / (\gamma_D \sqrt{\pi}) \right] \right\}^{1/2} \quad \text{for a Doppler line}$$

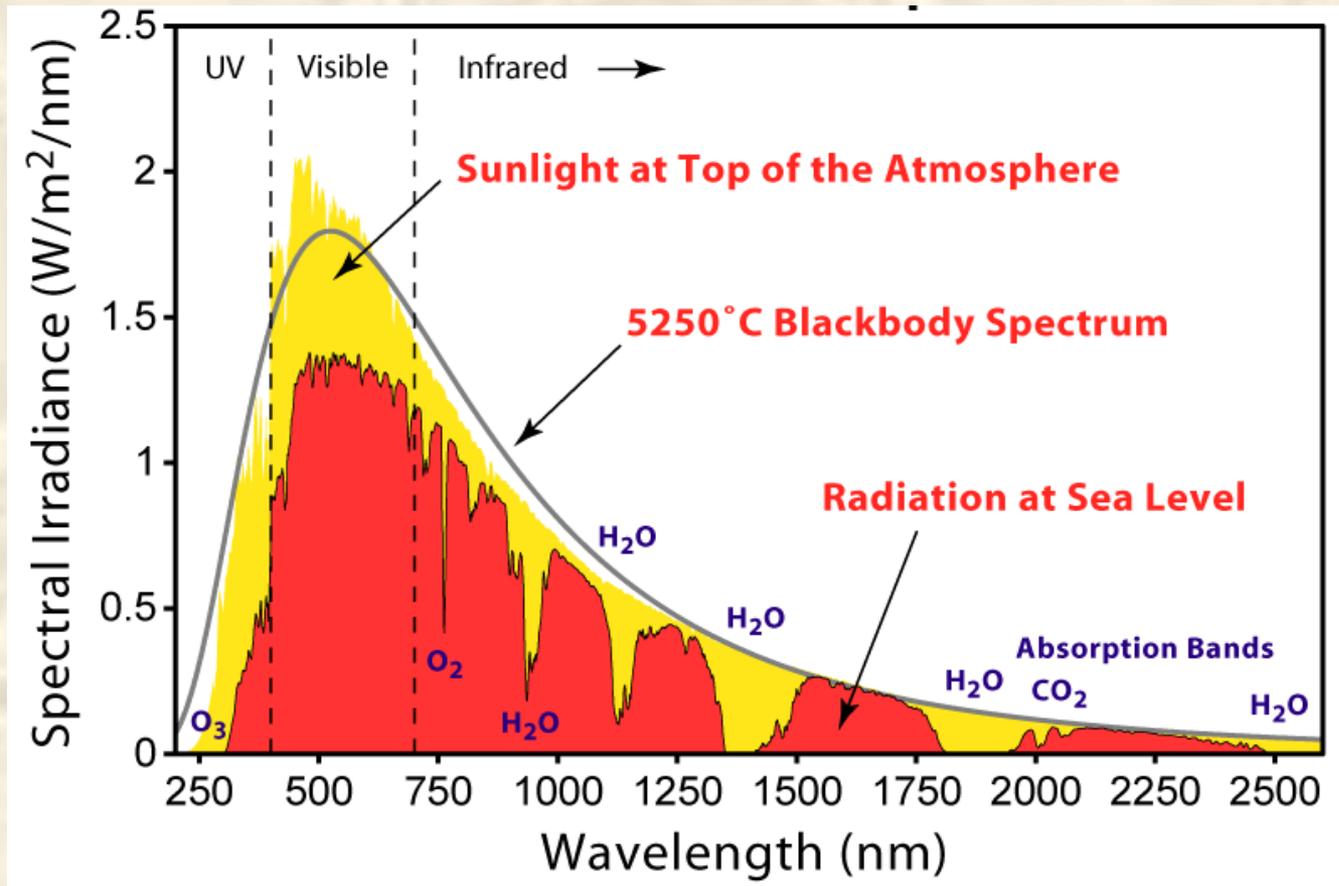
Absorption by atmospheric gases

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).



Solar Radiation Spectrum

