END
DATE
FILMED

1 - 84

OTIC

MICROCOPY RESOLUTION TEST CHART
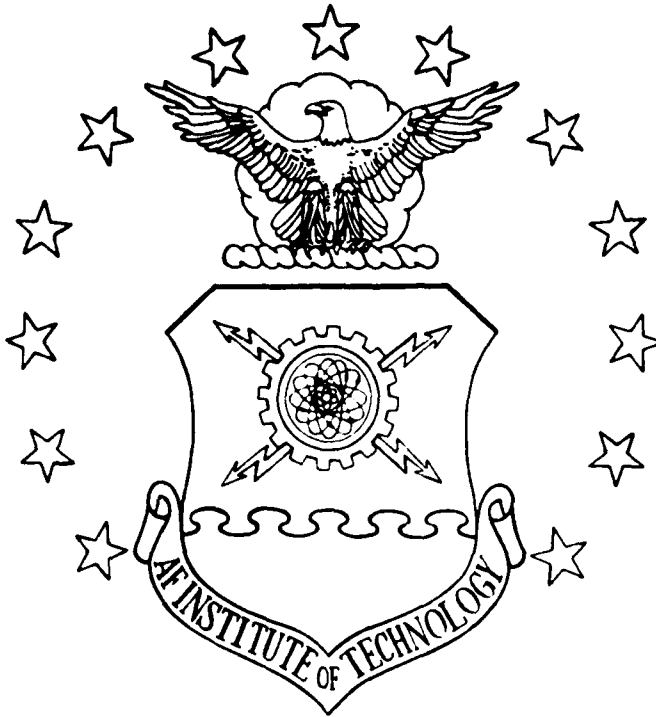
$$1.0$$
$$1.1$$
$$1.25 \quad 1.4 \quad 1.6$$

2.8 2.5
3.2 2.2
3.6
4.0 2.0
1.8

MASS SPECTROMETRY DETECTION

OF NEUTRAL DISSOCIATIVE FRAGMENTS

THESIS

AFIT/GEP/PH/82D-27

Mark E. Wunderlich
Captain   USAF

DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY (ATC)

AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

83 12 13 237

MASS SPECTROMETRY DETECTION

OF NEUTRAL DISSOCIATIVE FRAGMENTS

THESIS

AFIT/GEP/PH/82D-27 Mark F. Wunderlich
Captain   USAF

DTIC
SELECTED
DEC 1 4 1983

B

Approved for Public Release; Distribution Unlimited

MASS SPECTROMETRY DETECTION

OF NEUTRAL DISSOCIATIVE FRAGMENTS

THESIS

Presented to the Faculty of the School of Engineering

of the Air Force Institute of Technology

Air Training Command

in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

by

Mark E. Wunderlich, B.S.

Captain   USAF

Graduate Engineering Physics

December 1982

Acknowledgements

This thesis addresses a subject which is a matter of practical importance in the areas of both semiconductor and plasma physics. I would like to thank the Plasma Research Group of the Aero Propulsion Laboratory, Wright Aeronautical Laboratories, for suggesting this topic. This research, especially the opportunity to use a mass spectrometry system, has proven to be a tremendous learning experience.

In particular, I would like to thank Dr. Alan Garscadden, Captain Greg Schneider, and Captain Gary Duke for their time and helpful suggestions. Also, I would like to thank Dennis Grosjean for his suggestions with the computer system, and Bob Knight for his help in procuring the right tools and equipment to do the job.

I am especially indebted to my advisor, Captain John Prince, for extending to me his knowledge of mass spectrometry. His patience and willingness to help have been the biggest factor in the completion of this work. Special thanks go to my classmates, Major Greg Clark, Captain J.C. Mann, and Captain Tom Hermanson for their support and encouragement.

Final thanks are extended to my wife, Carolyn, and children, Mark and Benjamin, who have been so patient and understanding during the past 18 months.

Mark E. Wunderlich

(This thesis typed by Sharon A. Gabriel)

ii

Contents

List of Figures

List of Tables

v

Abstract

The feasibility of detecting neutral fragments from molecular dissociative processes has been investigated using a mass spectrometer. The mass spectrometer is equipped with dual ionizers. One ionizer is used to form neutral and ionic dissociation fragments. The neutral fragments proceed to the second ionizer for ionization and subsequent detection. The difference in the measured signal when the first ionizer is on or off will reveal information on the formation of neutrals as a function of electron energy. This study concentrates on the detection of the neutral nitrogen (N) and hydrogen (H) fragments from molecular nitrogen (N_2) and hydrogen (H_2).

No measurable experimental results from the two step, dissociation then ionization, process were obtained using the current experimental apparatus. The angular distribution of the dissociative fragments and the type and geometry of the apparatus prove to be important aspects which must be considered when detecting neutral fragments. Recommendations are given which may improve the possibility of detecting neutral fragments using this technique.

MASS SPECTROMETRY DETECTION

OF NEUTRAL DISSOCIATIVE FRAGMENTS

I. Introduction

Purpose

The detection of neutral atoms and molecules is not possible by common mass spectrometry techniques. This is due to the fact that a particle must possess a charge to be focused and detected. Thus, in mass spectrometry, the molecules or atoms under study are ionized using electron bombardment, photoionization, glow discharge, or one of the other numerous ionization techniques prior to mass filtering and detection. This inaccessibility to neutrals is a problem when one is interested in obtaining quantitative information about the neutrals and the processes in which they are involved.

As an example, consider the electron impact of a diatomic molecule (AB). There are several reactions which can take place, the relative magnitude of which depends on the energy of the bombarding electrons. Three of these reactions are:

$$e^- + AB \rightarrow AB^+ + 2e^- \quad \text{Ionization of parent molecule} \qquad (1)$$

$$e^- + AB \rightarrow A+B + e^- \quad \text{Dissociation} \qquad (2)$$

$$e^- + AB \rightarrow A + B^+ + 2e^-$$
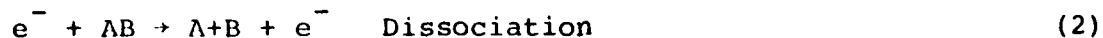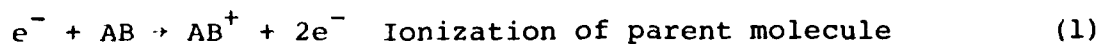
Dissociative Ionization (3)

$$\text{or } A^+ + B + 2e^-$$
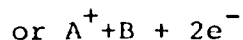
With all of these processes occurring in a reaction, it is possible through mass spectrometry to determine information such as the ionization efficiency for obtaining the ions AB^+ or B^+ from AB . However, quantitative information regarding the neutrals from straight dissociation, dissociative ionization or other secondary reactions cannot be obtained directly.

The purpose of this research is to determine the feasibility of detecting neutral dissociative fragments using a mass spectrometry system. The spectrometer is equipped with two electron impact ionizers. The first ionizer is used to form the reactions (1) - (3). The second ionizer is used to ionize the neutral fragments formed by the first ionizer for subsequent detection and analysis.

Background

Historical. The plasma deposition of Silane (SiH_4) is currently used in the preparation of Hydrogenated Amorphous Silicon (a-Si:H) thin films. These films play a major role in the production of many valuable semiconductor devices. One example is the production of highly efficient solar cells from the glow discharge deposition of silicon onto substrates

2

of indium-tin-oxide (ITO) (Ref 1). It has been determined that the incorporation of hydrogen into the film has a significant effect on the structural and electrical properties of the films (Ref 2). Conductivity is one of the properties which can be varied over wide ranges (Ref 3:31). Very little is known about the basic plasma processes which result in the incorporation of hydrogen into the film during the deposition process. Therefore, it is of interest to know the various plasma species involved in the film formation as well as t specific reactions leading to the incorporation of the hyd en. An understanding of this deposition chemistry is required optimization and control of the efficiency and properties of the semiconductor devices.

Reaction Process. The primary reaction taking place in a glow discharge deposition of SiH_4 is the collision of free electrons with the SiH_4 molecules. When SiH_4 is hit by an electron, there are a great number of possible ions, neutrals, and radicals which will result. Table I shows some of the possible fragments in the plasma. Of these fragments, mass spectrometry can reveal direct information on only the ionic species which are the net result of processes involving all species, neutral and ionic.

Turban, Catherine, and Grolleau (Ref 4) have concluded that the low ion fluxes which they obtained during experiments indicate that ions alone could not be responsible for the film growth. However, it has been impossible to obtain information

3

TABLE I	
Fragments of SiH_4	
Neutrals	Ions
SiH_4	SiH_4^+
SiH_3	SiH_3^+
SiH_2	SiH_2^+
SiH	SiH^+
Si	Si^+
H_2	H_2^+
H	H^+

about the neutral SiH_x groups, such as whether the primary source of SiH_2 was from dissociation of SiH_4, a secondary reaction involving SiH_3, or an even more complicated recombination reaction. Their mass spectrometry sampling of R.F. glow discharges of SiH_4 revealed little information on the role of the neutrals in the reaction (Refs 2,4). However, they indicate in Reference 5 that many intricate secondary reactions between neutrals, atoms and radicals, and ions occur.

4

Since so little is known about processes occurring involving the neutrals, further research is needed to determine the physical characteristics of all the processes involved in the plasma used in this formation.

The ultimate goal is to model all of the processes taking place in a SiH_4 plasma. Obtaining the electron impact cross-sections for all neutral and ionic processes is an important step in this direction. With the aid of computer analysis, these cross-sections will make it possible to totally model SiH_4 and other plasmas.

Scope

The fragmentation of Silane is extremely complex. This research concentrates on much simpler molecules, with the hope of extending the technique to the more complex molecules. H_2 and N_2 were two of the gases studied due to their simplicity and availability. The goal of this research is to detect the formation of neutral atomic nitrogen (N) or hydrogen (H) from molecular nitrogen (N_2) and hydrogen (H_2) as a function of electron bombardment energy. The electron impact ionization technique has been chosen to create the dissociative fragments. The choice of electron impact over the other ionization techniques is due to the nearly monoenergetic nature of the electrons from the ionizer. The small spread in electron energy will make it easier to model a discharge and hence optimize for specific reactions.

II.   Experimental Apparatus

The mass spectrometer system used in the present study
was a Modulated Beam Analytical Mass Spectrometer (EMBA-II),
manufactured by Extranuclear Laboratories, Inc. Figure 1 gives
the overall layout of the system and the necessary equipment
for its operation. For the purpose of discussion, the system
will be broken into three categories:

1) Mass Spectrometer

2) Spectrometer Control and Analysis

3) Vacuum and Gas System.

Mass Spectrometer

The spectrometer is divided into two differentially
pumped chambers. The first chamber contains an iridium fila-
ment (ionizer #1), five electrostatic optical elements, and
a chopper. The second chamber contains an array of four
tungsten filaments (ionizer #2), six electrostatic elements,
a quadrupole mass filter, and an electron multiplier. The
only connection between the chambers is a small 1/8 inch
aperture to allow neutral and ionic gas flow.

Figure 2 shows the physical arrangement of the ionizers,
chopper, and the ion optics. A small hole in the orifice plate
provides the entry point for the molecular beam. The orifice
is a "knife edge" in shape, with an entrance diameter of 50 μm,
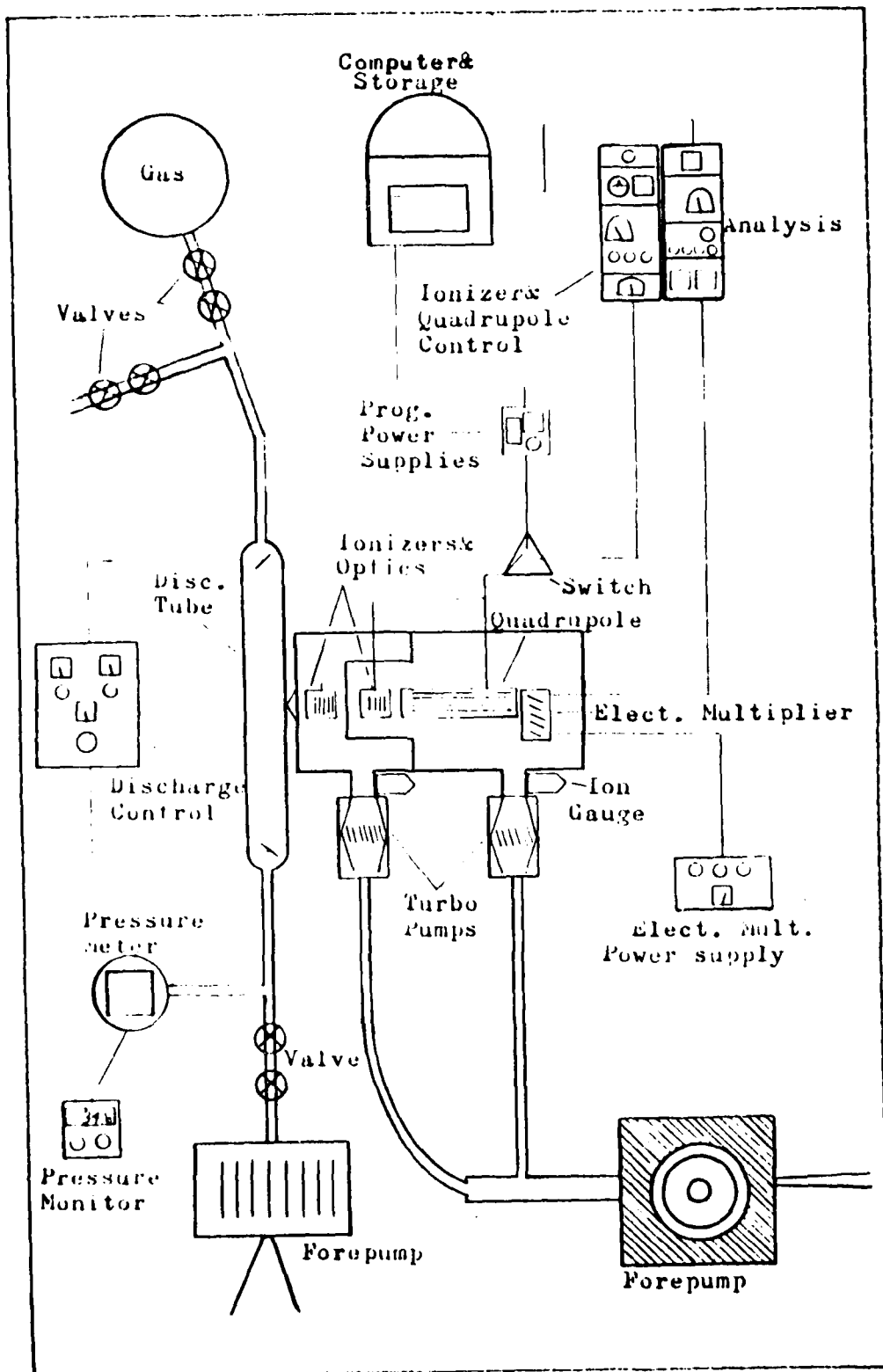exit diameter of 220 μm, and a depth of about 80 μm.

6

Figure 1. Mass Spectrometer and Associated Equipment
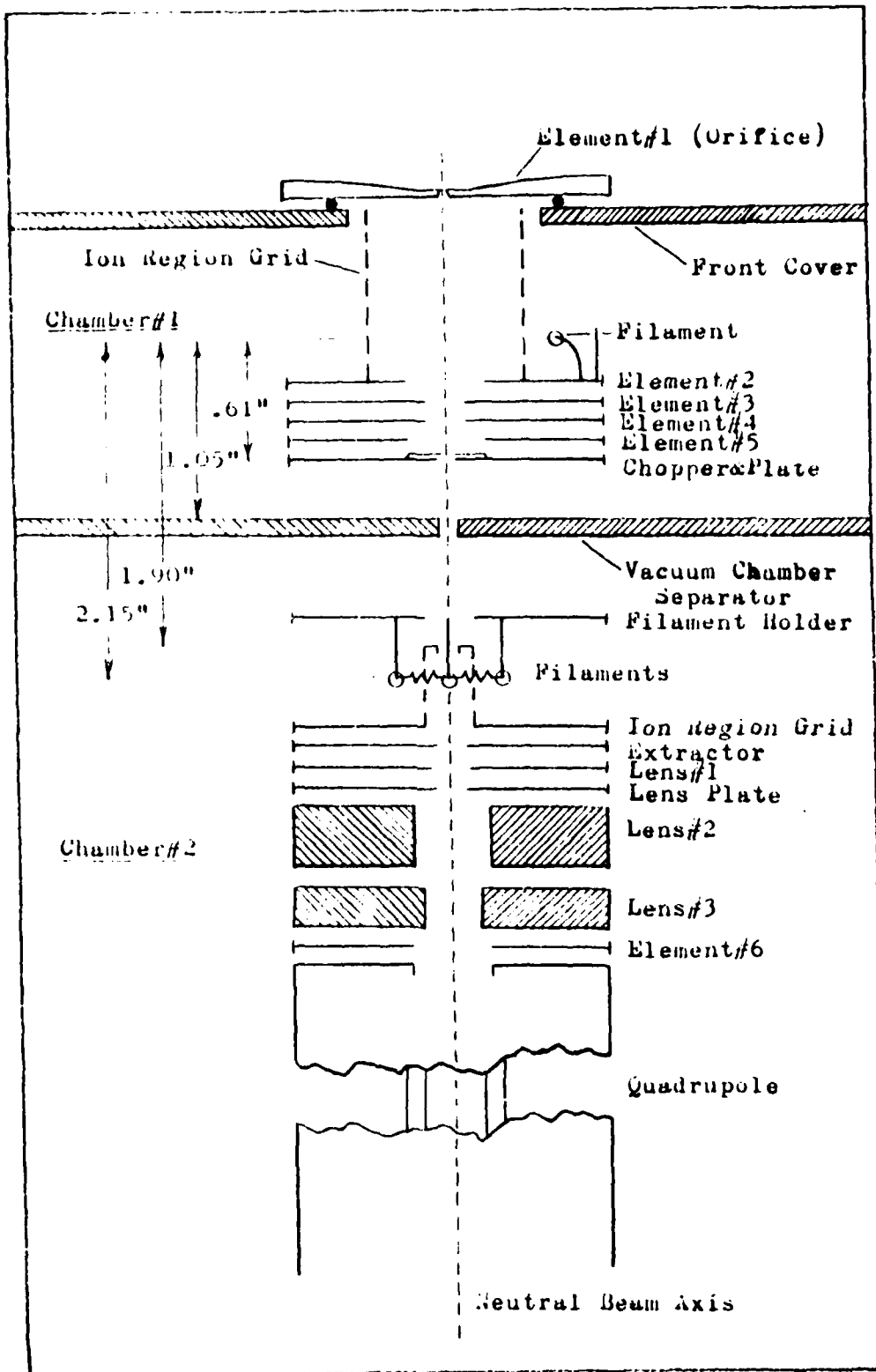
Figure 2. Arrangement of Ionizers, Chopper & Optics

8

The elements in chamber #1 can serve a dual purpose. The most proficient use is to extract and focus ions from an ion source, such as a glow discharge, into the second chamber. In this case, the filament of ionizer #1 is left off, and a potential is usually applied to element #1 (orifice plate) to give the incoming ions an initial energy.

In the present experiment, the filament of ionizer #1 was used to produce electrons for electron impact, and no potential was applied to element #1. Element #2 is a 1" x 1" wire mesh grid. The potential which is applied to this grid serves to accelerate the electrons from the filament into the center of the grid, thus forming an ionization region. Element #3 acts as an extractor to pull the ions out of the ionization region. Elements #4 and #5 are lenses which focus the ions. A motor driven tuning fork literally chops the beam on and off, producing a modulated molecular beam at 400 hz.

An array of four tungsten filaments and a grid form the second electron impact ionizer. An extractor and four lenses provide focusing of the ions from the second ion region into the quadrupole mass filter. The mass filter passes the ions of correct mass to charge ratio to a 14 stage venetian blind electron multiplier. Table II gives the values of the potentials and aperture sizes for all elements in both chambers. Ionizer #1 and its optics in chamber #1, and ionizer #2 and its optics in chamber #2 are operated with separate circuitry with the exception of element #6, which is run by the circuitry of ionizer #1.

9

TABLE II

Potentials and Aperture Sizes
of Electron Optics Elements

ELEMENT	POTENTIALS (Volts)	APERTURE SIZE Inches (unless specified)
Element #1	N/A	50 μm, 220 μm
Element #2	- 50 to + 50	1/2
Element #3	-260 to +260	1/4
Element #4	-260 to +260	1/4
Element #5	-260 to +260	1/2
Chopper Plate	N/A	7/64
Chamber Separator	N/A	1/8
Filament Holder	N/A	5/16
Ion Region Grid	0 to 60	5/32, 11/32
Extractor	- 10 to + 10	3/16
Lens #1	-250 to +100	1/4
Lens Plate	-250 to +100	3/16
Lens #2	-250 to +100	1/2
Lens #3	-250 to +100	3/8
Element #6	- 15 to + 15	1/2

Elements 1-6 Referenced to Ground

Extractor and Lenses 1-3 Referenced to Ion Grid

Spectrometer Control and Analysis

The equipment used for control and analysis is contained in an equipment rack. In this rack are the power supplies and controls for both ionizers and lens elements. The rack also contains the R.F. power source for the quadrupole, and the quadrupole control unit which selects the mass peak to be studied. A phase sensitive lock-in amplifier tuned to the 400 hz chopper frequency provides the capability to subtract background signal from the signal due to the incoming beam. The mass spectrum or individual mass peaks are displayed on an oscilloscope. The power source (-4000 V) for the electron multiplier is separate from the other power sources.

A Hewlett Packard 9845 computer, 9885M disc drive, and 9872A plotter enhance the capability of the system. Measurements of peak intensity can be taken manually from the scope or lock-in amplifier, or the computer can be used to externally control the system. Computer programs provide instructions to programmable power supplies which can operate the mass sweep function, or the energy sweep of ionizer #2. The lock-in amplifier signals for the mass or energy sweep are digitized and stored in the computer or on disc for future reference. Plotting routines are available to produce plots of the mass or energy spectra.

Vacuum and Gas System

A forepump is used to pump the chambers of the mass spectrometer. Once a pressure of 10^{-3} torr is obtained, two turbo-molecular pumps (450 ℓ/sec), one for each chamber, are used. The ionizers cannot be operated until a pressure below 10^{-5} torr is achieved. Equilibrium pressures in chambers #1 and #2 were typically 5×10^{-6} torr and 2×10^{-7} torr, respectively, as measured by ion gauges at the entrance to the turbo-molecular pumps. These pressures did not change appreciably when gas was fed into the system.

A glass discharge tube is attached to the orifice plate by suction. Commercial bottled gas was bled into the discharge tube by opening a series of on-off and needle valves. A forepump provided evacuation of the discharge tube. The required pressure was obtained by adjusting a needle valve at the end of the tube. This technique provides ease in varying the flow rate and pressure in the discharge tube. The pressure (in torr), as measured by a baratron pressure manometer, was read directly from a digital display.

A D.C. discharge source, with connection to an anode and cathode inside the tube, could provide a glow discharge. However, this capability was not used in the present experiment.

12

III. Experimental Procedure

When a diatomic molecule such as N_2 is bombarded with electrons from ionizer #1, the ionic species N_2^+ and N^+, and the neutrals N_2 and N, will result from the reactions previously mentioned in reactions (1)-(3). If the ions N_2^+ and N^+ cna be kept in chamber #1 by applying various potentials to the optical elements, then only the neutrals N_2 and N will get through to ionization region #2.

The tuning procedure was as follows. Ionizer #2 was turned on by itself, and tuned for the N^+ peak at mass 14. Then, ionizer #1 was turned on by itself, and tuned to reduce the N^+ signal to zero. This indicated that no N^+ ions were reaching the second ionizer. Ionizer #2 was then turned on, and a measurement was made of the signal from N^+ ions. Any additional signal that was present when ionizer #1 was turned on was due to the ionization in the second ionizer of neutral N from ionizer #1. A measure of this additive signal as a function of electron energy in ionizer #1 will lead to information regarding the production of neutrals by the first ionizer.

All measurements of signal were taken manually from a monitor on the lock-in amplifier.

IV.   Experimental Results

One of the biggest problems encountered using the two ionizer technique was the relative efficiency of the two ionizers.   Ionizer #1 consisted of one filament of length 1.2 cm, whereas ionizer #2 had four filaments of the same length.   This made ionizer #2 much more effective when it came to the ionization of neutrals.   Typical efficiencies of ionizer #2 are 1% of the incoming neutrals.   Of course, this depends on the electron energy, emission, and the atom or molecule being ionized.   Ionizer #1 was much less efficient in ionization or dissociation of the incoming molecules. Compounding this problem was the fact that, regardless of electron energy, ionizer #1 became unstable if it was operated at emission currents over .5 mA.   Thus, ionizer #2 had to be tuned at low emission currents (not necessarily optimum conditions) to ensure that the additive signal which would come from ionizer #1 was not overshadowed.

The operation at low currents required that the pressure in the flow tube be increased to obtain a strong enough signal at the detector.   Due to the combustibility of H_2, it was diluted in a 1:4 ratio with argon.   Thus, at 35 torr the partial pressure of H_2 was not sufficient to get a reliable signal from the H^+ ions.   Attempts to increase the pressure of H_2 by increasing the overall pressure resulted in a significant increase in the background pressure in both chambers.

14

Since H_2 is hard to pump from a vacuum due to its low molecular weight, the background signal increased to intolerable levels.

Figure 3 shows the results for the detection of N^+ ions where N_2 was fed into the discharge tube at 34.8 torr. These results were obtained with elements 3, 4, and 5 (see Figure 2) tuned to 0 volts. Following the experimental procedure mentioned earlier, element #2 was then tuned to a point where no ions came through to the detector. However, the neutrals should still be reaching ionizer #2. It might be noted at this point that this arrangement of the elements was the only one which kept the ions from reaching ionization region #2. During the data run of Figure 3, both ionizers were set at .5 mA emission, and ionizer #2 was varied from 5 to 100 eV.

There is an increase in the signal of N^+ ions when ionizer #1 is on. This increase is dependent on the energy of the ionizer #1 as expected. However, the additional signal is not present for ionizer #1 electron energies below 50 eV. One would expect to see an increase for energies down to the dissociation energy of N_2 at 9.80 eV (Ref 6:F-223). Also of interest is the existence and shape of the signals below the appearance potential for obtaining N^+ from N_2 at 24.5 eV (Ref 7:270). This signal should not normally exist below this energy of ionizer #2, since the creation of N^+ from ground state N_2 is impossible below this energy. The initial reaction was that this tail in the curve at low eV
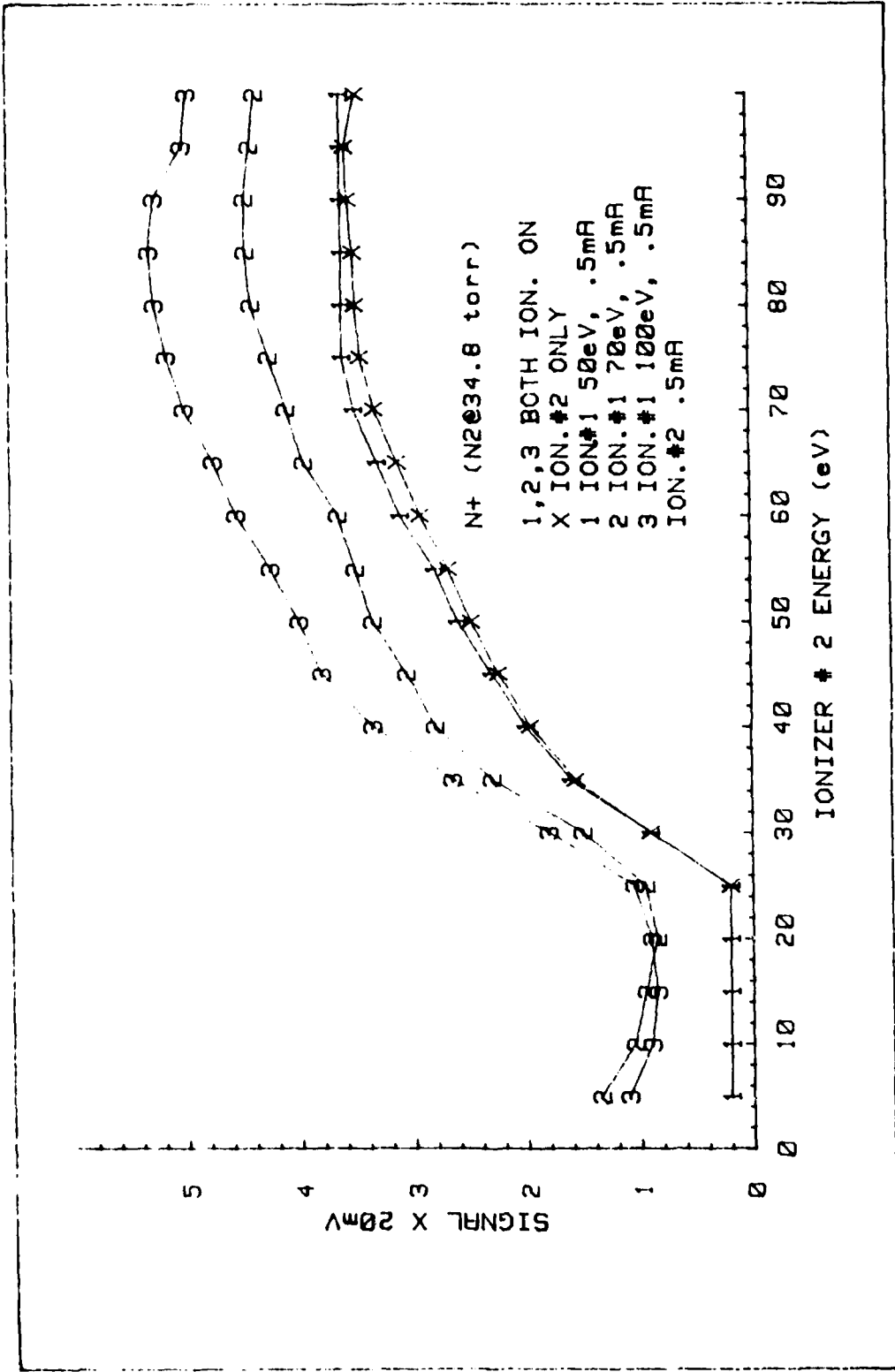
15

Figure 3. Measured Signals of N$^+$ Ions

16

was due to the ionization of excited state nitrogen atoms or molecules created by ionizer #1. These metastables would require a much lower energy for ionization.

Due to the suspicious nature of the data, other gases were investigated. Argon was chosen for investigation. Using the same procedure as with nitrogen, the ions from the first ionizer were kept in the first chamber. Figure 4 shows the results for argon. The same characteristics are evident in the data. In fact, Figures 5 through 9 show that this result is typical during the detection of many other ions, including N_2^+, Ar^{++}, H_2^+, O_2^+, and O^+. The results all show the same trend, a tail at low electron energies, followed by a sharp increase in signal at the ionization or appearance potential, and most importantly, an additive signal when ionizer #1 is turned on. The general shape of the curves is typical of an ionization efficiency curve, except for the low electron energy tail. The fact that the curves peak at other than normal energies can be explained by the fact that ionizer #2 was tuned at only a single energy for each data run. Thus, the shapes are not representative of true ionization efficiency curves. The low electron energy tail existed no matter where ionizer #2 was tuned.
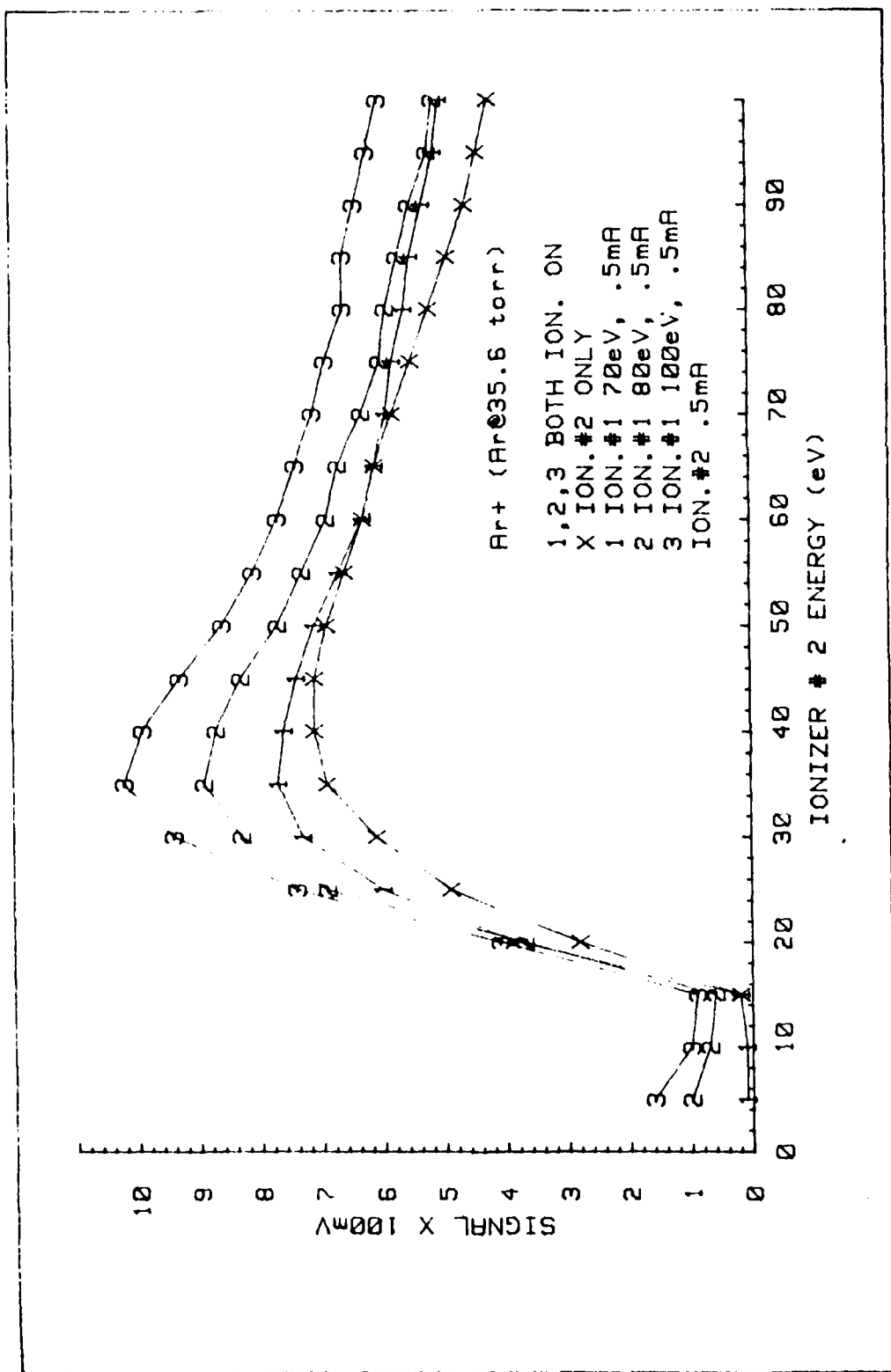
17

Figure 4. Measured Signals of Ar$^+$ Ions
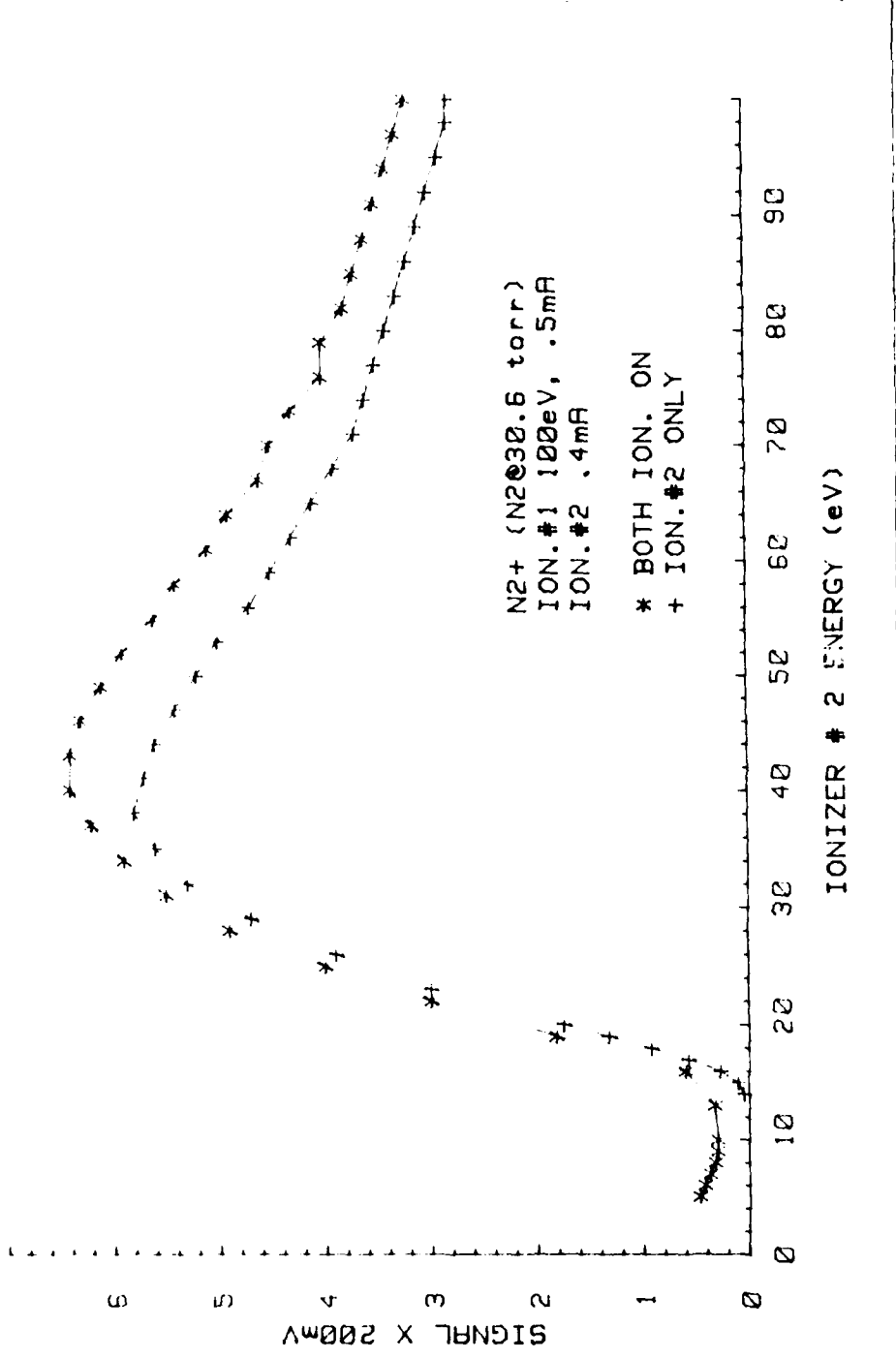
18

Figure 5. Measured Signals of N_2^+ Ions
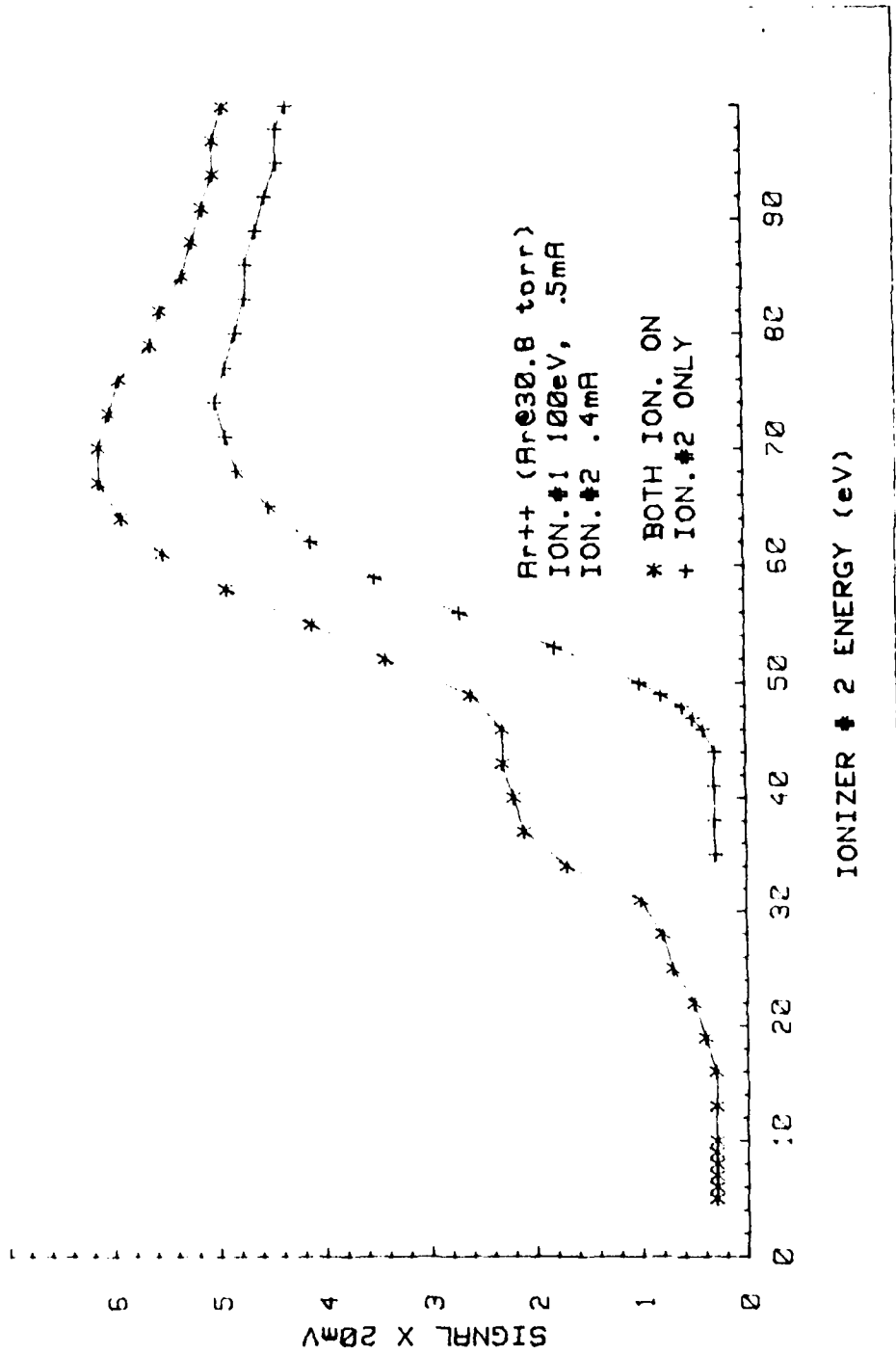
Figure 6. Measured Signals of Ar^{++} Ions

20
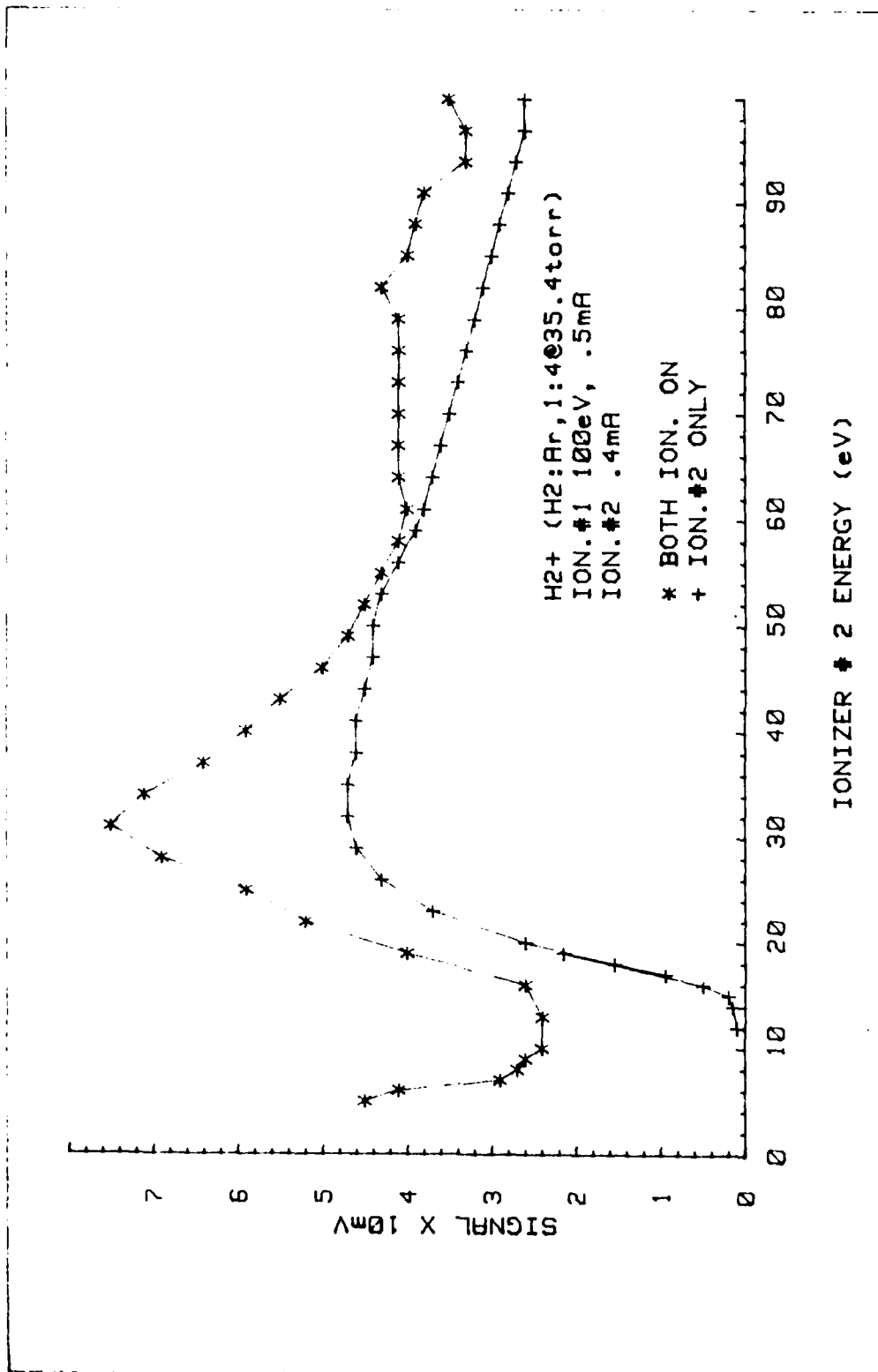
Figure 7. Measured Signals of H_2^+ Ions
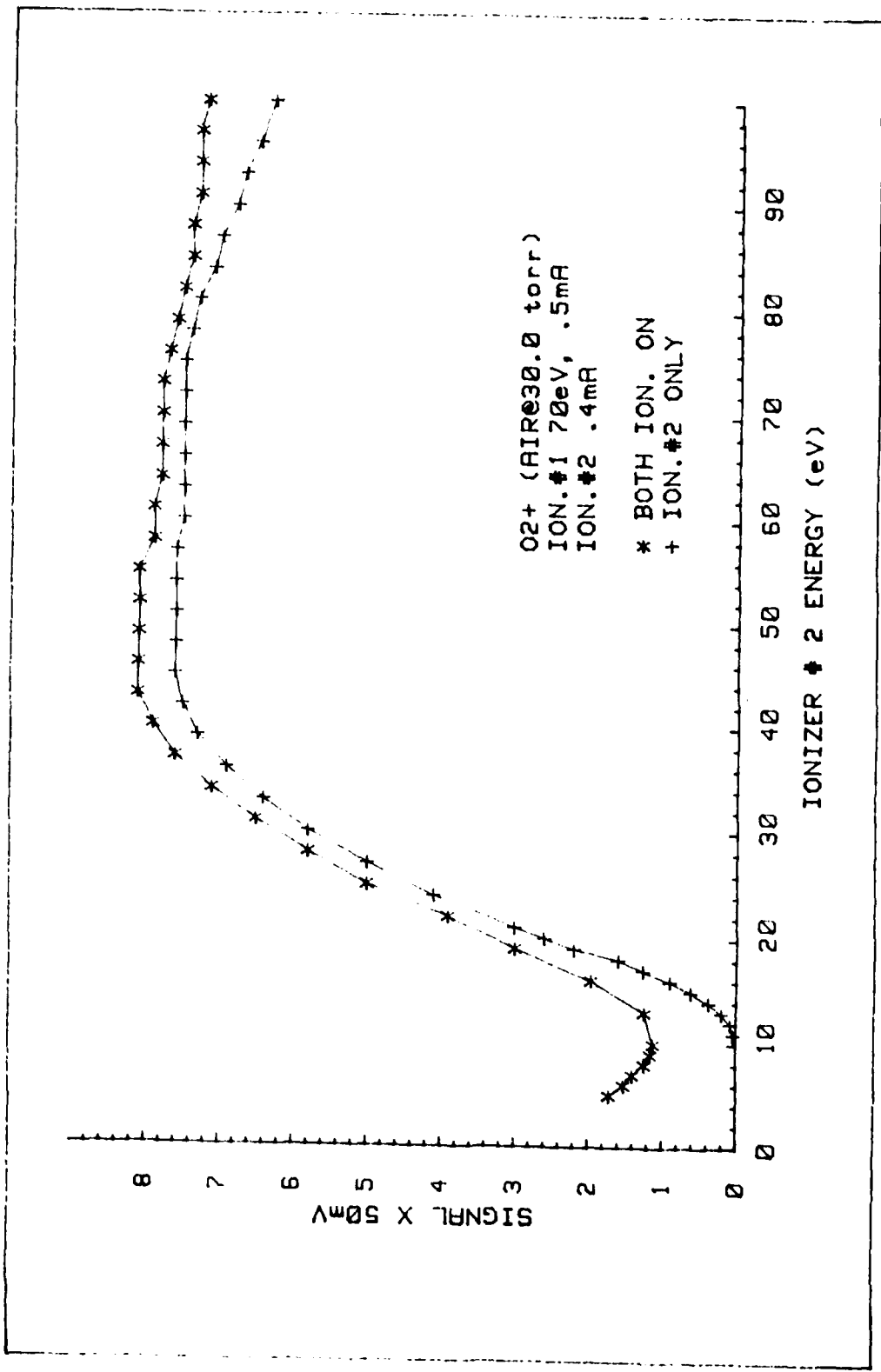
Figure 8. Measured Signals of O_2^+ Ions
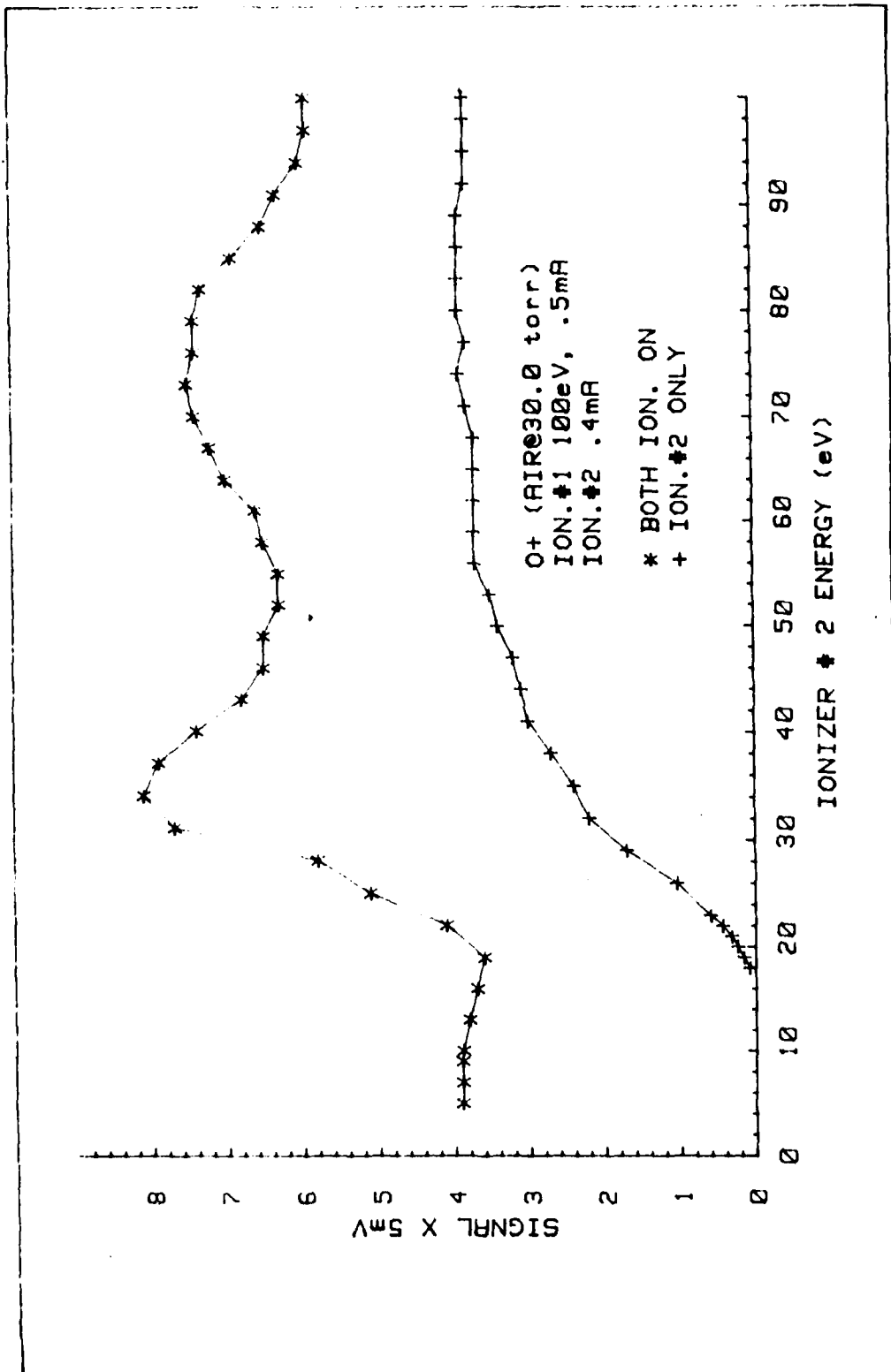
Figure 9. Measured Signals of O^+ Ions

23

V. Discussion

Ion Optics Interaction

It is obvious that, since ions such as Ar^+ show the additive signal, the additive signal for N^+ is not due to the ionization of neutral N fragments from ionizer #1. Rather, it is most likely due to an interaction between the optical elements. This conclusions is substantiated by several facts. First, the signals seem to change rapidly from time to time as if there were a building up of charge and subsequent discharge taking place. This effect was most evident at low electron impact energies in ionizer #2, and it tremendously affected the reproducibility of any data. It is known for a fact that the chopper and chopper plate were being charged by some means. An external connection provided the capability to ground the chopper plate. Doing so changed the signals significantly. However, this did not eliminate the low electron impact energy signals. Also, when the extractor of ionizer #2 was made positive with respect to the ion energy, no additive signal was detected for any ion, including N^+, and the low electron impact energy tail disappeared.

One explanation for the additive signal occurring on all ion signals is as follows: Ionizer #1 was adjusted with ionizer #2 off. In all cases, element #2 was tuned to reduce the signal from ionizer #1 to zero. When both ionizers were turned on, the negative space charge which existed in ionization

24

region #2 (i.e., inside the grid) could be large enough to pull or extract, into ionizer #2, some of those positive ions that normally wouldn't make it into ionization region #2 when just ionizer #1 is on. This seems reasonable since further tuning of element #2 when both ionizers were on could reduce the additive signal to zero. This "re-tuning" had the effect of offsetting the pulling power of the negative space charge.

Angular Distribution of Dissociative Fragments

If the above explanation is in fact true, then the question of why the signal from the neutrals was not detected remains to be answered. A clue to what is happening may lie in the electron-molecule collision process. It was Dunn (Ref 8) who first pointed out that the products of dissociation produced by electron impact depend upon the symmetries of the initial and final electronic states involved in the process. He stated that, when an electronic transition to an antibonding state occurs in a molecule, the impending dissociation normally takes place in a time small compared to the period of molecular rotation. To a good approximation, the dissociation products will then be traveling in a direction characteristic of the vibratory motion. The excess of the excitation energy over the energy of the final state is shared as kinetic energy in the out-going fragments. He concluded that the angular distribution

25

of the fragments depends critically on the initial and
final states of the fragments, and that anisotropies can be
expected for many molecules.

Rapp, Englander-Golden and Briglia pointed out in
their paper (Ref 9) regarding dissociative ionization of
H_2 that the resulting kinetic energy and angular distribution
of the fragments greatly hamper collection efficiency when
using a conventional slit system and ion optics. Thus,
accurate quantitative information regarding ionization of
molecules is difficult to obtain if the angular aspects are
not taken into account.

Much work, experiment and theory has been devoted to
the measurement and calculation of the kinetic energy and
angular distribution of the fragments from molecular dis-
sociation. By far, the most work has been done on hydrogen
(Refs 10, 11, 12, 13). However, work has also been done on
deuterium (Refs 10, 14), nitrogen (Refs 15, 16, 17, 18) and
oxygen (Ref 16).

It is worth presenting some of the data from these
studies. In general, the results show that the angular
distribution is a strong function of the fragment kinetic
energy and the electron impact energy. The typical geometry
used in the studies is shown in Figure 10. An electron beam
intersects either a static gas target, or a gas flow, where
the molecular flow velocity is related to the thermal energy
of the molecules. The angle θ is the angle in the plane
between the detector and the electron beam.
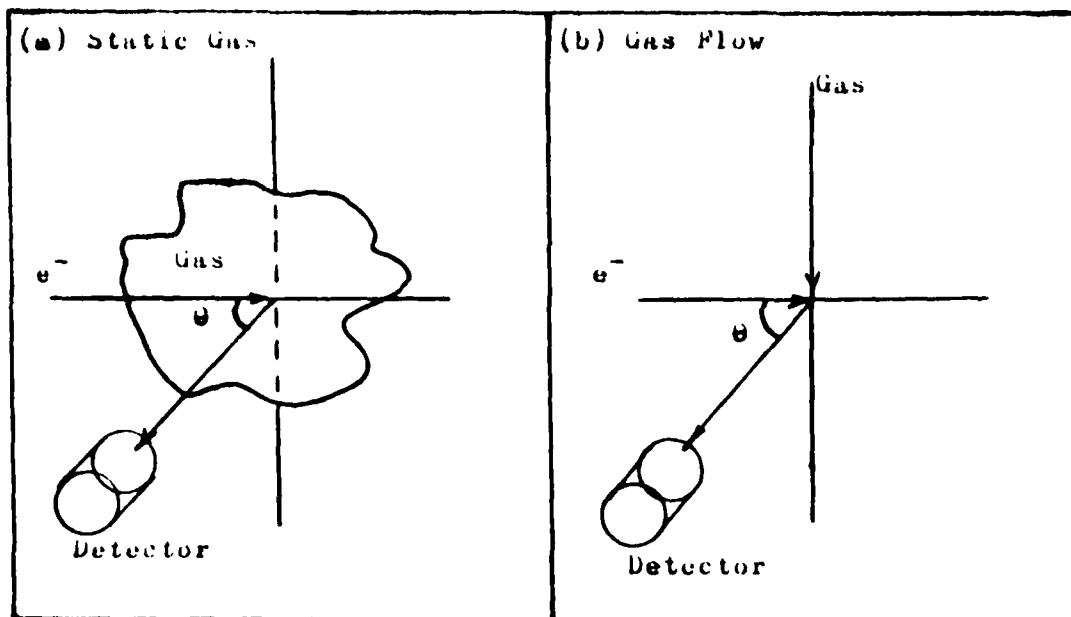
Figure 10.   Typical Geometries Used in
Angular Distribution Studies

Figure 11 shows the results of calculations by Zare
(Ref 11).   He used a Born approximation treatment to
calculate the angular distribution of 4.38 eV protons
ejected from the electron impact dissociation of H_2^+.
Dunn and Kieffer (Ref 13) did an experimental study of the
angular distribution of protons from dissociative ioniza-
tion of a static H_2 gas.   Their results for 8.6 eV protons
are given in Figure 12.   The results of both Figures 11 and
12 show that the anisotropy increases as the electron impact
energy decreases.   The forward-backward asymmetry in the
data of Figure 12 is due to linear momentum transfer effects
during the collision process (see Ref 19 or 20).
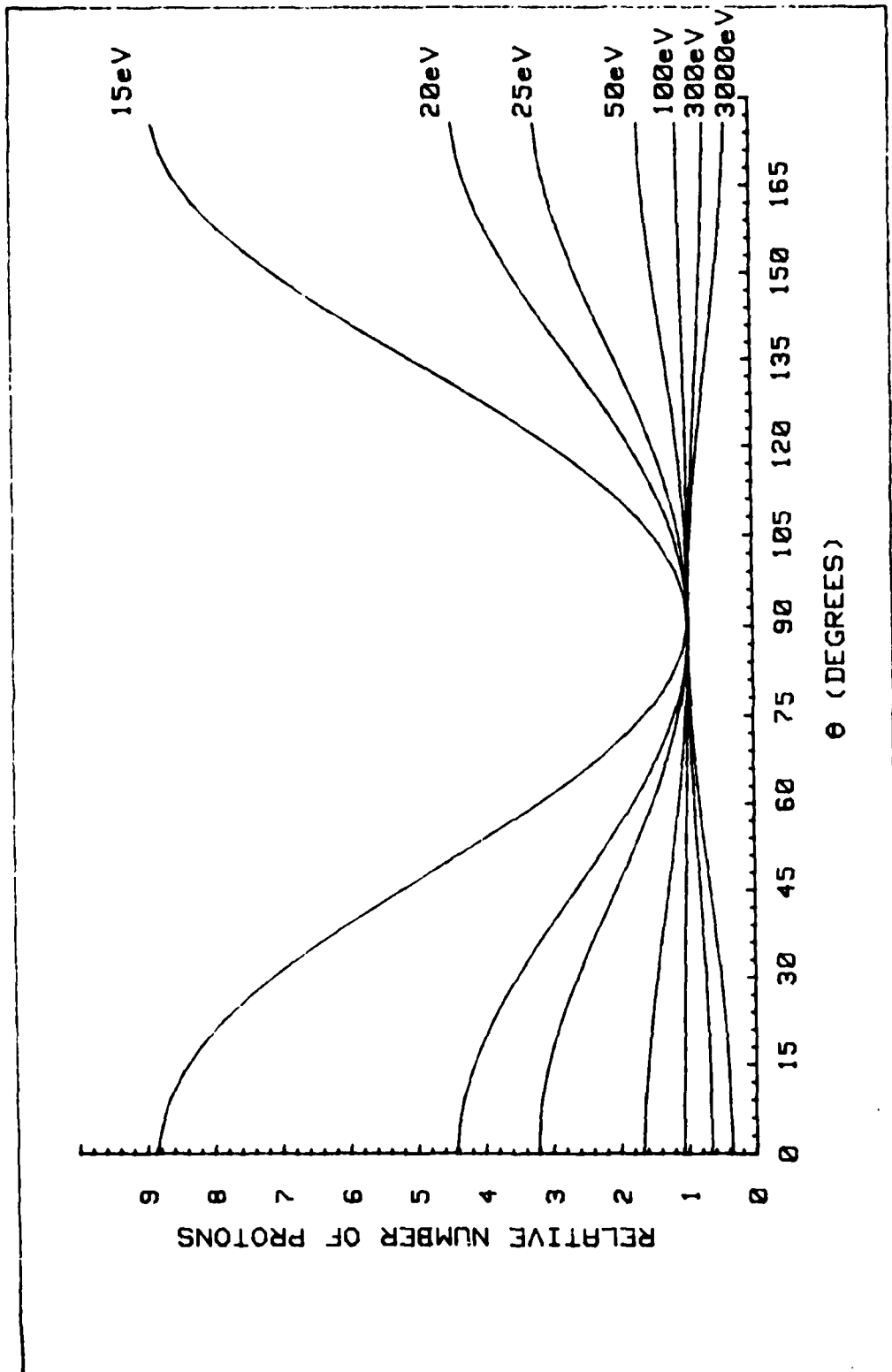
Figure 11. Calculated Angular Distribution of 4.38 eV Protons From Dissociative Ionization of H_2^+ (Data from Ref 11)
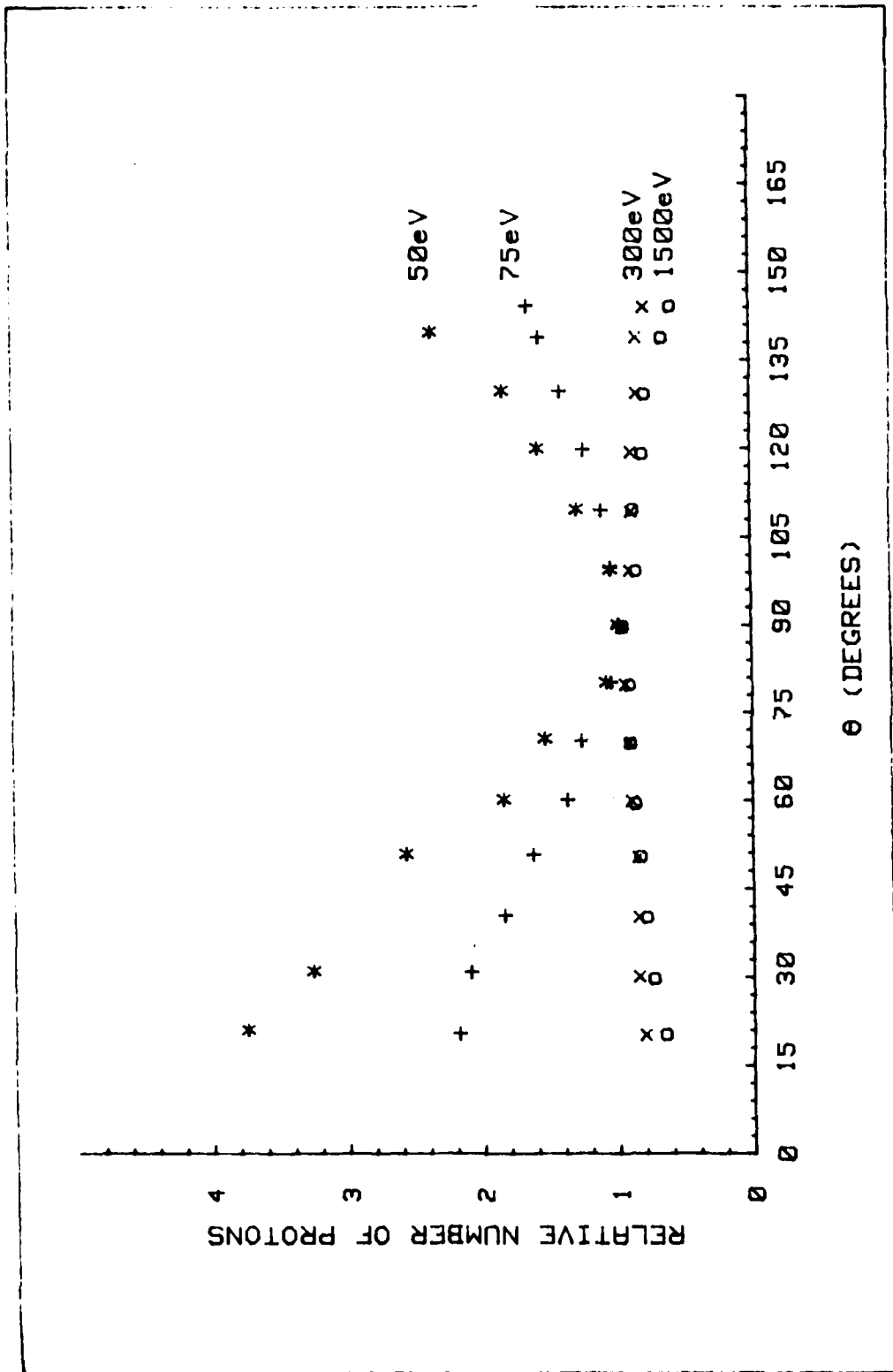
Figure 12. Angular Distributions of 8.6 eV Protons From Dissociative
Ionization of H_2 (Data from Ref 13)

Figure 13 shows the results of Crowe and McConkey for the angular distribution of N^+ ions of all energies from the dissociative ionization of N_2 in a static gas (Ref 15). These results are much different and show an almost isotropic distribution of ions. However, a slight increase in anisotropy with decreasing electron impact energy and the forward-backward decrease is still evident. The studies, using a gas flow perpendicular to the detector/electron beam plane, show that the distributions are not affected appreciably by the flow. Two such studies for N^+ (Ref 17) and O^+ (Ref 16) show a nearly isotropic distribution. Although the studies mentioned thus far have dealt with detection of ion fragments, a study (Ref 20) of the metastable H(2S) atoms from the dissociative excitation of H_2 show angular distributions which are also in agreement with the predictions of Dunn.

The point being made is that the angular distribution of the fragments is a very complex function of the molecular and atomic states, the fragment energies, and the electron impact energy. For detection of ions, the angular distribution does not hinder the collection as it does for neutral fragments. Since the neutral fragments cannot be focused by ion optics, quantitative information regarding neutrals becomes very dependent on the geometry of the apparatus. Relating this to the present experiment, consider the geometry given in Figure 2.

30
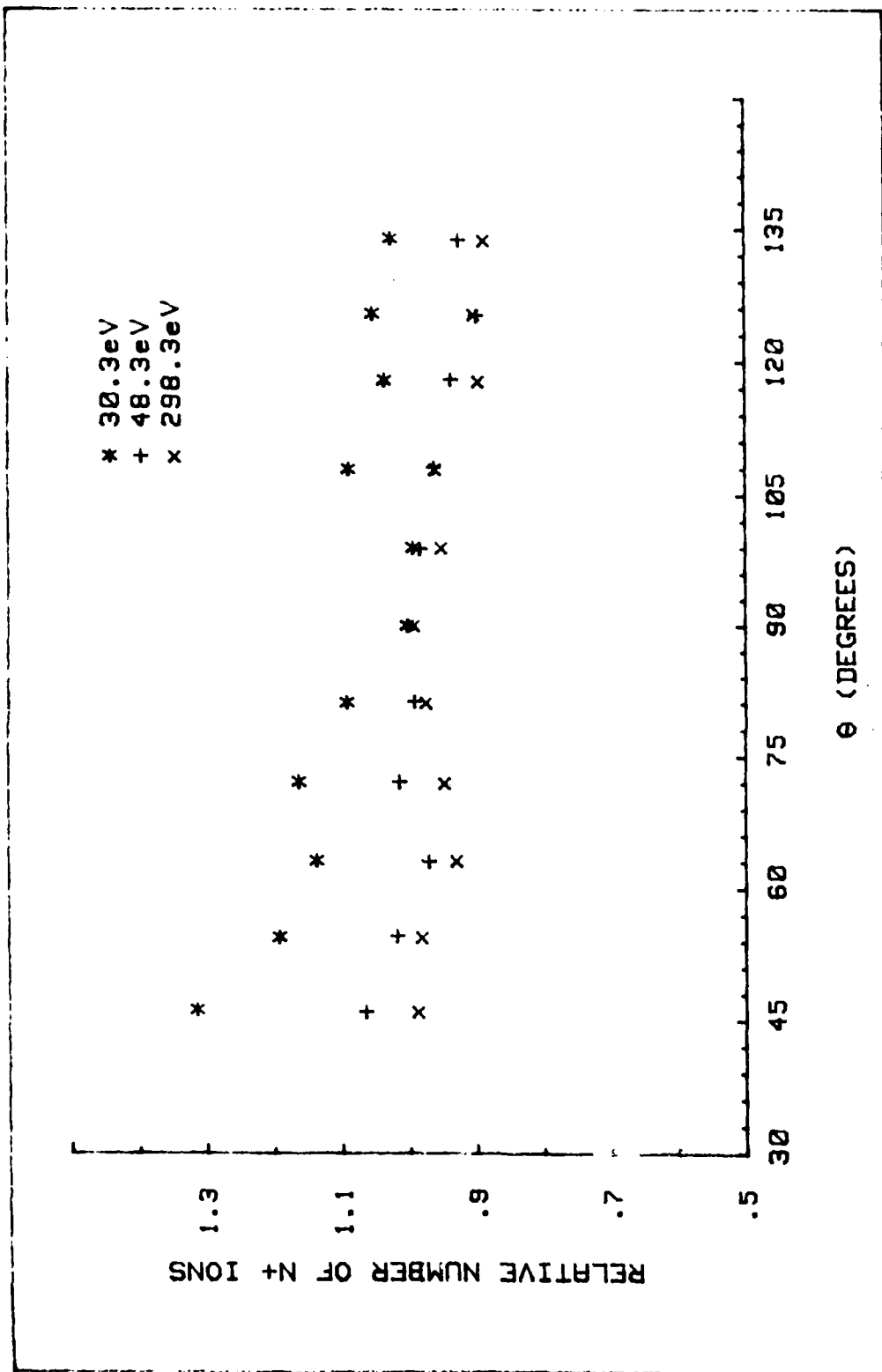
Figure 13. Angular Distribution of N⁺ Ions From Dissociative
Ionization of N_2 (Data from Ref 15)

In the present case, the detector axis and gas beam axis are the same. It must be determined if the initial molecular velocity will have an effect on the angular distribution of the fragments. To do this, consider a collision between an electron and a nitrogen molecule. Assume that the electron transfers all its energy to the molecule, and that dissociation will take place with the fragments exiting perpendicular to the beam axis, as shown in Figure 14. In such a collision, the fragment will share the energy in excess of the dissociation energy at 9.8 eV. The neutrals making it to ionizer #2 will be limited by the aperture between ionizer #1 and ionizer #2 that presents the smallest angle. The entrance to the ion region grid just before ionizer #2 creates the smallest angle (half angle 2.35°). To determine the effect of the molecular velocity, one must determine the resultant velocity vector obtained from vector addition of the molecular velocity and the velocity from the momentum transfer of the electron. The velocity component down the beam axis, V_t , will be the average velocity of the molecule due to its thermal energy

$$V_t = (8KT/\pi m)^{\frac{1}{2}} \tag{4}$$

where

K   is Boltzmann's constant

T   is temperature (kelvin)

m   is the mass of the molecule.
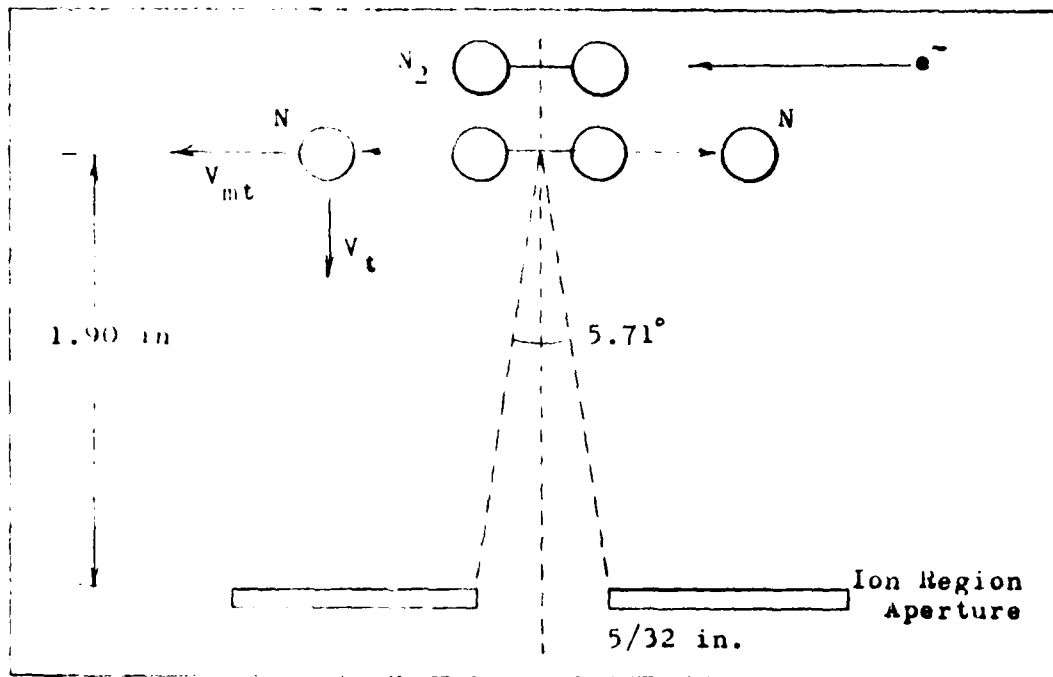
Figure 14.   Fragment Velocity Considerations

Using   T = 300° ,

$$V_t \;=\; 4.75 \times 10^4 \text{ cm/sec}$$

The velocity component perpendicular to the beam axis
will be related to the electron energy (ε) by:

$$\varepsilon \;=\; MV_{mt}^2 \;+\; 9.8 \text{ eV} \tag{5}$$

where

M   is the mass of the fragment.

33

To proceed to the second ionizer, the fragment's resulting velocity vector must fall within the 5.71 degree angle. A calculation shows that, to get through the aperture, the bombarding electron energy must be less than 5.52×10^{-5} eV above the dissociation energy. Since this energy is so small compared to the normal energy of separation, the velocity component resulting from the initial molecular velocity is negligible.

If we assume that the neutral N fragments have an isotropic distribution after their creation in ionizer #1, then the number of them getting to ionizer #2 will depend on the solid angle Λ of the aperture.

$$\Lambda = \frac{A}{d^2} \tag{6}$$

where

A is the area of the aperture

d is the distance from filament #1 to the aperture.

Substituting the correct values, one finds:

$$\Lambda = \pi[\tfrac{1}{2}(5/32 \text{ in})]^2/(1.90 \text{ in})^2 = .00531 \text{ rad}$$

Thus the fraction (F) of the neutrals in the isotropic distribution which would reach ionizer #2 is obtained by dividing by the spherical solid angle 4π .

$$F = \Lambda/4\pi = 4.2 \times 10^{-4} \tag{7}$$

In other words, only four neutrals out of every 10,000 created make it to the second ionizer. If you consider that the maximum ionization efficiency of the filament is about 1%, then only four in a million are ionized and subsequently detected. However, when determining the strength of the additive signal, the 1% efficiency factor is replaced by the relative strength between the two ionizers. Even if the ionizers were of equal efficiency, detecting an increase in signal of four on top of an existing signal of 10,000 is not within the detection limits or sensitivity of the system.

VI.   Conclusions and Recommendations

The detection of the neutral dissociative fragments from diatomic molecules using a double ionizer technique seems to be a formidable task. The deconvolution of the neutral products of an even more complex molecule may prove to be an insurmountable task. The neutrals from the first ionizer were not detected due to a combination of factors. In the case of N_2, the isotropic nature of the fragments and the specifications of the mass spectrometer system prevented most of the neutrals from reaching the second ionizer. Thus, the increase in signal was not strong enough to be detected.

Recommendations

Several problems have turned up in this first attempt to measure neutral dissociation products with the mass spectrometer. Some modifications to the system and technique may increase the possibility of detecting the neutral fragments.

(1)   Following Dushman (Ref 21:Ch 2), calculations were made to determine which flow regime the gas was in during its passage through the entrance orifice. Using the experimental conditions T = 300 degrees kelvin, P = 35 torr, the calculations for nitrogen (N_2) reveal that the gas

flow is intermediate. Both collisions with the orifice wall and collisions between molecules will be influential in determining the flow characteristics.

Further study is needed to determine if modification of the orifice and optical apertures would provide a better beam flow and collimation through the system. Better collimation would increase the overall efficiency of the first ionizer.

(2) One of the major problems encountered in the experiment was how to keep the ionic species created in ionizer #1 from getting to the second ionizer. In the mass spectrometer, all optics presently used are circular in shape, and have focusing properties similar to optical lenses. Element #2 was merely able to hold the ions in the ionization region. The installation of an ion attraction plate on one side of the first chamber will make it possible to draw ions to the side of the chamber. This will allow better flexibility with the other optics and may eliminate the optical interaction problems which were encountered.

(3) Make ionizer #1 more efficient. The possibility exists to install a four filament ionizer and ion region grid (like ionizer #2) in the place of the existing filament and wire mesh grid. This modifi-

cation should be fairly simple, -nd it would make ionizer #1 as efficient as ionizer #2. The wider range of emission currents would produce an increased amount of neutral fragments. The emission currents of both ionizers could be varied until the additive signal can be detected. It will have to be determined if the circuitry which presently operates ionizer #1 will be capable of operating the four filament arrangement.

(4) Create neutrals using a technique other than electron impact ionizer.

The possibility of detecting the neutral fragments from a glow discharge should be investigated. The system already has the capability for this kind of operation.

I recommend that the discharge of N_2 be sampled with and without one of the ionizers operating. The existence of neutral N in the discharge can be determined by operating the ionizer between the ionization energy of atomic N at 14.54 eV (Ref 7:270), and the appearance potential for obtaining N^+ from N_2 at 24.5 eV (Ref 7:270). Operation in this range will ensure that the N ions collected are coming from the ionization of N rather than dissociative ionization of N_2. When using a glow discharge, the monoenergetic nature of the bombarding electrons is lost. However,

the number of neutral fragments in the plasma will
be higher, and the angular distribution of the
fragments will be determined by only the orifice,
and should be much smaller.

Bibliography

1. Carlson, D.E. and C.R. Wronski. "Amorphous Silicon Solar Cell," Applied Physics Letters, 28: 671-673 (June 1976).

2. Turban, G., Y. Catherine, and B. Grolleau. "Ion and Radical Reactions in the Silane Glow Discharge Deposition of a-Si:H Films," Plasma Chemistry and Plasma Processing, 2: 61-80 (February 1982).

3. Adler, David. Amorphous Semiconductors. Cleveland OH: CRC Press, 1971.

4. Turban, G., Y. Catherine, and B. Grolleau. "Mass Spectrometry of a Silane Glow Discharge During Plasma Deposition of a-Si:H Films," Thin Solid Films, 67: 309-320 (April 1980).

5. Turban, G., Y. Catherine, and B. Grolleau. "A Study of the Silane Glow Discharge Deposition by Isotropic Labelling," Thin Solid Films, 77: 287-300 (March 1981).

6. Weast, Robert C., Ed. Handbook of Chemistry and Physics (57th Ed.). Cleveland OH: CRC Press, 1976.

7. Field, F.H. and J.L. Franklin. Electron Impact Phenomena and the Properties of Gaseous Ions. New York: Academic Press, 1957.

8. Dunn, Gordon H. "Anisotropies in Angular Distributions of Molecular Dissociation Products," Physical Review Letters, 8: 62-64 (January 1962).

9. Rapp, Donald, Paula Englander-Golden, and Donald D. Briglia. "Cross Sections for Dissociative Ionization of Molecules by Electron Impact," Journal of Chemical Physics, 42: 4081-4085 (June 1965).

10. Van Brunt, R.J. and L.J. Kieffer. "Angular Distribution of Protons and Deuterons Produced by Dissociative Ionization of H_2 and D_2 Near Threshold," Physical Review A2: 1293-1304 (October 1970).

11. Zare, Richard N. "Dissociation of H_2^+ by Electron Impact: Calculated Angular Distribution," Journal of Chemical Physics, 47: 204-215 (July 1967).

12. Crowe, A. and J.W. McConkey. "Dissociative Ionization by Electron Impact. I. Protons from H_2," *Journal of Physics*, B6: 2088-2107 (October 1973).

13. Dunn, Gordon H. and L.J. Kieffer. "Dissociative Ionization of H_2: A Study of Angular Distributions and Energy Distributions of Resultant Fast Protons," *Physical Review*, 132: 2109-2117 (December 1963).

14. Stockdale, J.A.D., V.E. Anderson, A.E. Carter, and Liliana Deleanu. "Dissociative Ionization of Molecules by Electron Impact. 1. Apparatus and Kinetic Energy Distributions of D^+ Ions from D_2," *Journal of Chemical Physics*, 63: 3886-3897 (November 1975).

15. Crowe, A. and J.W. McConkey. "Dissociative Ionization by Electron Impact. II. N^+ and N^{++} from N_2," *Journal of Physics*, B6: 2108-2117 (October 1973).

16. Stockdale, J.A.D. and Liliana Deleanu. "Dissociative Ionization of O_2 and N_2 by Electron Impact - N^+ and O^+ Kinetic Energies and Angular Distributions," *Chemical Physics Letters*, 22: 204-208 (September 1973).

17. Deleanu, L. and J.A.D. Stockdale. "Dissociative Ionization of Molecules by Electron Impact. II. Kinetic Energy and Angular Distributions of N^+ and N^{++} Ions From N_2," *Journal of Chemical Physics*, 63: 3898-3905 (November 1975).

18. Kieffer, L.J. and R.J. Van Brunt. "Energetic Ions From N_2 Produced by Electron Impact," *Journal of Chemical Physics*, 46: 2728-2734 (April 1967).

19. Misakian, M., J.C. Pearl and M.J. Mumma. "Linear Momentum Transfer Effects in Molecular Dissociation Produced by Electron Impact," *Journal of Chemical Physics*, 57: 1891-1895 (September 1972).

20. Misakian, Martin and Jens C. Zorn. "Dissociative Excitation of Molecular Hydrogen by Electron Impact," *Physical Review*, A6: 2180-2195 (December 1972).

21. Dushman, Saul. *Scientific Foundations of Vacuum Technique* (2d Ed.). New York: John Wiley & Sons, Inc., 1962.

41

Vita

Mark Edward Wunderlich was born on 18 August 1956 in Dubuque, Iowa. He graduated from high school in 1974, then attended Southeast Missouri State University at Cape Girardeau, where he received a Bachelor of Science degree in Engineering Physics. Upon graduation, he entered OTS and received a commission on 16 November 1978. His first assignment was to the Foreign Technology Division, AFSC, Wright-Patterson AFB, Ohio, where he served as a Laser Intelligence Signal Analyst. He entered the School of Engineering, Air Force Institute of Technology, in June 1981.

> Permanent Address: 8938 Autumgate
>   Huber Heights OH 45424

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1 REPORT NUMBER AFIT/GEP/PH/82D-27	2 GOVT ACCESSION NO. AD-A135 847	3. RECIPIENT'S CATALOG NUMBER
4 TITLE (and Subtitle) MASS SPECTROMETRY DETECTION OF NEUTRAL DISSOCIATIVE FRAGMENTS		5 TYPE OF REPORT & PERIOD COVERED MS Thesis
		6 PERFORMING ORG. REPORT NUMBER
7 AUTHOR(s) MARK E. WUNDERLICH CAPT USAF		8. CONTRACT OR GRANT NUMBER(s)
9 PERFORMING ORGANIZATION NAME AND ADDRESS Air Force Institute of Technology (AFIT-EN) Wright-Patterson AFB OH 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE December 1982
		13. NUMBER OF PAGES 48
14 MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16 DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

17 DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18 SUPPLEMENTARY NOTES

Approved for public release: IAW AFR 190-17.

LYNN E. WOLAVER
Dean for Research and Professional Development
Air Force Institute of Technology (AIC)
Wright-Patterson AFB OH 45433

9 SEP 1983

19 KEY WORDS (Continue on reverse side if necessary and identify by block number)

Mass Spectrometry   Ionization

Neutral Molecular Fragments   Nitrogen (N_2)

Dissociation

20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

The feasibility of detecting neutral fragments from molecular dissociative processes has been investigated using a mass spectrometer. The mass spectrometer is equipped with dual ionizers. One ionizer is used to form neutral and ionic dissociation fragments. The neutral fragments proceed to the second ionizer for ionization and subsequent detection. The difference in the measured signal when the first ionizer is on or off will reveal information on the formation of neutrals as a function of electron energy. This study
(Continued on Reverse)

DD FORM 1 JAN 73 1473   EDITION OF 1 NOV 65 IS OBSOLETE

BLOCK 20: ABSTRACT (Cont'd)

concentrates on the detection of the neutral nitrogen (N) and hydrogen (H) fragments from molecular nitrogen (N_2) and hydrogen (H_2).

No measurable experimental results from the two step, dissociation then ionization, process were obtained using the current experimental apparatus. The angular distribution of the dissociative fragments and the type and geometry of the apparatus prove to be important aspects which must be considered when detecting neutral fragments. Recommendations are given which may improve the possibility of detecting neutral fragments using this technique.

MED
8