The Fundamentals of Spectroscopy: Theory
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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
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Historical Background
Early History of Optical Spectra

1666: Sir Isaac Newton discovers solar spectrum
1802: William Hyde Wollaston identifies dark lines in solar spectrum
1812: Joseph von Fraunhofer studies these dark lines using a spectroscope
1853: August Beer recognizes the relationship between the absorption of light and concentration
1859: Gustav Kirchhoff & Robert Bunsen observe different colors from elements heated to incandescence
1868: Anders J. Angstrom measures the wavelengths of about 1,000 Fraunhofer lines
1882: Abney & Festing obtained infrared absorption spectra for over 50 compounds
Historical Background
1666 Observation of Visible Spectrum

Sir Isaac Newton's Experiment

Sir Isaac Newton, 1642-1726
English physicist and mathematician
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 Optican.**

**Img. 2: William Hyde Wollaston, 1766-1828, English Chemist.**
Historical Background
Kirchhoff and Bunsen’s Emission Experiment

Kirchhoff & Bunsen’s Experiment
Place Salt on Wire Loop and Hold in Flame

Burner
Lens
White Card
Prism
Emission Lines

Led to Discovery of Elements Rb and Cs

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


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
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 $3 \times 10^8$ 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).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>(E)</td>
<td>Energy (J)</td>
</tr>
<tr>
<td>(h)</td>
<td>Planck’s constant (6.62 (\times) 10^{-34} Js)</td>
</tr>
<tr>
<td>(\nu)</td>
<td>Frequency (s^{-1})</td>
</tr>
<tr>
<td>(c)</td>
<td>Speed of light (3(\times)10^8 ms^{-1})</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Wavelength (m)</td>
</tr>
</tbody>
</table>
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 (\(\gamma\) 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.
Key Parameters
Absorption and Emission

Here we see vibrational and rotational energy levels superimposed 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: $E_1, E_2, \ldots E_n$

*Energy level diagram for lead (Pb)*
Key Parameters
Light Absorbed vs. Energy Levels

Wavelength of light ($\lambda$) is inversely proportional to the spacing between energy levels:

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

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 (Io).

\[ T = \frac{I}{I_0} \]

(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 though it

Beer’s law
• Light absorption is proportional to the number of absorbing species in the sample
Absorbance is related to concentration by the Beer-Bouguer-Lambert law:

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

\( \varepsilon \) 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.

Source: Fundamentals of UV-visible spectroscopy

see notes for details
## Abbreviations

<table>
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<tr>
<td>A</td>
<td>absorbance</td>
</tr>
<tr>
<td>AAS</td>
<td>atomic absorption spectroscopy</td>
</tr>
<tr>
<td>AES</td>
<td>atomic emission spectroscopy</td>
</tr>
<tr>
<td>b</td>
<td>path length (cm)</td>
</tr>
<tr>
<td>c</td>
<td>speed of light (3 \times 10^8 \text{ ms}^{-1})</td>
</tr>
<tr>
<td>ε</td>
<td>extinction coefficient or molar absorption (\text{Lmol}^{-1}\text{cm}^{-1})</td>
</tr>
<tr>
<td>E</td>
<td>oscillating electric field</td>
</tr>
<tr>
<td>E</td>
<td>energy</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s constant (6.62 \times 10^{-34} \text{ Js})</td>
</tr>
<tr>
<td>I</td>
<td>transmitted radiation</td>
</tr>
<tr>
<td>I₀</td>
<td>incident radiation</td>
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</table>

<table>
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<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma – optical emission spectroscopy</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>inductively coupled plasma – atomic mass spectrometry</td>
</tr>
<tr>
<td>λ</td>
<td>wavelength</td>
</tr>
<tr>
<td>M</td>
<td>oscillating magnetic fields</td>
</tr>
<tr>
<td>MP-AES</td>
<td>microwave plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>T</td>
<td>transmittance</td>
</tr>
<tr>
<td>ν</td>
<td>frequency (\text{s}^{-1})</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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THANK YOU

Publication Number: 5991-6594EN