5 Mechanisms of Energy Transfer

5.1 Photophysics and Photochemistry.
General Principles

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The ultimate source of energy for all biological transformations is sunlight. Green plants, algae, and a few bacteria make use of the radiative energy in the visible wavelength range, from about 400 to 800 nm, for the synthesis of energy-rich organic compounds, such as glucose, from simple inorganic molecules, essentially water and carbon dioxide. Glucose is the prototype of food for higher organisms. The overall reaction of photosynthesis is represented by

\[ 6 \text{CO}_2 + 6 \text{H}_2\text{O} + \text{light} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \tag{5.1} \]

The first important, and yet very complex, stage is the reduction of NADP\(^+\) and the phosphorylation of ADP to ATP with the release of molecular oxygen. In a subsequent chain of "dark reactions", NADPH and ATP serve as energy sources for the reduction of CO\(_2\).

(For details, and other photochemical processes of biological relevance, see Chap. 13.)

In a photochemical reaction, as a consequence of the excitation of a molecule to a higher electronic state by absorption of light energy, chemical bonds can be broken, new bands formed, the molecule may be reduced or oxidized, and its conformation can change. Only absorbed light can be photochemically effective. Most molecules, however, are stable under illumination with visible light although they may absorb it.

There exist effective reaction "channels" for deactivating the optically excited state which are in competition with chemical reactions. All these processes, including the act of light absorption, are called "photochemical reactions". Generally, a photochemical reaction consists of a sequence of steps, only the first of which is truly photochemically induced (primary). For the example of Eq. (5.1), more than a hundred reaction steps are known. Eight elementary photochemical reactions, each consuming one photon, are involved to form one molecule of O\(_2\); all other steps are dark reactions. In this chapter, only photophysical and primary photochemical reactions will be considered.

5.1.1 Stationary States of Molecules

A free molecule may exist in a number of different "stationary" (long-lived) states. These states can be sufficiently well described by the solutions \(\psi_k\) of the time-independent, nonrelativistic Schrödinger equation of the system. To each of the different states correspond distinct values of energy and angular momentum, a characteristic distribution of electron density, and, in general a well-defined equilibrium geometry.

To a very good approximation, the internal energy in state \(\psi_i\) may be separated into three contributions:

\[ E_i = E_{\text{el}(i)} + E_{\text{v}(i)} + E_{\text{rot}(i)} \tag{5.2} \]

where

- \(E_{\text{el}(i)}\) is the electronic energy,
- \(E_{\text{v}(i)}\) the vibrational energy of the nuclei in the potential field of the electrons, and
- \(E_{\text{rot}(i)}\) the rotational energy of the whole molecule.

Valence electrons can be excited into higher states with energies in the range of \(\Delta E_{\text{el}} \approx 1\) to 5 eV, corresponding to light quanta of wavelengths \(\lambda \approx 1000\) to 200 nm. Internal vibrations and rotations require much lower-energy photons, typically \(\Delta E_{\text{v}} \approx 10^{-1}\) eV, \(\Delta E_{\text{rot}} \approx 10^{-3}\) eV, respectively (1 eV = 96.49 kJ/mol = 23.05 kcal/mol).

In "normal" photochemistry, as in photobiology, the energy range from 1 to 10 eV is of interest. From the solar spectrum, only photons with wavelengths \(\lambda > 300\) nm (energy < 2.7 eV) penetrate the atmosphere and reach the earth’s surface. Tungsten lamps with glass bulbs have a similar limit whereas helium and metal vapor lamps with quartz tubes emit very effectively quanta up to 6.2 eV (\(\lambda \approx 200\) nm).

The first ionization potential of most organic molecules is about 10 eV.

Spectroscopically relevant quantities, in particular wavelength \(\lambda\), wavenumber \(\tilde{\nu}\), quantum energy \(h\nu\), extinction coefficient \(\varepsilon\), have been introduced in Chap. 3.2.5.

5.1.1.1 Energy Level Diagrams; Multiplicity

The energies of the various states of a molecule are conveniently plotted in an energy level diagram. In condensed phases, rotation is hindered and vibrations are more or less damped; as a consequence, the corresponding energy levels are no longer sharp but instead are broadened. In the following we will disregard rotations and only deal with vibrationally excited electronic ("vibronic") states. Of great importance are their individual "natural" lifetimes \(\tau_i\) on
which the attainable population (concentrations) and
reaction rates strongly depend.

Almost all organic molecules have an even number of
electrons. In their lowest (ground) electronic states, the
intrinsic angular momenta (spins) of the electrons add
to a resultant spin of zero, characterized by a total spin
quantum number \( S = 0 \) and a "multiplicity" \( 2S + 1 = 1 \)
(singlet). Singlet states are diamagnetic. Another impor-
tant spin configuration is with \( S = 1 \) and \( 2S + 1 = 3 \)
(triplet), in which one pair of electrons has parallel spins
(see also Chap. 5.1.2.1). States with \( S \neq 0 \) are para-
magnetic. Transitions between states, and hence their
lifetimes, are governed by selection rules, one of the
most rigorous being the conservation of multiplicity.

Thus a triplet state is of relatively long life if there are
only singlet states below it on the energy scale. A change
in multiplicity, i.e., a spinforbidden reaction, is en-
\hanced by a strong internal magnetic field arising from
the orbital movement of electrons.

This "spin-orbit interaction" becomes more effective
when atoms with higher nuclear charge ("heavy
atoms") are introduced in a molecule, such as halogens,
metals, sulfur or phosphorus.

By far the most important molecule with a triplet
ground state is oxygen, \( \text{O}_2 \). It is especially reactive with
organic molecules in their lowest, long-lived, excited
triplet state. By oxidation (release of an electron) or
reduction (addition) of a molecule a paramagnetic
radical with an uneven number of electrons and \( S =1/2 \)
and \( 2S + 1 = 2 \) (doublet character) is formed.

In Fig. 3.63, a typical energy level diagram of an
organic molecule is schematically represented (Ja-
blonski diagram), including singlet \( (S_1) \) and triplet \( (T_1) \)
levels as well as some transitions. Typical lifetimes in
solution are: \( S_1 : 10^{-9} \ s = 1 \ \text{ns} \); \( T_1 : 10^{-6} \ s = 1 \ \mu \text{s} \); \( S_{n>1}, T_{n>1} : 10^{-12} \ s = 1 \ \text{ps} \).

In an ensemble, the occupation number \( n_k \) of mole-
cules in the excited state \( \psi_k \) decreases due to various
photophysical and photochemical reactions. In general,
the reaction rate \( v_i \) along channel \( i \) is given by first order
kinetics, \( v_i = k_i \cdot n_k \), where \( k_i \) is the rate constant of the
specific process. The yield of the reaction \( i \) is thus the
fraction
\[
\phi_i = \frac{k_i}{\sum k_j} \quad \sum \phi_i = 1. \quad (5.3)
\]

If the level \( \psi_k \) is populated (directly or indirectly) by
absorption of 1 quantum of light per molecule, \( \phi_i \) is
called the quantum yield of reaction \( i \). For photochemi-
cal primary reactions, \( \phi_i \leq 1 \); for photochemically
induced chain reactions, however, the number of
product molecules may be much greater than the
number of absorbed photons. Such a reaction is only
started, not driven, by light energy.

5.1.1.2 Solution Spectra

In Fig. 5.1 typical absorption and emission (fluores-
cence, phosphorescense) spectra of an organic molecule
in solution are shown. The energies of transitions to
pure electronic levels are indicated by symbols \( T_i, S_i \),
corresponding to an energy level diagram as in Fig.
3.63. Other maxima are caused by vibronic states. All
bands are broadened by energetic interactions with the
solvent (matrix). The apparent width originates from
the overlap of many much sharper spectra of individual
molecules, each of them "feeling" a somewhat different
interaction with its surroundings ("inhomogeneous
broadening"). A promising technique suitable for re-
vealing molecular lineshapes and yielding information
on these interactions should at least be mentioned; this
is "spectral hole burning". The intensity distribution
of vibronic transitions will be discussed below in Chap.
5.1.4.1 (see also Fig. 3.64).

With very few exceptions, emission transitions in
condensed phases only start from pure electronic levels
\( S_1 \) (fluorescence, decay time \( \tau_F \approx 1 \ \text{ns} \) to 1 \ \mu \text{s} \) and \( T_1 \)
(phosphorescence, \( \tau_P \approx 1 \ \mu \text{s} \) in liquids at 300 K to \( \approx 10 \ \text{s} \)
in solid solutions at \( T \leq 100 \ \text{K} \). All higher levels decay
or relax much faster via nonradiative channels.

A convenient measure for absorption intensities is
the "molar (decadic) extinction coefficient" \( \varepsilon (\tilde{\nu}) \), de-
defined by
\[
\varepsilon (\tilde{\nu}) = \frac{1}{cd} \log \frac{I_0}{I_\tilde{\nu}} \equiv \frac{E(\tilde{\nu})}{cd}, \quad (5.4)
\]
where \( c \) is the concentration in mol/l and \( d \) is the
thickness of sample in cm; \( I_0(\tilde{\nu}) \), \( I(\tilde{\nu}) \) are the incident and
transmitted light intensity at wavenumber \( \tilde{\nu} \), re-
respectively; and \( E(\tilde{\nu}) = \log \frac{I_0}{I_\tilde{\nu}} \), the "measured extinc-
tion", is measured with a spectrophotometer (cf. also