CHAPTER 3

MOLECULAR ELECTRON IONIZATION CROSS-SECTION
Molecular electron ionization cross-sections are of importance for evaluation of radiation chemical data, for mass spectroscopic studies; ion-molecule reactions and thermodynamic measurements and in plasma and Space Physics. Various models relating to polarizability and diamagnetic susceptibilities were offered. This chapter gives a brief account of literature, the relationships of cross-sections with polarizabilities and diamagnetic susceptibilities and the need to probe deeper in this direction. The relationships between Q and $\lambda_{\text{max}}$ on one hand and Q and $R_f$ on the other developed recently have also been discussed in brief and the utility of $\lambda_{\text{max}}$ and $R_f$ is outlined.
3.1 Molecular Electron Ionization Cross-Section

The 'ionization cross-section' does generally refer to the surface area of atom or molecule (assuming it to be spherical) which is susceptible for reactions and the electrons attached to an atom or molecule are in a field different from that when they are isolated. Electron ionization cross-sections for atoms and molecules are of importance for evaluation of radiation chemical data, for spectroscopic studies of ion-molecule reactions, for thermodynamic measurements and in plasma and Space Physics. There has been considerable work on both experimental and theoretical aspects of electron ionization cross-sections.\textsuperscript{1-7}

Total cross-sections\textsuperscript{8} of molecules for ionization by electrons form the basic calibration data for a variety of analytical instruments such as ionization manometers\textsuperscript{9}, ionization chambers\textsuperscript{10} and mass spectrometers\textsuperscript{11}. Further more, these quantities have the same basic significance for the initiation of reactions by ionization as do absorption coefficient for photochemical reaction initiation.

Although little attention has been paid to the manner in which the ionization cross-sections of individual substances vary with the energy of the ionizing reaction\textsuperscript{8}, relatively little is to be found in the literature concerning the variation of these cross-sections from substance to substance for a specific ionizing agent. The most detailed discussion of this aspect is that given by Dushman\textsuperscript{9} for the variation of the sensitivity of ionization manometers, with the substance whose pressure is to be measured. Dushman's discussion is purely empirical and the conclusion reached is that the best representation of the variation of ionization cross-sections is
obtained by taking the cross-section to be linearly related to the total number of atomic and molecular electrons.

The nature of Dushman's discussion of his correlation suggests that a theoretical result due to Bethe\textsuperscript{12} was advertently overlooked. This result of Bethe is that ionization cross-section ($Q_{ni}$) is approximately proportional to the mean square radius of the electron shell ($n, l$)\textsuperscript{13}. The ionization cross-sections of the outer electrons are proportional to their $r_{n1}^2$ those of inner electrons are proportional to $r_{n2}^2$ less a term in $Z_{\text{eff}}$ i.e. $(r_{n2}^2 - K \cdot Z_{\text{eff}}^6)$. These facts combined with the empirical observation that the energy lost by ionizing electrons is on the average 30 to 40 eV per ion pair, suggests that to calculate the ionization cross-section for an atom, one should sum the ionization potentials of all electrons (of energies less than 35 eV) and weight by $r_{n1}^2$.

Franklin\textsuperscript{4} critically studied and discussed various important aspects and applications of molecular electron ionization cross-sections. From the experimental measurement of molecular electron ionization cross-sections of various organic compounds, it is observed that the cross-sections increase rapidly with energy from threshold, reach a flat maximum between 50-80 eV and decrease slowly at higher energies. At high electron kinetic energy (71 K eV), there is good agreement between the experimental energy dependence of the cross-section and simple theory based on the Born approximation\textsuperscript{1}. However, the experimental dependence at cross-section on molecular structure is not satisfactorily predicted by theory. At lower electron energies which are relevant to mass spectroscopic
and radiation chemical studies (70 eV) the theory is even more approximate, and neither theory nor experiment show good in themselves or with each other. It is most desirable to find a correlation between cross-sections in the approximate energy dependent range near 70 eV and some ground-state molecular property.

One of the most fundamental measurements in the field of electronic and atomic impact phenomena is the absolute total cross-section for ionization of a gas by electron impact\(^2\). A new method was devised by Rapp and Englander-Golden\(^2\) to obtain absolute cross-sections of gases relative to hydrogen and they measured total ionization cross-sections of gases from threshold to 1000 eV in a total ionization tube. These cross-sections play a pivotal role in normalisation of modulated beam experiments and are also of importance in application to plasma physics, vacuum technology and the ionosphere.

According to Otvos and Stevenson\(^\text{3}\) ion-molecular reaction cross-section depends upon the polarizability of neutral molecules, and atomic ionization cross-sections (in the energy dependent range) could be calculated from average square radius of electrons. The total ionization cross-sections (sum of ion-molecular reaction cross-section and atomic electron ionization cross-sections) will give the molecular electron ionization cross-sections (Q). The above assumption was shown to be incorrect by Franklin, Field and Lamp.\(^4\) Franklin \textit{et al.}\(^4\) also proposed that the cross-sections might be proportional to polarizability as well as diamagnetic susceptibility. In 1961, Stevenson and Schissler\(^5\) reassessed the situation and they concluded as follows.
1. The additivity postulate does not hold good in general but holds within a given molecular class of compounds.

2. Simple classical theory indicates that cross-sections should be proportional to 0.5 power of the polarizability ($\alpha_{M}$) rather than 1.0 power as suggested by Lampe et al.

3. A general correlation may exist between electron ionization cross-section and diamagnetic susceptibility.

Beran and Kevan measured the molecular electron ionization cross-sections (Q) of hydrocarbons, fluoro compounds, halogen substituted hydrocarbons and fluorocarbons at 70 eV while Harrison measured 'Q' of hydrocarbons, ethers, ketones, aldehydes, esters and alkyl benzenes. Analysis of all results shows clearly that none of these proposed correlations is generally valid. They are however, valid within a given class of compounds.

It is quite unfortunate to see that with the limited literature available, no rigorous theory exists even today to explain the experimental dependence of cross-sections on molecular structure. Lacking rigorous predictive theory, one has to go through semi-empirical correlations to explain the observed facts. Beran and Kevan suggested the following three correlations to evaluate theoretically the molecular electron ionization cross-sections at 70 eV, from their extensive experimental work on fluoro and perfluoro organic molecules of several classes.

The above proposed correlations can be summarized as

1. Additivity of atomic cross-sections.
2. Linearity with polarizability.

3. Linearity with diamagnetic susceptibility.

From the figures obtained by Beran and Kevan\textsuperscript{7} it is clear that electron ionization cross-sections do not form a single correlation with polarizability, diamagnetic susceptibility or additivity of atomic cross-sections. However, linear correlations within a molecular class are found for each of the three molecular properties.

3.1.1 Linearity with Polarizability

Utilizing the concepts obtained from the figures Bervan and Kevan\textsuperscript{7} developed a semi-empirical equation (3.1), which gives total ionization cross-section at 70 eV as a function of molecular polarizability, $\alpha_M$, calculated by the $\delta$-function method with bond polarity corrections\textsuperscript{14,15}. The equation is designated as

\[
Q_{\text{exptl}} = \frac{1}{5.6 \times 10^{-9} \text{ cm}} \cdot \alpha_M + 4.2 \cdot (n_c - 2) \text{ ethers} + 4.3 \cdot n_c \text{ ketones} + 4.0 \cdot (n_c + 1) \text{ aldehydes} + 4.5 \cdot n_c \text{ esters} + 4.2 \cdot (n_c + 2) \text{ alkyl benzenes} \]

\[
0.91 \alpha_M \text{ (alkanes)} \quad 0.925 \text{ (mono fluoro compounds)} \\
0.91 \alpha_M \text{ (alkenes)} \quad 1.1 \text{ (monochloro compounds)} \\
\alpha_M + 4.2 - 4.0 \cdot (n_c - 2) \text{ ethers} \quad 1.1 \text{ (monobromo compounds)} \\
\alpha_M - 4.3 \cdot n_c \text{ ketones} \quad 1.1 \text{ (monoiodo compounds)} \\
\alpha_M - 4.0 \cdot (n_c + 1) \text{ aldehydes} \quad \ldots \quad \text{(3.1)}
\]

Here $n (> 1)$ denotes the number of atoms and if $n = 0$, $n^R$ will be considered as equivalent to one (i.e. $n^R = 1$). $\alpha_M$ is the $\delta$-function molecular-
polarizability\textsuperscript{15} with bond polarity corrections and is in units of \(10^{-24}\) cm\(^3\). This relation confirms the Lampe \textit{et al.}'s suggestion but is somewhat contradictory to Stevenson \textit{et al.}\textsuperscript{5} predictions.

3.1.2 Linearity with Susceptibility

The dependence of molecular electron ionization cross-section on fraction of susceptibility is shown by the relation which can be given as

\[
Q = 0.278 \chi_M (\text{cgs emu/mol}) \quad \ldots \quad (3.2)
\]

It forms a single correlation for all mono fluoro compounds, and agrees well with the Franklin\textsuperscript{4} and Stevenson\textsuperscript{5} suggestions.

3.1.3 Additivity of atomic cross-sections

Considering the conclusions of Stevenson and Schissler\textsuperscript{5}, Bervan and Kevan\textsuperscript{14} have formulated the following correlations.

\[
Q_{\text{expH}} = 1.34 \times \left( 2.21 n_c + 0.3 n_H + 0.16 n_F + 3.3 n_n (\text{chlorohydrocarbons}) + 2.9 n_n (\text{chloro halo hydro carbons}) + 4.33 n_{\text{Br}} + 0.7 (\text{alkynes}) + 5.3 n_l + 1.68 n_0 - 4.0 n_{\text{ce}} (\text{alkenes}) \times 10^{-16} \text{cm}^2 \right) \times \left( \text{no. of cc bonds} \right) \]

\[
= 1.34 \times 10^{-16} \text{cm}^2 \quad \ldots \quad (3.3)
\]
Here \( n_x \) is the number of \( x \) atoms and \( n_{C-C} \) refers to the number C-C bonds. This equation predicts experimental values with an average deviation of 4.5%. This correlation is the easiest of the three and has added feature that no other property of the molecule needs to be known except its molecular formula.

Beran and Kevan\(^7\) felt that the correlation with polarizability was the best among the three. These three are equally valid for a given class of compounds, with certain marginal errors.

### 3.2 ELECTRON IONIZATION CROSS-SECTION FROM DIAMAGNETIC SUSCEPTIBILITY.

Beran and Kevan\(^7\) suggested three correlations (3.1), (3.2) and (3.3) to evaluate theoretically the molecular electron ionization cross-sections. One of them (3.2) shows the dependence of molecular electron ionization cross-section as fraction susceptibility which reads as

\[
Q = 0.278 \chi_M
\]

It forms a single correlation for all monofluoro compounds and agrees with the Lampe and Stevenson's suggestions.

Subbaiah\(^16\) modified the above three correlations to make more effective in estimating the theoretical values of molecular electron ionization cross-section. According to his observation in unsaturated molecules like aldehydes and higher members of the ester series, it is suggested that the unsaturation in the molecule would effect the cross-section area. In order to compensate this, a factor (which
has later been termed as saturation factor) was introduced in the expression for 'Q'.

The modified relation of Beran and Kevan is as written as

\[ Q = 0.278 \gamma \chi_m \]  

... (3.4)

Here \( \gamma = (0.9)^n \) with \( n \) revealing the number of unsaturated bonds or rings in the molecule under consideration.

**Present status of the work on Molecular Electron Ionization Cross-sections**

Murthy and his group of scholars have reported the molecular electron ionization cross-sections of many systems along with molecular polarizabilities and diamagnetic susceptibilities and some of their work is given from references 17 to 22. Besides this school, one or two references could be found in literature and they are from Manguiter et al.\textsuperscript{23} and Beigmen et al.\textsuperscript{24}

**3.3 MOLECULAR ELECTRON IONIZATION CROSS-SECTION FROM \( \lambda_{\text{max}} \)**

An algebraic relation is developed between the molecular electron ionization cross-section (Q) and the wavelength corresponding to the maximum electronic absorption (\( \lambda_{\text{max}} \)) based on semi-theoretical grounds and is applied to some simple molecular systems by Sreenivasulu.\textsuperscript{21,22} The possibility of a relation between Q and \( \lambda_{\text{max}} \) is envisaged on the following concepts. The term 'ionization cross-section' does generally refer to the surface area of atom or molecule (assuming it to be spherical) which is susceptible for reactions and the electrons attached to an atom or molecule are in a field different from that when they are
isolated. A knowledge of the molecular electron ionization cross-section is useful in estimating the activity of the molecule. Similarly the wavelength at which maximum absorption of energy occurs ($\lambda_{\text{max}}$) does definitely throw light on the impact of electron with radiations. Thus an electron bound to an atom or molecule is responsible for the absorption of radiation as well as its reactivity. Both these molecular electron ionization cross-section ($Q$) and $\lambda_{\text{max}}$ are related to the number of free electrons which are readily responding to the electric and electromagnetic fields. So a relation between $Q$ and $\lambda_{\text{max}}$ is thought of now.

The molecular polarizability $\alpha_M$ is given by

$$\alpha_M = \frac{N \rho e^2}{4 \pi^2 M m c^2} \lambda_\infty^2$$

where $\lambda_\infty$, the wavelength corresponding to maximum absorption is far separated from $\lambda$, the wavelength of incident radiation.

In the above formula (3.5), $N$ is the Avagadro number, $e$ is the charge of electron, $\rho$ and $M$ are the density and molecular weight of the substance under consideration, '$c'$ is the velocity of light and $e$, $m$ are the charge and mass of the electron respectively.

The diamagnetic susceptibility $\chi_M$ can be given by the relation

$$-\chi_M = \gamma m \sigma' \alpha_M$$

where $\gamma = (0.9)^n$, $n$ reveals the number of unsaturated bonds or rings present in the molecule.
\[ \sigma' = \left[ \sigma_1^{1/n_1} \sigma_2^{1/n_2} \ldots \sigma_p^{1/n_p} \right]^{1/2} \quad \ldots \quad (3.7) \]

where \( \sigma_1, \sigma_2, \ldots, \sigma_p \) are the Pauling per cent covalence characters of the bonds. \( n_1, n_2, \ldots, n_p \) are the bond orders of various bonds present in the characteristic group and

\[
\sigma_i = \exp \frac{-(x_{a_i} - x_{b_i})^2}{4}
\]

where \( x_{a_i} \) and \( x_{b_i} \) are the electronegativities of the bonded atoms 'a' and 'b' of \( i^{th} \) bond. 'm' is characteristic constant equal to 0.72 \( \times 10^{19} \).

The modified relation of Beran and Kevan proposed by Rao et al.\(^{25} \) can be given by

\[
Q = 0.278 \gamma \chi_M
\]

\[
= 0.278 \left[ (0.9)^n \times (0.72 \times 10^{19}) \sigma' \alpha_M \right] \quad \ldots \quad (3.8)
\]

Substituting the value of \( \alpha_M (3.5) \) in the above equation (3.8)

\[
Q = 0.278 (0.9)^n (0.72 \times 10^{19}) \sigma' \frac{N \rho e^2}{4\pi^2 M m C^2} (\lambda_o)^2
\]

This can be written as

\[
Q = 0.278 (0.9)^n (0.72 \times 10^{19}) \sigma' \frac{\rho}{M} (\lambda_o)^2 \quad \ldots \quad (3.9)
\]
where

\[ \tau = \frac{N \rho e^2}{4\pi^2 M m C^2} = (4.77625 \times 10^{-12}) \]

Substituting the value of \( \tau \) in the above equation (3.9) it get reduced to

\[ Q = 0.95601 \times 10^7 \times (0.9)^n \sigma' \frac{\rho}{M} \sum \lambda_{max}^2 \quad \ldots \quad (3.10) \]

But this equation (3.10) needs modification in view of the part played by the effective number of electrons (\( p \)) which play very important role in the interaction of electromagnetic waves with the free electrons. As such the above equation gets modified to

\[ Q = -0.1 \rho \frac{0.95601 \times 10^7 \times (0.9)^n \sigma' \sum \lambda_{max}^2}{M} \]

\[ Q = 0.95601 \times 10^5 \times (0.9)^n \sigma' \frac{\rho}{M} \sum \lambda_{max}^2 \quad \ldots \quad (3.11) \]

The order of magnitude in (3.10) is so adjusted as to yield \( Q \) in \( 10^{-16} \text{ cm}^2 \). This equation can be applied to simple molecular systems.

### 3.4 Molecular Electron Ionization Cross-Section from \( R_t \)

Chromatography may be regarded as an analytical technique employed for the purification and separation of organic and inorganic substances. It is also found useful for the fractionation of complex mixtures, separation of closely related
compounds, such as isomers and in the isolation of unstable substances.

Chromatography can be divided into the following general areas.

1. Adsorption chromatography
2. Partition chromatography
3. Exclusion chromatography
4. Ion exchange chromatography.

The principles involved and the details of the above chromatographic methods can be studied from references 26 and 27.

Amongst all the chromatographic techniques known so far, paper chromatography is considered to be the simplest and most widely used since the time Consden and his group presented this method in 1994. In paper chromatography the analysis of an unknown substance is mainly done by the flow of solvents on specially designed filter paper. One of the two solvents is immiscible or partially miscible in the other solvent. The solvent rises up by the capillary action and by absorption on the paper, the separation is effected by the differential migration of the mixture of substances. This occurs due to differences in partition coefficients.

Paper chromatography can be divided into two classes.

1. Paper partition chromatography
2. Paper adsorption chromatography
The principle of chromatography lies in introducing a drop of a solution containing the sample of mixture at some point on the paper. The migration then occurs as a result of flow by mobile phase.

Paper chromatogram method has entirely different notation by which the results are represented. They are known as $R_f$ values. $R_f$ is defined as the ratio of the distance travelled by the compound at its point of maximum concentration to the distance travelled by the solvent. It is also called the relative rate of movement of the solute with respect to the solvent. $R_f$ values are different for different compounds, just as melting point, boiling point etc. They depend on the temperature, quality of the paper and the pH of the solution. So far $R_f$ is used as an identifying characteristic of the substance only.

A tentative explanation for relationship between $R_f'$ and 'Q' may be thought of due to the following reasoning. Electron ionization cross-section of an atom or a molecule give a measurement of the activity of the electrons. $R_f$ also expresses the activity of the molecule due to electrons. So a relation between these two is thought of.\(^2\) The relationship reads as

$$\log \frac{M \sigma^{1/4}}{(R_f Q) \beta} = \text{Constant}$$

where $M$ is molecular weight, $\sigma$ is its covalency factor (The details of $\sigma$ are discussed in Chapter 2). $\beta$ is a factor representing the dependence of $R_f$ and $Q$ on $P$, the number of carbon atoms in the homologous series of the molecule.
\[ \beta = 0.1 \left(1 + 0.19 P\right) \]  
This method of correlating \( Q \) with \( R_f \) has been applied to the homologous series of methanol, flavonoids, alkaloids by Sreenivasulu.\(^{21}\)

This method has an advantage of utilising \( R_f \) parameters to evaluate '\( Q \)'. So far \( R_f \) is only reported and extensive use of this is not made. This approach makes \( R_f \) to use for obtaining \( Q \).
REFERENCES


