# **Basic Environmental Spectroscopy**

The earth and its life are intimately connected to the intensity and colours of the solar light as it reaches the atmosphere, is transmitted and finally arrives at the surface of the earth. Furthermore, in the environmental sciences measurements often result in a spectrum, which comprises the intensity of waves as a function of wavelength or frequency. In this chapter we discuss what every physicist should know about the solar spectrum, which is the type of information contained in it. As an example we discuss the role of ozone in the upper atmosphere. In Chapter 7 we will discuss in more detail how to interpret spectral data and how to draw conclusions.

### 2.1 INTRODUCTION TO THE SOLAR SPECTRUM

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Light reaching the earth from the sun is essential for life. The detailed balance between the inflow and outflow of solar energy establishes the temperature of the earth's surface. The absorption of solar light by the photosynthetic pigments drives a unique energy conversion process that enables plants, algae and a variety of photosynthetic bacteria to store solar energy into chemical free energy for later use.

The photosynthetic process has been the basis for all fossil fuels present on earth and provides mankind with food and shelter. The development of artificial photosynthesis may be a way of coping with the energy crisis in the long run. Figure 2.1 shows the solar emission spectrum and how it overlaps with the absorption spectra of a variety of pigments, which play a role in photosynthesis.

The solar light that arrives on the earth's surface is composed of a wide range of frequencies characteristic for (a) the emitter, the sun, (b) specific elements at the solar surface, and (c) the composition of the atmosphere, since the light is partly absorbed by the earth's atmosphere. Similarly, light reflected by the atmosphere or by the earth's surface and detected by a satellite contains information about their chemical composition.

It is well known that the presence of ozone  $(O_3)$  in the atmosphere protects the earth from harmful solar UV radiation by the absorption of all light with a wavelength less than 295 nm. Decrease of the  $O_3$  layer will not only increase the amount of UV light at a particular wavelength but it will also allow the transmission of increasingly shorter wavelength radiation. This implies that important biomolecules such as DNA



**Figure 2.1** The solar spectrum as it reaches the top of the atmosphere. It overlaps with the absorption by the important pigments of a variety of photosynthetic organisms. Chlorophyll-*a*, the major pigment of higher plants, algae and cyanobacteria, absorbs red and blue light. In combination with carotenoids (such as  $\beta$ -carotene) they provide plants with their typical green colour. The major photosynthetic organisms of the world oceans, the cyanobacteria, absorb sunlight by a specialized pigment containing protein, the phycobilisome, which contains as major pigments phycoerythrin (±580 nm), phycocyanin (±620 nm) and allophycocyanin (±650 nm). All the light energy absorbed by the pigments can be used for photosynthesis. Bacteriochlorophyll-*a* and bacteriochlorophyll-*b* are the major pigments of two classes of photosynthetic bacteria absorbing in the near infrared part of the spectrum

and proteins, which were well protected against solar photons, may be increasingly damaged in the future.

Finally, the earth does not only absorb and reflect light, but it is also a light emitter. The emission is that of a black body at 288 K and therefore peaks far in the infrared (Fig. 1.2). The earth's energy balance is based on the emission and partial absorption of this infrared light and any change in any of these processes may disturb the balance. Since  $CO_2$  shows few strong absorption bands for infrared light, its presence in the atmosphere is of crucial importance in regulating the energy balance.

All the above-mentioned physical phenomena are intimately related to the field of atomic and molecular spectroscopy. Why are specific colours of the light emitted or absorbed by atoms and molecules? Can we quantify the amount of absorption? Is an absorption band narrow or wide and what does this imply? Can we quantify the changes in the atmospheric transmission spectrum due to changes in  $O_3$  and  $CO_2$  concentration (or the presence of other gases)? How do we quantitatively analyse the data accumulated by satellites or by detection from the earth's surface? Of a more fundamental nature are questions related to the solar energy conversion by photosynthesis and the design of artificial photosynthetic systems.

Since answering these questions requires a basic understanding of the interaction of light with matter and some knowledge of the terminology of spectroscopy we shall

#### INTRODUCTION TO THE SOLAR SPECTRUM

introduce the necessary concepts. For a more quantitative treatise of many of the theories discussed in this chapter, we refer to some general sources on spectroscopy [1-4] and to Chapter 7. We shall finish this chapter with a short discussion of the O<sub>3</sub> problem as viewed from spectroscopy.

#### 2.1.1 BLACK BODY RADIATION

A black body, by definition, absorbs all thermal radiation falling on it; the body absorbs and emits electromagnetic radiation without favouring particular frequencies. In first-order approximation the sun may be considered as a black body radiating at 5800 K. The intensity and spectral properties of the light emitted by a black body were originally described by the Stefan–Boltzmann law and Wien's law (1894). The Stefan–Boltzmann law formulates how the total energy emitted by a black body relates to the temperature by

$$I(T) = \sigma T^4 \tag{2.1}$$

where *I* would be the energy per unit area emitted per second by the black body through a pinhole in its surface, *T* is the absolute temperature and  $\sigma$  is the Stefan–Boltzmann constant, which is independent of the material. With the numerical value given in Appendix C one finds that 1 cm<sup>2</sup> of a black body at a temperature of 1000 K radiates about 5.7 W.

Wien's displacement law shows how the maximum of the energy distribution of black body radiation depends on the temperature by

$$\lambda_{\max} T = \text{constant} \tag{2.2}$$

with the constant on the right-hand side equal to  $2.898 \times 10^{-3}$  mK. For instance, a black body at 6000 K will emit maximally at 500 nm.

In the beginning of the twentieth century Rayleigh attempted to calculate the spectral distribution of a radiating black body from classical physical theory. His result, as formulated by Jeans, is given by

$$\mathrm{d}U = \frac{8\pi\nu^2 kT}{c^3} \,\mathrm{d}\nu \tag{2.3}$$

where dU is the energy density in the frequency interval between v and v + dv, k is the Boltzmann constant and c is the speed of light. The energy distribution that this law predicts is not realistic, as it leads to infinite energy density at high frequencies and is in total disagreement with Wien's displacement law.

Planck solved the problem in a historic contribution to the emerging quantum mechanics field by making the assumption that the energy of an oscillator of the electromagnetic field is not continuously variable, but is restricted to integral multiples of the energy hv, where hv is called a quantum of energy and h is Planck's constant. Thus, Planck arrived at the Planck energy distribution:

$$dU = \frac{8\pi h\nu^3}{c^3} \left(\frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}\right) d\nu$$
 (2.4)

In the limit  $\nu \to 0$ , eq. (2.4) leads to the Rayleigh–Jeans law (2.3), while for  $\nu \to \infty$  we obtain Wien's law (2.2). Note that eq. (2.4) refers to an energy density. Usually one

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is more interested in the emitted energy  $I_{\nu} d\nu$  passing a m<sup>2</sup> per second with frequencies between  $\nu$  and  $\nu + d\nu$ . This quantity is found from eqs. (2.3) or (2.4) by multiplication with c/4. The energy flux  $I_E dE$  is the energy between  $E = h\nu$  and  $E + dE = h\nu + d(h\nu)$ , which passes a m<sup>2</sup> per second (in J m<sup>-2</sup> s<sup>-1</sup>). It is found as  $I_E = I_{\nu}/h$ :

$$I_E \,\mathrm{d}E = \frac{2\pi\nu^3}{c^2} \frac{1}{\mathrm{e}^{h\nu/kT} - 1} \,\mathrm{d}E \tag{2.5}$$

The function  $I_E$  has dimensions  $m^{-2} s^{-1}$  and is shown in Fig. 4.30. When we divide by  $h\nu$  we get the photon flux  $N_E dE$ , which is the number of photons (in  $m^{-2} s^{-1}$ ) with energies between E and E + dE.

### 2.1.2 THE EMISSION SPECTRUM OF THE SUN

Figure 2.2 shows the emission spectrum of the sun, both measured outside the earth's atmosphere and measured at the earth's surface. In addition, the spectral shape for black body radiation, as given by eq. (2.4) at a temperature of 5900 K is shown. The dotted areas in Fig. 2.2 indicate the specific contributions of the atmospheric gases to the absorption of solar radiation. We note the contribution of  $O_3$  to the absorption of UV light between 0.2 µm and 0.3 µm, the strong absorption of H<sub>2</sub>O in the near infrared and the strong infrared transitions of CO<sub>2</sub>.

Figure 2.3a shows the transmission curve of the atmosphere measured over a horizontal distance of 1.8 km at sea level which is equivalent to the vertical atmosphere



**Figure 2.2** Spectral distribution of incident solar radiation outside the atmosphere and at sea level. Major absorption bands of some of the important atmospheric gases are indicated. (Reproduced by permission of McGraw-Hill from [5], Fig. 16.1. The emission curve of a black body at 5900 K is shown for comparison, with its peak adjusted to fit the actual curve at the top of the atmosphere

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Figure 2.3 Absorption properties of the earth's atmosphere and of some of its major constituents in the infrared region of the spectrum. (a) Horizontal absorption spectrum measured over a distance of 1800 m at sea level. (Reproduced from [6], Fig. 4.6, p. 140.) (b) Vertical absorption spectrum of the earth's atmosphere and absorption of individual compounds. (Reproduced with permission of 'Les Editions Physique' from [7], Fig. 4,

(it has the same optical density, to be introduced in eq. (2.30)). Note the many and strong contributions of H<sub>2</sub>O and O<sub>2</sub> extending far into the infrared with the complete cut-off of IR radiation by CO<sub>2</sub> for  $\lambda > 14 \mu m$ . This latter aspect is further emphasized by the spectra of some of the individual atmospheric gases shown in Fig. 2.3b.

These spectra clearly demonstrate that the spectral distribution and intensity of sunlight reaching the earth's surface are to a large extent determined by the absorption and light scattering properties of the earth's atmosphere. Similarly, the amount of light absorbed by the earth's surface in a certain frequency interval is determined by the distribution and spectral properties of the pigments of the vegetation and the scattering properties of the surface.

To obtain a basic understanding of these phenomena we shall proceed to discuss the interaction of light with matter and overview the spectral properties of atoms and molecules in Section 2.2.

### 2.2 INTERACTION OF LIGHT WITH MATTER

When light impinges on a medium containing a variety of atoms and/or molecules a number of processes may occur. First of all, due to the interaction between the electromagnetic wave and the matter, energy may be absorbed or released. We will derive the equations governing the process, which lead to the well-known Einstein coefficients. Then we introduce the concept of optical density of a medium in connection with Lambert–Beer's law. Finally, we apply these concepts to the ozone layer in the atmosphere.

### 2.2.1 THE TRANSITION ELECTRIC DIPOLE MOMENT

Consider an atomic or molecular system with discrete energy levels  $E_k$  and wave functions  $\Psi_k^0$ , which are the unperturbed solutions of the time-independent Schrödinger equation of the system [8]

$$H_0 \Psi_k^0 = E_k \Psi_k^0 \tag{2.6}$$

with  $H_0$  the Hamiltonian that describes the system. By switching on light with frequency  $\omega$  we introduce a perturbation  $H_1(t)$ , which starts to mix the eigenfunctions  $\Psi_k^0$ . After some time t the system will be found in a state  $\Psi(t)$ , which is now a solution of the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = (H_0 + H_1(t))\Psi(t) \tag{2.7}$$

For a complete set of eigenfunctions  $\Psi_k^0$  the time-dependent wavefunction  $\Psi(t)$  can be expressed as

$$\Psi(t) = \sum_{k} c_k(t) \Psi_k^0 e^{-iE_k t/\hbar}$$
(2.8)

Insertion of this expression into eq. (2.7) yields a set of equations for the time derivatives of the coefficients  $c_k$  (t), given by

$$\frac{\mathrm{d}c_k(t)}{\mathrm{d}t} = -\frac{i}{\hbar} \sum_n c_n(t) \,\mathrm{e}^{i\omega_{kn}t} \langle \Psi_k^0 | H_1 | \Psi_n^0 \rangle \tag{2.9}$$

with  $\omega_{kn} = (E_k - E_n)/\hbar$ .

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Taking  $\Psi_1^0$  as the initial state, at t = 0 we have  $c_1(0) = 1$  and  $c_k(0) = 0 (\forall k \neq 1)$ . This allows us to integrate eq. (2.9) for a time sufficiently short that  $c_k(t) \approx 0 (\forall k \neq 1)$  and  $c_1(t) \approx 1$ , which yields

$$c_k(t) = -\frac{i}{\hbar} \int_0^t e^{i\omega_{k1}t'} \langle k|H_1|1\rangle \,\mathrm{d}t'$$
(2.10)

The probability of finding the atomic or molecular system in the excited state k, thereby having absorbed a quantum  $\hbar \omega_{k1}$  from the light beam, is given by  $|c_k(t)|^2$ . Equation (2.10) shows that  $|c_k(t)|^2$  is directly related to the quantity  $|\langle k|H_1|1\rangle|^2$ . To obtain a useful expression for the transition probability we have to find the form of the perturbation  $H_1(t)$ .

An electromagnetic light wave is described by in-phase oscillating, perpendicular electric ( $\mathbf{E}(t)$ ) and magnetic ( $\mathbf{B}(t)$ ) fields, that both obey a scalar wave equation, provided that the velocity of the electromagnetic wave is  $u = (\varepsilon \mu)^{-1/2}$ . For a linearly polarized wave the electric field is given by:  $\mathbf{E}(t) = \mathbf{E}_0 \cos \omega t$ , where we have assumed that our atom/molecule is in the origin of the coordinate system and that the atomic/molecular dimensions are much smaller than the wavelength  $\lambda$ . The response of the atom/molecule will be dominated by the interaction of the electric field with the electronic charge distribution. For electrically neutral molecules/atoms the leading term is the electric dipole and thus

$$H_1(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t) \tag{2.11}$$

where the electric dipole operator  $\boldsymbol{\mu} = \sum_{i} q_i \mathbf{r}_i$ , in which the sum is taken over all electronic charges  $q_i$  at positions  $\mathbf{r}_i$ .

Substitution of eq. (2.11) into eq. (2.10), writing  $\cos \omega t'$  as the sum of two exponentials, performing the integration and calculating the probability  $P_k(t) = |c_k(t)|^2$  that the system is in the state k at time t yields

$$P_k(t) = \frac{1}{\hbar^2} |\langle k|\mu|1\rangle|^2 \frac{|\mathbf{E}_0|^2 \cos^2\theta \sin^2\frac{1}{2}(\omega_{k1} - \omega)t}{(\omega_{k1} - \omega)^2}$$
(2.12)

where we have assumed that the frequency of the light is close to the resonant frequency of the transition  $1 \rightarrow k$ , and with  $\theta$  the angle between the vectors  $\mu$  and  $E_0$ .

In eq. (2.12) we see that the quantity

$$|\boldsymbol{\mu}_{k1}|^2 = |\langle k|\boldsymbol{\mu}|1\rangle|^2 \tag{2.13}$$

determines the probability  $P_k(t)$ : the larger  $|\boldsymbol{\mu}_{k1}|^2$ , the larger  $P_k(t)$  and the stronger the transition  $1 \rightarrow k$  in the absorption spectrum. The quantity  $\boldsymbol{\mu}_{k1}$  is called the *transition dipole moment*. Note that the rate of light absorption due to the transition  $1 \rightarrow k$  also depends on the orientation of  $\boldsymbol{\mu}_{k1}$  relative to the electric field vector  $\mathbf{E}_0$  by the term  $\cos^2 \theta$ . For isotropic solutions or gases we will have to average over all possible orientations of  $\boldsymbol{\mu}_{k1}$  relative to  $\mathbf{E}_0$ . For an ordered system eq. (2.12) leads to polarization effects.

The transition probability  $P_k(t)$  as expressed in eq. (2.12) shows a marked frequency dependence, which in addition depends on time. Intuitively we would like to associate the absorption of light energy to a 'rate' (a number of events per second) and this requires that the probability  $P_k(t)$  is a linear function of the time t. A closer inspection

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of eq. (2.12) shows that as time proceeds the function  $P_k(t)$  becomes sharply peaked around  $\omega = \omega_{k1}$ . If we further realize that in a normal spectroscopic experiment the incident light is far from monochromatic, it is more appropriate to sum eq. (2.12) over a band of frequencies. This directly leads to the rate of population of level k:

$$\frac{\mathrm{d}P_k}{\mathrm{d}t} = \frac{\pi}{3\varepsilon_0\hbar^2} |\boldsymbol{\mu}_{k1}|^2 W(\omega) \equiv B_{1k}W(\omega) \tag{2.14}$$

where  $W(\omega)$  represents the (time-averaged) energy density of the incident electromagnetic field at frequency  $\omega$ . Note that we have averaged eq. (2.12) over all possible orientations of  $\mathbf{E}_0$  relative to  $\mu_{k1}$ , which in three-dimensional space gives a factor 1/3 as the average over  $\cos^2 \theta$ .

The quantity  $B_{1k} = \pi |\mu_{k1}|^2 / 3\varepsilon_0 \hbar^2$  is known as the Einstein coefficient for absorption and is directly related to the extinction coefficient measured in an absorption experiment.

#### 2.2.2 THE EINSTEIN COEFFICIENTS

In this section we will derive a simple relation between the rates of absorption, stimulated emission and spontaneous emission in an atomic or molecular system, schematically depicted in Fig. 2.4. For simplicity we assume that two energy levels exist,  $E_1$  and  $E_2$ , populated by  $N_1$  and  $N_2$  atoms or molecules respectively. Three possible radiative processes which connect levels 1 and 2 are indicated. Absorption and stimulated emission only occur with the light on and their rates (2.14) are summarized by  $B_{12}W(\omega)$  and  $B_{21}W(\omega)$  respectively, in which  $B_{12}$  is the Einstein coefficient for absorption and  $B_{21}$  the Einstein coefficient for stimulated emission. We define  $A_{21}$ as the Einstein coefficient for spontaneous emission from level 2 to level 1 which may also occur in the dark.

For the rate of population of level 1 we have

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = -B_{12}WN_1 + B_{21}WN_2 + A_{21}N_2 \tag{2.15}$$

Assuming a steady state, i.e.  $dN_1/dt = 0$ , it directly follows that

$$W(\omega) = \frac{A_{21}}{B_{12}(N_1/N_2) - B_{21}}$$
(2.16)



**Figure 2.4** The three basic radiative processes. Indicated are the Einstein coefficients and the transition rates for two levels with energies  $E_1$  and  $E_2$  respectively and occupation  $N_1$  and  $N_2$  respectively

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If we now take the situation that there is no external radiation field and that the system is in thermal equilibrium at a temperature T, then the ratio  $N_1/N_2$  follows from the Boltzmann distribution between states of different energies

$$\frac{N_1}{N_2} = e^{\hbar\omega/kT} \tag{2.17}$$

Under these conditions the energy density frequency distribution is given by Planck's radiation law (2.4), in which it has already been averaged over polarizations. If we change (2.4) to the variable  $\omega$  and keep in mind that the density differs by a factor  $2\pi$ , because of  $d\omega = 2\pi d\nu$  we find:

$$W(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{\mathrm{e}^{\hbar\omega/kT} - 1}$$
(2.18)

Since (2.18) should be identical to (2.16) it follows from eq. (2.17) that

$$B_{12} = B_{21} \tag{2.19}$$

$$\frac{A_{21}}{B_{21}} = \frac{\hbar\omega^3}{\pi^2 c^3} \tag{2.20}$$

From eq. (2.14) we deduce  $B_{12}$  and we obtain

$$A_{21} = \frac{\omega^3}{3\pi c^3 \hbar \varepsilon_0} |\mu_{21}|^2 \tag{2.21}$$

The importance of this result is that the same quantity  $|\mu_{21}|^2$  determines the rates of all radiative processes and consequently common selection rules apply to them.

#### 2.2.3 LAMBERT-BEER'S LAW

The microscopic quantities  $\mu_{21}$ ,  $B_{12}$ ,  $B_{21}$  and  $A_{21}$  are connected to the macroscopic phenomenon of absorption by Lambert-Beer's law. When a beam of light passes through a sample of material, the light beam is usually absorbed, but sometimes amplified (in a laser). Absorption dominates when most of the atoms/molecules are in their ground states ( $N_1 \gg N_2$ ) and when the intensity of the light beam is weak. In that case the rate equation (2.15) for transitions between states 1 and 2 is given by

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = -B_{12}N_1W(\omega) + A_{21}N_2 \tag{2.22}$$

Here  $B_{12}N_1W$  is the rate at which light energy is removed from the incident light beam. Let the light beam be propagated along the z axis. Since the beam is attenuated its energy W will be a function of z. Consider now a small slice of thickness dz and surface a as illustrated in Fig. 2.5. The amount of beam energy in this slice in the frequency interval  $\omega$  and  $\omega + d\omega$  is given by  $W d\omega a dz$ . It then follows from energy conservation that the rate of decrease of the beam energy equals the rate at which the light energy is removed from the beam by absorption. We find

$$-\frac{\partial W}{\partial t} \,\mathrm{d}\omega \,a\,\mathrm{d}z = N_1 B_{12} W(\omega) \hbar \omega \frac{a\,\mathrm{d}z}{V} F(\omega) \,\mathrm{d}\omega \tag{2.23}$$





Figure 2.5 Passage of a light beam through a thin slice of sample perpendicular to the direction of the beam

in which a dz/V represents the fraction of atoms or molecules in the selected slice a dz where V is the volume of the sample. Moreover, we have assumed that not all the atoms absorb precisely at the frequency  $\omega_{k1}$ , but that some statistical spread in transition frequencies exists at which the atoms/molecules can absorb light. To account for this, we introduced  $F(\omega) d\omega$ , the fraction of transitions that occur in the frequency interval  $\omega$  and  $\omega + d\omega$  with

$$\int F(\omega) \, \mathrm{d}\omega = 1 \tag{2.24}$$

Rearranging eq. (2.23) yields

$$\frac{\partial W}{\partial t} = -N_1 F(\omega) B_{12} W \frac{\hbar \omega}{V}$$
(2.25)

To obtain Lambert-Beer's law we rewrite eq. (2.25) in terms of the change in intensity I in W m<sup>-2</sup> of the light beam upon passage through the sample slice a dz. Inspection of Fig. 2.5 shows that the difference between the amount of energy entering and leaving the sample slice per unit of time precisely equals the rate of decrease of the beam energy. Thus we obtain  $-\partial W/\partial t = -\partial I/\partial z$ . Moreover, W = I/cn, with c the speed of light and n the index of refraction of the medium. Substitution into eq. (2.25) yields the required expression

$$\frac{\partial I}{\partial z} = -\frac{B_{12}N_1\hbar\omega F(\omega)}{Vnc}I$$
(2.26)

The solution of eq. (2.26) is straightforward and gives Lambert-Beer's law, sometimes just called Beer's law:

$$I(z) = I(0) e^{-Kz}$$
(2.27)

with K the absorption coefficient, given by

$$K = \frac{N_1 B_{12} \hbar \omega F(\omega)}{V cn} \tag{2.28}$$

Since  $B_{12}$  was calculated from eq. (2.14) in which an integration over a band was performed, it follows that for any particular transition  $B_{12}$  is independent of the frequency  $\omega$ . From eqs. (2.24) and (2.28) one finds

$$B_{12} = \frac{Vcn}{N_1\hbar} \int_{\text{band}} \frac{K}{\omega} \,\mathrm{d}\omega \tag{2.29}$$

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Thus, from a simple integration of the measurable (!) absorption coefficient K over the absorption line, we obtain the Einstein coefficient for absorption (and consequently the two other Einstein coefficients). Moreover, since we have related  $B_{12}$  to  $|\mu_{21}|^2$ (eq. (2.14)) the quantity  $|\mu_{21}|^2$  is calculated directly.

It is common practice to use, instead of eq. (2.27), the following expression for the dependence of I on passage through a material with pathlength l:

$$I(l) = I(0) \times 10^{-\text{OD}} \tag{2.30}$$

where the optical density OD is defined as

$$OD = \varepsilon l C \tag{2.31}$$

Here,  $\varepsilon$  is the molar extinction coefficient (usually expressed in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), *l* the pathlength (usually in cm) and *C* the concentration of the sample (usually expressed in mol dm<sup>-3</sup>). For example, in a leaf chlorophyll *a* has in its absorption maximum at 680 nm an extinction coefficient of 10<sup>5</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. The chlorophyll concentration in a leaf is about 10<sup>-3</sup> mol dm<sup>-3</sup> and the pathlength for light passing through a leaf is about 0.02 cm. Thus the OD of a single leaf at 680 nm is OD = 10<sup>5</sup> × 10<sup>-3</sup> × 2 × 10<sup>-2</sup> = 2. Thus, the reduction in intensity of 680 nm light upon passage through a leaf is about a factor 100. As a consequence no red light is detected below the outer array of leaves of a tree.

It is not difficult to relate eqs. (2.30) and (2.31) to the expressions for K and  $B_{12}$  and we finally find for  $|\mu_{21}|^2$ :

$$|\boldsymbol{\mu}_{12}|^2 = 1.01 \times 10^{-61} \int_{\text{band}} \frac{\varepsilon}{\omega} \,\mathrm{d}\omega$$
 (2.32)

where  $|\mu_{12}|^2$  is obtained in  $(Cm)^2$  and all the other constants have been replaced by their numerical values with the index of refraction n = 1.

Returning to eqs. (2.30) and (2.31), we can relate the extinction coefficient  $\varepsilon$  to the absorption cross-section of a single molecule,  $\sigma$ , given by

$$\sigma = \pi r^2 P \tag{2.33}$$

with r the radius of the molecule in cm and P the probability that a photon is absorbed upon the passage through the surface  $\pi r^2$ . Then

$$\varepsilon = \frac{\sigma N_{\rm A} 10^{-3}}{2.303} = \frac{\pi r^2 P N_{\rm A} 10^{-3}}{2.303} \tag{2.34}$$

in which  $N_A$  is Avogadro's number. One may deduce this equation by using the technique of Fig. 4.39 with eqs. (4.240) and (4.241).

### 2.3 BIOMOLECULES, OZONE AND UV LIGHT

In this section we will briefly discuss the absorption of light in the UV region by biological molecules, such as proteins and nucleic acids. Since both the amount and the spectral composition of UV light incident on earth is totally determined by the ozone present in the atmosphere, we shall summarize processes that lead to the building

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up and destruction of the ozone layer and show that small variations in ozone concentrations may lead to dramatic biological effects. These effects are largely related to the highly non-linear properties of Lambert-Beer's law (eqs. (2.30) and (2.31)), where the concentration C appears in the exponent.

## 2.3.1 THE SPECTROSCOPY OF BIOMOLECULES

Figure 2.6 shows the solar emission spectrum below 340 nm at the earth's surface in combination with the absorption spectrum of two important biomolecules: DNA, the carrier of the genetic code and  $\alpha$ -crystallin, the major protein of the mammalian eyelens. The absorption of light by these biological molecules is essentially zero in the region  $320 < \lambda < 400$  nm, which is called the near-UV or UV-A, intense in the region 200-290 nm, which is called the far-UV or UV-C and only overlaps with the solar spectrum in the wavelength region  $290 < \lambda < 320$ , the mid-UV or UV-B.

The absorption of DNA is due to the aromatic DNA bases guanine, thymine, cytosine and adenine and it peaks at about 260 nm, with a maximum extinction of  $\varepsilon = 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  (expressed per mole of base). The electronic transitions which contribute to the absorption in the range 220–290 nm are predominantly oriented in the plane of the DNA base.

The absorption of proteins like  $\alpha$ -crystallin in the wavelength region 250–300 nm is mainly due to the aromatic amino acids tryptophan and tyrosine and it peaks at about 280 nm. For a protein with a number of  $n_{\text{TRP}}$  tryptophan amino acids and a number of  $n_{\text{TYR}}$  tyrosine amino acids the extinction at 280 nm is given by

$$\varepsilon_{280} = n_{\rm TRP} 5600 + n_{\rm TYR} 1100 \,\,\rm{dm^3 \, mol^{-1} \, cm^{-1}} \tag{2.35}$$





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#### **BIOMOLECULES, OZONE AND UV LIGHT**

For a typical biological cell the total absorption of solar UV due to proteins would be about 10% of the absorption of nucleic acids.

Often proteins carry additional cofactors which allow proteins to carry out their specific tasks. For instance, in haemoglobin the haem group, a porphyrin molecule, is attached to the protein in a haem-protein complex which is active in oxygen binding of blood. In those cases the absorption extends into the near-UV, visible and sometimes near-infrared region of the spectrum. Although in several cases the absorption of light in this wavelength range is crucial for the biological function (photosynthesis, vision) and high illumination might induce damage we shall not further discuss it here.

#### 2.3.2 SOLAR UV AND LIFE

The interaction of solar UV with biological cells may lead to severe damage of the genetic material (mutagenesis) or cell killing. In more complex, multicellular organisms exposure to solar UV may lead to damage of crucial parts of the organism and, in the case of humans, to skin cancer.

It is by now well-documented that in particular the light absorbing parts of the DNA, called the chromophores, form the prime target in the process that leads to photodamage. Figure 2.7 shows the action spectrum  $E(\lambda)$ , which is the damage done by a unit of irradiation of a certain wavelength, for the production of erythyma (sunburn) in human skin. It also shows the UV tail  $I(\lambda)$  of the solar spectrum. The damage done at wavelength  $\lambda$  is therefore given by the product  $E(\lambda)I(\lambda)$ . It may be noted that the efficiency  $E(\lambda)$  of producing erythyma increases by four to five orders of magnitude between 350 and 280 nm, precisely in the region where the solar UV spectrum on earth collapses.



**Figure 2.7** Erythema (sunburn) action spectrum, plotted together with the solar spectrum and the resultant 'solar erythemal effectiveness' (which is the product  $E(\lambda)I(\lambda)$  in eq. (2.36)). Note the logarithmic ordinate. (Reproduced by permission of Plenum Press from [9], Fig. 8.4, p. 119)

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The action spectrum must be largely ascribed to the direct absorption of solar UV by DNA. Although for  $\lambda > 320$  nm the action spectrum in Fig. 2.7 tends to be higher than the DNA absorption in Fig. 2.6 implying that there are more absorbers, the primary target is probably still DNA. Similarly, studies on cellular cultures where cell survival on cell mutagenesis was measured have identified the chromophores of DNA as the primary target molecules. The major product of photon absorption in DNA is the pyrimidine dimer, a covalent structure involving two thymine molecules or a cytosine-thymine pair. Its presence in DNA has major destructive effects on the reading and translation of the genetic code.

The damage D done to a biological system by solar UV can be calculated from the action spectrum  $E(\lambda)$  by

$$D = \int_0^\infty E(\lambda) I(\lambda) \, \mathrm{d}\lambda \tag{2.36}$$

Since  $E(\lambda)$  is a function with a large negative slope and  $I(\lambda)$  a function with a large positive slope, even a minor change in  $I(\lambda)$  may lead to major changes in D.

#### 2.3.3 THE OZONE FILTER

Ozone (O<sub>3</sub>) forms a thin layer in the stratosphere, with a maximum concentration between 20 and 26 km above the earth's surface (cf. Fig. 3.7). The atmospheric ozone absorbs essentially all the radiation below a wavelength of 295 nm, due to a strong optical transition at about 255 nm, which extends into the mid-UV region. Figure 2.8 shows the absorption spectrum of ozone between wavelengths of 240 and 300 nm. At the maximum (255 nm) the absorption cross-section is about  $10^{-17}$  cm<sup>2</sup>, it is about half-maximum at 275 nm and has decreased to about 10% of its maximum value at 290 nm. That ozone forms a very thin shield indeed is probably best demonstrated by the fact that the amount of O<sub>3</sub> in the atmosphere corresponds to a layer of 0.3 cm at standard temperature and pressure.

Ozone is constantly formed in the upper layer of the atmosphere through the combination of molecular oxygen (O<sub>2</sub>) and atomic oxygen (O). The latter is formed through the photodissociation of O<sub>2</sub> in the 100 km region by light of wavelengths shorter than 175 nm. Sunlight excites the electronic transition between the triplet ground state of O<sub>2</sub> ( $^3 \sum_u^-$ ) and a triplet excited state ( $^3 \sum_g^-$ ). Once excited, the O<sub>2</sub> molecule may dissociate into two oxygen atoms: one in the ground state O ( $^3$ P) and one in the excited state O ( $^1$ D). The latter is 2 eV above the ground state. As a consequence of these processes, the sunlight with  $\lambda < 175$  nm is totally extinguished above the stratosphere.

Once formed, atomic oxygen attaches to  $O_2$  to form  $O_3$ . The efficiency of  $O_3$  formation by UV light is sensitive to a large number of factors, amongst which are the availability of  $O_2$ , changes in stratospheric temperature, chemicals and dust from volcanic eruptions.

Most of the ozone is produced above the equator, where the amount of incident solar UV light is maximal. Ozone formed at these latitudes then diffuses towards the poles, where it is 'accumulated'. The effective thickness of the ozone layer may increase from  $\leq 0.3$  cm at the equator to  $\geq 0.4$  cm above the pole at the end of winter. The ozone concentration displays significant daily and seasonal fluctuations and tends to be highest in late winter and early spring.

## BIOMOLECULES, OZONE AND UV LIGHT



Figure 2.8 Absorption spectrum of ozone in the wavelength region 240–300 nm. (Reproduced by permission of the Optical Society of America from [10], Fig. 1, p. 871)



**Figure 2.9** Breakdown of ozone to molecular oxygen, by means of the free radicals CI, NO and OH. (Reproduced by permission of Greenwood Publishing, Westport, CT from [11], Fig. 9.2, p. 145)

Ozone is permanently being formed and broken down in the stratosphere and only a very small fraction of the formed ozone escapes down to the troposphere. There are basically two pathways for the destruction of ozone and the reformation of  $O_2$ :

$$0 + 0_3 \longrightarrow 20_2 \tag{2.37}$$

$$O_2 + O_2 \longrightarrow 3O_2$$
 (2.38)

These reactions are the net result of a complex set of reactions catalysed by various gases and radicals. We mention explicitly atomic chlorine Cl, nitric oxide NO and hydroxyl radicals OH; the pathway along which they operate is shown in Fig. 2.9. Look for example at the Cl radical. It strips off an O atom from  $O_3$  (right-hand side), forming ClO; then loses an O atom to a free O atom and returns to the radical Cl state again. The net effect is eq. (2.37). Note that the scheme requires free O atoms to be present at altitudes of 25 km or more.

How are the free radicals NO, Cl and OH produced? The OH radical is a product of the breakdown of  $H_2O$  vapour, for instance produced in the exhaust of supersonic

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aeroplanes. Although part of the Cl radical may be formed from HCl released by volcanoes, the major input of Cl into the stratosphere originates from chlorofluorocarbons (CFCs), which are used as foam-blowing agents, refrigerants and propellants. CFCs are extremely stable in the troposphere. However, a small fraction may escape into the stratosphere, eventually reaching the upper stratosphere where they may be decomposed under the influence of UV light, thereby producing Cl and ClO.

 $N_2O$  is partly of anthropogenic origin and is released from soils and waters where it has been formed as a fertilizer waste product. Like the CFCs, the  $N_2O$  released at the earth's surface may eventually be photodecomposed and NO is formed. These radicals, together with the OH radical, remove some 99% of the stratospheric ozone. The processes that determine the amount and distribution of ozone in the atmosphere are illustrated in Fig. 2.10.\*

The crux of the ozone problem is demonstrated by Figs. 2.6 and 2.8. Any small variation in the ozone concentration will lead to changes in both the amount of UV light at a particular wavelength and the transmission of shorter wavelength radiation. This is of course a direct consequence of Lambert–Beer's law (eq. (2.30)). A certain percentage change in concentration of ozone yields the same percentage change in OD. A decrease of one OD unit at a particular wavelength implies a tenfold increase in the amount of light of that wavelength reaching the earth's surface. Since the action spectrum for damage to living cells or tissue is an exponentially increasing function (with decreasing  $\lambda$ ; see Fig. 2.7) the amount of ozone. That the amount and spectral distribution of



Figure 2.10 Processes that determine the concentration of ozone in the stratosphere. (Reproduced with permission of Greenwood Publishing, Westport, CT from [16], reproduced in [11], Fig. 9.3, p. 146)

\* For a more detailed discussion of the ozone problem and details of all the (photo-)chemical processes that occur refer to Refs. 11 to 15

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the UV light is in fact a strong function of the ozone concentration is best illustrated by Fig. 2.11, where the irradiance at ground level has been measured at three different ozone concentrations.

Predictions from models for the atmospheric ozone production and breakdown indicate a stratospheric ozone depletion ranging from 5–20% due to CFC and N<sub>2</sub>O production. From results as presented in Figs. 2.6 and 2.8 one may predict that a 10% ozone depletion will result in a 45% increase in damage from UV-B radiation. These alarming numbers illustrate the necessity to monitor accurately the structure of the ozone layer and to quantify the effects of increased UV on living organisms.

#### **Exercises**

- 2.1 Show that eq. (2.4) leads to eq. (2.3) for  $\nu \to 0$  and to Wien's displacement law (2.2) for  $\nu \to \infty$ . Check the value of the constant in eq. (2.2).
- 2.2 Calculate the frequency distributions given by eq. (2.4) for T = 6000, 2000, 800 and 300 K.
- 2.3 Calculate the total radiation energy per second emitted by the sun from eq. (2.1). Take the radius of the sun as  $6.96 \times 10^8$  m. Compare with the data given in Section 1.2 (b).
- 2.4 Reproduce the calculation leading to eq. (2.32). Note that for the extinction  $\varepsilon$  one has to use the measured dimensions in the integral and work out the SI dimensions in which the left-hand side is expressed.
- 2.5 Write down the usual definition of cross-section and check eq. (2.33).
- 2.6 Reproduce eq. (2.34) being careful in sticking to the units defined in Section 2.2.3. Conclude that in the official SI units eq. (2.34) would have contained some other powers of 10. Also, derive eq. (2.34) by sticking to the same, possibly unspecified

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units everywhere. Find that any power of 10 disappears. Apply the new equation with r in cm and find that the factor  $10^{-3}$  appears in order to find the dimensions of  $\varepsilon$  agreed underneath eq. (2.31).

- 2.7 Consider the ozone filter at a wavelength of 255 nm. Calculate the optical density OD for a path length of 0.3 cm as described and use eq. (2.31) to calculate the reduction of intensity over the path. Conclude that the remaining intensity is negligible.
- 2.8 From Figs. 2.6 and 2.8 estimate that a 10% ozone depletion may result in approximately a 45% increase in damage from UV-B radiation. Note that the solar spectrum of Fig. 2.6 moves upward with the effect that the left-hand cut off of the spectrum moves to the left. Therefore one has to add two effects, both of the same order of magnitude: change in the boundaries of the integral and change of the integrand.
- 2.9 The emission spectrum of a black body is usually drawn as a function of wavelength  $\lambda$  (Figs. 1.2 and 2.2). For comparison draw the photon flux  $N_E$  from eq. (2.5) as a function of E in eV and also the energy flux  $EN_E$ . Indicate the visible region. Notice that the peaks appear in the near infrared (Fig. 4.30).

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