CHAPTER II

THEORETICAL SURVEY OF SCATTERING OF SLOW ELECTRONS BY MOLECULES

2.1 INTRODUCTION :-

In the first chapter we have seen the experimental methods, by which various factors of slow electron polar molecule intraction can be evaluated. In this chapter we would try to discuss theoretical development of the problem. Many aspects of the problem can be well explained by the different theories but some of the aspects are such that none of the theories can explain it perfectly well. For example a larger cross section of H_2O, H_2S, D_2O can not be explained satisfactorily till to-day.

2.2 CLASSICAL APPROACH TO THE SCATTERING PROBLEM :-

In the classical picture of a collision, a particle with a definite angular momentum about the scattering centre will undergo a definite deviation, but on the quantum theory, as would be expected, this is no longer the case. Associated with each quantized angular momentum there is an amplitude function which gives the distribution in angle of the associated scattered amplitude (not the scattered intensity). The total scattered amplitude is obtained by adding the contributions from the separate angular momenta, each of which contributes at all angles. A suitable weighing factor related to the probability of any deviation occuring must be included in each contribution. Therefore the contribution to the amplitude scattered between angle θ and $\theta + d\theta$ from the angular momentum $\{l(l+1)\}^{1/2}\hbar$ is of the form $g(n_l)\,F_l(\theta)$ where $F_l(\theta)$ = Angular function associated with the particular angular momentum and the weight factor $g(n_l)$ is a measure of the chance that any deviation will occur.

$$g(n_l) = 0, \text{ when } n_l \to 0 \text{ or } n\pi,\ n = \text{Integer}$$

$$g(n_l) = \text{Maximum, when } n_l = 1/2\, n'\pi = \qquad n' = \text{Odd integer}$$

Total scattered amplitude is

$$\sum_l g(n_l)\,F_l(\theta)$$

and scattered intensity is

$$\left|\sum_l g(n_l)\,F_l(\theta)\right|^2$$

$$F_l(\theta) = \text{Zonal Harmonics } P_l(\cos\theta)$$

$$g(n_l) = (2l+1)\left\{\exp(2i\,\delta_l) - 1\right\}$$

Differential cross section

$$I_0 (\theta) = \frac{1}{4k^2} \left| \sum (2l+1) \left\{ \mathrm{Exp}\ (2i\delta_l - 1) \right\} P_l(\mathrm{Cos}\,\theta) \right|^2 \quad \ldots\ldots\ 2.1$$

which is firstly worked out by Faxen & Holtsmark (1929). From this a total scattering cross section σ_T can be put up in the form

$$\sigma_T = 2\pi \int_0^{\pi} I_0 (\theta) \,\mathrm{Sin}\,\theta \, d\theta \quad \ldots\ldots\ 2.2$$

We may now obtain some idea of the forms to be expected for the angular distributions of slow elastically scattered electrons. At very low energies only δ_0 is important and

$$I_0(\theta) = \frac{1}{4k^2} \left| \left\{ \exp\ (2i\ \delta_0) - 1 \right\} P_0 \right|^2 \quad \ldots\ldots\ 2.3$$

For obtaining a theory of the elastic collision of slow electrons with molecule as satisfactory as that of atom it is necessary to extend the Faxen - Holtsmark method to scattering for a field which no longer posses spherical symmetry. Even if this could be done the theory would be hampered by the greater ignorance of molecular field in comparision with atomic field. Despite of this difficulty it has, however been proved possible to extend Faxen-Holtsmark theory to a sufficient extent by approximate methods to obtain some interesting results for certain molecules.

Where as the schrodinger equation for the motion of electrons in a spherically symmetrical field of force can always be solved in principle, the corresponding problem for an axially symmetrical field is, in general insoluble, However by using spheroidal coordinates it is possible to obtain solutions for certain forms of axially symmetrical field which are likely to be rather similar to the actual fields. Of diatomic molecules. Stier (1932) and later Fisk (1936) have taken advantage of this to develop a theory of the elastic scattering of slow electrons by diatomic molecules which is a direct generalization of the Faxen-Holtsmark method of Partial cross section.

The total angular momentum of the incident electron about the centre of the molecules is no longer a constant of the motion. On the other hand the component of the angular momentum in the direction of nuclear axis isconstant and is therefore quantized, the allowed values being $m\hbar$, $m = 0,1,2\ldots\ldots$ The incident wave may therefore be resolved in the partial waves for which $m = 0,1,2$ ------- etc. With the particular fields for which Schrodinger equation is separable in sphroidal co-ordinates a further resolution may be made for a given value of m, as follows. When the two foci the spheroidal coordinate system (the two nuclei) are allowed to come together (the united atom limit) the resolution in terms of the total angular momentum quantum number $l + m$ is again possible as the system is once more spherically symmetrical. In the spheroidal case a partial wave denoted by m, l is one in which the axial angular momentum is mh and the total angular momentum in the united atom limit is

$\{(l+m)(l+m+1)\}^{\frac{1}{2}}\hbar$. For each such partial wave a phase shift δ_{ml} is introduced by the scattering field. The total elastic scattering cross section averaged over all orientations of the molecular axis, becomes

$$\sigma_t = \sum_{m,l} q_{m,1} \quad \cdots\cdots \quad 2{\cdot}4$$

where
$$q_{m,1} = \frac{2}{k^2} \sin^2 \delta_{m1} \qquad m = 0$$
$$= \frac{4}{k^2} \sin^2 \delta_{m1} \qquad m \neq 0$$

and K is as usual equal to $mv/\hbar$ where v = electron velocity. Associated with each partial wave is an angular distribution function. This depends for a fixed orientation of the molecular axis, on the angles specifying the directions of the incident and scattered electrons with respect to the molecular axis.

If θ = Angle between the direction of scattered electron and molecular axis. ϕ = Azimuthal angle specifying the plane containing the molecular axis and the direction of scattering. While w, α are similar angles defining the direction of incidence. Under these conditions the scattered intensity $I(\theta)$ is found to be

$$I(\theta) = +K^{-2} \left| \sum_{m,l} (e^{2i\delta_{m,l}} - 1)\, S_{m,l}(kd, \cos\theta)\, S_{m,l}(kd, \cos w) \cos(\phi - \alpha) \right|^2 \quad \cdots\cdots\ \cdots\ 2.5$$

with $\cos\theta = \cos\theta \cos w + \sin\theta \sin w \cos(\phi - \alpha)$ 2.6

As pointed above, the expression 2.5 refers to a fixed molecular orientation and accordingly must be averaged over all possible orientations.

As $K \rightarrow 0$ i.e. For slow electrons all the partial cross section tend to zero except q_{00} which tends to a finite value. The corresponding angular function S_{00} also tends to a constant value as $K \longrightarrow 0$, so the averaged angular distribution tends to become spherically symmetrical for sufficiently slow electrons just as for atoms.

In carrying out detailed calculations involving determination of the phases $\delta_{m,l}$ it is necessary to confine oneself to axially symmetrical scattering potentials which permit the separation of the spheroidal coordinates in the wave equation. It has, nevertheless, been possible to choose forms which provide a satisfactory representation of the observed scattering by many molecules. In the first detailed study on these lines stier (Loc-cit) used for the potential of the molecular field

$$V = -2 Z \epsilon^{2} d^{-1} \rho f(\rho) / (\rho^{2} - \mu^{2}) \ldots\ldots 2.7$$

where $\rho = \frac{r + p}{d}$, $\mu = \frac{r - p}{d}$ Z = effective nuclear charge and r, p, refers to the distances from the centres of the two atoms in the molecule $f(\rho)$ was taken to be of the form

$$f(\rho) = (\rho - \rho_0)^2 / (\rho_0 - 1)^2$$
$$= 0 \qquad \rho > \rho_0$$

Two parameters ρ_0 and Z are thus available for adjustment of theory to agree with observation. Choice of the values $\rho_0 = 3.46$,

$Z = 4.08$ gave good agreement with observed cross section curves for electrons of energy less than 10 eV.

The most extensive calculations have been carried out by Fisk (Loc-cit) who was guided by the method of Morse and Allis (1931) for dealing with scattering by atoms. He also took V in the form (7) but with

$$f(\rho) = 1 - \frac{\rho_0}{\rho}\left\{\frac{\rho - 1}{\rho_0 + 1}\right\}^2 \qquad \ldots\ldots \quad 2.8$$

and studied the variation of $\delta_{m,l}$ and hence of the q_{ml}, with two parameters β and x exactly analogous to those introduced by Morse and Allis for atoms. Thus $\beta^2 = 1/4\ Z\ d\ \rho_0$ and $x = \rho_0\ kd$ The method was applied to hydrogen, nitrogen, oxygen and chlorine. These methods are not applicable to chlorine the observed total cross section for Cl_2 was very much greater than the theoretical cross section over the range of electron energies investigated. Hund (1932) tried to applied the approximate statistical method to molecular field.

One further type of molecular scattering problem was amenable to approximate theoretical treatment. This arise when the molecule possesses such a high degree of symmetry that its scattering field is nearly spherically symmetrical. Buckingham, Massey and Tibbs (1941) have calculated a spherically symmetrical average field for the methane molecule by first averaging the field due to protons over a sphere and then applying the usual self consistent field method of Hartree. Massey (1935) and Wu (1947) have calculated the probability of exciting a vibrational quantum of H_2 by applying the usual collision theory. Massey finds that it is necessary to allow for the variation with nuclear separation of the screening effect of one atom on the field of the other in order to obtain agreement with Ramien's (1931). This is equivalent to supposing that the electron acts not purely dynamically but by changing the relative energy of the atoms due to its Coulomb field, a possibility first pointed out by Franck (1926). It has also been pointed out by Massey (1932) that the excitation of rotational motion in molecule possessing a dipole moment is likely to be quite efficient. The small mass of the electron is partly compensated by the great range at which it can interact with the molecule, so the effective couple it can exert is not necessarily small. Bennett & Thomas (1942) have made a rough analysis of the observed value of for Hydrogen in which they show that the efficiancy of rotational excitation must be quite high even in this molecule which possesses no dipole moment.

For nonpolar molecules Vogt and Wannier (1954) assumed that the interaction potential between ions or electrons ~~moving ions or electrons~~ moving through a nonpolar gas of relatively small molecules is given by

$$V = -e^2 \alpha / 2r^4 \qquad \ldots\ldots \quad \ldots\ldots 2.9$$

They solved under certain assumptions the wave equation for particle moving in such a potential. In the limit of low velocities, they gave a quantum mechanical cross section for spiralling collisions equal to

$$\sigma_0 = 4\pi\,(e2\alpha / mv^2)^{1/2} \quad \ldots\ldots\ldots \quad 2.10$$

$$\text{or}\quad \sigma_0 = A/v \quad \ldots\ldots\ldots \quad 2.11$$

$$\text{where}\quad A = 4\pi e\, m^{-1/2}\, \alpha^{1/2}$$

An expression relating σ and W (drift velocity) was given by Allis (1956)

$$W = \frac{4}{3}\,\frac{e}{m}\,\frac{E}{P}\,\frac{1}{n}\int_0^{\sigma} f_0\,\frac{d}{dv}\left(\frac{v^2}{\sigma}\right)dv \quad 2.12$$

Where E is the electric field, P is the pressure of the gas at $300^{o}K$, N is the number density of the gas molecule at 1 torr and $300^{o}K$, V is the electron velocity and f_o is the spherically symmetrical term in the expansion of the electron velocity distribution. From equation 2.12, σ can be calculated in principle, from electron drift velocity data if the energy distribution $f(\epsilon, E/P)$ in the electron swarm is known. In practice, however an assumed velocity dependence of simplyfies the analysis.

In experiments, generally $f(\epsilon, E/P)$ is Maxwellian for low E/P where W varies liniarly with E/P thus f_o of equation 2.12 is

$$f_o = (m/ 2\pi k T)^{3/2} \exp(-mv^2/ 2kT) \quad \ldots .2.13$$

According to Vogt and Wanniar theory using of equation 2.11

and 2.13 gives

$$W = (e/m)\ (E/P)\ n^{-1}\ A^{-1} \quad \ldots\ldots\ldots\ 2.14$$

2.3 DESCRIPTION FOR NONPOLAR MOLECULES :-

I Rotational close coupling theory :-

A primary distinction between electron atom and electron molecule collision is the assuredly anisotrop~~h~~ic charge distribution of the target in the latter case. In the case of rotational excitation, this anisotrop~~h~~y is particularly important in that classicaly speaking, its interaction with the incident electron provides the necessary torque required to change the angular momentum of the molecule. Then it can be expected that the rotational excitation to be favoured by a long ' lever arm ' and it is indeed found that the long range portion of the electron molecule anisotropic interaction dominates the rotational excitation process at low energies. In fact for homonuclear diatomic target molecule the pure r^{-3} electron - quadrupole interaction sufficient to describe rotational excitation at least in the immediate vicinity of thresold as observed by Gerjouy & Stein (1955).

Dalgarno & Moffett (1963), further demonstrated that the r^{-4} adiabetic polarization interaction also anisotropic, is important just above thresold and can lead to much larger cross section at higher energies. However the question of how to include polarization has remained for some time and although much progress has been made is still not completely resolved, at least in the context of close coupling. The inclusion of an explicit polarization potential of this r^{-4} type assumes that the bound molecular electrons relax adiabatically in the field of the scattering electron. Such an assumption is clearly bad at high incident energies, and even the low energy range of applicability is not certain.

At incident electron energies so low that only rotational excitation channels are open, the incident electron speed has the convenient properties of being small compared to electron speeds in the target molecule (making plusible the assumption that the target electrons can relax adiabetically in the field of the incident electron), while simulteneously being large compared to the rotational speeds of the target nuclei (making plusible the fixed nuclei approximation).

The close couple approximation is obtained by making some hopefully wise truncation of the set of coupled equations. The first attempt at a close coupling calculation for electron molecule scattering was made by Lane & Geltman (1967). Since only the ground electronic state was included, the effects of polarization which can be described in terms of virtual electronic excitation (castillego etal, 1960) were not being taken in to account. The internuclear separation was taken as fixed at the equilibrium value $R_e = 1.4\ a_0$ and the exchange metrix elements were ignored. It was expected that this later approximation would primarily affect the S-Wave scattering field at that time to be unimportant in rotational excitation. The electron molecule polarization, however, being a long range and anisotropic interaction, was known to be important (Dalgarno & Moffett, 1963) and was included in a phenomenological manner. For purpose primarily of illustration, a short range modification of the potential was made to ' mock ' the effect of exchange.

There were two particularly disturbing features of these early closecoupling calculations by Lane & Geltman (1967)

(1) The need for a semiempirical determination of the polarization interaction.

(2) The neglect of exchange.

The polarization question seemed more pressing at the time, so an attempt was made by Lane & Henry (1968) to calculate a reasonable polarization potential from first principles. The procedure, akin to well known polarized oribital method of Temkin (1957) was based on the Ray leigh Ritz variational principle. Using the variationally determined polarization interaction, Henry & Lane (1969) began another close coupling calculations similar to the earlier calculations but including the exchange matrix elements explicitly in the coupled equation. No adjustable parameters were present. Ardill and Davison (1968) already has reported a distorted wave calculation of p-wave scattering including exchange, and found the contribution to be significent. They did not however include the important polarization effects.

Before the improved close coupling calculations were completed Crompton, Gibson and Mciontosh (1969) had begûn to obtain $j = 0 \rightarrow 2$ rotational cross section via electron drift and diffusion measurement in parahydrogen. That para hydrogen observation would provide good test of the theory had been suggested by Gerjuoy and Stain (1955).

At higher energies where $j = 1 \rightarrow 3$ transitions are sizable the agreement between these close coupling calcula--tions and the measurements is not quite so good with exchange as well as polariazation included in the close coupling calcula--tions, expected to be able to represent the S-wave scattering which is particularly sensitive to short range effects and dominates the elastic (and hance total) cross section below a few eV. Massey and Ridley (1956) being the first of such calculations. Hara (1969) considered two centre elastic scattering without polarization. Hara (1969 b) also had calculated cross section considering some what weak polarization potential which may account for the better agreement he obtains with experiments.

Though close coupling method gives better agreement with experiment for H_2, for heavier diatomic molecule it becomes very complicated. In fact the utility of the approximation still is in question. Even for H_2 in order to further improve the calculations, a full polarized orbital calculation probably will be necessary, needless to say, processes involving pure vibrational excitation or simultaneous vibrational and rotational excitation, are more complicated rather remains a chalange to the theorist, Similarly, the electronic excitation cross sections, with their observed resonance structure are a challange to the close coupling method, and a substential effort is being made in this direction at the present time. A review of resonance scattering is made by Bardsley and Mandal (1968). The theory of dissociative recombina--tion, a process resulting from the collision of an electron with a positively charged molecular ion has been reviewed by Bardsley and Binodi (1970).

II. Development of fixed nuclei approximation and the theory of rotational excitation :-

For the purpose of calculating purely elastic scattering amplitudes the molecule can be replaced by one in which the nuclie are fixed during the whole scattering process. If the electron velocity v is much faster than the nuclear rotational velocities V, this assumption is reasonable (though not rigorous). In terms of the incident electron energy E the condition $v > V$ implies $E = 1/2mv^2 >> 1/2mV^2 = 1/2(m/M) MV^2$ or $E >> (m/M)E_{rot}$. Where $E_{rot} = 1/2MV^2$, is the molecular rotational kinetic energy. Even in the lightest molecule H_2 this condition requires $E >> 10^{-4}$eV.

The first application of the fixed nuclei model was carried out by Stier and Fisk (1932). It is observed that fixed nuclei model yeilds total electron molecule scattering cross sections of the right order of magnitude. For H_2 Fisk's results fits below 5eV., Theoretical cross section are definitly too low. In this energy range the more sophisticated calculations are made by Lane and Geltman (1967). They made the distict improvement in Fisk's results. On the very low energy side ($\angle \approx 1$ eV.) Fisk's results are definitely too high and going in wrong direction, a feature also manifested by Lane and Geltman's theoretical results.

These low energy failures of the theory presumably are to be ascribed to the neglect of electron exchange in Fisk's and Lane and Geltman's calculations. Actually it took over twenty years beyond Fisk's calculations to demonstrate, that exchange is important in electron molecule collisions; Although even before Fisk the profound effect of exchange in electron atom scattering had been shown by Morse & Allis (1933). This demonstration of the effect of exchange in e - H_2 total cross section was first given by Massey and Rdley (1956). They employed complete antisymmetrized form

$$\Psi(1, 2, 3) = \sum F(\vec{r}_i)\ (\vec{r}_j, \vec{r}_k)\ X_i^{+}\ (X_j^{+}, X_K^{+} - X_j^{-} X_k^{+}) \qquad \ldots\ldots 2.15.$$

Where i is the subscript for incident electron, while j and k the molecular electron. $X_{\mp}$ are the usual single particle spin 1/2 eigen functions. The special part of the target molecular ground state eigen function employed by Massey and

and Ridley was

$$\phi (j, k) = W (j) \; W (k)$$
$$W (j) = N \exp (- q \lambda_j) \; (1 + f \mu_j^2 + g \lambda_j) \ldots . 2.16$$

From Coulson (1938) here q, f.g. are known constants and are the spheroidial variables (referring to the jth electron).

Massey and Ridley then were able to calculate the S - wave scattering phase shift δ_{00} from the asymptotic forms

$$F(r_{1s}) = 1 / (1+a2)^{1/2} - \left[C (\lambda_i -1) \right]^{-1} X \; (\sin C(\lambda_i -1)$$
$$\left\{ a + b \exp \left[- \gamma (\lambda_i -1) \right] \right\} X \left\{ 1 - \exp \left[- \gamma (\lambda_i - 1) \right] \right\} \cos$$
$$(c\lambda_i - 1) \longrightarrow \sin (C \lambda_i + \delta_{00}) / C \lambda_i \; . \; \lambda_i \rightarrow \infty \quad \ldots 2.17$$

Where a,b, and γ are as yet undetermined constants, and

$$c = 1/2 \, kR_{ab} \quad \ldots\ldots \quad \ldots\ldots \quad 2.18$$

The best value of a,b and were found using Kohn (1948) variational principle. In the Kohn principle one varies the expression

$$L = \int \varphi (H - E) \varphi \quad \ldots . \quad \ldots . \quad \ldots . \quad 2.19$$

Massey and Ridley, rewrote equation 2.19 in the form,

$$L = L_D + L_E$$

Where L_D involves only direct integrals and L_E involves exchange integrals only. When Massey and Ridley kept only L_D; the resultant

S - wave phase shift was such as to give huge low energy cross section, reminiscent of the Fisk result and in gross disagreement with experiment. With retention of I_E, however the cross section is lowered drametically. Thus for the first time, one could say that a fundamental electron molecule collision calculations was in semi quantitetive agreement with experiment. Similar behaviour of calculations including exchange but omitting polarization was made by Tulley and Berry (1969).

The calculation of Massey and Ridley can be regarded as the first quantitetive calculation of e - H_2 scattering cross section. The next step in improving the accuracy is to include higher partial waves. To do this in spheroidial coordinates, while at the same time retaining the electron - electron interaction as did Massey and Ridley one must go beyond the separable spheroidal analysis of Stier and Fisk, This was infact done first by Nagahara (1953). But his calculations for e-H_2 scattering did not include exchange and any agreement with experiment. The non separable spheroidial analysis has been reported by Takayanagi (1967) and by Hara (1969).

In summing let us note the disadvantage of spheroidial analysis, namely that the spheroidial harmonics in terms of which the scattering amplitude is expressed depends on the inter nuclear distance, R_{AB}, of the particular molecule being investifated. This means that the experimentalist would infer different scattering parameter for different molecules; even if their observed scattering rates were the same.

Not only is this in-convanient, but it is really unphysical, because the inter nuclear separation is something which is not observed in the scattering experiment at all. If we made the analysis in terms of the more customary spherical harmonics this problem would not arise.

III. Single Centre Expansion :-

A single - centre spherical Harmonic expansion for electron molecule collision first was systematically employed by Temkin and Vasavada (1967) whose work was extended in Temkin, Vasavada, Chang and Silver (1969).

The single centre spherical Harmonic partial wave expansion can be carried out consistantly even for the spherically non symmetric targets occuring in electron molecule collisions, moreover this expansion in principle yeilds a complete description of the collision. In order that the single centre expansion converge reasonably rapidly , the incident electron should not be able to penetrate in to the molecular core.

Historically Carter, March & Vincent (1958) calculated single centred approximation. Their calculations were extremely crude and exchange was taken into account only in an approximate way. Neverthless this was the first single centered electron molecule scattering calculations and it supported the conclusion of Massey and Ridley.

IV. Adiabetic Nuclei Theory of rotational excitation :-

Rotational excitation is only possible if the nuclei actually are capable of rotation. Which means that we must now abandon the fixed nuclei model. Incident electron velocity V often are large compared to nuclear rotational velocity V. Hence it is possible to develop theories of rotational excitation for which the fixed nuclei calculations serve as a starting point. Indeed such a theory has been developed and infact the basic formula first was derived by Chase (1956) in the context of nuclear physics, where the problem was the excitation of deformed nuclei. Use of Chase's theory to compute rotational excitation customarily is termed the adiabetic theory of rotational excitation, because the nuclei are moving showly compared to the incident electron.

Oksyuk (1966) was one of the first to apply Chase's theory seriously to electron diatomic molecule collisions. He did obtain useful expressions in the approximations that the partial waves (in the scattered electron wave functions) are uncoupled. However the phase shifts Oksyuk used were derived from a calculation along the lines of Fisk (1936) Mittleman, Peacher and Rozsnyai (1968), applied Chase's theory to rotational excitation of polar (i.e. hetronuclear) molecules, but again their calculation did not utilise scattering parameters, from a detailed fixed nuclei calculation, but used rather a special soluble model due to Mittleman & Vonholdt (1965) . The adiabetic nuclei cross sections in the full coupled form for homonuclear molecules in Σ states were worked out for neutrals by Chang & Temkin (1969) and for charged targets (molecular ions) by Chang and Temkin (1970). Independently Hara (1969) has derived the necessary formula and has applied the adiabetic nuclei theory to his spheroidial calculations of $e - H_2$ scattering. Finally Temkin & Feisal (1971) have derived the generalized formula for non Σ states.

Understanding of electron molecule scattering has progressed significantly in recent years. For the purpose of incorporating both exchange and polarization, the fixed nuclei theory provides a reliable and convenient method of calculating the average cross section, moreover coupled with the adiabetic nuclei theory, it becomes an extremely effective not very arduous method for calculating most aspects of rotational excitation. However the validity and utility of the fixed nuclei and adiabetic nuclei approximations must not be confused with the validity of single centre expansions, whose reliability is by no means established. Unquestionably single centre expansion do provide an approximately quantitetive description; on the other hand, the degree of accuracy practicably attainable with single centre expansion is suspect, particularly for heavier diatomics. This is seen in Burke and Sinfailen (1970) calculations of $e^- - N_2$ scattering

2.4 Description for Polar molecules :-

The large class of low symmetry molecules which possess a permanent electric dipole moment have, as a group received considerable attention in the last few years. Particularly significant are the large number of organic molecules which fall within this group many of which are strongly polar with dipole moments greater than 1.5×10^{-18} esu.cm. or 1.5 debye units.

A great deal of effort has been expanded in studying experimentally and theoretically the interaction of low energy electrons with such dipolar systems. These processes find application in a wide variety of problems in radiation chemistry atmoshpheric physics, astrophysics and gaseous electronics.

A succienct review of the subject of electron collision frequencies in polar gases was published in 1967 by Crawford, Dalgarno & Hays in which a number of theoretical questions were examined and clarified and the existing experimental data were symmarized . A number of more detailed theoretical studies of the general properties of elastic and inelastic low energy collision cross sections for electrons on dipolar system is made. Much of the motivation for recent studies of low energy electron collisions with dipolar target systems has stemmed from the discovery that in a quantum mechanical treatment, the electric dipole field exhibits a critical binding property for charged particles.

Several indepandent investigators have shown that no bound state exists for a particle of electronic charge and mass in the field of a fixed dipole moment, D is less than

$1{\cdot}625 \times 10^{-18}$ esu.cm. or $0{\cdot}639\ ea_0$ in atomic units where e is the electronic charged a_0 = Bohr radius and that an infinite number of bound states exists for D larger than this critical value. The existence of a critical moment for the dipole field has raised considerable speculation as to the behaviour of the scattering cross sections of low energy electrons on polar molecules whose dipole moments lie near $0{\cdot}639\ ea_0$. Conflicting predictions have been made of the presence or absence of large change in these cross sections for supercritical as compared to subcritical polar molecules.

More recently Garratt (1970-71) has shown that the critical binding property of a non stationary molecular type dipolar field is quite different from that of the stationary dipole and that the critical dipole moment is not a fixed number but is instead a function of the dipole length. The moment of inertia and the rotational state of the molecular source of the dipole field. Thus the value $0{\cdot}639\ ea_0$, which is the critical moment for a fixed dipolar system, can not be used as a basis ~~a~~for comparision in relating scattering cross sections between a number of different molecules whose dipole moments cover a specific range of values of D.

2.5 SCATTERING BY A STATIONARY DIPOLE :-

Electron collision with molecular target systems are characterized by projectile velocities which are large as compared to rates of nuclear motion in the target system. Thus even for thermal energy collision, the Born Oppenheimer approximation may be invoked and the scattering can be treated by a fixed molecular orientation and subsequently averaging over the orientation of the target. The problem of electron scattering by a dipolar system of fixed orientation was first solved by Altshuler (1957). In this solutions for a point dipole target the differential cross section diverged in the forward direction with the result that the total elastic scattering cross section also diverged. The momentum transfer cross section, averaged over dipole orientation took the form

$$\sigma_m = \frac{8\pi}{3K^2}\left[\frac{D\,e\,m}{\hbar^2}\right]^2 \qquad \ldots\ldots\ 2.20$$

Here D is the dipole moment of the target, e and m are the charged and mass of the electron and k is the wave vector.

Further the momentum transfer cross section was expressed in πa_0^2 units and energy was converted in Volt units the final expression is of the form

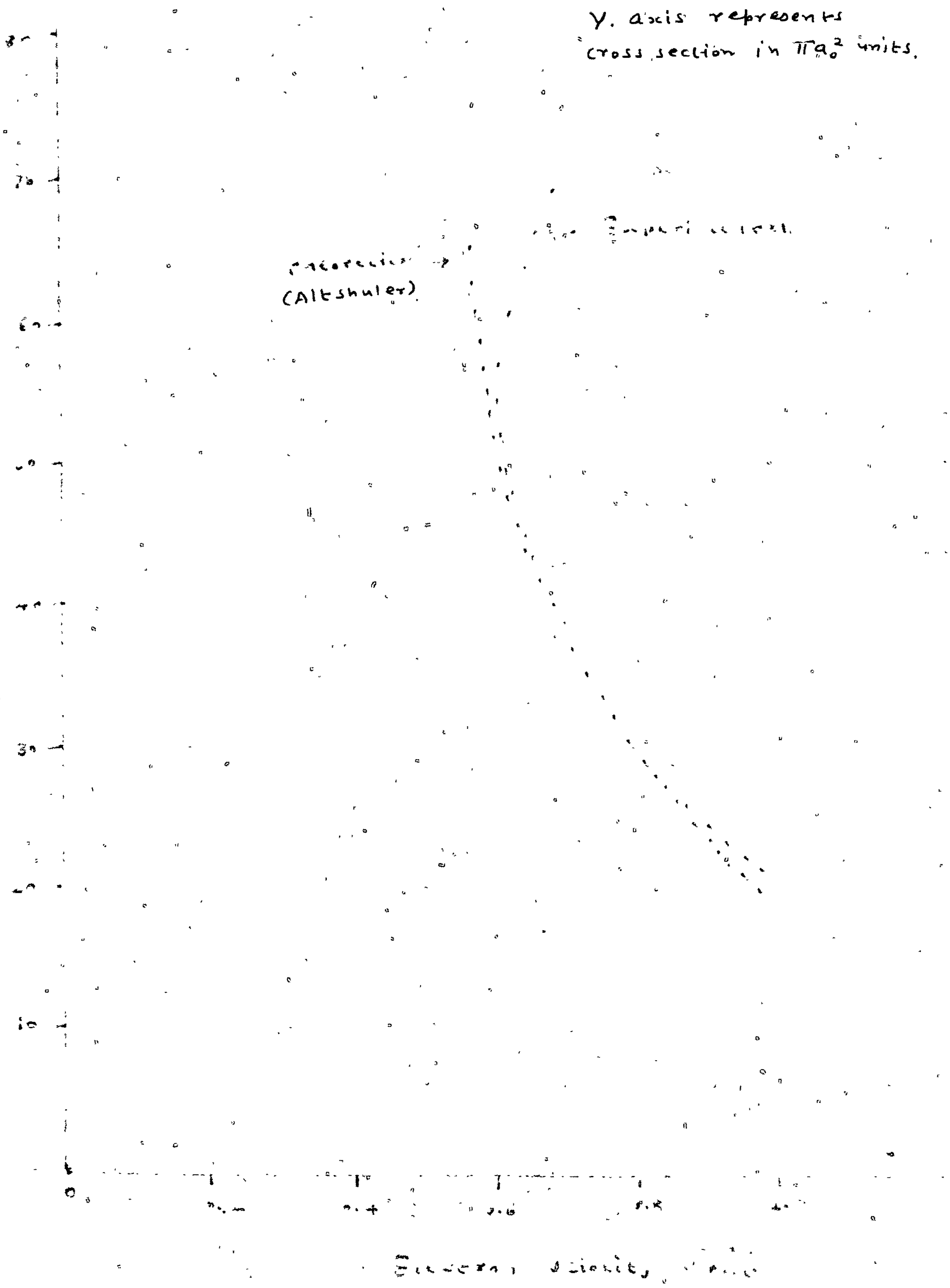
$$Q' = 5.6\ \left(\frac{D'^2}{E'^2}\right) \quad \text{where} \quad D' = \frac{D\ \text{esu.}}{10^{-18}} \qquad \text{---- } (2.21)$$

and E' = Electron energy in $\sqrt{\text{Volt}}$.

Altshuler's results are exhibited in graph I.

Altshuler further assumed that a possible source of error apart from the use of Born approximation may be the extrapolation of pure dipole interaction all the way

Graph. 1.


Y. axis represents cross section in πa_0^2 units.
Experiment
Theoretical (Altshuler)
80
70
60
50
40
30
20
10
0
0.2
0.4
0.6
0.8
1.0
Electron velocity

to the origin . An order of magnitude estimated was carried out by choosing a cut off point at a distance equal to $2a_0$. The correction term found in this way was

$$\Delta Q = 4\pi \left(\frac{16m}{3h^2} a_0^3 \quad v_0^3 \right)^2 \qquad \ldots\ldots \quad \ldots \; 2.22$$

where v_0 = Assumed constant potential for the spherically symmetric part of the potential. The correction is very small compared to cross section given in (2.21) especially for the lower incident energies . Conversely we may infer that in the case of very weak dipole moments the near field corrections can diminished the accuracy of the Altshuler's theory.

An exact solution for electron scattering by a point stationary dipole was obtained by Mittleman and Vonholdt (1965). By separating the wave function in spherical coordinates they obtained the exact solution for the scattering amplitude by using this amplitude they have calculated diffusion cross section. Their expression for momentum transfer cross section is

$$\sigma(\alpha) = \frac{2}{3} \frac{\pi}{k^2} \alpha^2 \qquad \ldots\ldots\ldots \quad \ldots \; 2.23$$

where $\alpha = 2\,D/ea_0$

Further they have observed that their results for NH_3 is about 12 % low, for H_2O it is about 20 % low and for HCN more than a factor of 2, too low. In short the total cross section diverged and that the momentum transfer cross section averaged over orientation of the dipole agreed with Altshuler's calculations for small D but increased rapidly for larger dipole moments with a singularity at the critical moment D = 0.639 ea_0. In a comparis~~i~~on with experimental cross sections for thermal energy electrons on polar molecules (Craford etal 1967). The momentum transfer cross section obtained in the exact treatment of scattering from a point dipole of fixed orientation (Mittleman 1965) gave much pooerer agreement with the data than did the Born treatment of the same ppoblem (Altshuler 1957). This was attributed to the difficulties associated with the strong singularity at the origin in the point dipole field.

Further Mittleman etal (1968) have studied the rotational excitation of polar molecules. They consider that the electron transit time is short compared to rotational periods with the result of an E^{-1} behaviour of the cross section. Diffusion cross section are also reported for Δl = 0,1,2 significant corrections to the Born approximation are obtained for larger dipole moments. The diffusion cross section was obtained as

$$\sigma_{l,l'} = \frac{2l+1}{k^2}\,\pi \sum_{\lambda=0}^{\infty} (2 \quad + 1) \begin{pmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 Z(\lambda) \quad \ldots 2.24$$

where

$$Z(\lambda) = \sum_{s,t} \Bigg\{ \big| Z_{\lambda st} + \mathrm{Re}\, Z_{\lambda st} Z^*_{\lambda, s+1, t+1} \sqrt{\frac{(\lambda+s+t+2)(\lambda+s+t+3)(s+t-\lambda+1)(s+t-\lambda+2)}{(2s+1)(2s+3)(2t+1)(2t+3)}} -$$

$$\mathrm{Re}\, Z_{\lambda st} Z^*_{\lambda, s+1, t-1} \sqrt{\frac{(\lambda+t-s-1)(\lambda+t-s)(\lambda+s-t+1)(s+t-\lambda+2)}{(2s+1)(2s+3)(2t-1)(2t+1)}} \Bigg\} \quad \ldots\ldots\ldots (2.25)$$

and $$Z_{\lambda st} = \sum_{m} \rho^{m}_{st} \, (-1)^{m} \begin{pmatrix} \lambda & s & t \\ o & m & m \end{pmatrix} \quad \ldots\ldots \quad \ldots \; 2.26$$

The λ sum in 2.24 was restricted by the 3j symbol to $|1 - 1'| \leq \lambda \leq 1 + 1'$.

The calculations for various transition was carried out and it was observed that $\Delta 1 = 0$. The diffusion cross section was observed to rise rapidly as α but almost, it was, flat function of 1. A small peak at 1 = 1 in each case was also observed. Further it was observed that $\Delta \ell = 0$ transition contributes significantly for $\alpha \geq 0.6$. The $\Delta \ell = 1$ cross section does not rise as rapidly as the $\Delta \ell = 0$ as a function of α but does grow some what more rapidly as a function of ℓ. Further in their work Mittleman etal have considered the high energy correction, low energy correction. Also they have tried the cross section for dipole moment greater than the critical value.

The variational approach to this problem is made by us. We have used the L. Mower's modified Schwinger's variational method. Our expression for momentum transfer cross section is

$$Q_d' = \frac{2}{3} \alpha^{2} \left[1 + 3 \, (\alpha/2)^{2} \Delta_{\ell} \right] \quad \ldots\ldots \quad 2.27$$

where α is the dimention less dipole moment $= 2D/ea_0$. For different values of ℓ momentum transfer cross section is calculated, it is found that for most of the molecules $\ell = 0$ term gives fairly good agreement with experiment also momentum transfer cross section for thermal electrons are calculated by these methods.

The point dipole approximation, with its associated difficulties due to the strong singularity of an r^{-2} term, was avoided by Shimizu (1963) and by Takayanagi and Itikawa (1968). These authors considered electron scattering by a finite dipole, composed of two fixed charges of opposite sign, separated by a distance 2a. Shimizu analyzed the problem in prolate spheroidial coordinates and obtained momentum transfer cross section (averaged over dipole orientations) which were significantly below the Born results of Altshuler (1957). Takayanagi and Itikawa expanded the calculations made by Shimizu, their expansion for total(σ) and momentum transfer cross section σ_m is given by

$$\left.\begin{aligned} \sigma &= I_o \\ \sigma_m &= I_o - I_1 \end{aligned}\right\} \qquad \cdots\cdots\cdots \quad 2.28$$

where $$I_o = \frac{4\pi}{k^2} \sum_{m \geq 0} \varepsilon_m \sum_{n' \geq m} \left| \sum_{l \geq m} D^m_{l,n}\; f^n_{l,m}\; \sin\eta^n_{l,m} \right|^2 \qquad \cdots\cdots \quad \cdots\cdots \quad 2.29$$

$$I_1 = \frac{4\pi}{k^2} \sum_{m \geq 0} \sum_{\bar m \geq 0} \sum_{l \geq m} \sum_{\bar l \geq \bar m} \sum_{n \geq m} \sum_{n' \geq m} \sum_{\bar n \geq \bar m} \sum_{\bar n' \geq m}$$

$$R_e\left(i^{n'-n}\, i^{n-n'}\, D^m_{ln'}\; D^{\bar m *}_{l\bar n} \right) \times f^n_{lm}\; f^{\bar n}_{\bar l \bar m} \sin\eta^n_{lm} \sin\eta^{\bar n}_{\bar l \bar m}$$

$$\Big[\varepsilon_m \delta_{m\,m} K^{(1)}(\eta_n ; m)\; K^{(1)}(\eta'_{\bar n}\; m) + 2\delta_{\bar m, m+1}$$

$$K^{(2)}(\bar\eta_{n,m})\; K^{(2)}(\bar\eta' n' ; m) \qquad \cdots \quad \cdots \quad 2.30$$

where $D^{m}_{l,m} = G^{m*}_{nl} = f^{n}_{lm} \exp (i \eta^{n}_{lm})$

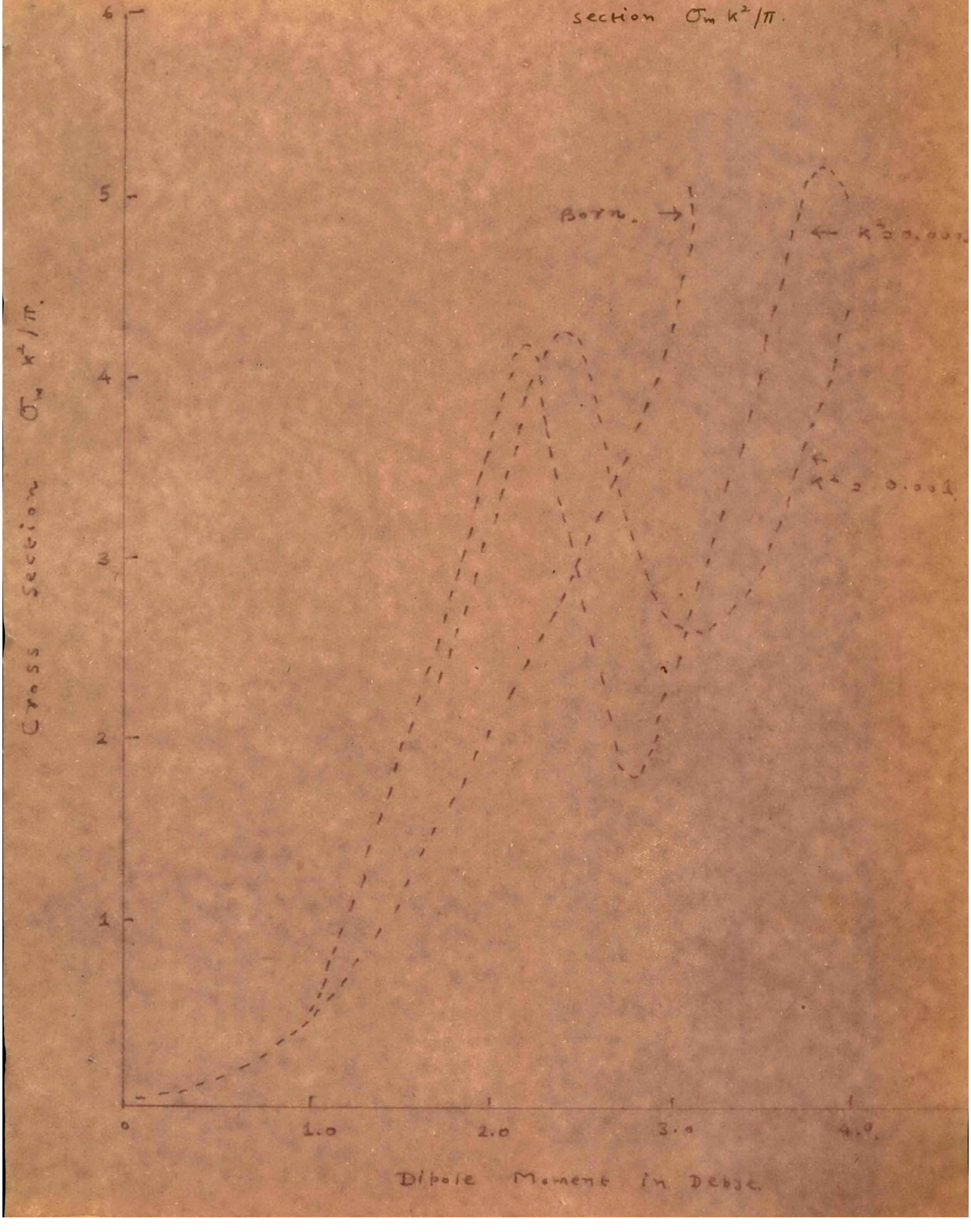
f^{n}_{lm} = Eigen vector which can be evaluated by secular equations. $\eta^{n}_{lm} = \Delta_{lm} + 1/2 (n - 1)\pi$

Δ_{lm} = phase shift.

In the graph 2, momentum transfer cross section's behaviour with dipole moment is shown. Born cross section is also drawn ofcourse Born cross section can not be compared with Takayanagi and Itikawa's calculations as former includes terms of all m. They covered a very small range of dipole moment(D 1 a.u.) In their calculations however they found that the contribution of the term of $m \geq 4$ to the momentum transfer cross section is very small so that comparision upto $m \leq 3$ can be made with Born cross section. From the graph 2 it is seen that for the electron with thermal energy ($K^2 \sim 0.001$, if we take 2a = 1 a.u.), the momentum transfer cross section calculated with the use of two centered dipolar field exceeds that obtained in the Born approximation. This may explain a large cross section of some polar molecules especially of ~~H_2O~~ H_2O . For $D < 0.5$ a.u. it can be observed that from the graph the cross section calculated by Takayanagi - Itikawa does not differ much from the Born approximation. Hence it seems that their mechanism can be effective for smaller dipole moment and that the anamalously large cross section of H_2S, remains unexplained.

Takayanagi - Itikawa also studied the short

Graph. 2.



Y. axis represents cross section $\sigma_m k^2/\pi$.

range effect on the potential by considering Coulomb two centered screening short range potential. It is observed that the addition of the short range attractive potential has the same effect as an increase of the dipole moment. Further a finite dipole calculations in more simpler way is made by us (1972). It is observed that the value of diffusion cross section agrees with point dipole approximation. Also an addition of short range force considering Coulomb one centered potential is made by us. The momentum transfer cross section for thermal electron is found less than experimental values. By the adjustment of a parameter from molecule to molecule exact agreement is found with the experiment .

The results of Takayanagi - Itikawa (1968) presented an interesting question in connection with scattering by a dipolar field. Since the total cross section for scattering by a point dipole diverges (Mittleman et al 196) and those of finite dipole (Takayanagi at al 1968) are finite the implication is that removal of the strong singularity at r = 0 in the potential function also removes the divergence in the forward scattering and in the total elastic scattering cross section. Garratt (1971) has shown that this is not the case. The total scattering cross section for a fixed dipolar system does diverge regardless of the presence or absence of a strong singularity at r = 0. The behaviour is due to the long range nature of the interaction which results in a very slow decrease in the partial wave phase shifts of the spheroidial wave decomposition of the scattering problem. The series expansion for the total scattering cross section does not converge and consequently this quantity is undefined. The finite results obtained by Takayanagi are due to numerical approximation in a nonconversant series.

By applying the close coupling method to polar molecules namely CN and HCl Takayanagi and Itikawa (1969) calculated rotational transition cross section and differential cross section. The transitions from the ground state of rotation are considered and the cross sections $\sigma(\ell = 0 \rightarrow \ell = 1).\sigma(\ell = 0 \rightarrow \ell = 2)$ are calculated. ℓ represents the rotational states of the molecule. For $\sigma(0 \rightarrow 1)$ they made the comparision with the calculation in Born approximation and it was observed that Born results are fairly accurate even for a quite large dipole moment (atleast upto 1 ea_o). These occurs a shape resonnance in the elastic process $0 \rightarrow 0$, which may explain the peak appearing at about 10 eV. of the incident energy in the measured total cross section for e - HCl collision.

Further they have observed that consideration of potential of the form

$$V(S.r) = -\frac{D}{r^2}\left[1 - \exp\left\{-(r/r_c)^6\right\}\right] X P_1 (S.r) \quad .2.31.$$

with a cut of distance $r_c = 1\ a_o$ for the incident energy 0.03 eV they observed a peak in total and elastic cross section at about D = 1 a.u. The partial wave analysis shows that this peak is due to the contribution of the incident S-wave. It may be attributed to a shape resonnance, When the term " resonnance " is used in a wider sense taking place for an appropriate depth of the potential well for p wave and the other partial waves of this kinds does not occur at least up to D = 1.5 a.u, so that the inelastic cross section for which s wave contribution is minor has no peaks in the region of D $\leqslant$ 1.5 a.u. Takayanagi and Itikawa have investigated an electron scattering by a fixed two centre dipole and shown that the scattering cross section has a peak at a certain value of the dipole moment. In that case the s wave contribution is dominant; particularly the rasonant type peak appears only in the s wave cross section for the dipole moment in the range of their calculations. This corresponds to the fact that for the partial waves other than s waves there exist no bound states in the dipole field, unless the dipole moment is much larger (Coulson et al 1967).

Further they have studied the behaviour of momentum transfer cross section dependence on dipole moment, with the same model and same energy, there also they found a peak at about D = 1 a.u. Crow ford (1967) has calculated the momentum transfer cross section for water molecule by close coupling method for which D = 0.73 a.u. He shows that the calculated value of is some what larger than Altshuler's Born approximation method.

A cross section formula for the rotational transition in a symmetric top molecule by electron collision was derived in Born approximation with adopting a general form of electron molecular interaction (Itikawa 1971). This result was applied to electron NH_3 collision. The cross section for the transitions $\Delta K \neq 0$ (K being the quantum number representing the angular momentum around the symmetry axis) was calculated, its magnitude was found to be much less than the dipole excitation cross section for which $\Delta K = 0$. In a large angle scattering however the differential cross section for $\Delta K = 0$ has a non - negligible effect. Further the rotational excitation of a polyatomic molecule by electron collision was considered as caused by the polarization interaction as well as by the electronic one (Itikawa 1970-71). This effect was incorporated in to the Born formula derived for the rotational cross section of symmetric top molecules.

A cross section formula was obtained for the electron impact rotational transition in an asymmetric top molecule, with use of the Born approximation. Selection rules were also derived on the basis of the symmetry properties of the molecular rotational wave function. Electron molecular multipole interaction were taken to be considered and rotational cross section are calculated for the transitions among some low lying states.

Y. Singh (1970) has also calculated momentum transfer cross section for CO, N_2O, and CO_2 molecules. CO and N_2O are having small dipole moment while CO_2 is not the polar molecule. He consdiered the potential of the form

$$V(\bar{r}.\bar{s}) = \sum_{\lambda=0} V_\lambda' P_\lambda (\hat{r}.\hat{s}) \qquad \ldots\ldots \quad \ldots\ldots \quad 2.32$$

$$= V_o(r) - \frac{e\mu}{r^2} P_1(\hat{r}\cdot\hat{s}) - \left(\frac{e\Theta}{r^3} + \frac{\alpha' e^2}{r^4}\right) P_2(\hat{r}\cdot\hat{s})$$

where μ and Θ are respectively dipole and quadrupole moments of the molecule and $\alpha' = 1/3\,(\alpha_{\parallel} - \alpha_{\perp})$; $\alpha_{\parallel}$ and $\alpha_{\perp}$ being the polarisabilities of the molecules along directions parallel and perpendicular to its axis; P_1 and P_2 are Legendra polynomials. V_o represents the spherically symmetric part of the potential including shortrange forces and r^{-4} dependent polarization force. He has used Born approximation to the problem. Their expression for momentum transfer cross section is

$$\sigma'_m(j) = \frac{8\pi}{3k^2} \left(\frac{me}{\hbar^2}\right) \Big\{ \mu^2 + \frac{2}{15}(\Theta k)^2 + \frac{2}{15}\pi\alpha' e\Theta k^3 + \frac{1}{80}\pi^2\alpha'^2 e^2 k^4 \Big\} \quad \ldots\ldots\ldots \quad 2{\cdot}33$$

the first term of the above equation is the standard result which appears in the equation of Altshuler (1957) and Crawford et al (1967). It is now evident that the inclusion of terms due to the quadrupole moment and anisotropy in polarizability in the potential energy of interaction leads to an increased cross section, but this is not sufficient to explain the entire difference in experiment and theory. Further for finding out the contribution of V_0 which generates the elastic scattering, the effective range theory originally introduced in nuclear scattering and which is developed for the scattering of a changed particle by a neutral polarizable system. In the effective range theory the scattering amplitude in a certain enery range is completely determimed to a certain accuracy by a small number of parameters and so in principle, just a few experimental points anywhere in the region are sufficient to determine the amplitude over the entire region. The momentum transfer cross section for V_o is thus

$$\sigma_m'' = 4\pi\left\{A^2 + \frac{4\pi}{5a_o} a\, A k + \frac{8}{3a_o} \alpha\, A^2 k^2 \log (ka_o) + C k^2\right\} \quad \ldots 2.34$$

A and C are parameters to be determined by experiment. A is generally referred to as the scattering length. The total momentum transfer cross section is some of the equations 2.33 & 2.34.

The condition for the validity of the derivations of the scattering cross sections, given above is that the distortion of the incoming and outgoing waves are negligible. Distorted wave calculations on H_2 and N_2 made by Takayanagi and Geltman (1965) and Sampson and Mjolsuness (1966) however suggests that for molecules of negative at least in part, can be counter-balanced in the low energy limit by neglecting the contributions of the anisotropy in polarizability.

Further Y.Singh has calculated inelastic cross sections for the same molecules and have compared it with Frost and Phelps (1962).Ultimately it is observed that at energies below the vibrational thresold, the Born approximations gives fairly accurate results and can be used to study the inelastic collision problems provided the transition probability is small and the first order perturbation treatment is appropriate. At energies near and above the vibrational thresold the more refind calculations of distorted wave should be followed.

For explaining the larger cross section for some of the molecules like H_2O, H_2S, D_2O Turner (1966) suggested the momentary capture of the electron. He then calculated the life time of temporarily formed negative ion and capture cross section. According to his theory electrons in addition to being scattered, might also be captured or at least momentarily held by the molecule (Hurst et al 1963). A passing electron can exert a torque on the molecular dipole and might excite the molecule to a higher rotational state. The electron might loose enough energy in doing this to form a bound ionic or quasi trapped state in the field of dipole. The natural decay of this temporary state would supply electrons back in to the swarm, thus introducing a contribution to the momentum transfer cross section not included in Altshuler's theory. Since spacing between rotational states is of the order of thermal energies (KT) stabilized negative ions are not formed by this mechanism. Applying Turner's mechanism Y. Itikawa (1867) have calculated captured cross section. The only change in Turner's calculations made is to treat capture process and the decay process in the unified manner i.e. they applied the second order perturbation theory in which the capture state is to be regarded as intermediate state. It is assumed that has a finite life time. By using a different wave function for final bound state of an electron and calculating scattering amplitude (Desai, Maru and Pandya 1974),by variational method. The life time for temporary negative ion and capture cross section is calculated just as Turner. Higher value of life time and lower value of capture cross section is observed. For the possibility of electron capture one has to examine whether or not a dipole field of arbitrary strength can possess bound states. A number of investigators have shown that bound states exist for an electron in the field of a permanent, finite, stationary electric dipole if the dipole moment D is greater than 1.625×10^{-18}esu.cm (= 0.639 ea_0) and that no bound states exist for D smaller than this critical value. Garrett (1970) has considered the problem of electron binding to a polar molecule in the case where the source of the field is not fixed in space but is a self part of the dymenical system. He found that the minimum moment is every where larger than that for the fixed dipole problem. This is to be expected since motion of the dipole would tend to lower the effective potential felt by a very loosely bound electron. The change in the critical moment due to nuclear motion is quite significant, especially for very small molecules where the D_{min} is as much as 30 % larger than that for fixed dipole. Secondly, the free dipole is unlike the stationary dipole in that the critical moment is no longer independent of the dipole length. Thirdly, it was observed that the minimum moment for an infinitely massive system corresponding to the fixed dipole is approached very slowly with increasing I. In fact, it is necessary to go to unrealistically large moment of inertia ($I = 10^8 \, m_e a_o^2$) in order to get within about 10 % of the fixed dipole value.

2.6 Non Adiabetic Dipolar Scattering :-

In treating electron scattering by polar molecules, the source of the dipolar field is not fixed in space, but is instead a part of the dynamical system and should be included as such in the total Hamiltonian. The dipole scattering problem was first treated by Massey (1932) who did include the rotational term of the target system in the scattering equation. His Born approximation treatment of scattering by a rigid rotator point dipole was later elaborated upon by Takayanagi (1966) and by Crawford et al (1967). In the Born approximation the inelastic cross section $\sigma(J; J')$ for transitions from initial rotational states j to final state j' takes the form,

$$\sigma(j, j+1) = \frac{8\pi}{3k_o^2}\left(\frac{D\,e\,m}{\hbar^2}\right)^2 \frac{j+1}{2j+1} \log \frac{|k_o + k_{jj'}|}{|k_o - k_{jj'}|} \quad \ldots\ 2.35$$

and

$$\sigma(j, j-1) = \frac{8\pi}{3k_o^2}\left(\frac{D\,e\,m}{\hbar^2}\right)^2 \frac{j}{2j+1} \log \frac{k_o + k_{jj'}}{|k_o - k_{jj'}|} \quad \ldots\ 2.36$$

The corresponding momentum transfer cross section are

$$\sigma_m(j, j+1) = \frac{8\pi}{3k_o^2}\left(D\,e\,m/\hbar^2\right)^2 \frac{j+1}{2j+1}\left[1 - \frac{(k_o - k_{jj'})^2}{2k_o\,k_{jj'}} \log \frac{k_o + k_{jj'}}{|k_o - k_{jj'}|}\right] \quad 2.37$$

and

$$\sigma_m(j, j-1) = \frac{8\pi}{3k_o^2}\left(D\,e\,m/\hbar^2\right)^2 \frac{j}{2j+1}\left[1 - \frac{(k_o - k_{jj'})^2}{2k_o\,k_{jj'}} \log \frac{k_o + k_{jj'}}{|k_o - k_{jj'}|}\right] \quad 2.38$$

The energy levels of the target rotator is given by

$$E_j = \frac{j\,(j+1)\hbar^2}{2I} \quad \ldots\ 2.39$$

Where I is the moment of inertia of dipolar system. The initial and final wave vectors k_o and $k_{jj'}$ for the scattered electrons are defined as

$$k_o = \sqrt{2m\,E/h^2}$$

and
$$k_{jj'} = 2m\left[E - (E^{r}_{g'} - E_j)/\hbar^2\right]$$

Thus the limit as $I \to \sigma$ the inelastic cross section 2.36 and 2.37 diverges.

Garrett (1971) has shown that the divergence in the inelastic cross section as $I \to \sigma$ is not a property of the point dipole Born approximation but is true for an exact treatment of the dipolar scattering problem This extreme importance of rotational energy terms in the total interaction Hemiltonian seems rather puzzling in view of their relative insignificance in other non polar scattering problems. The cause for this behaviour can be found in the extremely long range of the dipole field. In the limit of the fixed dipole the continuum states are characterized by phase shifts which decrease only as J^{-1}, where J is the total angular momentum plus dipole system. This yields a logarithmic divergence in the total cross section. The presence of rotational terms effectively decreases the interaction potential for distant collisions where the collision time becomes comparable to the rotational period of the target system. The phase shifts for large J thus decrease more rapidly and the total cross section is well behaved. The importance of the nonadiabetic nuclear terms show up in a similar fashion in critical binding of the electron to a dipolar system. The infinite degeneracy in the energy spectrum at $D = 0.639\ ea_0$ is removed in the treatment of the non stationary dipole problem and only 0 or a finite number of bound states exist for a given dipole magnitude.

The elastic cross section in the fixed nuclei approximation, σ, is related to the $I \to \infty$ limit of the cross sections in the nonadiabetic treatment through the relation,

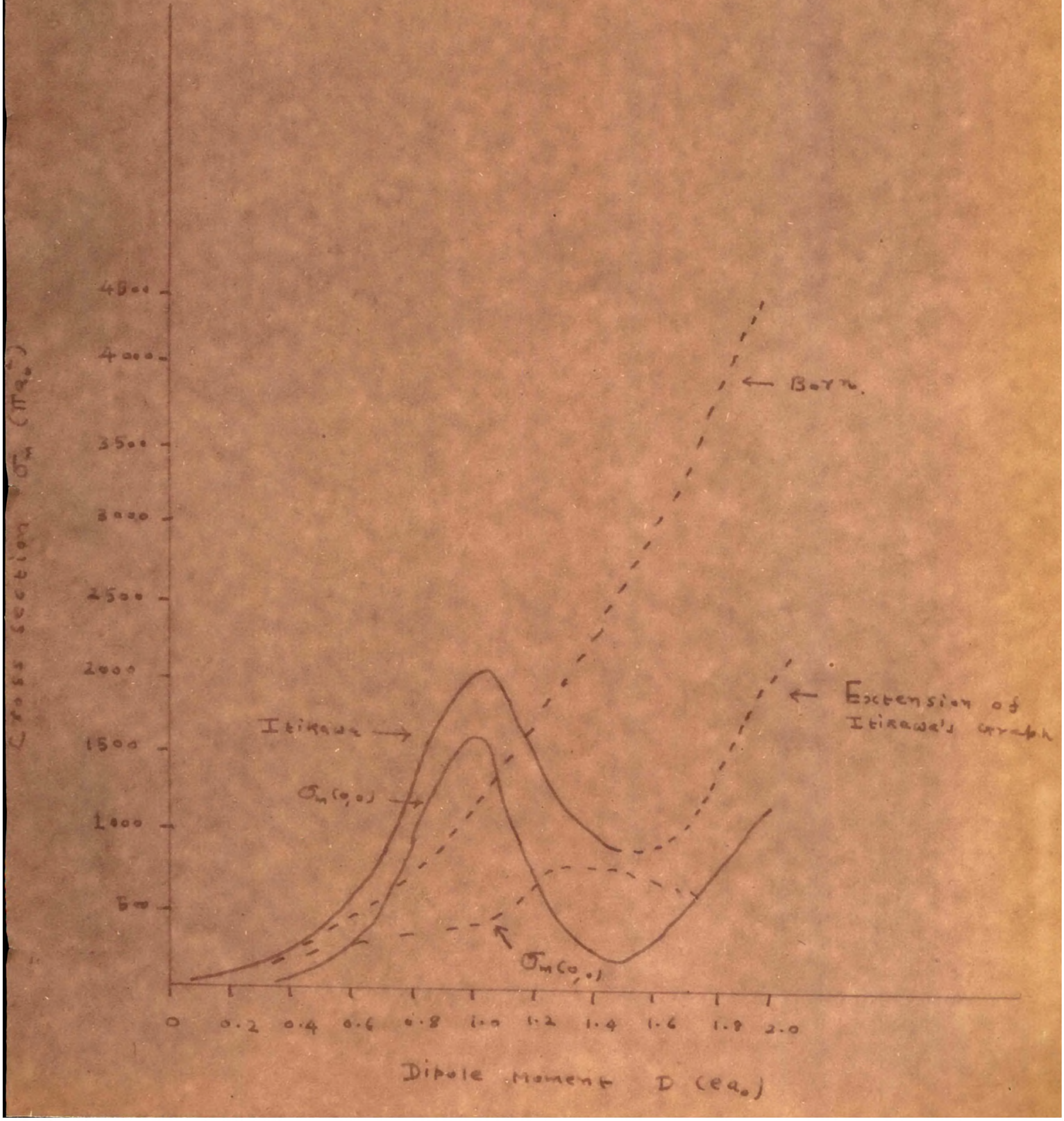
$$\sigma = \lim_{I \to \infty} \sum_{j'} \sigma(j, j') \qquad \ldots\ldots \qquad \ldots\ldots \qquad 2.40$$

where σ is the elastic cross section averaged over orienta-tions of the fixed nuclei and the sum extends ~~rathe~~ over all rotational states j' to which transitions are made from an initial state j. Thus the conclusion that the total elastic cross section diverges in the fixed nuclei approximation can also be reached by this indirect approach.

The most detailed understanding of electron scattering by dipolar system has been obtained through the close coupling method as formulated by Arthurs and Dalgarno (1960) close coupling calculations have been made of low energy elastic, inelastic and momentum transfer cross section

Graph. 3.

Y. axis. represents cross section σ_m (πa_0^2).



for eletrons incident on a pure dipolar rigid rotator and on a number of polar molecules. The same technique has been applied to the non adiabetic dipolar scattering. For thermal energy electrons ignoring vibrational and electronic degrees of freedom in the target system Garrett calculated total and momentum transfer cross section. The momentum transfer cross section for scattering in this case shown a strong maximum at $D = 1.0\ ea_0$ as shown in the graph 3. The S wave contribution dominates the cross section (Takayanagi and Itikawa, 1969) and is responsible for large peak in the calculated value of $\sigma_m(0,0)$.

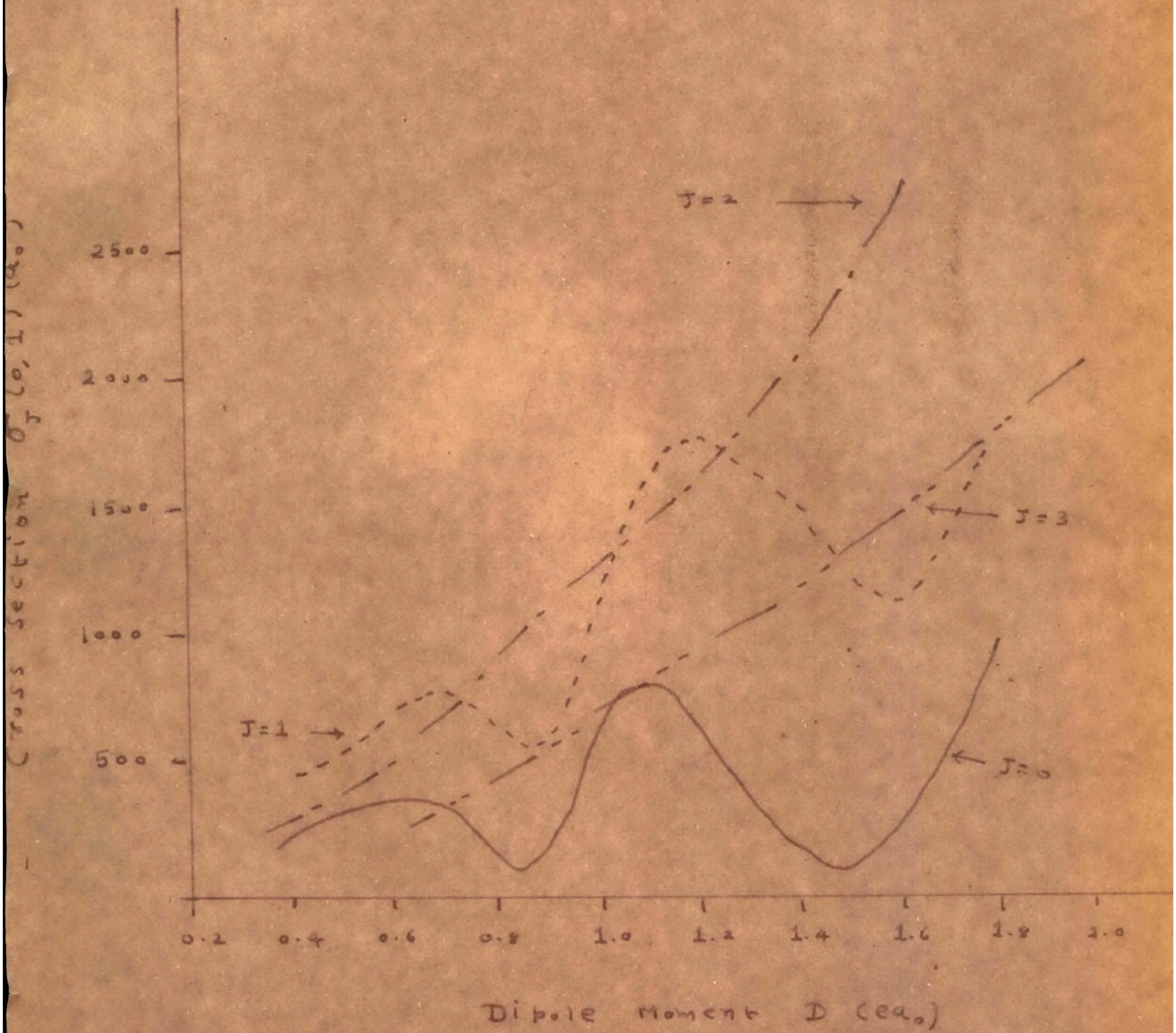
Finally for the investigation of the characteristic of the cross sections for a pure dipole rotator, the model potential (2.31) with a real dipole rotator consisting of charges + q and - q separated by a distance 2a and possessing moment of inertia I about the midpoint of the line separating the charges. The potential function for this dipole rotator is

$$V(r, \hat{s}) = -\sum_{\lambda=1,3\ldots} \frac{2eqr_<^{\lambda}}{r_>^{\lambda+1}} P_\lambda(\hat{s}\cdot\hat{r}) \qquad \ldots 2.41$$

where $\bar{s} = a/2$ is a vector from the centre of mass to one of the charges and $r_<$ is the lesser and $r_>$ the greater of r and s The dipole moment is $D = 2q\overset{a}{\cancel{s}}$ and 2a is the dipole length.

Graph. 4.

Y-axis represents cross section $\sigma_J(0,1)$ (a_0^2).



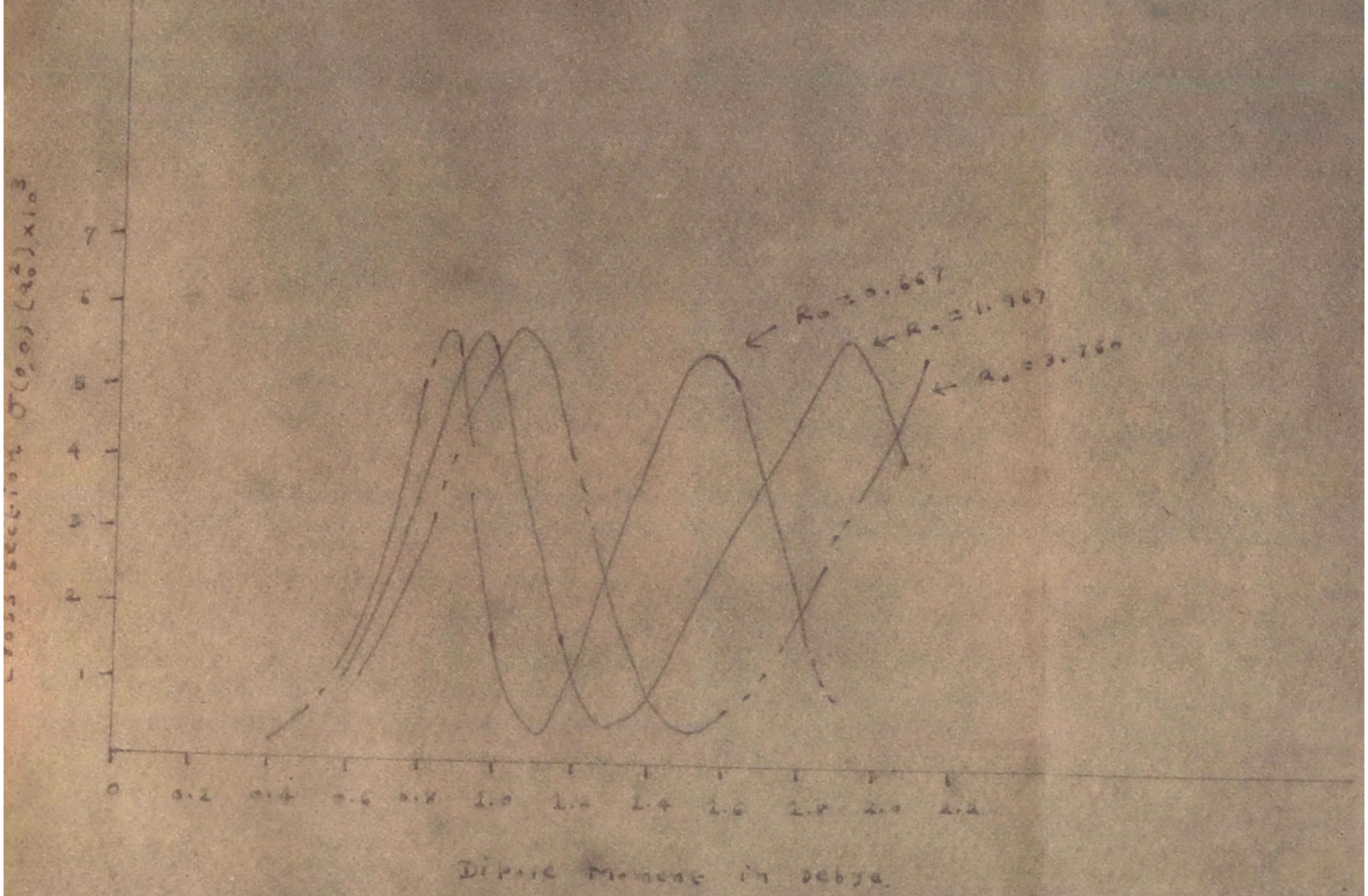
The calculation of momentum transfer cross section with such a dipole rotator is very lengthy and infact is prohibitive to the close coupling method. Fortunately, the maximum in σ_m which is the point of interest, is produced by the J = 0 componant of the elastic scattering channel. The results for J = 0 componant of the elastic channel are shown in graph 4 for scattering of 0.03 eV electron from a simple dipole rotator of three different dipole lengths. These results indicates that more than one maximum occurs in the cross section for this channel to depend on the dipole lengths. Thus the total thermal energy momentum transfer cross section for a simple dipole does not necessarily show a maximum at $D = 1.0\ ea_0$. Instead, the magnitude of σ_m for a fixed energy shows a more complicated dependence on D. With maxima and minima which occurs at points determine by the value of the dipole length. The critical dipole moments for simple dipole rotators shows this same behaviour, and are indicated on the figure. The The maxima in the elastic channel are associated with the critical moment for electron finding to the dipolar system and in the limit as $E \to 0$, where the inelastic channels are frozen out. The maxima would occur at the critical value of D and would correspond to transitions through $\pi/2$, $3\pi/2$ ---- radians in the S wave phase shift.

For the $0 \rightarrow 1$ inelastic channel, the presence of

Graph. 5.

Y-axis represents

Cross section $\sigma(0,0)\,(a_0^2) \times 10^3$.



strong maxima or minima in one channel of the total scattering cross section generally leads to corresponding excursions in the cross sections for other open channels at the same energy. Thus one would expect to find the behaviour demonstrated in graph 4 to be reflected in the inelastic cross section. In fact, this is the case but only in a restricted sense. This point is easily explained by the results shown in graph 5 . In this graph the partial wave components $J = 0, 1, 2$ of $\sigma(0, 1)$ are plotted for a specific dipolar system $R_o = 0.667\ a_o$, $I = 10^4 m\ a_o^2$.

This analysis of low energy electron scattering has indicated that even if polar molecules could be idealized as simple dipole rotators; there would be no particular value of dipolar magnitude at which dramatic differences would exist in momentum transfer cross section for molecules whose dipole moment are either above or below the given value, however one could say that for a fixed energy the total momentum transfer cross section for simple pure dipolar systems show a maximum for dipole moments in the region from approximately 0.7 to 1.1 ea_o. This first maximum is associated with the lowest critical moment for binding to this particular dipolar systems but before any cogent inferences can be made about scattering from real polar molecules. The study of the effects of monopole, dipole and induced dipole terms in the eletron molecule interaction potential have been investigated as to their -

individual and collective effects on the resultant theoretical cross sections.

Lastly in the scattering problem the study of phase shift is also an important factor because it is connected with the cross sections. For the phase shift calculations the knowledge of radial equation is essential. Mittleman et al (1968) have studied phase shift for using it in cross section. The numerical results of the phase shift is exhibited in ~~graph~~ chap III Garrett has also calculated the scattering phase shifts analogus to that for scattering from a spherically symmetric r^{-2} potential.

We have also attempted the problem of phase shift by various aspects. The summary of our results and comparision with others calculations are reported in chapter III.

Finally for any of the calculations the comparision with experiment is essential. The recent experiments are performed for thermal electrons and the diffusion cross section averaged over the Maxwellian distribution. The theoretical study for thermal electron is made by us and recently by Garrett. This has been discussed in detail in Chapter III.