Chemistry 4631

Instrumental Analysis

Lecture 1

Syllabus

Chemistry 4631 Spring 2024

Instructor: Dr. Teresa D. Golden
Chem 279, tgolden@unt.edu.

Office hours: MW 8:00-8:45 a.m. and 10:00-10:30 a.m. Chem 279

Lecture: MWF 9:00 – 9:50 a.m. Chem 352
Attendance is required.

Exams and Final will be taken in CHEM 352.

There will be several in-class exams and a final exam.

Dates for each exam will be announced in class and class website.

The final is scheduled for Wednesday May 10th (8:00-10:00 am) in CHEM 352 (notice earlier start time).

Syllabus

Chemistry 4631   Spring 2024

Course Material: **Text: Principles of Instrumental Analysis, 7th or 6th ed.; (Skoog/Holler/Nieman).**

Prereq: Chem 3451/3452 Quant. Analysis (w/ C or better)

This course covers electronics, spectroscopy, electrochemistry, chromatography, and selected topics.

This course does not use canvas – for latest info and announcements go to the Class Website at:

https://chemistry.unt.edu/~tgolden/courses/course_downloadsSpr24

Syllabus

Chemistry 4631 Spring 2024

Homework:

1) Problem sets will be assigned at the end of each chapter.

2) Also spectral interpretations will periodically be assigned.

Grading: Exams, quizzes, and assignments will each be given a total point value. The student's final grade will be: (the total number of points received/total number of points possible) x 100.

A – 90% B – 80% C – 70% D – 60% F < 60%

Syllabus

WEEK	CLASS ASSIGNMENT	TOPICS
1	Ch. 1 & 6 & Appendix Lab: No Lab	Intro, Stats, Data Analysis Intro Laboratory Principles, Electromagnetic Spectrum, Quantum Theory
2	Ch. 13-17 Lab: Check-in	UV-vis, FTIR, Fluorescence Theory
3	Ch. 6 & 7 Lab: UV-vis/FTIR	Components of Optical Instruments
4	Ch. 7 & 13-17 Lab: UV-vis/FTIR	Optical Instrument Design
5	Ch. 7 Lab: UV-vis/Fluorescence	Lasers, LEDs, and Semiconductors
6	Ch. 8-10 Lab: UV-vis/Fluorescence	Atomic Absorption and ICP Spectroscopy
7	Ch. 19 Lab: AAS/ICP/NMR	NMR
8	Ch. 22 Lab: AAS/ICP/NMR	Intro to Electrochemistry
9	Spring	Break
10	Ch. 23-25 Lab: Electrochemical Techniques	Electrochemical Techniques
11	Ch. 26 & 27 Lab: Electrochemical Techniques	Intro to Chromatography, Chromatography Theory, Gas Chromatography
12	Ch. 27 Lab:GC-FID/ GC-MS	Gas Chromatography Instrumentation
13	Ch. 28 Lab:GC-FID/ GC-MS	High Performance Liquid Chromatography Instrumentation
14	Ch. 11 & 20 Lab:HPLC-UV/HPLC-MS	Mass Spectroscopy Instrumentation and Spectra interpretation
15	Ch. 11 & 20 Lab:HPLC-UV/HPLC-MS	Mass Spectroscopy Instrumentation and Spectra interpretation
16	QA/QC & Review Lab: Final	Assessing Quality Assurance & Quality Control in the Lab
17	Final Exam (ACS)	8:00 -10:00 a.m.

Syllabus

Chemistry 4632 **Spring 2024**

Laboratory: M or W 1:30 – 5:20 p.m. Room 280 and 283 Chemistry

Instructor: Dr. Teresa D. Golden (Room 279 Chemistry, 565-2888 tgolden@unt.edu)

Teaching Assistants: Alireza Aminifazl Chem 225 T 9-10 am (aa1198@unt.edu); Saeed Hemmati Chem 225 Th 10-11 am (SaeedHemmati@my.unt.edu); Richard McCrary Chem 225 W 10-11 am (Richardmccrary@my.unt.edu).

Course Material: Lab Manual (handouts). The labs will cover spectroscopy, electrochemistry, chromatography, and selected topics. A pen, calculator, goggles, ruler, mask, and bound lab notebook are required for every lab. All notations, calculations and results are to be included in this lab notebook for each experiment. The TA must sign this book at the end of each lab.

Syllabus

Chemistry 4632 Spring 2024

Lab Reports: A formal lab report will be due at the next class period for every lab. This report must include: introduction and theory, experimental section, results, discussion, calculations, graphs, answers to questions, etc. The student will not only be graded on content but also neatness and readability. <u>No late reports will be accepted</u>.

<u>All Instrument diagrams must be drawn by hand.</u>

Exams: Lab practicums given during lab time.

Grading: The final lab grade will be calculated using the following: 10% lab book, 10% lab technique and 80% lab reports.

Syllabus

Week	Lab Assignment*
2	Laboratory Practicum: Proper Lab Techniques, Assign Drawers and Glassware
3 & 4	UV Spectroscopy: Mole-ratio and Slope-ratio Method
3 & 4	Infrared Spectroscopy: Spectra of Aldehydes and Ketones
5 & 6	UV Spectroscopy: Electronic Transitions in Organic Molecules
5 & 6	Fluorescence Spectroscopy: Determination of Fluorescein in Antifreeze
7 & 8	Atomic Absorption Spectroscopy or ICP-OES
7 & 8	NMR of Various Compounds
9	Spring Break
10 & 11	Potentiometry: Ion selective electrode, Fluoride in Water and Toothpaste
10 & 11	Voltammetry: CV of Vitamin C w/ Graphite Electrodes
12 & 13	GC-FID: Hydrocarbons & Gasoline
12 & 13	GC-MS: Volatile Organics
14 & 15	HPLC-UV-vis: Caffeine Analysis
14 & 15	HPLC-UV-MS: Drug Analysis
16	Final Exam: Laboratory Practicum, QA/QC, check-out

Syllabus

Chemistry 4632 Spring 2024

Laboratory Write-up Procedure

I. Title Page

Contains name, title of experiment, date of experiment, date due.

II. Introduction (3 to 8 pages) (30 pts)

III. Instrumentation (30 pts)

IV. Results and Discussion (40 pts)

All lab reports are due one week from the date performed and must be turned in to the TA at the beginning of lab. No late reports will be accepted.

How to Study For Class

Chemistry 4631

California State University Study – Multitasking
take notes
Purdue University Study - Spacing Effect
restudy previous material
Washington University – Self-testing (Active testing)
study groups
Harvard Study – Memory and fine motor skill
take notes

Study Tips:

1. Attend Class
2. Reread/Rewrite Notes Each Week
3. Write and Draw to Study (Practice Testing)

Introduction

Why Instrumental Analysis?

Instrumentation - used by scientist to solve analytical problems.

- **Measurement of physical properties**
- **Identification of unknowns**
- **Preparation of components**

TABLE 1-1 Chemical and Physical Properties Employed in Instrumental Methods

Characteristic Properties	**Instrumental Methods**
Emission of radiation	Emission spectroscopy (X-ray, UV, visible, electron, Auger); fluorescence, phosphorescence, and luminescence (X-ray, UV, and visible)
Absorption of radiation	Spectrophotometry and photometry (X-ray, UV, visible, IR); photoacoustic spectroscopy; nuclear magnetic resonance and electron spin resonance spectroscopy
Scattering of radiation	Turbidimetry; nephelometry; Raman spectroscopy
Refraction of radiation	Refractometry; interferometry
Diffraction of radiation	X-Ray and electron diffraction methods
Rotation of radiation	Polarimetry; optical rotary dispersion; circular dichroism
Electrical potential	Potentiometry; chronopotentiometry
Electrical charge	Coulometry
Electrical current	Amperometry; polarography
Electrical resistance	Conductometry
Mass	Gravimetry (quartz crystal microbalance)
Mass-to-charge ratio	Mass spectrometry
Rate of reaction	Kinetic methods
Thermal characteristics	Thermal gravimetry and titrimetry; differential scanning colorimetry; differential thermal analyses; thermal conductometric methods
Radioactivity	Activation and isotope dilution methods

The response is almost always represented by peaks,

But can also be color or a number (i.e. temperature, pH, etc…)

Chemist choose the correct analytical method or instrument to solve a problem.

In order to do this, the scientist must understand a wide variety of instruments and the limitations of each one.

Cost analysis is important.

To correctly select the instrument, the problem must be clearly defined.

1. What accuracy is required?
2. How much sample is available?
3. What is the concentration range of the analyte?
4. What components of the sample will cause interference?
5. What are the physical and chemical properties of the sample matrix?
6. How many samples are to be analyzed?

See Lab
Lecture 1

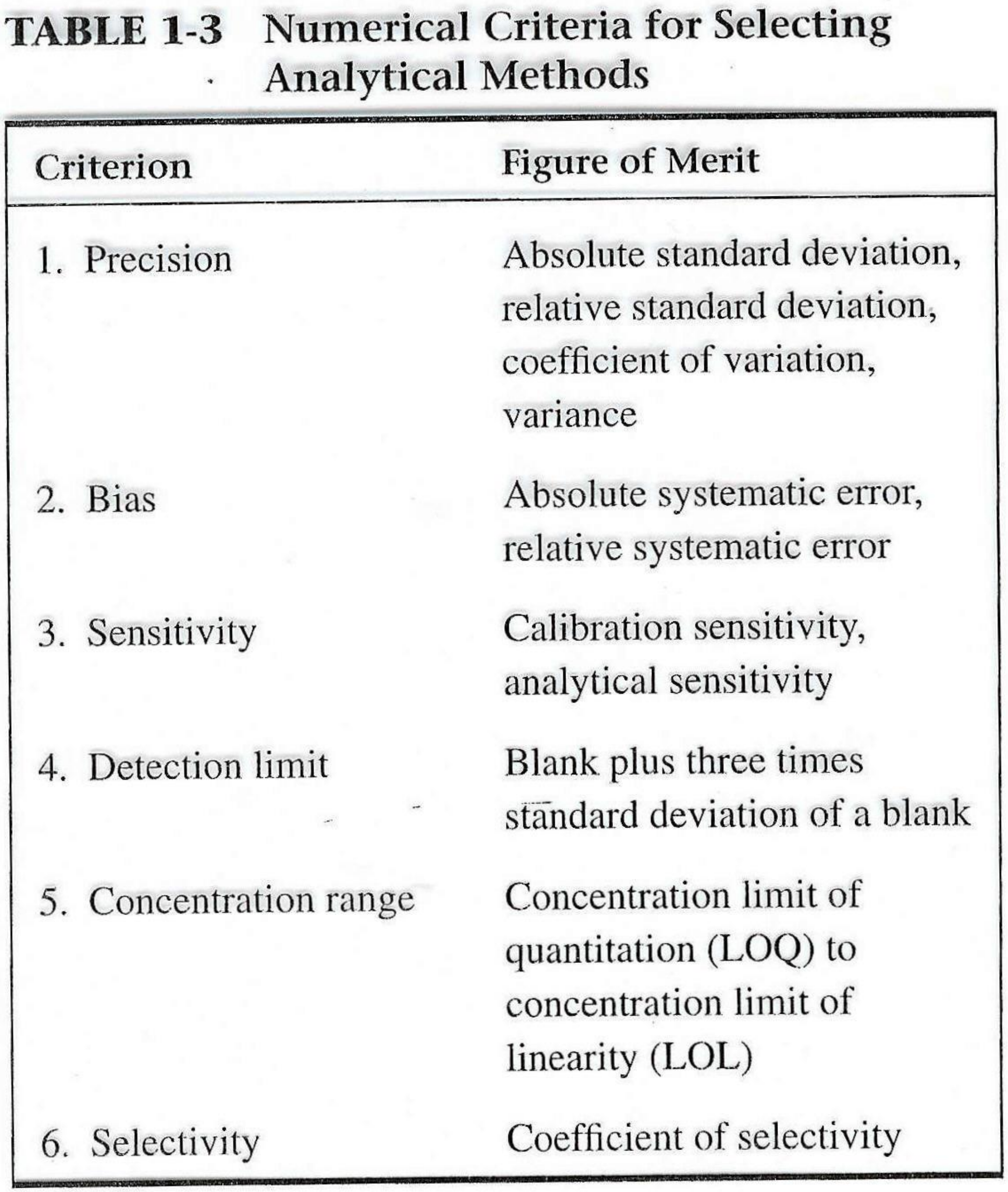


TABLE 1-3 Numerical Criteria for Selecting Analytical Methods

Criterion	Figure of Merit
1. Precision	Absolute standard deviation, relative standard deviation, coefficient of variation, variance
2. Bias	Absolute systematic error, relative systematic error
3. Sensitivity	Calibration sensitivity, analytical sensitivity
4. Detection limit	Blank plus three times standard deviation of a blank
5. Concentration range	Concentration limit of quantitation (LOQ) to concentration limit of linearity (LOL)
6. Selectivity	Coefficient of selectivity

Applications of UV/vis Spectrometry

Calibration curve – see Lab Lecture 1

Calibration standards need to approximate the composition of sample to be analyzed

If cannot match the matrix – best to use the standard addition method (Chapter 1).

Calibration

See Lab Lecture 1

- Standard Addition Method
- Internal Standard

Data Analysis

See Lab Lecture 1 – for how to do calculations on UV-vis Lab

Determination of Stoichiometry of Complex Ions

- Mole-ratio method
- Method of continuous variation

Applications of UV/vis Spectrometry

Quantitative Analysis

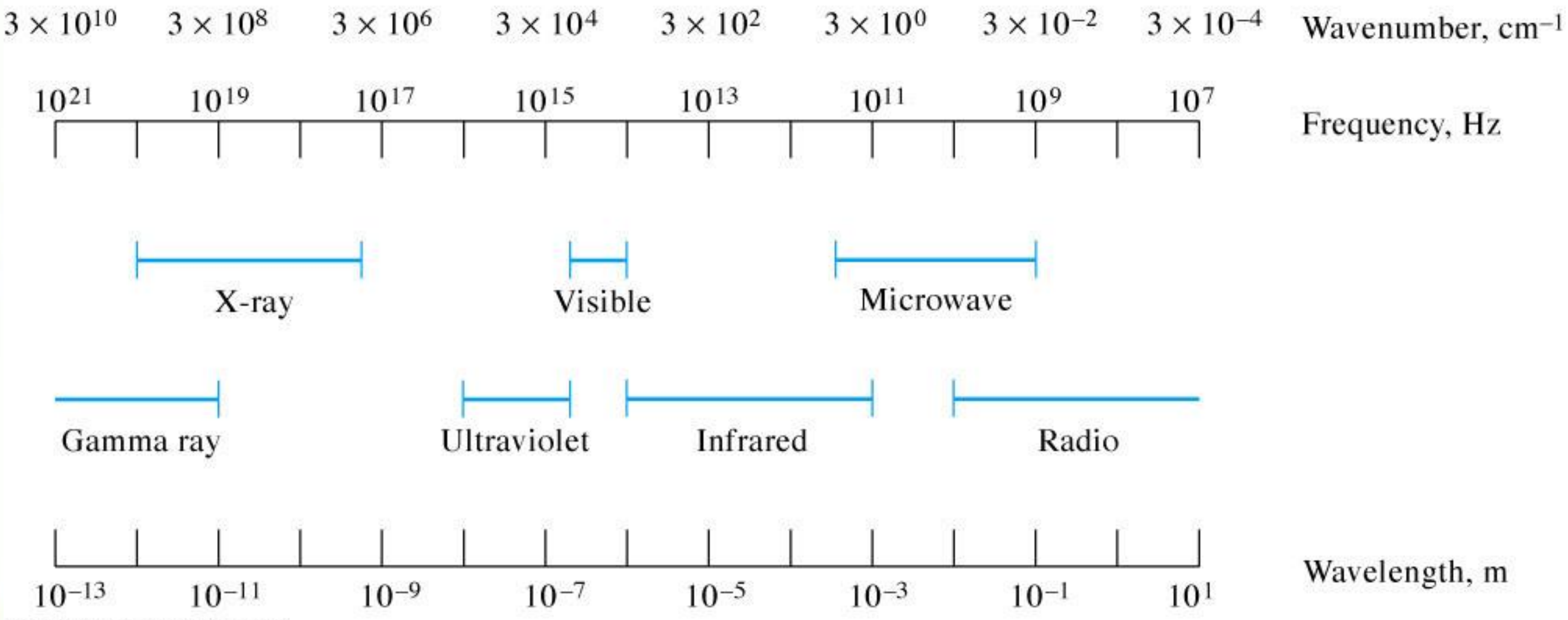
- Useful for both organic and inorganic systems
- Sensitive (10^{-4} to 10^{-5} M)
- Moderately selective
- Good accuracy
- Easy and convenient to use

Applications of UV/vis Spectrometry

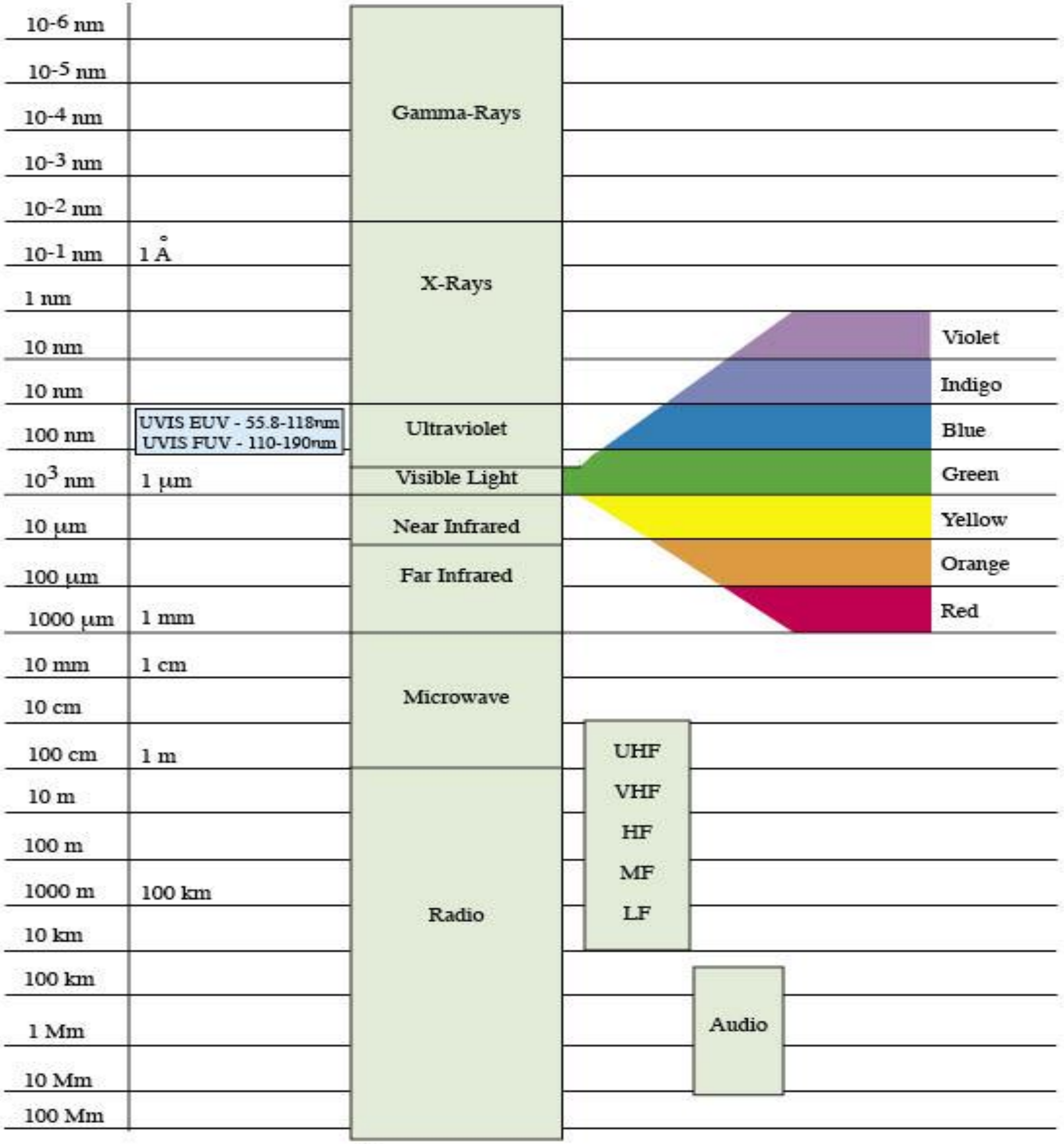
Let’s begin with some theory to help us understand instrumentation.

Atomic Spectroscopy

Electromagnetic Radiation



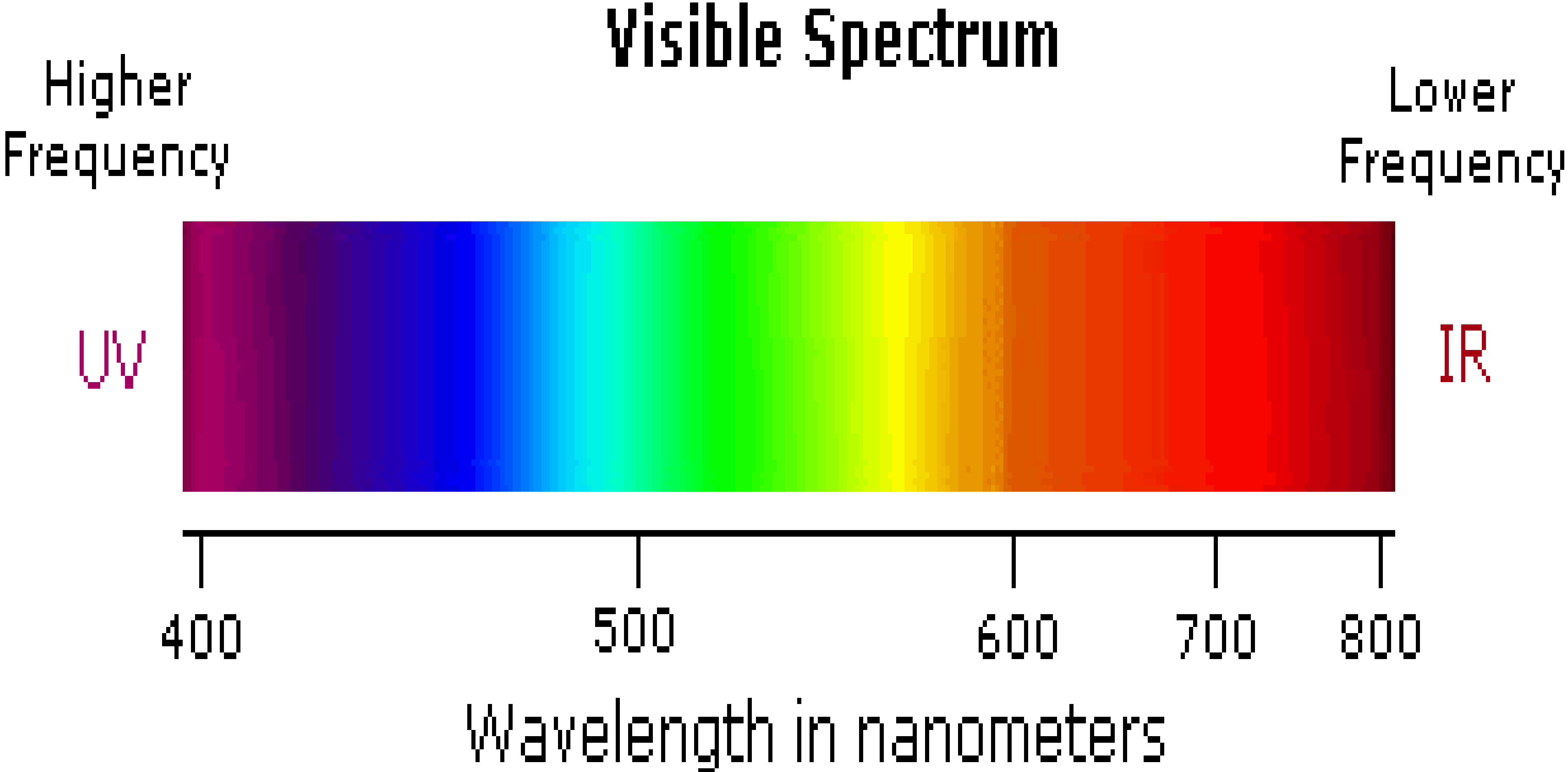
The Electromagnetic Spectrum



nm=nanometer, Å=angstrom, µm=micrometer, mm=millimeter,
cm=centimeter, m=meter, km=kilometer, Mm=Megameter

Atomic Spectroscopy

Electromagnetic Radiation



Atomic Spectroscopy

Electromagnetic Radiation

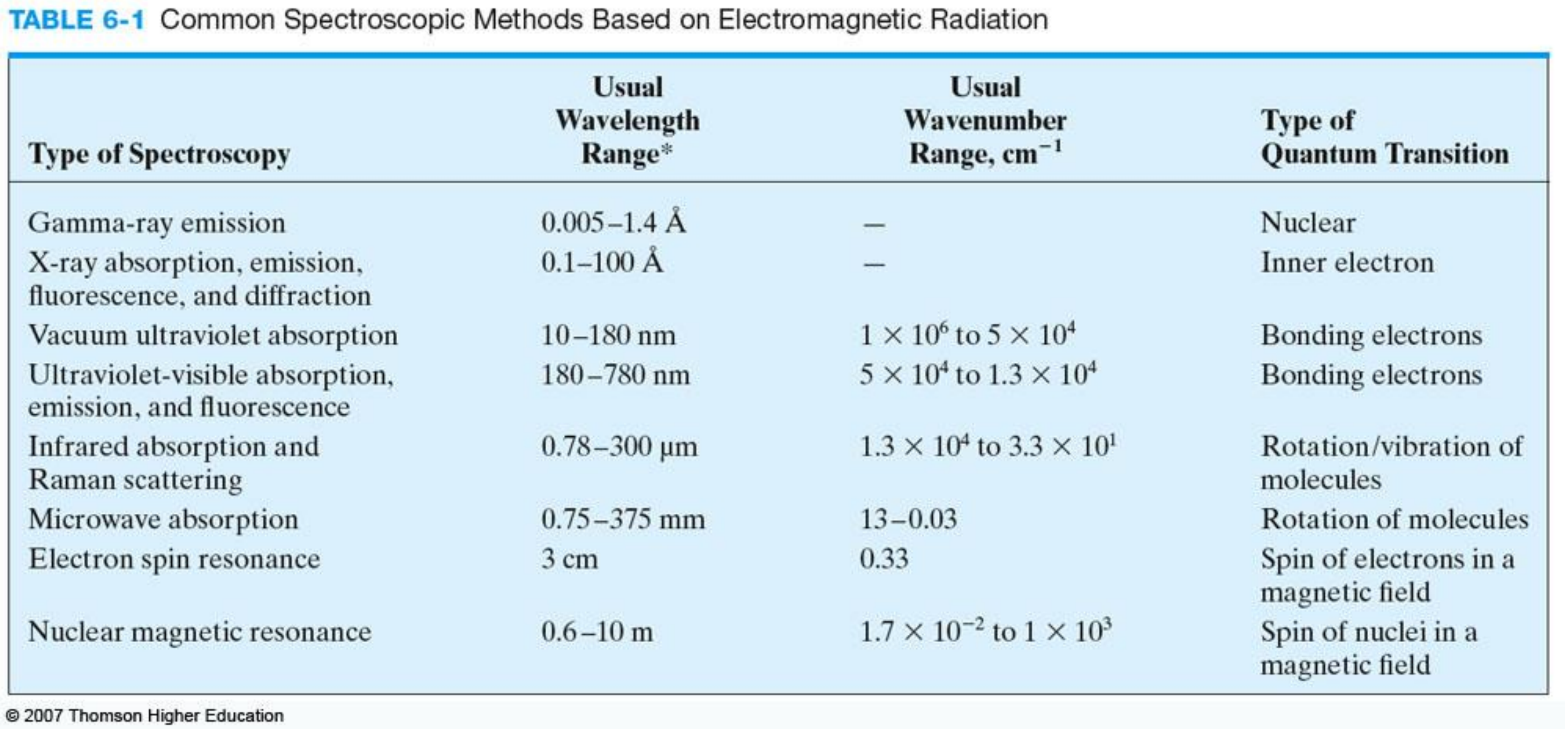
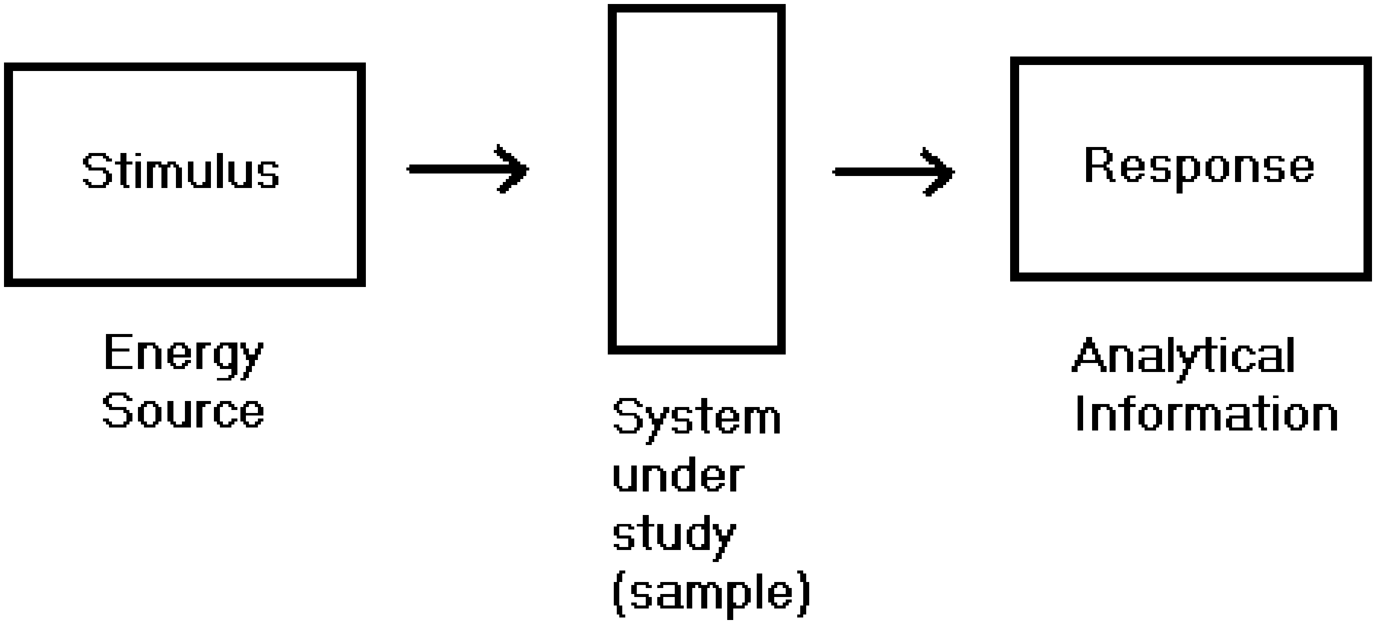


TABLE 6-1 Common Spectroscopic Methods Based on Electromagnetic Radiation

Type of Spectroscopy	Usual Wavelength Range*	Usual Wavenumber Range, cm^{-1}	Type of Quantum Transition
Gamma-ray emission	0.005–1.4 Å	–	Nuclear
X-ray absorption, emission, fluorescence, and diffraction	0.1–100 Å	–	Inner electron
Vacuum ultraviolet absorption	10–180 nm	1×10^6 to 5×10^4	Bonding electrons
Ultraviolet-visible absorption, emission, and fluorescence	180–780 nm	5×10^4 to 1.3×10^4	Bonding electrons
Infrared absorption and Raman scattering	0.78–300 μm	1.3×10^4 to 3.3×10^1	Rotation/vibration of molecules
Microwave absorption	0.75–375 mm	13–0.03	Rotation of molecules
Electron spin resonance	3 cm	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6–10 m	1.7×10^{-2} to 1×10^3	Spin of nuclei in a magnetic field

Instruments

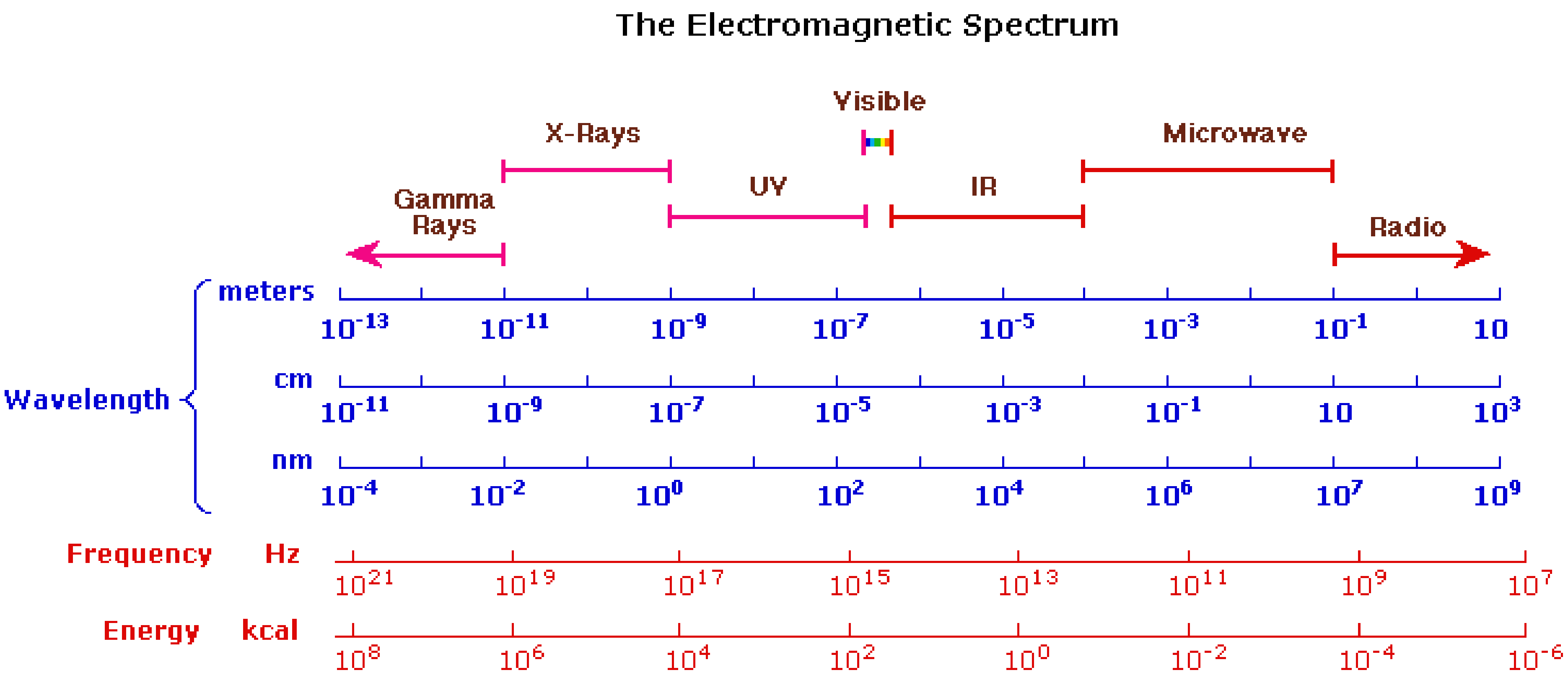
All instruments have the same basic components:



Stimulus → System under study (sample) → Response

Energy Source

Analytical Information


The Electromagnetic Spectrum
Visible
X-Rays
Microwave
UV
IR
Gamma Rays
Radio
Wavelength
meters
10^{-13} 10^{-11} 10^{-9} 10^{-7} 10^{-5} 10^{-3} 10^{-1} 10
cm
10^{-11} 10^{-9} 10^{-7} 10^{-5} 10^{-3} 10^{-1} 10 10^{3}
nm
10^{-4} 10^{-2} 10^{0} 10^{2} 10^{4} 10^{6} 10^{7} 10^{9}
Frequency Hz
10^{21} 10^{19} 10^{17} 10^{15} 10^{13} 10^{11} 10^{9} 10^{7}
Energy kcal
10^{8} 10^{6} 10^{4} 10^{2} 10^{0} 10^{-2} 10^{-4} 10^{-6}

Atomic Spectroscopy

Quantum Transitions

When electromagnetic radiation is emitted or absorbed, a permanent transfer of energy occurs.

The emitted electromagnetic radiation is represented by discrete particles known as photons or quanta.

Atomic Spectroscopy

Quantum Transitions

Photoelectric Effect

One use of electromagnetic radiation is to release electrons from metallic surfaces and imparts to these electrons sufficient kinetic energy to cause them to travel to a negatively charged electrode.

Atomic Spectroscopy

Quantum Transitions

Photoelectric Effect

- Heinrich Hertz in 1887
- Found that light whose frequency was lower than a certain critical value did not eject any electrons at all.
- This dependence on frequency didn't make any sense in terms of the classical wave theory of light.

Atomic Spectroscopy

Quantum Transitions

Photoelectric Effect

- Heinrich Hertz in 1887
- This dependence on frequency didn't make any sense in terms of the classical wave theory of light.
- It should have been amplitude (brightness) that was relevant, not frequency.

Atomic Spectroscopy

Quantum Transitions

Photoelectric Effect (Einstein 1905)

$$eV_o = h\upsilon - \omega$$

eV_o – maximum kinetic energy

h – Planks constant = 6.6254×10^{-34} J s

υ – frequency

ω – work function (depends on the surface material of photocathode)

Atomic Spectroscopy

Quantum Transitions

Photoelectric Effect

$$eV_o = h\upsilon - \omega$$

if $E = h\upsilon$, then

$$E = h\upsilon = eV_o + \omega$$

so the energy of an incoming photon is equal to the kinetic energy of the ejected photoelectron plus energy required to eject the photoelectron from the surface being irradiated.

Atomic Spectroscopy

Quantum Transitions

The energy of a photon can also be transferred to an elementary particle by adsorption if the energy of the photon exactly matches the energy difference between the ground state and a higher energy state. This produces an excited state (*) in the elementary particle.

$$M + h\nu \text{ -----> } M^*$$

Atomic Spectroscopy

Quantum Transitions

Molecules also absorb incoming radiation and undergo some type of quantitized transition.

The transition can be:

- **<u>Electronic transition</u> - transfer of an electron from one electronic orbital to another.**
- **<u>Vibrational transition</u> - associated with the bonds that hold molecules together.**
- **<u>Rotational transitions</u>**

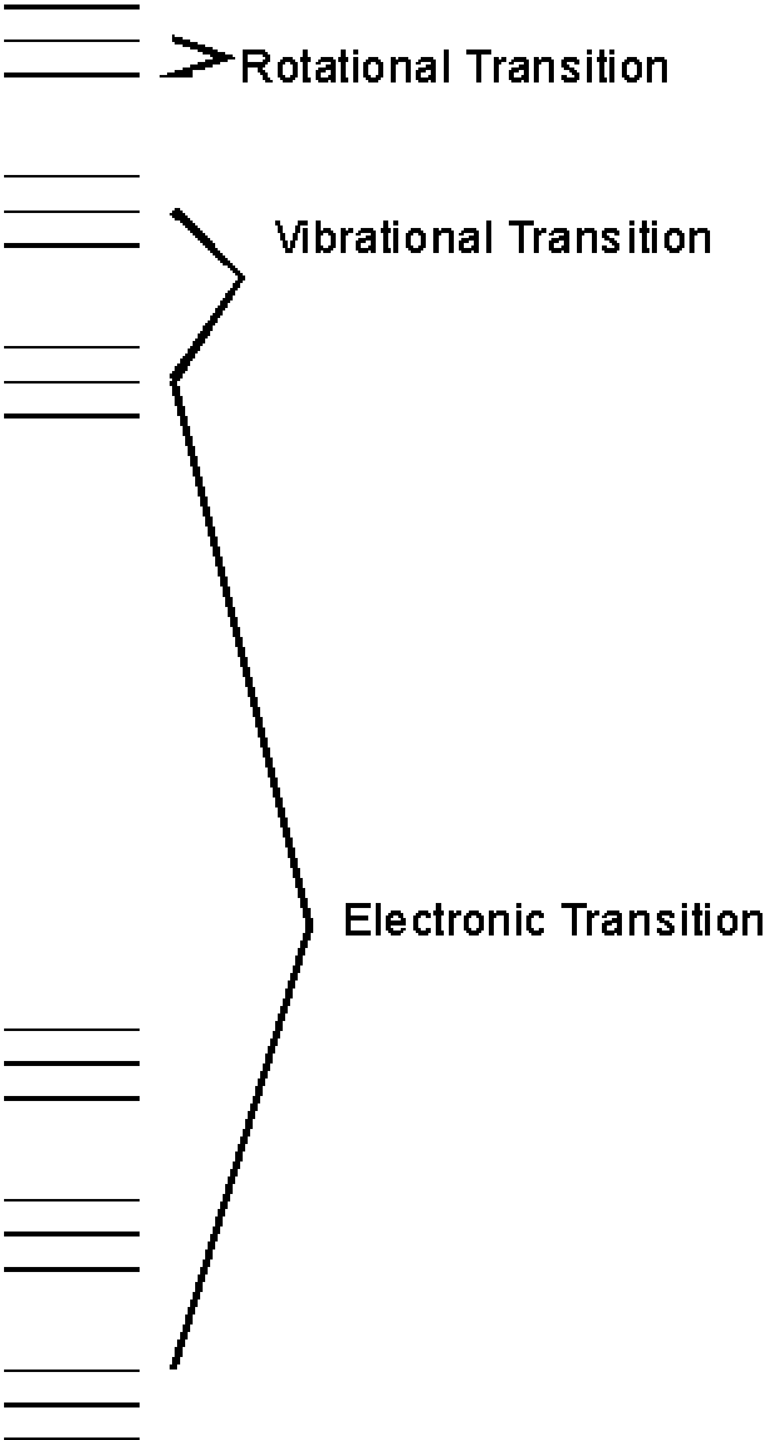
Atomic Spectroscopy

Quantum Transitions

Overall energy of a molecule:

$$E = E_{electronic} + E_{vibrational} + E_{rotational}$$

$$\Delta E_{electronic} \sim 10\Delta E_{vibrational} \sim 10\Delta E_{rotational}$$



Rotational Transition

Vibrational Transition

Electronic Transition

Atomic Spectroscopy

Quantum Transitions

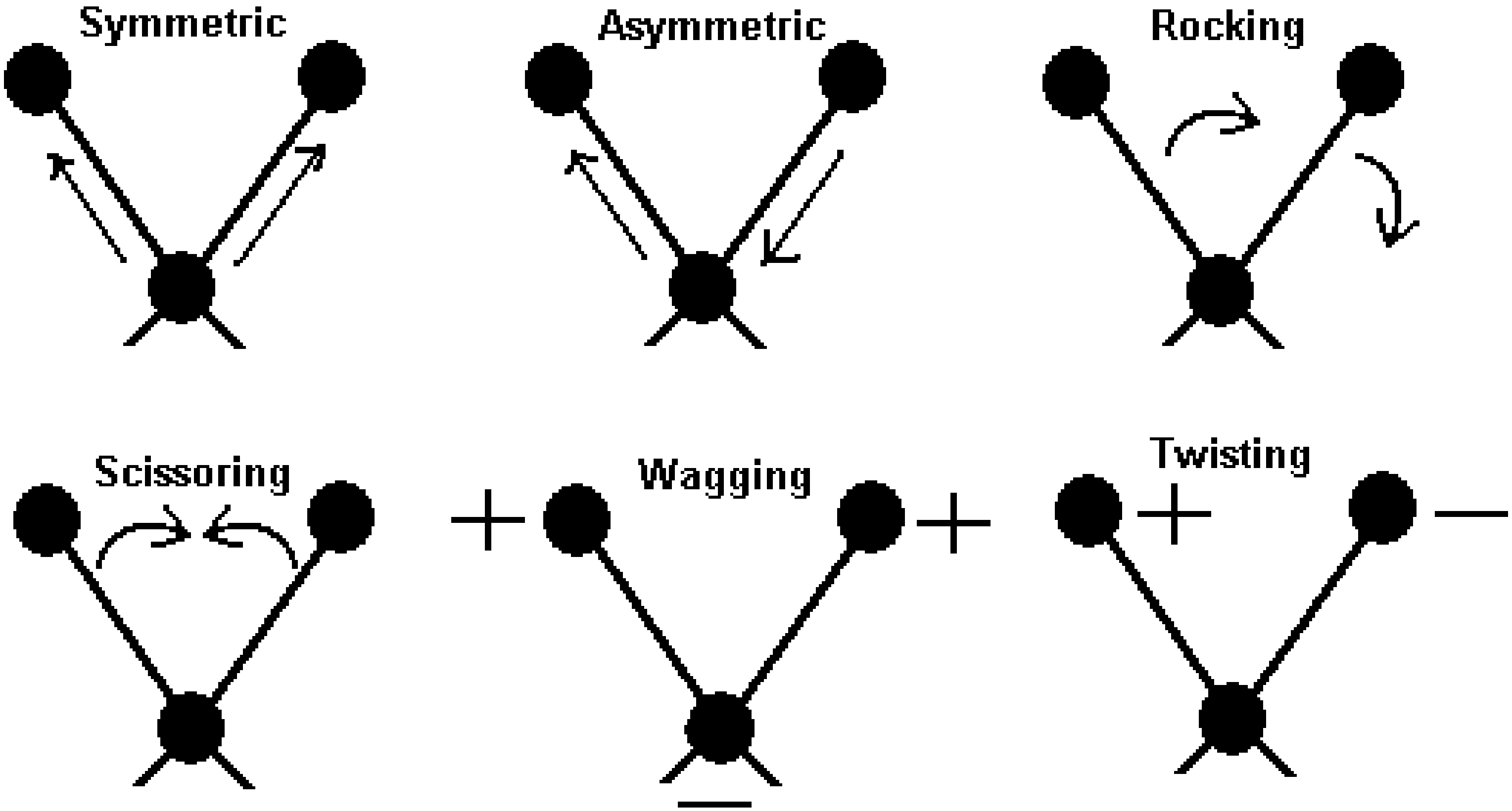
Overall energy of a molecule:

$$E = E_{electronic} + E_{vibrational} + E_{rotational}$$

$$\Delta E_{electronic} \sim 10\Delta E_{vibrational} \sim 10\Delta E_{rotational}$$

Molecular vibrations include:

- Symmetric stretching, asymmetric stretching, in-plane rocking, in-plane scissoring, out of plane wagging (bending), out of plane twisting.



We will Start with the UV-vis, (Fluorescence), and IR transitions and how to build an Instrument to measure these transitions.

- Infrared Absorption
  - IR radiation is not energetic enough to cause electronic transitions - so used to probe the vibrational and rotational states of the molecule.
- Ultraviolet Radiation
  - UV radiation is energetic enough to cause electronic transitions.

Assignment

- Read Chapter 1
- Read Appendix 1
- Go over Lab Lecture 1
- Homework 1: Ch. 1: 11 and

  Appendix 1: 1, 2, 10, and 12

  (extra credit) – Due Jan 24th