Computer Applications in Chemistry- Part III (M.Sc. II sem. Chemistry)

INTERNET AND ITS USES

By

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Networking

- A **computer network** or **data network** is a telecommunications network that allows computers to exchange data.
- In computer networks, networked computing devices pass data to each other along data connections.
- Data is transferred in the form of packets.
- The connections (network links) between nodes are established using either cable media or wireless media.
- The best-known computer network is the Internet.

Personal area network

- A personal area network (PAN) is a computer network used for communication among computer and different information technological devices close to one person.
- Some examples of devices that are used in a PAN are personal computers, printers, fax machines, telephones, PDAs, scanners, and even video game consoles.
- A PAN may include wired and wireless devices.
- The reach of a PAN typically extends to 10 meters.
- A wired PAN is usually constructed with USB and FireWire connections while technologies such as Bluetooth and infrared communication typically form a wireless PAN.

Local area network

- A local area network (LAN) is a network that connects computers and devices in a limited geographical area such as a home, school, office building, or closely positioned group of buildings.
- Each computer or device on the network is a node.
- Wired LANs are most likely based on Ethernet technology.
- Newer standards such as ITU-T G.hn also provide a way to create a wired LAN using existing wiring, such as coaxial cables, telephone lines, and power lines

Metropolitan area network

- A Metropolitan area network (MAN) is a large computer network that usually spans a city or a large campus.

Wide area network

- A wide area network (WAN) is a computer network that covers a large geographic area such as a city, country, or spans even intercontinental distances.
- A WAN uses a communications channel that combines many types of media such as telephone lines, cables, and air waves.
- A WAN often makes use of transmission facilities provided by common carriers, such as telephone companies.

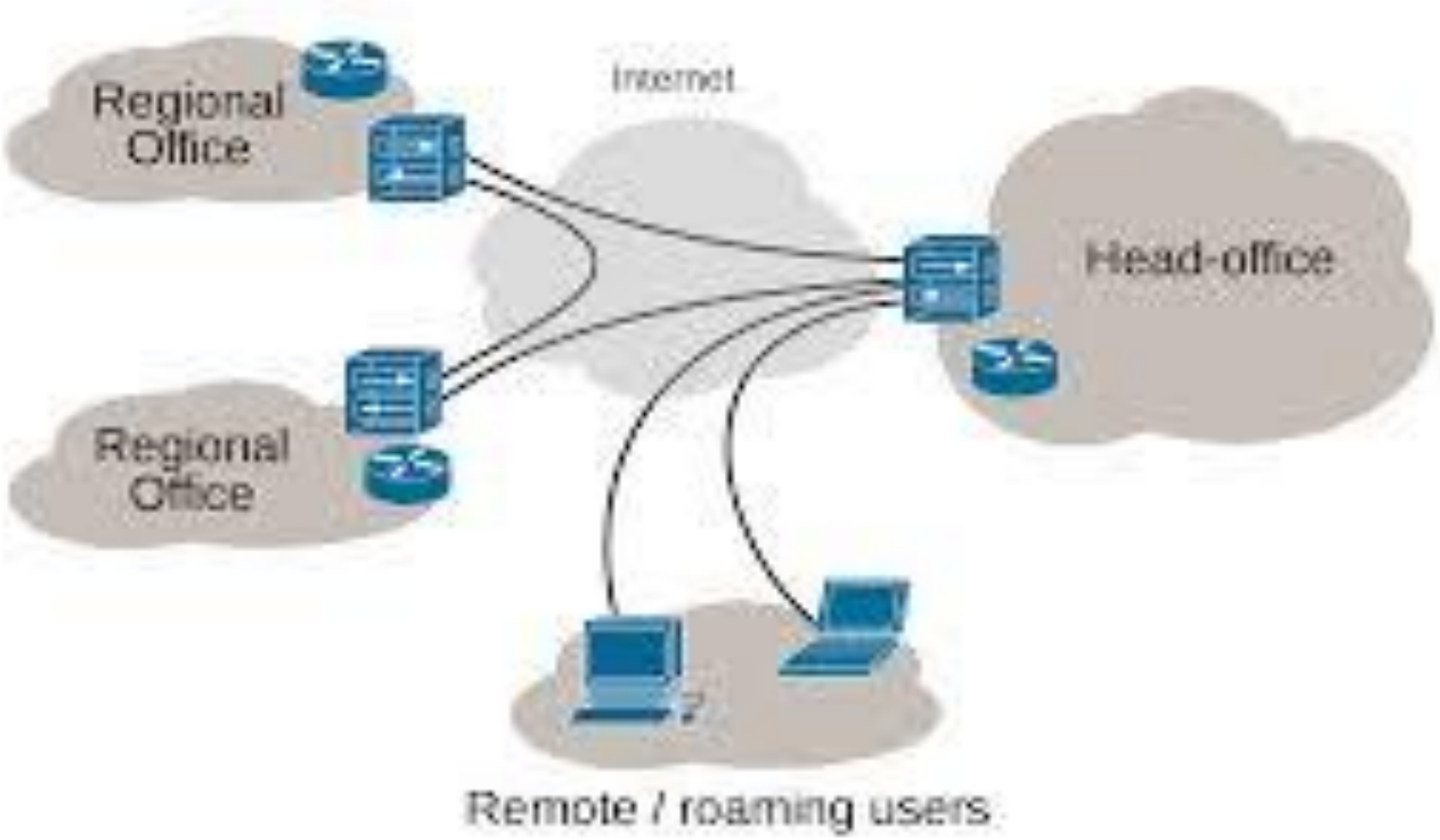
Enterprise private network

- An enterprise private network is a network that a single organization builds to interconnect its office locations (e.g., production sites, head offices, remote offices, shops) so they can share computer resources.

Virtual private network

- A virtual private network (VPN) is an overlay network in which some of the links between nodes are carried by open connections or virtual circuits in some larger network (e.g., the Internet) instead of by physical wires.
- The data link layer protocols of the virtual network are said to be tunneled through the larger network when this is the case.
- One common application is secure communications through the public Internet, but a VPN need not have explicit security features, such as authentication or content encryption.
- VPNs, for example, can be used to separate the traffic of different user communities over an underlying network with strong security features.

Internet VPN



Global area network

- A global area network (GAN) is a network used for supporting mobile across an arbitrary number of wireless LANs, satellite coverage areas, etc.
- The key challenge in mobile communications is handing off user communications from one local coverage area to the next.

Campus area network

- A campus area network (CAN) is made up of an interconnection of LANs within a limited geographical area.
- The networking equipment (switches, routers) and transmission media (optical fiber, copper plant, Cat5 cabling, etc.) are almost entirely owned by the campus tenant / owner (an enterprise, university, government, etc.).
- For example, a university campus network is likely to link a variety of campus buildings to connect academic colleges or departments, the library, and student residence halls.

Storage area network

- A storage area network (SAN) is a dedicated network that provides access to consolidated, block level data storage.
- SANs are primarily used to make storage devices, such as disk arrays, tape libraries, and optical jukeboxes, accessible to servers so that the devices appear like locally attached devices to the operating system.
- A SAN typically has its own network of storage devices that are generally not accessible through the local area network by other devices.
- The cost and complexity of SANs dropped in the early 2000s to levels allowing wider adoption across both enterprise and small to medium sized business environments.

Home area network

- A home area network (HAN) is a residential LAN used for communication between digital devices typically deployed in the home, usually a small number of personal computers and accessories, such as printers and mobile computing devices.
- An important function is the sharing of Internet access, often a broadband service through a cable TV or digital subscriber line(DSL) provider.

Intranet

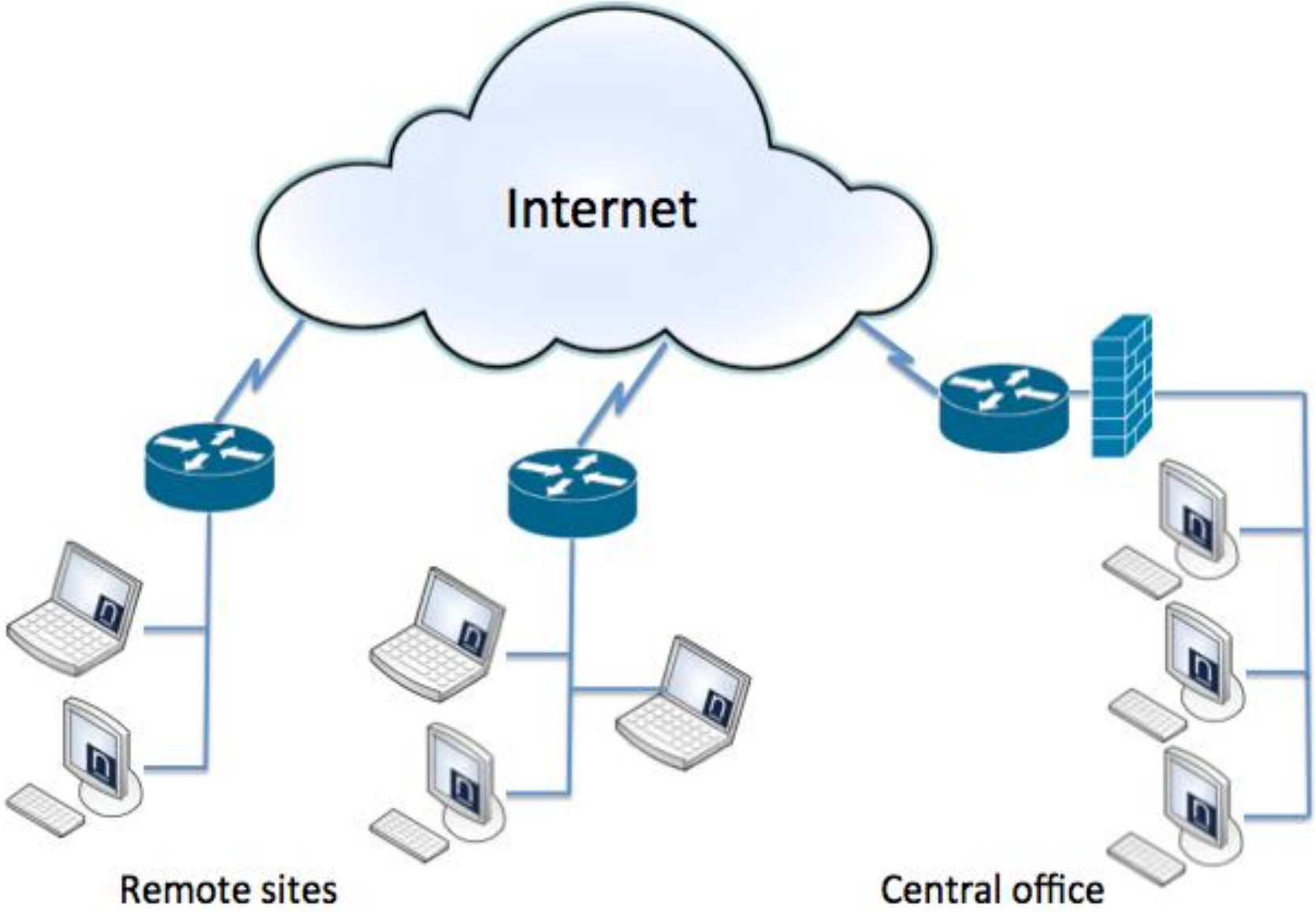
- An intranet is a set of networks that are under the control of a single administrative entity.
- The intranet uses the IP protocol and IP-based tools such as web browsers and file transfer applications.
- The administrative entity limits use of the intranet to its authorized users.
- Most commonly, an intranet is the internal LAN of an organization.
- A large intranet typically has at least one web server to provide users with organizational information.
- An intranet is also anything behind the router on a local area network.

Extranet

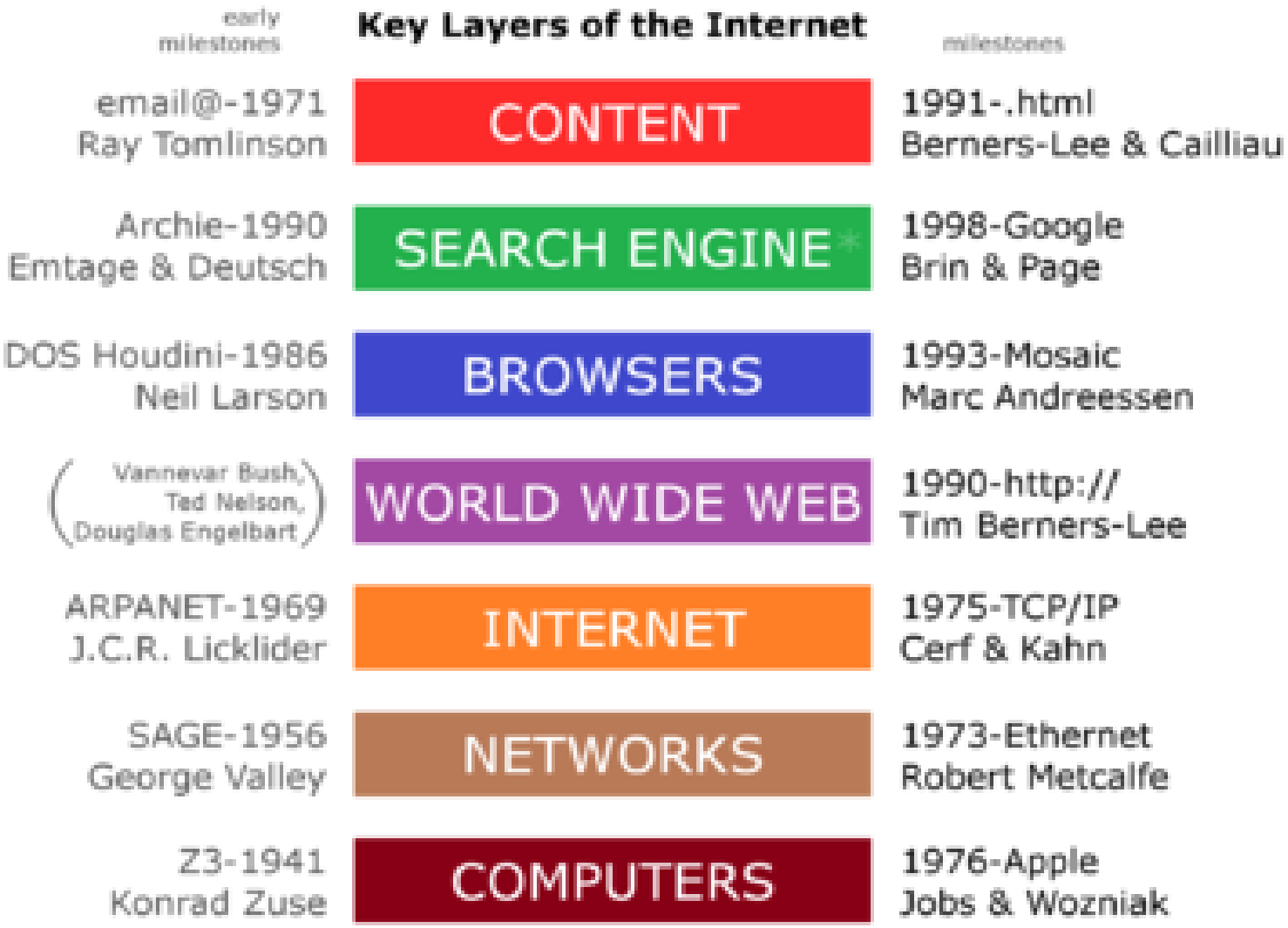
- An extranet is a network that is also under the administrative control of a single organization, but supports a limited connection to a specific external network.
- For example, an organization may provide access to some aspects of its intranet to share data with its business partners or customers.
- These other entities are not necessarily trusted from a security standpoint. Network connection to an extranet is often, but not always, implemented via WAN technology.

Internet

- The Internet is the largest example of an internetwork.
- It is a global system of interconnected governmental, academic, corporate, public, and private computer networks.
- It is based on the networking technologies of the Internet Protocol Suite.
- It is the successor of the Advanced Research Projects Agency Network (ARPANET) developed by DARPA of the United States Department of Defense.
- The Internet is also the communications backbone underlying the World Wide Web (WWW).
- Participants in the Internet use a diverse array of methods of several hundred documented, and often standardized, protocols compatible with the Internet Protocol Suite and an addressing system (IP addresses) administered by the Internet Assigned Numbers Authority and address registries.
- Service providers and large enterprises exchange information about the reach ability of their address spaces through the Border Gateway Protocol (BGP), forming a redundant worldwide mesh of transmission paths.


Internet
Remote sites
Central office

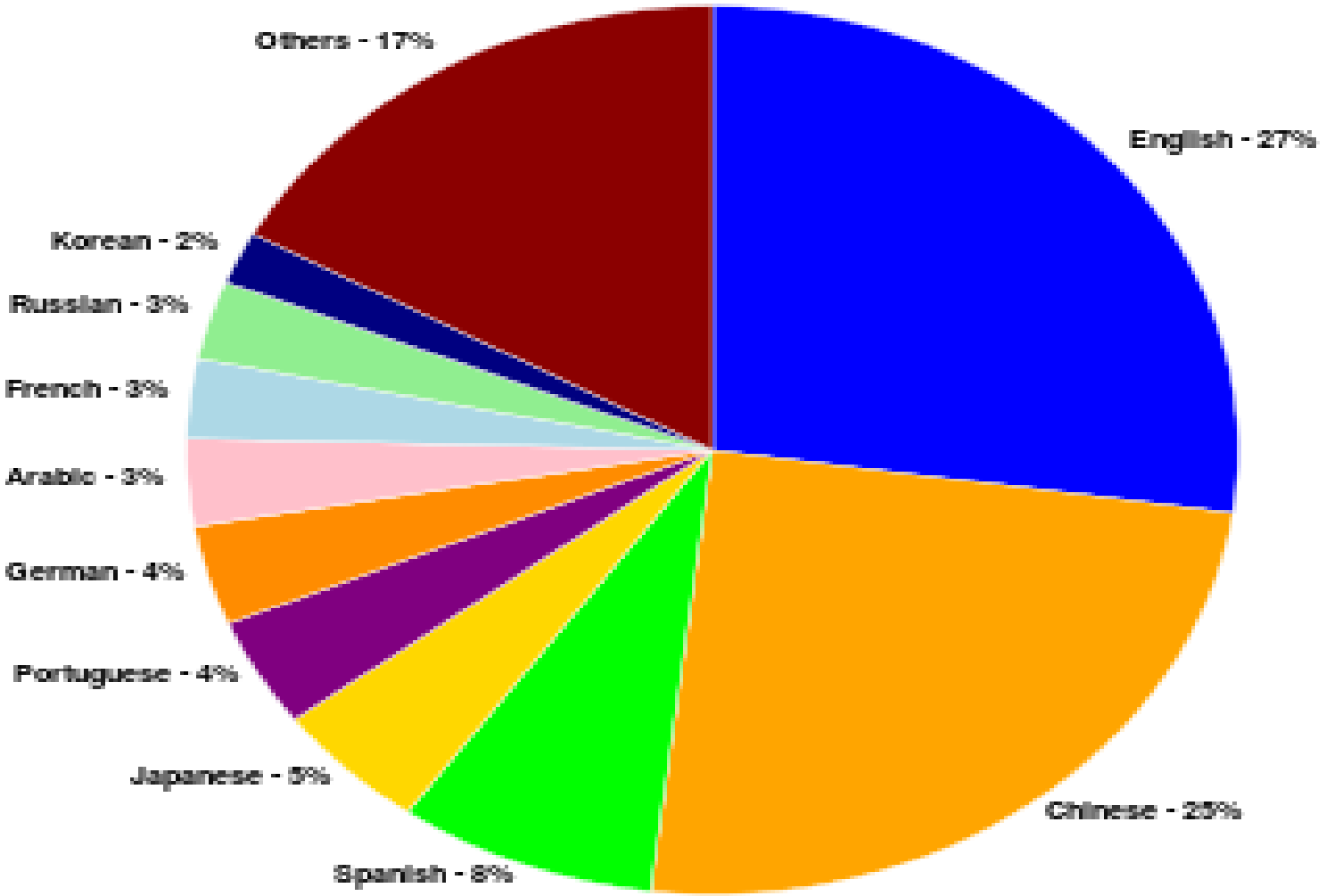
Kev lavers of the Internet



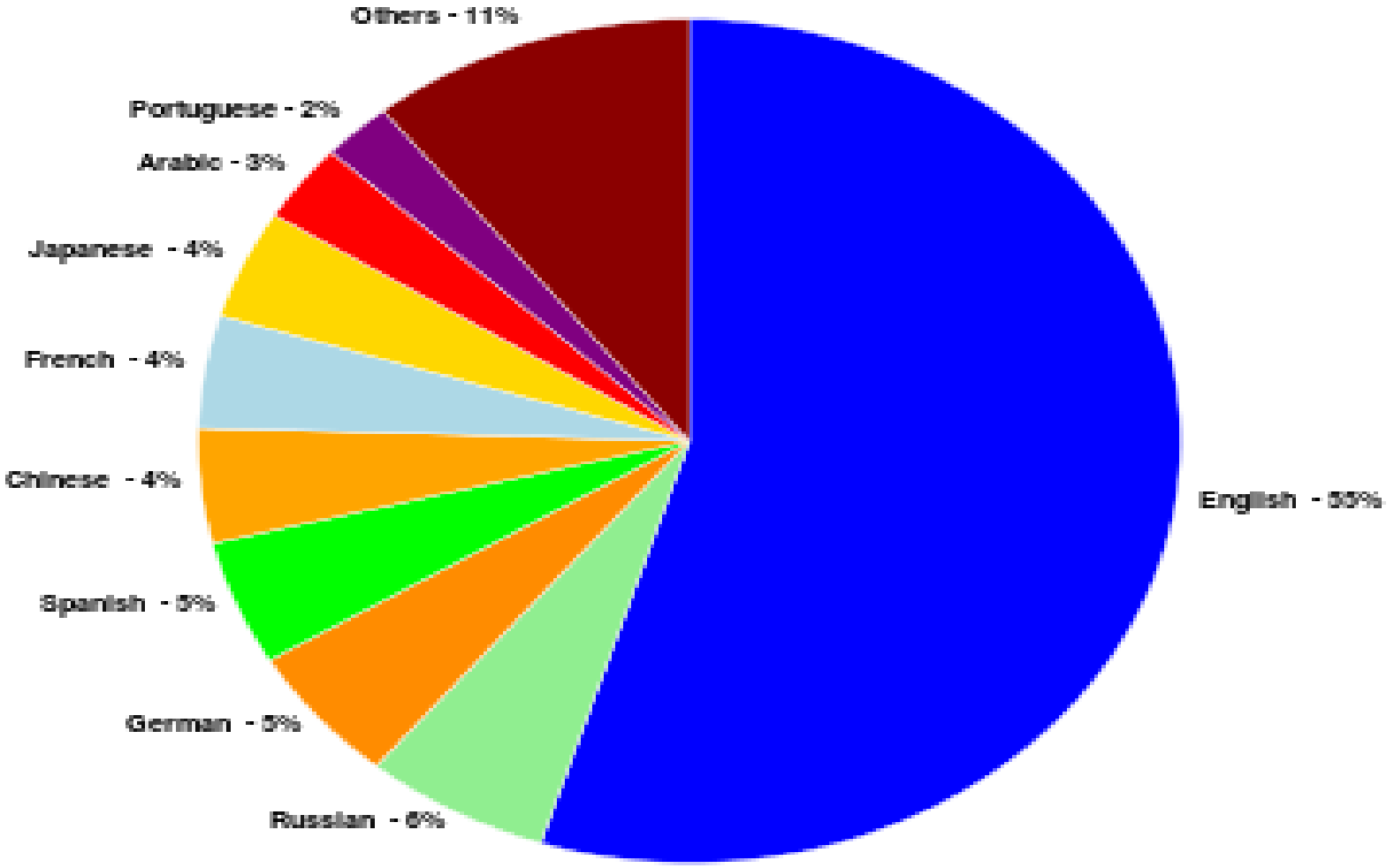
World wide internet users

	2005	2010	2013
World population[	6.5 billion	6.9 billion	7.1 billion
Not using the Internet	84%	70%	61%
Using the Internet	16%	30%	39%
Users in the developing world	8%	21%	31%
Users in the developed world	51%	67%	77%

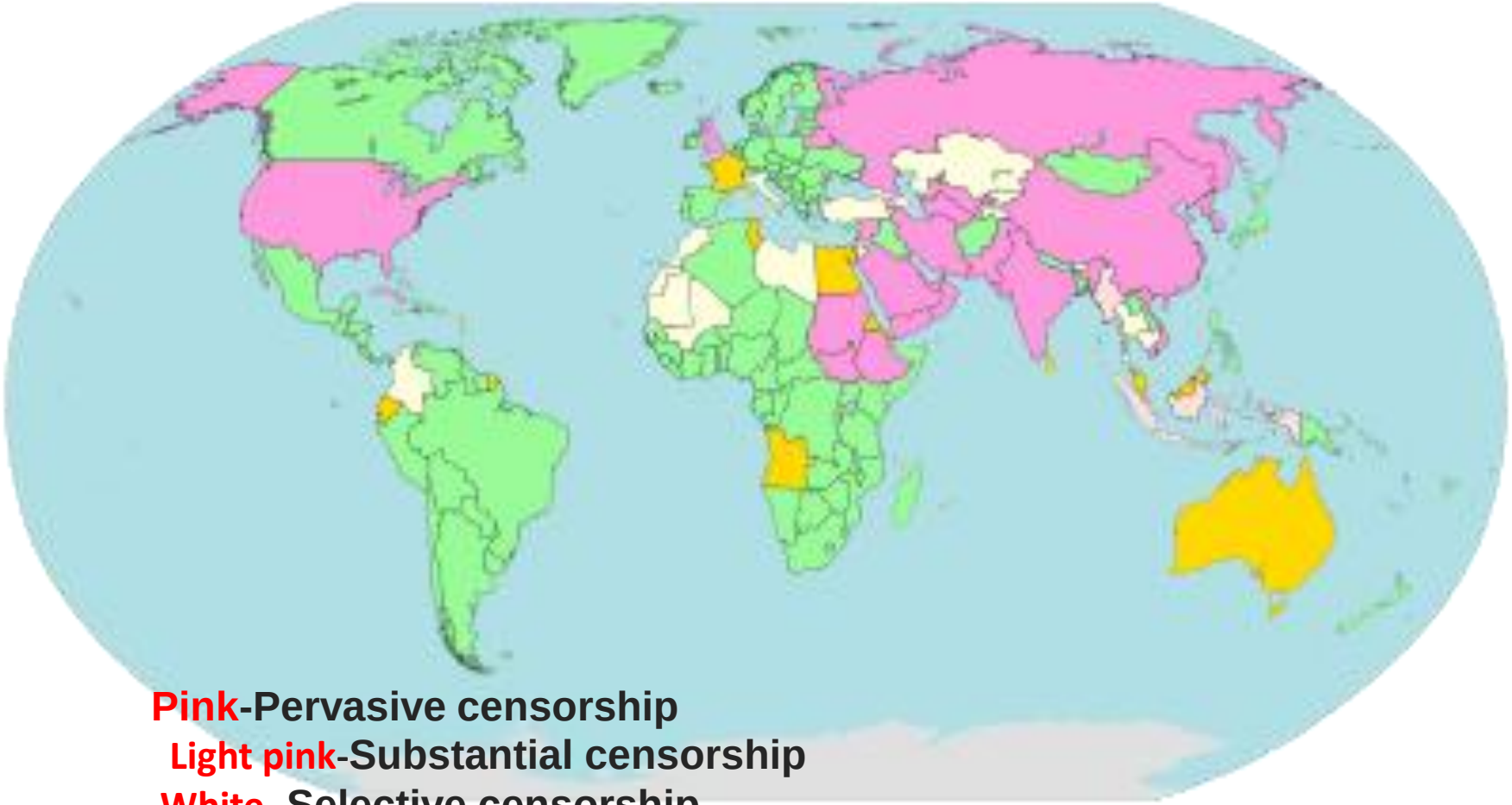
Internet User by language



Website Content languages



Internet censorship and surveillance by country



Pink-Pervasive censorship
Light pink-Substantial censorship
White- Selective censorship
Yellow-Changing situation
Green- Little or no censorship
Grey- Not classified / no data

Terms related to Internet

- *ADSL* Asymmetric Digital Subscriber Line is a technology for transmitting digital information at a high bandwidth on existing phone lines to homes and businesses. ADSL is asymmetric in the sense that it uses most of the channel to transmit downstream to the user and only a small part to receive information from the user. This means, high download rates and slower upload rates. Generally if it is 2Mb ADSL broadband, it refers to 2 Mbit/s Max d/load rate. The upload rate will probably be around 256 kbit/s Max. (ADSL has a maximum download rate of 8 Mbit/s, ADSL2 is capable of up to 16 Mbit/s and ADSL2+ is rated at 24 Mbit/s maximum.)
- *blogging*writing on or otherwise using online journals known as web logs or blogs

Terms related to Internet

- *cable modem* Primary competitor to ADSL, uses digital information transmitted over a cable television infrastructure.
- *CSS* Cascading Style Sheets; while HTML dictates the content of page, CSS regulates the format, including headers, footers, navigation bars, etc. While all of these elements can be created in HTML, such a method would have to be repeated on every web page. CSS on the other hand, is applied to all pages of a website.
- *Cyber bully* A bully who harasses his or her victims online through various means such as spamming, defaming or negative impersonation of the victim.

Terms related to Internet

- *dial-up* A method of connection to the internet using existing copper phone lines using a modem on the client's end to send information at a slow speed, normally reaching maximum speed at about 56 k bit/s. This technology uses the voice spectrum of the telephone lines to transmit data using a system of sounds that only the receiving modem or ISP understand.
- *egosurfer*someone who searches the Internet for references of himself/herself
- *Fail* The opposite of "win", "fail" expresses an ability to incorrectly perform acts ranging from idiotically simple to impossibly difficult, often consisting of an amusing element.
- *Flamer* A flamer is someone who makes degrading or insulting remarks on a forum or other Internet message board, the verb of which is "flame".

Terms related to Internet

- *Friending* the act of making and adding friends online through social networking sites such as Facebook and MySpace
- *FTP* Protocol to exchange files between two computers.
- *the Game* A popular mind game, often referred to on public message boards as a way to irritate other users.
- *Googling* searching through the Google search engine
- *Griefer* A player of an online game who harasses other players.

Terms related to Internet

- *HTML* HyperText Markup Language, the coding language used to create hypertext documents for the World Wide Web. In HTML, a block of text can be surrounded with tags that indicate how it should appear (for example, in bold face or italics). Also, in HTML a word, a block of text, or an image can be linked to another file on the Web. HTML files are viewed with a World Wide Web browser.
- *ID-10-T* clueless user; everybody giving a hard time to (computer) administrators

Terms related to Internet

- *Noob* A new or un-experienced person, someone who does not know the rules of a website, or has only recently joined.
- *Phishing* The act of attempting to obtain private or sensitive information such as user names, passwords and credit card information through the use of fake emails from trustworthy sites.
- *PHP*PHP Hypertext Preprocessor, the coding language to create interactive web pages and so forth.
- *POP3*Protocol to retrieve email.

Terms related to Internet

- *Redditor* A person who scours the Internet for media and posts the findings on the Reddit website. Once posted, other members can up vote or down vote the material based on their evaluation of it.
- *SMTP* Protocol to send email.
- *Spamming* the act of sending unsolicited email or posting many useless messages in a forum website.

Terms related to Internet

- *Trashers* someone who searches for information via whatever means needed which would compromise the security of a site. This activity often includes searching trash or refuse disposed in recycle bins of from the facility.
- *Troll* someone who attempts to gain infamy in chat or on forums by use of but not limited to links to disturbing items, bashing (fighting, put down) with others, copying or mimicking other's real posts into perverted messages.
- *Tweet* a small message sent by a user of the website Twitter.
- *Unfriend* The act of removing someone from a list of friends on social networking profiles of Facebook, MySpace or Bebo. It is also the Oxford dictionary's 2009 Word of the Year.
- *Win* Similar to "leet", "win" expresses an ability to perform an otherwise impossible act through pure luck or practice, or an object or statement that constitutes an amusing or amazing element.

Application of Internet

Internet has general applications in :-

- Surfing/ Searching about data
- Getting knowledge
- E- mailing
- Chatting/ video chatting
- Reservations/ e tickets
- E- governance
- video conferencing etc.
- Status checking of trains/ planes etc.

Application of Internet

- Social media networking
- Enterprise networking
- Doing project works
- Getting information about any thing
- Making Contacts
- Online form fillings
- Online bill deposits etc.
- Online interviews etc.

Applications of Internet

- Online jobs/ working
- Online tutorials
- Entertainment activities
- Watching films/ Videos etc.
- Geo mapping/ surfing of locations etc.
- Online shopping
- Online Banking

Some specific applications

- *Virtual Class Room:*
- **Virtual Education is a term describing on-line education using the Internet. This term is primarily used in higher education.**
- **Virtual Universities have also been established.**
- A **virtual classroom (VCR) is an advanced learning environment, created using internet, computers, supplicated video conferencing devices,**
- **Basically for remote learning or for distance education**

Some specific Applications

- ***Class Activities in VCR (Virtual Class room):***
- Group and individual learning activities
- Full on-line courses with modules
- On-line quizzes and surveys
- E-discussions and chats with students, parents and guests
- Forums and synchronous chat sessions
- Web Quests, etc.
- Homework activities and assessment documents

Advantages of VCR (Virtual Class room)

- **Offers Anytime Access:**
- **Ensures Comprehension:**
- **Electronic white board and polls, quizzes, and surveys:**
- **Flexible content area:**
- **Recording of the Class:**
- **Access to persons with disabilities:**
- **Appeal to Different Learning Styles:**
- **Create Community:**
- **Application sharing:**
- **Public & private text chat:**
- **Technology appropriate for Online Education:**

- Specific Applications in Research

Literature Survey

- Literature Survey may be done using Internet
- Abstract or Complete Research Paper/s may be obtained
- Websites are :-

✓ Google/ Google scholar

✓ Springer

✓ Elsevier

✓ Research Gate

✓ Pubmed

- A **web search engine** is a software system that is designed to search for information on the World Wide Web. The search results are generally presented in a line of results often referred to as search engine results pages (SERPs).
- Search Engine in common use:-

Google

Yahoo

Baidu

Bing

Excite

Ask

AOL

- **Search engine Market share in October 2014**

Google58.01%

Baidu29.06%

Bing8.01%

Yahoo!4.01%

AOL0.21%

Ask0.10%

Excite0.00%

- **Search engine Market share in July 2014**

Google68.69%

Baidu17.17%

Yahoo!6.74%

Bing6.22%

Excite0.22%

Ask0.13%

AOL0.13%

-

- Specific Applications In Research

Online Journals

Online Journals

- Many Journals are available in the subject/s.
- May /may not charge for publication.
- ISSN number is to be checked.
- Indexing and abstracting service should be checked.
- T& F/ Elsevier / Scopus/ Springer/web of science indexed journals should be preferred.
- Journals with impact factor should be selected.

Web camera and its uses

- A **webcam** is a video camera that feeds or streams an image or video in real time to or through a computer to a computer network, such as the Internet. Webcams are typically small cameras that sit on a desk, attach to a user's monitor, or are built into the hardware. Webcams can be used during a video chat session involving two or more people, with conversations that include live audio and video.

Uses of Web Camera

- Health care
- Video monitoring
- Commerce
- Videocalling and videoconferencing
- Video security
- Video clips and stills
- Input control devices
- Astro photography
- Laser beam profiling

PDF format of File

- The **Portable Document Format** (**PDF**) (redundantly: PDF format) is a file format developed by Adobe in the 1990's to present documents, including text formatting and images, in a manner independent of application software, hardware, and operating systems. Based on the PostScript language, each PDF file encapsulates a complete description of a fixed-layout flat document, including the text, fonts, vector graphics, raster images and other information needed to display it. PDF was standardized as ISO 32000 in 2008, and no longer requires any royalties for its implementation.
- PDF files may contain a variety of content besides flat text and graphics including logical structuring elements, interactive elements such as annotations and form-fields, layers, rich media (including video content) and three dimensional objects using U3D or PRC, and various other data formats. The PDF specification also provides for encryption and digital signatures, file attachments and metadata to enable workflows requiring these features.

JPG or JPEG format of File

- **JPEG** is a commonly used method of lossy compression for digital images, particularly for those images produced by digital photography. The degree of compression can be adjusted, allowing a selectable tradeoff between storage size and image quality. JPEG typically achieves 10:1 compression with little perceptible loss in image quality. Since its introduction in 1992, JPEG has been the most widely used image compression standard in the world, and the most widely used digital image format, with several billion JPEG images produced every day as of 2015.
- The term "JPEG" is an initialism/acronym for the Joint Photographic Experts Group, which created the standard in 1992. The basis for JPEG is the discrete cosine transform (DCT), a lossy image compression technique that was first proposed by Nasir Ahmed in 1972. JPEG was largely responsible for the proliferation of digital images and digital photos across the Internet, and later social media.

JPG or JPEG format of File

- JPEG compression is used in a number of image file formats. JPEG/Exif is the most common image format used by digital cameras and other photographic image capture devices; along with JPEG/JFIF, it is the most common format for storing and transmitting photographic images on the World Wide Web. These format variations are often not distinguished, and are simply called JPEG.
- The MIME media type for JPEG is *image/jpeg*, except in older Internet Explorer versions, which provides a MIME type of *image/pjpeg* when uploading JPEG images. JPEG files usually have a filename extension of .jpg or .jpeg. JPEG/JFIF supports a maximum image size of 65,535×65,535 pixels, hence up to 4 giga pixels for an aspect ratio of 1:1. In 2000, the JPEG group introduced a format intended to be a successor, JPEG 2000, but it was unable to replace the original JPEG as the dominant image standard.

Feel Free to contact on

- Via College Email id: pgcdatia@rediffmail.com

- Best of Luck

Applications of Computers In Chemistry- Part IV (M.Sc. II Sem. Chemistry)

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This PPT contains

- Assignment and
  set of Questions on Part- I,II and III

1. What do you understand by a computer?
2. Draw and explain the block diagram of a PC.
3. Enlist the Input/ Output devices used in a computer.
4. Differentiate between:

   (a) Hardware and software,

   (b) Operating system and Programming language,

5. What is flow charting?

6. Explain the Symbols used in flow charting.

7. Draw the flow charts for the following problems:

(a) addition of numbers.

(b) solution of quadratic equation

(c) system of simultaneous equation.

(d) ideal gas equation.

(e)computing lattice energy on the basis of Born Haber's cycle.

(f) computing rate constant and half life for a reaction obeying first order kinetics.

(g) computing rate constant and half life for a reaction obeying zero order kinetics.

(h) computing normality, molarity and molality of a solution.

(i) computing bond distance and atomic radius .

8. What is a programming language?
9. Enlist the features of either BASIC/ FORTRAN / C- language.
10. Which of the following are valid variables:
    (a) A1
    (b) 1A
    (c)ALLAHABAD
    (d) ab
    (e)AB 1
11. Which of the following are valid string variables:
    (a) A1$
    (b) 1A$
    (c)ALLAHABAD
    (d) ab
    (e)AB 1$

12. Express the following statements as in the BASIC language

    (a) A+B

    (b) (A+B)X(C+D)

    (c) {(A+B)X(C+D)} /{A2x B2}

    (d) {(A+B)X(C+D)}/{exp (2)}

13. Write and explain the programs for the problems mentioned in question no. 7

14. Explain Simpson rule.

15. Write the program for computing slope and intercept for a line using methods of least square.

16. Write a note on internet.
17. What are the devices required for the use of internet.
18. Differentiate between LAN and WAN .
19. Write a note on softwares which are in use in chemistry.
20. Explain the uses of internet.
21. Explain the applications of internet in study and research.
22. Write a note on PDF file
23. Write a note on JPEG file.
24. What is a web camera? Explain its uses.

Feel free to contact further

- Via College email pgcdatia@rediffmail.com

- Best of Luck

Applications of Spectroscopy, Part –I, M.Sc. IV Semester

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This presentation includes

- Unit – I UV Visible spectroscopy
- ✓ Introduction
- ✓ Wave nature of light
- ✓ Electromagnetic spectrum
- ✓ Colorimetery
- ✓ Spectroscopes / Spectrophotometers
- ✓ Instrumentation
- ✓ Beer Lambert's Law
- ✓ Block Diagram of Spectrophotometer
- ✓ Absorbance Vs. Transmittance
- ✓ Origin of electronic spectra
- ✓ Electronic transitions
- ✓ Solvent effect
- ✓ Effect of Conjugation
- ✓ Franck Condon Rule
- ✓ Woodward Fieser Rules and Application in the calculation of λmax
- ✓ Types of absorption shift
- ✓ Bathochromic shift
- ✓ Hypso chromic shift
- ✓ Hypo chromic shift
- ✓ Hyper chromic Shift
- ✓ Assignment/ set of Questions

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

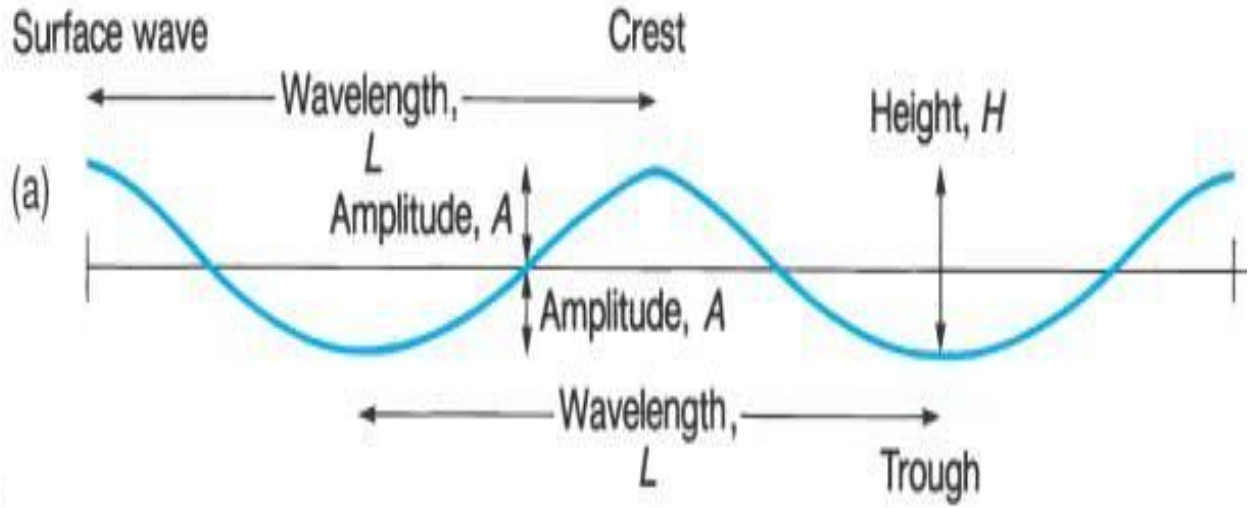
- Any application that deals with chemical substances or materials can use this technique. In biochemistry, for example, it is used to determine enzyme-catalyzed reactions.
- In clinical applications, it is used to examine blood or tissues for clinical diagnosis.

Introduction

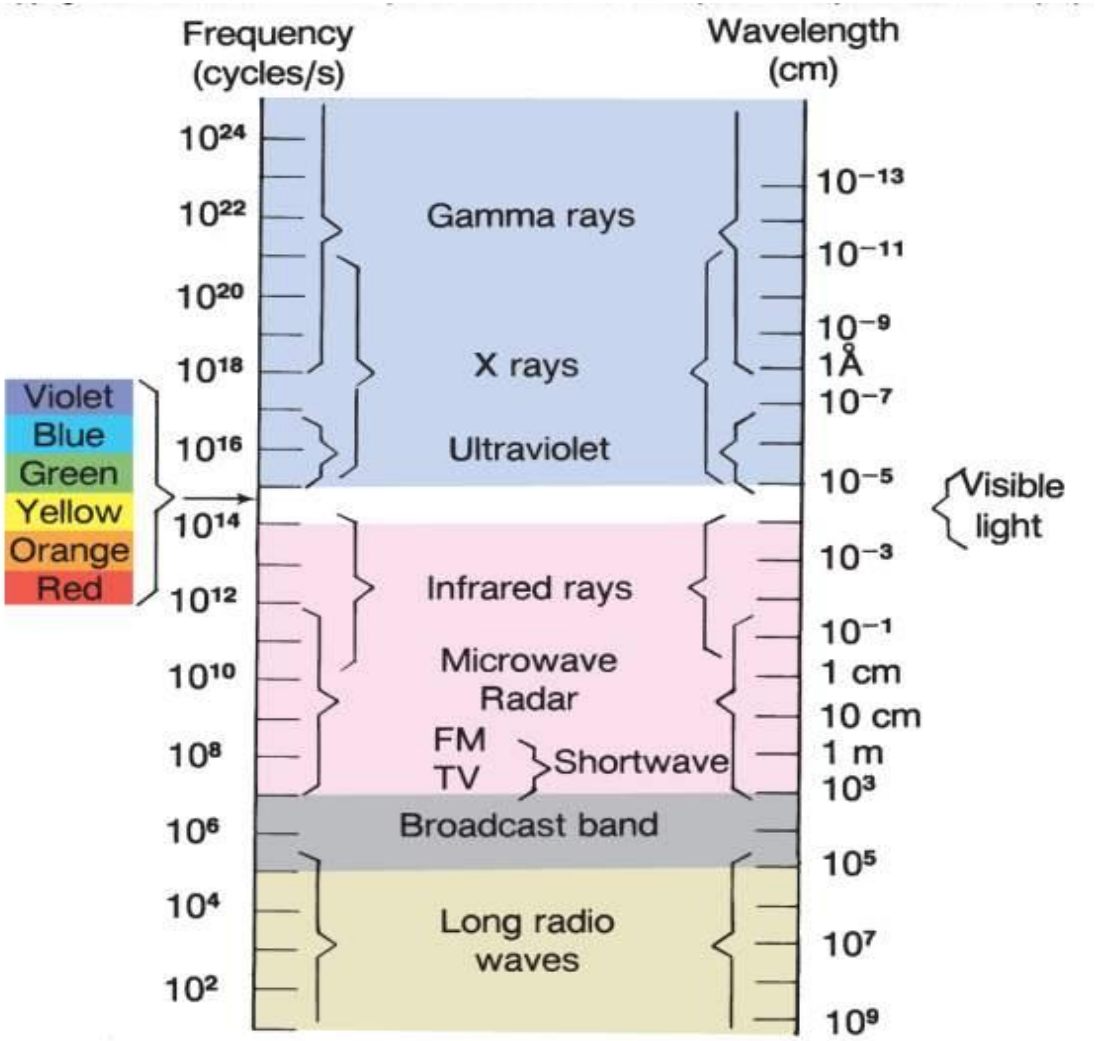
- There are also several variations of the spectro-photometry such as atomic absorption spectro-photometry and atomic emission spectro-photometry.

Wave Nature of Light

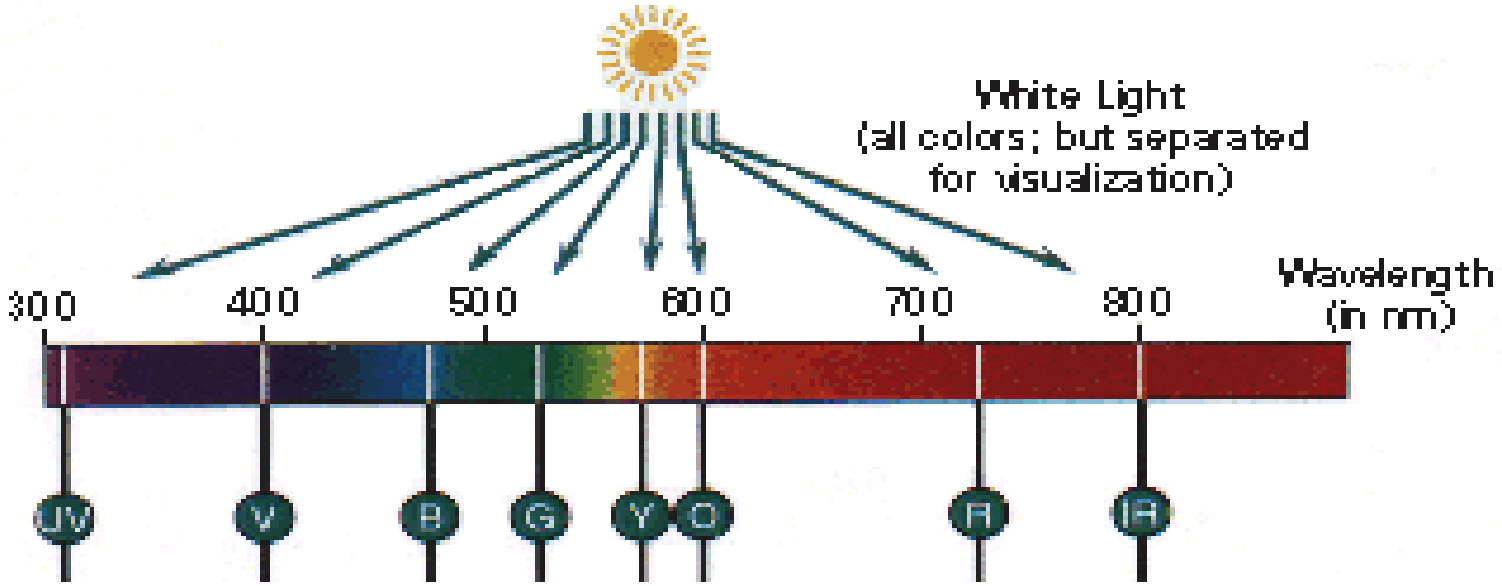
- *Electromagnetic radiation* moves in waves



Electromagnetic Spectrum



VIBGYOR


White Light
(all colors; but separated
for visualization)
300
400
500
600
700
800
Wavelength
(in nm)
UV
V
B
G
Y
O
R
IR

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

Colorimetery

- 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:

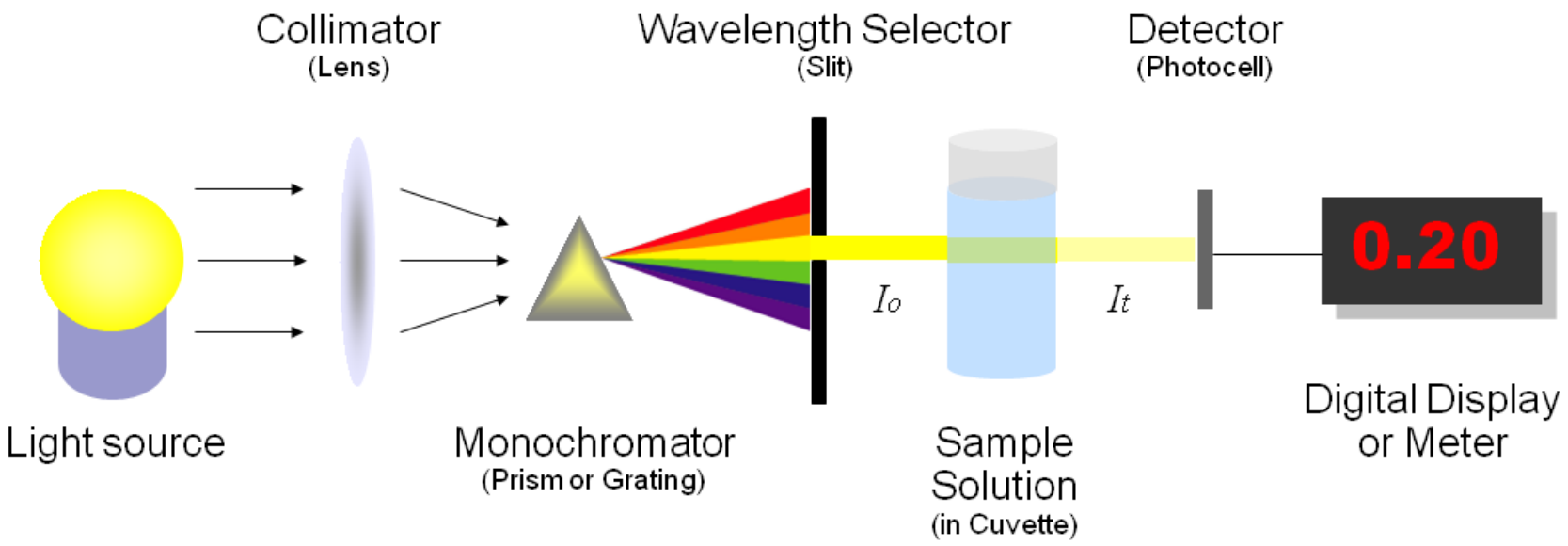
Instrumentation

- **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.

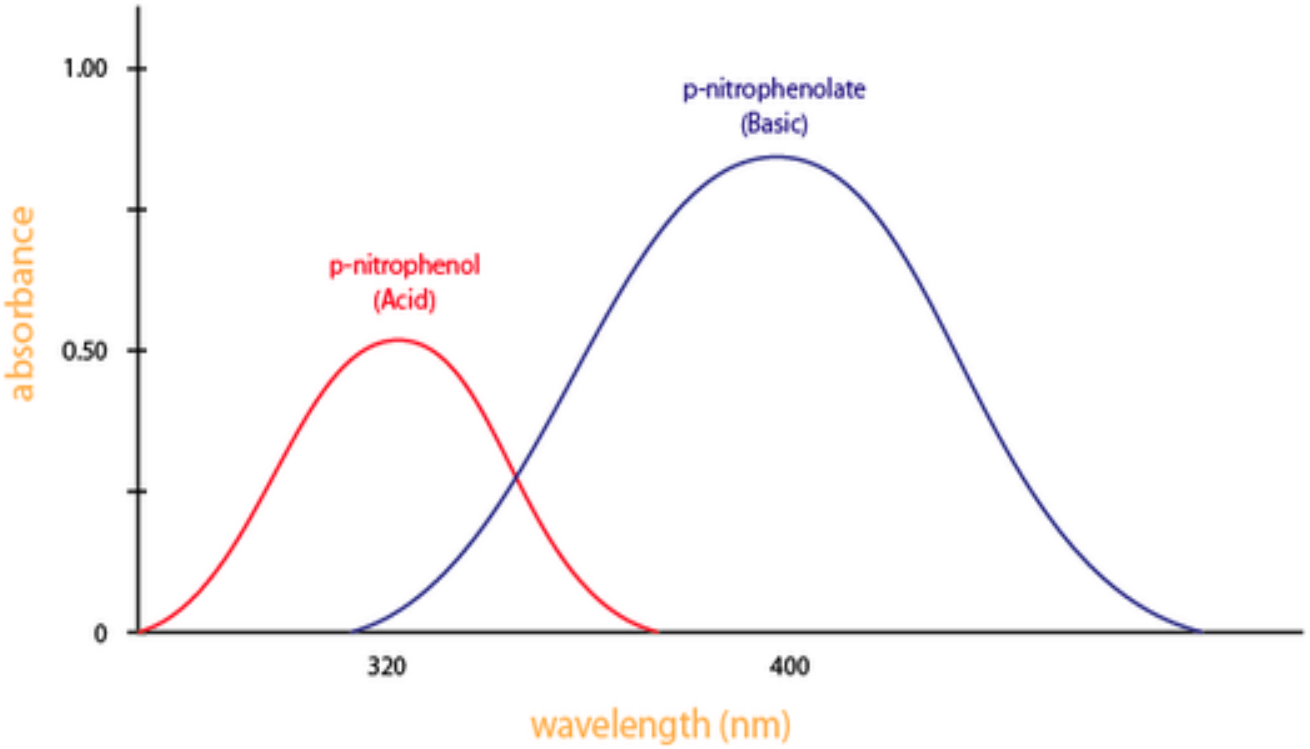
Block Diagram



Instrument


MODE
CONCENTRATION / FACTOR
540
.081
TRANSMITTANCE
ABSORBANCE
CONCENTRATION
FACTOR
MILTON ROY COMPANY
SPECTRONIC 20D

A typical Spectrum



Beer- Lambart 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),

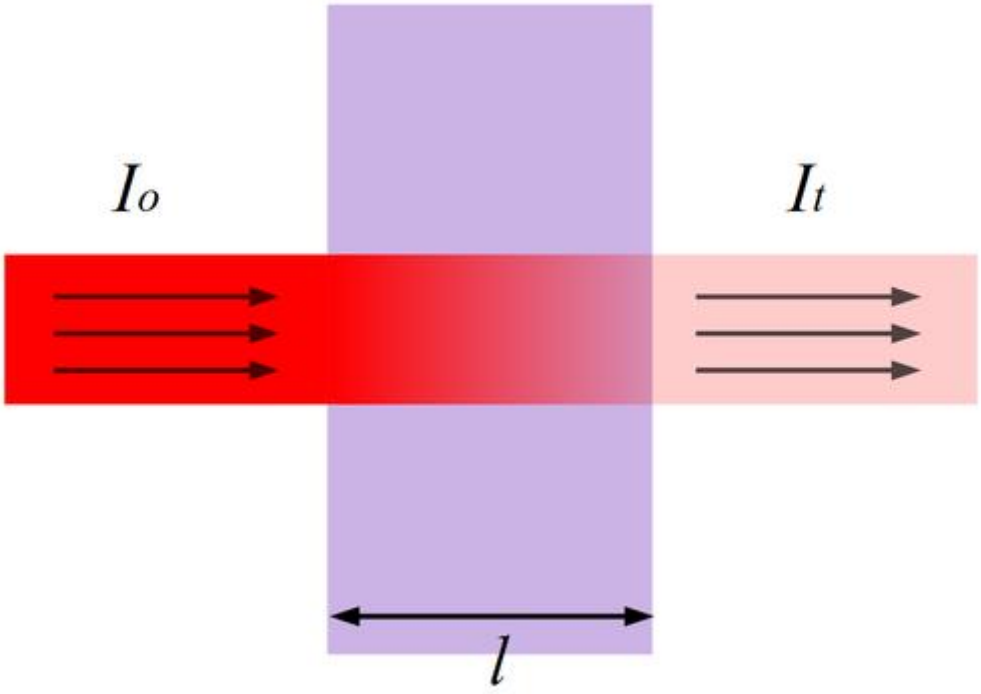
Beer Lambart Law

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: $L \cdot mol^{-1} \cdot cm^{-1}$.

Beer Lambart Law



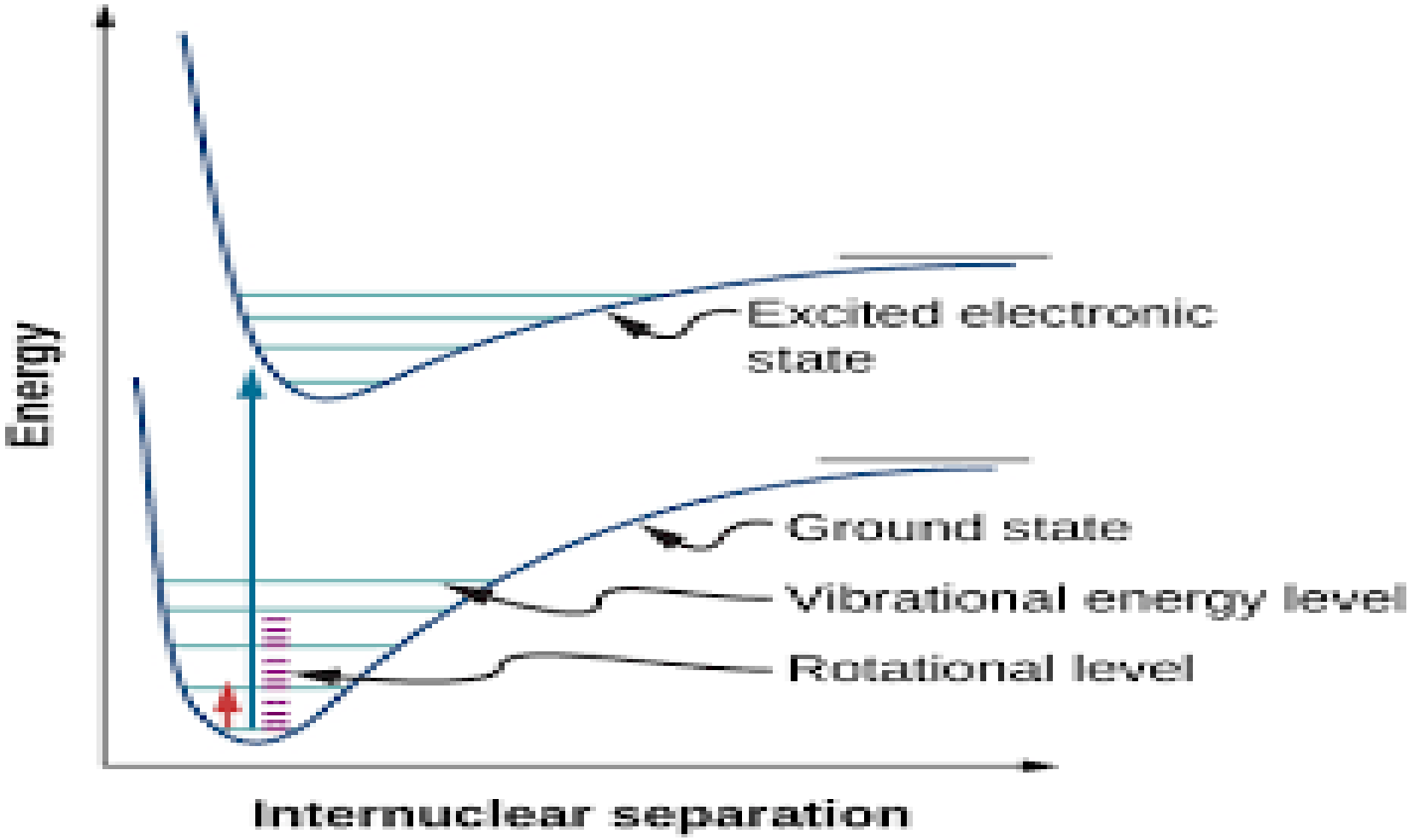
Absorbance Vs. Transmittance

- Transmittance is the fraction of light that passes through the sample. This can be calculated using the equation:
- Transmittance(T)=ItIo
- Transmittance is related to absorption by the expression:
- Absorbance(A)=−log(T)=−log(ItIo)

Introduction to Electronic Spectroscopy (UV-Visible Spectroscopy)

- **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.

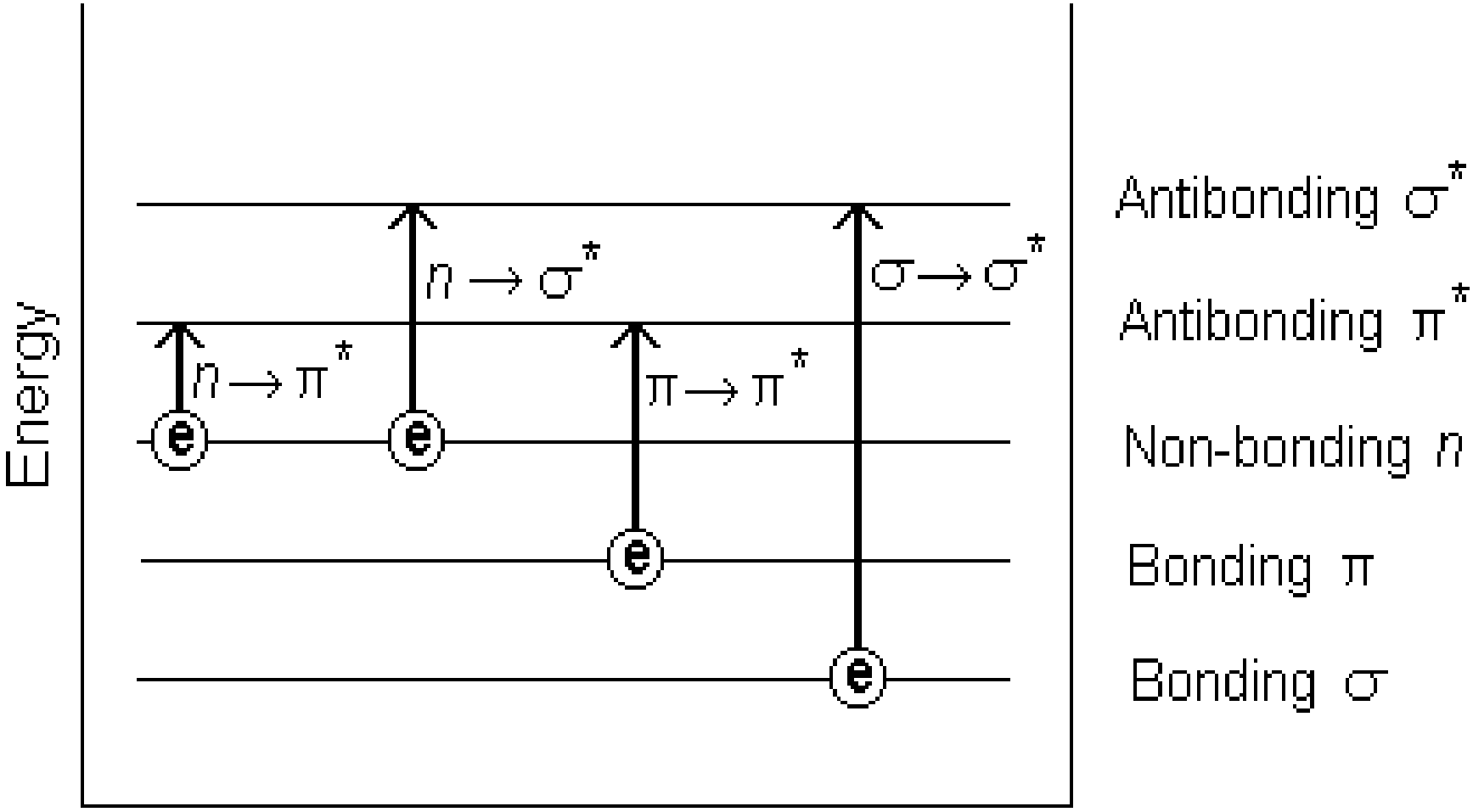
Introduction-Electronic Spectra origin



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.
- π–π^*,
- n–π^*,
- σ–σ^*, and
- n–σ^*,
- These can be ordered as follows :σ–σ^* > n–σ^* > π–π^* > n–π

Electronic Transitions



Electronic Transitions

- **s ® 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 ® s* transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to s ® s* transitions are not seen in typical UV-Vis. spectra (200 - 700 nm)

- ***n* ® s* Transitions**

  Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of *n* ® s* transitions. These transitions usually need less energy than s ® 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* ® s* peaks in the UV region is small.

- ***n* ® p* and p ® 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 absorbtivities from *n* ® p* transitions are relatively low, and range from 10 to100 L mol^{-1} cm^{-1} . p ® p* transitions normally give molar absorbtivities between 1000 and 10,000 L mol^{-1} cm^{-1} .

{where s =σ ; p = π and n= non bonding orbitals]

Electronic Transitions (Appearance in Compounds)

σ→σ* Alkanes

σ→π* Carbonyl compounds

π →π* Alkenes, carbonyl compn, alkyne etc.

n→σ* Oxygen, nitrogen, sulfur and halogen compounds

n →π* Carbonyl compounds (Usually Forbodden)

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 π →π* transition shifts towards lower wavelength side.
- Shown in the next slide

Effect of conjugation

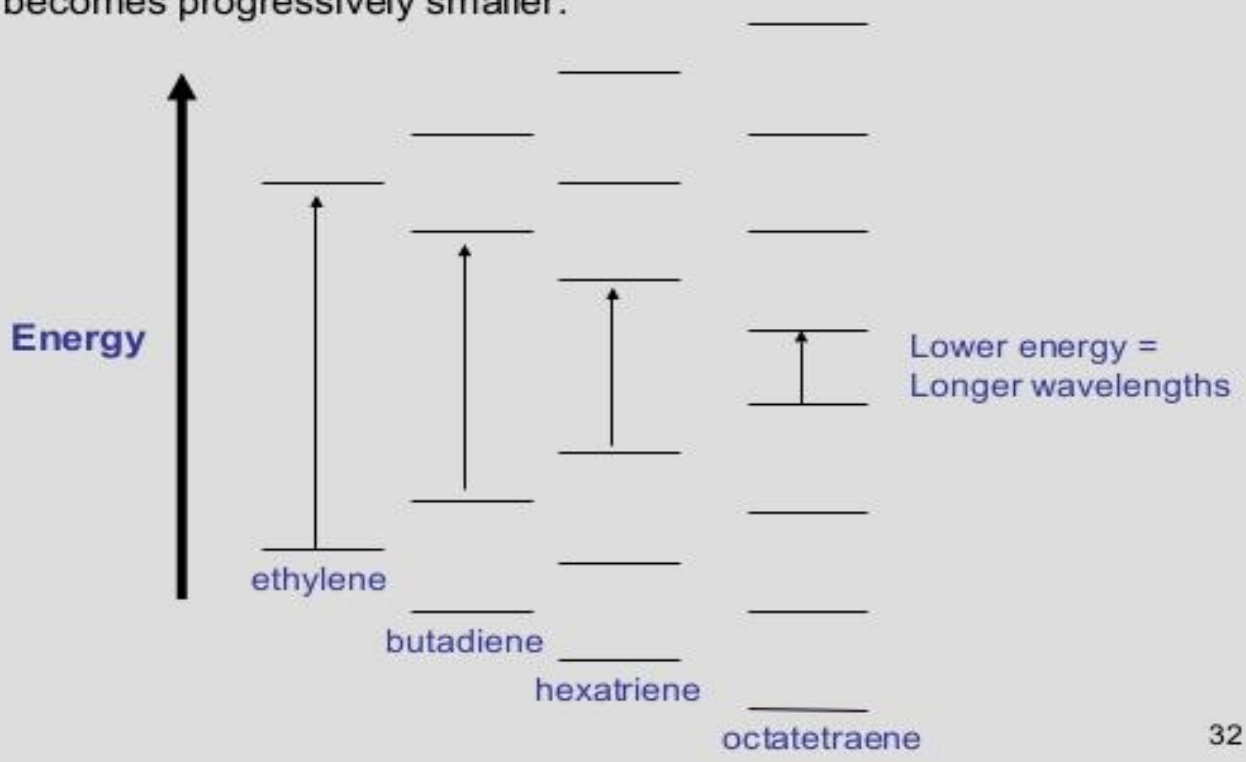
UV Spectroscopy

III. Chromophores

A. Substituent Effects

2. Conjugation – Alkenes

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



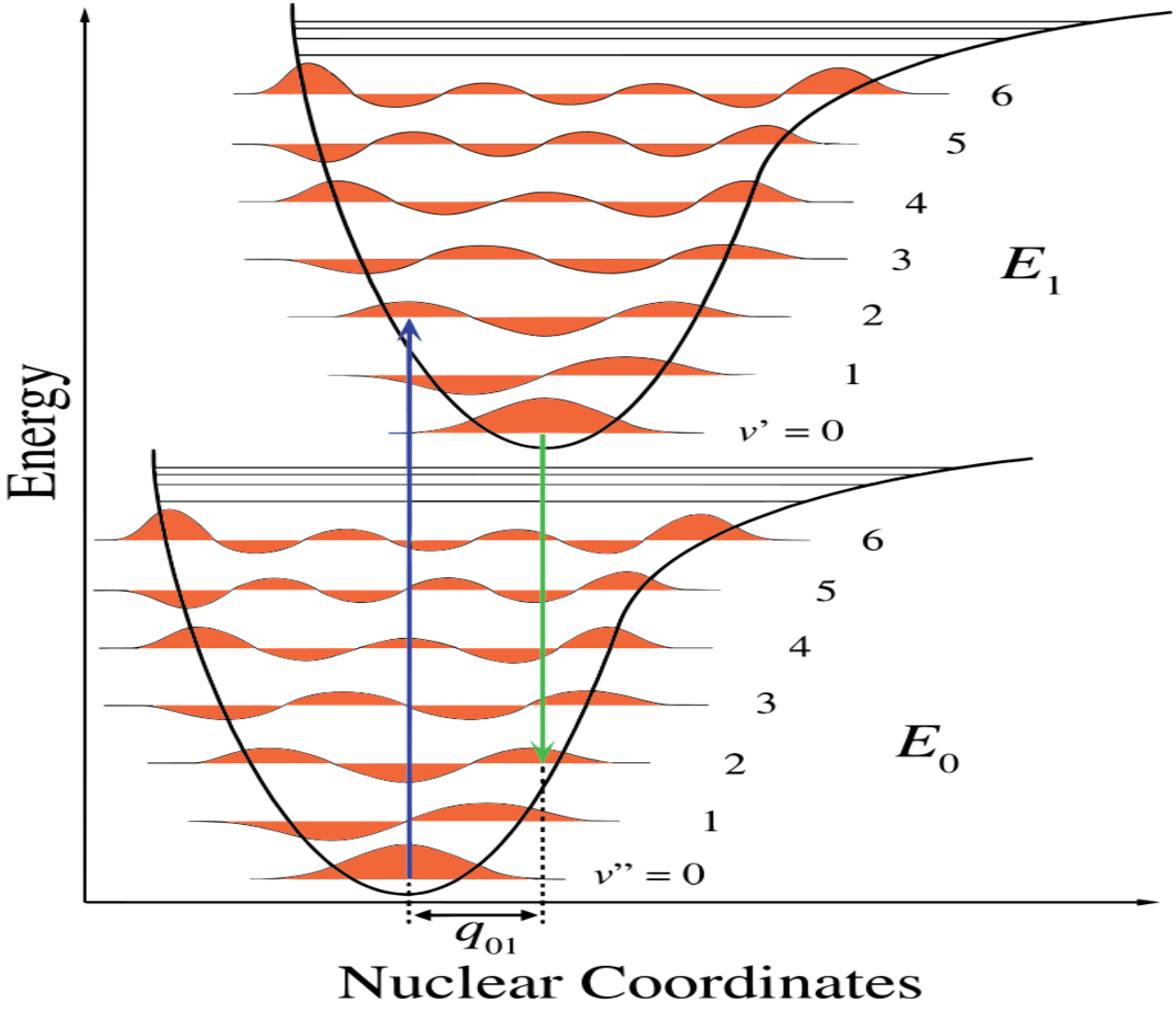
Charge Transfer Spectra

- 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 absorbtivities from charge-transfer absorption are large (greater that 10,000 L mol^{-1} 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

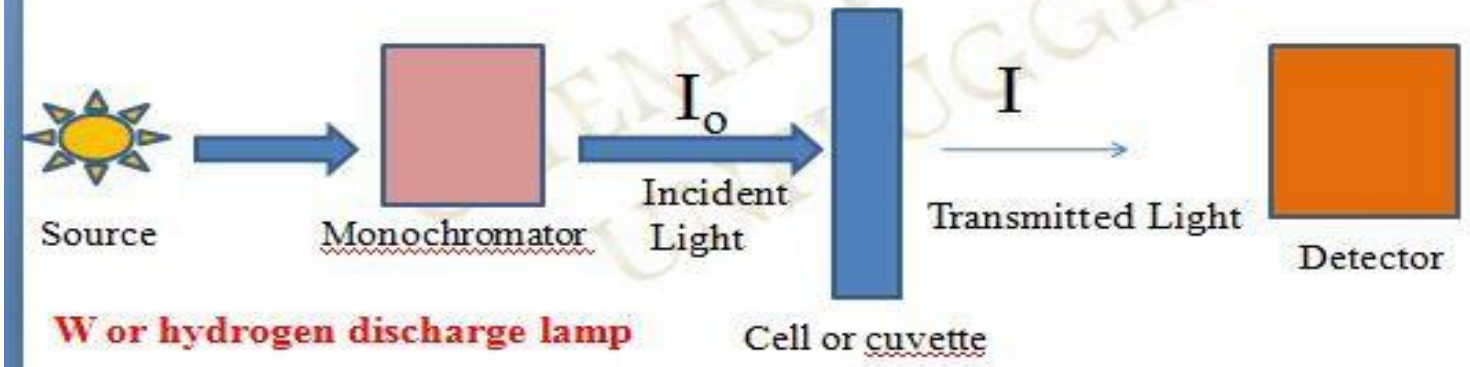
- Absorbance is directly proportional to concentration of the solution.

$$A = \varepsilon cl = \log(I_o/I)$$

where, c= concentration (mol/litre)

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

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



Woodward Fieser Rules

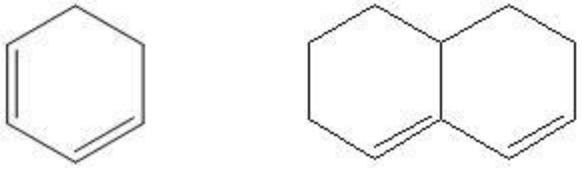
- In 1945 Robert Burns Woodward gave certain rules for correlating λ_{max} with molecular structure. In 1959 Louis Frederick Fieser modified these rules with more experimental data, and the modified rule is known as Woodward-Fieser Rules. It is used to calculate the position and λ_{max} for a given structure by relating the position and degree of substitution of chromophore.

WOODWARD- FIESER RULES:

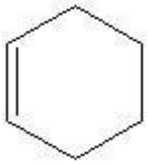
- Each type of diene or triene system is having a certain fixed value at which absorption takes place; this constitutes the ***Base value or Parent value***. The contribution made by various alkyl substituents or ring residue, double bond extending conjugation and polar groups such as –Cl, -Br etc are added to the basic value to obtain λ_{max} for a particular compound

WOODWARD- FIESER RULES:

- **CONJUGATED DIENE CORRELATIONS:**
- **a) Homoannular Diene:-** Cyclic diene having conjugated double bonds in same ring
- **b) Heteroannular Diene:-** Cyclic diene having conjugated double bonds in different rings.

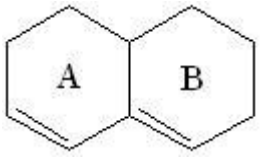


- **c) Endocyclic double bond:-** Double bond present in a ring.



WOODWARD- FIESER RULES:

- **d) Exocyclic double bond: -** Double bond in which one of the doubly bonded atoms is a part of a ring system.



- Here Ring A has one exocyclic and endocyclic double bond. Ring B has only one endocyclic double bond.

WOODWARD- FIESER RULES:

- **PARENT VALUES AND INCREMENTS FOR DIFFERENT SUBSTITUENTS/GROUPS:**

- **I) CONJUGATED DIENE CORRELATIONS:**

- i) Base value for homoannular diene = 253 nm
- ii) Base value for heteroannular diene = 214 nm
- iii) Alkyl substituent or Ring residue attached to the parent diene = 5 nm

- iv) Double bond extending conjugation = 30 nm

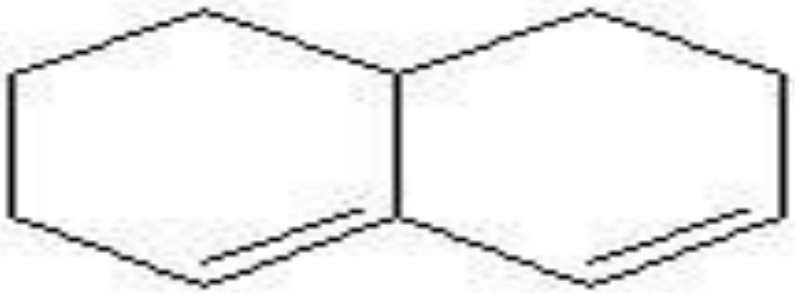
- v) Exocyclic double bonds = 5 nm

- vi) Polar groups: a) -OAc = 0 nm
- b) -OAlkyl = 6 nm

- c) -Cl, -Br = 5 nm

WOODWARD- FIESER RULES:

- **Eg:**
- Base value = 214 nm
- Ring residue = 3 x 5 = 15 nm
- Exocyclic double bond = 1 x 5 = 5 nm
- λ_{max} = 214 + 15 + 5 = 234 nm



WOODWARD- FIESER RULES:

- **II) α, β UNSATURATED CARBONYL COMPOUNDS OR KETONES:**

- 1. Base value: a) Acyclic α, β unsaturated ketones = 214 nm

- b) 6 membered cyclic α, β unsaturated ketones = 215 nm

- c) 5 membered cyclic α, β unsaturated ketones = 202 nm

- d) α, β unsaturated aldehydes = 210 nm

- e) α, β unsaturated carboxylic acids & esters = 195 nm

WOODWARD- FIESER RULES:

- 2. Alkyl substituent or Ring residue in α position = 10 nm

- 3. Alkyl substituent or Ring residue in β position = 12 nm
- 4. Alkyl substituent or Ring residue in γ and higher positions = 18 nm

- 5. Double bond extending conjugation = 30 nm

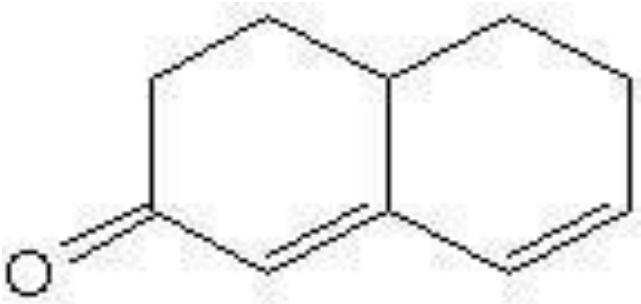
- 6. Exocyclic double bonds = 5 nm
- 7. Homodiene compound = 39 nm

WOODWARD- FIESER RULES:

- 8. Polar groups: a) –OH in α position = 35 nm
- –OH in β position = 30 nm
- –OH in δ position = 50 nm
- b) –OAc in α, β, γ, δ positions = 6 nm
- c) –OMe in α position = 35 nm
- –OMe in β position = 30 nm
- –OMe in γ position = 17 nm
- –OMe in δ position = 31 nm
- d) –Cl in α position = 15 nm
- –Cl in β position = 12 nm
- e) –Br in α position = 25 nm
- –Br in β position = 30 nm
- f) $–NR_2$ in β position = 95 nm

WOODWARD- FIESER RULES:

- **Eg:**
- Base value = 214 nm
- β- Substituents = 1 x 12 = 12 nm
- δ- Substituents = 1 x 18 = 18 nm
- Double bond extending conjugation =1 x 30 = 30 nm
- Exocyclic double bond = 5 nm
- λ_{max} = 279 nm



WOODWARD- FIESER RULES:

- **III) AROMATIC COMPOUNDS:**
- 1) Base value: for a) ArCOR = 246 nm
- b) ArCHO = 250 nm
- c) $ArCO_2H$ = 230 nm
- d) $ArCO_2R$ = 230 nm
- 2) Alkyl group or ring residue in ortho and meta position = 3 nm
- 3) Alkyl group or ring residue in para position =10 nm
- 4) Polar groups: a) –OH, $–OCH_3$, –OAlkyl in o, m position = 7 nm
- b) –OH, $–OCH_3$, –OAlkyl p position = 25 nm
- c) –O (oxonium) in o position = 11 nm
- d) –O (oxonium) in m position = 20 nm

WOODWARD- FIESER RULES:

- **III) AROMATIC COMPOUNDS: (Cont'd)**

- e) –O (oxonium) in p position = 78 nm
- f) –Cl in o, m position = 0 nm
- g) –Cl in p position = 10 nm
- h) –Br in o, m position = 2 nm
- i) –Br in p position = 15 nm
- j) $-NH_2$ in o, m position = 13 nm
- k) $-NH_2$ in p position = 58 nm
- l) $-NHCOCH_3$ in o, m position = 20 nm
- m) $-NHCOCH_3$ in p position = 45 nm

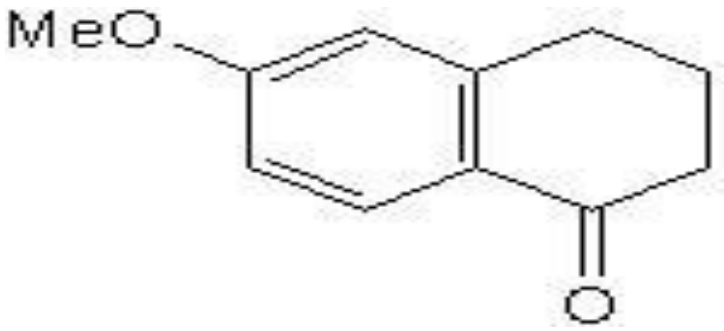
WOODWARD- FIESER RULES:

- n) $-NHCH_3$ in p position = 73 nm
-
- o) $-N(CH_3)_2$ in o, m position = 20 nm
-
- p) $-N(CH_3)_2$ in p position = 85 nm

- **Eg:**

Base value =246 nm

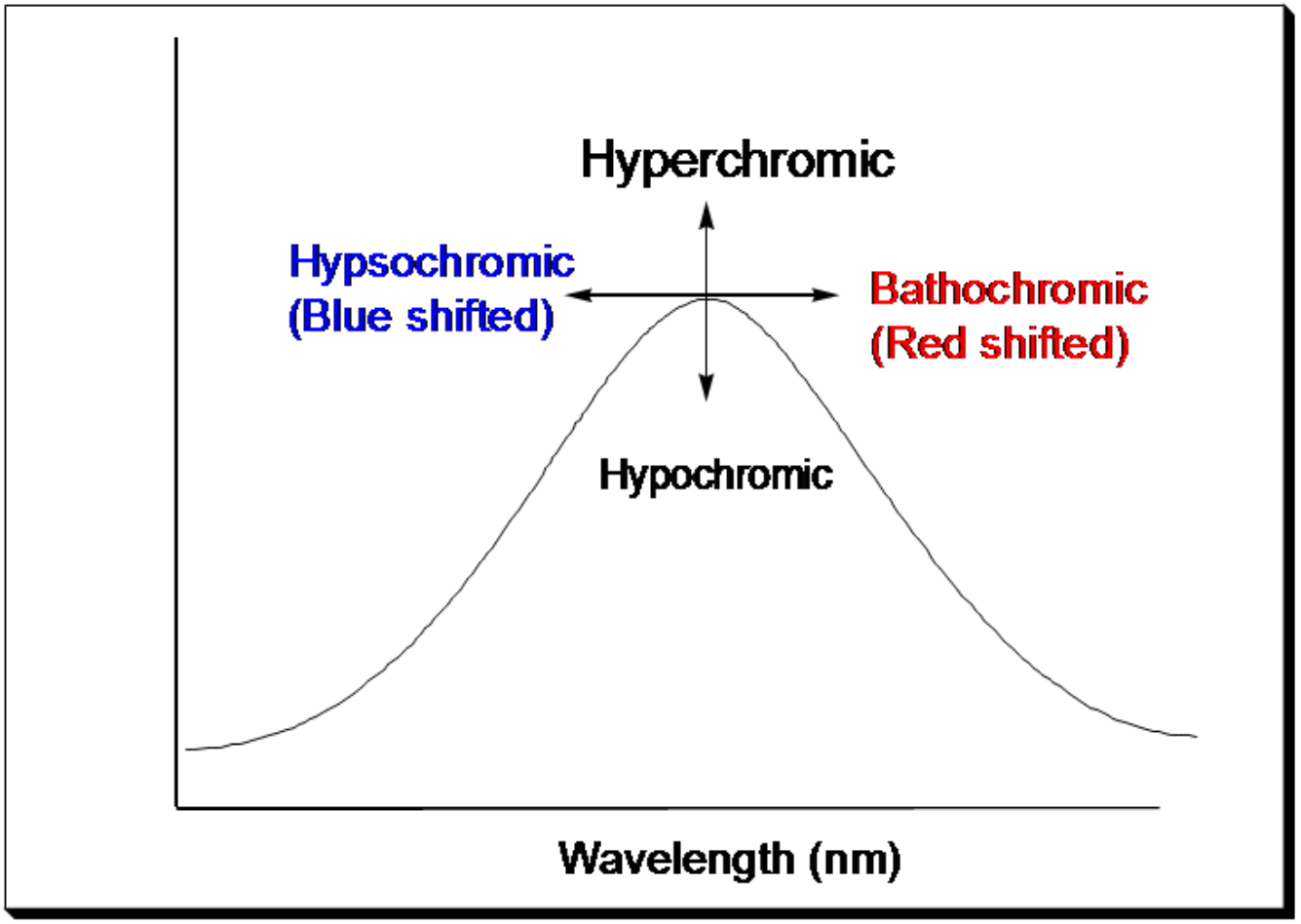
- Ring residue in o- position = 1 x 3 = 3 nm
- Polar group $-OCH_3$ in p- position = 25 nm
- λ_{max} = 274 nm



Terminology for absorption shifts

- Changes in chemical structure or the environment lead to changes in the absorption spectrum of molecules and materials. There are several terms that are commonly used to describe these shifts, that you will see in the literature, and with which you should be familiar.
- **Bathochromic**: a shift of a band to lower energy or longer wavelength (often called a red shift).**Hypsochromic**: a shift of a band to higher energy or shorter wavelength (often called a blue shift).**Hyperchromic**: an increase in the molar absorptivity.**Hypochromic**: an decrease in the molar absorptivity.

Terminology for absorption shifts



Assignment/ Set of Questions

Q1. What do you understand by spectroscopy?

Q2. What do you understand by electromagnetic spectrum.

Q3. State and explain Beer- Lambert's Law.

Q4. What do you understand by the term absorbance. How it differs from transmittance.

- Q5. What do you understand by electronic transitions?
- Q6. Explain solvent effect.
- Q7. Explain the effect of conjugation on electronic transition.
- Q8. What is charge transfer spectra?

Assignment/ Set of Questions

- Q9. What is the principle of electronic spectroscopy?
- Q10. Explain Franck Condon Rule
- Q11. Explain the terms:- Red shift, Blue shift, hypso chromic shift, batho chromic shift, hyper chromic shift, hypochromic shift
- Q12. Explain the instrumentation used in UV –visible spectroscopy.
- Q13 Explain the applications of electronic spectroscopy
- Q14. Explain Woodward Fieser Rules.
- Q15. Discuss the applications of Wood ward Fieser Rules.

- Best Of Luck