CHAPTER I

EXPERIMENTAL BACKGROUND

1.1 INTRODUCTION:-

The problem of interaction of low energy electrons ($\sim <$ 15eV) with atoms and molecules are of interest not only in the field of physics but also in Chemistry, Biology, Engineering and Medical sciences. The study of this problem is fundamentally attached with the radiation science because almost all kinds of ionizing radiations when interact with matter ultimately produce low energy electrons and as matter consists of atoms and molecules the study of slow electrons interaction with atoms and molecules is necessary.

When an electron interacts with gas atoms or molecules different effects are observed. They are distinguished as elastic collision, inelastic collision etc.

In an elastic collision conservation principles of energy and momentum is well applicable or in other words no energy exchange take place between the internal motion of a molecule and an electron. The electron loses some energy in such encounters but only because of the finite ratio of their masses, it results in transfer of some velocity to the center of mass of the molecule as a whole.

In an inelastic collision some kinetic energy of the electron is lost in exciting internal motion in the molecule~~s~~. In this type the distinction may be made between ionizing and non-ionizing impacts depending on whether or not sufficient energy is transferred to lead to ejection of one or more electrons from the atom.

Super elastic collision takes place only between an~~d~~ electron and an excited atom or molecule, such that electron gains some energy from the internal motion of the atom or molecule. Important instances of collisions of this type occur between electron and metastable atoms.

Collision may also occur in which electromagnetic radiation is emitted. They are essentialy inelastic as far as the electron is concerned, but differ in that the whole or part of the additional energy is lost as radiation. If the loss is great enough the electron may be captured to form a negative ion.

The complete picture of the slowing down of radiation in matter requires knowledge of the various processess through which low energy electrons interact with matter and lose energy. Thus if the kinetic energy of the electron in a gaseous medium is below the ionization potential of the molecule, the electron loses energy -

to electronic excitation as long as its kinetic energy is above the first excitation potential of the medium. When the electron energy is below the first excitation potential, moderation occurs through elastic collisions and through inelastic collision leading to vibrational and rotational excitation.

A subexcitational electron may lose energy also through various type of electron attachment processes and through the excitation of compound negative ion states. Compound negative ion state can decay purely elastically (see Ref.161) give vibrationally excited molecules (162) (eg. H_2 N_2 CO) or lead to dissociative attachment (e.g. N_2O, Halogenated Benzene derivatives (Schulz 1961, Compton etal 1966) or all the three processes may be in competition. The knowledge of the cross sections for the above processes for various molecules and as a function of electron energy is of primary interest to radiation research.

The process of formation of negative ions is very important because these studies often provide information about molecular structure, while the ability of molecule to capture low energy electrons and to form stable or temporary negative ions is believed to play an important role in the biological action of molecules; such as to the cancer inducing ability of chemical carcinogens (163). While the toxicity of certain compounds (e.g. CCl_4) has been related to electron Capture (Gregory 1966).

Nuclear physicists finds interest in negative ions for acceleration purposes.

The importance of low energy electron interaction particularly electron capture and electron diffusion has received much recognition.recently. Interaction of slow electrons with Polar molecules is also the subject of greatest importance. Many experiments are performed and theoretical explanations are also given to the various aspect of these types of interaction. Still we are not perfectly acquaint with the nature and behaviour of the polar molecules.

1.2 COLLISION CROSS SECTION.

Consider a parallel beam of electrons of homogeneous velocity which is passing through a gas having "N" identical molecules. Molecules are imagine to have spherical shape in nature and having cross sectional area as 'Q'.

Chances for an electron to collide with molecules within a small distance δx is according to probability theory equals to $NQ\delta x$.

Now there are all chances that an electron can be removed from the beam during such an impact, for such an escape some of the beam current strength will be lost, this loss of current is given by

$$\delta I = N Q I \delta x.$$

$$\therefore \frac{\delta I}{I} = N Q \delta x$$

On integrating

$$\Big[\log I\Big]_{I_0}^{I_p} = N Q \Big[x\Big]_{x}^{0}$$

$$\log I_p - \log I_o = - N Qx$$

$$\log \left(\frac{I_p}{I_o}\right) = - N Q x$$

Where P is any point from which electrons starts to travel distance δx and the current at P is I_p.

$$\therefore \quad \frac{I_p}{I_o} = e^{-NQx}$$

$$I_p = I_o \, e^{-NQx} \text{ - - - - - } 1.1$$

If I_p / I_o is measured as a function or x and N, Q may thus be found.

In actual experiment a beam of electrons of homogeneous velocity is fired in to the gas. In traversing a certain distance x in the gas a fraction proportional to x of the electron will be deviated from their original paths and lose energy by collision with gas molecules. All electrons so affected are considered to be lost from the beam. If measurements are made of the rate at which the current remaining in the beam varies with x, it will again be found that,

$$I = I_o \, e^{-\alpha x} \quad \ldots\ldots\ldots 1.2$$

α = Absorption coefficient of the gas for the electron beam. If P is a gas pressure in mm. of Hg. Then,

$$N = 2.7 \times 10^{19} P / 760$$

and as Q is effective collision cross section = α / N

$$\therefore \quad Q = 2.81 \times 10^{-17} \alpha / P \ \text{Cm}^2 \quad \ldots\ldots 1.3$$

This quantity is called the total collision cross section of the gas molecules for electrons of the beam velocity.

Our definition of Q includes all types of collisions presented by a gas molecules; towards electron of a given velocity v. For specifying various types of collision i.e. Elastic, Inelastic Superleastic and Radiative collision a different probabilities which can specify the types of collision should be included.

(1) DIFFERENTIAL CROSS SECTION.

So far we have paid no attention to the specification of the angular distribution of electrons undergoing a particular type of collision. Consider for moment an elastic collision. The elastic collision cross section Q_0 may be further broken down as follows.

$P(\theta) \sin\theta \, d\theta \, d\phi$ is the probability that in an elastic collision the electron is scattered in to the solid angle $d\Omega$ ($= \sin\theta \, d\theta \, d\phi$). Then $P(\theta) \; Q_0 \; \sin\theta \, d\theta \, d\phi$ is called the differential cross section for elastic scattering in to the solid angle $d\Omega$. It is usually written

$$I_0(\theta) \sin\theta \, d\theta \, d\phi$$

therefore we have $P(\theta) = I_0(\theta) / Q_0$

$$\text{and} \quad Q_0 = \int_0^{\pi}\int_0^{2\pi} I_0(\theta) \sin\theta \, d\theta \, d\phi \quad \ldots\ldots\ldots \; 1.4$$

In the same way differential cross section for inelastic collision may also defined. Thus ~~XH~~ $I_n(\theta) \sin\theta \, d\theta \, d\phi$ is the differential cross section for scattering in to the solid angle $d\Omega$ in an inelastic collision involving excitation of n^{th}

state of atom.

(ii) DIFFUSION OF ELECTRONS THROUGH GASES :-

Consider the diffusion of a swarm of electrons through a gas at pressure P under the influence of a constant electric field of strength E. This is of interest, not only from its application to electric discharge and other phenomena, but also because it can provide valuable information about the collision cross section of atoms and molecules towards slow electrons. It is particularly useful in determining the mean energy loss suffered by a slow electrons in collision with the gas molecules. The electrons concerned may have too small an energy to produce any electronic excitation within the molecule but may excite vibrational or rotational states. It is important to study diffusion as it is of historical interest also in as much as Townsend and Bailey (Loc. Cit.) observed in this way the anomalous behaviour of slow electrons in argon as long as 1921, independently of Ramsauer's investigations. It is observed that two sets of results are entirely compatible. We are much interested in applying the diffusion method to the study of energy losses due to excitation of molecular vibration and rotation and to the negative ion formation.

The principle of the method which may be used to determine the mean free path and mean energy loss collision is as follows,

In the steady state let

w = Mean drift velocity in the field direction.

ϵ = Mean kinetic energy.

l = Mean free path of the electrons in a gas.

λ = Fraction of energy loss by an electron while colliding with gas molecules.

c = Mean velocity of the random motion of the electron.

Therefore number of collisions made in traversing a distance x in the direction of field cx / wl since xc / w is actual length of path.

The energy lost in this collision will be $\lambda \epsilon c x / w l$ For a stedy state $\lambda \epsilon c x / w l = E e x$. and as $\epsilon = 1/2 \, mc^2$, m = mass of an electron.

$$\text{therefore} \quad \lambda c^3 / w = 2 E e l / m \qquad \ldots\ldots\ldots \quad 1.5$$

Now let the mean distance traversed in the direction of field in the interval δt between collisions = $w \, \delta t$

$$\text{therefore} \quad 1/2 \; \frac{E e \, \delta t^2}{m} = w \, \delta t.$$

Apart from the numerical factor of order unity, δt may be taken as l/c giving

$$2 \, w \, c = E e \, l / m.$$

Since 'l' is inversly proportional to the gas pressure 'P', both 'c' and 'w' are function of E/p. If c and w are measured for a fixed value of E/p then l and λ can be obtained.

In practice l will not be a constant and the measurements of ~~m~~ c and w will give certain mean values of l and λ over the velocity distribution of the electrons. We can not therefore hope to derive from experiments on electron swarm, any - information as definate about collision cross section as may be obtained from experiments of the Ramsauer type. It is possible however, to work with electrons of lower energy than in the more direct experiments and to obtain information about the energy losses of electrons on collision with molecules which can not be got in any other way.

To analyse the diffusion phenomena in more detail in relation to collision cross section, we shall consider a swarm of such small mean energy that inelastic collision with the gas atom do not occur. The only loss of energy in elastic collision therefore arises from definite value of the ratio of the mass of an electron to that M of a gas molecule. On the other hand, we shall suppose that the mean energy of molecule is very much smaller than that of the electrons. We also suppose that the electron concentration in the stream is so small that the inter action between the electrons can be ignored. Under these conditions it becomes possible given the results of Ramsauer experiment and also of measurements on the angular distributions of elastically scattered electrons to compute both the drift velocity and the mean kinetic energy as a function of f/p. These may than be compared with values observed by various methods and good agreement is found. This enables one to apply the technique with confidence to molecular gases in which the mean energy loss is not known before hand, and in which attachment may occur.

(iii) MOMENTUM TRANSFER (DISSFUSION) CROSS SECTION (M. T. C. S.)

With the assumptions made, the fraction of its energy lost per impact by an electron which is scattered through an angle θ is given by

$$2\ (1 - \cos\theta)\ m/M$$

if $(m/M)^2$ is ignored.

Since $P(\theta)\sin\theta\, d\theta\, d\phi$ is the probability that on collision, the electron be scattered in to the solid angle $d\Omega$ about θ, the mean fractional energy loss per collision, will be

$$2\ (m/M)\int_0^{\pi}\int_0^{2\pi}(1 - \cos\theta)\ P(\theta)\ \sin\theta\ d\theta\ d\phi$$

In terms of total and differential scattering cross section Q_o and $I_o d\Omega$ for elastic scattering

$$P(\theta) = I_o(\theta)/Q_o$$

so that mean fractional energy loss per collision becomes

$$2\ (m/M)\ \frac{Q_d}{Q_o}$$

where

$$Q_d = \int_0^{\pi}\int_0^{2\pi} I_o(\theta)\ (1 - \cos\theta)\ \sin\theta\ d\theta\ d\phi \quad .....1.6$$

and is usually referred as the momentum transfer cross section, which is some times called diffusion cross section also on account of its importance in the discussion of diffusion phenomena.

Thus the fractional amount of energy lost by an electron in traversing a distance x in a gas containing N molecules/c.c. is $2\ (m/M)\ N\ Q_d\ x$. Just as if the total elastic cross section Q_o when replaced by Q_d and the fractional energy lost per collision by $2m/M$ thus for purely elastic collisions we should take $l = 1/N\ Q_d$ and $\lambda = 2m/M$. It must be remembered however that in general Q_d will be functions of electron energy.

Q_d differes appreciably from Q_o only when there is a pronounced contribution of scattering in either backward direction or forward directions. If $I_o(\theta)$ is a constant independent of θ, then Q_d and Q_o are equal.

If the mean energy ϵ of the gas molecules can not be ignored the expression for the mean fractional energy loss per collision must be modified by multiplication by the factor $(1 - 4/3\ \epsilon_o/\bar{\epsilon})$. If the electrons themselves have a Maxwellian distribution of mean energy $\bar{\epsilon}$, the corresponding factor becomes modified by an amount to $4/3\ (1 - \epsilon_o/\bar{\epsilon})$.

1.3 BASIC EXPERIMENTAL PROCEDURE.

There are three classes of measurements which can be performed. Most desirable, ofcourse, would be a set of measurements of the differential scattering cross section as a function of incoming and outgoing energy and angle. From such a set of measurements, one can directly obtain either the total cross section or the momentum transfer cross section. In principle, at least, a direct measurement of the differential cross section is straight forward. All one need do is scatter a monoenergetic parallel electron beam by a monoenergetic line gas target. One than studies the scattered electrons ariving at a detector of infinite angular resolution as a function of angle, and as a function of incoming and outgoing energy.

In practice, the problems associated with making a low energy quasimonoenergetic electron beam and quasiline was target together with detecting the scattered electrons at even some finite angular resolution have proven to be some what difficult. The problem of unknown or at best variable detection efficiancy arising from finite angular resolution can be, to a certain extent, over ~~s~~come by a total scattering measurements. However the problems associated with finite energy resolution becomes more serious as one goes to lower and lower energies. Ultimately the problem of space charge (leading to loss of si~~ng~~gnal at very low energies) makes it impossible to measure scattering cross section directly. In any case as the energy is lowered a measurement of scattering cross section as a point function of energy gradually becomes a measurement of the average value of the product of the cross section and collisional relative velocity divided by the average value of the relative velocity. Thus at sufficiently low energies even a so called direct measurement ends up with the problem of unfolding the desired cross section for monoenergetic particles from measurements averaged over the energy distribution functions of the colliding particles.

For experimental findings the essential thing is to have low energy electrons. There are three important techniques generally used to produce low energy electrons. (1) Electron swarm technique (2) Electron beam technique (3) Swarm beam combination.

In electron swarm technique a swarm of electron of known energies is used while in beam technique a monoenergy electron beam is taken in to consideration. Some investigators have found the advantage of the combination of both the mthods.

Electron swarm experiments have provided the useful informations concerning the interaction of the low energy electrons with and the transport of electrons through gases (164).

The direct measurements of the electron scattering cross section both total and differential was first made by Ramsauer & Kollath (1930, 32), in the early years of this century, which was based on the principle that is used by Ramsauer (1921) for electron atom scattering.

The difficulties associated with direct measurements of the low energy electron scattering cross section has led to the re-emergence of the so called indirect methods of cross section measurements, where in the desired cross section is extracted from the data only after a fairly complicated analysis. The oldest of these methods which determines the momentum transfer cross section from measurements of transport properties of electron swarm, was pointed out by Townsend & Bailey (1922).

In the indirect measurement usually measured are the drift velocity and the ratio of the diffusion co-efficiants to mobility as functions of the ratio of electric field strength E to density N.

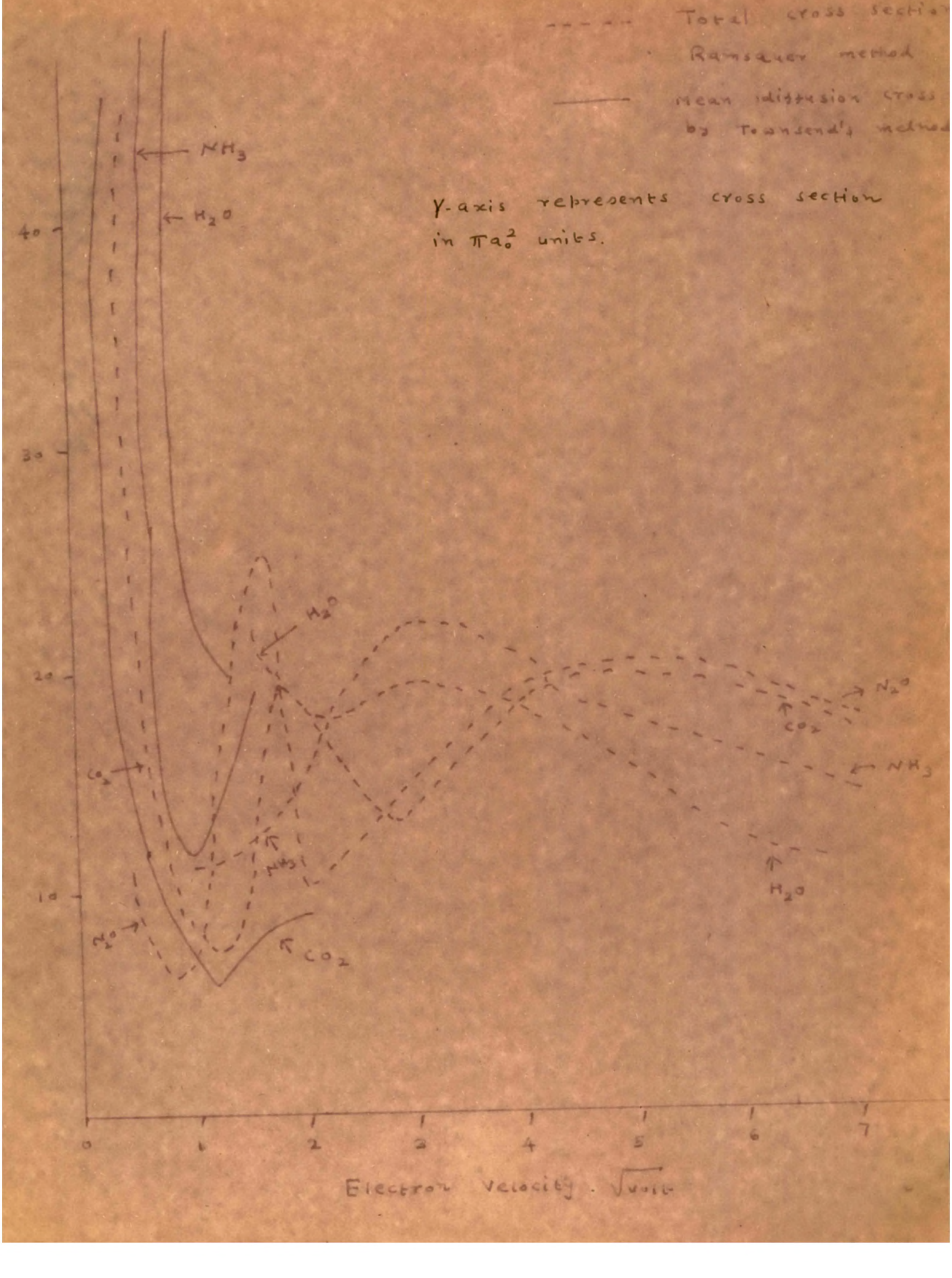
The total scattering cross section can be measured by Ramsauer's method while momentum transfer cross section can be measured by Townsend's method. Some of the results obtained by these methods are discussed in the next section.

1.4 OBSERVED CROSS SECTION

The method of Ramsauer and Townsend have been applied to the tdetermination of the total cross sections for a number of molecules for slow electron.

The Ramsauer effect is used to study the molecular structure. When slow electrons pass through a gases we observe a peculiar dependence upon the electron velocity, of the total cross section for the interaction of electrons with the gas molecules. The effective cross section is taken as the sum of the cross sections of the molecules contained in 1 Cm^3 at 1 mm. of Hg, and 0^o C. This varies with electron velocity in accordance with a curve that is characteristics of the given compound or given class of compounds. The data observed by the Ramsauer method is interesting from the view point of Grimm's law of displacement of hydride. The inter molecular field that acts on the electrons and determines the magnitude of the effective cross section (for a given electron velocity) - in molecules that belongs to each of two classes under consideration has similar structure within the limits of a given class. It is interesting to find that the effective cross section is a sensitive indicator of the type of valance molecule.

The diatomic molecules which have been investigated in early days are H_2, O_2, N_2, Cl_2, Br_2, I_2, CO, Graph. 1.



Y-axis represents cross section in πa_0^2 units.

NO, HCl (165).

The total cross section for a number of molecule of organic series have been measured in an attempt to observe a cross section corelation with the nature of the chemical binding. The contrast was observed between the behaviour of ethane, ethylene, and acetyline (Bannon & Brose 1928. Bruche 1927, 29,30). While in paraffin series from methane (CH_4) to butane (C_4H_{10}) a close similarity behaviour was observed; by Bruche (1930). It is also of interest to note the remarkable similarity in behaviour between Methane and Argon (Ramsauer & Kollath 1930, Bruche 1927, 30, Brode 1925). The detailed structure of a hydrocarbon does not seem to exert any important influence. Isomers behave in very nearly the same way as the normal and isomeric forms of butane and pantane (Bruche 1930). Even Isomers which differ very considerably in structure such as ethyle-alchohol and methyl ether , do not seem to behave very differently towards slow electrons, Schemieder 1930. Other groups of related organic molecules which have been investigated are the singly substituted methanes CH_3F, CH_3OH, CH_3NH compared with CH_4, $(CH_3)_3CH$, $(CH_3)_3N$, Schemieder 1930 and CH_3Cl, CH_2Cl, $CHCl_3$, CCl_4, Holts & Holts Mark 1931.

Results are also obtained for the polar molecules which contains dipole moments. H_2O, NH_3, CO_2, and N_2O (166) are studied by both the classical methods. The results are as illustated in graph-1.

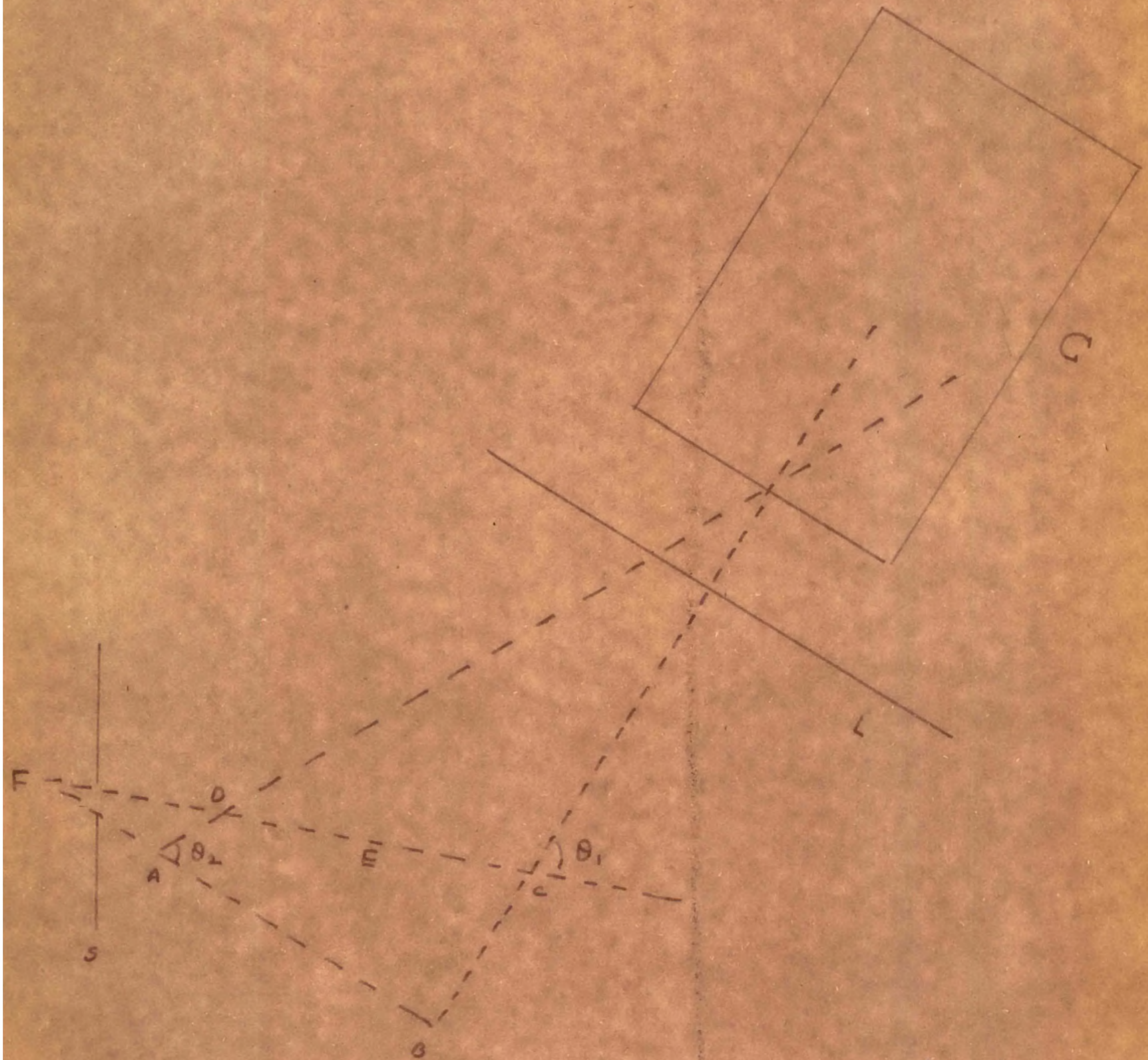


Fig. 1.1.

1.5 FURTHER DEVELOPMENTS IN EXPERIMENTS.

After the Ramsauer and Townsends experimental investigations a various changes are introduced in these standard methods. Some of the new instruments are also built up for measuring the various factors.

A very extensive measurements have been made for the angular distribution function for the electrons scattered elastically and non elastically. A general principle of such an instrument is illustrated in fig. 1.1. A beam of electrons of definite energy emerges from a source " S " in to the gas contained in a region free from electrostatic fields. Those electrons scattered from the area ABCD of the beam through the angles in the small range θ_1, and θ_2 pass through the entrance slit L of a collector. This collector include some analysing device to ensure that only scattered electrons with energies in the required range are measured. By the rotation of the collector C the variation in θ may be measured. From that the scattering itensity per unit solid angle can be obtained. By changing the design of the collector various attempts are made. Bullard and Massey (1931) used shielded Faraday cylinder. Some of the investigator used electrostatic analyser (167). For studying slow electrons scattering Ramsauer and Kollath (1932) prepared a special instruments where number of plate collectors usually called zones are used .

Another important factors of which experimental investigation is essential are the drift velocity of the electron in the molecular gas and the diffusion coefficients. Although the drift velocities obtained by the various swarm techniques are reasonably compatible there seems to be a substential disagreement between the swarm methods for the measurements of the diffusion coefficient D. Diffusion co-efficients have been studied principally by the well established lateral diffusion method of Townsend (171). Recently a time of flight (TOF) method has been developed (Hurst etal 1963,1966), which gave D values generally smallar in magnitude than those obtained by the Townsend method by an amount which increases with E/P and depended strongly on the gas. A basic difference between the two methods is that the Townsend method measures D in a direction perpendicular to the applied electric field, while the TOF method measures D in parallel direction. Since the possible instrumental errors seem to be excluded the difference between the D values obtained by the two methods may be suggestive of an anisotropic electron scattering at low energies; i.e. D has a tensor character.

The useful information about the interaction potential involved in the electron molecule collision can be obtained from measurement of W (Drift velocity), D/W, D/μ (μ = electron mobility). The measurements of w provide the measurements of cross section. The velocity dependence of the cross section is difficult to determine, however measurement of w as f a function of temperature T, has provide such information (Pack & Phelps 1961, Frost 1962, Christophorou etal 1966). For example, the measurement of w for C_2H_4 as a function of T yielded a velocity independent cross section for thermal electron energies (Christophorou etal 1966) equal to (4.37 ± 0.26) X 10^{-16} cm.2

The direct excitation of vibrational states of molecule by electron impact is generally very small due to the small electron to molecule mass ratio. Few beam experimants have been designed to study vibrational excitation. This is due in part to the small cross sections involved in the direct vibrational excitation and the fact that the direct excitation begins at very low energies where beam experiments are difficult to perform. The trapped electron data of Schulz and Dowell (1962) however were interpreted as vibrational excitation of the $\nu=1$ to $\nu=8$ states of O_2. The literature appears to be devoid of experiments reporting on direct vibrational excitation by electron impact. On the other hand swarm experiments which otherwise are ideally suited for the extreme low energy region present serious difficulties in the deductions of cross sections for elastic and in-elastic processes from the measured swarm parameters. A detail analysis of swarm data requires solution of the appropriate Boltzman transport equation for time independent electric fields and some knowledge of the energy dependence of the cross section for the elastic and inelastic processes.

Other swarm experiments (168) have further shown that rotational and vibrational excitation of molecules by electrons occur at low energies. Direct rotational excitation is not expected to be large, but it may be enhanced through the long range interaction of low energy electrons with polar and quadrupolar molecules (Gerjuoy & Stein, 1955 O'Mally 1964, Sampson etal 1966). The possibility of vibrational excitation in an electron - molecule collision will be small unless the duration of the collision, T_{coll}, is approximately equal to the natural vibrational period of the molecule T_{vib} i.e.

$$\frac{T_{col}}{T_{vib}} = 1 \qquad \ldots\ldots \qquad \ldots\ldots \qquad (1.7)$$

For energies in the electron volt range the electron passes by the molecule much too fast to allow sufficient energy transfer and thus the electron must be temporarily bound to the molecule in order to fulfill equation (1.7). The large vibrational excitation processes in N_2 observed in swarm experiments and later in beam experiments were interpreted as proceeding through such temporary negative ion intermediates. It may be possible that rotational excitation is enhanced through temporary negative ion states in a similar fashion. Temporary negative ion resonance were also observed for H_2, D_2, HD, N_2, CO, N_2O some hydrocarbons (Bowman and Miller 1965) and benzene derivatives. When disso - -ciative attachment is possible, the temporary negative ion may dissociate the dissociative process being in competition with autoionization .

Several theoretical studies have treated the direct vibrational excitation of molecules by electron impact and have been successful in treating the phenomena of vibrational excitation of molecules via temporary negative ion stated.(169)

In general, low energy electron impact spectroscopy provides a unique tool to investigate the structure of molecules and excitation functions in particular. Optical selection rules involving change of multiplicity, angular momentum and symentry are greatly relaxed, and a study of both optically allowed and optically forbidden transitions becomes possible. A large portion of the work on electronic excitation, however was also done with energy sufficiently high ($\geq$ 100 e_V).

Electron capture has been studied by both swarm and beam methods. The swarm data are usually compared by plotting the attachment coefficient, α, or the probability of attachment per collision, h, Vs. E/P or Vs. the mean energy of agitation, $\bar{\epsilon}$ (170). Most of the early work on electron capture achieved by the swarm method is complicated because of unknown electron energy distribution. The beam data on the other hand are usually given as negative ion yields I (ϵ), in relative units Vs. the electron energy, ϵ . Recent improvement in beam method and its combination with swarm experiment allowed determination of capture cross section as a function of electron energy.

If the capture process remains an isolated events, the electron will be ejected by autodetachment generally within a typical vibration time (10^{-13} - 10^{-14} sec). Diatomic negative ions formed by unimolecular electron capture have never been detected directly because of their short life times (stabilization is necessary). However a number of molecules are known (Compton etal 1966 Henglein etal 1961) to attach electrons by unimolecular electron capture for $T > 10^{-6}$ Sec. These molecules are large and generally symetric, so that the excess energy of the captured electron is shared with the many molecular degrees of freedom for a time long enough to be detected in a conventional mass spectrometer. The mean life times were determined by modified Bendix TOF mass spectrometer (Compton etal 1966). In general large cross section and long life time can be visualised in two manners (I) Weak transitions from the initial state of the neutral molecule directly to a large number of final state of the ion, and (II) the transition to the neutral molecule to the negative ions is strongly allowed but the excess energy is distributed among the various internal degrees of freedom. Under the assumption (I) large cross sections results because of the large number of final states, and long lifetimes are accounted for by the weak coupling between the initial and any of the final states. Under the assumption (II) large cross section result from the large transition probabilities, and the long life times are due to the time required for the system to return to a configuration which will lead to autodetechment.

A detailed determination of the various quantities of slow electron polar molecule interaction has been made recently by L.G. Christophorou and his coworkers and many interesting data has been discovered by this method. A brief discussion of the method is therefore necessary.

A block diagram of the experimental arrangement is given in fig. 1.2. The main part of the apparatus is ionization chamber, which contains two parallel gold plates, cylindrical in shape. Thelower plate B, which forms lower end of the drift space, is held at a negative potential and constitutes the photo surface from which electrons are ejected by ultraviolet irrediation. A gas discharge tube (G.M.) is mounted on to upper plate T, which is held at zero potential and constitutes the upper end of the drift space.

The carrier gas and total gas pressure were measured by a Wallac and Tireman mechanical gauge, while the sample gas pressure was measured by a Barton pressure meter.

The sample gas was introduced in to the chamber first, and the sample gas pressure were measured within a tenth of a micron accuracy. Pumping on the samples removed traces of air and dissolved oxygen. None the compound studied, was purified further except the ethyline carrier gas. Ethyline was passed through a deoxo purifire, a molecular trap, and was distilled three to four times by liquid nitrogen before use. The purified ethyline was introduced in to the ionized chamber at a pressure P_E (usually 100 torr) and the drift velocity in pure ehtyline were measured. This purification procedure was repeated before each series of experiments to insure the same working conditions and purity of ethyline.

The electron swarm drift velocities were measured as follows. The ultraviolet light emitted by a mercury pulshed flash tube strikes the center of the lower plates B, and releases photoelectrons. These electrons quickly come into the equilibrium with the molecules of the carrier gas and through the action of the applied electric field, travell the drift space B and ultimately trigger the gas discharge tube.

The ultra violet pulse which generate the electron swarm also triggers a photodiode, and the output pulse is fed to an oscilloscope at some time " t ", after the display of the light pulse, the pulse from the gas discharge tube is also seen on the oscilloscope. The time lapse " t " between the two pulses is the electron drift time.

By the help of this technique Christophorou etc. have studied various types of nonpolar, polar, and molecules with the mixture of ethyline. The necessity for studying molecules in a mixture with a carrier gas is mainly because a number of interacting compounds have low vapour pressure at room temperature. Also some compounds have high capture cross section for low energy electrons, thus if used without dilution, no electrons would be left to trigger the electron detector used in this work.

In the electron swarm experiments electrons undergo many collisions and diffuse in the gaseous medium through which they drift under the influence of the electric fields, Their energy has a considerable spreading which is characterized by a function f (ϵ ,E/P), defined by f (ϵ ,E/P) $d\epsilon$ = fraction of electrons in an energy range $d\epsilon$, about ϵ ,E/P is the " pressure reduced electric field " usually expressed in volts Cm^{-1} $torr^{-1}$. Energy distributions in electron swarm f (ϵ, E/P) are known for various gases and mixture of gases.

In the swarm experiments no direct identifications of the product is made but certain parameters such as the rate of electron attachment can be measured absolutely. Also swarm experiments are performed at high pressure and allow studies of processes which are stabilized by collision. In general swarm experiments are relatively easy to perform but in many cases difficult to interpret.

1.6 GENERAL COMMENTS ON BEAM TECHNIQUE AND SWARM BEAM COMBINATIONS.

BEAM TECHNIQUE.

The beam technique in contrast with swarm experiments, deal with nearly monoenergetic electrons and single collision processes. Usually they are restricted to electron energies above 2eV; which excludes studies in the interesting range below this energy.

Most electron - molecule collision processes have a sharp dependence on the kinetic energy of the incident electron. Thus the most important quality of the beam experiments in addition to correct energy scale, is a narrow electron energy distribution.

The retarding potential difference method (RPD) considerably improved the beam technique, allowing an energy resolution of 0.1eV to be generally obtained. More recently improved electrostatic analyzers allowed energy resolution of 0.012eV was reported in the energy loss spectrum of electron through H_2.

The various techniques based on RPD method (e.g. trapped electron method) and the various improved electrostatic analyzers provided the informations on the position and intensity of allowed and forbidden electronic transitions, existence of the temporary negative ion states, and oscillator strength of excitation processes. Also the light omitted from the states excited by an electron impact has been studied with considerable success. While the well known Ramsauer method (with various modifications) has provided the most useful results on total scattering cross section.

The beam experiments are easily adopted for identifying the product of electron molecule interaction and measuring their kinetic energy. However the various ions yeilds are measured in relative units. Thus limiting the determination of cross sections to total ionization experiments. This shortcoming can be over come by incorporating swarm data with beam studies.

(II) SWARM BEAM COMBINATION .

There are certain unique advantages in the combination of electron swarm and electron beam technique. Such a swarm beam has been performed, (Christophorou etal 1965) and has provided a new tool for the determination of electron capture cross sections, briefly from electron swarm experiments the absolute rate of electron attachment, $\alpha(E/P) \times W(E/P)$ is obtained. Where $\alpha(E/P)$ is the probability that an electron will be captured in travelling 1 Cm. in the field direction when the attaching gas pressure is 1 torr and $W(E/P)$ is the electron swarm drift velocity.

The capture rate is related to the capture cross section $\sigma_c(\epsilon)$ and to $f(\epsilon, E/P)$ by

$$\alpha(E/P) \times W(E/P) = N_0 (2/m)^{1/2} \int_0^\infty f(\epsilon, E/P)\, \epsilon^{1/2} \sigma_c(\epsilon)\, d\epsilon \qquad \ldots 1.8$$

where N_0 is the number of attaching gas molecule per cm.^{3} at 1 torr, and " m " is the electron mass.

From the electron beam experiments the negative ion yeilds $I(\epsilon)$, as a function of electron energy are obtained in relative units and an identification of the product of electron molecule collision is made. Provided the width of the electron beam is small compared with the width of the negative ion current, a trial function can be constructed as

$$\sigma_{bj}(\epsilon) = K_j T_j I(\epsilon) \qquad \ldots\ldots 1.9$$

Where T_j is a simple translation of the $I(\epsilon)$ curve along the ϵ axes to correct for any uncertainities in the original energy calibration and K_j is a constant for each T_j which transform the $I(\epsilon)$ curves from relative to absolute units.

To obtain both T_j and K_j equation (1.9) is introduced in to equation (1.8) and a double least square procedure is performed, where one obtains for each value of E/P the best fit between the calculated and the experimental results through equation (1.10)

$$\frac{d}{dT_j}\left\{ \sum_i \left[N_0 \left(\frac{2}{m}\right)^{\frac{1}{2}} K_j \int_0^{\infty} \epsilon^{\frac{1}{2}}\, T_j\, I(\epsilon) \times f_i(\epsilon)\, d\epsilon - \alpha_i w_i \right]^2 \right\} = 0 \qquad \cdots\ \cdots\ (1.10)$$

Equation (1.10) forms the bases of the swarm beam technique. It combines informations from the beam experiments $[I(\epsilon)]$ with that from the swarm experiments (αXW) and provides K_j (thus σ_i) and T_j (thus energy scale calibration).

The method is very sensitive in determining the absolute magnitude of the cross section and in establishing the correct energy scale.

1.7 DISCUSSION OF THE EXPERIMENTAL RESULTS.

As discussed above many experiments are performed for different measurements of low energy electron interaction with molecules. Our aim is to study polar molecules only. Some of the interesting results are plotted in the above pages. In this particular section we would like to discuss the results obtained on the mthod developed by Christophorou, which is explained in detail in the last section. Some of the important results for polar molecules are as follows.

(I) Data are reported on the temperature dependence of electron swarm drift velocities " W " in ethyline. The analysis of the data gave a velocity independent cross section for momentum transfer, σ_ε for ethyline at thermal electron energies. Using a constant σ_ε the dependence of W_e/W_m on gas concentration is investigated. Where we is the drift velocity in the ethyline and w_m that in mixtures of ethylene with a polar impurity P. Three regions of concentration were distinguished : initial, intermediate and final. The initial region can provide information about the velocity dependence of σ_m , the intermediate (better suit for experimentation) can easily provide σ_m if the velocity dependence of σ_m is known, and the final region provides a new way to measure the drift velocity for pure polar compounds P by simply measuring w_e/w_m in mixtures of P with ethylene. The latter is extremely important when P can not be studied alone. (Christophorou etal 1966).

(II) Drift velocities were measured for thermal electron swarms traselling through gases and gas mixtures. The " w " data are used to calculate average cross sections for momentum transfer, σ's, which are assumed to have a v^{-1} and v^{-2} dependence for nonpolar and polar molecules respectively. An effort is made to corelate the experimental values of σ with the molecular polarizability and/or the molecular dipole moments. The theoretically predicted corelations are discussed and compared with experiments. It was observed that Born approximation theory gives better agreement with experiment (Christophorou etal 1966).

III. Mean scattering cross sections and drift velocities data for thermal electrons for polar molecules in the pure form and in mixtures with ethylene are also observed. The electrical molecular dipole moment D ranges from 0 to about 4.1 debye. A conclusion can be drawn that the overall dependence of the experimental cross sections on D indicates the possible effect of the binding of an electron to a molecule (when $D > D_{min}$) and the possible effect of a potential resonance was predicted by Takayanagi and Itikawa (Christophorou etal 1969).

IV. The temperature dependence of the drift velocity of thermal electrons travelling through polar gases has also been investigated and the data have been determined more accurately the magnitude and the velocity dependence of the momentum transfer cross section σ_m. experessed as $\sigma_m = A_\alpha / v^\alpha$, where A_α is a constant for each value of α. The values for different polar molecules are found to be close to the value of 2, predicted by the Born approximation. There is a considerable spreading in σ_m for permanent electric dipole moments D in the region $1.65 \leq D \leq 3$ debye (Christophorou & Pittman 1970)

V. The mobility μ of thermal electrons in π electron containing orgenic molecules (linear, cyclic and aromatic hydrocarbons) decreases with increasing number of doubly occupied π orbitals, For linear hydrocarbons with two doubly occupied π orbitals, μ increases with increasing separation of the two π orbitals (Christophorou etal 1973)

VI. Long lived parent negative ions formed via nuclear excited Feshbach resonances at thermal electron energies have been observe for various molecules. The measured life time depend on the electron donor - acceptor properties of the substituent group, and the intramolecular interaction between them, which is a function of their relative position around the benzene perypherу. It can be concluded that NO_2 containing benezene derivetives, CN substituted orgenic molecules, higher aromatic hydrocarbons, strained structures and orgenic molecules containing the functional groups - COCO - - COCH (OH), - COOH and CHCHO, capture thermal electrons and formed long lived parent negative ions via nuclear excited Feshbach resonance (Hadjaintoniou etal 1973) .