4

Electromagnetic Absorption and Emission by Atoms and Molecules

4.1 Photochemistry

In a photochemical process a molecule denoted AB is promoted into a usually short lived intermediate excited (highly reactive) state AB^*. Possible processes for the molecule to attaining thermochemical equilibrium are

$$\text{photolysis} \qquad AB^* \rightarrow A + B \tag{4.1}$$

$$\text{ionization} \qquad AB^* \rightarrow AB^+ + e \tag{4.2}$$

$$\text{luminescence} \qquad AB^* \rightarrow AB + h\nu' \tag{4.3}$$

$$\text{intramolecular transfer} \qquad AB^* + AB \rightarrow AB + AB^{**} \tag{4.4}$$

$$\text{intermolecular transfer} \qquad AB^* + M \rightarrow AB + M^* \tag{4.5}$$

$$\text{collisional deactivation} \qquad AB^* + M \rightarrow AB + M \tag{4.6}$$

$$\text{photochemical reaction} \qquad AB^* + M \rightarrow C_1 + C_2 \tag{4.7}$$

where B, B_1, B_2, C_1, C_2 and M denote other molecules. Following the absorption of a photon there is the possibility that more than one pathway may occur. For each process this is represented by the quantum yield which denotes the probability of a processes occurring when a photon is absorbed. The sum of the quantum yields of all process is unity. If a single process occurs then the quantum yield for that process is one.

The bond energies of several atmospheric gases whose are shown in Table 4.1 along with the photon wavelength that has the equivalent energy of the bond. For photolysis the photon must have at least enough energy to break a bond. The lowest energies capable of producing photolysis occur in the visible. Only solar photons are available in sufficient number to generate significant atmospheric photolysis.

Photolysis is usually treated as a first order process so that the rate at which a molecule is split into fragments is the product of a photolysis frequency, J, and the concentration of the molecule. Hence the rate of loss of a molecule A is expressed

$$\text{Loss Rate} = \frac{d\,[A]}{dt} = J\,[A]$$

where [A] denotes the concentration in molecules per unit volume. The photolysis rate is calculated by integrating over the portion of the solar spectrum whose photons

TABLE 4.1

Bond Energies of Some Atmospheric Gases

Bond	**Energy kJ mol^{-1}**	**Equivalent Photon Wavelength nm**
C≡C	812	147.3
C=O	728	164.3
C=C	615	194.5
O=O	498	240.2
H-H	436	274.4
H-O	464	257.8
C-H	414	289.0
C-O	360	332.3
C-C	347	344.7
Cl-Cl	244	490.3
F-F	158	757.1

TABLE 4.2

Principal Photolitic and Associated Reactions in the Earth's Atmosphere

Reaction	**Location**	**Comment**
$O_2 + h\nu \rightarrow O + O$	stratosphere	the creation of ozone
$O_3 + h\nu \rightarrow O_2 + O$	stratosphere	the balance of atomic oxygen and ozone
$O_3 + h\nu \rightarrow O_2 + O^{1D}$ $O^{1D} + H_2O \rightarrow 2OH$	troposphere	the creation of the hydroxyl radical
$NO_2 + h\nu \rightarrow NO + O$ $O + O_2 + N_2 \rightarrow O_3 + N_2$	troposphere	the creation of ozone

have sufficient energy to dissociate the molecule.

$$J = \int_{\lambda_1}^{\lambda_2} q(\lambda)\sigma(\lambda)\epsilon(\lambda)\, d\lambda$$

where $q(\lambda)$ is the photon flux, $\sigma(\lambda)$ is the absorption cross-section, $\epsilon(\lambda)$ is the quantum yield. All the terms inside the integral are dependent on wavelength but additionally the absorption cross-section is dependent on pressure and temperature; the quantum yield is dependent on temperature. The photon flux is dependent not just on the solar input but on the absorption and scattering above the level of interest and, in some case, on the light reflected back from the atmosphere/surface below.

Ionization becomes possible at shorter wavelengths e.g. NO at 135 nm.

The principal photolysis reactions are shown in Table 4.2.

4.2 Atomic Absorption

In general a molecule may carry translational, electronic, vibrational and rotational energy. As atoms in a simple monatomic gas cannot vibrate or rotate they can only carry translational energy or electronic excitation.

4.2.1 The Bohr Atom

To understand how light interacts with matter we must first recall the atomic description. In the case of the hydrogen atom *Bohr* [1913] presented a simple picture of a single electron of mass m and charge $-e$ moving in a circular orbit about a positively charged nucleus of mass M ($\gg m$) and charge $+e$. Balancing the forces on the electron gives

$$\frac{mv^2}{r} = \frac{ke^2}{r} \tag{4.8}$$

where r is the radius of the electron's orbit, v its velocity and $k = 1/4\pi\epsilon_0$. Bohr assumed that the angular momentum of the electron was quantized such that

$$mvr = \frac{nh}{2\pi} = n\hbar \tag{4.9}$$

where n is an integer ≥ 1, h is Planck's constant and $\hbar = h/2\pi$. The quantization of angular momentum means that an electron is not free to move in any orbit but must adopt given quantized orbits whose radii are given by combining equations 4.8 and 4.9, i.e.

$$r = n^2 \frac{h}{2\pi me^2 k} \tag{4.10}$$

In consequence the total energy of the electron, given by the sum of its electrostatic potential energy and its kinetic energy is also quantized, i.e.

$$\begin{aligned} E_{\text{tot}} &= E_{\text{pot}} + E_{\text{kin}} && (4.11)\\ &= -k\frac{e^2}{r} + k\frac{e^2}{2r} && (4.12)\\ &= -\frac{me^4k^2}{2n^2\hbar^2} && (4.13) \end{aligned}$$

The lowest energy state is the ground state of the atom. When the atom gains energy through the absorption of a photon the electron moves to a higher energy level and the atom is said to be in an excited state. For energy to be conserved the frequency of light, ν, absorbed by atom is

$$h\nu = E_i - E_f \tag{4.14}$$

where E_i is the total energy in the initial orbit and E_f is the total energy in the final orbit. As E_i and E_f can only have specific values their differences are can also only

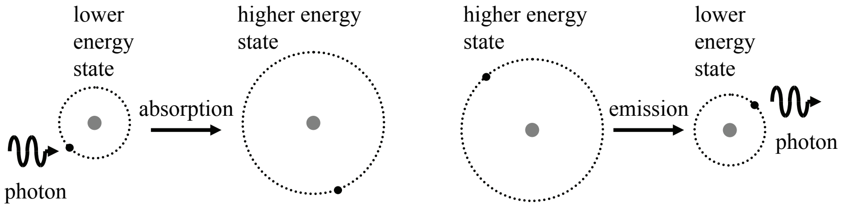


FIGURE 4.1
Electronic transitions occur through absorption or emission of a photon whose energy matches the change in energy state of the atom.

have certain values. These quantized values result in the emitted light having discrete frequencies called an emission spectrum. Conversely an atom is absorbs photons at specific frequencies corresponding to the energy change in exciting the atom from the lower to the higher energy sate. Figure 4.1 summarises the processes of absorption and emission.

4.2.2 Wave Functions

The Bohr model of an atom has long been superseded by a description that uses wave mechanics. In this approach the probability of finding the electron at coordinate $(\mathbf{r}, t)[= (r, \theta, \phi, t)]$ is proportional to the squared magnitude of the wave function, $\psi(\mathbf{r}, t)$. The wave function is a solution of Schrödinger's equation

$$-\frac{\hbar}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{4.15}$$

where V is the potential energy of the electron. The solution to this equation for the hydrogen atom is

$$\psi_n = f\left(\frac{r}{a_0}\right)\exp\left(-\frac{r}{na_0}\right) \tag{4.16}$$

where r is the radial distance from the nucleus, $f\left(\frac{r}{a_0}\right)$ is a power series, a_0 is a constant and n is the principal quantum number. The value of n is an integer in the range $[1, \infty]$. The principal quantum number governs the approximate energy and size of the orbital. The complete state of the atom is described by a further three quantum numbers l, m and s.

The orbital quantum number l determines the shape of the orbital and so the angular momentum of the electron. It can only take integer values up to one less than the principal quantum number.

The magnetic quantum number m denotes the behaviour of the electron when the atom is in a magnetic field. It can only take integral values from - l to + l.

The spin quantum number s measure the angular momentum an electron possesses. It has magnitude 1/2.

This is an example of what is called a *selection rule*. Transitions that break a selection rule are called *forbidden transitions*.

TABLE 4.3
Atomic Quantum Numbers

Name	Designation	Values
Principal	n	$1, 2, 3 \ldots$
Orbital	l	$0, \ldots (n-2), (n-1)$
Magnetic	m	$-l, -(l-1), \ldots, 0, \ldots, (l-1), l$
Spin	s	$\frac{1}{2}$

4.3 Molecular Absorption and Emission

The absorption spectrum of a molecule is substantially more complex than that of an atom as there can be transitions between energy states of the atoms that make up the molecules, and transitions between energy states associated with movement of the atoms. In the Born-Oppenheimer approximation the electronic energy E_e, the vibrational energy E_v and the rotational energy E_r of an isolated molecule are completely independent so that the total energy, E, is found from

$$E = E_e + E_v + E_r$$

Each of these energies are quantised so that the total energy can only take discrete values. It is the changes between these quantised states that gives rise to finite energy changes associated with the absorption and emission spectra of atmospheric gases. The energy associated with each change is highest for electronic transitions (1 eV), intermediate for vibrational transitions (10^{-3} eV) and lowest for rotational transitions (10^{-6} eV). Electronic changes in state, i.e. electrons changing their orbital configurations, extend from the near infrared to the ultraviolet. These high energy transitions are usually accompanied by lower energy transition so the molecular spectra have fine structure associated with vibrational and rotational transitions. Vibrational transitions and concomitant rotational changes give rise to bands in the infrared known as vibration-rotation bands. Rotational transitions alone occur at low energies in the microwave region.

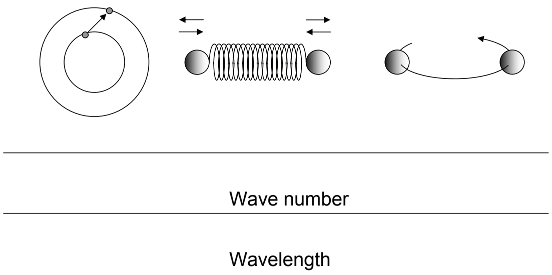


TABLE 4.4
Types of Rotator

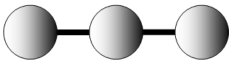
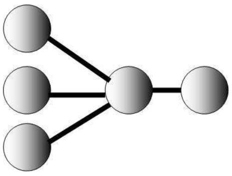
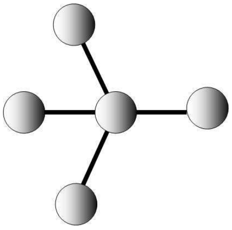
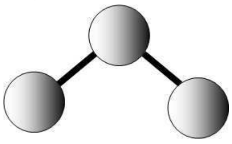
	Moments of Inertia	**Examples**
Linear Molecules 	$I_A = 0, I_B = I_C$	HCl, OCS, CO_2, N_2O, all diatomic molecules
Symmetric Tops	Prolate $I_B = I_C > I_A, I_A \neq 0$	CH_3F, NH_3, CH_3Cl, CF_3Cl
	Oblate $I_B = I_C < I_A, I_A \neq 0$	BCl_3
Spherical Tops 	$I_A = I_B = I_C$	CH_4
Asymmetric Tops 	$I_A \neq I_B \neq I_C$	H_2O, O_3

FIGURE 4.1
needs caption, check oblate & prolate

For absorption to take place the molecule must interact with the incident field of electromagnetic radiation. The gas must possess an electric dipole moment which is permanent due to the configuration of the molecule or is induced by vibration. The majority gases in the atmosphere, N_2 and O_2, do not possess electric dipole moments, nor are they generated by distortion of the molecule during vibration. Hence there are no absorption spectra due to these gases in the infrared. The trace gases H_2O, CO_2 and O_3 are more complex and possess permanent electric dipole moments or vibrationally induced ones.

4.3.1 Molecular Shape

The rotational kinetic energy of a freely rotating molecule is

$$E_r = \frac{1}{2} I_{\mathrm{x}} \omega_{\mathrm{x}}^2 + \frac{1}{2} I_{\mathrm{y}} \omega_{\mathrm{y}}^2 + \frac{1}{2} I_{\mathrm{z}} \omega_{\mathrm{z}}^2 \tag{4.17}$$

where x, y, and z are the principal axes of rotation and I_{x}, I_{y} I_{z} are the moments of inertia about each of these axes respectively. Molecules are classified according to their three moments of inertia into four categories shown in Table 4.4 and described as follows:.

Linear molecules For these molecules the moment of inertia along the inter nuclear axis is zero and is equal about the other two axes.

Symmetric top molecules These possess two moments of inertia that are equal.

Spherical symmetric top molecules One in which all three principal moments of inertia are equal.

Asymmetric top molecules Possess three different moments of inertia.

Using angular momentum about each axis instead of inertia gives

$$E = \frac{L_{\mathrm{x}}^2}{2I_{\mathrm{x}}} + \frac{L_{\mathrm{y}}^2}{2I_{\mathrm{y}}} + \frac{L_{\mathrm{z}}^2}{2I_{\mathrm{z}}} \tag{4.18}$$

The Hamiltonian for a freely rotating molecule is accomplished by replacing the angular momenta with the corresponding quantum mechanical operators. Molecules can be divided into four types of rotators based on their geometric structure and resulting moment of inertia:

4.4 Line Shape

The three factors that characterise line absorption — position $\tilde{\nu}_0$, strength S and shape $f(x)$— combine to define the **mass absorption coefficient**, as

$$k^{\mathrm{abs}}(\tilde{\nu}) = S\, f(\tilde{\nu} - \tilde{\nu}_0), \tag{4.19}$$

where $\tilde{\nu}$ is the frequency of absorbed radiation and the strength of the line is defined by

$$S = \int_0^\infty k^{\mathrm{abs}}(\tilde{\nu})\, d\tilde{\nu}. \tag{4.20}$$

TABLE 4.6
Typical Line Width needs checking

Line Broadening Process	**FWHM** **cm^{-1}**
Natural	$10^{-2} - 10^{-5}$
Doppler	$10^{-4} - 10^{-6}$
Collision at the	
Surface (~ 1000 hPa)	0.1
Tropopause (~ 300 hPa)	0.027
Stratopause (~ 1 hPa)	9.6×10^{-5}
Mesopause (~ 0.003 hPa)	2.9×10^{-7}

The term line centre is used for $\tilde{\nu}_0$ while frequencies far from the centre of the line are called the line wings. By definition the shape factor is normalized to unity, i.e.

$$\int_0^\infty f(\tilde{\nu} - \tilde{\nu}_0)\, d\tilde{\nu} = 1. \tag{4.21}$$

The broadening of lines is caused by slight changes to the energy levels involved in a transition. The three processes that give rise to broadening are, natural broadening, Doppler broadening and collision broadening. The width of the broadened line is measured by its full width at half maximum (FWHM) and typical values are shown in Table 4.6.[*] From the Table it is apparent that natural broadening is practically negligible compared to the broadening caused by collisions and the Doppler effect.

4.4.1 Natural Broadening

The emission of waves by a atom of molecule as it changes state is within a limited time. The oscillations can be described by

$$f(t) = \begin{cases} 0 & t < 0 \\ Ae^{-t/\Delta t} exp(i2\pi f t) & t \geq 0 \end{cases} \tag{4.22}$$

where Δt is an average lifetime. The Fourier transform of this function gives the frequency spectrum of the emitted radiation,

$$g(\nu) = \int_{-\infty}^{\infty} f(t)\, dt = \int_0^\infty Ae^{-t/\Delta t} e^{i2\pi\nu t} \tag{4.23}$$

$$= \frac{A}{1/\Delta t - i2\pi(\nu - \nu_0)} \tag{4.24}$$

If the average lifetime is long the decay is slow and the wave is almost monochromatic. If Δt is short then the frequency spectrum comprises a continuous interval of

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[*] As noted by *Thorne* [1988] care has to be taken as FWHM is usually the full width however sometimes it is half of this.

width $\Delta\nu$ such that

$$\Delta\nu\Delta t \geq \frac{1}{4\pi} \tag{4.25}$$

The energy contained in the wave is proportional to the square of the modulus of $g(\nu)$,

$$|g(\nu)|^2 = \frac{A}{1/(\Delta t)^2 + 4\pi^2(\nu - \nu_0)^2} \tag{4.26}$$

This function is plotted in Figure XX and shows a sharp maximum at ν_0. The line shape of a transition with only natural broadening is a Lorentzian and is the same shape as a purely pressure broadened line. The FWHM points are

$$\nu = \nu_0 \pm \frac{1}{2\pi\Delta t} \tag{4.27}$$

Hence the halfwidth of the spectral line is inversely proportional to the decay time.

This result can also be obtained from a quantum mechanical approach. The natural linewidth of an energy level is determined by the lifetime of the excited state of an atom before radiative decay. The uncertainty principle $\Delta E\Delta t \sim \hbar$ relates the life of an excited state to the precision with which the energy level can be expressed. Whereas the ground energy state has an effectively infinite lifetime so that the natural broadening is dominated by the lifetime of the excited state.

The rate of loss of atoms from an excited state j to a lesser energy state i is given by

$$-\frac{dN_j}{dt} = N_j \sum_{i=1}^{j-1} A_{ji} \tag{4.28}$$

where the A_{ji}s are the Einstein spontaneous emission coefficients for all of the radiative transitions originating from level j. Integrating this equation produces

$$N_j(t) = N_j(0)e^{-t/\tau_j} \tag{4.29}$$

where τ_j is the radiative lifetime, i.e.

$$\tau_j = \frac{1}{\sum_{i=1}^{j-1} A_{ji}} \tag{4.30}$$

Strong atomic transitions have A_{ji}s of 10^8 to 10^9 s^{-1}, so lifetimes are 1 to 10 ns, corresponding to a natural linewidth of about 10^{-3} cm^{-1}.

4.4.2 Doppler Broadening

Doppler broadening resulting from the thermal velocities of atoms and molecules. In the frame of reference of the observer there is an apparent shift in wavelength of emitted light as a function of the motion of a molecule along the line-of-sight. The higher the temperature of the gas, the larger the velocity range and the broader the line.

The line shape can be derived by considering a gas that is sufficiently rarefied so that collision are infrequent. If a molecule which has a velocity component, v_z, along the line-of-sight radiates at a frequency ν_0, then the frequency ν seen by a stationary observer is:

$$\nu = \nu_0 \left(1 + \frac{v_z}{c}\right) \tag{4.31}$$

which has the same form when expressed in terms of wavenumbers

$$\tilde{\nu} = \tilde{\nu}_0 \left(1 + \frac{v_z}{c}\right) \tag{4.32}$$

Let $p(v)\, dv$ represent the probability that the velocity of the molecule along the line of sight lies between v and $v + dv$. If the translational states are in thermodynamic equilibrium then $p(v)$ is given by the Maxwell-Boltzmann distribution according to

$$p(v_z)\, dv_z = (m/2\pi k_\mathrm{B} T)^{1/2} \exp(-m v_z^2 / 2k_\mathrm{B} T)\, dv_z, \tag{4.33}$$

where m is the mass of the molecule, k_B is the Boltzmann constant, T is the temperature. The shape of a Doppler broadened line is proportional to the probability of an emitted photon having a wavenumber in the range $\tilde{\nu} + d\tilde{\nu}$ which is found by substituting in Equation 4.32 to give

$$f_\mathrm{D}(\tilde{\nu} - \tilde{\nu}_0) \propto p(\tilde{\nu})\, d\tilde{\nu} = \frac{c}{\tilde{\nu}_0} \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{1/2} \exp\left[-\frac{m}{2k_\mathrm{B} T}\left(c\frac{\tilde{\nu} - \tilde{\nu}_0}{\tilde{\nu}_0}\right)^2\right] d\tilde{\nu} \tag{4.34}$$

The constant of proportionality in this expression is unity (see Problem 4.1) so the shape factor is

$$f_\mathrm{D}(\tilde{\nu} - \tilde{\nu}_0) = \frac{1}{\alpha_\mathrm{D} \pi^{1/2}} \exp\left[-\left(\frac{\tilde{\nu} - \tilde{\nu}_0}{\alpha_\mathrm{D}}\right)^2\right], \tag{4.35}$$

where

$$\alpha_\mathrm{D} = \frac{\tilde{\nu}_0}{c}\left(\frac{2k_\mathrm{B} T}{m}\right)^{1/2}. \tag{4.36}$$

The value of α_D is the $1/e$-width, i.e. the point at which the absorption drops to 1/e of that of the line centre. The Doppler FWHM, α'_D, is a factor $\sqrt{\ln(2)}$ greater, i.e. $\alpha'_\mathrm{D} = \sqrt{\ln(2)}\alpha_\mathrm{D}$.

4.4.3 Pressure Broadening

The interaction between emitting or absorbing atom or molecule and other particles or fields can widen and shift the transition energy levels. Processes involved include:

Impact pressure broadening: The collision of other particles with the emitting particle interrupts the emission process for a period much shorter than the lifetime of the emission process.

Quasistatic pressure broadening: In this case collisions are so frequent that the energy levels are influenced for a period much longer than the lifetime of the emission process.

Resonance broadening: Resonance broadening (self-broadening) occurs only between identical species and is confined to lines with the upper or lower level having an electric dipole transition (resonance line) to the ground state.

van der Waals broadening: Van der Waals broadening arises from the dipole interaction of an excited atom with the induced dipole of a ground state atom.

Stark broadening: Stark broadening due to charged perturbers, i.e., ions and electrons, usually dominates resonance and van der Waals broadening in discharges and plasmas.

Much fuller descriptions of these processes are provided by *Thorne* [1988] (also Goody & Yung??) and references therein.

The shape of spectral lines due to pressure broadening is given by the **Lorentz profile**,

$$f_{\mathrm{L}}(\tilde{\nu}-\tilde{\nu}_0) = \frac{\alpha_{\mathrm{L}}}{\pi((\tilde{\nu}-\tilde{\nu}_0)^2 + \alpha_{\mathrm{L}}^2)}, \tag{4.37}$$

where α_{L} is the half-width of the line and is defined by

$$\alpha_{\mathrm{L}} = \alpha_0 \left(\frac{p}{p_0}\right)\left(\frac{T_0}{T}\right)^{\frac{1}{2}}, \tag{4.38}$$

where α_0 is the half-width at standard temperature ($T_0 = 273$ K) and pressure ($p_0 =$ 1000 mb). From kinetic theory it is possible to show that the rate of collisions within a gas is proportional to $pT^{-1/2}$. Hence the width of a line is proportional to the collision frequency within the gas.

An example of the impact of line broadening is shown in Figure 4.4.3 where the increase in width associated due to a change in the gas obliterates the line structure.

The Lorentz description generally underestimates the absorption in the far wings of actual absorption lines. This is important in the atmospheric windows where the continuum absorption is composed of the contribution from many distant lines. In addition the Lorentz model fails to describe lines when $\alpha_{\mathrm{L}} \gg \tilde{\nu}_0$ i.e. when the line width is large compared to the centre frequency and the line wing is unable to extend below zero frequency. In this case, especially in the microwave, it is appropriate to use the asymmetric van Vleck-Weisskopf shape [*van Vleck and Weisskopf*, 1945] which is defined by

$$f_{\mathrm{VW}}(\tilde{\nu}-\tilde{\nu}_0) = \frac{1}{\pi}\left(\frac{\tilde{\nu}}{\tilde{\nu}_0}\right)^2 \left[\frac{\alpha_{\mathrm{L}}}{(\tilde{\nu}-\tilde{\nu}_0)^2 + \alpha_{\mathrm{L}}^2} + \frac{\alpha_{\mathrm{L}}}{(\tilde{\nu}+\tilde{\nu}_0)^2 + \alpha_{\mathrm{L}}^2}\right]. \tag{4.39}$$

Figure 4.4.3 compares the Lorenz and the van Vleck-Weisskopf line shapes.

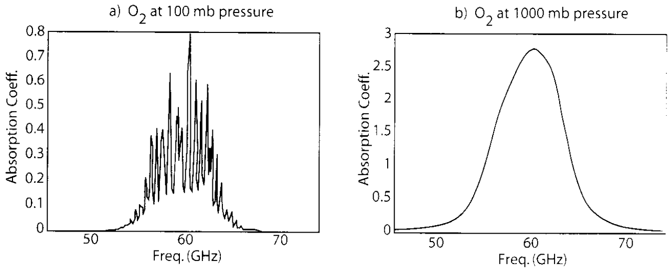


FIGURE 4.2

redo using rfm - can we show this in the ir or does it have to be the microwave?

4.4.4 The Voigt Line Shape

The Voigt line shape covers those regimes where both collision broadening and Doppler broadening contribute to the line shape. If the two process are assumed to be independent then the resultant profile is the convolution of the two line shapes i.e.

$$f_V(\tilde{\nu}-\tilde{\nu}_0) = \int_{-\infty}^{\infty} f_{\mathrm{D}}(\tilde{\nu}'-\tilde{\nu}_0)\, f_{\mathrm{L}}(\tilde{\nu}'-\tilde{\nu}_0)\, d\tilde{\nu}' \tag{4.40}$$

$$= \frac{\alpha_{\mathrm{L}}}{\alpha_{\mathrm{D}}\pi^{3/2}} \int_{-\infty}^{\infty} \frac{1}{(\tilde{\nu}'-\tilde{\nu}_0)^2+\alpha_{\mathrm{L}}^2} \exp\left[-\left(\frac{\tilde{\nu}-\tilde{\nu}'}{\alpha_{\mathrm{D}}}\right)^2\right] d\tilde{\nu}' \tag{4.41}$$

This integration has no analytic solution and must be done numerically. For small values of $\alpha_{\mathrm{L}}/\alpha_{\mathrm{D}}$ the Lorentz component determines the central part of the Voigt profile. As the Lorentz profile drops much more slowly than the Doppler profile the line wings are determined almost entirely by pressure broadening. A problem with the Voigt shape is that pressure and velocity can be correlated.

4.4.5 Comparison of Doppler and Pressure Broadening

Figure 4.4.5 shows the change in line half width as a function of altitude. Above about 60 km the collisions between molecules are so infrequent that the Doppler broadening is the dominant broadening process. As the collision half width increase with pressure, collision broad becomes the dominant process below about X km. The region in between where both process contribute to the line width is where the Voigt line shape is adopted.

The principal absorption bands of carbon dioxide and water vapour bands consist of a large number of lines which are independent (i.e. non-overlapping) broadening by collision processes only for levels in the stratosphere between ≈ 20 to 60 km in altitude. At lower levels the lines overlap substantially.

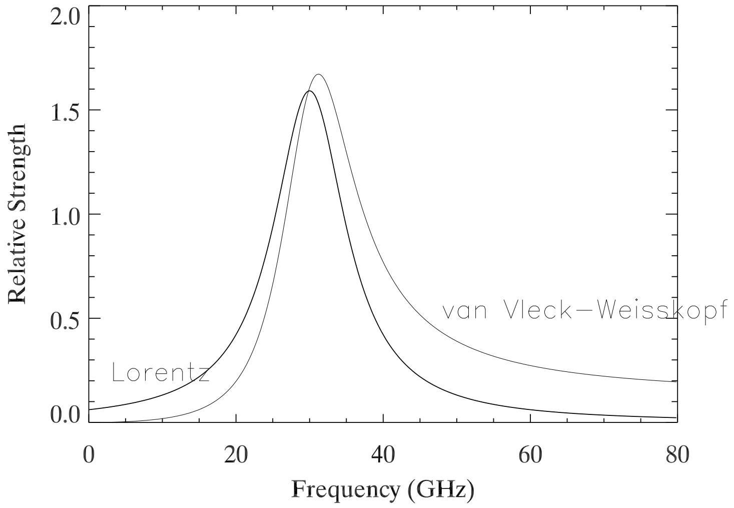


FIGURE 4.3
Comparison between the Lorenz and the van Vleck-Weisskopf line shapes. Choose actual line??

4.4.6 Continuum Absorption

The total energy of the molecule includes the translational energy which is not quantized. Therefore process that fragment a molecule can absorb a range of energies. Continuum absorption/emission has a smooth frequency dependence making it impossible to ascribe to specific molecular transitions. Continuum absorption/emission is most apparent in the windows regions to be less transparent than predicted by discrete molecular absorption alone. The processes identified giving rise to continuum absorption/emission are

Photoionization Absorption occurs when the photon has enough energy to strip an electron completely from an atom or molecule. Ionization require a large amount of energy so that it primarily occurs from X-ray and gamma radiation. Although the ionization requires a discrete amount of energy any excess energy carried by the photon can be absorbed as part of the kinetic energy of the ion or electron. As translational kinetic energy is not quantised there is no constraint on the energy of the photon.

Photodissociation Sufficiently energetic electrons can also dissociate a molecule into two pieces. In this case the photon must have at least the of the chemical bonding energy. Any energy in excess of this appears in the unquantised kinetic energy of the fragments.

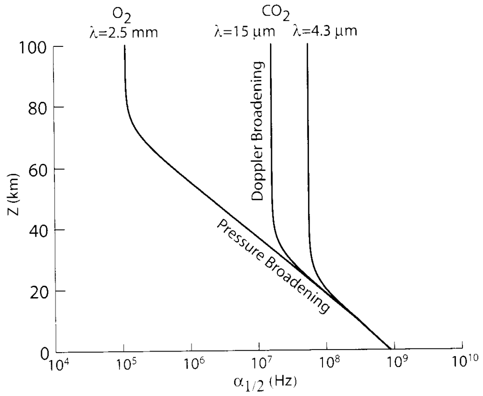


FIGURE 4.4

show two bands say then on right show the transmission over 1km horizontal path i.e. can resolve lines high up but not lower down

Wing absorption absorption/emission. One is that it is due to the residual effects of the far wings of strong lines which are not accurately modelled. If there are many strong lines some distance away (in frequency) the effect of the individual lines can accumulate.

Polymer absorption the interaction is caused by molecular polymers (e.g. water vapour dimer) which being large floppy molecules might be expected to have broad transitions and hence broad spectral features.

■ check ■

4.5 Radiative Penetration of the Earth's Atmosphere

4.5.1 Atmospheric Windows

The depth of penetration of Sunlight into the atmosphere or the escape of terrestrial radiation to space is determined by the energy loss through scattering or absorption within the atmosphere. Figure 4.6 shows the absorption of the atmosphere as a function of wavelength for a number of radiatively important gases. In general each region of absorption by a particular gas is made up of many individual lines.

The first observation to make on Figure 4.6 is that a number of gases contribute to make the atmosphere opaque to radiation with the exception of a few transparent regions called atmospheric windows. The principal of these are

- the visible window

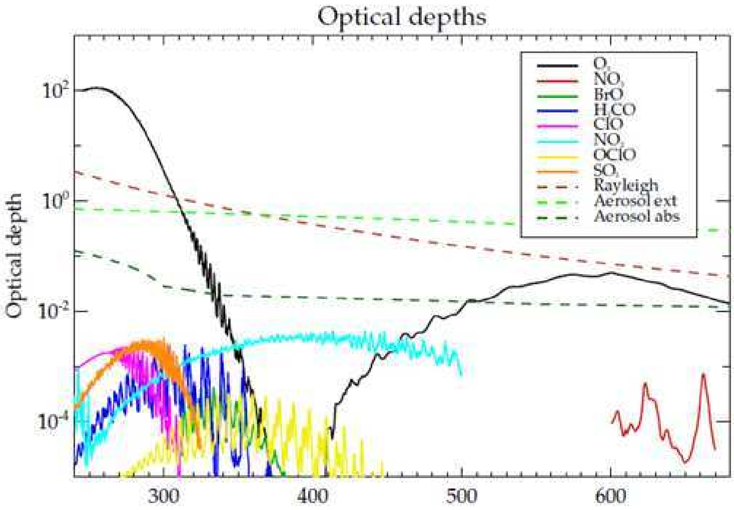


FIGURE 4.5
Optical depth in shortwave.

- the infrared window from about 7 to 13 μm which is interrupted by a strong O_3band centred at about 9.6 μm.

In addition there are many trace gases that have very little contribution to the total atmospheric absorption but have to be included because the gas has spectral features that dominate a very narrow waveband. This feature is shown in Figure 4.8 where successive increase of resolution at about 12 μm releals the contribution by individual lines.

■ go further to 200 um ■

photo ionization - ionosphere Transmission of the atmosphere is cut off at short wavelengths by o2 and o3 through the visible there are weak h2o bands

A band of o2 at 760 nm also at 1.27 um water vapour most important absorber in the infrared

atmospheric window at about 3-5 um and 8 - 14 um. co2 at 4.3 um ch4 at 3.3 o3 at 9.6

4.5.2 O_2

At wavelengths less than 1 um bands of O_2 are caused by electronic transitions. Figure 4.5.2 shows the absorption cross section for O_2 below 250 nm. O_2 consists of a band system overlying a continuum 220 - 300 nm

at about 220 Schumann-Runge

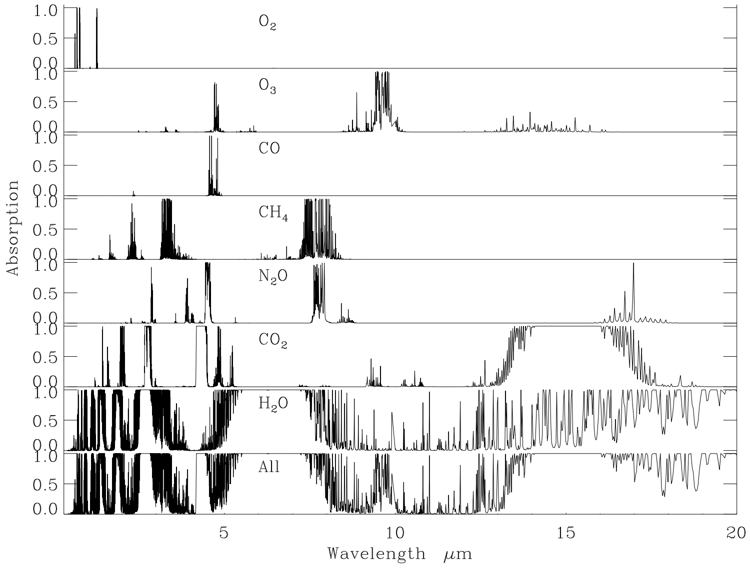


FIGURE 4.6
Spectral absorption for a vertical path from the surface to the top of the atmosphere.

4.5.3 O_3

At wavelengths less than 1 um bands of O_3 are caused by electronic transitions. Figure 4.5.3 shows the principal shortwave ozone bands centred at 250 nm, 320 nm and 600 nm.

gases that matter h20 co2 o3 n2o co and ch4 then no so2 and no2

4.6 Spectroscopic Data Bases

Most complete and widely used HITRAN 1992 edition lists 709, 308 lines species? wavelength range.

Problem 4.1 By using the normalization criterion defined in Equation 4.21 show that the constant of proportionality in Equation 4.34 is unity.

Additional Reading

Atkins, P., and R. S. Friedman, *Molecular Quantum Mechanics*, Oxford University Press, New York, 2005.
Banwell, C. N., and E. M. McCash, *Fundamentals of Molecular Spectroscopy*, McGraw-Hill, Maidenhead, 1994.
Thorne, A., *Spectrophysics: Principles and Applications*, Springer, Berlin, 1988.

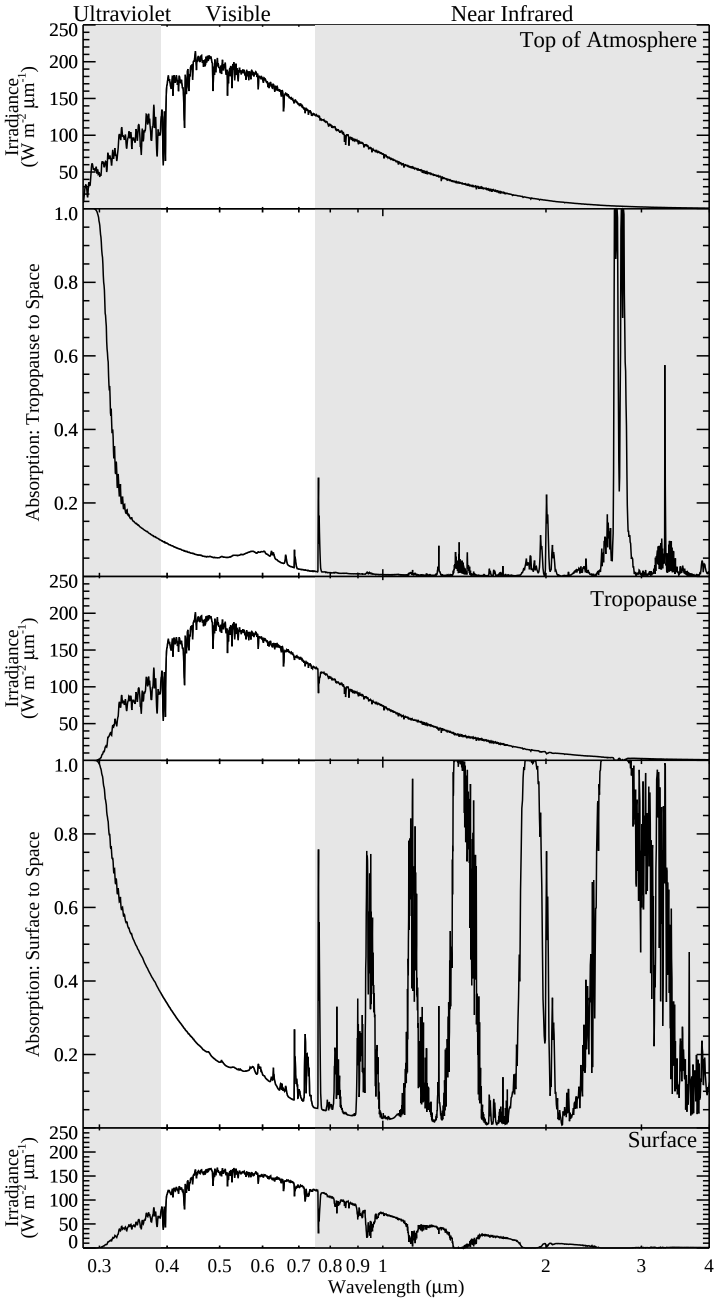


FIGURE 4.7
Spectral absorption for a vertical path from the surface to the top of the atmosphere.

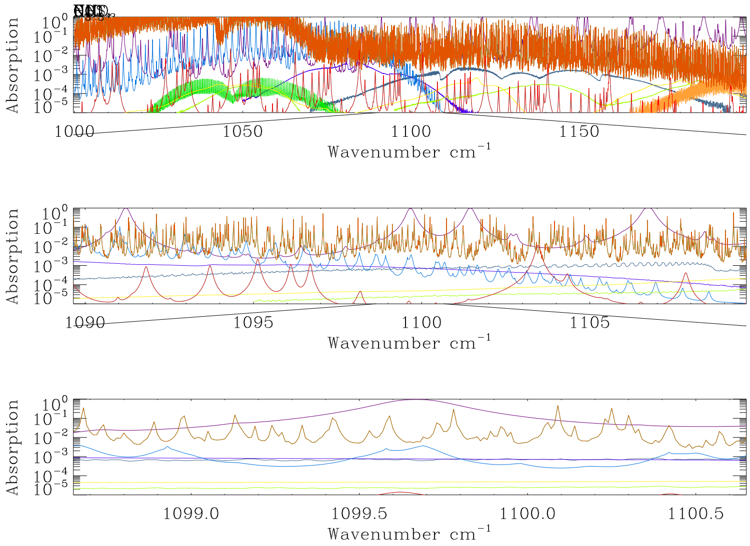
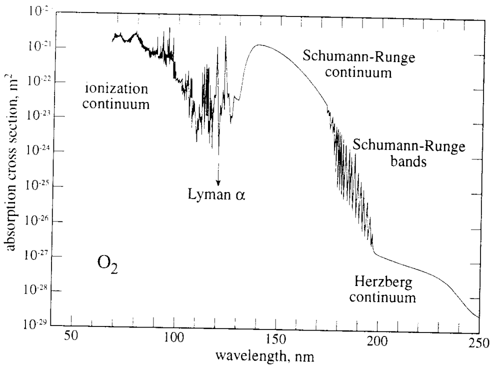
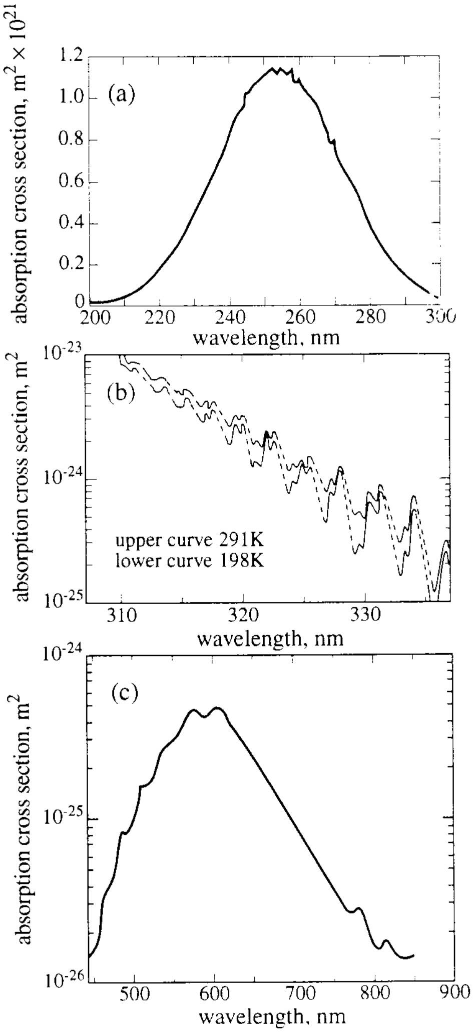


FIGURE 4.8
Spectral absorption for a vertical path from the surface to the top of the atmosphere.




(a)
absorption cross section, m^2 × 10^{21}
1.2
1.0
0.8
0.6
0.4
0.2
0
200
220
240
260
280
300
wavelength, nm
(b)
absorption cross section, m^2
10^{-23}
10^{-24}
10^{-25}
upper curve 291K
lower curve 198K
310
320
330
wavelength, nm
(c)
absorption cross section, m^2
10^{-24}
10^{-25}
10^{-26}
500
600
700
800
900
wavelength, nm