

1

Interaction of Radiation with Matter

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1.1

Introduction

The interaction of light with matter is at the basis of one of the primary participants in human perception, because a significant part of the cerebral cortex is dedicated to visual processing. This complex mechanism starts with the light-induced isomerization of a retinal molecule that triggers a messenger cascade to produce the transmission of a nerve impulse from the retina. And it is through sight that we gather most of our knowledge of our environment (sizes, colors, shapes, etc.).

However, the chemical properties of the visual pigments in our retinas, together with the structure of the eye, limit our perceptions to light wavelengths between 390 and 750 nm and objects larger than 0.1 mm. Application of our knowledge about the interaction of light with matter and the development of optical instruments allowed us very early to use optical devices to immensely expand the range of objects accessible to our study, from the organelles in cells to faraway galaxies. In parallel, the discovery of electromagnetic radiation outside of the visible range provided incentives and tools for the elaboration of unifying concepts about light and for a myriad of technological applications.

In this chapter, we summarize the main laws that govern the interaction of electromagnetic radiation with matter, and the way in which these laws can be applied to the different phenomena that can arise from this interaction. This information is necessarily limited, and will be developed in more detail as needed in each of the following chapters on specific techniques.

1.2

Spectroscopy: A Definition

Spectroscopy is the study of the interaction of electromagnetic radiation with matter involving either absorption, emission, or scattering of radiation by the system under study. Atomic and molecular spectra can provide detailed

information about the structure and chemical properties of the system. Spectroscopic techniques are one of the main sources of molecular geometries, that is, bond lengths, bond angles, and torsion angles, and can also yield, as will be seen, significant information about molecular symmetry, energy level distributions, electron densities, or electric and magnetic properties [1–15].

Spectroscopy has been an essential tool in the development of models for atomic and molecular structure, prompting scientists to refine existing models to accurately reproduce the experimentally observed spacing between energy states. A dramatic example of this is the birth of quantum theory (to explain the discrete nature of electronic transitions in atoms) or the discovery of the element helium in the spectrum of the Sun, well before it was found on Earth [16–19]. Nowadays, spectroscopic tools are routinely used in quantitative and qualitative chemical analysis and in the characterization of new molecules and materials, and play an essential role in such diverse fields as the elaboration and testing of theoretical models, synthetic chemistry, the study of reaction mechanisms, or biochemistry and materials science [20–23].

Atomic and molecular spectroscopies are mainly related to the absorption or emission of electromagnetic radiation and the changes taking place in those systems as a consequence of the energy of the radiation. Diffraction methods, however, involve the wave nature of the radiation, and rely on the interpretation of the interference patterns between waves upon their encounter with obstacles of dimensions roughly close to their wavelength. When these waves correspond to electromagnetic waves in the X-ray region of the spectrum or particles such as electrons or neutrons, their wavelengths are similar to the spacing between atoms in condensed phases such as liquids or crystals and they can be employed to obtain useful information about the atomic positions in these materials. X-ray diffraction produced the key images for unraveling the double-helix structure of DNA, and is routinely used to elucidate the structure of large biomolecules, surfaces, or materials [24–26].

1.3

Electromagnetic Radiation

According to elementary physics, a charge is surrounded by an electric field, and a moving charge, that is, an electrical current, also generates a magnetic field. Besides this, accelerated charges emit electromagnetic radiation, while radiation accelerates charged particles. Maxwell's equations condense all these phenomena describing the dynamics of free charges and currents and providing the foundation of classical electromagnetic theory and the interaction of light and matter. These equations describe macroscopically the behavior of charges in electric and/or magnetic fields, both in vacuum and in materials. Among these, propagation of light in vacuum is easier to describe, since light in matter is constantly absorbed and re-emitted, so that the solution of Maxwell's equations in matter requires detailed knowledge about the structure of the material, a simplified model

for the material, or some empirical information about the interaction between light and matter.

Solution of Maxwell's equations without sources (charges or currents) leads to the equation of a propagating electromagnetic wave [27]. Thus, electromagnetic radiation can be described as a wave phenomenon formed by the combination of electric (E) and magnetic (H) fields, which oscillate in phase orthogonal to each other and orthogonal to the direction of propagation as well. For a given direction of propagation, these two orthogonal fields can be oriented in any direction in the plane perpendicular to it. However, if restrictions are imposed on the oscillation planes of the wave, polarized radiation can be obtained. Thus, for a plane-polarized (also known as linearly polarized) wave traveling in the x direction, the electric and magnetic fields of the electromagnetic radiation given by

$$E = E_0 \sin \left[2\pi \left(\frac{x}{\lambda} - \nu t \right) \right] \quad (1.1)$$

$$H = H_0 \sin \left[2\pi \left(\frac{x}{\lambda} - \nu t \right) \right] \quad (1.2)$$

are always in the same two orthogonal planes. The plane of polarization is conventionally taken to be the plane containing the electric field (the xy plane in Figure 1.1) because, as seen below, radiation and matter usually interact through the electric component. E_0 and H_0 in the previous equations correspond to the amplitudes, that is, the maximum values of the electric and magnetic fields, respectively.

The radiation wavelength, λ , can be defined as the distance between adjacent crests at a given point in time, and the frequency, ν , is the number of oscillations passing by a point in a given time (that is, the inverse of the wave period), usually with units of s^{-1} or Hz. The relation between frequency and wavelength is given by

$$\nu = \frac{c}{\lambda} \quad (1.3)$$

where c is the velocity of propagation of the wave. In vacuum, c equals the speed of light (c_0), but in general $c = c_0/n$ where n is the index of refraction of the propagation medium. For historical reasons, the use of the inverse of the wavelength is

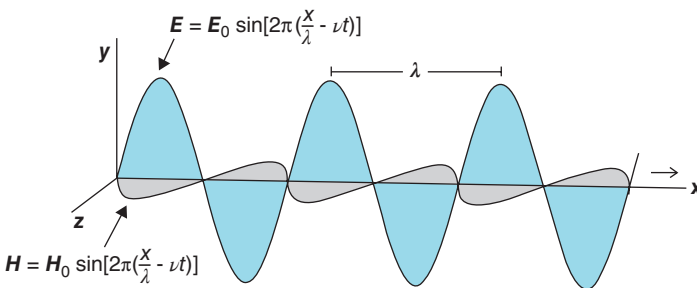


Figure 1.1 Plane-polarized electromagnetic radiation.

also very common in spectroscopy;

$$\tilde{\nu} = \frac{1}{\lambda} \quad (1.4)$$

It is known as wavenumber and is usually given in units of cm^{-1} .

Ondulatory and corpuscular theories of light coexisted and replaced each other since the seventeenth century, but the wave nature of the electromagnetic radiation was firmly established by Maxwell in the nineteenth century. However, at the beginning of the twentieth century Planck and Einstein showed that radiation also presents the properties of a particle. According to the corpuscular theory, electromagnetic radiation can be described as quantum energy packets named *photons* that possess an energy given by

$$E = h\nu \quad (1.5)$$

where ν is the radiation frequency and h is Planck's constant.

Later, in 1924 de Broglie stated that if electromagnetic waves present properties associated with particles, the particles can also display wavelike properties and proposed that the wavelength of a particle behaving as a wave depends on its linear momentum, p , according to the expression

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad (1.6)$$

where m is the particle mass and v is its velocity. Further experiments of diffraction with electron beams confirmed the wavelike properties of particles, and nowadays neutron and electron diffraction techniques, such as X-ray diffraction, are used in laboratories all over the world for the characterization of materials.

According to the previous 1.6, electromagnetic radiation is considered to have a dual nature, as a wave and as a particle, which manifests in different phenomena. As will be seen below, the description of the interaction of light and matter in spectroscopic methods where radiation is absorbed or emitted is based on the corpuscular behavior of the radiation since photons are absorbed or emitted depending on their energy. Diffraction methods, however, are based on the wave behavior of radiation or on the wavelike properties of particles.

1.4 Electromagnetic Spectrum

Depending on its frequency or wavelength, an electromagnetic wave is included in one of the several regions in which the electromagnetic spectrum is divided. As can be seen in Table 1.1, the electromagnetic spectrum covers a large range of radiation frequencies, of which the visible region is only a small part. The traditional division of the electromagnetic spectrum into regions is artificial because there are no fundamental differences between radiations in these regions beyond the energies involved. However, each region can be usually related to particular technological applications (from radio communications to gamma knife surgery) or a

Table 1.1 Electromagnetic spectrum.^{a)}

Region	Frequency (s^{-1})	Wavelength	Wavenumber (cm^{-1})	Energy (eV)	Spectroscopy
Radio	$10^6 \rightarrow 3 \times 10^9$	300 m \rightarrow 10 cm	$3 \times 10^{-5} \rightarrow 0.1$	$4.1 \times 10^{-9} \rightarrow 1.2 \times 10^{-5}$	Nuclear magnetic resonance
Microwave	$3 \times 10^9 \rightarrow 3 \times 10^{12}$	10 cm \rightarrow 0.1 mm	0.1 \rightarrow 100	$1.2 \times 10^{-5} \rightarrow 0.012$	Electron spin resonance and rotational spectroscopy
Infrared	$3 \times 10^{12} \rightarrow 3 \times 10^{14}$	0.1 mm \rightarrow 1 μ m	100 \rightarrow 10 000	0.012 \rightarrow 1.2	Rotational spectroscopy and vibrational spectroscopy
Visible	$4.3 \times 10^{14} \rightarrow 7.5 \times 10^{14}$	700 nm \rightarrow 400 nm	14 300 \rightarrow 25 000	1.7 \rightarrow 3.1	UV-visible
Ultraviolet	$7.5 \times 10^{14} \rightarrow 3 \times 10^{16}$	400 nm \rightarrow 10 nm	25 000 \rightarrow 10^6	3.1 \rightarrow 120	UV-visible
X-rays	$3 \times 10^{16} \rightarrow 10^{19}$	100 \AA \rightarrow 0.3 \AA	$10^6 \rightarrow 3 \times 10^8$	$120 \rightarrow 4 \times 10^4$	Electronic transition (internal electrons)
γ -rays	$10^{19} \rightarrow 10^{22}$	0.3 \AA \rightarrow 0.003 \AA	$3 \times 10^8 \rightarrow 3 \times 10^{10}$	$10^4 \rightarrow 10^9$	Nuclear transitions

a) Most commonly used spectroscopic units:

Radio frequency radiation: MHz = 10^6 Hz ($\text{Hz} = s^{-1}$). Microwave radiation: GHz = 10^9 Hz.

Infrared radiation: cm^{-1} (wavenumbers). Visible and ultraviolet radiation: nm = 10^{-9} m.

X-ray and γ -ray radiation: nm = 10^{-9} m and \AA = 10^{-10} m.

certain spectroscopic method, the latter depending on the energy levels between which the radiation causes a transition or the processes that may occur in atoms or molecules exposed to that radiation. It must be noted, however, that the limits between regions are diffuse and that the type of energy transition associated with each spectroscopic region is only approximate.

1.5

Interaction of Radiation with Matter

The study of spectroscopic methods requires the use of quantum mechanics concepts [17–19]. From the early work of Bohr on atomic spectra, it could be established that absorption or emission of radiation is possible because of the quantization of atomic and molecular energy levels. Thus, Bohr's frequency condition indicates that a system can experiment on a transition between two states 1 and 2 if the energy of the electromagnetic radiation *absorbed* equals the energy difference between the two states

$$\Delta E_{1 \rightarrow 2} = E_2 - E_1 = h\nu \quad (1.7)$$

On the other hand, *emission* of radiation is due to the return of an atomic or molecular system from an excited state to a lower energy state, and the energy of the emitted radiation also corresponds to the energy difference between the states involved in the transition (Figure 1.2).

The application of quantum mechanics to atoms and molecules shows that these systems display a large number of quantized energy levels. The energy of a molecule is then the result of the contributions from electronic configuration, vibration, rotation and translation, and various electron–electron, nuclear–nuclear and nuclear–electron interactions. Most often, these contributions can be considered independent and treated separately because their energies usually differ by several orders of magnitude. As a consequence, the energy differences between different types of levels in molecular systems (electronic and vibrational, for example) correspond to electromagnetic radiation of different frequency and, as seen above, this causes each region of the spectrum to be related with a characteristic type of spectroscopy. The occurrence of quantized energy levels together with electromagnetic radiation of proper energy is not, however, a sufficient condition for absorption or emission of radiation. The probability of a transition and the amount of radiation absorbed or emitted

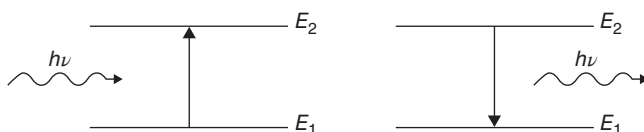


Figure 1.2 (a,b) Absorption and emission between quantized energy levels.

depends on the nature of the interaction between the molecular system and the radiation.

The mechanism of interaction between electromagnetic radiation and matter relies on the interaction between the oscillating electric and magnetic fields of the radiation with the electric or magnetic dipole moment of an atom or molecule. Thus, a molecular system can experience a force as a consequence of the electrostatic interaction between its electric dipole moment and the oscillating electric field of the electromagnetic radiation. On the other hand, the interaction between the permanent magnetic moment of a nucleus or an electron and the magnetic field of the electromagnetic radiation is the foundation of nuclear magnetic resonance, electron spin resonance, and related spectroscopic techniques. According to this, the interaction between atoms or molecules and the electromagnetic radiation requires the existence of a permanent electric or magnetic dipole or the instantaneous creation of an electric dipole due to internal motions. As is shown below, the magnitude of this interaction depends on the size of the molecular dipole moment.

The quantitative study of the interaction of electromagnetic radiation with matter can be done using a simple semi-classical model. In this model the electromagnetic radiation is treated classically, while the energy levels are obtained by solving the time-dependent Schrödinger equation. It is due to the time dependence of radiation shown in Equations 1.1 and 1.2 that the interaction of radiation with atoms and molecules requires solving the time-dependent Schrödinger equation.

For a single particle described by means of a wave function depending on coordinates and time, $\Psi(x, y, z; t)$, the form of the Schrödinger equation is

$$\hat{H} \Psi(x, y, z; t) = i \frac{\hbar}{2\pi} \frac{\partial \Psi(x, y, z; t)}{\partial t} = i\hbar \frac{\partial \Psi(x, y, z; t)}{\partial t} \quad (1.8)$$

or

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + \hat{V} \right) \Psi(x, y, z; t) = i\hbar \frac{\partial \Psi(x, y, z; t)}{\partial t} \quad (1.9)$$

where the Hamiltonian operator \hat{H} is the combination of the Laplacian operator, given by $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, and the potential energy operator \hat{V} , which depends only on the spatial coordinates (x, y, z) .

If the potential energy is considered to be time independent, the wave function $\Psi(x, y, z; t)$ can be written as the product of a time-independent function $\psi(x, y, z)$ and a function of time $\phi(t)$

$$\Psi(x, y, z; t) = \psi(x, y, z)\phi(t) \quad (1.10)$$

From now on, to simplify the notation, explicit inclusion of coordinates and time is discontinued. Introducing the above function allows us to separate the Schrödinger equation into two equations. The first,

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + \hat{V} \right) \psi = E\psi \quad (1.11)$$

corresponds to the time-independent Schrödinger equation whose solution provides the energy of the particle in a state n ($E = E_n$) and the wave function $\psi(x, y, z)$, from which physical properties can be deduced. The second,

$$i\hbar \frac{d\phi}{dt} = E\phi \quad (1.12)$$

is a first order differential equation on time with a solution given by

$$\phi(t) = e^{-iE_n t/\hbar} \quad (1.13)$$

It must be noted here that this time-dependent factor in the solution of the Schrödinger equation always has the same form; therefore the total wave function for a single particle can be written as

$$\Psi_n = \psi_n e^{-iE_n t/\hbar} \quad (1.14)$$

More complex quantum mechanical systems, such as atoms or molecules, usually possess several stationary states described by total wave functions $\Psi_0, \Psi_1, \Psi_2, \dots$, with discrete energies E_0, E_1, E_2, \dots . For a transition between two nondegenerate m and n states caused by a photon of adequate frequency, the Ψ_m and Ψ_n wave functions describing the states involved in the transition are solutions of the Schrödinger equation, and their linear combination

$$\Psi = c_m(t)\Psi_m + c_n(t)\Psi_n \quad (1.15)$$

should be also a solution of the equation. Such a superposition of states is the general solution for systems in transition between two states. The initial state Ψ_m is described by $c_m = 1/c_n = 0$ and the final state Ψ_n is described by $c_m = 0/c_n = 1$. During an absorptive transition, the coefficients change from $c_m = 1 \rightarrow 0$ to $c_n = 0 \rightarrow 1$, while they change from $c_m = 0 \rightarrow 1$ and $c_n = 1 \rightarrow 0$ if radiation is emitted. Time enters this way into the solution of the problem, since the coefficients $c_i(t)$ are only functions of time.

If we want to model how this radiation-induced transition between states Ψ_m and Ψ_n takes place, we can consider that the time-dependent radiation field associated to exposure to an electromagnetic radiation is a perturbation $\hat{H}'(x, y, z, t)$ that must be added to the Hamiltonian for the unperturbed system H_0

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (1.16)$$

If the potential due to the electromagnetic radiation is small compared to the molecular potential, the Schrödinger equation during irradiation becomes

$$(\hat{H}_0 + \hat{H}') \Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (1.17)$$

which can be solved by means of perturbation theory. After some algebra, the rate of increase of c_n , that is, the rate of transition from initial state m to final state n can be obtained as

$$\frac{dc_n}{dt} = \frac{c_m}{i\hbar} \int \Psi_n^* \hat{H}' \Psi_m dv \quad (1.18)$$

According to Equation 1.18, explicit forms for the Ψ_m and Ψ_n wave functions and the \hat{H}' Hamiltonian are needed to evaluate the intensity of a transition. To obtain further insight into the form of the \hat{H}' Hamiltonian, the interaction between the electromagnetic radiation and the system must be analyzed. As cited above, the electric and magnetic components of the radiation can interact with the electric or the magnetic dipole of the system. For the sake of brevity, in our analysis we will consider the system as an electric dipole moving only on one dimension x . Extension of this derivation to the three-dimensional case and to magnetic properties is straightforward. In this framework, the magnitude of the dipole moment (μ_x) depends on the displacement of an electric charge (e) by a distance x from its equilibrium position

$$\mu_x = ex \quad (1.19)$$

The Hamiltonian representing the classical interaction between the electric dipole moment and the electric field of the electromagnetic radiation is

$$\hat{H}' = -\boldsymbol{\mu}\mathbf{E} = -\mu E \cos \theta \quad (1.20)$$

where θ is the angle between the dipole and the electric field. For a polarized electromagnetic radiation traveling along the x direction, the amplitude of the electric field is

$$E_x = 2E_x^0 \cos 2\pi\nu t = E_x^0(e^{i2\pi\nu t} + e^{-i2\pi\nu t}) \quad (1.21)$$

where E_x^0 is the maximum amplitude of the electric field (Figure 1.1). If we assume that the dipole and the electric radiation field are parallel

$$\hat{H}' = -\mu_x E_x = -exE_x \quad (1.22)$$

and introducing the above expressions it can be shown that

$$c_n = E_x^0 \int \psi_n^* \mu_x \psi_m \, d\nu \left(\frac{1 - e^{i(E_n - E_m + h\nu)t/\hbar}}{E_n - E_m + h\nu} + \frac{1 - e^{i(E_n - E_m - h\nu)t/\hbar}}{E_n - E_m - h\nu} \right) \quad (1.23)$$

where the integral $\int \psi_n^* \mu_x \psi_m \, d\nu$ is usually represented as $\mu_x^{nm} = \langle n | \mu_x | m \rangle$ and is known as the transition dipole moment integral.

According to the initial conditions, if the energy of the initial state m is lower than that of the final state n , the energy difference ($E_n - E_m$) will be positive for a transition $\Psi_m \rightarrow \Psi_n$ caused by absorption of radiation, and will be negative for a transition $\Psi_m \leftarrow \Psi_n$ with emission of radiation. If we only consider now the absorption process, the above expression can be simplified because when the frequency of the radiation fulfills that

$$h\nu = E_n - E_m \quad (1.24)$$

the denominator of the second term in the addition becomes very small and the entire second term can take large values, so that the first term containing

$E_n - E_m + h\nu$ can be neglected. Under these conditions, the probability of finding the system in the upper state n after irradiation is given by

$$|c_n^2| = c_n^* c_n = 4(E_x^0)^2 (\mu_x^{nm})^2 \left(\frac{\sin^2 [\pi t (E_n - E_m - h\nu) / h]}{(E_n - E_m - h\nu)^2} \right) \quad (1.25)$$

This expression applies only when the radiation is monochromatic. By integration over all the frequencies, the total transition probability, that is, the probability of finding the system in state n after interaction with the radiation, is

$$|c_n^2| = c_n^* c_n = 4(E_x^0)^2 (\mu_x^{nm})^2 \int_{-\infty}^{\infty} \frac{\sin^2 [\pi t (E_n - E_m - h\nu) / h]}{(E_n - E_m - h\nu)^2} d\nu = \frac{(E_x^0)^2}{\hbar^2} (\mu_x^{nm})^2 t \quad (1.26)$$

According to this, the probability of a system in state Ψ_m undergoing a transition to state Ψ_n due to irradiation is proportional to the transition dipole moment integral, the square of the incident electric field amplitude (the intensity of the radiation), and the time of irradiation.

In order to compare with experimental results on the amount of radiation absorbed, it is convenient to rewrite the previous expression substituting the electric field strength by the energy density (ρ), that is, the energy per unit volume that is irradiated by the electromagnetic radiation. These magnitudes are related by the expression

$$\rho = \frac{(E_x^0)^2}{2\pi} \quad (1.27)$$

Further differentiation of the transition probability with respect to time and extension of the complete procedure for isotropic radiation (where the three x , y , z components of the radiation–dipole interactions are equal) gives the transition probability per unit time as

$$\frac{d[c_n^* c_n]}{dt} = \frac{8\pi^3}{3\hbar^2} \mu_{nm}^2 \rho(\nu) = B_{nm} \rho(\nu) \quad (1.28)$$

where

$$\mu_{nm}^2 = \sum_{i=x,y,z} (\mu_i^{nm})^2 \quad (1.29)$$

and

$$B_{nm} = \frac{8\pi^3}{3\hbar^2} \mu_{nm}^2 \quad (1.30)$$

called Einstein's coefficient of induced absorption. Expression (1.28) shows that the rate of the $\Psi_m \rightarrow \Psi_n$ transition depends on the square of the dipole moment integral and the energy density of the radiation.

If we change the initial conditions in Equation 1.15 to those for a system in an upper energy state, that is, with $c_m = 0$ and $c_n = 1$, the previous treatment for induced absorption would be formally identical for the emission of radiation from an excited state Ψ_n to state Ψ_m induced by an electromagnetic radiation.

Thus, the expression for induced emission from an excited state is identical to that for induced absorption with $B_{mn} = B_{nm}$.

However, the procedure presented here has not considered the possibility of spontaneous emission from the upper state Ψ_n to the lower energy state Ψ_m , a process that can be of importance when the population of the upper energy state is significant. Following Equation 1.28, in the presence of radiation the population change of the upper state due to induced absorption must be proportional to the population of the lower state according to

$$\left(\frac{dN_n}{dt}\right)_{\text{absorption}} = N_{m \rightarrow n} = N_m B_{mn} \rho(\nu) \quad (1.31)$$

However, there is also a population change of the upper state n due to induced emission

$$\left(\frac{dN_n}{dt}\right)_{\text{emission}} = N_{m \leftarrow n} = -N_n B_{nm} \rho(\nu) \quad (1.32)$$

and the possibility of spontaneous emission

$$\left(\frac{dN_n}{dt}\right)_{\text{emission}} = N_{m \leftarrow n} = -N_n A_{nm} \quad (1.33)$$

where A_{nm} is the Einstein coefficient for spontaneous emission. The relationship between the A_{nm} and B_{nm} coefficients can be established using the radiative energy density given by the Planck radiation law

$$\rho(\nu) = \frac{8\pi h\nu_{mn}^3}{c^3 (e^{h\nu_{mn}/kT} - 1)} \quad (1.34)$$

and the relationship between the upper and lower state populations given by the Boltzmann distribution law

$$N_n = N_m e^{-(E_m - E_n)/kT} = N_m e^{h\nu_{mn}/kT} \quad (1.35)$$

For a system in equilibrium, absorption and emission rates must be equal and the net change of the upper state population is zero:

$$\left(\frac{dN_n}{dt}\right) = N_{m \rightarrow n} + N_{m \leftarrow n} = (N_m - N_n) B_{mn} \rho(\nu) - N_n A_{nm} = 0 \quad (1.36)$$

which gives the relation between spontaneous and induced Einstein's coefficients

$$A_{nm} = \frac{8\pi h\nu_{mn}^3}{c^3} B_{nm} \quad (1.37)$$

According to Equation 1.36, when a system is irradiated there will be competitive induced and spontaneous emissions that reduce the intensity of the absorption lines. However, only induced emission is coherent with the incident radiation, that is, they travel in the same direction and have the same phase, so that the net absorption intensity equals the difference between the absorbed and induced emission intensities according to

$$N_n B_{mn} \rho(\nu) - N_n B_{nm} \rho(\nu) = B_{mn} \rho(\nu) (N_m - N_n) \quad (1.38)$$

which states that the intensity for a given absorption depends on the population difference between the initial and final states. It must be also noted here that, due to the ν_{mm}^3 factor, the importance of spontaneous emission increases as the radiation frequency increases (which is of importance in lasers). However, for transitions with frequencies below 10^{12} s^{-1} the magnitude of A_{mm} compared to B_{mm} is insignificant and spontaneous emission can be neglected.

1.6

Magnetic Spectroscopies

All the above discussion is focused on the changes experienced by matter as a consequence of the electric field of the electromagnetic radiation. In addition, we will now comment briefly on some aspects of nuclear magnetic resonance methods and electron spin resonance methods that are instead related to the action of the magnetic field of the radiation.

The phenomenon of magnetic resonance is due to the interaction of an external magnetic field with the magnetic moment associated with the spin of a nucleus or an electron. In the absence of an external magnetic field, the states of a spin system are degenerated, that is, they have the same energy, and no spectroscopic transitions can be observed. However, when the spin system interacts with an external magnetic field, the energy degeneracy is removed and absorption or emission of radiation can be observed [7, 28–30].

If we consider initially the nuclear magnetic resonance, the interaction energy between a nuclear magnetic moment, $\boldsymbol{\mu}_m$, and the external magnetic field, \boldsymbol{H} , is given by

$$E = -\boldsymbol{\mu}_m \cdot \boldsymbol{H} \quad (1.39)$$

The nuclear magnetic moment is proportional to the nuclear spin angular momentum \boldsymbol{I}

$$\boldsymbol{\mu}_m = g_N \frac{e}{2m_p} \boldsymbol{I} = \frac{1}{\hbar} g_N \beta_N \boldsymbol{I} \quad (1.40)$$

where the nuclear magneton, β_N , depends on the proton mass, m_p , and the values of the nuclear g_N factor must be determined experimentally for each nucleus. As a consequence of the effect of the magnetic field, the orientations of the nuclear magnetic moment along the z direction of the incident field are quantized and can only take values according to

$$I_z = \hbar M_I \quad (1.41)$$

where the values of the magnetic quantum number are $M_I = -I, \dots, 0, \dots, I$. For the common case of protons in $^1\text{H-NMR}$ and carbons in $^{13}\text{C-NMR}$ with $I = 1/2$, the orientation with $M_I = +1/2$ is parallel to the field direction and is energetically preferred, while the orientation with $M_I = -1/2$ is antiparallel. Following the expressions above, the energies for these spin states are given by

$$E_{M_I} = -g_N \beta_N H_z M_I \quad (1.42)$$

and the energy separation between two levels is

$$\Delta E = h\nu = E_{-1/2} - E_{1/2} = g_N \beta_N H_z \quad (1.43)$$

or

$$\omega = 2\pi\nu = \gamma H_z \quad (1.44)$$

where γ is called the magnetogyric ratio and includes a combination of factors given by

$$\gamma = \frac{g_N \beta_N}{\hbar} \quad (1.45)$$

It must be recalled here that the expression for the NMR quantum mechanical transition frequency ω is similar to that of the Larmor angular frequency obtained for the classical description of the precessional motion experimented by the nuclear magnetic moment around the direction of the external electromagnetic field.

According to the above, the energies needed for transitions between nuclear magnetic levels depend both on the intensity of the applied magnetic field and on the value for the magnetogyric ratio for each nucleus (Figure 1.3). However, it must be noted that the energy separation between levels is very small compared with the average energy of thermal motion and, as a consequence, the populations of the separated energy levels are nearly equal and signal sensitivities are small. Some characteristic resonance frequencies and common magnetic fields are shown in Table 1.2.

Quantitative treatment for electron magnetic resonance is similar to that presented here. However, due to its lighter mass, the value of γ_e for an electron is larger than that for a proton and, as a consequence, the energy separation between the energy levels for the electron is approximately 2000 times greater than for the proton. For these reasons, one of the main difficulties of electron resonance spectroscopy is generation and detection of resonance frequencies above 35 000 MHz, which fall into the microwave range of the electromagnetic spectrum. Furthermore, electron resonance spectroscopy is only useful for the study of systems with unpaired electrons and its use is much more limited than that of nuclear magnetic techniques [31].

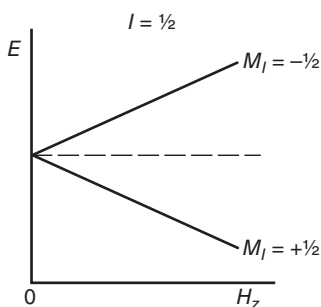


Figure 1.3 Spin energy differences in an external magnetic field for a nucleus with $I = 1/2$.

Table 1.2 Some magnetic resonance parameters for selected nuclei with $I = 1/2$.

Nucleus	μ_m ^{a)}	$\gamma \times 10^7 \text{ s}^{-1} \text{ T}^{-1}$	NMR frequency (MHz) ^{b)}	Relative sensitivity
¹ H	2.79285	23.751	42.5775	1.00000
¹³ C	0.70241	6.726	10.7084	0.01591
¹⁹ F	2.62887	25.167	40.0776	0.83400
³¹ P	1.13160	10.830	17.2515	0.06652

a) Nuclear magnetic moments in units of the nuclear magneton β_N .

b) These values correspond to nuclei in a magnetic field $H = 1.0 \text{ T}$.

1.7

Pulse Techniques in NMR Spectroscopy

According to the above discussion, continuous NMR spectra can be obtained by keeping constant the radiation frequency while varying the intensity of the external magnetic field until the resonance condition given in Equation 1.43 is achieved, or by keeping constant the value of the external magnetic field while the frequency of electromagnetic radiation is varied. However, these procedures are only suitable for sensitive nuclei with large magnetic moments and high natural abundance, and to obtain the NMR spectra of insensitive nuclei of low abundances, the use of pulse NMR techniques is mandatory.

For a sample immersed in a magnetic field with nuclei with different resonant frequencies, all the nuclear magnetic moments precess around the applied field direction. As a consequence of the small energy difference between the nuclear spin levels, the number of nuclei in the lower energy state (n_α) is greater than that in the upper energy state (n_β) and the components of the nuclear magnetic moments along the field direction can be added to obtain a macroscopic magnetization, usually described by the vector M_0 (Figure 1.4). This magnetization vector M_0 is used to describe the interaction between the nuclear dipoles and the magnetic vector of the radiofrequency pulse.

In NMR pulse methods, all the nuclei in a sample are excited simultaneously by a radiofrequency pulse. A radiofrequency generator can produce a pulse if it is switched on only for a short time, containing not a single frequency but a continuous band of frequencies around a given frequency center. Only a part of the frequency interval is effective in exciting transitions, and the choice of the pulse duration and the generator frequency depends on the magnetic field employed and on the nuclei to be studied. During the application of a pulse, the macroscopic magnetization vector M_0 is moved away from its equilibrium position through a pulse angle that depends on the angle between the direction of the static field and the direction in which the radiofrequency pulse is applied. Once the pulse is switched off, the magnetization vector M_0 reverts to its equilibrium state through a complicated motion, named relaxation. Bloch showed that the behavior of M_0 , both during the application of the pulse and the subsequent relaxation, can be

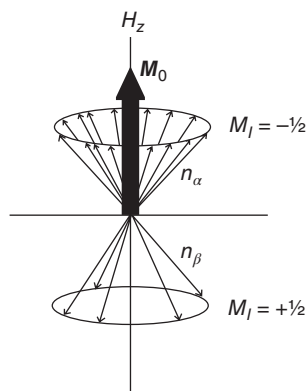


Figure 1.4 Macroscopic magnetization M_0 .

easily described in a rotating coordinate system by means of three magnetization components varying with time. Thus, the return of the M_z component to its equilibrium condition, named longitudinal relaxation and occurring at a rate determined by the spin-lattice relaxation time, T_1 , depends on the way the energy of the spin system is transferred to the surroundings. On the other hand, transverse relaxation determines how rapidly the M_x and M_y magnetization components decay, and the rate constant for this process depends on the spin-spin relaxation time, T_2 , which can be classically visualized as the energy transferred by the spin system during relaxation to the adjacent nuclei through fluctuating magnetic fields.

In samples containing nuclei with different resonant frequencies, the decay curves of the transverse components of the magnetization superimpose and interfere producing a complex signal (Figure 1.5) that can be detected by a receiver coil. This free induction decay (FID) signal is obtained in the time domain and contains the resonance frequencies and intensities of the sample. However, the FID signal cannot be interpreted directly and must be transformed into a useful spectrum in the frequency domain by means of a mathematical operation named Fourier transformation. Additional details on the NMR pulse techniques will be given in subsequent chapters and can be found in more specialized literature [28–30].

1.8

Line Widths

The transitions between energy levels should result in the absorption or emission of discrete frequencies of the electromagnetic spectrum, resulting in line spectra. However, in the experiments, spectral lines are always broadened, due to different effects: natural line width, Doppler shift, Lorentz broadening, and other physical or technical (depending on the experimental setup) phenomena.

Natural line width does not depend on the experimental setup and is inherent to any studied system. It arises from the uncertainty principle, which states that

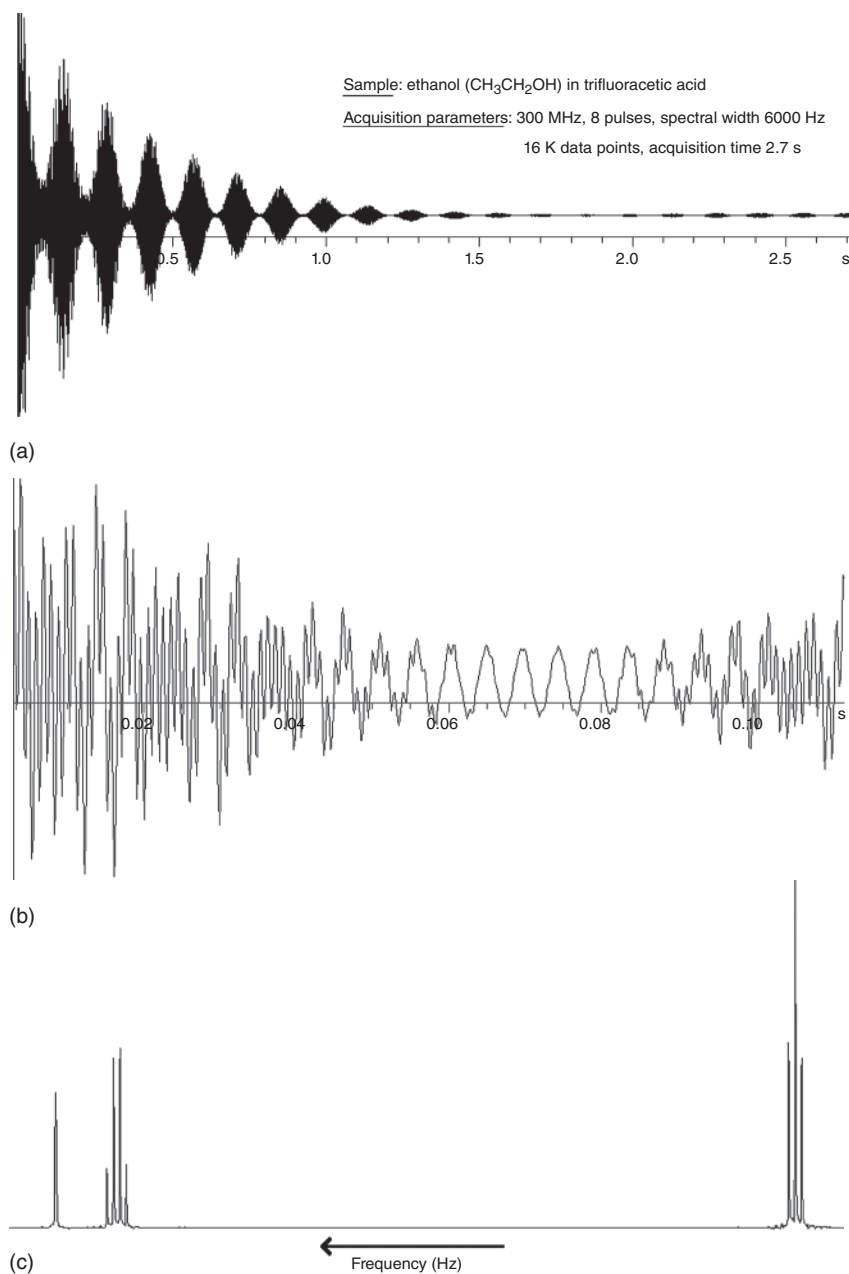


Figure 1.5 Free induction decay (FID) and Fourier transformation. (a) ^1H NMR time domain spectrum of ethanol. (b) Zoomed area of the time domain spectrum between 0 and 0.1 s. (c) Frequency domain spectrum obtained by Fourier transform of the time domain spectrum.

two conjugated variables cannot be exactly determined at the same time, so that, for example,

$$\Delta E \Delta t \geq \frac{\hbar}{2} \quad (1.46)$$

In this case, Δt would represent the lifetime of the excited state and ΔE the uncertainty in the energy of this state, which will be reflected in an uncertainty in the frequency of the radiation associated with this transition.

The Doppler effect is another source of bandwidth, due to the thermal motion of the atoms or molecules emitting radiation. The atoms or molecules that travel in the direction of the observer emit light at a higher frequency than those traveling away from him

$$\nu = \nu_0 \left(1 \pm \frac{v}{c} \right) \quad (1.47)$$

where ν_0 is the frequency of the transition, v is the speed of the atom or molecule, and c is the speed of light.

Pressure broadening is an umbrella term that includes the different effects that neighboring particles can have in the emission of an individual particle. Collision of other particles with the emitting particle can result in a decreased lifetime of the excited state, enhancing the uncertainty in its energy beyond that corresponding to the natural broadening, leading to what is called impact pressure broadening or Lorentz broadening. Other particles can also shift the energy levels of the target molecule through their electric fields (Stark broadening), through resonance (an energy exchange between particles of the same type), or other interactions (van der Waals broadening).

Of the broadening mentioned above, natural line broadening is the smallest, while the others can be reduced changing the experimental conditions. Thus, pressure broadening can be removed working at low pressures, while Doppler broadening can be reduced using effusive or molecular beams where the velocity component of the sample in the direction of observation is small.

1.9 Selection Rules

As noted in Equation 1.26, the probability of the absorption or emission of a photon due to a transition between two states depends on the transition dipole moment integral. Application of symmetry considerations to the two states involved in the transitions can help identify when the integral is going to be zero without the need of explicitly solving it, resulting in what are called “selection rules.” Selection rules determine which transitions are allowed and are expected to appear in the spectrum, and which are forbidden and will not appear in the spectrum. Selection rules can be quite varied and depend on the type of spectrum considered and the properties of the system under study [17, 32].

The key requirement for a transition to be forbidden, that is, to have a zero probability of occurring, is that the dipolar transition moment $\mu_x^{nm} = \int \psi_n^* \mu_x \psi_m dv$ is

zero. For this, the product $\psi_n^* \mu_x \psi_m$ needs to be antisymmetric, under the symmetry operations of the system. This condition can be easily checked by using the character table corresponding to the symmetry point group of the system and bearing in mind that the electric dipole operator transforms as x, y, z , the magnetic dipole as R_x, R_y, R_z and the electric polarizability (used, for instance, in Raman spectra) as $x^2, y^2, z^2, xy, xz, yz$. Using this, it is easy to explain, for instance, why the symmetric stretch in CO_2 is inactive in IR spectroscopy while it is active in Raman spectroscopy [17, 19, 33–35].

Selection rules are expressed in terms of quantum numbers with physical significance derived from the system wave function, and some simple examples follow. Thus, selection rules governing atomic electronic spectra are $\Delta n = 0, 1, 2, \dots$ with $\Delta L = \pm 1$ for single electron transitions and $\Delta L = 0, \pm 1$ for multielectron transitions, $\Delta S = 0$ and $\Delta J = 0, \pm 1$ (except for the forbidden $J = 0 \rightarrow J = 0$ transition), where n is the principal quantum number, L the orbital angular momentum, S , the spin angular momentum, and J , the total angular momentum. In molecular systems, the observation of pure rotational transitions requires the molecule to have a non-zero permanent electric dipole moment and the selection rules are $\Delta J = 0, \pm 1$ and $\Delta M = 0$ or ± 1 , where J is the rotational angular momentum and M corresponds to the component of the rotational momentum along a given axis. For vibrational spectra, transitions are allowed within the harmonic oscillator model when the change in the vibrational quantum number is $\Delta v = \pm 1$ if, at the same time, the molecular dipole moment changes with the nuclear motion. When the Hamiltonian used for the system does not take spin into account, transitions between different spins are not allowed.

It must be noted here that the distinction between allowed and forbidden transitions is strictly based on the assumptions made in the development of the model, but sometimes in experimental spectra allowed transitions are not appreciated due to very low intensities, while some forbidden transitions appear as low-intensity peaks. This happens usually if the transition takes place through a mechanism not involving the electrical dipole or due to the simplifications introduced in the quantum description of the system. Some examples are spin-orbit coupling, which allows the mixing of states of different multiplicity and explains phosphorescence, and vibronic coupling (the coupling between electronic and vibrational motions) or the mixture of ligand orbitals d of the metal, which explain the appearance of unexpected forbidden transitions in the electronic spectra in transition metal complexes [7, 8, 16, 17, 36].

1.10

Summary of Spectroscopic Techniques

The following summary and the associated classification of spectroscopic techniques are in no way comprehensive. Their purpose is just to provide a brief outlook of the wealth of methods available, highlighting the common principles behind very diverse experimental setups. The assignment of one

specific technique to one set or another is sometimes ambiguous, since two or more phenomena can be exploited at a time (scattering of emitted electrons, for example, or the side-by-side analysis of excitation and fluorescence spectra).

1.10.1

Absorption-Based Methods

A photon (sometimes two in two-photon spectroscopy) is destroyed while the absorbing medium (atom, molecule, or material) increases its energy by $h\nu$. The most common experimental setup implies the measurement of the amount of radiation absorbed at different wavelengths, resulting in a spectrum where absorbance is plotted against frequency.

Absorption of photons in different region of the electromagnetic spectrum leads to transitions between different levels of energy in atoms, molecules, or materials. As a result, radiation of different wavelengths can be used to obtain geometries, electronic structures, and so on, or as a probe for the presence of certain functional groups or atoms in a sample.

Microwave spectroscopy uses microwave radiation to analyze transitions between molecular rotational energy levels, thus providing information on moments of inertia and, with the use of isotope substitutions, detailed and accurate molecular geometries [37–39].

Infrared radiation promotes transitions between vibrational energy levels, leading to spectra that allow for the identification of functional groups and which represent a very characteristic and sensitive fingerprint of a specific molecule [33–35, 40–43].

Irradiation of atoms and molecules with visible and near-UV light can lead to excitation of electronic states providing information on their electronic structure. Its most extended use is in quantitative analysis [32, 36].

The absorption of higher energy photons can result in the excitation of electrons to higher energy non-bound states in the continuum region and/or from deeper (core) orbitals. The study of the absorbance *vs.* frequency curves, and the dynamic behavior of the emitted electrons and their interactions with surrounding atoms (backscattering) provides information on the electronic energy levels of the substrate, its composition, and structure. This is the case of photoelectron spectroscopy, where an X-ray (XPS/electron spectroscopy for chemical analysis (ESCA)), far ultraviolet, or ultraviolet (UPS) photon excites a core or valence electron that is emitted (photoelectric effect) [44]. The kinetic energy of the emitted electron is then measured and used to infer information about the binding energy of electrons in the material. These techniques are very useful in the analysis of surfaces. X-ray absorption spectroscopy (XAS) is another example, which provides information on the energies of core electrons (it can be used to identify atoms) through analysis of the absorbance profile and on the environment of a certain atom through the features in the spectrum due to backscattering by neighboring atoms [25, 26].

Beyond the X-ray region, Mössbauer spectroscopy uses gamma rays to produce nuclear transitions. Changes in absorbance reflect with great accuracy information about the environment of the nuclei [45].

Finally, it must be recalled that some materials display different refractive indices for right and left circularly polarized light waves, resulting in a rotation of the plane of linearly polarized light when traversing a sample, a phenomenon called optical activity. In certain anisotropic media, the absorption coefficient can depend on the direction of polarization of the incoming radiation, resulting in preferential absorption of one polarization component. This phenomenon is named dichroism [46, 47]. More information on these two phenomena will be given in subsequent chapters of this book.

1.10.2

Emission-Based Methods

A photon is generated while the energy in the medium decreases by $h\nu$. For this to happen, the atom, molecule, or material needs to be in an excited state, emitting radiation in the decay to the ground state (or a less energetic state). The initial excitation can be achieved with irradiation, thermally, by collision with a beam of particles, and so on. As with the absorption spectroscopies, photons of different wavelengths can be involved in this process, depending on the kind of transitions being studied.

One of the most common techniques in this family, used for both quantitative and qualitative analysis, is atomic emission spectroscopy, where electronic states of atoms are thermally excited and the wavelength and intensity of the UV–visible radiation emitted during relaxation to the ground state is used to identify and quantify them [11, 13, 48].

Fluorescence spectroscopies fall in this classification as well. In them, excitation of the material is produced by incoming electromagnetic radiation, and the radiation emitted has a very small delay and a lower frequency than the irradiating light. The most commonly used technique involves using the UV–visible frequency range to excite a molecule to a higher electronic state in an excited vibrational state. After excitation, the molecule undergoes vibrational relaxation and then emits a photon with an energy corresponding to that of the transition between the lowest vibrational level of the excited electronic state and the ground state. Phosphorescence is a similar phenomenon, where instead of just undergoing vibrational relaxation between the absorption and emission of a photon, the electron exerts intersystem crossing that traps it in an electronic state from which the radiation-emitting transitions to the ground state are forbidden and thus very slow [49–52].

Fluorescence spectroscopy is not restricted, however, to UV–visible light, and X-ray fluorescence spectroscopy is used for elemental analysis in materials. In this technique, atoms in a sample are bombarded by X-rays or gamma radiation, energetic enough to remove an electron from the core. The resulting ion is unstable

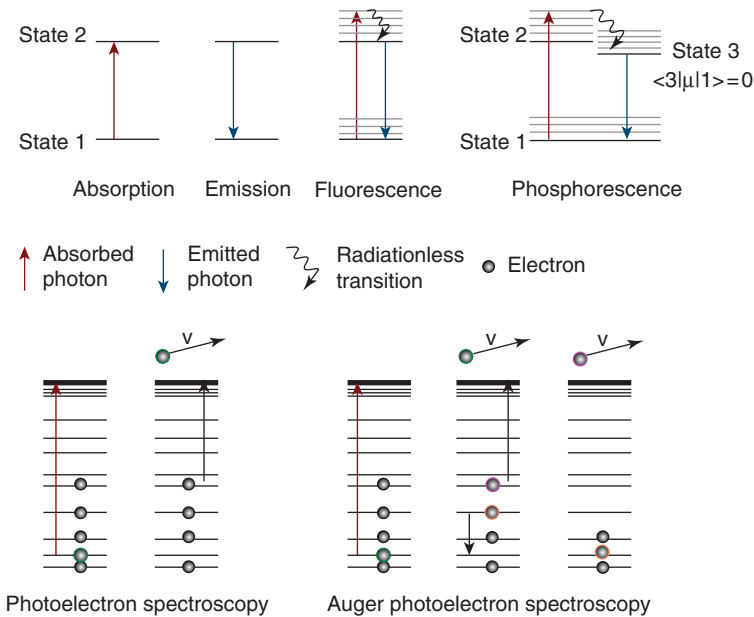


Figure 1.6 Schematic examples of the phenomena involved in some absorption and emission spectroscopies.

and the atom rearranges through a light-emitting transition that fills the hole with an electron from a higher orbital.

Again, radiation does not need to be the only measurable output of a relaxation process. Auger electron spectroscopy (mainly used for surfaces and materials) excites a sample with radiation or an electron beam, ejecting an electron from a core orbital. Upon relaxation, an outer shell electron fills this hole and the energy liberated in this process is used to emit a second electron whose kinetic energy is measured by a detector [4, 8, 44] (Figure 1.6).

1.10.3

Scattering and Diffraction Methods

It has been established above that when electromagnetic radiation passes through an atomic or molecular sample it may be absorbed if the energy of the radiation corresponds to the energy separation of two stationary states of the atoms or molecules in the sample. If this is not the case, most of the radiation passes through the sample unaffected, but a small percentage of the light is *scattered* in all directions by the particles in the sample.

Radiation scattering can be elastic or inelastic. If the wavelength of the scattered radiation is the same as the wavelength of the incoming beam, radiation is scattered elastically. This process, in a classical way, can be explained because the

oscillating electromagnetic field of the incoming radiation provokes that the electron cloud of the atoms or molecules in a sample vibrates at the same frequency of the incident radiation, and the system formed by the positive nuclei and the vibrating electron cloud constitutes an oscillating dipole that immediately radiates at the same frequency in random directions [27]. From a molecular point of view, scattering can be interpreted as a two-step process in which the incident photon collides with a molecule and excites it to a virtual state, which then relaxes back to its original state emitting a photon of the same energy as that of the incoming photon. It must be remarked that the two steps are simultaneous, and no stationary state exists in the interval between them. Therefore, scattering is a non-resonant process that should not be confused with fluorescence or phosphorescence, in which atoms or molecules absorb one photon and form an excited state (that lasts long enough to be characterized as a stationary state) and then decay by emitting a second photon [13, 16, 17].

Elastic scattering depends on the size of the particles that scatter radiation. Thus, if the incoming radiation wavelength is larger than the particle size of the matter with which it interacts, Rayleigh scattering is observed, and the intensity of the scattered light, I_s , is proportional to the wavelength of the radiation according to $I_s \propto 1/\lambda^4$. This expression indicates that light of shorter wavelengths (blue) is more scattered by the particles in the atmosphere than light of longer wavelengths (red), so that Rayleigh scattering is one of the reasons for the blue color of the sky. When the wavelength of the incoming radiation is similar to the size of the particles, Mie scattering is observed. The intensity of Mie scattering depends only weakly on wavelength and becomes independent of it when the size of the particle exceeds that of the incoming wavelength radiation. For this reason, clouds in the sky, containing large droplets of water, scatter white light and do not present appreciable colors [13, 27].

If radiation scattering is inelastic, the frequency of the scattered radiation is different than that of the incoming beam. In this case, the incident radiation excites the atoms or molecules in the sample to a virtual state that takes part of the energy of the incoming light, and relaxation from this virtual excited state to a second state, higher or lower in energy than the initial state, results in a shift in frequency of the scattered light.

Among the techniques based in inelastic scattering, Raman spectroscopy is one of the most popular. There are different applications of the Raman effect, but the most widely used makes visible or near-infrared light from a high intensity laser source pass through a sample, exciting molecular vibrational or rotational states. Most of the incoming radiation is scattered without a change in frequency (Rayleigh scattering) when the molecules relax to their initial state, but when some of the excited molecules relax to vibrational states higher or lower in energy than the initial state, Stokes or anti-Stokes Raman scattering is observed, respectively. Raman spectroscopy is widely used in the study of molecular vibrations, and provides complementary results to IR absorption spectroscopy, since some forbidden transitions in one case are allowed in the other and vice versa [33, 34, 40, 53–56].

Another extensively used group of techniques are those based on diffraction. The term diffraction refers to those phenomena that occur when a wave encounters an obstacle. According to Huygens, each point on a wave front can be considered as a source of secondary waves and the secondary waves that propagate beyond an obstacle may interfere and produce different diffraction patterns. Furthermore, since matter also has wavelike properties, small particles can also diffract [57–60]. For these reasons, X-rays and electrons or neutrons are especially suitable for the study of molecular structures, because their wavelengths roughly match the spacing between atoms in condensed phases, resulting in diffraction patterns that can be used to build a model of the electronic density of the studied material. X-ray diffraction is an essential tool in the structural elucidation of crystals, and can be also used to detect periodicity in complex materials. It is the structural characterization tool of choice for small molecules that can be crystallized, since it provides detailed information about the atomic positions, and is widely used in biochemistry to resolve the structure of proteins, DNA and RNA chains, or other biological structures such as viruses [61, 62].

Complementary tools can be electron diffraction (usually carried out in a transmission electron microscope), which provides information about both long-range and short-range order in solids, and neutron diffraction. The latter particles, in contrast with electrons or X-rays, scatter from nuclei, instead of interacting with the electron density, resulting in higher precision in the resolution of atomic positions and sensitivity to isotopes [63–65].

In the following chapters, the reader will acquire a deeper understanding of recent developments in spectroscopic techniques and their application to the structural elucidation of systems of chemical interest. For a more detailed discussion of the interaction of radiation with matter, the quantum mechanics needed for the calculation of the different energy levels and wave functions describing the states involved in the spectroscopic transitions, or specifics on any of the mentioned methods, the reader is referred to the texts cited in the references section.

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