

Introduction to Spectroscopy –IV, B.Sc. III Year

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This presentation contains

- Set of Assignment/ Set of questions on
“Introduction of Spectroscopy”

Assignment/ set of questions

Q1. Write a note on rotator.

Q2. Explain criteria for a molecule to be IR active

Q3. Explain selection rules.

Q4. What do you understand by electromagnetic spectrum.

Q5. State and explain Beer- Lambert's Law.

Q6. Which of the following will be IR active:

Water, carbon dioxide, ethylene, ammonia, hydrochloric acid, carbon monoxide

And why

Assignment / Set of questions (Cont'd)

- Q7. Explain instrumentation of IR spectroscopy.
- Q8. Explain the types of vibrations
- Q9. Explain application of IR spectroscopy in the structural elucidation of molecule
- Q10. Explain Theory of Vibration- Rotation Spectroscopy.
- Q11. Explain the application of IR spectroscopy in determination of force constant
- Q12. Explain Application of IR/ Microwave spectroscopy in the determination of bond length.

Assignment/ Set of Questions (Cont'd)

- Q13. What is isotopic effect.
- Q14. Explain the theory of microwave spectroscopy.
- Q15. Explain the estimation of moment of inertia and bond length.
- Q16. What is the condition of a molecule to be microwave active?
- Q17. Explain selection rules for microwave spectroscopy.
- Q18. What do you understand by PQR branches ?

Assignment/ Set of Questions (Cont'd)

- Q19. Explain basic principle of NMR spectroscopy
- Q20. What is chemical shift?
- Q21. What do you understand by Iso bestic point?
- Q22. What is nuclear shielding?
- Q23. What do you understand by nuclear spin.?
- Q24. Explain the instrumentation used in NMR spectroscopy.

Assignment/ Set of Questions (Cont'd)

- Q25. What do you understand by electronic transitions?
- Q26. Explain solvent effect.
- Q27. Explain the effect of conjugation on electronic transition.
- Q28. What is charge transfer spectra?
- Q29. What is the principle of electronic spectroscopy?
- Q30. Explain Franck Condon Rule.

Assignment/ Set of questions (cont'd)

- Q31. Explain the terms:- Red shift, Blue shift, hypsochromic shift, batho chromic shift.
- Q32.Explain the terms : Fluorescence, Phosphorescence
- Q33. Draw and explain Jablonski diagram.
- Q34. Explain the terms: dissociation, pre- dissociation
- Q35. Explain the instrumentation used in UV –visible spectroscopy.
- Q36. Explain the applications of electronic spectroscopy

Assignment/ Set of Questions (Cont'd)

- Q37. Explain Raman Effect.
- Q38. Write a note on quantum theory of Raman effect.
- Q39. Write a note on classical theory of Raman effect.
- Q40. Explain the origin of Stokes' and anti-Stokes' lines.
- Q41. Explain the applications of Raman spectroscopy.
- Q42. Explain Rotation Raman Spectroscopy.

- Best of Luck

Introduction To Spectroscopy, Part – II, B.Sc. III year, Paper-I

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This lecture Includes

- IR spectroscopy
Introduction
Features
Selection Rule/ Normal modes
Types of Vibrations
IR spectrophotometers
A typical IR Spectrum
Applications of IR spectroscopy
- NMR spectroscopy
Introduction
Magnetic Moment and Gyro Magnetic Ratio
Principle
Orientation of Spins
Distribution of Energy Levels
Frequency of Absorption
Nuclear Shielding
A typical NMR Spectrum
Relaxation
Applications of NMR

IR Spectroscopy

- **Introduction**
- **Infrared spectroscopy** (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light.
- It covers a range of techniques, mostly based on absorption spectroscopy.
- it can be used to identify and study chemicals.
- For a given sample which may be solid, liquid, or gaseous, the method or technique of infrared spectroscopy uses an instrument called an **infrared spectrometer**

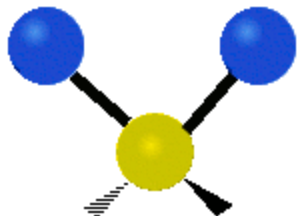
IR Spectroscopy

- Features
- The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far-infrared, named for their relation to the visible spectrum.
- The higher-energy near-IR, approximately $14000\text{--}4000\text{ cm}^{-1}$ ($0.8\text{--}2.5\text{ }\mu\text{m}$ wavelength) can excite overtone or harmonic vibrations.
- The mid-infrared, approximately $4000\text{--}400\text{ cm}^{-1}$ ($2.5\text{--}25\text{ }\mu\text{m}$) may be used to study the fundamental vibrations and associated rotational-vibrational structure.
- The far-infrared, approximately $400\text{--}10\text{ cm}^{-1}$ ($25\text{--}1000\text{ }\mu\text{m}$), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

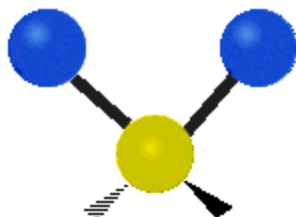
IR Spectroscopy

- Selection Rules/ Normal Modes
- In the Born–Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighborhood of the equilibrium molecular geometry, the resonant frequencies are associated with the normal modes corresponding to the molecular electronic ground state potential energy surface.
- The resonant frequencies are also related to the strength of the bond and the mass of the atoms at either end of it. Thus, the frequency of the vibrations are associated with a particular normal mode of motion and a particular bond type.

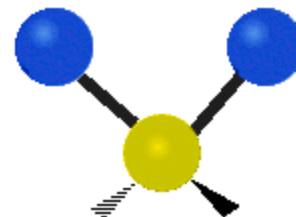
Types of Vibrations



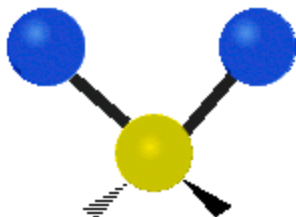
**Symmetrical
stretching**



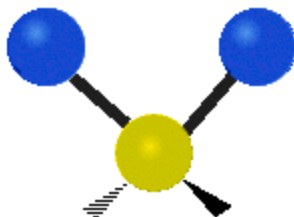
**Antisymmetrical
stretching**



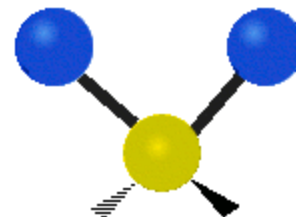
Scissoring



Rocking

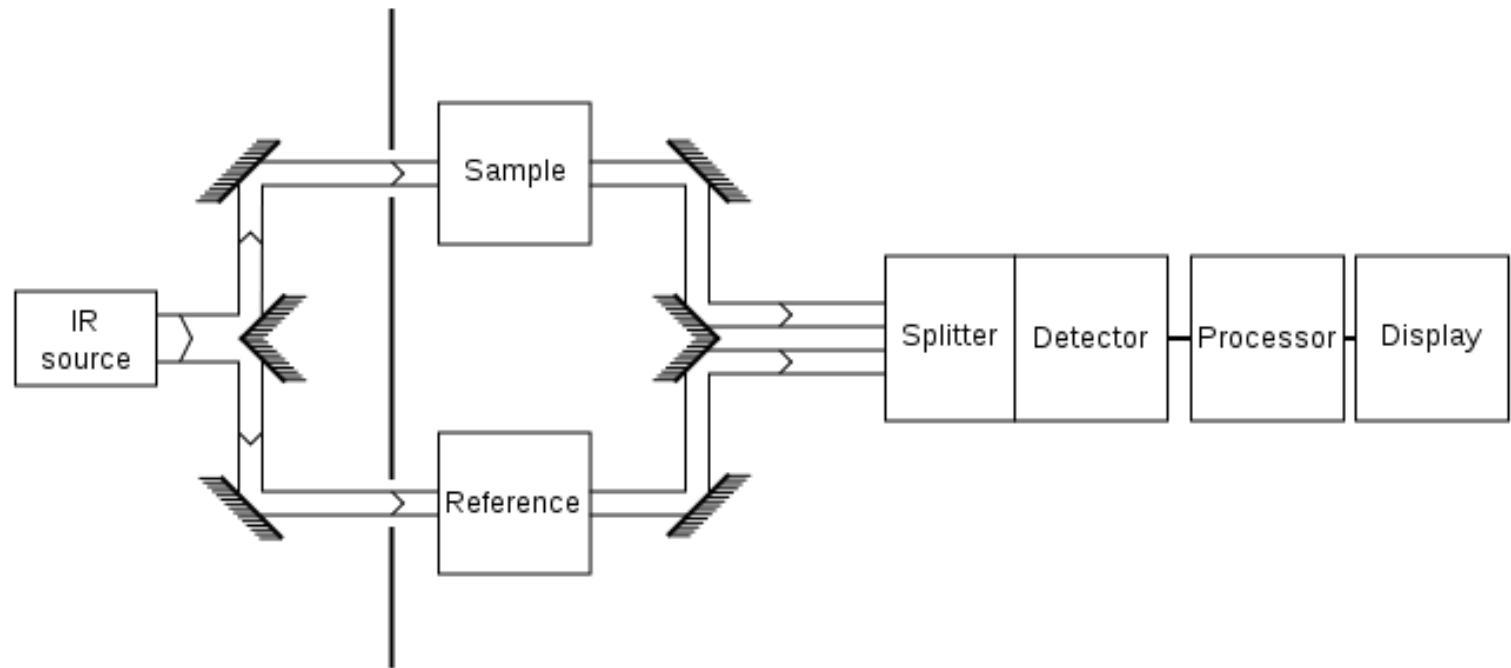


Wagging

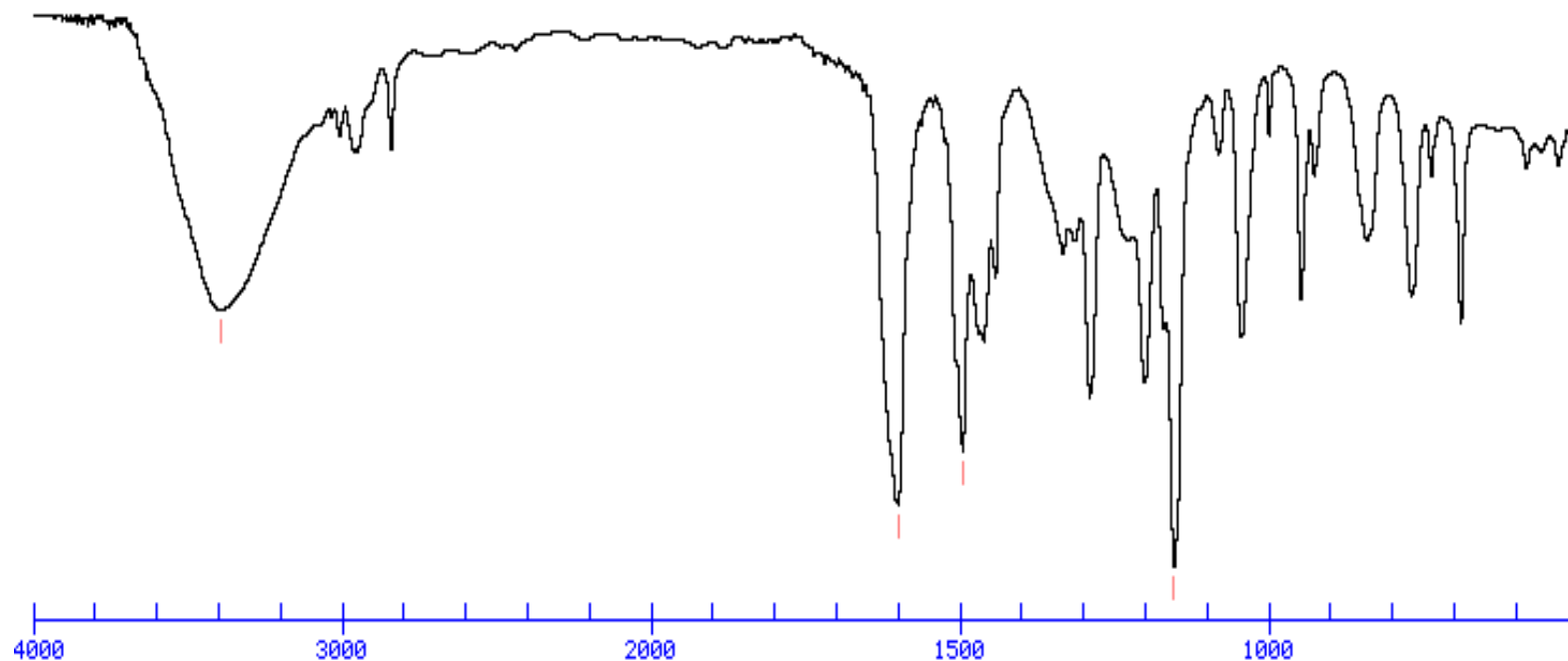


Twisting

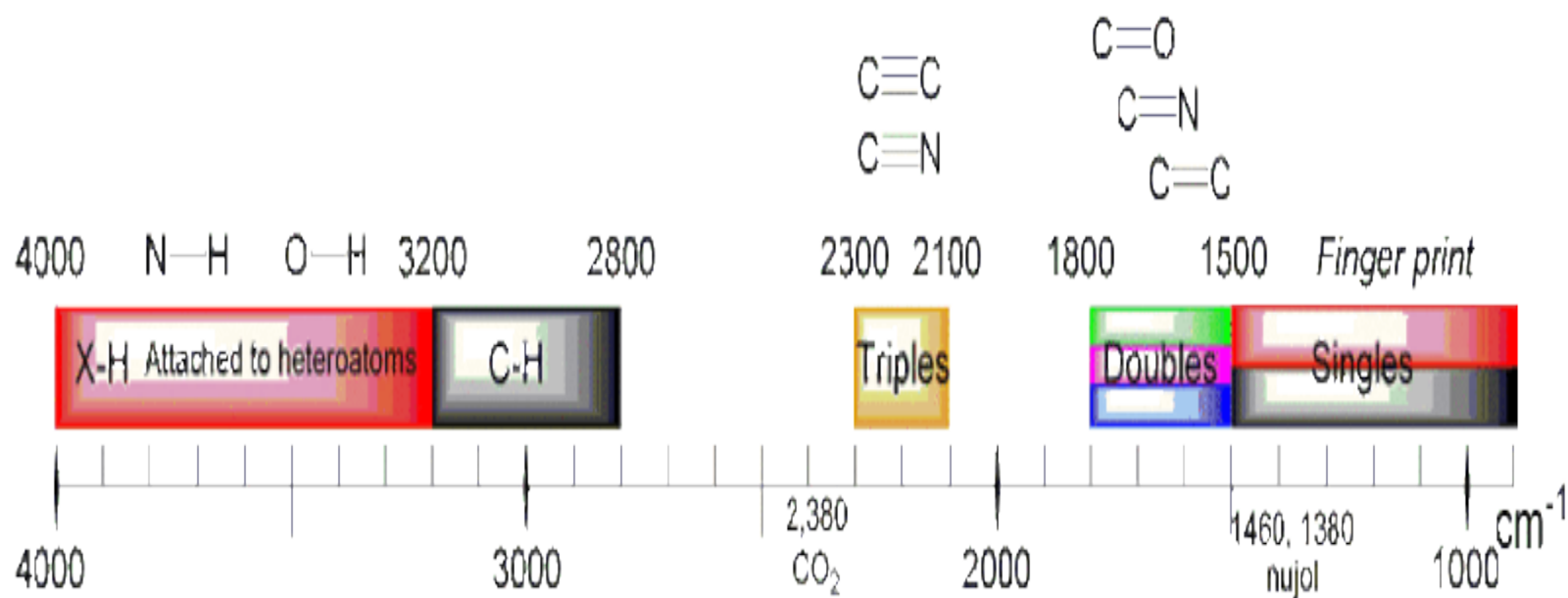
IR Spectrophotometer



A typical IR Spectrum



Applications of IR Spectrophotometer



Applications of IR Spectroscopy

- Infrared spectroscopy is a simple and reliable technique widely used in both organic and inorganic chemistry, in research and industry. It is used in quality control, dynamic measurement, and monitoring applications such as the long-term unattended measurement of CO₂ concentrations in greenhouses and growth chambers by infrared gas analyzers.
- It is also used in [forensic analysis](#) in both criminal and civil cases, for example in identifying [polymer degradation](#). It can be used in determining the [blood alcohol content](#) of a suspected drunk driver.

Applications of IR Spectroscopy

- A useful way of analysing solid samples without the need for cutting samples uses ATR or attenuated total reflectance spectroscopy. Using this approach, samples are pressed against the face of a single crystal. The infrared radiation passes through the crystal and only interacts with the sample at the interface between the two materials.
- With increasing technology in computer filtering and manipulation of the results, samples in solution can now be measured accurately (water produces a broad absorbance across the range of interest, and thus renders the spectra unreadable without this computer treatment).

Applications of IR Spectroscopy

- Infrared spectroscopy is also useful in measuring the degree of polymerization in [polymer](#) manufacture. Changes in the character or quantity of a particular bond are assessed by measuring at a specific frequency over time. Modern research instruments can take infrared measurements across the range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate.
- Infrared spectroscopy has also been successfully utilized in the field of semiconductor microelectronics: for example, infrared spectroscopy can be applied to semiconductors like [silicon](#), [gallium arsenide](#), [gallium nitride](#), [zinc selenide](#), amorphous silicon, [silicon nitride](#), etc.
- The instruments are now small, and can be transported, even for use in field trials.

NMR Spectroscopy

- Introduction
- Nuclear Magnetic Resonance (NMR) is a nuclei (Nuclear) specific spectroscopy that has far reaching applications throughout the physical sciences and industry.
- NMR uses a large magnet (Magnetic) to probe the intrinsic spin properties of atomic nuclei. Like all spectroscopies, NMR uses a component of electromagnetic radiation (radio frequency waves) to promote transitions between nuclear energy levels (Resonance).
- Most chemists use NMR for structure determination of small molecules.

NMR Spectroscopy

- In 1946, NMR was co-discovered by Purcell, Pound and Torrey of Harvard University and Bloch, Hansen and Packard of Stanford University.
- The discovery first came about when it was noticed that magnetic nuclei, such as ^1H and ^{31}P (proton and Phosphorus 31) were able to absorb radio frequency energy when placed in a magnetic field of a strength that was specific to the nucleus.

NMR Spectroscopy

- Upon absorption, the nuclei begin to resonate and different atoms within a molecule resonated at different frequencies.
- This observation allowed a detailed analysis of the structure of a molecule.
- Since then, NMR has been applied to solids, liquids and gasses, kinetic and structural studies, resulting in 6 Nobel prizes being awarded in the field of NMR.

Magnetic Moment & Gyro magnetic Ratio

- All molecules with a non-zero spin have a magnetic moment, μ , given by
- $\mu = \gamma I$
- where γ is the gyro magnetic ratio, a proportionality constant between the magnetic dipole moment and the angular momentum, specific to each nucleus.

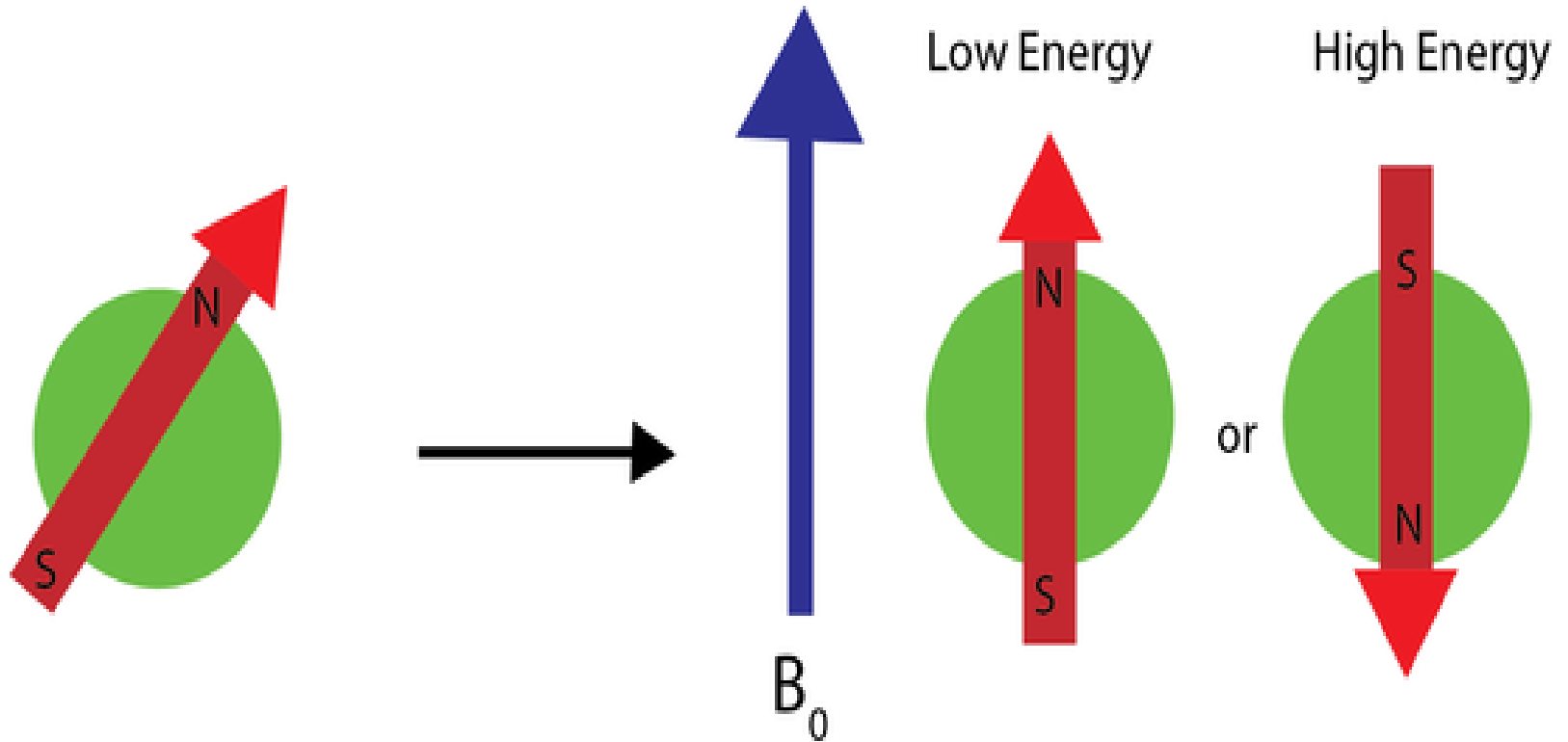
Gyromagnetic Ratio

Nuclei	Spin	Gyromagnetic Ratio (MHz/T)	Natural Abundance (%)
^1H	1/2	42.576	99.9985
^{13}C	1/2	10.705	1.07
^{31}P	1/2	17.235	100
^{27}Al	5/2	11.103	100
^{23}Na	3/2	11.262	100
^7Li	3/2	16.546	92.41
^{29}Si	1/2	-8.465	4.68
^{17}O	5/2	5.772	0.038
^{15}N	1/2	-4.361	0.368

Principle

- The magnetic moment of the nucleus forces the nucleus to behave as a tiny bar [magnet](#).
- In the absence of an external magnetic field, each magnet is randomly oriented.
- During the NMR experiment the sample is placed in an external magnetic field, B_0 , which forces the bar magnets to align with (low energy) or against (high energy) the B_0 .
- During the NMR experiment, a spin flip of the magnets occurs, requiring an exact quanta of energy.

Orientation of Spins



Distribution in Energy Levels

- An exact quanta of energy must be used to induce the spin flip or transition. For any m , there are $2m+1$ energy levels. For a spin $1/2$ nucleus, there are only two energy levels, the low energy level occupied by the spins which aligned with B_0 and the high energy level occupied by spins aligned against B_0 . Each energy level is given by

$$E = -m\hbar\gamma B_0$$

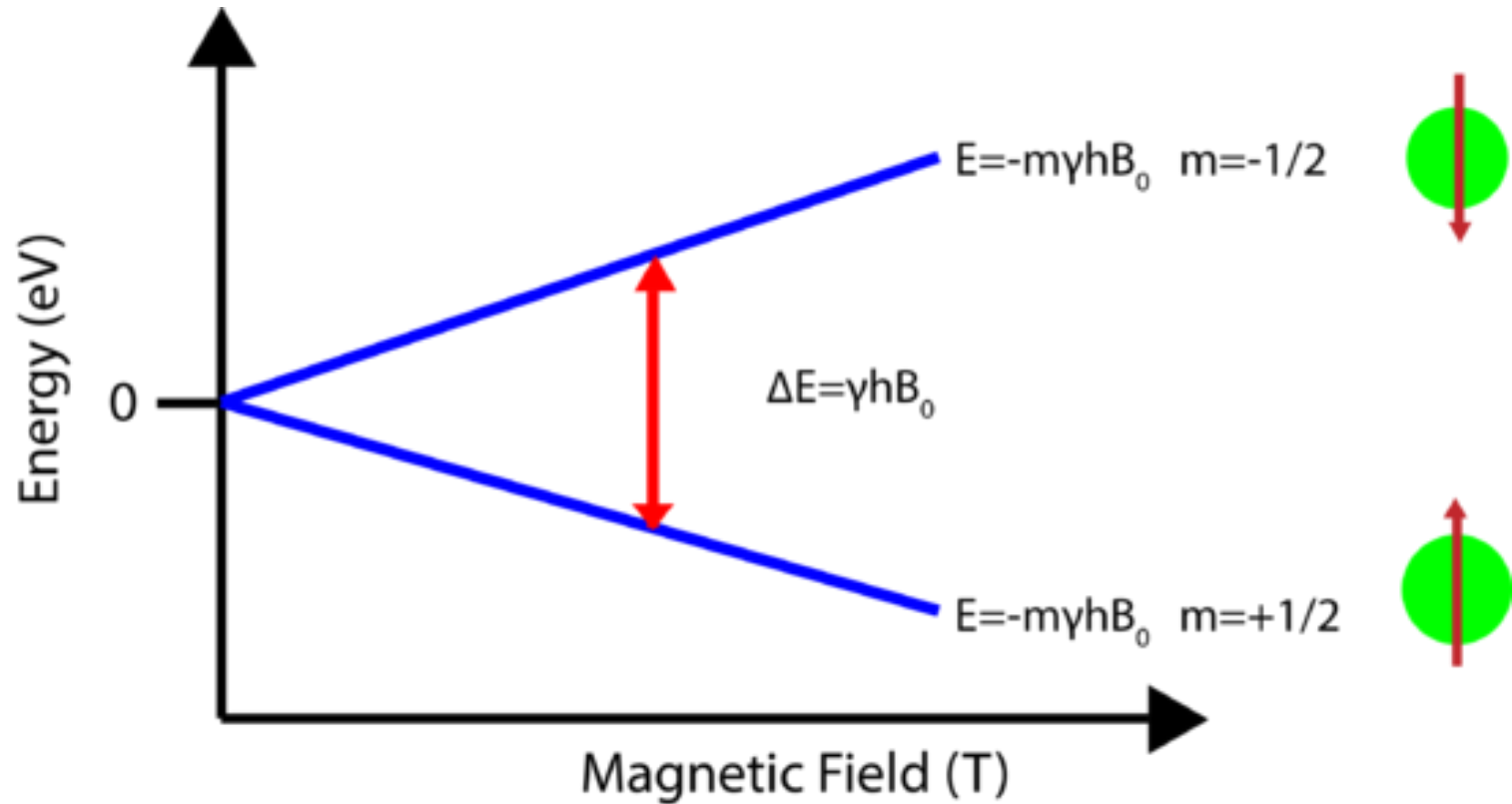
where m is the magnetic quantum number, in this case $\pm 1/2$.

- The energy levels for $m > 1/2$, known as quadrupolar nuclei, are more complex and information regarding them can be found [here](#).
- The energy difference between the energy levels is then

$$\Delta E = \hbar\gamma B_0$$

- where \hbar is Planks constant.

Energy Levels



Frequency for absorption

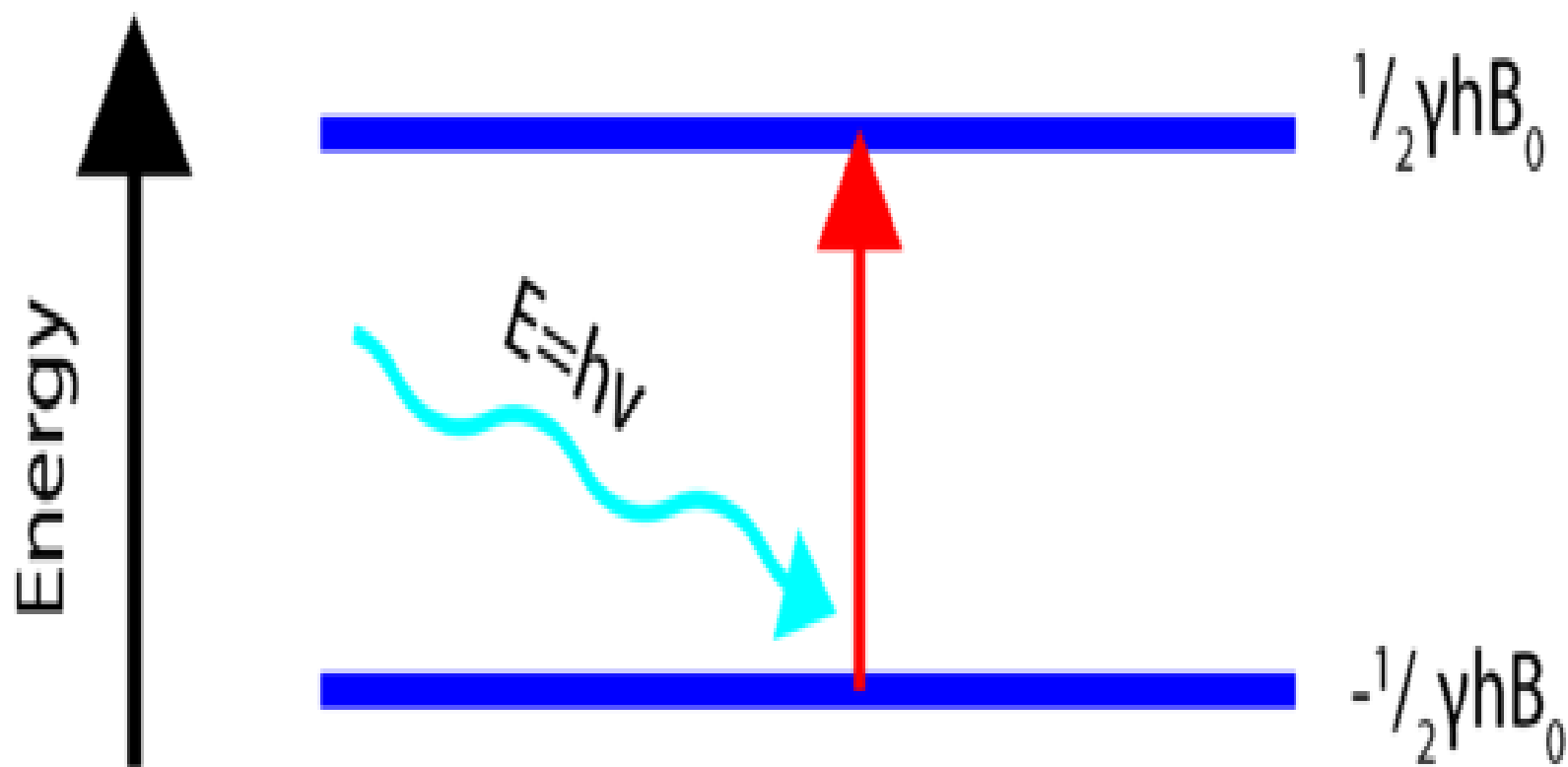
- For most NMR spectrometers, B_0 is on the order of Tesla (T) while γ is on the order of 10^7 . Consequently, the electromagnetic radiation required is on the order of Hz. The energy of a photon is represented by

$$E=h\nu$$

- and thus the frequency necessary for absorption to occur is represented as:

$$\nu=\gamma B_0/2\pi$$

Frequency of Absorption



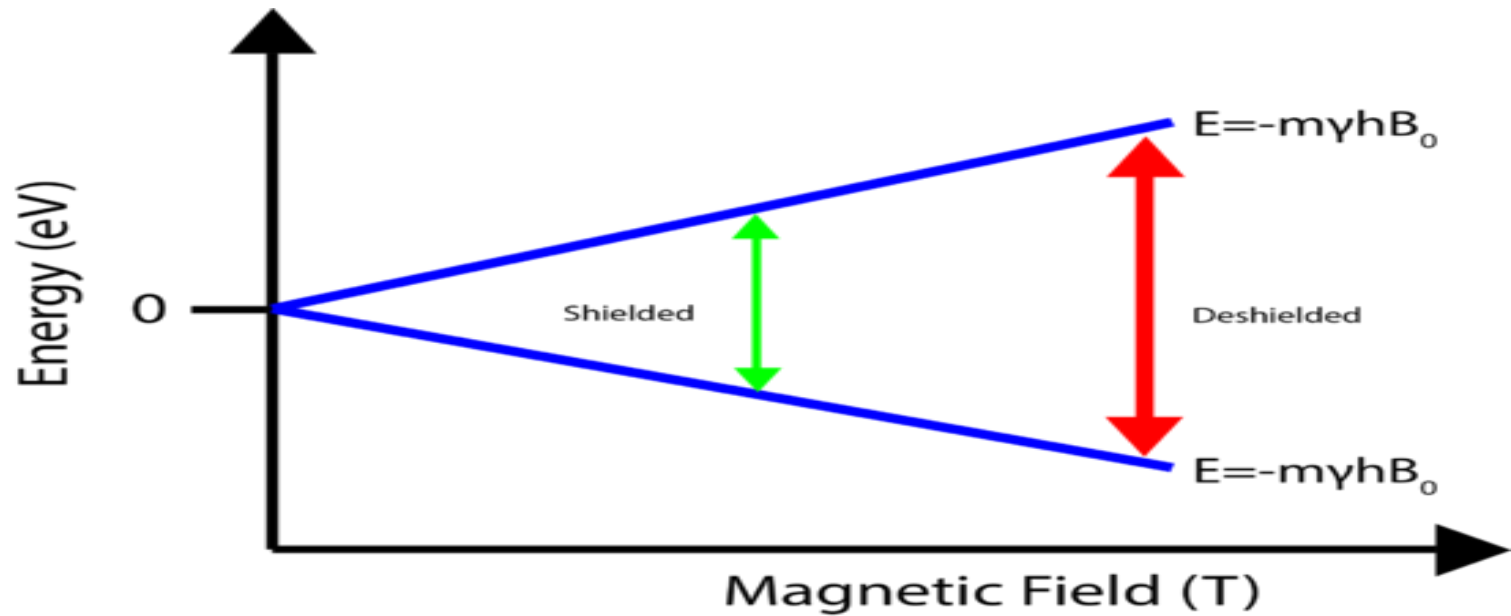
Nuclear Shielding

- The power of NMR is based on the concept of nuclear shielding, which allows for structural assignments.
- Every atom is surrounded by electrons, which orbit the nucleus.
- Charged particles moving in a loop will create a magnetic field which is felt by the nucleus.
- Therefore the local electronic environment surrounding the nucleus will slightly change the magnetic field experienced by the nucleus, which in turn will cause slight changes in the energy levels! This is known as shielding.

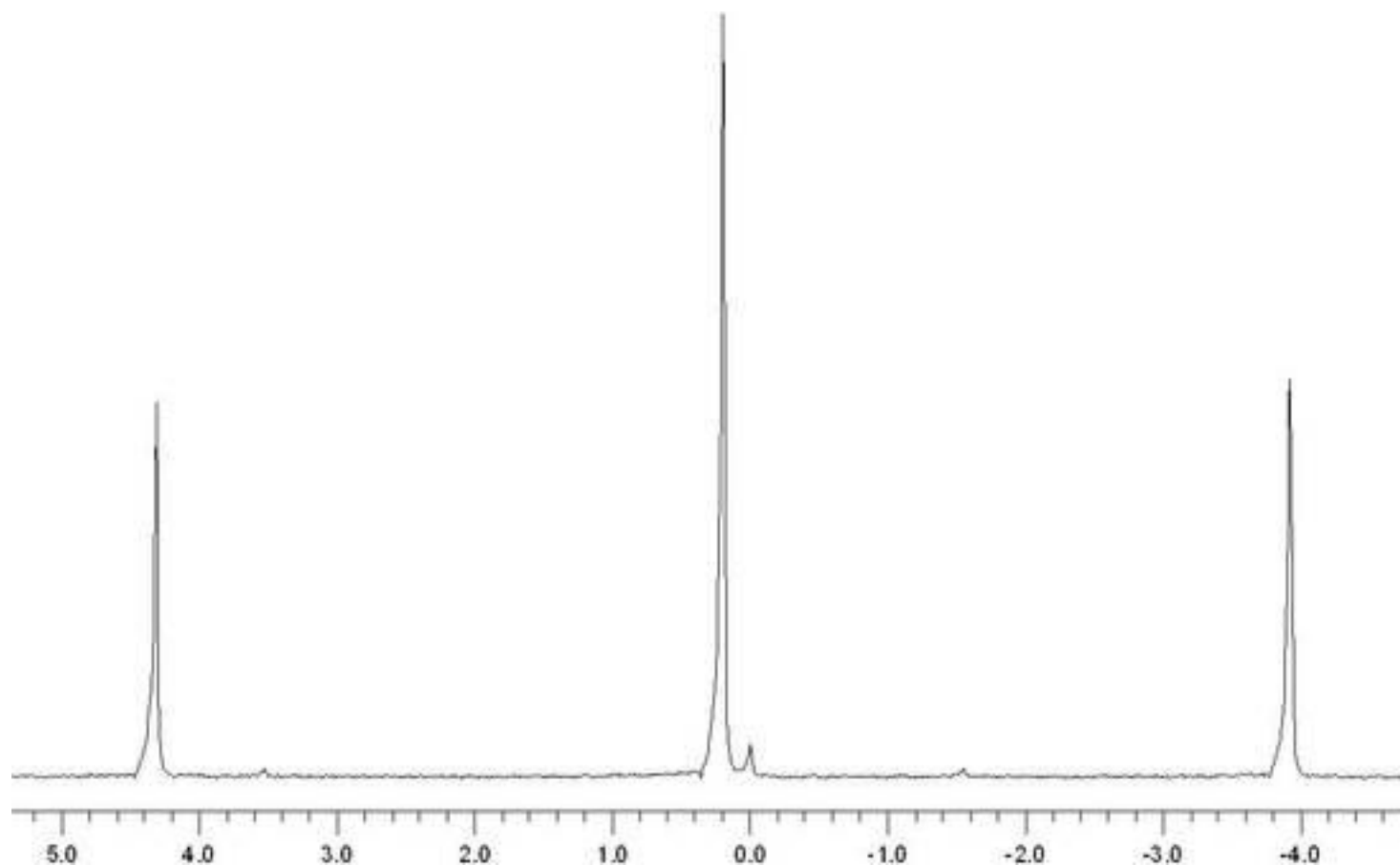
Nuclear Shielding

- Nuclei that experience different magnetic fields due to the local electronic interactions are known as inequivalent nuclei.
- The change in the energy levels requires a different frequency to excite the spin flip, which as will be seen below, creates a new peak in the NMR spectrum.

Nuclear Shielding



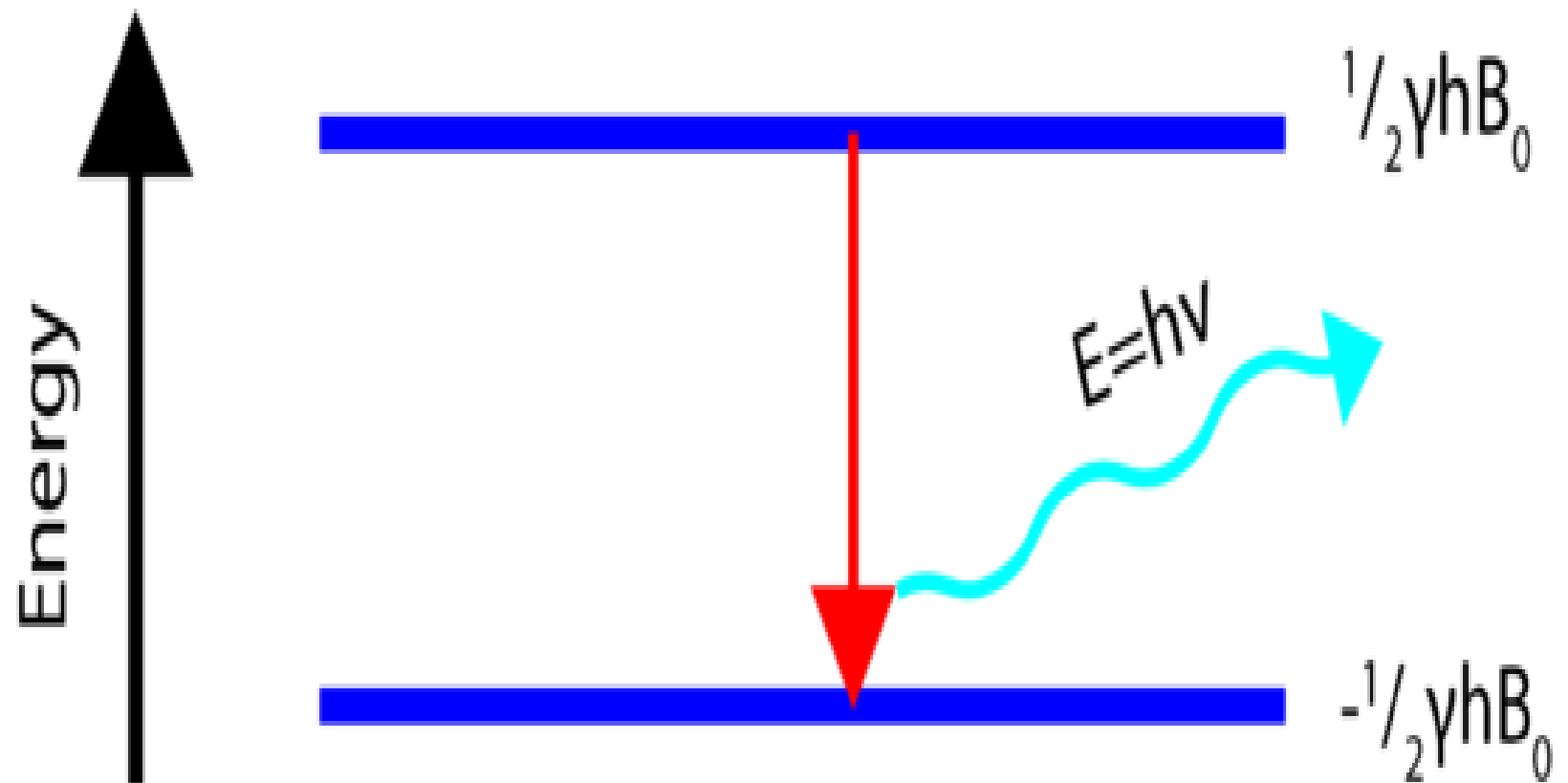
A Typical NMR Spectrum



Relaxation

- Relaxation refers to the phenomenon of nuclei returning to their thermodynamically stable states after being excited to higher energy levels.
- The energy absorbed when a transition from a lower energy level to a high energy level occurs is released when the opposite happens.
- This can be a fairly complex process based on different timescales of the relaxation.
- The two most common types of relaxation are spin lattice relaxation (T_1) and spin spin relaxation (T_2).

Relaxation



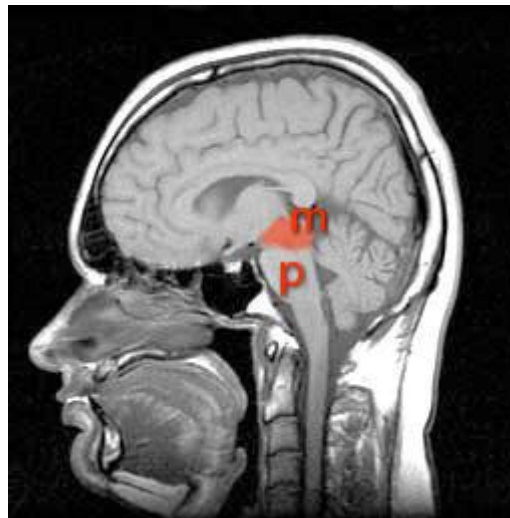
Relaxation

- To understand relaxation, the entire sample must be considered.
- By placing the nuclei in an external magnetic field, the nuclei create a bulk magnetization along the z-axis.
- The spins of the nuclei are also coherent. The NMR signal may be detected as long as the spins are coherent with one another

Applications

- **Medicine**

Nuclear magnetic resonance imaging, better known as magnetic resonance imaging (MRI) is an important medical diagnostic tool used to study the function and structure of the human body. It provides detailed images of any part of the body, especially soft tissue, in all possible planes and has been used in the areas of cardiovascular, neurological, musculoskeletal and oncological imaging.



Application

- **Chemistry**

In many laboratories today, chemists use nuclear magnetic resonance to determine structures of important chemical and biological compounds.

In NMR spectra, different peaks give information about different atoms in a molecule according specific chemical environments and bonding between atoms.

The most common isotopes used to detect NMR signals are ^1H and ^{13}C but there are many others, such as ^2H , ^3He , ^{15}N , ^{19}F , etc., that are also in use

Application

- **Other Fields**
- NMR has also proven to be very useful in other area such as environmental testing, petroleum industry, process control, earth's field NMR and magnetometers.

Non-destructive testing saves a lot of money for expensive biological samples and can be used again if more trials need to be run.

The petroleum industry uses NMR equipment to measure porosity of different rocks and permeability of different underground fluids.

- Best of Luck

Introduction to spectroscopy, Part –III, B.Sc. III year

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This Presentation Contains

- UV –Visible Spectroscopy

- Introduction
- It's Principle
- Electronic Transitions
- Solvent Effect
- Effect of conjugation
- Charge Transfer Spectra
- Franck Condon Principle
- Basic Laws
- Some terms related to UV-Visible Spectroscopy
- Dissociation and Pre-dissociation
- Fluorescence and phosphorescence
- Jablonski Diagram

- Applications
- Instrumentation

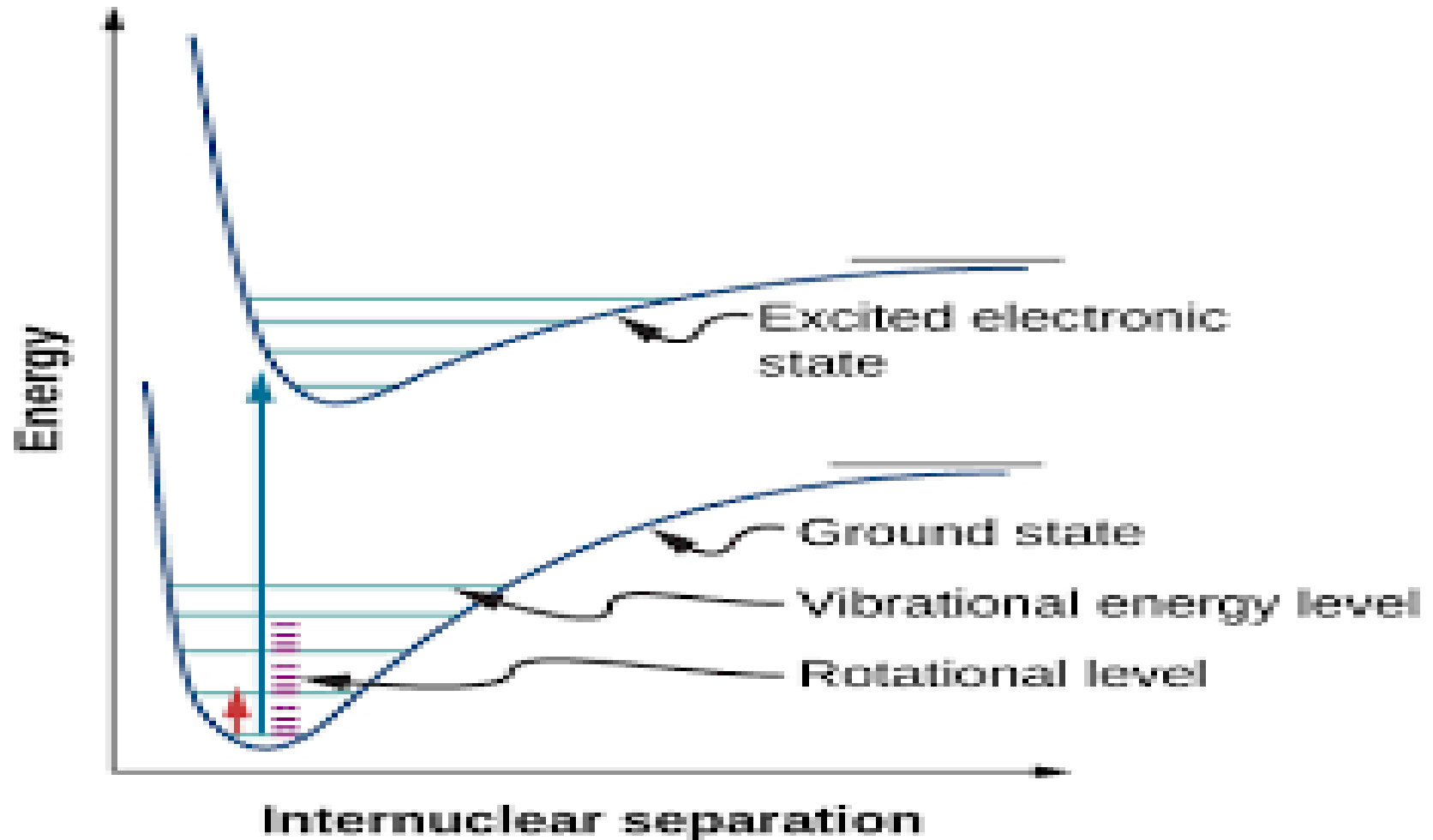
- Raman Spectroscopy-

- ✓ Raman Effect
- ✓ Rayleigh Scattering
- ✓ Quantum Theory of Raman Effect
- ✓ Classical Theory Of Raman Effect
- ✓ Stroke's and Anti-Stroke's Lines
- ✓ Selection Rules
- ✓ Rotation Raman Spectra
- ✓ Applications

Introduction

- **Ultraviolet–visible spectroscopy** or **ultraviolet–visible spectrophotometry** (**UV–Vis** or **UV/Vis**) refers to [absorption spectroscopy](#) or reflectance spectroscopy in part of the [ultraviolet](#) and the full, adjacent [visible](#) spectral regions.
- This means it uses light in the visible and adjacent ranges. The absorption or reflectance in the visible range directly affects the perceived [color of the chemicals](#) involved.
- In this region of the [electromagnetic spectrum](#), [atoms](#) and [molecules](#) undergo [electronic transitions](#). Absorption spectroscopy is complementary to [fluorescence spectroscopy](#), in that [fluorescence](#) deals with transitions from the [excited state](#) to the [ground state](#), while absorption measures transitions from the ground state to the excited state.

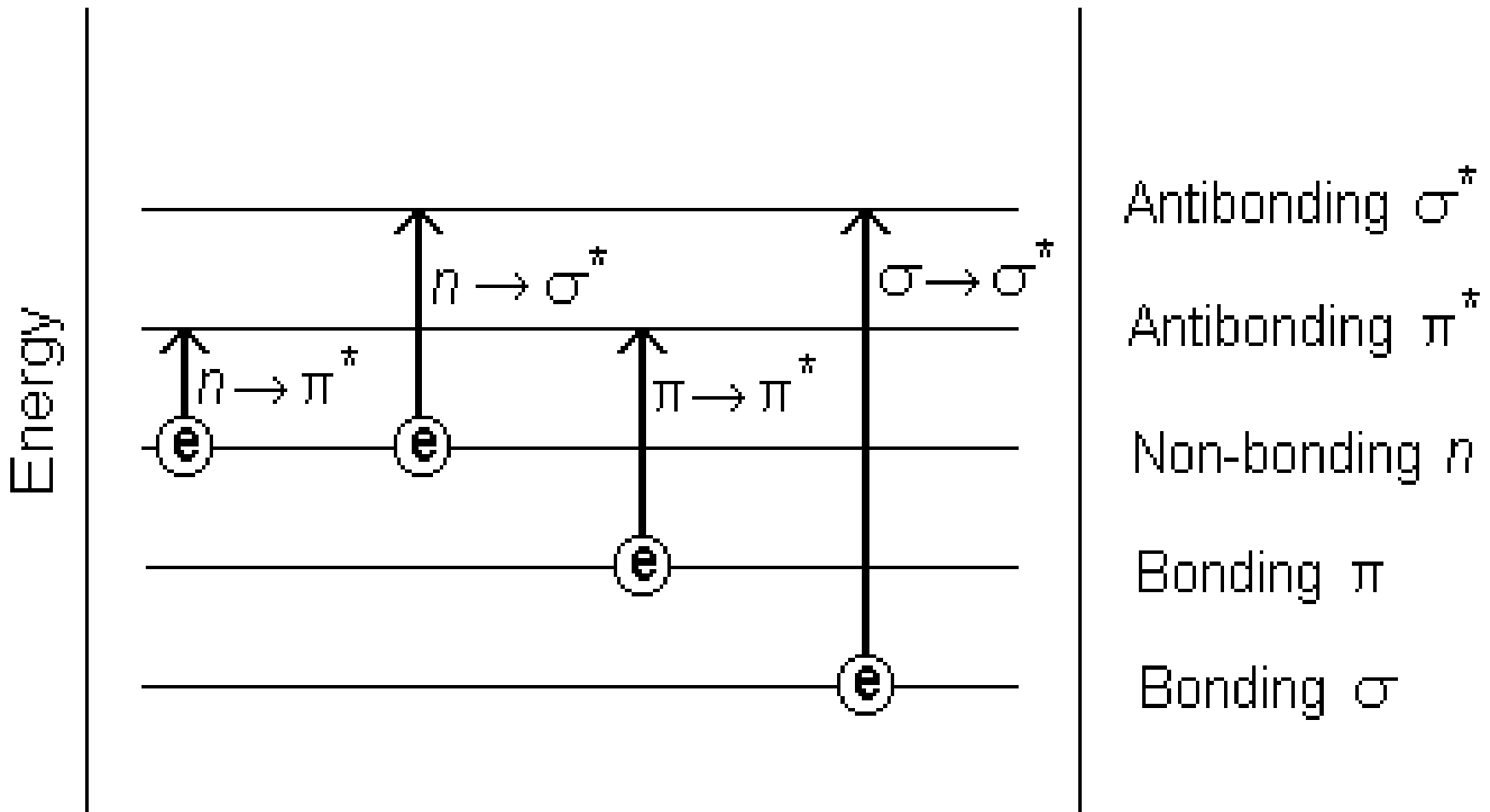
Introduction-Electronic Spectra origin



Principle

- Molecules containing bonding and non-bonding electrons (n-electrons) can absorb energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals.
- The more easily excited the electrons (i.e. lower energy gap between the [HOMO](#) and the [LUMO](#)), the longer the wavelength of light it can absorb.
- There are four possible types of transitions viz.
 - $\pi-\pi^*$,
 - $n-\pi^*$,
 - $\sigma-\sigma^*$, and
 - $n-\sigma^*$,
- These can be ordered as follows : $\sigma-\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi$

Electronic Transitions



Electronic Transitions

- **$s \rightarrow s^*$ Transitions**

An electron in a bonding s orbital is excited to the corresponding antibonding orbital. The energy required is large. For example, methane (which has only C-H bonds, and can only undergo $s \rightarrow s^*$ transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to $s \rightarrow s^*$ transitions are not seen in typical UV-Vis. spectra (200 - 700 nm)

- **$n \rightarrow s^*$ Transitions**

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n \rightarrow s^*$ transitions. These transitions usually need less energy than $s \rightarrow s^*$ transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with $n \rightarrow s^*$ peaks in the UV region is small.

- **$n \rightarrow p^*$ and $p \rightarrow p^*$ Transitions**

Most absorption spectroscopy of organic compounds is based on transitions of n or p electrons to the p^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the p electrons.

- Molar absorptivities from $n \rightarrow p^*$ transitions are relatively low, and range from 10 to 100 $\text{L mol}^{-1} \text{cm}^{-1}$. $p \rightarrow p^*$ transitions normally give molar absorptivities between 1000 and 10,000 $\text{L mol}^{-1} \text{cm}^{-1}$.

{where $s = \sigma$; $p = \pi$ and $n =$ non bonding orbitals}

Electronic Transitions (Appearance in Compounds)

$\sigma \rightarrow \sigma^*$ Alkanes

$\sigma \rightarrow \pi^*$ Carbonyl compounds

$\pi \rightarrow \pi^*$ Alkenes, carbonyl compn, alkyne etc.

$n \rightarrow \sigma^*$ Oxygen, nitrogen, sulfur and halogen compounds

$n \rightarrow \pi^*$ Carbonyl compounds (Usually Forbidden)

Solvent Effect

- The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. Peaks resulting from $n \rightarrow p^*$ transitions are shifted to shorter wavelengths (*blue shift*) with increasing solvent polarity. This arises from increased solvation of the lone pair, which lowers the energy of the n orbital. Often (but *not* always), the reverse (i.e. *red shift*) is seen for $p \rightarrow p^*$ transitions. This is caused by attractive polarisation forces between the solvent and the absorber, which lower the energy levels of both the excited and unexcited states. This effect is greater for the excited state, and so the energy difference between the excited and unexcited states is slightly reduced - resulting in a small red shift. This effect also influences $n \rightarrow p^*$ transitions but is overshadowed by the blue shift resulting from solvation of lone pairs.

Effect of conjugation

- Increase in conjugation decreases the energy gap between π and π^* orbitals, as a result of which $\pi \rightarrow \pi^*$ transition shifts towards lower wavelength side.
- Shown in the next slide

Effect of conjugation

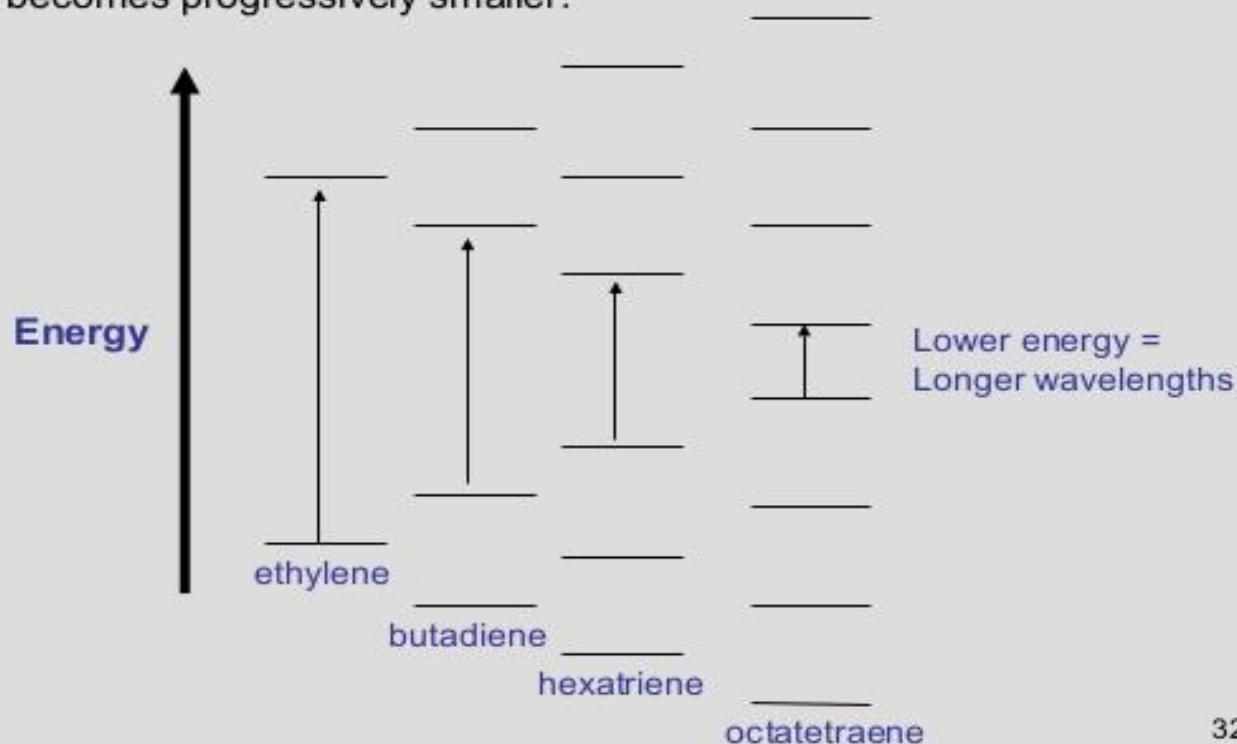
UV Spectroscopy

III. Chromophores

A. Substituent Effects

2. Conjugation – Alkenes

Extending this effect out to longer conjugated systems the energy gap becomes progressively smaller:



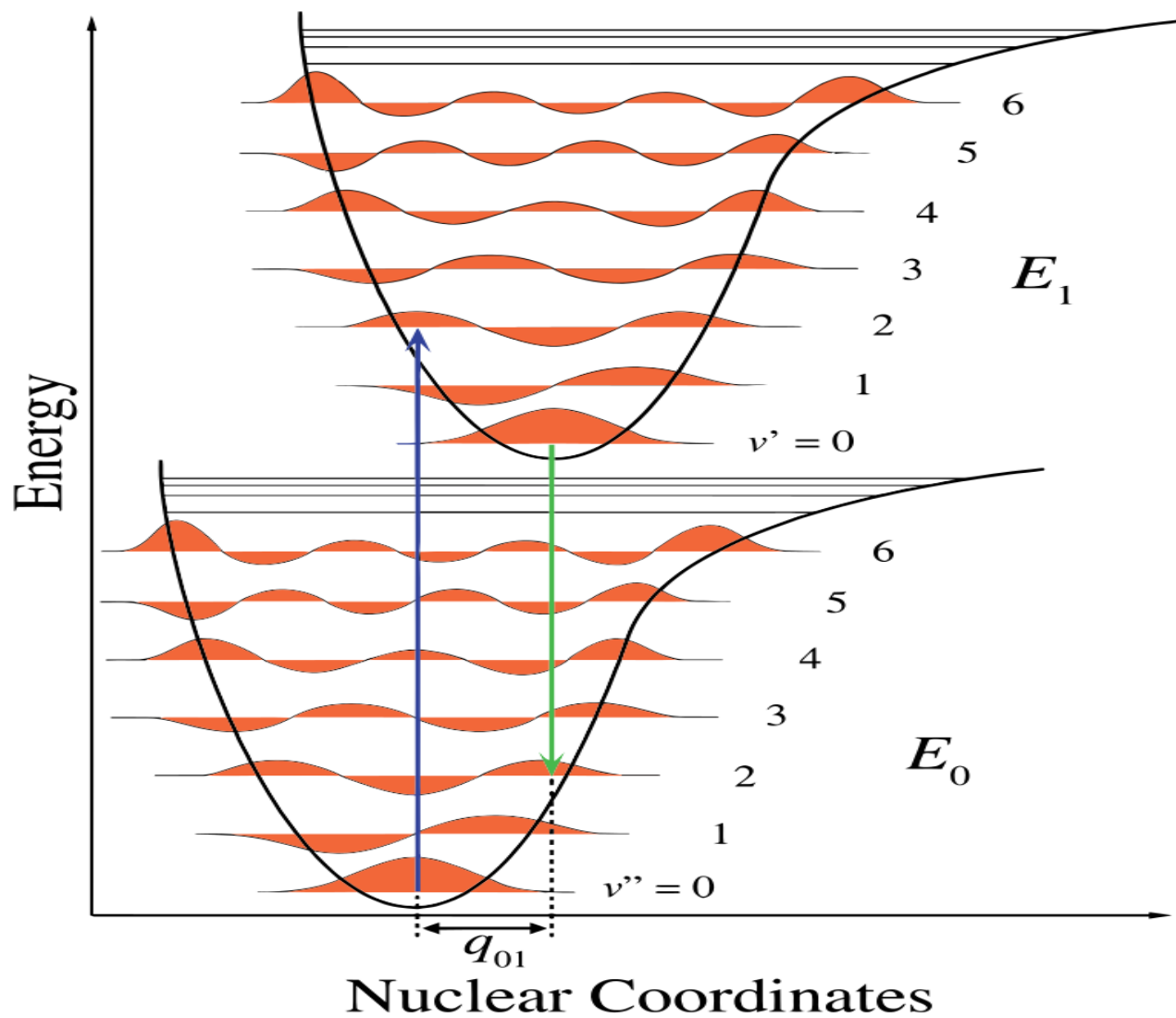
Charge Transfer Spectra

- Many inorganic species show charge-transfer absorption and are called *charge-transfer complexes*. For a complex to demonstrate charge-transfer behaviour, one of its components must have electron donating properties and another component must be able to accept electrons. Absorption of radiation then involves the transfer of an electron from the donor to an orbital associated with the acceptor.
- Molar absorptivities from charge-transfer absorption are large (greater than $10,000 \text{ L mol}^{-1} \text{ cm}^{-1}$).

Franck –Condon Principle

- The Franck–Condon principle is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy. The principle states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly.

Franck Condon Principle



Basic Laws of UV- Visible Spectroscopy

Beer-Lambert's Law

CHEMISTRY
UNPLUGGED

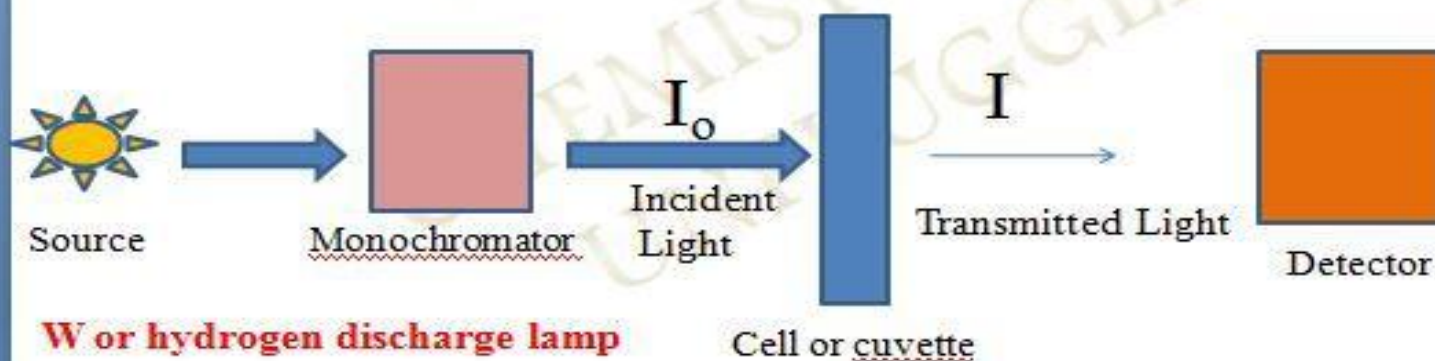
- Absorbance is directly proportional to concentration of the solution.

$$A = \epsilon c l = \log(I_0/I)$$

where, c = concentration (mol/litre)

l = length of light path through the cell (cm)

ϵ = molar absorption coefficient ($\text{L mol}^{-1} \text{cm}^{-1}$)



Basic Law $\{c=v\lambda\}$

What is the frequency of violet light with wavelength 400 nm?

$$c = \lambda v$$

$$v = \frac{c}{\lambda}$$

$$c = 2.998 \times 10^8 \text{ ms}^{-1}$$

$$\lambda = 400 \text{ nm} = 400 \times 10^{-9} \text{ m}$$

$$= \frac{2.998 \times 10^8 \cancel{\text{ms}^{-1}}}{400 \times 10^{-9} \cancel{\text{m}}}$$

$$= 7.50 \times 10^{14} \text{ Hz}$$

Some important terms related to Electronic Spectra

Bathochromic shift (red shift): a shift to lower energy or longer wavelength.

Hypsochromic shift (blue shift): a shift to higher energy or shorter wavelength.

Hyperchromic effect: An increase in intensity.

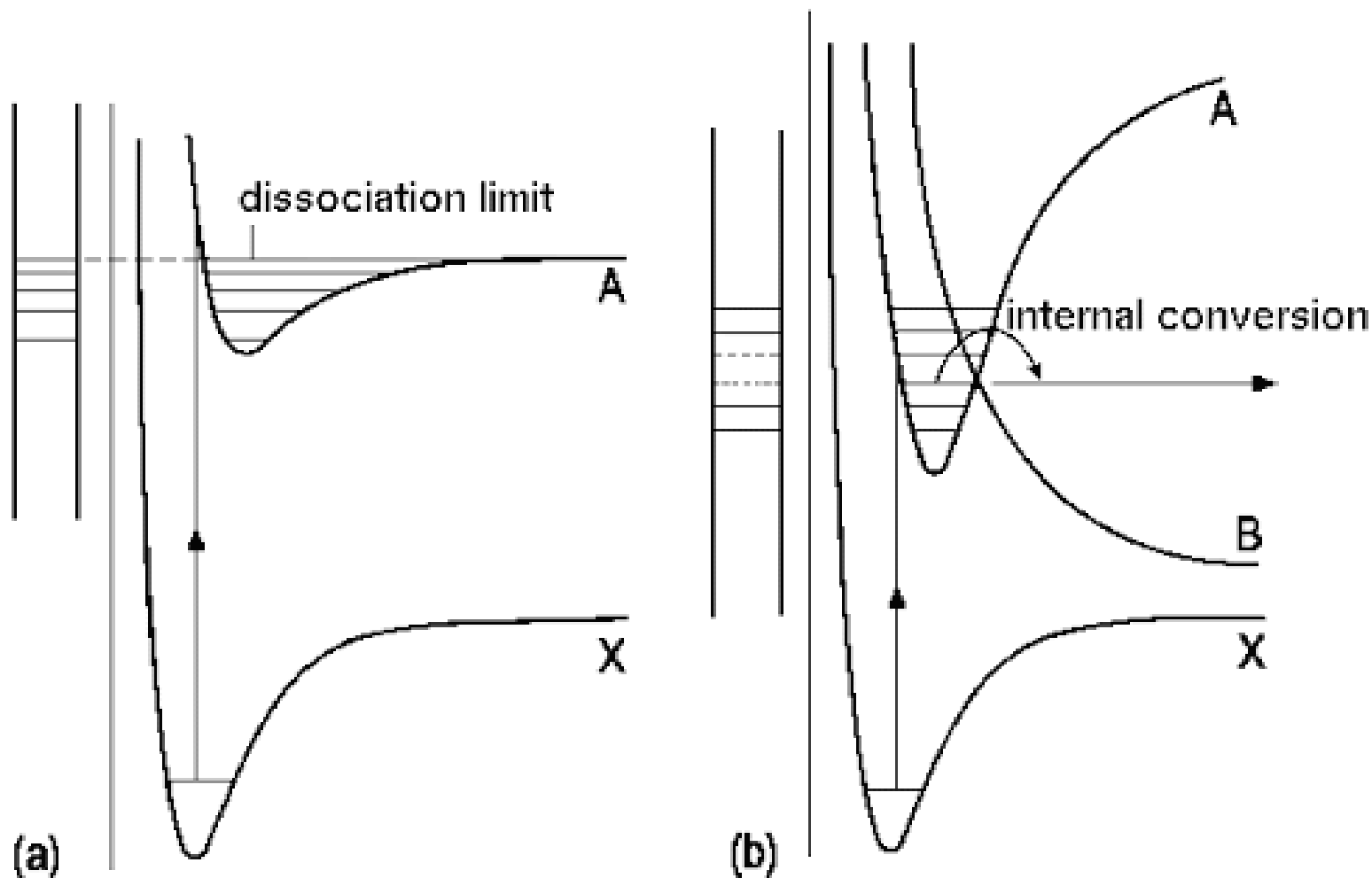
Hypochromic effect: A decrease in intensity.

Dissociation and Pre- dissociation

- If excitation transfers a molecule in a state containing more energy than the separated components (atoms, or molecules), **dissociation** takes place. Above the dissociation limit the energy is not quantized and energy continuum appears instead of discrete energy levels. The **dissociative state** is not stable, which means that the molecule disassembled into the separated components very quickly (approximately during the time of one vibration). In some spectra the discrete energy level structure disappears already for energies which are below the dissociation limit but reappears again at some higher energies. This phenomenon is called **predissociation**.
- **Predissociation** can be usually explained as a result of internal conversion from an excited state A into a dissociative state B. We assume relationship between the vibrational states closely above the level of intersection and the translational motion during dissociation. These circumstances allow a separation of a molecule via state B without supplying the energy of dissociation for state A. Note that, in the range beyond the blurred caused by predissociation, discrete lines are found. An interpretation would be that for higher vibrational states, a conversion towards state B is excluded again.
- Sometimes, predissociation is a result of some additional external factors. For example, we can imagine a molecule to be pushed from state A to state B due to collision with another atom, or molecule. Alternatively, an external electric, or magnetic field can cause to the predissociation of an initially stable molecule. In such cases, we speak of **collision- or field- induced predissociation**.

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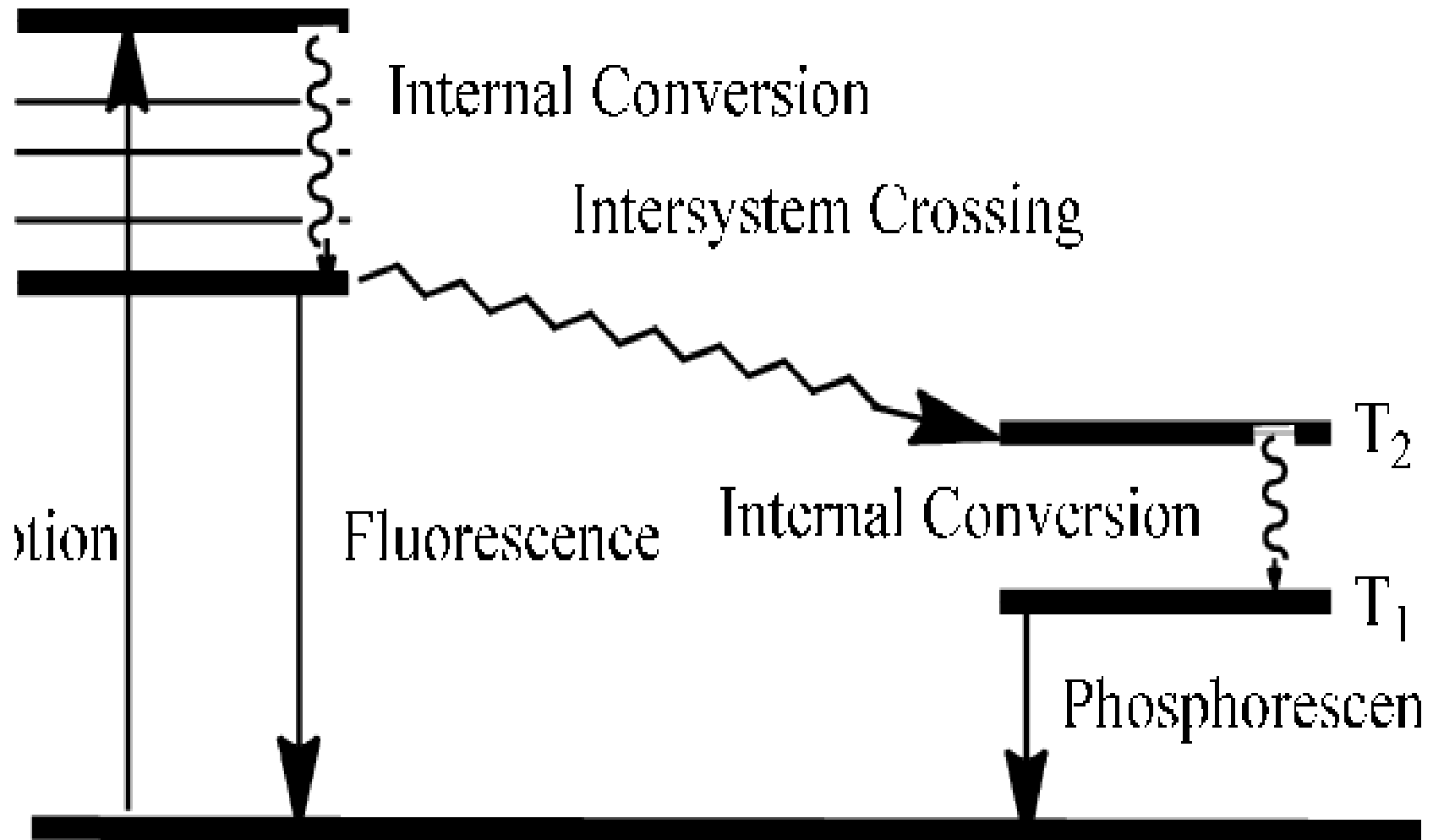
Dissociation and Pre-dissociation



Fluorescence and phosphorescence

- Fluorescence and phosphorescence are types of molecular luminescence methods. A molecule of analyte absorbs a photon and excites a species. The emission spectrum can provide qualitative and quantitative analysis. The terms fluorescence and phosphorescence are usually referred to as photoluminescence because both are alike in excitation brought by absorption of a photon. Fluorescence differs from phosphorescence in that the electronic energy transition that is responsible for fluorescence does not change in electron spin, which results in short-lived electrons ($<10^{-5}$ s) in the excited state of fluorescence. In phosphorescence, there is a change in electron spin, which results in a longer lifetime of the excited state (second to minutes). Fluorescence and phosphorescence occurs at longer wavelength than the excitation radiation.

Fluorescence and phosphorescence

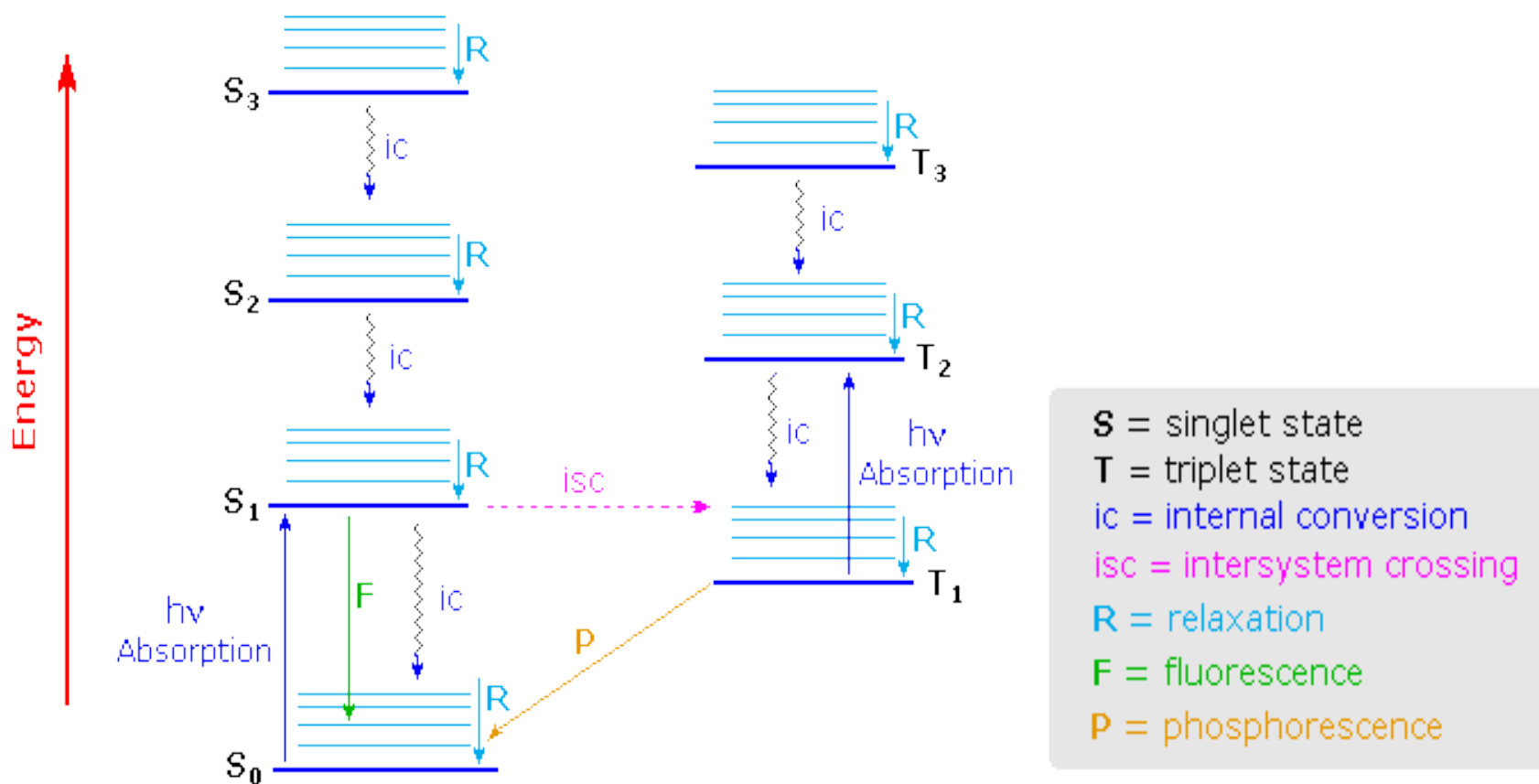


Jablonski Diagram

- The Jablonski diagram that drawn below is a partial energy diagram that represents the energy of photoluminescent molecule in its different energy states. The lowest and darkest horizontal line represents the ground-state electronic energy of the molecule which is the singlet state labeled as S_0 . At room temperature, majority of the molecules in a solution are in this state.

Jablonski Diagram

A Jablonski Diagram



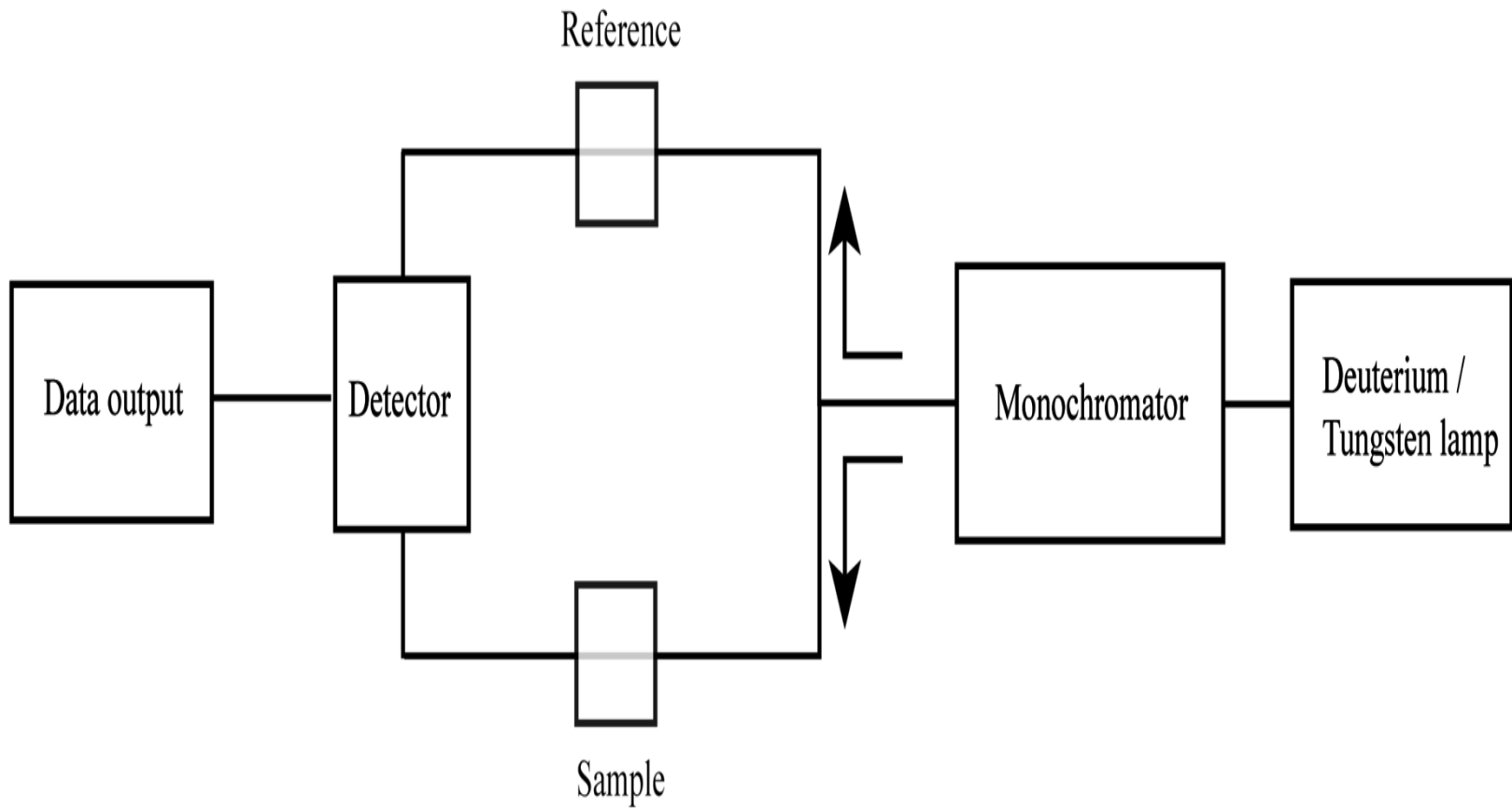
Applications of UV Visible Spectroscopy

- UV/Vis spectroscopy is routinely used in [analytical chemistry](#) for the [quantitative](#) determination of different analytes, such as [transition metal](#) ions, highly [conjugated organic compounds](#), and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.
- Solutions of transition metal ions can be colored (i.e., absorb visible light) because [d electrons](#) within the metal atoms can be excited from one electronic state to another. The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or [ligands](#). For instance, the colour of a dilute solution of [copper sulfate](#) is a very light blue; adding [ammonia](#) intensifies the colour and changes the wavelength of maximum absorption (λ_{max}).
- [Organic compounds](#), especially those with a high degree of [conjugation](#), also absorb light in the UV or visible regions of the [electromagnetic spectrum](#). The solvents for these determinations are often water for water-soluble compounds, or [ethanol](#) for organic-soluble compounds. (Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy. Ethanol absorbs very weakly at most wavelengths.) Solvent polarity and pH can affect the absorption spectrum of an organic compound. Tyrosine, for example, increases in absorption maxima and molar extinction coefficient when pH increases from 6 to 13 or when solvent polarity decreases.
- While [charge transfer complexes](#) also give rise to colours, the colours are often too intense to be used for quantitative measurement.

Instrumentation

- The basic parts of a spectrophotometer are a light source, a holder for the sample, a [diffraction grating](#) in a [monochromator](#) or a [prism](#) to separate the different wavelengths of light, and a detector. The radiation source is often a [Tungsten](#) filament (300–2500 nm), a [deuterium arc lamp](#), which is continuous over the ultraviolet region (190–400 nm), [Xenon arc lamp](#), which is continuous from 160 to 2,000 nm; or more recently, light emitting diodes (LED)^l for the visible wavelengths. The detector is typically a [photomultiplier tube](#), a [photodiode](#), a photodiode array or a [charge-coupled device](#) (CCD). Single photodiode detectors and photomultiplier tubes are used with scanning monochromators, which filter the light so that only light of a single wavelength reaches the detector at one time. The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that its intensity may be measured as a function of wavelength. Fixed monochromators are used with CCDs and photodiode arrays. As both of these devices consist of many detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelengths on different pixels or groups of pixels simultaneously.
- Simplified schematic of a double beam UV–visible spectrophotometer
- A spectrophotometer can be either *single beam* or *double beam*. In a single beam instrument (such as the [Spectronic 20](#)), all of the light passes through the sample cell. Initial intensity must be measured by removing the sample. This was the earliest design and is still in common use in both teaching and industrial labs.

Instrumentation



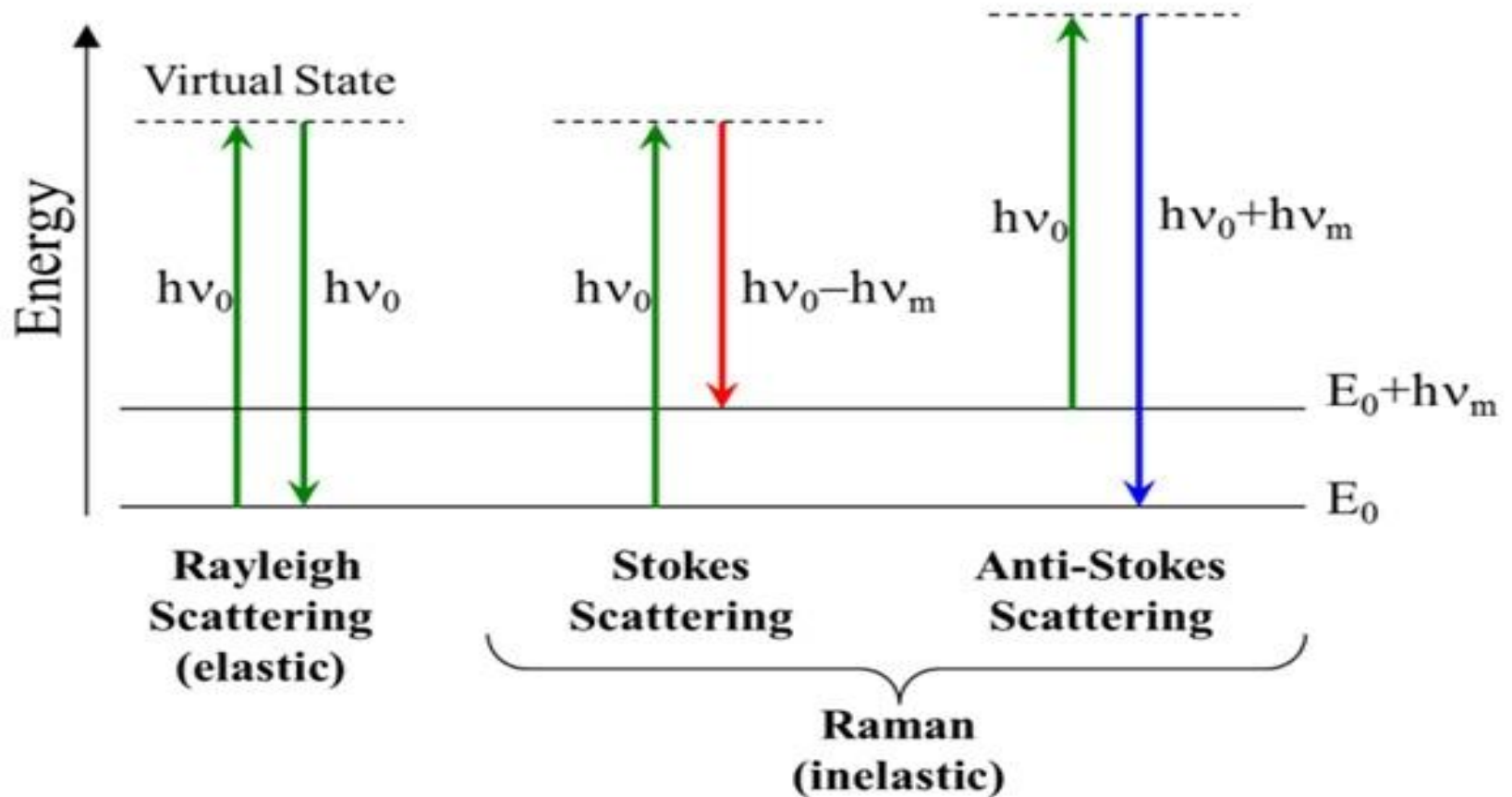
Raman Spectroscopy

- Raman scattering or the Raman effect is the inelastic scattering of photons by matter, meaning that there is an exchange of energy and a change in the light's direction. Typically this involves vibrational energy being gained by a molecule as incident photons from a visible laser are shifted to lower energy. This is called normal Stokes Raman scattering. The effect is exploited by chemists and physicists to gain information about materials for a variety of purposes by performing various forms of Raman spectroscopy.
- Many other variants of Raman spectroscopy allow rotational energy to be examined (if gas samples are used) and electronic energy levels may be examined if an X-ray source is used in addition to other possibilities.
- More complex techniques involving pulsed lasers, multiple laser beams and so on are known.

Rayleigh scattering

- Light has a certain probability of being scattered by a material. When photons are [scattered](#), most of them are [elastically scattered](#) ([Rayleigh scattering](#)), such that the scattered photons have the same energy ([frequency](#), [wavelength](#) and color) as the incident photons but different direction. Rayleigh scattering usually has an intensity in the range 0.1% to 0.01% relative to that of a radiation source. An even smaller fraction of the scattered photons (approximately 1 in 10 million) can be scattered *in-elastically*, with the scattered photons having an energy different (usually lower) from those of the incident photons—these are Raman scattered photons. Because of [conservation of energy](#), the material either gains or loses energy in the process.
- Rayleigh scattering was discovered and explained in the 19th century. The Raman effect is named after Indian scientist [C. V. Raman](#), who discovered it in 1928 with assistance from his student [K. S. Krishnan](#). Raman was awarded the Nobel prize in Physics in 1930 for his discovery although [Grigory Landsberg](#) and [Leonid Mandelstam](#) observed the effect in crystals the same year as Raman. The effect had been predicted theoretically by [Adolf Smekal](#) in 1923

Quantum Theory of Raman Effect



Classical Theory

- The electric field E_i of the light wave acts on the charges in the material
- Interaction of light with a single molecule considered
- Induced dipole moment P_i of a molecule (vector)

$$(1) \quad P_i = p_i + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \dots$$

Raman effect

Hyper Raman effect

- p_i – induced permanent dipole moment
- α_{ij} – polarizability (tensor)
- i, j, k, l – subscripts running over directions x, y, z

Origin of Raman Scattering

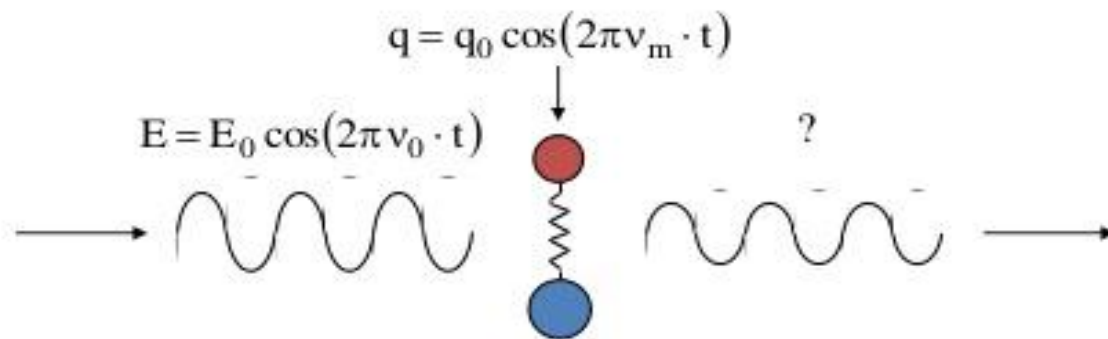
The electric field strength (E) of an EM radiation (normally laser beam with frequency ν_0) with an amplitude E_0 fluctuates with time (t) according to:

$$E = E_0 \cos 2\pi\nu_0 t$$

When this light irradiates a diatomic molecule, an electric dipole moment (P) will be induced because of the movement of nuclei and electrons as a response for the applied electric field:

$$P = \alpha E = \alpha E_0 \cos 2\pi\nu_0 t$$

Scattering of radiation from a diatomic molecule



Induced dipole moment: $P = \alpha E = \alpha E_0 \cos(2\pi\nu_0 \cdot t)$

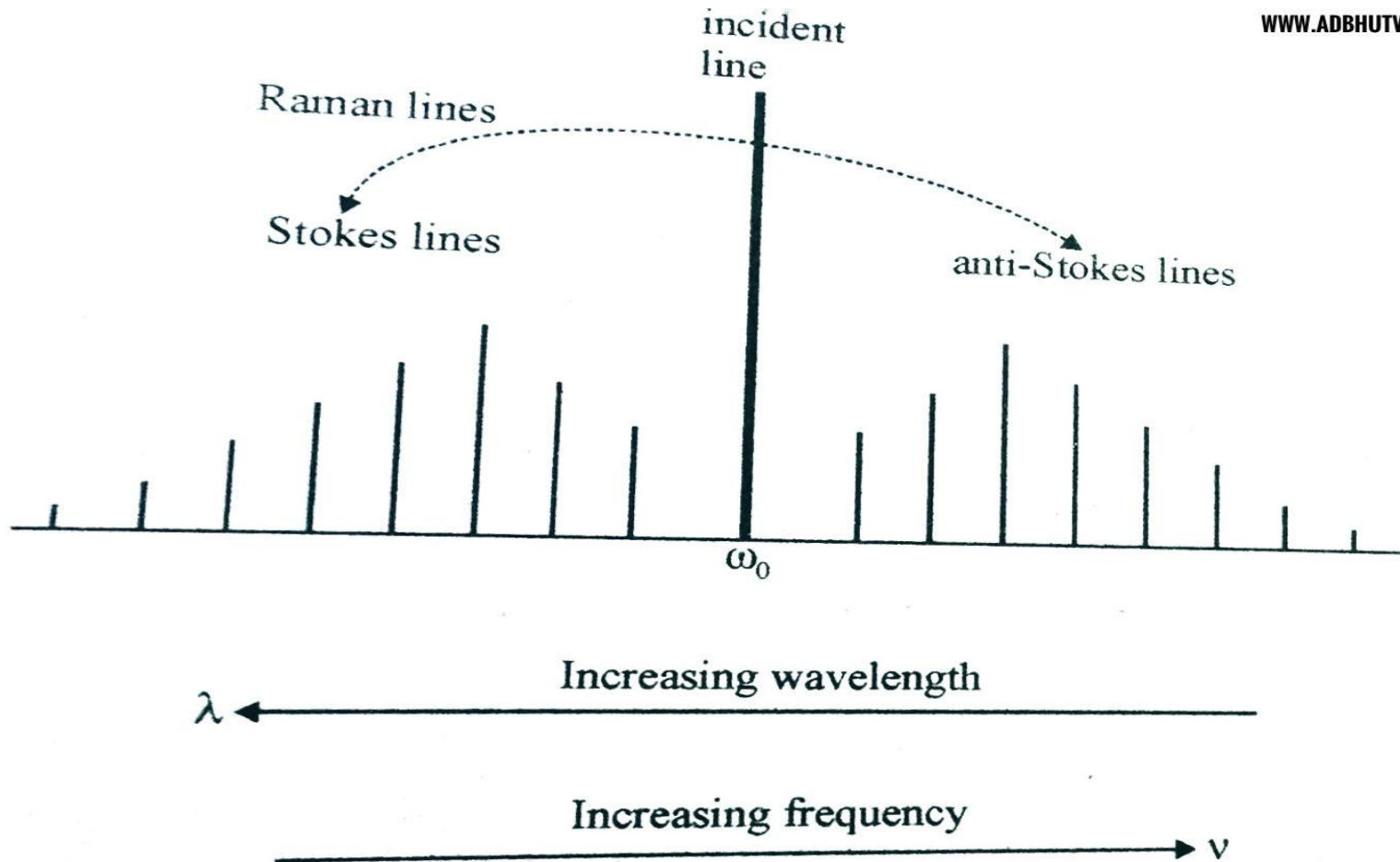
For a small amplitude of vibration, the polarizability α is a linear function of q :

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q} \right)_{q=0} \cdot q + \dots$$

$$\begin{aligned} \Rightarrow P &= \alpha_0 E_0 \cos(2\pi\nu_0 \cdot t) + \left(\frac{\partial \alpha}{\partial q} \right)_{q=0} \cdot q_0 \cos(2\pi\nu_m \cdot t) \cdot E_0 \cos(2\pi\nu_0 \cdot t) = \\ &= \underbrace{\alpha_0 E_0 \cos(2\pi\nu_0 \cdot t)}_{\text{Rayleigh scattering}} + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q} \right)_{q=0} q_0 E_0 \left[\underbrace{\cos(2\pi\{\nu_0 - \nu_m\} \cdot t)}_{\text{Stokes scattering}} + \underbrace{\cos(2\pi\{\nu_0 + \nu_m\} \cdot t)}_{\text{Anti-Stokes scattering}} \right] \end{aligned}$$

Stroke's and Anti-Stroke's Lines

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Selection Rules

- In contrast to IR spectroscopy, where there is a requirement for a change in dipole moment for vibrational excitation to take place, Raman scattering requires a change in polarizability. A Raman transition from one state to another is allowed only if the molecular polarizability of those states is different. For a vibration, this means that the derivative of the polarizability with respect to the normal coordinate associated to the vibration is non-zero: In general, a normal mode is Raman active if it transforms with the same symmetry of the quadratic which can be verified from the [character table](#) of the molecule's point group. As with IR spectroscopy, only fundamentals are allowed according to the QHO. There are however many cases where overtones are observed.
- The [rule of mutual exclusion](#), which states that vibrational modes cannot be both IR and Raman active, applies to certain molecules.
- The specific selection rules state that the allowed rotational transitions are $\Delta J = 0, \pm 2$, where J is the rotational state. This generally is only relevant to molecules in the gas phase where the Raman linewidths are small enough for rotational transitions to be resolved.
- A selection rule relevant only to ordered solid materials states that only phonons with zero phase angle can be observed by IR and Raman, except when [phonon confinement](#) is manifest.

Rotation Raman Spectra

- Molecular rotational transitions can also be observed by [Raman spectroscopy](#). Rotational transitions are Raman-allowed for any molecule with an [anisotropic polarizability](#) which includes all molecules except for spherical tops. This means that rotational transitions of molecules with no permanent dipole moment, which cannot be observed in absorption or emission, can be observed, by scattering, in Raman spectroscopy. Very high resolution Raman spectra can be obtained by adapting a [Fourier Transform Infrared Spectrometer](#). An example is the spectrum of $^{15}\text{N}_2$. It shows the effect of nuclear spin, resulting in intensities variation of 3:1 in adjacent lines. A bond length of 109.9985 ± 0.0010 pm was deduced from the data.

Applications

- [Raman spectroscopy](#) employs the Raman effect for substances analysis. The spectrum of the Raman-scattered light depends on the molecular constituents present and their state, allowing the spectrum to be used for material identification and analysis. Raman spectroscopy is used to analyze a wide range of materials, including gases, liquids, and solids. Highly complex materials such as biological organisms and human tissue can also be analyzed by Raman spectroscopy.
- For solid materials, Raman scattering is used as a tool to detect high-frequency phonon and [magnon](#) excitations.
- Raman [lidar](#) is used in atmospheric physics to measure the atmospheric extinction coefficient and the water vapour vertical distribution.
- Stimulated Raman transitions are also widely used for manipulating a trapped ion's energy levels, and thus basis [qubit](#) states.
- Raman spectroscopy can be used to determine the [force constant](#) and [bond length](#) for molecules that do not have an infrared [absorption spectrum](#).
- [Raman amplification](#) is used in [optical amplifiers](#).
- The Raman effect is also involved in producing the appearance of the blue sky (see [Rayleigh Scattering](#): 'Rayleigh scattering of molecular nitrogen and oxygen in the atmosphere includes elastic scattering as well as the inelastic contribution from rotational Raman scattering in air').

References

- “Rasaynik Spectroscopy”, O.P. Srivastava and Kishor Arora, M.P. Hindi Granth Academy publication.
- Chemistry B.Sc. Part - III, Shivrul Agarwal and Company.
- Wikipedia

- Best Of Luck

Introduction to Spectroscopy

B.Sc. III year Paper –I, Part I

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Govt. P.G. College (Auto.) ; Datia (M.P.) -
475661

This Lecture Includes

- Introduction to spectroscopy
- Wave nature of light
- Electromagnetic spectrum
- Colorimetry
- Spectrophotometers / spectroscopes
- Instrumentation
- A typical spectrum
- Beer- Lambert's Law/ Absorbance and transmittance
- Isobestic Point
- Selection Rule (In General)

Introduction

- Spectro-photometry is a method to measure how much a chemical substance absorbs light by measuring the intensity of light as a beam of light passes through sample solution.
- The basic principle is that each compound absorbs or transmits light over a certain range of wavelength.
- This measurement can also be used to measure the amount of a known chemical substance.

Introduction

- Spectro-photometry is one of the most useful methods of quantitative analysis in various fields such as chemistry, physics, biochemistry, material and chemical engineering and clinical applications.
- Spectro-photometry is widely used for quantitative analysis in various areas (e.g., chemistry, physics, biology, biochemistry, material and chemical engineering, clinical applications, industrial applications, etc).

Introduction

- Any application that deals with chemical substances or materials can use this technique. In biochemistry, for example, it is used to determine enzyme-catalyzed reactions.
- In clinical applications, it is used to examine blood or tissues for clinical diagnosis.

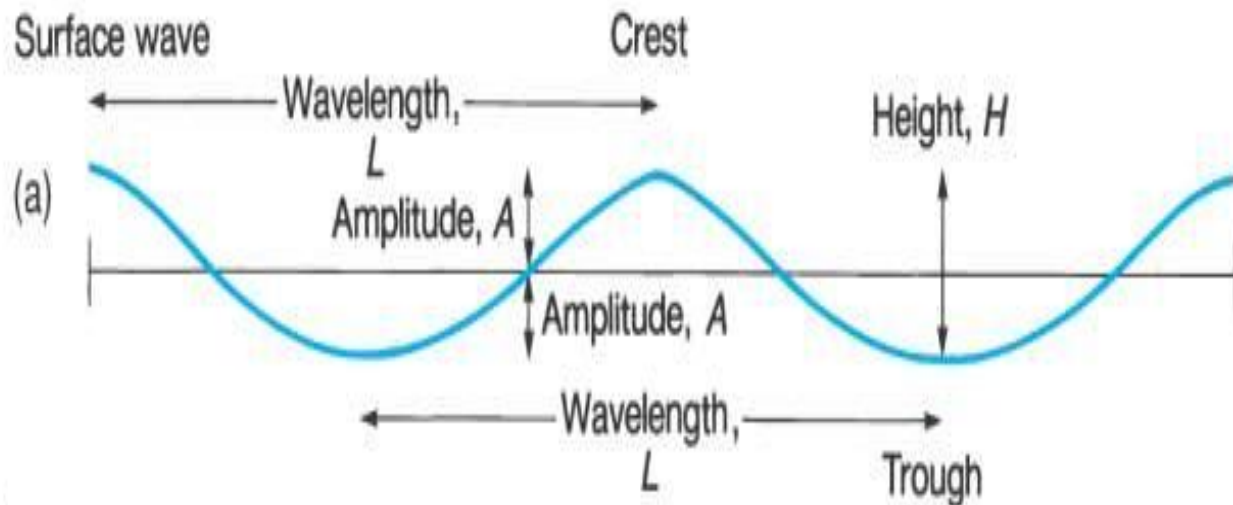
Introduction

- There are also several variations of the spectro-photometry such as atomic absorption spectro-photometry and atomic emission spectro-photometry.

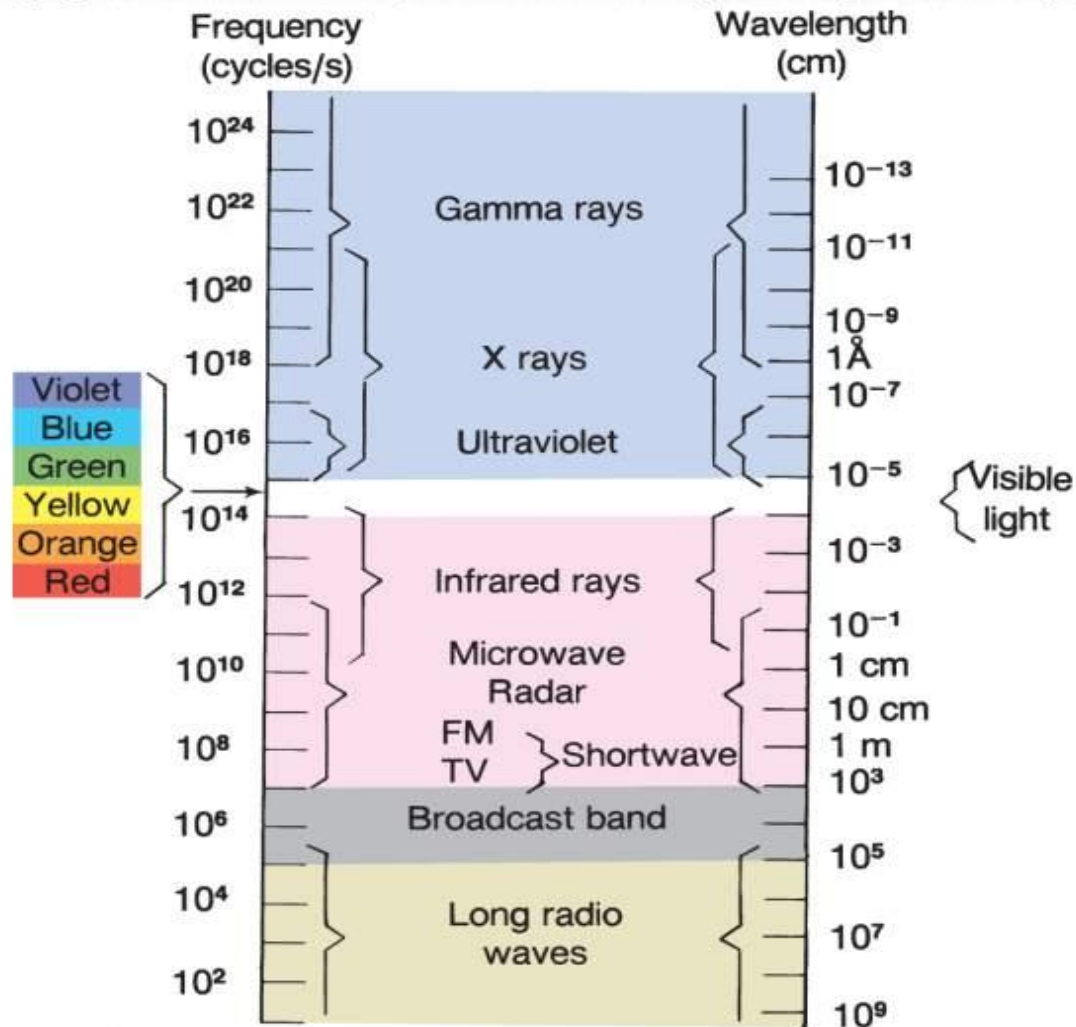
Wave Nature of Light

- *Electromagnetic radiation* moves in waves

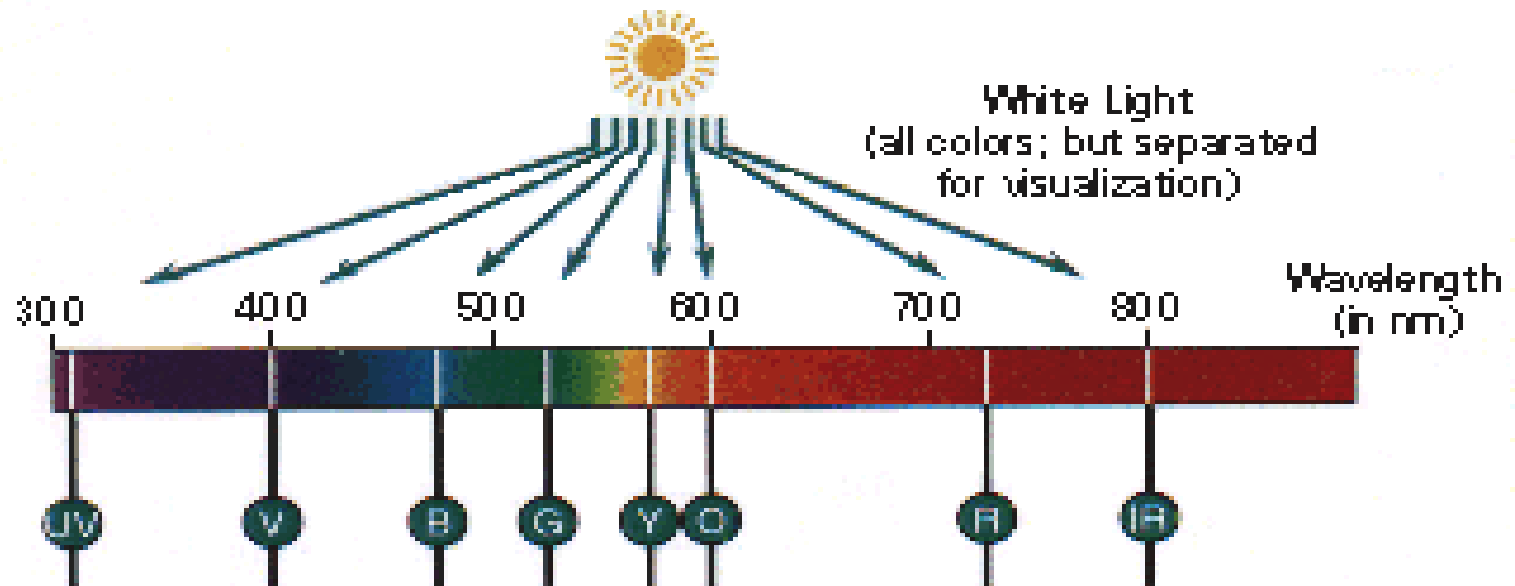
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Electromagnetic Spectrum



VIBGYOR



Electromagnetic Spectrum

COLOR	WAVELENGTH (λ in nm)
Ultraviolet	< 380
Violet	380 – 435
Blue	436 – 480
Greenish-blue	481 – 490
Bluish-green	491 – 500
Green	501 – 560
Yellowish-green	561 – 580
Yellow	581 – 595
Orange	596 – 650
Red	651 – 780
Near Infrared	> 780

Colorimetry

- The solutions of many compounds have characteristic colors.
- The intensity of such a color is proportional to the concentration of the compound.

Spectroscopes Vs. Spectrophotometers

- Light can either be *transmitted* or *absorbed* by dissolved substances
- Presence & concentration of dissolved substances is analyzed by passing light through the sample
- Spectroscopes measure electromagnetic ***emission***
- Spectrophotometers measure electromagnetic ***absorption***

Instrumentation

- What do visible spectrophotometers measure?
 - Amount of light absorbed by the dissolved substance
 - Qualitative
 - Quantitative

Instrumentation

- A spectrophotometer is an instrument that measures the amount of photons (the intensity of light) absorbed after it passes through sample solution.
- With the spectrophotometer, the amount of a known chemical substance (concentrations) can also be determined by measuring the intensity of light detected.
- Depending on the range of wavelength of light source, it can be classified into two different types:

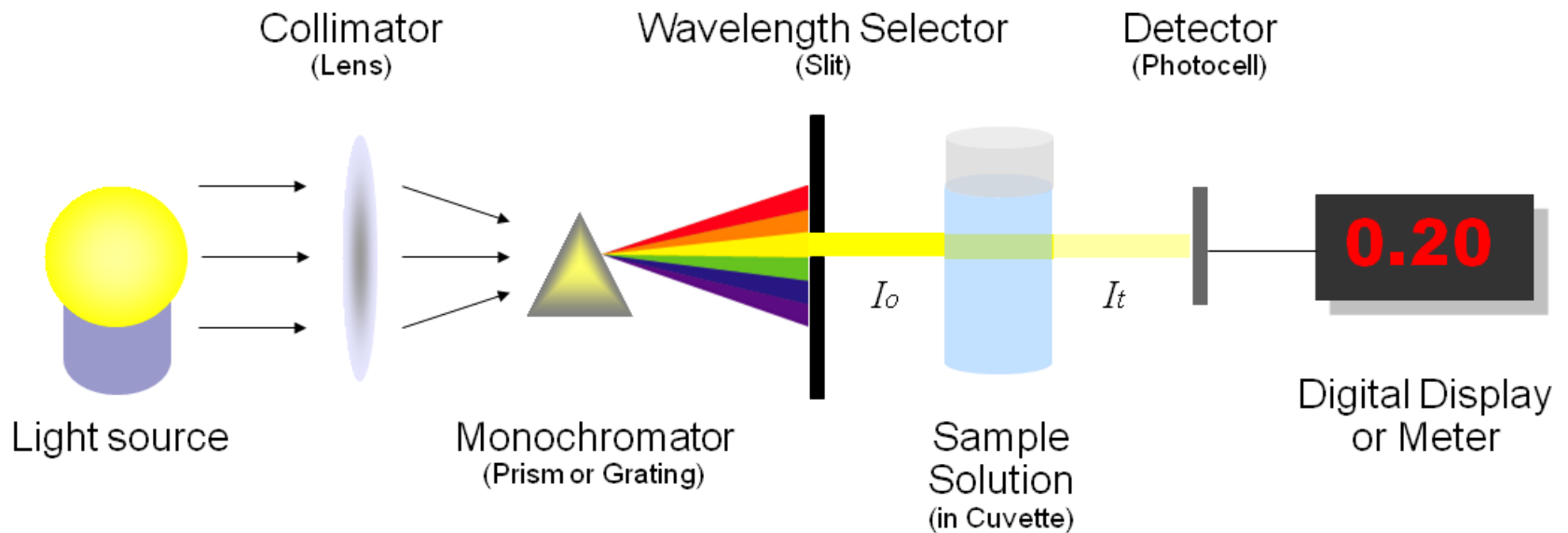
Instrumentation

- **UV-visible spectrophotometer:** uses light over the ultraviolet range (185 - 400 nm) and visible range (400 - 700 nm) of electromagnetic radiation spectrum.
- **IR spectrophotometer:** uses light over the infrared range (700 - 15000 nm) of electromagnetic radiation spectrum.

Instrumentation

- **Spectrometer:** It produces a desired range of wavelength of light. First a collimator (lens) transmits a straight beam of light (photons) that passes through a monochromator (prism) to split it into several component wavelengths (spectrum). Then a wavelength selector (slit) transmits only the desired wavelengths.
- **Photometer:** After the desired range of wavelength of light passes through the solution of a sample in cuvette, the photometer detects the amount of photons that is absorbed and then sends a signal to a galvanometer or a digital display.

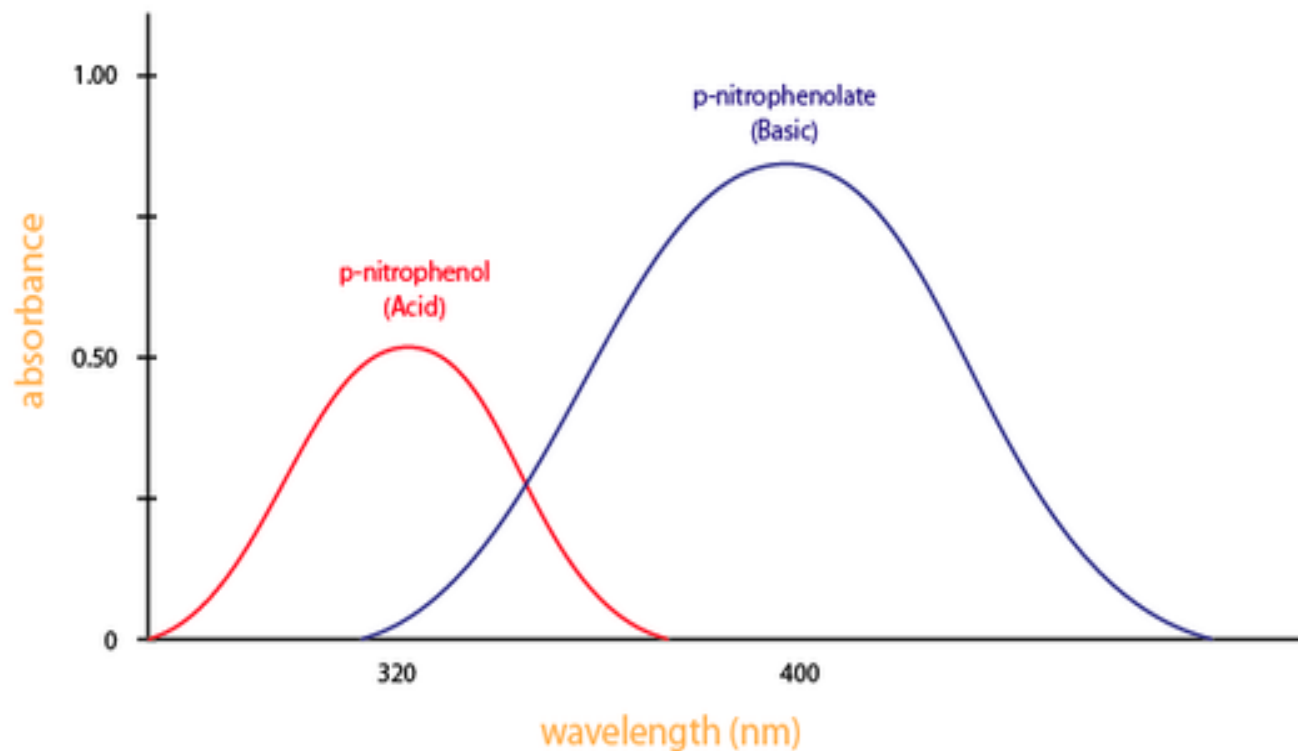
Block Diagram



Instrument



A typical Spectrum



Beer- Lambert Law

- [Beer-Lambert Law](#) (also known as Beer's Law) states that there is a linear relationship between the absorbance and the concentration of a sample. For this reason, Beer's Law can *only* be applied when there is a linear relationship.

Beer's Law is written as:

- $A = \epsilon lc$

where

A is the measure of absorbance (no units),

ϵ is the molar extinction coefficient or molar absorptivity (or absorption coefficient),

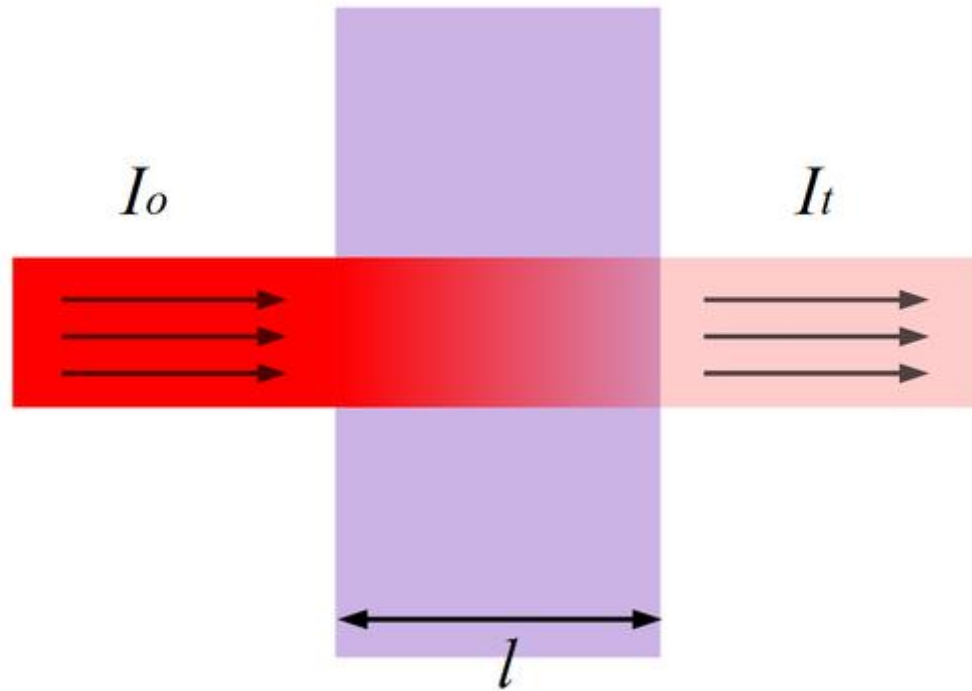
Beer Lambert Law

l is the path length, and

c is the concentration.

- The molar extinction coefficient is given as a constant and varies for each molecule. Since absorbance does not carry any units, the units for ϵ must cancel out the units of length and concentration. As a result,
- ϵ has the units: $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

Beer Lambert Law



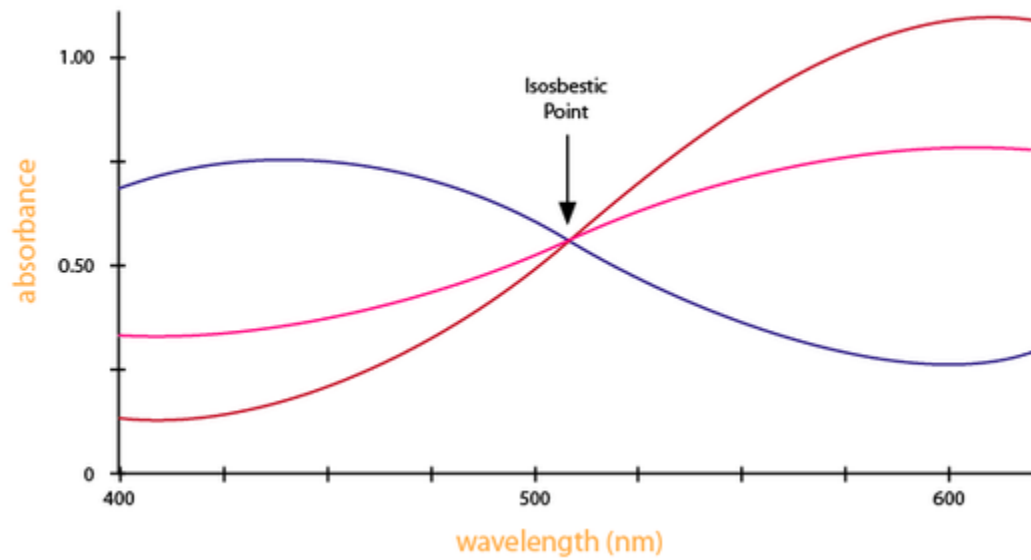
Absorbance Vs. Transmittance

- Transmittance is the fraction of light that passes through the sample. This can be calculated using the equation:
- $\text{Transmittance}(T) = I_t / I_o$
- Transmittance is related to absorption by the expression:
- $\text{Absorbance}(A) = -\log(T) = -\log(I_t / I_o)$

Isobestic Point

- An **isosbestic point** is the wavelength in which the absorbance of two or more species are the same. The appearance of an isosbestic point in a reaction demonstrates that an intermediate is NOT required to form a product from a reactan

Isobestic Point



Selection Rules (In General)

- In [physics](#) and [chemistry](#), a **selection rule**, or **transition rule**, formally constrains the possible transitions of a system from one [quantum state](#) to another. Selection rules have been derived for [electromagnetic](#) transitions in [molecules](#), in [atoms](#), in [atomic nuclei](#), and so on. The selection rules may differ according to the technique used to observe the transition. The selection rule also plays a role in [chemical reactions](#), where some are formally [spin-forbidden reactions](#), that is, reactions where the spin state changes at least once from [reactants](#) to [products](#).

Selection Rules (In General)

- In quantum mechanics the basis for a spectroscopic selection rule is the value of the transition moment integral

$$\int \psi^* \mu \psi d\tau$$

Selection Rules (In General)

- Where these are the wave functions of the two states involved in the transition and μ is the transition moment operator
- This integral represents the propagator (and thus the probability) of the transition between states; therefore if the value of this integral is zero then the transition is forbidden.
- If the symmetry of this function spans the totally symmetric representation of the point group to which the atom or molecule belongs then its value is (in general) not zero and the transition is allowed. Otherwise, the transition is forbidden.

Selection Rules (In General)

- **Symmetry characteristics of transition moment operator. Following table shows transition type along with dipole moment operator and type of spectra**

Transition type	μ transforms as	note
Electric dipole	x, y, z	Optical spectra
Electric quadrupole	$x^2, y^2, z^2, xy, xz, yz$	Constraint $x^2 + y^2 + z^2 = 0$
Electric polarizability	$x^2, y^2, z^2, xy, xz, yz$	Raman spectra
Magnetic dipole	R_x, R_y, R_z	Optical spectra (weak)

- Best Of Luck

Photo Chemistry, B.Sc. III Year, Paper --I

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This presentation Contains

- Photo chemical reactions- Introduction
- Differences between Photochemical and thermal reactions
- Basic Laws of Photochemistry
 - ❖ Grothous Drapper's Law
 - ❖ Stark Einstein's Law
 - ❖ Beer Lambert's law
- Quantum Yield
- Low and high quantum yield
- Fluorescence and Phosphoresce
- Jablonski Diagram
- Photo- sensitization
- Sensitizers
- Actinometers
- Norrish type 1 and 2 Reactions
- Assignment and Set of questions

Introduction

- **Photochemistry** is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400–750 nm) or infrared radiation (750–2500 nm).

Introduction

- In nature, photochemistry is of immense importance as it is the basis of photosynthesis, vision, and the formation of [vitamin D](#) with sunlight.
- Photochemical reactions proceed differently than temperature-driven reactions.
- Photochemical paths access high energy intermediates that cannot be generated thermally, thereby overcoming large activation barriers in a short period of time, and allowing reactions otherwise inaccessible by thermal processes.
- Photochemistry is also destructive, as illustrated by the [photodegradation](#) of plastics.

Photochemical vs Thermal Reaction

More Information Online WWW.DIFFERENCEBETWEEN.COM

Photochemical Reaction

Thermal Reaction

DEFINITION

A photochemical reaction is a form of chemical reaction in which the reactants get energy as photons.

A thermal reaction is a form of chemical reaction in which the reactants get energy as heat.

MECHANISM OF INITIATION

Photochemical reactions initiate when the reactants get energy from photons.

Thermal reactions initiate when the reactants get heat energy.

EFFECT OF LIGHT

The presence of an appropriate light source is a necessity for a photochemical reaction.

The thermal reactions may occur even in the absence of light.

EFFECT OF TEMPERATURE

Temperature of the reaction mixture has no direct effect on the initiation and progression of the reaction.

Temperature has a direct effect on the thermal reactions.

ACCELERATION

There is no need of a catalyst for almost all the photochemical reactions.

Most of the thermal reactions need a catalyst to accelerate the reaction.

Basic Laws of Photo Chemistry

(Grothous Draper's Law)

- The **Grotthuss–Draper law** (also called the **Principle of Photochemical Activation**) states that only that light which is absorbed by a system can bring about a photochemical change. Materials such as [dyes](#) and [phosphors](#) must be able to absorb "light" at optical frequencies.
- This law provides a basis for [fluorescence](#) and [phosphorescence](#).
- The law was first proposed in 1817 by [Theodor Grotthuss](#) and in 1842, independently, by [John William Draper](#).^[5]
- This is considered to be one of the two basic laws of [photochemistry](#).

Basic Laws of Photochemistry

(Stark- Einstein's Law)

- The **Stark–Einstein law** is named after German-born physicists [Johannes Stark](#) and [Albert Einstein](#), who independently formulated the law between 1908 and 1913. It is also known as the **photochemical equivalence law** or **photoequivalence law**. In essence it says that every photon that is absorbed will cause a (primary) chemical or physical reaction.
- The photon is a quantum of radiation, or one unit of radiation. Therefore, this is a single unit of EM radiation that is equal to Planck's constant (h) times the frequency of light. This quantity is symbolized by γ , $h\nu$, or $\hbar\omega$.
- The photochemical equivalence law is also restated as follows: for every [mole](#) of a substance that reacts, an equivalent mole of quanta of light are absorbed.
- The formula is: $\Delta E = N_A h\nu$
- where N_A is [Avogadro's number](#).

Basic Laws of Photochemistry

(Stark- Einstein's Law)

- The photochemical equivalence law applies to the part of a light-induced reaction that is referred to as the primary process (i.e. [absorption](#) or [fluorescence](#)).
- In most photochemical reactions the primary process is usually followed by so-called secondary photochemical processes that are normal interactions between reactants not requiring absorption of light. As a result, such reactions do not appear to obey the one quantum–one molecule reactant relationship.
- The law is further restricted to conventional photochemical processes using light sources with moderate intensities; high-intensity light sources such as those used in [flash photolysis](#) and in laser experiments are known to cause so-called biphotonic processes; i.e., the absorption by a molecule of a substance of two photons of light.

Quantum yield

- The **quantum yield (Φ)** of a radiation-induced process is the number of times a specific event occurs per photon absorbed by the system. The "event" is typically a kind of chemical reaction.

Quantum yield

- The quantum yield for the decomposition of a reactant molecule in a decomposition reaction is defined as:

$$(\Phi) = (\text{No. of molecules decomposed}) / (\text{No. of photons absorbed})$$

- Quantum yield can also be defined for other events, such as fluorescence:

$$(\Phi) = (\text{Photons emitted}) / (\text{Photons absorbed})$$

- Here, quantum yield is the emission efficiency of a given fluorophore.

Low and High Quantum yield

- **High Quantum Yield** : When two or more molecules are decomposed per photon, the **quantum yield** $\phi > 1$ and the reaction has a **high quantum yield**.
- **Low Quantum Yield** : When the number of molecules decomposed is less than one per photon, the **quantum yield** $\phi < 1$ and the reaction has a **low quantum yield**.

Basic Laws of Photochemistry

Beer-Lambert's Law

CHEMISTRY
UNPLUGGED

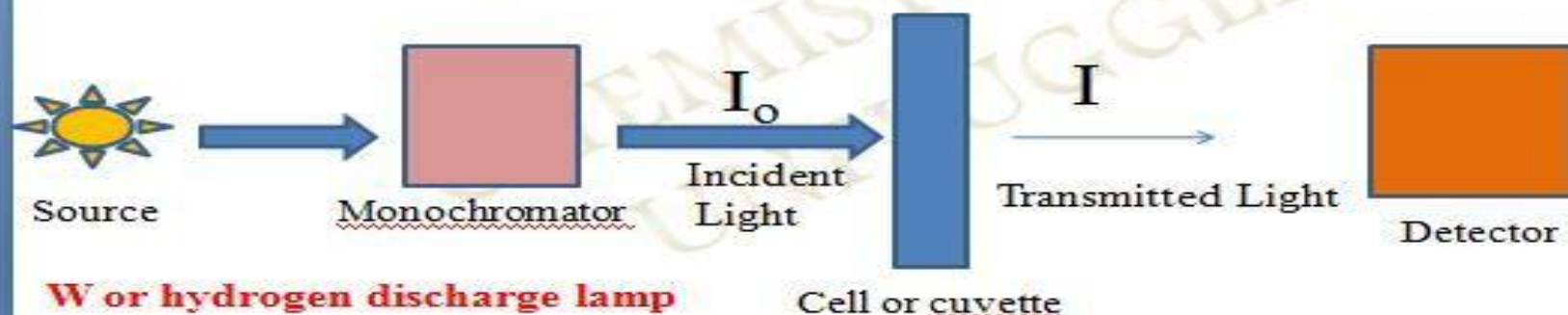
- Absorbance is directly proportional to concentration of the solution.

$$A = \epsilon c l = \log(I_0/I)$$

where, c = concentration (mol/litre)

l = length of light path through the cell (cm)

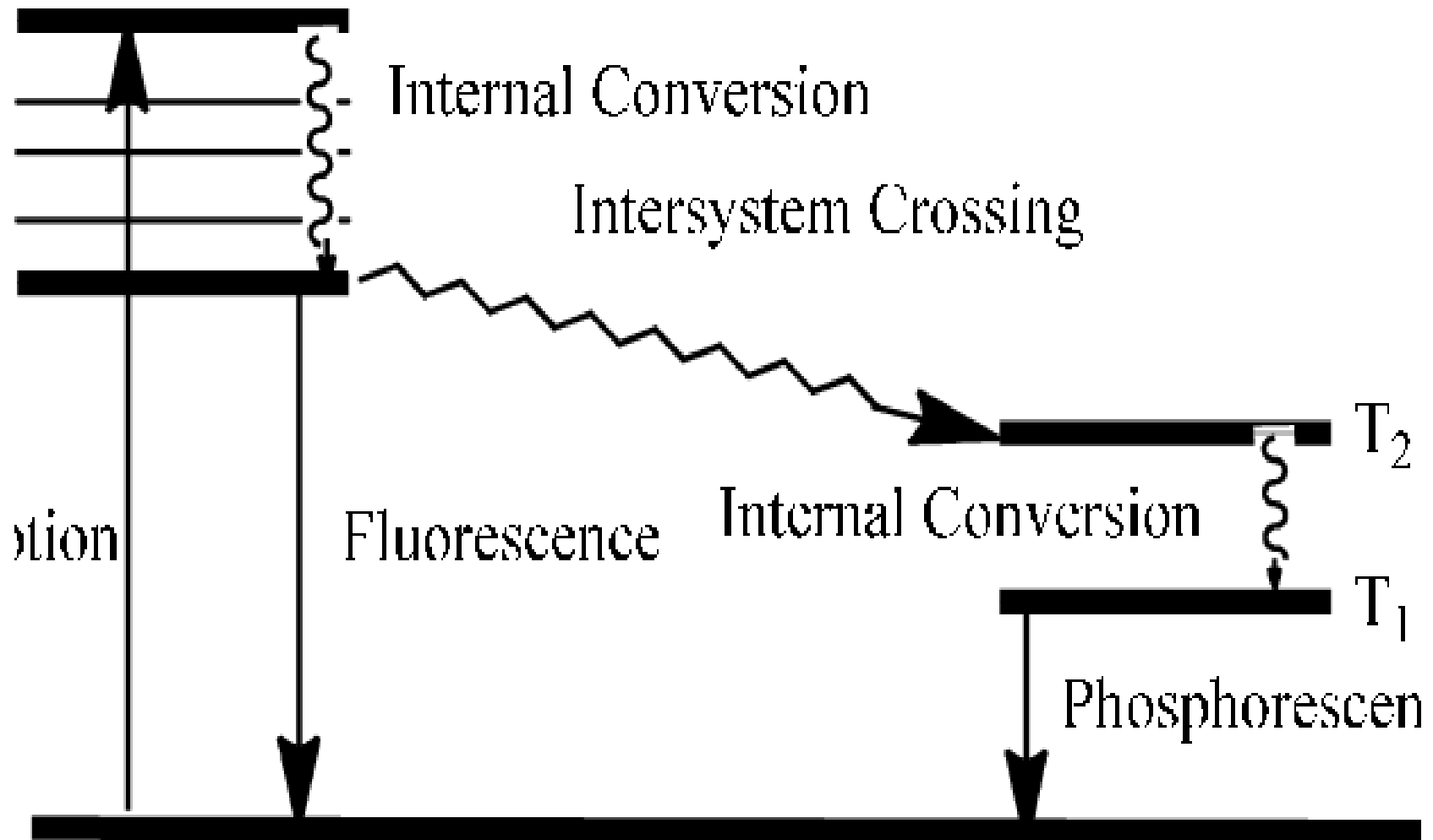
ϵ = molar absorption coefficient ($\text{L mol}^{-1} \text{cm}^{-1}$)



Fluorescence and phosphorescence

- Fluorescence and phosphorescence are types of molecular luminescence methods. A molecule of analyte absorbs a photon and excites a species. The emission spectrum can provide qualitative and quantitative analysis. The terms fluorescence and phosphorescence are usually referred to as photoluminescence because both are alike in excitation brought by absorption of a photon. Fluorescence differs from phosphorescence in that the electronic energy transition that is responsible for fluorescence does not change in electron spin, which results in short-lived electrons ($<10^{-5}$ s) in the excited state of fluorescence. In phosphorescence, there is a change in electron spin, which results in a longer lifetime of the excited state (second to minutes). Fluorescence and phosphorescence occurs at longer wavelength than the excitation radiation.

Fluorescence and phosphorescence



Jablonski Diagram

- The Jablonski diagram that drawn below is a partial energy diagram that represents the energy of photoluminescent molecule in its different energy states. The lowest and darkest horizontal line represents the ground-state electronic energy of the molecule which is the singlet state labeled as S_0 . At room temperature, majority of the molecules in a solution are in this state.

Jablonski Diagram

A Jablonski Diagram

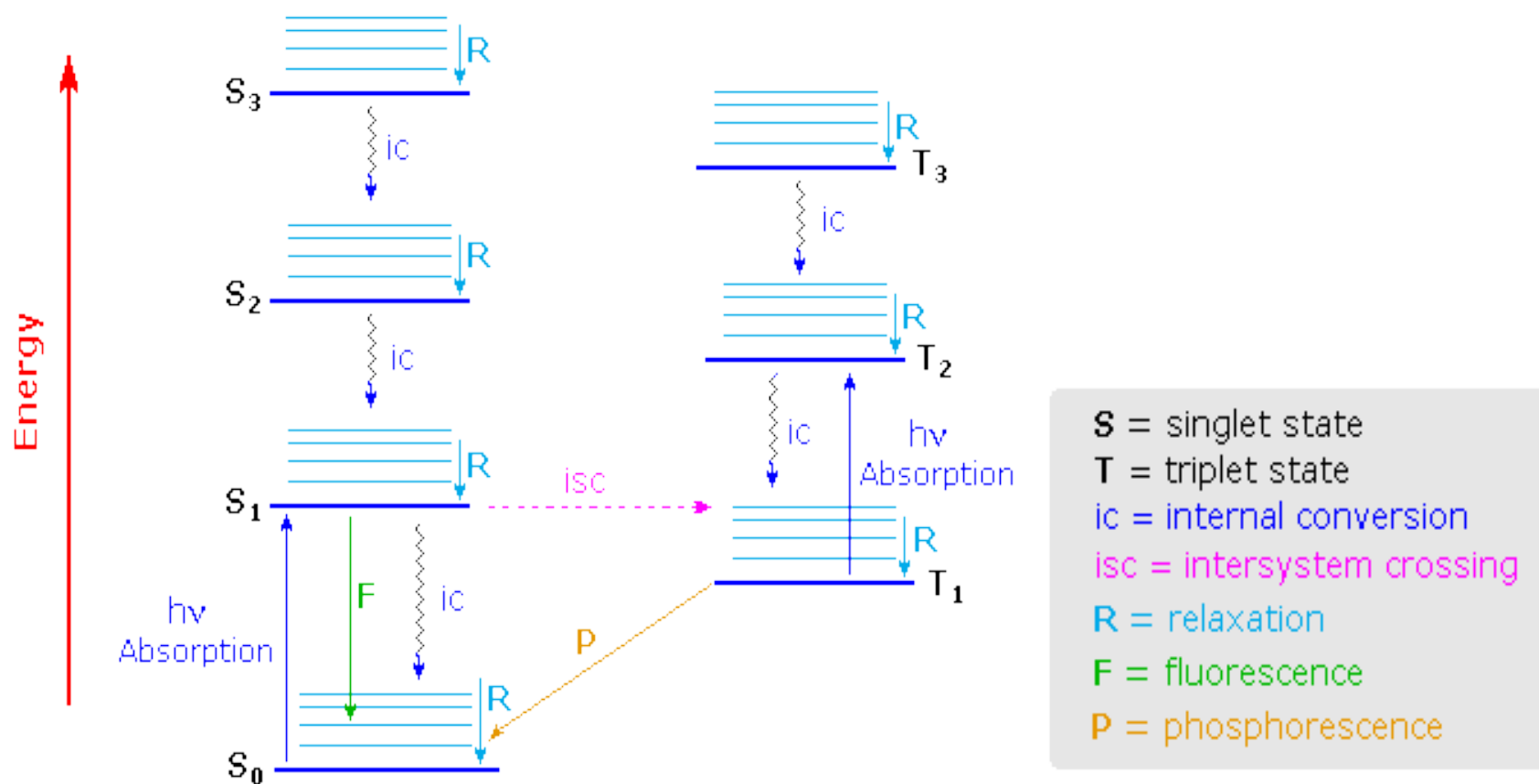


Photo Sensitization

- [Photosensitization](#) is a process of transferring the [energy](#) of absorbed light. After absorption, the energy is transferred to the (chosen) [reactants](#). This is part of the work of [photochemistry](#) in general. In particular this process is commonly employed where reactions require light sources of certain [wavelengths](#) that are not readily available.
- For example, [mercury](#) absorbs radiation at 1849 and 2537 [angstroms](#), and the source is often high-intensity [mercury lamps](#). It is a commonly used sensitizer. When mercury vapor is mixed with [ethylene](#), and the compound is [irradiated](#) with a mercury lamp, this results in the photodecomposition of ethylene to acetylene. This occurs on absorption of light to yield excited state mercury atoms, which are able to transfer this energy to the ethylene molecules, and are in turn deactivated to their initial energy state.
- [Cadmium](#); some of the [noble gases](#), for example [xenon](#); [zinc](#); [benzophenone](#); and a large number of organic dyes, are also used as sensitizers.
- [Photosensitisers](#) are a key component of [photodynamic therapy](#) used to treat cancers.

Sensitizer

- A **sensitizer** in [chemiluminescence](#) is a chemical compound, capable of [light emission](#) after it has received energy from a molecule, which became excited previously in the chemical reaction. A good example is this:
- When an alkaline solution of [sodium hypochlorite](#) and a concentrated solution of [hydrogen peroxide](#) are mixed, a reaction occurs:
- $\text{ClO}^-(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{O}_2^*(\text{g}) + \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{OH}^-(\text{aq})$ O_2^* is excited oxygen – meaning, one or more electrons in the O_2 molecule have been promoted to higher-energy [molecular orbitals](#). Hence, oxygen produced by this chemical reaction somehow 'absorbed' the energy released by the reaction and became excited. This energy state is unstable, therefore it will return to the [ground state](#) by lowering its energy. It can do that in more than one way:
- it can react further, without any light emission
- it can lose energy without emission, for example, giving off heat to the surroundings or transferring energy to another molecule
- it can emit light
- The intensity, duration and color of emitted light depend on [quantum](#) and [kinetical](#) factors. However, excited molecules are frequently less capable of light emission in terms of brightness and duration when compared to sensitizers. This is because sensitizers can store energy (that is, be excited) for longer periods of time than other excited molecules. The energy is stored through means of [quantum vibration](#), so sensitizers are usually compounds which either include systems of [aromatic](#) rings or many conjugated double and triple [bonds](#) in their structure. Hence, if an excited molecule transfers its energy to a sensitizer thus exciting it, longer and easier to quantify light emission is often observed.
- The color (that is, the [wavelength](#)), brightness and duration of emission depend upon the sensitizer used. Usually, for a certain chemical reaction, many different sensitizers can be used.

Actinometers

- **Actinometers** are instruments used to measure the heating power of radiation. They are used in meteorology to measure solar radiation as pyranometers, pyrheliometers and net radiometers.
- An actinometer is a chemical system or physical device which determines the number of photons in a beam integrally or per unit time. This name is commonly applied to devices used in the ultraviolet and visible wavelength ranges. For example, solutions of iron(III) oxalate can be used as a chemical actinometer, while bolometers, thermopiles, and photodiodes are physical devices giving a reading that can be correlated to the number of photons detected.

Norrish Type 1 and 2 Reactions

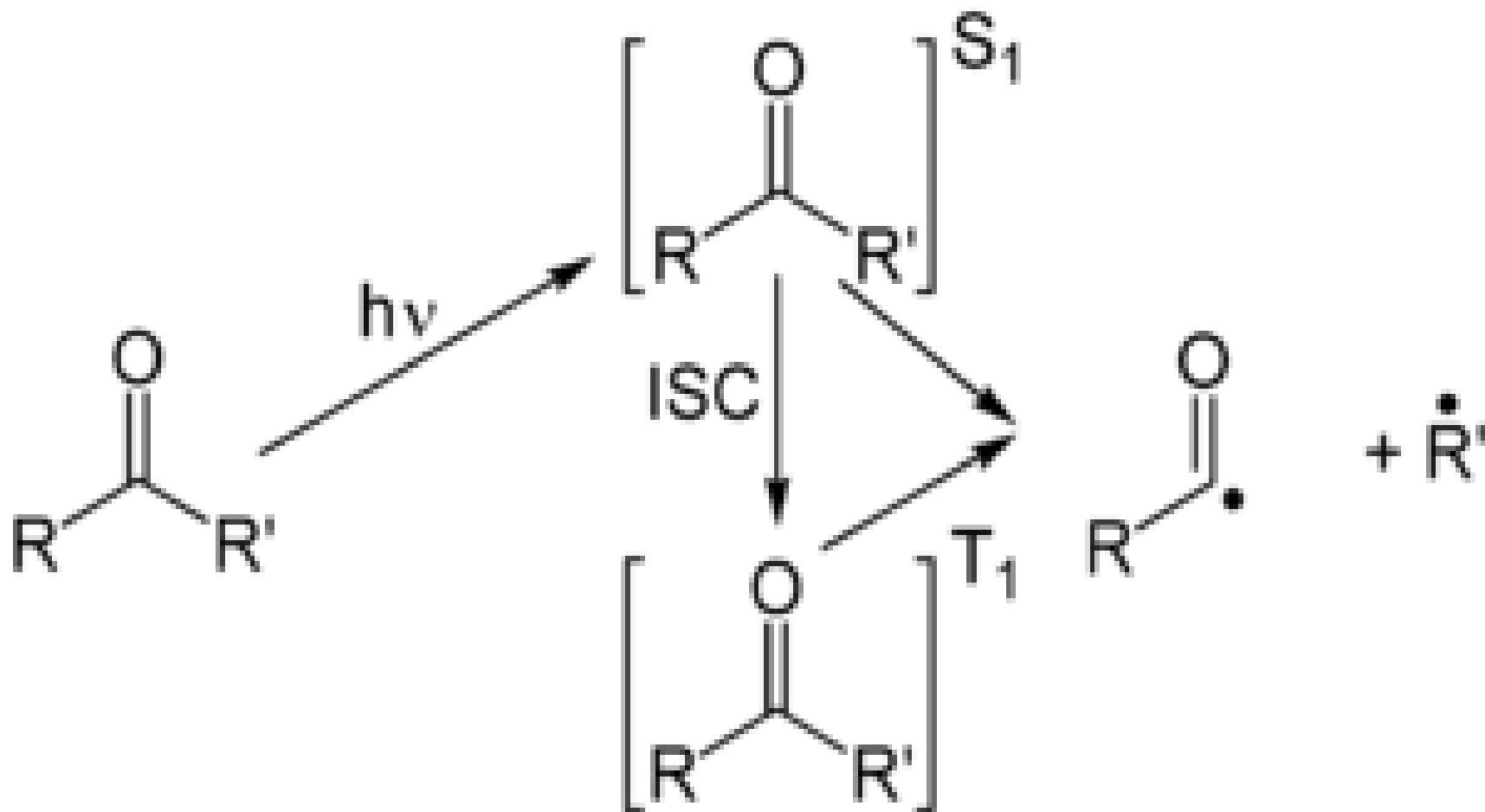
- The **Norrish reaction** in organic chemistry describes the photochemical reactions taking place with ketones and aldehydes.
- This type of reaction is subdivided in **Norrish type I reactions** and **Norrish type II reactions**.
- The reaction is named after Ronald George Wreyford Norrish.

Norrish type I reaction

- The Norrish type I reaction is the photochemical cleavage or homolysis of aldehydes and ketones into two free radical intermediates. The carbonyl group accepts a photon and is excited to a photochemical singlet state. Through intersystem crossing the triplet state can be obtained. On cleavage of the α -carbon bond from either state, two radical fragments are obtained. The size and nature of these fragments depends upon the stability of the generated radicals; for instance, the cleavage of 2-butanone largely yields ethyl radicals in favor of less stable methyl radicals.

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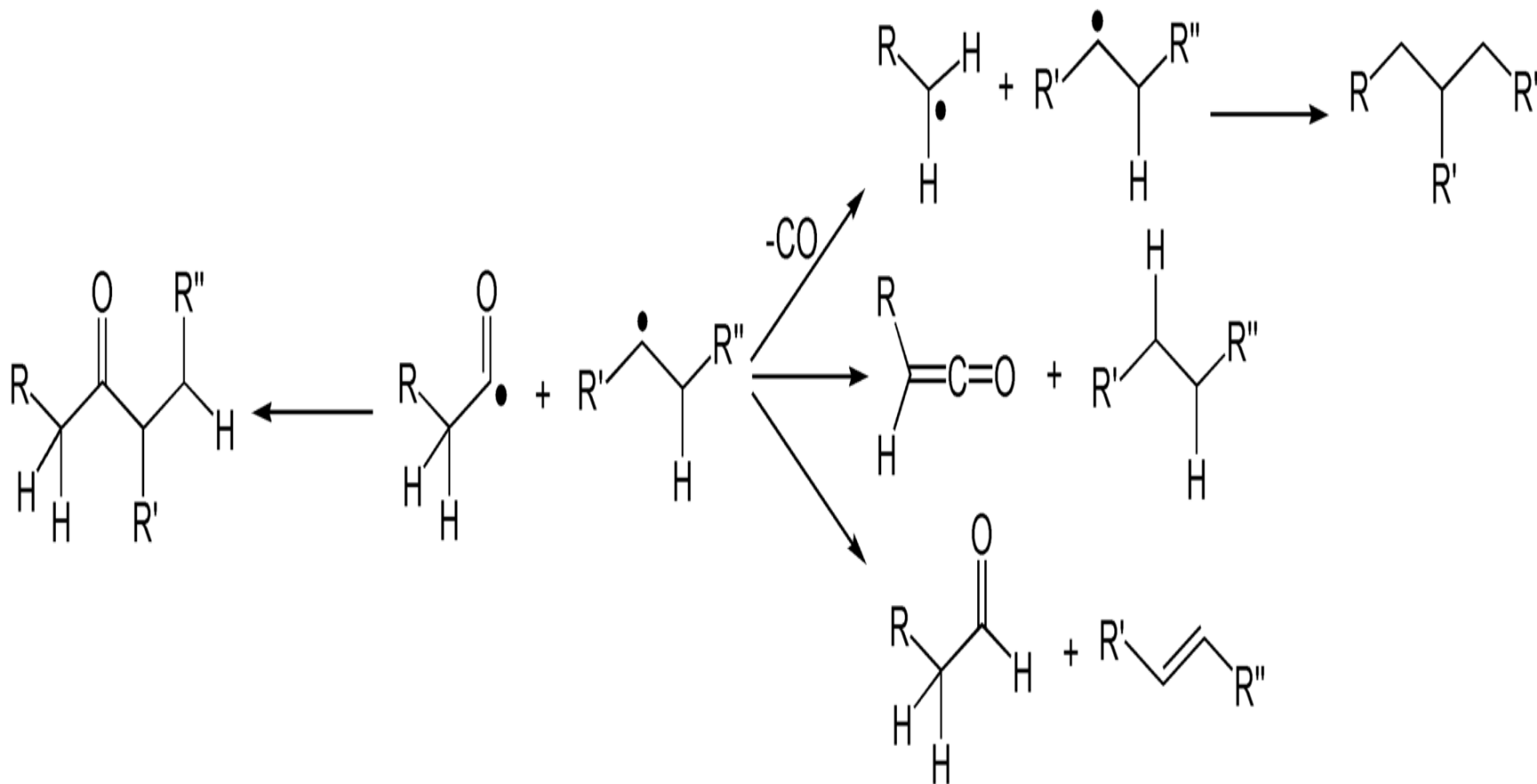
Norrish type 1 reaction



Norrish type 1 reaction

- Several secondary reaction modes are open to these fragments depending on the exact molecular structure.
- The fragments can simply recombine to the original carbonyl compound, with [racemisation](#) at the α -carbon.
- The acyl radical can lose a molecule of [carbon monoxide](#), forming a new carbon radical at the other α -carbon, followed by formation of a new carbon–carbon bond between the radicals. The ultimate effect is simple extraction of the carbonyl unit from the carbon chain. The rate and yield of this product depends upon the [bond-dissociation energy](#) of the ketone's [\$\alpha\$ substituents](#). Typically the more α substituted a ketone is, the more likely the reaction will yield products in this way.
- The abstraction of an α -[proton](#) from the carbonyl fragment may form a [ketene](#) and an alkane.
- The abstraction of a β -proton from the alkyl fragment may form an [aldehyde](#) and an [alkene](#).

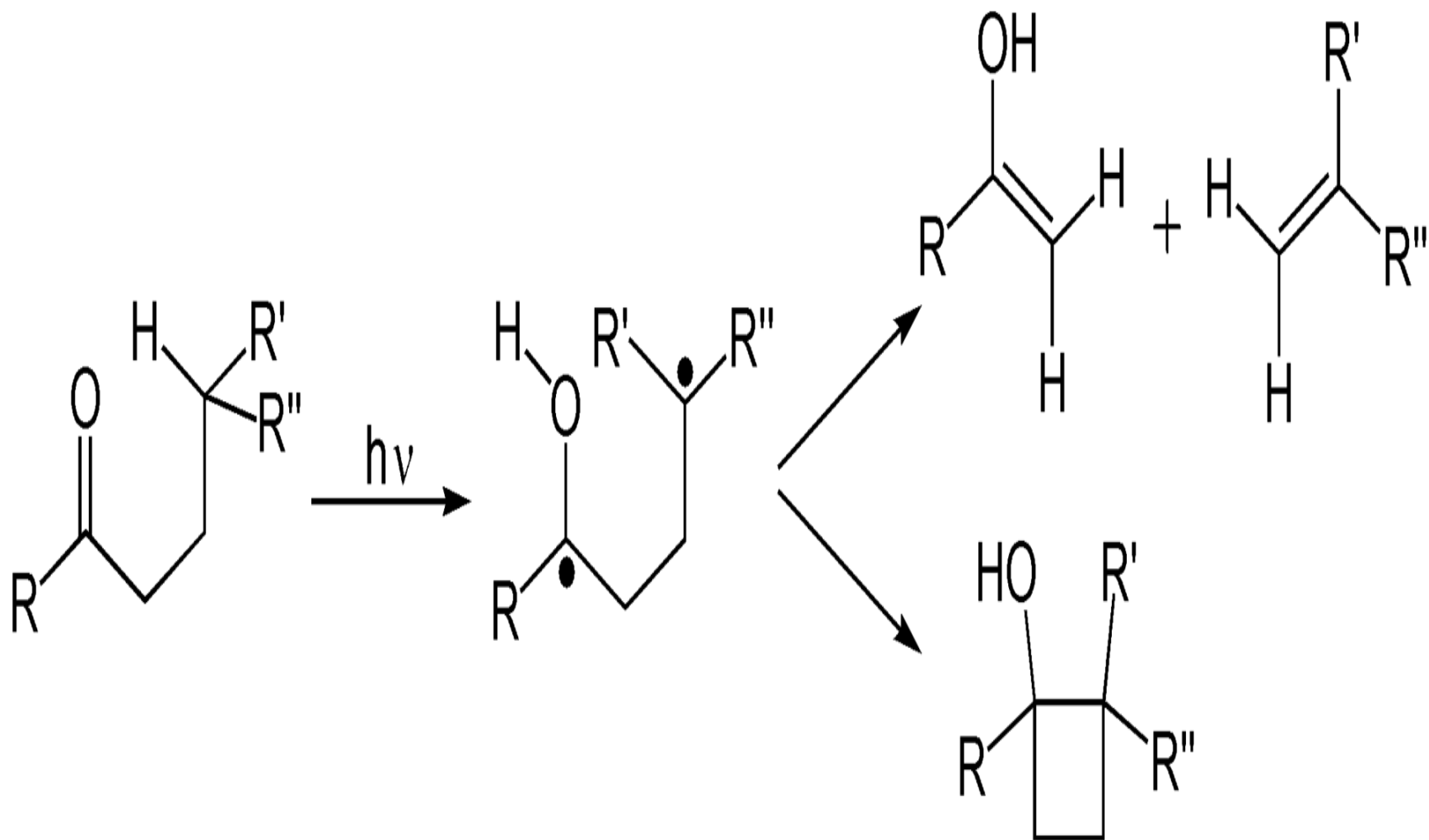
Norrish type 1 Reaction



Norrish Type 2 Reaction

- A Norrish type II reaction is the photochemical intramolecular abstraction of a γ -hydrogen (a hydrogen atom three carbon positions removed from the carbonyl group) by the excited carbonyl compound to produce a 1,4-biradical as a primary photoproduct. Norrish first reported the reaction in 1937.

Norrish type 2 Reaction



Assignment and set of questions

- Q1. What do you understand by photochemistry?
- Q2. What are the types of photo chemical reactions?
- Q3. What are the differences between photochemical and thermal reactions?
- Q4. State and explain Grothous Draper's law
- Q5. State and explain Stark's Einstien's law.
- Q6. What do you understand by quantum yield?

Assignment and set of questions

- Q7. Explain low and high quantum yield.
- Q8. State and explain Beer Lambert's Law
- Q9. Differentiate between fluorescence and phosphorescence
- Q10. What do you understand by internal conversion and intersystem crossing?
- Q11. Draw and explain Jablonski diagram.
- Q12.

Assignment and set of questions

- Q13 What is photo sensitization? Write a note on sensitizers.
- Q14.What are actinometers?
- Q15.Write short note on :
 - Norrish type 1 reaction and
 - Norrish type 2 reaction

- Best of Luck

Physical properties and Molecular Structure, B.Sc. III year, Paper I

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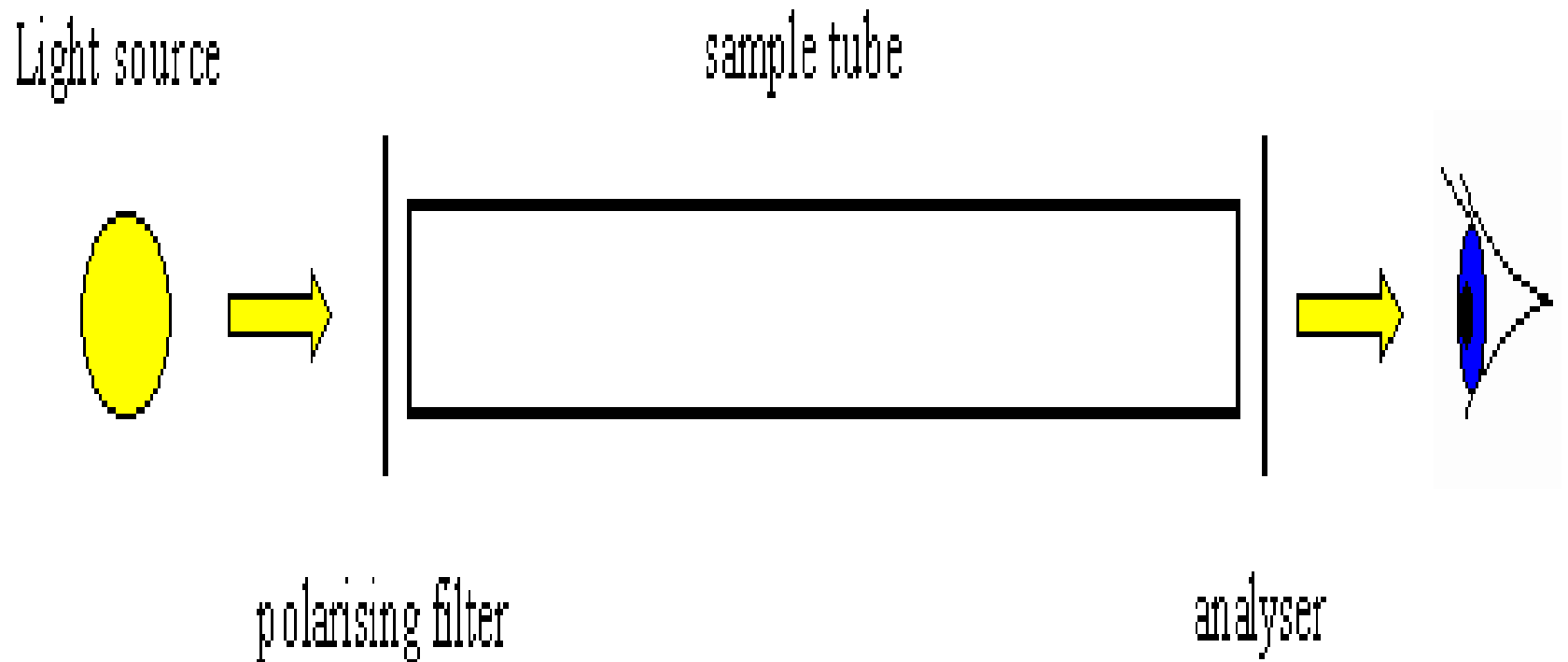
This Presentation Includes

- Optical activity
- Polari meter
- Measuring Optical Activity: Enantiomers
- Optical Activity: Areas of Use
- Clausius–Mossotti equation
- Lorentz–Lorenz equation
- Dipole Moment
- Dipole Moment: Examples
- Dipole Moment: Formula
- Debye Equation
- Magnetic Moment
- Magnetic Susceptibility
- Types of Magnetic materials

Optical Activity

- **Optical activity** is the ability of a chiral molecule to rotate the plane of plane-polarised light, measured using a **polarimeter**.
- A simple polarimeter consists of a light source, polarising lens, sample tube and analysing lens.
- When light passes through a sample that can rotate plane polarised light, the light appears to dim because it no longer passes straight through the polarising filters. The amount of rotation is quantified as the number of degrees that the analysing lens must be rotated by so that it appears as if no dimming of the light has occurred.

Optical Activity: Polari meter



Measuring Optical Activity

- When rotation is quantified using a polarimeter it is known as an **observed rotation**, because rotation is affected by path length (l , the time the light travels through a sample) and concentration (c , how much of the sample is present that will rotate the light). When these effects are eliminated a standard for comparison of all molecules is obtained, the **specific rotation**, $[\alpha]$.
- $[\alpha] = 100 \alpha / cl$ when concentration is expressed as g sample /100ml solution

Optical Activity: Enantiomers

- Enantiomers will rotate the plane of polarization in exactly equal amounts (same magnitude) but in opposite directions.
- **Dextrorotary** designated as *d* or (+), clockwise rotation (to the right)
Levorotary designated as *l* or (-), anti-clockwise rotation (to the left) If only one enantiomer is present a sample is considered to be **optically pure**.
- When a sample consists of a mixture of enantiomers, the effect of each enantiomer cancels out, molecule for molecule.

Optical Activity: Areas of use

- For a pure substance in solution, if the color and path length are fixed and the [specific rotation](#) is known, the observed rotation can be used to calculate the concentration. This usage makes a [polar meter](#) a tool of great importance to those trading in or using sugar syrups in bulk.
- In the presence of an applied [magnetic field](#), it is possible for samples of all compounds to exhibit optical activity. A magnetic field aligned in the direction of light propagating through a material will cause the rotation of the plane of linear polarization. This [Faraday effect](#) is one of the first discoveries of the relationship between light and electromagnetic effects.

Clausius–Mossotti equation

- The **Clausius–Mossotti relation** expresses the dielectric constant (relative permittivity, ϵ_r) of a material in terms of the atomic polarizability, α , of the material's constituent atoms and/or molecules, or a homogeneous mixture thereof. It is named after Ottaviano-Fabrizio Mossotti and Rudolf Clausius. It is equivalent to the Lorentz–Lorenz equation. It may be expressed as:

Polarization of nonpolar liquids

- The molar polarization P_i ($\text{m}^3\text{mol}^{-1}$) is defined by the Clausius-Mossotti equation as

$$P_i = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho}$$

- Where:
 - M is the molar mass (molecular weight) in kgmol^{-1}
 - ϵ is the dielectric constant
 - ρ is the density (in kgm^{-3}).

Lorentz–Lorenz equation

- The **Lorentz–Lorenz equation** is similar to the Clausius–Mossotti relation, except that it relates the refractive index (rather than the dielectric constant) of a substance to its polarizability. The Lorentz–Lorenz equation is named after the Danish mathematician and scientist Ludvig Lorenz, who published it in 1869, and the Dutch physicist Hendrik Lorentz, who discovered it independently in 1878.

Lorentz–Lorenz equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N \alpha_m$$

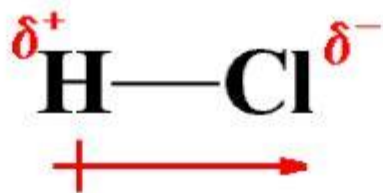
The Lorentz–Lorenz equation is similar to the Clausius–Mossotti relation, except that it relates the refractive index (rather than the dielectric constant) of a substance to its polarizability.

Dipole moment

- A dipole moment arises in any system in which there is a separation of charge. They can, therefore, arise in ionic bonds as well as in covalent bonds. Dipole moments occur due to the difference in electronegativity between two chemically bonded atoms.
- A bond dipole moment is a measure of the polarity of a chemical bond between two atoms in a molecule. It involves the concept of electric dipole moment, which is a measure of the separation of negative and positive charges in a system.

Dipole Moment

- The bond dipole moment is a vector quantity since it has both magnitude and direction. An illustration describing the dipole moment that arises in an HCl ([hydrochloric acid](#)) molecule is provided below



**Dipole Moment has a
Magnitude and a Direction**

Dipole Moment

- **Important Points**
- The dipole moment of a single bond in a polyatomic molecule is known as the bond dipole moment and it is different from the dipole moment of the molecule as a whole.
- It is a vector quantity, i.e. it has magnitude as well as definite directions.
- Being a vector quantity, it can also be zero as the two oppositely acting bond dipoles can cancel each other.
- By convention, it is denoted by a small arrow with its tail on the negative center and its head on the positive center.
- In chemistry, the dipole moment is represented by a slight variation of the arrow symbol. It is denoted by a cross on the positive center and arrowhead on the negative center. This arrow symbolizes the shift of electron density in the molecule.
- In the case of a polyatomic molecule, the dipole moment of the molecule is the vector sum of the all present bond dipoles in the molecule.

Dipole Moment Formula

- A dipole moment is the product of the magnitude of the charge and the distance between the centers of the positive and negative charges. It is denoted by the Greek letter ' μ '.
- Mathematically,
- **Dipole Moment (μ) = Charge (Q) * distance of separation (r)**
- It is measured in Debye units denoted by 'D'. $1 \text{ D} = 3.33564 \times 10^{-30} \text{ C.m}$, where C is Coulomb and m denotes a meter.
- The bond dipole moment that arises in a chemical bond between two atoms of different electronegativities can be expressed as follows:
- **$\mu = \delta.d$**
- Where: μ is the bond dipole moment,
- δ is the magnitude of the partial charges δ^+ and δ^- ,
- And d is the distance between δ^+ and δ^- .

Dipole Moment

- The bond dipole moment (μ) is also a vector quantity, whose direction is parallel to the bond axis. In chemistry, the arrows that are drawn in order to represent dipole moments begin at the positive charge and end at the negative charge.
- When two atoms of varying electronegativities interact, the electrons tend to move from their initial positions to come closer to the more electronegative atom. This movement of electrons can be represented via the bond dipole moment.

Example: Dipole moment of BeF_2

- In a beryllium fluoride molecule, the bond angle between the two beryllium-fluorine bonds is 180° . Fluorine, being the more electronegative atom, shifts the electron density towards itself. The individual bond dipole moments in a BeF_2 molecule are illustrated below.



Bonds Diploes in BeF_2

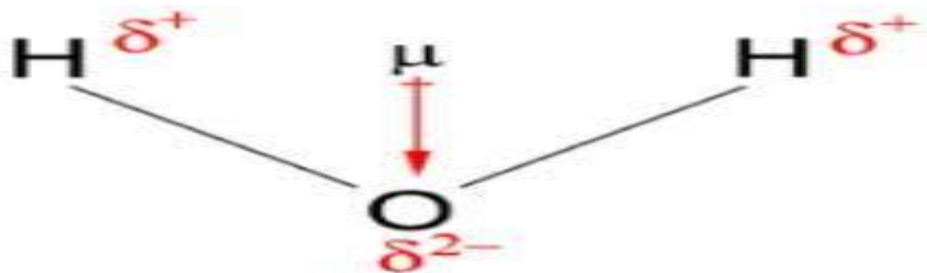


Total Bond Moment in BeF_2

Example: Dipole moment of H₂O (Water)

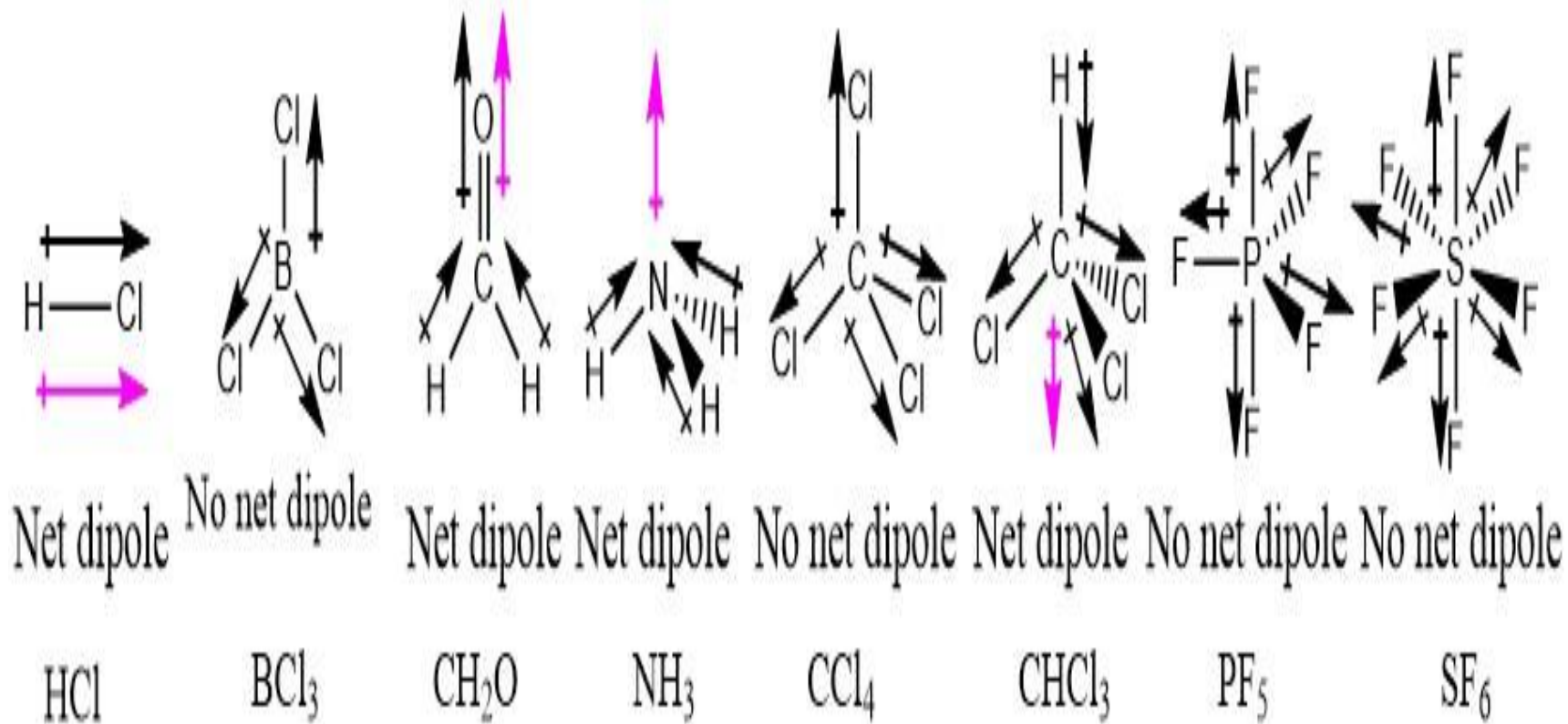
- In a water molecule, the electrons are localized around the oxygen atom since it is much more electronegative than the hydrogen atom. However, the presence of a lone pair of electrons in the oxygen atom causes the water molecule to have a bent shape (as per the [VSEPR theory](#)). Therefore, the individual bond dipole moments do not cancel each other out as is the case in the BeF₂ molecule. An illustration describing the dipole moment in a water molecule is provided below.

Example: Dipole moment of H₂O (Water)

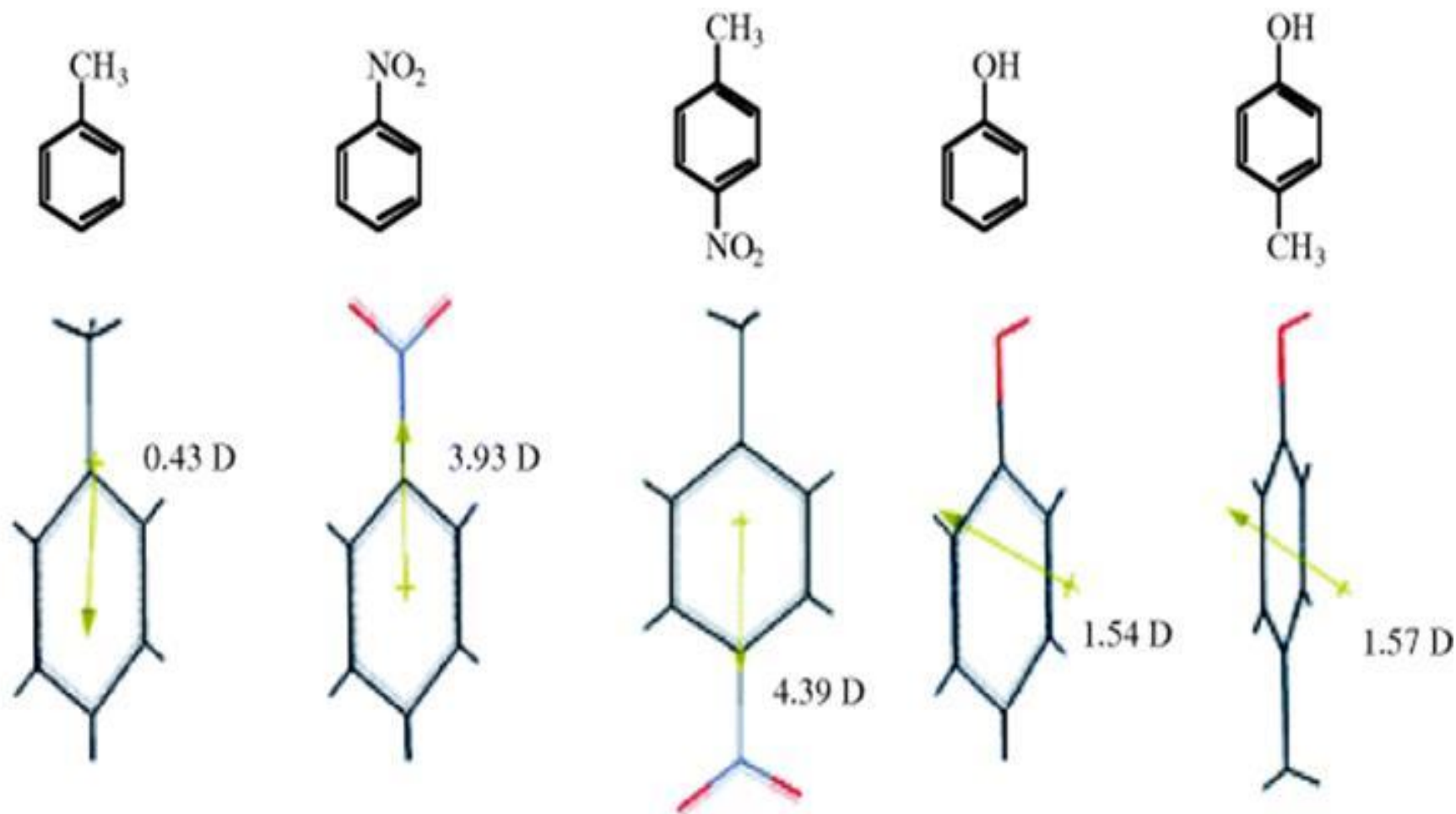


The bond angle in a water molecule is 104.5°. The individual bond moment of an oxygen-hydrogen bond is 1.5 D. The net dipole moment in a water molecule is found to be 1.84D

More Examples: Dipole Moment



More Examples : Dipole Moment



Measurement of Dipole Moment :Relative Permittivity, Polarization, and Polarizability

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = P_E + P_V + P_O = \frac{N_A}{3\epsilon_0} \left(\alpha_e + \alpha_v + \frac{\mu^2}{3kT} \right)$$

Debye Equation

This is generally called the Debye equation. It was the first relationship that made the connection between the *molecular parameter* of the substance being tested and the *phenomenological (macroscopic)* parameter that can be experimentally measured.

Using the molar polarization $[P]$, defined by (2.57)

$$[P] = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d}$$

we can write the *Debye equation* for a pure compound as:

$$[P] = \frac{4\pi}{3} N_A \left(\alpha + \frac{\mu^2}{3kT} \right) \quad (3.2)$$

Thus, according to the *Debye equation*, the molar polarization of a compound at a given temperature *is constant*. It must be independent of the pressure and have the same value in gaseous and the liquid state.

Magnetic Moment

$$\mu_{\text{so}} = \sqrt{4S(S+1)}$$

$$\mu_{\text{S+L}} = \sqrt{4S(S+1) + L(L+1)}$$

$$\mu_{\text{eff}} = \mu_{\text{so}} \left(1 - \frac{\alpha \lambda}{\Delta} \right)$$

Magnetic Susceptibility

- Magnetic susceptibility is a dimensionless proportionality constant that indicates the degree of magnetization of a material in response to an applied magnetic field. It is caused by interactions of electrons and nuclei with the externally applied magnetic field.
- What is Magnetic Susceptibility?
- *In electromagnetism, magnetic susceptibility is defined as:*
- The measures of how much a material will be magnetized in an applied magnetic field.
- *It is denoted by χ .*
- Magnetic Susceptibility Formula
- The mathematical definition of magnetic susceptibility is the ratio of magnetization to applied magnetizing field intensity. This is a dimensionless quantity.
- $\chi = M/H$
- *Where,*
- **χ** : magnetic susceptibility
- **M** : magnetization
- **H** : field intensity

Types of Magnetic Materials

- *With the help of magnetic susceptibility, magnetic materials can be classified as:*
- **Paramagnetic material:** Magnetic materials which align with the magnetic field are known as paramagnetic materials. Magnetic susceptibility is $\chi > 0$ which means it is always a small positive value for paramagnetic materials. These materials are temperature dependent and are weakly attracted by magnets with relative permeability 1.00001 to 1.003. Alkaline earth metal, aluminium, oxygen etc are some of the examples of paramagnetic materials.

Types of Magnetic Materials

- **Diamagnetic material:** Magnetic materials which align against the magnetic field are known as diamagnetic materials. Magnetic susceptibility is $\chi < 0$ which means it is always a negative value for diamagnetic material. These materials are repelled by the magnets and they move from a stronger field to a weaker field. These materials are independent of temperature. As these materials magnetize in the opposite direction, they do have a small amount of magnetization intensity. Gold, tin, mercury, water, etc are examples of diamagnetic materials. Diamagnetic materials have a constant relative permeability.

Types of Magnetic Materials

- **Ferromagnetic material:** Magnetic materials that are highly magnetized in a magnetic field are known as ferromagnetic materials. These are highly attracted by the magnets and move from weaker fields to stronger fields. Ferromagnetic materials do not have a constant relative permeability and vary from 1000 to 100000. Magnetic susceptibility is very high and positive and depends on the applied field. Iron, cobalt, nickel and their alloys are examples of ferromagnetic materials.

Assignment/ Set of Questions

- Q1. What do you understand by optical activity?
- Q2. What are Enantiomers?
- Q3. Explain the construction of polar meter
- Q4. Define optical activity and its areas of uses.
- Q5. Write and explain Clausius–Mossotti equation
- Q6. Write and explain Lorentz–Lorenz equation.
- Q7. What do you understand by Dipole Moment?
- Q8. What is the formula for dipole moment? What is its unit?
- Q9. How can you correlate dipole moment with the structure of any compound.

Assignment / Set of Questions

Q10. Which of the following molecules will have the permanent dipole moment and why?

Water, boron tri fluoride, carbon mono oxide, carbon di oxide, ammonia, sulfur tri oxide, benzene, m- di nitro benzene

Q11. Explain the measurement of dipole moment.

Q12. What do you understand by magnetic moment?

Q13. What is magnetic susceptibility?

Q14. Write and Explain Debye equation.

Q15. Write a note on the following: (i) Diamagnetism (ii) paramagnetism (iii) Ferromagnetism

- Best of Luck