Light and the Magic of Life through Excited States

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Abstract

When we speak of light, we are really speaking about electromagnetic waves and this includes visible light, x-rays, microwaves and radio waves, all of which are familiar in our daily lives. In fact, the core ingredients for life comprise of light (energy), water, oxygen and minerals, as depicted in the picture below. Light interfering with water in the sky in an oxygen atmosphere and minerals on the ground. Critically, it is energy that is core to the growth of all things.

Introduction

Figure 1: Depiction of the 4 main elements of life, water, air, minerals and light [1]

It is one of these core elements we will explore, light or energy, given its crucial role and our understating of how this energy actually works.

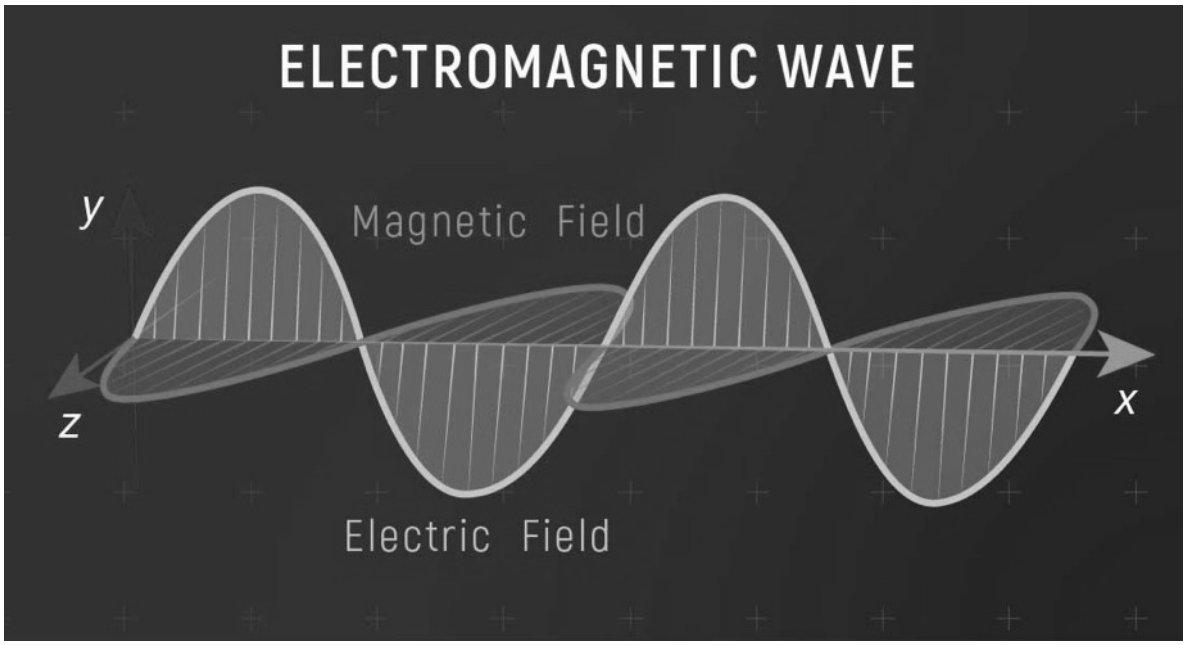

Figure 2: Electromagnetic waves are from both electric fields and magnetic fields, 90 degrees traveling in the same direction and a key source of energy [2].

If a molecule is irradiated by light with sufficient energy, photons may be absorbed, exciting the molecule from the ground electronic state to some excited electronic state. In addition, each electronic state of the molecule contains multiple vibrational and rotational energy levels.

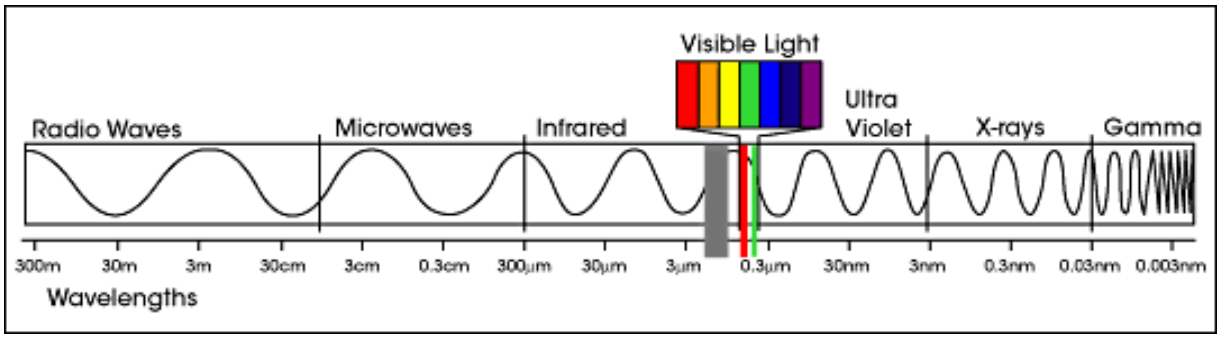

Figure 3: Spectrum shows radio waves to gamma rays, with the all-important ones of the visible spectrum showing just how thin a sliver of the EM waves. Because the vibrational levels are a fine splitting of the electronic energy levels, and the rotational levels are an even finer splitting of the vibrational levels, typically only the vibrational levels are considered when discussing absorption and emission. Thus, in general, after absorption of a photon, the molecule is in some vibrational level of an excited electronic state. http://ffden-2.phys.uaf.edu/webproj/212_spring_2014/Greg_Klupar/practice.html

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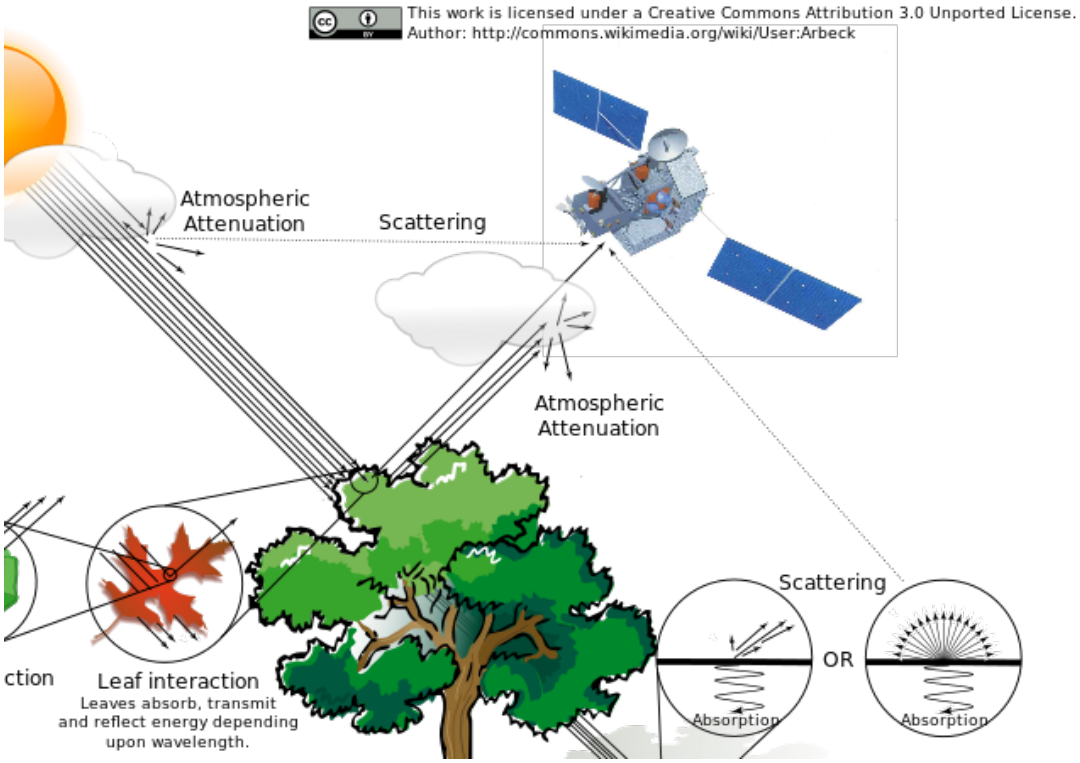
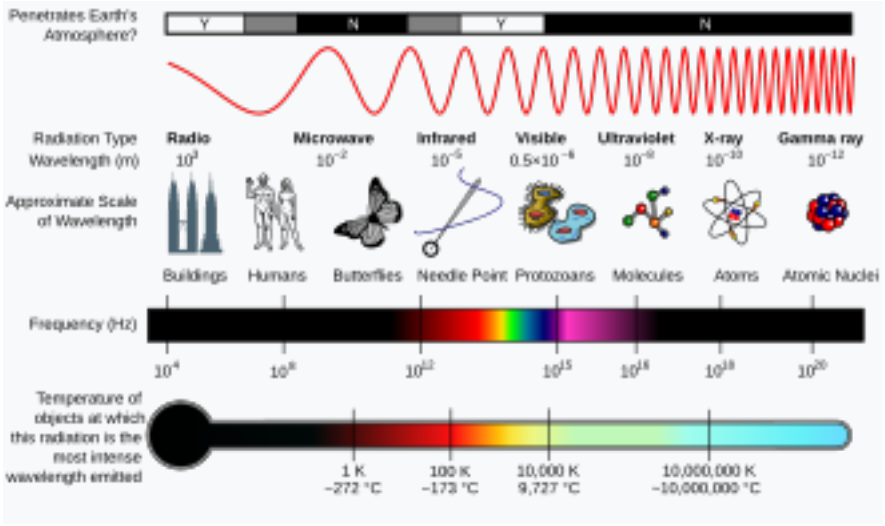


Figure 4: Light, absorption, and reflection in the natural world. [3]



Absorption and Emission

Description of the absorption and emission process is typically done through what is known as a Jablonski energy diagram, shown in figure 2. It should be noted that the ground electronic state is split into vibrational energy levels, even though this is not depicted in the Jablonski energy diagram in figure 5.

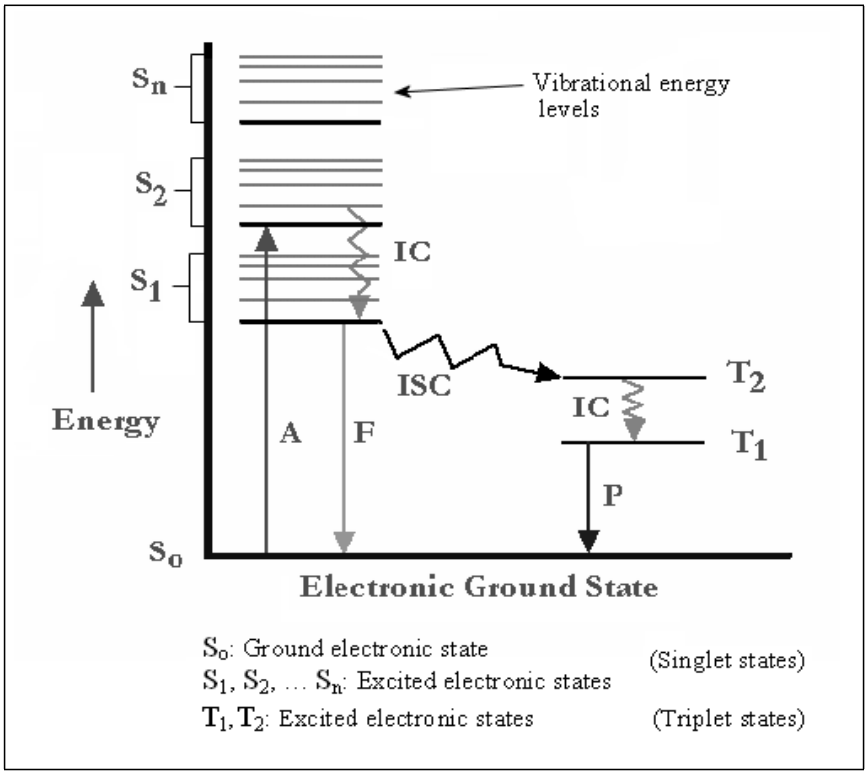


Figure 5: Jablonski energy diagram of absorption and emission. (Note: IC = internal conversion, ISC = inter-system crossing, A = absorption, F = fluorescence, and P = phosphorescence.)

Also, at room temperature, before excitation, organic molecules are almost always in the ground electronic state. Electronic states are also characterized by their *multiplicity*. The spin quantum number (S) of a molecule is the absolute value of the sum of the electron spins of the molecule. The multiplicity is defined as 2S + 1, and can be either a *singlet* or a *triplet*. A singlet state is when all the electrons in the various orbitals have their spins paired (opposite). In this case, there are equal numbers of electrons with positive (up) and negative (down) spins. Therefore, S = 0, and the multiplicity is 1. Singlet states are typically denoted as S_O (ground

state), S_1, S_2, … S_n. A triplet state occurs when there is one unpaired set of electron spins. In this case, S = 1, and the multiplicity is 3. The ground electronic state for organic molecules is almost always a singlet state. Absorption can excite the molecule to any one of the excited singlet states, S_1, S_2, … S_n [5].

Absorption of a photon typically occurs practically instantaneously; on the order of a femtosecond. Typically, excitation is considered as occurring from the lowest vibrational level of the ground electronic state. Ultimately, the extra energy of the excited molecule is lost, with the molecule eventually returning to the lowest vibrational level of the ground electronic state. Typically, this involves some energy being converted to heat, and the rest of the energy being released in the form of an emitted photon, with energy less than the exciting photon. This photon emission is known as photoluminescence, of which there are two types; fluorescence and phosphorescence.

Upon photon absorption, several processes are possible, but the most probable is that the molecule will relax to the lowest vibrational energy level of the first excited electronic state, S_1. This process is referred to as *internal conversion* or *vibrational relaxation*, converting excess energy into heat, and occurring without the emission of light. This time for this process to occur is typically on the order of a picosecond. Molecules will almost always undergo complete vibrational relaxation during their excited lifetimes since a very large number of vibrational cycles will occur during the lifetime of the excited electronic states. Typically, an excited molecule will exist in the lowest vibrational level of the first excited state, S_1, for a timescale on the order of nanoseconds. From this level, the molecule can relax to the various vibrational levels of the ground electronic state through the emission of a photon. In this case, the photoluminescence process is called fluorescence. Other relaxation processes other than fluorescence emission are also possible. The molecule can decay from the excited singlet state to the ground state without the emission of light

by dissipating energy in the form of heat, or it can also undergo quenching. Another possible pathway is for the molecule to go from the excited singlet state into an excited triplet state, in a process known as *intersystem crossing*, which is also a radiationless transition. After this has occurred, the molecule can undergo vibrational relaxation, falling to the lowest vibrational level of the first excited triplet state. Finally, the molecule may return to the ground electronic state through the emission of a photon. In this case, the process of photon emission is known as phosphorescence. Because this process involves a triplet-singlet transition, it is less probable, and thus phosphorescence is a much slower process than fluorescence. Typically, the lifetime of a triplet excited state ranges from about 100 μs to 1 second. Typically, the energy of a triplet state is lower than its corresponding singlet state, therefore photons emitted through phosphorescence are longer in wavelength than those emitted through fluorescence.

It should be noted that the fluorescence process occurs with a much greater probability than phosphorescence. This is due to the fact that intersystem crossing occurs with a relatively low probability. In this process, the molecule must undergo spin conversion, producing unpaired electrons, which occurs with relatively low probability. In other words, the only highly probable transitions are those in which $\Delta S = 0$ (singlet-singlet transition). Any transition in which the initial and final spin states differ ($\Delta S \geq 1$, triplet-singlet transition) occur with far lower probability.

Comparison of Absorption and Fluorescence

Because fluorescence emission is the favored process for photoluminescence for molecules, it is worthwhile to examine a few important characteristics of a fluorescence spectrum, and its relationship to the corresponding absorption spectrum. Figure 6, below depicts hypothetical absorption and fluorescence emission spectra for a molecule. In figure 6, only absorption due to transitions to the first excited state is shown.

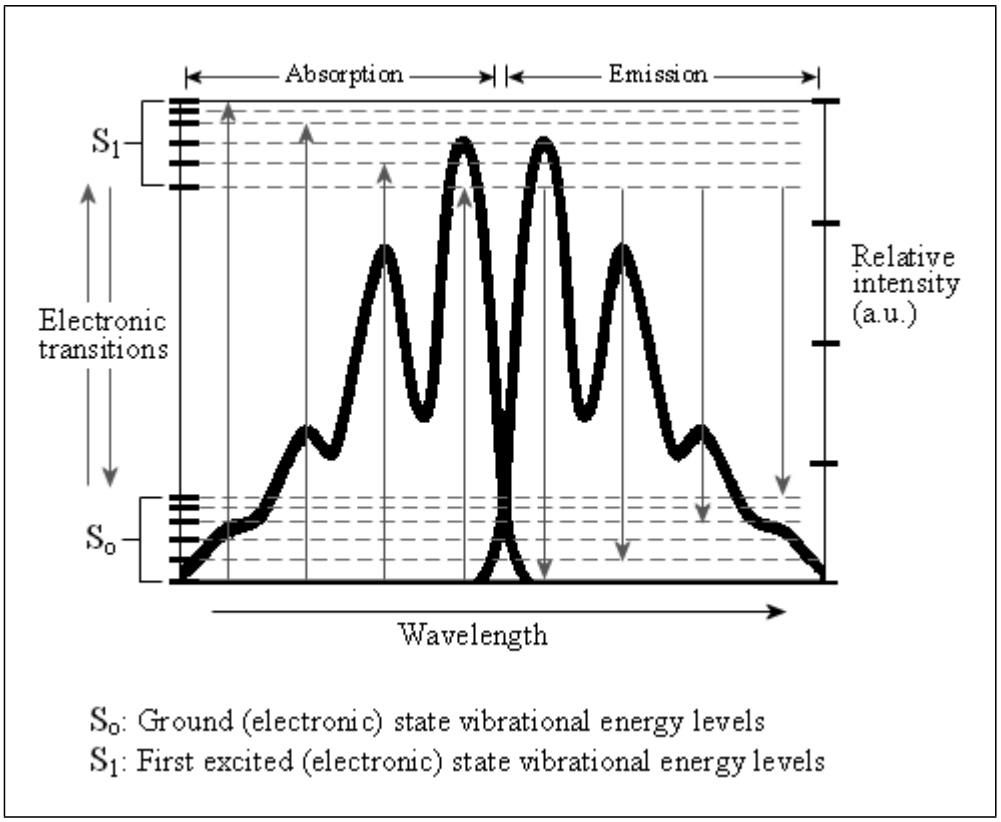


Figure 6: Hypothetical absorption and fluorescence emission spectra for a molecule

In figure 6, absorption for transitions from S_o to S_1 is shown on the left-hand side, while the fluorescence emission spectra is shown on the right-hand side. Hypothetical vibrational levels for the S_o and S_1 electronic states are also shown in the diagram.

Vertical upward arrows indicate absorption transitions to various (hypothetically) preferred vibrational levels of the first excited electronic state, while downward arrows indicate fluorescence emission from the lowest vibrational level of the first excited state to various vibrational levels of the ground electronic state. Figure 6 illustrates the fact that the absorption spectrum and the fluorescence spectrum can quite often be mirror images of each other, at least when speaking only of S_o to S_1 absorption transitions. Of course, higher energy photons can create absorption transitions to higher excited electronic states (S_2, S_3, etc.), but these transitions will not be mirrored in the fluorescence spectrum, since almost all emissions take place from the

lowest level of the first excited electronic state (due to vibrational relaxation). However, it must be noted that this mirror-image relationship will not always strictly hold in practice. It will most likely be satisfied if the vibrational modes in the excited state are comparable to those of the ground state. Another way of looking at it is that the most probable transitions are the same for both absorption and emission. However, factors such as differences in dipole orientations and geometry between the two states can modify this mirror-image relationship.

The fluorescence spectrum is independent of the excitation wavelength, higher energy photons can give rise to higher energy bands in the absorption spectrum, since transitions to electronic states higher than the first excited state are possible. But, since vibrational relaxation causes virtually all emission to occur from the lowest vibrational level of the first excited state, fluorescence spectra should not be affected by the energy of excitation. Obviously, the only requirement is that the excitation photon energy is large enough to cause a transition from the ground state to the first excited state ($S_o \rightarrow S_1$). The fluorescence spectrum depicted in figure 6, is an example of what is known as *Stokes fluorescence.* It is called this because it involves the emission of photons that have lower energy (longer wavelength) than the excitation photons. This is the type of fluorescence typically observed in practice, and the wavelength difference between the absorption and emission maxima are known as the Stokes shift. However it is possible to have emission of photons with higher energy, which is known as anti- Stokes fluorescence. Typically, the extra energy required would come from excess thermal energy, and thus would be more likely to is possible to have emission of photons with higher energy, which is known as anti-Stokes fluorescence. Typically, the extra energy required would come from excess thermal energy and would be more likely to be observed at high temperatures.

Experimental

Beer-Lambert Law

The extent to which light is absorbed in passing through a material is typically described by the well-known Beer-Lambert law. Figure 7, below, illustrates light with initial intensity, I_o, passing through a sample.

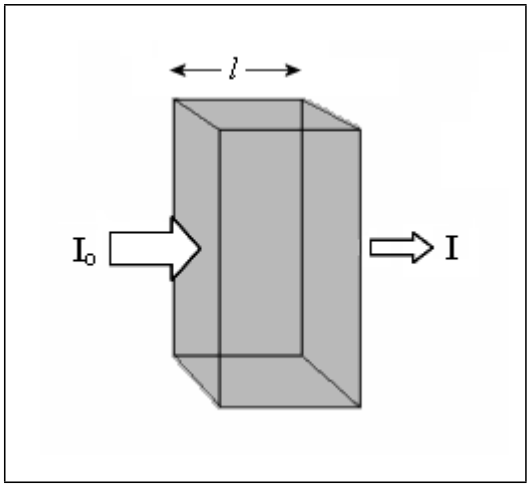


Figure 7. Simple illustration of light passing through a sample.

$$I = I_o e^{-\alpha lc}$$

where I_o is the initial light intensity before passing through the sample, I is the light intensity after having passed through a sample of path length, *l*. The sample is Io characterized by an absorption coefficient, α, and c is the concentration of absorbing species in the sample. The absorbance, A, is defined as:

$$A = \alpha lc$$

and the absorption coefficient, α, is often written as:

$$\alpha = \frac{4\pi k}{\lambda}$$

Optical absorption spectroscopy of materials was performed using a Perkin Elmer Lambda 20 UV/Vis spectrometer. This spectrometer uses an all-reflecting optical system. A schematic diagram of the optical system is shown in Figure 8, below.

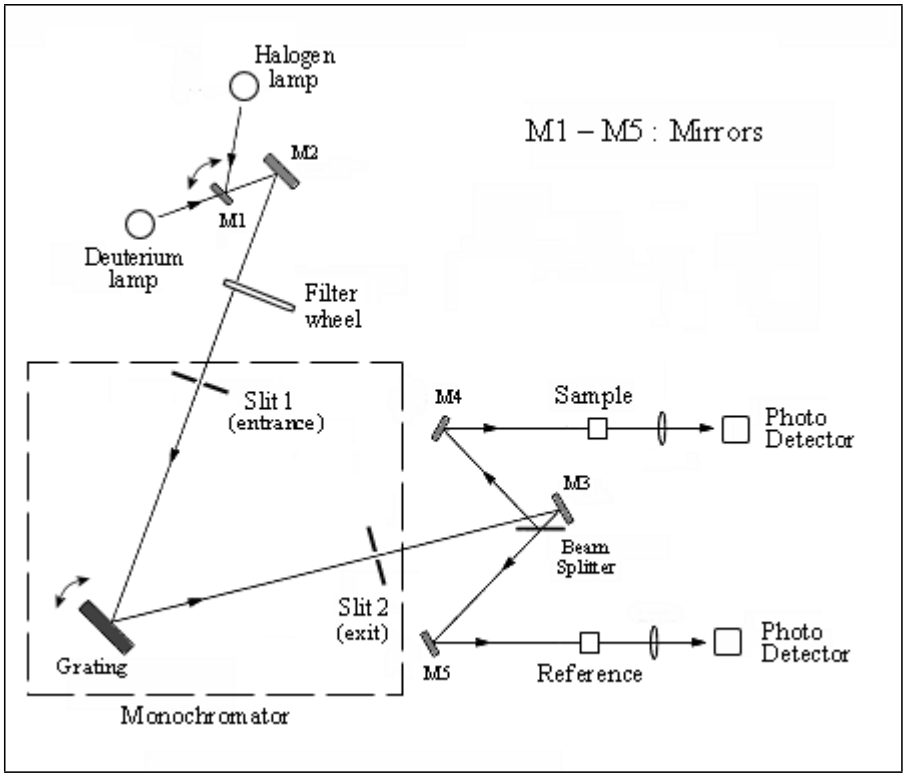


Figure 8: Schematic diagram of the optical system of the Lambda 20 UV/Vis spectrometer.

The halogen lamp acts as the source for the visible range, while the deuterium lamp is the source for the ultraviolet range. During operation in the visible range, mirror M1 reflects the incident radiation from the halogen lamp onto the source mirror M2, while simultaneously blocking the radiation from the deuterium lamp. While scanning in the ultraviolet range, mirror M1 moves out of the way, allowing radiation from the deuterium lamp to impinge on the source mirror M2. Incident radiation from the source mirror M2 then passes through an optical filter on the filter wheel assembly. This is done to pre- filter the incident radiation before it enters the monochromator. Depending on the wavelength being produced, the appropriate optical filter on the filter wheel is placed in the beam path, while a stepping motor

drives the filter wheel in order to be in synchronization with the monochromator. After passing through the appropriate optical filter on the filter wheel, the incident beam passes through the entrance slit (slit 1) of the monochromator. The incident beam then strikes the grating. The grating disperses the incident beam into a continuous spectrum. Thus, the rotational position of the grating selects a small portion of the spectrum to be incident on the exit slit (slit 2) of the monochromator. During measurement, the grating continuously scans through an angular range, causing a continuous variation of wavelength to be incident on the exit slit. The grating is a concave grating with 1053 lines/mm at the center. The exit slit restricts the light exiting the monochromator to an almost monochromatic beam, with a spectral bandpass of approximately 2 nm. The light beam exiting the monochromator is then reflected off mirror M3 onto a beam splitter. The beam splitter splits the incident beam into two paths, allowing 50 percent of the incident light to pass through and strike mirror M4, while 50 percent of the radiation is reflected onto mirror M5. Mirror M4 reflects one incident beam onto a sample cell, whereas M5 reflects the other incident beam onto a reference cell. In both cases, after the light has passed through the sample or reference cell, it passes through a convex lens and is incident on a photodiode detector w here k is called the extinction coefficient, and λ is the wavelength of the incident light. Often, the functional form for the absorption or attenuation of light as it passes through a material will be seen written as:

$$I(z) = I_o e^{-az}$$

where again I_o is the initial light intensity and I(z) is the light intensity after the light has passed through a distance, z, of the sample. (This relation is analogous to the Beer-Lambert law, but technically is not called the Beer-Lambert law.) In this case, also, α is typically referred to as the absorptivity or absorption coefficient. It also sometimes referred to as the attenuation coefficient

or extinction coefficient. This form of the law is applied to absorption as well as to light scattering (from gas molecules, for instance).

It must be noted that this situation is specific to performing measurements on materials in solution, which are contained in quartz cells. For measurements on thin films, only the optical path corresponding to mirror M_4 is utilized. For thin films, a solution is first drop-casted onto a glass microscope slide and allowed to dry. For these thin film measurements, a blank glass microscope slide was first placed in the sample spot (optical path of mirror M_4) and reference measurement was performed. This measurement was then used as the reference for subsequent measurements of the thin films. A photograph of the Lambda 20 UV/Vis spectrometer is shown in Figure 9 below.

Figure 9: Photograph of the Perkin Elmer Lambda 20 UV/Vis absorption spectrometer.

When light is incident on an organic semiconductor, a molecule is excited by absorbing a photon of sufficient energy to produce a transition from the ground state S_0 to an excited state S_n. The absorption and emission process in a molecule may be explained using a Jablonski diagram shown in Figure 5. Assuming that initially the molecule was at its lowest energy state, excitation will occur from the lowest vibrational energy level of S_0 to some vibrational energy level of the excited state. The molecule will return to its lowest vibrational level of the ground state by losing the excess energy either in the form of heat or using it partly to emit a quantum of radiation and converting the rest to heat.

Energy Band Theory

When two identical atoms are brought closer together, their wave functions will start to overlap. As a result of the Pauli exclusion principle, where two identical electrons cannot share the same electronic state, the two atomic states will split into two different energy states with different binding energies. When more atoms are put together, there will be a further splitting of energy levels. The energy interval between each level becomes smaller and finally the energy levels will be nearly continuous and form an energy band.

Due to the boundary conditions of the Brillouin zone, there will be gaps between certain bands. The lowest energy band that doesn't have any electrons occupied at a temperature of 0 K is called the conduction band. The highest energy band in which all energy states are occupied by electrons at 0 K is the valence band. Conductors such as metals are the materials in which the valence band and the conduction band overlap to some extent. There will be no energy gap between the two bands and the electrons can move from conduction band to valence band easily and introduce conduction. Insulators on the other hand, typically have energy gaps exceeding 3

eV, making it very difficult for the electrons to get to the conduction band and generate any electric current. The semiconductors are materials with a slightly smaller band gap than insulators, usually in the range of 0.1 to 3eV.

Conclusion

When broadband electromagnetic radiation is passed through a transparent material, a fraction of it is absorbed. The remaining light may then be dispersed through a prism to observe the missing portions of the spectrum denoted as an absorption spectrum. The absorption of light by the material leads to electronic energy level transitions and indeed it is appropriate to more accurately label UV-vis spectroscopy as electronic spectroscopy. Excitation light from the laser source is directed at the sample which is placed in a mount at an angle relative to the laser beam path. This ensures that a large portion of the incident laser light intensity is reflected away from the detector allowing the lower intensity PL to be collected.

References

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