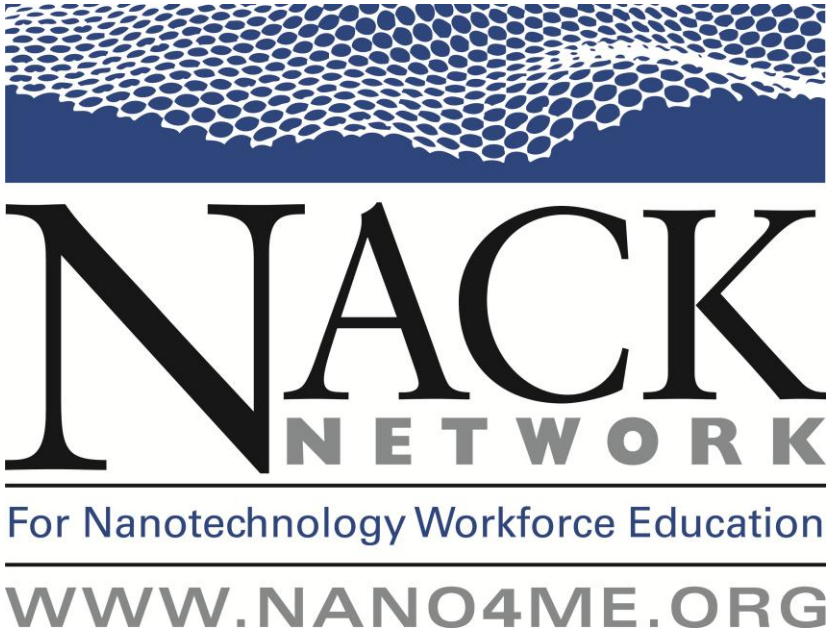


Characterization, Testing of Nanotechnology Structures and Materials

E SC 216

Unit 2
Common Spectroscopic Measurements

Lecture 1
Introduction to Photon-Based Spectroscopies

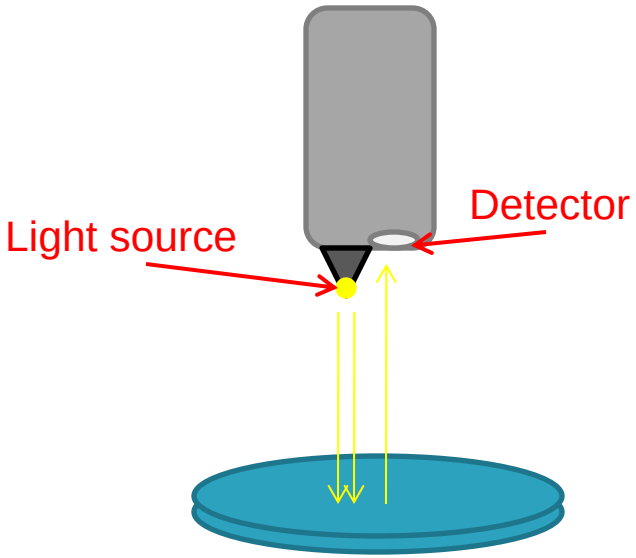
Outline

- Reflective Spectroscopy
- FTIR
- UV-vis Spectrophotometry

Reflection Spectroscopy

- Reflection spectroscopy is the analysis of light that has been reflected or scattered from a solid, liquid or gaseous medium.
- Commonly used to determine film thickness and index of refraction.
- Non-destructive and non-contact.
- Simple and relative low cost

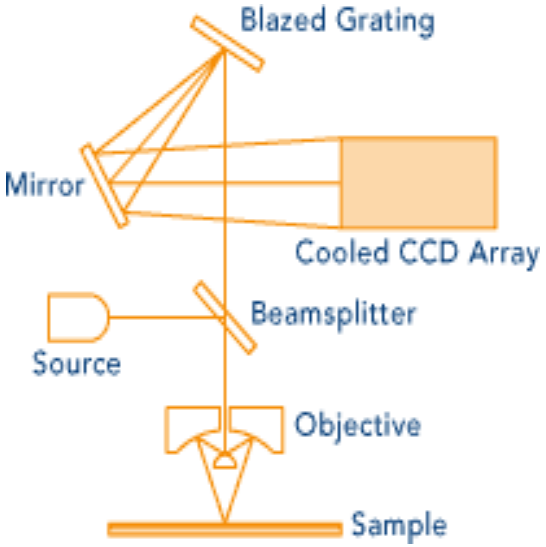
Reflection Spectroscopy



- A broadband light source is reflected off the sample at normal incidence.
- The intensity of the reflected light is measured over the range of wavelengths.
- Computer software utilizes the property of dispersion (the wavelength dependence of a medium's index of refraction) to determine the film thickness

Reflection Spectroscopy

The reflection spectroscopy equipment in the Lab is a Nanometrics Nanospec AFT model 010-180.



Nanometrics Inc

Reflection Spectroscopy

Advantages and Disadvantages:

- Able to analyze multilayer films.
- Can measure organic films like photoresist.
- Usually requires a reference sample of known composition and thickness

Outline

- Reflective Spectroscopy
- FTIR
- UV-vis Spectrophotometry

FTIR Spectroscopy

- FTIR spectroscopy stands for Fourier Transform Infra Red spectroscopy
- This technique measures the infrared light absorbed by a sample.
- Fourier math principle is used to correlate the absorbed band of light from the incident laser to a specific bond.
- This technique is based on the principle that bonding between atoms is like a spring. The bonds vibrate at frequencies that match those of infrared light. Therefore, a specific portion of the infrared (IR) light spectrum can excite these unique bonds.
- Simply stated, different bonds vibrate at different frequencies and will absorb only radiation that matches that frequency.

FTIR Spectroscopy

- This absorption can therefore be used to identify bonds using IR radiation.
- Used to detect and identify molecules present on a surface or detect and identify the chemical bonding in a thin film in a non-destructive manner.
- Basically, IR light is split into two beams. One of he beams interacts with the sample, and it is destructively added to the known beam. The resultant waveform show the amplitude and specific frequency absorbed. This is a popular testing algorithm.

FTIR Uses

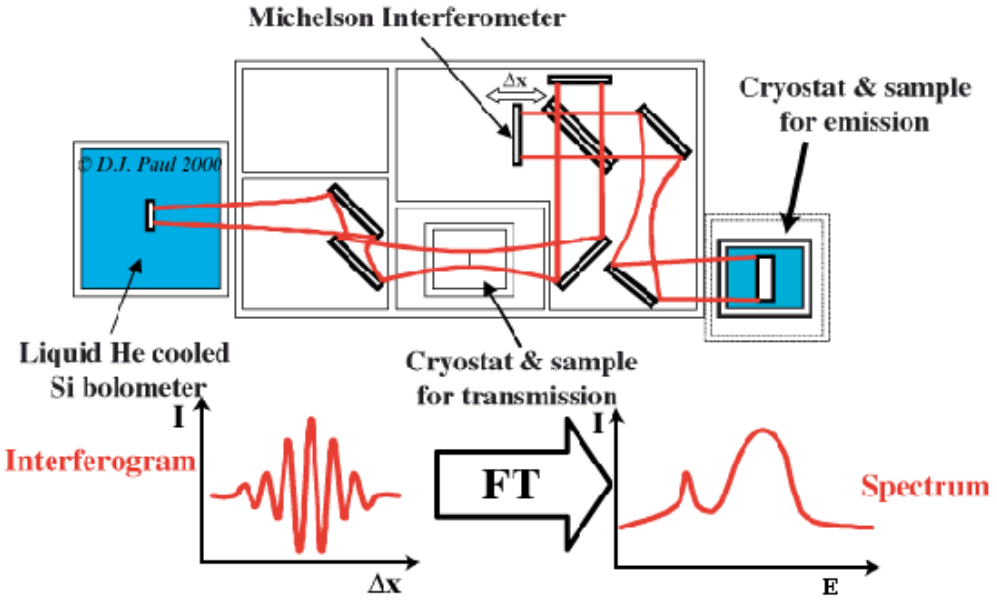
- Confirm the identity of a pure compound by seeing bonding types present
- Detect the presence of specific impurities by seeing bonding
- Detection of biological entities by seeing bonding
- Detection of bonding and therefore chemical composition of thin films.
- Used as a non-destructive characterization tool

FTIR Equipment

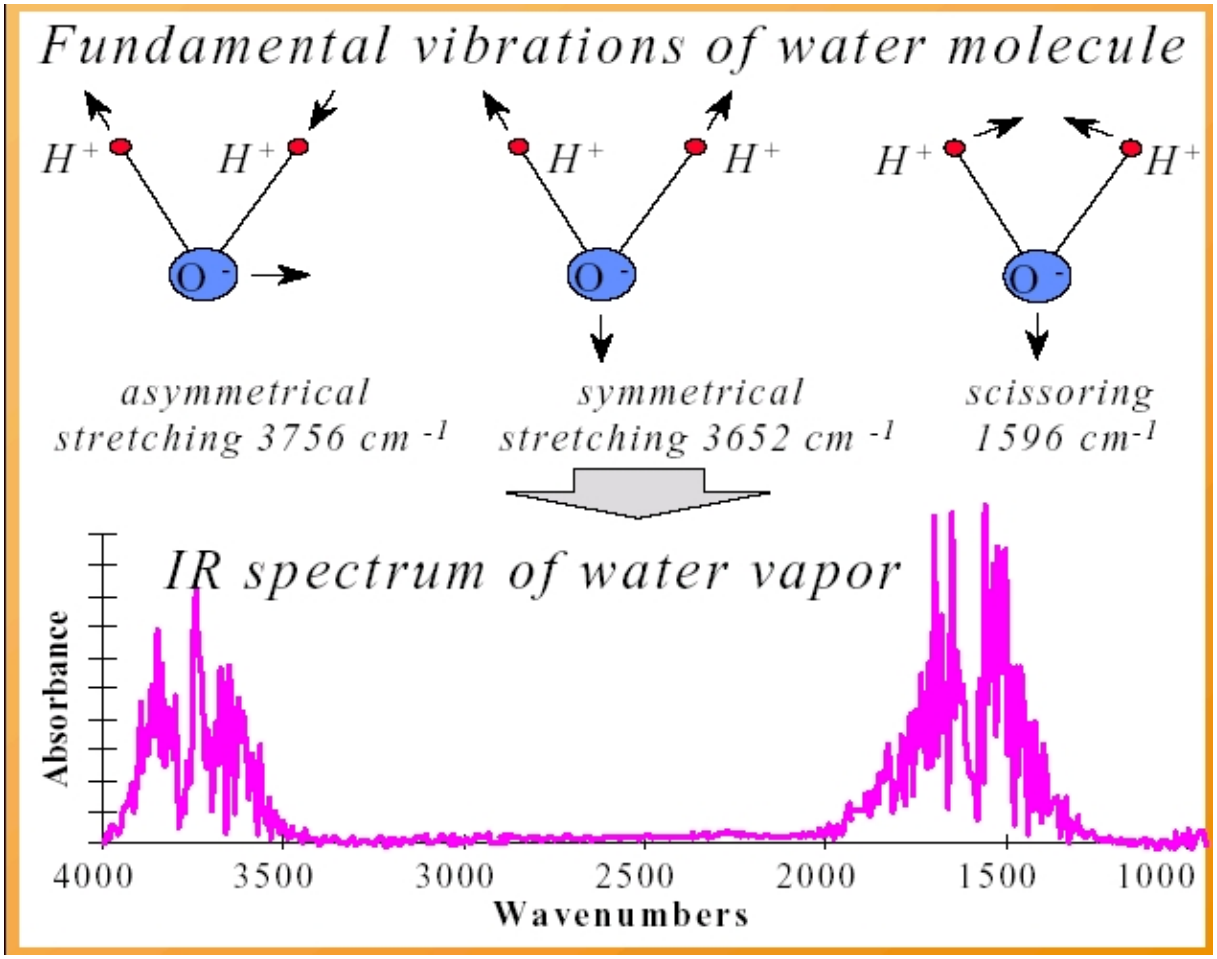
The beamsplitter transmits half the beam to the moving mirror and half to the fixed mirror. They reflect and then recombine in the comparator. The mirrors move to recombine the beams constructively or destructively.

The detector reads the beam as a continuous electrical signal called an interferogram.

The computer converts the interferogram into an absorption graph.

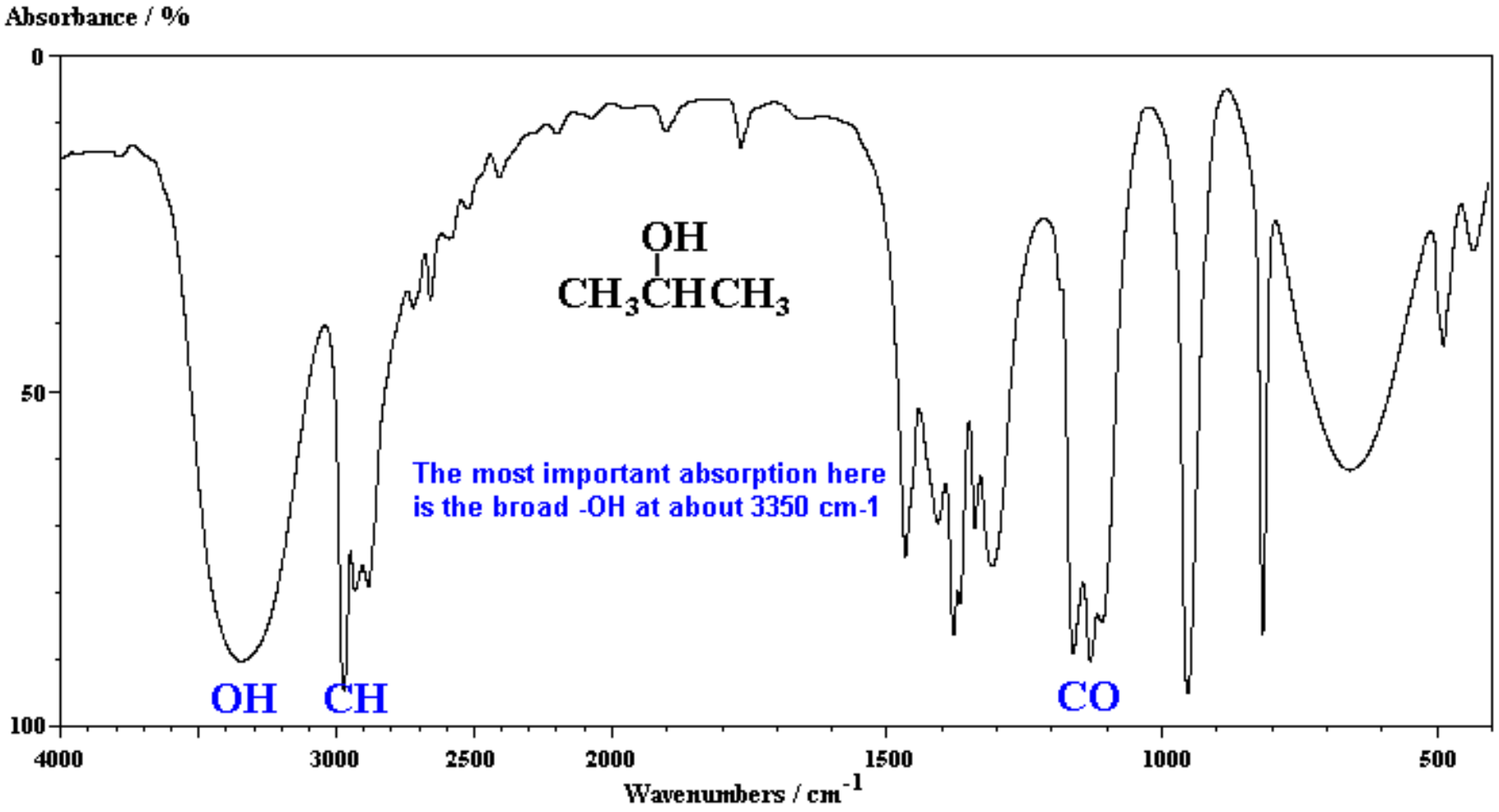


Absorbance of IR light by Water



Infrared vibrational modes

FTIR Spectra of Isopropanol



Carey, F. *Organic Chemistry Online*. McGraw Hill 2000

Absorbance and Transmittance

- Transmittance (T) is the percentage of energy that a bond transmits with respect to the amount of energy that is being exposed to.
- T = 1- (Fraction of Light Absorbed)
- Every bond has its own absorbance and transmittance energy.

Absorbance, Reflectance and Transmittance

- Radiation causes excitation of bonds
- Bonds between atoms start to vibrate and move towards and away from each other when excited by the appropriate IR frequency
- When excitation occurs energy is taken out of the IR light (absorbed) and converted into a mechanical motion. The IR light that isn't absorbed gets reflected or transmitted.

Spectrophotometer

- A spectrophotometer is used to measure reflectance and absorbance as a function of the wavelength
- The system uses the UV-Visible range of E-M energy
- Sample can be liquid, solid or gas
- Can be used to measure plasmon frequencies in metal nanoparticles, and the bandgap of a semiconductor
- It detects absorption caused by plasmons, electronic transitions, and by molecular excitations whereas FTIR, because of its wavelength range (IR), detects absorption by bond vibration

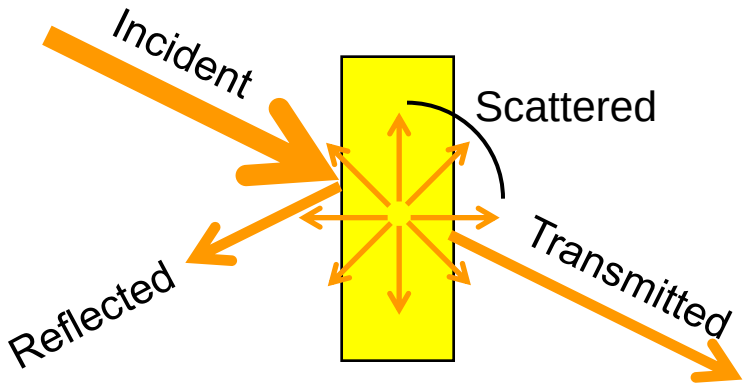
Cary 300 UV-Vis Spectrophotometer

Modes	Single/double/dual single beam
UV light source	Deuterium arc lamp
Visible light source	Incandescent bulb
Accessories	Specular reflectance, Diffuse reflectance

Interaction of Light with Matter

When light strikes a sample, many processes can occur:

- Reflection
- Scattering
- Diffraction
- Absorption
- Transmission



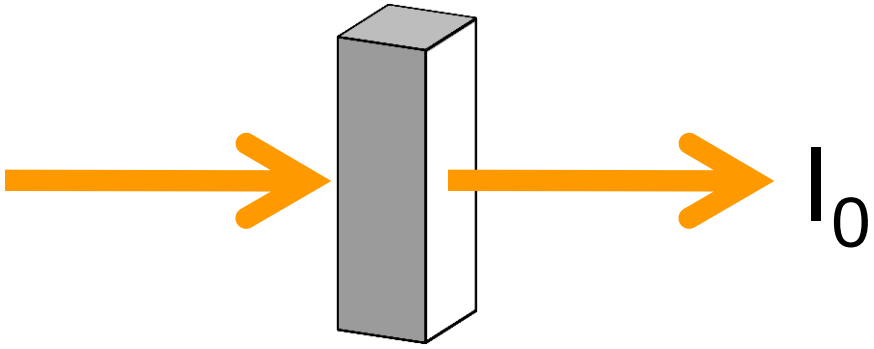
The interaction depends both on the wavelength of the light and the properties of the sample.

UV-vis Spectrophotometer

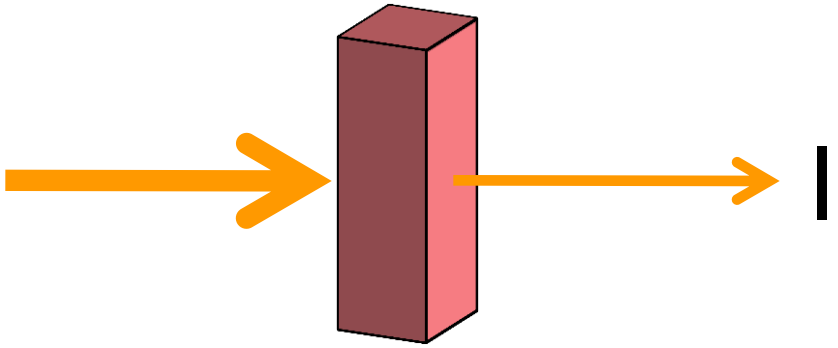
- Measures difference in intensity between two beams of light:
  - One is the reference (or initial) beam and has intensity = I_0
  - One beam passes through the sample and has intensity = I
  - Note: $I < I_0$
- The measurements can be performed in at least two different ways:
  - Single beam (sequential: ref then sample)
  - Double beam (simultaneous: ref and sample)

Single Beam Measurement

Step 1: Measure blank sample and use this as the “baseline” which will be factored out of all future sample measurements. This corrects for absorption by the solvent and other uncontrolled variables.

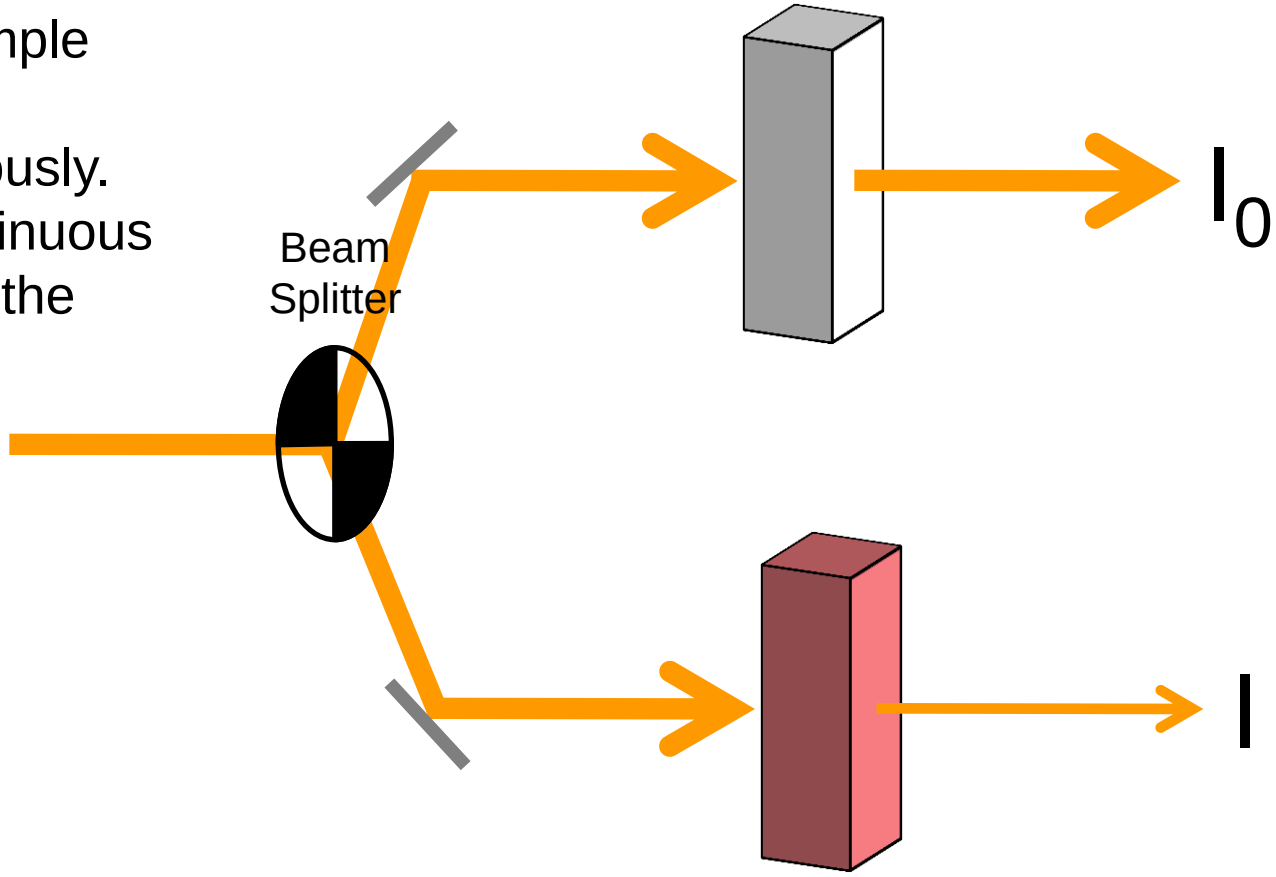


Step 2: Measure actual sample in the exact same solvent that was used for the baseline.



Double Beam Measurement

In this set-up, the sample and reference are measured simultaneously. This allows for a continuous comparison between the two samples.



Measurement Considerations

- What is measured by the spectrophotometer?
  - The intensity of light striking the detector
- When done correctly, the difference between the measured intensity and the reference intensity is due only to events occurring in the sample.
- Most often, absorption by molecules in the sample reduces the light intensity as the beam passes through the sample.

Measurement Considerations

However, other processes (in addition to absorption) can be happening during the measurement. For example:

- Reflection
- Scattering

→ These *decrease* the amount of light reaching the detector

- Fluorescence
- Phosphorescence

→ These *increase* the amount of light reaching the detector

Measurement Considerations

- The Cary 300 instrument measures transmitted light and can calculate the amount of light absorbed.
- It can also compensate for reflection when proper references (baselines) are used.
- Also, with the “integrating sphere” detector, our instrument can directly measure reflected light.
- However, our set-up cannot account for scattering or light emission from the sample (e.g., fluorescence). Other instruments can be used to measure these quantities, if needed.

Terminology

- Consider the simple case of a well-behaved homogeneous solution (no scattering or emission processes).
- When light passes through the sample it can be reflected (R), absorbed (A), or transmitted (T).
- The sum of these 3 processes must account for all of the incident light. If the initial intensity was 100:

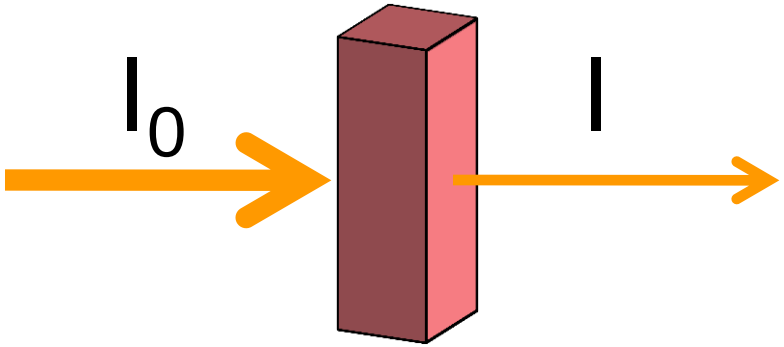
$$100 = R + A + T$$

- With appropriate baseline measurements, reflection is factored out, so the only processes we need to consider are A and T:

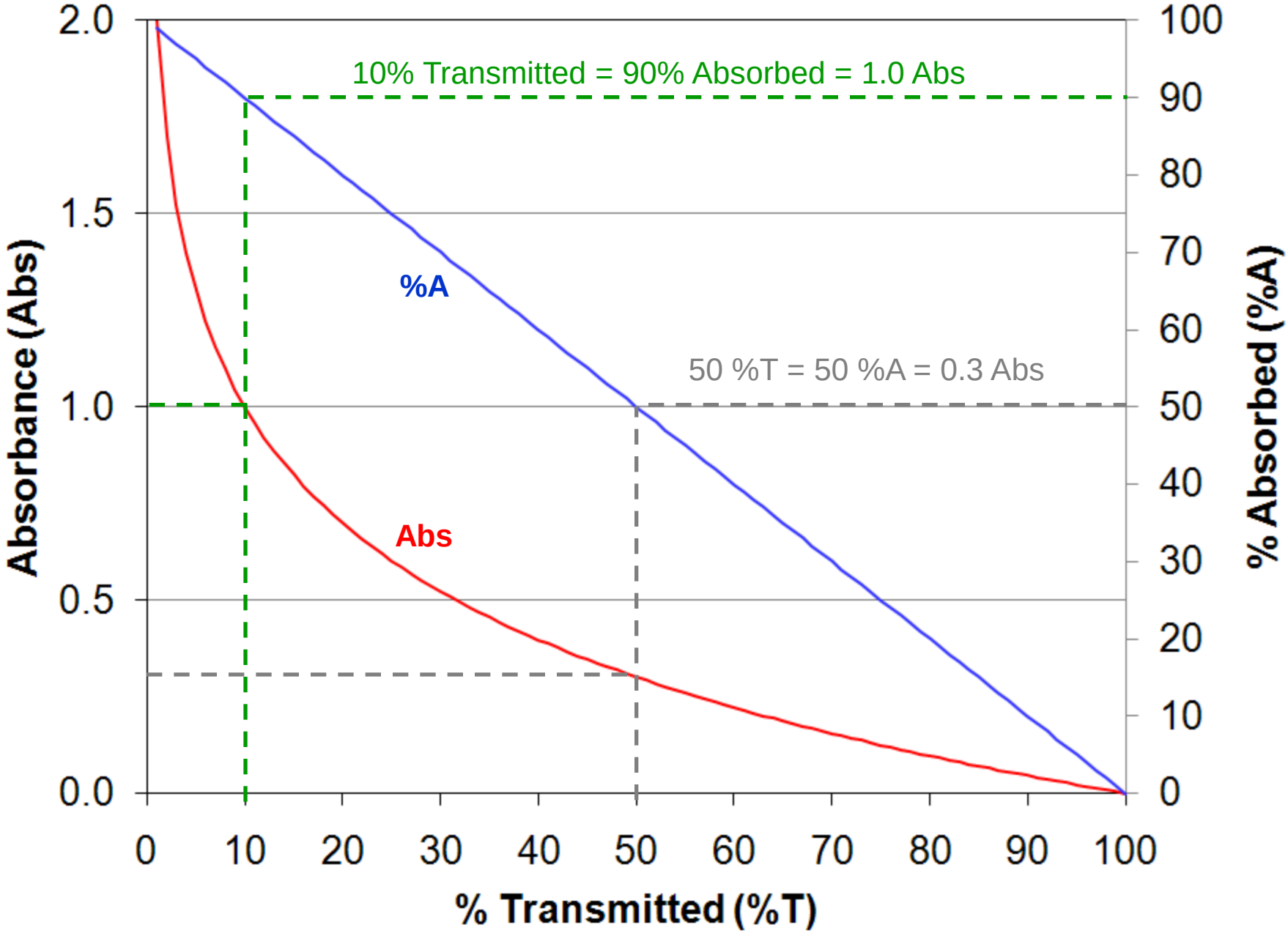
$$100 = A + T$$

Terminology

Quantity	Description	Range	Calculation
Transmittance (T)	Ratio of intensities between incident and transmitted light	$0 \leq T \leq 1$	$T = \frac{I}{I_0}$
% Transmittance (%T)	Transmittance expressed as a percentage	$0\% \leq \%T \leq 100\%$	$\%T = \frac{I}{I_0} \times 100$
% Absorbed (%A)	The percentage of light absorbed by the sample	$0\% \leq \%A \leq 100\%$	$\%A = 100 - \%T$
Absorbance (Abs)	A logarithmic quantity that is directly proportional to concentration	$Abs \geq 0$	$Abs = -\log(T) = -\log\left(\frac{I}{I_0}\right)$



Note: I_0 is usually baseline corrected to factor out absorption by the solvent and reflection caused by the sample holder



Absorbance (Abs)

Q: Why use a logarithmic quantity instead of a simple linear one?
A: The absorbance is directly proportional to concentration.

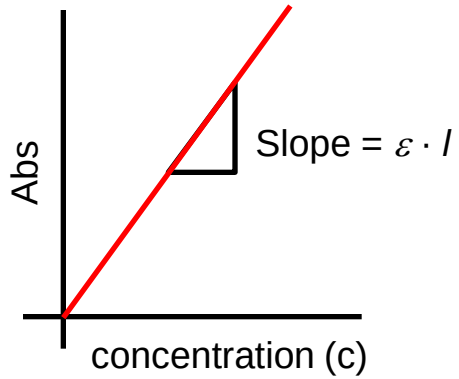
The Beer-Lambert Law
The absorbance of a beam of collimated monochromatic radiation in a *homogeneous isotropic medium* is proportional to:

•the absorption path length (*l*), which is commonly 1 cm (thickness of the cuvette)
•the concentration (*c*).

The law can be expressed as: $\text{Abs} = -\log(I/I_0) = \varepsilon\, c\, l$

where the proportionality constant (ε) is called the molar absorption coefficient.

SI units:
Abs = dimensionless
l = cm
c = mol/L
ε = L/mol·cm



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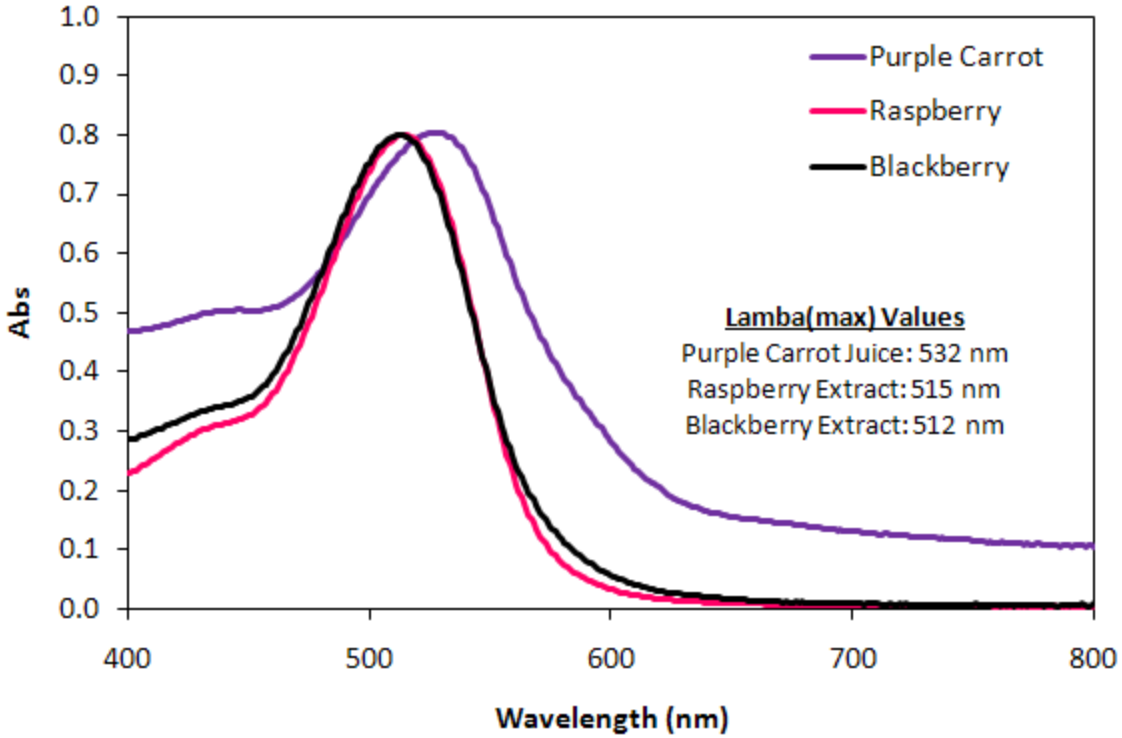
UV-vis Example

Dye solutions used in solar cell experiment



Absorbance = 0.80 at λ_{max}

Abs = -log(T)

0.80 = -log(T)

$T = 10^{-0.80} = 0.16$

16% Transmitted
84% Absorbed