1

Fundamentals of Spectroscopy

La lumière (...) donne la couleur et l'éclat à toutes les productions de la nature et de l'art; elle multiplie l'univers en le peignant dans les yeux de tout ce qui respire.

Light (...) gives colour and brilliance to all works of nature and of art; it multiplies the universe by painting it in the eyes of all that breathe.

Abbé Nollet, 1783

1.1 INTRODUCTION

"Science is spectral analysis. Art is light synthesis", so wrote Karl Kraus, Austrian writer. Light has intrigued both poets and scientists. What exactly is light? What effect does it have on matter? These are questions that have baffled scientists for many years, prompting Einstein in 1917 to say "For the rest of my life I will reflect on what light is". The branch of science that deals with the study of electromagnetic radiation (of which visible light is a part) and its interaction with matter is called *spectroscopy*. The word is derived from the Latin: *spectron* – spectre (ghost or spirit), or the Greek: *σκοπειν* – to see. This literally means that in spectroscopy, you do not look directly at the molecule – the matter – but what you see is its 'ghost' or image. To begin our study, we must, therefore, first discuss the nature of electromagnetic radiation and matter, and then the interaction between the two.

We start this chapter by giving basic formulae and definitions relating to waves, including travelling waves. We then go on to the wave description of electromagnetic radiation and its manifestations, and then discuss the properties emerging from a particulate description of radiation. The entire electromagnetic spectrum, its divisions and sub-divisions, the kind of spectroscopy observed in each region, are the topics of the next section. The populations of energy levels play an important role in the observed intensities. Einstein's coefficients and their interrelation are introduced in this chapter, but the quantum mechanical treatment is reserved for the next chapter. We wind up this chapter with a discussion of line shapes and broadening, followed by a brief introduction to Fourier transform spectroscopy, the almost magical transformation of a time decay to a line width, and the experimental recording of spectra. This chapter sets the foundation for the future chapters. The entire treatment in this chapter is semi-classical, i.e., we recognize that the energy levels of atoms and molecules are quantized, but do not go beyond Bohr's theory. This makes the various processes easier to comprehend, and gives us guidelines for the next chapter, where we bring in quantum mechanics.

1.2 SOME PROPERTIES OF WAVES

A wave is a disturbance that travels and spreads out through some medium. Familiar examples are ripples on the surface of water and vibrations in a string. A wave is characterized by its *frequency*, *wavelength*, *speed*, *direction* and *phase*. These parameters are best understood by imagining an object, such as a ball, moving in a circular path, as shown in Figure 1.1. If, at time $t = 0$, the object is in the horizontal (or 3 o'clock) position, its vertical (y) coordinate is zero. Let the object now start rotating counter-clockwise in a circular path of radius A with an *angular frequency* ω. The angular frequency (ω) is a scalar measure of the rotation rate, measured in radian per second, and is given by $\omega = |\vec{v}| / |\vec{r}|$, where $v = |\vec{v}|$ is the tangential speed at a point about the axis of rotation (measured in m s^{-1}), and $r = |\vec{r}|$ is the radius of rotation. (In this book, all vector quantities are denoted by an arrow above the symbol and $|\vec{r}|$, for example, refers to the magnitude of $\vec{r}$.)

Then, in time t, the object executes an angle $\theta = \omega t$ radian, and its y coordinate is now

$$y(t) = A \sin\theta\,(t) = A \sin\,(\omega t)$$

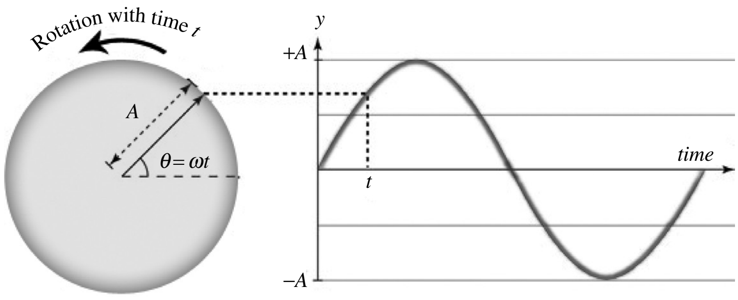

Figure 1.1. Oscillation of a ball in circular motion

When θ reaches $\pi / 2$ (12 o'clock position), the vertical component y achieves its maximum value, i.e., $y = A \sin\,(\pi / 2) = A$. At $\theta = \pi$ (9 o'clock position), y is again zero, and at $\theta = 3\pi/2$ (6 o'clock position), $y = -A$. We can trace $y(t)$ as a function of time as in the panel on the right-hand side of Figure 1.1 until the object reaches its original position when $\theta = 2\pi \equiv 0$. This completes one cycle. Subsequent motion is a repetition of the previous cycle, since $\sin\,(\theta + 2\pi) = \sin\,(\theta)$.

The maximum value of $y(t)$, i.e., A, is called the *amplitude* of the wave. The time taken for completion of a cycle is called the *time period* (T) of the wave and is measured in second (s). A cycle is completed when θ spans 2π; therefore, $\omega T = 2\pi$, or $T = 2\pi / \omega$. Since the pattern repeats itself every T seconds, the number of cycles completed per second is the reciprocal of T. This is called the *frequency* of the wave and is given the symbol ν ($= 1 / T$) with unit s^{-1} (Hz). The maxima in the peaks are called *crests* and the minima are named *troughs* (Figure 1.2). The distance traversed by the object in one cycle, called the *wavelength*, is denoted by the symbol λ.

It is measured as the distance between two successive peaks or crests, troughs or corresponding zero crossings, and is expressed in metre (m).

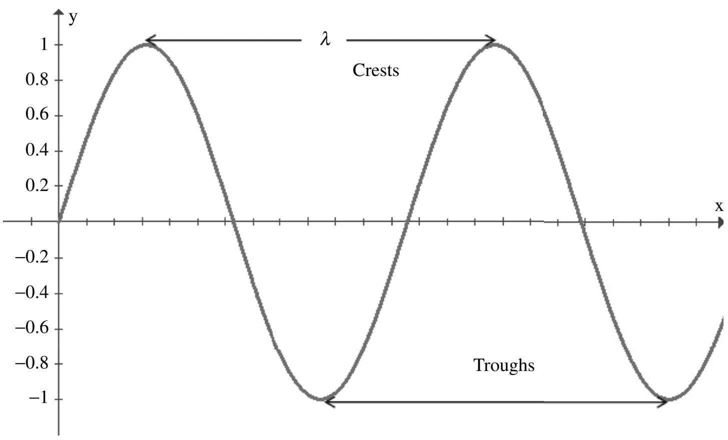

Figure 1.2. The wavelength of a sine wave, λ, measured between crests

The *speed* of light in vacuum is represented by c_0, and is equal to ~3×10^8 m s^{-1} (precisely 299,792,458 m s^{-1}). For media other than vacuum, the speed of light in vacuum, c_0, is replaced by c, the speed in the medium, given by c_0 / n, where n is the refractive index of the medium. Henceforth, we shall use the symbol c for the speed of light in any medium (with $n = 1$ for vacuum). The frequency and wavelength are related by the expression $\lambda\nu = c$; hence, short wavelength radiation has high frequency. The frequency is a more fundamental property than the speed and wavelength of the radiation, and remains constant when radiation propagates through media of different densities, whereas the other two change with the medium.

Another quantity frequently used by spectroscopists is the *wavenumber* ($\tilde{\nu}$), defined as a count of the number of wave crests (or troughs) in a given unit of length: $\tilde{\nu} = \nu / c = 1 / \lambda$. The dimensions of wavenumber are inverse length. The SI unit for the wavenumber is m^{-1}, but the unit cm^{-1} is still in use. For example, light of 400 nm wavelength is given a wavenumber of 25,000 cm^{-1}, rather than 2.5×10^6 m^{-1}. The conversion from cm^{-1} to m^{-1} may be performed by multiplying the wavenumber in cm^{-1} by 100. Alternatively, to express the wavenumber in cm^{-1}, use the value $2.99792458 \times 10^{10}$ cm s^{-1} for c, in place of its value in m s^{-1} to convert wavelength to wavenumber.

Note: Conversion from the wavelength in nm to wavenumber in cm^{-1}:

$$\tilde{\nu}[\mathrm{cm}^{-1}] = \frac{10^7\ \mathrm{cm}^{-1}\mathrm{nm}}{\lambda[\mathrm{nm}]}$$

since 1 nm = 10^{-7} cm.

There is still another term that needs to be defined. The case of a wave starting at zero and immediately increasing (Figure 1.1) is a special one. In general, the oscillation may start from any point, even the highest, as shown in Figure 1.3. In such a case, one may express this wave in terms of the cosine function, since we know that the cosine of zero radian is unity. However, there is another way of expressing this function without changing the general form of our equation. As Figure 1.3 shows, the cosine function is just the sine function, started a little earlier, and the cosine function can be expressed in terms of the sine function just by adding the starting angle. Thus, for the wave shown in Figure 1.3, we may equivalently write

$$y(t) = A\cos\theta(t) \equiv A\sin\left(\theta(t) + \frac{\pi}{2}\right) \tag{1.1}$$

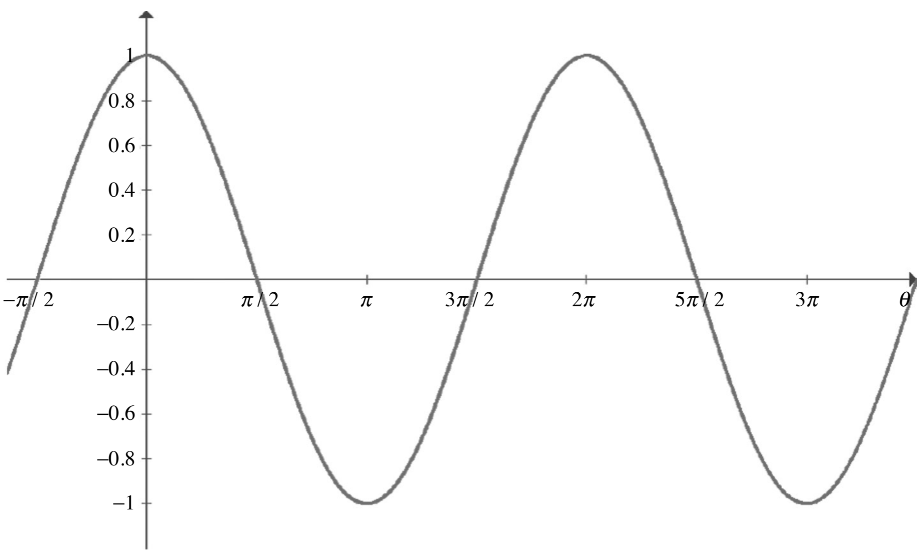

Figure 1.3. A cosine wave expressed as a sine wave with $\phi = \pi / 2$

The angle at which an oscillation starts is referred to as the *phase angle*, or simply the *phase* of an oscillation. It is commonly given a symbol ϕ and is expressed in radian. The general form of the equation is thus $y = A\sin(\theta + \phi') \equiv A\cos(\theta + \phi)$. We have seen that the wave shown in Figure 1.3 can be equivalently expressed in terms of the cosine function, with a phase angle of zero or as a sine function with a phase of $\pi / 2$ [equation (1.1)]. Using the relationship $\cos\theta = \sin\left(\theta + \frac{\pi}{2}\right)$, it is possible to completely describe wave motion in terms of either the sine or cosine functions, just by changing the phase angle.

A trigonometrically more tractable formulation is in terms of the complex exponential $y = Ae^{i(\theta+\phi)}$. Only the real part of this expression has any physical interpretation, and this can be extracted using Euler's formula $y = Ae^{i(\theta+\phi)} = A\left(\cos(\theta+\phi) + i\sin(\theta+\phi)\right)$. Since the cosine function represents the real part of the exponential function, we shall follow the cosine function in our future derivations.

In terms of the various quantities that we have developed, we are now in a position to express $y(t)$ in a variety of forms:

$$\begin{aligned} y(t) &= A\cos(\theta+\phi) = A\cos(\omega t+\phi) = A\cos(2\pi\nu t+\phi) \\ &= A\cos\left(\frac{2\pi t}{T}+\phi\right) = A\cos\left(\frac{2\pi ct}{\lambda}+\phi\right) \end{aligned} \tag{1.2}$$

Of these, the relations in terms of the frequencies (ω and ν) will be used in what follows.

1.2.1 Travelling waves

Light waves are travelling waves and we now discuss the form taken by equation (1.2) for a travelling wave. A travelling wave is any kind of wave that propagates in a single direction (say, z) with negligible change in shape. Hence, it is a function of both spatial (z) and temporal (relating to time, t) variables. We now combine the two dependencies and write

$$y(z,t) = A\cos\phi(z,t) = A\cos(\alpha z + \beta t) \tag{1.3}$$

For this oscillation to move through space, i.e., towards positive z, the point z_0 in space at a time t_0 must move to $z_1 > z_0$ at time $t_1 > t_0$ (Figure 1.4).

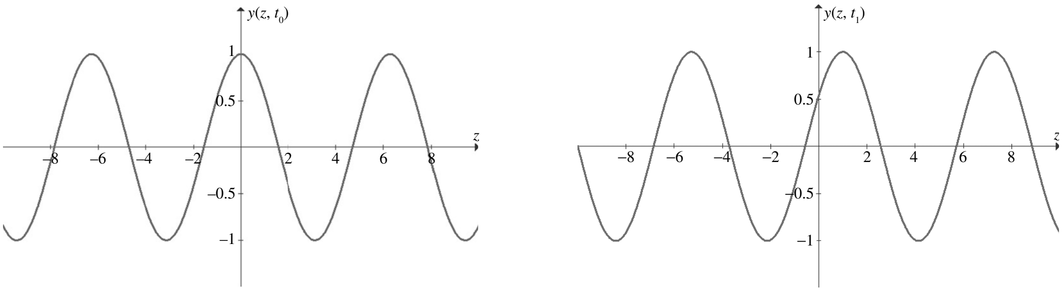

Figure 1.4. 'Snapshots' of a sinusoidal wave at two different times t_0 and $t_1 > t_0$, showing motion of the peak originally at the origin at t_0. The wave is travelling towards $z = +\infty$

The phase of the first wave (t_0) at the origin is zero, but that of the second (at t_1) is negative. Since the wave at location z_1 and time t_1 has the same phase as the wave at location z_0 and time t_0, we can say that:

$$y(z_0, t_0) = y(z_1, t_1)$$

In addition, for the wave to maintain its shape, the phase must be a linear function of z and t; otherwise the wave would compress or stretch out at different locations in space or time. Therefore:

$$\alpha z_0 + \beta t_0 = \alpha z_1 + \beta t_1, \text{ or } \alpha(z_1 - z_0) = -\beta(t_1 - t_0).$$

As discussed, if $t_1 > t_0 \Rightarrow z_1 > z_0$ (i.e., the wave moves towards $z = +\infty$), then α and β must have opposite algebraic signs:

$$\phi(z,t) = |\alpha|z - |\beta|t$$

Since it is the argument of the cosine function, $|\alpha|z - |\beta|t$ has the 'dimensions' of angle (radian). We have already identified $\beta = \omega$ [equation (1.2)], the angular frequency of the oscillation. Similarly, since z has the dimensions of length, α must have the dimensions of rad m^{-1}, i.e., α tells us how many radians of oscillation exist per unit length – the angular spatial frequency of the wave, commonly denoted by k ($= 2\pi / \lambda$): $y_+(z,t) = A\cos(kz - \omega t + \phi)$ – travelling harmonic wave towards $z = +\infty$ with arbitrary phase ϕ. Similarly, for a harmonic wave moving towards $z = -\infty$, $y_-(z,t) = A\cos(kz + \omega t + \phi)$ – travelling harmonic wave towards $z = -\infty$ with arbitrary phase ϕ.

1.3 ELECTROMAGNETIC RADIATION

Up till now, we have not defined $y(t)$; it could be any variable that changes as the wave passes. In the case of light waves, it is their vibrating electric and magnetic fields. Electromagnetic radiation is so named because it consists of mutually perpendicular electric and magnetic fields, normal to the direction of propagation of the wave. The connection of optics with electricity and magnetism was first realized by Maxwell through his equations, which form the basis of all electricity and magnetism. However, towards the end of the nineteenth century, some puzzling phenomena regarding light could not be explained by classical physics, and the quantum theory had to be invoked to explain these. For example, the wave theory of light could explain most phenomena relating to light, such as propagation in a straight line, reflection, refraction, superposition, interference, diffraction, polarization and the Doppler effect, but it could not explain certain other observations regarding blackbody radiation (electromagnetic radiation emitted by a heated object), photoelectric effect (emission of electrons by an illuminated metal) and spectral lines (emission of sharp spectral lines by gas atoms in an electric discharge tube). Young's double slit experiment firmly established the quantum mechanical explanation that both light and matter have dual nature, i.e., they can behave *as either wave or particle, depending on what question you ask: there is a 'wave' aspect and a 'particle' aspect, too*. Thus, the intensity of light depends on the square of the amplitude of the wave, and its energy depends on the frequency of the photon. Since we are more familiar with the wave nature of light, we first characterize electromagnetic radiation as a wave.

1.3.1 Wave nature of light

Light is energy that travels in a straight line in the form of electromagnetic waves. Like all waves, when it encounters an object, light may get absorbed, diffracted, reflected, refracted, scattered or transmitted, depending on the shape and composition of the object, and on the light's wavelength. In fact, many of these processes may occur simultaneously, because objects have uneven compositions or shapes, and beams of light are not monochromatic, i.e., they may include many wavelengths.

Light can be considered as oscillations of an electromagnetic field – characterized by electric ($\vec{E}$) and magnetic ($\vec{B}$) components – perpendicular to the direction of light propagation and to each other (Figure 1.5).

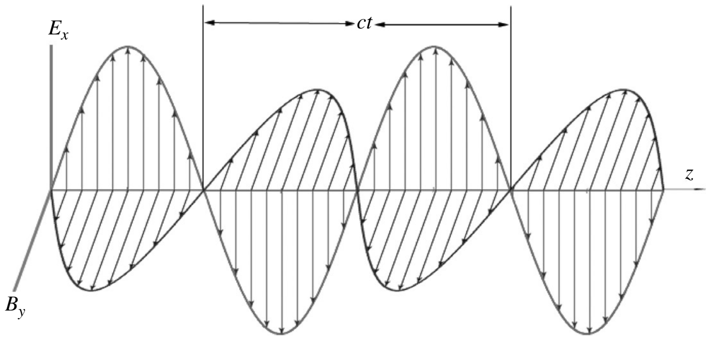

Figure 1.5. A schematic view of an electromagnetic wave propagating along the *z*-axis

It can be shown from Maxwell's relations that the magnitudes of the electric and magnetic fields are related by the wave speed, i.e., $|\vec{E}| = c|\vec{B}|$. The electric and magnetic fields oscillate in the *xy* plane perpendicular to the direction of propagation (Figure 1.5). As the electric field changes, so does the magnetic field in tandem. The wave represented in this figure has its electric fields aligned in the *xz* plane and pointing in the *x* direction. The magnetic fields are aligned in the *yz* plane and all vectors point in the *y* direction.

1.3.1.1 Polarization

Electromagnetic radiation has another (and sometimes important to spectroscopists) property: *polarization*. In contrast to sound waves, electromagnetic waves are *transverse waves*, i.e., the oscillations occur perpendicular to the direction of propagation of the wave. For an electromagnetic wave propagating in the *z*-direction, there are two transverse directions along which the electric and magnetic fields can lie. The $\vec{E}$ vectors could lie either in the *x* or *y* directions, or anywhere in the *xy* plane, i.e., $\vec{E} = \hat{i}E_x + \hat{j}E_y$, where $\hat{i}$ and $\hat{j}$ are unit vectors along the *x* and *y* directions, respectively. The polarization of light is defined by the orientation of the wave's electric field. Natural light is generally unpolarized, i.e., its electric field vectors are in all random directions in the *xy* plane (Figure 1.6). The electromagnetic wave shown in Figure 1.5 is an example of a *plane* polarized light since all the electric field vectors lie in a single plane, the vertical plane (*xz*), pointing in the *x* direction. The electric and magnetic fields for this wave are given by

$$\vec{E} = E_0 \cos(kz - \omega t)\hat{i}$$

$$\vec{B} = B_0 \cos(kz - \omega t)\hat{j} = \frac{E_0}{c}\cos(kz - \omega t)\hat{j}$$

This wave has $\vec{E}$ always pointing in the *x* direction and $\vec{B}$ always pointing in the *y* direction. A wave like this, where the fields always point along given directions, is also said to be *linearly polarized*. The example wave is linearly polarized in the *x* direction because the electric field vectors are all in this direction.

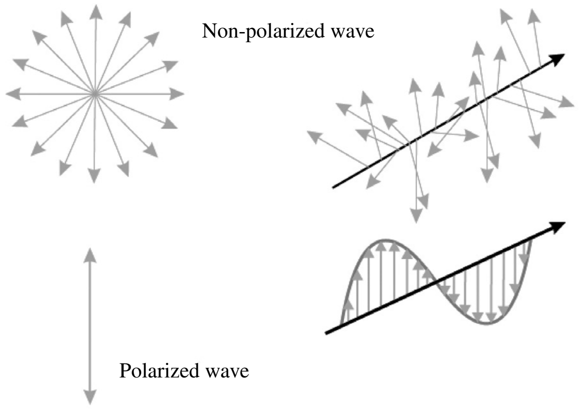

Figure 1.6. Electric field $\vec{E}$ orientation for polarized and non-polarized electromagnetic waves

1.3.2 Particulate nature of radiation

Radiation can be also described in terms of particles of energy, called *photons*. A photon has energy but has neither mass nor charge. Its energy (in Joule) is given as:

$$\varepsilon_{\text{photon}} = h\nu = hc/\lambda = hc\tilde{\nu} \tag{1.4}$$

where h is Planck's constant ($h = 6.626075 \times 10^{-34}$ J s). Equation (1.4) relates the energy of each photon of the radiation to the electromagnetic wave characteristics ($\tilde{\nu}$ and λ). It was Planck who, in 1901, first postulated this relation more as a matter of mathematical necessity to explain blackbody radiation (discussed in Section 1.4), than out of a belief that light consisted of discrete quanta. Einstein, on the other hand, took this mathematical 'trick' and interpreted it literally: if light could only possess energies which were integer multiples of the Planck discrete energy, $E = h\nu$, perhaps light was actually *composed* of discrete packets (photons), each possessing an energy $h\nu$.

By extending Planck's hypothesis of energy quantization to include not just the absorption and emission mechanism but to the light itself, Einstein succeeded in explaining certain puzzling phenomena related to the photoelectric effect. Experiments on the emission of photoelectrons from the surface of metals showed that low-frequency radiation had no effect, but once a threshold frequency was crossed, emission occurred with no time lag. The threshold frequency was dependent on the 'work function' (ionization energy) of the metal. Higher frequencies of the incident radiation led to ejection of electrons with higher kinetic energies. All these observations could be explained if it was assumed that the incident radiation consists of photons of energy $h\nu$, and the maximal kinetic energy of the ejected electrons is given by $E_k = h\nu - \phi$, where ϕ is the work function of the metal, equal to $h\nu_0$, where ν_0 is the threshold frequency.

The photon energy is directly proportional to the wavenumber. However, spectra are usually recorded in terms of the wavelength, so a conversion to energy is required. Putting in the values of h and c, we find that the conversion factor from wavelength to photon energy is

$$hc = 1.986447 \times 10^{-25} \text{ J m} = 1.986447 \times 10^{-16} \text{ J nm}$$

Table 1.1 summarizes some of the characteristics of electromagnetic radiation studied so far, their relationship with wavelength and their common units of measurement.

The internal energies of atoms are small (~10^{-19} J) because of their small size (~10^{-10} m). The individual photon energies are also of the same order and may be more conveniently expressed in *electron volt* (eV), a unit equal to the kinetic energy imparted to an electron when it is accelerated by a potential of 1 V. The conversion factor between electron volt and Joule is numerically equal to the charge on an electron.

$$1 \text{ eV} = 1.60217733 \times 10^{-19} \text{ C} \times 1 \text{ V} = 1.60217733 \times 10^{-19} \text{ J}$$

Combining this with equation (1.4) gives the following conversion factor when the photon energy is expressed in electron volt and wavelength in nanometre.

$$\varepsilon_{\text{photon}}[\text{eV}] = 1240/\lambda[\text{nm}]$$

Table 1.1. Characteristics of electromagnetic radiation

Characteristic	Common units	Relationship with wavelength
Wavelength	m μm (10^{-6} m) nm (10^{-9} m)	
Wavenumber	m^{-1} cm^{-1}	$\tilde{\nu} = \frac{1}{\lambda}$
Frequency	s^{-1} (Hz) kHz (10^3 s^{-1}) MHz (10^6 s^{-1}) GHz (10^9 s^{-1})	$\nu = \frac{c}{\lambda}$
Speed	m s^{-1}	$c = \nu\lambda$
Energy	Joule (J)	$E = \frac{hc}{\lambda}$

To appreciate the vast range of photon energies, consider that yellow light ($\lambda \approx 600$ nm) has a photon energy of ~2 eV, while X-rays from a copper source, with a wavelength of 0.154 nm, have a photon energy of about 8000 eV. This shows that at least 8000 V is needed to give electrons sufficient energy to produce these X-rays.

The energies discussed above, although small by macroscopic standards, are very significant at the level of individual atoms or molecules. This can be seen by multiplying them by Avogadro's number (N_A), so as to give the energy per mole. The conversion factor from electron volt per molecule to Joule per mole is eN_A, giving

$$1 \text{ eV per molecule} = 96.5 \text{ kJ mol}^{-1}$$

Table 1.2 summarizes the conversion factors amongst various energy units.

Table 1.2. Conversion factors between radiation frequency, wavenumber, photon energy and the corresponding energy per mole

	Corresponding value in			
Unit	**Hz**	**cm^{-1}**	**eV**	**kJ mol^{-1}**
1 Hz	1	3.336×10^{-11}	4.136×10^{-15}	3.990×10^{-13}
1 cm^{-1}	2.998×10^{10}	1	1.236×10^{-4}	1.196×10^{-2}
1 eV	2.418×10^{14}	8066	1	96.49
1 kJ mol^{-1}	2.506×10^{12}	83.60	1.036×10^{-2}	1

Example 1.1 A light bulb of 60 W emits at a wavelength of 0.5 μm. Calculate the number of photons emitted per second.

Solution

The energy of one photon is $\varepsilon_{\text{photon}} = hc / \lambda$; thus, since 60 W = 60 J s^{-1}, the number of photons per second, N, is

$$N = \frac{60\,(\text{J s}^{-1})\ \lambda(\text{m})}{h\ (\text{J s})\ c\ (\text{m s}^{-1})} = \frac{60 \times 0.5 \times 10^{-6}}{6.6256 \times 10^{-34} \times 2.9979 \times 10^{8}} = 1.510 \times 10^{20}\ \text{s}^{-1}$$

Note: A large number of photons is required because Planck's constant h is very small! It is hardly surprising that the quantum nature of this light is not usually apparent.

Example 1.2 Calculate the energy in Joule and the wavenumber in cm^{-1} of:
(a) A photon with wavelength 1 μm
(b) A photon with frequency 6.00×10^{14} Hz

Solution

(a) Energy, $E = hc / \lambda$; hence for a wavelength 10^{-6} m:

$$E = (6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^{8}\ \text{m s}^{-1}) / (10^{-6}\ \text{m}) = 1.986 \times 10^{-19}\ \text{J}$$

Wavenumber, $\tilde{\nu} = 1 / \lambda$; hence $\tilde{\nu} = 1 / (10^{-6}\,\text{m}) = 10^{6}\ \text{m}^{-1} = 10^{4}\ \text{cm}^{-1}$

(b) Energy $E = h\nu$; hence, $E = (6.626 \times 10^{-34}\,\text{J s}) \times (6.00 \times 10^{14}\ \text{s}^{-1}) = 3.98 \times 10^{-19}$ J

$\tilde{\nu} = \nu / c = (6.00 \times 10^{14}\ \text{s}^{-1}) / (2.998 \times 10^{8}\ \text{m s}^{-1}) = 2.00 \times 10^{6}\ \text{m}^{-1} = 2.00 \times 10^{4}\ \text{cm}^{-1}$

Example 1.3 Two energy levels are separated in wavenumber by 200 cm^{-1}. Convert this energy to Joule.

Solution

$$E = hc\tilde{\nu} = (6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{8}\ \text{m s}^{-1}) \times (20000\ \text{m}^{-1}) = 3.97 \times 10^{-21}\ \text{J}$$

Note: It is essential to convert from cm^{-1} to m^{-1} if we want the final answer in SI units of Joule.

Example 1.4 k_BT, where k_B is Boltzmann's constant, is an important property in chemistry with units of energy. Calculate the value of k_BT at 10 K, 100 K and 300 K, giving your answer in J, kJ mol^{-1} and cm^{-1}.