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 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, \( \theta \), and the angle of refraction, \( \phi \):  

\[
I_s = -\frac{\sin(\phi - \theta)}{\sin(\phi + \theta)} \\
I_p = -\frac{\tan(\phi - \theta)}{\tan(\phi + \theta)}
\]

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°.
**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 $\lambda$ constructively interferes when the following relationship is satisfied:

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

where $m$ is the **order** and $\theta$ 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 $\theta$ 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.**
Photomultiplier Tubes

One type of photon detector is the photomultiplier tube (or PMT). A PMT is similar to a phototube in that it has a photoelectric cathode that absorbs light and emits a photon. 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.
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.

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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 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.
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:

\[ d\rho = \frac{8\pi hc}{\lambda^5} \left( \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \right) d\lambda \]
In spectroscopy, light is typically the perturbation on an atomic or molecular system. The perturbation Hamiltonian is
\[ \hat{H}' = A_0 \cos 2\pi vt = A_0 \cdot \frac{e^{2\pi vt} + e^{-i2\pi vt}}{2} \]
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:
\[ P(t) = \frac{4}{(2\pi \nu_\Delta - 2\pi \nu)^2} \cdot \sin^2 \left[ \frac{1}{2} (2\pi \nu_\Delta - 2\pi \nu) \cdot t \right] \]
where \( \nu_\Delta \) 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, \( \nu \), nears the energy difference between the two wavefunctions, \( \nu_\Delta \). 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
\[ P(t) = 2 \cdot \left| \int \psi^*_f \hat{H} \psi_i d\tau \right|^2 \cdot t \]
\[ \times \int_{-\infty}^{\infty} g(\nu) \cdot \sin^2 \left[ \frac{1}{2} (2\pi \nu_\Delta - 2\pi \nu) \cdot t \right] \frac{1}{(2\pi \nu_\Delta - 2\pi \nu)^2} d\nu \]
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
\[ P(t) = 2\pi \cdot g(\nu_{\text{max}}) \cdot \left| \int \psi^*_f \hat{H} \psi_i d\tau \right|^2 \cdot t \]
This implies a transition rate of
\[ \text{Rate} = 2\pi \cdot g(\nu_{\text{max}}) \cdot \left| \int \psi^*_f \hat{H} \psi_i d\tau \right|^2 \]
This is known as **Fermi's golden rule.**
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:

\[ h\nu = BE + \frac{1}{2}mv^2 \]

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.