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Electromagnetic Radiation

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Symbols

$\mathbf{B}$	magnetic field vector
B_0	magnetic field amplitude
c	speed of light
c_0	speed of light *in vacuo*
E	photon energy
$\mathbf{E}$	electric field vector
E_0	electric field amplitude
h	Planck constant
$\hbar$	Planck constant/2π
$\mathbf{k}$	wave vector
n_λ	refractive index at wavelength λ
$\mathbf{p}$	photon momentum
$\mathbf{S}$	spin
t	time
λ	wavelength
ν	frequency
$\bar{\nu}$	wavenumber
ω	circular frequency

Electromagnetic radiation is the technical term for light; not just visible light, but any light, ranging right through from radio frequencies to gamma rays. As the name suggests, light of all kinds is radiated through conjoined electric and magnetic fields, as shown by Maxwell in the mid-nineteenth century. To fully appreciate the nature of electromagnetic radiation, however, we first have to consider both its wave-like and photonic aspects.

Waves and Photons

In the case of monochromatic (single-frequency) radiation, light propagates as a wave with a well-defined repeat or wavelength λ (Figure 1). Travelling at the speed of light, c, these waves oscillate at a characteristic frequency ν given by c/λ. The electric field, the magnetic field and the direction of propagation are mutually perpendicular, and for convenience may be chosen to define a set of Cartesian axes (x, y, z), respectively. With propagation in the z direction, the electric field vector points in the x direction and oscillates in the xz plane:

$$E(z,t) = E_0 \sin(kz - \omega t) \qquad [1]$$

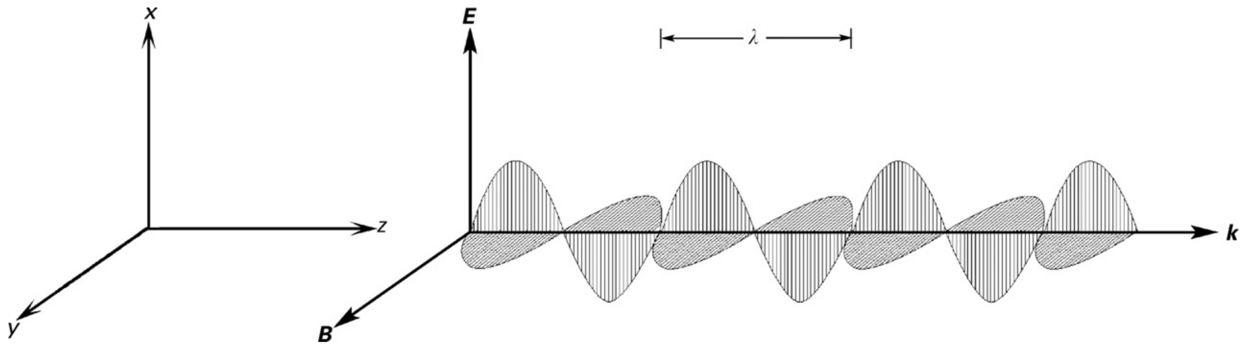

Figure 1 Oscillating electric field E and magnetic field B associated with mononchromatic radiation.

where E_0 is the field amplitude and where also for conciseness we introduce $k = 2\pi/\lambda$ and $\omega = ck = 2\pi\nu$. The magnetic field vector accordingly points in the y direction and oscillates in the yz plane:

$$B(z, t) = B_0 \sin(kz - \omega t) \qquad [2]$$

with amplitude B_0. Given that the electric and magnetic fields oscillate in phase and in mutually perpendicular planes, eqns [1] and [2] together satisfy Maxwell's equations provided the amplitudes are related by $E_0 = cB_0$. In fact most spectroscopy involves the interaction of matter with the electric rather than the magnetic field of the radiation, because of its stronger coupling – usually by a factor of a thousand or more – with atomic and molecular charge distributions.

The speed of travel of an electromagnetic wave as described above can be understood in terms of the motion of any part of the waveform, such as the crest. The interval Δt between the arrival of two successive crests at any given point is given by $\omega\Delta t = 2\pi$, while at any time their spatial separation Δz also satisfies $k\Delta z = 2\pi$. So the speed of propagation $\Delta z/\Delta t = \omega/k = c$, which *in vacuo* takes the value $c_0 = 2.9979 \times 10^8\ \mathrm{m\,s^{-1}}$.

On the radiation travelling through any substance, the electronic influence of the atoms or molecules traversed by the light reduces the propagation speed to a value less than c_0; then one obtains $c = c_0/n_\lambda$ where n_λ is the refractive index of the medium for wavelength λ; accordingly, $k = 2\pi n_\lambda/\lambda$. The significance of the refractive correction is greatest in the solid or liquid phase, especially at wavelengths close to an optical absorption band of the medium.

A fundamental paradox in the nature of electromagnetic radiation, to some extent apparent even in the earliest scientific studies by Newton and others, is that it exhibits not just wave-like but also particle-like (corpuscular) properties, and both prove to be of key importance in spectroscopy. In particular, it is only through the association of discrete units of energy with electromagnetic radiation of any given frequency that we can properly understand atomic and molecular transitions and the appearance of spectra.

In the modern quantum representation of light developed by Planck, Einstein, Dirac and others, we now understand the twin wave and particle attributes through a description in terms of *photons* (a term in fact first introduced by the thermodynamicist Lewis). As such, electromagnetic radiation of a given frequency ν is seen to propagate as discrete units of energy $E = h\nu$, where h is the Planck constant.

With the key concepts in place, we can now take a look at some of the more detailed aspects of electromagnetic radiation in two stages — first by more fully enumerating the properties of photons in general terms, and then by examining those more specific features that relate to particular wavelength or frequency regions of the electromagnetic spectrum.

Photon Properties

Mass

Photons are elementary particles with zero rest mass – necessarily so, since, from special relativity theory, no particle with a finite mass can move at the speed of light.

Velocity

The speed of light is normally quoted as speed *in vacuo*, c_0, with refractive corrections applied as appropriate; the free propagation of any photon also has a well-defined direction, usually denoted by the unit vector $\hat{k}$.

Energy

Photon energy is linked to optical frequency ν through the relation $E = h\nu$ (where $h = 6.6261 \times 10^{-34}$ J s). Each photon essentially conveys an energy E from one piece of matter to another, for example from a television screen to a human retina.

Frequency

The optical frequency ν expresses the number of wave cycles per unit time. Also commonly used in quantum mechanics is the circular frequency $\omega = 2\pi\nu$ (radians per unit time), in terms of which the photon energy is $E = \hbar\omega$ where $\hbar = h/2\pi$. The lower the optical frequency, the more photons we have for a given amount of energy; and the larger the number of photons, the more their behaviour approaches that of a classical wave (this is one instance of the 'large numbers' hypothesis of quantum mechanics). It is for this reason that electromagnetic radiation becomes increasingly wave-like at low frequencies, and why we tend to think of radiofrequency and microwave radiation primarily in terms of waves rather than particles.

Wavelength

The wavelength λ of the electric and magnetic waves is given by $\lambda = c/\nu$. In spectroscopy, common reference is made to its inverse, the *wave number* $\bar{\nu} = 1/\lambda$, usually expressed in $\mathrm{cm^{-1}}$.

Momentum

Each photon carries a linear momentum p, a vector quantity of magnitude $h/\lambda = \hbar k$ pointing in the direction of propagation. It is then convenient to define a *wave vector or propagation vector* $k = k\hat{k}$ such that $p = \hbar k$. Since the photon momentum is proportional to frequency, photons of high frequency have high momenta and so exhibit the most particle-like behaviour. X-rays and gamma rays, for example, have many clearly ballistic properties not evident in electromagnetic radiation of lower frequencies.

Electromagnetic Fields

The electric and magnetic fields, *E* and *B*, respectively, associated with a photon are vector quantities oriented such that the unit vectors ($\hat{E}$, $\hat{B}$, $\hat{k}$) form a right-handed orthogonal set.

Polarization

For plane-polarized (also called linearly polarized) photons, the plane within which the electric field vector oscillates can sit at any angle to a reference plane containing the wave vector, as shown in Figures 2a and 2b. Other polarization states are also possible: in the right- and left-handed circular polarizations depicted in Figures 2c and 2d, the electric field vector sweeps out a helix about the direction of propagation. Elliptical polarization states are of an intermediate nature, between linear and circular. Together, the wave vector and polarization of a photon determine its *mode*.

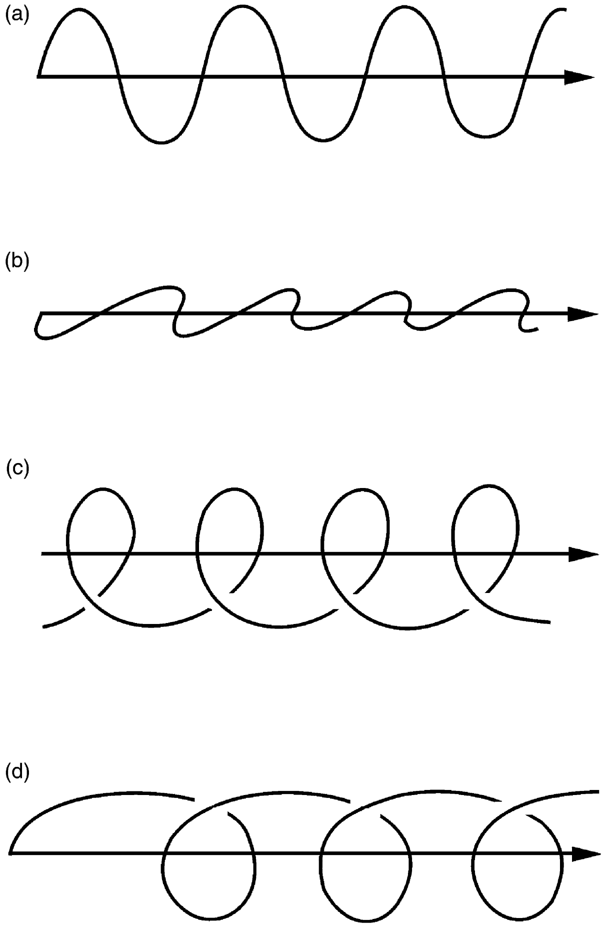

Figure 2 Polarization states: (a) and (b) plane; (c) and (d) circular.

Spin

Many of the key properties of photons as elementary particles relate to the fact that they have an intrinsic spin $S = 1$, and so are classified as *bosons* (particles with integer spin as opposed to half-integer spin particles of matter such as electrons). As such, photons collectively display a behaviour properly described by a Bose–Einstein distribution. At simplest, this means that it is possible for their oscillating electromagnetic fields to keep in step as they propagate. Through this, coherent beams of highly monochromatic and unidirectional light can be produced; this is of course the basis for laser action.

Angular momentum

The intrinsic spin of each photon is associated with an angular momentum, a feature that plays an important role in the selection rules for many spectroscopic processes. Circularly polarized photons have the special property of quantum angular momentum: the two circular polarization states, left- and right-handed, respectively carry $+1$ or -1 unit of angular momentum, $\hbar$.

Regions of the Spectrum

We can now delineate the properties of the various spectral regions shown in Figure 3. Looking across the electromagnetic spectrum, it is immediately apparent that there is enormous difference in scale between the extremes of wavelength (or frequency), and it is not surprising to find that they encompass an enormous range of characteristics.

Gamma-Rays

This is a region of highly penetrating radiation with the highest optical frequencies (exceeding 3×10^{19} Hz), and an upper bound of 10 pm on the wavelength. Spectroscopy in this region primarily relates to nuclear decay process, as in the Mössbauer effect.

X-rays

This region encompasses both ‘hard’ X-rays (wavelengths down to 10 pm) and less penetrating ‘soft’ X-rays (wavelengths up to 10 nm) with optical frequencies lying between 3×10^{19} and 3×10^{16} Hz. With the capacity to produce ionization by electron detachment, photon energies in this region are often reported in electronvolts (eV), and run from around 10^5 eV down to

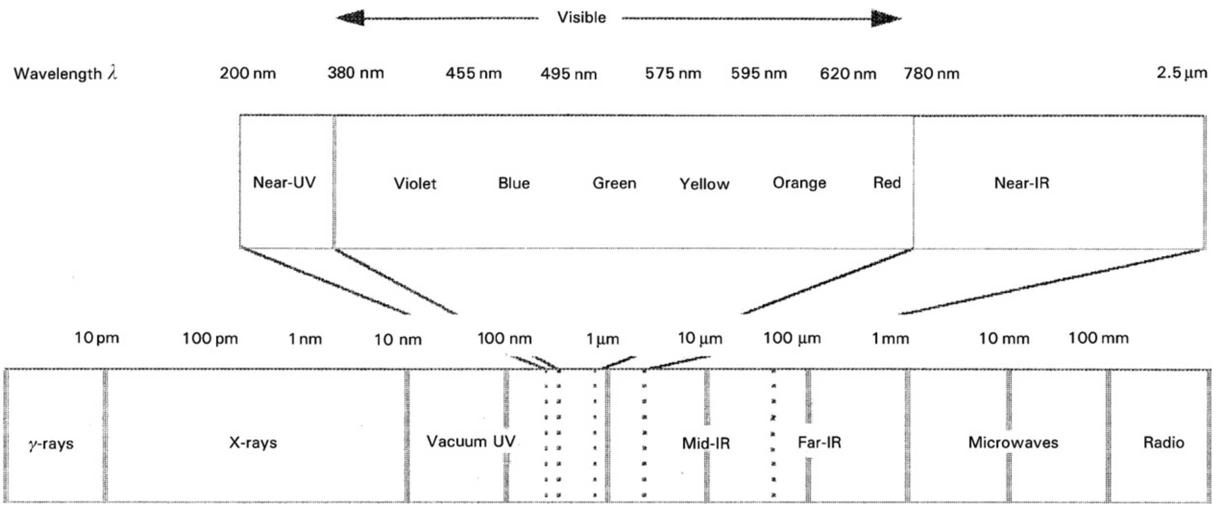

Figure 3 The electromagnetic spectrum.

100 eV (1 eV = 1.602 × 10^{-19} J). X-ray absorption and fluorescence spectra as such mostly relate to atomic core electronic transitions.

Ultraviolet

With UV wavelengths running from 10 nm up to the violet end of the visible range at around 380 nm, this region is commonly divided at a wavelength of 200 nm into the 'far-UV' region (wavelengths below 200 nm, often referred to as 'vacuum UV' because oxygen absorbs here) and the near-UV (200–380 nm). With photon energies from 100 eV down to less than 10 eV – the latter being typical of the lowest atomic or molecular ionization energy – photoionization processes are associated with many of the techniques of ultraviolet spectroscopy. At the lower end of this region, photon energies are comparable with valence bond energies. As such they are commonly scaled by Avogadro's number and reported in units of kJ mol^{-1}; for example, the wavelength of 240 nm corresponds to 500 kJ mol^{-1}, a typical bond energy. One other form of division often applied to the near-UV region relates to its photobiological effects and applies principally to solar radiation; UV-A (320–380 nm) is the relatively safe region closest to the visible range; UV-B (280–320 nm) signifies radiation that can produce extensive tissue damage; UV-C radiation with wavelengths below 280 nm is potentially more damaging but is mostly filtered out by atmospheric gases that absorb here, the most important being ozone.

Visible

The visible range extends from approximately 380 nm (violet) to 780 nm (red) (Table 1). The precise divisions are a little arbitrary and depend on individual perceptions, but the wavelengths given in Table 1 are a reasonable guide. Note that the link with perceived colour is not 1:1 – for example, light containing an equal mixture of red and green wavelengths appears yellow, although no yellow wavelengths are present. The visible range spans near enough an octave of frequencies and is a region in which photon energies are comparable with the bond energies of some of the weaker chemical bonds, running up from around 150 kJ mol^{-1} at the red end to over 300 kJ mol^{-1} at the other. Most of the spectroscopy in this range of wavelengths relates to electronic transitions unaccompanied by chemical change, and of course all absorption or fluorescence processes responsible for colour.

Table 1 The visible spectrum

Colour	*Wavelengths (nm)*
Red	780–620
Orange	620–595
Yellow	595–575
Green	575–495
Blue	495–455
Violet	455–380

Infrared

This is another region commonly subdivided, in this case into the near IR (wavelengths running from the red end of the visible spectrum at 780 nm out to 2.5 μm), the mid-IR (from 2.5 to 50 μm) and the far IR (50 μm to 1 mm). The absorption of near-IR radiation is commonly associated with the excitation of low-lying electronic excited states and overtones or combinations of molecular vibrations. In spectroscopic connections, the unqualified term 'infrared' generally refers to the mid-range, where spectral positions are usually cited by reference to wavenumbers $\bar{\nu} = 1/\lambda$. In the mid-IR range between 200 and

4000 cm^{-1}, it is principally vibrational transitions that accompany the absorption of radiation, with the corresponding nuclear motions less localized at the lower-wave number end of the scale. The far-IR region beyond relates mostly to low-frequency molecular vibrations and inversions, or rotations in small molecules.

Microwave

With wavelengths in the 1–100 mm range and frequencies on the GHz (10^9 Hz) scale, spectroscopy in the microwave region relates primarily to transitions involving molecular rotation, or others involving states of different electron spin orientation (electron spin resonance).

Radio

With radiation of wavelengths exceeding 100 mm we finally run into the radio wave region, where frequencies are commonly reported in MHz (10^6 Hz). Photon energies here are too small to lead to transitions associated with electronic or nuclear movement, but they can produce transitions between spin states (nuclear magnetic resonance).

As a caveat by way of conclusion, it should be pointed out that the nature of transitions studied by a particular spectroscopic technique is not always so obviously linked with a particular optical frequency or wavelength region if the elementary interaction involved in the spectroscopy entails more than one photon. For example, Raman spectroscopy allows molecular vibrational transitions to be studied with visible or ultraviolet light, while multiphoton absorption of IR radiation can lead to electronic excitations.

See also: Light Sources and Optics.

Further Reading

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