

10.2.1.3 Molecular spectroscopy

10.2.1.3.1 Introduction

Molecular radiation results from the *rotational, vibrational and electronic energy transitions* of molecules. *Band spectra* are the combination of many different spectral lines resulting from vibrational, rotational and electronic transitions. *Unresolved band spectra* may appear as a spectral continuum.

10.2.1.3.2 Fundamentals of molecular absorption spectroscopy (UV/VIS)

The terms symbols and units used in molecular absorption spectroscopy are summarised in Table 10.3.

10.2.1.3.3 The UV/VIS absorption spectrum

Molecules which absorb photons of energy corresponding to wavelengths in the range 190 nm to about 1000 nm exhibit *UV/VIS absorption spectra*. The *quantized internal energy* E_{int} of a molecule in its electronic ground or excited state can be approximated with sufficient accuracy for analytical purposes by

$$E_{int} = E_{el} + E_{vib} + E_{rot}$$

where E_{el} is the electronic, E_{vib} the vibrational and E_{rot} the rotational energy, respectively. Absorption of a photon results in a change of the electronic energy accompanied by changes in the vibrational and rotational energies. Each *vibronic transition*, i.e. a particular electronic plus vibrational transition, corresponds to an *absorption band* consisting of rotational lines. In liquids and solids the rotational lines are broad and overlap so that no rotational structure is distinguishable.

Highly structured spectra can be obtained when the UV/VIS absorption of a solute in certain *polycrystalline matrices* (e.g. n-alkanes, cycloalkanes, inert gases such as rare gases) is measured at low temperatures. For all spectra the solvent, solvent temperature and solute concentration should be specified (see Note 1).

10.2.1.3.4 The Beer-Lambert-Bouguer Law

The *Beer-Lambert-Bouguer Law*, generally called the *Beer-Lambert law*, may be written for a single absorber either gaseous or in solution,

Note 1 . For the term *Shpol'skii spectra* see section 10.3.6.1.

$$-\log_{10} (\phi_t/\phi_o) = -\log_{10} \tau_i = \epsilon c b = A$$

where ϕ_t is the monochromatic radiant power transmitted by the absorbing medium, ϕ_o is the monochromatic radiant power incident on the medium, τ_i is the *internal transmittance* ($=\phi_t/\phi_o$), ϵ is the *molar (decadic) absorption coefficient*, c is the *concentration*, b the *absorption path length* and A the (decadic) *absorbance*.

Internal transmittance τ_i , i.e. transmittance of the medium itself, disregarding boundary effects, has to be distinguished from the *total transmittance* τ . The difference, which is mainly due to reflection losses associated with cell windows, can be compensated by using *matched cells* (see section 10.3.5.1.2).

Absorptance α is defined by $\alpha = 1 - \tau$ where reflection is assumed to be negligible.

The Beer-Lambert law holds only if the absorbing species behave independently of each other, and if the absorption occurs in a uniform medium. Furthermore, the incident radiation must be parallel, monochromatic (see Note 2) and there should be no measurable *saturation effect* due to depletion of the ground state molecules.

10.2.1.3.5 Molecular luminescence spectroscopy

The various types of molecular luminescence observed can be classified by (a) the mode of excitation to the excited state capable of emission and (b), the type of molecular excited state (Table 10.4). *Fluorescence* is the spin-allowed radiative transition while *phosphorescence* is the result of a spin-forbidden radiative transition. The definitions of the various radiative and radiationless transitions which occur in molecules are illustrated in the term scheme in Fig. 10.1.

Note 2 . In practice parallel, monochromatic radiation is not always used. Convergence or divergence of the light beam as found in practice, will cause only minor deviations from the Beer-Lambert law.

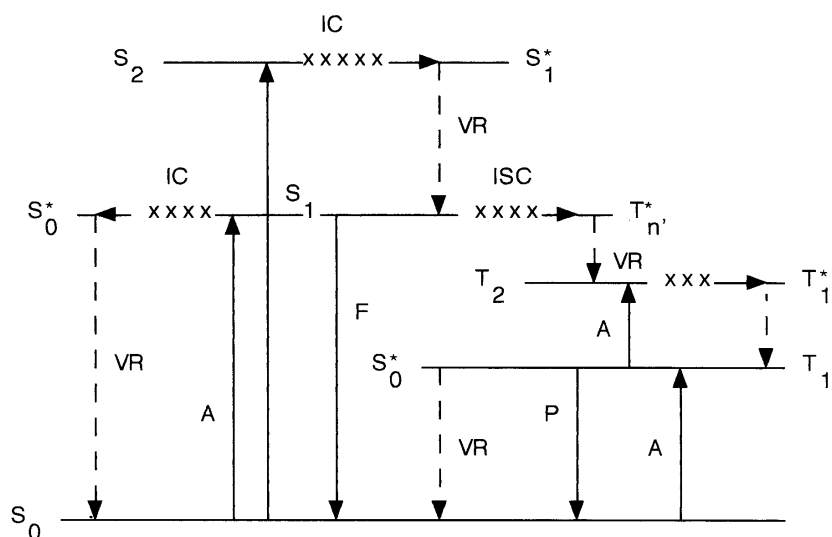


Fig. 10.1 Schematic diagram of radiative (—), radiationless (xxx), and vibrational relaxation (- - -) transitions between electronic states in a π -electronic system.

Notation:

States: S_0 = ground state, S_1 = first excited singlet state, S_2 = second excited state

Transitions: A = absorption ($S_0 \rightarrow S_n$, $S_0 \rightarrow T_1$, $T_1 \rightarrow T_n$)
 IC = internal conversion ($S_n \rightarrow S_1$, $S_1 \rightarrow S_0$, $T_n \rightarrow T$),
 ISC = intersystem crossing ($S_1 \rightarrow T_n$, $T_1 \rightarrow S_0$),
 VR = vibrational relaxation, F = fluorescence ($S_1 \rightarrow S_0$), and
 P = phosphorescence ($T_1 \rightarrow S_0$)

Fluorescence, *delayed fluorescence*, and phosphorescence can also arise from excited states higher than the first and, therefore, the transition should be indicated by a subscript. However, the quantum yields of radiative processes from higher excited states are generally several orders of magnitude lower than the quantum yields of emission from the first excited state. Therefore, if no special indication is given, the quantum yields are those of the respective first excited states. Three types of delayed fluorescence are known:

- (i) *E-type delayed fluorescence*: The first excited singlet state becomes populated by a thermally activated radiationless transition from the first excited triplet state. Since in this case the population of the singlet and triplet states are in thermal equilibrium, the lifetimes of delayed fluorescence and the concomitant phosphorescence are equal.

- (ii) *P-type delayed fluorescence*: The first excited singlet state is populated by interaction of two molecules in the triplet state (triplet-triplet annihilation) thus producing one molecule in the excited singlet state. In this biphotonic process, the life-time of delayed fluorescence is half the value of the concomitant phosphorescence.
- (iii) The first excited singlet state becomes populated by recombination of radical ions with electrons or by recombination of radical ions of opposite charge.

TABLE 10.3 Terms, symbols and units used in molecular absorption spectroscopy

Term	Symbol	Practical Unit	Notes
radiant energy	Q	J	
radiant power	$\phi = dQ/dt$	W	
radiant intensity	I	W sr ⁻¹	
spectral radiance	$L_\lambda(B_\lambda)$	W m ⁻² sr ⁻¹ nm ⁻¹	
radiant power incident on absorbing medium	ϕ_0	W	
radiant power transmitted by absorbing medium	ϕ_t	W	
radiant power reflected by sample	ϕ_r	W	
radiant power absorbed by medium	ϕ_a	W	
transmittance or transmission factor	τ	1	= ϕ_t/ϕ_0
reflectance or reflection factor	ρ	1	= ϕ_r/ϕ_0
absorptance or absorption factor	α	1	= $1 - \tau$
internal transmittance	τ_i	1	
internal absorptance	α_i	1	
(decadic) internal absorbance	A	1	= $-\log_{10} \tau_i$
linear (decadic) absorption coefficient	a, K	cm ⁻¹	= A/b
molar (decadic) absorption coefficient	ϵ	L mol ⁻¹ cm ⁻¹	= $A/(c b)$
specific (decadic) absorption coefficient	d	L g ⁻¹ cm ⁻¹	
molar concentration of absorber	c	mol L ⁻¹	
wavelength	λ	nm	
wavenumber		cm ⁻¹	= $1/\lambda$
spectral bandwidth of spectrometer	$\Delta\lambda$	nm	
wavelength modulation interval	$\Delta\lambda_{\text{mod}}$	nm	wavenumber may also be used
absorption pathlength	b	cm	
cell pathlength	l	cm	

TABLE 10.4 Classification of types of luminescence

(a) Excitation Mode	Luminescence Type
absorption of radiation (UV/VIS)	photoluminescence
chemical reaction	chemiluminescence, bioluminescence
thermally activated ion recombination	thermoluminescence
injection of charge	electroluminescence
high energy particles or radiation	radioluminescence
friction	triboluminescence
sound waves	sonoluminescence
(b) Excited State (Assuming Singlet State)	Luminescence Type
first excited singlet state	fluorescence, delayed fluorescence
lowest triplet state	phosphorescence

10.2.1.3.6 Absorption and deactivation processes

In principle, *radiative* and *radiationless transitions* can be distinguished in molecules. In both, transitions between terms of the same multiplicity are spin-allowed, while transitions between terms of different multiplicity are spin-forbidden (*spin conservation rule*).

Singlet-singlet absorption results in the transition from the singlet ground state of the molecule into singlet excited states ($S_0 \rightarrow S_n$) and leads to the UV/VIS absorption spectrum.

The analogous *triplet-triplet absorption* takes place in the transition from the lowest triplet state of the molecule to higher triplet states ($T_1 \rightarrow T_n$), thus leading to the triplet-triplet absorption spectrum.

Each absorption transition is characterized by the energy of the absorbed radiation, the oscillator strength and the polarization of the transition as well as the vibrational structure of the band system.

10.2.1.3.7 Radiationless transitions

Intrachromophoric radiationless transitions take place within the term system of the molecule, *interchromophoric radiationless transitions* between the term system of two non-conjugated parts of the molecule and *intermolecular radiationless transitions* between two molecules of identical or different species.

Interchromophoric and intermolecular radiationless transitions are *electronic energy transfer* processes.

Intrachromophoric radiationless transitions between states of the same multiplicity are termed *internal conversion* (IC): $S_n \rightarrow S_1$, $S_1 \rightarrow S_0$, $T_n \rightarrow T_1$ being distinguished.

Intrachromophoric radiationless transitions between states of different multiplicity are termed *intersystem crossing* (ISC): $S_1 \rightarrow T_n$, $T_1 \rightarrow S_0$, $T_1 \rightarrow S_1$ are known.

The following electronic energy transfer processes are known: singlet-singlet (spin-allowed), triplet-triplet (spin-allowed), singlet-triplet (spin-forbidden) and triplet-singlet transfer (spin-forbidden).

The most important property of radiationless transitions for analytical work is the transition probability, because this determines the yield of luminescence. The *quantum yields of fluorescence*, Y_F , and *phosphorescence*, Y_P , are related to the radiative and radiationless rate constants as follows:

$$Y_F = k_{FM} / (k_{FM} + k_{TM} + k_{GM})$$

$$Y_P = [k_{TM} / (k_{FM} + k_{TM} + k_{GM})] [k_{PT} / (k_{PT} + k_{GT})]$$

where the rate constants relate to the transitions as follows:

Rate constant	Transition
k_{FM}	fluorescence
k_{TM}	ISC ($S_1 \rightarrow T_n$)
k_{GT}	ISC ($T_1 \rightarrow S_0$)
k_{GM}	IC ($S_1 \rightarrow S_0$)
k_{PT}	phosphorescence

Luminescence quenching is defined as the radiationless redistribution of the excitation energy *via* interaction (electronic energy or charge transfer) between the emitting species and the quencher. Quencher and emitter can be molecules of the same species (*concentration quenching*) or of different species. The deactivation of the primarily excited emitter can lead to the activation of the quencher followed by radiative deactivation (*sensitized luminescence*). In some cases, concentration quenching is

accompanied by the formation of a new bimolecular species, which is capable of emission (*excimer-* and *exciplex-luminescence*).

In special cases luminescence quenching effects can be used to enhance sensitivity and/or selectivity in the luminescence analysis of mixtures, for example the strong depopulation of the fluorescing singlet excited state by external heavy atom perturbers can lead to a large population of the phosphorescing triplet excited state (*enhanced phosphorescence analysis*). Other special cases of luminescence quenching effects are applied in *quenched fluorescence analysis*.

10.2.1.3.8 Radiative transitions

Fluorescence radiation occurring at wavelengths longer than the absorption wavelengths i.e., the normal case, is said to be of the *Stokes type*. Fluorescence radiation occurring at shorter wavelengths than the absorption wavelengths is classified as the *anti-Stokes type*.