CHAPTER 3

ABSORPTION, EMISSION, REFLECTION, AND SCATTERING

3.1   Absorption and Emission

As noted earlier, blackbody radiation represents the upper limit to the amount of radiation that a real substance may emit at a given temperature. At any given wavelength λ, emissivity is defined as the ratio of the actual emitted radiance, R_λ, to that from an ideal blackbody, B_λ,

$$\varepsilon_\lambda = R_\lambda / B_\lambda .$$

Emissivity is a measure of how strongly a body radiates at a given wavelength; it ranges between zero and one for all real substances. A gray body is defined as a substance whose emissivity is independent of wavelength. In the atmosphere, clouds and gases have emissivities that vary rapidly with wavelength. The ocean surface has near unit emissivity in the visible regions.

For a body in local thermodynamic equilibrium the amount of thermal energy emitted must be equal to the energy absorbed; otherwise the body would heat up or cool down in time, contrary to the assumption of equilibrium. In an absorbing and emitting medium in which I_λ is the incident spectral radiance, the emitted spectral radiance R_λ is given by

$$R_\lambda = \varepsilon_\lambda B_\lambda = a_\lambda I_\lambda ,$$

where a_λ represents the absorptance at a given wavelength. If the source of radiation is in thermal equilibrium with the absorbing medium, then

$$I_\lambda = B_\lambda ,$$

so that

$$\varepsilon_\lambda = a_\lambda .$$

This is often referred to as Kirchhoff's Law. In qualitative terms, it states that materials that are strong absorbers at a given wavelength are also strong emitters at that wavelength; similarly weak absorbers are weak emitters.

3.2   Conservation of Energy

Consider a layer of absorbing medium where only part of the total incident radiation I_λ is absorbed, and the remainder is either transmitted through the layer or reflected from it (see Figure 3.1). In other words, if a_λ, r_λ, and τ_λ represent the fractional absorptance, reflectance, and transmittance, respectively, then the absorbed part of the radiation must be equal to the total radiation minus the losses due to reflections away from the layer and transmissions through it. Hence

$$a_\lambda I_\lambda = I_\lambda - r_\lambda I_\lambda - \tau_\lambda I_\lambda ,$$

or

$$a_\lambda + r_\lambda + \tau_\lambda = 1 ,$$

which says that the processes of absorption, reflection, and transmission account for all the incident radiation in any particular situation.   This is simply conservation of energy.   For a blackbody $a_\lambda = 1$, so it follows that $r_\lambda = 0$ and $\tau_\lambda = 0$ for blackbody radiation. In any window region $\tau_\lambda = 1$, and $a_\lambda = 0$ and $r_\lambda = 0$.

Radiation incident upon any opaque surface, $\tau_\lambda = 0$, is either absorbed or reflected, so that

$$a_\lambda + r_\lambda = 1 \ .$$

At any wavelength, strong reflectors are weak absorbers (i.e., snow at visible wavelengths), and weak reflectors are strong absorbers (i.e., asphalt at visible wavelengths). The reflectances for selected surfaces for the wavelengths of solar radiation are listed in Table 3.1.

From Kirchhoff's Law we can also write

$$\varepsilon_\lambda + r_\lambda + \tau_\lambda = 1 \ ,$$

which says emission, reflection, and transmission account for all the incident radiation for media in thermodynamical equilibrium.

3.3   *Planetary Albedo*

Planetary albedo is defined as the fraction of the total incident solar irradiance, S, that is reflected back into space. Radiation balance then requires that the absorbed solar irradiance is given by

$$E = (1 - A) S/4.$$

The factor of one-fourth arises because the cross sectional area of the earth disc to solar radiation, πr^2, is one-fourth the earth radiating surface, $4\pi r^2$. Recalling that S = 1380 Wm^{-2}, if the earth albedo is 30 percent, then E = 241 Wm^{-2}.

3.4   *Selective Absorption and Emission*

The atmosphere of the earth exhibits absorptance that varies drastically with wavelength. Atmospheric absorptance is small in the visible part of the spectrum, while it is large in the infrared. This has a profound effect on the equilibrium temperature at the surface of the earth. The following problem illustrates this point. Assume the earth behaves like a blackbody and the atmosphere has an absorptance a_S for incoming solar radiation and a_L for outgoing longwave radiation. E is the solar irradiance absorbed by the earth-atmosphere system, a known function of albedo. What is the implied irradiance emitted from the earth's surface Y_s and the irradiance emitted by the atmosphere Y_a (both upward and downward)? Radiative equilibrium requires at the surface

$$(1-a_S) E - Y_s + Y_a = 0 \ ,$$

and at the top of the atmosphere

$$E - (1-a_L) Y_s - Y_a = 0 \ .$$

Solving for Y_s yields
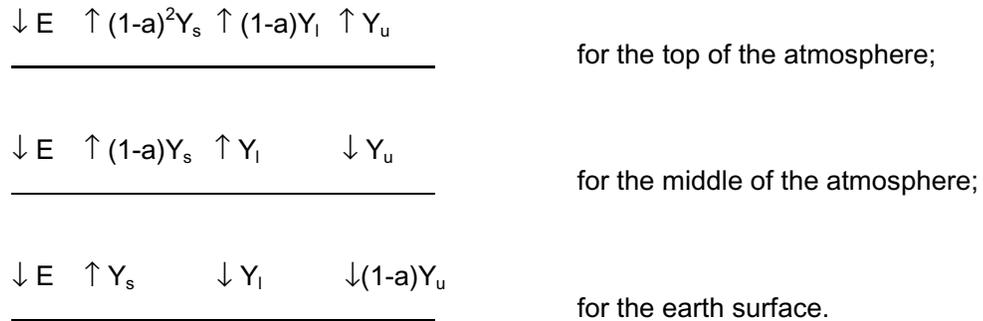
$$Y_s = \frac{(2-a_S)}{(2-a_L)} E \ ,$$

and

$$Y_a = \frac{(2-a_L) - (1-a_L)(2-a_S)}{(2-a_L)} E \ .$$

Since $a_L > a_S$, the irradiance and hence the radiative equilibrium temperature at the earth surface is increased by the presence of the atmosphere. With $a_L = .8$ and $a_S = .1$ and $E = 241$ Wm^{-2}, Stefans Law yields a blackbody temperature at the surface of 286 K, in contrast to the 255 K it would be if the atmospheric absorptance was independent of wavelength ($a_S = a_L$). The atmospheric gray body temperature in this example is 245 K.

A gas in a planetary atmosphere that is a weak absorber in the visible and a strong absorber in the infrared contributes toward raising the surface temperature of the planet. The warming results from the fact that incoming irradiance can penetrate to the ground with relatively little absorption, while much of the outgoing longwave irradiance is "trapped" by the atmosphere and emitted back to the ground. In order to satisfy radiation balance, the surface must compensate by emitting more radiation than it would in the absence of such an atmosphere. To emit more, it must radiate at a higher temperature.

Trapping of the longwave radiation also can explain the gradual decrease of effective blackbody temperature of atmospheric layers as altitude increases. Expanding on the previous example, assume the atmosphere is represented by two layers and let us compute the vertical profile of radiative equilibrium temperature. For simplicity in this two layer atmosphere, let $a_S = 0$ and $a_L = a = .5$, u indicate upper layer, l indicate lower layer, and s denote the earth surface. Schematically we have:

$$\downarrow E \quad \uparrow (1-a)^2 Y_s \quad \uparrow (1-a)Y_l \quad \uparrow Y_u$$
—————————————————————— for the top of the atmosphere;

$$\downarrow E \quad \uparrow (1-a)Y_s \quad \uparrow Y_l \quad \downarrow Y_u$$
—————————————————————— for the middle of the atmosphere;

$$\downarrow E \quad \uparrow Y_s \quad \downarrow Y_l \quad \downarrow (1-a)Y_u$$
—————————————————————— for the earth surface.

Radiative equilibrium at each surface requires

$$E = .25\, Y_s + .5\, Y_l + Y_u \, ,$$

$$E = .5\, Y_s + Y_l - Y_u \, ,$$

$$E = Y_s - Y_l - .5\, Y_u \, .$$

Solving yields $Y_s = 1.6\, E$, $Y_l = .5\, E$ and $Y_u = .33\, E$. The radiative equilibrium temperatures (blackbody at the surface and gray body in the atmosphere) are readily computed.

$$T_s = [1.6E / \sigma]^{1/4} = 287 \text{ K} \, ,$$

$$T_l = [0.5E / 0.5\sigma]^{1/4} = 255 \text{ K} \, ,$$

$$T_u = [0.33E / 0.5\sigma]^{1/4} = 231 \text{ K} \, .$$

Thus, a crude temperature profile emerges for this simple two-layer model of the atmosphere.

3.5   Absorption (Emission) Line Formation

The Planck explanation of the continuous spectra of the blackbody was founded in the idea of quantization of available energy levels. Planck successfully explained the nature of radiation from heated solid objects of which the cavity blackbody radiator formed the prototype. Such radiation generates continuous spectra and is contrary to line spectra. However, when properly extended, the theory of quantization also led to the understanding of the line spectra of the atom. Let us investigate the development of the Bohr atomic model briefly.

In 1913, Bohr postulated that: (a) the angular momentum of the electrons in their circular orbits about the nucleus are quantized,

$$mvr = nh/2\pi ,$$

where m is the electron mass, v the velocity, r the radius, n the quantum number, and h Planck's constant; and (b) the atoms radiate (absorb) only when the electron makes a transition from one energy state to another state of lower (higher) energy,

$$E_{n1} - E_{n2} = hf .$$

The mechanical stability of the electron in a circular orbit about a proton is given by the Coulomb force offset by the centrifugal force

$$\frac{e^2}{r^2} = \frac{mv^2}{r} ,$$

where e is the electron charge. The total energy of the electron n^{th} state is given by

$$E_n = \frac{1}{2}mv^2 - \frac{e^2}{r}$$

$$= -\frac{2\pi^2 me^4}{h^2} \frac{1}{n^2} .$$

Therefore, the frequency of the emission (absorption) lines in the hydrogen spectrum is given by

$$f = \frac{2\pi^2 me^4}{h^3} (\frac{1}{n_2^2} - \frac{1}{n_1^2})$$

or

$$f = K (\frac{1}{n_2^2} - \frac{1}{n_1^2}) ,$$

where K = 3.28 x 10^{15} Hz.

Monochromatic emission is practically never observed. Energy levels during energy transitions are normally changed slightly due to external influences on atoms and molecules, and due to the loss of energy in emission. As a consequence, radiation emitted during repeated energy transitions is non-monochromatic and spectral lines are caused by: (1) the damping of vibrations of oscillators resulting from the loss of energy in emission (the broadening of lines in this case is considered to be normal); (2) the perturbations due to collisions between the absorbing molecules

and between the absorbing and non-absorbing molecules; and (3) the Doppler effect resulting from the difference in thermal velocities of atoms and molecules. The broadening of lines due to the loss of energy in emission (natural broadening) is practically negligible as compared with that caused by collisions and the Doppler effect. In the upper atmosphere, we find a combination of collision broadening and Doppler broadening, whereas in the lower atmosphere, below about 40 km, the collision broadening prevails because of increased pressure.

In general, spectral lines are assumed to be symmetric about the central wavelength λ_o which corresponds to a maximum absorbing power. In the case of a symmetric line, well separated from neighbouring lines of the absorption spectrum, the line shape may be fitted by the Lorentz form

$$k_\lambda = \frac{k_o \, \alpha^2}{(\lambda - \lambda_o)^2 + \alpha^2} \quad ,$$

where k_λ is a measure of the absorbing power and a is the half width of the line. The half width is the displacement from the line centre to the wavelength where $k_\lambda = k_o/2$. In such an individual spectral line, the absorbing power approaches zero asymptotically at increasing distance in the line wings from the centre. More generally, however, the absorbing power does not become zero between lines because of the overlapping effects of many lines.

3.6 *Vibrational and Rotational Spectra*

The Bohr theory of the hydrogen atom explained the quantized energy states available to an electron in orbit about a hydrogen nucleus. Additional consideration of elliptical orbits, relativistic effects, and magnetic spin orbit interaction was needed to explain the observed emission spectra in more detail (including the fine structure). Explanation of molecular emission lines requires still more work. Gaseous emission spectra are found to have atomic spectral lines with many additional molecular emission lines superimposed. As indicated earlier, three major types of molecular excitation are observed.

(a)   The electronic excitation when the orbital states of the electrons change in the individual atoms;

(b)   The vibrational excitation when the individual atoms vibrate with respect to the combined molecular centre of mass;

(c)   The rotational excitation when the molecule rotates about the centre of mass.

To understand the vibrational spectra more clearly, consider a typical potential energy curve for a diatomic molecule (shown in Figure 3.2). Stable equilibrium occurs with the nuclei separated by a distance R_o. If the nuclei are separated by a slightly greater or smaller distance R, the energy is raised and a spring-like restoring force is effected. This restoring force can be represented by

$$F = -\left(\frac{d^2E}{dR^2}\right)_{R=R_o} (R - R_o) \quad ,$$

which has a classical frequency of vibration

$$f_o = \frac{1}{2\pi\mu^{1/2}} \left(\frac{d^2E}{dR^2}\right)_{R=R_o}^{1/2} \quad ,$$

with the reduced mass of the vibrating system

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \quad .$$

The energy levels can be shown to have the form of the Planck postulate

$$E_m = (m + 2) hf_o, \quad m = 0, 1, 2, ...$$

where the additional 2 is a consequence of solving the Schroedinger wave equation for a harmonic oscillator. The vibrational energy levels of a diatomic molecule are shown in Figure 3.2, the upper energy levels are not equally spaced since the actual energy well is wider than the parabolic approximation and hence these energy levels are closer together than the lower levels.

The rotational spectra appears as fine structure of the combined electronic and vibrational lines. The kinetic energy of rotation of the nuclei about their common centre of mass is readily solved with the Schroedinger equation and the following energy levels emerge:

$$E_J = \frac{h^2}{8\pi^2 \mu R_o^2} J (J + 1), \quad J = 1, 2, 3, ...$$

These rotational energies are very small, and therefore, lines of the pure rotation spectrum are in the far infrared or microwave regions of the spectrum.

The total energy of a molecule is given by

$$E = E_{electronic} + E_{vibration} + E_{rotation} .$$

The typical separation between the lowest state and the first excited state is about 2 to 10 eV for electronic energies, about .2 to 2 eV for vibration energies and about 10^{-5} to 10^{-3} eV for rotation energies. Note that 1 eV = 1.6 x 10^{-19}J which corresponds to emission at a wavelength of 1.24 μm. Figure 3.3 illustrates this schematically.

Each transition involving a change in electron energy produces a whole series of emission or absorption lines, since many combinations of changes in vibration and rotation energy are possible. If such a system of lines is observed under low resolution conditions, it appears to be a band with practically a continuous distribution of frequencies. With higher resolution the individual lines can be resolved and the energy differences measured. In this way, the energies of the vibrational states and of the rotational states can be measured. It is apparent that in the higher vibrational states the average internuclear distance R is larger because of the asymmetry of the binding energy curve. This fact produces a higher moment of inertia μR^2 when the vibrational quantum number is large and a correspondingly smaller separation in the rotational energy levels. Thus, precision measurement of the rotational levels as a function of vibrational quantum number permits the study of the asymmetry of the binding energy curve; it is this asymmetry that is responsible for the thermal expansion of molecules.

3.7 Summary of the Interactions between Radiation and Matter

One basic type of interaction between radiation and matter can be summarized by a photon transferring all of its energy to an atom or a molecule and thus being removed from the radiation field. The energy of the photon raises an electron to a higher energy level or a molecule to higher rotational or vibrational states. This increase in energy of the receiving atom or molecule can be released in several different ways.

One mechanism is for the activated molecule to collide with another molecule, and to drop back into a lower energy state; the energy thus freed becomes kinetic energy of the molecules and corresponds to warming the gas. This is absorption. The photon is permanently lost or attenuated from the radiation field.

A second mechanism for release of the energy increase is the spontaneous transition of the molecule (in about one nanosecond) into its original state by emitting a photon which is identical to the absorbed one except for its direction of propagation. This is scattering, where the photon remains part of the radiation field but the direct beam is attenuated.

A third mechanism is the activated molecule releases its energy spontaneously but in two stages. Two photons with different lower energies result; the sum of the energies of the two photons equals the energy of the absorbed photon. The direct beam is attenuated; the original photon has been replaced by two photons at longer wavelengths and is no longer part of the radiation field. This is Raman-scattering.

Other mechanisms for energy release are fluorescence and phosphorescence. These occur when the energy is not released spontaneously, but after relaxation times of nanoseconds to hours.

Another basic type of interaction involves the conversion of molecular kinetic energy (thermal energy) into electromagnetic energy (photons). This occurs when molecules are activated by collisions with each other and the activation energy is emitted as photons. This is emission.

3.8   Beer's Law and Schwarzchild's Equation

In the absence of scattering, the absorption of parallel beam radiation as it passes downward through a horizontal layer of gas of infinitesimal thickness dz is proportional to the number of molecules per unit area that are absorbing radiation along the path. This relationship can be expressed in the form

$$da_\lambda \ = \ - \, dI_\lambda \, / \, I_\lambda \ = \ - \, k_\lambda \, \rho \, \sec \varphi \, dz \ ,$$

where ρ is the density of the gas and φ is the zenith angle. Here absorbed monochromatic radiance is expressed as an incremental amount of depletion of the incident beam. dI_λ and dz are both negative quantities, so da_λ is positive. The product $\rho \sec \varphi \, dz$ is the mass within the volume swept out by a unit cross-sectional area of the incident beam as it passes through the layer, as pictured in Figure 3.4. The absorption coefficient k_λ is a measure of the fraction of the gas molecules per unit wavelength interval that are absorbing radiation at the wavelength in question. k_λ is a function of composition, temperature, and pressure of the gas within the layer. It has units of square metres per kilogram, which makes the product $k_\lambda \rho \, dz$ dimensionless. Integrating from z up to the top of the atmosphere yields

$$\ln I_{\lambda\infty} \ - \ \ln I_\lambda \ = \ \sec \varphi \ \int_{z}^{\infty} \ k_\lambda \, \rho \, dz \, .$$

Taking the anti-log of both sides and assuming k_λ is independent of height,

$$I_\lambda \ = \ I_{\lambda\infty} \ \exp \, (- \, k_\lambda \, u) \ ,$$

where

$$u \ = \ \sec \varphi \int_{z}^{\infty} \ \rho \, dz \, .$$

This relation, often referred to as Beer's Law, states that radiance decreases monotonically with increasing path length through the layer. The quantity u is called the density weighted path length. $k_\lambda u$ is a measure of the cumulative depletion that the beam of radiation has experienced as a result of its passage through the layer and is often called the optical depth σ_λ. The transmittance of the layer of gas lying above the level z is given by

$$\tau_\lambda = I_\lambda / I_{\lambda\infty} = e^{-k_\lambda u}$$

and it follows that, in the absence of scattering, the absorptance

$$a_\lambda = 1 - \tau_\lambda = 1 - e^{-k_\lambda u}$$

approaches unity exponentially with increasing optical depth. At wavelengths close to the centre of absorption lines, k_λ is large so that a very short (density weighted) path length is sufficient to absorb virtually all the incident radiation. At wavelengths away from absorption lines, a path length many orders of magnitude longer may be required to produce any noticeable absorption.

Indirect calculation of the spectrum of solar radiation incident on the top of the atmosphere, on the basis of ground-based measurements, provides an interesting example of the application of Beer's law. Such calculations were made quite successfully many years before direct measurements of undepleted solar radiation were available from satellites. Writing Beer's Law in another form, we have

$$\ln I_\lambda = \ln I_{\lambda\infty} - \sec \varphi \int_z^\infty k_\lambda \rho \, dz .$$

Over the course of a single day, I_λ is measured at frequent intervals at a ground station. During this period, the numerical value of the integrand changes very little in comparison to the large changes in solar zenith angle. Thus, to a good approximation, the above expression assumes the form

$$\ln I_\lambda = A - B x ,$$

where $x = \sec \varphi$ and A and B are constants; that is to say, when the individual data points for I_λ are plotted on a logarithmic scale as function of $\sec \varphi$, they tend to fall along a straight line. Since the path length is directly proportional to x, it is possible to deduce the radiance upon the top of the atmosphere simply by extending the straight line that makes the best fit to the data points back to x = 0 (that is, zero path length through the atmosphere).

At the wavelengths of solar radiation, atmospheric emission is negligible, and only absorption needs to be considered. However, at the wavelengths of terrestrial radiation, absorption and emission are equally important and must be considered simultaneously. The absorption of terrestrial radiation along an upward path through the atmosphere is described with the sign reversed by the relation

$$-dL_\lambda{}^{abs} = L_\lambda k_\lambda \rho \sec \varphi \, dz .$$

The emission of radiation from a gas can be treated in much the same manner as the absorption. Making use of Kirchhoff's law it is possible to write an analogous expression for the emission,

$$dL_\lambda{}^{em} = B_\lambda d\varepsilon_\lambda = B_\lambda da_\lambda = B_\lambda k_\lambda \rho \sec \varphi \, dz ,$$

where B_λ is the blackbody monochromatic radiance specified by Planck's law. Now we subtract the absorption from the emission to obtain the net contribution of the layer to the monochromatic

radiance of the radiation passing upward through it:

$$dL_\lambda = -(L_\lambda - B_\lambda) k_\lambda \rho \sec \varphi \, dz \; .$$

This expression, known as Schwarzchild's equation, is the basis for computations of the transfer of infrared radiation. For an isothermal gas, with constant k_λ, this may be integrated to obtain

$$(L_\lambda - B_\lambda) = (L_{\lambda o} - B_\lambda) \exp(-k_\lambda u) \; ,$$

where $L_{\lambda o}$ is the radiance incident on the layer from below. This expression shows that L_λ should exponentially approach B_λ as the optical thickness of the layer increases. For a layer of infinite optical thickness the emission from the top is B_λ regardless of the value of $L_{\lambda o}$; that is to say, such a layer behaves as a blackbody.

It is often useful to transform the height variable z to pressure p through the hydrostatic equation and the definition of mixing ratio $q = \rho/\rho_a$ where ρ and ρ_a are the density of gas and air respectively,

$$g \rho \, dz = -q \, dp \; .$$

Thus, the optical depth becomes

$$u(p) = \sec \varphi \int_0^p q \, g^{-1} \, dp \; ,$$

and the monochromatic transmittance (the probability that a photon of wavelength l leaving pressure level p will reach the top of the atmosphere) is given by

$$\tau_\lambda(p) = \exp\left[-\sec \varphi \int_0^p k_\lambda g^{-1} q \, dp \right] \; .$$

3.9   *Atmospheric Scattering*

Scattering is a physical process by which a particle in the path of an electromagnetic wave continuously abstracts energy from the incident wave and re-radiates that energy in all directions. Therefore, the particle may be thought of as a point source of the scattered energy. In the atmosphere, the particles responsible for scattering cover the sizes from gas molecules ($\sim 10^{-8}$ cm) to large raindrops and hail particles (~ 1 cm). The relative intensity of the scattering pattern depends strongly on the ratio of particle size to wavelength of the incident wave. If scattering is isotropic, the scattering pattern is symmetric about the direction of the incident wave. A small anisotropic particle tends to scatter light equally into the forward and backward directions. When the particle becomes larger, the scattered energy is increasingly concentrated in the forward directions. Distribution of the scattered energy involving spherical and certain symmetrical particles may be quantitatively determined by means of the electromagnetic wave theory. When particles are much smaller than the incident wavelength, the scattering is called Rayleigh scattering. For particles whose sizes are comparable to or larger than the wavelength, the scattering is customarily referred to as Mie scattering.

Rayleigh scattering indicates that the intensity scattered by air molecules in a specific direction is inversely proportional to the fourth power of the wavelength. A large portion of solar energy, lying between the blue to red portion of the visible spectrum, is Rayleigh scattered by the atmosphere. Blue light ($\lambda \approx 0.425$ μm) has a shorter wavelength than red light ($\lambda \approx 0.650$ μm).

Consequently, blue light scatters about 5.5 more than red light. It is apparent that the λ^{-4} law causes more of the blue light to be scattered than the red, the green, and the yellow, and so the sky, when viewed away from the sun's disk, appears blue. Moreover, since the molecular density decreases drastically with height, it is anticipated that the sky should gradually darken to become completely black in outer space in directions away from the sun. And the sun itself should appear whiter and brighter with increasing height. As the sun approaches the horizon (at sunset or sunrise), sunlight travels through more air molecules, and therefore more and more blue light and light with shorter wavelengths are scattered out of the beam of light, and the luminous sun shows a deeper red colour than at the zenith.

Larger particles in the atmosphere such as aerosols, cloud droplets, and ice crystals also scatter sunlight and produce many fascinating optical phenomena. However, their single scattering properties are less wavelength selective and depend largely upon the particle size. As a result of this, clouds in the atmosphere generally appear white instead of blue. In a cloudy atmosphere, the sky appears blue diluted with white scattered light, resulting in a less pure blue sky than would have been expected just from Rayleigh scattering. Scattering by a spherical particle of arbitrary size has been treated exactly by Mie in 1908 by means of solving the electromagnetic wave equation derived from the fundamental Maxwell equations.

It is possible to formulate an expression analogous to absorption for ds_λ, the fraction of parallel beam radiation that is scattered when passing downward through a layer of infinitesimal thickness, namely

$$ds_\lambda \ = \ dI_\lambda / I_\lambda \ = \ K \, A \sec \varphi \, dz \ ,$$

where K is a dimensionless coefficient and A is the cross-sectional area that the particles in a unit volume present to the beam of incident radiation. If all the particles which the beam encounters in its passage through the differential layer were projected onto a plane perpendicular to the incident beam, the product $A \sec \varphi \, dz$ would represent the fractional area occupied by the particles. Thus, K plays the role of a scattering area coefficient which measures the ratio of the effective scattering cross section of the particles to their geometric cross section. In the idealized case of scattering by spherical particles of uniform radius r, the scattering area coefficient K can be prescribed on the basis of theory. It is convenient to express K as a function of a dimensionless size parameter $\alpha = 2\pi r/\lambda$, which is a measure of the size of the particles in comparison to the wavelength of the incident radiation. Figure 3.5a shows a plot of α as a function of r and λ. The scattering area coefficient K depends not only upon the size parameter, but also upon the index of refraction of the particles responsible for the scattering. Figure 3.5b shows K as a function of a for two widely differing refractive indices. When $\alpha \ll 1$ we have Rayleigh scattering ($K \sim \alpha^4$), and between .1 and 50 we are in the Mie regime. For $\alpha > 50$ the angular distribution of scattered radiation can be described by the principles of geometric optics. The scattering of visible radiation by cloud droplets, raindrops, and ice particles falls within this regime and produces a number of distinctive optical phenomena such as rainbows, halos, and so forth.

It should be noted that the scattering of terrestrial radiation in the atmosphere is of secondary importance compared to absorption and emission of terrestrial radiation.

3.10   The Solar Spectrum

The solar spectrum refers to the distribution of electromagnetic radiation emitted by the sun as a function of the wavelength incident on the top of the atmosphere. The solar constant S is a quantity denoting the amount of total solar irradiance reaching the top of the atmosphere. We recall that it is defined as the flux of solar energy (energy per time) across a surface of unit area normal to the solar beam at the mean distance between the sun and earth. The solar spectrum and solar constant have been extensively investigated for some time. Abbot undertook a long series of ground-based measurements, resulting in a value of about 1350 Wm^{-2} for the solar constant.

Subsequent to Abbot's work and prior to more recent measurements carried out from high-altitude platforms, solar constant values of 1396 and 1380 Wm^{-2}, proposed by Johnson and Nicolet respectively, were widely accepted. Since July 1985, the Earth Radiation Budget Experiment (ERBE) has been monitoring the sun's radiation . The solar constant measurements from Nimbus 7 indicate a value of 1372 Wm^{-2} with generally less than a 0.1% variation. There are some significant short term fluctuations due to decreases associated with the development of sunspots.

The standard solar spectrum in terms of the spectral irradiance is shown in the top solid curve of Figure 3.6. Also shown in this diagram is the spectral solar irradiance reaching sea level in a clear atmosphere. The shaded areas represent the amount of absorption by various gases in the atmosphere, primarily H_2O, CO_2, O_3, and O_2. Absorption and scattering of solar radiation in clear atmospheres will be discussed later. If one matches the solar spectral irradiance curve with theoretical blackbody values, we find that a temperature around 6000 K fits the observed curve closely in the visible and infrared wavelengths. Most of the electromagnetic energy reaching the earth originates from the sun's surface, called the photosphere. Of the electromagnetic energy emitted from the sun, approximately 50% lies in wavelengths longer than the visible region, about 40% in the visible region (0.4-0.7 μm), and about 10% in wavelengths shorter than the visible region.

3.11   Composition of the Earth's Atmosphere

To describe the interaction of the earth's atmosphere with solar radiation, the atmosphere's composition must be understood. The atmosphere is composed of a group of nearly permanent gases and a group of gases with variable concentration. In addition, the atmosphere also contains various solid and liquid particles such as aerosols, water drops, and ice crystals, which are highly variable in space and time.

Table 3.2 lists the chemical formula and volume ratio for the concentrations of the permanent and variable gases in the earth's atmosphere. It is apparent from this table that nitrogen, oxygen, and argon account for more than 99.99% of the permanent gases. These gases have virtually constant volume ratios up to an altitude of about 60 km in the atmosphere. It should be noted that although carbon dioxide is listed here as a permanent constituent, it's concentration varies as a result of the combustion of fossil fuels, absorption and release by the ocean, and photosynthesis. Water vapour concentration varies greatly both in space and time depending upon the atmospheric condition. Its variation is extremely important in the radiative absorption and emission processes. Ozone concentration also changes with respect to time and space, and it occurs principally at altitudes from about 15 to about 30 km, where it is both produced and destroyed by photochemical reactions. Most of the ultraviolet radiation is absorbed by ozone, preventing this harmful radiation from reaching the earth's surface.

3.12   Atmospheric Absorption and Emission of Solar Radiation

The absorption and emission of solar radiation in the atmosphere is accomplished by molecular storing of the electromagnetic radiation energy. Molecules can store energy in various ways. Any moving particle has kinetic energy as a result of its motion in space. This is known as translational energy. The averaged translational kinetic energy of a single molecule in the x, y and z directions is found to be equal to kT/2, where k is the Boltzmann constant and T is the absolute temperature. A molecule which is composed of atoms can rotate, or revolve, about an axis through its centre of gravity and, therefore, has rotational energy. The atoms of the molecule are bounded by certain forces in which the individual atoms can vibrate about their equilibrium positions relative to one another. The molecule, therefore, will have vibrational energy. These three molecular energy types (translational, rotational, and vibrational) are based on a rather mechanical model of the molecule that ignores the detailed structure of the molecule in terms of nuclei and electrons. It is possible, however, for the energy of a molecule to change due to a change in the energy state of the electrons of which it is composed. Thus, the molecule also has electronic energy. The energy

levels are quantized and take discrete values only. As we have pointed out, absorption and emission of radiation takes place when the atoms or molecules undergo transitions from one energy state to another. In general, these transitions are governed by selection rules. Atoms exhibit line spectra associated with electronic energy levels. Molecules, however, also have rotational and vibrational energy levels that lead to complex band systems.

Solar radiation is mainly absorbed in the atmosphere by O_2, O_3, N_2, CO_2, H_2O, O, and N, although NO, N_2O, CO, and CH_4, which occur in very small quantities, also exhibit absorption spectra. Absorption spectra due to electronic transitions of molecular and atomic oxygen and nitrogen, and ozone occur chiefly in the ultraviolet (UV) region, while those due to the vibrational and rotational transitions of triatomic molecules such as H_2O, O_3, and CO_2 lie in the infrared region. There is very little absorption in the visible region of the solar spectrum.

3.13   Atmospheric Absorption and Emission of Thermal Radiation

The earth also emits electromagnetic radiation covering all frequencies. However, the global mean temperature of the earth-atmosphere system is only about 250 K, a temperature that is obviously much lower than that of the sun's photosphere. As a consequence of Planck's law and Wien's displacement law discussed earlier, the radiance (intensity) peak of the Planck function is smaller for the earth's radiation field and the wavelength for the radiance (intensity) peak of the earth's radiation field is longer. The energy emitted from the earth-atmosphere system is called thermal infrared (or terrestrial) radiation. Figure 1.1 showed the earth radiance to space measured by the Infrared Interferometer Spectrometer Instrument (IRIS) on board Nimbus IV as well as the spectral distribution of radiance emitted by a blackbody source at various temperatures in the terrestrial range (in terms of wavenumber). In some spectral regions the envelope of the emission spectrum is very close to the spectrum emitted from a blackbody with a temperature of about 300 K, which is about the temperature of the surface. In these spectral regions, the atmosphere is transparent to that radiation. In other spectral regions the emission spectrum is close to the spectrum emitted from a blackbody with a temperature of about 220 K, which is about the temperature at the tropopause. This occurs in spectral regions where the atmosphere is opaque or absorbing to that radiation and the atmosphere is said to be trapping the radiation.

Figure 3.7 shows more recent measurements from an airborne interferometer; clearly, in certain portions of the infrared spectrum, radiation is trapped by various gases in the atmosphere. Among these gases, carbon dioxide, water vapour, and ozone are the most important absorbers. Some minor constituents, such as carbon monoxide, nitrous oxide, methane, and nitric oxide (which are not shown in Figure 3.7) are relatively insignificant absorbers insofar as the heat budget of the earth-atmosphere is concerned. Carbon dioxide absorbs infrared radiation significantly in the 15 μm band (in the wavenumber domain from about 600 to 800 cm^{-1}, which also corresponds to the maximum intensity of the Planck function). Water vapour absorbs thermal infrared in the 6.3 μm band (from about 1200 to 2000 cm^{-1}) and in the rotational band beyond 20 μm (< 500 cm^{-1}). Except for ozone, which has an absorption band in the 9.6 μm region (about 1040 cm^{-1}), the atmosphere is relatively transparent from 8 to 12 μm (800 to 1200 cm^{-1}). This region is referred to as the atmospheric window. Carbon dioxide also has an absorption band in the shorter wavelength of the 4.3 μm region (2325 cm^{-1}). The global distribution of carbon dioxide is fairly uniform, although there has been observational evidence indicating a continuous global increase over the past century owing to increased combustion of fossil fuels. This leads to the question of the earth's climate and possible climatic changes due to the increasing carbon dioxide concentration. Unlike carbon dioxide, however, water vapour and ozone are highly variable both with respect to time and the geographical location. These variations are vital to the radiation budget of the earth-atmosphere system and to long-term climatic changes.

Figure 3.8 shows the radiance from .1 μm to 10 cm emitted by the earth-atmosphere system transmitted to space. In a clear atmosphere without clouds and aerosols, a large portion (about 50%) of solar energy transmits through the atmosphere and is absorbed by the earth's

surface. Energy emitted from the earth, on the contrary, is absorbed largely by carbon dioxide, water vapour, and ozone in the atmosphere as evident in Figure 3.7. Trapping of thermal infrared radiation by atmospheric gases is typical of the atmosphere and is, therefore, called the atmospheric effect.

Solar radiation is referred to as shortwave radiation because solar energy is concentrated in shorter wavelengths with its peak at about 0.5 μm. Thermal infrared radiation from the earth's atmosphere is referred to as longwave radiation because its maximum energy is in the longer wavelength at about 10 μm. The solar and infrared spectra are separated into two spectral ranges above and below about 4 μm, and the overlap between them is relatively insignificant. This distinction makes it possible to treat the two types of radiative transfer and source functions separately and thereby simplify the complexity of the transfer problem.

3.14   Atmospheric Absorption Bands in the Infrared Spectrum

Inspection of high resolution spectroscopic data reveals that there are thousands of absorption lines within each absorption band. The fine structure of molecular absorption bands for the 320-380 cm^{-1} is due to water vapour, and for the 680-740 cm^{-1} region it is due to carbon dioxide. The optically active gases of the atmosphere, carbon dioxide, water vapour, and ozone are all triatomic molecules. Figure 3.9 shows the absorption spectra for H_2O and CO_2. Spectroscopic evidence indicates that the three atoms of CO_2 form a symmetrical straight line array having the carbon atom in the middle flanked by oxygen atoms in either side. Because of linear symmetry it cannot have a static electric dipole moment. Figure 3.10a shows the three normal modes of vibration of such a configuration. The symmetrical motion v_1 should not give rise to an electric dipole moment and, therefore, should not be optically active. The v_1 vibration mode has been identified in the Raman spectrum near 7.5 μm. In the v_2 vibration mode, the dipole moment is perpendicular to the axis of the molecule. The 15 μm band represents this particular vibration. The band is referred to as a fundamental because it is caused by a transition from the ground state to the first excited vibrational state. Another fundamental corresponding to the v_3 vibration mode is the 4.3 μm band, which appears at the short-wave edge of the blackbody curve of atmospheric temperatures.

The water molecule forms an isosceles triangle which is obtuse. Figure 3.10b shows the three normal modes of vibration for such a structure. The 6.3 μm band has been identified as the v_2 fundamental. The two fundamentals, v_1 and v_3, are found close together in a band near 2.7 μm, i.e., on the shortwave side of the infrared spectral region.

The band covering the region from 800 to 400 cm^{-1} shown in Figure 3.7 represents the purely rotational spectrum of water vapour. The water molecule forms an asymmetrical top with respect to rotation, and the line structure of the spectrum does not have the simplicity of a symmetrical rotator such as found in the CO_2 molecule. Close inspection shows that the absorption lines have no clear-cut regularity. The fine structure of the 6.3 μm band is essentially similar to that of the pure rotational band.

In the region between the two water vapour bands, i.e. between about eight and 12 μm, the so-called atmospheric window, absorption is continuous and is primarily due to water vapour. Absorption by carbon dioxide is typically a small part of the total in this region. The overlap of water vapour with ozone in this region is insignificant in the computations of cooling rates since water vapour is important mainly in the lower atmosphere, while cooling due to ozone takes place primarily in the stratosphere and higher.

The ozone molecule is of the triatomic nonlinear type (Figure 3.10b) with a relatively strong rotation spectrum. The three fundamental vibrational bands v_1, v_2, and v_3 occur at wavelengths of 9.066, 14.27, and 9.597 μm, respectively. The very strong v_3 and moderately strong v_1 fundamentals combine to make the well-known 9.6 μm band of ozone. The v_2 fundamental is well-

masked by the 15 μm band of CO_2. The strong band of about 4.7 μm produced by the overtone and combination frequencies of O_3 vibrations is in a weak portion of the Planck energy distribution for the atmosphere. Note that the absorption bands of O_3 in the UV part of the solar spectrum are due to electronic transitions in the ozone molecule.

3.15   Atmospheric Absorption Bands in the Microwave Spectrum

While most of the focus of this chapter has been the visible and infrared spectral regions, a brief summary of the absorption lines in the microwave spectral region follows. Molecular oxygen and water vapour are the major absorbing constituents here. Figure 3.11 shows the transmittance for frequencies below 300 GHz. Below 40 GHz only the weakly absorbing pressure broadened 22.235 GHz water vapour line is evident; this line is caused by transitions between the rotational states. At about 60 and 118.75 GHz, there are strong oxygen absorption lines due to magnetic dipole transitions. For frequencies greater than 120 GHz, water vapour absorption again becomes dominant due to the strongly absorbing line at 183 GHz.

A special problem in the use of microwave from a satellite platform is the emissivity of the earth surface. In the microwave region of the spectrum, emissivity values of the earth surface range from .4 to 1.0. This complicates interpretation of terrestrial and atmospheric radiation with earth surface reflections. More will be said about this later.

3.16   Remote Sensing Regions

Several spectral regions are considered useful for remote sensing from satellites. Figure 3.12 summarizes this. Windows to the atmosphere (regions of minimal atmospheric absorption) exist near 4 μm, 10 μm, 0.3 cm, and 1 cm. Infrared windows are used for sensing the temperature of the earth surface and clouds, while microwave windows help to investigate the surface emissivity and the liquid water content of clouds. The CO_2 and O_2 absorption bands at 4.3 μm, 15 μm, 0.25 cm, and 0.5 cm are used for temperature profile retrieval; because these gases are uniformly mixed in the atmosphere in known portions they lend themselves to this application. The water vapour absorption bands near 6.3 μm, beyond 18 μm, near 0.2 cm, and near 1.3 cm are sensitive to the water vapour concentration in the atmosphere.

In summary, incoming solar radiation (mostly visible) drives the earth-atmosphere (which emits infrared). The atmosphere transmits, absorbs (by H2O, O2, O3, dust) reflects (by clouds), and scatters (by aerosols) incoming visible; the earth surface absorbs and reflects the transmitted visible.   Atmospheric H2O, CO2, and O3 selectively transmit or absorb the outgoing infrared radiation. The outgoing microwave is primarily affected by H2O and O2. The atmosphere has window regions where radiation is mostly transmitted (but some absorption occurs in all parts of the spectrum). The earth surface emits with efficiency less than blackbody at all wavelengths (but in the infrared window regions the emissivity is close to one for some surfaces). Figure 13.3 summarizes the infrared atmospheric absorptance and selected earth surface emissivities.

Table 3.1 Reflectance (in percent) of various surfaces in the spectral range of solar radiation
(using the US Standard Atmosphere of 1976)

Bare soil	10 - 25
Sand, desert	25 - 40
Grass	15 - 25
Forest	10 - 20
Snow (clean, dry)	75 - 95
Snow (wet, dirty)	25 - 75
Sea surface (sun angle) > 25	< 10
Sea surface (low sun angle)	10 - 70

Table 3.2 Composition of the Atmosphere (from the US Standard Atmosphere of 1976)

Permanent Constituents		Variable Constituents	
Constituent	% by volume	Constituent	% by volume
Nitrogen (N_2)	78.084	Water vapour (H_2O)	0-0.04
Oxygen (O_2)	20.948	Ozone (O_3)	$0-12 \times 10^{-4}$
Argon (Ar)	0.934	Sulfur dioxide (SO_2)[1]	0.001×10^{-4}
Carbon dioxide (CO_2)	0.033	Nitrogen dioxide (NO_2)[1]	0.001×10^{-4}
Neon (Ne)	18.18×10^{-4}	Ammonia (NH_3)[1]	0.004×10^{-4}
Helium (He)	5.24×10^{-4}	Nitric oxide (NO)[1]	0.0005×10^{-4}
Krypton (Kr)	1.14×10^{-4}	Hydrogen sulfide (H_2S)	10.00005×10^{-4}
Xenon (Xe)	0.089×10^{-4}	Nitric acid vapour (HNO_3)	Trace
Hydrogen (H_2)	0.5×10^{-4}		
Methane (CH_4)	1.5×10^{-4}		
Nitrous oxide (N_2O)[1]	0.27×10^{-4}		
Carbon monoxide (CO)[1]	0.19×10^{-4}		

[1]Concentration near the earth's surface.
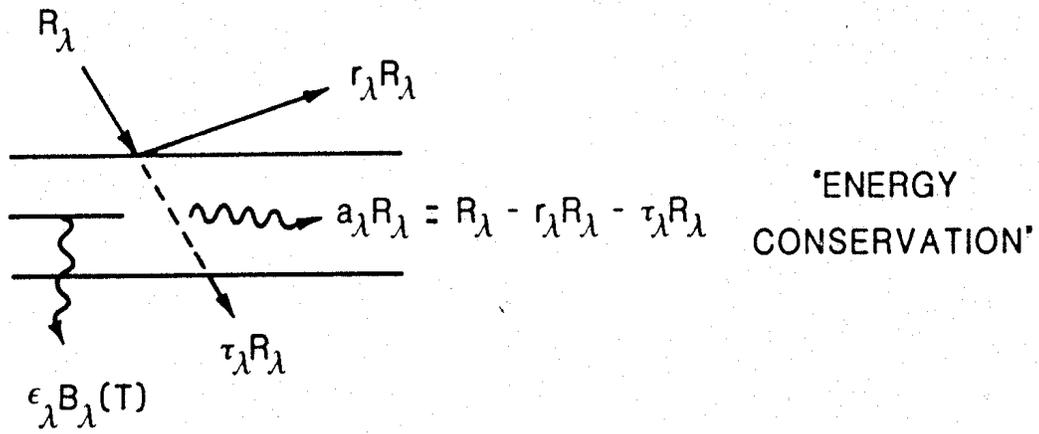
Figure 3.1: Schematic for reflectance, absorptance, and transmittance in a layer of gases.
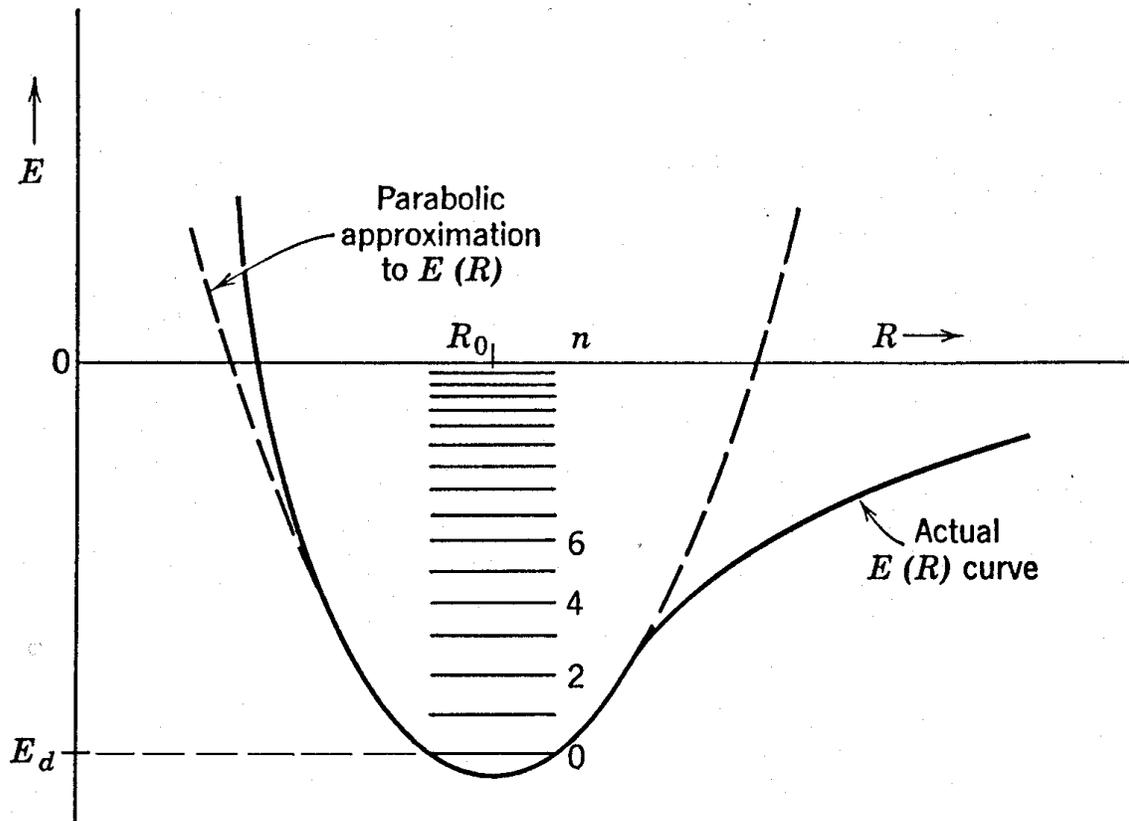
Figure 3.2: Vibrational energy levels of a diatomic molecule.
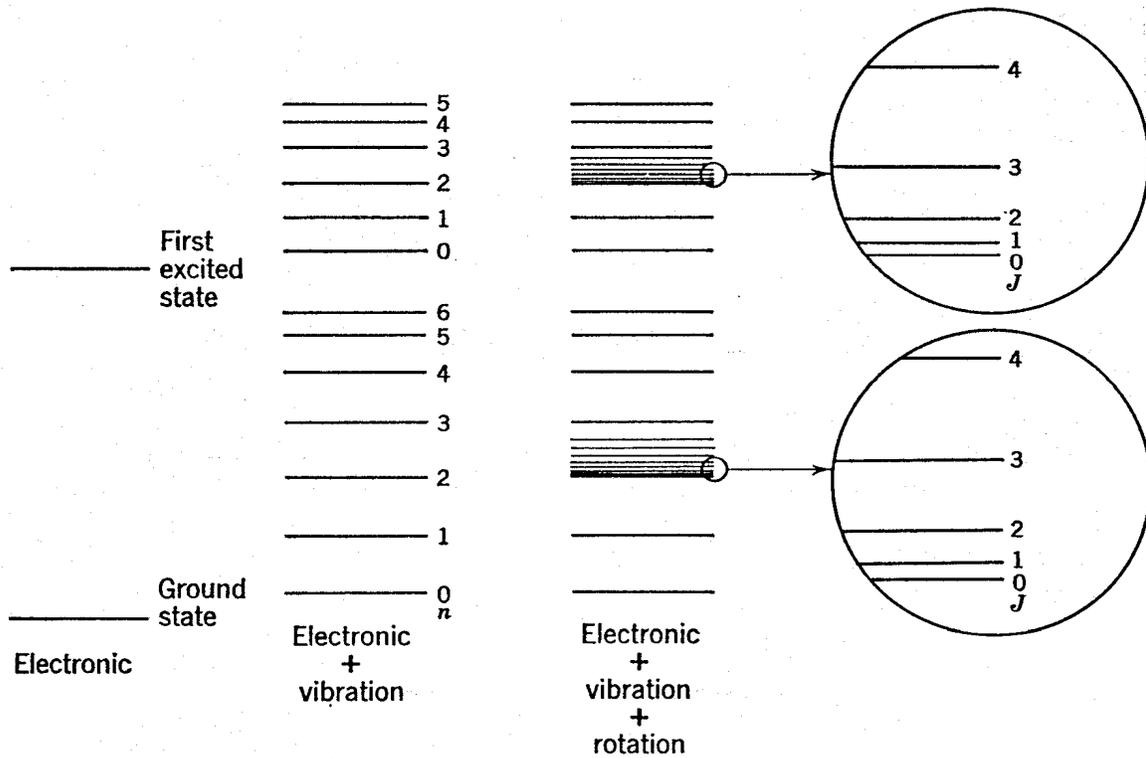
Figure 3.3: Energy levels of a diatomic molecule. Every level of electronic + vibrational energy has rotational fine structure, but this structure is illustrated only for the n = 2 states.
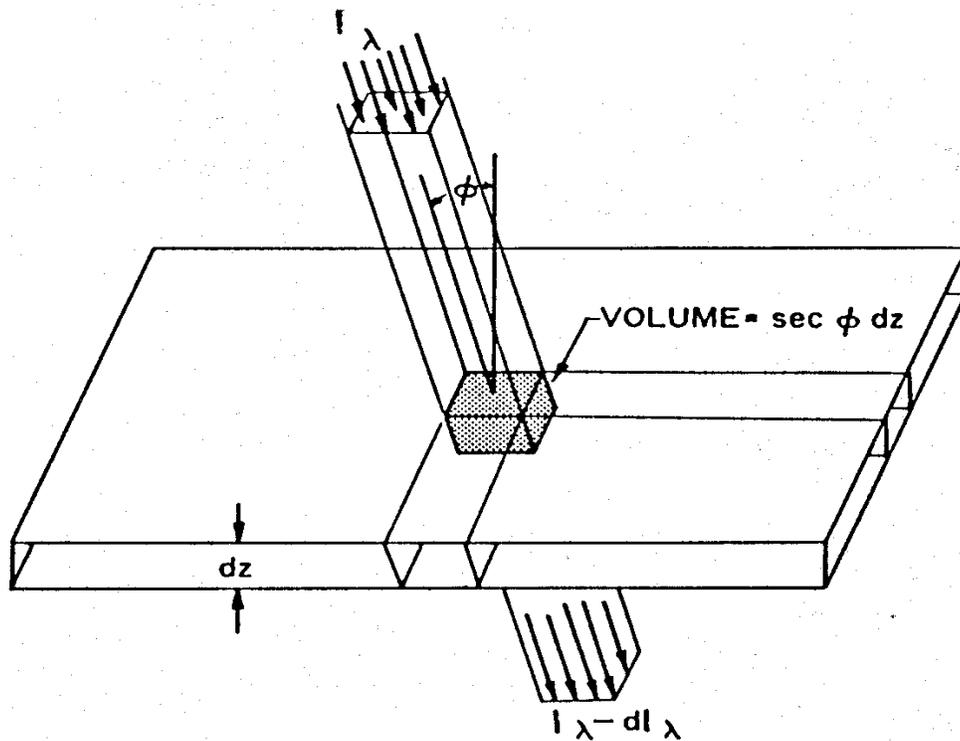
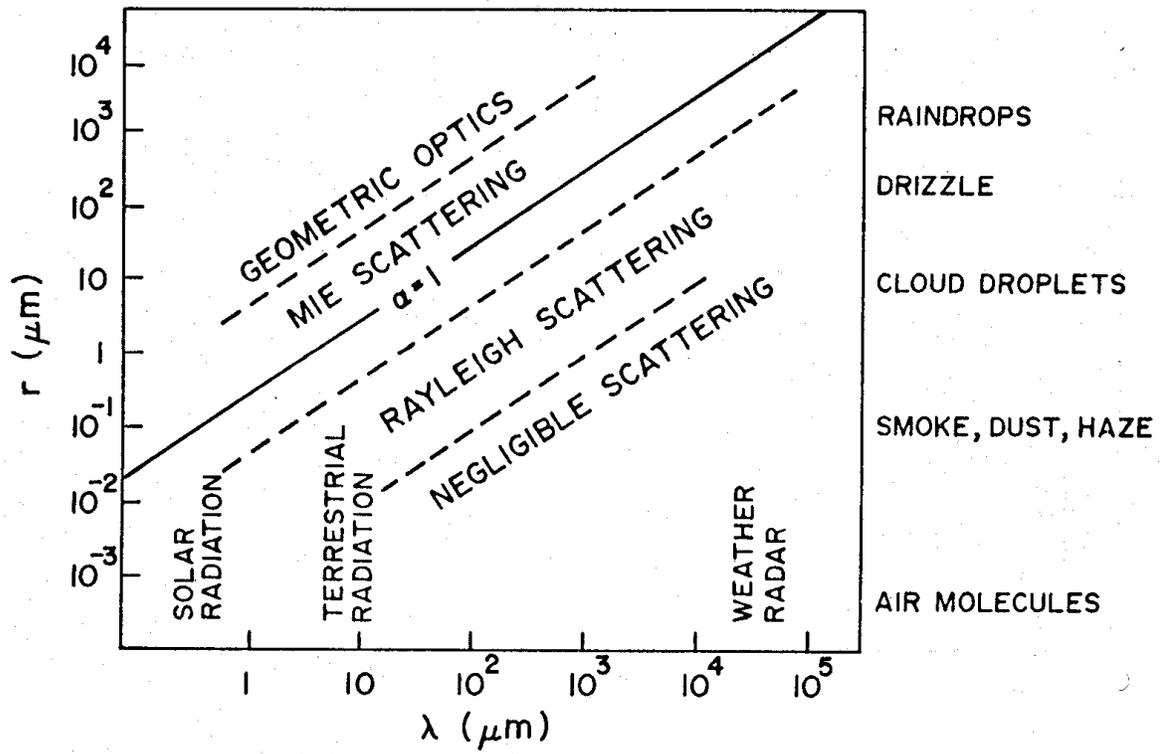**Figure 3.4**: Depletion of an incident beam of unit cross-section while passing through an absorbing layer of infinitesimal thickness.

Figure 3.5a: Size parameter a as a function of incident radiation and particle radius.
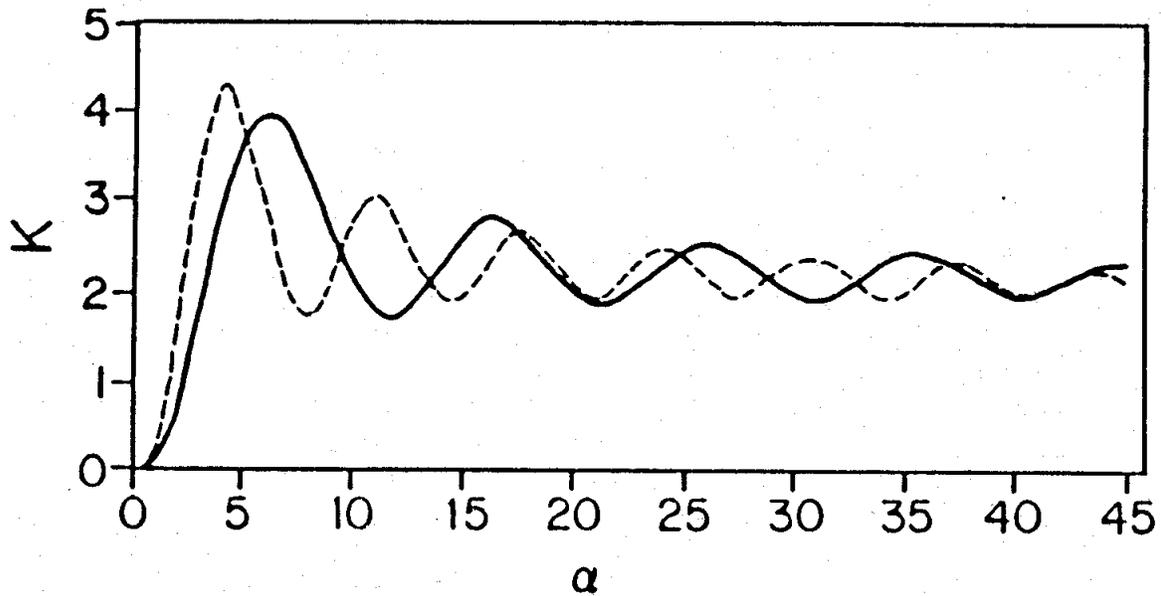
Figure 3.5b: Scattering area coefficient K as a function of size parameter for refractive indices of 1.330 (solid curve) and 14.86 (dashed curve).
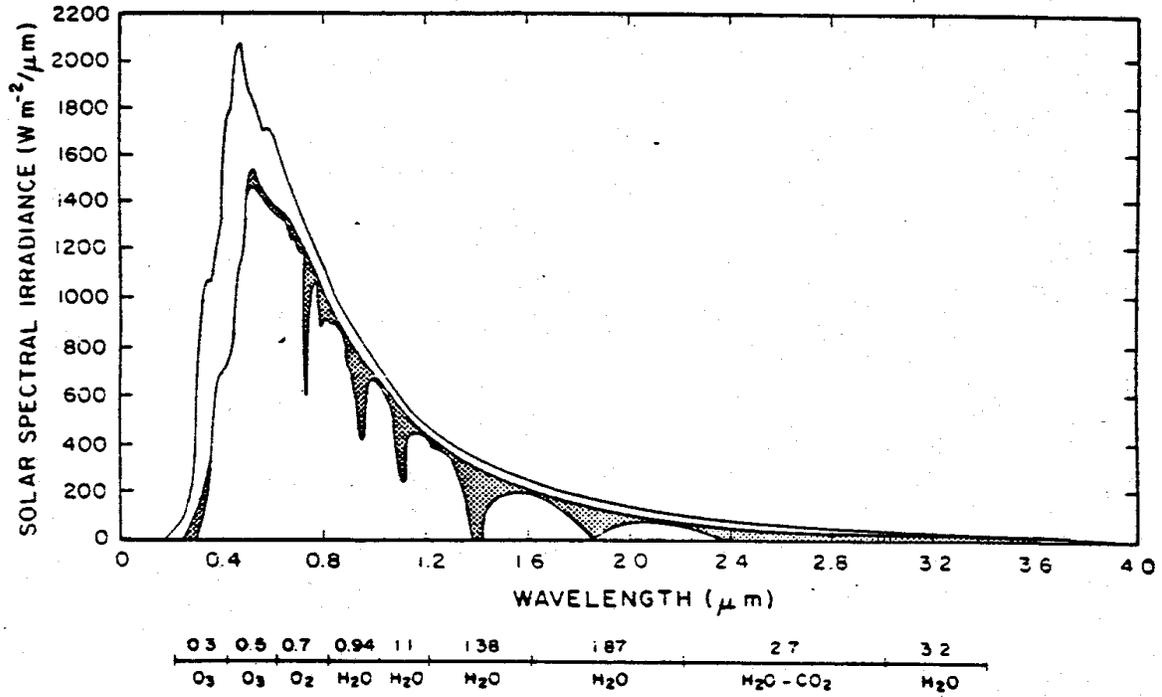
Figure 3.6: Spectral irradiance distribution curves related to the sun: (1) the observed solar irradiance at the top of the atmosphere (after Thekaekara, 1976); and (2) solar irradiance observed at sea level. The shaded areas represent absorption due to various gases in a clear atmosphere.
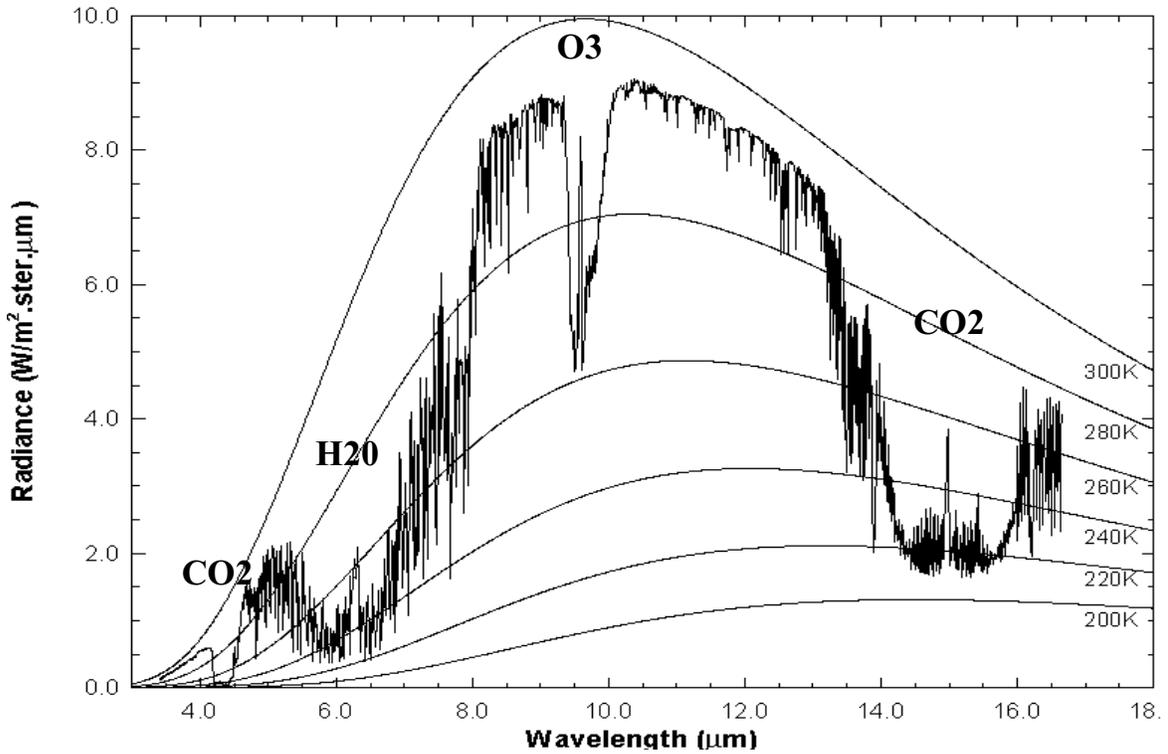
Figure 3.7: Earth-atmosphere emitted radiances overlaid on Planck function envelopes.
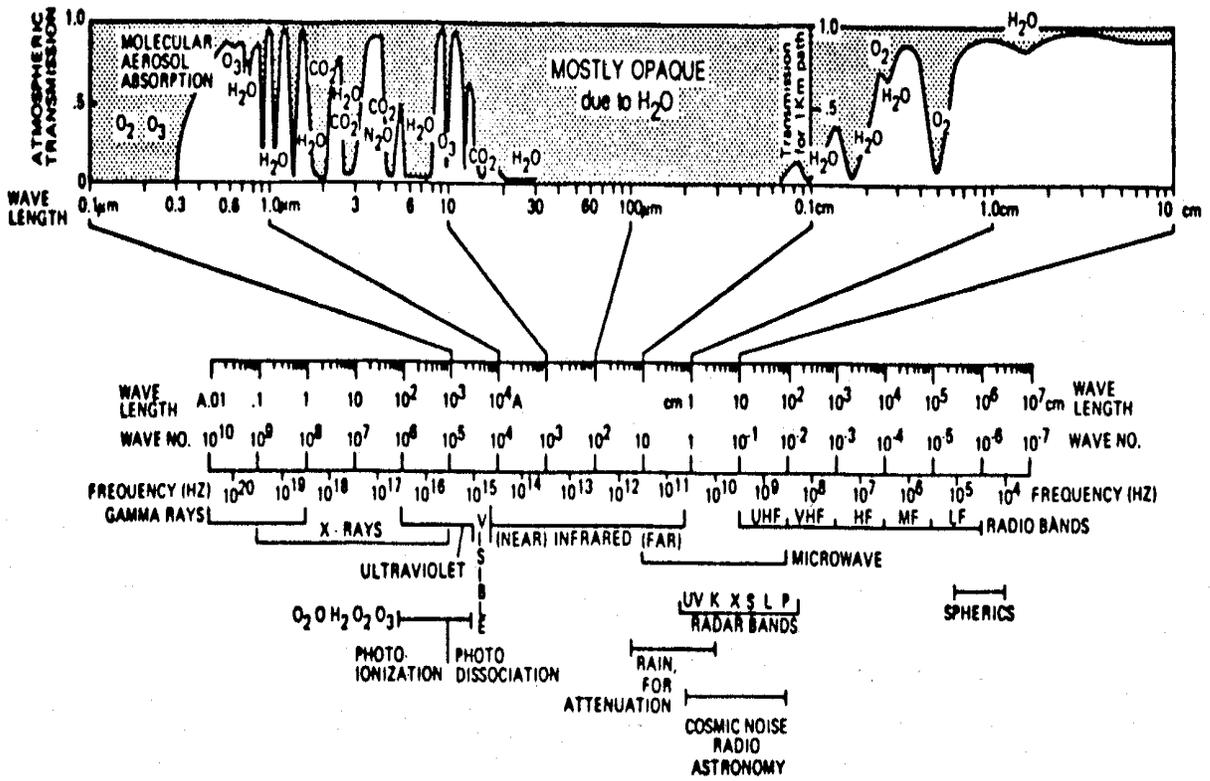
Figure 3.8a: Atmospheric transmission characteristics showing the major absorption bands.
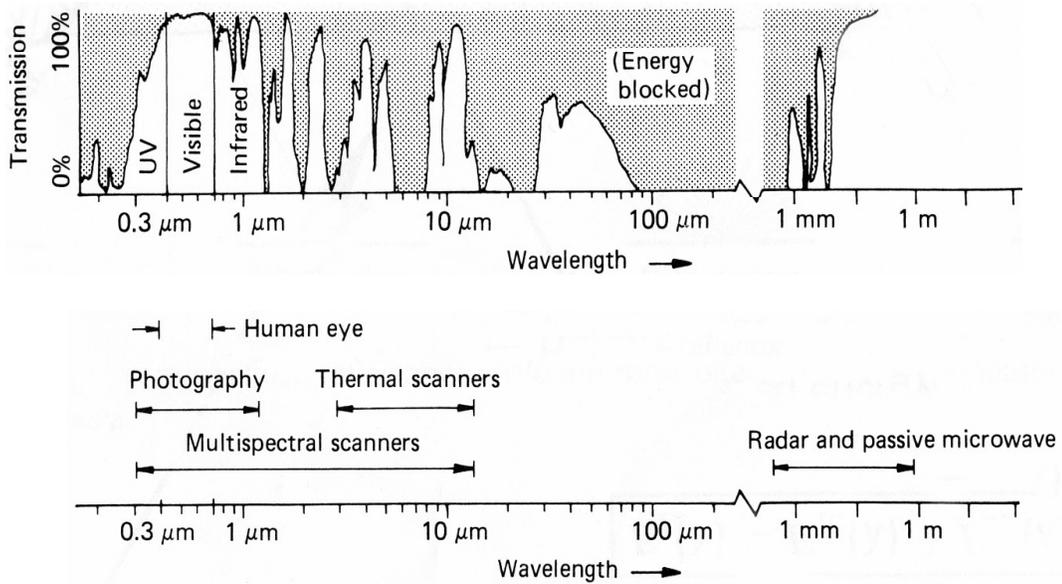
Figure 3.8b: Atmospheric transmission characteristics and the associated remote sensing technologies.
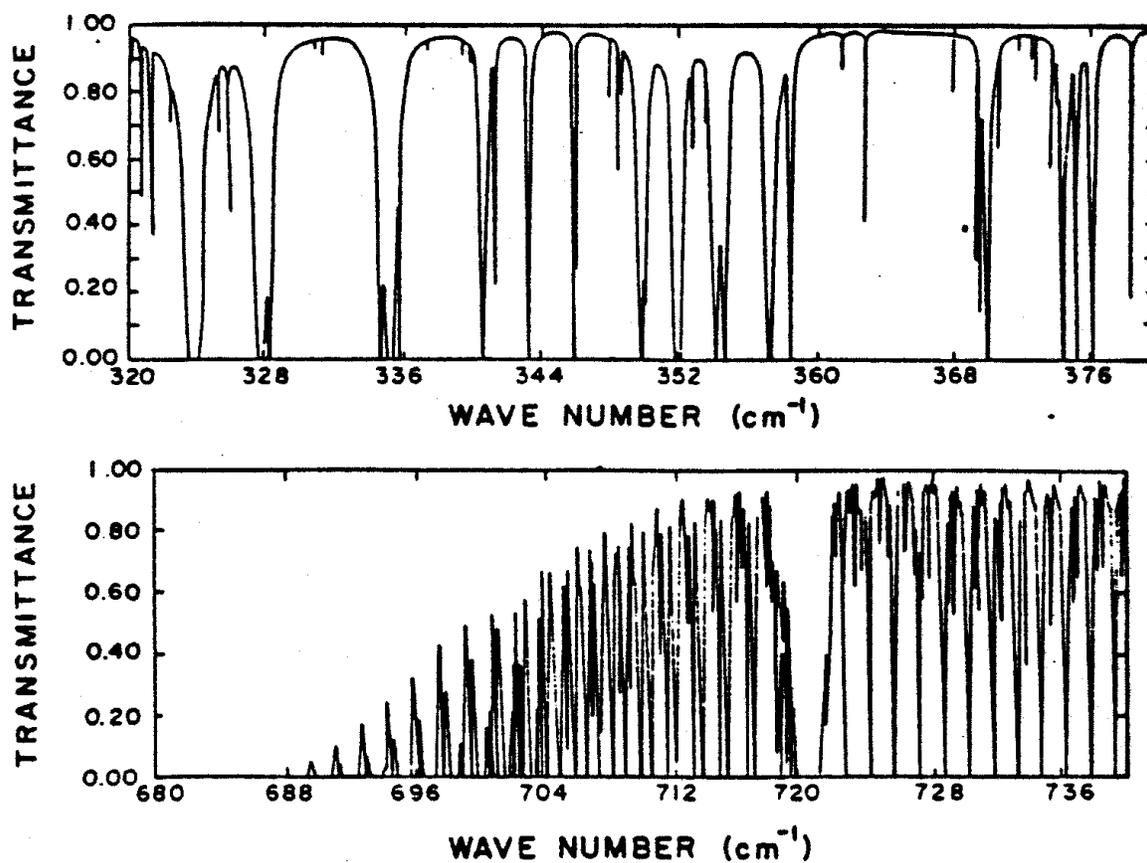
Figure 3.9: Absorption spectrum of the water vapour rotational band (beyond 18 μm) and the carbon dioxide band (near 15 μm) at high spectral resolution.

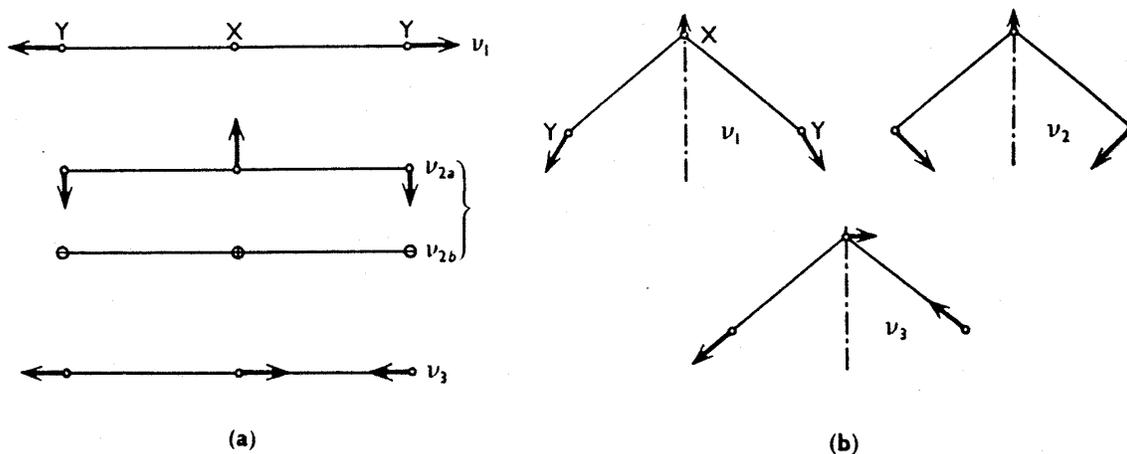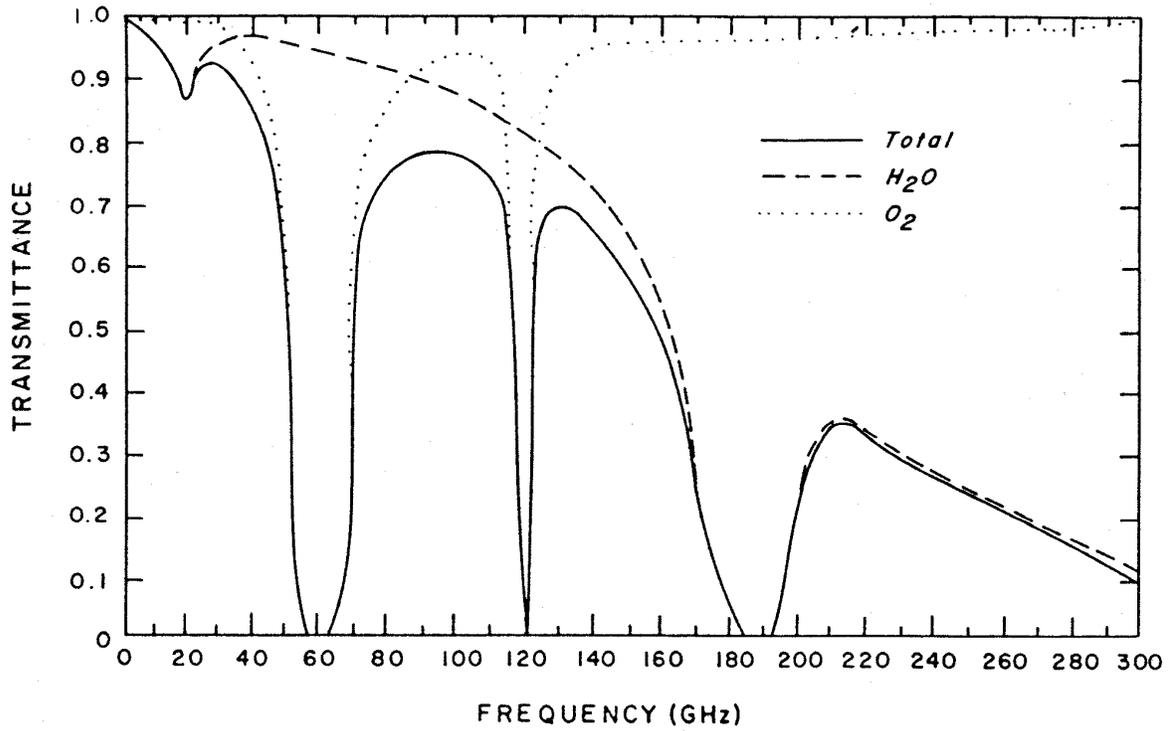**Figure 3.10**: Normal modes of a linear (a) and triangular (b) molecules.

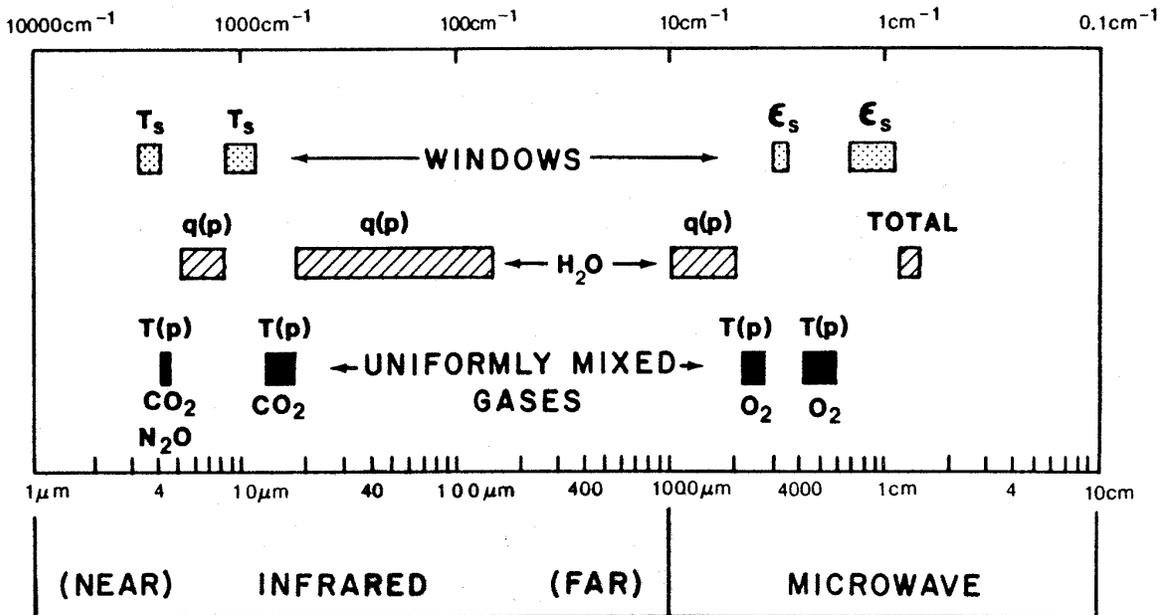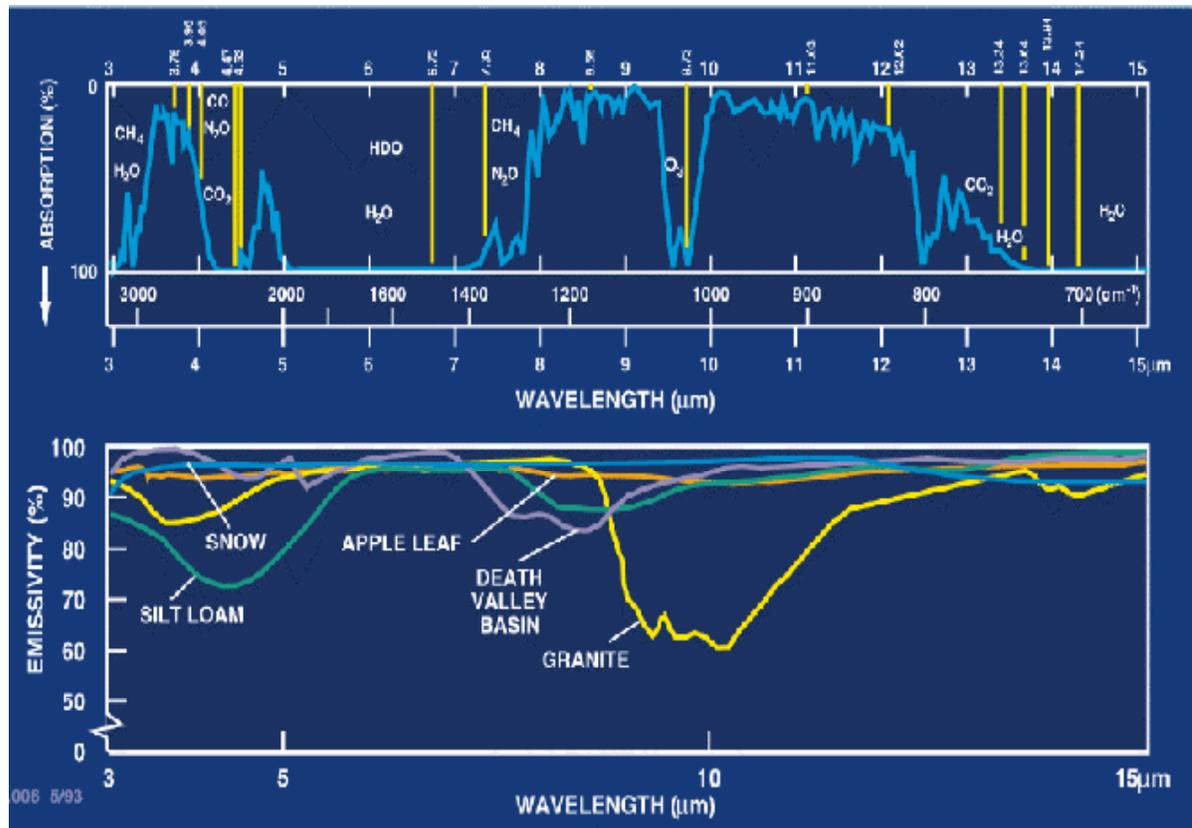**Figure 3.11**: Atmospheric transmittance in the microwave region of the spectrum as a function of frequency.

Figure 3.12: Spectral regions used for remote sensing of the earth atmosphere and surface from satellites. ε indicates emissivity, q denotes water vapour, and T represents temperature.

Figure 3.13: Infrared atmospheric absorption (top) and earth surface emissivity for some surfaces (bottom).