

Table 4.5 Characteristic parameters of optical radiation

		Wavelength (λ)	Frequency (ν) in Hz	Quantum energy (E) in eV
Terahertz-radiation	<1 mm	$3 \cdot 10^{11}$ – $3 \cdot 10^{12}$	$<1.24 \cdot 10^3$	
Infrared	IRC	3,000 nm–1 mm	$3 \cdot 10^{11}$ – $1 \cdot 10^{14}$	$1.24 \cdot 10^3$ –0.41
	IRB	1,400–3,000 nm	$1 \cdot 10^{14}$ – $2.1 \cdot 10^{14}$	0.41–0.89
	IRA	700–1,400 nm	$2.1 \cdot 10^{14}$ – $4.3 \cdot 10^{14}$	0.89–1.77
Visible light		400–700 nm	$4.3 \cdot 10^{14}$ – $7.5 \cdot 10^{14}$	1.77–3.09
Ultraviolet	UVA	315–400 nm	$7.5 \cdot 10^{14}$ – $9.5 \cdot 10^{14}$	3.09–3.94
	UVB	280–315 nm	$9.5 \cdot 10^{14}$ – $1.1 \cdot 10^{15}$	3.94–4.42
	UVC	100–280 nm	$1.1 \cdot 10^{15}$ – $3.0 \cdot 10^{15}$	4.42–12.4
Ionizing radiation		<100 nm	$>3.0 \cdot 10^{15}$	>12.4

Here the nomenclature of high frequency engineers on the one hand, and the specialists in optical spectroscopy on the other hand overlap. The THz region from 0.3 to 3 THz, corresponding to a wavelength (λ) from 0.1 to 1 mm, overlaps with the far infrared, the so-called IRC, which is defined in the large region between 3 μ m and 1 mm (see Table 4.5). Therefore, the THz range spans the transition from radio-electronics to photonics.

In contrast to Fig. 4.26, in Fig. 4.32, the quantum energy of the radiation is additionally included (E in eV) as a third coordinate. The relation between E and the frequency (ν) is given by Planck's constant $h = 6.626 \cdot 10^{-34}$ J s = $4.136 \cdot 10^{-15}$ eV s, corresponding to the relation $E = h\nu$.

In the lower frequency region the quantum energy of radiation is far too low to be considered as a possible reason for interactions with matter. But if it rises up to the levels of molecular vibrations, this parameter becomes of increasing importance. At first it exceeds the energy of thermal noise (kT). Finally, it achieves the energy of covalent bonds, and therefore the energy of ionization. Therefore, in Fig. 4.32 two remarkable points in the scale are included: First the value of 0.026 eV, which corresponds to the energy of thermal noise at 300 K ($E = kT = 8.617 \cdot 10^{-5} \cdot 300$ eV = 0.026 eV), and then the energy of ionization, i.e., the quantum energy which is sufficient to break a covalent bond of water, which amounts to around 12 eV. This second point in the frequency spectrum is considered as the border line to ionizing radiation (see Sect. 4.9).

It is important to note that these two points indicate the general range of energetic transformations in biological processes. From the point of view of thermodynamics, effective mechanisms of energy transformation are possible only above the level of thermal noise. Conversely, the quantum energy must not be as large, as it could destroy the machinery itself. Therefore, the upper limit of biological existence is the quantum energy of ionization, where the quantum energy of the radiation starts to break the covalent bonds of proteins and other biologically important molecules. In fact, only the tiny frequency region of “visible light” between 400 and 700 nm, i.e., 1.77–3.09 eV is suitable to be used by biological systems to extract energy from sunlight, and to recover optical information.

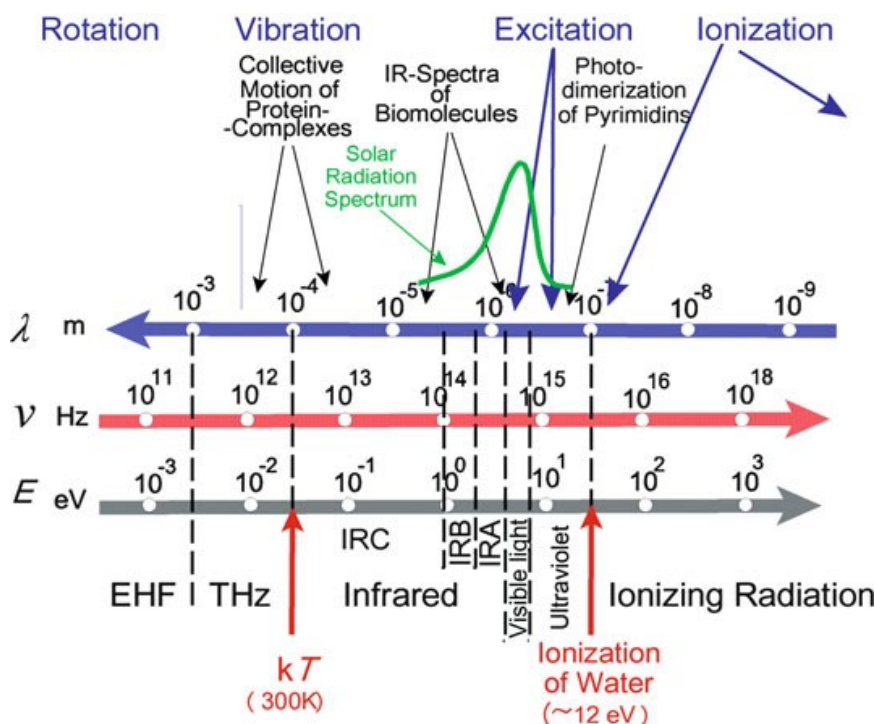


Fig. 4.32 The spectrum of optical frequencies and ionizing radiation (continuation of technical-used frequencies shown in Fig. 4.26)

The scientific literature for this frequency spectrum is largely dominated by spectroscopic investigations. This aspect is quite important for research on the structure and functions of molecular systems, and presented in a number of excellent monographs. Corresponding to the aim of this textbook, the following explanations, however, will concentrate on the mechanisms of molecular interactions, and on aspects of biological influences of this kind of radiation.

It should be noted here that in optical spectroscopy, as a peculiarity, the parameter *wave number* is used to characterize absorption spectra. This parameter is reciprocal to the wavelength. The wavelength (λ) of $3,000 \text{ nm} = 3 \cdot 10^{-4} \text{ cm}$, for example, corresponds to the wave number of: $1/3 \cdot 10^{-4} = 3,330 \text{ cm}^{-1}$. Unfortunately, this parameter is sometimes called “frequency” by spectroscopists, which of course has the correct dimension: $1/\text{s} = \text{Hz}$. Furthermore, the abscissae of absorption spectra are sometimes plotted in a decreasing, and sometimes in an increasing version. In the following text we will only use the three parameters λ (m), ν (Hz), and E (eV) as depicted in Fig. 4.32, plotting them always in the same orientation.

4.8.1 THz and Infrared: The Vibration-Inducing Frequencies

The frequency spectrum which will be considered in this chapter can be characterized in general as thermal radiation, emitted by the sun, by heated materials, and also by the human body. As shown in Figs. 4.32 and 4.37 the thermal

radiation which arrives at the earth's surface from the sun occurs mainly at frequencies $>10^{14}$ Hz, i.e., in the frequency region of IRA, and to a lesser extent at IRB. This also corresponds to the warm sensation of animals, which, however, is considered a temperature sensation according to the Arrhenius law (Sect. 2.1.5), rather than a perception of photons of the infrared radiation. Even the infrared orientation of some snakes, which helps them in the hunting of warm-blooded animals, are not based on particular quantum processes but rather on a temperature-sensitive membrane inside a particular pinhole camera (see Sect. 4.1).

Only in the last decennium has the technical possibilities been developed to produce and to indicate radiation in the THz-frequency range. The THz technologies now receive increasing attention, and various devices use this wavelength. Therefore this frequency band becomes increasingly important in diverse applications. It opens the way to extend infrared spectroscopy into these parts of the spectrum. Because the THz-radiation is strongly absorbed by water molecules, it penetrates just several millimeters of fatty tissue with low water content. This also complicates the THz-spectroscopy of biomolecules in their natural water environment. Conversely the dependence of THz absorption on the water content of the tissue may become important for some diagnostic methods, for example to detect some kinds of epithelial cancer. Some frequencies of terahertz radiation can be used for 3D imaging of teeth and may be more accurate and safer than conventional X-ray imaging in dentistry.

The frequency dependence of absorption of infrared radiation by water and CO_2 is best illustrated by the absorption spectrum of the normal atmosphere, not loaded with fog or rain (Fig. 4.33). It shows a maximum in the frequency region between 10^{12} and 10^{13} Hz. Therefore, it is somewhat unsuitable for use in technical telecommunications, at least under outdoor conditions.

The molecular mechanism of direct interaction of THz and infrared radiation with biological systems can finally be deduced from the data of absorption spectroscopy and by inelastic scattering of photons (*Raman spectroscopy*). The absorption of photons leads to vibrational movements of the molecules and their components. Depending on the structure of the molecule, a more or less large number of vibrational modes are possible. The vibrational modes of proteins are mostly influenced by their secondary structure, and furthermore by their kinds of hydration.

As already discussed in Sect. 2.1.6 (see also Fig. 2.8) the vibration frequency of a C–C bond is in the infrared frequency range of 10^{14} Hz which corresponds to a wavelength of 3 μm . The modes of rotation of these bonds, in contrast, are much lower, and correspond to a frequency below 1 THz. As shown in Fig. 4.32, this is below the energy of thermal movement (kT). The vibration modes, however, may also shift to lower frequencies if collective molecular motions or those of strongly hydrated macromolecules are considered. Collective motions of proteins can involve subdomains of hundreds of atoms with corresponding frequencies up to the THz regime. In these complexes the vibrational energy may flow in a concerted manner, to produce conformational changes.

Recently methods of THz time-domain spectroscopy have been developed. In this case short THz-pulses are applied to the sample material. This allows one to

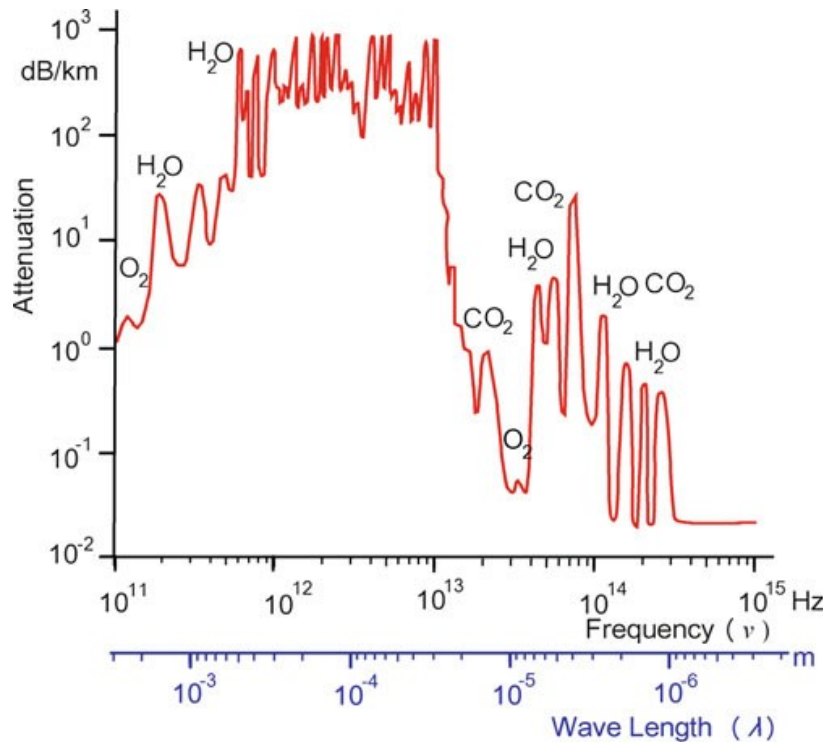


Fig. 4.33 Light absorption in the earth's atmosphere (Data from Sizov 2010)

register both the amplitude and the phase shifts, which contain far more information than a conventional image formed with a single-frequency source.

Exposure of human skin to infrared radiation resulting from solar irradiation, or from IR-emitting devices is used in medical treatments, as a preventative measure, and more recently in the “wellness” sector. Terahertz radiation is nonionizing, and thus is not expected to damage tissues and DNA, unlike X-rays. Single overexposures to IR radiation, however, can lead to acute damage in the form of skin burns, or collapse of the circulatory system. In cases of chronic or frequent repeated exposure, squamous cell carcinoma can result, especially in combination with other sources, like UV radiation. To date the recommendations for protecting humans from the risks of skin exposure to IR are only defined in terms of acute effects.

Further Reading

IR-spectroscopy: Siebert and Hildebrandt 2008; THz-spectroscopy: Plusquellic et al. 2007; Balu et al. 2008; safety aspects: Piazena and Kelleher 2010.

4.8.2 Visible Light: Processes of Excitation and Energy Transfer

The wavelength of visible light lies between 400 and 700 nm. This corresponds to quantum energies between 3.09 and 1.77 eV (see Fig. 4.32 and Table 4.5). This

quantum energy therefore, is far below that of ionizing radiation, a value, which is arrived at only in short-wave ultraviolet light (UVC). Conversely it is larger than that of thermal noise (kT), which at temperatures of biological importance amounts to only about 0.026 eV. As already mentioned in the preface to this Sect. (4.8) the organism uses exactly, this gap between the quantum energy of thermal noise, and the quantum energies causing ionization for photosynthesis and communication with the environment. The photons of light are strong enough for electron excitation, i.e., to lift electrons into a higher energetic state. This is the basic step for effective photochemical processes of energy conversion and photoreception, whilst not endangering the stability of biomolecules.

To understand the basic biophysical processes of photon absorption, let us first consider briefly the process of molecular excitation as illustrated in the so-called *Jablonski diagram* (Fig. 4.34). In a first step, the absorption of a photon leads to the raising of an electron to an orbit of higher quantum number. This can occur in the framework of the following two series of energetic states, which are qualitatively different: S_0, S_1, S_2, \dots , and T_1, T_2, T_3, \dots . Between these steps with increasing quantum numbers additionally, small energetic steps of thermal excitations are positioned. In the case of *singlet states* (S), the electrons of a pair have antiparallel oriented spins. The spin quantum numbers, therefore, have different signs. In the case of *triplet states* (T), the spins of the electrons of the pair are oriented in parallel, thus their spin quantum numbers are identical. The occurrence of electrons in which all quantum numbers are equal is ruled out by *Pauli's exclusion principle* stating that it is impossible for two electrons with identical quantum numbers to occur in the same atom. Thus, if the triplet state represents an electron pair with identical spin quantum numbers, these two electrons must differ with regard to other energy parameters although their orbitals can be energetically very similar. A triplet is a so-called *degenerated state*.

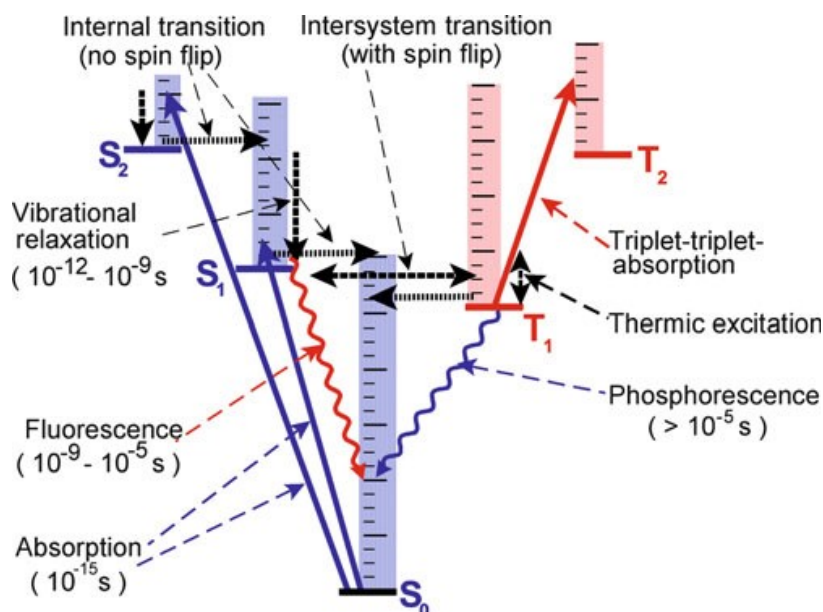


Fig. 4.34 Jablonski diagram of molecular excitations

These two states of excitation differ substantially in their life span. Figure 4.34 shows that the transition $S_1 \rightarrow S_0$ occurs under emission of *fluorescent light* within 10^{-9} – 10^{-5} s, whereas the transition $T_1 \rightarrow S_0$, recordable as *phosphorescence*, will occur at a much slower rate. Consequently, triplet states are characterized by an increased stability when compared with excited singlet states.

In photobiological systems of energy harvesting, as well as in photoreceptor processes the light energy absorbed by the chromophores must be transferred, in order to produce an excitation of the corresponding effector molecules. This transfer from a donor to an acceptor molecule occurs either by charge carriers, i. e., in an electron transfer as a redox-process, by way of fluorescence, or by Förster resonance energy transfer (abbreviated FRET transfer).

The mechanism of this *resonance transfer* can be envisioned as some sort of coupling between oscillating dipoles. It is a process in which a $S_1 \rightarrow S_0$ transition in the donor molecule induces an $S_0 \rightarrow S_1$ excitation in the acceptor. The excited electron of the donor molecule undergoes oscillations and returns to its basic state thus inducing excitation of an electron in the acceptor molecule. This process requires an overlapping of the fluorescent bands of the donor with the absorption band of the acceptor, i.e., the resonance of both oscillators. The smaller the difference of the characteristic frequencies between donor and acceptor, the faster the transfer will be. These so-called strong dipole-dipole couplings are possible to distances of up to 5 nm. This distance is in fact much smaller than the wavelength of emitted light. Therefore a real photon is undetectable, and this mechanism is classified as radiation-less. The term *Förster resonance energy transfer* (FRET) therefore seems to be more appropriate than *fluorescence resonance transfer*.

In general, an *energy transfer by radiation* is also possible. In this case the energy transfer occurs actually by fluorescent radiation emitted by one, and absorbed by the neighboring molecule. Such mechanisms are capable of transferring energy over distances which are large when compared with the other processes described in this context. However, the efficiency of this process is quite low. In fact, such mechanisms do not play a significant role in biological processes.

In contrast to FRET, which usually occurs as a radiation-less singlet-singlet transfer, the *Dexter electron transfer* is a mechanism which allows the energy transfer from triplet states. This is a particular case of electron transfer, in which an excited electron transfers from one molecule (the donor) to a second (the acceptor), maintaining its spin. Typically it may occur at distances below 10 nm.

In the most common metabolic reactions the energy transfer occurs by charge carriers as a classical example of a redox reaction. It consists basically of the transfer of one or two electrons from the donor, to the acceptor molecule. In this way, the donor becomes oxidized, and the acceptor reduced.

For these processes of electron transfer, donor and acceptor molecules must be in exactly defined positions to each other, and at a minimum distance, so that overlapping of respective electron orbitals can occur. In the first place, donor and acceptor will form a complex of highly specific steric configuration, a so-called *charge transfer complex*. This process of complex formation occasionally requires steric transformations of both molecules. It takes place at lower rates when