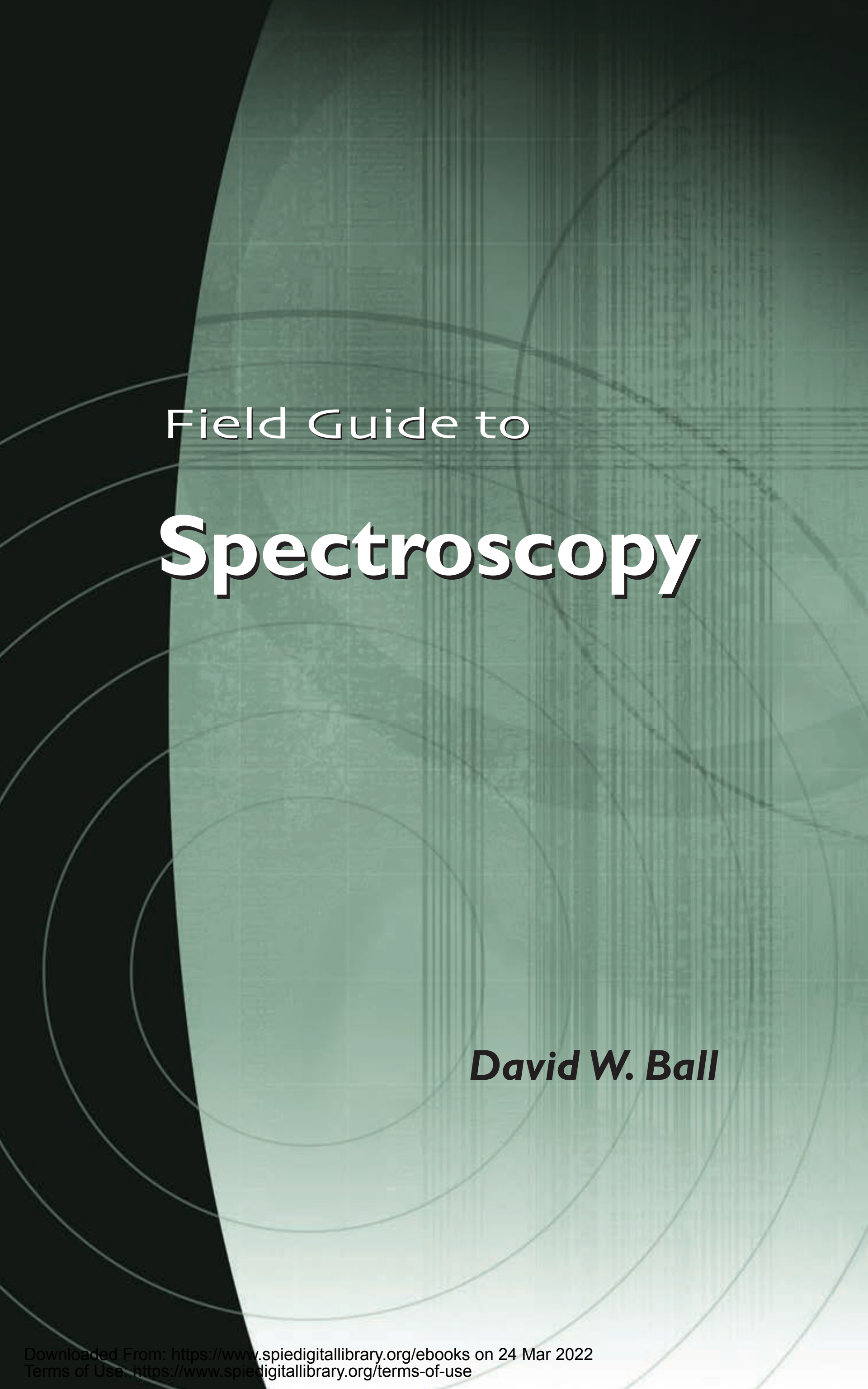

Field Guide to
Spectroscopy

David W. Ball

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John E. Greivenkamp, Series Editor

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Field Guide to Spectroscopy

Of all the *Field Guides* published to date, this one may stand out due to its relatively broad topic: the field of spectroscopy. Indeed, entire field guides can be written on what is covered here in one or two pages (witness the two pages on polarization here versus an entire *Field Guide* devoted to that topic published previously). Whatever limitations this may impart on this volume, I accept them and expect that the reader will understand them, too.

This material is derived from several sources, including my own training in infrared and circular dichroism spectroscopy from Rice University and the Lawrence Berkeley Laboratory; from courses I have taught in spectroscopy at Cleveland State University; and from personal research I conducted in the course of authoring "The Baseline" column in *Spectroscopy* magazine since 1994. Writing is a form of self-education, and I have been blessed with fast (though not always accurate) typing skills with which I can benefit by increased writing and, as a result, learning.

Thanks go to my colleague, John F. Turner II, for his review of the initial Table of Contents. I would also like to thank reviewers Brad Stone of San Diego State University and Vidi Saptari of MKS Instruments, Inc., for their thoughtful comments on the manuscript, and John E. Greivencamp of the University of Arizona, series editor, for leadership in the *Field Guides* series. Thanks are also due to Dr. Koji Masutani of Micro Science Inc. for corrections made while preparing the Japanese translation of this book.

This *Field Guide* is dedicated to my family: my wife, Gail, and my sons, Stuart and Casey.

David W. Ball
Department of Chemistry
Cleveland State University

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Glossary

a	Absorptivity
a	Hyperfine coupling constant
a	Width
A	Ammeter
A	Einstein coefficient of spontaneous emission
$A(\lambda)$	Absorbance at some wavelength λ
ATR	Attenuated total reflection
b	Path length
B	Beamsplitter
B	Magnetic flux strength
B	Einstein coefficient of stimulated absorption
B	Rotational constant
$\mathbf{B}$	Magnetic flux density
BE	Binding energy of electron
c	Concentration
c	Speed of light in vacuum
c'	Speed of light in transparent medium
c_n	Linear combination expansion coefficient
C	Compensator
CCD	Charge coupled device
CD	Circular dichroism
CID	Charge injection device
d	Distance between grating grooves
D_a	Angular dispersion
D_l	Linear dispersion
D1, etc.	Dynode 1, etc.
e	Charge on the electron
$\mathbf{E}$	Electric field
E	Energy
ΔE	Change in energy
$\langle E \rangle$	Average energy
EPR	Electron paramagnetic resonance
ESR	Electron spin resonance
f	Focal length
$f(t)$	Time-dependent function
F	Focal point
F	Force

Glossary

$F(\omega)$, $F(\nu)$	Fourier transform
$F(\nu)$	Lineshape function
FID	Free induction decay
FIR	Far infrared
FT	Fourier transform
FTIR	Fourier transform infrared spectroscopy
FT-NMR	Fourier transform nuclear magnetic resonance spectroscopy
FWHM	Full width at half maximum
g_e	Electron *g* factor
g_J	Landé *g* factor
g_N	Nuclear *g* factor
G	Grating
h	Planck's constant
$\hbar$	Planck's constant divided by 2π
HCL	Hollow-cathode lamp
$\mathbf{H}$	Magnetic field
$\hat{H}$	Hamiltonian operator for energy
$H(\alpha^{1/2}x)$	Hermite polynomial
i	The square root of -1
I	Intensity
I	Moment of inertia
I	Nuclear spin quantum number
I_a	Intensity of absorbed light
I_p	Intensity of p-polarized light
I_r	Intensity of reflected light
I_s	Intensity of s-polarized light
I_t	Intensity of transmitted light
ICP	Inductively coupled plasma
IR	Infrared
$\mathbf{J}$	Free current density
J	Rotational quantum number
J	Total (spin + orbital) angular momentum
ΔJ	Change in rotational quantum number
k	Boltzmann's constant
k	Force constant
ℓ	Length

Glossary

ℓ	(3D) Angular momentum quantum number
LED	Light-emitting diode
L, L_{tot}	Total angular momentum
L_{z}	Z-component angular momentum
$\hat{L}_z$	*Z*-component angular momentum operator
$\hat{L}_{\mathrm{tot}}^2$	Squared total angular momentum operator
m	Mass
m	Order of refraction
m_{e}	Mass of the electron
m_ℓ	(2D) Angular momentum quantum number
m_{s}	*Z*-component of spin angular momentum quantum number
M	Mirror
M	Transition moment
M_I	*Z*-component of nuclear spin angular momentum
M_J	*Z*-component of total angular momentum
n	Index of refraction
n	Quantum number (principal)
Δn	Change in quantum number
NIR	Near infrared light
NMR	Nuclear magnetic resonance
$\langle O \rangle$	Average value of property O
p	Momentum, linear
$\hat{p}$	Momentum operator, linear
$P(t)$	Probability, time-based
PDA	Photodiode array
PMT	Photomultiplier tube
QM	Quantum mechanics
r	Distance
R	Radius of curvature
R	Resolution
R_{d}	Reciprocal linear dispersion
S	Source

Glossary

S	Spin angular momentum quantum number
$2S+1$	Multiplicity
S1, S2	Slits
SNR	Signal-to-noise ratio
t	Time
T	Temperature, absolute
T	Transmittance
$\%T$	Percent transmittance
TDSE	Time-dependent Schrödinger equation
TISE	Time-independent Schrödinger equation
UPS	Ultraviolet photoelectron spectroscopy
UV	Ultraviolet light
UVA	Ultraviolet A
UVB	Ultraviolet B
v	Velocity
V	Verdet constant
V	Potential energy
$\hat{V}$	Potential energy operator
x	Position
$\hat{x}$	Position operator
XPS	X-ray photoelectron spectroscopy
α	Angle of incoming light
β	Angle of preferential refraction
γ	Blaze angle
γ	Magnetogyric ratio
δ	Chemical shift parameter
Γ	Irreducible representation of point group
ε_0	Permittivity of free space
$\varepsilon(\lambda)$	Molar extinction coefficient
θ	Angle of dispersion
θ	Angle of rotation
θ_c	Critical angle
θ, θ_i	Angle of incidence
θ_r	Angle of reflection
λ	Wavelength of light
λ_{max}	Maximum wavelength
$\Delta\lambda$	Wavelength range

Glossary

μ	Magnetic permeability
μ	Reduced mass
μ_0	Permeability of free space
μ_B	Bohr magneton
μ_N	Nuclear magneton
$\hat{\mu}$	Dipole moment operator
ν	Frequency of light
ν	Larmor frequency
$\tilde{\nu}$	Wavenumber of light
ρ	Free electric charge density
ρ, $\rho(\nu)$	Radiation density
σ	Screening constant
ϕ	Angle
ϕ	Angle of refraction
ϕ	Work function
ϕ, Φ	Trial wave function
Ψ	Wavefunction
Ψ^*	Wavefunction, complex-conjugated
ω	Angular frequency

Spectroscopy Defined

Spectroscopy is the study of **matter** using **electromagnetic radiation** (light).

Spectroscopy is based on **quantum mechanics**, the prevailing theory of the behavior of atoms and molecules. One of the conclusions of quantum mechanics is that the energies of the various forms of motion within atoms and molecules are limited to certain discrete values; that is, they are **quantized**. When an atomic or molecular system absorbs or emits light, the system goes from one quantized energy level to another. The **Bohr frequency condition** states that the difference in the energy levels must equal the energy of the light absorbed or emitted. Spectroscopy uses this principle to probe the energy levels of the matter under study. Ultimately, spectroscopy helps us learn how matter and energy interact.

Most of what we know about the universe comes from studying the interaction of light and matter, which makes spectroscopy a fundamental technique in understanding the world around us.

Light is not the only probe used in spectroscopy. Several types of spectroscopy use **magnetic fields** in conjunction with light to probe the nature of matter. In some cases, like **nuclear magnetic resonance spectroscopy**, it is clear from the name of the method that magnetic fields are involved. In other cases, like **Zeeman spectroscopy**, it is not clear from the name of the technique.

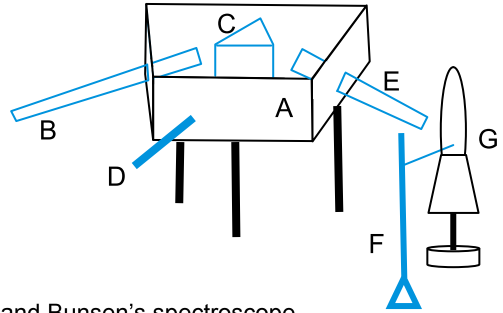
Spectrometry is a more restrictive term. It refers to the measurement of the intensity of absorption or emission of light at one or more specific wavelengths, rather than a range of wavelengths.

Spectrometer, Spectroscope, and Spectrograph

A **spectrometer** is any instrument used to probe a property of light as a function of its portion of the electromagnetic spectrum, typically its wavelength, frequency, or energy. The property being measured is usually intensity of light, but other variables like polarization can also be measured. Technically, a spectrometer can function over any range of light, but most operate in a particular region of the electromagnetic spectrum.

A **spectroscope** is a device that measures the spectrum of light. Early versions had a slit, a prism, and a screen with markings to indicate various wavelengths or frequencies; later versions were calibrated to electronic detectors. Although the apparatus Isaac Newton used in his work on the spectrum of light can be considered a crude spectroscope, it is generally recognized that the spectroscope was invented by Gustav Kirchhoff and Robert Bunsen around 1860.

A **spectrograph** is an instrument that separates incoming light by its wavelength or frequency and records the resulting spectrum in some kind of multichannel detector, like a photographic plate. Many astronomical observations use telescopes as, essentially, spectrographs.



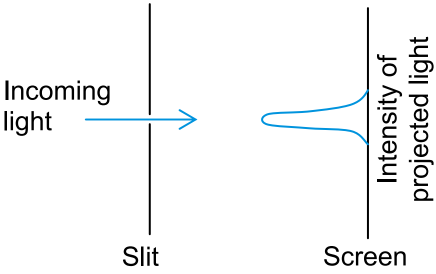
Kirchhoff and Bunsen's spectroscope

A – Spectroscope box	B – Viewing optics
C – Prism	D – Turning handle
E – Focusing optics	F – Sample holder
G – Flame	

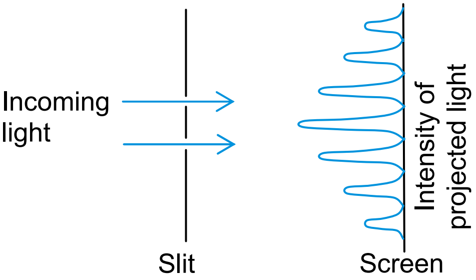
Light as a Wave

Is light a particle or a wave? This question occupied the minds of many brilliant scientists in the past. Newton favored light as a particle. His contemporary, Christiaan Huygens, thought that light was a wave.

In 1803, English scientist Thomas Young conclusively demonstrated that light was a wave by performing what is incorrectly called the **double-slit experiment**. (Young actually split a narrow beam of sunlight with a card.) In a single-slit experiment, a beam of light is projected onto a screen. The intensity of light on the screen varies according to the perpendicular distance away from the center of the slit.



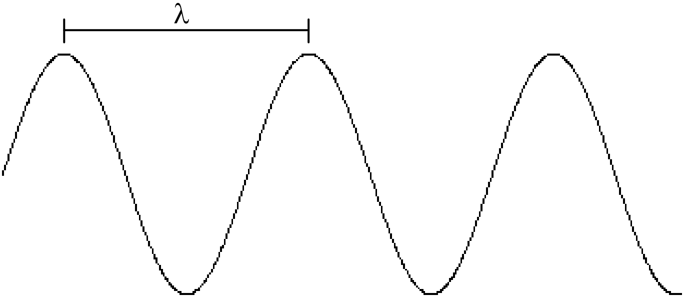
However, when Young used two tiny slits of light close together, instead of two images as might be expected, a pattern of interference fringes appeared. Only waves can interfere, so this result demonstrated that light was a wave.



Light as a Wave (con't)

As a wave, light has two characteristic properties: a **wavelength** and a **frequency**.

The wavelength λ (lambda) is the distance between two corresponding positions of adjacent waves. It can be illustrated as follows:



Wavelengths have units of length: meter, centimeter, micrometer (or micron), nanometer, and Ångstrom are common units.

The frequency ν (nu) is the number of waves that pass a given point per second. The units of frequency are s^{-1}, also known as Hertz (Hz).

Another way to express a frequency is the number of waves per unit length, such as per meter or per centimeter. This type of frequency is called **wavenumber**. Its units are m^{-1} or cm^{-1}. Wavenumber is defined as 1/λ and represented as $\tilde{\nu}$.

Like any wave, the product of the frequency and wavelength of light is its **velocity**. However, in a vacuum the velocity of light is a constant, labeled *c*. Thus, we have

$$c = \lambda \cdot \nu$$

The speed of light in a vacuum is 2.99792458×10^8 m/s.

Light as a Particle

In 1905, Albert Einstein proposed that a wave of light had a specific amount of energy that depended on its frequency. Building on Planck's **quantum theory**, Einstein used this proposal to explain the **photoelectric effect**. In essence, Einstein was suggesting that a light wave acted as a particle of energy, E, having a value of

$$E = h \cdot \nu$$

where h is **Planck's constant** (6.626×10^{-34} J · s), and ν is the frequency of the light wave. Thus, like the energy levels of an atom or molecule, the energy of a light wave is quantized. As a particle, a wave of light is called a **photon**.

Light also has **momentum**, another property previously ascribed only to particles. A photon of wavelength λ, frequency ν, wavenumber $\tilde{\nu}$, and energy E has a momentum p given by the following expressions:

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda} = h\tilde{\nu}$$

Light has both wave and particle properties. Scientists once thought that something could be *either* a particle or a wave, but not both. Science now recognizes that the two attributes are not mutually exclusive. But light does not act as a particle and a wave simultaneously; whether light behaves as a particle or a wave depends on the property being measured.

The Electromagnetic Spectrum

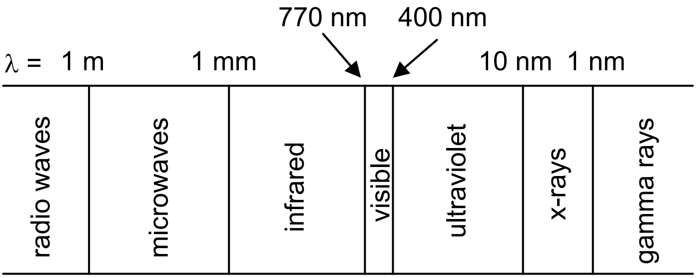
In the common vernacular, light refers to **visible light**. Technically, light also refers to wavelengths or frequencies of **electromagnetic radiation** that cannot be seen but whose effects can be measured. The entire range of wavelengths/frequencies of electromagnetic radiation comprises the **electromagnetic spectrum**.

In order of increasing frequency (increasing energy, decreasing wavelength), the electromagnetic spectrum is divided (somewhat arbitrarily) into the following regions:

- **radio waves**
- **microwaves**
- **infrared (IR) light**
- **visible light**
- **ultraviolet (UV) light**
- **x-rays**
- **gamma rays**

Some of these regions are themselves broken down into subregions; for example, UV light can be separated into longer-wavelength ultraviolet B (UVB) light and shorter-wavelength ultraviolet A (UVA) light.

The regions of the electromagnetic spectrum are roughly separated as shown (not to scale):



Maxwell's Equations of Electromagnetism

Maxwell's equations are a set of four equations that describe the behavior of electric and magnetic fields and how they relate to each other. Ultimately they demonstrate that electric and magnetic fields are two manifestations of the same phenomenon.

In a vacuum with no charge or current, Maxwell's equations are, in differential form:

$$\nabla \cdot \mathbf{E} = 0$$
$$\nabla \cdot \mathbf{B} = 0$$
$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$
$$\nabla \times \mathbf{B} = \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$

where **E** and **B** are the **electric field** and **magnetic flux density**, and $\nabla\cdot$ and $\nabla\times$ are the divergence and curl operators, respectively. The variables μ_0 and ε_0 are the fundamental universal constants called the **permeability of free space** and the **permittivity of free space**, respectively. In a vacuum with no electrical charges present, the mathematical solutions to these differential equations are sinusoidal plane waves, with the electric field and magnetic fields perpendicular to each other and to the direction of travel, having a velocity

$$v = \frac{1}{\sqrt{\mu_0 \varepsilon_0}} \equiv c$$

where c is recognized as the speed of light.

Maxwell's equations are macroscopic expressions; they apply to the average fields and do not include quantum effects.

Maxwell's Equations: General Form

In their most general form, Maxwell's equations can be written as

$$\nabla \cdot \mathbf{D} = \rho \text{ (Gauss' law of electricity)}$$
$$\nabla \cdot \mathbf{B} = 0 \text{ (Gauss' law of magnetism)}$$
$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \text{ (Faraday's law of induction)}$$
$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \text{ (Ampère's law)}$$

For linear materials, the relationships between **E**, **D**, **B**, and **H** are

$$\mathbf{D} = \varepsilon \mathbf{E}$$
$$\mathbf{B} = \mu \mathbf{H}$$

Here, ε is the **electrical permittivity**, and μ is the **magnetic permeability.** For nonlinear materials, ε and μ are dependent on the field strength. In isotropic media, ε and μ are independent of position. In anisotropic media, ε and μ can be described as 3 × 3 matrices that represent the different values of permittivity and permeability along the different spatial axes of the medium. In all media, ε and μ also vary with the frequency of the radiation.

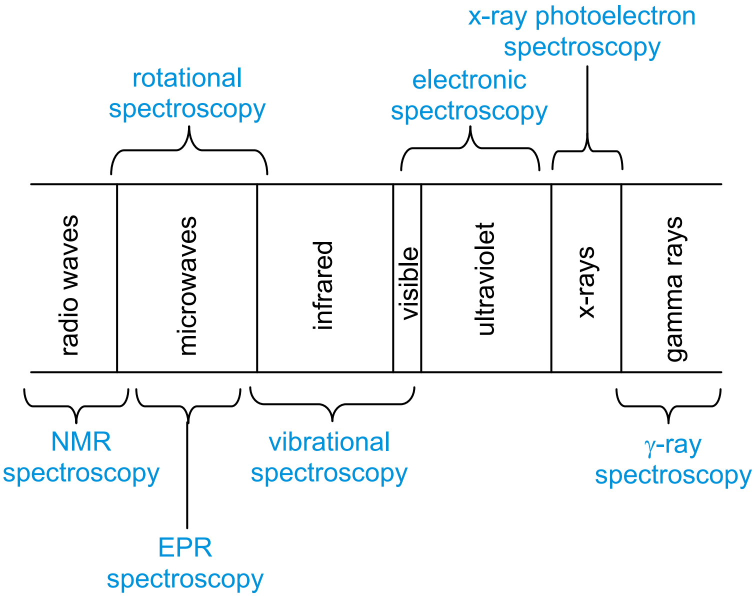
To be consistent with Maxwell's equations, the magnitudes of the electric and magnetic field vectors must satisfy the following relationship:

$$\frac{|\mathbf{E}|}{|\mathbf{B}|} = c$$

Thus, in electromagnetic radiation, the electric field vector has a much larger amplitude than the magnetic field vector.

Spectroscopy and Regions of the Spectrum

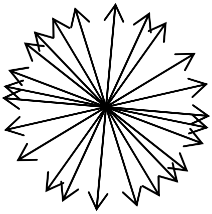
Different regions of the spectrum probe different types of energy levels of an atomic or molecular system. It is not uncommon to refer to a spectroscopic technique by the region of the electromagnetic spectrum involved; synonymously, a type of spectroscopy may be referred to by using the types of energy levels involved.



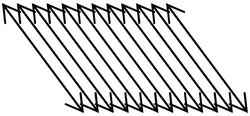
Thus, the term **vibrational spectroscopy** is sometimes used interchangeably with **infrared spectroscopy**, although some vibrational transitions may occur in the microwave region of the spectrum and some electronic transitions may occur in the IR region of the spectrum. In other cases, no such substitution is done; rarely, if ever, are **nuclear magnetic resonance** (NMR) or **electron paramagnetic resonance** (EPR) spectroscopies referred to as radio spectroscopy or microwave spectroscopy, respectively.

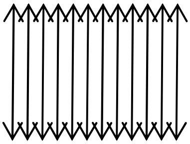
Polarization

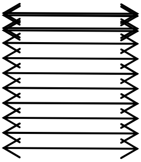
The electric field vectors of the transverse waves of light usually have random orientation about their direction of travel. Such light is called **unpolarized light**. If viewed head-on, unpolarized light can be represented like this:



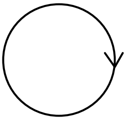
A **polarizer** is an optical device that allows only light of a certain direction of polarization to pass. **Polarized light** is light whose field vectors show a preferred orientation. Light can be completely or partially polarized. **Linear polarized light** has the field vectors lined up in a parallel fashion; if viewed head-on, linear polarized light can be represented by any of the following:



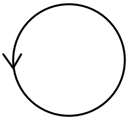




Light can also be **circular polarized** by taking 45° linearly polarized light and retarding either the *x*- or *y*-component with a quarter-wave plate. The result is an electric field vector that traces a helix as it traverses through space. Seen head-on, circular polarized light looks like the following:



right circular polarized

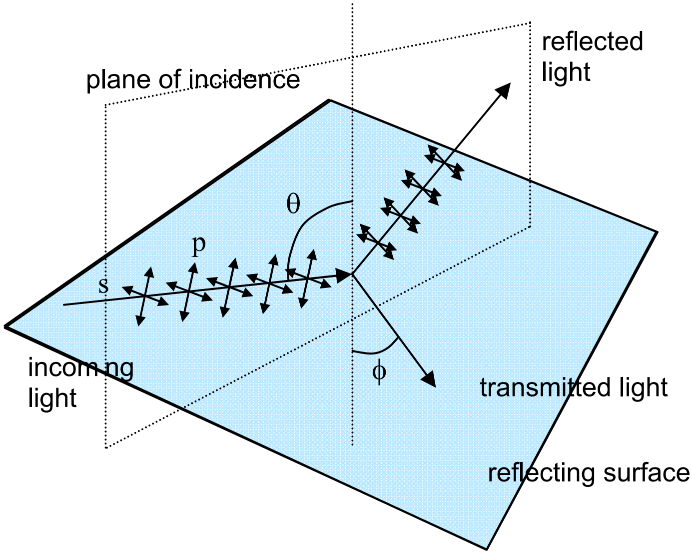


left circular polarized

Light that is not perfectly circular polarized is said to be **elliptical polarized**.

Polarization and Reflection

The linear polarization of light can be defined with respect to a plane that contains the incoming and reflected light. This plane is called the **plane of incidence**. The term **s polarization** is used to describe light whose electric field is perpendicular to the plane of incidence, while the term **p polarization** describes light whose electric field is parallel (or contained in) the plane of incidence.



Reflected light does not have the same intensities of s- and p-polarized light as does the incoming light. **Fresnel's equations** give the intensities of s- and p-polarized reflected light in terms of the angle of incidence, θ, and the angle of refraction, ϕ:

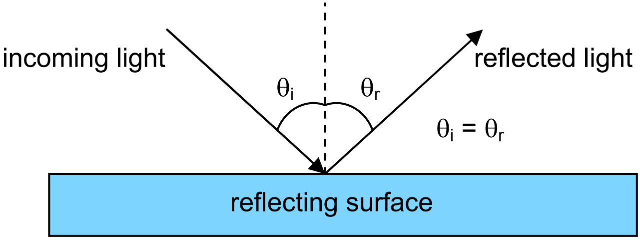
$$I_s = \frac{\sin(\phi - \theta)}{\sin(\phi + \theta)} \qquad I_p = \frac{\tan(\phi - \theta)}{\tan(\phi + \theta)}$$

At a certain incident angle, I_p becomes zero and all of the p-polarized light becomes transmitted, not reflected. This angle is called **Brewster's angle**, and for regular glass is about 53°.

Interactions of Light with Matter

Light can interact with bulk matter in three ways: it can be **reflected**, **transmitted**, or **absorbed**. In many cases, a combination of two or three effects occurs.

Reflection is a redirection of the propagation vector of a light wave by a surface. If the reflection is by a smooth surface, then the angle between the incoming propagation vector with the normal to the reflecting surface, θ_i, equals the angle of the outgoing propagation vector with respect to the same normal, θ_r. This is usually spoken as "the angle of incidence equals the angle of reflection."



If the surface is flat so that reflection occurs in a particular direction, it is called **specular reflection**. If the surface is rough so that light is reflected in a variety of directions, this is **diffuse reflection**.

Light is **transmitted** if a medium is transparent to that particular wavelength(s) of light. Different media are transparent to different regions of the spectrum. The speed of light is slower in any nonvacuum medium than it is in a vacuum, and varies with wavelength.

Light is **absorbed** if the energy of the light equals the energy difference between two energy states of the matter involved. Most spectroscopy is based on the absorption of light.

The combined intensities of the three interactions equals the original intensity; this is known as the **conservation law**:

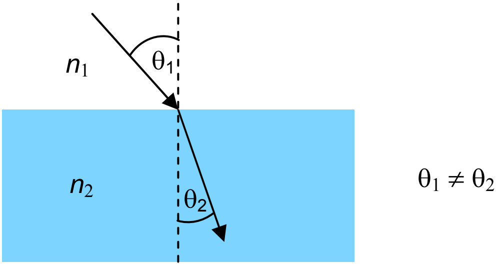
$$I_0 = I_r + I_t + I_a$$

Index of Refraction

The speed of light in a transmitting medium is less than that of the speed of light in a vacuum. The **index of refraction**, n, is the ratio of the speed of light in a vacuum, c, to the speed of light in a medium, c':

$$n = \frac{c}{c'}$$

One consequence of this difference in speed is that when light goes from one medium to another at an angle, the propagation vector in the new medium has a different angle with respect to the normal.



This change in direction of propagation is called **refraction**. The relationship between the indices of refraction and the angles is

$$n_1 \sin\theta_1 = n_2 \sin\theta_2$$

This relationship is called **Snell's law**.

Indices of refraction are temperature-dependent and wavelength-dependent.

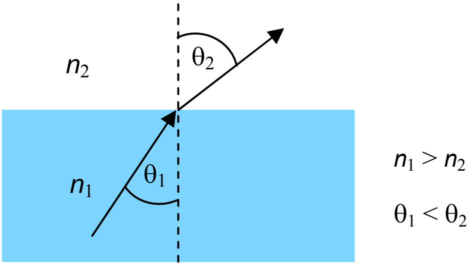
Indices of refraction of common materials*

Material	n	Material	n
air	1.0003	water	~1.33
flint glass	1.55	rock salt	1.544
quartz	1.544, 1.553	diamond	2.417

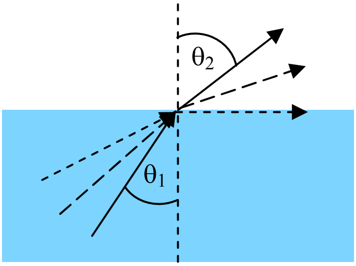
*for light having a wavelength of ~550–590 nm

Internal Reflection

When light enters a medium that has a lower index of refraction, Snell's law indicates that the light refracts so that it makes a greater angle with respect to the normal.



As the incoming ray increases its angle with respect to the normal, the outgoing ray in the second medium increases its angle also, and at some point reaches 90°.



At this particular value of θ_1, the angle of refraction is ≥ 90° and the light does not leave the first medium. This is **total internal reflection**. The **critical angle** θ_c at which total internal reflection will occur is given by the expression

$$\theta_c = \sin^{-1}\frac{n_2}{n_1}$$

Not only is total internal reflection important in fiber optics transmission and polarizers, but a form of spectroscopy—**attenuated total reflectance** (ATR) spectroscopy—is based on this phenomenon.

Dichroism

The concept of **dichroism** (literally, “two-colored”) comes from mineralogy. Certain minerals, like tourmaline, have different colors when viewed along different crystal axes.

In spectroscopy, dichroism occurs when a material absorbs left circular polarized light in different amounts than right circular polarized light. This is the basis of **dichroism spectroscopy**.

There are at least three major areas of **circular dichroism (CD) spectroscopy**:

- Analysis of chiral molecules. Although there is yet no relationship between the absolute chirality and the preference for polarization type, CD spectroscopy can be used to track the **chirality** in a sample.
- The interaction between a vibrational mode and the electronic state of a molecule can cause **vibrational circular dichroism**, wherein the vibrational modes of a molecule preferentially absorb one circular polarization of light over another.
- **Magnetic circular dichroism** occurs because the selection rules for right circular polarized light are different than for left circular polarized light. In the presence of a magnetic field, previously degenerate absorptions now differ in energy and there is a difference in the absorptions between the two polarizations.

Circular dichroism spectra are typically displayed as difference spectra—the absorption of one polarization minus the absorption of the other polarization.

Light Sources

Sources of electromagnetic radiation come in two types: **continuum sources** that emit a broad distribution of radiation, and **line sources** that emit narrow distributions of radiation. Some sources are combinations of both types.

Common continuum sources for UV and visible light include **incandescent lamps** with tungsten filaments and **high-pressure arc lamps** that contain a high pressure of inert gas like xenon. For strictly UV light, **hydrogen** or **deuterium arc lamps** are available; these have only a small amount of gas in them. In the IR region, **Nernst glowers** (a semiconducting rod of Zr-, Y-, or Th-based ceramic) and **globars** (SiC rods) are available.

In magnetic resonance spectroscopy, the source is usually near monochromatic and the magnetic field is varied. Standard **klystrons** or other microwave generators are used to produce microwaves, and **radio transmitters** generate radio waves.

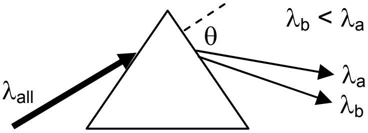
Common line sources are **low-pressure arc lamps** containing elements such as Hg, Cd, Zn, or Na, with Hg being the most common. **Hollow-cathode lamps** (HCL) use a cathode of one or more metals. Ionized gas inside the lamp sputters the cathode, creating a low-pressure atmosphere of the metal atoms, which get excited by the surrounding plasma and emit very narrow lines of characteristic light. **Light-emitting diodes** (LEDs) also give off a wavelength of light characteristic of the semiconducting diode.

Lasers are useful sources because they can be operated in a continuous or pulsed fashion, and their output distribution can be single line or practically continuum. Lasers can be so bright, however, that the spectral properties of a nonvacuum medium can change due to the strength of the electric field. This leads to **nonlinear optical effects** that can be useful or not useful in spectroscopy.

Prisms

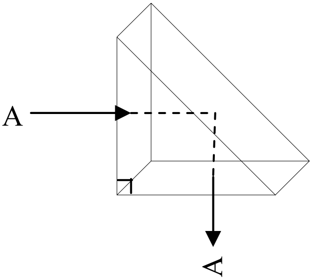
A **prism** is a transmitting optical component that has three major spectroscopic functions: dispersion, reflection, or polarization.

A **dispersing prism** separates light into its constituent wavelengths. This is because the index of refraction of the prism material varies with wavelength. As the two interfaces of the prism are nonparallel, the outgoing light rays of differing wavelength will travel in slightly different directions, becoming dispersed by wavelength. Typically, lower wavelengths of light are refracted more than higher wavelengths. The **angular dispersion**, D_a, is the variation of the **angle of dispersion**, θ, with respect to wavelength:

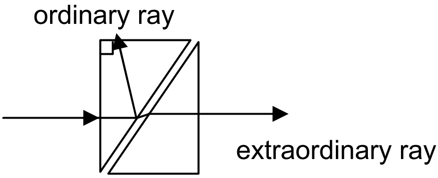


$$D_a = \frac{d\theta}{d\lambda}$$

A **reflecting prism** takes advantage of total internal reflection to change the direction and/or orientation of an incoming light beam.



A **polarizing prism** takes advantage of birefringent materials (like calcite) and is constructed to separate the ordinary and extraordinary rays. Examples include the **Nicol prism**, the **Glan-Foucault prism** (shown), and the **Wollaston prism**.



Gratings

Although **gratings** can be used in reflection or transmission mode, the vast majority used in spectroscopy are reflective. A reflection grating is a surface that has been lined with closely spaced grooves. Upon reflection of a collimated incoming broadband light source, each groove acts as an independent slit. Reflections from multiple slits constructively and destructively interfere so that light of a particular wavelength constructively interferes at a particular angle. As such, the broadband incoming light becomes angularly diffracted.

The relationship between the angle of incoming light α, the direction of preferential diffraction β of light having wavelength λ, and the distance between consecutive grooves d is given by the **grating formula**:

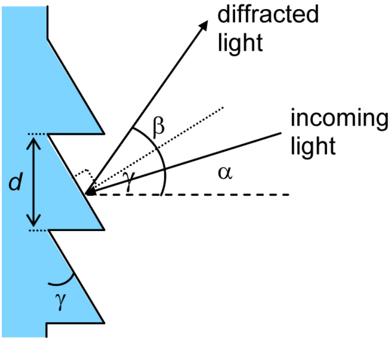
$$d(\sin\alpha + \sin\beta) = m\lambda$$

where m is called the **order of the diffraction**. A value of $m = 0$ corresponds to specular reflection, which occurs to most of the incoming light. A value of $m = 1$ is called the **first order diffraction**; $m = 2$ is the **second order diffraction**, etc.

High-efficiency gratings are **blazed**; their grooves make a **blaze angle** γ with the face of the grating. In a blazed grating, also called an **echellette**, specular reflection occurs at an angle of 2γ and not at the angle for which $m = 0$. The efficiency of the grating is greatest when

$$\lambda = 2d\sin\gamma\cos\left(\frac{\beta-\alpha}{2}\right)$$

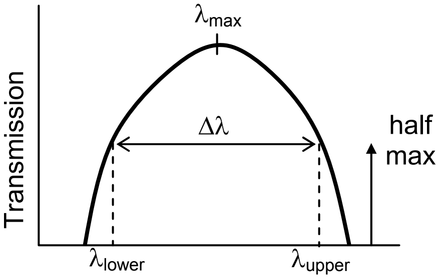
so gratings can be chosen to maximize their diffraction efficiency at a particular wavelength by choosing γ.



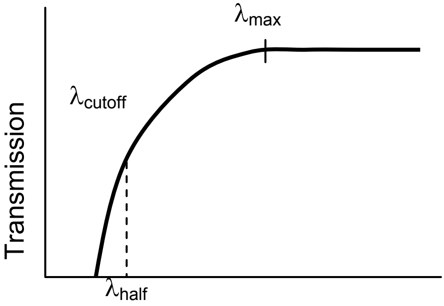
Absorption Filters

Filters come in two types. A **bandpass filter** allows a range of wavelengths to pass, while a **cutoff filter** only allows light above or below a certain wavelength to pass. Most filters use either absorption or interference to eliminate all but the desired regions of light.

An **absorption filter** contains a pigment that absorbs all but a range (or ranges) of light. For a **bandpass filter**, the **range** Δλ is expressed by the wavelengths at which the transmission is half the maximum transmission for the full width of the range (abbreviated "**full width at half maximum**," or **FWHM**). A filter with an exceptionally narrow Δλ is a **notch filter**.



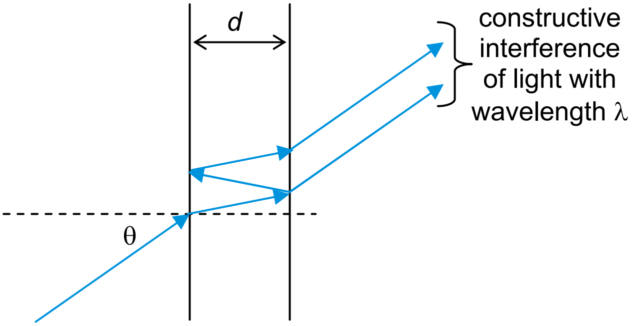
Cutoff filters are either **short-wavelength cutoff** or **long-wavelength cutoff**, depending on whether they absorb all light below or above a specified wavelength.



Interference Filters

An **interference filter** uses destructive interference of most light to isolate and transmit a narrow range of wavelengths of light.

One type of interference filter is the **Fabry-Perot filter**. It is a thin layer (several hundred nanometers) of low refractive index, usually mounted between glass sheets. Incoming polychromatic light experiences some internal reflection and mostly undergoes destructive interference. However, light of a particular wavelength undergoes constructive interference and passes through the filter.



As with gratings, more than one order, m, are possible. The relationship between the passed wavelength λ, the angle of incidence θ, the index of refraction n, and the thickness of the filter medium d is

$$2d\left(n^2 - \sin^2\theta\right)^{1/2} = m\lambda$$

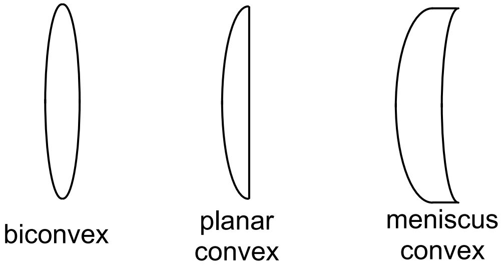
Interference filters are **tunable**; the exact wavelength that passes can be varied by changing the characteristics of the filter, typically the angle of incidence θ or the thickness d.

A **multicavity interference filter** has multiple layers of high- and low-refractive index materials. Its mechanism of operation is the same as the Fabry-Perot filter, but it can achieve a much narrower distribution of transmitted light.

Types of Lenses: Convex

The formal definition of a **lens** is any optical component that has two or more refracting surfaces. By this definition, a flat pane of glass is a lens. In practical terms, a lens has at least one curved surface. A lens composed of a single element with one or two curved surfaces is a **simple lens**. A lens composed of two or more simple lenses is a **compound lens**.

A lens that is thicker in the center than it is at the edges is called a **convex lens**.



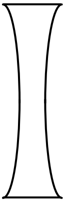
A convex lens takes collimated light and converges the light rays. Because the index of refraction varies with wavelength, polychromatic incoming light can converge at different points based on wavelength. This is called **chromatic aberration**. Incoming light rays that enter the lens off-axis can also converge at different points; this is **spherical aberration**.

The curves of the convex lens surfaces can be **spherical**, **aspherical**, or **cylindrical**. Aspherical lenses minimize spherical aberration and other deficiencies of spherical-surface lenses, while cylindrical lenses refract light in only one plane.

A lens can be thought of as a prism with one or two curved surfaces.

Other Types of Lenses

A lens that is thinner in the center than it is at the edges is called a **concave lens**.



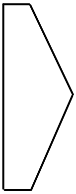
biconcave

planar concave

meniscus concave

A concave lens takes collimated light and diverges the light rays. Concave lenses suffer from the same aberrations that convex lenses have.

An **axicon** is a type of convex lens with a conical surface. Axicons are used to converge incoming monochromatic light into a ring.



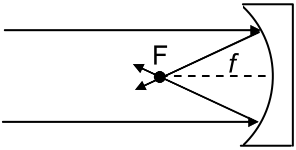
axicon

An **achromat lens** is a compound lens that minimizes aberrations. The combination of lenses can be referred to as doublets, triplets, etc., depending on the number of simple lenses in the combination.

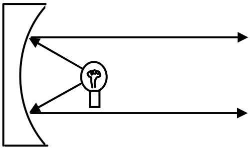
Many lenses have a **coating**—a thin layer of a substance that has an intermediate index of refraction between the lens material and air. This minimizes reflection losses at the interfaces of the transmitting medium. Magnesium fluoride, MgF_2, and calcium fluoride, CaF_2, are common **antireflection coatings** for the visible range. Thorium fluoride, ThF_4, is also used for the UV, visible, and near-IR ranges. Multiple coatings can also be used to improve transmission in specific wavelength ranges.

Mirrors

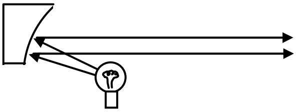
A **mirror** is an optical component that has a highly reflective surface. The surface can be on the top of some substrate, like glass. This is a **front surface mirror**. On a **rear surface mirror**, the reflecting surface can also be on the back of a transparent substrate. For visible-light applications, the reflecting surface can be aluminum or silver. Infrared mirrors use a gold reflecting surface. Like lenses, many front surface mirrors have a thin coating to protect the reflecting surface.



A flat mirror, or **plane mirror**, is used to change the direction of a beam of light but not its divergence. A **spherical mirror** can take a collimated beam of light and focus the light at a point, called the **focal point**, F. The distance between the mirror and the focal point is called the **focal length** *f* of the mirror. For a spherical mirror, the focal length is half of the radius of curvature, *R*, of the mirror surface.



A source of light located at the focal point produces a collimated beam of light after the rays reflect off the spherical mirror surface. An **off-axis** spherical mirror can be used so that the beam path of the collimated light is not blocked by the source.



An **aspherical mirror** can be either parabolic or ellipsoidal. Like a spherical mirror, a **parabolic mirror** forms a collimated beam of light if a source is located at its focus. An **ellipsoidal mirror** focuses light from one focal point to the other focal point.

Lens and Mirror Equations

A thin spherical biconvex lens whose surfaces have a **radius of curvature** R and is composed of a material having index of refraction n has a **focal length** f given by the expression

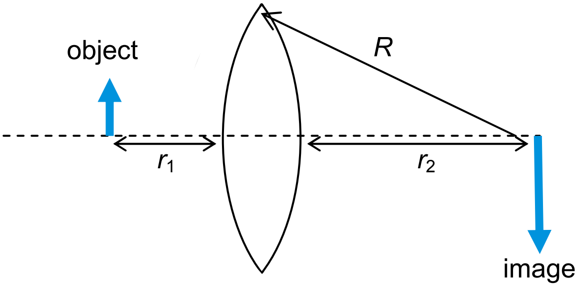
$$\frac{1}{f} = \frac{2(n-1)}{R}$$

If an object is positioned some distance r_1 from the lens, an image of that object appears at a distance r_2 on the other side of the lens such that

$$\frac{1}{r_1} + \frac{1}{r_2} = \frac{1}{f}$$

Thus, an object that appears to be at infinity (or a collimated beam of light) appears at the focal length of the lens. Depending on the defined coordinate scheme, either r_1 or r_2 may be negative; however, focal lengths for convex lenses are positive. The image is magnified by a factor equal to the ratio of the distances; that is,

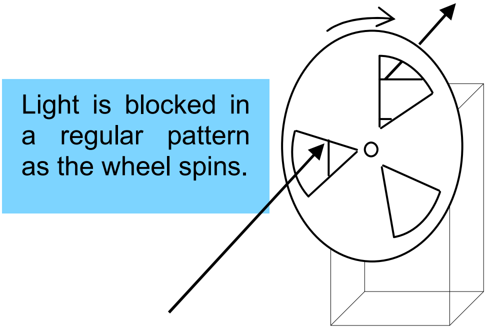
$$\text{magnification} = -\frac{r_2}{r_1}$$



Concave spherical mirrors, which by convention have negative values of R, follow similar equations, as do thin convex lenses.

Modulators: Mechanical Choppers and Shutters

Some types of spectroscopy work better if the intensity of the light source increases and decreases in a regular pattern. Such a signal is **modulated**. Rather than fluctuating the source, the light from the source is interrupted mechanically or optically. A **modulator** is a device that interrupts the light.



A mechanical modulator is called a **chopper**. It physically blocks the light beam periodically. The frequency of the interruption depends on the angular velocity of the wheel and the pattern of openings. The intensity pattern of the light from the source approaches a square wave. Chopping speeds can vary from almost 0 to over 50,000 Hz.

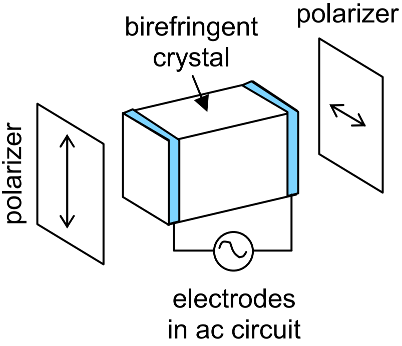
Designs based on tuning forks are also available. This type of design is called a **resonant chopper**. Resonant choppers are designed to have a certain fixed frequency. As the tines on the fork vibrate, an aperture between the tines opens and closes with fixed frequency. Since the motion is sinusoidal, the light intensity varies sinusoidally. Chopping rates of over 5 kHz are possible.

Intermittent chopping is performed with a **shutter**. A shutter can be as simple as a card mounted on a rotating axis, or as complex as an iris used in a camera. Unlike choppers, which are controlled electronically, a shutter may be controlled electronically or manually.

Electro-Optical Modulators

An **electro-optical modulator** is based on the change in the refractive index of a birefringent material due to the presence of an electric field.

The **Pockels effect** is the change in refractive index of a medium in the presence of an electric field. The change in refractive index is directly proportional to the strength of the field. As polarized light travels through the medium, it changes its polarization. If the medium is sandwiched between crossed polarizers, light will only pass if the change in birefringence is enough to make the resulting polarization the same as the outgoing polarizer. By modulating the electric field (up to more than 100 MHz), the **Pockels cell** becomes a modulator. The electric field is parallel to the propgation vector of the light. Materials used for crystals include potassium dihydrogen phosphate (KDP), deuterated potassium dihydrogen phosphate (KD*P), lithium niobate ($LiNbO_3$), and beta-barium borate (BBO; β-BaB_2O_4).



A **Kerr cell** is similar to a Pockels cell except it depends on the **Kerr effect**, a transverse effect on the refractive index that depends on the square of the electric field. The electrodes are mounted on the sides, not the ends, of the cell. Modulations of over 10 MHz are possible. Nitrobenzene is a common medium.

Magneto- and Acousto-Optical Modulators

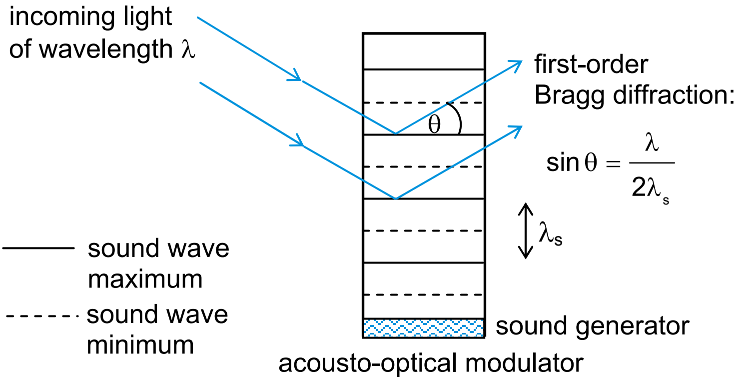
A **magneto-optical modulator** uses the **Faraday effect**, a change in the refractive index due to the presence of a magnetic field. The magnetic field must be parallel to the propagation of the light.

The magneto-optical modulator differs from the electro-optical modulator in that it can rotate the plane of linear polarized light by any angle, whereas electro-optical modulators typically rotate the plane of polarized light by 90°. The relationship between the rotation angle and the strength of the magnetic field is

$$\theta = B \cdot V \cdot \ell$$

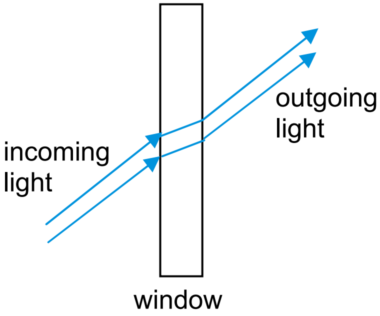
where θ is the angle of rotation, B is the strength of the magnetic field in tesla, ℓ is the length of the active medium, and V is the **Verdet constant**, the proportionality constant in the equation that is characteristic of the medium. The Verdet constant is wavelength-dependent.

When passing a sound wave of given wavelength through a medium, the pressure of the sound waves can change the refractive index of the medium. Since these variations occur at regular intervals (equal to the wavelength of the sound wave), incoming light will be diffracted in much the same way as a crystal diffracts x-rays (**Bragg diffraction**). This is an **acousto-optical modulator**.



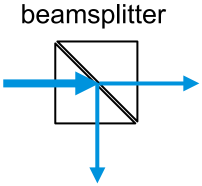
Other Components

A **window** is an optical component whose main function is to separate environments or serve as a substrate, but it has minimal effects on the spectral characteristics of the probing radiation. Windows typically have flat, parallel surfaces. The path of the light rays may be deflected but should not be dispersed.



Window materials can be any substance that does not absorb the light of interest. Transparent materials like glass, quartz, and sapphire are used in visible and UV regions. Ionic crystals like KBr, NaCl, CaF_2, or KRS-5 (mixed TlBr/TlI) can be used for the IR region, as can diamond. Polyethylene is used in the far-IR. Beryllium windows are used in x-ray and gamma ray spectroscopy.

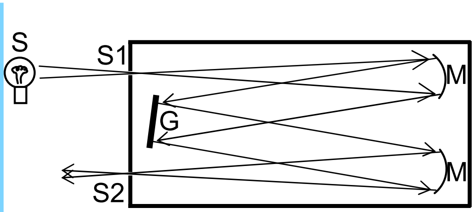
A **beamsplitter** is an optical component that allows part of an electromagnetic beam to pass through and reflects the rest. Beamsplitters can be cemented right prisms or partially silvered mirrors.



A **waveguide** is a rectangular or cylindrical tube that propagates radio waves or microwaves. They are mostly found in magnetic resonance spectrometers. **Fiber optics** can be thought of as a waveguide for visible light.

Grating Monochromators

A **monochromator** is a combination of elements that disperses polychromatic light. The most important element of a monochromator is the **dispersing element** itself, which can be a prism or a grating, with gratings being more common.



Czerny-Turner monochromator:
S – source
S1, S2 – slits
G – grating
M – focusing mirrors

An **entrance slit** limits the image of the incoming polychromatic light. A **mirror** collimates light onto a grating or other dispersing element. Another mirror focuses light of a selected wavelength range onto an **exit slit**. Typically, the dispersing element rotates to allow light of varying wavelengths to be focused on the exit slit. The range of wavelengths coming out of the exit slit is given by the **linear dispersion**, D_l:

$$D_l = \frac{dx}{d\lambda}$$

Linear dispersion depends on the focal length of the mirrors and the dispersing power of the dispersing element. The **reciprocal linear dispersion** R_d can also be used to express the dispersing power of a monochromator:

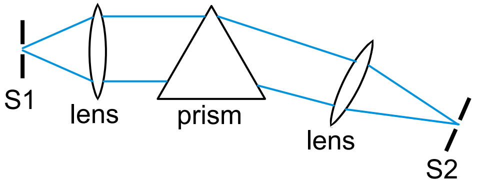
$$R_d = \frac{d\lambda}{dx}$$

A **Fastie-Ebert monochromator** is similar to a Czerny-Turner monochromator except that it uses a single symmetrically placed curved mirror instead of two smaller ones. High-quality monochromators may have curved slits to compensate for mirror effects.

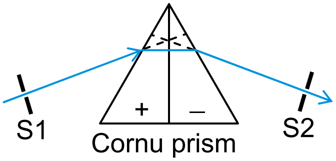
Prism Monochromators

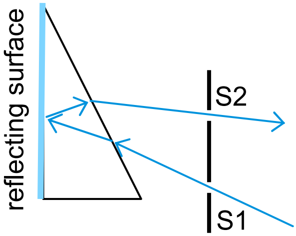
Prism monochromators may be preferred in shorter-wavelength UV spectroscopy and when the radiation power is high, as in laser spectroscopy. The details of the optics may vary, but the dispersing element is a prism.

The **Bunsen prism monochromator** is one of the earliest types of monochromator. It uses two lenses, one on either side of the prism.



A **Cornu prism monochromator** uses a compound prism that consists of two 30°-60°-90° quartz prisms cemented to each other. One prism is left-handed quartz; the other is right-handed quartz, so that birefringence effects cancel overall.

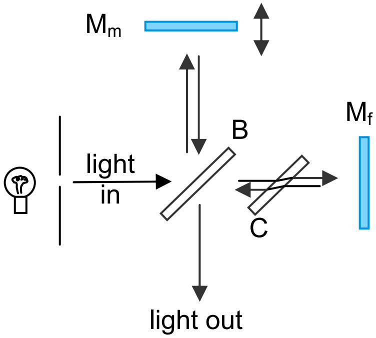




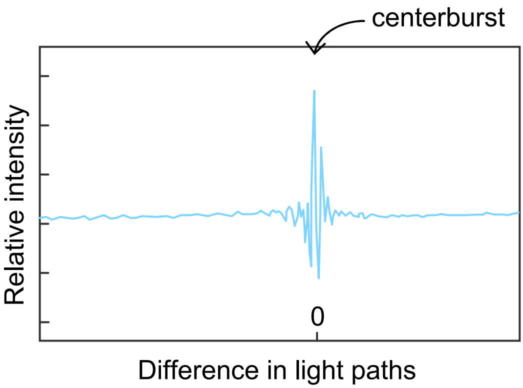
A **Littrow prism monochromator** uses a single right triangular prism whose longer leg is mirrored to reflect the incoming light back. A spectrograph based on a Littrow monochromator can be very compact.

Michelson Interferometer

A **Michelson interferometer** uses a **beamsplitter** B to separate a beam of polychromatic light into two beams. These beams travel to different mirrors, one fixed (M_f) and one moving (M_m). A **compensator** C is used in one optical path to ensure that all light passes through a transparent medium the same number of times. When recombined, all of the different wavelengths of light constructively interfere when the two light paths are exactly the same length, indicated by a maximum in the intensity of the recombined light. When the wavelengths of light travel different lengths, they rapidly destructively intererfere, resulting in some baseline intensity of recombined light.



A plot of light intensity versus mirror position is called an **interferogram**. The central region of brightness is called the **centerburst**.



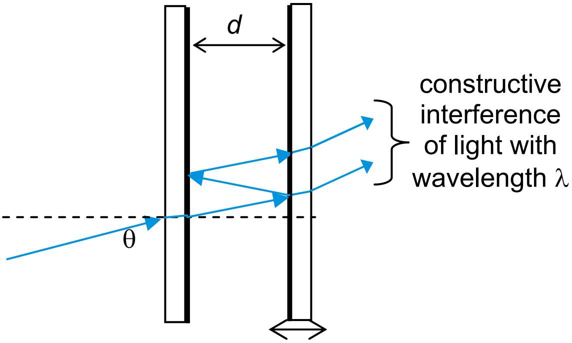
Fabry-Perot Interferometer

A **Fabry-Perot interferometer** is very similar to a Fabry-Perot filter. However, instead of a thin layer of some medium sandwiched between two mirrors, the Fabry-Perot interferometer has two parallel, highly reflective mirrors separated by an air gap several millimeters to several centimeters in width.

Light of wavelength λ constructively interferes when the following relationship is satisfied:

$$m\lambda = 2d\cos\theta$$

where m is the **order** and θ is the angle of the incoming light.



If one of the mirrors is mechanically moved back and forth (most systems use a piezoelectric crystal), the wavelength that constructively interferes at a particular angle θ varies, and the system acts as an interferometer. Since the angle of refraction also depends on the index of refraction of the gap between the mirrors, Fabry-Perot interferometers can also be used with constant d but by changing the pressure of some filler gas.

> Fabry-Perot interferometers are capable of very high resolution, able to distinguish spectral lines less than a nanometer apart.

Detectors

A **detector**, or **radiation transducer**, is any device that converts an amount of radiation into some other measurable phenomenon. Ultimately, most of these other measurable phenomena will be tied to an electrical signal.

There are two main types of detectors: **photon detectors** and **thermal detectors**. All detectors have similar characteristics:

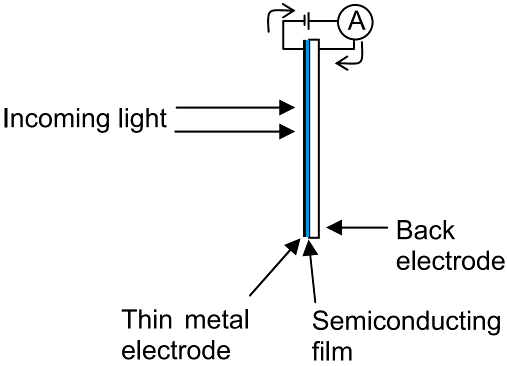
- The output of a detector must respond to changes in the incident light intensity. The ability to respond is expressed by quantities such as **responsivity**, **sensitivity**, and **dynamic range**.
- The output of a detector must respond quickly to quick changes in incident light intensity. This can be quantified by a detector **time constant**.
- A detector must have a minimal **dark signal** (also called **dark current** if current is the measurable of the detector). The dark signal is the signal when no light impinges on the detector.
- A detector must have an acceptable level of noise. **Noise** is unwanted signal from any source other than the signal of interest.

The earliest detectors were human eyes, followed by photographic methods. Eyes are extremely sensitive detectors; their dynamic range is 10^{10}–10^{14}, while photographic film and modern electronic detectors have a dynamic range of only 10^{3}–10^{5}. It is said that the human eye can detect up to 7 million different colors, meaning it can differentiate light that varies by as little as 0.000056 nm in wavelength! However, the eye is notoriously unreliable and its response is difficult to quantify. Certain forms of spectroscopy still use photographic methods, in part because photographic film can be sensitive to regions other than visible light.

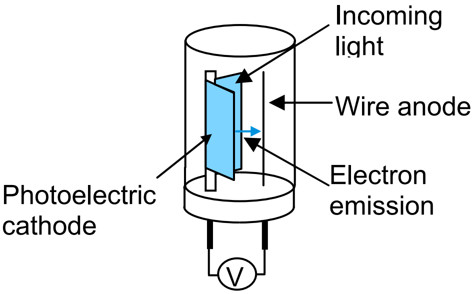
Photon Detectors

Photon detectors count photons of light. A photon detector has some surface that absorbs photons and produces some effect (current, voltage) proportional to the number of photons absorbed.

A **photovoltaic cell** consists of a layer of semiconductor (like selenium, Hg-Cd-Te, Cu_2O, etc.) sandwiched between two metallic electrodes, with the exposed electrode thin enough to be transparent. Photons of light are absorbed by the semiconductor, forming electrons and holes that create a current proportional to the number of photons absorbed.

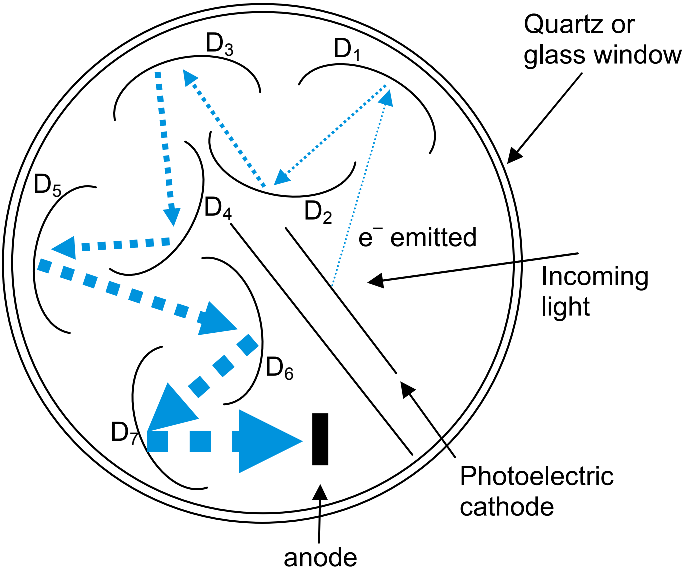


A **phototube** uses the photoelectric effect to generate a current from absorbed light. Light is absorbed by a metallic surface with a low work function. Electrons are emitted and attracted to a positively biased anode. Electronics measure the current, which is proportional to the number of photons absorbed.



Photomultiplier Tubes

One type of photon detector is the **photomultiplier tube (PMT)**. A PMT is similar to a phototube in that it has a photoelectric cathode that absorbs light and emits an electron. A PMT also contains other electrodes in sequence called **dynodes**. Each dynode is kept at a higher positive voltage than the preceding one, with a total voltage drop that can exceed 2500 V. Electrons are attracted to each successive dynode, and upon striking the dynode they knock off several additional electrons from the dynode. As the electron stream travels from dynode to dynode, more and more electrons are emitted as part of a cascade. At the final anode, 10^4–10^8 electrons may be produced for every electron emitted from the cathode.

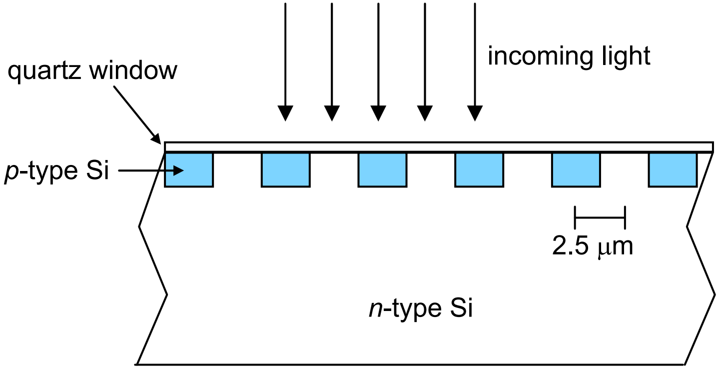


PMTs can detect IR, visible, and UV light, and can be very sensitive and have very fast response times. Some are cooled to minimize dark current. Many are so sensitive that they can be burned out if the incoming light is too bright.

Multichannel Photon Detectors

A **multichannel photon detector** measures dispersed radiation simultaneously. Photographic detection methods are the oldest instrumental forms of multichannel detectors.

A **photodiode array (PDA)** has small (25–50 μm by 2.5 mm) *p*-type semiconductor diodes embedded in an *n*-type Si substrate. Each diode is reverse-biased. Incoming light causes charge to build up, which is neutralized by either the electrons or holes. The amount of neutralized charge is proportional to the number of incident photons. After exposure, each diode is interrogated (a process that takes microseconds) by recharging; the amount of current needed to recharge each diode is measured. Arrays of 1024 diodes are common, with sizes ranging from 64 to 4096 diodes. Total interrogation times are in the millisecond range.



PDAs have a wide spectral response, from IR to UV. They can also be constructed from GaAs (gallium arsenide) or InGaAs (indium gallium arsenide) semiconductors.

Multichannel Detectors: Charge-Transfer Devices

A **charge-transfer device** is a two-dimensional array of semiconductive **pixels** that accumulate charge upon absorption of incident radiation, much like a PDA. Each pixel is about 10–20 μm by 10–20 μm; a **megapixel** device can be as small as 1 cm^2. Two types of charge-transfer devices are charge-injection devices and charge-coupled devices. Their physical makeups are similar; the main difference is how they measure the charge buildup caused by incident photons.

In a **charge injection device (CID)**, the buildup of holes in the *n*-type semiconductor under each pixel is measured by two electrodes. The holes are transferred from one electrode to another by varying the voltages on the electrodes. The amount of charge (and, by extension, the relative number of incident photons) is determined by the difference in net voltage on the two electrodes.

In a **charge-coupled device (CCD)**, each pixel has three electrodes, called **gates**. Electrons build up under each pixel just as they do in PDAs and CIDs. At a particular time, the electrons are moved to one side of the pixel, and ultimately into a detector by ramping up the negative voltage on the gates sequentially.

CCDs are extremely sensitive and can detect very low light levels, especially if cooled to minimize dark current. This makes them desirable as detectors in astronomy. Digital cameras also use CCDs as their “film.” To generate a color image, either a single CCD with a red/green/blue Bayer filter is used, or three different CCDs with a single filter is used and a composite image is reconstructed.

Thermal Detectors

A **thermal detector** absorbs radiation and changes temperature. Because the power in absorbed radiation is typically rather small (<10^{-7} W), the detector itself should be small so that it has a low heat capacity.

A **thermocouple** is the joining of two dissimilar-metal or metal alloy wires or films. When this occurs, a potential difference is formed between the other ends of the metals. Since potential differences are temperature-dependent (called the **Seebeck effect**), temperature values or changes in temperatures can be determined by calibration.

Thermocouple Types	
Type J	Fe vs. Cu-Ni
Type K	Ni-Cr vs. Ni-Al
Type E	Ni-Cr vs. Cu-Ni
Type T	Cu vs. Cu-Ni
Type S, R	Pt-Rh vs. Pt
Type N	Ni-Cr-Si vs. Ni-Si-Mg

A **bolometer** is a semiconductor or thin metal strip whose resistance decreases with temperature. They are small, and typically painted black to better absorb radiation.

A **Golay detector** is a small pneumatic chamber filled with gas and covered with a thin membrane. When radiation strikes the detector, the gas warms, increasing the internal pressure and deforming the membrane. Deflection of the membrane can be measured mechanically or optically.

A **pyroelectric detector** uses a crystal of a **pyroelectric material**, which has a strong temperature-dependent electric polarization. The change in electric polarization causes a measurable current, which changes fast enough to respond to the output of an interferometer. The most common material used is deuterated triglycine sulfate, (dTGS). Lithium tantalate ($LiTaO_3$) and lead zinc titanate (PZT) are also used.

Fourier Transform

The **Fourier transform** is a mathematical transformation that re-expresses a function in terms of sinusoidal functions, and vice versa. Although there are several different specific definitions and conventions, the form of the Fourier transform with unitary normalization constants is

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt$$

where $f(t)$ is a function of time, i is the square root of –1, and the function $F(\omega)$ is the Fourier transform of $f(t)$ and is a function of $(\text{time})^{-1}$, or frequency. If the original function f is a function of distance, its Fourier transform is a function of $(\text{distance})^{-1}$, or wavenumber.

For real, even functions, the above definition becomes

$$F(\nu) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) \cos\left(2\pi\nu t\right) dt$$

which is also called the **cosine transform**.

The function $f(t)$ is related to $F(\nu)$ via a Fourier transform; that is,

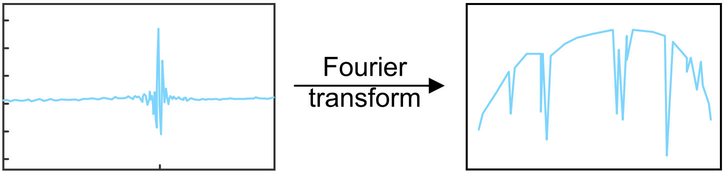
$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\nu) \cos\left(2\pi\nu t\right) d\nu$$

In 1892, Lord Rayleigh recognized that a spectrum was related to its interferogram via a Fourier transform. The conversion of an interferogram into a spectrum was first accomplished by Fellgett in 1949. However, it was not until the introduction of spectrometer-dedicated computers and the development of the Cooley-Tukey algorithm, called the **fast Fourier transform**, in 1965 that Fourier transform-based spectroscopy began to grow in popularity.

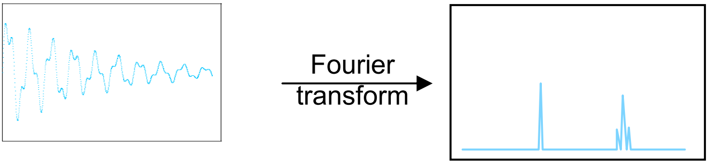
Fourier Transform Spectroscopy

Two forms of spectroscopy commonly use the Fourier transform as an integral part of the signal analysis: IR absorption spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The Fourier transform is occasionally seen in conjunction with Raman spectroscopy or UV-visible spectroscopy, but the IR and magnetic resonance techniques are dominated by Fourier transform spectroscopy.

In **Fourier transform infrared (FTIR)** or **(FT-IR)** spectroscopy, a Michelson interferometer is used to generate an interferogram, which is passed through a sample. A detector digitizes the interferogram, and a Fourier transform is performed to generate a **single-beam spectrum**.



In **Fourier transform nuclear magnetic resonance (FT-NMR)**, a strong pulse of radio frequency radiation illuminates a sample, causing the nuclei that are exposed to a magnetic field to orient together and create a net magnetization in one plane (labeled the x,y plane). This creates an alternating current that can be detected by a coil in the x,y plane. A plot of the intensity of this current versus time is called a **free induction decay (FID)** signal. The Fourier transform of the FID signal generates an NMR spectrum.



Absorption

There are two spectroscopically important processes: absorption and emission.

Absorption is when an atomic or molecular process takes in a photon and goes to a higher energy such that the increase in energy equals the energy of the photon:

$$\Delta E \equiv E_{\mathrm{f}} - E_{\mathrm{i}} = h\nu$$

In 1917, Albert Einstein defined a **rate of stimulated absorption** as

$$\text{rate of stimulated absorption} = B \cdot \rho(\nu) \cdot c$$

where $\rho(\nu)$ is the density of radiation having frequency ν, c is the concentration of the absorbers in the lower energy level, and B is the **Einstein coefficient of stimulated absorption** and is given by

$$B = \frac{\pi e^2}{4\pi\varepsilon_0 h m_e \nu}$$

where:

e—charge on electron, 1.6022×1^{-19} C
ε_0—permittivity of free space, 8.8542×10^{-12} $\mathrm{C^2/J \cdot m}$
h—Planck's constant, 6.6261×10^{-34} $\mathrm{J \cdot s}$
m_e—mass of the electron, 9.1094×10^{-31} kg

Absorption of photons is probably the most common measurement in spectroscopy. The **absorptivity** of a chemical substance, $\varepsilon(\lambda)$, is a measure of how strongly that substance absorbs light of a particular wavelength. It is commonly expressed in molar terms and is also referred to as the **molar absorptivity** or the **molar extinction coefficient**. The **absorbance**, $A(\lambda)$, of a sample depends on the molar absorptivity, the concentration of the chemical substance, and the distance the light passes through the sample.

Emission

Emission occurs when a substance goes from a higher energy state to a lower energy state, giving off a photon whose energy is equal to the difference in the energies of the states:

$$\Delta E \equiv E_{\mathrm{f}} - E_{\mathrm{i}} = h\nu$$

In 1917, Albert Einstein defined a **rate of spontaneous emission** as

$$\text{rate of spontaneous emission} = A \cdot c$$

where c is the concentration of absorbers in the upper energy state and A is the **Einstein coefficient of spontaneous emission** and is given by

$$A = \frac{8\pi^2 e^2 \nu^2}{4\pi\varepsilon_0 m_e c^3}$$

where:

e – charge on electron, 1.6022×10^{-19} C
ε_0 – permittivity of free space, 8.8542×10^{-12} C^2/J · m
c – speed of light, 2.9979×10^8 m/s
m_e – mass of the electron, 9.1094×10^{-31} kg

Einstein also demonstrated that there is also a **rate of stimulated emission**:

$$\text{rate of stimulated emission} = B' \cdot \rho(\nu) \cdot c$$

where B' is the **Einstein coefficient of stimulated emission** and $\rho(\nu)$ is the density of radiation having frequency ν. Einstein was able to show that B′ = B, the coefficient of stimulated absorption. Further, the ratio of spontaneous emission to stimulated emission is proportional to ν^3:

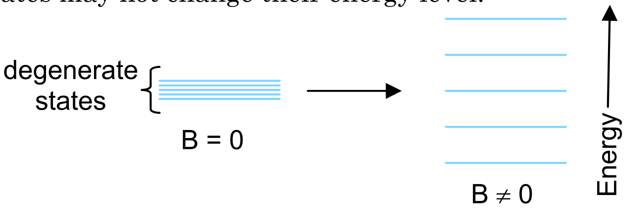
$$\frac{A}{B} = \frac{\left(8\pi^2 e^2 \nu^2 / 4\pi\varepsilon_0 m_e c^3\right)}{\left(\pi e^2 / 4\pi\varepsilon_0 h m_e \nu\right)} = \frac{8\pi h \nu^3}{c^3}$$

The higher the frequency of light involved, the greater the rate of spontaneous emission over stimulated emission.

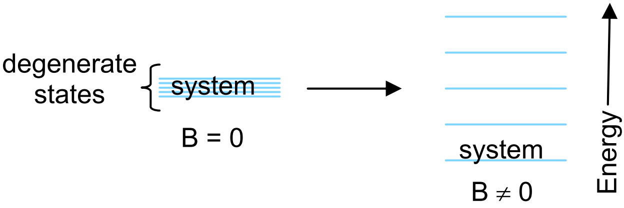
Magnetic Resonance

In many atomic and molecular systems, the constituent atoms and/or molecules have several states that have exactly the same energy. Such states are called **degenerate states**.

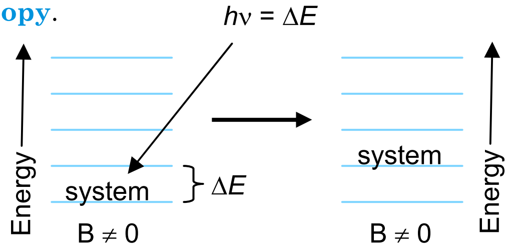
In the presence of a magnetic field, however, many sets of degenerate states split, with some states rising slightly in energy and some states lowering slightly in energy. Some states may not change their energy level.



In most cases, a system adopts its lowest-energy state (although low-lying excited states can be populated by thermal energy). Without a magnetic field, a system can be in any one of the degenerate states, but in the presence of a magnetic field, the lowest energy state is normally preferred.

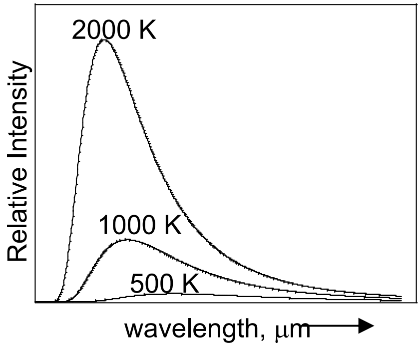


If electromagnetic radiation of the correct energy were to impinge on a system exposed to a magnetic field, the system can absorb the light and transfer to a higher energy state. This is **magnetic resonance spectroscopy**.



Quantum Theory

A **blackbody** is a perfect absorber or emitter of light. It can be approximated by a cavity with a small hole in it. In studying blackbodies, it is easier to study how they emit light rather than how they absorb light. Rather than having all wavelengths of light being emitted at equal intensities, the intensities of **blackbody radiation** vary, and the exact distribution depends on temperature.



In 1900, Max Planck rationalized this behavior by assuming that the atoms in the blackbody acted like little oscillators whose energies were proportional to their frequencies (rather than their amplitudes, as is normal with the energies of waves):

$$E \propto \nu$$

The proportionality constant used to generate an equation is known as h, and is known as **Planck's constant**:

$$E = h\nu$$

The value of h is $6.62608676 \times 10^{-34}$ J · s. Because the energy of the oscillator is specified by frequency, we say that the energy of the oscillator is **quantized**. Planck was then able to derive the following **radiation distribution law** that correctly predicted the intensity of blackbody radiation:

$$d\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) d\lambda$$

Quantum Theory of Light and Its Application

In 1905, Albert Einstein suggested that Planck's equation $E = h\nu$ applied to light itself; that is, the energy of light is **quantized**.

Einstein used this proposal to explain the **photoelectric effect**, in which light shone on a metal in a vacuum caused the emission of electrons. The photoelectric effect had several anomalous features:

1. Below a certain frequency of light that was characteristic of the metal, no electrons were emitted. This frequency is called the **threshold frequency**.
2. Increasing the frequency of light did not increase the number of electrons emitted, but did increase the kinetic energy of the emitted electrons.
3. Increasing the intensity of light did not increase the speed of emitted electrons, but did increase the number of electrons emitted.

Einstein demonstrated that he could explain the photoelectric effect if the energy of light were, indeed, equal to $h\nu$. He postulated that each metal had some binding energy he called a **work function**, ϕ, which had to be overcome before an electron could be ejected. An electron absorbed the energy of a ray of light, later called a **photon**, and when it had enough energy to escape the metal, it used part of the photon's energy to overcome the work function. The remaining energy went into kinetic energy of the moving electron. Thus, the following relationship was followed:

$$h\nu = \phi + \frac{1}{2}mv^2$$

Increasing the intensity of light did not increase the energy of the individual photons but did increase the number of photons, so more electrons were emitted. Increasing the frequency did, however, increase the energy of the individual photon, so the emitted electrons had more kinetic energy when they were emitted.

Quantum Mechanics—Postulates

The behavior of electrons in atoms and molecules is best described by the theory of **quantum mechanics** (also known as **wave mechanics**, because electrons are known to have wave properties). Quantum mechanics (QM) is based on several postulates.

Postulate #1. The state of a system of particles is given by a **wavefunction** Ψ, which is a function of the coordinates and time. Ψ contains all information that can be determined about the state of the system. Ψ must be single-valued, continuous, and bounded, and $|\Psi|^2$ must be integrable.

Postulate #2. For every physical observable, there exists a corresponding Hermitian **operator** $\boldsymbol{\hat{O}}$. Operators are constructed based on the definitions

$$\text{the position operator: } \hat{x} \equiv x\,\cdot$$

$$\text{the momentum operator: } \hat{p}_x = -i\hbar\frac{\partial}{\partial x}$$

where $\hbar$ is $h/2\pi$ and is called "h-bar" and i is the square root of $^-1$.

Postulate #3. The only values of observables that can be observed in any single measurement are the **eigenvalues** of the **eigenvalue equation** constructed between the proper operator and the wavefunction Ψ of the system:

$$\hat{O}\Psi = K\Psi$$

where K is the **eigenvalue** and is a constant. The wavefunction Ψ is called an eigenfunction of the operator $\hat{O}$.

> Postulates are assumed, not proven. If the conclusions based on the postulates agree with experiment, the postulates are assumed to be correct—but they are never formally *proven*.

Quantum Mechanics—More Postulates

Postulate #4. Wavefunctions need not be functions of most operators. However, proper wavefunctions must satisfy the following equation involving the total energy operator, $\hat{H}$, called the **Hamiltonian operator**:

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

This equation is called the **time-dependent Schrödinger equation (TDSE)**. If the time dependence can be separated from the wavefunction, the TDSE simplifies into the (one-dimensional) **time-independent Schrödinger equation (TISE)**:

$$\hat{H}\Psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}\right]\Psi = E\Psi$$

where m is the mass of the particle, $\hat{V}$ is the specific potential energy operator for the system, and E is the **energy** eigenvalue for the system. *This is the central postulate of quantum mechanics.*

Postulate #5. The **average value** (or **expectation value**) of an observable, $\langle O\rangle$, is given by

$$\langle O\rangle = \int_{\substack{\text{all}\\ \text{space}}} \Psi^*\hat{O}\Psi\, d\tau$$

where "all space" refers to the complete dimensionality of the system and $d\tau$ represents the appropriate dimensional infinitesimal for the system. The Ψ^* represents the complex conjugate of Ψ.

Postulate #6. The set of all eigenfunctions for an operator is a complete mathematical set of functions.

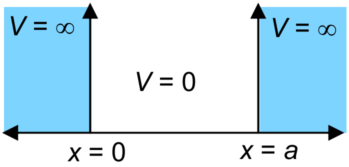
Postulate #7. In a given system, if the wavefunction is a linear combination of nondegenerate wavefunctions

$$\Psi = \sum_n c_n\Psi_n \quad \text{and} \quad \hat{A}\Psi_n = a_n\Psi_n$$

then the probability that a_n will be the value of any particular measurement is $|c_n|^2$.

QM—Particle-in-a-Box

The one-dimensional particle-in-a-box is an ideal system that assumes a particle exists between two infinitely-high potential energy barriers separated by some length a. Inside the box, the potential energy is 0.



The wavefunction Ψ in the regions in which $V = \infty$ is exactly 0. The Schrödinger equation for the region in which $V = 0$ is

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi = E\Psi$$

In order for the wavefunction to be continuous, the function must go to zero at the boundaries of the box, $x = 0$ and $x = a$. Such requirements are called **boundary conditions**.

Acceptable wavefunctions for a particle-in-a-box are sine functions of the form

$$\Psi = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}, \quad n = 1, 2, 3, \ldots$$

The variable n is a **quantum number**. The energy eigenvalues are

$$E = \frac{n^2h^2}{8ma^2}$$

Since the energies of a particle-in-a-box are restricted based on the n quantum number, the energy of a particle-in-a-box is quantized.

The particle-in-a-box ideal system can be applied to the energy levels and spectra of molecules that have linear conjugated double-bond systems. The delocalized electrons can be approximated as particles in a "box."

QM—Harmonic Oscillator

A classical harmonic oscillator is a mass that undergoes some periodic motion and follows **Hooke's law**:

$$F = -kx$$

where F is the restoring force on the mass, x is the displacement from an equilibrium position, and k is the **force constant**. The potential energy for a harmonic oscillator is

$$V = \frac{1}{2}kx^2$$

Classically, a harmonic oscillator has a frequency ν given by the expression

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

Quantum mechanically, the Schrödinger equation for an ideal harmonic oscillator is

$$\hat{H}\Psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right]\Psi = E\Psi$$

This differential equation has known solutions. The wavefunctions are

$$\Psi = \left(\frac{\alpha}{\pi}\right)^{1/4}\left(\frac{1}{2^n n!}\right)^{1/2} H_n\left(\alpha^{1/2}x\right)e^{-\alpha x^2/2},\ n = 0,1,2,3,\ldots$$

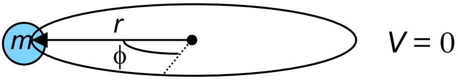
where $\alpha = 2\pi\nu m/\hbar$, $H_n(\alpha^{1/2}x)$ is a **Hermite polynomial** of n^{th} order, and n is a quantum number. The energy eigenvalue has the expression

$$E = h\nu\left(n + \frac{1}{2}\right)$$

where ν is the classical frequency of the oscillator. For the lowest possible value of the quantum number, the energy is nonzero; this is **zero point energy**. The harmonic oscillator system is used as an approximation to describe vibrations of atoms in molecules. When there is more than one mass on a harmonic oscillator, the **reduced mass** μ must be used in place of the mass m.

QM—Two-Dimensional Rotations

Two-dimensional (2D) rotational motion assumes rotation of a mass m about a center at a fixed radius r.



It is mathematically more convenient to rewrite the Hamiltonian operator in terms of the angle ϕ instead of the two dimensions x and y:

$$\hat{H}\Psi = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\Psi = E\Psi$$

where I is the **moment of inertia** and equals mr^2.

In order to be single-valued, the wavefunction must have the same value after it travels a full circle, or 2π radians. This is the **circular boundary condition**.

Acceptable wavefunctions for two-dimensional rotation are exponential functions of the form

$$\Psi = \frac{1}{\sqrt{2\pi}}e^{-im\phi}, \quad m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

where m is a **quantum number**. The energy eigenvalues are

$$E = \frac{m^2\hbar^2}{2I}$$

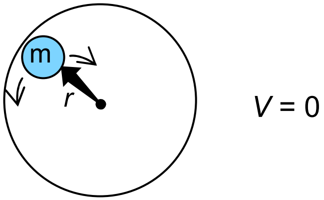
The energy of two-dimensional rotation is quantized. Except for $m = 0$, each value of energy can be produced by either $+m$ or $-m$; thus, each energy level is **doubly degenerate**. Angular momentum is also quantized:

$$\hat{L}_z\Psi = -i\hbar\frac{\partial}{\partial\phi}\Psi = m\hbar\Psi$$

The angular momentum can have values of $m\hbar$. Two-dimensional motion can be used to model the energy levels of electrons in benzene and other aromatic systems. If there is also a mass at the center, the system is called a **two-dimensional (2D) rigid rotor**.

QM—Three-Dimensional Rotations

Three-dimensional (3D) rotational motion assumes rotation of a mass *m* on the surface of a sphere having fixed radius *r*.



Using two **spherical polar coordinate** angles θ and ϕ, the Schrödinger equation for this system is

$$\hat{H}\Psi = -\frac{\hbar^2}{2I}\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Psi = E\Psi$$

If we assume the solutions to this differential equation can be separated into a Θ function and a ϕ function, solutions are

$$\Psi = \Theta_{\ell,m_\ell} \cdot \frac{1}{\sqrt{2\pi}} e^{-im_\ell\phi},\ \ell = 0,1,2,3\ldots;\ |m_\ell| \le \ell$$

where Θ_{ℓ,m_ℓ} is an **associated Legendre polynomial** with indices ℓ and m_ℓ, which are both quantum numbers. Collectively, the product of the two functions of Θ and ϕ are called **spherical harmonics**.

The energy eigenvalues are quantized:

$$E = \frac{\ell(\ell+1)\hbar^2}{2I}$$

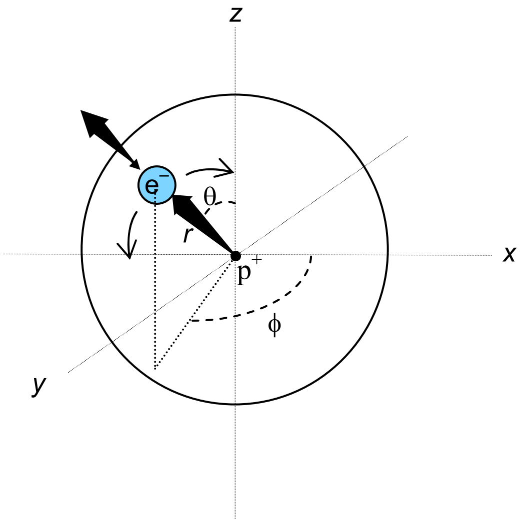
and each energy level is $2\ell+1$—fold degenerate. The **square of the total angular momentum**, L^2_{tot}, and the ***z* component of the total angular momentum**, L_z, are quantized as well:

$$L^2_{\text{tot}} = \ell(\ell+1)\hbar^2 \qquad L_z = m_\ell\hbar$$

If there is a mass at the center of the sphere, this system is known as the **three-dimensional (3D) rigid rotor**. This ideal system can be used to approximate the electronic energy levels of buckminsterfullerene, C_{60}.

QM—The Hydrogen Atom: Setup

In quantum mechanics, the **hydrogen atom** is defined as an ideal system of a **central force** type—the potential energy is a function of the distance between the protonic nucleus and the electron only, not the angle.



Quantum mechanically, the hydrogen atom is much like a 3D rigid rotor except that the distance between the nucleus and electron, *r*, is also allowed to vary. The potential energy is also not zero: it is the coulombic attraction between oppositely charged particles,

$$V = -\frac{e^2}{4\pi\varepsilon_0 r}.$$

The complete three-dimensional, spherical polar coordinate Schrödinger equation for the hydrogen atom is

$$\hat{H}\Psi = \left\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] - \frac{e^2}{4\pi\varepsilon_0 r}\right\}\Psi = E\Psi$$

QM—The Hydrogen Atom: Solutions

If it is assumed that the wavefunctions of the hydrogen atom are **separable** into an r part, a θ part, and a ϕ part, the differential equation that is the Schrödinger equation for the hydrogen atom system is solvable. It can be represented as

$$\Psi = \mathrm{R}(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$$

The functions $\Theta(\theta) \cdot \Phi(\phi)$ are the spherical harmonics from 3D rotational motion. They introduce the quantum numbers ℓ and m_ℓ, which have the same restrictions in the hydrogen atom system as they have in the 3D rotational motion system.

The functions $\mathrm{R}(r)$ are a set of polynomials called the **associated Laguerre polynomials**. These polynomials introduce a new index, n, which is a quantum number. Because of the Laguerre polynomials, there are also additional restrictions on the values of n, ℓ, and m_ℓ:

$$n = 1, 2, 3, \ldots$$

$$\ell < n$$

$$|m_\ell| \le \ell$$

The quantum number n is called the **principal quantum number** and designates a **shell**. The quantum number ℓ is the **orbital angular momentum quantum number** and designates a **subshell**. The m_ℓ quantum number is the **z component of the orbital angular momentum quantum number** (sometimes called the **magnetic quantum number**) and designates an **orbital**. There are $2\ell + 1$ orbitals in every subshell, and n^2 orbitals in every shell.

Subshells are labeled by a combination of the n and l quantum numbers in a "number + letter" combination. The letters s, p, d, and f represent ℓ values of 0, 1, 2, and 3. Thus, the designation "3p" represents the wavefunction that has $n = 3$ and $\ell = 1$. Subscripts can be used to specify the m_ℓ quantum number if necessary.

QM—Other Systems

Very few other systems that can be defined in quantum mechanics have **analytic solutions**: specific equations that can be produced to satisfy the differential equation, which is the Schrödinger equation. In all other cases, including all atoms larger than hydrogen and all molecules, wavefunctions must be approximated.

The reason for this inability to determine analytic solutions can be illustrated by considering the Hamiltonian operator for helium:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\nabla^2_{e\#1} + \nabla^2_{e\#2}\right) - \frac{2e^2}{4\pi\varepsilon_0 r_{e\#1}} - \frac{2e^2}{4\pi\varepsilon_0 r_{e\#2}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

where ∇^2 ("del-squared") is the abbreviation for the three-dimensional spherical polar coordinate kinetic energy operator of the Hamiltonian operator. Although the usual tactic has been to assume that the solution $\Psi(r,\theta,\phi)$ of the Schrödinger equation is separable, here we cannot do that because of the last term. It contains r_{12}, the distance between the two electrons, which simultaneously depends on six cooridinates: r, θ, and ϕ for electron #1, and r, θ, and ϕ for electron #2.

Despite the fact that analytic solutions are not available for any system larger than a hydrogen atom, there are alternatives. First, **numerical solutions** can be determined for many systems. Second, two major **approximation methods** are available. In these ways, even very large systems can be studied using the tools of quantum mechanics.

> Many students are dismayed when they learn that the Schrödinger equation cannot be solved for atoms larger than hydrogen. Quantum mechanics provides other tools to understand larger systems, and is still the best theory available to understand subatomic behavior.

Spin

In 1925, Uhlenbeck and Goudsmit suggested that the properties of the electron could be explained if the electron had its own intrinsic angular momentum, which was called **spin**.

All subatomic particles, including electrons, have a characteristic spin. All electrons have a spin of (½)$\hbar$, so we define a new quantum number s, the **spin angular momentum quantum number**. The **z component of the spin angular momentum**, whose quantum number is m_s, ranges from $+s$ to $-s$ in unit steps, or (for an electron) +½ ("spin up" or α) and –½ ("spin down" or β).

Although all electrons have the same value of s, electrons can have different values of m_s. Thus, there are four variable quantum numbers that can be specified for any one electron. The **Pauli principle** states that in an atom, no two electrons can have the same set of four variable quantum numbers. The Pauli principle is what causes electrons to fill the shells and subshells of multielectron atoms in the order they do, following a scheme called the **aufbau principle**.

Like orbital angular momentum, spin angular momentum is a vector quantity, and the different spin angular momenta of multiple electrons can combine together for a larger overall spin angular momentum—or they can combine against each other, or **pair**, to cancel their spin angular momenta. All completely filled electron subshells have the electron spins paired, so the combined spin angular momentum of a filled subshell is always zero.

Quantum Number Recap

n—principal quantum number—1, 2, 3, 4, …

ℓ—orbital angular momentum quantum number—$\ell < n$

m_ℓ—z-component of the orbital angular momentum quantum number—$|m_\ell| \leq \ell$ ($2\ell+1$ possible values)

s—spin quantum number—½ for all electrons

m_s—+½ or –½ for any electron ($2s+1$ possible values)

Approximation Methods—Variation Theory

There are two major methods used to approximate systems larger than the hydrogen atom: variation theory and perturbation theory.

Variation theory is based on the **variation theorem**, which states that any trial wavefunction ϕ for a system will produce an average energy, $\langle E \rangle$, equal to or higher than the true energy E_{true} of the system:

$$\langle E \rangle = \int \phi^* \hat{H} \phi \, d\tau \geq E_{\text{true}}$$

That is, the lower the energy, the better the wavefunction.

Trial wavefunctions can be any function that satisfies the general conditions of the system, i.e., continuous, single-valued, etc. Usually, functions are selected for ease of mathematical manipulation. In many cases, one or more variables are included in the function and a value of $\langle E \rangle$ is determined as a function of those variables. Then, this expression is minimized with respect to these variables:

$$\frac{\partial \langle E(a,b,\ldots) \rangle}{\partial a} = \frac{\partial \langle E(a,b,\ldots) \rangle}{\partial b} = \ldots = 0$$

Linear variation theory uses a linear combination of individual functions, called **basis functions**, which have different expansion coefficients:

$$\Phi_i = \sum_j c_{i,j} \Psi_j$$

In a similar fashion, the average energy $\langle E \rangle$ is calculated, then minimized in terms of the expansion coefficients $c_{i,j}$:

$$\frac{\partial \langle E(c_{i,1}, c_{i,2}, \ldots) \rangle}{\partial c_{i,1}} = \frac{\partial \langle E(c_{i,1}, c_{i,2}, \ldots) \rangle}{\partial c_{i,2}} = \ldots = 0$$

Much of the determination of the energy minima can be performed using linear algebra techniques on a computer.

Approximation Methods—Perturbation Theory

Perturbation theory assumes that the Hamiltonian operator of a real system can be written as the sum of an ideal system Hamiltonian $\hat{H}^{\circ}$ and some correction $\hat{H}'$ called the **perturbation**:

$$\hat{H}_{\text{system}} = \hat{H}^{\circ} + \hat{H}'$$

Now, the average energy $\langle E \rangle$ is evaluated using this Hamiltonian and ideal-system wavefunctions Ψ°:

$$\begin{aligned}\langle E \rangle &\approx \int \Psi^{\circ *} \hat{H}_{\text{system}} \Psi^{\circ}\, d\tau = \int \Psi^{\circ *} \left(\hat{H}^{\circ} + \hat{H}' \right) \Psi^{\circ}\, d\tau \\ &= \int \Psi^{\circ *} \hat{H}^{\circ} \Psi^{\circ}\, d\tau + \int \Psi^{\circ *} \hat{H}' \Psi^{\circ}\, d\tau \\ &= E_{\text{ideal}} + \int \Psi^{\circ *} \hat{H}' \Psi^{\circ}\, d\tau = \langle E_{\text{ideal}} \rangle + \langle E^{(1)} \rangle\end{aligned}$$

The average energy $\langle E^{(1)} \rangle$ is called the **first-order correction** to the ideal energy. If the perturbation is well-defined, the integral definition of $\langle E^{(1)} \rangle$ can be evaluated analytically or numerically.

Even if the first-order energy correction can be evaluated analytically, the overall energy is not the exact energy of the system because the wavefunctions of the ideal system, Ψ°, were used. First-order corrections to the wavefunction can also be determined, typically by using the other wavefunctions in the set of wavefunctions of the ideal system, $\Psi_n^{(0)}$:

$$\Psi_{n,\text{real}} = \Psi_n^{(0)} + \sum_m a_m \Psi_m^{(0)}, \text{ where}$$

$$a_m = \frac{\int \left(\Psi_m^{(0)} \right)^* \hat{H}' \Psi_n^{(0)}\, d\tau}{E_n^{(0)} - E_m^{(0)}}, \; m \neq n$$

Higher-order corrections can also be defined, both for the energy and the wavefunction; the expressions get progressively more complex.

Approximation Methods Applied to Spectroscopy

In spectroscopy, light is typically the perturbation on an atomic or molecular system. The perturbation Hamiltonian is

$$\hat{H}' = A_0 \cos 2\pi\nu t = A_0 \cdot \frac{(e^{i2\pi\nu t} + e^{-i2\pi\nu t})}{2}$$

If this perturbation Hamiltonian is applied using time-dependent perturbation theory, the following expression can be derived for the probability, $P(t)$, of a system to be in an excited state:

$$P(t) = \frac{4 \cdot \left|\int \Psi^*_{\text{final}} \hat{H}' \Psi_{\text{initial}}\ d\tau\right|^2}{\left(2\pi\nu_\Delta - 2\pi\nu\right)^2} \cdot \sin^2\left[\frac{1}{2}\left(2\pi\nu_\Delta - 2\pi\nu\right) \cdot t\right]$$

where ν_Δ is the difference in the energies of the initial and final states, expressed in frequency units.

This probability maximizes when the frequency of the light probing the system, ν, nears the energy difference between the two wavefunctions, ν_Δ. As time gets very large (that is, approaches infinity), it can be shown that the area under this probability approaches $\pi t/2$; that is, the probability that a transition will occur increases with time. Many light sources yield a range of frequencies. If the distribution function of source output is given by $g(\nu)$, the probability of a system absorbing light is given by

$$P(t) = 4 \cdot \left|\int \Psi^*_{\text{final}} \hat{H}' \Psi_{\text{initial}}\ d\tau\right|^2 \cdot \int_{-\infty}^{\infty} g(\nu) \cdot \frac{\sin^2\left[{}^{1}\!/_{2}\left(2\pi\nu_\Delta - 2\pi\nu\right) \cdot t\right]}{\left(2\pi\nu_\Delta - 2\pi\nu\right)^2} d\nu$$

If the light source is sufficiently narrow that the distribution function can be replaced with its value at the maximum of the sine function, this probability simplifies to

$$P(t) = 2\pi \cdot g(\nu_{\text{max}}) \cdot \left|\int \Psi^*_{\text{final}} \hat{H}' \Psi_{\text{initial}}\ d\tau\right|^2 \cdot t$$

This implies a transition rate of

$$\text{Rate} = 2\pi \cdot g(\nu_{\text{max}}) \cdot \left|\int \Psi^*_{\text{f}} \hat{H}' \Psi_{\text{i}}\ d\tau\right|^2$$

This is known as **Fermi's golden rule**.

The Transition Moment

It can be shown that the Einstein coefficient of stimulated absorption can be expressed as

$$B = \frac{\left| \int \Psi^{*}_{\text{final}} \hat{\mu} \Psi_{\text{initial}} \; d\tau \right|^{2}}{6\varepsilon_{0}\hbar^{2}}$$

where $\hat{\mu}$ is the dipole moment operator and is defined as $-e\mathbf{r}$, where $\mathbf{r}$ is the distance vector.

The integral in the numerator, $\int \Psi^{*}_{\text{final}} \hat{\mu} \Psi_{\text{initial}} \; d\tau$, is defined as the **transition dipole moment**, or simply the **transition moment**, M:

$$\mathrm{M} \equiv \int \Psi^{*}_{\text{final}} \hat{\mu} \Psi_{\text{initial}} \; d\tau$$

The value of the transition moment dictates how well two wavefunctions will participate in a transition (because all other terms in the expression for B are constant). If the value of the integral is exactly zero (and there are certain circumstances in which the integral must be exactly zero), the coefficient of absorption is exactly zero and the transition is **forbidden**. If the integral is nonzero, no matter how nonzero, the transition is **allowed**. Allowed transitions have a wide range of probability because the integral may have a very large value or a very small, but still nonzero, value.

Transition moments can be calculated if one knows or can approximate the wavefunctions involved in a transition; for example, for the $2s \rightarrow 2p_z$ transition in a hydrogen atom, $\mathrm{M} = -2.54\times10^{-29}$ C · m. The negative sign is arbitrary and aproblematic, because the absorption coefficient depends on the square of the transition moment.

Quantum-Mechanical Selection Rules

Quantum-mechanical selection rules are simple statements based on quantum number changes that yield nonzero values of M, the transition moment. These transitions are allowed. Other changes in the various quantum numbers are technically forbidden. In reality, some allowed transitions may be so weak that they cannot be observed; also, because atoms and molecules are not ideal, some forbidden transitions still may have significant intensities.

By evaluating the circumstances under which the integral in the definition of the transition moment is nonzero, the following quantum-mechanical selection rules can be derived:

- For changes in atomic electronic wavefunctions:
  Δn = anything
  $\Delta \ell = \pm 1$
  $\Delta m_\ell = 0, \pm 1$
- For changes in vibrational wavefunctions:
  $\Delta n = \pm 1$
- For changes in rotational wavefunctions:
  $\Delta J = \pm 1$
- For changes in nuclear spin wavefunctions:
  $\Delta I = \pm 1$
- For changes in electron spin wavefunctions:
  $\Delta m_{\mathrm{s}} = \pm 1$

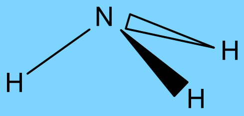
Other quantum-mechanical selection rules can be defined, depending on the system.

Violations of quantum-mechanical selection rules are not uncommon. In vibrations, $\Delta n = \pm 2\ \pm 3\ \pm 4\ \ldots$ are not unusual; such transitions are called **overtone transitions**.

Group Theory

Group theory is the mathematical study of symmetry.

Every object, even a molecule, has symmetry. Symmetry is described by various **symmetry elements**, of which there are five types: **identity**, **axes of rotation**, **centers of inversion**, **reflection planes**, and **improper axes of rotation**. Because of mathematical constraints, only certain combinations of symmetry elements are possible. These combinations are called **point groups**.



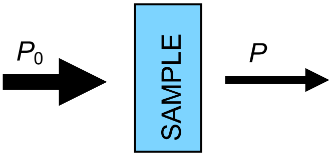
The pyramidal ammonia molecule has six symmetry elements: identity, rotation by 120°, rotation by 240°, and three reflection planes, each one coincident with a N-H bond. Its point group is labeled C_{3v}.

In turn, each point group has a specific number of sets of behaviors with respect to each individual symmetry element in the group. Each of these sets is an **irreducible representation**.

Because molecules have shapes that are dictated by their wavefunctions, the wavefunctions must belong to the same point group as the molecule. Each wavefunction can be labeled with the irreducible representation that corresponds to the wavefunction's behavior with regard to all the symmetry elements of the point group. The irreducible representation has many of the same mathematical properties as the wavefunction itself, and typically it is easier to manipulate the irreducible representation than the wavefunction. As such, in many cases the irreducible representation is used instead of the wavefunction. Operators also have irreducible representations in every point group, so certain wavefunction-operator integrals, like transition moments, can be evaluated in terms of their symmetry properties.

Plotting a Spectrum—The Ordinate

Most spectra are represented by simple graphical plots. There are several ways to plot a spectrum.



The **ordinate** is the y-axis of a plot. There are several common ways to represent the ordinate of a spectrum. If the incident power of light entering a sample is P_0 and the power leaving the sample is P, then **transmittance**, T, is defined and their ratio is

$$T = \frac{P}{P_0}$$

Percent transmittance, $\%T$, is the transmittance × 100%:

$$\%T = T \times 100\% = \frac{P}{P_0} \times 100\%$$

The baseline for transmittance spectra is typically at the top of the plot.

Absorbance, A, is the negative logarithm of the transmittance:

$$A = -\log T = -\log\left(\frac{P}{P_0}\right)$$

The baseline for absorbance spectra is typically at the bottom of the plot. Absorbance is useful because it can be shown that A is directly related to concentration of the absorbing species in the sample. Because absorbance is logarithmically related to T, absorbance values larger than 3 or 4 may be questionable because a small change in light intensity can lead to a large absorbance change.

% Power Absorbed	T	A
0	1.00	0
90	0.1	1
99	0.01	2
99.9	0.001	3
99.99	0.0001	4

Plotting a Spectrum—The Abscissa

The **abscissa** is the x-axis of a plot. There are various ways a spectrum can be represented on its x-axis.

In many cases, a spectrum is plotted versus one of the properties of the light waves used in that particular spectroscopic technique. Thus, UV-visible spectra can be plotted in units of wavelength (Å or nm) or wavenumber (cm^{-1}). Infrared spectra are also plotted in units of wavelength (μm; sometimes called microns but improperly labeled μ) or wavenumber (cm^{-1}), while microwave spectra are usually plotted in units of frequency (MHz or GHz). Of the three common photonic properties, frequency and wavenumber are directly proportional to the energy of the photon; wavelength is inversely proportional to the energy of the photon.

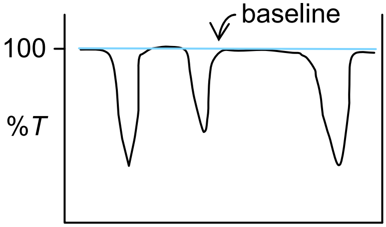
X-ray photoelectron spectra are plotted in terms of the difference between the energy of the source (usually a near-monochromatic x-ray emitter) and the binding energy of the ejected electron. The unit used is electron-volt (eV).

Magnetic resonance spectra are typically plotted in terms of the strength of the magnetic field needed to achieve resonance. The unit is gauss (G). Nuclear magnetic resonance spectra can be plotted in units of parts per million (ppm), which describes the change in the actual magnetic field experienced by the nucleus rather than the imposed field.

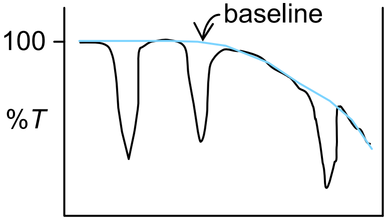
Mössbauer spectroscopy uses the slight shift in absorption frequency due to the chemical environment of a nucleus. This shift is so small that resonance can be achieved by moving a sample at some velocity and taking advantage of the resulting Doppler effect. Mössbauer spectra are typically plotted in units of cm/s.

Baselines

A **baseline** is a known value of transmittance or absorbance to which a signal can be compared when measured. Typically (but not always), the baseline of a transmittance spectrum should be at 1 (100%), while the baseline of an absorbance spectrum should be at 0.



Baselines may not always be at 100% transmittance or 0% absorbance because of effects other than absorption occurring to the incoming light. Scattering, for example, causes less light to pass through a sample via a mechanism other than absorption, usually resulting in a curved baseline.



For digitized spectra, a computational **baseline correction** can be applied to straighten the baseline. This must be done with care, because usually the value of the transmittance or absorbance of some signals may change. Computer programs used to collect and process spectra digitally may have a variety of algorithms for applying a baseline correction.

Beer's Law

Beer's law (sometimes called the **Beer-Lambert law**) states that the absorbance is proportional to the path length, *b*, through the sample and the concentration of the absorbing species, *c*:

$$A \propto b \cdot \mathrm{c}$$

The proportionality constant is sometimes given the symbol *a*, giving Beer's law an alphabetic look:

$$A = a \cdot b \cdot c$$

The constant *a* is called the **absorptivity**. More formally, the proportionality constant is represented by ε and is called the **extinction coefficient**:

$$A = \varepsilon \cdot b \cdot \mathrm{c}$$

If ε has molar units, it is called the **molar extinction coefficient**, or the **molar absorptivity**. The molar absorptivity varies with wavelength, and Beer's law is more accurately written as a function of λ:

$$A(\lambda) = \varepsilon(\lambda) \cdot b \cdot \mathrm{c}$$

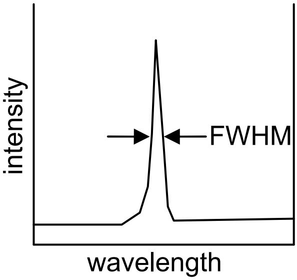
Most substances follow Beer's law at low to moderate concentrations of absorbing species. Beer's law may not be followed very well due to saturation effects in highly concentrated samples, changes in the refractive index of the sample, solute-solvent interactions, stray light effects, or the polychromaticity of the spectrometer light.

The direct relationship between absorbance and concentration illustrated by Beer's law often makes absorbance a more useful mode for spectra than transmittance.

Linewidths

Although spectroscopic transitions are spoken of as having specific energies, no spectral line is infinitely narrow. Every spectroscopic spectral line has some nonzero **linewidth**. The quality of modern spectrometers is such that the linewidths in most spectra are caused by one or more physical phenomenon, rather than instrumental factors.

The width of a spectral signal is typically expressed as some range of wavelength, frequency, or wavenumber as measured halfway to the peak maximum. This is called the **half-width** or the **full width at half maximum** (FWHM).



The shapes of lines can be approximated by three types of functions. A **Gaussian** lineshape has the general formula

$$F(\nu) \propto e^{-k(\nu-\nu_0)^2}$$

where k is some constant and ν_0 is the frequency of the center of the line. A **Lorentzian** lineshape has the form

$$F(\nu) \propto k\left[\frac{1}{1+(\nu-\nu_0)^2}\right]$$

Because the different mechanisms of line broadening produce different line shapes, most spectral signals are a combination of Gaussian and Lorentzian shapes called a **Voight profile**. For given normalized band shapes, a Gaussian shape is taller and narrower, while a Lorentzian shape is shorter and broader and a Voight shape somewhat in between.

Types of Line Broadening

Spectral lines have finite width for a variety of reasons. Most fundamentally, excited states have some finite lifetime that produces a natural line width called **natural broadening**, which has a Lorentzian shape. Natural broadening can have a value of 1 milliÅngstrom (mÅ) or less and in most cases is overwhelmed by other forms of broadening.

In a gas-phase sample, the motion of particles toward or away from the detector when light is emitted imposes a Doppler effect on the emitted photon; this is **Doppler broadening** and has a Gaussian shape. Doppler broadening and natural broadening determine the lower limit to the width of a spectral line.

In a gas, collisions between particles (of the sample itself and its container) can impart a very slight variation in the exact energy of transition. This is **collisional** or **pressure broadening**. It, too, is Lorentzian in shape.

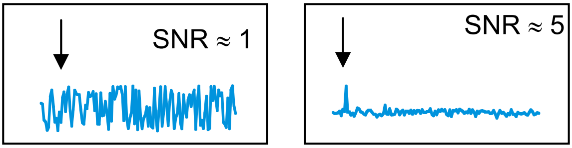
If the radiation impinging on the sample is powerful enough, **saturation broadening** can occur. This happens when the sample absorbs light faster than the excited state can decay. Since absorption occurs less in the center of the line than near the sides, an apparent broadening is seen.

Broadening is either homogeneous or inhomogeneous. **Homogeneous broadening** occurs when all particles have the same probability of contributing to the broadening of a spectral line. Natural broadening is homogeneous. **Inhomogeneous broadening** occurs when different particles have a different probability of contributing to the overall broadening. For example, in Stark broadening, molecules with permanent dipole moments can affect the exact energy of transition based on the exact position of a molecule in a sample, such as in an imperfect crystal.

Noise

Noise is unwanted fluctuation in a signal. Some level of noise can never be eliminated, because it results from the particulate nature of matter and light; this is **fundamental noise**. However, **excess noise** comes from imperfections in equipment, instrumentation, conditions, etc., and theoretically can be minimized or eliminated.

While too much noise is not good, it is irrelevant if the signal itself is strong enough. Thus, the concept of **signal-to-noise ratio (SNR)** is important. In the left spectrum below, a signal (in the position as indicated by the arrow) is obscured by the noise. In the right spectrum, the magnitude of the noise is lower, allowing for the signal to be detected without question. A SNR of at least 3 is necessary to demonstrate that a true signal exists.



There are different types of noise. **Thermal noise** comes from the temperature of electrical components. **Shot noise** arises from the existence of junctions in electrical components that charged particles (electrons) must cross. **1/*f* noise**, also called **pink noise** or **frequency noise**, is random noise of indeterminate origin but which has a larger magnitude at lower frequencies. **White noise** is random noise whose magnitude is constant no matter what the frequency.

The most controllable form of noise is **environmental noise**, which arises from the interactions of the system with the surroundings. Noise occurs at 60 Hz and its multiples (in the U.S.; 50 Hz and its multiples in other countries) because of AC power. Components picking up radio or TV signals (essentially acting as antennae) can convert those signals to voltage or current fluctuations. Flickering sources, power variations, shared electrical circuits, elevators, temperature and other weather fluctuations, and pedestrian traffic all cause noise.

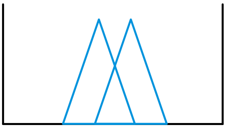
Resolution

Resolution is a measure of how close two different spectral signals can be but still be differentiated as separate signals. For dispersive spectrometers, resolution is largely a function of slit width, W, and the reciprocal linear dispersion, R_d, of the monochromator. The **resolving power** R of a spectrometer is defined as

$$R = \frac{\lambda}{\Delta\lambda}$$

where λ is the average wavelength between the two signals and $\Delta\lambda$ is the difference between them.

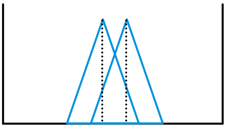
Experimentally, there are two common criteria used to decide if two nearby signals are resolved or not. The **baseline criterion** requires that the plot of the spectrum return to baseline at some point between the two signals.



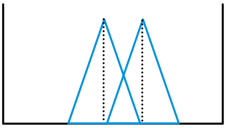
Not resolved by baseline criterion

Resolved by baseline criterion

The **Rayleigh criterion** requires that the maximum of one signal must be at a wavelength that corresponds to a minimum of the other. Deconvolution of the spectrum may be necessary to determine if two signals are considered resolved according to this criterion.



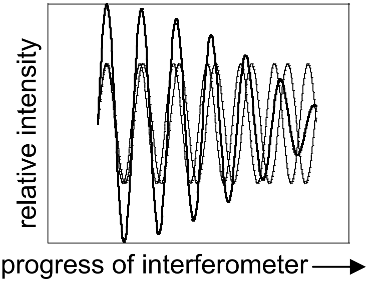
Not resolved by Rayleigh criterion



Resolved by Rayleigh criterion

Resolution in Fourier Transform Spectrometers

Because all wavelengths of light come through simultaneously in an interferometer, resolution is determined differently for these spectrometers.



If we assume that a spectrum contains two infinitely sharp lines at slightly different frequencies, their interferogram signal should be the combination of two sine waves (thin lines), as pictured. Note that as the path along the interferogram progresses, the two sine waves get increasingly more asynchronous. The closer the two initial sine waves are, the farther out the interferometer must travel to note that their sum (thicker line), which is what the detector ultimately measures,) is not a single, simple sine wave. Thus, we have

$$\text{resolution} \propto \frac{1}{\text{interferometer displacement}}$$

Two waves of dissimilar frequency combine constructively and destructively in a regular fashion called a **beat**. The beat frequency, ν_{beat}, equals the difference of the frequencies of the component waves:

$$\nu_{\text{beat}} = \Delta\nu = \nu_1 - \nu_2$$

In order to properly resolve the two signals, the interferometer must travel the wavelength of one beat, λ_{beat}. Since wavelength and frequency are inversely related, we have

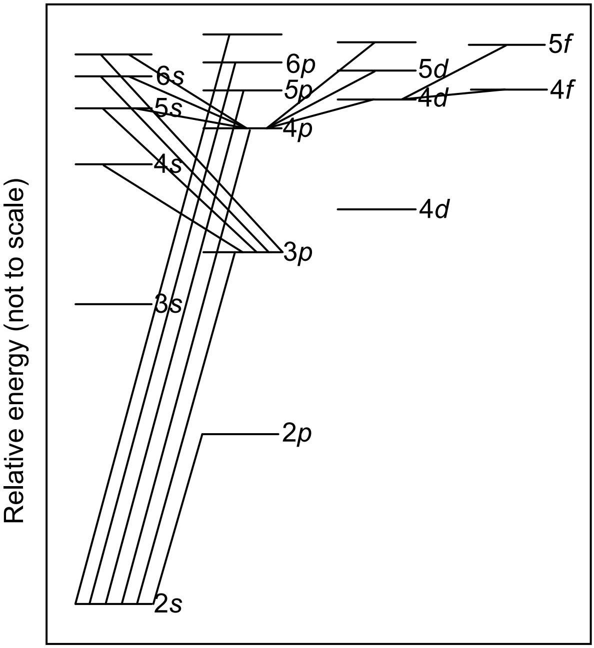
$$\text{interferometer travel} = \lambda_{\text{beat}} = \frac{1}{\Delta\nu}$$

Thus, an interferometer that moves 1 cm can resolve signals that are 1 cm^{-1} apart.

Atomic Electronic Spectroscopy

In the absence of a magnetic field, atoms have only electronic energy levels that can be easily probed. (We will ignore nuclear energy levels, which are on the order of tens of millions of electron volts higher than the ground state.) Atoms and monatomic ions, then, only have **electronic spectra**.

Most atomic electronic spectra occur in the visible and UV regions of the spectrum, although many inner transition metal atoms have electronic spectra in the IR region. Most atomic electronic spectra have been well-mapped and are displayed in a **Grotrian diagram**, which illustrates the observed transitions among energy levels, sometimes using a variable line thickness to represent the relative intensity of the transition.



Grotrian diagram (partial) for Li atoms, by subshell

Atomic Term Symbols

Atomic energy levels are usually labeled by a construction called a **term symbol** that symbolically indicates the values of the angular momenta for each particular energy state. Because angular momenta are vectors, they can combine, or **couple**, in a variety of ways to generate different values of total angular momenta.

In the **Russell-Saunders scheme**, a term symbol can be represented as

$$^{2S+1}L_J$$

where L is the total orbital angular momentum and is represented by a capital letter (S, P, D, F, etc.) that indicates the value of L; S is the total spin angular momentum; and J is the total angular momentum as determined by the coupling of L and S. J can have the values

$$J = L + S \rightarrow |L - S| \text{ in unit increments}$$

The amount $2S + 1$ is called the **multiplicity** and is a measure of the maximum number of J values a term will have. The terms **singlet**, **doublet**, **triplet**, etc., are used in cases in which the multiplicity is 1, 2, 3, etc. In addition, each term will be $2J + 1$-fold degenerate because there will be that number of M_J values, or z-components of the total angular momentum.

Within a given electron configuration, there may be many possible term symbols because of the differing ways the electrons may couple their angular momenta. However, **Hund's rules** the lowest-energy term symbol can be determined by:

1. The term having largest multiplicity will be the ground state.
2. If more than one term symbol has the highest multiplicity, the one having the highest value of L will be the ground state.
3. If the valence shell is less than half filled, the lower J will have lower energy; if greater than half filled, the higher J will have lower energy.

Electronic Spectra Selection Rules

For hydrogen, the selection rules are based on possible changes in the four variable quantum numbers:

$$\Delta n = \text{anything}$$
$$\Delta \ell = \pm 1$$
$$\Delta m_\ell = 0, \pm 1$$
$$\Delta m_s = 0$$

For polyelectronic atoms and ions, the electric dipole selection rules are based on the possible changes in the total orbital angular momentum L, the total spin angular momentum S, and the total angular momentum J:

$$\Delta L = 0, \pm 1$$
$$\Delta S = 0$$
$$\Delta J = 0, \pm 1 \text{ (but } J_{\text{initial}} = 0 \not\leftrightarrow J_{\text{final}} = 0\text{)}$$

The selection rule $\Delta S = 0$ is useful because it implies that the multiplicity does not change during the course of allowed electronic transitions. Thus, in absorption spectroscopy, allowed excited states will have the same overall spin as the ground state. Forbidden transitions to a state having a different spin do occur because atoms are not ideal systems, but these transitions have lower probability. Grotrian diagrams are sometimes drawn with states of different multiplicity in different sections, referred to as **manifolds**. Thus, for helium, we find the **singlet manifold** (containing only states that have $S = 0$), the **triplet manifold** (containing only states that have $S = 1$), etc.

In molecules, a transition is allowed only if the irreducible representation of the initial and final wavefunctions, Γ_i and Γ_f respectively, and the dipole moment operator's irreducible representation Γ_M contain the totally symmetric irreducible representation when multiplied together. That is,

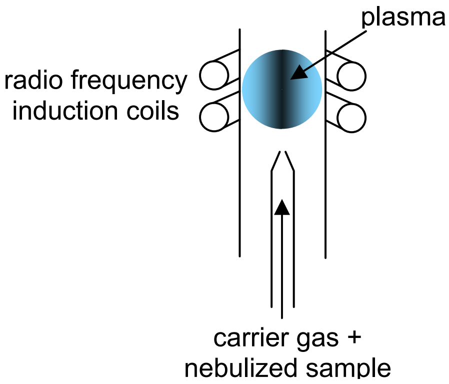
$$\Gamma_f \otimes \Gamma_M \otimes \Gamma_i \supset \text{ totally symmetric}$$

Atomic Emission Spectroscopy

If atoms can be excited by some energy source, light emitted by these atoms can be analyzed as the excited atoms release energy and return to a lower-energy or ground state. This is **atomic emission spectroscopy**. If the intensity of only one or a few emission lines are considered, as for example in quantitative or qualitative analysis, this is **atomic emission spectrometry**.

There are two main methods of exciting atoms from samples. The first is a **flame**. A flame uses thermal energy to excite atoms into upper electronic energy levels. The temperature of a flame can range from 1700°C (natural gas + air) to over 3300°C (acetylene + oxygen). However, because many chemical processes occur in any flame, emission can come from many species. A flame also serves as the **atomizer** of the spectroscopic apparatus.

The second main method for generating emission spectra is a **plasma**. In an **inductively coupled plasma (ICP)**, a carrier gas—usually argon—is doped with some nebulized sample, and the combination is subjected to the magnetic field from radio frequency induction coils, forming a plasma. Although most of the emission from the plasma is from the carrier gas, some emission comes from the atoms or ions in the sample. Light from the plasma can be analyzed for presence and quantity of more than 60 elements. Detection limits go to the part per billion (ppb) range.

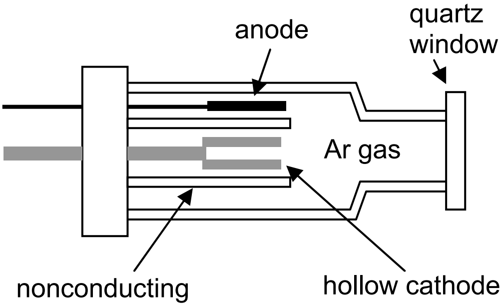


Electric arcs can also be used to generate emissions for spectroscopic or spectrometric analysis.

Atomic Absorption Spectroscopy

In **atomic absorption spectroscopy/spectrometry**, a dissolved solute is nebulized and atomized in a flame. Then, light coming from a lamp composed of the element being analyzed is passed through the flame. The atomized element in the flame absorbs the lamp emission, allowing one to identify and quantify the amount of element in the sample.

Typically, a **hollow-cathode lamp** is used. One advantage is that the light emitted by a hollow-cathode lamp consists of lines that have a very narrow width, a width that may be narrower than the absorption profile of the sample. In addition, the sample in the flame may also be emitting some characteristic light. This potential problem is solved by using a modulator, like a chopper, in the light path before the flame. A detector will see a constant signal from the flame emission, and a variable signal from the modulated source. A lock-in amplifier isolates the variable signal and amplifies it.



Hollow-cathode lamps can have cathodes constructed of more than one element for simultaneous analysis of more than one element in a sample.

Careful calibration must be done in atomic absorption spectrometry if it is to be used for quantitative purposes. Lamp voltages and currents, emission and absorption profiles, and instrumental factors can introduce deviations from Beer's law.

The Born-Oppenheimer Approximation

Technically, the quantum mechanical wavefunction of a molecule is a function of all nuclear coordinates and all electronic coordinates simultaneously:

$$\Psi_{\mathrm{molecule}} = \Psi(r_{\mathrm{e}}, r_{\mathrm{n}})$$

The Hamiltonian operator for a molecule is composed of the kinetic energies of translation, rotation, vibration, and electrons, plus the potential energies of electron-electron repulsion, nucleus-nucleus repulsion, and electron-nucleus attraction:

$$\hat{H} = K_t + K_r + K_v + K_e + V_{ee} + V_{nn} + V_{en}$$

The **Born-Oppenheimer approximation** states that since the nuclear motion is so slow with respect to the electronic motion, the motions of the nuclei are separable from those of the electrons, and the nuclei move in the presence of an average electronic potential. The **nuclear Hamiltonian operator** is thus

$$\hat{H}_n = K_t + K_v + K_r + \mathrm{E}_{\mathrm{el}}$$

which considers translational, vibrational, and rotational energies; the **electronic Hamiltonian operator** $\hat{H}_e$ is composed of the other four terms. Furthermore, the wavefunction can also be separated as

$$\Psi_{\mathrm{molecule}}(r_{\mathrm{e}}, r_{\mathrm{n}}) \approx \Psi(r_{\mathrm{e}}, r_{\mathrm{n}}) \cdot \Psi_n(r_{\mathrm{n}})$$

where the nuclear wavefunction Ψ_n depends only on the nuclear coordinates, and the electronic wavefunction Ψ depends on variable electronic coordinates but fixed nuclear coordinates.

The Born-Oppenheimer approximation allows us to interpret and calculate spectra in terms of individual molecular processes rather than all processes at once.

Molecular Spectroscopy

The spectra of molecules can be separated into four general types, although overlap of and influences on each type can occur:

- **electronic spectroscopy**
- **vibrational spectroscopy**
- **rotational spectroscopy**
- **nuclear resonance spectroscopy**

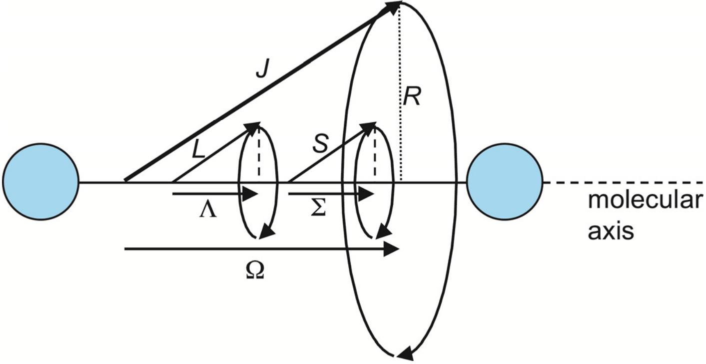
Overlaps include **rovibrational spectroscopy**, in which rotational behavior is superimposed on a vibrational spectrum; and **vibronic spectroscopy**, in which vibrations influence the electronic spectrum. Also, certain behaviors of a molecule (like vibrations) may effect the transition moments of other behaviors (like electronic transitions), causing violations of selection rules and the appearance of absorptions or emissions that ideally would not occur.

The imposition of a magnetic field can change the details of an electronic spectrum, as can an electric field. A magnetic field can also be used in systems that have unpaired electrons or nuclei with nonzero overall spin. Use of circularly polarized light takes advantage of differences in the selection rules in electronic and vibrational spectroscopy.

Sampling techniques vary widely. Gases can be contained in deceptively small chambers that, utilizing mirrors, can have an effective path length of tens of meters. Liquids—either pure liquids or liquid solutions—can be held in a small cup or **cuvette** made of plastic, glass, or quartz; in a tube of similar composition; or sandwiched in a thin film between two appropriately transparent windows. Alternately, a probe can be immersed into a liquid or liquid solution. Solids can be transparent crystals, fine powders embedded in plastic or an ionic solid, or polished surfaces kept in a vacuum chamber.

Diatomic Molecule Term Symbols

Because of their symmetries, diatomic molecules have a slightly different system for expressing angular momenta in term symbols.



A term symbol for the electronic energy levels of a diatomic molecule is similar to the Russell-Saunders term symbol for an atom. It is

$$^{2\Sigma+1}\Lambda_{\Omega}$$

where Λ is the Greek letter representing the magnitude of the orbital angular momentum on the molecular axis (Σ for 0, Π for 1, Δ for 2, Φ for 3, etc.), Σ is the numerical value of the spin angular momentum component in the molecular axis, and Ω has up to 2Σ+1 possible values as given by

$$\Omega = \Lambda + \Sigma \;\longrightarrow\; |\Lambda - \Sigma| \text{ in unit increments}$$

Electronic states of diatomic molecules have up to two additional labels on them. If a molecule is a homonuclear diatomic molecule, a right subscript "**g**" (for "**gerade**") or "**u**" (for "**ungerade**") is added to indicate whether the electronic wavefunction is symmetric or antisymmetric with respect to the center of inversion. Finally, for Σ states of any diatomic molecule, a right superscript + or – is included to indicate whether an electronic wavefunction is **symmetric** or **antisymmetric** with respect to a σ plane of symmetry that includes the molecular axis.

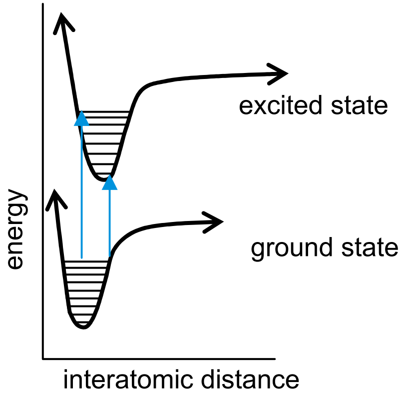
Molecular Electronic Spectroscopy

It is difficult to make generalizations about most electronic spectra because the electronic wavefunctions are specific to each individual molecule. The general selection rule

$$\Gamma_f \otimes \Gamma_M \otimes \Gamma_i \supset \text{ totally symmetric}$$

still holds, however.

One influence on electronic transitions is the exact position of the nuclei, which are changing due to molecular vibrations. Because electronic transitions are fast compared to nuclear motions (according to the Born-Oppenheimer approximation), nuclei are in the same positions before and after a transition. This can be illustrated easily for a diatomic molecule, which only has one internuclear distance.



Within each electronic state are a manifold of vibrational levels. Electronic transitions are essentially vertical (no change in interatomic distance), an idea called the **Franck-Condon principle**. Thus, transitions at the turning point of the two vibrational levels involved (as seen for the shorter arrow) have a high probability of transition because of the law of conservation of momentum. However, transitions involving vibrational levels at different stages of vibration (the longer arrow) have a lesser probability because in the lower-energy state the momentum of the atoms is high but in the higher-energy state the momentum of the atoms is low.

Hückel Approximations

In a **Hückel approximation**, the molecular orbital wavefunctions of the π electronic orbitals can be assumed to be linear combinations of atomic orbital wavefunctions. Variation theory can be applied to these molecular orbitals, and in consequence two types of interactions between the atomic orbitals are formed:

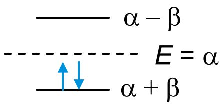
- An **energy integral**,

$$H_{xy} = \int \Psi_x^* \hat{H} \Psi_y \, d\tau \equiv \begin{cases} \alpha \text{ if } x = y \\ \beta \text{ if } x,\ y \text{ adjacent} \\ 0 \text{ if } x,\ y \text{ not adjacent} \end{cases}$$

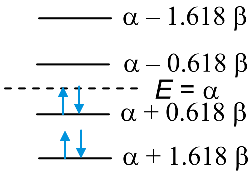
- An **overlap integral**,

$$S_{xy} = \int \Psi_x^* \Psi_y \, d\tau \equiv \begin{cases} 1 \text{ if } x = y \\ 0 \text{ if } x \neq y \end{cases}$$

In solving for the energies of the π molecular orbitals of ethylene, we find that $E = \alpha \pm \beta$. For 1,3-butadiene, the same treatment finds that $E = \alpha \pm 0.618\beta$ and $\alpha \pm 1.618\beta$. Thus, the total π energy of butadiene is 0.472β greater than expected if it were assumed to be two ethylene units. This is **energy of delocalization**.



Hückel treatment of the π electrons of ethylene

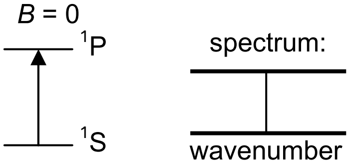


Hückel treatment of the π electrons of butadiene

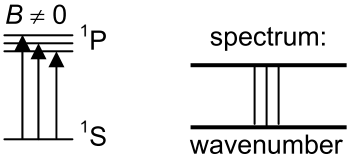
Energy of delocalization is maximized in planar circular systems that have $4n + 2$ π electrons, where $n = 0, 1, 2, 3,$ etc., which is referred to as the **$4n + 2$ rule**. The most well-known molecule that illustrates this is benzene, C_6H_6. This property of unexpected stability is called **aromaticity**.

The energies α and β are measured spectroscopically, with β being the more useful parameter. It is about 6270 cm^{-1}, or about 75 kJ/mol.

The Zeeman Effect



In the absence of a magnetic field, a ^{1}S → ^{1}P transition will show only a single line despite the fact that in the *p* subshell there are three orbitals with different M_L values.



However, in the presence of a magnetic field of strength *B*, the orbitals having different M_L values interact with the magnetic field differently and have a slightly different energy. The single line splits into a **triplet** of equally spaced lines. This is called the **Zeeman effect**, and the spectroscopic technique is called **Zeeman spectroscopy**.

There is an additional selection rule because now the M_L values are no longer degenerate. The new selection rule is

$$\Delta M_L = 0, \pm 1 \text{ (but } M_L = 0 \not\leftrightarrow M_L = 0 \text{ if } \Delta J = 0)$$

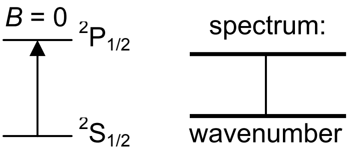
As in this case, when $S = 0$ and only singlet states are involved, the change in energy of the electronic M_L states depend only on orbital angular momentum; this rather straightforward effect is called the **normal Zeeman effect**. The change in energy of the electronic state due to the magnetic field is

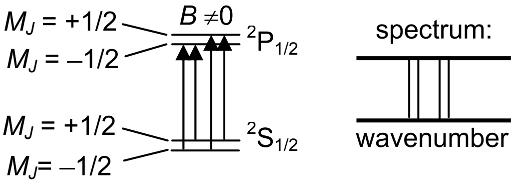
$$\Delta E_{\text{mag}} = \mu_B \cdot M_L \cdot B$$

where μ_B is a proportionality constant called the **Bohr magneton** and equals 9.274×10^{-24} J/T (where T stands for tesla, a unit of magnetic field strength). Values of ΔE_{mag} can be positive or negative depending on the value of M_L, but the energy changes are only on the order of 1 cm^{-1}.

The Anomalous Zeeman Effect

In the normal Zeeman effect, $S = 0$, so $J = L$. When $S \neq 0$, $J \neq L$ and the pattern of splitting of lines in a magnetic field depends on S, L, and J. This is the **anomalous Zeeman effect**. The splitting also depends on the M_J value of the individual electronic state.





In the case of the anomalous Zeeman effect, the energy change due to the magnetic field is

$$\Delta E_{\text{mag}} = g_J \cdot \mu_{\text{B}} \cdot M_L \cdot B$$

where g_J is a constant called the **Landé g factor**, which is given by

$$g_J = 1 + \left[\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right] (g_e - 1)$$

where, in turn, g_e is called the **electron g factor** and is the proportionality constant that relates the spin angular momentum vector **S** of the electrons to the magnitude of the magnetic dipole m of the electrons. Its value is 2.002319304… and can be approximated as 2. Thus, the final term in the Landé g factor can be approximated as $(2 - 1) = 1$, and the definition of g_J is simplified.

The pattern of line splitting in the presence of a magnetic field is not regular; this is why this form of the Zeeman effect is considered anomalous.

Nuclear Magnetic Resonance: Theory

Many atomic nuclei have nonzero overall spin, I (with quantized z-component spin, M_I). In the absence of a magnetic field, all orientations of the nuclear spin have the same energy. In the presence of a magnetic field, the orientations have different energies, and transitions can occur between the spin states of different energies. This is **nuclear magnetic resonance (NMR)** spectroscopy.

In the presence of a magnetic field of strength B, a nucleus changes its energy by

$$\Delta E_{\text{mag}} = -g_{\text{N}} \cdot \mu_{\text{N}} \cdot B \cdot M_I$$

where g_{N} is the **g factor** for the particular nucleus and μ_{N} is the **nuclear magneton**. Because the selection rule is

$$\Delta M_I = \pm 1$$

we can combine the two equations to determine the energy change that accompanies the transition:

$$\Delta E = g_{\text{N}} \cdot \mu_{\text{N}} \cdot B$$

It is customary to express this energy change as an equivalent angular frequency $\omega = 2\pi\nu$:

$$\omega = 2\pi\nu = \frac{g_{\text{N}}\mu_{\text{N}}}{\hbar} B$$

The ratio $(g_{\text{N}}\mu_{\text{N}})/\hbar$ is defined as γ and is called the **magnetogyric ratio** for the particular nucleus. The frequency ν in the above expression is called the **Larmor frequency** and is the frequency with which the magnetic dipole of the nucleus precesses about the applied magnetic field.

The energy difference between the spin orientations is dependent on the magnetic field strength. Thus, when the two have the correct values so that electromagnetic radiation is absorbed, they are said to be in **resonance**. Radio waves are in the right frequency range for most magnetic fields.

NMR: The Chemical Shift

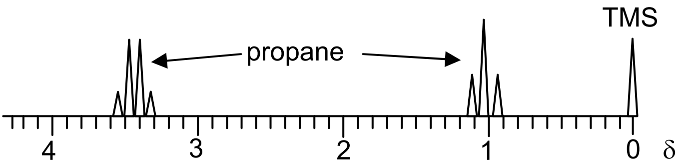
The exact magnetic field experienced by a nucleus, which in turn determines the resonant frequency needed for absorption, depends on the exact chemical environment of the nucleus. These differences cause what is called **chemical shift**, a change in the exact frequency needed for resonance. One way of expressing the exact magnetic field, B_{nuc}, is

$$B_{\text{nuc}} = B_{\text{appl}}(1 - \sigma)$$

where B_{appl} is the applied magnetic field, and σ is called the **screening constant**. Because the exact frequency depends on a magnetic field whose strength may also vary, it is typical to use an internal standard in NMR samples. For ^{1}H and ^{13}C NMR, the internal standard is **tetramethylsilane**, $Si(CH_3)_4$, or TMS. An NMR spectrum is typically plotted in terms of the difference, in parts per million (ppm), of the screening constant of a sample versus the screening constant of TMS. The **chemical shift parameter**, δ, is defined as

$$\delta = (\sigma_{\text{TMS}} - \sigma_{\text{sample}}) \times 10^6$$

and has units of ppm. An NMR spectrum is a plot of absorbed radio frequency radiation versus δ. The greater the δ, the higher the frequency of radio waves absorbed and the lower the magnetic field at the nucleus.

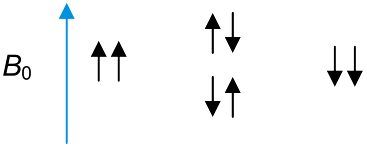


The NMR spectrum of propane, for example, shows two signals: one for the CH_3 groups (which have equivalent environments), and one for the central methylene group. Since the hydrogen atoms on each of these groups experience different chemical environments, their signals appear at different δs.

NMR: Spin-Spin Splitting

The NMR spectrum of propane consists of a quartet of equally spaced lines and a triplet of equally spaced lines. The splitting comes from an interaction of spins of the nuclei of the atoms in the molecule, so the phenomenon is called **spin-spin splitting**. It is caused by the interactions of the spin orientations in one group of nuclei with those of another set of nuclei.

The two hydrogen atoms in the central methylene group of propane have four possible orientations with regard to the magnetic field:



Each column of spin combinations exerts the same overall influence on the magnetic field because it has the same overall spin. This influence is felt on the adjacent methyl group, so that its hydrogen atoms instantaneously experience one of three different magnetic fields, two of the same magnitude and a median one of twice the magnitude. Thus, the signal from the methyl group hydrogen atoms shows a triplet in a 1:2:1 intensity pattern. Similarly, there are eight possible spin orientations of the three hydrogen atoms in the methyl group, and according to their net spins, they can be combined into four groups having 1, 3, 3, and 1 possibilities. Thus, the methylene group hydrogen atoms can experience one of four possible fields and will split into a quartet with intensity ratios of 1:3:3:1.

Spin-spin splitting is a major advantage in NMR spectroscopy because it gives clues about molecular structure. This, along with the characteristic chemical shift for atoms in various environments, makes NMR a very useful tool.

NMR is typically operated in pulsed, Fourier transform mode, rather than absorption mode.

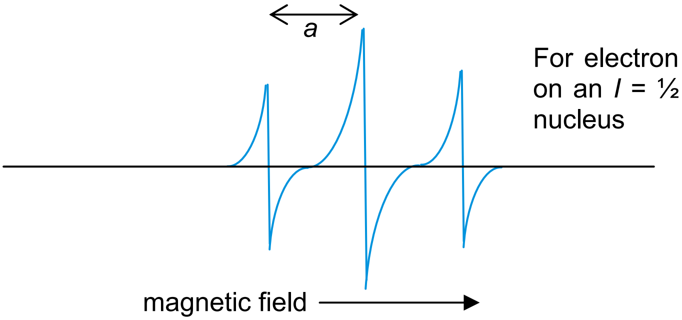
Electron Spin Resonance

Electron spin resonance (ESR), also called **electron paramagnetic resonance (EPR)**, is very similar to NMR. In ESR (or EPR), an unpaired electron—either from a radical species or from a partially filled, unpaired subshell—has a net spin that can adopt two different energy states in the presence of a magnetic field. One major difference compared to NMR is that resonance in ESR occurs with radiation in the microwave portion of the spectrum.

Not all unpaired electrons absorb the same microwave radiation at the same magnetic field. The exact value of the electron g factor, g_e, depends strongly on the local environment. In particular, because many nuclei have a nonzero spin I, there is an interaction, or coupling, between the unpaired electron's spin and the spin of the nuclei. This is **hyperfine coupling**. The size of the coupling is represented by a, the **hyperfine coupling constant**, such that the local magnetic field experienced by an electron, B_{local}, is given by

$$B_{\text{local}} = B_0 + a \cdot M_I$$

ESR spectra are plotted as derivative spectra rather than absorption spectra. Also, it is easier to keep the microwave radiation fixed and vary the magnetic field. Thus, ESR spectra are plots of absorbed radiation versus a varying magnetic field.



Rotational Spectroscopy

Rotational spectroscopy can be modeled by assuming a molecule acts as a quantum mechanical 3D rigid rotor. A linear molecule has two equal rotations; a nonlinear molecule has three distinct rotations that may all be equivalent (such molecules are called **spherical tops**), may have two equivalent and one unique (**symmetric tops**), or may have all three different (**asymmetric tops**).

In order to have a pure rotational spectrum, a molecule must have a permanent dipole moment. The quantum mechanical selection rule is based on the molecular rotational quantum number, J:

$$\Delta J = \pm 1$$

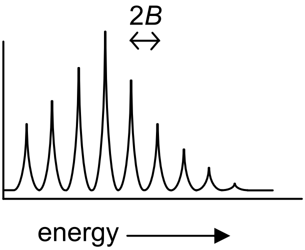
This selection rule allows us to determine an expression for the energy change for a linear or spherical top molecule, assuming absorption:

$$\Delta E = \frac{(J+1)\hbar^2}{I}$$

If we define the **rotational constant** B as $\hbar/2I$, this expression becomes

$$\Delta E = 2B(J+1), \quad J = 0, 1, 2, 3, \ldots$$

Successive absorptions thus appear at $2B$, $4B$, $6B$, $8B$, etc.—a series of lines equally spaced by $2B$. The lines will have varying intensities depending on the thermal population of the molecules in each rotational state.



Experimentally determined rotational spectra can be used to determine I, and from that, the structure of the molecule. Most pure rotational spectra are measured using microwave radiation. Rotational spectra of symmetry and asymmetric tops are more complicated.

Vibrational Spectroscopy

A molecule of N atoms has $3N - 6$ **vibrations** ($3N - 5$ for linear molecules), called **normal modes** of vibration, whose motions do not change the center of mass of the molecule. The frequencies of those vibrations, from Hooke's law, is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where k is the **force constant** and μ is the **reduced mass**. Vibrations of molecules are treated as QM harmonic oscillators (although real molecules exhibit some **anharmonicity**, a measure of deviation from ideality). The energy of a QM harmonic oscillator is

$$E = h\nu\left(n + \frac{1}{2}\right)$$

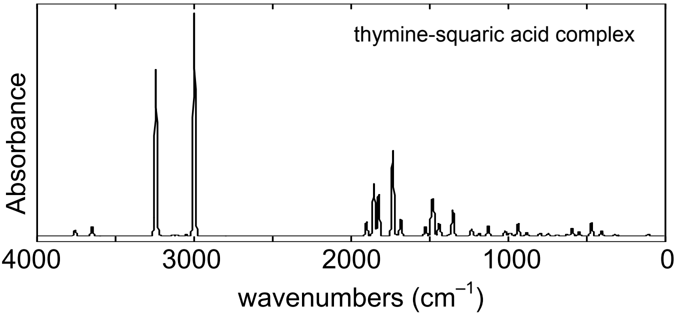
In order for a vibration to absorb light, the vibration must be accompanied by a change in dipole moment of the molecule. Quantum mechanically, the selection rule is

$$\Delta n = \pm 1$$

This selection rule allows us to determine an expression for the energy change for a vibration:

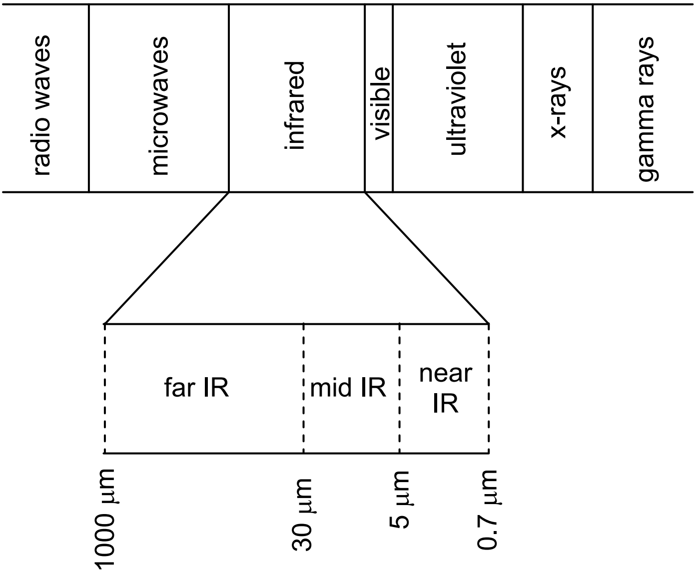
$$\Delta E = h\nu$$

Thus, a vibration absorbs light whose frequency is the same as the vibration. This typically occurs in the IR region of the spectrum. Vibrational spectra are typically expressed in micrometers (μm) or cm^{-1}.



Near- and Far-Infrared Spectroscopy

The **near-infrared (NIR)** region of the electromagnetic spectrum spans wavelengths from about 5000 nm to 770 nm, where visible light starts. The light is energetic enough to detect combinations and overtones of molecular vibrations, especially O-H, N-H, and C=O functional groups. Because NIR spectrometers are absorption-type spectrometers, they are simpler and more convenient than modern mid-IR spectrometers, most of which are FT devices. NIR spectrometers are used in process control and on-line monitoring in the food, pharmaceutical, and agriculture industries.



The **far-infrared (FIR)** region of the spectrum spans wavelengths from about 30 μm to 1000 μm, where the microwave region begins. FIR spectroscopy is used to probe low-frequency vibrations of molecules, including molecules with heavy atoms and solid state vibrational modes. Low frequency motions of large molecules like proteins can also be studied. FIR spectroscopy often must be used with specialized optics that is not appropriate for mid- or near-IR spectroscopy.

Overtones and Combination Bands

Because of violations of or approximations in selection rules, two types of absorptions can appear in a vibrational spectrum.

An **overtone band** is an absorption whose selection rule is a change in vibrational quantum number that is something other than ±1 (which is called the **fundamental absorption**):

$$\Delta n = \pm 2, \pm 3, \text{ etc. for overtone band}$$

Typically, the absorption frequency of an overtone band is somewhat less than a perfect multiple of the $\Delta n = \pm 1$ absorption frequency because of anharmonicity.

Frequencies of Overtone Absorptions of HCl (fundamental = 2886.0 cm^{-1})

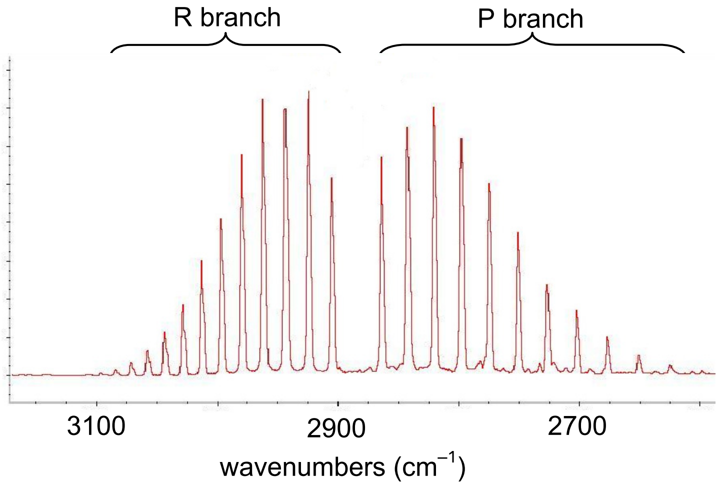
Δn =	Frequency (cm^{-1})	Variation from Multiple
+2	5668.0	–104.0 cm^{-1}
+3	8346.8	–311.2 cm^{-1}
+4	10922.8	–621.2 cm^{-1}
+5	13396.2	–1033.8 cm^{-1}

A **combination band** is an absorption whose frequency is very near the sum or difference of two or more fundamental vibrations of a molecule. Essentially, two ore more vibrational modes are excited by the same photon. Not all combinations are possible. The product of the irreducible representations of the two (or more) fundamental vibrations must include the irreducible representation of the dipole moment operator in that particular symmetry.

Because of overtone and combination bonds, the vibrational spectrum of a molecule may contain more than $3N - 6$ absorptions. Perhaps ironically, combination bands may appear whose component fundamental vibrations are not IR-active. The identification of combination bands can be verified using isotopic substitution.

Rovibrational Spectroscopy

Although pure rotational transitions typically occur at lower energies than pure vibrational transitions, a combination of the two processes can occur, essentially superimposing a rotational spectrum on a vibrational spectrum. This is **rotational-vibrational spectroscopy**, or **rovibrational spectroscopy**.

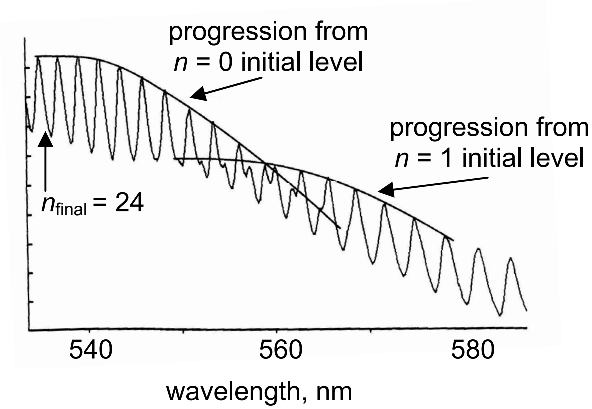


In rovibrational spectra, ΔJ can be either +1 or –1. When ΔJ is –1, a molecule is going to an energy level that is overall lower in energy than the pure vibrational transition. The series of lines in which $\Delta J = -1$ is the **P branch**. When ΔJ is +1, a molecule is going to an energy level that is overall higher in energy than the pure vibrational transition. The series of lines in which $\Delta J = +1$ is the **R branch**. When ΔJ is 0, ideally the rovibrational transition occurs at exactly the vibrational energy change; this is the **Q branch**, which may not be allowed in all molecules. In reality, the energy changes in the Q branch may vary because of centrifugal distortions that occur at high values of J.

The peaks in the rovibrational spectrum show the characteristic intensity pattern of rotational state populations that are due to thermal excitation into upper-J states.

Vibronic Spectroscopy

Although there is no selection rule for changes in vibrational quantum number in an electronic transition, the Franck-Condon principle does limit the possibilities for vibrational transitions during electronic transitions, a process called vibrational-electronic or **vibronic spectroscopy**.



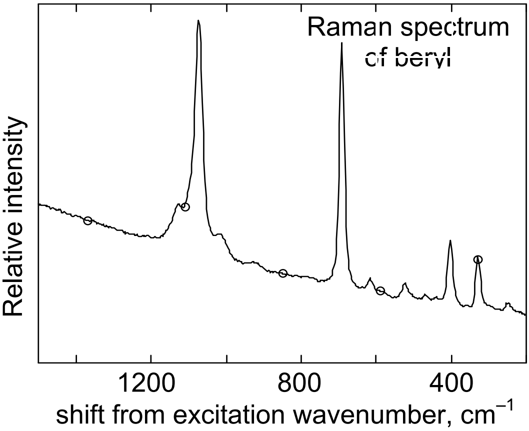
In the electronic spectrum of purple I_2 vapors going from the ground electronic state to the first excited electronic state, a series of almost equally spaced lines is the vibrational structure of the molecule in either the $n = 0$ or $n = 1$ vibrational quantum number of the ground electronic state to a different vibrational quantum number in the excited electronic state. Each series of vibrational signatures having the same initial or final vibrational quantum number is called a **progression**. Vibrational structure that illustrates the same change in vibrational quantum number (e.g. $\Delta n = 1$, $\Delta n = 2$, etc.) is called a **sequence**.

The intensities of the individual vibrational transitions also reflect thermal populations, as do rotational spectra. For molecules having small atoms (like H), the thermal excitation needed is usually too much at room temperature, while for molecules with heavy atoms (like I_2), normal temperatures may be enough to populate excited vibrational states.

Raman Spectroscopy

Of all the photons that may pass through a sample, approximately 1 in 10^7 may gain or lose an amount of energy equal to the energy of rotational or vibrational transition of the molecules in the sample. This is called the **Raman effect** or **Raman scattering** and forms the basis of **Raman spectroscopy**.

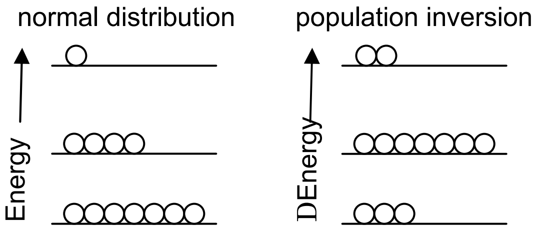
Because so few photons experience the Raman effect, acceptable spectra are produced only with long exposures or with very intense light sources like lasers. Most photons that interact with molecules without absorption come away with the same energy as they had initially (**Rayleigh scattering**). Some photons come away with less than their initial energy; these are **Stokes lines**. A lesser number of photons come away with more than their initial energy; these are **anti-Stokes lines**. The group of Stokes lines mirrors the group of anti-Stokes lines on the other side of the Rayleigh scattering signal.



The selection rule for vibrational Raman activity is $\Delta n = \pm 1$; for rotational Raman activity $\Delta J = 0$, it is ± 2. Absorption spectra and Raman spectra can give complementary information about a system. Some modes may produce strong IR absorptions but weak Raman signals, or vice versa.

Lasers

Under normal circumstances, the higher an energy level is, the less it is populated by thermal energy. Under some circumstances (for example, the presence of an upper energy level that has a relatively long lifetime), a system can be constructed so that there are more atoms/molecules in an upper energy level than is allowed under conditions of normal thermodynamic equilibrium. Such an arrangement is called a **population inversion**.

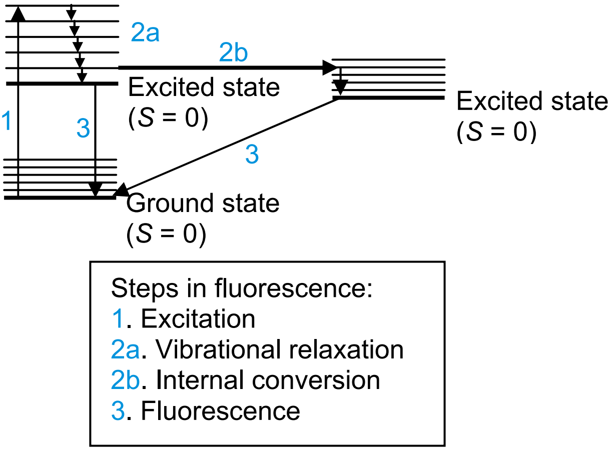


When a population inversion exists, an upper-state system will eventually give off a photon of the proper wavelength and drop to the ground state. This photon, however, can stimulate the production of other photons of exactly the same wavelength because of stimulated emission of radiation. Thus, many photons of the same wavelength (and phase, and other similar characteristics) can be generated in a short time. This is light amplification by stimulated emission of radiation, or LASER—usually seen in lowercase as **laser**. Lasers typically have a very narrow wavelength range of emission.

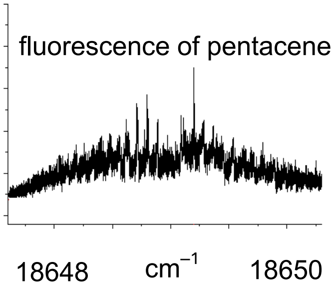
Many types of energy levels—electronic, vibrational, bands in semiconductors—are used to make lasers. Many materials are active laser sources, including Cr^{3+} ions in ruby and alexandrite crystals, Ti^{3+} in sapphire, Nd^{3+} in garnet, and a variety of doped semiconductors. Gases or gas mixtures like He/Ne, Ar, Kr, CO_2, N_2, even Cu(g) can be made to lase. Certain organic dyes can also be made to lase; one advantage is that their laser action has a broader range of wavelengths (20–30 nm) and they can be **tuned** to a particular wavelength.

Fluorescence

In some atomic or molecular systems, light is absorbed by the system, undergoes some radiationless internal relaxation—either through vibrational states (**vibrational relaxation**), electronic states (**internal conversion**), or both—and then de-excites to the ground state by emitting a photon having a lower energy than the exciting photon. This process is called **fluorescence**.



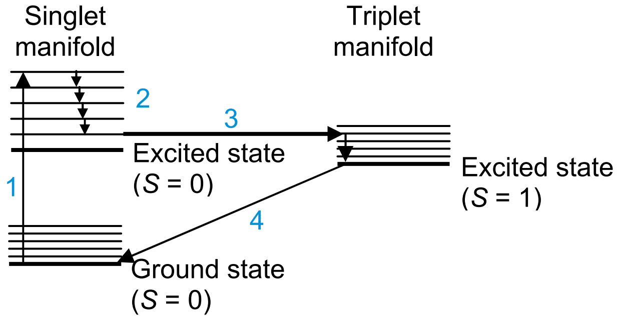
Fluorescence is a relatively fast process: 10^{-5}–10^{-8} s. **Fluorescence spectroscopy** has three aspects: a plot of fluorescence versus wavelength of incident light; a plot of fluorescence versus the wavelength of emitted light; and the time frame in which the fluorescence is emitted. A diagram of the energy levels involved in a fluorescence process is called a **Jablonski diagram**. Because of the relaxation processes, fluorescence will usually be of a lower energy (i.e., lower frequency, higher wavelength) than the excitation light. High-resolution fluorescence spectra can show vibrational and, in the gas phase, rotational structure.



Phosphorescence

Phosphorescence is similar to fluorescence except that after excitation, there is a violation of the $\Delta S = 0$ selection rule as the system undergoes a radiationless **intersystem crossing** into the triplet manifold. (Alternatively, there could be excitation directly into the triplet manifold by an intense light source, like a laser.) Once in the triplet manifold, relaxation to the singlet ground state is also a spin-forbidden process; while it does happen, it is relatively slow. Most phosphorescence occurs in the 10^{-4}–10^2 s timeframe. In order for phosphorescence to be favored, the system must be protected from other potential mechanisms of de-excitation. Intermolecular collisions or the presence of dissolved oxygen causes **quenching**, which lowers the efficiency of the phosphorescence process.

Phosphorescence and fluorescence can occur in the same system. Phosphorescence is typically lower in energy than fluorescence because the triplet state involved is usually lower in energy. Because heavy-atom molecules are less ideal, systems having heavy atoms are more likely to violate the spin selection rule and show phosphorescence.



Steps in phosphorescence:
1. Excitation
2. Vibrational relaxation
3. Intersystem crossing
4. Phosphorescence

Photoelectron Spectroscopy

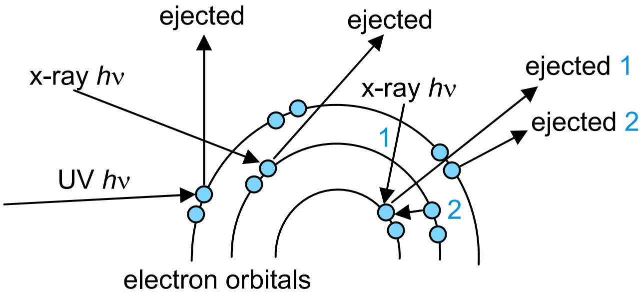
If an electron in an atom absorbs a high-energy photon, the electron can be ejected from the atom. If the incoming photons have a given energy (i.e., are monochromatic), then the electrons will be ejected with a characteristic kinetic energy. The characteristic kinetic energy depends on the **binding energy** (BE) of the electron in its orbital:

$$h\nu = \text{BE} + \frac{1}{2}mv^2$$

Because electrons, especially nonbonding valence and core electrons, have a particular energy depending on the element, this type of spectroscopy, called **photoelectron spectroscopy**, can be used to identify elements in a sample.

Far-UV light has enough energy to remove valence electrons. This is **ultraviolet photoelectron spectroscopy (UPS)**. Relatively low-energy x-rays have enough energy to remove core electrons; this is **x-ray photoelectron spectroscopy (XPS)**. The basic mechanisms in both forms of spectroscopy are the same, although the instrumentation is different to accommodate the different spectral regions.

In **Auger spectroscopy**, a core electron is ejected and a higher-level electron falls down to fill the hole; in doing so, it releases enough energy to emit a second electron, called the **Auger electron**. It is the energy of the Auger electron that is measured in this form of spectroscopy.



Equation Summary

Light

$$c = \lambda \cdot \nu \qquad \mathrm{E} = h\nu$$

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda} = h\tilde{\nu}$$

Maxwell's equations

$$\nabla \cdot \mathbf{E} = 0 \qquad \nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \qquad \nabla \times \mathbf{B} = \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$

Polarization equations

$$I_{\mathrm{s}} = \frac{\sin(\phi - \theta)}{\sin(\phi + \theta)} \qquad I_{\mathrm{p}} = \frac{\tan(\phi - \theta)}{\tan(\phi + \theta)}$$

Snell's law

$$n_1 \sin\theta_1 = n_2 \sin\theta_2 \qquad \theta_{\mathrm{c}} = \sin^{-1}\frac{n_1}{n_2}$$

Dispersion

$$D_{\mathrm{a}} = \frac{d\theta}{d\lambda} \qquad D_{\mathrm{l}} = \frac{dx}{d\lambda}$$

$$R_d = \frac{d\lambda}{dx}$$

Grating and filter formulas

$$d(\sin\alpha + \sin\beta) = m\lambda \qquad 2d\left(n^2 - \sin^2\theta\right)^{1/2} = m\lambda$$

Lens and mirror equations

$$\frac{1}{f} = \frac{2(n-1)}{R} \qquad \frac{1}{r_1} + \frac{1}{r_2} = \frac{1}{f}$$

$$\text{magnification} = -\frac{r_2}{r_1}$$

Equation Summary

Fourier transform

$$F(\nu) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) \cos\left(2\pi\nu t\right) dt$$

$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\nu) \cos\left(2\pi\nu t\right) dt$$

Einstein coefficients

$$B = \frac{\pi e^2}{4\pi\varepsilon_0 h m_e \nu} \qquad A = \frac{8\pi^2 e^2 \nu^2}{4\pi\varepsilon_0 m_e c^3}$$

Planck’s radiation distribution law

$$d\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) d\lambda$$

The photoelectric effect

$$h\nu = \phi + \tfrac{1}{2} m v^2$$

Operator algebra

$$\hat{x} \equiv x \cdot \hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

$$\hat{O}\Psi = K\Psi$$

The Schrödinger equation

$$\hat{H}\Psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}\right]\Psi = E\Psi$$

Average values

$$\left\langle O \right\rangle = \int_{\substack{\text{all}\\ \text{space}}} \Psi^* \hat{O} \Psi \, d\tau$$

Equation Summary

Particle-in-a-box

$$\Psi = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}, \quad n = 1, 2, 3, \ldots \quad E = \frac{n^2 h^2}{8ma^2}$$

Harmonic oscillator

$$\Psi = \left(\frac{\alpha}{\pi}\right)^{1/4}\left(\frac{1}{2^n n!}\right)^{1/2} H_n\left(\alpha^{1/2}x\right)e^{-\alpha x^2/2}, n = 0, 1, 2, 3, \ldots$$

$$E = h\nu\left(n + \frac{1}{2}\right)$$

2D rotational motion

$$\Psi = \frac{1}{\sqrt{2\pi}}e^{-im\phi}, \quad m = 0, \pm 1, \pm 2, \pm 3, \ldots \qquad E = \frac{m^2\hbar^2}{2I}$$

3D rotational motion

$$\Psi = \Theta_{\ell, m_\ell} \cdot \frac{1}{\sqrt{2\pi}}e^{-im_\ell\phi}, \ \ell = 0, 1, 2, 3 \ldots; \left|m_\ell\right| \le \ell$$

$$E = \frac{\ell(\ell+1)\hbar^2}{2I} \quad L^2_{\text{tot}} = \ell(\ell+1)\hbar^2 \qquad L_z = m_\ell\hbar$$

Hydrogen atom

$$\Psi = \mathrm{R}(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$$

Perturbation theory and spectroscopy

$$P(t) = \frac{4 \cdot \left|\int \Psi^*_{\text{final}}\hat{H}'\Psi_{\text{initial}}\, d\tau\right|^2}{\left(2\pi\nu_\Delta - 2\pi\nu\right)^2} \cdot \sin^2\left[\frac{1}{2}\left(2\pi\nu_\Delta - 2\pi\nu\right) \cdot t\right]$$

$$P(t) = 4 \cdot \left|\int \Psi^*_{\text{final}}\hat{H}'\Psi_{\text{initial}}\, d\tau\right|^2 \cdot \int_{-\infty}^{\infty} g(\nu) \cdot \frac{\sin^2\left[{}^1\!/_2\left(2\pi\nu_\Delta - 2\pi\nu\right) \cdot t\right]}{\left(2\pi\nu_\Delta - 2\pi\nu\right)^2} d\nu$$

$$\text{Rate} = 2\pi \cdot g(\nu_{\text{max}}) \cdot \left|\int \Psi^*_{\text{f}}\hat{H}'\Psi_{\text{i}}\, d\tau\right|^2$$

Equation Summary

Transition moment

$$\mathrm{M} \equiv \int \Psi^{*}_{\text{final}} \hat{\mu} \Psi_{\text{initial}} \, d\tau$$

Absorbance and transmittance

$$T = \frac{P}{P_0} \qquad \%T = T \times 100\% = \frac{P}{P_0} \times 100\%$$

$$A = -\log T = -\log\left(\frac{P}{P_0}\right)$$

Beer's Law

$$A(\lambda) = \varepsilon(\lambda) \cdot b \cdot c$$

Magnetic spectroscopy

$$\Delta E_{\text{mag}} = g_J \cdot \mu_{\text{B}} \cdot M_L \cdot B \quad \Delta E_{\text{mag}} = -g_{\text{N}} \cdot \mu_{\text{N}} \cdot B \cdot M_I$$

$$g_J = 1 + \left[\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right](g_e - 1)$$

$$B_{\text{nuc}} = B_{\text{appl}}(1 - \sigma) \qquad \delta = (\sigma_{\text{TMS}} - \sigma_{\text{sample}}) \times 10^6$$

$$B_{\text{local}} = B_0 + a \cdot M_I$$

Rotational spectroscopy

$$\Delta E = 2B(J + 1), \quad J = 0, 1, 2, 3, \ldots$$

Photoelectron spectroscopy

$$h\nu = \text{BE} + \frac{1}{2} m v^2$$

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David W. Ball is a Professor in the Department of Chemistry at Cleveland State University (CSU) in Ohio. He received a Ph.D. in chemistry from Rice University in 1987 and, after post-doctoral research at Rice University and at Lawrence Berkeley Laboratory in Berkeley, California, joined the faculty at CSU in 1990, rising to the rank of Professor in 2002. He has authored more than 160 publications, equally split between research papers and works of a more educational bent, including five books currently in print (and one more on the way). Dr. Ball's research interests include low-temperature infrared spectroscopy and computational chemistry. His wife, Gail, is an engineer who keeps him on his toes. His two sons, Stuart and Casey, also keep him on his toes, especially since his older son Stuart is currently (at this writing) experiencing the cataclysmic educational process of Fourth Grade.

Professor Ball has a doppelgänger, David W. Ball, who writes historical fiction and lives in the Rocky Mountains. David (the chemistry professor) has read some of David's (the real author's) books and has enjoyed them. There is no word if the favor has been returned.

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