A BRIEF TOUR OF ELECTRONIC SPECTROSCOPY

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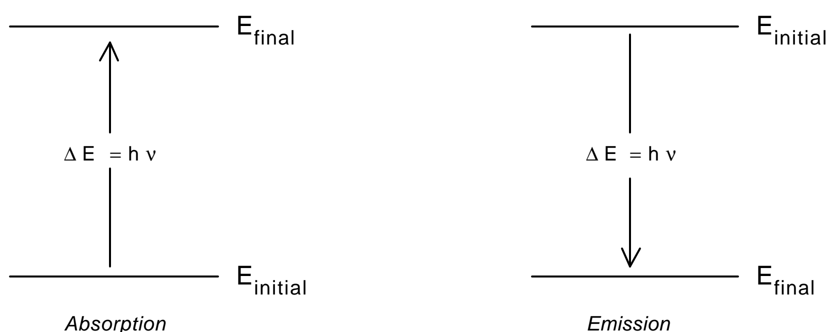
1. ELECTRONIC STATES OF MOLECULES

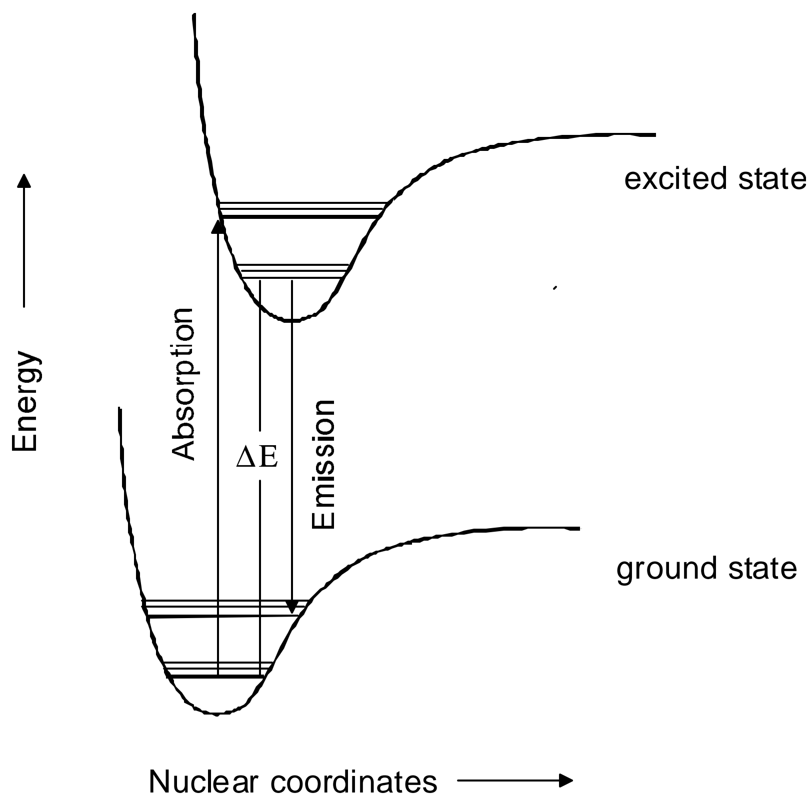
The energy states of electrons in atoms and molecules are quantized. The exact pattern of quantization (spacing between energy levels, number of states available to electrons) is related to the chemical nature of the atom or molecule. Electronic spectroscopy probes directly the quantization of electronic energy. The technique is based on the interaction between the electrons in the sample and electromagnetic radiation. For a system in a low energy state, energy from a photon will be absorbed, raising the system's energy to a higher, quantum mechanically allowed state. This process is called *absorption*. Conversely, a system in a high energy state may decay to a low energy state by emission of a photon whose energy corresponds to the difference in the energy of allowed quantum states. This process is called *emission*. In either case, a strict relationship exists between the photon's energy ($h\nu$) and the difference between quantum states (ΔE):



In reality, the energy states associated with large molecules are more complex than depicted above. Namely, each electronic state of a molecule also has vibrational and rotational levels. Quantum mechanics dictates that these vibrational and rotational states are quantized.

Each electronic state can be described mathematically by a multi-dimensional Morse potential, with vibrational and rotational levels within it. The well associated with the ground state of the molecule lies lower in energy than wells associated with excited states.

Typically, the structure of the excited state is different from that of the ground state. This is because the distribution of electrons around the nuclei is different in different states of the molecule. This situation is shown below, where each electronic state is drawn as a Morse potential, with the excited state displaced relative to the ground state along the nuclear coordinate axis. Vibrational and rotational levels are denoted by thick and thin horizontal lines, respectively.



Absorption occurs from the very lowest energy level of the ground state, i.e., the lowest vibrational level of the lowest electronic state. Upon absorption, the energy of the system is raised "vertically", leaving the molecule in an excited electronic state that is also slightly vibrationally excited. This occurs because the two curves are offset along the nuclear coordinate.

Before emission, the system has time to release some of the extra vibrational energy as heat to the surroundings. Hence, emission occurs from the lowest vibrational level of the excited electronic state. Emission occurs "vertically", leaving the system in the ground electronic state but slightly vibrationally excited.

As a result of this interplay between electronic and vibrational states of the system, the wavelength of radiation required to induce absorption tends to be shorter than the wavelength of emitted radiation. Put differently, the emission spectrum of a molecule tends to be shifted to longer wavelengths (a **red shift**) relative to the absorption spectrum.

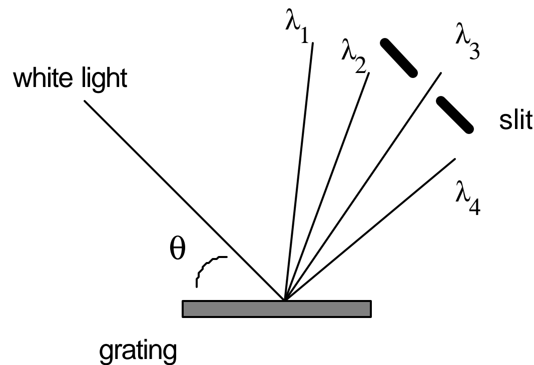
2. ABSORPTION

Materials owe their color to the absorption of specific wavelengths of visible light ($400 \text{ nm} < \lambda < 800 \text{ nm}$) and their "glow" to emission of specific wavelengths of visible light. Nowhere are these principles more important than in photosynthesis, where natural organic dyes (chlorophylls and carotenes) absorb visible light from the sun and convert it to useful metabolic energy.

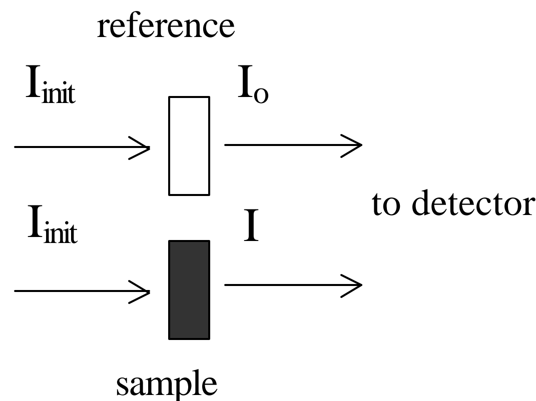
The relationship between chemical structure and the wavelength of light emitted or absorbed makes spectroscopy a very powerful technique for chemists, physicists, and biologists. Biologists

and analytical chemists use the specific pattern of absorption or emission by a sample to identify its components. Physical chemists and physicists use spectroscopy to describe in detail the structure of low and high energy states of atoms and molecules.

Experimentally, absorption and emission measurements are made with a *spectrophotometer*. For an absorption measurement, white light (from a deuterium or tungsten lamp) passes through a monochromator. The monochromator contains a *diffraction grating*, which decomposes light into its component wavelengths. By rotating the grating relative to the axis of propagation of the white light beam (i.e., changing θ), a narrow band of wavelengths can be let out of the monochromator through a narrow slit.



This light of specific wavelength is split into two beams of equal intensity, I_{init}. One half of the intensity goes through a cell ("cuvette") that contains a reference for the experiment, typically the solvent. The intensity of this beam is I_o. The other half of the intensity passes through a cuvette containing a solution of the compound of interest (in the same solvent that is used as a reference.) The intensity of this beam is I.



If the sample absorbs at a particular wavelength λ, then $I(\lambda) < I_o(\lambda)$. At each wavelength, a light detector samples I_o and I, converts them to electrical current, and reports the absorbance (A) of the sample, defined as:

$$A(\lambda) = -\log \frac{I(\lambda)}{I_o(\lambda)}$$

A plot of $A(\lambda)$ versus λ is the *absorption spectrum* of the sample. For solutions of large molecules, the absorption spectrum will show broad bands centered at wavelengths of light that correspond to ΔE's for specific pairs of states. The more bands in a spectrum, the more information may be gathered about the electronic structure of the molecule.

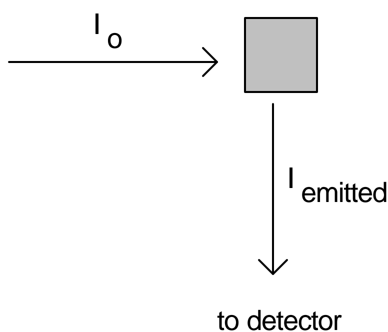
The Beer-Lambert Law relates the absorption $A(\lambda)$ at a particular wavelength to three parameters: the pathlength ℓ of the sample holder (often in units of cm), the concentration of solute C (often in units of M), and the molar extinction coefficient $\varepsilon(\lambda)$ (often in units of $M^{-1}cm^{-1}$):

$$A(\lambda) = \varepsilon(\lambda) \cdot C \cdot \ell$$

The molar extinction coefficient is related to the probability that the solute will absorb light. The wavelength dependence of ε is a signature of the solute and is a consequence of the molecular structure of the solute and its interaction with the environment (e.g., the solvent).

3. EMISSION

An emission measurement is conducted in a slightly different fashion. White light passes through a grating and slit as before. Energy from this beam excites the sample to a high energy state. This state can release energy by emission of a photon. The emitted light may be detected all around the sample. However, detecting along the direction of propagation of the incident beam will provide absorption information primarily. For this reason, emission is often detected at 90° relative to the direction of the incident beam.



The intensity of emitted light will be highest at those wavelengths that correspond to energy separations between pairs of quantum states in the molecule. A plot of $I_{emitted}(\lambda)$ versus λ is the *emission spectrum* of the sample. Again, the spectrum of large molecules in solution will have broad bands.

There are two types of emission events: fluorescence and phosphorescence. Fluorescence occurs when the high- and low-energy states have the same net electronic spin. Phosphorescence

occurs when emission of a photon is accompanied by a change in the electronic spin state of the molecule. The laws of quantum mechanics forbid spin state changes during optical transitions. In reality, though phosphorescence does occur but with much lower efficiency than fluorescence. For this reason, fluorescence has been embraced by biologists and chemists as a sensitive probe of structure and concentration.

The fluorescence intensity at a specified emission wavelength λ is given by the equation below:

$$F_\lambda = I_o(2.303\varepsilon(\lambda_A)Cl\Phi_f Z)$$

where, as before, I_o is the incident light intensity at a wavelength λ_A, $\varepsilon(\lambda_A)$ is the molar extinction coefficient of the solute at λ_A, C is the concentration, l is the pathlength, Φ_f is the fluorescence quantum yield, and Z is an instrumental factor. The factor Z arises from the fact that only a small amount of light emitted by the sample is collected by the spectrometer (typically at 90° relative to the exciting beam from a lamp or laser).

The fluorescence quantum yield Φ_f is a measure of the intrinsic probability that a species will fluoresce at the wavelength λ. It depends on a number of factors, including:

- The electronic structure of the species. For example, of the naturally occurring aminoacids, only tryptophan and tyrosine are highly fluorescent.
- The polarity of the solvent. For example, the side chain of tryptophan is highly fluorescent in non-polar solvents or when buried in the hydrophobic interior of a protein. However, the emission intensity decreases in polar solvents, such as water.
- Reactions involving the excited electronic state of the solute. Such reactions make up the field of **photochemistry**, which we will study later in the course.