

## Absorption and scattering

When a beam of radiation goes through the atmosphere, it encounters gas molecules, aerosols, cloud droplets, and ice crystals. These objects perturb the radiation field. Part of the radiation can pass the object unchanged, which is called *transmission*, part of it can change direction without a change in energy/frequency, which is called *scattering*<sup>1</sup>, and part of it can disappear with the energy transferred to the object, which is called *absorption*. Both scattering and absorption remove radiation from the beam and are together called *extinction*. This can be demonstrated by projecting the images of two Petri dishes on the screen, one with inky water and another with milky water. Both images are dark, yet their darkness is caused by different mechanisms. Light incident on the inky water is not transmitted mostly because of absorption, whereas light incident on the milky water is not transmitted mostly because of scattering. It is important to remember that absorption and scattering depend not only on the object but also on the wavelength. A shallow layer (say 1cm) of clean water transmits visible light but is almost opaque to infrared radiation.

### Absorption by gases

The atmosphere is composed mostly of N<sub>2</sub> and O<sub>2</sub> (see table below), yet the most important greenhouse gases are H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub> and O<sub>3</sub>. To understand why, we need to look at how gas molecules absorb radiation.

chemical species	molecular weight ( $g\ mol^{-1}$ )	proportion by volume	chemical species	molecular weight	proportion by volume
N <sub>2</sub>	28.01	78%	O <sub>3</sub>	48.00	~500ppb
O <sub>2</sub>	32.00	21%	N <sub>2</sub> O	44.01	310ppb
Ar	39.95	0.93%	CO	28.01	120ppb
H <sub>2</sub> O (vapor)	18.02	~0.5%	NH <sub>3</sub>	17.03	~100ppb
CO <sub>2</sub>	44.01	380ppm	NO <sub>2</sub>	46.00	~1ppb
Ne	20.18	19ppm	CCl <sub>2</sub> F <sub>2</sub>	120.91	480ppt
He	4.00	5.2ppm	CCl <sub>3</sub> F	137.37	280ppt
CH <sub>4</sub>	16.04	1.7ppm	SO <sub>2</sub>	64.06	~200ppt
Kr	83.8	1.1ppm	H <sub>2</sub> S	34.08	~200ppt
H <sub>2</sub>	2.02	~500ppb	AIR	28.97	

<sup>1</sup> Raman scattering changes the frequency of the photon but since it is rare, we shall not include it in our discussion of atmospheric radiation.

The energy of a molecule can be stored in electronic (energy states of the electrons), vibrational (individual atoms vibrate about their equilibrium positions), rotational (the molecule rotates about an axis through its center of mass), or translational (translational motion of the molecule) forms. The first three are quantized.

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}}$$

A molecule in the atmosphere can absorb a photon only if the energy of the photon corresponds to the difference between the energy of two allowable states of the molecule. This energy difference is the sum of the difference in each mode of the energy storage. Transitions in each mode of the energy storage correspond to different range of energies. Roughly speaking, electronic transitions correspond to energies in photons with wavelengths between 0.1 and 1  $\mu\text{m}$ , vibrational transitions correspond to energies in photons with wavelengths between 1 and 100  $\mu\text{m}$  and rotational transitions correspond to energies in photons with wavelengths between 100-10<sup>4</sup>  $\mu\text{m}$ . At 300K, a typical translational energy ( $kT$ ) corresponds to  $\sim 250\mu\text{m}$ . In addition, photons shorter than  $\sim 100\text{nm}$  can remove electrons from an atom. This is called photoionization and is responsible for the ionosphere. If no transitions between two allowable states correspond to the energy of the photon, then the molecule will not absorb this photon.

Transition probability between states is governed by selection rules in quantum mechanics. However, for infrared radiation, the wavelength is much greater than the size of the molecule, so that we can take a more classical view of the coupling between a molecule and the electromagnetic field, where the molecule is sitting in a large-scale (smooth on the scale of the molecule) fluctuating electric and magnetic field provided by the light. In order to have coupling required for radiative transitions (so that energy exchanges can take place), the molecular, being neutral in charge, needs to have an electric dipole moment, so that it will rotate and vibrate in response to the (fluctuating) electric and magnetic field<sup>2</sup>. Coupling due to higher moments are too weak to be important for the present purpose. An electric dipole moment exists when the effective centers of the positive and negative charges of the molecule have nonzero separation and is equal to  $ql$ ,  $q$  being the charge and  $l$  being the separation distance. Molecules like  $\text{H}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$  have permanent electric dipole moments due to their asymmetrical charge distributions (see figure below; note that electrons are not shared equally among the atoms) so they are very active radiatively. On the other hand, molecules like  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2$  do not have permanent electric dipole moments. When the  $\text{CO}_2$  molecules are vibrating in the  $\nu_2$  (bending) or  $\nu_3$  (asymmetric stretching) modes, temporary dipole moments are developed, allowing coupling with electromagnetic field. These vibrational transitions, typically accompanied by rotational transitions, are important in the infrared (4-100 $\mu\text{m}$ ) as discussed above, allowing  $\text{CO}_2$  to become active at infrared wavelengths. The  $\nu_1$  (symmetric stretching) mode does not produce an electric dipole and is radiatively inactive.  $\text{N}_2$  and  $\text{O}_2$  molecules have only one vibration mode, which does not produce electric dipoles, so that they are mostly inactive in the infrared. (One way to think about it is that as an  $\text{N}_2$  or  $\text{O}_2$  molecule vibrates, there is no change in the electrical dipole moment, thus no radiation of energy.)  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{H}_2$  molecules are only active in the

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<sup>2</sup> This part follows closely Section 1.3 of An Introduction to Atmospheric Radiation by K. N. Liou.

infrared when there are frequent collisions that temporarily break the symmetry, which are seen in high density atmospheres such as those on the giant planets. Such frequent collisions produce continuum absorptions that are smooth functions of wavelength.

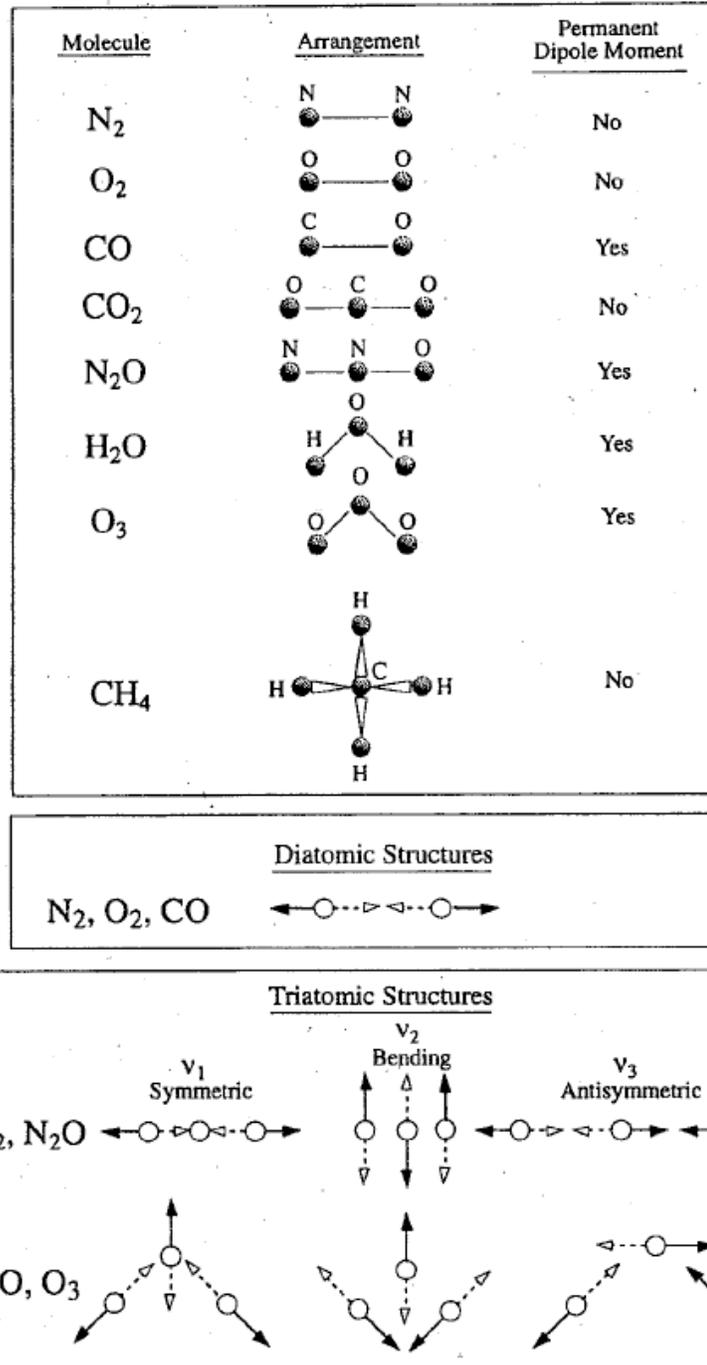
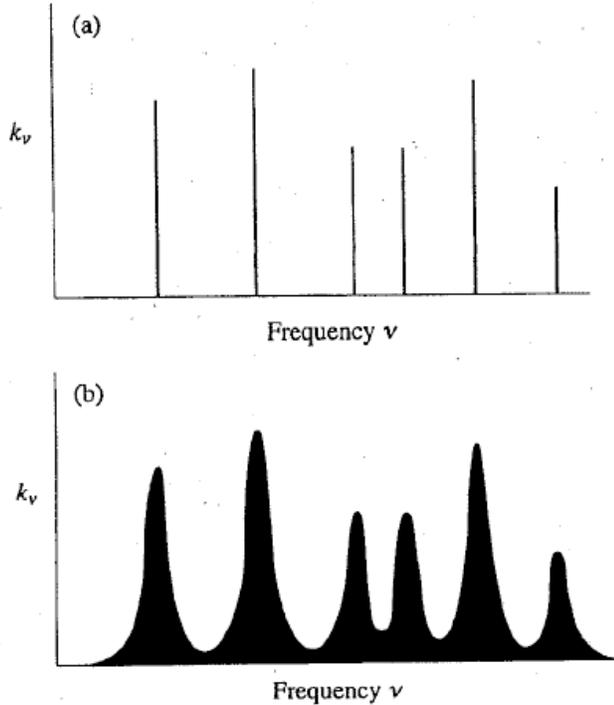


Fig. 3.3 Schematic diagrams showing the vibrational modes of diatomic and triatomic molecules. [From McCartney (1983). Reprinted with permission from Wiley and Sons, Inc.]

(Fig3.3 of Hartmann)

Each allowed transition gives an absorption line. The collection of such absorption lines in a particular frequency interval is called an absorption band. The position and strength of these lines are measured and/or calculated based on quantum mechanics and archived. The absorption lines however are not delta functions. Instead, they are broadened by the following processes.



**Fig. 3.5** Hypothetical line spectrum (a) before broadening, (b) after broadening.

(Fig. 3.5 of Hartmann)

Natural broadening: An excited state will decay spontaneously to a lower state even if it is completely undisturbed. From the energy-time uncertainty principle, the finite lifetime of the excited state implies it possesses a finite but narrow range of energies. This gives the natural broadening when transitions take place, which has the Lorentz line shape

$$f_L(\nu - \nu_0) = \frac{\alpha_L}{\pi \left[ (\nu - \nu_0)^2 + \alpha_L^2 \right]} \quad (1)$$

with  $\alpha_L = (2\pi\bar{t})^{-1}$ . This is normalized so that

$$\int f_L(\nu - \nu_0) d\nu = \frac{1}{\pi} \tan^{-1} \frac{\nu}{\alpha_L} \Big|_{-\infty}^{\infty} = 1$$

The typical lifetime of an atomic energy state is  $\sim 10^{-8}$  s, so this broadening is about  $10^7$  Hz (or  $3 \times 10^4 \text{ cm}^{-1}$ ) and generally negligible for our purposes.

Pressure broadening (collision broadening): Detailed processes and calculations of pressure broadening are complicated. But roughly speaking, it is similar to natural broadening and can be approximated by the Lorentz line shape, with the natural lifetime

of excited states replaced by the averaged time between collisions, which is a lot shorter. So pressure broadening is much greater than natural broadening. For the atmosphere, the half width is roughly

$$\alpha_c = \alpha_0 \left( \frac{p}{p_0} \right) \left( \frac{T_0}{T} \right)^{1/2} \quad (2)$$

where  $\alpha_0 \sim 0.1 \text{ cm}^{-1}$  (or  $3 \times 10^9 \text{ Hz}$ ) is the half-width at standard atmosphere temperature  $T_0=273\text{K}$  and and pressure  $P_0=1\text{bar}$ . The functional form in (2) can be understood from kinetic theory. The time between collisions is proportional to the mean free path divided by the mean velocity, so

$$\alpha \propto nu \propto pT^{-1/2}$$

Doppler broadening: The movement of molecules can Doppler-shift the frequency of radiation.

$$v = v_0 \left( 1 \pm \frac{u}{c} \right)$$

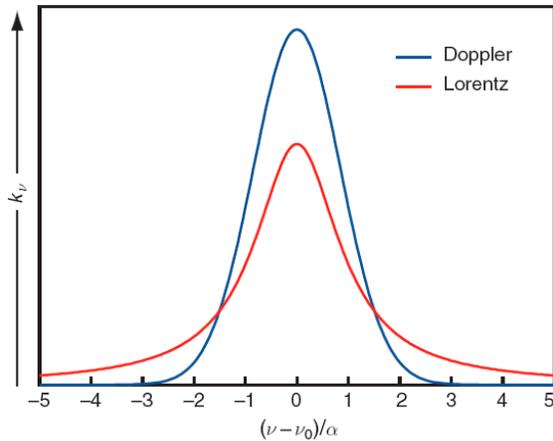
Given the Maxwell-Boltzmann distribution

$$\text{probability}(u) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mu^2}{2kT}\right)$$

this allows a broader range of frequencies of radiation to effect a particular transition, gives a Doppler line shape:

$$f_D(v - v_0) = \frac{1}{\alpha_D \sqrt{\pi}} \exp\left(-\left(\frac{v - v_0}{\alpha_D}\right)^2\right) \quad (3)$$

where  $\alpha_D = \frac{v_0}{c} \sqrt{\frac{2kT}{m}}$ . This is the dominant mechanism at high altitudes. But because of the pressure dependence in Eq.(2), in the troposphere and lower stratosphere, the pressure is sufficient high and collision between molecules is sufficiently frequency, pressure broadening dominates.



Broadening is important. With it, a transition, instead of causing absorption only at the line center, can affect a much wider range of the spectrum.

Below we briefly talk about some of the climatically important absorption features.

O<sub>2</sub> and O<sub>3</sub>:

At wavelengths less than ~310nm, the absorption cross sections of O<sub>3</sub> and O<sub>2</sub> are extraordinarily large so that no solar radiation penetrates to the ground. These absorptions result in the dissociation of the molecule (break the bond).

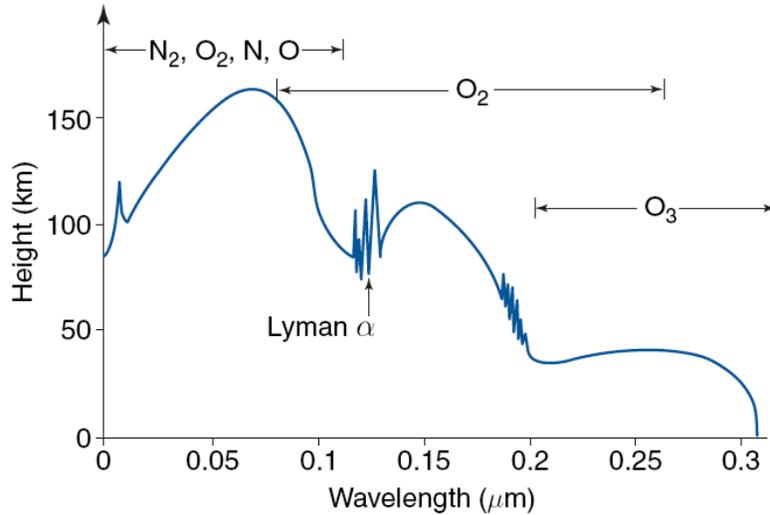
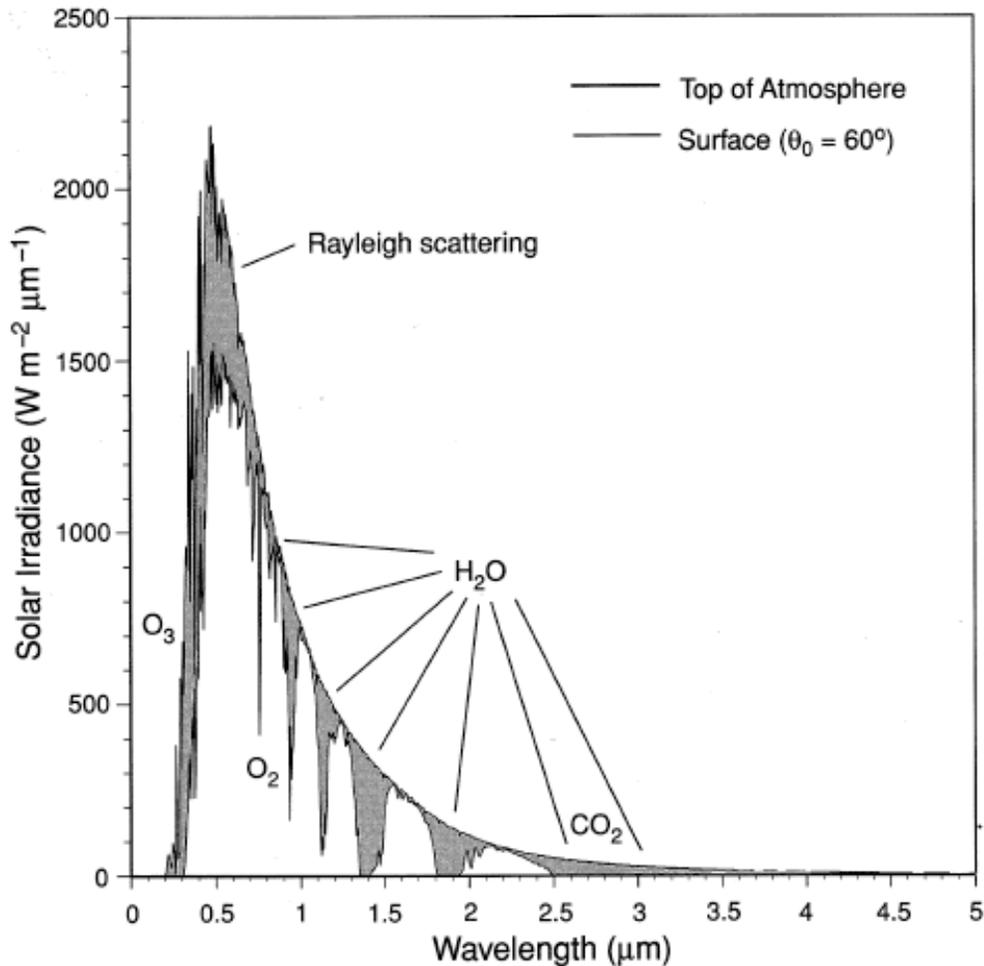


Figure: Height that sunlight can penetrate through.

In the near infrared (1-4 micron), there is some significant absorption by vibration-rotation bands of atmospheric gases, mostly by water vapor and with some contribution from carbon dioxide. These account for most of the absorption of solar radiation by air molecules in the atmosphere. The visible wavelengths are virtually free of gaseous absorption features, and the chief attenuation is by Rayleigh scattering.

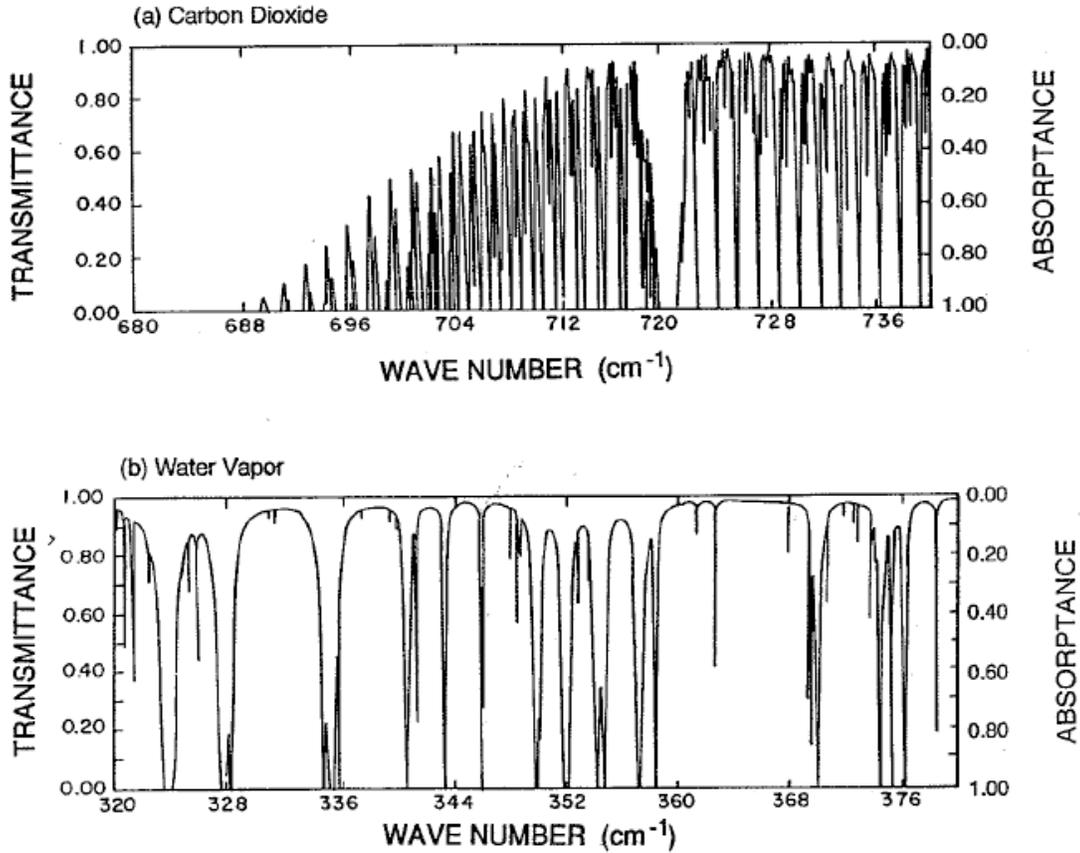


**Figure 3.9** Solar irradiance curve for a  $50 \text{ cm}^{-1}$  spectral interval at the top of the atmosphere (see Fig. 2.9) and at the surface for a solar zenith angle of  $60^\circ$  in an atmosphere without aerosols or clouds. Absorption and scattering regions are indicated. See also Table 3.3 for the absorption of  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{NO}_2$ .

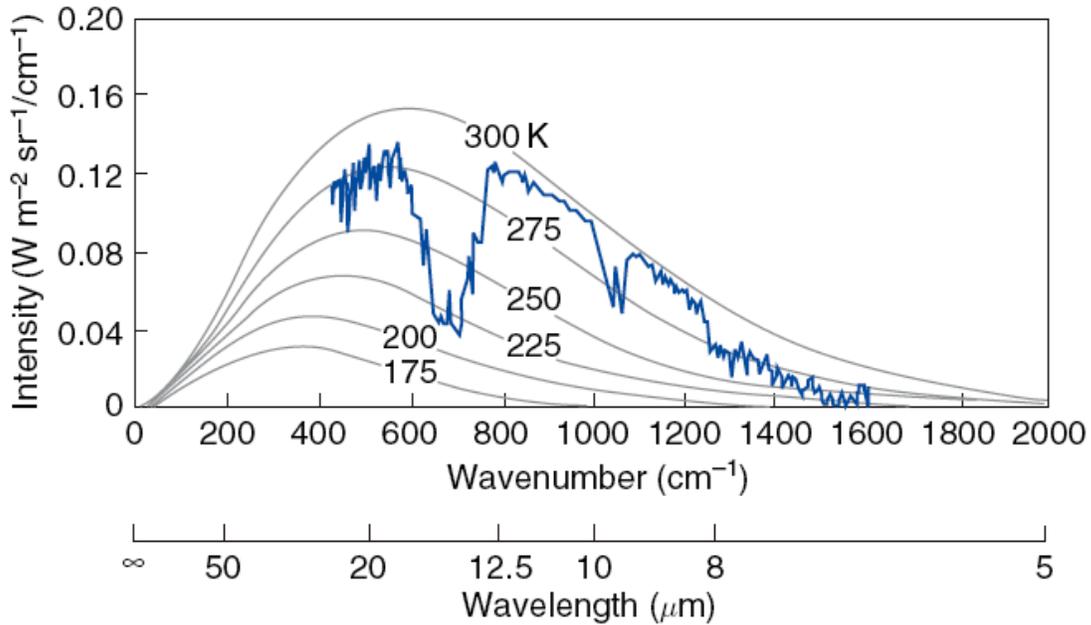
Vibration-rotation bands and pure rotation bands of polyatomic molecules account for the longwave absorption of the clear atmosphere:

The bending mode of  $\text{CO}_2$  produces a very strong vibration and rotation absorption band near  $15 \mu\text{m}$ . This is very important for climate and critical for the stratosphere where it accounts for much of the longwave absorption. This is particularly true as it occurs near the peak of the terrestrial emission spectrum.

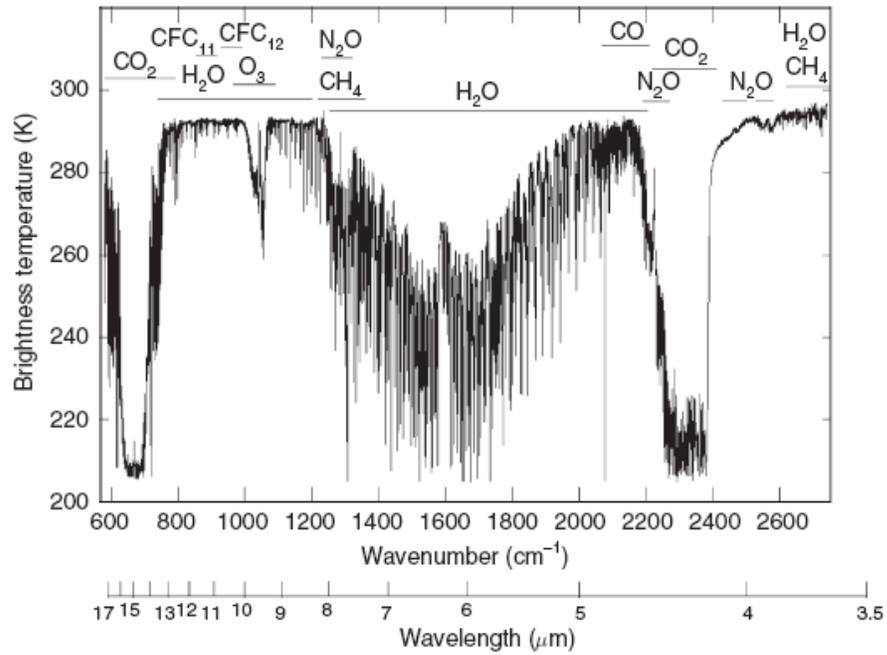
Water vapor has an important vibration-rotation band near  $6.3 \mu\text{m}$ , and a densely spaced band of pure rotational lines of water vapor increasingly absorbs terrestrial emission at wavelengths in excess of about  $12 \mu\text{m}$ . The region in between is called the water vapor window. In this window sits the  $9.6 \mu\text{m}$  band of ozone.



**Figure 8.11** Absorption spectra in (a) the  $14\text{-}\mu\text{m}$  band of  $\text{CO}_2$  and (b) the rotational band of  $\text{H}_2\text{O}$  at  $27$  to  $31\ \mu\text{m}$ . Adapted from McClatchey and Selby (1972).



Monochromatic intensity of radiation emitted from a point on the Earth measured by an infrared spectrometer.



Finer resolution data from NASA ER-2 aircraft

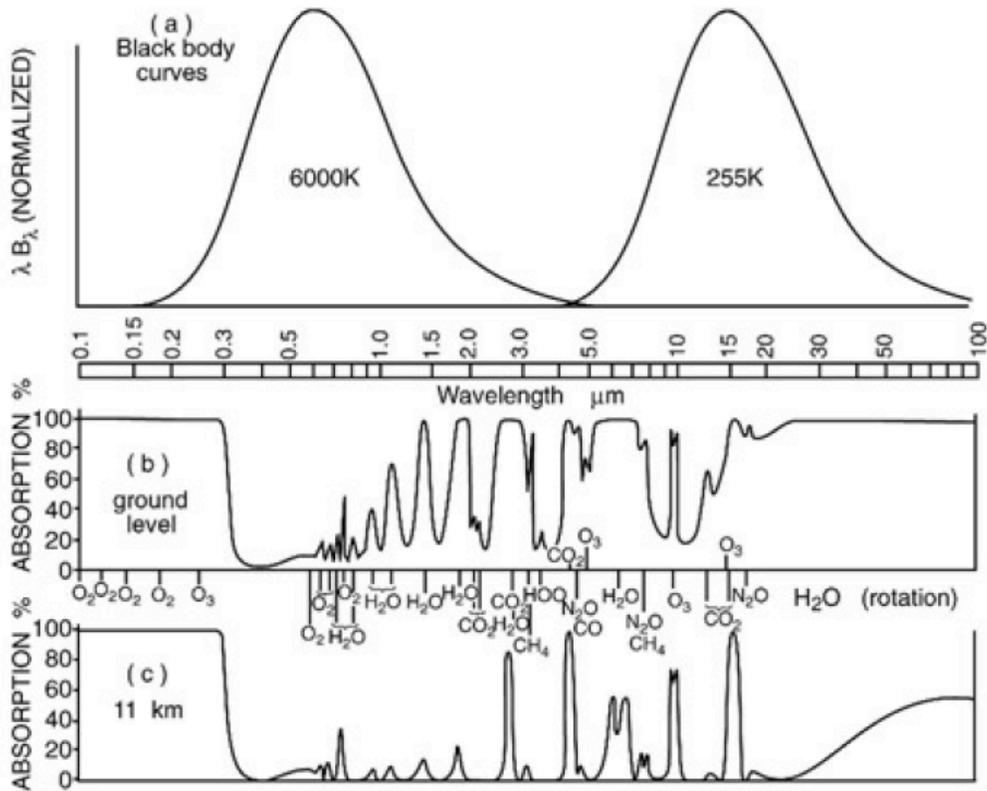


Figure 2.6: (a) The normalized blackbody emission spectra,  $T^{-4}\lambda B_\lambda$ , for the Sun ( $T = 6000 \text{ K}$ ) and Earth ( $T = 255 \text{ K}$ ) as a function of  $\ln\lambda$  (top) where  $B_\lambda$  is the black body function (see Eq.(13.2)) and  $\lambda$  is the wavelength (see the Appendix for further discussion.) (b) The fraction of radiation absorbed while passing from the ground to the top of the atmosphere as a function of wavelength. (c) The fraction of radiation absorbed from the tropopause (typically at a height of 11 km) to the top of the atmosphere as a function of wavelength. The atmospheric molecules contributing the important absorption features at each frequency are also indicated. After Goody and Yung (1989).

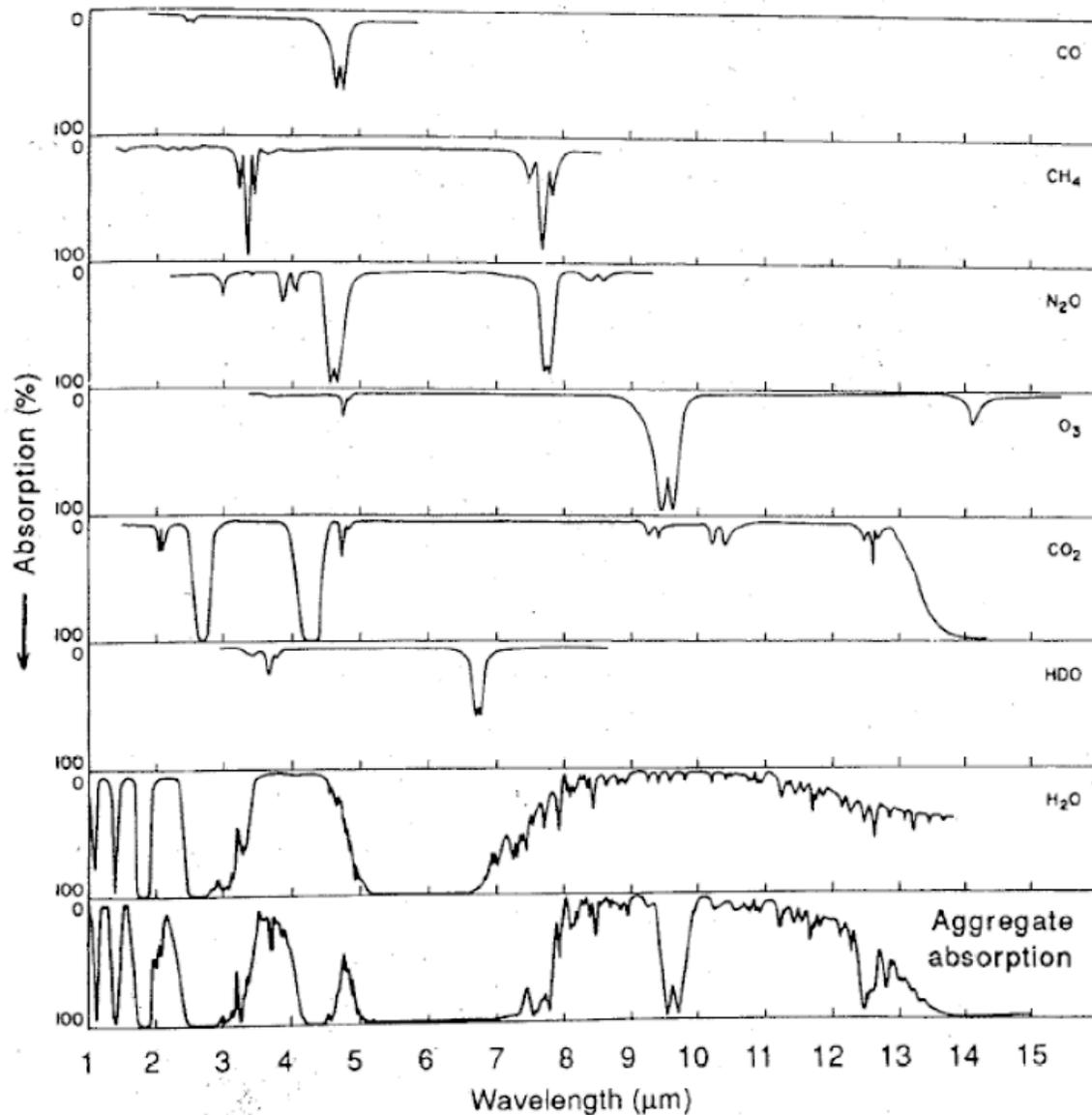


Fig. 3.4 Infrared absorption spectra for various atmospheric gases. [From Valley (1965). Used with permission from McGraw-Hill, Inc.]

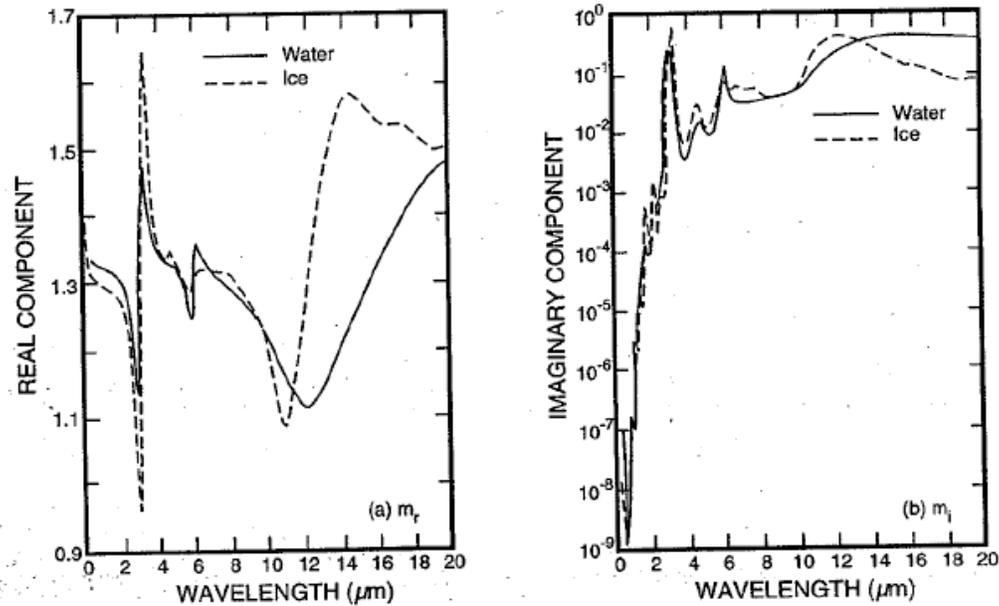
### Scattering:

Scattering of radiation by dielectric spherical objects is described by a theory developed by a German physicist Gustav Mie (1868-1957) in 1908. Mie solved Maxwell's equations for the electromagnetic field about a dielectric sphere in terms of an expansion in spherical harmonics and Bessel functions. Properties of the scattered wave field are functions of the index of refraction and a dimensionless size parameter

$$x = \frac{2\pi r}{\lambda}$$

where  $r$  is the radius of the sphere. The real component of the index of refraction,  $m_r$ , is the phase speed of light in a vacuum divided by that in the medium and imaginary component  $m_i$  indicates the amount of absorption. The following figure shows that for

water and ice. For air molecules at visible wavelengths,  $m_i$  is small and  $m_r$  is close to unity.



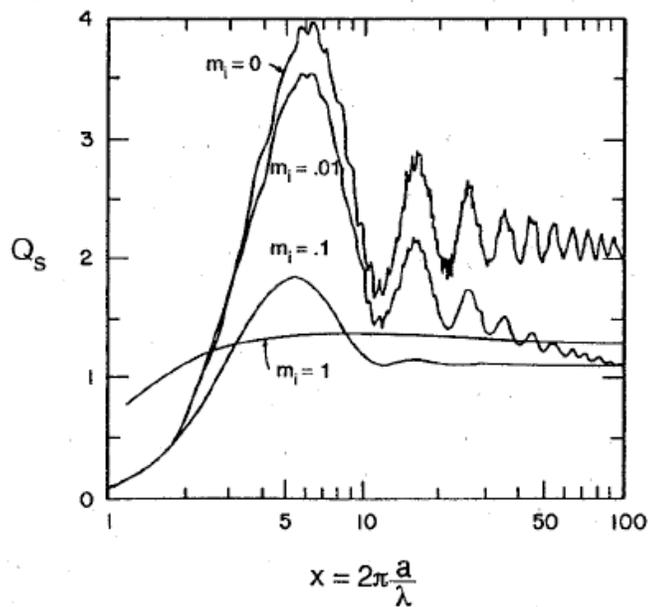
**Figure 9.25** Index of refraction for water (solid line) and ice (dashed line) as functions of wavelength. (a) Real component and (b) imaginary component. Adapted from Liou (1990).

It is useful to define dimensionless scattering and extinction efficiencies

$$Q_s = \frac{s}{\pi r^2}$$

$$Q_e = \frac{e}{\pi r^2}$$

where  $s$  and  $e$  are the scattering and extinction cross sections. The cross sections are a way to quantify scattering/absorption/extinction by a mechanical analogy. Consider an object that scatters photons. The number of photons scattered is the same as the number of photons scattered by an object with a cross section of  $s$  sitting in the light beam colliding with the incoming photons (the actual physics is of course not the collision of photons with the object). Note that it's a property of the object and doesn't depend on the intensity of the incoming radiation.



**Figure 9.26** Scattering efficiency from a dielectric sphere having real component of refractive index  $m_r = 1.33$  for several imaginary components  $m_i$ , as functions of the dimensionless size parameter  $x = 2\pi(a/\lambda)$ . After Hansen and Travis (1974). Reprinted by permission of Kluwer Academic Publishers.

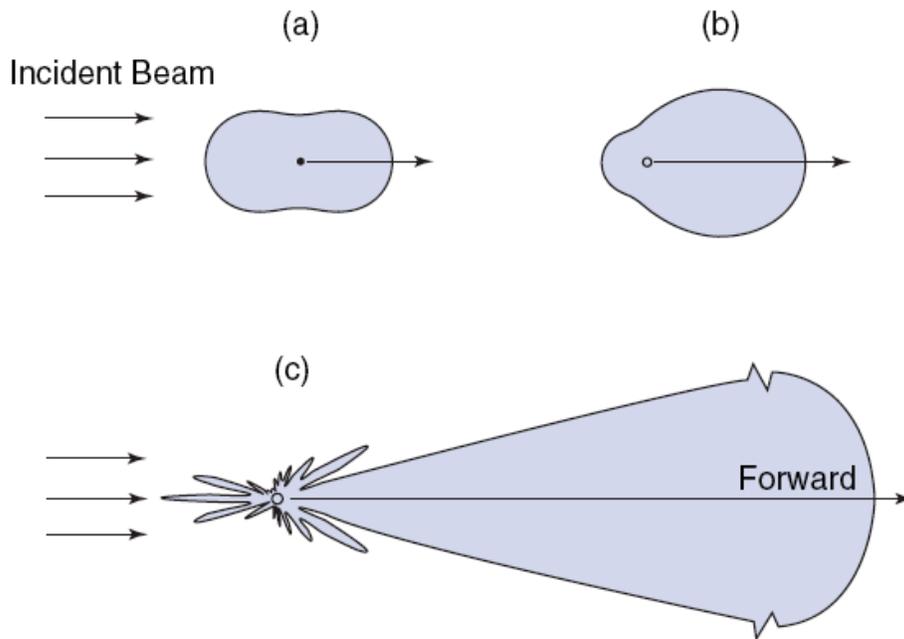
In the limit of small  $x$ ,  $Q_s$  increases as  $x^4$ , known as Rayleigh scattering, (Lord Rayleigh, 1871). This behavior can be understood in the following way. For small  $x$ , the molecular is small compared to the wavelength of the incidence radiation. Therefore, one can consider the molecular as sitting in a relatively homogeneous (but oscillating) electromagnetic field. From classical electromagnetic theory, the induced electric dipole moment  $p$  (charge times the separation between positive and negative charges) is proportional to the incidence strength of the electric field, and the amplitude of the electric field that the induced dipole produces is proportional to the acceleration of the dipole moment or  $\partial^2 p / \partial t^2$ . This gives a dependence on the frequency squared. Since intensity is proportional to the wave amplitude squared, it depends on frequency to the 4<sup>th</sup> power.

Therefore, in the Rayleigh limit, scattering is stronger at shorter wavelengths. This is why the sky is blue: air molecules scatter more of the blue light which is the light we see coming from the sky away from the sun. In the limit of large  $x$ ,  $Q_s$  does not depend on wavelength, and approaches 2, i.e. the effective scattering cross section is twice its physical cross section. It is greater than 1 due to diffraction in addition to reflection and refraction. This is why clouds are white (more later). In the limit of large  $x$  and large  $m_i$  (strongly absorbing medium),  $Q_s$  asymptotes to 1 as only the diffraction component is left.

Directionality of scattering:

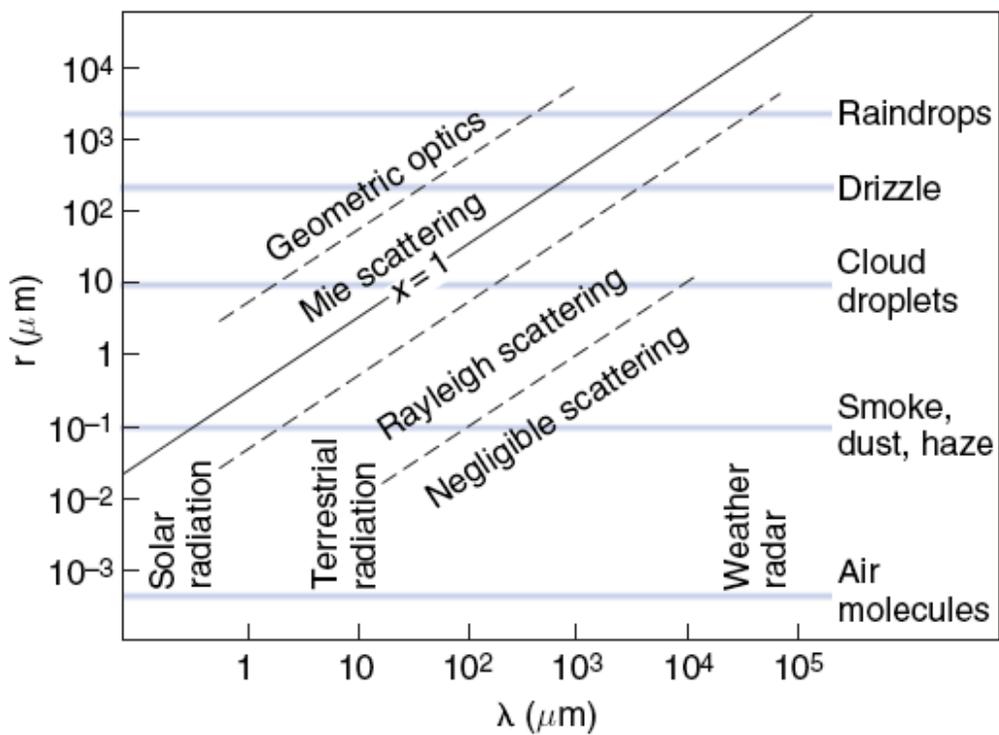
Scattering depends on the direction relative to the incident light. This dependence can be quite complicated. The main feature to note is the strong forward scattering for large size

parameters, a result of diffraction. Rayleigh scattering scatters equal amount of energy forward and backward.



(Fig. Schematic showing the angular distribution of the radiation at visible ( $0.5 \mu\text{m}$ ) wavelength scattered by spherical particles with radii of  $10^{-4} \mu\text{m}$ ,  $0.1 \mu\text{m}$  and  $1 \mu\text{m}$ )

Scattering regimes of different atmospheric scatterers.



(Fig. 4.11, Wallace and Hobbs)

It is fun to consider implications for geoengineering, for which size parameter =1 appears optimal. If the size parameter is too small, Rayleigh scattering makes the scattering efficiency small. If the size parameter is too large, the asymmetry factor becomes large (forward scattering dominates), and the cross section per unit mass also becomes small.

Scattering by nonspherical ice particles is complicated and remains a research topic. It can be treated with numerical techniques.

Light can be scattered once (single scattering) or multiple times (multiple scattering).

Adding milk to an aquarium illustrates some of the points of scattering. With only clean water, there are few scatterers. So we don't quite see a laser beam going through the aquarium unless it's pointed at you. Add a slight amount of milk, you see a beam of light going through the aquarium. This "beam" of light is actually light scattered out of the beam into our eyes by single scattering. Add more milk, we see the whole water body is illuminated because of multiple scattering.

Now putting the aquarium on the overhead projector, we see it's blue. This is because particles in milk scatter more blue light than red. So why is a glass of milk white? A glass of milk is optically thick so light is scattered many many times before reemerging (One evidence that a glass of milk is optically thick is that a larger glass looks no different than a smaller glass). This makes the single scattering characteristics irrelevant. Particles in milk are very weakly absorbing. Even though red light are scattered fewer times, they still get scattered enough times to remerge like the blue light, with little absorption. This is why a glass of milk is white<sup>3</sup>.

In the above, we discussed briefly absorption and scattering by gas molecules and particles. A detailed study of these is beyond the scope of the course and requires a separate course on spectroscopy and radiative transfer.

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<sup>3</sup> These experiments and more are described in the book *Clouds in a glass of beer* by Craig Bohren. Very interesting reading.