Lecture No. 1

ADVANCES IN SPECTROSCOPY

by

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ADVANCES IN SPECTROSCOPY

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Analytical atomic spectroscopy utilises the emission, absorption or fluorescence of light at discrete wavelength by atoms in a vaporised sample for the determination of the elemental composition of the sample. Spectroscopy is thus an analytical technique concerned with the measurement of the interaction of radiant energy with matter. A display of such data is called a spectrum, that is a plot of the intensity of the emitted or absorbed radiant energy (or some function of the intensity) versus the energy of that light. Spectra due to the emission of radiant energy are produced as energy is emitted from matter, after some form of excitation, then collimated by passage through a slit, then separated into components of different energy by transmission through a prism or by reflection from a ruled grating and finally detected. Spectra due to the absorption of radiant energy are produced when radiant energy from a stable source collimated and separated into its components in a monochromator passes through the sample whose absorption spectrum is to be measured and is detected.

Historical Development

The history of the spectroscopy dates back to the 17th Century when Newton discovered that a prism will divide light into spectral colours. Some of the major advancements in spectroscopy are listed below in a chronological order.

1666 - Newton finds that a prism will divide sunlight into its constituent colours.

1802 - Wollaston finds dark lines in a solar spectrum using a primary slit as an aperature.

1817 - Frauenhofer produces the first diffraction grating and builds the first spectroscope.

1859 - Kirchhoff and Bunsen discover the utility of spectroscopy in chemical analysis.

1900 to 1920 - Direct, alternating and high voltage sources are developed.

1930 - Gerlach and Schweitzer develop the internal reference technique.

1940 - Begining of spectrometers with photoelectric measurement.

Spectroscopic Units

The radiant energy can be described in terms of a number of properties or parameters. The "frequency ν" is the number of oscillations per unit time described by the electromagnetic wave; the usual unit of frequency is the hertz (1 H_z = 1 cycle per second). The velocity C of propagation is 2.9979×10^{8} ms^{-1} for radiation travelling through vacuum, and somewhat less for passage through a transparent medium.

The wavelength λ is the distance between adjacent crests of the wave in a beam of radiation. It is given by the ratio of the velocity to the frequency. The units of wavelength are the micrometer (1 mm = 10^{-6} m; formerly called the micron μ) and the 'nanometer' (1 nm = 10^{-10} m; formerly called the millimicron $m\mu$). The 'angstrom' (1 A = 10^{-10} m) although not sanctioned by the SI system is widely used in spectroscopy. Another quantity which is often convenient is the 'wavenumber' $\bar{\nu}$, the number of waves per unit distance. The unit most commonly used for the wavenumber is the reciprocal centimeter (cm^{-1}).

The velocity, wavelength and wavenumber, in vacuo, are related to the frequency by the expression

$$\nu = \frac{C}{\lambda} = \bar{\nu} C$$

The energy content E of a photon is directly proportional to the frequency.

$$E = h\nu = \frac{hC}{\lambda} = hc\bar{\nu}$$

where h is Planck's constant.

Spectral Regions

Visible light constitutes only a small part of the spectrum of radiant energy, or electromagnetic spectrum. The principal spectral regions and fields of spectroscopy are given in the following table.

Table

Spectral region	Approximate wavelength range	Typical source	Typical detector	Energy transitions studied in matter
Gamma	1-100pm	Radioactive nuclei	Geiger counter Scintillation counter	Nuclear transitions
X-ray	6pm-100nm	X-ray tube	Geiger counter	Ionisation by inner electron removal

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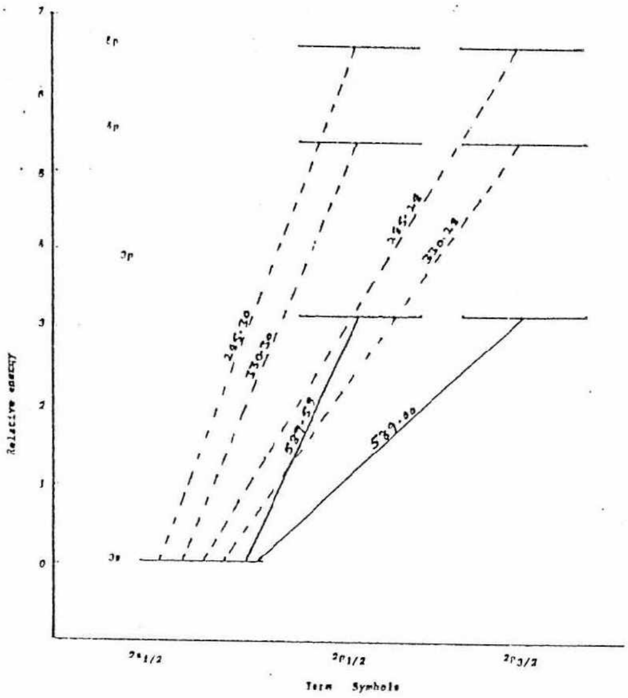
Table (cont'd)

Spectral region	Approximate wavelength range	Typical source	Typical detector	Energy transitions studied in matter
Vacuum ultraviolet	10-200nm	High voltage discharge, high vacuum spark	Photo-multiplier	Ionisation by outter electron removal
Ultraviolet	200-400nm	Hydrogen discharge lamp	Photo-multiplier	Excitation of valence electron
Visible	400-800nm	Tungsten lamp	Phototubes	-do-
Near infrared	0.8-2.5μm	-do-	Photocells	-do-
Infrared	2.5-50μm	Nernst glower globar lamp	Thermocouple bolometer	Molecular vibrations
Far infrared	50-1000μm	Mercury lamp (high pressure)	-do-	Molecular rotations
Microwave	0.1-30cm	Klystrons magnetrons	Si-W crystal bolometer	Molecular rotations; electron spin resonable
Radio-frequency	10^{-1}-10^{3}m	Radio transmitter	Radio receiver	Molecular rotations; nuclear magnetic resonance

Origin of Spectra

An atom consists of a positively charged nucleus surrounded by a number of electrons in rapid motion around the nucleus. The nucleus is made up of positively charged protons and the electrically neutral neutrons. In any atom there will be as many number of electrons as there are protons in the nucleus. For each electron in each atom there is a discrete set of energy levels that the electron can occupy. The spacing of the energy levels is different for each electron in the atom, but for similar atoms corresponding electrons will have identical spacing. As an example let us consider the neutral sodium atom. The figre shows a few of the energy levels of the valence electron of the neutral sodium atom, in accordance with the current theories. Under ordinary conditions essentially all the atoms in a body of sodium vapour are in the ground state, that is, their valence electrons lie in the 3s level. If irradiated with a beam of energy including wavelengths 589.00 and 589.59 nm, the outer electrons of many of the atoms will absorb photons and will be accelerated to 3p levels. (The two very close 3p levels differ only in their spin characteristics). The excited electrons has a strong tendency to return to its ground (3S) state, and in so doing emits a photon. This emitted photon posseses a definite amount of energy, dictated by the spacing of this energy levels. In the present example, this emitted radiation constitutes the familar yellow light of the sodium flame or lamp.

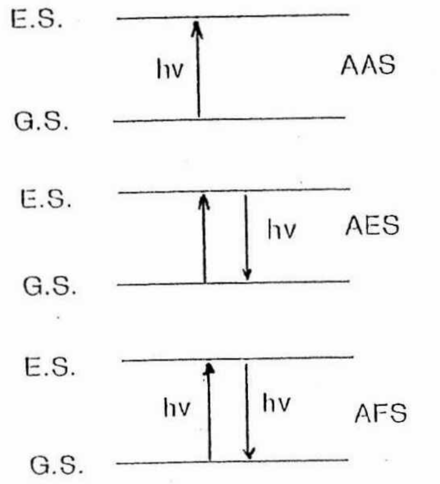


Partial energy level diagram for the valence electron in the sodium atom

If this electron is given more energy, it may be raised to some higher level than 3p, such as 4p or 5p. In such a case it may not drop back to 3s by a single process but may pause at intermediate levels like a ball rolling down steps. This situation can be quite complex. For one thing, not all conceivable transitions are actually possible, some are forbidden by the selection rules of quantum mechanics.

With a highly energetic source of excitation many electrons (not only the outer most) in any element can be excited to varying degrees, and the resulting emitted radiation may contain upto several thousand discrete and reproducible wavelengths, mostly in the UV and visible regions. This is the basis of the analytical method of emission spectroscopy. There are three basic analytical atomic spectrometric techniques, atomic emission spectrometry (**AES**); atomic absorption spectrometry (**AAS**) and atomic fluorescence spectrometry (**AFS**). It is possible to distinguish between these by considering the following figures where two electronic energy levels of a ground state atom are considered. The ground state is labelled 0 and the excited state is labelled 1. In general, the transition from the ground state to one or another of the lowest lying excited state is the one most used for atomic spectrometric measurements.

Comparison of AAS, AES & AFS



Atomic Emission Spectrometry (AES)

The simplest example of atomic emission is the experiment of putting common salt into a flame. A yellow colour is seen in the flame. This occurs because of the following sequence of events. First, the sodium chloride is broken down by heat of the flame into its constituent atoms, sodium and chloride. Considering the sodium only, it then exists in the flame in its neutral ground state form. Second, heat energy from the flame is able to excite the sodium atom from the ground 0 state to an excited state 1. This represents collisional or non-radiative excitation to the excited state. In a flame, this is essentially a thermally generated collisional excitation process whose efficiency depends on the temperature of the flame. The sodium atom in the excited state then spontaneously decays back down to the ground state by two main processes. One is by collisional transfer of energy to other species in the flame gasses. The other process is atomic emission and is the loss of energy by emission of a photon of light. The wavelength of this emitted photon depends upon the energy difference between this excited state and the ground state. The amount of light that is emitted depends on the number of atoms emitting this radiation. Hence, it can be both a qualitative as well as a quantitative analytical technique. Apart from the flame, the other commonly used excitation sources for atomic emission are, high energy arcs or sparks and inductively coupled plasma.

Atomic Absorption Spectrometry (AAS)

In AAS the excitation from the ground state to the upper state is by the absorption of energy in the form of light (radiation). An atom cell, for example, a flame is used to break down compounds, but the energy for excitation is drawn from a light source, usually a hollow cathode lamp. The way the measurement is made is fundamentally different from the AES case. In AAS the detection system looks at the light source directly and sees an intensity of the light source I_0 before any atoms are put into the atom cell. When atoms are put into the atom cell, they absorb some of this radiational energy and are excited from the ground state to the upper state. The detection system see~~m~~s this absorption as a drop in the intensity of the light source from I_0 to I the ratio I/I_0 is called the transmittance and is related to concentration logarithmically. Hence, AAS can be used to measure precisely the concentration of atoms in the flame.

Atomic Fluorescence Spectrometry (AFS)

AFS can be considered a combination of AES and AAS in that the excitation from the ground state to the upper state is carried out radiationally (as in AAS) but the measurement is made by detection of radiation emitted by the atom as it relaxes back from the excited state to the ground state (as in AES). The only difference between AFS and AES is the way in which the atoms are excited in the first place. In AES the atoms are excited only by the collisional energy inherent in the high temperature of the atom cell. In AAS and AFS the atoms are excited primarily by radiation from a light source.