Absorption of Light and Fate of Excitation Energy in Plant Cells

In Chapter 8, we became acquainted with the stage on which the drama of photosynthesis is enacted. We know (from Chapter 6) that this drama is in two acts: one played, as it were, on a lighted, the other on a darkened stage. In the following chapters, we shall consider a little closer what is known about the text of these two acts. A great amount of research has been done in recent years both on the biochemical and on the photochemical (biophysical) stages of photosynthesis. The study of the dark steps has profited greatly from the discovery of the long-lived radioactive isotope, [14]C. Its use has facilitated the identification of the sequence of biochemical reactions that occurs in the seconds and minutes following the beginning of illumination of a photosynthetic organism (see Chapter 17).

The photochemical stage requires a different approach. In this case, we want to learn something about the nature and sequence of processes that occur in fractions of a second. We must follow rapid changes in the composition and properties of the photosynthetic apparatus; the approach must be physical rather than chemical.

The photochemical part of photosynthesis begins with light absorption. Let us review some general aspects of this process; its knowledge is

essential for the understanding of the mode of action of the photosynthetic pigments.

What happens when light is absorbed by matter? The peculiar thing is that light spreads like a wave, but is absorbed like a stream of particles. The whole world picture of modern physics has this duality; everything is both wave and particle. More precisely, some aspects of the behavior of all physical objects are best described by means of the wave picture, and others, by means of the particle picture. When we talk here about physical objects, we mean primarily the so-called elementary particles of matter—electrons, protons, and neutrons, as well as particles of light, called photons or light quanta.

Heisenberg's *uncertainty principle* permits us to use both, on the face of it, mutually exclusive pictures. This principle states that every time we try to measure the magnitudes that characterize a wave, such as its wavelength or amplitude, the experiment causes the magnitudes characteristic of the particle, such as its location in space and its velocity, to become indefinite, and vice versa. Consequently, it is impossible to devise an experiment that would prove one of the two pictures correct, and the other wrong. We can, therefore, continue using one picture in describing certain aspects of a phenomenon, and the other picture in describing other aspects of it. For example, in the case of light, its propagation, reflection, and interference are best described using the wave picture, while its emission and absorption by atoms and molecules are best described by means of the particle picture.

From experiments on light *propagation* (refraction and interference) the characteristic properties of a light wave, its *wavelength*, λ, wave number, $\bar{\nu}$ and *frequency*, ν, can be derived. They are related by the equation

$$\lambda \nu = \frac{\nu}{\bar{\nu}} = c \qquad (10.1)$$

where c is the velocity of propagation of light (3.0×10^{10} cm/sec in vacuum). As mentioned before, the wavelengths of visible light lie, roughly, between 400 and 800 nm. Below 400 nm lies the ultraviolet, above 800 nm, the infra-red. From experiments on light absorption and emission, we derive the size of the particles, that is, energy quanta (or photons), E. They are the energy packages the light derives from matter in the process of emission, and imparts to it in the process of absorption.

A light wave hits a material object exposed to it like rain hits the pavement, in single drops, each carrying the energy E.

The fundamental relation between E and the properties of the corresponding wave is:

$$E = h\nu = hc\bar{\nu} \qquad (10.2)$$

where h is fundamental constant of physics, called Planck's constant (after Max Planck, the German physicist who first proposed the concept of an energy quantum in 1900). Its dimensions are that of action, that is, energy multiplied by time. Its value in absolute units is 6.62×10^{-27} erg sec.

Equation 10.2 establishes a connection between the wave properties $(\lambda, \bar{\nu})$ and the particle properties of light (E). The higher the frequency—that is, the shorter the wavelength—the larger the quantum. Table 10.1 shows the wave numbers $(\bar{\nu})$, frequencies (ν), and energy quanta, E, corresponding to certain wavelengths of the electromagnetic spectrum.

The quantum size is given in ergs, which is the absolute mechanical energy unit in the so-called CGS system; in Kcal (which is the commonly used unit in chemistry) and in electron-volts (the unit used in atomic physics). The figures 10×10^{-12} to 1.25×10^{-12} erg and 6.3 to 0.79 eV, are the energy contents of a single quantum of 200 to 1600 nm light; while 144 to 18 Kcal are the total energies of an einstein

TABLE 10.1   Optical Radiations

Wavelength, λ, (nm[a])	200	400	800	1,600
Wave number $(\bar{\nu})(\text{cm}^{-1})$	50,000	25,000	12,500	6,250
Frequency, ν (sec^{-1})	15×10^{14}	7.5×10^{14}	3.75×10^{14}	1.88×10^{14}
Photons (quanta), E, in erg/quantum	10×10^{-12}	5×10^{-12}	2.5×10^{-12}	1.25×10^{-12}
in Kcal/einstein[b]	144	72	36	18
in electron volts/quantum	6.3	3.15	1.57	0.79

[a] 1 nm $= 10^{-7}$cm   [b] One einstein $= 6.0 \times 10^{23}$ quanta.

(6×10^{23} quanta). In Chapter 2 we gave about 112 Kcal/mole as the energy stored in photosynthesis, when one mole of CO_2 is reduced and one mole of O_2 produced. We note now that this corresponds to the energy of approximately three einsteins of 800 nm light.

PROPERTIES OF SOLAR RADIATION

The sun emits a continuous spectrum of radiation, from the ultraviolet through the visible into the infrared. It is the spectrum of a hot body having a surface temperature of 6000°C. The higher the temperature, the further the maximum of thermal radiation moves toward the shorter waves. (This is why metals appear, upon heating, first red, then yellow, and ultimately white or even bluish.)

As temperature rises and the total heat radiation increases, the *average size*, E, of quanta grows, too. At 6000°C, the maximum intensity of the emitted light lies in the orange part of the visible spectrum, at about 600 nm. According to Planck's radiation formula, it drops slowly towards the longer waves and sharply towards the shorter waves.

Only a relatively small amount of solar radiation falls into the ultraviolet, $\lambda < 400$ nm. Of the ultraviolet light present when this radiation reaches the top of the atmosphere, the larger part does not penetrate to the surface of the earth. The shorter-wave ultraviolet (<300 nm) is absorbed by the oxygen molecules, O_2, which are thus chemically activated, and react to form ozone molecules: $3O_2 \rightarrow 2O_3$. The ozone molecules themselves absorb in the nearer ultraviolet, between 300 and 350 nm, and react back to O_2.

Together, the two forms of oxygen form a screen that prevents most of the sun's ultraviolet light, except that above 350 nm, from reaching the surface of the earth. This is a very important protection. All organic molecules absorb light in the far ultraviolet; all living matter on land would have been destroyed if organisms were continuously exposed to unscreened sunlight. Only aquatic organisms could survive under a sufficiently thick layer of water.

About one half of the solar energy flux, as it reaches the surface of the earth, consists of visible light, that is, light with wavelengths from 400 to 800 nm. The other half is infrared light, with wavelengths

above 800 mm. Some bands in the infrared region are absorbed in the air by water vapor and carbon dioxide.

Since, in photosynthesis, light has to be used to induce a chemical change, long-wave infrared light is of no use for it. In order to cause a chemical change, the quantum must be large enough to affect significantly the chemical stability of a molecule, that is, it must not be too small compared to the energies of the chemical bonds.

The quantum does not need to be so large as to break a chemical bond and decompose the molecule into free atoms or radicals; usually, it is enough for it to "energize" the molecule, transferring it into a sufficiently energy-rich *excited state* to surmount the "activation barrier" and permit a chemical reaction. (A chance of immediate remarriage makes divorce from the original partner easier!)

Excitation of a stable molecule is, however, unlikely to be chemically effective unless the absorbed quantum weakens a chemical bond *substantially*. The energies of stable chemical bonds in organic molecules are, as stated in Chapter 5, of the order of 50–100 Kcal/mole. Light quanta must be, say, half, as large, 25–50 Kcal/einstein, to weaken them significantly.

Coming from the infrared side, light quanta reach 25 Kcal/mole (or about 1 ev) at 1200 nm. They reach 50 Kcal/mole, or about 2 ev, in the middle of the visible spectrum. In other words, ultraviolet light and short-wave visible (violet, blue, and green) light, can be expected to be photochemically fully active. Certain photochemical reactions are possible also in the long-wave visible light (yellow and red) and even in the near-infrared. Quanta belonging to the long-wave infrared can cause only slight perturbations of stable chemical bonds, insufficient to lead to photochemical reactions.

Since vision itself is based on a photochemical action of light, its long-wave limit, (that is, the limit between infrared and visible spectrum), coincides approximately with the above-suggested limit of photochemical activity. The limit of visibility toward the shorter waves is imposed by the absorption of ultraviolet light in the tissues separating the retina from the air. This made it useless for animals to equip their retinas with photosensitive compounds absorbing further in the ultraviolet. The human eye can see up to about 760–800 nm on one end of the spectrum, and down to about 360–400 nm on the other hand.

Bacterial photosynthesis occurs mainly in the near-infrared, up to

1000–1100 nm. Properly sensitized photographic plates respond to light up to 1500 nm.

BEER'S LAW

When a beam of photons having appropriate frequencies strikes an absorbing substance, this beam is progressively weakened as it penetrates into the medium. This weakening follows Beer's Law:

$$I = I_0 10^{-\alpha cx} \tag{10.3}$$

where I_o is the intensity of the incident beam (the number of quanta striking each second one cm^2 of the surface normal to the direction of the beam), I is the residual intensity in depth x, and αc, a constant of the material, characterizing its absorption capacity. The product αc can be separated, in the case of solutions of colored molecules in a colorless medium, into a concentration factor, c, and an intrinsic factor, α. If c is expressed in moles/liter, α is the so-called *molar absorption coefficient*. It depends on the wavelength of light. If the beam is not monochromatic, that is, if it contains a variety of photons (for example, if it is a beam of white light), its spectral composition changes as it passes through the absorbing layer. The wavelengths for which the α values are highest are eliminated first, and those for which the α values are smallest penetrate deepest, or emerge on the other side of the absorbing layer.

The dependence of I on depth x in Eq. 10.3 is exponential. Differentiation converts Eq. 10.3 into Eq. 10.4, which applies to a thin layer, dx:

$$\frac{dI}{dx} = -I_0 \alpha c \ 10^{-\alpha cx} \ln 10 \tag{10.4}$$

By using natural logarithms, ln e (logarithms to the base e), instead of decadic ones, one can get rid of the factor ln 10. This is sometimes done, but more often, the decadic absorption coefficient is used instead of the natural. (The latter is often designated as ϵ, with $\epsilon = \ln 10 \times \alpha$.)

Equation 10.4 suggests that whenever light penetrates a certain distance dx, it is weakened in the same proportion. If it is weakened by 50% in the first 1 cm layer, it is weakened again by 50% in the next
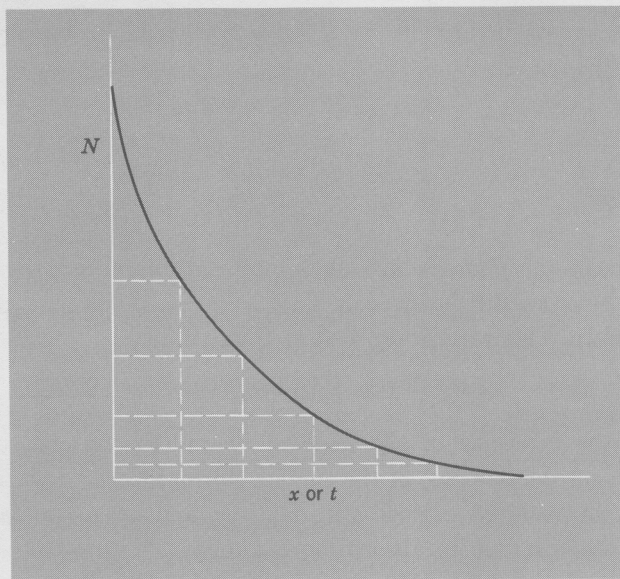
FIG. 10.1 Exponential decay curve.

1 cm layer, and so on. This is called exponential decay, a law of decay characteristic of all processes consisting of individual events not related to each other. (In our case, a molecule picks up a quantum without relation to what happened to any other quantum or any other molecule.) This is a so-called *first order process*. The number of absorption acts occurring in each layer of thickness, dx, is, under these conditions, proportional to the intensity of the beam incident on it.

Similar relations prevail in "first order" chemical reactions and in the transformation of radioactive elements; only there, the time coordinate, t, takes the place of the space coordinate x. The number of reacting molecules (or of nuclear transformations), dN, in each time element, dt, is proportional to the number of unchanged reactants (or radioactive atoms) present at the beginning of this period (Fig. 10.1). The decay is logarithmic *in time;* it is logarithmic *in space* in the case of light absorption.

One can rewrite Eq. 10.3 in the form:

$$\log \frac{I_0}{I} = \alpha c x \qquad (10.5)$$

The expression log (I_0/I) is often called *optical density* or *"absorbance"* of the absorbing material. Optical density 1 means that the light is weakened by a factor of 10; optical density 2, that it is weakened by a factor of 100, etc. The optical density of 1 cm thick layer is 1 if $\alpha = 1/c$. Strong organic pigments are characterized by α-values of the order of 10^4, so that an optical density of 1 is that of a 1 cm layer of an approximately 10^{-4} molar solution.

The exponential decay of light intensity upon penetration into an absorbing medium is a nuisance in quantitative photochemical work. To study the kinetics of photochemical reactions, one would like to illuminate the photosensitive system *uniformly*, but Beer's law makes this impossible. It is helpful to use an optically very thin (or dilute) system, with a low αc-value. When I is *almost* equal to I_0, the exponential can be expanded into a series, and the series broken off after the first term, giving:

$$I = I_0(1 - \alpha cx \ln 10) \tag{10.6}$$

Exponential decay is thus replaced by *linear* decay. This approximation is permissible as long as the term αcx is large compared to the next, neglected term in the series, $(\alpha cx)^2/2$. If the optical density αcx is 0.1, the neglected term is 0.005, so that neglecting it means an error of 5 percent. If the optical density is 0.01, the neglected term is 0.00005; this means an error of 0.5%. If errors up to 1 percent can be tolerated, linear approximation can be used for samples with absorbances of the order of 0.02.

In working with photosynthesizing plant cells, one has to contend with the fact that a single chloroplast may absorb 50 or 60 percent of incident light in the peak of the absorption band (675 nm). It is, therefore, impossible to achieve uniform illumination of all chlorophyll molecules in a single chloroplast, except by using monochromatic light far from the peak of the absorption band of chlorophyll.

MECHANISM OF LIGHT ABSORPTION AND EMISSION

What happens to an atom or molecule that absorbs a photon? When light is absorbed by matter, each quantum is taken up by a single atom

or molecule and the whole energy of the quantum is communicated to it. The absorbing atom or molecule is thus *excited*, that is, lifted from its normal state of lowest energy (highest stability) to an *excited*, energy-rich state. According to Bohr's theory of atomic and molecular structure, an atom or molecule can exist only in a series of discrete states of electronic energy. This is represented in Fig. 10.2, in which
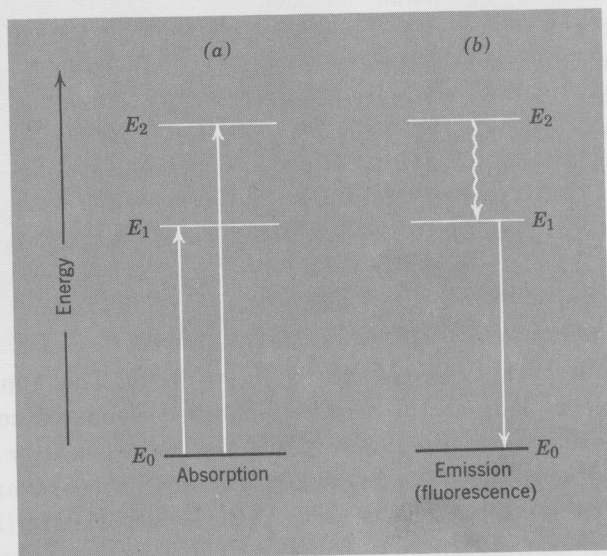

FIG. 10.2. Ground state (E_0) and two excited states (E_1, E_2) of a molecule (vibrational and rotational levels not shown).

energy levels are indicated, as they usually are in spectroscopy, by properly spaced horizontal lines. The lowest line represents the ground state, E_0, of the atom or molecule in which it exists in the absence of external activation. The higher lines (E_1 and E_2) represent *excited electronic* states—the only kind of excited states possible in an atom.

In a diatomic or polyatomic *molecule*, one or several series of (also quantized) *vibrational* and *rotational* states are superimposed on each electronic state. If the molecule is complex, the various vibrational and rotational states lie so close together that sharp absorption and emission lines of atoms, or structured bands of simple molecules, are replaced by broad, continuous bands.

The absorption lines (or bands) are represented, in schemes of this

type, by arrows directed upwards (Fig. 10.2a) and the emission lines or bands by arrows directed downwards (Fig. 10.2b). The energy of the quanta of emission or absorption are proportional to the lengths of the arrows. An atom or molecule can absorb only energy quanta corresponding to the distances between the permitted energy states. Once it is excited, say to state E_2, it can emit only light quanta represented by downward arrows, leading from E_2 to a lower energy state, and finally to E_0 (Fig. 10.2b).[1] In *fluorescence*, light absorption leading, say, from E_0 to E_1 is reversed by light emission leading from E_1 to E_0.

When a photon is absorbed, the molecule usually is not merely transferred into an excited electronic state, but also acquires some vibrational energy. According to the so-called *Franck-Condon principle*, the absorption of a photon is a practically instantaneous process, since it involves only the rearrangement of practically inertia-free electrons. The much heavier atomic nuclei have no time to readjust themselves during the absorption act, but have to do it after it is over, and this readjustment brings them into vibrations. This is best illustrated by potential energy diagrams, such as that in Fig. 10.3. It is an expanded energy level diagram, with the abscissa acquiring the meaning of distance between the nuclei, r for example, distance x-y in a diatomic molecule xy). The two potential curves show the potential energy of the molecule as function of this distance for two electronic states, a ground state and an excited state. Excitation is represented, according to the Franck-Condon principle, by a *vertical* arrow (A). This arrow hits the upper curve, except for very special cases, not in its lowest point, corresponding to a nonvibrating state, but somewhere higher. This means that the molecule finds itself, after the absorption act, in a nonequilibrium state and begins to vibrate like a spring. This vibration is described, in Fig. 10.3, by the molecule running down, up, down again, etc., along the upper potential curve, like a pendulum. The periods of these vibrations are of the order of 10^{-13} or 10^{-12} seconds. Since the lifetimes of excited electronic states are of the order of 10^{-9} sec (or longer), there is enough time during the excitation period for many thousands of vibrations. During this time much if not all of the extra vibrational energy

---

[1] The wavy arrow in Fig. 10.2b relates to another, radiationless way in which a transition can occur—by energy loss to surrounding molecules, or by its "internal" conversion into vibrational energy of the excited molecule.

can be lost by energy exchange (temperature equalization) with the medium. The molecule, while it remains extremely "hot" as far as its electronic state is concerned, thus acquires the ambient "vibrational temperature." Fluorescence, when it comes, originates from near the bottom of the upper potential curve, and follows a vertical arrow down (F), until it strikes the lower potential curve. Again, it does not hit it in its deepest point, so that some excitation energy becomes converted into vibrational energy. The cycle absorption-emission thus contains two periods of energy dissipation. Because of this, the fluorescence arrow (F) is always shorter (that is, the fluorescence frequency is lower) than that of absorption (A). In other words, the wavelengths of the fluorescence band are longer than those of the absorption band. This displacement of fluorescence bands towards the longer waves compared to the absorption bands ("Stokes' shift") was a long-established experimental
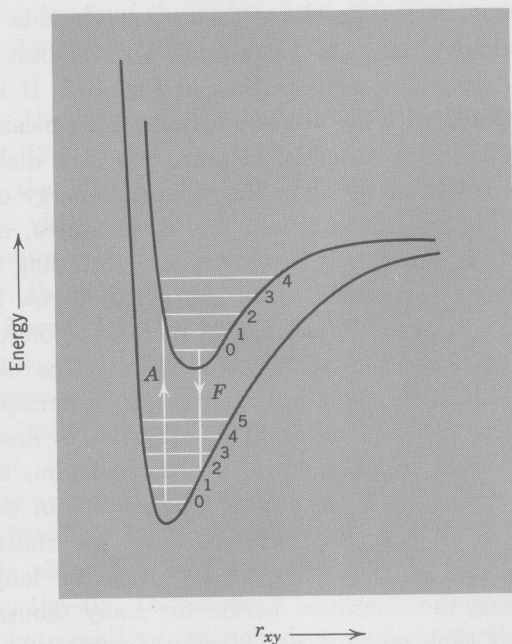

FIG. 10.3 Potential energy curves for the ground state and an excited state of a diatomic molecule. (r, interatomic distance; A, absorption; F, fluorescence; numbers indicate vibrational states.)
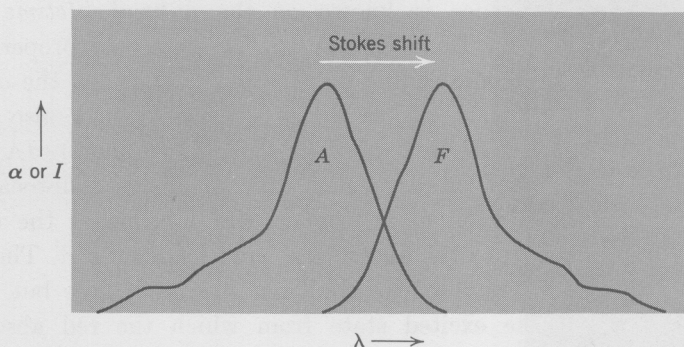
FIG. 10.4 The Stokes' shift (displacement of fluorescence band compared to the absorption band of a molecule). Approximate mirror symmetry of the two bands exists when the shapes of the potential curves in the ground state and the excited state are similar.

fact (Fig. 10.4), before the Franck-Condon principle provided its interpretation. Obviously, the extent of the shift depends on the difference between the two potential curves. The same difference determines the width of the absorption band. Chlorophyll a, the major pigment of all green plants, has (in organic solvents) a very narrow absorption band (half-band width, 18 nm) and a very small Stokes' shift (of the order of 7–10 nm).

FATE OF EXCITATION ENERGY
IN PHOTOSYNTHESIZING CELLS

We must now consider the fate of the energy quantum absorbed by a molecule—for example, a chlorophyll molecule in a chloroplast—and the way in which it can be utilized for a photochemical reaction. A molecule, M^*, in an electronically excited state, faces several possibilities. If it is well protected from interaction with other molecules, it will have to get rid of its excitation energy "all by itself." The simplest way is for it to emit a photon back into space. This is *fluorescence*. The average time a molecule has to spend in the excited state between

absorption and fluorescence is known as the *natural lifetime* τ_o of the excited state. Its duration depends on the electronic properties of the two states. An electronic charge distribution that favors the *absorption* of a quantum (that is, makes the absorption strong) also favors its *emission* (makes the lifetime of the excited state short). (A heavy earner is a heavy spender, or easy come, easy go!) This reciprocal relation permits the calculation of τ_o, the natural lifetime of the excited state, from the intensity of the absorption band leading to it. The exact relationship is rather complex,[2] we shall not discuss it here but simply mention that τ_o of the excited state from which the red absorption band of chlorophyll *a* is emitted is about 1.5×10^{-8} sec (15 nsec).

The excited molecule has, however, very rarely the chance to live out its whole natural lifetime because other ways to lose its excitation energy are offered to it (Fig. 10.5). One is intrinsic: instead of by fluorescence, the molecule can lose its electronic excitation energy by so-called *internal conversion*, that is, by conversion of the large electronic excitation quantum into smaller vibrational quanta within the molecule itself (see Figs. 10.2 and 10.5). Very often, the loss of only one or a few vibration quanta suffices to transfer the molecule from its original excited state into a nonfluorescent, *metastable* state. This is a peculiar excited electronic state, with a much longer natural lifetime. This "metastability" is due to the fact that the emission of a light quantum, transferring the molecule from the metastable state into the ground state, is extremely improbable (because it would violate certain "conservation rules"). For reasons of reciprocity, whatever is unlikely in emission is also unlikely in absorption, so that metastability of an excited state also implies weakness of the absorption band leading to it.

Usually, the ground state of a valence-saturated organic compound, that is, of a molecule having only paired electrons in the outermost

---

[2] An approximate relationship is:

$$\frac{1}{\tau_o} = 3 \times 10^{-9} \left(\frac{1}{\lambda}\right)^2 \Delta \left(\frac{1}{\lambda}\right) \epsilon_{max}$$

where $\dfrac{1}{\lambda}$ = wave number (in cm^{-1}) at the peak of the absorption band; ϵ_{max}, the corresponding absorption coefficient, and $\Delta \left(\dfrac{1}{\lambda}\right)$, the half-band width in wave numbers (cm^{-1}).
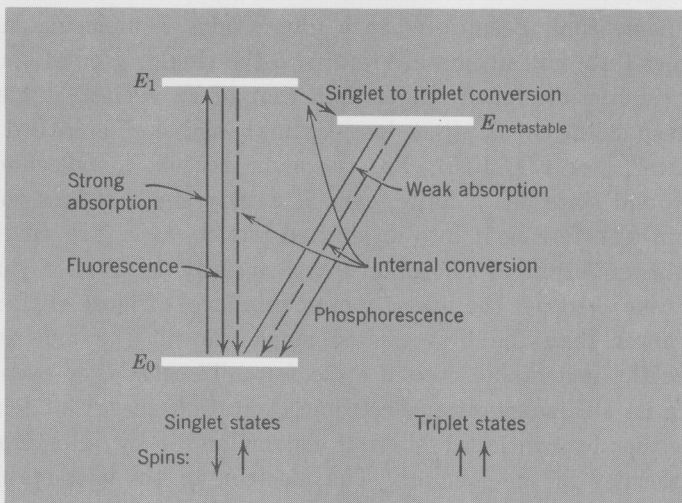
FIG. 10.5 Excitation and deexcitation processes in a valence-saturated molecule (with a singlet ground state and a metastable triplet state). (Vibrational and rotational levels are not shown.)

orbit, is a *singlet* state with an electron spin of zero, while its most important metastable state is a *triplet* state, with the net electron spin of 1, in quantum units $\lambda/2\pi$ (as indicated in Fig. 10.5).

Electrons are supposed to spin (that is, rotate around an axis passing through the electron). A triplet state is characterized by two parallel spins ($\uparrow\uparrow$): both valence electrons spin in the same sense; a singlet state, by antiparallel spins ($\uparrow\downarrow$): one electron spins clockwise, the other anticlockwise. A triplet state is so called because, upon closer examination, it proves to consist of three close components (three closely-spaced energy levels). Transition from a triplet to a singlet state or vice versa by emission or absorption of a photon is prohibited because the photon has no "handle" to accept (or to supply) the rotational momentum needed to compensate the change in rotational momentum associated with the "flipping" of one spin from parallel to antiparallel orientation in respect to the other spin.[3] The prohibited transition may, nevertheless, take place if some other rotating system (in the same molecule, or in its surroundings) offers itself to maintain the law of conservation of

[3] Conservation of rotational momentum is a basic law of mechanics.

angular momentum. Because of such interactions, a molecule in an excited triplet state will ultimately return to the singlet ground state—but only after a lifetime much longer than that of an excited singlet state. The corresponding weak (but long-lasting) emission is called "phosphorescence" (see Fig. 10.5). For the same reason, a molecule in the singlet ground state has a finite, even if a very small chance to absorb a quantum transferring it into an excited triplet state. The energy content of the quantum of phosphorescence usually is smaller than that of fluorescence because the lowest metastable level of most organic molecules is lower than the first excited singlet level. The molecule may survive in the metastable excited state for milliseconds, or even longer, dispersing its still substantial electronic excitation energy at leisure, as it were, either by continued internal conversion, or by interaction with other molecules in the medium. The electron in the metastable state may be kicked back up to the singlet-excited state (E) by acquiring some energy from the medium; fluorescence following such an action will be delayed (delayed fluorescence). It seems that many photochemical reactions occur through the intermediary of metastable states. These states give the light-excited molecule a better chance to encounter a reaction partner than do the fleeting fluorescent singlet states. The existence of triplet states has been proven in chlorophyll dissolved in organic solvents, but not yet clearly demonstrated in vivo; there are, however, various indications that the triplet state of chlorophyll may be involved in photosynthesis.

Fluorescence, internal conversion, and transition to the triplet state are competing spontaneous (or "monomolecular") processes, by which excited states can lose their excitation energy. In addition, there can be "induced" deactivation, as well as photochemical reactions, caused by interaction of the excited molecule with different collision partners.

In a condensed (that is, solid or liquid) system, where an excited molecule is crowded by other molecules, it is particularly strongly threatened by accidents, which can deprive it of its excitation energy. One can say that, in addition to the two inescapable "first order" death causes, the "heart disease" of fluorescence and the "cancer" of internal conversion, the life of an excited molecule in a condensed medium is threatened also by a variety of "second order" processes—communicable diseases or injuries caused by encounters with other molecules.

Measurements have shown that the fluorescence yield of chlorophyll

a in solution (for example, in diethyl ether, or ethanol) is about 30 percent. This means that out of 100 excited molecules, 30 die by emitting a quantum of fluorescence and 70 by internal conversion (presumably initiated by transfer into the metastable state).

In the living cell, the fluorescence yield of chlorophyll *a* is much lower, In weak light, it does not exceed 3 percent, that is, at best, only 3 out of 100 excited molecules are deactivated by fluorescence. What of the others? In low light, when photosynthesis proceeds with its maximum quantum yield, they may be all, or practically all, utilized for the primary photochemical reaction of photosynthesis by interaction of the excited molecule (either before or after its conversion into the metastable stage) with a "primary reactant."

Photochemical utilization of excitation energy will or will not affect the quantum yield of fluorescence, depending on whether it precedes or follows the conversion into the metastable state. In the first case, photochemical sensitization is in direct competition with fluorescence; in the second, it is not.

According to Bohr's theory, excitation of an atom (or molecule) means the shifting of one of its electrons from its closest permitted orbit around the nucleus (energy E_0), into a wider one (energy E_1). The primary photochemical process in photosynthesis was described, in Chapter 5 as an *oxidation-reduction* (that is, in essence, shifting of an electron from the reductant to the oxidant). Photosynthesis thus requires the replacement of electron transfer from one orbit to another within a single molecule of Chl *a*, by electron transfer from one molecule (reductant) to another (oxidant). In principle, this can be imagined to occur in three steps, as represented by the three arrows in Fig. 10.6. The vertical arrow represents the excitation of an electron in pigment *P* to a higher energy level. (This must be, specifically, the pigment molecule in or near the "reaction center.") The upper slanted arrow represents the transfer of this high-energy electron to the oxidant, and the lower downward-slanted arrow, the replacement of this electron in *P* by an electron supplied by the reductant. The two dashed arrows are slanted downward, because spontaneous dark reactions must occur with some loss of free energy. The net result is oxidation of the reductant *R* and reduction of the oxidant *O*, with the energy of light utilized to move the electron "uphill" from its more stable association with *R* to a less stable association with *O*.
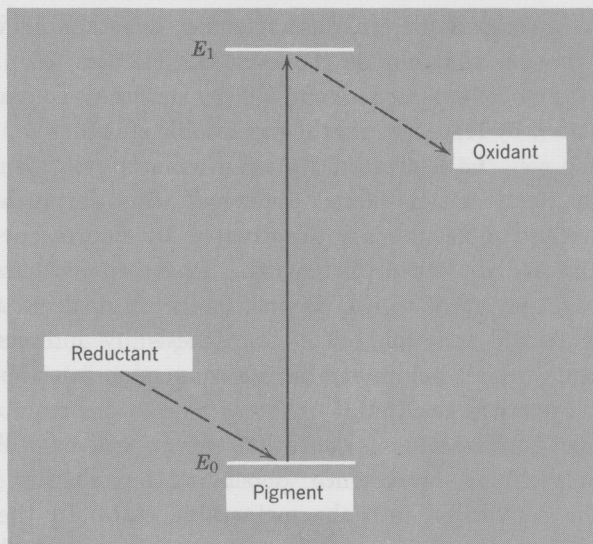
FIG. 10.6 Pigment-sensitized electron transfer from reductant to oxidant, with storage of energy. (E_0, ground state; E_1, excited state.)

In practice, of course, the process is more complicated. To begin with, it seems to involve a *transfer of energy quanta* from pigment molecule to pigment molecule in the "photosynthetic unit" (see Chapters 6 and 8) and their *trapping* in a reaction center. Recently we have begun to acquire some understanding of this process (Chapters 11 and 12). Furthermore, it seems to require two photochemical reactions in succession, with an enzymatic reaction sequence between them (Chapters 14–16).