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ENERGY AND ANGULAR DISTRIBUTIONS OF FRAGMENT IONS ARISING FROM THE DISSOCIATIVE IONIZATION OF NITROUS OXIDE BY ELECTRON IMPACT

by

Fred Judson Hadley

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

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INTRODUCTION

Electron-induced dissociation of molecules has been fundamental to mass spectroscopy since its earliest days. Such processes yield a wealth of information, particularly bond energies, ionization potentials, electron affinities and other thermodynamic quantities of interest. All of these are essential to the determination of the shapes and positions of potential energy curves for a given molecule. In addition to the items mentioned above, kinetic energy distributions of fragment ions are useful in determining the number and positions of various excited electronic states of the parent ion. The reader has only to glance briefly at the literature [1,2,3,23,29] to realize how much work has been done concerning these matters.

The symmetries of the excited states of molecules has received wide attention only recently [11,12,13,16,18]. These have been determined by measuring relative cross-sections for ionization as a function of the angle included between the incident electron beam and the axis along which the fragment ions are detected. Angular distribution studies began as early as the 1930's with the work of Nakao and Sasaki [25]. Their theoretical and experimental work on H₂ [25,26] was neglected, however, and interest in the problem was not renewed until fifteen or twenty years ago. Kerner [4] had treated H₂⁺ in the early 1950's, deriving a cos²θ dependence for the fragments using
Born's first approximation. This was for the transition from the ground $^2E_g$ of $N_2^+$ to the $^2E_u$ state.

More recently, Dunn [18] has employed symmetry arguments to show that the fragments of such ionization processes would not be ejected isotropically, thus throwing in doubt the absolute cross-section measurements of dissociative attachment processes as well as ionization processes. Since Dunn's theoretical treatment, many experimental studies of angular distributions have been made, almost exclusively treating the simple diatomic, homonuclear molecules [5, 6, 7, 8, 11, 12, 13, 14, 15]. The results, by and large, have agreed well with Dunn's predictions.

In the present work, we address ourselves to two questions:

(1) Do Dunn's selection rules hold for triatomic species (in the present case, $N_2O$)? For example, the excited state of $N_2O^+$ which leads to the products $O^+$ and $N_2^+$ appears to have $^2\pi$ symmetry, these being the $(\Lambda^2\pi)$ and $(\Sigma^2\pi)$ states. Since the ground state for $N_2O$ has $^\Sigma^+$ symmetry, Dunn's rules would predict vanishing intensity when the electron beam is parallel to the axis of observation, and would maximize at an angle of $\pi/2$ radians. We wish to investigate this process as well as those leading to the $N^+$, $N_2^+$ and $NO^+$ fragments.

(2) Are the kinetic energy distributions of these fragment ions a function of the angle of incidence of the electron? In light of Dunn's rules, one would expect to find the intensities in the energy distributions changing with the electron's angle of incidence. We expect this to be
the case since the different peaks in a kinetic energy
distribution arise from different excited states of the
parent ion, which may or may not have the same symmetries.
More important, however, will be to ascertain whether the
energies of these states change. That is, is there a
shift in energy associated with the angle of incidence?
THEORY

It will be in our interest to outline briefly, at the outset, some of the important points in the mathematical treatment of scattering. For a vigorous analysis, the reader is referred to any of a number of texts on the subject, especially those of Massey and Burhop [1] and Craggs and Massey [2] or Zare's paper [16]. Much of the material has been distilled from these treatises.

Let us first consider an electron of some given energy, $E_0$, approaching a molecule. In Figure 1, we have set the atom or molecule at the origin, while the electron approaches along the z-axis. We will first discuss how this electron is scattered by the molecule, since the mathematics are formulated most easily in that reference frame. Once this is done, we can then change coordinate systems and discuss how the molecular fragments behave, since these fragments are the species observed.

The approaching electron can be described as a plane wave, incident upon the molecule, having associated with it a wave number, $k_0$, where

\[ k_0 = \frac{mv}{nh} = \left[ \frac{2m}{nh^2} E_0 \right]^{1/2} \]  

(1)
Figure 1

Scattering of an Electron by a Target Molecule
The value of $k_0$ is related to the flux density, $A$, of the incoming wave. Upon scattering by the molecular field, we wish to measure the intensity of the scattered wave which passes out through a solid angle, $d\omega$, described by the angles $\Theta'$ and $\Phi'$. The intensity of the scattered wave will be a function of the solid angle, $d\omega$, and the initial flux density of the incoming wave. The number of electrons passing out through $d\omega$, then, is $A \cdot I(\Theta', \Phi') \ d\omega$ where $I(\Theta', \Phi')$ is the differential cross-section for scattering. It gives the angular dependence of the scattered intensity and is also a function of the incident electron energy. Therefore, we shall subscript it with $K$, the magnitude of the momentum transferred to the molecule.

After scattering, the electron is described as an outgoing spherical wave, having the form,

$$\psi_{\text{scattered}} = \frac{e^{ik_n r}}{r} (f_K(\Theta, \Phi))$$ (2)

Here we have added subscripts to indicate the loss of electron momentum to the molecule. If $k_n$ is the magnitude of momentum after scattering, then, $\hat{K}$, the change in momentum, is

$$K = |\hat{k}_0 - \hat{k}_n|$$ (3)

This relationship is diagrammed in Figure 2. The scattered wave function of equation (2) can be seen to have sinusoidal character $e^{ik_n r}$, decreasing intensity with distance from the scattering
center \(\frac{1}{r}\) and angular dependence \(f_K(\Theta, \phi)\) which is a function of the amount of momentum transferred. The last term is designated the scattering amplitude and is related to the scattering cross-section, \(I_K(\Theta, \phi)\), by

\[
I_K(\Theta, \phi) = \frac{k}{k_0} |f_K(\Theta, \phi)|^2
\]

We can now write the total wave function for the scattering process as a sum of the incoming plane wave and the outgoing spherical wave,

\[
\psi_{r\rightarrow\infty} = e^{ik_0 z} + e^{i\frac{k}{n} r} f_K(\Theta, \phi)
\]

Equation (5) gives the asymptotic limits to the wave function. We can now solve Schrödinger's equation, using these boundary conditions, and write,

\[
\nabla^2 \psi + \frac{2m}{\hbar^2} [E_0 - V(r)] \psi = 0
\]

Letting \(U(r) = \frac{2m V(r)}{\hbar^2}\), we rewrite (6) as

\[
\nabla^2 \psi + [k_0^2 - U(r)] \psi = 0
\]
Figure 2

Relationship between the incident momentum vector and the momentum transfer vector. Also, the relationship between the internuclear axis and the vector representing the dissociating fragments.
Matters are very much simplified if we can assume that $V(r)$ in (6) is much less than the initial energy, $E_0$.

$$V(r) \ll E_0 \quad (8)$$

This is Born's Approximation, essentially. It serves to determine approximate values of $\psi$, and is valid when the incident electron energy is somewhat above the threshold of ionization. We are interested in finding an expression for $\psi$ since this can be put into (5) and give us an expression for $I_k(\theta, \phi)$, which leads to $I_k(\theta, \phi)$. We can write (7) as

$$\nabla^2 \psi + k_n^2 \psi = U\psi \quad (9)$$

and, using the method of Green's function [30], derive an integral expression for $\psi$.

$$\psi(r) = \psi_0(r) - \frac{1}{4\pi} \frac{ik_n}{U(r')} \psi(r') e^{ik_n|r-r'|} \, \text{dr'} \quad (10)$$

where $r'$ is a dummy variable running over the range of $r$. Born's approximation can be seen in (10). It is an iterative process. The first term on the right, $\psi_0(r)$, is just the wave function if $U(r)$ in (7) were equal to zero. Born's first approximation consists in putting $\psi_0(r)$ into the integral portion of (10), in place of $\psi(r')$, as a first approximation to the wave function, $\psi(r)$. We then get,
\[ \psi(r) = e^{i k_0 \cdot Z} - \frac{1}{4\pi} \int e^{i k_0 \cdot Z'} U(r') \frac{e^{i k_0 |r-r'|}}{|r-r'|} \, dr' \]  

(11)

From (5) we can now see that the differential scattering amplitude will have the form,

\[ f_K(\Theta, \Phi) = -\frac{1}{4\pi} \int e^{i \hat{K} \cdot \hat{r}} U(r') \, dr' \]  

(12)

where we have used the approximation,

\[ \frac{i k_0 |r-r'|}{|r-r'|} \approx \frac{i k_0 r - i k_0 \cdot \hat{r}}{r} e^{-i k_0 \cdot \hat{r}} \]  

(13)

We now have an expression for the Born scattering amplitude and can use it to determine the scattering cross-sections for ionization processes.

Let us write the wave function for a target molecule as a product of electronic, vibrational and rotational terms,

\[ \phi_{n\nu, Jm} = \psi_n(r_i, R) \chi_{n\nu}(R) \rho_{Jm}(\Theta, \Phi) \]  

(14)

Here, \( r_i \) and \( R \) are the electronic coordinates and internuclear separation, respectively, while \( \Theta \) and \( \Phi \) give the orientation of the molecule relative to the momentum transfer vector, \( \hat{K} \). Suppose the fragments move apart through a solid angle described by the polar angles \( \lambda \) and \( \mu \), which are also relative to \( \hat{K} \). The angles \( \Theta, \Phi \) and \( \lambda, \mu \)
will be nearly identical since we consider cases in which the molecule does not rotate appreciably in the time it takes to separate into fragments. If the rotation is appreciable, we lose information as to the angular distribution of the fragments. The two vectors will differ most when the kinetic energy of the recoiling fragments is near zero. The situation is drawn in Figure 2. The vector \( \hat{p} \) is the asymptotic limit of the direction the recoiling fragments move apart.

Using equations (4) and (12), we can now write down an expression for the differential cross-section, \( I \), as,

\[
I_{n\nu JM} \, \frac{d\omega}{\omega} = \left| JG(R_0, \theta, \phi) \chi_{n\nu}(R) \rho_{JM}(\theta, \phi) F(\lambda, \mu; R, \theta, \phi) \right|^2 \, d\omega \quad (15)
\]

The term \( G(R_0, \theta, \phi) \) in (15) is the amplitude one would get if the nuclear coordinates were held fixed. The last term in (15) is the wave function for the dissociating fragments. This wave function can also be written as the sum of a plane wave and an outgoing spherical wave. Thus

\[
F(\lambda, \mu; R, \theta, \phi) \sim e^{i\vec{P} \cdot \vec{R}} + \frac{e^{iP_R}}{R} f(\lambda, \mu; \theta, \phi) \quad (16)
\]

The magnitude of the vector \( \hat{p} \) will depend on the kinetic energy of the dissociating fragments. To put \( F \) in the most general terms possible, we expand it as a series in Legendre polynomials with the argument \( \gamma \), and have,

\[
F = \sum_{s} (2s+1) \, F_s(R) \, P_s(\cos \gamma) \quad (17)
\]
where

\[ \cos \gamma = \cos \lambda \cos \Theta + \sin \lambda \sin \Theta \cos (\Phi - \mu) . \]  

(18)

By expressing \( F \) in terms of the included angle, \( \gamma \), between the molecular axis and the recoil vector, \( \vec{p} \), we insure that the plane wave and spherical wave parts of (16) interfere properly so that \( F \) will appear as a radial flux.

Let us also express \( G(R_0, \Theta, \Phi) \) in terms of Legendre functions, and write,

\[ G(R_0, \Theta, \Phi) = \sum_p (2p+1) G_p(R_0) P_p(\cos \Theta) \]  

We have not included \( \Phi \) in (19) since the scattering amplitude should be symmetric about the vector \( \hat{k} \).

Now let us consider a target molecule in its ground rotational state so that \( \rho_{jm} = 1 \). Combining (15), (17) and (19), we have, for the differential cross-section,

\[ I \propto \left| \sum_p (2p+1) G_p(R_0) P_p(\cos \Theta) \chi_{nm}^{(R)} \sum_s (2s+1) F_s(R) P_s(\cos \gamma) \int dR \right|^2 \]  

(20)

Using the addition theorem for Legendre polynomials, as given in Whittaker and Watson [28], this product of Legendre polynomials in (20) becomes,

\[ I \propto \left| \sum_p (2p+1) G_p(R_0) \int \chi_{nm}^{(R)} P_p(R) R^2 dR \right| \left| \sum_p (2p+1) \cos \lambda \right|^2 \]  

(21)
Now we have the differential scattering cross-section as a function of \( \lambda \), the angle of the fragments with respect to the momentum transfer vector, \( \vec{K} \). Since we are considering allowed and forbidden transitions to various electronic states, we shall express the amplitude, \( G(R_0,\Theta,\Phi) \), in terms of dipole moment components associated with an electronic transition. We write,

\[
G(R_0,\Theta,\Phi) \propto [X \cos \Theta \cos \Phi + Y \sin \Theta \sin \Phi + Z \cos \Theta]
\]

(22)

We are now in a position to consider particular cases of molecular transitions. First let us consider a \( \Sigma \rightarrow \Sigma \) transition in the target molecule. In this case, the dipole moment change is along the internuclear axis, so that \( x = y = 0 \). Therefore, we are left with \( G \propto Z \cos \Theta \). This means that in (21) we need only the first term \( P_1(\cos \lambda) \), which is just \( \cos \lambda \), so that \( I \) varies as \( \cos^2 \lambda \). Actually, the \( P(\cos \Theta) \) terms are Associated Legendre functions and we are considering, above, the \( P_1^0(\cos \Theta) \) term, which in hydrogen-like wave functions corresponds to a \( p_z \) term.

When we consider, on the other hand, a transition such as a \( \Sigma \rightarrow \pi \) transition, we have \( Z = 0 \) in (22). \( G(R_0,\Theta,\Phi) \) then becomes,

\[
G \propto X \cos \Theta \cos \Phi + Y \sin \Theta \sin \Phi
\]

(23)

which gives just the \( P_1^{\pm 1}(\cos \lambda) \) associated Legendre function, and thus behaves as \( \sin \lambda \). Therefore, I will behave as \( \sin^2 \lambda \).
We must now convert from the coordinate system in which the momentum transfer vector is the principal axis to one in which \( \hat{k}_0 \) serves as the symmetry axis. This is convenient since, in the laboratory, we measure the angle between the electron beam and the fragment ion beam. Thus, we wish to change from the \((\lambda, \mu)\) coordinates into the \((\theta, \phi)\) frame as shown in Figure 3. If \( K \) is related to \( \hat{k}_0 \) by the angles \((\eta, x)\), we have

\[
\cos \lambda = \cos \theta \cos \eta + \sin \theta \sin \eta \cos (\phi - x) \tag{24}
\]

To get the dependence of \( I \) on the angle \( \theta \), we must average \( \cos^2 \lambda \) over all values of \( x \) (in cases of \( \Sigma - \Sigma \) transitions). From (24), this average will be,

\[
<\cos^2 \lambda> = \frac{1}{2\pi} \int_0^{2\pi} \cos^2 \lambda \ P(x) \ dx \tag{25}
\]

\[
= \frac{1}{2\pi} \int_0^{2\pi} \cos^2 \lambda \ dx \tag{26}
\]

\[
= \cos^2 \theta \cos^2 \eta + \frac{1}{2} \sin^2 \theta \sin^2 \eta \tag{27}
\]

For \( \Sigma \leftrightarrow \pi \) transitions, we need to average \( \sin^2 \lambda \), which is just \( 1 - <\cos^2 \lambda> \). Thus,

\[
<\sin^2 \lambda> = \cos^2 \theta \sin^2 \eta + \frac{1}{2} \sin^2 \theta (1 + \cos^2 \eta) \tag{28}
\]
Figure 3

The transformation from the $(\lambda, \mu)$ coordinate system into the $(\theta, \phi)$ coordinate system.
We now recall, from Figure 3, that \( \eta \) is the angle included between \( \hat{k}_0 \) and \( \hat{k} \). Near threshold, there will be a large amount of momentum transferred to the molecule. Therefore, \( \hat{k} \) and \( \hat{k}_0 \) will be nearly equal. As a result, the angle \( \eta \) is small. Thus, for \( \Sigma-\Sigma \) transitions, we should, from (27) see \( \cos^2 \theta \) dependence for the dissociating fragments. Similarly, for \( \Sigma-\Pi \) transitions, we see \( \sin^2 \theta \) dependence.

At first glance, one would assume that \( \Sigma-\Sigma \) transitions can give rise to either \( \sin^2 \theta \) or \( \cos^2 \theta \) distributions. Dunn's selection rules give non-vanishing intensities in both instances. That we observe only a \( \cos^2 \theta \) dependence is a result of the angle \( \eta \) behaving as it does near threshold.

As the electron energy increases, the vector \( \hat{k}_n \) increases and so will the angle \( \eta \). We then would expect to see \( \Sigma-\Sigma \) transitions show \( \sin^2 \theta \) dependence while \( \Sigma-\Pi \) transitions would show \( \cos^2 \theta \) dependence. The total reversal is not seen, however, although the trend is in that direction. Zare [16] has shown this to be due to the fact that, in averaging, small values of \( K \) are weighted strongly, and, as a result, small values of \( \eta \) contribute heavily to \( I(\theta, \phi) \).

Also, one generally finds that although a \( \cos^2 \theta \) or \( \sin^2 \theta \) distribution is to be expected, the intensity never falls completely to zero at \( \theta = 90^\circ \) or \( 0^\circ \), respectively. This is due to the fact that more than one excited state may be responsible for the dissociated fragments, states of mixed symmetry.
EXPERIMENTAL

In scattering experiments, one often has the choice of moving either the ion source or the detector. Since, in our system, the former is much smaller and more compact, we have chosen to fix the detection system while rotating the electron gun. The gun assembly rotates about the center of the scattering chamber, producing ions which then pass through an ion-optics system (for energy analysis) and then through a mass filter to a detector. A general schematic of the apparatus is presented in Figure 4. A quadrupole mass filter is ideal for mass analysis since it involves no magnetic fields which would interfere with angular distribution measurements.

The inlet tube for the gas being studied, can be fitted with small circular apertures so as to form a molecular beam, or can be used without these, allowing for distribution measurements in a static gas.

A. Main Chamber and Electron Gun

The main chamber and quadrupole housing, with much of the attendant apparatus is shown in Figure 5. The body was constructed of 304 stainless steel (non-magnetic). The chamber height and diameter were 11 inches and 10 7/16 inches, respectively. The length of the quadrupole housing was 19 3/4 inches while the diameter was 6 3/8 inches. All welding of the chamber was done on the inside so as to prevent virtual leaks from occurring. Feedthroughs for the quadrupole
Figure 4

General Schematic of the Apparatus
Figure 5

Diagram of the Main Chamber and Quadrupole Housing
and ion-optics, as well as for the detector system were made through the flange at the end of the quadrupole housing tube. Feedthroughs for the electron gun were made through the top plate of the main chamber.

Directly below the main chamber was attached an NRC model 0326-6 cryobaffle 6 inches in diameter. This, in turn, led to an NRC VHS-6 oil diffusion pump having a rated pumping speed of 2400 liters per second. A Precision Scientific 500 mechanical forepump was used to back up the diffusion pump. A smaller NRC HS-2 oil diffusion pump, along with an NRC-325 2-inch cryobaffle was used to remove the bulk of the gas from the system if we used molecular beams. In any event it served to provide extra pumping speed. A smaller Precision Scientific model 150 forepump backed up the smaller diffusion pump. The baffles were charged with freon instead of the usual liquid nitrogen, the former being more convenient and economical and also entirely adequate for our purposes. The whole chamber and quadrupole housing were also bakeable with the use of heating tape. This, however, was not done often, as we noticed condensation of pump oil at the rear of the quadrupole housing, near the ion detector. Also, the ultimate background pressure of about $3 \times 10^{-7}$ torr precluded the need for frequent baking.

Magnetic fields had to be eliminated inside the main chamber, if meaningful measurements of angular distributions were to be made. The easiest and most direct way to do this is to use metal foil of high magnetic susceptibility, covering the chamber as completely as possible. Thus, the inside walls of the main chamber were lined with Co-netic AA
mu-metal, an alloy of chromium, cobalt, nickel and aluminum. Measurements using a Hewlett-Packard 4288 D.C. milliammeter with a Hall-effect probe indicated the magnetic field at the center of the chamber was not more than 20 milligauss in any direction. The radius of curvature of 25eV electrons (the lowest energy used in these experiments) in this field was found to be about 840 cm, acceptable for our purposes. Thermal ions have an even greater radius of curvature. For example, the ion of lowest mass in this work, the nitrogen ion, will have a radius of curvature of 5400 centimeters if its energy is thermal.

All wires leading to the electron gun and ion optics were carefully shielded with brass shim stock or with braided metal sheathing to eliminate any stray electric fields.

The electron gun was mounted on a stainless steel table which moved over stainless steel ball bearings, as shown in Figure 5. The gun was of a filament wire (.007 inch Rhenium) and two stainless steel grids. The slits on the grids were 17mm long and 0.5mm wide. They were also milled so as to reduce the 0.050 inch thickness of the metal to a knife edge.

In most of the work, we did not use an electron trap, as this would limit the range the gun table could be rotated. In order to prevent excessive scattering of electrons around the chamber, the mu-metal shield was coated with several layers of graphite (Aquadag). This had the added advantage of reducing light scatter which the ion detector might be sensitive to.
The two grids of the electron gun were placed 1/2 inch apart, allowing a beam divergence of about 2 degrees. Space change effects will, of course, widen this if they are appreciable. To avoid this, the filament was normally run with a current of about 3 amperes rather than the normal 3.5 amperes. The second grid was placed about 1 inch from the center of the chamber. At this point, then, the beam width would be about 0.9mm. This width is important when considering thermal ions, for, if any stray electric fields or contact potentials are present, ions formed on one side of the beam will be accelerated more than ions formed on the other side of the beam, resulting in a widening of the thermal energy distributions. This effect was seen in the present work, thermal distributions housing a considerably larger full-width at half-maximum (FWHM) than one would calculate. To reduce contact potentials in the chamber, the ion-optics housing was gold-plated while many of the surrounding parts were coated with graphite. Collimating magnets could not, of course, be used as this would interfere with angular measurements.

The filament consisted of two flexible stainless steel arms over which was strung .007 inch Rhenium wire. The filament power was supplied by a hamda LH 122 FM power supply. The electron energy was controlled by two Kepco model PCX-100 voltage regulators placed in series. This allowed for electron energies up to 200 eV. When an electron trap was used, it was connected to a Simpson D.C. microammeter. The collector plate of the electron trap was held at 6 volts positive with respect to ground.
The electron gun table was attached to a Norton model 1301 rotary motion feedthrough with sealed bellows. An indicating pointer was fastened to the shaft on the outside and scanned over angles marked off at intervals of ten degrees.

Finally, the pressure gauges for the chamber were placed at the end of the quadrupole housing tube and in the exhaust tube leading to the 2" diffusion pump. The gauges were standard Veeco RG-75 tubes used in conjunction with a Veeco RGL-7 ionization gauge control. Normal pressures in the chamber, while running, were anywhere from 2 to $10 \times 10^{-6}$ torr while the background pressures ranged from $3 \times 10^{-7}$ to $1 \times 10^{-6}$ torr.

B. Ion Optics

The ion optics system served a dual purpose in the present work. The first function, of course, was to transport ions from the interaction region to the detector with as little discrimination as possible. The second was to perform translational energy analysis of these ions. For the latter purpose, a retarding field analyzer was employed. It has the advantage of reducing kinetic energy discrimination since the ions see only a potential wall as opposed to deflection analyzers where ions of differing energy follow different trajectories. The system is shown in Figure 6. The whole assembly was constructed of brass, the outer sheathing being gold-plated, as noted above. The insulating spacers were made of Delrin, a commercial polymer. The
Figure 6

Diagram of the Ion Optics System
various grids and circular rings were insulated from the sheath with a coat of clear epoxy.

The angular resolution of the apparatus was determined by two circular apertures at the front of the optics assembly. The holes were 0.070 inches in diameter and were spaced 0.610 inches apart. This resulted in an angular resolution of 6 degrees. To determine the "true" angular distribution of any ion, one would actually need to deconvolute the measured distribution against the angular function representing the interaction region between the electron beam and the region of acceptance into the optics assembly. This is not necessary, however, since the general shape of a distribution is all that is needed to determine the symmetries of excited molecular ion states.

Both of the apertures were maintained at ground potential, so that the space between them was essentially field free. There would be a small penetration from the extraction grid immediately behind the second aperture, but this can be shown to be negligible. Indeed, if the extraction grid is placed at 80 volts with respect to ground, it is seen that the potential at the center of the field-free region is of the order of 0.01 volts.

The extraction grid was normally held at 80 volts negative with respect to ground. This served to prevent scattered electrons from traversing the flight path and also to accelerate the ions of interest, to the energy analyzer. The diameter of the extraction grid was 3/16 inches.
Behind the extraction grid was placed an einzel lens, responsible for the energy analysis of the ions. The two outer grids were of 1/8 inch diameter and were covered with molydenum mesh, having 100 lines to the inch. The mesh was used for two reasons. First, it reduces field penetration from adjacent grids. Secondly, it presents a flat potential field to the ion being analyzed. Because of this, they will have negligible transverse motion and will be collected more efficiently. The mesh had a rating of 90% optical transparency.

As Simpson has pointed out [36], we must remember that a retarding field analyzer does not actually measure the total kinetic energy of a particle. Rather, it affords us a measure of the particle's momentum perpendicular to the equipotential field lines. The distinction between the two can often be overlooked if the defining apertures preceding the retarding grid limit the angle of divergence sufficiently. Specifically, he has that

\[
\frac{\text{transverse energy}}{\text{axial energy}} = \tan^2 \theta
\]

where the transverse energy is that associated with motion perpendicular to the ion-optic axis. As noted above, \( \theta \) in our system is 3 degrees (6 degree angular spread divided by two). Therefore, the energy measured by our retarding analyzer, is essentially all axial energy, and represents the total kinetic energy of the particles.

Locht and Schopman [31] have found that the performance of retarding grids is much improved if two layers of mesh, placed a small
distance apart, are used, instead of a single layer. With the latter, the electric field is inhomogeneous due to the small bends in the wire, as well as the effects from neighboring grids. The use of a set of parallel pieces of mesh on the retarding grid eliminates the latter and creates a small region of field homogeneity. The two authors noted that, by increasing the distance between the two layers, one can make the field inside more homogeneous. However, as this lessens the field gradient across the retarding grid, space charge effects become important. Thus, one attempts to strike a balance. In the present arrangement, the two layers were placed 1 mm apart, the diameter of the mesh aperture being 3/8 inch. The distance from the center of the retarding grid to the outer two grids of the einzel lens was set at 1/8 inch.

The einzel lens, as used in the present experiments, acted as a diverging lens, when translational energy distributions were being studied, and as a converging lens when angular distributions were measured. This can be seen using Grivet's [20] formulation, in which he chooses the voltage ratios to be

$$\sigma = \frac{V_R - V_A}{V_A}. \quad (29)$$

where VR and VA are the potentials applied to the retarding and outer accelerating grids, respectively. For mesh lenses, divergence occurs for $\sigma$ values less than zero, convergence for $\sigma$ values greater than zero. There is no lens action if $\sigma$ equals zero. During kinetic
energy measurements, the accelerating potential, VA, was held anywhere from 20 to 40 volts negative with respect to ground, while VR scanned from small positive potentials to small negative potentials. This gave rise to σ values which were negative. For angular distributions, on the other hand, both VR and VA were negative, in many cases VR being the more negative. This gives σ values which are positive.

Locht and Schopman [31] have found that the magnitude of the potential on the outer accelerating grids is critical to the operation of the retarding analyzer. Specifically, the FWHM (full width at half-maximum) of the thermal energy distributions decrease with a decrease in the potential of the accelerating grids. Their optimum conditions were to place VA at 1-10 volts negative. We did indeed find this to be the case, although to a lesser extent. One loses ion intensity at potentials this low, so in our arrangement, we placed VA at higher potentials, ranging from -40 to -20 volts with respect to ground. The FWHM was somewhat wider, but did not present a serious problem.

To eliminate many of the problems of the diverging lens, mentioned above, a series of coaxial cylinders was placed immediately behind the einzel lens, and in front of the quadrupole housing. These cylinders, five in number, acted as a series of two-element electrostatic lenses, the properties of which are discussed in any of a number of books [20,21] on ion and electron optics. Using Grivet's expression for the problem, the potential along the axis of the cylinders can be expressed as,

$$\phi(z) = \frac{V + V}{2} \left[ 1 + \frac{1-\gamma}{1+\gamma} \frac{1}{2\omega d} \ln \frac{\cosh \omega(z+d)}{\cosh \omega(z-d)} \right]$$ (30)
where \( \omega = \frac{1}{d} \tanh(1.318d) \) and \( d \) is the separation of adjacent cylinders expressed in units of the cylinder radius. In the present case, \( d \) is equal to 0.33. The term \( \gamma \) is the voltage ratio, \( V_1/V_2 \), between any two adjacent cylinders. The focal lengths of two-element coaxial cylindrical lenses are functions of \( \gamma^{-1/4} \). A graph of the focal lengths, given in units of the cylinder radius, along with the potential distribution along the symmetry axis is given in Figures 7a and 7b. The \( z \) axis of Figure 7b is the symmetry axis of the lens, while \( \phi_1 \) and \( \phi_2 \) are the potentials of adjacent cylinders. The center line of Figure 7b indicates the midpoint between the two cylinders. It is seen from above, that the focal lengths of any set of two-element lenses will be equal if their voltage ratios are equal. This arrangement has been used previously (e.g. Futrell, Vestal [24]). All ratios will be equal if the potentials decrease or increase exponentially. In our system, the voltage ratios were always nearly 2:1, giving a focal length of about 6 inches. The first cylinder was held at about -10 volts while the fifth was placed at -80 volts. The cylinders were connected by resistors, rendering unnecessary the use of individual voltage supplies.

The retarding potential was scanned using a ramp generator designed by James Grannan and Bruce Wagner of this department. The ramp was designed to scan any of a number of voltage ranges over several different time periods. Specifically, the voltage ranges were 2, 4, 6, 8, and 10 volts, while the scanning times were 16, 38, 56, 80,
Figure 7a

The Focal Length of a Cylindrical Two-Element Lens as a Function of \( \gamma \), the ratio of the two potentials.

Figure 7b

The Potential Distribution in a Cylindrical Two-Element Lens.
110, 145 and 272 seconds. A schematic diagram of the ramp generator is presented in Figure 8, along with a typical ramp output in Figure 9. The ramp was powered by an Ortec Bin power supply, and was biased with a 90-volt battery supply, enabling the operator to start scans over a wide range of voltages.

C. Mass Filter and Detection System

Mass analysis of the ions was achieved using an Extranuclear Model 324-9 quadrupole mass filter. The rods were 3/4 inch in diameter and 12 inches long. RF power was supplied to the rods by an Extranuclear Model QPS power supply. Routine tuning of the mass filter as well as mass scanning was aided by a Tetronix model 545A oscilloscope.

The filter was fixed rigidly to the end flange of the quadrupole housing tube, the front of the filter being supported by a Y-shaped yoke fitted with adjusting screws for purposes of alignment.

For the mathematics of quadrupole mass filtering, the reader is referred to any of several texts (e.g. R. Kiser [23]). A block diagram of the ion detection system is seen in Figure 10. The detector used was a Mullard channel electron multiplier, having a rated gain of $2 \times 10^8$. The cone of the detector was displaced off of the optical axis of the quadrupole filter and ion-optics system, so that spurious counts arising from UV radiation would be eliminated. Nakao and Yamamoto [19] have recently tested an off-axis detector with a deflection plate to increase intensity. Such a deflection system was not used in the present work, however.
Figure 8

Schematic of the Ramp Generator
Figure 9

A Sample Output Ramp Voltage Scan from the Ramp Generator.
Figure 10

Block Diagram of the Ion Detection System.
High voltage (3000 volts) was supplied to the detector by means of a Fluke 415B high voltage power supply. All connections to the channeltron were made with RG-62U high voltage coaxial cable with BNC connectors. The signal from the channeltron led to an Ortec model 113 preamplifier followed by a 485 amplifier. From this, the signal passed through an Ortec single channel analyzer to both a rate meter and tuner-scaler system. A Leeds-Northrup dual pen chart recorder was connected to the output of the rate meter. This arrangement allowed for both time averaging (for angular distribution measurements) and for direct chart recording (for kinetic energy distributions).

D. Angular and Energy Distributions

Normally, if one has a static gas in a chamber, and rotates an electron gun about the center, the interaction volume in which ions are formed and reach the detector follows a cosecant \( \theta \) dependence, where \( \theta \) is the supplement of the included angle between the electron gun and the ion detection axes. This is shown in Figure 11, where the quadrilateral ABCD defines the interaction region. Thus, one normally multiplies all angular measurements by \( \sin \theta \) to get the actual distribution and account for this changing volume.

In the present system, however, the electron beam profile was not the normal conical shape, but rather a rectangular shape. Multiplication by \( \sin \theta \) would not be valid, and in addition, one has to contend with stray magnetic and electric fields in the chamber that might affect the angular distribution measurements. To take into
Figure 11

Diagram of Interaction Volumes for Ionization.
account all of these factors, we decided to measure distributions of ions we knew to be thermal, isotropic species. The most convenient way to do this is to measure the distribution of the parent ion, in our case, \( \text{N}_2\text{O}^+ \). The use of the parent ion allows for correction factors at each angle, eliminating all of the above effects. The correction factors, of course, are values which, when multiplied by the measured intensities of the parent ion, give an isotropic distribution. In addition to the parent ion, noble gas ions were often used in the event the background signal at mass 44 (\( \text{N}_2\text{O}^+ \)) was large. Neon was most often used.

The use of the parent ion calibrant also provided a means for calibrating the energy scale. Since the energy of an \( \text{N}_2\text{O}^+ \) ion will be thermal, the maximum in the kinetic energy distribution should occur at 0.04eV. In actual practice, the energy is shifted slightly, due to contact potentials, stray field, etc. When measuring kinetic energy distributions, then, we set the maximum of the parent ion peak to be zero volts, adjusting all others in that particular run likewise.

Angular measurements were taken in increments of ten degrees, beginning at \( \theta = 20^\circ \) or \( 30^\circ \) and proceeding to \( \theta = 120^\circ \). At each angle, the signal was integrated for anywhere from 20 sec to 80 sec, depending on its strength. All intensities were divided by the intensity recorded at \( \theta = 90^\circ \). Normally, two or three sets of readings were taken and the average used. These were then multiplied by the appropriate correction factors, determined in a separate experiment and labeled \( \text{N}_2\text{O}^+ \) factor, to get \( I(\theta) \), the angular distribution of the species. A
sample distribution of an angular measurement is presented in Table I. In the table, I have presented two sets of data, labeled count I and count II. These are the number of counts at the detector over a period of 20 seconds, measured at the various angles, \( \theta \). The two columns labeled Norm I and Norm II are just the first two columns normalized at \( \theta = 90^\circ \). All of the angular distributions have been normalized in this fashion. The next column, count, is just the average of the two sets of normalized data. The \( N_2O^+ \) factor column represents the results of a separate experiment. As mentioned previously, it represents the angular distribution of thermal \( N_2O^+ \) ions and consists of the inverses of the measured ion intensities. Thus, multiplication by these factors should account for variations in magnetic and electric fields with impact angle as well as variation in the interaction volume in which ionization occurs. The final column, \( I(\theta) \) is the calculated angular distribution for the ion of interest, in this case, \( O^+/N_2O \).

Kinetic energy measurements were made at several angles to determine whether there were any angular effects. The retarding curves, recorded on the chart paper, were, of course, differentiated to determine the energy distributions. This was accomplished using a simple APL computer program written by the author.

The retarding potential difference method has its advantages and disadvantages. As mentioned previously, it does not discriminate to the degree that deflection methods do. On the other hand, what is measured is a small change in a large quantity. One has to live with
Table I

Angular Distribution Measurements for $O^+/N_2O$ at 50 eV.
Table I

<table>
<thead>
<tr>
<th>θ</th>
<th>$0^+_{\text{signal count I}}$</th>
<th>$0^+_{\text{signal count II}}$</th>
<th>normalized count I</th>
<th>count II</th>
<th>$\frac{N_20^+}{\text{count}}$</th>
<th>factor</th>
<th>I(0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>15196</td>
<td>11956</td>
<td>2.68</td>
<td>2.20</td>
<td>2.44</td>
<td>.063</td>
<td>.026</td>
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<tr>
<td>40</td>
<td>10418</td>
<td>8966</td>
<td>1.83</td>
<td>1.65</td>
<td>1.74</td>
<td>.085</td>
<td>.049</td>
</tr>
<tr>
<td>50</td>
<td>7226</td>
<td>6731</td>
<td>1.27</td>
<td>1.24</td>
<td>1.26</td>
<td>.137</td>
<td>.109</td>
</tr>
<tr>
<td>60</td>
<td>6124</td>
<td>5987</td>
<td>1.08</td>
<td>1.10</td>
<td>1.09</td>
<td>.268</td>
<td>.246</td>
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<td>70</td>
<td>5791</td>
<td>5615</td>
<td>1.02</td>
<td>1.03</td>
<td>1.02</td>
<td>.653</td>
<td>.641</td>
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<tr>
<td>80</td>
<td>5609</td>
<td>5704</td>
<td>.99</td>
<td>.99</td>
<td>.99</td>
<td>.925</td>
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<td>5678</td>
<td>5432</td>
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<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
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<tr>
<td>100</td>
<td>5887</td>
<td>5456</td>
<td>1.04</td>
<td>1.00</td>
<td>1.02</td>
<td>.935</td>
<td>.917</td>
</tr>
<tr>
<td>110</td>
<td>6555</td>
<td>5804</td>
<td>1.15</td>
<td>1.07</td>
<td>1.11</td>
<td>.476</td>
<td>.429</td>
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<tr>
<td>120</td>
<td>6267</td>
<td>5847</td>
<td>1.10</td>
<td>1.08</td>
<td>1.09</td>
<td>.652</td>
<td>.599</td>
</tr>
</tbody>
</table>

$0^+_{N_20}$ 50 eV
more serious signal-to-noise problems than one sees in other methods. For this reason, the ramp generator scanning the retarding voltage was normally run at its slowest speed as was the chart recorder. This provided a rough means of time-averaging the signal.

Finally, the nitrous oxide used in this work was Matheson C.P. grade. It was introduced into a 3-liter flask with no freeze thaw cycles. The vacuum line was pumped using only a mechanical forepump, the background pressure being about 60 microns. Since the $N_2O$ pressure was of the order of 700 torr, no problems with impurities were considered.
RESULTS AND DISCUSSION

Energy Distributions

In Figure 12 we show a retarding curve (in this case for \( \text{O}^+/\text{N}_2\text{O} \) at 70 eV) as recorded on the present instrument. Error bars have been included at several points on the translational energy distribution curve, \( P(E) \). These bars were determined in the following manner. Each point on the retarding curve has an uncertainty in its value, the degree depending on the amount of noise in the signal. The limits of this uncertainty are estimated by inspection. The upper limit to the point is used, along with adjacent points, to calculate a differential between neighboring points. This differential will determine one point on the energy curve, \( P(E) \). In a similar manner, the lower limit to the point is used to calculate a new point on the energy curve. These two points will correspond to the same energy. The distance between the points is the measure of error and is drawn as an error bar. In the translational energy distributions to follow, only one, or perhaps two, error bars are drawn, as these did not vary in size significantly over the range of the distribution, as can be seen in Figure 12.

We wished to compare our translational energy distributions with several determined by other workers. Thus, in Figure 13, we have
Figure 12

Retarding Curve and Translational Energy Distribution for $O^+ / N_2O$ at 70 eV.

"The curve was obtained by differentiating the retarding potential curve."
Figure 13

Translational Energy Distributions for N⁺/NO and O⁺/NO at 100 eV at 0°.
plotted the translational energy distributions for two ionic species, as recorded on our apparatus, along with the distributions found by Hagstrum [10].

The distributions for low energy ions, in this case $N^+/NO$, seem to correlate well with Hagstrum's results. Our distribution becomes slightly higher at higher ion energy while it is very slightly lower near zero energy. The difference, however, is within the accuracy of either instrument.

When we consider ions with appreciable kinetic energy, on the other hand, we see a marked discrepancy. In the distributions, for $O^+/NO$ in Figure 13, we see that high energy ions are collected more efficiently (or, conversely, low energy ions are collected less efficiently) in the present apparatus. This seems reasonable when we consider the two systems. In Hagstrum's arrangement, ions formed in the source were accelerated out through defining slits, mass analyzed and then retarded. As Hagstrum noted, ions formed with considerable energy would have large velocity components perpendicular to the ion flight path leading to the analyzer. These ions, then, would be lost for failure to pass through the defining slits. It was for this reason that he was unable to obtain appreciable ion currents for high energy processes such as $O^+/NO$ and $O^+/CO$.

Since, in the present arrangement, ions drift after being formed, those with low energies will suffer more attenuation due to space charge, stray fields and contact potentials. Ions with high velocities will not be affected to nearly the same degree. Thus, we
expect to see a larger contribution from ions of high energy. The "true" energy distribution would seem to lie somewhere between our results and those of Hagstrum.

**Potential Energy Diagrams**

For later reference, let us draw a potential energy diagram for dissociative ionization processes. In this diagram (Figure 14), we, of course, can represent only one internuclear distance, but this will suffice. For \( \text{N}_2\text{O} \), there would be two such coordinates, representing the \( \text{N}-\text{N} \) and \( \text{N}-\text{O} \) bond distances. In Figure 14, we have drawn the Franck-Condon region for excitation (within the vertical dashed lines), along with two upper states to which the target molecule may be excited. At the appearance potential, the lower of the two curves will give rise to ions having thermal or near-thermal energy, while ions resulting from transitions to the upper curve will have appreciable excess energy. The total excess energy, represented by \( E^* \) in Figure 14, will consist mainly of vibrational and translational energy, with a small amount of rotational energy.

Classically, the fraction of \( E^* \) appearing as translation is just the total excess energy divided by the number of vibrational modes [33]. The assumption here is that all vibrational modes in the molecule absorb energy equally. Thus,

\[
\varepsilon_T = \frac{E^*}{N}
\]

(31)
Figure 14

Potential Energy Diagram
for Dissociative Ionization.
where $\varepsilon_T$ is the total translational energy and $N$ is the number of vibrational modes. It has long been known, however, that all vibrational modes do not absorb energy equally. That is, there is not a statistical distribution. Following Franklin and Hansey [33], we shall include a factor, $a$, in the denominator to represent the fraction of vibrational modes activated. This factor has been empirically determined to be about 0.44. Thus,

$$\varepsilon_T = \frac{E^*}{aN}$$  \hspace{1cm} (32)

In an experiment, one never actually measures $\varepsilon_T$ directly, since it includes the energy of the neutral species formed after dissociation. What is observed is the kinetic energy of the particular ion of interest, which we label $\varepsilon_1$. The two are related by virtue of the conservation of momentum, so we write

$$\varepsilon_T = [(M_1 + M_n) \varepsilon_1 - M_1\left(\frac{3}{2} kT\right)] \frac{1}{M_n}$$  \hspace{1cm} (33)

where $M_1$ and $M_n$ are the masses of the ionic and neutral species, respectively. The last term in the brackets represents the thermal motion of the parent ion, and can usually be disregarded if the fragment ion has appreciable energy.

Energy and Angular Distributions

$\frac{N^+}{N_{20}}$

As seems evident from the kinetic energy distributions in Figure 15, only one electronic state of the parent ion is involved in
Figure 15

Translational Energy Distributions
for $N^+/N_2O$. ..
the formation of $N^+$ fragment ions. The translational energy
distribution becomes quite broad as the electron energy is increased.
Referring to the potential curves of Figure 14, this would be true if
the uppermost curve were sharply rising in the Franck-Condon region.
This is suggested by Hagstrum's treatment of diatomic molecules [10]
in which he mirrors the square of the wave function of the ground
state of the molecule onto the potential curve of the excited state.
This gives an approximate form to the kinetic energy of the fragments.
This is not rigourously true in the present case since the fragment
products will have vibrational energy as well as translational.
Nevertheless, the treatment is qualitatively correct.

That only one state of the parent ion is involved in $N^+$
formation is apparent when we consider the energetics of this process.
From Figure 15, at an electron energy of 30 eV, the average ion
energy, $\bar{e}_1$, appears to be about 1 eV. From equation (33), we find
that the total vibrational and translational energy, $E^*_{v,t}$, is

$$
E^*_{v,t} = 0.44 \times 4 \times \frac{44}{30} \times \bar{e}_1 = 2.58 \bar{e}_1
$$

resulting in a value of 2.58 eV for $E^*_{v,t}$. The measured appearance
potential for $N^+$ formation has been determined to be about 20 eV [34].
Thus, we can determine the fraction of excess electron energy appearing
as vibrational and translational energy in the products. At an
electron energy of 30 eV, this fraction is just,

$$
\frac{E^*_{v,t}}{(30-20)\text{eV}} = \frac{2.58}{10} = .26 \text{ at } 30 \text{ eV}
$$

50
The remaining three quarters of the energy is presumably carried off by the scattered electrons.

Similarly, from Figure 15, we estimate the ion energies at 50 eV and 70 eV to be about 3.3 eV and 4.4 eV, respectively. Thus, these fractions becomes,

$$\frac{E^*_{V,t}}{(50-20)\text{eV}} = \frac{2.58(3.3)}{30} = 0.28 \text{ at 50 eV}$$  \hspace{1cm} (36)

$$\frac{E^*_{V,t}}{(70-20)\text{eV}} = \frac{2.58(4.4)}{50} = 0.23 \text{ at 70 eV}$$  \hspace{1cm} (37)

This nearly constant fraction would indicate that only one state is involved in the dissociation process. If new states of the products were formed, with, say, thermal energy, the fraction calculated above would abruptly change.

Considering now, the angular distribution for $N^+/N_2O$ (Figure 16), we find the distribution peaking at 90° where the angle is defined in Figure 17. While this relationship roughly follows a $\sin^2\theta$ dependence, we note that the present results are more sharply peaked. This seems most likely to be an instrumental artifact, arising from the differences in collection efficiencies of the $N^+$ ions and $N_2O^+$ calibrant ions.

We conclude from the shape of the distribution that the symmetry of the excited parent ion state must be $^2\pi$. In Table II, we present several possible transitions leading to $N^+$, along with the correlated symmetries.
Figure 16

Angular Distributions for $N^+/N_2O$. 

52
Table II

<table>
<thead>
<tr>
<th>Correlated Symmetry of Fragments</th>
<th>A.P.(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2\text{O}^+ \rightarrow \text{N}^{+}(3_P^g) + \text{NO}^{2\pi} )</td>
<td>( 4,2_\Sigma^+ \quad 2,4_\Sigma^- )</td>
</tr>
<tr>
<td>( \quad \downarrow \quad 2,4_\pi \quad 2,4_\Delta )</td>
<td></td>
</tr>
<tr>
<td>( \rightarrow \text{N}^{+}(1\Omega) + \text{NO}^{2\pi} )</td>
<td>( 2_\Sigma^+ 2_\Sigma^- 2_\pi 2_\Delta )</td>
</tr>
<tr>
<td>( \rightarrow \text{N}^{+}(1\Sigma) + \text{NO}^{2\pi} )</td>
<td>( 2_\pi )</td>
</tr>
<tr>
<td>( \rightarrow \text{N}^{+}(3_P^g) + \text{NO}^{2\Sigma} )</td>
<td>( 2_\pi 2_\Sigma^- )</td>
</tr>
</tbody>
</table>
Figure 17

Translational Energy Distributions
for NO⁺/N₂O
As in the case of \( N^+ / N_2O \), there seems to be only one electronic state involved in the dissociation process leading to \( NO^+ \) ions. The kinetic energy distributions, presented in Figure 17, are smooth and give no indication of competing reactions. Dibeler, et. al., have found three ionizative processes for \( NO^+ \) formation, using photoionization techniques. They recorded onsets at 15.01 eV, 16.53 eV and 17.74 eV. The corresponding reactions and their symmetries are presented in Table III.

Upon inspection of the angular distribution for \( NO^+ \) (Figure 18), we see a \( \cos^2 \theta \) dependence as the electron energy is lowered. This would indicate that the last reaction in Table III (17.74 eV) is the predominant process. Indeed, Dibeler [34] found the process at 15.01 eV to be very weak, as it is spin forbidden and breaks the \( + \leftrightarrow - \) rule. He did find a sharp onset at 16.53 eV which would imply some contribution from the \( ^2\pi \) state of \( N_2O^+ \). This would result in a \( \sin^2 \theta \) dependence, which is not observed, so we conclude that the contribution is small. The largest intensity seen by Dibeler [34] was the process at 17.74 eV which, we conclude, is the main process. It is also interesting to note that Collin and Lossing [35] have observed wide curvature in the ionization efficiency curve near onset. Such curvature would result from a number of low-lying states such as the first two in Table III.

One matter that is puzzling is why these forbidden transitions (reaction 1 in Table III) occur at all. The symmetry rules governing
Figure 18

Angular Distributions for 
\( NO^+/N_2O \)
### Table III

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Symmetry</th>
<th>A.P. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2O^+ \rightarrow NO^+(\Sigma_e^+) + N(^4S_u)$</td>
<td>$^4\Sigma^-$</td>
<td>15.01</td>
</tr>
<tr>
<td>$\rightarrow NO^+(\Sigma_e^+) + N(^2D_u)$</td>
<td>$^2\Sigma^-, \pi, \Delta$</td>
<td>16.53</td>
</tr>
<tr>
<td>$\rightarrow NO^+(\Sigma_e^+) + N(^2P_u)$</td>
<td>$^2\Sigma^+, \pi$</td>
<td>17.74</td>
</tr>
</tbody>
</table>
multiplicity ($\Delta \Sigma = 0$) and wave function sign (+ ↔ −) no longer apply. The best explanation seems to be a combination of large spin-orbit coupling in the parent molecule and predissociation of the parent ion involving vibrationally excited states of the products.

In addition to our work on translational and angular distributions, we wished to determine whether the kinetic energy distributions were a function of the angle of incidence of the electron. We have measured energy distributions for NO$^+$ ions at a number of angles and present them in Figures 19 and 20. With the exception of the distribution at 45°, all seem to be equivalent, within the limits of the accuracy of our instrument. The difference at 45° appears to be instrumental. The peak maximum is shifted by about 0.25eV. This is possibly due to contact potentials, although this seems unlikely since all runs were made within a short period. Thus, any contact potential would appear in the other distributions as well. Hagstrum [10] has noted that any variations in electric or magnetic fields might shift the energy scale by as much as 0.2eV. We can only surmise that the movement of the electron gun caused some change in the electric fields in the chamber. Based on the other three distributions in Figures 19 and 20, we conclude that there is no appreciable angular effect on translational distributions.

It is interesting to note that Van Brunt, Kieffer, et. al. [5] found no angular dependence of the translational energy distributions.
Figure 19

Translational Energy Distributions
for NO\(^+\)/N\(_2\)O at 0° and 90°
Figure 20

Translational Energy Distributions
for NO$^+$/N$_2$O at 45° and 120°
for $0^+/O_2$. Crowe and McConkey [12] have noted that their angular
distribution for $0^+/CO_2$ shows a slight, irregular hump in the forward
scattering direction. They have attributed this to a momentum
transfer from the incident electron to the molecule. That this would
show up in the translational energy distributions seems unlikely
since, on the one hand, the effect is very slight, and also since one
distribution is a measure of intensity of ions while the other is a
measure of kinetic energy.

$0^+/N_2O$

Two separate processes are evident in the case of $0^+$ formation.
Dibeler, et. al. [34] have found a very weak transition onsetting at
15.31eV with an intensity on the order of 0.02% of the $N_2O^+$ intensity.
This process, reaction (1) in Table IV, correlates to a $^4\Sigma^-$ which is
in violation of both the $++++$ and the multiplicity rule, $\Delta\Sigma = 0$.
Hence, the low intensity.

We do not believe the first process is seen in our experiments.
A second process, onsetting at 19.02eV has been noted by Eland [27].
The products correlate to a $^2\Pi$ state of the molecular ion. As seen in
Figure 21, we observe a $\sin^2\theta$ dependence for $0^+/N_2O$, implying that the
second process is responsible for $0^+$ production.
Table IV

| (1) $N_2O^+$ → $O^+(4S_u) + N_2(1\Sigma^+_g)$ | $4\Sigma^-$ | 15.31eV |
| (2) $N_2O^+$ → $O^+(2D_u) + N_2(1\Sigma^+_g)$ | $2\Sigma^-, 2\pi, 2\Delta$ | 19.02eV |
| (3) $N_2O^+$ → $O^+(2P_u) + N_2(1\Sigma^+_g)$ | $2\Sigma^+, 2\pi$ | 20.7eV |
Figure 21
Angular Distributions
for \(0^+/N_{2}O\)
We suggest that the kinetic energy distributions, shown in
Figure 22 be interpreted as follows: The peak seen at 30eV electron
energy is attributed primarily to reaction (2) in Table IV. This
becomes the high energy peak in the 70eV distribution. Considering
the energetics of the process, we find the total translational and
vibrational excess energy is just,

\[ E^*_{v,t} = 0.44 \times 4 \times \frac{44}{28} \times \frac{\epsilon}{1} = 2.77 \frac{\epsilon}{1}. \]  

(38)

The average ion energies at 30 and 70eV are 0.5eV and 2.2eV,
respectively. Thus, the fraction of excess electron energy appear as
\( E^* \) is,

\[ \frac{E^*_{v,t}}{11} = \frac{2.77(0.5)}{11} = 0.13 \quad \text{at 30eV} \]  

(39)

\[ \frac{E^*_{v,t}}{51} = \frac{2.77(2.2)}{51} = 0.12 \quad \text{at 70eV} \]  

(40)

The second process, appearing as a thermal or quasi-thermal
peak at 70eV must arise from a still more energetic process. The
most likely reaction is the last reaction in Table IV, in which the \( \text{O}^+ \)
ion is in an even higher electronic state. The \( \text{O}^+ \) ion in the \( 2p_u \)
state is found to be about 1.7eV higher in energy than the \( 2d_u \) state [32].
Thus, this process should onset at about 20.7eV. It has not been
reported by the photo electron spectroscopists.

We have measured the kinetic energy distributions for \( \text{O}^+/\text{N}_2\text{O} \) at
two different angles, 0° and 90° (Figure 23). Within the accuracy of
Figure 22

Translational Energy Distributions
for $O^+/N_2O$
Figure 23

Translational Energy Distributions
for $\text{O}^+/\text{N}_2\text{O}$ at $0^\circ$ and $90^\circ$
$O^+ / N_2O \quad 70\,EV \quad 0^\circ$

$O^+ / N_2O \quad 70\,EV \quad 90^\circ$
our instrument, we find no difference in the two distributions, except for the fact that one seems broader than the other. The positions of the peaks do not differ, appreciably, however. It is also noted that the intensity of high-energy ions is slightly greater at 0° than at 90°.

\[
\frac{N_2^+}{N_2O}\]

\(N_2^+\) formation is considerably more complicated than the preceding processes. The reactions to be considered are presented in Table V. Based on his photoionization studies, Dibeler has suggested that the onset for \(N_2^+\) formation is 17.29eV. The products of this process correlate to both a \(2\Sigma^+\) and a \(2\pi\) state for \(N_2O^+\). The former is forbidden, and hence, weak, while the latter would lead to a \(\sin^2\theta\) dependence which is not apparent from our results, although possible.

The angular distributions for \(N_2^+\) (Figure 24) are somewhat curious in that they are enhanced as the electron energy increases to 70eV. It would appear that we are seeing a \(\cos^2\theta\) distribution at high energies (which should flatten out as the electron energy is raised above 70eV) which becomes partially masked by a \(\sin^2\theta\) distribution at low energies. The \(\cos^2\theta\) dependence still predominates, even at 30eV. We conclude that reaction (1) in Table V becomes more important as the energy is lowered to onset, while a reaction with products correlating to a \(2\Sigma^+\) state predominate as the energy is increased. The most plausible reactions for the latter process are reactions 2, 3 and 4 in Table V.
Table V

Electronic Processes Leading to $N_2^+$ formation
Table V

(1) $N_2O^+ \rightarrow N_2^+(2\Sigma_g^+) + O(^3P_u)$  
17.29eV$^{[34]}$  
$^2\Sigma^-, ^2\pi$

(2) $N_2O^+ \rightarrow N_2^+(2\Sigma_g^+) + O(^1D_u)$  
19.3eV$^{[32]}$  
$^2\Sigma^+, ^2\pi, ^2\Delta$

(3) $N_2O^+ \rightarrow N_2^+(2\Sigma_g^+) + O(^1S)$  
21.5eV  
$^2\Sigma^+$

(4) $N_2O^+ \rightarrow N_2^+(\Delta S_{\pi_u}) + O(^3P_u)$  
18.42eV  
$^2\Sigma^+, ^2\epsilon^-, ^2\pi, ^2\Delta$

(5) $N_2O^+ \rightarrow N_2^+(\epsilon \Sigma_g^+) + O(^5P_u)$  
20.5eV  
$^2\epsilon^-, ^2\pi$

(6) $N_2O^+ \rightarrow N_2^+(\epsilon \Sigma_g^+) + O(^3P_u)$  
25.3eV  
$^2\epsilon^-, ^2\pi$

(7) $N_2O^+ \rightarrow N_2^+(2\Sigma_g^+) + O(^1S)$  
29.3eV  
$^2\Sigma^+$
Figure 24
Angular Distributions for $N_2^+/N_2O$
When we consider the translational energy distributions (Figure 25), we observe two processes occurring. At 30eV, we see only one peak, presumably arising from processes (2) or (4) in Table V (these having the lowest onsets). This peak then is the high-energy process seen in the energy distributions at 50eV and 70eV. At 30eV, the fraction of excess electron energy appearing as $E^*_{v,t}$ is

$$\frac{E^*_{v,t}}{11eV} = \frac{0.44 \times 4 \times 2.75 \times e^{-1}}{11eV} = \frac{1.45eV}{11eV} = 0.13$$  \hspace{1cm} (41)$$

The high energy processes at 50eV and 70eV give a fraction of,

$$\frac{E^*_{v,t}}{31} = \frac{4.8 \times 1.1}{31} = 0.17 \hspace{1cm} \text{at 50eV}$$  \hspace{1cm} (42)$$

and

$$\frac{E^*_{v,t}}{51} = \frac{4.8 \times 1.7}{51} = 0.16 \hspace{1cm} \text{at 70eV}.$$  \hspace{1cm} (43)$$

We observe a second process occurring at 50eV and 70eV, presumably onsetting somewhere near 30eV. Since the angular dependence becomes more pronounced at high energy, we conclude that this new process must correlate to a $^2\Sigma^+$ state of the parent ion. Reaction 7 in Table V seems to support this conclusion. It would be of low intensity at 30eV and, hence, would not be seen. Taking into account the overlapping distributions at 50eV and at 70eV, we
Figure 25

Translational Energy Distributions for $\text{N}_2^+)/\text{N}_2\text{O}$
\[ \text{N}_2^+/\text{N}_2\text{O} \quad 70 \text{ EV} \quad 0^\circ \]

\[ \text{K.E. (volts)} \]

\[ \text{P(E)} \]

\[ \text{N}_2^+/\text{N}_2\text{O} \quad 50 \text{ EV} \quad 0^\circ \]

\[ \text{K.E. (volts)} \]

\[ \text{P(E)} \]

\[ \text{N}_2^+/\text{N}_2\text{O} \quad 30 \text{ EV} \quad 0^\circ \]

\[ \text{K.E. (volts)} \]

\[ \text{P(E)} \]
estimate the average ion energies for this second process to be 0.5eV and 1.0eV, respectively. The corresponding fractions would be, following the calculations above,

\[
\frac{E^*_{v,t}}{20} = \frac{2.4\text{eV}}{20} = 0.12 \quad \text{at 50eV} \tag{44}
\]

and

\[
\frac{E^*_{v,t}}{40} = \frac{4.8\text{eV}}{40} = 0.12 \quad \text{at 70eV} \tag{45}
\]

We conclude that both peaks arise from process (7) in Table V.

At this point, it is in order that we demonstrate the validity of Born's approximation as it applies to the work presented here. As we noted above, the approximation is most valid for high incident electron energy with a minimum of momentum transfer to the molecule. We shall, therefore, consider our most marginal case in this respect, \(O^+/N_2\) at 30eV. Our results show that roughly 25% of the incident energy is lost to the molecule, the remaining 75% being carried off by the scattered electrons.

Following Van Brunt [17], we consider the magnitude of the momentum transfer vector, \(K\), and write,

\[
k^2 = k_0^2 + k_n^2 - 2k_0k_n \cos \omega \tag{46}
\]

where \(\omega\) is the included angle between \(\mathbf{k}_n\) and \(\mathbf{k}_0\). As the collision becomes more and more inelastic, \(k_n\) will approach zero and \(K \to k_0\).
If the incident electron energy is 30eV, we find that $k_0$ is just $4.5 \times 10^7 \text{ cm}^{-1}$.

As Zare has pointed out for the case of $\text{H}_2^+$ [16], Born's approximation is valid if $K < \frac{1}{a_0}$ where $a_0$ is the Bohr radius. This is equivalent to saying that the wavelength of the incident electron wave be larger than an atomic dimension. Otherwise, we get diffraction effects. The limit then, is,

$$K < \frac{1}{a_0} = 18.9 \times 10^7 \text{ cm}^{-1}$$

and we see that our $K_{\text{max}}$ is indeed, less than $\frac{1}{a_0}$. Thus, the approximation is valid in this, the most marginal case, and is therefore valid for all others considered.
SUMMARY

We have demonstrated that fragment ions, produced in the dissociation of a polyatomic molecule, exhibit angular dependence relative to the incident beam of electrons. This angular dependence has also been shown to behave in the manner predicted on theoretical grounds, using Born's approximation; namely, that one sees the angular distributions becoming isotropic as the energy of the electrons increase, being most sharply peaked at low energy. Furthermore, we have shown Born's approximation to be valid in the particular reactions presented here. Heretofore, with the exception of Crowe and McConkey's work on CO₂ [12], the Born approximation has been applied to only diatomic species.

More important is the fact that Dunn's selection rules [18] for diatomic species also seem to hold in the present case for a triatomic molecule. That this is so is supported by the fact that plausible electronic states have been assigned to the various reactions in accordance with their angular dependence. It is significant to note that our assumption that the fraction of excess electron energy (above the ionization threshold) that appears as translational energy of the fragments is constant for a given electronic process was successful in correlating these processes to the various peaks in the translational energy distributions. Our conclusions agree, for the most part, with the results of other workers.
Lastly, we find no appreciable angular dependence on the translational energy distributions of the various fragment ions. This is in agreement with the results of Van Brunt, Kieffer, et. al., in their work on $^{16}O/^{18}O$. We, in fact, expected no such angular dependence, since the translational energy of a fragment ion is most strongly a function of the vibrational modes within a molecule and the energy partitioning among these modes.

In Table VI, we have summarized the reactions we think predominate in the dissociation of $N_2O$. 
Table VI

Summary of $N_2O$ Reactions
Table VI

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2O(1^+_{1g}) \rightarrow N_2O^+(2\pi) \rightarrow N^+(3\text{P}_g) + NO(2\pi)$</td>
<td>19.47eV</td>
</tr>
<tr>
<td>$\rightarrow N_2O^+(2\pi) \rightarrow N^+(1\text{D}) + NO(2\pi)$</td>
<td>21.4eV</td>
</tr>
<tr>
<td>$\rightarrow N_2O^+(2\pi) \rightarrow N^+(1\text{S}) + NO(2\pi)$</td>
<td>23.5eV</td>
</tr>
<tr>
<td>$\rightarrow N_2O^+(2\pi) \rightarrow N^+(3\text{P}_g) + NO(2\Sigma_g^+)$</td>
<td>24.9eV</td>
</tr>
<tr>
<td>$N_2O(1^+_{1g}) \rightarrow N_2O^+(2\Sigma_g^+) \rightarrow NO^+(1\Sigma_g^+) + N(2\text{Pu})$</td>
<td>17.74eV</td>
</tr>
<tr>
<td>$N_2O(1^+_{1g}) \rightarrow N_2O^+(2\pi) \rightarrow O^+(2\text{Du}) + N_2(1\Sigma_g^+)$</td>
<td>19.02eV</td>
</tr>
<tr>
<td>$\rightarrow N_2O^+(2\pi) \rightarrow O^+(2\text{Pu}) + N_2(1\Sigma_g^+)$</td>
<td>20.7eV</td>
</tr>
<tr>
<td>$N_2O(1^+_{1g}) \rightarrow N_2O^+(2\Sigma_g^+) \rightarrow N_2^+(2\Sigma_g^+) + O(1\text{Dg})$</td>
<td>19.3eV</td>
</tr>
<tr>
<td>$\rightarrow N_2O^+(2\Sigma_g^+) \rightarrow N_2^+(A \ 2\pi_u) + O(3\text{Pg})$</td>
<td>18.42eV</td>
</tr>
<tr>
<td>$\rightarrow N_2O^+(2\Sigma_g^+) \rightarrow N_2^+(C \ 2\Sigma_u^+) + O(1\text{S})$</td>
<td>29.3eV</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY


