CHAPTER 2.0

EXPERIMENTAL APPROACH

(2.1) Introduction

Electron-impact ionization is basic collision process and is used significantly in areas such as plasma physics and radiobiology etc. Electron-electron coincidence \([e, \ 2e]\) experiments gives complete information about the collision process and electron impact ionization is studied frequently using this technique. For molecular targets, a lot of data is available from electron momentum spectroscopy studies. EMS uses the electron-electron coincidence technique to probe the electronic structure of the target.

(2.2) Mass Spectrometry (MS)

It is a method to calculate mass and charge ratio of particles. MS is used to calculate chemical structure of molecules and composition of molecules. The procedure of MS is as follows-

1. A target molecule is put into the MS instrument.
2. The molecule is fragmented by interaction of molecule with electron beam then different ions can be produced.
3. The produced ions are separated in analyzer.
4. The produced ions are detected by quantitative technique.
5. The ion signal is converted into mass spectra.

MS contains three parts:

- **Ion source-** It is used to convert sample molecules into ions.
- **Mass analyzer-** The produced ions are arranged according to masses by applying electromagnetic energy.
- **Detector-** It is used to determine the produced ions and provided data for measurements.

This technique is used qualitatively and quantitatively. MS is to study the characteristics of compounds.

In mass spectroscopy the role of electron impact ionization is to convert the sample before mass analysis into ion and fragmented form. The source in electron impact have a heated filament which as a function to generate electrons and are accelerated by the ion trap. The accelerating potential has a function to control the energy of the incident electrons. On
providing sufficient energy to this sample compound it will give fragmented ions. It has been found that on supplying of higher energy range of electrons, chances of getting molecular ions are very few in contrast with fragmented ions. However we can get the molecular ions even at low energy range. After the ions are formed, they are forced to move in the accelerating section, where we can take mass analysis. It will be useful to view ion trajectories in two or more dimensions with at least one being time.

![Mass Spectrometer diagram](image)

**Figure 2.1: View of mass spectrometer**

(2.3) **Time of flight**

This method is used to determine the time when object, particle and electromagnetic wave can travel in a medium.

It is used to measure velocity and path length of medium. The moving particle can be observed directly or indirectly.

- It is used for determination of low-conductive thin films.
- In TOF-MS, the ions are moved have same kinetic energy.
- The TOF method in infrared spectroscopy is used to determine optical path length.
- TOF is used in ultrasonic flow meter to determine the speed of signal propagation in media.
- The TOF method in optical interferometer is used to measure the path length difference between sample and reference arms.
- TOF in kinematics is used for the determination of time in which a projectile is travel in air.

(2.4) Time-of-flight mass spectrometry (TOFMS)

The technique in which electric field is applied then ions are moved. The acceleration of moving electrons shows that the produced ions have same energy and mass. The time of produced ions can be detected in detector and this time depends in mass and charge ratio.

![Linear TOF Mass Spectrometer](image)

Figure 2.2: View of Linear TOF mass spectrometer

(2.5) Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS)

In this method, ion beam is used for removal of molecules from the surface of sample. TOF-SIMS uses a focused and pulsed beam to remove chemical species on material surface.
The produced particles are close to dissociated ions that are positive and negative. The moving particles can be detected in a detector.

When low ion current is produced, TOF-SIMS is known as static SIMS but the ion current is high, TOF-SIMS is known as dynamic SIMS.

It is used to study the characteristics of materials and semiconductors [83-84].
to effusive secondary beam source. Formation of ions takes place in the collision zone
after that they are extracted, focused, and by a quadrupole filter their mass analysis
done and then detected by a channel electron multiplier. Figure 2.4 shows the equipment
schematically. It has three vacuum chambers:

The first is for the rare gas beam source.

The rare gas beam is formed by a standard effusive source coupled with an electron
bombardment device. The electron bombardment source consists of a spiral-shaped
tungsten filament, supplied with 10 V and 6 A, located just after the skimmer and
parallel to the beam direction for a length of about 1 cm. The electrons emitted by the
filament are accelerated through the beam by a plate, with a positive potential, placed
below the filament.

The plate potential is chosen to maximize the beam intensity. Possible ions and high
Rydberg state atoms, which are also formed by the electron bombardment exciter, are
detached by a quenching electrostatic field. By heating the 1 mm diameter orifice of the
source, it is likely to change the argon beam velocity distribution.

This allows the measurement of cross sections in a large kinetic energy range: by using
source temperatures of 300 and 900K, it is likely to cover up a collision energy range
from 0.04 to 0.3eV. The collision velocity selection was accomplished by the use of a
time of flight (TOF) device.

The secondary beam of randomly oriented sample say, CH$_3$Cl molecules at room temperature
is prepared by effusion from a glass micro capillary array.

After the scattering center the metastable atom beam is detected and placed beside the beam
direction. The secondary beam intensity is examined by the detector.
Figure 2.4: Experimental Set up for the collision between target molecules and metastable rare gas atoms.

By use of TOF technique, which is mentioned above, velocity of the metastable atom can be analyzed. The function of multi scaler is to count the metastable atoms.

The average velocity resolution of metastable atoms by TOF analysis is around 5%. In other words, the overall energy resolution of the cross section energy dependence is defined essentially by the thermal spread of the target molecules from the source.

At the collision zone time, the time spectra of the product ion intensity are recorded. After that for a given delay time then relative cross sections and collision velocity are obtained. Through the mass filter the time spectra of product ions are corrected by the ion
flight time. Metastable atoms are produced in the electron bombardment exciter, where many photons are also formed which can photo-ionize the target molecules.

On the other hand, the division of photo-ions and Penning-ions is easy by the TOF technique, the previous being detected at practically zero delay time. The photo-ion peak in the TOF spectrum is used to calibrate the ion flight time through the quadrupole filter.

**(2.7) Transverse-Field Method**

The first successful ionization measurement was made by Keene (1949). To determine the charge transfer and for ionization measurement Goldman used this technique to measure proton-impact [85].

**(2.7.1) Basic Set up of Apparatus**

The equipment is shown in Figure (2.5). To suppress secondary electrons from collimator C, pursued by a collimator suppressor CS, the ion beam enters the system. After this it will enter into cell GC and in Faraday cup FC.

By the use of magnetic field and electric field within the cup the suppression of electron can be accomplished and this can be done in few cases.

EP is the electron collecting plate and IP is the ion collecting plate, we will apply positive potential to the EP and a negative potential to IP. The function of GP, which is a guard plates to maintain the field constant over the measurement area.

When the ions hit a grid G, which is placed between the beam and the ion collecting plate the purpose of this is just to contain secondary electrons produced at the plate.
Figure 2.5: Equipment of transverse-field method to determine ionization cross-sections.

Above representation shows:-

The beam collimator is represented by C
The collimator suppressor is represented by CS
The gas cell is represented by GC

IP, EP, and GP represent the ion collection plate, the electron collection plate and the guard plates, respectively.

Secondary electron suppressor grid is represented by G, FCS is represented as the Faraday cup suppressor and FC is represented as the Faraday cup. To get the cross sections $\sigma_+$ and $\sigma_-$ the currents $I_+$ and $I_-$ are calculated.

If $l_0$ is the length of the electron and ion collecting plates having target gas density $n$,

with the incident beam current $I_B$, further we assume that $n$ is very small that can make single collision, for production of positive ion current $I_+$ and for negative with the
electron current $I$, beam is responsible for their production. In that case

$$\sigma_\pm = \frac{I_\pm}{nll_B}$$

(1)

The concept of experiment is quite simple concept wise but in real practice if the measurements of cross sections are done perfectly, a lot of safety measures and corrections are required. We will discuss them in the subsequent sections.

(2.7.2) **Groundwork and Gathering of the Proton Beam**

In general proton beam is analyzed magnetically due to the fact that it contains only protons. Electron capture at about 250 keV is enough to cause neutralization of large part of beam. If high vacuum is not maintained then electron capture becomes prominent all along beam path. Beam neutralization also occurs in gas cell and along beam path resulting in two paths –

First, before it reaches the cup. Second, before getting the measuring area if a proton is neutralized, here ionization will take place which will cause different cross section.

If fairly accurate values are available for $\sigma_c$, the capture cross section, and for $\sigma_+^0$ and $\sigma_-^0$, by neutral atom impact we can make correction in the measured ionization cross section, these are responsible for the production of electrons and positive ions.

The cross sections for modified equations are

$$\sigma_\pm = \frac{I_\pm}{nll_B}\exp(-nl_1\sigma_c) - \sigma_+^0\left[\exp(nl_1\sigma_c) - 1\right]$$

(2)

Where the effective path length of target gas is represented by $l_1$, the effective path length of Faraday cup from the area to be determined is represented by $l_2$ and the beam current is represented by $I_B$.

Characteristically, at an energy range of 1-35 keV, the corrections for beam neutralization are found to be major. However, correction has been made; 15% neutralization has been
observed when a 5 keV beam travels 10 cm all the way through nitrogen at $3 \times 10^{-4}$ Torr.

A collimation is used for collecting the entire beam passing through target gas. Secondary electrons are eliminated by having a suppressor. Secondary electrons are produced when beam strikes aperture edges. To stay away from secondary electron apply either a negative bias on suppressor or a positive bias on aperture. The faraday cup is shielded to avoid field penetration into collision area.

As the beam passes all the way through the transverse field and guard plates, the beam gets deflected. This results in problem of incomplete collection by Faraday cup.

(2.7.3) **Determination of Target Gas Density**

Ideal gas law is applied to measure pressure and temperature for stationary gas targets. In earlier days for the measurement of pressure McLeod gauge was used. Pirani gauges calibrated against McLeod gauge were also used for the purpose.

Vapors of mercury after condensing due to trap action flow away from gauge. The resulting measured value of pressure is different from actual pressure due to pumping effect. As measured value of pressure is smaller, the measured cross section comes out to be larger. Streaming effect of mercury proved that there was error in pressure readings. In 1966, Schram et al (1966) showed that the error depend on diameter of tubing, mercury temperature of gauge [86]. The error becomes prominent for heavier gases. Thus the mercury reservoir in gauge is cooled as a remedial action to reduce streaming, mercury rate and vapor pressure. To reduce the flow rate of mercury vapors the diameter of tube has given a size of capillary.

At moment of measurement, when mercury rises to stop point at that point of time the gas cell is closed. The variation in pressure between two sides controls/varies the position of membrane. The membrane forms two capacitors in bridge network and the amplified output is recorded. Pressure can be calculated directly from measured quantities as the gauge is not absolute. To achieve greater accuracy, compare the gauge with McLeod gauge. The reference pressure has to be insignificant compared to pressure under measurement, as the capacitance manometer is a differential gauge.

In order to have better results, high temperature is kept at head of capacitance manometer.
Thermal transpiration causes variation in gas cell pressure and gauge pressure [87]. The equation \(P_1/P_2 = (T_1/T_2)^{1/2}\) can be used for corrections when aperture separates regions at different temperatures and helps in overcorrecting when tubing connects two regions.

If we use regulator valves, gas lines, leak valves as safety measures which will prevent the formation of oil grease, rubber or other vapors. Static gas conditions can be understood better for experimental arrangements having large volume of gas cell with small entrance.

(2.7.4) The Path Length

The length of collecting plates in transverse field is the path length \(l\) in the direction of beam. Guard plates serve the purpose of avoiding edge effects and will provide uniform field. Few ions or electrons having component of velocity in forward direction go after trajectories and will not be collected. In the forward direction if ions and electrons which are collected have a velocity component, near to forward edge these will go after the edge of the plate and finally we will not collect them. Before the collecting plate region in reimbursement, along the beam path the ions or electron formed, they will appear at the collector. A longitudinal electric field adjacent to beam exists if a biased suppressor is used.

(2.7.5) Ion Collection and Electron

Ejection of extremely slow recoil ions is due to immense collisions with the atoms. Using the screened Coulomb potential the energy allocation of these ions is explained by calculation. Consider \(m_A\) is the mass of target atom with nuclear charge \(Z\), recoil energy \(E_r\), by proton impact to the target is

\[
\left(\sigma/dE_r\right)_{\text{recoil}} = 4\pi a_0^2 R^2 Z^2 T^{-1} \times \left[ E_r + R \left(1 + Z^{2/3}\right) m_e / m_A\right]^{-2} m_e / m_A
\]

We have to multiply the energy \(E_r(d\sigma/dE_r)_{\text{recoil}}\) by ionization efficiency for finding cross section. Here we have ignored the momentum, so that the recoil energy value \(E_r\) shows maximum value of the recoil energy.

Recoil energy \(E_r\) is expressed in Equation (3).

In this equation we see that from monoatomic targets collision no complexity is involved.
However, the ejected fragments may have energies up to 20 eV for molecular target.

Here, all the ions can be collected by applying a potential difference of moderate value. The electrons may have twice the velocity of projective or even higher [88]. At higher energy a better approximation is provided by Rudd model.

Ejection energy is given by

\[
E = (IT)^{1/2} \ln \left( \frac{1}{f} \right)
\]  \hspace{1cm} (4)

Here \(T = E_p / 1836\), \(f\) is the fraction of ejected electron and \(I\) is the binding energy of the target atom.

The ejection of electrons take place in the collision process that occurs at low energy range, at intermediate energy range it occurs strongly and move in forward direction and then becomes peaked at higher energy range.

In general saturation is observed when we off the current levels. A plot of Electron current Vs. collection voltage is the common test for this. We do not have any method that will provide us the knowledge about how much fraction of electron are collected. However, the curves attain zero slopes for electron collection. By the use of available information regarding ejected electrons we can determine the electrode biases needed for nearly complete collection. Moreover, proton energy is responsible for the energy of electrons, is the impact energy changes the biases should be adjusted accordingly. The beam will be deflected when the collecting field is large.

It becomes necessary to make correction in ion current value which is calculated for transparency of grid when grid is at positive ion plate and used for electron suppression. Usually ion transmission and geometrical transmission is considered to be equal but it is an approximation as the ion trajectories are deflected by grid potentials and plate [89]. Rudd showed that the genuine transmission \(t\) and geometrical transmission \(t_0\) are related as
\[ t = \left[ 1 + \left( t_0^{-1} - 1 \right) \left( V/gV_i \right)^n \right]^{-1} \]  

(5)

Where \( V_i \) = Potential of the ion plate.

\[ V_g \] = Potential of the grid

\[ b \] = Ratio of the distance between beam to plate and distance between beam to grid.

The above equation holds well only when the energy of initial ion is lower in comparison to grid or plate energy. Experimental data holds well when \( n=1/2 \), for \( t_0 = 90\% \), to be used in place of which would give an error of 5-9%.

**2.7.6 Spurious Currents and the Grid**

Spurious currents must be avoided, such current are caused due to followings reasons:-

*a. Secondary electrons striking the grid*

While passing through grid, a small portion of electron hit it and produces secondary electron; these secondary’s must be taken in to consideration from collision in while determining electron current.

At higher range of energy, this correction may be neglected but at low energies, more positive ions are formed than electron due to electron capture affected by protons. The electron formed may fall to plate because for negative charges grid has highest potential energy. Majority of ions hit the grid from that end which is away from ion collecting plates. As a result, many secondary electrons go to collecting plate giving rise to spurious currents [90].

It was observed by (Ghosh & Sheridan, 1957) that secondary emission coefficient have dependency on mass of ion and their energy besides composition. Further it has been found that for specific surfaces we can find the secondary emission coefficient.
b. Generation of Photoelectrons

Photoelectron is generated on most of the metal surfaces by ultraviolet photons with energy from 10-40 eV. The production of photoelectron takes place when the beam of proton is responsible for excitation in any of the surfaces, solid or gas [91].

It has been observed by Rudd et al (1983) that this will not cause any error reason being low photons cause low cross section.

c. Secondary electrons from surfaces

Scattering of protons take place from edge of collimator aperture and from collision with target gas. These secondary protons emit secondary electron after hitting surfaces of metal. This may be beam suppressor or grid.

Scattering from collimator edges can be minimized by making them razor-sharp. Other method is to have a shield near the collimator so as to pass the main beam and prevent the scattered particles. Such scattering is prominent at low energies of protons and for heavy targets.

d. Reflection of ions

Additional ionization is caused if the bottom of Faraday cup is knocked by protons, after this they are reflected back and enter into the target gas [92]. It has been observed by (Thomas, 1985) that at an energy range about 5 keV the reflection coefficient had the value more than 10% for protons.

This can cause a serious problem. Another kind of ionization results when Faraday cup emits radiation by the beam of ions in bombardment process.

(2.7.7) The Transverse-Field Method and Variations

Since, according to (Gilbody & Lee, 1963), to deal with the spurious electrons is a hard task [93]. Variation of transverse field method electron current are measured by one plate ion current and for both plates, which correspond to total current. Thus the $\sigma_+$, which is cross section, is calculated from $\sigma_+$ and $\sigma_c$. The above approach increases ambiguity as two quantities are involved. At low energies, if $\sigma_c$ is less significant hence contributes to more
errors.

It has been observed by (Fite et al, 1960, Gilbody & Ireland, 1964) that cross beam method has been used by researchers at preferred target is not stable [94-95]. We define path length of beam by the size of target beam only. The production of secondary electron and end effects do not cause any hurdle. As the beam may be non-uniform, profile of beam determines the overlap integral of their densities.

On changing the direction of beam during overlap integral, an error is observed. Beam neutralization problems are avoided as target densities are small. Normalization of cross section is needed as complete target densities cannot be determined easily.

Information about products of ionization can be observed in transverse field apparatus by knowing the mass-to-charge ratio. During proton ionization which was first noticed by (Keene, 1949) that by collision the dissociation of H₂ takes place. Wexler (1964) found the variety of ions by the collision process [96]. This method is used to find the values of cross sections for producing charge states. By the use of collision one can find ionization cross sections, single ionization, double ionization, triple ionization, capture with dissociation and with ionization of H⁺ + H₂.

Finding a transverse field is very tough especially at low impact energies, which can collect all ions and electrons. The field should be such that the beam is not deflected outside the detection region. Ions and electrons are produced by the beam passing in a field-free region. By turning off the beam and making collecting field so that it can push the ions and the values of m/z can be recorded.

### (2.8) One Photon Ionization Model

In this model a photon can be interacted with target molecule for production of ions, if the energy of photon is greater than ionization potential of molecule. Plasmas in fusion energy devices consist of central hot plasmas with the colder regions near the edge. The temperatures are much lower in the edge region than in the core and there is a relatively high population of neutral species. Neutral and charged molecular species can form in this region and influence of plasma diagnostics.

A variety of molecules including hydrocarbon species are formed in the edge region and hydrocarbon species can be produced to C₃H₈. As plasma interacts with the surface of the
containment vessel, the erosion of the surface will take place. Therefore, there is the potential for a series of chemical reactions that occur near the surface.

A wide variety of interaction processes take place involvement of these molecules in the edge region. Is not well understood how these processes affect the efficiency of the diverter itself. Therefore there is a need for collecting spectroscopic data and collision to better understand the extent to which these processes are important in the edge regions, including data derived from infrared spectroscopy [97-101].

Carbon-based materials are used in current tokomaks evident advantages due to its low capacity as radioactive and high heat resistance. Dissociative ionization is used in fusion reactors and mass spectrometry

\[
XY + e \rightarrow X^+ + Y + KER
\]

The fragment ion \((X^+)\) and the neutral fragment \((Y)\) produced through dissociative ionization. Distribution of kinetic energy release (KERD) calculate energy transfer path in the plasmas i.e. for modeling such environments not only the relative abundance ion fragments. The general considerations, it is clear that a minimal model should be able to account for the memory and the threshold behavior of real photon detectors.

**2.8.1 Experimental setup**

When a partial hit of a photon on an electron in the detector may not cause ionization but sets the electron up to ionize the atom on a second hit from a photon coming later from the other slit.

Counting these hits over time that would never ionize an atom at this location through one slit accounts for the interference pattern with two slits. The key in the detector is partial hits. All experiments are used double-focusing mass spectrometer that has been amended several times.

A detailed description can be found in previous publications. Under neutral gas molecules introduced through a gas inlet system capillary leak in the collision chamber of the ion source. Ions are produced on one type of ion source Nier electron impact (electron currents typical 10 µA) which is maintained at a temperature of about 200 °C.
The kinetic energy of the electrons may vary from about 0 to 1000 eV, which is set by a computer. The dispersion of the electron energy distribution is about 0.5 eV. The ions enter the analyzer section of the mass spectrometer through the entrance slit are moved by a potential drop of 3 kV. A current flows and electron transit time reveals atom or molecule ionization time is about 0.1 psec. Therefore, the probability of ionization is high. Thus, the integration of the equations of motion of the electrons in the plasma component time step requires approximately $10^{-12} - 10^{-11}$ s.

![Figure 2.6: Experimental setup of one photon ionization model](image)

Larmor rotation does not calculate the rate of ion production in ECR plasma [103-109]

(2.8.2) **The amounts of macro particles and cells for adequate description of plasma**

The amount of macro-particles in ion charge state on an elementary cell equals 10-15. To obtain the number of macro particles should be in the order of $(2-3) \times 10^5$ for the description of suitable plasma in consideration of two dimensions (2D).
Each particle finite has 6 coordinates in the 6D-phase space. This means having the spatial coordinates (x, y, z coordinates) and coordinates pulse velocity. The equations of motion can be obtained by numerical methods; more economical with respect to computer resources is a leap frog method of the second order.

Electron impact ionization is basically a collision process that occurs in artificial plasmas data and ionization cross section is necessary to understand precise quantitatively these environments [110-116].

This method is simple and lead to reliable data. An alternative technique that incorporates a white neutral beam fast charge transfer obtained was used by Peterson and McDowell.

This approach is used to study that chemically unstable neutral for is less attractive to study stable species due to need to calculate the beam overlap function [117-121].

(2.9) **Energy-Loss Method**

After collision, we get secondary products, instead of these, beam itself is analyzed in “energy loss method” after being passed through target gas.

If particles of beam are losing their energies by a process then the cross sections for them can be calculated [122]. For production of ions energy-loss spectroscopy can be used, but this cannot be used for proton impact cross sections. Those processes which involve metastable states, energy-loss method is quite appropriate for them. Even we can find the cross sections by use of this method.

This made easier the analysis of those beams which involved energies up to 200 keV. In source emits ions and they are accelerated to pass through target. The equipment used by Park and his co-workers is shown in Figure (2.11).

The undesired charge states are then removed by using a magnetic analyzer. Before entering electrostatic analyzer, deceleration takes place. The energy loss spectrum is thus obtained by keeping analyzer potential constant. As decelerating system is referenced to accelerator, fluctuation of any kind has little effect on results. Sweeps can be prepared with or without gas targets.

To calculate total cross sections this technique can be used because during atomic collisions, the immense number of ions get deflected even at very small angles. Errors occur when
scattered beam fails to be collected in to angular acceptance of analyzer. Due to high angular
deflection of beam particles, only small portion of total beam is lost. Error can be avoided
(Park, 1983) by integrated over angular dependence of cross section [123].

In figure 2.7, the ion source is IS, the acceleration column is AC, collision chamber with
target gas is CC, deflecting magnet is M, decelerating column is DC, energy analyzer is EA,
electron multiplier detector is EM, high voltage is HV and an offset voltage is $\Delta V$.

Protons making Ions by collisions have almost equal chances of neutralization in comparison
to those which do not make collision. So, ratio is not affected from which cross section is
measured.

The technique has no influence if the particles of beam loss their energies. Similarly if a beam
gets neutralization does not make any change in the results. However this method provides
the cross section which does not explain same set of specific processes as other two
techniques.

For instance, no process is involved which occupy a change in charge states. Also no
information about the ejected electrons can be got owing to diverse decay schemes. Such
disagreement occurs at energy below 100 keV as electron capture is much prominent at these
energies.
Figure 2.7: Representation of the equipment for making energy-loss measurements.