

The Fundamentals of Spectroscopy: Theory

BUILDING
BETTER SCIENCE

AGILENT AND YOU





Agilent is committed to the educational community and is willing to provide access to company-owned material.

This slide set was created by Agilent for teaching purposes only.

If you wish to use the pictures, sketches, or drawings for any other purpose, please contact Agilent first.



Introduction

Spectroscopy is the study of the interaction between matter and electromagnetic radiation. Historically, spectroscopy originated through the study of visible light dispersed according to its wavelength, by a prism. Later the concept was expanded greatly to comprise any interaction with radiative energy as a function of its wavelength or frequency. Spectroscopic data is often represented by a spectrum, a plot of the response of interest as a function of wavelength or frequency.

- Spectrum (Latin): ghost
- Skopos (Greek): watcher
- Spectroscopist = ghost watcher



Table of Contents

Historical Background

- [Early History of Optical Spectra](#)
- [1666 Observation of Visible Spectrum](#)
- [1802 Fraunhofer Absorption Lines](#)
- [Kirchhoff & Bunsen's Emission Experiment](#)
- [Kirchhoff & Bunsen's Absorption Experiment](#)

Definitions

- [The Milton Spectrum](#)
- [Spectroscopy and Spectrometer](#)
- [Electromagnetic Spectrum](#)
- [Light](#)

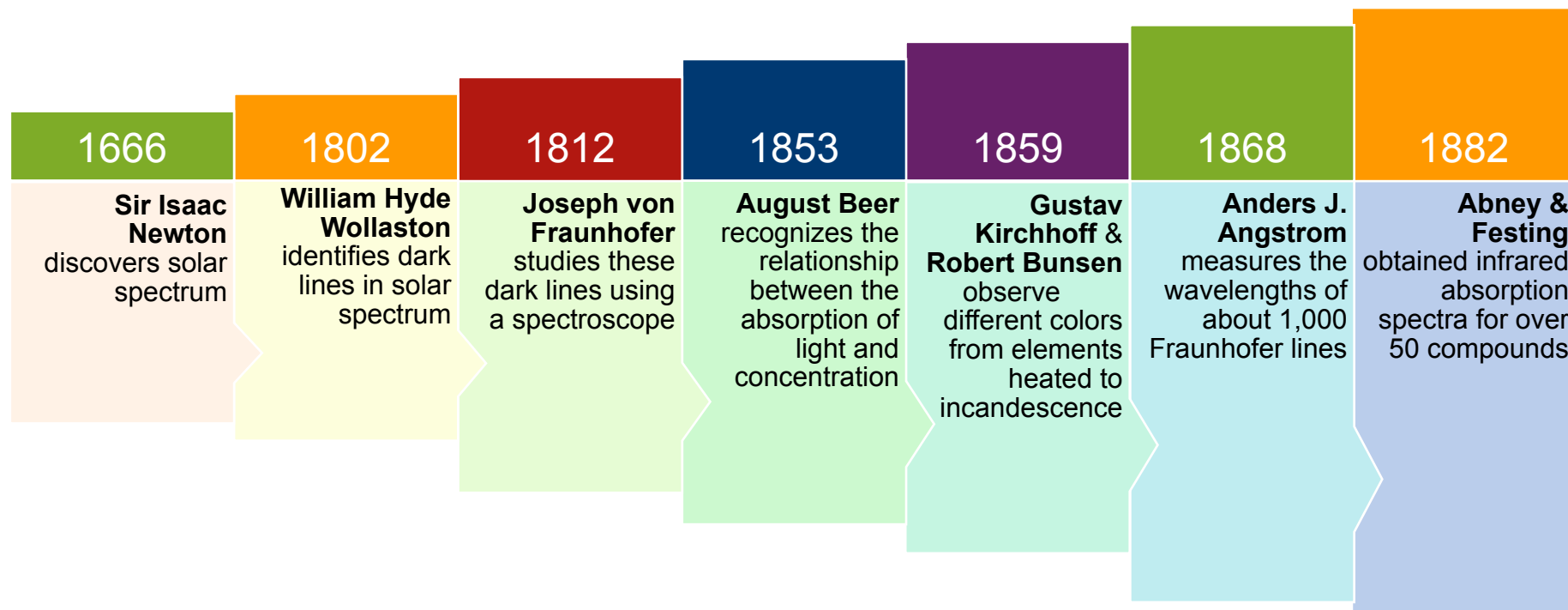
Key Parameters

- [Wavelength and Frequency](#)
- [Absorption and Emission](#)
- [Light Absorbed vs. Energy Levels](#)
- [Characteristics of Atomic Spectra](#)
- [Absorbance and Transmittance](#)
- [Absorbance: Concentration Relationship](#)
- [Beer-Bouguer-Lambert Law](#)



Historical Background

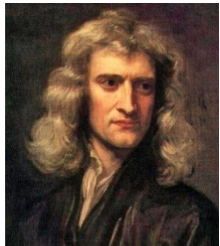
Early History of Optical Spectra



Historical Background

1666 Observation of Visible Spectrum

Sir Isaac Newton's Experiment

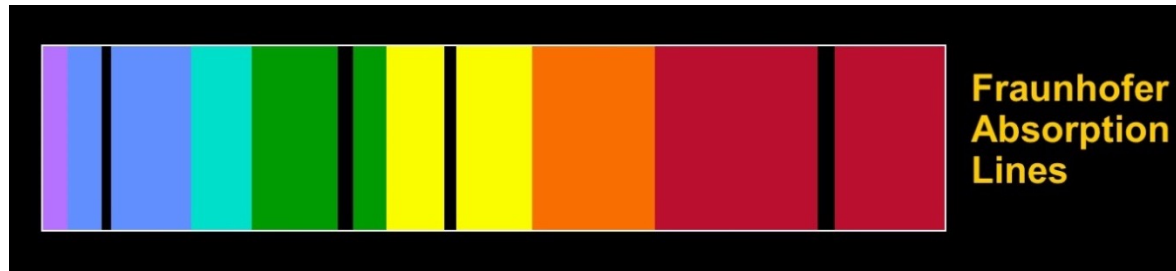


Sir Isaac Newton, 1642-1726
English physicist and mathematician
Source: [Wikipedia](#)

Historical Background

1802 Fraunhofer Absorption Lines

Wollaston and Fraunhofer, working independently, discover dark lines in the solar spectrum.



Fraunhofer introduces diffraction grating which obtains better spectral resolution.

Fraunhofer proposes that dark lines are due to the sun's own atmosphere absorbing light.



Img. 1: Joseph von Fraunhofer, 1787-1826, German Optician.
Source: [Wikipedia](#),

Img. 2: William Hyde Wollaston, 1766-1828, English Chemist.
Source: [Wikipedia](#)

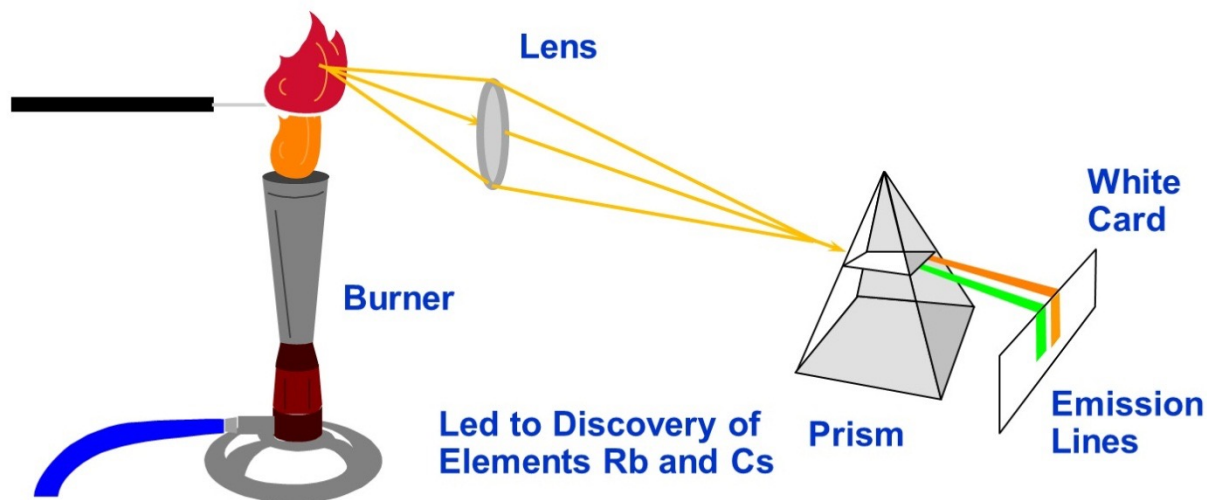
see notes for details

Historical Background

Kirchhoff and Bunsen's Emission Experiment

Kirchhoff & Bunsen's Experiment

Place Salt on Wire Loop
and Hold in Flame



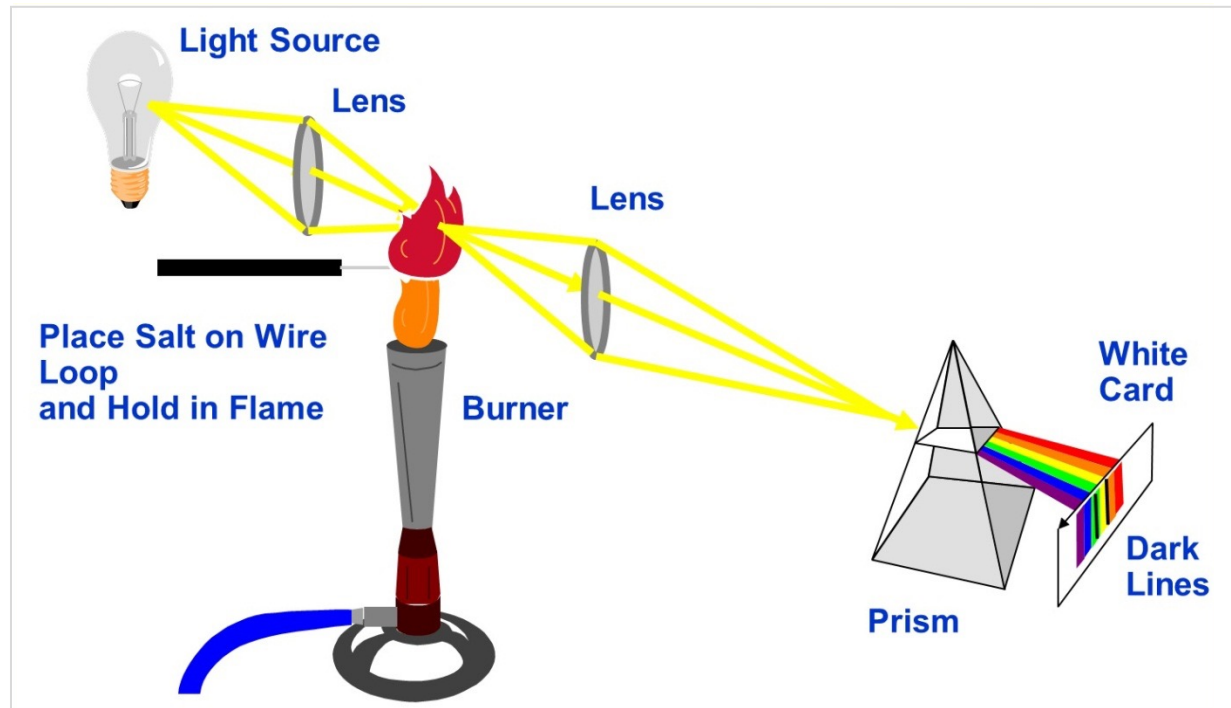
Robert Bunsen (1811-1899)
German Chemist,
Source: [Wikipedia](https://en.wikipedia.org/wiki/Robert_Bunsen)

Gustav Robert Kirchhoff (1825-1887) German
Physicist,
Source: [Wikipedia](https://en.wikipedia.org/wiki/Gustav_Robert_Kirchhoff)

Kirchhoff and Bunsen observed different colors from elements heated to incandescence.

Historical Background

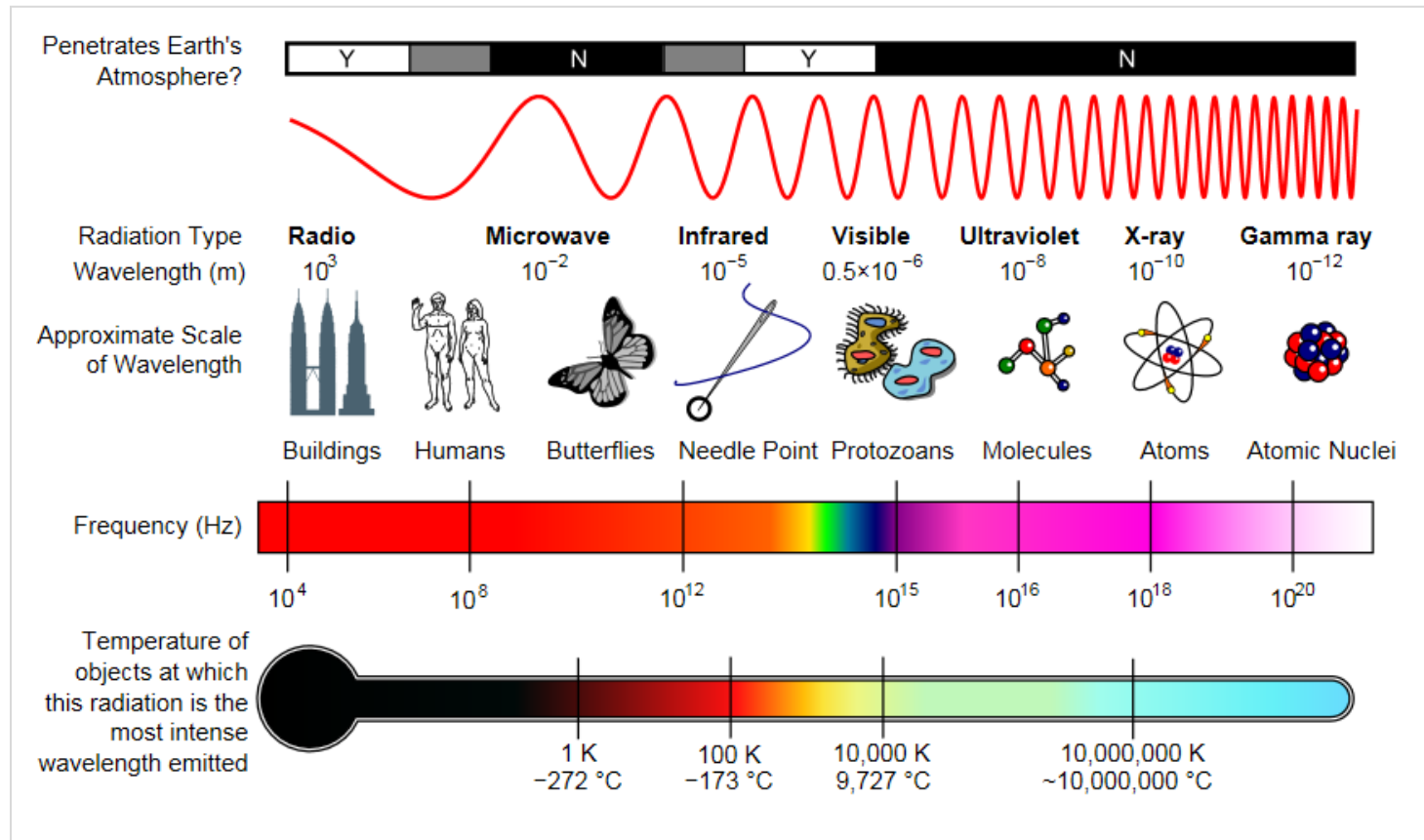
Kirchhoff and Bunsen's Absorption Experiment



Kirchhoff and Bunsen passed a light beam through the heated metallic salt and obtained Fraunhofer absorption lines.

Definitions

The Milton Spectrum



This diagram of the Milton spectrum shows the type, wavelength (with examples), frequency, and black body emission temperature.

Source: [Wikipedia](#); adapted from [EM_Spectrum3-new.jpg](#), which is a NASA image

Definitions

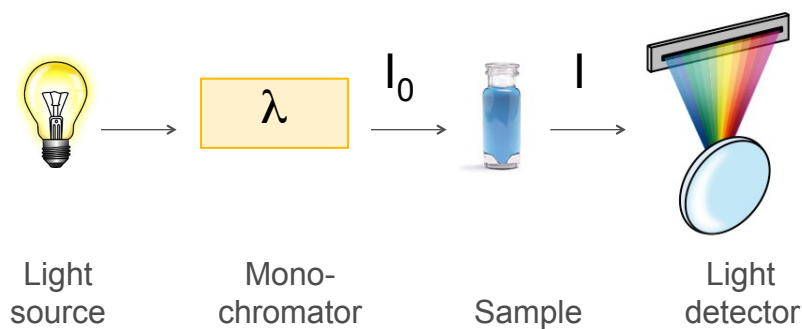
Spectroscopy

The measurement of a sample's interaction with light of different wavelengths from different regions of the electromagnetic spectrum.

The measurement of such signals as a function of wavelength results in the collection of a spectrum, and leads to the term “spectroscopy.”

Spectrometer

An instrument for making relative measurements in the optical spectral region, using light that is spectrally dispersed by a dispersing element.

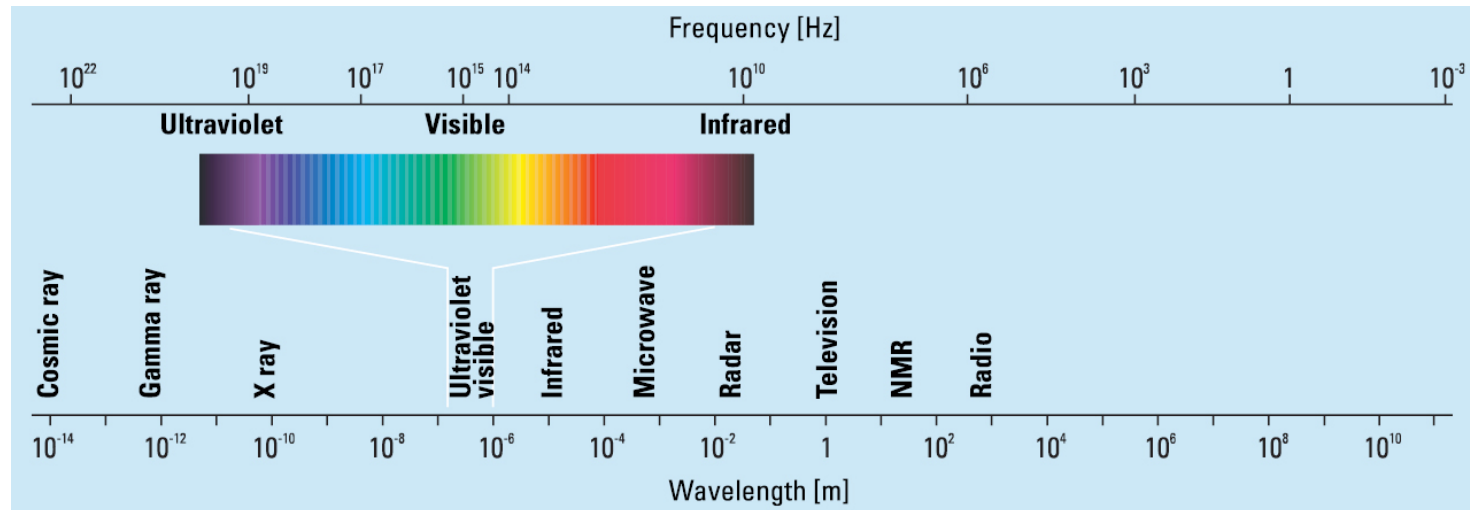


Definitions

Electromagnetic Spectrum

The electromagnetic spectrum covers many orders of magnitude in frequency and wavelength.

- Names of the regions are purely historical
- No abrupt or fundamental change in going from one region to the next
- Visible light represents only a small fraction of the electromagnetic spectrum



The electromagnetic spectrum

Definitions

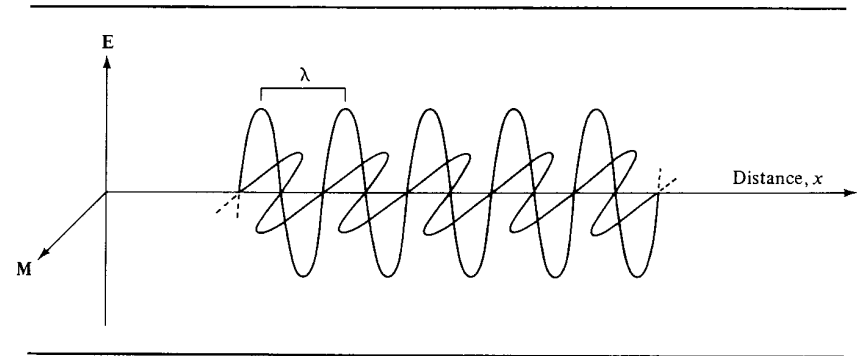
Light

Light can be described in two ways:

- Wave-like properties Terms such as wavelength and frequency are often used.
- Particle-like properties These are expressed in terms of packets of energy called photons.

These terms are valid throughout the entire electromagnetic spectrum and are not limited to what is normally considered to be “light” (visible, ultra-violet, and infrared).

Light is considered wave-like in nature as it consists of oscillating electric (E) and magnetic (M) fields. These fields are at right angles to each other, and travel at a constant velocity in a given medium. In a vacuum, this velocity is $3 \times 10^8 \text{ ms}^{-1}$.



Key Parameters

Wavelength and Frequency

The energy associated with electromagnetic radiation can be defined as follows:

$$E = h \cdot \nu$$

Frequency is related to wavelength by:

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

Note: In spectroscopy, wavelength is generally expressed in micrometers, nanometers, or wavenumbers ($1/\lambda$; expressed in reciprocal centimeters).

E	Energy (J)
h	Planck's constant (6.62×10^{-34} Js)
ν	Frequency (s^{-1})
c	Speed of light (3×10^8 ms $^{-1}$)
λ	Wavelength (m)

Key Parameters

Absorption and Emission

Interactions of electromagnetic radiation with matter may be broadly classified into:

- **Absorption processes:**

Electromagnetic radiation from a source is absorbed by the sample and results in **a decrease** in the radiant power reaching a detector

- **Emission processes:**

Electromagnetic radiation emanates from the sample, resulting in **an increase** in the radiant power that reaches a detector



Key Parameters

Absorption and Emission

Absorption and emission processes involve **transitions** between different energy levels or states.

For a transition to occur, an incident photon must have energy **equal to the difference in energy between the two states**. If this is the case, the energy can be absorbed, and a transition to an excited state can occur.

Such transitions can involve changes in

- Electronic energy
- Vibrational energy
- Rotational energy

$$\Delta E_{\text{electronic}} > \Delta E_{\text{vibrational}} > \Delta E_{\text{rotational}}$$

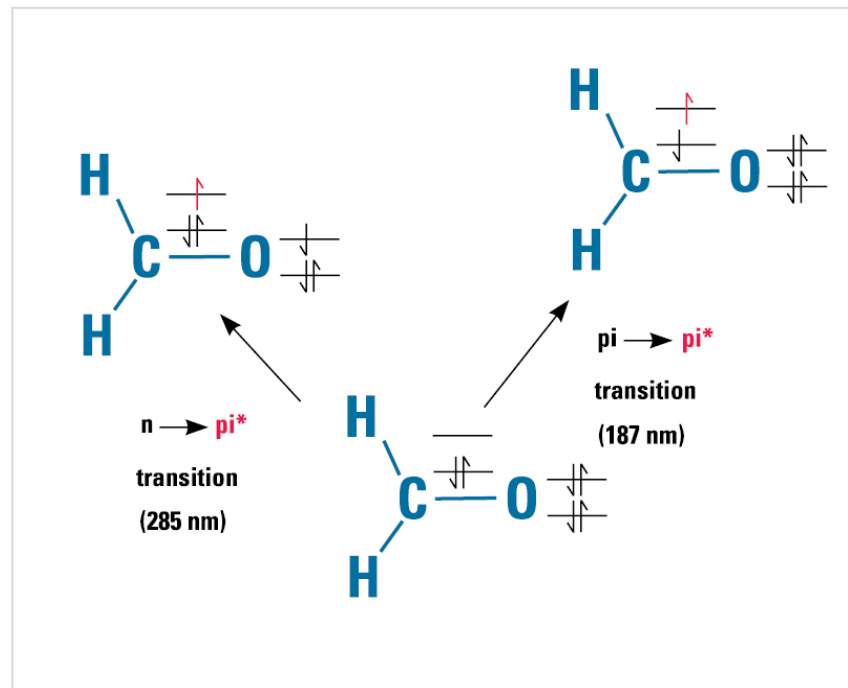
Changes in nuclear energy levels can be observed at very high energies (γ rays), while changes in nuclear spin states can be observed at much lower energies (microwaves and radiowaves).

Key Parameters

Absorption and Emission

This figure shows an example of electronic transitions in formaldehyde and the wavelengths of light that cause them.

These transitions should result in very narrow absorbance bands at wavelengths highly characteristic of the difference in energy levels of the absorbing species.



Electronic transitions in formaldehyde

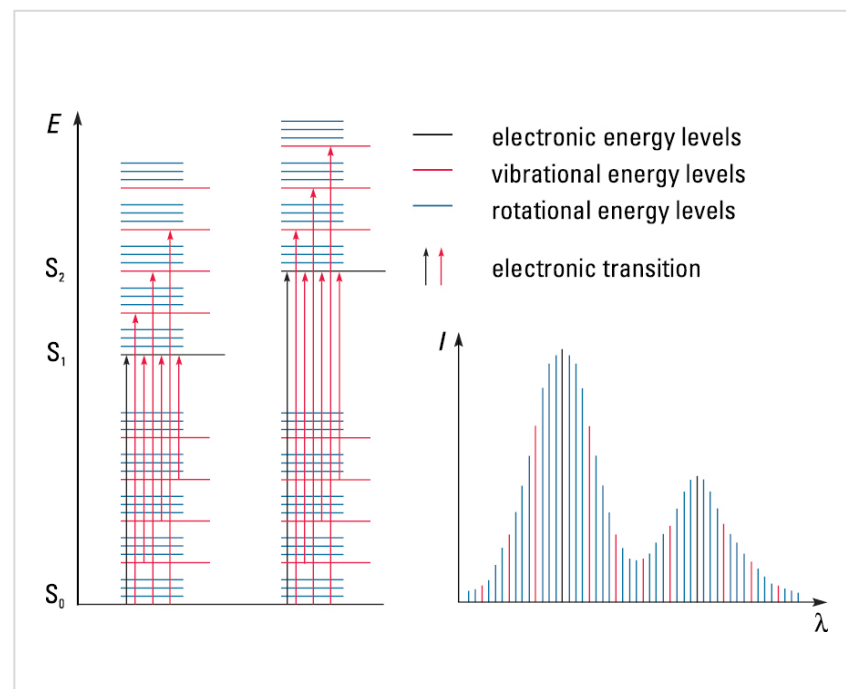
Key Parameters

Absorption and Emission

Here we see vibrational and rotational energy levels super-imposed on the electronic energy levels.

Because many transitions with different energies can occur, the bands are broadened.

The broadening is even greater in solutions owing to solvent-solute interactions.



Electronic transitions and UV-visible spectra in molecules

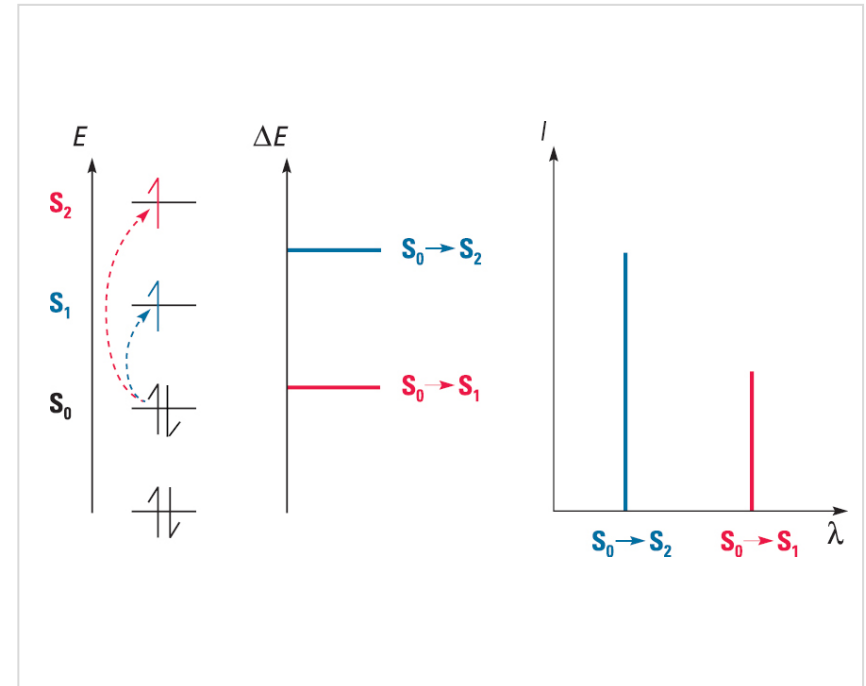
Key Parameters

Absorption and Emission

This figure shows an example of electronic transitions in atoms.

These transitions should result in very narrow absorbance bands at wavelengths highly characteristic of the difference in energy levels of the absorbing species.

Unique wavelengths exist for each absorption/emission of energy from the atom.



Electronic transitions and spectra in atoms

Key Parameters

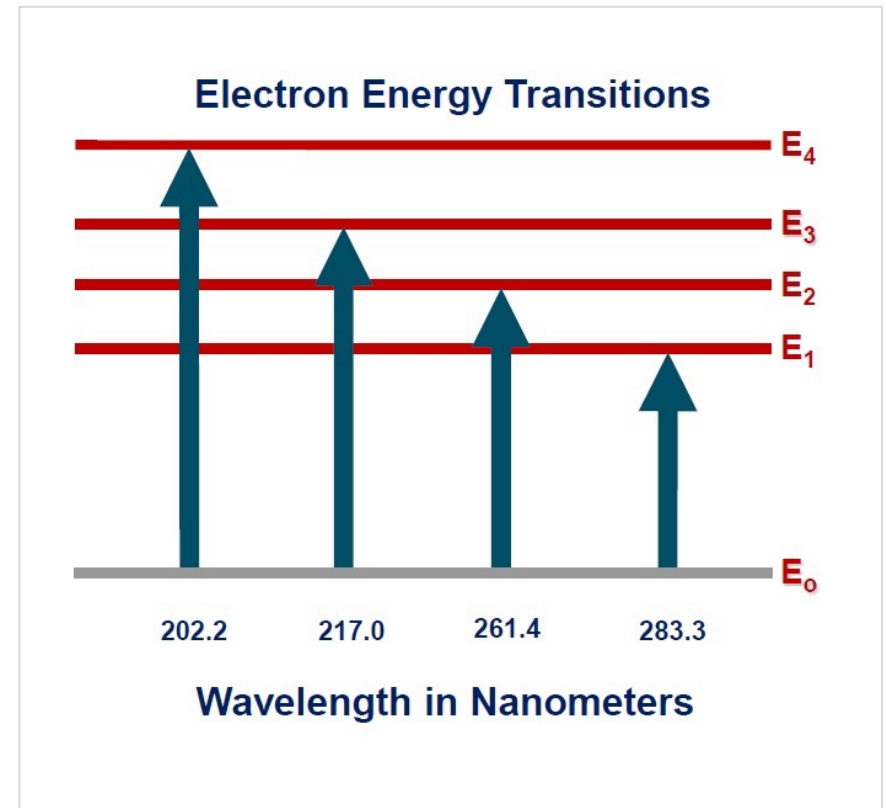
Absorption and Emission

Atoms can absorb discrete amounts of energy:

- Heat
- Light at discrete wavelengths

An electron may change energy levels:

- Energy to change levels = energy of absorbed light
- Atoms become “excited”
- Electron moves to higher energy level: $E_1, E_2, \dots E_n$



Energy level diagram for lead (Pb)

Key Parameters

Light Absorbed vs. Energy Levels

Wavelength of light (λ) is inversely proportional to the spacing between energy levels:

$$\lambda = \frac{c}{\Delta \cdot E} \quad (\text{wider spacing} = \text{shorter wavelength})$$

Each transition has different spacing and energy and therefore different wavelength.

Atoms will also have emission lines. An excited atom relaxes to ground state releasing energy as emitted light.

- Same energy as absorption
- Same wavelength as absorption

Key Parameters

Characteristics of Atomic Spectra

Sharp peaks (compared to broad peaks in UV-Vis)

Most significant lines originate from ground state

- Resonance lines:
 - Most intense lines
 - Most interest in atomic absorption

They can occur from one excited state to another

- Non-resonance lines:
 - Weaker lines
 - Generally **not** useful for atomic absorption



Key Parameters

Absorbance and Transmittance

When radiation interacts with matter a number of processes can occur:

- Absorbance
- Reflection
- Scattering
- Fluorescence/phosphorescence
- Photochemical reactions

When light passes through or is reflected from a sample, the amount of light absorbed is equal to the ratio of the transmitted radiation (I) to the incident radiation (I_0).

$$T = \frac{I}{I_0} \quad T = \left(\frac{I}{I_0} \right) \cdot 100$$

(*Transmittance*)

$$A = -\log_{10} T$$

(*Absorbance*)

Key Parameter

Absorbance/Concentration Relationship

Lambert's law

- The portion of light absorbed by a transparent medium is independent of the intensity of the incident light
- Each successive unit of thickness of the medium absorbs an equal fraction of the light passing through it

Beer's law

- Light absorption is proportional to the number of absorbing species in the sample



UV-Vis Spectroscopy

Beer-Bouguer-Lambert Law

Absorbance is related to concentration by the Beer-Bouguer-Lambert law:

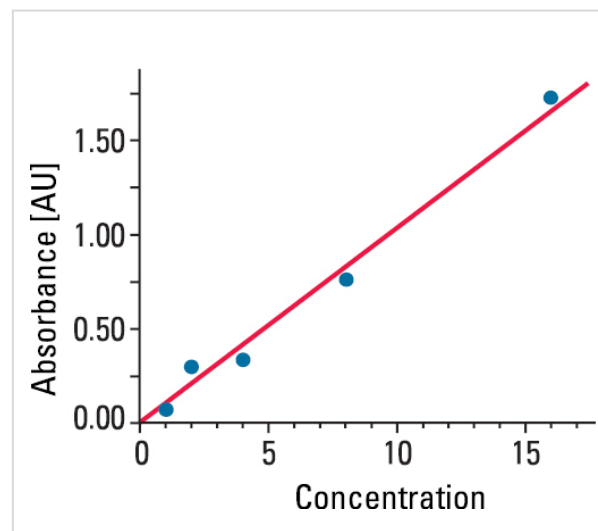
$$A = -\log_{10} T = \varepsilon \cdot b \cdot c$$

ε extinction coefficient or molar absorption ($\text{Lmol}^{-1}\text{cm}^{-1}$)

b pathlength (cm)

c concentration

Absorption can be attributed to interaction with the sample and/or losses due to reflection and scattering.



Example of calibration curve. Calibration is done by measuring A as c varies.

Source: [Fundamentals of UV-visible spectroscopy](#)
see notes for details

Abbreviations

Abbreviation	Definition
A	absorbance
AAS	atomic absorption spectroscopy
AES	atomic emission spectroscopy
b	path length (cm)
c	speed of light ($3 \times 10^8 \text{ ms}^{-1}$)
ϵ	extinction coefficient or molar absorption ($\text{Lmol}^{-1}\text{cm}^{-1}$)
E	oscillating electric field
E	energy
h	Planck's constant ($6.62 \times 10^{-34} \text{ Js}$)
I	transmitted radiation
I_0	incident radiation

Abbreviation	Definition
ICP-OES	inductively coupled plasma – optical emission spectroscopy
ICP-MS	inductively coupled plasma – atomic mass spectrometry
λ	wavelength
M	oscillating magnetic fields
MP-AES	microwave plasma atomic emission spectroscopy
T	transmittance
ν	frequency (s^{-1})
XRF	X-ray fluorescence
XRD	X-ray diffraction

Learn More

For more information on products from Agilent, visit www.agilent.com or www.agilent.com/chem/academia

Have questions or suggestions to this presentation?
Contact academia.team@agilent.com

Publication	Title	Pub. No.
Primer	Atomic spectroscopy applications in the contract environmental laboratory	5991-5326EN
Primer	Fundamentals of UV-visible spectroscopy	5980-1397EN
Brochure	Atomic Spectroscopy Portfolio Brochure	5990-6443EN
Web	CHROMacademy – free access for students and university staff to online courses	
Videos	www.agilent.com/chem/teachingresources	
Images	www.agilent.com/chem/teachingresources	





THANK YOU

Publication Number: 5991-6694EN

 ToC

For teaching purpose only

February 22, 2016

28



Agilent Technologies

ACADEMIC
& INSTITUTIONAL
RESEARCH