UNIT-1 <u>MPHYCC-10</u>

Chemicals can be analyzed both quantitatively and qualitatively through a number of different analytical methods, but one big area of analysis is by using spectroscopy. Spectroscopy studies are the interaction between electromagnetic radiation and matter, with the interactions giving rise to electronic excitations, molecular vibrations or nuclear spin orientations.

Spectroscopy methods can be categorized depending on the *types of radiation, interaction between the energy and the material, the type of material and the applications the technique is used for*. There are many different types of spectroscopy, but the most common types used for chemical analysis include *atomic spectroscopy, ultraviolet and visible spectroscopy, infrared spectroscopy, Raman spectroscopy and nuclear magnetic resonance.*

Classifications

Spectroscopy can be defined by the type of radiative energy involved. The intensity and frequency of the radiation allow for a measurable spectrum. Electromagnetic radiation is a common radiation type and was the first used in spectroscopic studies. Both infrared (IR) and near IR use electromagnetic radiation, as well as microwave techniques. Both electrons and neutrons are also a source of radiation energy due to their de Broglie wavelength. Mechanical methods can be applied to solids for radiation, and acoustic spectroscopy uses radiated pressure waves.

Another way of classifying spectroscopy is by the nature of the interaction between the energy and the material. These interactions include absorption, emission, resonance spectroscopy, elastic and inelastic scattering. The materials used can also define the spectroscopy type, including atoms, molecules, nuclei and crystals.

Atomic Spectroscopy

Atomic spectroscopy was the first application of spectroscopy developed, and it can be split into *atomic absorption, emission and fluorescence spectroscopy*. Atoms of different elements have distinct spectra so atomic spectroscopy can quantify and

identify a sample's composition. The main types of atomic spectroscopy include atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES) and atomic fluorescence spectroscopy (AFS).

In AAS atoms absorb ultraviolet or visible light for transition to higher levels of energy. AAS quantifies the amount of absorption of ground state atoms in the gaseous state. AAS is commonly used in the detection of metals.

In AES, atoms are excited from the heat of a flame, plasma, arc or spark to emit light. AES used the intensity of light emitted to determine the quantity of an element in a sample. Techniques that use AES include flame emission spectroscopy, inductively coupled plasma atomic emission spectroscopy, and spark or arc atomic emission spectroscopy.

In AFS, it is a beam of light that excites the analytes, causing them to emit light. The fluorescence from a sample is then analyzed using a fluorometer, and it is commonly used to analyze organic compounds.

Ultraviolet and Visible Spectroscopy

Ultraviolet (UV) and visible (Vis) spectroscopy analyses compounds using the electromagnetic radiation spectrum from 10 nm to 700 nm. Many atoms are able to emit or absorb visible light, and it is this absorption or reflectance that gives the apparent color of the chemicals being analyzed.

The absorption of visible and UV radiation is associated with excitation of electrons from a low energy ground state into a high energy excited state, and the energy can be absorbed by both non-bonding n-electrons and π-electrons within a molecular orbital.

Wavelengths of all lights have a particular energy associated with them, and it is only light with the right amount of energy that causes transitions from one level to another for absorption. *For larger gaps between energy levels, more energy is*

required for promotion to the higher energy level, so there will be higher frequency and shorter wavelength absorbed.

UV and visible spectroscopy can be used to measure the concentration of samples using the principles of the Beer-Lambert Law, which states that *absorbance is proportional to the concentration of the substance in solution and the path length.* As well as for measuring the concentration of a sample, UV and visible spectroscopy can be used to identify the presence of the free electrons and double bonds within a molecule. In addition to being an analytical technique that can be used alone, a UV/Vis spectrometer can be used as a detector for high-performance liquid chromatography.

Infrared Spectroscopy

Infrared (IR) analyses compounds using the infrared spectrum, which *can be split into near IR, mid-IR and far IR. Near IR has the greatest energy and can penetrate a sample much deeper than mid or far IR, but due to this, it is also the least sensitive.* Infrared spectroscopy is not as sensitive as UV/Vis spectroscopy due to the energies involved in the vibration of atoms being smaller than the energies of the transitions.

IR uses the principle that molecules vibrate, with bonds stretching and bending, when they absorb infrared radiation. IR spectroscopy works by passing a beam of IR light through a sample, and for an IR detectable transition, the molecules of the sample must undergo dipole moment change during vibration. When the frequency of the IR is the same as the vibrational frequency of the bonds, absorption occurs and a spectrum can be recorded.

Different functional groups absorb heat at different frequencies depending on their structure, and thus a vibrational spectrum can be used to determine the functional groups present in a sample. When interpreting the data obtained by an IR, results can be compared to a frequency table to find out which functional groups are present to help determine the structure.

Raman Spectroscopy

Raman spectroscopy is similar to IR in that it is a vibrational spectroscopy technique, but it uses inelastic scattering. The spectrum of Raman spectroscopy shows a

scattered *Rayleigh line and the Stoke and anti-Stoke lines*, which is different from the irregular absorbance lines of IR.

Raman spectroscopy works by the detection of inelastic scattering, also known as Raman scattering, of monochromatic light from a laser in the visible, near-infrared or ultraviolet range. *For a transition to be Raman active, there must be a change in the polarizability of the molecule during the vibration and the electron cloud must experience a positional change.*

The technique provides a molecular fingerprint of the chemical composition and structures of samples, but Raman scattering gives inherently weak signals. Techniques such as Surface Enhanced Raman Spectroscopy (SERS) have been developed to enhance sensitivity when using Raman spectroscopy.

Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) uses resonance spectroscopy and nuclear spin states for spectroscopic analysis. All nuclei have a nuclear spin, and the spin behavior of the nucleus of every atom depends on its intramolecular environment and the external applied field.

When nuclei of a particular element are in different chemical environments within the same molecule, there will be varied magnetic field strengths experienced due to shielding and de-shielding of electrons close by, causing different resonant frequencies and defines the chemical shift values.

Spin-spin coupling takes into account that the spin states of one nucleus affect the magnetic field that is experienced by neighboring nuclei, via intervening bonds. Spin-spin coupling causes absorption peaks of each group of nuclei to be split into a number of components.

There are multiple types of NMR analyses, which are hydrogen NMR, carbon 13 NMR, DEPT 90 and DEPT 135 NMR. The NMR spectrum of a compound shows the

resonance signals that are emitted by the atomic nuclei present in a sample, and these can be used to identify the structure of a compound.

Molecular Spectra

Molecular energy levels are more complicated than atomic energy levels because molecules can also vibrate and rotate. The energies associated with such motions lie in different ranges and can therefore be studied separately. Electronic transitions are of the order 1 eV, vibrational transitions are of the order 10^{-2} ev and rotational transitions are of the order 10^{-3} ev. For complex molecules, these energy changes are difficult to characterize, so we begin with the simple case of a diatomic molecule.

## The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is one of the basic concepts underlying the description of the quantum states of molecules. This approximation makes it possible to separate the motion of the nuclei and the motion of the electrons. This is not a new idea for us. *We already made use of this approximation in the particle-in-a-box model*. Then we discussed the translational, rotational and vibrational motion of the nuclei without including the motion of the electrons. Here, we will examine more closely the significance and consequences of this important approximation. Note, in this discussion nuclear refers to the atomic nuclei as parts of molecules not to the internal structure of the nucleus.

The Born-Oppenheimer approximation neglects the motion of the atomic nuclei when describing the electrons in a molecule. The physical basis for the Born-Oppenheimer approximation is the fact that *the mass of an atomic nucleus in a molecule is much larger than the mass of an electron (more than 1000 times).* Because of this difference, the nuclei move much more slowly than the electrons. In addition, due to their opposite charges, there is a mutual attractive force of Ze^2/r^2 acting on an atomic nucleus and an electron. This force causes both particles to be accelerated. Since the magnitude of the acceleration is inversely proportional to the mass, a = F/m, the acceleration of the electrons is large and the acceleration of the atomic nuclei is small; the difference is a factor of more than 2000. Consequently, the electrons are moving and responding to forces very quickly, and the nuclei are

not. You can imagine running a 100-yard dash against someone whose acceleration is a 2000 times greater than yours. That person could literally run circles around you.

Example: *Coupled Oscillators with Dissimilar Masses* (Just to understand)

If two particles interact in some way, and one is much heavier than the other, the light particle will move essentially as a "slave" of the heavy particle. That is, it will simply follow the heavy particle wherever it goes, *and*, it will move rapidly in response to the heavy particle motion. As an illustration of this phenomenon, consider the simple mechanical system pictured below:
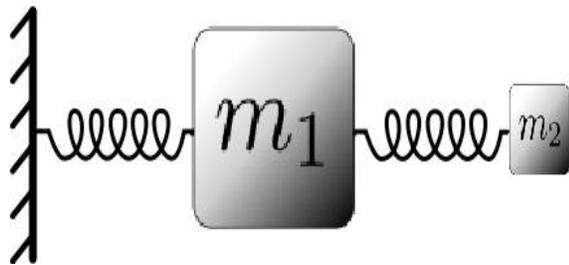
Considering this as a classical system, we expect that the motion will be dominated by the large heavy particle (m1), which is attached to a fixed wall by a spring. The small, light particle (m2), which is attached to the heavy particle by a spring will simply follow the heavy particle and execute rapid oscillations around it.

So a good approximation is to describe the electronic states of a molecule by thinking that the nuclei are not moving, i.e. that they are stationary. The nuclei, however, can be stationary at different positions so the electronic wave function can depend on the positions of the nuclei even though their motion is neglected.