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An apparatus for electron impact ionization cross-section measurements

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AN APPARATUS FOR ELECTRON IMPACT IONIZATION CROSS SECTION MEASUREMENTS

By

Pascal Renault

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MASTER OF ARTS

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ABSTRACT

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Cross sections for electron impact ionization of molecules and rare gases are necessary for the modeling of phenomena related to the earth's upper atmosphere and to plasmas. The construction of an apparatus to improve the accuracy of measurements of such cross sections is reported.

The ions are produced in a static gas target crossed by an electron beam and are counted with a new ion detector technology, which insures a increased accuracy of the ion flux measurement and of the target length. The target gas density is measured using an ionization gauge calibrated against a high accuracy capacitive transducer. This apparatus also features a pulsed mode of operation, which allows a product analysis through time of flight measurement.
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INTRODUCTION

Electron impact ionization processes are of fundamental importance and the measurements of the corresponding cross sections supply the information necessary to the modeling of various natural environments ranging from planetary atmospheres to hot astrophysical plasmas\(^{(46,47)}\), as well as laboratory work on controlled fusion and mass spectrometry applications.

In the case of atmospheric phenomena, energetic electrons are produced through three processes. First the photoionization of upper atmosphere atomic and, to a lesser degree, molecular species by solar X-ray and UV photons is responsible for photoelectrons of energy typically less than 1 eV. Electrons arising from the second phenomenon, or polar cusp electrons, are initially trapped in the Earth's magnetic field and penetrate deeply into the atmosphere through cleft regions in this field. The energy distribution of these electrons can often be described as Maxwellian with a characteristic temperature of approximately 40 eV. Finally, electrons originating from the solar wind also enter the Earth's atmosphere with an energy of approximately 10 eV.

Electron impact ionization has received significant experimental attention. The earliest absolute total cross section measurements were performed in 1932 by Tate, Smith, and Hagstrum \(^{(1-7)}\), while Rapp \textit{et al} \(^{(20-23)}\) made in 1965 the first attempt at studying dissociative and non-dissociative ionization separately:

\[
\begin{align*}
e^{-} + AB & \rightarrow AB^+ + 2 e^{-} & \text{non-dissociative ionization} \\
e^{-} + AB & \rightarrow A + B^+ + 2 e^{-} + \text{kinetic energy} & \text{dissociative ionization}
\end{align*}
\]
Other groups performed similar measurements on gases of aeronomic interest (see for example the reviews by Kieffer and Dunn\(^{(12)}\) in 1966 and Märk\(^{(34)}\) in 1981). However, discrepancies remain between the results of the different groups, and the measurements of ratios of non-dissociative to dissociative ionization cross sections of molecules as well as total absolute cross sections are still uncertain. This problem has also been the subject of much theoretical work. However, in regard to the theoretical difficulties encountered in the three-body, spherically asymmetrical problem of electron impact, reliance on laboratory measurement of cross sections is still necessary.

Dissociative ionization cross sections have been measured differentially with respect to the energy and angular distributions of the fragments for oxygen, nitrogen, and hydrogen. In the latter case results are in good agreement with calculations\(^{(10,11,14,16)}\).

The apparatus described in this thesis has been designed and built over the past two years and is expected to yield better cross section values than those available for electron impact ionization of both molecules and rare gases. The improvement is two-fold. It lies first in the use of a high-accuracy capacitive transducer and of a broad range ionization gauge for the measurement of the target gas density. The capacitive transducer is used as the primary source of absolute pressure measurement and is insensitive to the gas composition. The ionization gauge is used to extrapolate this absolute standard. Previous measurements \(^{(1-7,20-23,18)}\) ultimately relied on a McLeod gauge for their absolute calibration. However, the pumping action of the mercury\(^{(22)}\) reduces the accuracy of this method, especially for gases of large atomic number. Rapp and co-workers addressed this issue by using a McLeod gauge for hydrogen and normalizing cross sections of other gases to that of hydrogen by a dynamic effusive flow technique\(^{(22)}\). However, they could not apply this technique to the species NO and O\(_2\) for which they used the McLeod gauge reading approximately corrected. The second improvement lies in the pulsed operation.
mode of the apparatus, which allows the identification of the products and the measurement of partial cross-sections, coupled with the complete collection of the fragment ions, checked through position information from the ion detector. The product identification is done through time of flight mass spectrometry and made possible by the use of the new ion detection technology. Time of flight information is also used to eliminate events due to secondary electrons, which appear later than valid counts, and background events, which correspond to different mass peaks, principally the water peak. This is a significant improvement over the use of the retarding field technique in Rapp's experiment\(^{(21)}\) and results in a better treatment of the secondary electrons problem than in previous experiments.

The present apparatus is therefore expected to result in an improved accuracy of the absolute partial cross section values for electron impact ionization phenomena.

The gases of interest are atmospherically relevant species such as oxygen, nitrogen, and rare gases. The electron energy ranges from threshold to 2500 eV.
CHAPTER I

THE PHYSICS OF ELECTRON IMPACT IONIZATION

In this chapter the physics of electron impact ionization of atoms and molecules is described. Results derived for the simplest case of the hydrogen atom are extended to the case of multi electron atoms. Following is a description of non dissociative and dissociative ionization of diatomic molecules.

Ionization can be described as the transition undergone by an atom initially in its electronic ground state having one or more of its electrons acquiring enough energy to go into the continuum. This transition results from the perturbation caused by the Coulomb interaction between the incident electron and the atom or molecule. Single electron impact ionization of an atom A is schematically represented by the following reaction:

\[ A + e_i^- \rightarrow A^+ + e_s^- + e_e^- \]  \hspace{1cm} (1a)

and multiple ionization of order n is represented by

\[ A + e_i^- \rightarrow A^{n+} + e_s^- + (n+1) e_e^- \]  \hspace{1cm} (1b)

where \( e_i^- \), \( e_s^- \), and \( e_e^- \) are the incident, scattered, and ejected electrons respectively.

The main difficulties encountered in the calculation of electron impact ionization cross sections arise from the three body nature of the problem. It is not possible to solve it
exactly and one must resort to approximations. In the domain of impact energies large compared to the binding energy of the atom, the Born approximation usually gives satisfactory results. In the case of near threshold collisions however the Born approximation is out of its range of validity. Furthermore, in the regime of low energy collision, non negligible exchange effects arise from the antisymmetrical nature of the wave function with respect to the exchange of the incident and ejected electrons, required in order to satisfy the Pauli principle. We now present the application of the Born approximation to the electron impact ionization of atomic hydrogen, its simplest application.

The problem consists in solving the Schrödinger equation for a system consisting of an atom made up of a proton and its bound electron and the incident electron. This equation reads:

\[
\left( \nabla_1^2 + \nabla_2^2 + \frac{8\pi^2m}{\hbar^2} \left( E + \frac{e^2}{r_1} + \frac{e^2}{r_2} - \frac{e^2}{r_{12}} \right) \right) \psi = 0 \tag{2}
\]

where \( r_1 \) and \( r_2 \) are the distances from the nucleus to the incident and atomic electrons respectively, \( r_{12} \) is the inter electron distance, and \( E = E_0 + E_i \) is the sum of the energy of the atom in its ground state and the kinetic energy of the incident electron respectively. The first simplifying assumption that can be made consists in solving the Schrödinger equation in the approximately inertial reference frame of the atomic nucleus. The reason for the validity of this assumption is that the conservation of momentum and the negligible value of the ratio of the mass of the electron to that of the nucleus (always less than \( 10^{-3} \)) imply a negligible change in the nucleus velocity. This approximation amounts to neglecting the \( \nabla^2 \) term in the Schrödinger equation (2).

The solution to this equation can always be written in the following form:
\[ \Psi = e^{i k_0 \cdot r_1} \psi_0(r_2) + \phi(r_1, r_2) \]  

(3)

The term \( e^{i k_0 \cdot r_1} \) represents the incident wave moving along the wave vector \( k_0 \) and \( \psi_0(r_2) \) is the wave function describing the atom in its ground state. The incident electron energy \( E_t \) is related to the norm of the wave vector \( k_0 \) through the equation

\[ E_t = \frac{\hbar^2 k_0^2}{8\pi^2 m} \]  

(4)

In the absence of interaction between the incident electron and the atom the complete solution would be limited to:

\[ \Psi = e^{i k_0 \cdot r_1} \psi_0(r_2) \]  

(5)

The \( \phi(r_1, r_2) \) term appears solely because of the interaction between the incident electron and the atom and contains all of the information about the collision. In the case where \( E_t \) is much larger than \( E_0 \) we can assume that it is a relatively small correction term, which can be calculated by perturbation theory. Expanding this term on the different atomic states and the continuum, we obtain:

\[ \phi(r_1, r_2) = \sum_n F_n(r_1) \psi_n(r_2) + \int F_v(r_1) \psi_v(r_2) \, dv \]  

(6)

where the \( \psi_n \) factors are the wave functions of the different atomic states and the \( F_n \) the expansion coefficients. By simple substitution of (6) into (2), we find that the expansion coefficients are solutions to the system of coupled equations:
\[(\nabla_1^2 + k_n^2) F_n = U_{0n} e^{ik_0 \cdot r_1} + \sum_m U_{nm}(r_1) F_m(r_1) \]

(7)

where

\[U_{nm} = \frac{8\pi^2 m e^2}{\hbar^2} \int \psi^*_n(r_2) \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) \psi_m(r_2) \, dr_2\]

(8)

and

\[k_n^2 = \frac{8\pi^2 m}{\hbar^2} (E_1 - E_n + E_0)\]

(9)

So far no approximation concerning the electronic wave functions has been made. If we now take into account the fact that the incident energy is much larger than the binding energy inside of the atom, the system giving the \(F_n\) reduces to the uncoupled system:

\[(\nabla_1^2 + k_n^2) F_n = U_{0n} e^{ik_0 \cdot r_1}\]

(10)

Equations (10) are insufficient to determine the \(F_n\) unless their asymptotic form is specified. Physically, this asymptotic form has to be that of an outgoing spherical wave:

\[r^{-1} e^{ik_0 \cdot r} f_{0n}(\theta, \phi)\]

(11)

Applying Green's theorem to equations (10) and (11) one gets:

\[f_{0n}(\theta, \phi) = -\frac{1}{4\pi} \int U_{0n} e^{i(k_0 - k_n) \cdot r} \, dr\]

(12)

where \(k_n\) is a vector in the direction of the scattering and of magnitude \(k_0\)
The differential cross section can then be expressed as:

\[ \frac{k_n}{k_0} |f_{on}(\theta,\phi)|^2 \]  

(13)

The previous results can be expanded to the case of multi electron atoms. Let \( r_1, \ldots, r_N \) be the coordinates of the N atomic electrons. The differential cross section is again given by equation (13) where now

\[ \tilde{U}_{0\alpha}(\vec{r}) = \frac{8\pi^2 me^2}{\hbar^2} \left\{ \sum_{s=1}^{N} \frac{1}{|\vec{r}-\vec{r}_s|} \right\} \Psi_0(r_1,\ldots, r_N) \Psi_n^*(r_1,\ldots, r_N) \, dr_1\ldots dr_N \]  

(14)

By integration over the coordinates of the incident electron the expression for the differential cross section can be simplified and reduces to:

\[ I_{on} = \frac{4\pi^2 m e^4 k_n}{\hbar^4} \left( \frac{4\pi}{k^2} \int \psi_0 \left( \sum e^{i(k_0 - k_n)\cdot r_i} \right) \psi_n^* \, dr_1\ldots dr_N \right)^2 \]  

(15)

where \( K^2 = k_0^2 + k_n^2 - 2 k_0 k_n \cos(\theta) \)
For a more complete description of the Born approximation applied to electron impact ionization of atoms see for example Massey and Burhop (49). Figure I-1 presents a comparison of calculated and observed cross-sections for ionization of atomic hydrogen by electrons with energies up to 800 eV.

In the case of electron impact on molecules, cross section calculations are based on the same principle as for atoms, the atomic wave function being replaced by the molecular wave function. However, calculations are complicated by the fact that the diatomic molecule does not present the spherical symmetry of the atom. Besides one must also take into account the relative motion of the nuclei in the frame of the center of mass of the molecule. The two possible types of motion in a bound molecule are described by discrete vibrational and rotational states and, in an unbonded molecular ion, a continuum corresponding to the motion of fragments.

In order to describe the processes involved, one must refer to the potential energy diagrams for both the molecule and the molecular ion. These diagrams represent the potential energy as a function of the internuclear distance for individual electronic states. These diagrams assume it is possible to decouple the electronic quantum states from the nuclear motion. This is the case in the Born-Oppenheimer approximation, which states that because of the small value of the mass of the electron compared to that of the nuclei, the electronic states adjust themselves adiabatically to the much slower motion of the nuclei.

First, in the case of non dissociative ionization two states are to be considered: the ground state of the molecule and the final bonding state of the molecular ion. An illustration is given in figure I-2. In the initial state, the ground state of the molecule, the nuclei oscillate in the bonding part of the curve and could therefore be in different excited
Figure I-1: Calculated and experimental cross sections for ionization of atomic hydrogen by electron impact
vibrational states. An approximate value of the energy difference between consecutive vibrational states is given by the following formula:

$$\Delta E = \frac{0.55}{\sqrt{m}} \text{ eV}$$  \hspace{1cm} (16)

where $m$ is the reduced mass of the molecule. In the example of nitrogen this spacing is about 0.15 eV. This value being about an order of magnitude higher than the thermal energy (0.025 eV at room temperature), the molecule is almost always in its ground vibrational state at room temperature. Besides the vibration of the molecule, one must consider its rotational excited states. Typical values of the energy difference between rotational levels are of the order of 1/100 eV, which is of the same order of magnitude as thermal energy. At room temperature the molecule is in a number of excited rotational states according to a Boltzman distribution. However the rotational energy is small compared to the bonding and vibrational energies. The reaction of single ionization can be schematically represented by the following formula:

$$e^- + XY \rightarrow XY^+ + 2 e^-$$  \hspace{1cm} (17)

According to the Frank-Condon principle, the electronic transition is much faster than the motion of the nuclei. It may therefore be said that the internuclear distance is conserved during the electronic transition. As a consequence, as illustrated in figure I-2, the molecular ion is usually formed with an internuclear distance different than its classical equilibrium position: it is usually in a vibrationally excited state.

In the case of direct dissociative ionization,
Figure I-2: Energy diagram of an hypothetical molecule $X_2$ and its bonded molecular ion $X_2^+$. The classical internuclear distance being smaller for the molecule than for the ion, the molecular ion vibrational state is a combination of a number of excited states.
\[ e^- + XY \rightarrow X^+ + Y + 2e^- \] (18)

the final state is an antibonding state. As illustrated in figure I-3 in the example of hydrogen, the molecule is initially in the \( ^1\Sigma_g^+ \) ground state and is ionized to the final antibonding state \( ^2\Sigma_u^+ \) state. The molecular ion formed is unstable and its constituents fly apart. Dissociative ionization can also occur if the energy diagram of the final state presents a minimum corresponding to a bonded molecular ion such as in the case of the \( ^2\Sigma_u^+ \) state (see figure I-3), provided that the energy of the vibrational motion is larger than that of the chemical bond.

The Frank-Condon principle applied to dissociative ionization allows a theoretical determination of the fragment kinetic energy distribution. The internuclear distance distribution corresponding to the vibration in the potential well of the initial state is conserved during the electronic transition, therefore the reflection of this distribution on the final state curve corresponds to the kinetic energy distribution. An illustration is given in figure I-3. An interesting comparison between calculations and laboratory measurements of the energy distribution of the fragments has been carried out by G. H. Dunn and L. J. Kieffer (11) in the simplest case of the hydrogen molecule. Experimental results on oxygen and nitrogen are given by J. A. D. Stockdale and L. Delanu (26), Van Brunt and Kieffer (13, 17), and Dunn (10, 11).

The angular distribution of the fragments is characteristic of the angular dependance of the ionization probability since the dissociation occurs in the direction of the vibrational
Figure I-3: Direct dissociative ionization and predissociative ionization by electron impact in the hydrogen molecule. The unstable molecular ion in the state $^1\Sigma_u^+$ leads to direct dissociative ionization. If the molecule is ionized into the $^1\Sigma_g^+$ molecular ion state, the system can remain bonded or unbonded, depending on the value of $R$ at the moment of the ionization.
motion, which is much faster than the rotation of the molecule. Calculations of the angular distributions in the case of hydrogen were carried out by R. N. Zare (38) and experimental data are presented by G. H. Dunn and L. J. Kieffer (11).
CHAPTER II

DESCRIPTION OF THE APPARATUS

The scheme used in the present experiment to perform electron impact cross sections measurements is similar to that of the early work of Tate and Smith in that in both cases a static gas target is crossed by an electron beam. The cross section is a measure of the probability that the collision of an electron with an atom or a molecule will result in the formation of a specific ion. Assuming a thin target it is defined according to the following formula:

$$\sigma = \frac{N_{\text{ion}}}{N_{e^-}} \cdot \frac{1}{nL}$$

where $N_{\text{ion}}$ and $N_{e^-}$ are the number of ions formed and the number of electrons entering the target respectively. $L$ is the target length and $n$ is the target gas density. The product $nL$ is the target thickness.

The main improvements of the present experiment over Tate and Smith's design lie in the use of a pulsed operation mode and of a new ion detector technology. Use of the position and time sensitive detector allows the complete collection of fragment ions as well as the precise measurement of the target length $L$. The pulsed operation mode allows the different ions formed to be identified according to their mass to charge ratio through time of flight measurement. In the case of homonuclear diatomic molecules the present apparatus allows one to distinguish between fragment ions and ions due to double non-dissociative ionization, from information on the ion impact location on the detector. The present
experiment also includes a pressure measurement technique that uses the absolute reading of a Baratron and an averaging procedure that extends its range into the low pressure domain, allowing a determination of the target gas density $n$.

The new design therefore provides a measurement of the path length and of the target gas density along with the complete collection and identification of reaction products.

The geometry adopted for the apparatus is given in figure II-1. The main constituents of this apparatus are contained in a vacuum chamber: an electron beam source, an electron collector, a magnetic shield, two parallel copper plates, and an ion detector.

The source used for the electron beam is a CRT electron gun manufactured by Southwest Vacuum Devices, reference 73Z. These electron guns were originally designed to operate at an energy of 25 keV in a $10^{-7}$ Torr vacuum. They can however be used at higher pressures with a shorter life time and can operate at lower energies. Tests have been performed down to a 15 eV electron beam energy.

For the electron beam to travel along a straight line, it is necessary to create a field free region at the beam location. This implies first isolating the apparatus from external magnetic fields such as the earth's magnetic field and locally generated magnetic fields by placing the apparatus inside a magnetic shield made of $\mu$ metal. The residual magnetic field inside the shield was measured to be less than $10^{-6}$ Tesla, corresponding approximately to 1/50 of the Earth's magnetic field. In a magnetic field of this strength the cyclotron radius of a 10 eV electron is 10 m, a value large enough to neglect the curvature of the electron beam. One must also insure that all the materials used inside the magnetic shield are non magnetic. The bulkiest parts required to conduct electricity are made of OFHC copper. Brass is used for nuts and bolts, all magnetic materials have been eliminated and use of
Figure II-1: Geometry of the apparatus
stainless steel is kept to a minimum. Besides magnetic fields, one must also eliminate electrostatic fields. This is accomplished by insuring that while the electron beam is on, no applied voltage will modify the electrons trajectories.

The second concern related to the electron beam is space charge divergence. It can easily be calculated that in a 10 eV electron beam of 1 nA, assuming that all the electrons are on the same geometrical line, the electrons are spaced by approximately .3 mm one from the other and, because of this wide spacing, one can presume their mutual repulsion to have little effect on the beam diameter and energy. The current is fixed by the upper limit on the count rate imposed by the ion detector.

The electron gun is turned on for approximately 10 ns, typically. The electrons emitted are directed through the gas to be studied into a Faraday cup where they are collected. The cup design must allow collection of all electrons. It must also enable a measurement of the electron beam current during an actual experiment and therefore has to be shielded from high voltages pulses present in its immediate vicinity. Finally it must allow a rough determination of the beam diameter. The technical solutions adopted are presented in figure II-2. The bottom of the cup is stuffed with steel wool which contribute to preventing electrons from exiting the cup. The entrance of the cup is an aperture slightly larger than the electron beam diameter and the cup is enclosed in a shield serving the double purpose of collecting electrons in the outer part of the beam and isolating the cup from high voltage pulses. The Faraday cup is connected to an ammeter which allows the measurement of the electron beam current after it has crossed the target. Within the resolution of the ammeter, the current collected in the cup is equal to the electron flux $N_e$ above the ion detector since the beam attenuation is very small, as proved by the independence of the measured current on the target gas pressure. The electrons travel in a straight path from gun to cup in a time inversely proportional to the square root of their
Fig II-2: Faraday cup
energy. In the case of a low value of this energy, say 10 eV, this time is approximately 60 ns.

The positive ions created by the short burst of electrons are initially located on the beam axis and are formed with a range of kinetic energies, up to a few eV typically. The velocity of a 10 eV oxygen atom is approximately 1.3 cm μS⁻¹. A short time after all of the electrons have been collected in the cup, an intense electric field perpendicular to the electron beam direction is applied in the interaction region and the ions are accelerated towards the ion detector. This field is created by a high positive voltage applied to the top copper plate while the bottom plate remains solidly tied to ground.

At this point we must make sure that both the geometry of the interaction region and the field strength insure the realization of two conditions, the total collection of fragment ions and time of flight resolution of the different species. Detailed calculations, presented in the appendix, lead to values for the spacing of the copper plates and for the voltage to be applied to the top plate.

The fast-rising high voltage required is provided by a high power Velonex pulser model 360 with a plug in unit V1742. This pulser can deliver voltages of up to 2500 V with a rise time of 50 nS. However the load it drives has to be resistive with a 300 Ω value. The pulser is limited in the power it can put out, which limits the repetition rate of the experiment.

Another requirement is that the apparatus allow a determination of the target length L. This physical quantity corresponds to the length of the part of the electron beam that produces the actually detected ions. The collisions between the ions and the molecules of the target gas are very rare since the mean free path in the high vacuum used is large compared to the dimensions of the interaction region. These length are typically a few meters for the mean free path and a few centimeters for the apparatus. Under this condition
Figure II-3: In a uniform extraction field $E$, the trajectories followed by different particles such as $A$ and $B$ are parabolas that are functions of the direction and magnitude of the initial velocity of the ions only, which results in the equivalence of $L_2$ and $L_1$ if $A$ and $B$ are formed in the same conditions. The uniform distribution of events along the ion beam implies that the target length and the length over which the ions are collected are identical.
the trajectories correspond to the motion of charged particles in an electric field and are parabolas. Moreover, if the electric field is uniform, the ions will follow trajectories that depend on their initial velocity, both in direction and magnitude, but not on the location of their formation. As illustrated in figure II-3, the field uniformity and collision-free trajectory conditions result in the equivalence of the target length and the length over which ions are detected, the former being the number $L$ necessary to the calculation of the cross section and the latter the physical quantity determined by the ion detector.

In order to reduce the end effects responsible for the non-uniformity of the electric field, we used plates as large as allowed by the dimensions of the existing vacuum chamber and a modified version of the parallel plates capacitor geometry. This geometry features wings on the top plate and two guard rails. This setup has been modelled using the computer program SIMION. The criterion used to determine the field uniformity is the identity of the ion trajectories in the actual field with those of ions in an ideally flat field: any detected ion must travel the same distance in the directions parallel to the plates as it would in the ideal case. As a worst case, we considered oxygen atomic ions having a high kinetic energy (15 eV) and an initial velocity parallel to the plates, either parallel or perpendicular to the electron beam, that are detected at the edge of the ion collector. The computer simulation resulted in differences of less than 0.2 mm. The calculated trajectories and equipotential lines are shown in figures II-4 and II-5.

The ion detector used is a position sensitive detector (PSD). The operation of this detector has previously been described by Gao et al.(46) The PSD detects individual particles for which it gives information on the time and position of the impact, both of which are used to infer time of flight and target length. A description of the PSD is given in figure II-6.
Figure II-4: Equipotentials in the direction orthogonal to the beam corresponding to 250, 500, 750, 1000, 1250, 1500, and 1750V obtained by computer simulation using the SIMION program. The "winged" shape of the top plates makes the field seen by the ions more uniform. The trajectories drawn correspond to a 15 eV O$^+$ ion with its initial velocity parallel to the bottom plate and perpendicular to the beam. The distance travelled sideways as calculated by the SIMION program is 10.56 mm, to be compared to the value 10.33 mm for an ideally flat field.
Figure II-5: Equipotentials in the direction parallel to the beam corresponding to 250, 500, 750, 1000, 1250, 1500, and 1750V obtained by computer simulation using the SIMION program. The winged shape of the top plate and the "guard rails" make the field seen by the ions more uniform. The top plate is held at 2000V and the guard rails at 1325 V. The four trajectories drawn correspond to 15 eV O+ ions with their initial velocities directed along the beam and detected at the edge of a 40 mm PSD. The distances travelled sideways are 10.67 mm and 10.44 mm for ions having their initial velocity parallel and antiparallel to the electron beam respectively, to be compared with a value of 10.33 mm in an ideally flat field.
Figure II-6: Position and time-sensitive detector
It is interesting to note that the highly sensitive PSD is located some 7 cm away from the top plate on which a 2000 V pulse with a rise time of 100 nS is applied. In order to prevent pick up on the detector from the extraction pulse through capacitive coupling of the PSD to the top plate, the PSD and all its leads are entirely shielded, both inside and outside the vacuum chamber. The active part of the detector is shielded by a grid, which both insures the flat geometry of the bottom plate and prevents the high voltages present on the ion detector from modifying the trajectories of the ions and electrons in the interaction region. In spite of this shielding some pick up still remains and is removed by electronically gating the counting events.

In order to accurately count the ions, one must calibrate the PSD. As shown by Gao et al.\(^{(46)}\) the detection efficiency increases towards its theoretical limit with increasing detected particle energy. This theoretical limit corresponds to the fraction of open area on the microchannel plate and can be up to 66\%. The amount of energy required for a particle to be detected with this maximum efficiency is a function of its mass. Therefore, in order to have a detection efficiency independent of mass and the same for all species, one must accelerate the particles to be detected, typically up to an energy of 3 keV. In the present experiment, this is achieved by biasing the front face of the PSD to a high negative voltage, which incidentally also confers the advantage of repelling stray electrons from the PSD. Two potential problems inherent to this high front voltage however are, first, a lens effect in front of the PSD and, second, a great number of secondary electrons emitted from the front microchannel plate leading to unwanted ionizations. Tests have shown these problems to be non-existent for front voltages up to 2 kV, which correspond to a total ion impact energy of approximately 3.5 keV. Finally the detection efficiency has to be measured absolutely. We intend to perform this measurement by rastering the detector with an ion beam, the current of which can be determined by directing the beam into a Faraday cup.
With the PSD calibrated, it is possible to perform measurements of $N_{\text{ion}}$ and $L$, which leaves only the target gas density to be measured.

The nominal operating pressure for the electron gun is $10^{-7}$ Torr and the PSD should not be operated at pressures higher than $10^{-5}$ Torr in order to prevent arcing. The maximum allowed pressure is therefore $10^{-5}$ Torr, which corresponds to a gas density of $n = 3.3 \times 10^{17}$ m$^{-3}$.

We can then verify that the single collision condition corresponding to a thin target is satisfied: the probability that an electron ionizes a molecule over the diameter of the PSD must be small compared to one. Using a typical value of $10^{-16}$ cm$^2$ for the cross section, the maximum allowed value for $n$, and 25 mm for the PSD diameter, we calculate the value of this probability to be: $p = L \sigma n = 8.2 \times 10^{-5}$: the single collision condition is amply satisfied.

The pressure measurement technique used is one in which the source of absolute measurement is a baratron head, the full range of which is 1 Torr. The technique adopted also makes use of an ion gauge, the absolute calibration of which is known not to be accurate by more than 10% at best, used as a relative linear pressure measuring device. The ionization gauge stops being linear at high pressures because the single collision condition is not satisfied or because of electric charges accumulated on the gauge walls, and at low pressures because of the secondary electrons created by X-rays. For the Varian 564 broad range gauge used, the X-ray limit claimed by the manufacturer is $10^{-10}$ Torr and the highest operating pressure is $10^{-2}$ Torr.

Therefore it is possible to calibrate the ion gauge against the baratron at a pressure high enough for the latter to be accurate (typically $10^{-4}$ Torr with an accuracy of 5% claimed by the manufacturer) and use it in a pressure range where the Baratron becomes
unreliable. However, in order to check the gauge linearity and to perform the gauge calibration at a pressure as close as possible to the pressure at which the actual experiment is done, we have extended the baratron range down by two orders of magnitude by sampling the baratron output a great number of times and averaging it. Figure II-7 shows the pressure reading of the baratron versus that of the ion gauge. This graph indicates that the baratron can be used down to $10^{-5}$ Torr.

Knowledge of the pressure allows the determination of the target density $n$, the last of the four physical quantities that enter in the calculation of the electron impact cross section. The data collection and analysis schemes are now presented.

The data gathered during an experiment consist of a series of counts, each corresponding to time of flight and impact position information on an individual ion or on a background event. A schematic of the electronics used is shown in figure II-8.

The ions are detected after a time of flight proportional to the square root of their mass to charge ratio. The data are accumulated as "reverse" time of flight, in which one measures the time elapsed between the actual detection of the particle (start pulse) and a pulse occurring some set delay after the electron gun is fired (stop pulse) as illustrated in figure II-9. The reason for the use of this reverse time of flight scheme is that there are cycles during which no particle is detected. Those cycles can be ignored by the data acquisition electronics if no start pulse occurs before the stop pulse.

An example of the mass spectrometer output is illustrated in figure II-10. When these data were taken, the chamber contained some argon and nitrogen. The centers of the different peaks are indicated in table II-1. The channel zero corresponds to a time of flight equal to the time delay at which the delay unit was set: 2500 ns in the present example. Increasing abscissa corresponds to shorter time of flight as a consequence of reverse
timing. The self consistency of the peak locations can be checked using the fact that the time of flight is proportional to the square root of the mass to charge ratio. The calculated values agree with the actual center to about a tenth of a channel.

One can also verify the consistency of theoretically predicted and measured time of flight. In the instance of Ar⁺ the time of flight is measured to be 1600 ns. The expected value is given by the following formula:

\[ T = \sqrt{\frac{2xdm}{Ve}} = 1300 \text{ ns} \]

The 300 ns discrepancy can be accounted for by the delay before the onset of the extraction field and its finite rise time, which make the actual time of flight longer. Using the same set of data, it is possible to plot the position distribution of different species. See figures II-11 to II-15.

Since the species Ar⁺, Ar⁺⁺, and N₂⁺⁺ do not have any initial kinetic energy, except for the negligible thermal energy, the width of their position distributions is representative of the width of the electron beam. However, in the case of N⁺ which does have non-negligible initial kinetic energy, the distribution spreads out more in the direction perpendicular to the electron beam. This fact is illustrated in figures II-16 and II-17 where the spatial distribution measured orthogonally to the electron beam and integrated over the length of the PSD is presented for N⁺ and N₂⁺⁺. It can be verified that no fragment ion flies sideways so far as to miss the detector.

The final value of N₁ is obtained by integration of the areas subtended by the different peaks, discarding the counts too close to the edge of the PSD (see figure II-10).
Figure II-7: Gauge reading vs. baratron reading
Figure II-8: Electronics
Note: the output of the pulse generator is used to inhibit the discriminator during the rising edge of the extraction field to eliminate pick up.

Figure II-9: Cycle timing
<table>
<thead>
<tr>
<th>Peak</th>
<th>Channel</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>149</td>
<td>Ar$^+$</td>
</tr>
<tr>
<td>2</td>
<td>191</td>
<td>N$_2^+$</td>
</tr>
<tr>
<td>3</td>
<td>223</td>
<td>Ar$^{++}$</td>
</tr>
<tr>
<td>4</td>
<td>232</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>5</td>
<td>252</td>
<td>N$_2^{++}$ &amp; N$^+$</td>
</tr>
<tr>
<td>6</td>
<td>365</td>
<td>H$^+$</td>
</tr>
</tbody>
</table>

Table II-1: TOF peak centroids corresponding to Fig II-10
Figure II-10: Time of flight spectrum for nitrogen and argon. The centers and species corresponding to the peaks are shown in table II-1. Channel 0 corresponds to a time of flight of 2500 ns.
Figure II-11: Position distribution of the events happening between channel 130 and 170, attributed to Ar⁺.
Figure II-12: Position distribution of the events happening between channel 175 and 200, attributed to $N_2^+$. 
Figure II-13: Position distribution of the events happening between channel 215 and 228, attributed to Ar++.
Figure II-14: Position distribution of the events happening between channel 228 and 240, attributed to H$_2$O$^+$. 
Figure II-15: Position distribution of the events happening
between channel 240 and 270, attributed to N+. 
Figure II-16: Space distribution of $N_2^+$ measured perpendicularly to the electron beam and integrated over the length of the PSD.
Figure II-17: Space distribution of $N^+$ measured perpendicularly to the electron beam and integrated over the length of the PSD.
CONCLUSION

Electron impact ionization cross sections are of great interest for the study and modeling of aeronomic phenomena. The apparatus described in this thesis and its principle of operation are believed to represent a great improvement over the previous measurements, both for the accuracy and the nature of the results.

At this time the proper functioning of this apparatus has been checked and some preliminary data have been obtained as illustrated in the second chapter of this work. However, no cross section measurement has yet yielded reliable values principally for lack of proper calibration of the ion detector.

Work is still in progress and the main tasks that now need to be addressed are the calibration of the PSD and naturally the actual data taking, for gases relevant to the atmosphere over a wide range of energies.

This new apparatus design is hoped to be fruitfully used for experiments involving reactions other than electron impact, performed in a set up where the electron beam would be replaced by an atomic or molecular beam.
APPENDIX

Determination of the interaction region dimensions

The two conditions to be satisfied here are that all fragment ions will be collected irrespective of their initial kinetic energy and that a time of flight analysis will allow a discrimination between parent and fragment ions. Throughout this chapter we will consider the case of a 15 eV oxygen fragment.

Let us first consider the former condition: the distance travelled sideways has to be less than the radius of the PSD.

This distance can be calculated as:

\[ D = t \nu_0 \quad \text{(1)} \]

where \( t \) is the time of flight and \( \nu_0 \) the transverse velocity. Considering the case of a 15 eV oxygen fragment ion, \( \nu_0 \) is given by:

\[ \nu_0 = \sqrt{ \frac{2e}{m} } = 1.3 \text{ cm/\mu s} \quad \text{(2)} \]

We deduce from equations (1) and (2) that for \( D \) to be equal to 1 cm (to be compared to the 1.2 cm radius of the PSD) the time of flight has to be 730 ns:

\[ T = 730 \text{ ns} \quad \text{(3)} \]
Assuming that the extraction field turns on instantly after the ion is formed, the time of flight for an oxygen ion having no initial energy is:

\[ T = \sqrt{\frac{2xdm}{Ve}} \tag{4} \]

where \( x \) is the distance separating the electron beam from the PSD, \( V \) the potential applied to the top plate, \( d \) the distance separating the two plates, and \( m \) the mass of the ion.

The extraction field contributes to the final energy of the ions. As has been shown by Gao \textit{et al}, the higher the energy of the particle, the better the detection efficiency of the PSD. In order to have the highest possible detection efficiency, we choose to operate at the maximum voltage \( V \) allowed by the pulser: 2000V

Equations (3) and (4) yield:

\[ xd = \frac{T^2Ve}{2m} = 31 \text{ cm}^2 \tag{5} \]

Let us choose \( x = 5 \text{ cm} \), \( d = 6.2 \text{ cm} \) and check these values against the other requirements.

The next constraint is that the ions never hit the top plate. This may occur because of the fact that some of the energetic ions will see their initial velocity directed towards the top plate and will therefore get closer to it than the electron beam is. We can estimate the distance those particles travel towards the top plate as the sum of the distance covered while they drift freely before the onset of the pulse and the distance travelled in a linearly rising field. The field cannot be turned on till all the electrons have reached the Faraday cup if we
want to have the ability to monitor the electron beam current during the experiment. A worst case value for this time lag is 200 ns. The first distance is readily estimated:

\[ L_1 = v_0 t_1 = 2.6 \text{ mm} \quad (6) \]

We have used \( v_0 = 1.3 \text{ cm/ms} \) and \( t_1 = 200 \text{ ns} \)

Let us now calculate the second distance \( L_2 \). During the rising edge of the extraction field, which last 100 ns typically, the acceleration is a function of time given by:

\[ a = \frac{eVt}{mdT} \quad (7) \]

where \( V \) is the maximum voltage (2000 V), \( T \) the rise time, and \( d \) the distance separating the two plates. By integration with respect to time we deduce the velocity:

\[ v = \frac{eVt^2}{2mdT} - v_0 \quad (8) \]

The ion will be closest to the top plate when \( v = 0 \). The time is then calculated to be:

\[ t = \sqrt{\frac{2dmTv_0}{eV}} = 110 \text{ ns} \quad (9) \]

We see that it corresponds approximately to the duration of the rising edge itself.

By integration of the velocity, we calculate the distance travelled to be:
\[ L_2 = T v_0 + \frac{VeT^2}{6dm} = 1.3 \text{ mm} \quad (10) \]

The total distance is therefore 4 mm, which is safe since the distance from the electron beam to the top plate is 1.2 cm.

Our last requirement is that a measurement of the time of flight allows us to distinguish between parent and fragment ions.

The time of flight for a parent ion, using an instantly rising pulse is

\[ t = \sqrt{\frac{2xm}{Ve}} = 1.0 \mu s \quad (11) \]

The longest time of flight for a fragment ion corresponds to an energetic ion being formed with an initial velocity directed away from the detector and formed on the edge of the electron beam farthest from the detector. The time of flight is the solution of the equation:

\[ x + r = \frac{VeT^2}{2dm} + v_0 t \quad (12) \]

Where \( r \) is the diameter of the electron beam, estimated to be approximately 1 mm. We calculate:

\[ t = \frac{v_0 + \sqrt{v_0^2 + \frac{2Ve(x+r)}{dm}}}{\frac{Ve}{dm}} = 780 \text{ ns} \quad (13) \]
Conversely, the shortest time of flight will be given by:

\[
    t = \frac{-v_0 + \sqrt{v_0^2 + \frac{2Ve(x-r)}{dm}}}{\frac{Ve}{dm}} = 630 \text{ ns}
\]  

(14)

Therefore, in the case of oxygen, we expect to see in a time of flight spectrum a narrow parent ion peak at 1 \( \mu \)s and a fragment ion peak at 700 ns with a width of 150 ns. The two peaks do not overlap and a time of flight analysis does allow us to distinguish fragment and parent ions.
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