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Appearance Potentials and Kinetic Energies of Ions from $N_2$, CO, and NO

by

Peter Marston Hierl

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INTRODUCTION

One of the principal applications of mass spectrometry has been the study of ionization and dissociation processes, primarily, but not exclusively, those induced by electron impact. Such studies have yielded valuable information on molecular structure, such as bond strengths, ionization potentials of unstable species (radicals), molecular energy levels, etc.

The subject of electron-induced ionization and dissociation has been the subject of periodic review articles. Massey and Burhop (138) have discussed the theoretical and experimental work done before 1950, while another review by Massey (137) covered electron-induced excitation and ionization of atoms to 1955. Craggs and Massey (38) discussed experimental and theoretical studies of electron-molecule collisions to 1958. Fite (53) emphasized the work done since the publication of the book by Massey and Burhop. Field and Franklin (52) discussed in detail the experimental techniques involved and listed a great deal of experimental data gathered before 1957. Mott and Massey (159) and Seaton (172) have presented advanced discussions of the theory. McDaniel (140) has summarized much of the work done on excitation and ionization by electron impact. Other reviews of the subject include those by Hasted (89), Collin (31), and Kiser (114).

In general, the dissociative ionization of a molecule may be represented by the equation

\[ R_1 R_2 \rightarrow R_1^+ + R_2 + e^- \]  

(1)

where \( R_1^+ \) is a fragment ion and \( R_2 \) is the neutral fragment. The
appearance potential of the ion, $AP_0 (R_1^+)$, is defined as the minimum energy required to form the ion and its accompanying neutral fragment, both in their ground states, from the ground state of the parent molecule. This process may be regarded energetically as the breaking of the $R_1$-$R_2$ bond, followed by the ionization of the radical, $R_1$. That is,

$$AP_0 (R_1^+) = D (R_1-R_2) + I (R_1)$$  \(2\)

where $D(R_1-R_2)$ is the strength of the $R_1$-$R_2$ bond and $I(R_1)$ is the ionization potential of the radical, $R_1$. However, in case one or both of the products possess excess energy, the experimentally observed appearance potential, $AP(R_1^+)$, will be given by

$$AP(R_1^+) = AP_0 (R_1^+) + E$$  \(3\)

where $E$ represents the excess energy of the products. For a polyatomic molecule, this will equal the relative translational energy of the particles plus any electronic, vibrational, or rotational energy they may possess above their ground states.

Accurate interpretation of the energetics of electron impact data, then, depends upon the accurate determination of both (1) the experimental appearance potential, and (2) the excess energy, if any. Failure to correctly measure the excess energy could result in experimental appearance potentials that are from a tenth of an electron volt to several electron volts higher than the true or "adiabatic" appearance potential, $AP_0$.

Various methods have been proposed for the determination of appearance potentials and for the measurement of excess translational energy. These methods will be discussed in detail in the following sections of this work.
A. APPEARANCE POTENTIAL MEASUREMENTS

Appearance potential data are usually presented in the form of ionization efficiency (IE) curves, which are graphical representations of the intensity of the ion as a function of the energy of the ionizing agent. For standard electron impact experiments, a typical IE curve consists of a curved portion for the first volt or so above onset, a linear segment for the next 10 to 20 volts, a broad maximum up to about 100 volts, and then a gradual decrease (52).

The shape of IE curves has been treated theoretically by a number of workers (5, 6, 138, 210). A theoretical quantum-mechanical treatment was proposed by Wigner (205) and further developed by Wannier (200) which predicted that, for single ionization of atoms, the ionization yield should increase as the 1.127th power of the energy by which the electron energy exceeds the ionization potential of the atom. Geltman (72), however, predicted that the probability of ionization should vary as the n-th power of the excess energy, where n is the degree of ionization. Experimental evidence (43, 44, 54, 57-59, 93-95, 157) has, in general, supported the prediction of n-th power dependence of intensity upon electron energy for n-fold ionization.

Thus, it should be possible, in principle, to plot the n-th root of the ion intensity against the electron energy to obtain a straight line which intersects the energy axis at the appearance potential of the ion under investigation. Such a method of determining appearance potentials, however, fails for several reasons. First,
because of such factors as contact potentials, surface polarization, space charges, field penetration, and charge exchange, there will be some uncertainty as to the absolute energy of the electron beam (4, 52, 135, 167). Although some efforts have been made to calculate an absolute energy scale (2), the usual procedure is to calibrate the energy scale by use of a reference gas of known ionization potential. Generally, the reference gas is a rare gas (Ar, Kr, or Xe) and is admitted into the mass spectrometer simultaneously with the sample.

The second problem in determining appearance potentials is the interpretation of the IE curve itself. It has been found that this curve approaches the energy axis asymptotically rather than linearly, thus making the exact point of onset difficult to determine. This curvature is caused primarily by the fact that the electrons are not strictly homogeneous in energy. Most mass spectrometers use a hot filament as a source of electrons, resulting in a beam of electrons with a Maxwellian distribution of energies (101, 163). Both graphical and experimental methods have been suggested to correct for the non-homogeneity of the electron beam, but none so far has been completely satisfactory. Because this problem has been discussed at length in many books (4, 31, 52, 142, 144, 167) only a brief summary of the various methods will be presented here.

The vanishing current method (174) assumes that the electron energy at which the ion just appears is equivalent to the appearance potential. It has been widely used and yielded surprisingly good results in many cases, considering the unavoidable subjectivity involved in the determination of onset.
The extrapolated difference method of Warren (201) plots the intensity of the ion under investigation so that its linear segment is parallel to that of the reference gas. The differences of voltage between the curves are then plotted as a function of ion intensity and extrapolated to zero ion current.

The "linear extrapolation method," in which the linear segment of the IE curve was extrapolated to zero ion intensity, often yielded poor results (especially for fragment ions) and is now generally abandoned.

The "critical slope method" attempts to account mathematically for the electron energy distribution. The application of this method is difficult because the experimenter must know the exact temperature of the filament. Moreover, some of the assumptions used in its derivation are questionable. It has, however, yielded excellent results (101).

Another logarithmic method is the "energy compensation method," first proposed by Lossing, et al. (127), and subsequently modified by Kiser (115). The voltage at which the ion intensity has fallen to 1% (or, 0.1%) of its value at 50 volts is taken as the appearance potential. Because it generally gives excellent and reproducible results (30) this method is very often used now.

The "derivative method" of Morrison (150-154) is another mathematical attempt to eliminate the curvature due to the spread in electron energies.
Two instrumental techniques have been applied to the problem of obtaining monoenergetic electron beams. The more straightforward method is to use an electron energy selector or electron spectrometer in which deflection of electrons in a magnetic or electrostatic field is used to select an electron beam of narrow energy spread. Such a method was first used by Nottingham (163) in 1939, but because of the very low electron currents obtainable, it was not widely used until the development of more sensitive detecting devices. Recent workers (26, 107, 108, 134, 135), however, have reported very informative studies by use of this method.

The second method of obtaining monoenergetic electrons was first proposed by Fox and his colleagues in 1951 (60) and further developed in 1955 (58). The "Retarding Potential Difference" (RPD) method employs a retarding potential, \( V_R \), to provide a sharp cut-off on the low energy side of the electron energy distribution. After recording the ion intensity at a given value of electron energy and \( V_R \), the retarding potential is increased by a small amount (dV) and the ion intensity is measured a second time. The decrease in ion intensity (dI) is equivalent to the ion current which would be produced by the portion of electrons of energy spread dV. In effect, the ion intensity observed at the higher retarding potential is considered to be background, and if dI is plotted as a function of electron energy, the resulting IE curve will be equivalent to that obtained with monoenergetic electrons with an energy spread of dV. A modified RPD source that uses the properties of space-charge-limited diodes to produce the retarding potential has been proposed by Clothier and Schiff (27).
B. KINETIC ENERGY MEASUREMENTS

The formation of dissociation products with excess energy is explained by the Franck-Condon Principle (32, 33, 62). The basis of this principle, in the case of photon or electron ionization, is that the time of interaction is so short ($10^{-15}$ sec or less) compared to the time necessary for a vibration ($10^{-12}$ to $10^{-13}$ sec), that the nuclei may be considered as fixed at their equilibrium distances during the ionization process. In other words, the point on the potential energy curve of the molecule representing the configuration before the transition lies directly below the point on the potential energy curve of the molecule-ion representing the configuration after the transition. If the equilibrium internuclear distance of the neutral molecule and the molecule-ion differ, such a "vertical" transition will form the ion in an excited state. (The Franck-Condon Principle is discussed at length by Craggs and Massey (38), Field and Franklin (52), and Massey and Burhop (138). The validity of this principle has been demonstrated by studies of hydrogen in which the dissociation processes predicted by the Franck-Condon Principle have been observed experimentally (8, 10, 34, 35, 49, 128, 134).

The detection of vibrational excitation requires energy resolution better than 0.1 eV because of the close spacing of the vibrational energy levels. Using an electron velocity selector, Marmet and Morrison (135) observed vibrational structure in H$_2$, N$_2$ and NO, and determined the spacings of the vibrational levels. Other investigations have revealed vibrational fine structure in the IE curves obtained by electron impact (134, 155, 196) and by photo-
ionization (42, 63, 80, 155, 162).

The most direct evidence for the formation of electronically excited ions by electron impact is to be found in the work of Fox, et al. (57-59, 93-95) on the determination of IE curves with electrons essentially homogeneous in energy (RPD technique), and in the work of Morrison (91, 150-154) on the determination of the first and second derivatives of ionization efficiency curves.

Using these techniques, it became possible in many cases to show that when ionization can proceed by a single process to a single energy level, the ionization yield is a linear function of the electron energy in excess of the ionization potential. The application of this linear threshold law to the ionization probability curves for the formation of Kr\(^+\) and Xe\(^+\) produced breaks which could be correlated with the known electronic energy levels of these ions (59). Similar results have been reported by Frost and McDowell (66), who studied the ionization and dissociation of molecular oxygen, using the RPD method. They reported observing all the spectroscopically known states of the molecular ion and one additional state. The vertical ionization potentials thus determined were in very good agreement with those calculated from available spectroscopic data. Moreover, six different dissociation processes leading to the production of the atomic ion were observed and identified.

The detection and measurement of initial translational energy usually involves one of two basic methods: the use of retarding potentials, or an analysis of the focusing properties of ions formed with translational energy.
The earliest retarding potential measurements (180) were of limited use because of the lack of mass analysis. Nevertheless, this method has been applied to the study of a number of simple molecules such as hydrogen (8, 11, 128, 129, 131); water (129); nitrogen (131, 132, 180); carbon monoxide (133, 180); nitric oxide (87); hydrogen chloride (87); and iodine (17). Recent studies include those by Schultz (168-171).

More recently, retarding potential studies of ions separated by mass analysis have been made by a number of workers (8, 40, 56, 61, 82, 97, 109-111, 161, 178).

Since the focusing and ion collection properties of a mass spectrometer are different for ions formed with and without initial translational energy, discrimination and peak contour studies can be used to detect and, in some cases, to measure the initial kinetic energy of the ions.

The most extensive study of discrimination effects arising from ionic translational energies has been carried out by Berry (7), with additional contributions made by several other workers (21, 22, 28, 29, 202). A variation of this method, involving electrostatic or magnetic deflection of the ion beam, has been developed by Reese and Hippel (166) and applied by others (7, 12, 49, 148, 158, 176, 177, 183-189).

The possibility of deriving information on initial energies from the contours of peaks obtained from conventional mass spectrometry has been demonstrated qualitatively by McDowell and Warren (143) and quantitatively by Hagstrum and Tate (85). This method also has been applied successfully by others (81, 86, 98, 106, 118, 121, 147, 193, 194, 199).
C. OBJECTIVE OF THE PRESENT STUDY

Because the previously discussed methods of measuring initial translational energies of fragment ions had all been developed for either conventional mass spectrometers or for specially built instruments, this present study is designed to develop a method by which these measurements can be made with a time-of-flight mass spectrometer. A mathematical analysis of the peak shapes obtained with such an instrument indicates considerable peak broadening for ions formed with excess translational energy. Employing this fact, a method is developed by which the translational energy can be readily determined from the peak width. The validity of this method is demonstrated by a comparison of the results obtained for several ions with the results obtained by a number of other workers employing other techniques. Finally, the present method is applied to the re-examination of the ions formed by electron impact in nitrogen, carbon monoxide, and nitric oxide.

II. EXPERIMENTAL WORK

The instrumentation employed for the experimental ionization and dissociation studies is briefly described. The basic theory of the operation of a time-of-flight mass spectrometer is discussed in detail because of its importance in the method developed in this paper for the measurement of initial translational energy. The instrumentation and methods employed in the determination of appearance potentials are also discussed in some detail.

A. MASS.SPECTROMETER

Measurements were made on a Bendix Time-of-Flight (TOF) mass
Figure 1. Schematic Representation of a Time-of-Flight Mass Spectrometer, Showing the 5-Grid Electron Gun for RPD Work.
spectrometer, Model 12, using a S14-107 ion source and a flight tube of 180 cm. This instrument and the theory of its operation have been described in detail by a number of workers (20, 79, 88, 113, 206, 207).

Figure 1 shows the major elements of a time-of-flight mass spectrometer. There are three principal regions: the ionization region, bounded by the backing plate and the ion focus grid; the ion acceleration region, bounded by the ion focus grid and the ion energy grid; and the drift tube, a field-free region extending from the energy grid to the collector cathode.

The Bendix TOF mass spectrometer employed was operated at a repetition rate of 10 kc/sec with a 3000 volt ion accelerating potential. Thus, 10,000 complete mass spectra were produced each second.

The gas sample was ionized by bombardment with a pulsed electron beam in the ionizing region of the ion source. The electrons were produced by continuous emission from a heated .005 inch tungsten filament. The control grid was biased negatively with respect to the filament, preventing electrons from passing continuously into the ionizing region. These electrons were permitted to enter the ionization chamber by a 0.25 micro-second duration positive pulse applied to the control grid only at the beginning of each cycle. The electron beam was collimated by a system of slits and by a weak (approximately 100 gauss) magnetic field, resulting in a beam of small but finite thickness, s. The center of the electron beam is at distance $s_0$ from the ion focus grid. During the period of electron bombardment, the ionization region was essentially field free, with both the backing plate and the ion focus grid at zero
potential.

The nominal electron energy was taken as the voltage difference between the DC filament potential and the ground potential on the final grid of the electron gun. Hence, the electron energy was determined by the filament potential, which was variable between 0 and 100 volts.

Molecules bombarded by electrons of sufficient energy broke down into positive and negative ions and neutral fragments. Immediately after the electron beam was shut off, the ion focus grid was pulsed negatively to analyze positive ions. The ion focus pulse was continuously variable from zero to -250 volts and of about 2.5 micro-seconds duration. It produced an electric field $E_s$ in the ionization region which drew all positive ions toward the grid with approximately 80% passing through the grid into the accelerating region.

The ion energy grid was maintained at a potential of -3000 volts, resulting in an electric field ($E_d$) in the accelerating region which imparted to all positive ions an energy impulse of magnitude $q_dE_d$, where $d$ is the distance from the ion focus grid to the ion energy grid and $q$ is the charge on the ion.

About 80% of these ions passed through the energy grid and entered the field-free region of the drift tube, which was maintained at the same potential as the ion energy grid.

Since all ions received an equal energy impulse, the velocity of a particular ion was inversely proportional to the square root
of its mass-to-charge (m/e) ratio. That is, the lighter ions had the higher velocities and reached the collector sooner. Since all ions left the accelerating region practically simultaneously and were allowed to drift some distance prior to striking the collector, those of equal mass bunched together and collectively separated from packets of ions of different mass.

Ions reaching the stainless steel collector cathode with 3000 electron volts of energy dislodged electrons from its surface. (See Figure 2.) These electrons were directed onto the dynode strip of the Wiley multiplier (206). After about 50 cycloids along the dynode strip, the initial electron current had been increased by a factor of about $10^5$. As long as gates 1 through 6 were held at ground potential, the electrons continued to cycloid in space along the equipotential line until reaching the oscilloscope anode. If, however, one of the gates received a negative pulse, any electrons adjacent to that gate at that instant were deflected 90° towards the corresponding anode, resulting in a signal which was subsequently amplified by the analog unit.

The scanning device on one analog unit was modified by the insertion of a 1 Megohm resistor in the scan rate control unit in what previously had been the "Off" position. This was done to provide an extremely slow scan which, in conjunction with a Honeywell chart recorder running at 8 inches per minute, enabled 10 nanoseconds of real time to be displayed by 0.328 inches of chart paper. The mass spectrometer was normally run at an ion accelerating voltage of 3.0 kv. The tungsten wire filament was operated at 3.0 amperes
Figure 2. Multiplier Operation
and the trap current was 0.250 microamperes. To ensure optimum resolution, the ion lens was not used when recording peak shapes, but it was used to give maximum sensitivity in appearance potential measurements. For negative ions the spectrum, displayed on a Hewlett-Packard Model 175A oscilloscope, was scanned with a 1782A display scanner and the results were again recorded with the Honeywell chart recorder.

The peak shapes and appearance potentials were measured at sample pressures between $2 \times 10^{-6}$ and $2 \times 10^{-5}$ mm of Hg, maintained with a mechanical forepump and a mercury diffusion pump. The cold trap-baffle arrangement was always refrigerated with liquid nitrogen during the operation of the instrument. Before admission of the sample, the background pressure was $2 - 10^{-7}$ mm Hg, resulting mainly from nitrogen, oxygen and water.

B. APPEARANCE POTENTIAL MEASUREMENTS

Three different techniques were used for the determination of appearance potentials. The retarding potential difference (RPD) method of Fox (58,60,146) was used for all positive ions (with the exception of several of the doubly charged atomic ions, whose intensities were too low to yield good results with this method). The standard five-grid electron gun was used, and Figure 3 shows the circuit used for the production of the appropriate potentials. To keep the ionization region as free as possible of field penetration, the voltage on the trap anode was reduced from its normal value of +150 volts to approximately +10 volts. The control grid bias was reduced to a few tenths of a volt to give maximum electron current
Figure 3. Schematic Diagram of RPD Circuit
while still maintaining pulsed operation. RPD grids #1 and #3 were maintained at about +0.5 volts, relative to the electron energy, while the retarding grid (RPD grid #2) was kept at a potential of -2.5 volts, relative to the electron energy. Empirically, this value was found to give the greatest variation in ion current for a given value of ΔV. All measurements were made with a ΔV of 0.10 volts. A rare gas (either argon or neon) was used to calibrate the electron energy scale. It was admitted to the ionization region simultaneously with the sample gas and at sufficient pressure to give a peak approximately equal in intensity to the ion under investigation at that time.

A variation of the energy compensation method (115,127) was used to determine the appearance potential of several of the doubly charged atomic ions whose intensities were too low for the RPD method. In these cases a semi-log plot of the ion intensity was made as a function of the electron energy. The appearance potential was assumed to be that electron energy at which the ion intensity had fallen to 0.1% of its value at 100 ev. The appearance potential of the ion Ne^+ was determined in the same manner in order to calibrate the electron energy. While the choice of the value 0.1% was somewhat arbitrary, it represented, in most cases, the limit of the detection ability of the instrument for these ions.

The vanishing current method (174) was used to determine the appearance potentials of the negative ions investigated. Because of the difficulty in recording negative ions, the point at which the given ion first appeared was determined visually on the oscilloscope. The precision of this method was surprisingly good, the
standard deviation for five trials usually being less than 0.2 ev. The ion SF$_6^-$ was used to calibrate the electron energy scale in all cases.

III. MEASUREMENT OF INITIAL TRANSLATIONAL ENERGY IN A TOF MASS SPECTROMETER

Wiley and McLaren (207) have given a detailed analysis of the focusing action of the time-of-flight mass spectrometer. They found that the peak shape was a function of the initial energy of the ion. The following section describes a method by which the initial energy effect can be distinguished from the other effects, thus permitting the calculation of the initial translational energy of the ion based on its peak shape.

A. FLIGHT TIMES

The total flight time for an ion formed in the electron beam is defined as the time from the application of the ion focus (drawout) pulse to the time the ion strikes the collector cathode. This time is composed of three terms: $T_s$, the residence time in the ionization region; $T_d$, the time of passage through the acceleration region; and, $T_p$, the time of flight down the drift tube. Each of these terms can be calculated from a consideration of the dynamical equations governing the motion of a charged particle in an electric field.

An ion of mass $m$ and charge $e$, formed in the source, will, upon application of the ion focus pulse, experience a force given by

$$ F = M \frac{dv}{dt} = eE_s. \quad (1) $$
If the zero of time is taken as the time of application of the ion focus pulse, then \( T_s \), the time required for the ion to travel from the point of its formation in the electron beam to the ion focus grid, can be obtained from the integral

\[
\int_0^{T_s} dt = \frac{m}{eE_s} \int_{v'}^{v''} dv
\]

(2)

where \( v' \) and \( v'' \) refer to the initial and final velocities, respectively, of the ion. Carrying out the integration, we obtain

\[
T_s = \frac{m(v'' - v')}{eE_s}.
\]

(3)

If the ion possesses, at the time of its formation, any translational energy with a component \( U_x \) directed along the axis of the flight tube, the initial velocity is given by

\[
v' = \pm (2U_x/m)^{1/2}
\]

(4)

where the plus and minus signs refer to initial velocities directed toward and away from the collector, respectively.

Similarly, if an ion is formed at a distance \( s \) from the ion focus grid, in falling through the electric field \( E_s \) in the source, the ion will acquire an additional amount of energy given by \( sE_s \). The ion will reach the ion focus grid with a total \( x \)-component of translational energy given by \( U_x + sE_s \), and, consequently, it will leave the ionization region with a final velocity given by

\[
v'' = \left( \frac{2}{m} \right)^{1/2} \left( sE_s + U_x \right)^{1/2}.
\]

(5)

Substitution of equations (4) and (5) into equation (3) yields the expression for the residence time of the ion in the ionization
region after the ion focus pulse has been applied. That is,

\[ T_s = \frac{(2m)^{1/2}}{eE_s} \left[ (esE_s + U_x)^{1/2} \pm (U_x)^{1/2} \right] \]  \hspace{1cm} (6)

where the + and - signs now refer to initial velocities directed away from and toward the collector, respectively. An identical treatment for the acceleration of a charged particle in an electric field yields the time for the ion to pass through the acceleration region. By analogy with equation (3), we obtain

\[ T_d = \frac{m}{eE_d} \left( v_d'' - v_d' \right) \]  \hspace{1cm} (7)

where \( v_d' \) refers to the velocity of the ion as it enters the acceleration region, and \( v_d'' \) refers to the velocity of the ion as it leaves the acceleration region.

The ion will enter the acceleration region with just the velocity that it left the ionization chamber, and therefore,

\[ v_d' = v'' = \left( \frac{2}{m} \right)^{1/2} \left( esE_s + U_x \right)^{1/2} \]  \hspace{1cm} (8)

from equation (5). In passing through the acceleration region the ion will acquire an additional amount of translational energy, \( edE_d \). Thus, it leaves the acceleration region with a total translational energy given by \( edE_d + esE_s + U_x \), and its final velocity is given by

\[ v_d'' = \left( \frac{2}{m} \right)^{1/2} \left( edE_d + esE_s + U_x \right)^{1/2} \]  \hspace{1cm} (9)

Substitution of equations (8) and (9) into equation (7) yields
\[ T_d = \left( \frac{2m}{eE_d} \right)^{1/2} \left[ (eE_d + eE_s + U_x)^{1/2} - (eE_s + U_x)^{1/2} \right]. \] (10)

Since the drift tube is a field-free region, the ion experiences no further acceleration or change in velocity while travelling the length of the drift tube. Its velocity is that with which it left the acceleration region, \( v_d'' \), and consequently the time of flight down the drift tube is given by

\[ T_D = \frac{D}{v_d''} = \left( 2m \right)^{1/2} \frac{D}{2(eE_d + eE_s + U_x)^{1/2}}. \] (11)

If one maintains constant operating conditions \((E_s, E_d \text{ constant})\) and considers only ions of identical m/e ratio, the flight time depends only upon the point \((s)\) of formation and the initial translational energy \((U_x)\) of the ion. The total flight time can then be written as

\[ T(U_x, s) = T_s(U_x, s) + (T_d(U_x, s) + T_D(U_x, s)) \] (12)

where \(T_s(U_x, s), T_d(U_x, s)\) and \(T_D(U_x, s)\) are given as \(T_s, T_d, \text{ and } T_D\) in equations (6), (10), and (11), respectively.

Table 1 lists typical values for the parameters involved in these equations, as well as the calculated flight times. For the sake of convenience, it was assumed that \(U_x\) was zero, and \(s\) was \(s_0\). Moreover, \(E_d\) was calculated for a potential of -3000 volts on the ion energy grid, and \(E_s\) was calculated for an ion focus pulse of -120 volts. (The selection of this value will be explained later.) Thus, the total flight time for a singly charged ion should be \(2.442 \ M^{1/2}\) microseconds, under the given operating conditions.

B. RESOLUTION

If all the ions were formed at rest \((U_x = 0)\) and if they were
### TABLE I: TYPICAL PARAMETERS FOR BENDIX TOF INSTRUMENT

<table>
<thead>
<tr>
<th>Distance (cm)</th>
<th>Electric Fields (volts/cm)</th>
<th>Energies (ergs/molecule)</th>
<th>Times* (microseconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D = 170</td>
<td>$E_s = 227$</td>
<td>$U_x = 7.25 \times 10^{-14}$</td>
<td>$T_s = 0.066 , M^{1/2}$</td>
</tr>
<tr>
<td>d = 0.711</td>
<td>$E_d = 4008$</td>
<td>$esE_s = 1.76 \times 10^{-9}$</td>
<td>$T_d = 0.016 , M^{1/2}$</td>
</tr>
<tr>
<td>$s_o = 0.483$</td>
<td></td>
<td>$edE_d = 4.57 \times 10^{-9}$</td>
<td>$T_D = 2.360 , M^{1/2}$</td>
</tr>
</tbody>
</table>

$\Delta s = 0.020$

*Masses expressed in atomic mass units.
all in a plane parallel to the ion focus grid \((s = s_o)\), then the flight times would depend only upon the ratio \(m/e\). Every ion of a given \(m/e\) ratio would arrive at the collector at the same instant, resulting in a mass spectrum consisting entirely of sharp lines or delta functions at the appropriate mass numbers.

As can be seen from the equation for the total flight time, any variation in either initial position or initial energy will result in a slight variation in the flight time of the ion and a consequent broadening of the ion signal.

Thus, the peak width depends upon both the point of formation of the ion (space resolution) and upon the initial translational energy of the ion (energy resolution). If one can calculate the contribution of each of these effects to the peak width or even eliminate the contribution from space broadening (as it turns out, one can), an analysis of the peak width will yield information on the translational energy with which an ion is formed.

Instead of being formed in a plane parallel to the ion focus grid, the ions are actually formed throughout the entire thickness of the electron beam, \(\Delta s\). The initial space distribution of the ions can be considered as a deviation of the initial position (as measured from the ion focus grid) about its average, \(s_o\), so that

\[
   s_{\text{max}} = s_o + 1/2 \Delta s
\]

and

\[
   s_{\text{min}} = s_o - 1/2 \Delta s.
\]

The space resolution problem is to reduce the time spread, \(\Delta T\).
which is defined as the variation in flight time introduced by a small variation, \( \Delta s \), in the position variable, \( s \), about its average, \( s_o \).

That is, \( \Delta T_{\Delta s} \) is defined by the equation

\[
\Delta T_{\Delta s} = T(U_x,s) - T(U_x,s_o).
\]

(14)

The reduction of space broadening may be accomplished by making \( \Delta s \) small compared with \( s_o \) (using a narrow electron beam); or by employing "space focusing," a technique which gives each ion a velocity dependent upon \( s \) in such a way as to minimize \( \Delta T_{\Delta s} \). Qualitatively, space focusing is based on the fact that ions farther away from the ion focus grid (and consequently of larger \( s \) value) fall through a larger potential when accelerated by the focus pulse than do those ions formed nearer to the ion focus grid. Although they have a greater distance to travel to reach the collector, the former, because of their greater energy, will eventually overtake the latter at some distance down the flight tube. By a careful adjustment of the focus pulse, all of the ions will reach this "cross-over point" just at the collector cathode. That is, the proper choice of the focus pulse will cause ions formed initially at position \( (s_o + ds) \) to overtake those formed at position \( (s_o - ds) \) exactly at the detector, and \( \Delta T_{\Delta s} \) will be zero, thus eliminating the space resolution problem.

If, for the moment, one assumes that \( U_x \) equals zero and considers ions that differ only in their initial positions, one can calculate \( \Delta T_{\Delta s} \), the change in flight time corresponding to a small change, \( \Delta s \), in the variable \( s \) about its average value, \( s_o \). Expansion of the term \( T(0,s) \) in a Taylor series about the point \( s_o \) yields (175,207)

25
\[ T(0, s) = T(0, s_0) + \left[ \frac{dT(0, s)}{ds} \right]_{s_0}^s \frac{(s-s_0)}{1!} + \left[ \frac{d^2T(0, s)}{ds^2} \right]_{s_0}^s \frac{(s-s_0)^2}{2!} + \ldots (15) \]

Substitution of this equation into equation (14) shows that \( \Delta T_{\Delta s} \) can be calculated from the following series

\[ \Delta T_{\Delta s} = \sum_{n=1}^{\infty} \frac{1}{n!} \left[ \frac{d^nT(0, s)}{ds^n} \right]_{s_0}^s (\Delta s)^n \]

(16)

where \( \Delta s = (s-s_0) \). Calculation of the first three terms of this rapidly converging series shows that \( \Delta T_{\Delta s} \) goes through zero at a focus pulse of -120 volts for the ion source used. Focus pulse values smaller than this do not permit the cross-over to occur before the ions reach the collector, while larger values of the focus pulse will cause the cross-over point to occur prematurely in the drift tube. A value of -120 volts, however, causes the cross-over to occur at the collector cathode, thus eliminating the effect of variations in initial position on the peak shape. Consequently, the broadening of the ion packet is caused solely by variations in the initial translational energy of the ions.

An ion that is formed with a component in initial translational energy, \( U_x \), parallel to the axis of the drift tube will have a total flight time differing from that of an ion formed with no such translational energy. This time difference, \( \Delta T_u \) is defined by the expression

\[ \Delta T_u = T(U_x, s_0) - T(0, s_0). \]

(17)

Since the energy terms \( esE_s \) and \( edE_d \) are normally much greater than
U_x, one can make the following approximations:

\[(e s E + U_x)^{1/2} \cong (es E_s)^{1/2}\]  \hspace{1cm} (18a)

\[(ed E_d + es E_s + U_x)^{1/2} \cong (ed E_d + es E_s)^{1/2}\]  \hspace{1cm} (18b)

Combining these approximations with the expressions for T_s, T_d, and T_D, one obtains the results

\[T_s(U_x, s_o) \cong T_s(0, s_o) + \frac{(2m)^{1/2}(U_x)^{1/2}}{e E_s}\]  \hspace{1cm} (19a)

\[T_d(U_x, s_o) \cong T_d(0, s_o)\]  \hspace{1cm} (19b)

\[T_D(U_x, s_o) \cong T_D(0, s_o)\]  \hspace{1cm} (19c)

Thus, to a good approximation, initial translational energies affect only the residence time in the ionization region. Substitution of this result into the definition of \(\Delta T_u\) given by equation (17) yields

\[\Delta T_u = \pm \frac{(2m)^{1/2}(U_x)^{1/2}}{e E_s}\]  \hspace{1cm} (20)

This means that an ion formed with a component \(U_x\) of initial energy will have a total flight time slightly greater or slightly less than that of an ion formed with no initial energy, depending upon whether the initial velocity is directed away from or toward the collector, respectively. Moreover, the magnitude of this difference in flight times is given by equation (20).

The physical meaning of this equation is more easily understood if one considers the case of two identical ions, A and B, formed at the same initial position, s, with equal but oppositely directed veloc-
ity components, $v_o$, along the axis of the drift tube.

$$-v_o \leftarrow A$$

$$B \rightarrow +v_o$$

Upon its formation, ion A moves away from the collector, decelerating due to the electric field, $E_s$, in the ionization region. Applying Equation (1) for the motion of a charged particle in an electric field, one finds that this ion comes to rest at time, $\Delta T_u$, given by the integral

$$\int_{-v_o}^{T_u} dt = \int_{-v_o}^{0} \frac{m}{eE_s} dv . \quad (21)$$

Integration of Equation (21) yields

$$\Delta T_u = \frac{mv_o}{eE_s} . \quad (22)$$

At this time, the ion reverses direction and is accelerated toward the collector by the electric field $E_s$. Because the ion is accelerated by the same electric field that had decelerated it previously, it returns to its original position (point of formation) with its original energy (i.e., speed) but this time with its velocity directed toward the collector. Subsequently, its motion is identical to that of ion B, which, however, it continues to lag behind in time by the "turn-around time." This turn-around time is simply twice the deceleration time, $mv_o/eE_s$. An ion formed with zero initial translational energy will have a flight time halfway between the flight times of these two excited ions. That is,

$$T(U_x, s_o) = T(0, s_o) \pm \Delta T_u \quad (23)$$

where $\Delta T_u$ equals $mv_o/eE_s$, and where the plus and minus signs refer to
initial velocities directed away from and toward the collector, respectively.

Figure 4 illustrates the relative magnitude of each of these effects and their dependence upon the magnitude of the focus pulse. The dotted line represents $\Delta T_{\Delta s}$, the peak width produced by the finite thickness, $\Delta s$, of the electron beam. The solid lines represent $\Delta T_u$, the peak width resulting from ions formed with initial translational energy $U_x$. Two curves for $\Delta T_u$ are shown, one representing ions of thermal energy (0.04 eV) and the other representing ions with a typical initial energy value (0.50 eV). The dotted curve was calculated from Equation (16), using the first three terms of the series, while the solid lines were calculated from Equation (20). It should be noted that even for ions of thermal energy, energy broadening is a more significant cause of peak broadening than is space broadening. This is even truer for ions formed with excess translational energy. Consequently, as long as the focus pulse equals or nearly equals -120 volts, the peak broadening may be considered to arise entirely from variations in initial velocities of the ions.

C. PEAK SHAPES

The shape of an ion peak is simply the representation of the number of ions arriving at the collector as a function of time; i.e., the intensity of the signal at time $T$ is proportional to the number of ions whose total flight time is $T = T(U_x, s)$.

Proper use of space focusing will give each ion a velocity dependent upon $s$ in such a way as to minimize $\Delta T_{\Delta s}$. The flight times
Figure 4. Calculated Effect of Focus Pulse on Peak Width.
will be independent of the point at which the ions are formed, and all ions will act as if they had been formed at $s_0$. If this focus condition is obeyed (focus pulse = -120 volts) and if the operating conditions are kept constant, the total flight time will depend only upon $U_x$ for ions of a given m/e ratio. (Consequently, the notation may be simplified by using the term $\Delta T$ to represent $\Delta T_u$.)

The number of ions that are formed with a given initial velocity ($v_x$) parallel to the axis of the drift tube will equal the number of ions reaching the collector at time $T = T(0, s_0) + \frac{mv_x}{eE_s}$, so that if one knows the probability distribution for one component of the velocity, one can calculate the probability distribution for the quantity $\Delta T$. This will permit a calculation of the relative intensity of the ion signal as a function of flight time and, consequently, a calculation of the shape of the ion peak.

If $P(v)$ is a known distribution function for the variable $v_x$, and if $v_x = f(\Delta T)$, then the corresponding distribution function in the variable $\Delta T$ will be

$$Q(\Delta T) = P\left[f(\Delta T)\right] \frac{d f(\Delta T)}{d \Delta T}.$$  

(24)

From equation (22)

$$v_x = \frac{eE_s}{m} \Delta T.$$  

(25)

Hence

$$\frac{d f(\Delta T)}{d \Delta T} = \frac{eE_s}{m}.$$  

(26)

And Equation (24) becomes
\[ Q(\Delta T) = \frac{eE_s}{m} P \left[ f(\Delta T) \right] . \] (27)

The function \( Q(\Delta T) \) represents the probability that an ion of given \( m/e \) ratio will have a total flight time differing by a small amount \( \Delta T \), from the flight time of an identical ion formed with zero initial translational energy, \( T(0,s_0) \). This distribution function, if known, enables one to calculate the relative intensity of the ion signal as a function of time; i.e., to calculate the peak shape as a function of initial energy, or, conversely, to calculate the initial energy distribution from the peak shape.

In the case of ions formed by the direct ionization of the molecule or in the case in which fragment ions are formed with no excess translational energy, the initial energy of these ions is merely whatever thermal energy they might possess at the temperature at which the source is operated. For such thermal or quasi-thermal energy distributions, the molecular velocities are distributed according to the well-known Gaussian distribution (124)

\[ P(v_x) = \frac{1}{\alpha(2\pi)^{1/2}} \exp \left( -\frac{v_x^2}{2\alpha^2} \right) \]

\[ \alpha = \frac{(kT/m)^{1/2}}{\exp} \] (28)

Since the dependence of \( v_x \) upon \( \Delta T \) is known from Equation (25), the change of variables indicated by Equation (27) results in the equation

\[ Q(\Delta T) = \frac{1}{\sigma(2\pi)^{1/2}} \exp \left[ -\frac{(\Delta T)^2}{2\sigma^2} \right] \]

\[ \sigma = \frac{m\alpha/eE_s}{\exp} \] (29)

where \( k \) is the Boltzmann constant and \( T \) is the absolute temperature.
For ions of a given m/e ratio and a thermal or quasi-thermal distribution of initial energies, the intensity of the ion signal as a function of flight time will be a Gaussian or bell-shaped distribution about the average value, $T_0^s$, as shown in Figure 5.

From the known distribution it is possible to calculate the time at which the intensity has fallen to one-half of its maximum value and to express this time, $\Delta T_{1/2}$, in terms of the constant $\sigma$, which in turn is a known function of the parameters $e$, $m$, $E_s$ and $k$, and of the temperature of the gas, $T$, from which one can determine the average value of the initial translational energy, $\overline{U}$.

The time at which the ion peak has fallen to one-half of its maximum value is obtained from the expression

$$\frac{1}{2} = \exp \left[ \frac{-(\Delta T_{1/2})^2}{2\sigma^2} \right]$$

which yields

$$\left(\frac{\Delta T_{1/2}}{\sigma}\right)^2 = 2 \ln 2.$$  (31)

Equivalently, this relationship can be expressed in terms of the full width at half height, $2\Delta T_{1/2}$, a quantity that is more conveniently measured experimentally. Since the ion peak is symmetrical,

$$2\Delta T_{1/2} = 2(2 \ln 2)^{1/2} \sigma = 2.36 \sigma.$$

Substituting into this equation the definitions of $\alpha$ and $\sigma$ given in Equations (28) and (29), one obtains

$$2\Delta T_{1/2} = 2.36 \frac{(kTm)^{1/2}}{eE_s}.$$  (33)
Figure 5. Peak Shape for Thermal Ions.
$Q(\Delta T)$

Relative Intensity

$\Delta T$ (in units of $\sigma$)

$\Delta T_0$

$2 \Delta T_{1/2}$
With $\bar{U}$ equal to $(3/2)kT$, the average value of the initial translational energy for a thermal distribution is given by

$$\bar{U} = \frac{N_o}{3.69} \left(\frac{eE_s}{E_s}\right)^2 \frac{(2\Delta T_{1/2})^2}{M}$$

(34)

where $N_o$ is Avogadro's number and $M$ is the molecular weight of the ion in grams/mole.

In the case of ions formed with excess translational energy, the exact distribution function for the excess energy is generally unknown. Nevertheless, some qualitative information on the form of the distribution function as well as quantitative information on the magnitude of the excess energy can be obtained from an analysis of the peak shapes. This information, in turn, can yield information on the potential energy curves of the excited states leading to the observed dissociation. For example, ions for which the most probable excess energy is zero will have peaks very similar in shape to, but considerably broader than those for thermal ions. At the other extreme, when the dissociation process yields ions with a high initial translational energy that is distributed over a relatively narrow range, the resulting ion peak is nearly rectangular. This can be shown if one considers the case in which a number of ions are formed at the same point with equal but randomly directed velocities, $v_o$. The velocity vectors will form a uniform sphere of radius $v_o$, as shown in Figure 6. The probability that the component of velocity in a given direction (e.g., $v_x$) has a value in the range between $v_x$ and $v_x + dv_x$ is proportional to the area of the sphere's surface lying between a plane perpendicular to and intersecting the $x$-axis at distance $v_x$ from the origin, and a second such perpendicular plane.
Figure 6. Velocity Distribution for Monoenergetic Ions.
\[ A(\text{zone}) = 2\pi v_0 \, dv_x \]
at distance \( v_x + dv_x \) from the origin. That is, an ion whose velocity vector ends on the surface of this zone will have a component of velocity along the \( x \)-axis in the desired range, \( v_x \) to \( v_x + dv_x \). The probability, \( P(v_x)dv_x \), that the velocity component is in this range is given by the ratio of the area of this zone to the total area of the sphere. That is,

\[
P(v_x)dv_x = \frac{2\pi v_o^2 dv_x}{4\pi v_o^2} = \frac{1}{2v_o} dv_x
\]

Thus, the probability distribution is independent of the velocity. This means that all velocities in a given direction are equally probable over the range \(-v_o\) to \(v_o\). Substitution of Equation (35) into Equation (27) for the distribution function for the flight times results in the equation

\[
Q(\Delta T) = \frac{1}{2(\Delta T_o)} - \Delta T_o \leq \Delta T \leq \Delta T_o
\]

where

\[
\Delta T_o = \frac{mv_o}{eE_s}
\]

This type of distribution function results in ion peaks rectangular in shape, as shown in Figure 7. As will be discussed in the next section, ion peaks very similar to this shape have been observed experimentally, indicating that the fragment ions under observation were formed by a process which gives them all the same or very nearly the same amount of initial energy, \( U_o \). Since \( U_o \) equals \( 1/2 \, mv_o^2 \), and the relationship between the experimentally observed peak width and the velocity is given by Equation (37), one can determine the trans-
Figure 7. Peak Shape for Monoenergetic Ions.
\[ Q(\Delta T) = \frac{1}{2(\Delta T_0)} \quad \text{for} \quad -\Delta T_0 \leq \Delta T \leq \Delta T_0 \]
lational energy with which the ions are formed by a measurement of the peak width. For the sake of convenience, one defines $W_o$, the full width of the ion peak at its base, by the equation

$$W_o = 2 \Delta \tau_o$$  \hspace{1cm} (38)

which yields the relationship

$$U_o = \frac{N_o}{8} (eE_s)^2 \frac{W_o^2}{M}$$  \hspace{1cm} (39)

where $N_o$ is Avogadro's number and $M$ is the molecular weight of the ion in grams per mole, as before.

For all ions whose energy distributions are clearly not thermal or quasi-thermal, the procedure has been to measure the width at the base of the peak ($W_o$). Using the width, $W_o$, and the relationship expressed in Equation (39) one can calculate a characteristic energy, $U_o$, which represents the maximum initial translational energy possessed by a detectably significant number of ions. $W_o$ is, in effect, the "turn-around time" for ions of initial energy $U_o$ whose velocities are directed entirely along the flight axis.

One additional factor that affects the peak shape is the manner in which the instrument itself detects the ion signal. As explained in the section on the TOF mass spectrometer, when an ion packet strikes the ion cathode, electrons are knocked from its surface and are directed onto the multiplier. The current produced in the multiplier by an individual ion packet is measured by deflecting the electron pulse for that mass from the electron pulse train (which normally follows the equipotential line to the oscilloscope anode) to one of the gated anodes of the multiplier. This is accomplished by a
precisely timed pulse which gates the desired mass peak to the appropriate anode.

The effect of this gate pulse is such that instead of measuring the intensity of the ion signal at some particular instant in time, the instrument actually measures the sum of the ion signals for all ions of that mass whose secondary electrons are passing the gate during the small but finite period of time during which the gate is pulsed. This effect is illustrated in Figure 8. The shaded area represents that fraction of the ion signal which is actually being recorded by the instrument at time $T$. Consequently, if the actual intensity of the ion packet itself at time $\Delta T$ is given by the function $Q(\Delta T)$, the observed ion signal as given by the instrument has a relative intensity at time $\Delta T$, given by the integral

$$I(\Delta T) = \int_{\Delta T - T_g/2}^{\Delta T + T_g/2} Q(t) \, dt$$

(40)

where $Q(t)$ is the distribution function, defined in Equation (27), which gives the intensity of the ion beam at some particular time. The duration of the gate pulse, $T_g$, was 20 nanoseconds.

The problem of eliminating instrumental effects on peak shapes was recognized by Gur'yev et al. (81) in their study of kinetic energy measurements by peak form analysis for a conventional sector field instrument. They treated the problem by using the convolutional integral to analyze peak forms and developed a method for solving the integral based on the particulars of the problem at hand.
Figure 8. Effect of Gate Pulse on Peak Width.
The problem of obtaining the actual distribution function, \( Q(\Delta T) \) from the observed function, \( I(\Delta T) \), may also be solved graphically. By substituting appropriate trial distribution functions for \( Q(t) \) into Equation (40) and carrying out the integration to obtain \( I(\Delta T) \), one can construct a family of peak forms \( I(\Delta T) \), each of which arises from a distinctive distribution function, \( Q(\Delta T) \). Then, by comparing an experimentally determined peak form with those calculated for \( I(\Delta T) \), one can deduce the distribution function, \( Q(\Delta T) \), actually possessed by the ions. For example, in the case of thermal ions, whose distribution function \( Q(\Delta T) \) is given by the Gaussian distribution about the average, \( T(0, s_o) \), substitution of \( Q(t) \) from Equation (29) into the integral of Equation (40) yields the following expression for the observed relative intensity of the ion signal as a function of time:

\[
I(\Delta T) = \int_{\Delta T - 1/2 \, T_g}^{\Delta T + 1/2 \, T_g} \frac{1}{\sigma \sqrt{2\pi}} \exp \left(-\frac{t^2}{2\sigma^2}\right) dt. \tag{41}
\]

Substitution of the dimensionless parameter \( x = \Delta T/\sigma \) in the equation results in the expression

\[
I(\Delta T) = \int_{x_1}^{x_2} \frac{1}{\sqrt{2\pi}} \exp \left(-\frac{x^2}{2}\right) dx \tag{42}
\]

where

\[
x_2 = (\Delta T + 1/2 \, T_g)/\sigma = x + T_g/2\sigma \tag{43a}
\]

\[
x_1 = (\Delta T - 1/2 \, T_g)/\sigma = x - T_g/2\sigma \tag{43b}
\]

Further, if an area integral, \( A(c) \), is defined by the expression

\[
A(c) = \int_{0}^{c} \frac{1}{\sqrt{2\pi}} \exp \left(-\frac{x^2}{2}\right) dx \tag{44}
\]
then Equation (41) may be rewritten as

\[ I(\Delta T) = A(x_2) - A(x_1). \]  \hfill (45)

Values for the area integrals appear in standard mathematical tables (100). From these tables, the expected peak shapes, \( I(\Delta T) \), can be constructed and the corresponding half-widths predicted.

An example of such a construction is illustrated in Table 2. The actual distribution function for the ion flight times, \( Q(\Delta T) \), has been calculated from probability tables, assuming \( \sigma \) equals 10 nanoseconds. Then, using the values listed in the same table for the area integrals, the peak shape as recorded by the instrument \( I(\Delta T) \), has been calculated, assuming a gate pulse duration \( (T_g) \) of 20 nanoseconds. These results are illustrated in Figure 9. The term \( 2\Delta T_{1/2} \) represents the full width at half-height for the actual ion distribution, while \( W_{1/2} \) represents the full width at half-height for the ion peak as drawn by the instrument. It can be seen that the net effect of the gate pulse is to make the peak seem wider than it actually is. (In this example, an ion packet of actual half-width \( (2\Delta T_{1/2}) \) 23.2 nanoseconds is recorded by the instrument as having a half-width \( (W_{1/2}) \) of 27.2 nanoseconds.) By constructing several such peaks in this manner, a calibration curve can be made from which it is possible to deduce the true width of the ion packet \( (2\Delta T_{1/2}) \) from the experimentally observed width \( (W_{1/2}) \). Such a calibration curve is shown in Figure 10. The use of this curve is illustrated for the previous example, in which a peak measuring 27.2 nanoseconds wide at half-height is produced by an ion signal whose true distribution measures only 23.2 nanoseconds wide at half-height. Two significant features should be noted in this curve.
<table>
<thead>
<tr>
<th>$\Delta T$ $x 10^9$ sec</th>
<th>$Q(\Delta T)^*$</th>
<th>$x_2^{**}$</th>
<th>$x_1^{**}$</th>
<th>$A(x_2)$</th>
<th>$A(x_1)^{***}$</th>
<th>$I(\Delta T)^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.399</td>
<td>1.0</td>
<td>-1.0</td>
<td>.341</td>
<td>-.341</td>
<td>.682</td>
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<tr>
<td>2</td>
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<td>1.2</td>
<td>- .8</td>
<td>.385</td>
<td>-.288</td>
<td>.673</td>
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<tr>
<td>4</td>
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<td>1.4</td>
<td>- .6</td>
<td>.419</td>
<td>-.226</td>
<td>.645</td>
</tr>
<tr>
<td>6</td>
<td>.333</td>
<td>1.6</td>
<td>- .4</td>
<td>.452</td>
<td>-.155</td>
<td>.607</td>
</tr>
<tr>
<td>8</td>
<td>.290</td>
<td>1.8</td>
<td>- .2</td>
<td>.464</td>
<td>-.079</td>
<td>.543</td>
</tr>
<tr>
<td>10</td>
<td>.242</td>
<td>2.0</td>
<td>0.0</td>
<td>.477</td>
<td>.000</td>
<td>.477</td>
</tr>
<tr>
<td>12</td>
<td>.194</td>
<td>2.2</td>
<td>0.2</td>
<td>.486</td>
<td>.079</td>
<td>.407</td>
</tr>
<tr>
<td>14</td>
<td>.150</td>
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<td>.337</td>
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<tr>
<td>16</td>
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<td>0.8</td>
<td>.497</td>
<td>.288</td>
<td>.209</td>
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<td>.036</td>
<td>3.2</td>
<td>1.2</td>
<td>.499</td>
<td>.385</td>
<td>.114</td>
</tr>
<tr>
<td>24</td>
<td>.022</td>
<td>3.4</td>
<td>1.4</td>
<td>.500</td>
<td>.419</td>
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<td>.008</td>
<td>3.8</td>
<td>1.8</td>
<td>.500</td>
<td>.464</td>
<td>.036</td>
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<tr>
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<td>.004</td>
<td>4.0</td>
<td>2.0</td>
<td>.500</td>
<td>.477</td>
<td>.023</td>
</tr>
</tbody>
</table>

* $Q(\Delta T) = Q (-\Delta T); \ I(\Delta T) = I (-\Delta T)$

** $x_2 = (\Delta T + 1/2 \ T_g)/\sigma$ with $T_g = 20$ nsec

** $x_1 = (\Delta T - 1/2 \ T_g)/\sigma$ with $\sigma = 10$ nsec

*** $A(x) = -A(-x)$
Figure 9. Comparison of True Ion Distribution, $Q(\Delta T)$, with Recorded Ion Distribution, $I(\Delta T)$. 
Figure 10. Calibration Curve to Deduce True Peak

Width \((2\Delta T_{1/2})\) from Observed Peak

Width \((W_{1/2})\).
CALIBRATION CURVE

Calculated from Equation (41)
First, the limiting factor in resolution is the finite width of the gate pulse (lower limit, 20 nanoseconds); second, as the peak width increases the value of \(2\Delta T_{1/2}\) approaches asymptotically that for \(W_{1/2}\).

**IV. RESULTS AND DISCUSSION**

The experimental work was divided into two major portions. The first was a test of the method derived to measure initial translational energies. The second portion was the application of this method to a detailed study of three diatomic gases, nitrogen, carbon monoxide, and nitric oxide.

**A. PRELIMINARY INVESTIGATIONS**

As a test of the accuracy of the analytical expressions derived for the flight time of an ion, the expected time difference between two different mass peaks was first calculated and then measured experimentally on the oscilloscope. Using the expression \(T(0, s_0) = 2.442 M^{1/2}\) microseconds, it was estimated that the ion \(O_2^+\) should arrive at the detector 0.894 microseconds after the arrival of the ion \(N_2^+\). On the oscilloscope, the ions were separated by 0.90 microseconds. In a second such test, the separation between the \(Ar^+\) ion and the \(N_2^+\) ion was calculated to be 2.53 microseconds. The observed separation was 2.55 microseconds. This agreement is well within the accuracy of the experimental method and confirms the correct derivation of the expression for the ion flight times. There were no observable factors (such as field penetration into the ionization region) which might alter the flight times of the ions.
The second test involved the accurate prediction of peak widths for ions of precisely known initial energies, i.e., thermal ions. The expected peak widths at half-height for ions of thermal energy (assuming a source temperature of 300° K) were calculated from Equation (33) and were also obtained graphically from the peak shapes constructed mathematically from Equation (42), as explained previously. Figure 11 compares the results of these calculations with a number of experimentally determined peak widths for ions over a wide mass range.

As discussed previously these calculations show that the gate pulse causes significant broadening of the narrower peaks (those for ions of small mass and low energy). However, the excellent agreement between the peak widths observed and those calculated \( (W_{1/2}) \) by means of Equation (42) shows that this broadening effect due to the gate width can be accurately calculated and the appropriate corrections made to obtain the true peak width \( (2\Delta T_{1/2}) \) and hence the true value of the initial energy.

Moreover, this instrumental factor becomes decreasingly important for thermal ions whose peak width at half-height is greater than about 25 nanoseconds, which is approximately the peak width expected for thermal ions with a m/e ratio of 28. For thermal ions of greater mass, the effect of the gate pulse may be neglected and the peak width may be accurately predicted from the simpler relationship expressed in Equation (33). The gate effect may likewise be neglected for any excited ions with a half-width greater than 25 nanoseconds.

The third test of the method involved the measurement of ions formed with a considerable amount of excess translational energy.
Figure 11. Calculated and Experimental Peak Widths.
Such ions have long been known to exist in the mass spectra of molecules. In his 1930 study of the hydrogen molecule, Blackney (8) found, in addition to protons of thermal energies, a number of \( H^+ \) ions with about 4.5 eV of kinetic energy. Such high energy fragments were subsequently observed in the mass spectra of polyatomic molecules. Hustrulid, Kusch and Tate (106), for example, found excess-kinetic energy ions of masses 12 to 15 and 25 to 27 in the mass spectrum of benzene. However, whereas Blackney had determined that the high energy protons in hydrogen resulted from excitation to a repulsive state of the hydrogen molecule ion followed by dissociation, Hustrulid, et al. tentatively ascribed the high-energy ions in the benzene spectrum to the dissociation of doubly charged ions into two smaller, singly charged fragments. This conclusion was supported by the observation that the high energy fragments had appearance potentials of about 30 volts (typical ionization potential value for doubly charged, polyatomic organic molecules), while the thermal fragment ions were observed to have appearance potentials in the neighborhood of 20 volts. Moreover, as demonstrated by Mohler, Dibeler and Reese (147), the kinetic energy of the correlated pair of fragment ions is in most cases nearly equal to the Coulomb energy of two ions at a distance equal to the greatest distance between valence electrons in the molecule. Measurements of appearance potentials and kinetic energies in subsequent investigation have supported this mechanism (12, 50, 67, 68, 96, 164, 193-195). Success in finding pairs of fragment ions with matching kinetic energies (same authors as above) has not been shared by others (86, 176). Such failures to detect excited pairs of ions have been explained by an alternative method proposed by Monahan and
Stanton (148) who postulate a single ionization with the simultaneous excitation of a second electron. A recently constructed instrument (139) capable of detecting the products from the dissociative ionization of a single molecule has permitted the direct observation of the decomposition of a doubly-charged molecule-ion into two singly charged fragments of high translational energy.

Whatever their origin, such high-energy fragment ions have been observed by numerous workers with good agreement as to the actual value of the translational energy. Consequently, two typical ions of this type where chosen to test the ability of the method previously developed to accurately determine high translational energies.

Figure 12 shows the chart recording for the methyl ion peak resulting from the bombardment of ethyl bromide with 50 volt electrons. In addition to the relatively narrow peak caused by ions with a quasi-thermal energy distribution, there is a much wider peak produced by ions with an obviously much different energy distribution. It should be noted that the high-energy group of methyl ions produces a symmetric peak whose center appears at exactly the same mass number as the center of the peak produced by the quasi-thermal group of methyl ions. That is, $T(O, s_o)$ is the most probable flight time for both types of methyl ions.

The methyl ion from ethyl bromide has been investigated previously by workers (164) using a somewhat different method of measuring initial translational energies. In Table 3, results are compared with those obtained in this work.
Figure 12. Peak Shape for CH$_3^+$ Ion from C$_2$H$_5$Br.
<table>
<thead>
<tr>
<th></th>
<th>This Work</th>
<th>Olmsted, Street and Newton (164)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K.E. of Quasi-thermal ion</td>
<td>0.15</td>
<td>0.21</td>
</tr>
<tr>
<td>K.E. of ion with excess K.E.</td>
<td>3.26</td>
<td>3.31</td>
</tr>
</tbody>
</table>
The methyl ion from propane is also formed with two entirely different energy distributions. Table 4 compares the value obtained in this investigation for the initial translational energy of the high-energy fragment with the values obtained by several other workers.

The very good agreement obtained with the values reported by other workers in both of these cases shows that the method developed in this work is a very accurate method which may be applied to the measurement of initial translational energies over a wide range of values.

B. DIATOMIC MOLECULES

Despite the fact that the diatomic molecules nitrogen, carbon monoxide and nitric oxide were among the most thoroughly investigated compounds in the development of mass spectrometric methods, their bond strengths remained the source of great controversy for nearly a quarter of a century. Not until the advent of practical methods for producing monoenergetic electron beams in the mid-1950's was the problem finally settled. This subject has been extensively reviewed in a number of works (37,46,52,70,141).

These three gases have been chosen for further study in this work for two principal reasons: first, such an investigation serves as a classical example of the problems, methods, and limitations of the electron impact method of determining molecular properties; second, it is hoped that additional information on these compounds will result from this investigation.
TABLE 4: KINETIC ENERGY OF CH$_3^+$ FRAGMENT IONS FROM C$_3$H$_8$

<table>
<thead>
<tr>
<th>This Work</th>
<th>MOHLER et al. (147)</th>
<th>STANTON (176)</th>
<th>BRACHER et al. (12)</th>
<th>TSUCHIVA (194)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.21</td>
<td>2.2</td>
<td>2.3</td>
<td>2.2</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>
1. NITROGEN

Some of the earliest work (130,131) on nitrogen reported a bond strength in the range 6.73 to 7.90 eV, but by the mid-1950's thorough spectroscopic studies (45, 48) had narrowed the value down to just one of two possibilities, 7.373 eV or 9.756 eV. It had been shown (82, 180) that the fragmentation products are formed with zero translational energy at the appearance potential of N\(^+\). The uncertainty in the bond strength resulted from the inability of the experiment to identify the electronic states of the products formed at the dissociation limit 24.297 eV.

Lozier (131,132) and Hagstrum (82) reported evidence supporting the assumption that the nitrogen atom produced is excited electronically. At the time the lower value for D(N\(_2\)) was also supported by a number of other investigators (92,122,125,126). Douglas (46), however, pointed out that the available spectroscopic data could be more easily interpreted if one assumes D(N\(_2\)) equals 9.756 eV. This higher value had been advanced by a number of workers (15,24,47,69, 71,75-78,90) and had been supported by indirect experimental evidence from shock wave studies (116,117,191,192); combustion studies (190); and from the study of dissociation on a hot wire (51). Burns (19) and Clarke (26), employing monoenergetic electron beams, produced evidence that could be explained only by assuming the higher value (9.76 eV) for the bond strength. Subsequently, Hagstrum (83) and Lindholm (123) reinterpreted their earlier results and found them to be consistent with the value 9.76 eV for D(N\(_2\)). Frost and McDowell (65), also employing monoenergetic electrons, found results in good
agreement with those of Clarke.

Because of its importance in the identification of electronically excited products, the method used in the monoenergetic electron impact studies is summarized here. Burns (19), using the RPD technique of producing monoenergetic electrons, found an ionization efficiency curve for \(N^+\) that was composed of several linear segments. With onset occurring at 24.3 eV, the first three upward breaks in the curve were at 26.2, 26.8, and 27.9 eV. According to the linear threshold law for ionization discussed previously, these breaks indicated ionization to various electronic levels of the products. Clarke (26), using a velocity selector to produce monoenergetic electrons, reported onset at 24.35 eV, with breaks occurring at 26.71 and 28.1 eV, while Frost and McDowell (65), also using RPD techniques, found onset at 24.32 eV and breaks at 26.66 and 27.92 eV. Since the various electronic states of the products (a nitrogen atom and an atomic nitrogen ion) are well known from spectroscopy, one set of expected breaks in the IE curve could be predicted for \(D(N_2) = 7.37\) eV, while a second set could be predicted for \(D(N_2) = 9.76\) eV. Whichever set of predicted levels gave the best agreement with the observed breaks was assumed to be the set based on the correct value for \(D(N_2)\). The predicted energy levels are listed in Table 5 and are compared with the experimental data available in Figure 13. Clearly, the assumption that \(D(N_2) = 9.76\) eV gives better agreement with the experimental data, and this is the presently accepted value for the bond strength of the nitrogen molecule.

The four principal ions observed in the mass spectrum of nitrogen
<table>
<thead>
<tr>
<th>State</th>
<th>Relative Energy (eV)</th>
<th>Absolute Energy (eV) If D(N₂) = 9.75 eV</th>
<th>Absolute Energy (eV) If D(N₂) = 7.37 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>I N(4S) + N⁺(3P)</td>
<td>0.00</td>
<td>24.3</td>
<td>21.9</td>
</tr>
<tr>
<td>II N(4S) + N⁺(1D)</td>
<td>1.90</td>
<td>26.2</td>
<td>23.8</td>
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<tr>
<td>III N(2D) + N⁺(3P)</td>
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<tr>
<td>IV N(2P) + N⁺(3P)</td>
<td>3.58</td>
<td>27.9</td>
<td>25.5</td>
</tr>
<tr>
<td>V N(4S) + N⁺(1S)</td>
<td>4.05</td>
<td>28.4</td>
<td>26.0</td>
</tr>
<tr>
<td>VI N(2D) + N⁺(1D)</td>
<td>4.28</td>
<td>28.6</td>
<td>26.2</td>
</tr>
<tr>
<td>VII N(2P) + N⁺(1D)</td>
<td>5.48</td>
<td>29.8</td>
<td>27.4</td>
</tr>
<tr>
<td>VII N(2D) + N⁺(1S)</td>
<td>6.43</td>
<td>30.7</td>
<td>28.3</td>
</tr>
</tbody>
</table>
Figure 13. Predicted and Observed Dissociation States for $N_2$. 
are shown in Figure 14, where their relative intensities are plotted as a function of the electron energy. The most important ions in the low pressure (2 x 10^-6 mm Hg.) mass spectrum of nitrogen are N_2^+, N^+, N_2^{++} and N^{++}. At an electron energy of 100 volts, their relative intensities were observed to be in the ratio of 377 : 38.5 : 12.3 : 1. (It should be noted that the intensity of the ion N_2^{++}, determined from the peak at m/e 14.5 from N^{14}_2 N^{15}, had to be corrected by the subtraction of a relatively constant factor appearing as a background and assumed to result from the interference caused by the much more intense peaks at m/e 14 and 15, which could not be completely resolved from the 14.5 peak.) No negative ions were observed in the mass spectrum of nitrogen.

Using argon (IP = 15.755 eV) as a reference gas, the ionization potential of the nitrogen molecule-ion was determined. Figure 15 shows a typical ionization efficiency curve. The average of five trials indicated that the first ionization potential of nitrogen was 15.59 ± 0.05 eV. This is in excellent agreement with the value of 15.577 eV determined spectroscopically (160,209,211) for the ionization of the ground state of N_2(^1Σ^+ g) to the ground state of the N_2^+ ion (X^2Σ^+ g). The X^2Σ^+ g state is well known (16,23,36,39,45,165) and 21 vibrational levels have been observed.

The first noteworthy feature in the fine structure of the IE curve is the deviation of the experimental points from linearity in the region 16.2 to 17.2 eV. This deviation occurred in all the trials. Other workers have observed such curvature in the region 16.0 to 17.5 eV (26,55,112,156,208). (It was not, however, observed by Frost and McDowell (64)). According to Clarke's (26) explanation, the shape of
Figure 14. Positive Ions in the Mass Spectrum of Nitrogen.
Figure 15. Ionization Efficiency Curve for $N_2^+$ from Nitrogen.
the curve for \( N_2^+ \) is due to excitation of the vibrational levels of the ionized molecule, which are known from spectroscopy (45) and from photoelectron spectroscopy (1).

Following the technique of Clarke (26), the curvature was ignored and the linear portions extrapolated to meet at \( 16.87 \pm 0.10 \text{ eV} \). This break has been observed by others (26,27,57,64,112,208) and attributed by them to the \( \text{A}^2\Pi_u \) state identified spectroscopically by Meinel (145) and Dalby and Douglas (41) and situated at 16.691 eV. As Clarke (26) pointed out, "the interpretation indicates that once the electrons have sufficient energy to excite the \( \text{2}\Pi_u \) state, then vibrational levels are no longer excited. This is not in disagreement with optical spectrometry, where the bands attributed to the \( \text{2}\Pi_u \) state have recently been found to be quite weak."

Another break in the IE curve was observed at \( 18.75 \pm 0.20 \text{ eV} \) (average of five trials). This break has been observed in other mass spectrometric investigations (26,57,64,208) and has been interpreted as formation of the \( N_2^+ \) ion in the \( \text{B}^2\Sigma_u^+ \) state. This state, observed spectroscopically to occur at 18.746 eV (102), is well known and 29 vibrational levels are known (16,23,36,39,45,165).

A fourth ionization potential was observed at \( 23.86 \pm 0.20 \text{ eV} \). This has been interpreted as being the \( \text{C}^2\Sigma_u^+ \) state (64), known spectroscopically to occur at 23.581 eV (3,173,204). The high value obtained by electron impact is reasonable in view of the differences in the equilibrium internuclear distance between this state and the ground state of the nitrogen molecule. As can be seen in Figure 16,
Figure 16. Potential Energy Curves for the Electronic States of $N_2^+$. 
which shows the pertinent electronic states of the $N_2^+$ ion, the minimum of the potential energy curve for the $C^2\Sigma_u^+$ state lies to the right of the effective Franck-Condon region (assumed to be 0.1 Å in width.) Consequently, one would expect the vertical ionization potential from electron impact data to be somewhat higher than the adiabatic ionization potential from spectroscopy.

Since the ground electronic state of the nitrogen molecule has the configuration $KK(\sigma_\text{g}^2 \pi_\text{u}^2 \pi_\text{u}^2 \pi_\text{u}^2 \pi_\text{g}^2)$, the first ionization potential (15.577 eV) corresponds to the removal of a $(\sigma_\text{g}^2 \pi_\text{u}^2 \pi_\text{u}^2 \pi_\text{g}^2)$ electron, the second (16.694 eV) to the removal of a $(\pi_\text{u}^2 \pi_\text{g}^2)$ electron, the third (18.746 eV) to the removal of a $(\sigma_\text{u}^2 \pi_\text{g}^2)$ electron, while the fourth (23.581 eV) probably corresponds to the removal of a $(\sigma_\text{u}^2 \pi_\text{g}^2)$ electron and the simultaneous excitation of a second electron (64).

The appearance potential of the doubly-charged molecule-ion $N_2^{++}$ was determined. Using the value of 43.38 eV (149) for the appearance potential of doubly-charged argon to calibrate the electron energy, the average of four trials indicated that $AP(N_2^{++}) = 44.2 \pm 0.5$ eV. This value must be considered uncertain, however, because of the high background at m/e 14.5 due to interference from the adjacent peaks. (The sample was approximately 90% $^{14}\text{N}_2^{15}\text{N}$, prepared by the decomposition of an isotopically labelled diazonium salt.) The RPD curve for $N_2^{++}$ did not go to zero but remained constant below a certain value of the electron energy. This value was taken as the appearance potential of the ion, and hence there is some uncertainty regarding its value. Earlier investigators (82,181,197) reported
values of $40.3 \pm 1$, $47.4 \pm 1$ and $49.5 \pm 0.5$ eV for the appearance potential of this ion. More recently, Dorman and Morrison (43) have reported the value $43.5 \pm 0.3$ eV, while Hurley and Maslen (105) found a value of $42.7$ eV, with a second process occurring above $43.8$ eV.

Hurley (104) has calculated the potential energy curves for a number of states of the doubly-charged nitrogen molecule. On the basis of these calculations, he compared his experimental ionization potentials with those that he calculated (see Figure 17.) He concluded that the lower value ($42.7$ eV) could arise from ionization to either the $a_1 \Sigma_g^+$ state or the $X^2\Pi_u$ state, while the higher value ($43.8$ eV) might arise from ionization to either the $b^1\Pi_u$ state or the $3\Sigma_g^-$ state. On the basis of these calculations, it would seem that both the value reported in this work ($44.2$ eV) and that ($43.5$ eV) reported by Dorman and Morrison (43) could be interpreted as representing ionization to either the $b^1\Pi_u$ state or the $3\Sigma_g^-$ state.

The appearance potential of the $N^+$ ion was determined by the RPD method, and a typical IE curve is shown in Figure 18. The initial translational energy of the ion as a function of the electron energy was also determined, and the results are shown in Figure 19. The ion $N^+$ was found to be formed with little or no excess translational energy at its appearance potential, which agrees with the earlier findings of Hagstrum (82) and others (110, 131, 132). The appearance potential was found to be $24.32 \pm 0.03$ eV, which agrees very well with the spectroscopically determined dissociation limit of $24.297$ eV (45,48). Literature values (18,19,26,64,82,85,110,131,180,197) indicate an appearance potential of 23.0 to 24.6 eV, with a most probable value
Figure 17. Potential Energy Curves for the Electronic States of \( \text{N}_2^{++} \).
Figure 18. Ionization Efficiency Curve for N$^+$ from Nitrogen.
$\Delta I$ (Arbitrary Units)

$N^+$ from $N_2$

ELECTRON ENERGY (eV)
Figure 19. Kinetic Energy vs. Electron Energy for $N^+$ from Nitrogen.
of 24.3 eV.

There is a definite break, occurring in the IE curve at 26.2 eV. The curved portion in the region 26.2 to 26.6 eV is almost identical in shape to that observed by Burns (19) and interpreted by him as representing the onset of a process in which the N⁺ ion is formed in an excited state. This break, however, was not observed by Clarke (26), using a velocity selector, nor was it observed by Frost and McDowell (65), who repeated Burns' RPD experiments in order to clear up this discrepancy. Although this anomalous curvature occurred in each of the five appearance potential measurements on N⁺, and although it appears to be identical in shape to that reported by Burns (19), it is not believed to be caused by the onset of a new process forming excited N⁺ ions as Burns claimed. The irregular curvature is not consistent with such an interpretation, nor could this interpretation explain the failure of Frost and McDowell (65) to observe such a process. It is possible that the curvature arises from some auto-ionization process.

Ignoring the curvature and extrapolating the linear segments of the IE curve, there is clearly a break occurring at 26.65 ± 0.15 eV (average of five trials). A second break was observed at 28.0 ± 0.2 eV. Such breaks have been observed in all previous investigations of the dissociative ionization of nitrogen with monoenergetic electrons (19, 26, 65). From the energy levels listed in Table 5, the observed breaks in the IE curve may be explained by the following processes:

\[ \text{N}_2 + 24.32 \text{ eV} \rightarrow \text{N}(^4S) + \text{N}^+ (^3P) + e \]  \hspace{1cm} \text{(R1)}
\[ \text{N}_2 + 26.75 \text{ eV} \rightarrow \text{N}^\text{+} (^2\text{D}) + \text{N}^\text{+} (^3\text{F}) + \text{e} \quad (\text{R2}) \]
\[ \text{N}_2 + 28.0 \text{ eV} \rightarrow \text{N}^\text{+} (^2\text{F}) + \text{N}^\text{+} (^3\text{P}) + \text{e} . \quad (\text{R3}) \]

It can be seen that the first three processes leading to the production of \text{N}^\text{+} ions involve the production of the nitrogen atom in its three lowest states, while the \text{N}^\text{+} ion is always produced in its lowest state. The failure to observe the formation of the \text{N}^\text{+} ion in its first excited state \( ^1\text{D} \) has been explained (52) by the fact that, according to the Wigner-Witmer correlation rules (92), such dissociation products correlate only with quartet states, but no quartet states of \text{N}_2^+ have been observed spectroscopically.

Information as to the state of the \text{N}_2^+ ion which gives rise to the observed dissociation products can be inferred from the kinetic energy data. As can be seen from Figure 19, \text{N}^\text{+} ions are formed with zero translational energy at the appearance potential, which indicates that the turning point of the dissociation asymptote lies within the effective Franck-Condon region. As the electron energy is increased, however, the total kinetic energy of the fragments increases and levels off at an average value of about 2 eV. This indicates that the potential energy curve for the \text{N}_2^+ ion involved lies about 2 volts above the dissociation asymptote at an internuclear distance equal to the equilibrium internuclear distance of the nitrogen molecule \( r_e = 1.094 \text{A} \).

This information indicates that the \text{N}^\text{+} ion observed at 24.3 eV probably does not arise from any of the first three levels of the \text{N}_2^+ ion. The \( ^2\text{S}_u \) state of \text{N}_2^+, which McDowell (141) thinks is responsible for the production of \text{N}^\text{+} ions, has the proper shape in the Franck-Condon
region but does not correlate with the products formed at 24.3 eV. It does, however, correlate with the products observed at 26.7 eV and very possibly could be the state of the $N_2^+$ ion which dissociates according to process II. The potential energy curves given by Gilmore (74) (see Figure 16) are not complete enough to answer the question unambiguously, but it seems possible that a state such as the $D_2^T \Pi_g$ state is the one which gives rise to the products observed at 24.3 eV.

Vaughan (197) reported a sharp increase in the efficiency of production of the $N^+$ ion at 47 eV. Hagstrum and Tate (85) noted a similar increase at 49.5 eV, and interpreted this increase as the onset of the formation of $N_2^{++}$ ions. This explanation, however, may be questioned for three reasons. First, although $N_2^{++}$ ions unquestionably contribute to the m/e = 14 peak at these electron energies, the increase in intensity reported by Hagstrum seems much larger than is justified by the intensities reported for the $N_2^{++}$ ion in the present investigation. Second, the value of the electron energy for onset is considerably above the more recent (43,105) values for the appearance potential of $N_2^{++}$. Third, and most important, this present study indicates a sudden and sharp increase in the kinetic energies of the fragment ions at 48 ± 2 eV. This sudden increase, which could not be caused by $N_2^{++}$ ions, is interpreted as resulting from the formation of an unstable $N_2^{++}$ ion and its subsequent dissociation into two $N^+$ ions of high kinetic energy. $N^+$ ions with 4 to 8 eV of kinetic energy were reported by Tate and Lozier (180) when nitroene was bombarded with electrons of 46 to 54 volts of energy. They, too, interpreted this as the formation of two singly charged atomic nitrogen ions.
Such an explanation is based on two facts. First, as mentioned previously, such behavior has been widely observed to occur for polyatomic organic molecules. Moreover, Lozier (128) observed the formation of protons with kinetic energies of 7.5 to 12.5 volts in the bombardment of hydrogen with electrons of 46 to 56 volts, in complete agreement with theoretical predictions based on the removal of two electrons from hydrogen. Second, according to Hurley's calculations (104), there is a state \( A^3 \Pi_g \) of the \( N_2^{++} \) ion which passes through the Franck-Condon region (see Figure 17) in such a manner that dissociation into two \( N^+ (^3P) \) ions should occur at about 46.5 eV. If his postulated dissociation products are correct, the ions should be formed with a minimum of about 8 volts total kinetic energy, which is precisely what the present measurements indicate. Consequently, a fourth process for the production of \( N^+ \) ions can be postulated:

\[
N_2 + 47 \pm 1 \text{ eV} \rightarrow N^+ (^3P) + N^+ (^3P) + 2e. \quad \text{(R4)}
\]

The appearance potential of the \( N^{++} \) ion was measured by the RPD method, using \( \text{Ne}[\text{AP(Ne}^{++}) = 62.63 \text{ eV (149)] as the calibrating gas. The average of three trials indicated that the appearance potential of \( N^{++} \) is } 63.65 \pm 0.20 \text{ eV. The ion was observed to be formed with } 5.0 \pm 0.4 \text{ eV of kinetic energy at the appearance potential. Since the bond strength of the nitrogen molecule is } D(N_2) = 9.76 \text{ eV, and since } 14.54 + 29.61 = 44.15 \text{ eV (149) are required to remove two electrons from the nitrogen atom, the relationship}

\[
\text{AP(N}^{++}) = D(N_2) + IP(N \rightarrow N^{++}) + E_e(N) + E_e(N^{++}) + (28/14)E_e(N^{++}) \quad \text{(1)}
\]

becomes

\[
63.6 \pm 0.2 = 9.76 + 44.15 + 2(5.0 \pm 0.4) + E_e(N) + E_e(N) \quad \text{(2)}
\]
or

\[ -0.3 \pm 1.0 = E_e(N) + E_e(N^{++}). \]  

(3)

Since the lowest electronic state of the N atom is 2.4 eV above the ground state, while the lowest electronic state of the \( N^{++} \) ion is about 7 eV above the ground state (149), it would appear that in the observed process, both products are formed in their ground electronic states.

That is,

\[ N_2^+ (63.6 \pm 0.2 \text{ eV}) \rightarrow N(^4S) + N^{++}(^3P) + 2e + (10 \pm 0.8 \text{ eV}). \]  

(R5)

2. CARBON MONOXIDE

The dissociation energy of carbon monoxide and the related quantity, the heat of vaporization of carbon, had been subjects of a long controversy (14, 46, 52, 69). The values under consideration for \( D(\text{CO}) \) were 9.14, 9.61, 9.85 and 11.11 eV, while the corresponding values for \( L(\text{C}) \) were 125.0, 135.8, 141.3, and 170.4 kcal/mole respectively.

The existence of a dissociation limit of CO at 11.1078 eV was observed spectroscopically (48). In electron impact studies, \( C^+ \) ions were observed to be formed at 28.9 and at 22.8 eV (82,84,85,133), while \( O^+ \) ions were observed to be formed at 23.2 eV (82,85,182). The difficulty in all of these experiments, however, was the proper identification of the electronic states of the dissociation products.

The first value for the appearance potential of \( C^+(20.9 \text{ eV}) \) was interpreted as representing an ion pair process (\( O^- \) being the other product). Because the electron affinity of oxygen was not well known at the time, however, this result could not be used to determine
D(CO) unambiguously. Moreover, there was uncertainty as to the
process by which O⁺ ions were produced at 23.2 eV. Chupka and Inghram
(25) claimed C⁻ was the other product, while Hagstrum (82) failed to
observe the C⁻ ion in the mass spectrum of carbon monoxide.

Branscomb and Smith (13) found a value of 1.48 eV for the electron
affinity of oxygen. This value, which is now generally accepted as
correct, was used by Lægsgren (121) to interpret the results of his
electron impact study of carbon monoxide. His conclusion, that
D(CO) equals 11.11 eV, has since been supported by a number of
experiments which indicated that the heat of sublimation of carbon
was 170 kcal/mole (25,73,99,158,192).

In the present study the relative intensities of the positive
ions observed in the low pressure (5 x 10⁻⁶ mm Hg) mass spectrum of
carbon monoxide are shown in Figure 20. This would appear to be the
first time that the doubly charged atomic ions C^{++} and O^{++} have been
reported in the mass spectrum of carbon monoxide. In addition, the
negative ions C⁻ and O⁻ were observed.

The ionization potential of carbon monoxide was determined by
RPD techniques, using argon (IP = 15.755 eV) (149) to calibrate the
electron energy. The average of five trials indicated that IP(CO)=
14.00 ± 0.05 eV. This is in excellent agreement with the spectroscopic
value of 14.009 eV (92) and the value 14.1 ± 0.1 eV reported from mass
spectrometric investigations (82,85,181,197). This value is interpret-
ed as representing ionization to the X^2−_g state of the CO⁺ ion.

A typical IE curve for CO⁺ is shown in Figure 21. This is in
Figure 20. Positive Ions in the Mass Spectrum of Carbon Monoxide.
Figure 21. Ionization Efficiency Curve for CO⁺ from Carbon Monoxide.
agreement with RPD data (57,112) that the IE curve is linear for at least 1.5 eV above onset. This result was also obtained by Winters (208) using a different method.

A break was observed to occur at 16.5 ± 0.1 eV in the IE curve, as can be seen from Figure 21. A similar break has been reported by Fox (55,57), who interpreted it as the onset of ionization to the A\(^2\)\(\Pi\) \(_u\) state of CO\(^+\), which is known to be 2.52 eV above the ground state of the ion (92). The present measurements are consistent with such an interpretation.

The appearance potential of the doubly-charged molecule-ion, CO\(^{++}\), could not be determined with any accuracy because of interference from a strong background peak at m/e 14 resulting from a small air leak. Published values, however, indicate that the appearance potential for CO\(^{++}\) is in the range 41.8 to 46 eV (43,85,197).

The negative ion O\(^-\) was observed to be formed by a resonance process, with onset occurring at 9.7 ± 0.2 eV. The width of the ion peak seemed to indicate that the ion was formed with excess translational energy. However, it was found that all negative ion peaks were unusually wide, even those for ions which were known to possess little or no excess translational energy. The conclusion was that kinetic energy measurements could not be made on negative ions, at least under the present conditions. It is suggested that perhaps the peak broadening for negative ions results from the negative square well potential of several tenths of an electron volt produced by the electron beam. If, however, it is assumed that the O\(^-\) ion was formed
with little or no excess translational energy, the observed appearance potential of 9.7 eV agrees very well with the value of 9.63 eV calculated for the process

$$\text{CO} + \text{e} + (9.63 \text{ eV}) \rightarrow \text{C}(^3\text{P}) + \text{O}^- (^2\text{P}). \quad (R6)$$

The ion O$^-$ was also observed to be formed by an ion pair process with onset occurring at 20.9 ± 0.2 eV. Since this value agrees very well with the value of 20.82 ± 0.05 eV observed for the appearance potential of the C$^+$ ion (using Ne$^+$ to calibrate the electron energy), it is concluded that these ions were formed simultaneously by the process

$$\text{CO} + 20.89 \text{ eV} \rightarrow \text{C}^+ (^2\text{P}) + \text{O}^- (^2\text{P}). \quad (R7)$$

Since the C$^+$ ion was formed with no excess translational energy, no correction need be made on the observed appearance potentials, which agree very well with the value of 20.89 eV calculated for the ion pair process (R7), assuming EA (0) = 1.48 eV (13) and with the previously observed value of 20.9 eV (82,83,133). As shown in Figure 22, there is a sharp increase in the production of C$^+$ ions at 22.45 ± 0.10 eV. The ions were observed to be formed with zero translational energy at this appearance potential, which agrees with the results of Hagstrum and Tate (85) and of Berry (7). If the products are assumed to be C$^+ (^2\text{P},^0)$ and O$^-(^2\text{P})$, the calculated value is 22.37 eV. Previous workers (82,83,121,123,133) have reported values in the range 22.4 to 22.8 eV. The electron energy was not increased enough to observe additional breaks in the curve, if any exist.

The results obtained for the O$^+$ ion are in complete disagreement with the previously published results of Hagstrum (85) and of Berry (7), who reported that very few, if any, O$^+$ ions of less than about
Figure 22. Ionization Efficiency Curve for $\text{C}^+$ from Carbon Monoxide.
C\(^+\) from CO
0.65 eV of translational energy are formed, and that appreciable numbers are formed with more than 2.5 eV. The present investigation, while observing maximum translational energies of about 0.5 eV for $O^+$ ions (Figure 23), found that the average excess translational energy was zero at the appearance potential. The broadening at the base of the ion peak (yielding the value of 0.5 eV for the maximum excess energy) was probably caused by a small number of ions which were produced by the high-energy electrons in the Maxwellian distribution of electron energies. These results have been interpreted as indicating that the potential energy curve involved in the formation of $O^+$ from CO probably passes through the Franck-Condon region rather steeply, so that it is possible that electrons of energy slightly greater than the threshold value can produce some ions with appreciable kinetic energy.

A typical IE curve for the production of $O^+$ ions from carbon monoxide is shown in Figure 24 ($Ne^+$ was used to calibrate the electron energy.) Onset occurred at 23.2 eV, with breaks observed at $24.65 \pm 0.06, 26.0 \pm 0.10, 27.45 \pm 0.10$ and $28.0 \pm 0.10$. These observed values, uncorrected for any excess translational energy, agree very well with the appearance potential values calculated (with $EA(C) = 1.5$ eV (136) for the following processes:

$\text{CO} + 23.22 \text{ eV} = C^-(^4S) + O^+(^4S)$ \hspace{1cm} (R7)

$\text{CO} + 24.72 \text{ eV} = C(^3P) + O^+(^4S) + \epsilon$ \hspace{1cm} (R8)

$\text{CO} + 25.99 \text{ eV} = C(^1D) + O^+(^4S) + \epsilon$ \hspace{1cm} (R9)

$\text{CO} + 27.40 \text{ eV} = C(^1S) + O^+(^4S) + \epsilon$ \hspace{1cm} (R10)

$\text{CO} + 28.04 \text{ eV} = C(^3P) + O^+(^2D) + \epsilon$. \hspace{1cm} (R11)
Figure 23. Kinetic Energy vs. Electron Energy
for $O^+$ and $C^+$ from Carbon Monoxide.
Figure 24. Ionization Efficiency Curve for $O^+$ from Carbon Monoxide.
However, because of the complete lack of agreement with previously published work on this subject, it is felt that a re-examination of the present data is in order.

The possibility of the process

\[ \text{CO} + e \rightarrow \text{CO}^{++} + 3e \rightarrow \text{C}^+ + \text{O}^+ + 3e \]  

(R12)

was investigated. As pointed out by Vaughan (197), 35.98 eV are needed to form the two singly charged atomic ions in their ground states, while the minimum energy required to form CO\(^{++}\) is about 43 eV. This would result in dissociation products with a total translational energy of 43-36=7.0 eV. By the law of conservation of momentum, the C\(^+\) ion would have \((16/28)(7.0) = 4.0\) eV of energy, while the O\(^+\) ion would have \((12/28)(7.0) = 3.0\) eV of energy. As indicated in Figure 23, the observed translational energies were 1.2 and 0.8 eV for the O\(^+\) ion and the C\(^+\) ion, respectively, in the electron energy range under consideration. The observed energies are much lower than would be expected for this process. Even if one assumes that part of the 7.0 eV of excess energy is used to form excited electronic states of the product ions, one would still expect, by conservation of momentum, that the C\(^+\) ion would have more translational energy than the O\(^+\) ion, if they were produced by the dissociation of CO\(^{++}\). Since this was not the case, it is concluded that this process did not occur. This finding is in agreement with the conclusion reached by Vaughan (197). Dorman and Morrison (43), however, thought that such a process was fairly reasonable, and since the corresponding process was observed in nitrogen, it is felt that this subject should also be reinvestigated.
The appearance potential of the ion $C^{++}$ was determined by the energy compensation method (115), using $Ne^{++}$ ($AP = 62.63$) (149), to calibrate the electron energy. The results indicated that the ion $C^{++}$ is formed with $4.7 \pm 0.5$ eV of translational energy at its appearance potential, $54.2 \pm 0.2$ eV. Substituting these values into the equation

$$AP(C^{++}) = D(CO) + I(C \rightarrow C^{++}) + \left(\frac{28}{16}\right) E_t(C^{++}) + E_e$$ (4)

gives the result

$$54.2 \pm 0.2 = 11.11 + 35.64 + \left(\frac{28}{16}\right)(4.7 \pm 0.5) + E_e$$ (5)

$$-0.8 \pm 1.1 = E_e$$ (6)

Thus, it appears that the products are both formed in their ground electronic states, since the first electronic level, $O^1D$, is $1.97$ eV above the ground state. That is, the observed process is

$$CO + (54.2 \pm 0.2 \text{ eV}) \rightarrow C^{++}(1S) + O^3P + (8.2 \pm 0.9 \text{ eV}) (R13)$$

A similar conclusion is drawn for the ion $O^{++}$, which was observed to appear with $0.7 \pm 0.3$ eV of translational energy at an electron energy of $61.3 \pm 0.3$ eV. Substituting these values into the appropriate equation, one finds that

$$61.3 \pm 0.3 = 11.11 + 48.76 + \frac{28}{12} (0.7 \pm 0.3) + E_e$$ (7)

$$-0.2 \pm 1.0 = E_e.$$ (8)

Since the first excited state of either produce is $1.27$ eV above the ground state, it seems that both products are formed in their ground state. That is, the observed process is

$$CO + (61.3 \pm 0.3 \text{ eV}) \rightarrow C^3P + O^{++}(4S) + (1.6 \pm 0.7 \text{ eV}) (R14)$$

3. **NITRIC OXIDE**

Since the value for $D(O_2)$ is well established and since $D(N_2)$ and
D(NO) are related through the equation

\[ D(N_2) = 2D(NO) - D(O_2) + 2\Delta H_f(NO) \]  

(9)

the molecule NO had been investigated (82) as a means of determining D(N\(_2\)) (52). That study indicated that D(NO) = 5.29 eV, which led to the conclusion that D(N\(_2\)) = 7.37 eV. The calculations, however, were based on a value (2.33 eV) for the electron affinity of oxygen which is quite a bit higher than the presently accepted value (1.48 eV). Moreover, some of the results could be interpreted only on the rather doubtful assumption that the O\(^-\) ion is formed with an excitation energy about equal to EA (O). When it was demonstrated (19,26) that D(N\(_2\)) = 9.76 eV, Hagstrum (83) reinterpreted his previous data and concluded that D(NO) was 6.49 eV. The agreement between observed and calculated appearance potentials, however, was still not completely satisfactory.

The relative intensities of the positive ions observed in the low pressure (5 \( \times \) 10\(^{-6}\) mm Hg) mass spectrum of NO are shown in Figure 25. The results are similar to those for CO, in that doubly-charged atomic ions (N\(^{++}\), O\(^{++}\)) were observed. The only negative ion observed was O\(^-\).

The average of five trials indicates that the ionization potential of the NO molecule is 9.28 \( \pm \) 0.03 eV. The value was obtained by the RPD technique, using CH\(_3\)I (IP = 9.55 eV) (203) to calibrate the electron energy. An indirect spectroscopic value can be calculated as 9.258 \( \pm \) 0.005 eV or 9.267 \( \pm \) 0.005 eV, following either Tanaka's (179) or Huber's (103) measurements. Previous electron impact investigations have indicated an ionization potential of 9.24 \( \pm \) 0.04 eV (201). This
Figure 25. Positive Ions in the Mass Spectrum of Nitric Oxide.
value corresponds to the formation of NO$^+$ in its ground electronic state (X$^1\Sigma^+$). Ionization to higher electronic levels was not observed in the limited range of electron energies (9 to 14 eV) investigated.

The O$^-$ ion was observed to be formed by a resonance process with onset occurring at $5.0 \pm 0.1$ eV. It was not possible to determine the initial translational energy of the ion, but if it is assumed that the ion is formed with zero excess translational energy, the observed value agrees very well with the value of 5.01 eV calculated for the process

$$\text{NO} + e \rightarrow \text{N}(^4\text{S}) + \text{O}^-(^2\text{P}). \quad (\text{R13})$$

The O$^-$ ion is also formed by an ionic dissociation process, with onset occurring at $19.8 \pm 0.1$ eV. This agrees well with the value of $19.94 \pm 0.14$ eV determined by the RPD technique for the appearance potential of N$^+$. The value of $19.9 \pm 0.2$ eV had been reported previously (82,85) for the appearance potential of N$^+$. This agreement indicates that these two ions are formed simultaneously by an ion pair process. Since the N$^+$ ion was observed to be formed with $0.34 \pm 0.10$ eV of translational energy at onset, the present data indicate that the corrected appearance potential, $A_{p0}$, for the ion pair process is $19.30 \pm 0.32$ eV. Assuming $EA(0) = 1.48$ eV (13), this experimental value agrees well with the value of 19.55 eV calculated for the process

$$\text{NO} + e \rightarrow \text{N}^+(^3\text{F}) + \text{O}^-(^2\text{P}) + e \quad (\text{R14})$$

As shown in Figure 26 a sharp upward break in the IE curve for N$^+$ was observed at $21.78 \pm 0.11$ eV (average of six determinations).
Figure 26. Ionization Efficiency Curve for $N^+$ from Nitric Oxide.
$N^+ \text{ from NO}$

$\Delta I$ (arbitrary units) versus Electron Energy (eV)
A graph of the translational energy of the \( \text{N}^+ \) ion versus electron energy also showed a sudden increase at this electron energy. This increase to 0.48 \( \pm \) 0.10 eV of translational energy is interpreted as representing the translational energy of the \( \text{N}^+ \) ions formed by a new process occurring at electron energies greater than 21.78 eV. Consequently, the appearance potential corresponding to the formation of ions with zero initial energy is 20.88 \( \pm \) 0.29 eV. This value agrees very well with the value of 21.03 eV calculated for the process

\[
\text{NO} + 21.03 \text{ eV} \rightarrow \text{N}^+ (^3\text{P}) + \text{O} (^3\text{P}) + \text{e}. \tag{R15}
\]

There was also some indication of an additional break in the region 23.2 \( \pm \) 0.2 eV. There was no observed increase in peak width, so it is assumed that the \( \text{N}^+ \) ions arising from this new process were formed with less than 0.48 eV of translational energy. Since a lower limit for the translational energy cannot be set, the corrected value for this appearance potential must be in the range 23.2 \( \pm \) 0.4 eV. This could correspond to either of the following processes:

\[
\begin{align*}
\text{NO} + 22.93 \text{ eV} & \rightarrow \text{N}^+ (^1\text{D}) + \text{O}(^3\text{P}) + \text{e} \tag{R16} \\
\text{NO} + 23.00 \text{ eV} & \rightarrow \text{N}^+ (^3\text{P}) + \text{O}(^1\text{D}) + \text{e}. \tag{R17}
\end{align*}
\]

Gilmore's (74) potential energy curves for \( \text{NO}^+ \) are not complete enough to allow a determination of the state of the \( \text{NO}^+ \) ion giving rise to the observed dissociation products. However, the contention that \( \text{N}^+ \) ions are formed with kinetic energy at the first appearance potential 21.78 eV is supported by the fact that Gilmore does not list any states whose dissociation asymptote lies within the Franck-Condon region. There is one state (\(^1\Delta\)), however, that seems to intercept the
Franck-Condon region at about 1 volt above its dissociation asymptote, and it is entirely possible that this is the state involved in process II.

The \( O^+ \) ion was observed to have an appearance potential of \( 20.46 \pm 0.10 \) eV (average of five determinations). This is in agreement with the previously reported value of \( 20.6 \pm 0.2 \) (82). This value was at first (82) assumed to refer to \( O^+ \) ions produced with about \( 0.8 \) eV of translational energy in order to correspond to \( D(NO) = 5.29 \) eV. After it was shown that \( D(NO) = 6.49 \) eV, it was assumed (83) that the \( O^+ \) ions were actually formed with zero kinetic energy. The present measurements, however, indicate that the \( O^+ \) ions are formed with \( 0.25 \pm 0.15 \) eV of translational energy. The value of the appearance potential, corrected for initial energy, is then \( A\Phi_o(O^+) = 19.96 \pm 0.40 \) eV. This is in good agreement with the value of 20.10 eV calculated for the process

\[
NO + 20.10 \text{ eV} \rightarrow N(^4S) + O^+ (^4S) + e. \quad (R18)
\]

A break was observed to occur in the IE curve at \( 22.59 \pm 0.15 \) eV. Because there was no increase in the translational energy of the \( O^+ \) ions, it is assumed that this process results in \( O^+ \) ions with zero to \( 0.25 \) eV of translational energy. This indicates that the process has an appearance potential, corrected for any translational energy, in the range 22.0 to 22.9 eV. This probably corresponds to the process

\[
NO + 22.48 \text{ eV} \rightarrow N(^2D) + O^+ (^4S) + e. \quad (R19)
\]

As in the case of carbon monoxide, there was no evidence of the process

\[
NO + e \rightarrow (NO^{++})^* + 3e \rightarrow N^+ + O^+ + 3e \quad (R20)
\]
A study of the translational energies of the fragments indicates that $0^+$ ions are formed with a maximum of 7.5 eV of translational energy, while $N^+$ ions are formed with a maximum of 5.7 eV. If the ions were produced by the decomposition of a doubly charged molecular ion, it would be expected (from conservation of momentum) that the $N^+$ ions would possess slightly more translational energy than do the $0^+$ ions.

The $N^{++}$ ion was observed to appear at $56.0 \pm 0.2$ eV, with $2.0 \pm 0.5$ eV of translational energy. Assuming a bond strength of 6.49 eV (92) and a value of 44.15 eV (149) for the removal of two electrons from a nitrogen atom, one calculates that

$$56.0 \pm 0.2 = 6.49 + 44.15 + \frac{30}{16} (2.0 \pm 0.5) + E_e$$  \hspace{1cm} (10)

or

$$1.6 \pm 1.2 = E_e.$$  \hspace{1cm} (11)

Since the first excited level of the products is the $^1D$ state of the oxygen atom, which lies 1.97 eV (149) above the ground state, it is postulated that the observed process is

$$\text{NO} + (52.60 \text{ eV}) \rightarrow N^{++}(^2P) + O(^1D).$$  \hspace{1cm} (R21)

No explanation can be offered for the formation of electronically excited products when, in every other example studied, the products had always been observed to have been formed in their ground electronic states.

The $O^{++}$ ion had an appearance potential of $61.62 \pm 0.15$ eV (average of five trials). This ion was observed to be formed with $2.5 \pm 0.5$ eV of translational energy at its appearance potential. With 48.76 eV (149) required to remove two electrons from an oxygen atom, one finds
61.62 \pm 0.15 = 6.49 + 48.76 + \frac{30}{14} \ (2.5 \pm 0.5) + E_e \quad (12)

or

1.1 \pm 1.2 = E_e. \quad (13)

Since the first excited state of the N atom \(^2\text{D}\) is 2.38 eV above the ground state, it is not possible to indicate the proper process from this data.

V. SUMMARY AND CONCLUSIONS

The focusing action of a time-of-flight mass spectrometer has been analyzed mathematically. First, an equation was derived for \(T(U_x, s)\), the total flight time of an ion. Second, it was found that the width of an ion peak is determined by the following three factors: (1) variations in \(s\), the initial position of an ion; (2) variations in \(U_x\), the initial translational energy of an ion; and (3) the manner in which the instrument itself records an ion signal.

It was shown that the effect of variations in initial position could be eliminated by using a focus pulse of the proper magnitude. To a first approximation this focus pulse is given by the focus condition \(dT(0, s)/ds = 0\), where the derivative is evaluated at \(s_0\). Moreover, the peak broadening due to instrumental factors may either be calculated by use of the appropriate equations or be ignored completely for ions of high initial translational energy.

Under these conditions, then, the distribution of initial translational energies may be deduced from the shape and width of the ion peak. It was found that this method gave very good agreement.
with initial energy measurements carried out on a number of fragment ions by other workers employing a variety of techniques.

Subsequently, this method was applied to the study of the ionization and dissociation of three diatomic molecules: nitrogen, carbon monoxide, and nitric oxide. The RPD method of determining appearance potentials, in conjunction with this method of measuring excess translational energy, permitted the observation and identification of 30 different ionization and dissociation processes. These results are summarized in Tables V to VII, where the measured appearance potentials, corrected for any excess translational energy, are compared both with the value calculated for the indicated process and with previously reported values obtained by other workers.

These results plainly show that the techniques employed in the present study provide a very powerful method for the investigation of the energetics of dissociative ionization induced by electron impact.

The logical continuation of this research program would involve the study of the dissociation of polyatomic molecules, with special emphasis being placed on the high-kinetic energy fragment ions which have been postulated to result from the decomposition of a doubly charged ion. A number of fragment ions from any of the ethyl halides, for example, exhibit such properties. By correlating such data as relative intensities, appearance potentials, and excess translational energies, new information, both experimental and theoretical, could be obtained on the ionization and dissociation of polyatomic molecules.
VI: BIBLIOGRAPHY

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VII: VITAE

The author was born in Brooklyn, New York, on May 17, 1941, the son of Joseph Wolfgang Hierl and Dorothy McMeekan Hierl. He attended public school in New York and in New Jersey and was graduated from Plainfield High School, Plainfield, New Jersey. In September of 1959 he entered the Massachusetts Institute of Technology and was graduated with a Bachelor of Science degree in June, 1963. While at the Massachusetts Institute of Technology the author wrote his senior thesis under the supervision of Professor John W. Irvine, Jr. In September, 1963, he began a period of graduate study under the supervision of Professor Joe L. Franklin at the William Marsh Rice University in Houston, Texas. He was awarded the degree of Doctor of Philosophy in June, 1967.

While studying under Professor Franklin's direction, the author has had several publications in scientific journals and has presented papers at scientific meetings.

The author is married to the former Jeanne Marie Verville.

He is a member of the American Chemical Society, the American Association for the Advancement of Science, and the Society of the Sigma Xi.
### APPENDIX A: SUMMARY OF RESULTS

#### TABLE I: NITROGEN

<table>
<thead>
<tr>
<th>Process</th>
<th>Products</th>
<th>This Work</th>
<th>Previous Studies</th>
<th>Spectroscopic</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $N_2^+$ ($X^2\Sigma_g^+$)</td>
<td>15.59 ± 0.05</td>
<td>15.7 (82)</td>
<td>15.58 (92)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.60 (208)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.60 (57)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.63 (64)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) $N_2^+$ ($A^2\Pi_u^-$)</td>
<td>16.87 ± 0.10</td>
<td>16.71 (208)</td>
<td>16.69 (145)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.93 (57)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.84 (64)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3) $N_2^+$ ($B^2\Sigma_u^+$)</td>
<td>18.75 ± 0.20</td>
<td>18.60 (208)</td>
<td>18.75 (92)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.84 (57)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.76 (64)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) $N_2^+$ ($C^2\Sigma_u^+$)</td>
<td>23.86 ± 0.20</td>
<td>23.53 (64)</td>
<td>23.58 (92)</td>
<td></td>
</tr>
<tr>
<td>(5) $N_2^{++}$ ($b^1\Pi_u$) or ($3\Sigma_u^-$)</td>
<td>44.2 ± 0.5</td>
<td>42.7 (105)</td>
<td>43.8 (104)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>43.5 (43)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>43.8 (105)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6) $N^+$ ($^3P$) + $N(4S)$</td>
<td>24.32 ± 0.03</td>
<td>24.35 (26)</td>
<td>24.30 *</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>24.32 (65)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>24.3 (82)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7) $N^+ (^3P)$ + $N(2D)$</td>
<td>26.65 ± 0.15</td>
<td>26.71 (26)</td>
<td>26.68 *</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.7 (19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.66 (65)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8) $N^+ (^3P)$ + $N(2P)$</td>
<td>28.0 ± 0.2</td>
<td>28.1 (26)</td>
<td>27.88 *</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.93 (65)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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### APPENDIX A: SUMMARY OF RESULTS

**TABLE I: NITROGEN**

(continued)

<table>
<thead>
<tr>
<th>Process</th>
<th>Products</th>
<th>This Work</th>
<th>Previous Studies</th>
<th>Spectroscopic</th>
</tr>
</thead>
<tbody>
<tr>
<td>(9)</td>
<td>$2 N^+ (^3P)$</td>
<td>$39.0 \pm 2.0$</td>
<td>-</td>
<td>$38.84$ *</td>
</tr>
<tr>
<td>(10)</td>
<td>$N^{++} (^3P) + N(^4S)$</td>
<td>$53.6 \pm 1.0$</td>
<td>-</td>
<td>$53.9$ *</td>
</tr>
</tbody>
</table>

* Calculated assuming $D(N_2) = 9.76$ eV (19,26). Ionization potentials and electronic energy levels from reference 149.
<table>
<thead>
<tr>
<th>Process</th>
<th>Products</th>
<th>This Work</th>
<th>Previous Studies</th>
<th>Spectroscopic</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) CO$^+$ ($X^2\Sigma_g^+$)</td>
<td>14.00 ± 0.05</td>
<td>14.1 (82)</td>
<td>14.009 (92)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14.05 (208)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13.98 (57)</td>
<td></td>
</tr>
<tr>
<td>(2) CO$^+$ ($A^2\Pi_u^-$)</td>
<td>16.5 ± 0.1</td>
<td>16.4 (57)</td>
<td>16.53 (92)</td>
<td></td>
</tr>
<tr>
<td>(3) O$^-$ ($^2\Pi$) + C($^3\Pi$)</td>
<td>9.7 ± 0.2</td>
<td>9.6 (82)</td>
<td>9.63 *</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.5 (85)</td>
<td></td>
</tr>
<tr>
<td>(4) ${O^- (^2\Pi) + C^+ (^2\Pi)}$</td>
<td>20.9 ± 0.2</td>
<td>21.1 (82)</td>
<td>20.89 *</td>
<td></td>
</tr>
<tr>
<td>${C^+ (^2\Pi) + O^- (^2\Pi)}$</td>
<td>20.82 ± 0.05</td>
<td>20.9 (82)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5) C$^+$ ($^2\Pi$) + O($^3\Pi$)</td>
<td>22.45 ± 0.10</td>
<td>22.8 (82)</td>
<td>22.37 *</td>
<td></td>
</tr>
<tr>
<td>(6) ${O^+ (^4\Pi) + C^- (^4\Pi)}$</td>
<td>23.20 ± 0.05</td>
<td>23.2 (82)</td>
<td>23.22 *</td>
<td></td>
</tr>
<tr>
<td>${C^- (^4\Pi) + O^+ (^4\Pi)}$</td>
<td>23.3 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7) O$^+$ ($^4\Pi$) + C($^3\Pi$)</td>
<td>24.65 ± 0.05</td>
<td>-</td>
<td>24.72 *</td>
<td></td>
</tr>
<tr>
<td>(8) O$^+$ ($^4\Pi$) + C($^1\Delta$)</td>
<td>26.00 ± 0.10</td>
<td>-</td>
<td>25.99 *</td>
<td></td>
</tr>
<tr>
<td>(9) O$^+$ ($^4\Pi$) + C($^1\Sigma$)</td>
<td>27.45 ± 0.10</td>
<td>-</td>
<td>27.40 *</td>
<td></td>
</tr>
<tr>
<td>(10) O$^+$ ($^2\Delta$) + C($^3\Pi$)</td>
<td>28.0 ± 0.1</td>
<td>-</td>
<td>28.04 *</td>
<td></td>
</tr>
<tr>
<td>(11) C$^{++}$ ($^1\Sigma$) + O($^3\Pi$)</td>
<td>46.0 ± 1.1</td>
<td>-</td>
<td>46.75 *</td>
<td></td>
</tr>
<tr>
<td>(12) O$^{++}$ ($^4\Pi$) + C($^3\Pi$)</td>
<td>59.7 ± 1.0</td>
<td>-</td>
<td>59.87 *</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated assuming D(CO) = 11.11 eV (121).

EA(O) = 1.48 eV (13), and EA(C) = 1.5 eV (136).

Ionization potentials and electronic energy levels from reference 149.
<table>
<thead>
<tr>
<th>Process</th>
<th>Products</th>
<th>This Work</th>
<th>Previous Studies</th>
<th>Spectroscopic</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>NO$^+(X^1\Sigma^+)$</td>
<td>9.28 ± 0.03</td>
<td>9.4 (82)</td>
<td>9.26 (92)</td>
</tr>
<tr>
<td>(2)</td>
<td>O$^-(^2P)$ + N($^4S$)</td>
<td>5.0 ± 0.1</td>
<td>3.2 (82)</td>
<td>5.01 *</td>
</tr>
</tbody>
</table>
| (3)     | \{O$^-(^2P)$ + N$^+(^3P)$
       | N$^+(^3P)$ + O$^-(^2P)$ | 19.3 ± 0.3  | 19.8 (82)       | 19.55 *       |
| (4)     | N$^+(^1D)$ + O($^3P$) | 20.88 ± 0.29 | 21.7 (82)      | 21.03 *       |
| (5)     | \{N$^+(^1D)$ + O($^3P$)
       | or N$^+(^3P)$ + O($^1D$)} | 22.8 ± 0.8  | -               | 22.93 *       |
| (6)     | O$^+(^4S)$ + N($^4S$) | 19.96 ± 0.40 | 18.9 (82)     | 20.10 *       |
| (7)     | O$^+(^4S)$ + N($^2D$) | 22.4 ± 0.4  | -               | 22.48 *       |
| (8)     | \{N$^+(^2P)$ + O($^3P$)
       | or N$^+(^2P)$ + O($^1D$)} | 52.2 ± 1.2  | 50.64 *         |
| (9)     | \{O$^+(^3P)$ + N($^4S$)
       | or O$^+(^3P)$ + N($^2D$)} | 56.4 ± 1.2  | -               | 55.25 *       |

* Calculated assuming D(NO) = 6.49 eV (83) and EA(O) = 1.48 eV (13).

Ionization potentials and electronic energy levels from reference 149.