1

Introductory Concepts

AIMS AND OBJECTIVES

After you have completed your study of all the components of Chapter 1, you should be able to:

- Understand the concept of the quantised nature of light and matter and be able to draw simple diagrams showing quantised energy levels in atoms and molecules.
- Relate the wavelength of electromagnetic radiation to its frequency and energy.
- Understand the relationship between the wavelength of electromagnetic radiation absorbed by a sample and its potential to produce chemical change.
- Understand how absorption, spontaneous emission and stimulated emission occur in matter–light interactions.
- Explain how quantum mechanics has led to the concept of atomic and molecular orbitals.
- Use and interpret simple atomic and molecular orbital energy diagrams.
- Describe the relative merits as light sources of mercury lamps and lasers.
- Describe the mode of action of a laser and the characteristic properties of laser light.
- Distinguish between electronic configuration and electronic state.
- Recognise experimental situations in which lasers are essential and those in which mercury lamps are more appropriate.

Principles and Applications of Photochemistry Brian Wardle

- Understand the importance of quantum yield as a measure of the efficiency of a photoreaction.

1.1 THE QUANTUM NATURE OF MATTER AND LIGHT

Photochemical reactions occur all around us, being an important feature of many of the chemical processes occurring in living systems and in the environment. The power and versatility of photochemistry is becoming increasingly important in improving the quality of our lives, through health care, energy production and the search for 'green' solutions to some of the problems of the modern world. Many industrial and technological processes rely on applications of photochemistry, and the development of many new devices has been made possible by spin-off from photochemical research. Important and exciting light-induced changes relevant to everyday life are discussed throughout this text.

Photochemistry is the study of the chemical reactions and physical changes that result from interactions between matter and visible or ultraviolet light.

The principal aim of this introduction is to familiarise the reader with basic ideas relating to light and matter and the interaction between them. Quantum mechanics underpins an understanding of the nature of both light and matter, but a rigorous treatment of quantum theory involves complex mathematical analysis. In order to make the ideas of quantum mechanics available to a wider readership, conceptually simple models are presented.

The development of the **quantum theory** in the early twentieth century allowed predictions to be made relating to the properties and behaviour of matter and light. The electrons in matter have both wavelike and particle-like properties, and quantum theory shows that the energy of matter is **quantised**; that is, only certain specific energies are allowed.

The quantised energy levels of matter have a separation that is of the same order as the energy of visible or ultraviolet light. Thus the absorption of visible or ultraviolet light by matter can excite electrons to higher energy levels, producing electronically-excited species.

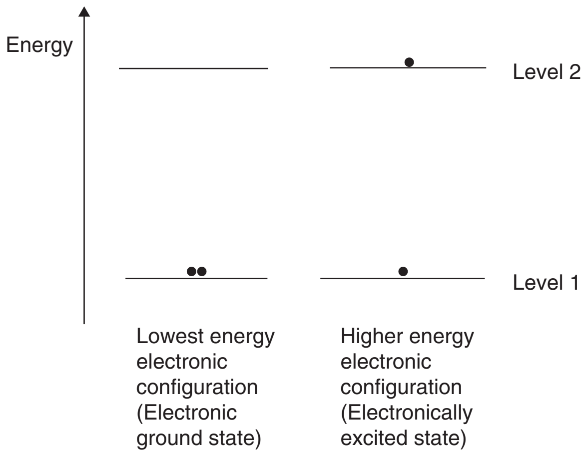


Figure 1.1 Quantised energy levels in matter, where an electron (•) may be found in either of the two energy levels shown

According to the quantum theory, light is also quantised. The absorption or emission of light occurs by the transfer of energy as **photons**. These photons have both wavelike and particle-like properties and each photon has a specific energy, E, given by **Planck's law**:

$$\boxed{E = h\nu}$$

where h is **Planck's constant** (6.63×10^{-34} Js) and ν is the **frequency** of oscillation of the photon in units of s^{-1} or Hertz (Hz).

The term 'hν' is used in equations for photophysical and photochemical processes to represent a photon.

For example, for a molecule R in its ground state which absorbs a photon to produce an electronically-excited molecule, R*, we may write the process as:

$$R + h\nu \rightarrow R^*$$

Each photon oscillates with wavelength λ, where $\lambda = c/\nu$ and where c is the speed of light. Thus:

$$\boxed{E = h\nu = hc/\lambda}$$

This equation demonstrates the important properties relating to the energy of photons:

The energy of a photon is proportional to its frequency and inversely proportional to its wavelength.

The units most commonly used are:

- J or kJ for the energy of a photon. The energy of one mole of photons (6.02×10^{23} photons) is called an **einstein** and is measured in units of kJ mol^{-1}. One einstein of light of wavelength λ is given by $N_A\,hc/\lambda$, where N_A is the **Avogadro constant** ($6.02 \times 10^{23}\,\mathrm{mol}^{-1}$). Sometimes energy is measured in **electronvolts** (eV), where 1 eV = 1.602×10^{-19} J.
- s^{-1} or Hz for frequency, where 1 Hz = 1 s^{-1}.
- nm (nanometre) or Å (angstrom) for wavelength, where 1 nm = 10^{-9} m and 1 Å = 10^{-10} m.

In some literature accounts, the term **wave number** ($\bar{\nu}$) is used. This is the number of wavelengths per centimetre, and consequently wave number has units of reciprocal centimetres (cm^{-1}).

Table 1.1 shows the properties of visible and ultraviolet light.

The production of the electronically-excited state by photon absorption is the feature that characterises photochemistry and separates it from other branches of chemistry.

Table 1.1 Properties of visible and ultraviolet light

Colour	**λ/nm**	**$\nu/10^{14}$ Hz**	**$\bar{\nu}/10^{4}$ cm^{-1}**	**E/kJ mol^{-1}**
red	700	4.3	1.4	170
orange	620	4.8	1.6	193
yellow	580	5.2	1.7	206
green	530	5.7	1.9	226
blue	470	6.4	2.1	254
violet	420	7.1	2.4	285
ultraviolet	<300	>10.0	>3.3	>400

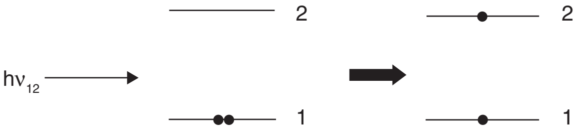


Figure 1.2 The process of light absorption

Sometimes electronic excitation can result in chemical changes, such as the fading of dyes, photosynthesis in plants, suntans, or even degradation of molecules. On other occasions, the electronically-excited state may undergo deactivation by a number of physical processes, either resulting in emission of light (luminescence) or conversion of the excess energy into heat, whereby the original ground state is reformed. Electronically-excited states can also interact with ground-state molecules, resulting in energy-transfer or electron-transfer reactions provided certain criteria are met.

There are three basic processes of light–matter interaction that can induce transfer of an electron between two quantised energy states:

1. In **absorption** of light, a photon having energy equal to the energy difference between two electronic states can use its energy to move an electron from the lower energy level to the upper one, producing an electronically-excited state (Figure 1.2). The photon is completely destroyed in the process, its energy becoming part of the total energy of the absorbing species.

   Two fundamental principles relating to light absorption are the basis for understanding photochemical transformations:
   - The **Grotthuss–Draper law** states that only light which is absorbed by a chemical entity can bring about photochemical change.
   - The **Stark–Einstein law** states that the primary act of light absorption by a molecule is a one-quantum process. That is, for each photon absorbed only one molecule is excited. This law is obeyed in the vast majority of cases but exceptions occur when very intense light sources such as lasers are used for irradiation of a sample. In these cases, concurrent or sequential absorption of two or more photons may occur.
2. **Spontaneous emission** occurs when an excited atom or molecule emits a photon of energy equal to the energy difference between the two states without the influence of other atoms or molecules (Figure 1.3(a)):

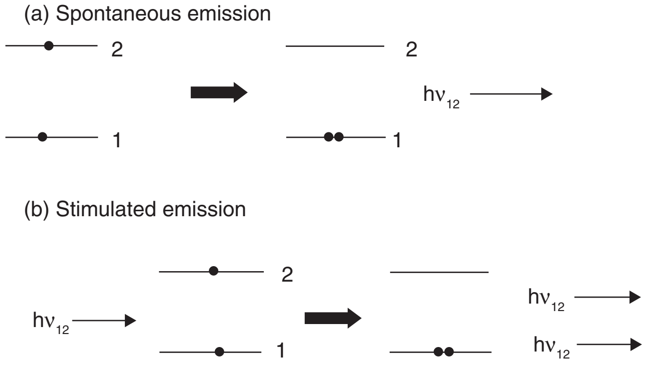


Figure 1.3 The processes of (a) spontaneous emission and (b) stimulated emission

$$R^* \rightarrow R + h\nu_{12}$$

Light is emitted from the bulk material at random times and in all directions, such that the photons emitted are out of phase with each other in both time and space. Light produced by spontaneous emission is therefore called **incoherent light**.

3. **Stimulated emission** occurs when a photon of energy equal to the energy difference between the two states interacts with an excited atom or molecule (Figure 1.3(b)):

$$R^* + h\nu_{12} \rightarrow R + 2h\nu_{12}$$

The photons produced by stimulated emission are in phase with the stimulating photons and travel in the same direction; that is, the light produced by stimulated emission is **coherent light**. Stimulated emission forms the basis of laser action.

1.2 MODELLING ATOMS: ATOMIC ORBITALS

Erwin Schrödinger developed an equation to describe the electron in the hydrogen atom as having both wavelike and particle-like behaviour. Solution of the **Schrödinger wave equation** by application of the so-called **quantum mechanics** or **wave mechanics** shows that electronic energy levels within atoms are quantised; that is, only certain specific electronic energy levels are allowed.

Solving the Schrödinger wave equation yields a series of mathematical functions called **wavefunctions**, represented by Ψ (Greek letter psi), and their corresponding energies.

The square of the wavefunction, Ψ^2, relates to the probability of finding the electron at a particular location in space, with **atomic orbitals** being conveniently pictured as boundary surfaces (regions of space where there is a 90% probability of finding the electron within the enclosed volume).

In this quantum mechanical model of the hydrogen atom, three **quantum numbers** are used to describe an atomic orbital:

- The **principal quantum number**, n, can have integral values of 1, 2, 3, etc. As n increases, the atomic orbital is associated with higher energy.
- The **orbital angular-momentum quantum number**, ℓ, defines the shape of the atomic orbital (for example, s-orbitals have a spherical boundary surface, while p-orbitals are represented by a two-lobed shaped boundary surface). ℓ can have integral values from 0 to (n – 1) for each value of n. The value of ℓ for a particular orbital is designated by the letters s, p, d and f, corresponding to ℓ values of 0, 1, 2 and 3 respectively (Table 1.2).
- The **magnetic quantum number**, m_l, describes the orientation of the atomic orbital in space and has integral values between –l and +l through 0 (Table 1.3).

In order to understand how electrons of many-electron atoms arrange themselves into the available orbitals it is necessary to define a fourth quantum number:

- The **spin quantum number**, m_s, can have two possible values, +½ or –½. These are interpreted as indicating the two opposite directions in which the electron can spin, ↑ and ↓.

Table 1.2 Values of principal and angular-momentum quantum numbers

N	ℓ
1	0 (1s)
2	0 (2s) 1 (2p)
3	0 (3s) 1 (3p) 2 (3d)
4	0 (4s) 1 (4p) 2 (4d) 3 (4f)

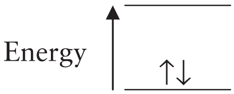
Table 1.3 Values of angular-momentum and magnetic quantum numbers

ℓ	**Orbital**	m_l	**Representing**
0	s	0	an s orbital
1	p	−1, 0, 1	3 equal-energy p orbitals
2	d	−2, −1, 0, 1, 2	5 equal-energy d orbitals
3	f	−3, −2, −1, 0, 1, 2, 3	7 equal-energy f orbitals

The total spin, S, of a number of electrons can be determined simply as the sum of the spin quantum numbers of the electrons involved and a state can be specified by its **spin multiplicity**:

$$S = \sum m_s$$
$$\text{Spin multiplicity} = 2S + 1$$

A ground-state helium atom has two paired electrons in the 1s orbital ($1s^2$). The electrons with paired spin occupy the lowest of the quantised orbitals shown below (the **Pauli exclusion principle** prohibits any two electrons within a given quantised orbital from having the same spin quantum number):



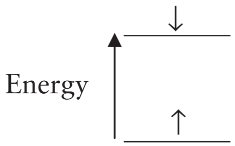
$$\text{Total spin } S = \frac{1}{2} - \frac{1}{2} = 0$$
$$\text{Spin multiplicity} = (2S + 1) = 1$$

This species is referred to as a **ground-state singlet** and is designated by S_0.

Electronic excitation can promote one of the electrons in the 1s orbital to an orbital of higher energy so that there is one electron in the 1s orbital and one electron in a higher-energy orbital. Such excitation results in the formation of an excited-state helium atom.

In the lowest excited-state helium atom there are two possible spin configurations:

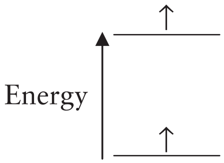
1. The two electrons have opposite spins:



$$\text{Total spin } S = \frac{1}{2} - \frac{1}{2} = 0$$
$$\text{Spin multiplicity} = (2S + 1) = 1$$

A species such as this is referred to as an **excited singlet state**.

2. The two electrons have parallel spins:



$$\text{Total spin } S = \frac{1}{2} + \frac{1}{2} = 1$$
$$\text{Spin multiplicity} = (2S + 1) = 3$$

In this case the species is referred to as an **excited triplet state**.

For a helium atom with two (paired) electrons in the 1s orbital in the ground state, the ground-state singlet is designated S_0, with S_1, S_2 … being used to designate excited singlet states of increasing energy. Similarly T_1, T_2 … are used to designate excited triplet states of increasing energy.

1.3 MODELLING MOLECULES: MOLECULAR ORBITALS

Some aspects of the bonding in molecules are explained by a model called **molecular orbital theory**. In an analogous manner to that used for atomic orbitals, the quantum mechanical model applied to molecules allows only certain energy states of an electron to exist. These quantised energy states are described by using specific wavefunctions called **molecular orbitals**.

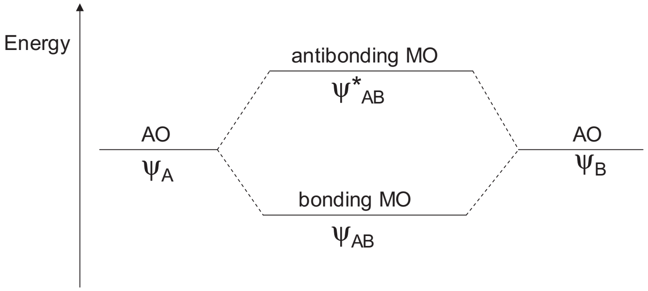


Figure 1.4 Formation of molecular orbitals (MO) by the interaction of two identical atomic orbitals (AO)

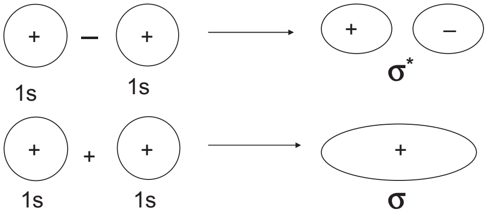


Figure 1.5 Boundary surfaces of σ (bonding) and σ* (antibonding) molecular orbitals

In order to examine molecular orbitals at their simplest, we shall consider the case of diatomic molecules. The interaction of the wavefunctions of two identical atomic orbitals gives rise to wavefunctions of two distinct molecular orbitals (Figure 1.4).

The lower-energy **bonding molecular orbitals** result when atomic orbital wavefunctions enhance each other in the region of the nuclei. The atoms are held together by attraction between the nuclei and the electrons in the bonding molecular orbital, and $\psi_{AB} = \psi_A + \psi_B$.

Higher-energy **antibonding molecular orbitals** are formed when the atomic orbital wavefunctions cancel each other in the region of the nuclei, repelling electrons from the region where $\psi^*_{AB} = \psi_A - \psi_B$. The antibonding molecular orbital therefore represents a situation which tends to separate the atoms rather than bonding them together.

If the two atomic orbitals are s-orbitals then the resulting molecular orbitals are called σ (**sigma**) bonding molecular orbitals and σ* (**sigma star**) antibonding molecular orbitals (Figure 1.5).

Molecular orbitals formed by mixing two parallel p-orbitals are called π (**pi**) if bonding and π* (**pi star**) if antibonding (Figure 1.6).

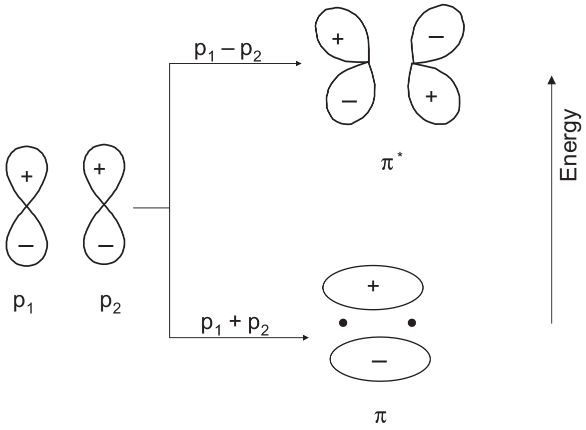


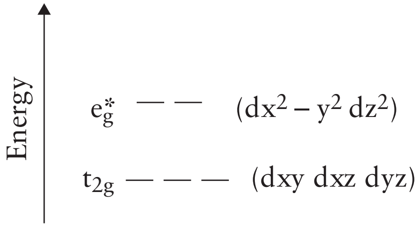
Figure 1.6 Boundary surfaces of π (bonding) and π* (antibonding) molecular orbitals

The **phasing** of the molecular orbitals (shown as +/–) is a result of the wavefunctions describing the orbitals. + shows that the wavefunction is positive in a particular region in space, and – shows that the wavefunction is negative.

In addition to bonding and antibonding molecular orbitals it is necessary to consider **nonbonding molecular orbitals** (n). These orbitals contain lone pairs of electrons that are neither bonding nor antibonding and so play no part in bonding atoms together, being localised on just one atom. Nonbonding orbitals generally have a higher energy than bonding orbitals.

Figure 1.7 shows a simple representation of the relative quantised energy levels found in organic molecules.

The molecular orbital model can also be applied to complexes of the d-block elements. In octahedral complexes the d-orbitals of the metal are not degenerate, as they are in the free metal, because of the interaction between the ligand and metal orbitals. The five d-orbitals are split into three t_{2g} (nonbonding) and two e_g^* (antibonding) MOs; that is:



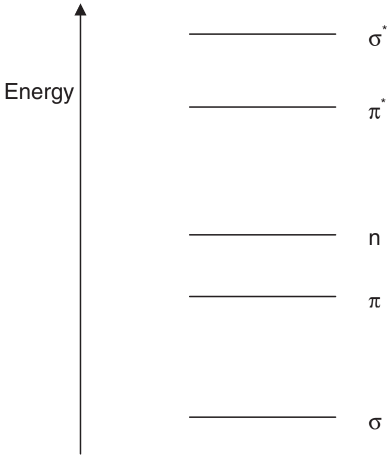


Figure 1.7 Schematic representation of molecular orbital energies in organic molecules

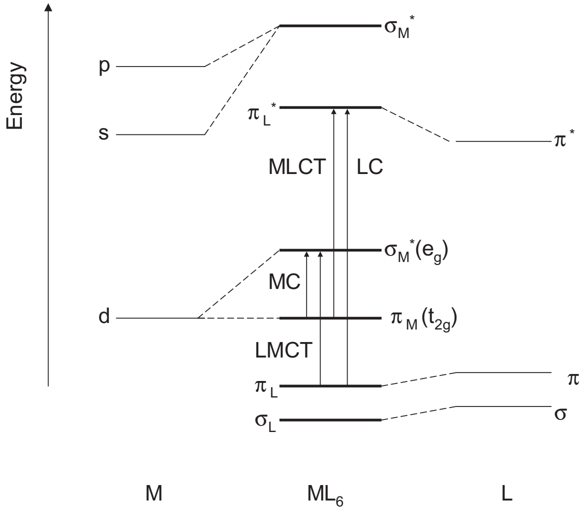


Figure 1.8 Molecular orbital diagram for an octahedral d-block metal complex ML_6. The vertical arrows indicate different types of electron transition that may be brought about by photon absorption

A representative molecular orbital diagram for an octahedral d-block metal complex ML_6 is shown in Figure 1.8. The MOs are classified as bonding (σ_L and π_L), nonbonding (π_M) and antibonding (σ_M^*, π_L^* and σ_M^*). The ground-state electronic configuration of an octahedral complex of a d^n metal has the σ_L and π_L MOs completely filled, while the n d-electrons are found in the π_M nonbonding MOs of t_{2g} symmetry and the σ^*_M antibonding MOs of e_g symmetry.

Photon absorption produces excited electron configurations by promotion of an electron from an occupied to a vacant MO. These electronic transitions are described as:

- Metal-centred (MC) transitions or d–d transitions between the nonbonding and antibonding metal-centred MOs. Such transitions are commonly found among the first-row d-block elements.
- Ligand-centred (LC) transitions between bonding and antibonding ligand-centred MOs. These transitions are expected for aromatic ligands with extended π- and π*-orbitals.
- Ligand-to-metal charge transfer (LMCT) transitions between the bonding ligand-centred MOs and antibonding metal-centred MOs. Such transitions are found where a ligand is easily oxidised and the metal is easily reduced.
- Metal-to-ligand charge transfer (MLCT) transitions between the nonbonding metal-centred MOs and antibonding ligand-centred MOs. Such transitions are found where a metal is easily oxidised and the ligand is easily reduced.

1.4 MODELLING MOLECULES: ELECTRONIC STATES

The physical and chemical properties of molecules are determined by the electronic distribution within the molecules. For example, the ground-state methanal molecule, like other organic molecules, has a **closed shell structure**; that is, its occupied molecular orbitals all contain two paired electrons. Let us consider the possible electronic configurations that can occur in ground-state and excited-state methanal molecules. The molecular orbital diagram for methanal (formaldehyde), $H_2C{=}O$, is shown in Figure 1.9. The highest occupied molecular orbital (HOMO) is the nonbonding n molecular orbital localised on the O atom of the carbonyl group, and the lowest unoccupied molecular orbital (LUMO) is the antibonding π* molecular orbital of the CO group.

Neglecting the filled low-energy σ-orbitals, the electronic configuration of the lowest electronic state (the ground state) is $\pi^2 n^2$. Photon absorption of the appropriate energy results in excited-state configurations by promotion of one electron from an occupied molecular orbital

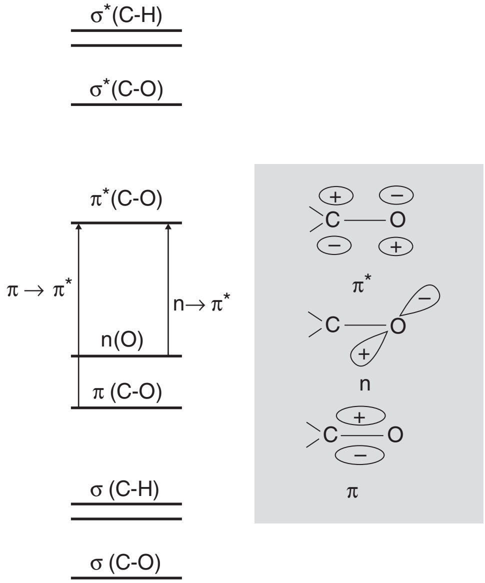


Figure 1.9 Molecular orbital diagram for methanal, showing the n → π* and π → π* transitions. The boundary surfaces of the π, n and π* molecular orbitals are also shown

to a vacant molecular orbital. The relatively low-energy n → π* (HOMO → LUMO) and π → π* electronic transitions lead to $\pi^2 n\pi^*$ and $\pi n^2\pi^*$ excited configurations.

In terms of the spin multiplicity of the ground state and excited states of methanal, the ground state is a singlet state (S_0), with the excited states being either singlets (S_1, S_2, etc.) or triplets (T_1, T_2, etc.) (Figure 1.10).

Both the S_1 and T_1 excited states arise from the promotion of an electron from the n molecular orbital to the π* molecular orbital. They are referred to as $^1(n,\pi^*)$ and $^3(n,\pi^*)$ states, respectively. The S_2 and T_2 states arise from the promotion of an electron from the π molecular orbital to the π* molecular orbital and are referred to as $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ states, respectively. The **state diagram** for methanal is shown in Figure 1.11. With regard to the different spin states in molecules, the following ideas are important:

- An excited triplet state always has a lower energy than that of the corresponding excited singlet state. This is in line with **Hund's rule**: when two unpaired electrons occupy different orbitals, there is a

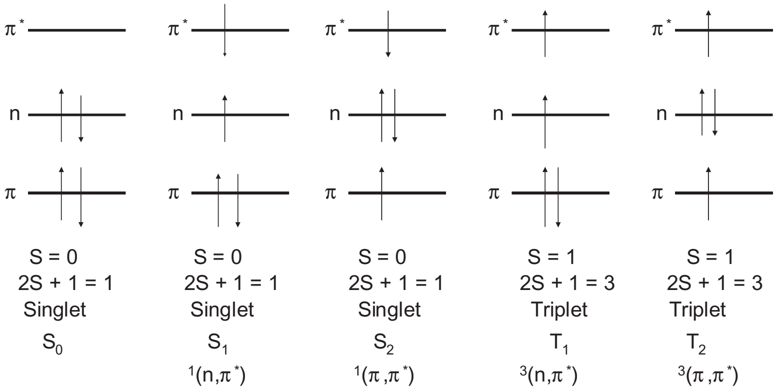


Figure 1.10 Configurations of the ground state and excited electronic states of methanal

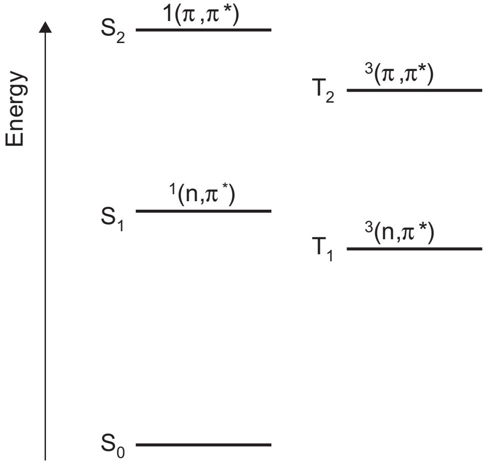


Figure 1.11 State diagram for methanal

minimum energy repulsion between the electrons when their spins are parallel.

- When electron excitation of a ground-state molecule, S_0, occurs, there is a tendency for the spin multiplicity to be retained. $S_0 \rightarrow T_1$ transitions are said to be **spin forbidden**; that is, they may be allowed but tend to be much less probable than $S_0 \rightarrow S_1$ transitions. Triplet excited states are generally accessed from the S_1 state only if the molecule or its environment favours the process of

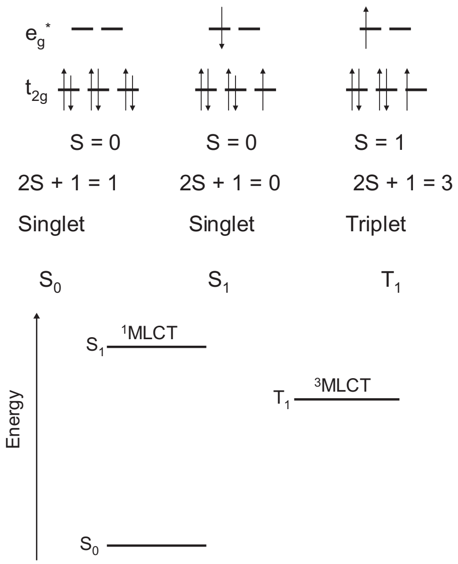


Figure 1.12 Electronic configurations and state diagram for the octahedral complex $Ru(bpy)_3^{2+}$. Only the lower-lying states are shown

intersystem crossing, whereby a molecule in the S_1 state is converted to a triplet state (see Section 2.6 and Chapter 5).

For octahedral complexes of Ru(III), and other d^6 ions, the σ_L and π_L MOs are fully occupied and the ground-state configuration is a closed shell because the HOMO π_M is fully occupied (t_{2g}^6). The ground state is a singlet state (S_0), with the excited states being either singlets or triplets (Figure 1.12).

However, in octahedral Cr(III) complexes, Cr^{3+} is a d^3 metal ion with three electrons in the HOMO orbitals π_M (t_{2g}^3). Thus the complexes of Cr(III) have an open-shell ground-state configuration, which on excitation produces quartet and doublet states (Figure 1.13).

1.5 LIGHT SOURCES USED IN PHOTOCHEMISTRY

Incandescent tungsten-filament lamps are good sources of visible light, with ultraviolet light down to 200 nm being generated by using a quartz tube. Below 200 nm, atmospheric oxygen absorbs ultraviolet light and so it is necessary to employ vacuum apparatus in order to work at these short wavelengths.

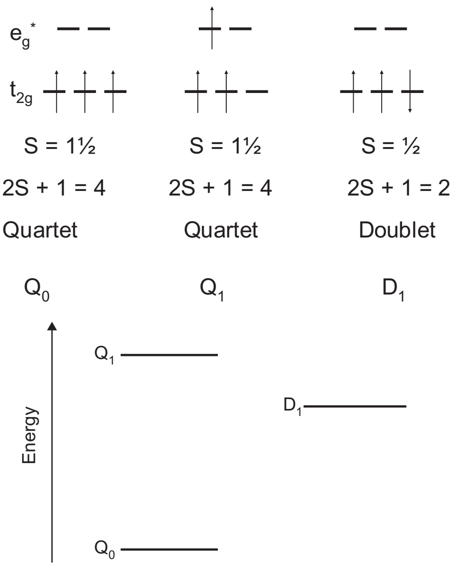


Figure 1.13 Electronic configurations and state diagram for a d^3 octahedral complex of Cr(III). Only the lower-lying states are shown

Discharge lamps contain xenon gas or mercury vapour through which an electric discharge is passed. At low pressure, the light they give out is emitted as a series of spectral lines characteristic of the element concerned. Discharge lamps have the ability to produce short pulses of light, and because of their high intensity at short wavelengths they are ideal for use as light pumping sources for lasers. Here, atoms are promoted to excited states, from which they can subsequently be stimulated to emit coherent monochromatic light.

Lasers are particularly important in photochemical research because their stimulated emission produces light which is monochromatic, coherent and very intense. Additionally, advances in laser technology have enabled lasers to deliver pulses of shorter and shorter duration such that today it is possible to produce pulses of the order of femtoseconds ($1\,\text{fs} = 10^{-15}\,\text{s}$).

1.5.1 The Mercury Lamp

The mercury lamp has been the conventional light source used in photochemistry. The ground-state mercury atom, Hg, has two electrons in its highest occupied orbital, the 6s atomic orbital. Excited mercury atoms can therefore exist as either singlet or triplet spin states, rather like the case of helium discussed earlier.

Light emitted from a mercury lamp is caused by electronic transitions from higher-energy-level atomic orbitals to lower–energy-level atomic orbitals. The electronic transitions are subject to certain constraints known as **selection rules**:

- An electronic transition must involve a change in the orbital angular momentum quantum number ℓ such that $\Delta\ell = \pm1$. Thus a 1s to 2p transition is allowed and a 1s to 3p transition is allowed, but a 1s to 2s or 1s to 3d transition is forbidden. This rule is sometimes called the **Laporte selection rule**.
- Where the electronic states involve singlets and triplets, transitions between the singlet and triplet states are forbidden by the **spin selection rule**, where there is no change in the spin multiplicity and thus $\Delta S = 0$. However, for electronic transitions in heavier atoms, such as mercury, there is a partial relaxing of the spin selection rule due to increased **spin–orbit coupling** in such atoms. Electrons in motion produce a magnetic field and spin–orbit coupling arises out of an interaction between the magnetic field due to the electron spin and the magnetic field due to the orbital motion of the electron. One of the consequences of this spin–orbit coupling is that the mixing of the states of different multiplicities occurs, so that the division into singlet and triplet states becomes less precise. The higher the atomic number, the greater the spin–orbit coupling and the less ‘forbidden’ the electronic transitions involving changes of multiplicity become.

The emission of a mercury lamp depends on its operating conditions. Low-pressure lamps have both the least intense emission and the fewest spectral output lines, the most prominent being a line at 254 nm. Medium-pressure lamps are brighter and produce a greater number of lines. High-pressure mercury lamps operating at high temperature and pressure have the most intense emission, which, because of extensive pressure-broadening, is continuous over a wide range of wavelengths, but the emission at 254 nm is absent because of the process of self-absorption.

1.5.2 Lasers

The word **laser** is an acronym for **light amplification by stimulated emission of radiation**.

Pulsed lasers emit pulses so short that even the fastest photoprocesses can be monitored, which would be impossible using conventional light sources.

The necessary conditions for the generation of laser light are:

1. A **laser medium** in a tube within the laser cavity, with a mirror at each end. A pump source must excite the atoms or molecules in the laser medium so that stimulated emission (Figure 1.3(b)) can occur. Lasers are classified by the nature of the medium, important ones being:
   - **Solid-state lasers**, such as the ruby laser, neodymium doped yttrium aluminium garnet (Nd-YAG) laser and the titanium doped sapphire laser.
   - **Gas lasers**, such as the helium-neon laser and the argon ion laser.
   - **Dye lasers**, in which the laser medium is a coloured fluorescent dye dissolved in a nonabsorbing solvent.
2. A **metastable state**, which is a relatively long-lived excited state with energy above the ground state. At thermal equilibrium the populations of the ground and metastable states are N_0 and N_1, respectively, where $N_0 >> N_1$. If a system is to act as a laser then the incident photons must have a greater probability of bringing about stimulated emission than of being absorbed. This occurs when the rate of stimulated emission is greater than the rate of absorption; that is, when $N_1 >> N_0$. This non-equilibrium condition is known as **population inversion**. Provided we can obtain a population inversion, light amplification can be achieved. We can now see why the metastable state needs to be relatively long-lived – it needs to exist for a sufficiently long time to allow a population inversion to build up.

   When a single photon of appropriate energy interacts with an excited-state atom, a second photon travelling in phase with and in the same direction as the initial photon will be emitted by stimulated emission. These two photons can cause further stimulated emission through interaction with two atoms, producing four photons by stimulated emission, and so on (Figure 1.14). Thus we have light **amplification**, which is also known as **gain**. The laser medium containing the atoms is sometimes known as the **gain medium**.
3. A **pumping mechanism**, in order to excite the atoms or molecules of the gain medium by supplying them with sufficient energy.

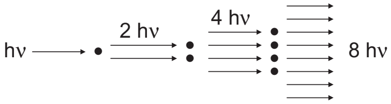


Figure 1.14 Light amplification resulting from stimulated emission (• represents an electronically-excited atom)

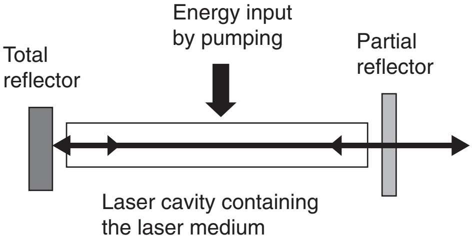


Figure 1.15 Schematic representation of a laser system

Depending on the type of laser used, this energy can come from a source of light, an electrical discharge or via chemical reactions.

4. An **optical resonance cavity** to sustain laser action. Even establishing population inversion and promoting stimulated emission is not enough to sustain laser action. In practice, photons need to be confined in the system to allow those created by stimulated emission to exceed all other mechanisms. This is achieved by the use of two mirrors bounding the laser medium, one totally reflecting, the other (in the direction of the output beam) partially reflecting (Figure 1.15).

1.5.2.1 How is a population inversion achieved in a laser?

At thermal equilibrium, according to the **Boltzmann distribution** (see Section 2.3), the population of atoms and molecules in the excited state can never exceed the population in the ground state for a simple two-level system.

However, laser action requires that N_1 be greater than N_0 in order to bring about the population inversion, but this can only be achieved when three or more energy levels are considered:

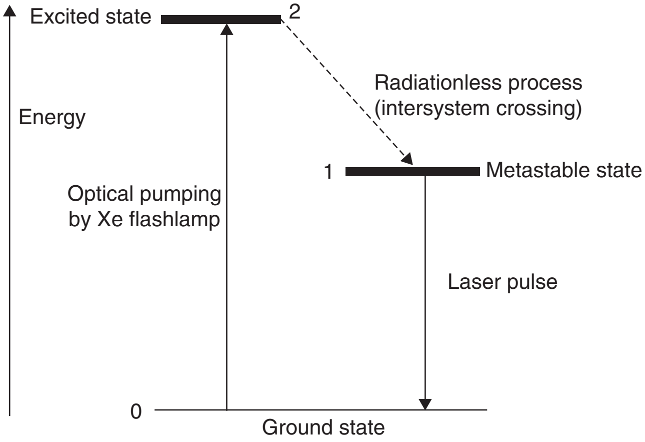


Figure 1.16 Transitions between energy levels in the ruby laser

- **The three-level ruby laser**. Ruby consists of Al_2O_3 containing traces of Cr^{3+}. A flash of white light from a xenon flashlamp excites the Cr^{3+} ions to state 2. They rapidly decay to state 1 by intersystem crossing. State 1 has a relatively long lifetime, allowing its population to build up so that it is greater than that of the ground state. In order to achieve population inversion, more than half of the ground-state Cr^{3+} ions must be excited (so that $N_1 > N_0$), which is not a particularly efficient process (Figure 1.16).
- **The four-level neodymium yttrium aluminium garnet (Nd-YAG) laser**. This solid-state laser consists of a rod of yttrium aluminium garnet doped with Nd^{3+} ions. The energy levels are shown in Figure 1.17. Optical pumping by a Xe flashlamp results in excitation of Nd^{3+} ions to level 3, followed by rapid radiationless decay to level 1. The lower laser level (level 2) has a very small population and so population inversion between levels 1 and 2 is easily achieved. The laser output (1064 nm) is in the infrared; **frequency-doubling** techniques allow it to be shifted into the visible and/or ultraviolet. Frequency-doubling, also known as **second harmonic generation**, involves absorption of two photons of frequency ν in a suitable crystal, such as KH_2PO_4, resulting in emission of a single photon of frequency 2ν. Frequency-doubling crystals can be used in series to produce other harmonics of the fundamental frequency of the laser.

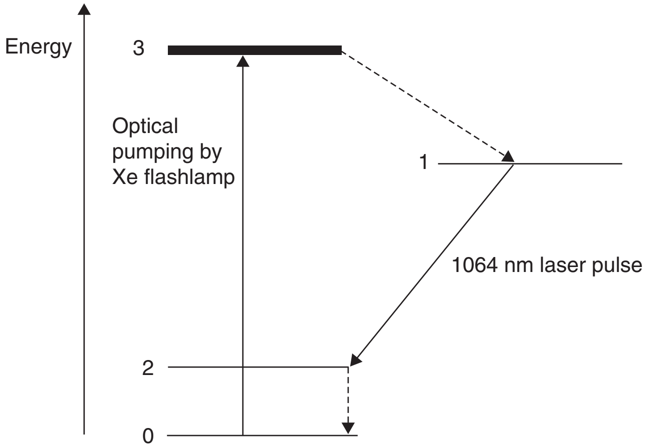


Figure 1.17 Transitions between energy levels in the neodymium laser

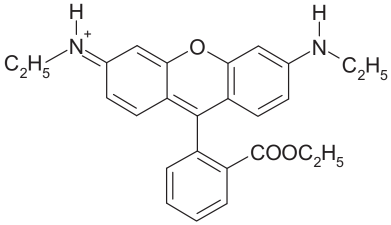


Figure 1.18 Rhodamine 6G

- **The four-level dye laser.** Whereas transitions between energy levels in atoms have a very narrow spread of energies, transitions between states of large molecules in solution are often very broad. This is the case for many solutions of dye molecules that have long conjugated chains and absorb in the visible region. The rhodamine 6G (Figure 1.18) laser allows the production of tuneable laser radiation where the output covers a broad spread of wavelengths (570–620 nm).

  Dye lasers are usually pumped by another laser, and a selection of around 25 dyes typically provides coverage of a wide region from 350 to 900 nm. Organic dye lasers are four-level lasers, even though only two electronic levels may be used (Figure 1.19).

  Vibrational relaxation (dotted arrows in Figure 1.19) is able to maintain a population inversion. The broad absorption and

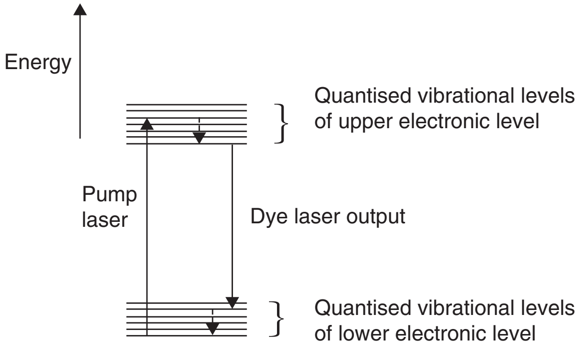


Figure 1.19 Energy levels and transitions in the rhodamine 6G dye laser

emission spectrum of rhodamine 6G, resulting from the broad upper and lower levels, enables the laser to be tuned to the required wavelength by use of a wavelength-selective device in the laser cavity.

1.5.2.2 Laser pulsing techniques

Some lasers produce a continuous-wave (CW) beam, where the timescale of the output cycle is of the same order as the time taken to remove photons from the system. CW lasers can be modified to produce a pulsed output, whereas other lasers are inherently pulsed due to the relative rates of the pumping and emission processes. For example, if the rate of decay from the upper laser level is greater than the rate of pumping then a population inversion cannot be maintained and pulsed operation occurs.

Pulsed lasers produce extremely short flashes of light, which means that photochemical events can be initiated very rapidly and subsequent physical and chemical events can be followed as they occur. In order to reduce the time of the laser pulse a number of techniques have been developed:

- Intense nanosecond pulses ($1\,\text{ns} = 10^{-9}\,\text{s}$) can be produced by **Q-switching**. A shutter is placed between the laser rod and one of the mirrors, thus inhibiting lasing. If the shutter is suddenly opened, the excitation is dumped in one huge burst. One type of shutter is the electro-optic **Pockels cell** (KH_2PO_4 crystal with a high applied potential).

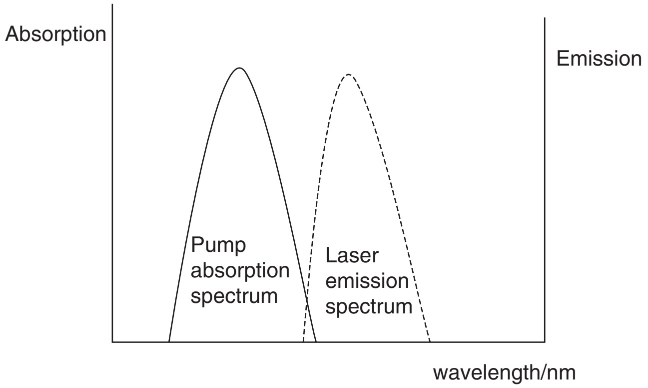


Figure 1.20 Absorption and emission spectra of Ti^{3+} ions in an alumina crystal

- Picosecond pulses (1 ps = 10^{-12} s) are produced by **mode locking**, where the electronics of the instrumentation open and close the shutter at the round-trip frequency of the cavity.

In the last decade or so, the most remarkable advances in laser pulse generation have been carried out using the Ti^{3+} doped aluminium oxide laser, known as the **titanium sapphire laser** (Ti:sapphire). The absorption band of Ti^{3+} is in the blue-green spectral range, while the emission spectrum is shifted to higher wavelength, as shown in Figure 1.20. The maximum absorption occurs around 510 nm, in the green part of the spectrum, and so Ti:sapphire lasers are pumped by either the green line of an argon laser (514 nm) or the frequency-doubled (green) line of the Nd-YAG laser (532 nm). The broad absorption band allows tuning between 700 and 900 nm and the high peak output intensity enables the Ti:sapphire laser to be used as an efficient source for frequency doubling, giving 350–450 nm photons.

Ti:sapphire lasers can operate both in CW mode and in pulsed mode. There are two types of pulsed Ti:sapphire laser:

- One which produces pulses of the order of 10 ns and is usually pumped by a Q-switched Nd-YAG laser.
- A mode-locked Ti:sapphire laser, which can produce sub-ps pulses and is usually pumped by CW argon or Nd-YAG lasers. The shortest pulses coming from this laser type are exceptionally short, of the order of a few femtoseconds.

1.6 EFFICIENCY OF PHOTOCHEMICAL PROCESSES: QUANTUM YIELD

The preparation of integrated circuit chips relies on a photochemical process using **photoresists** (polymer coatings designed to change some physical property on exposure to light, thus providing a means of distinguishing between exposed and unexposed areas). The surface of the substrate is coated with a thin layer of photoresist material, which is then selectively irradiated, through a stencil, with ultraviolet light. The light causes a chemical change in the exposed region and, depending on the system used, it is possible to wash away either the exposed or the unexposed region selectively, using an appropriate solvent. The process is repeated many times to produce the final, complex circuit board. Because of the vast scale on which this process operates, it is important to understand the photochemistry, so as to maximise the efficiency of the reaction and reduce the considerable energy costs needed to power the light source. The **quantum yield** is a measure of how efficiently the absorbed photons are utilised.

1.6.1 Primary Quantum Yield (ϕ)

After photon absorption there are different ways in which the excited state may be deactivated, so not every excited molecule will form a primary product. The quantum yield for this primary process is given by:

$$\phi = \frac{\text{number of bonds broken in the primary step}}{\text{number of photons absorbed}}$$

Consider the photodissociation of propanone in Scheme 1.1.

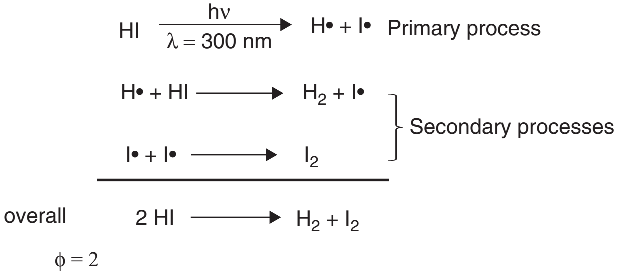
$$(CH_3)_2CO \xrightarrow[\lambda > 266\text{ nm}]{h\nu} (CH_3)_2CO^* \longrightarrow \bullet CH_3 + \bullet CH_3CO$$

$$\phi = 1$$

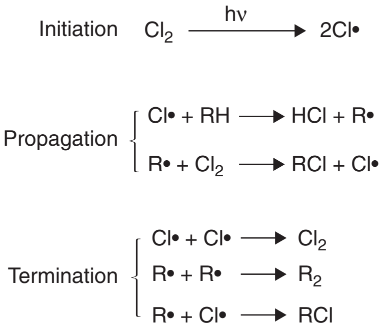
$$(CH_3)_2CO \xrightarrow[\lambda < 193\text{ nm}]{h\nu} (CH_3)_2CO^* \longrightarrow 2\bullet CH_3 + CO$$

$$\phi = 2$$

Scheme 1.1



Scheme 1.2



Scheme 1.3

The species $\cdot CH_3$ and $\cdot CH_3CO$ are **radicals**: species containing unpaired electrons. Radicals are formed by homolytic fission of a covalent bond, where the electron pair constituting the bond is redistributed such that one electron is transferred to each of the two atoms originally joined by the bond.

1.6.2 Overall Quantum Yield (Φ)

The overall quantum yield is the number of molecules of reactant, R, consumed per photon of light absorbed.

$$\Phi = \frac{\text{number of molecules of R consumed}}{\text{number of photons absorbed by R}}$$

According to the Stark–Einstein law, Φ should be equal to 1. However, if secondary reactions occur, Φ can be greater than 1.

Consider the photodissociation of hydrogen iodide in Scheme 1.2.

Φ can be very large for **chain reactions,** with the propagation reactions acting as an amplifier of the initial absorption step.

Irradiation of mixtures of hydrocarbons and chlorine at suitable wavelengths leads to chlorination of the organic molecule (Scheme 1.3). Reactions have overall quantum yields in excess of 10^6 ($>10^6$ propagation cycles for each termination step).