

Ionization of Nitrogen Molecules by Nitrogen Molecules*

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The ionization cross section for N_2 molecules on impact with N_2 molecules has been measured over the laboratory energy range from 30 to 1000 ev. The incident molecular beam was produced by the technique of ionization by electron impact, electrostatic acceleration and neutralization by charge transfer. The measurements were carried out in a low-pressure parallel plate ionization chamber. Particular attention was paid to the problem of secondary electrons. Ionization was observed a few volts above threshold. Cross sections which were obtained ranged from 10^{-20} to 10^{-16} cm². The curve of cross section vs incident particle energy showed structure indicative of competing processes.

INTRODUCTION

THE process of ionization by atomic particles has been the subject of very many investigations. Interest in ionization has ranged from the nature of the interaction itself to the indirect sensing of atomic particles through their ionizing effects. The vast bulk of the data available has dealt with high-energy particles (energies much greater than ionization potentials), and usually the particles have been charged. Reasonably accurate theories have been developed to deal with some of these cases. In contrast, the present experiment concerns ionizing interactions between relatively slow, uncharged particles. Theoretical analysis of the interactions under these conditions is extremely difficult and little experimental work has been done. However, the current interest in high-temperature phenomena involved in such fields of study as shock waves, plasma physics, and high-temperature chemistry has made the study of low energy ionizing interactions imperative. This paper presents data on such low-energy interactions between nitrogen molecules. Although one may argue that nitrogen is a poor choice on grounds of theoretical complexity, the atmospheric abundance of nitrogen makes these data immediately useful. Furthermore, it is hoped that the study of chemically active species will lead to the development of techniques applicable to chemical reaction kinetics in which fairly high activation energies are present. Specifically, it was the purpose of this experiment to determine the ionization cross section for nitrogen molecules on impact with nitrogen molecules having laboratory energies between 30 and 1000 ev.

The technique used consisted of three basic parts. First, a molecular N_2 beam was produced having the desired energy. Second, an N_2 thin gas target was provided for this beam between the plates of a parallel plate ionization chamber. Finally, the electrons produced in ionizing interactions were swept by the electrostatic field between the plates to the collector plate and this current was measured. It was possible to determine the ionization cross section through knowledge of the incident beam intensity, target particle density,

guarded collector length, and the collector current. Experimentally the most difficult problem arose in showing that the collector current corresponded to ionization electrons rather than secondary electrons produced at the chamber surfaces. A considerable part of the experimental discussion will be involved with this problem.

APPARATUS

Molecular N_2 Beam

The molecular N_2 beam apparatus has been discussed in detail elsewhere.¹ A short summary will be given here.

Figures 1 and 2 show the beam-producing apparatus. An N_2^+ ion beam was produced by the ion source and lens system of Fig. 1. The ion source was operated as an electron impact source. The electron energy was about 22 ev. The third lens (Fig. 2) determined the final ion-beam energy and focused the ion beam through the apertures which followed. A fraction (<20%) of

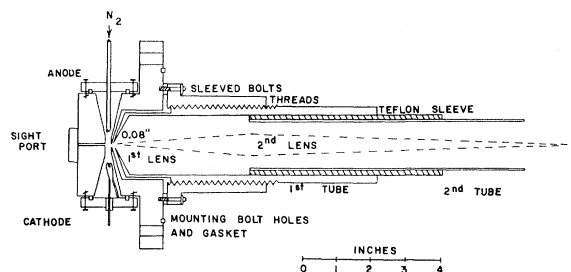


FIG. 1. Ion source and lens system.

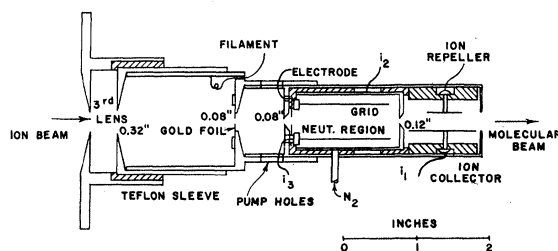


FIG. 2. Third lens and neutralizing region.

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¹ N. G. Utterback and G. H. Miller, Rev. Sci. Instr. 32, 1101 (1961).

the ion beam entering the neutralization chamber was neutralized by charge transfer with N_2 gas. The mixed ion and molecular beam passed between deflecting plates where the ion beam was removed. The neutral-beam energy was determined under the assumption that negligible momentum was transferred during charge transfer, and therefore that the molecular beam had the same energy and direction as the ion beam. The ion-beam energy was determined by using the neutralization chamber as a Faraday cage. Energy spread at half-maximum was found to be 0.5 eV.

The molecular N_2 beam intensity was determined by measuring three currents (Fig. 2) as follows. The ion collector current i_1 corresponded to those ions which had not undergone charge transfer or strong scattering. The current i_2 arose from the cup which was held at a potential positive enough to repel the slow ions arising from charge transfer, but not positive enough to repel scattered ions; i_2 therefore corresponded to ions strongly scattered which had not undergone charge transfer. The ions arising from charge transfer were driven by the positive cup to the grid and were collected as i_3 . Now $i_1 + i_2 + i_3$ was the total ion current entering the neutralization chamber. Thus β , the fraction of all entering ions which underwent charge transfer, was given by

$$\beta = i_3 / (i_1 + i_2 + i_3). \quad (1)$$

If I represents the unscattered ion beam in the event charge transfer had not occurred, the current i_1 was given by

$$i_1 = I - \beta I, \text{ or } I = i_1 / (1 - \beta). \quad (2)$$

It follows that the molecular beam intensity in molecules per second, B , was

$$B = \beta I = \beta i_1 / (1 - \beta) = i_3 / (1 + i_2 / i_1), \quad (3)$$

where the currents are in ions per second.

It is seen that if no scattering had been present ($i_2 = 0$), the molecular beam intensity would have been equal to i_3 , the slow ion current. A more detailed discussion of the assumptions implicit in Eq. (3) has been given previously.¹ It was also shown in that reference that the absolute intensity could be determined to within 20% by the use of this method. Beam intensities of the order of 10^9 molecules/sec were used in this work.

Ionization Chamber

Figure 3 shows the electrode arrangement for the ionization chamber. The beam was allowed to pass between the grid and the collector and guard plate in a direction parallel to the grid wires. The purpose of the grid was to suppress secondary electrons arising at the back plate behind the grid due to scattered molecules. The grid was composed of 0.0007-in. diam gold-plated tungsten wires spaced about 0.1 in. apart. It therefore presented a very small solid angle for molecules scat-

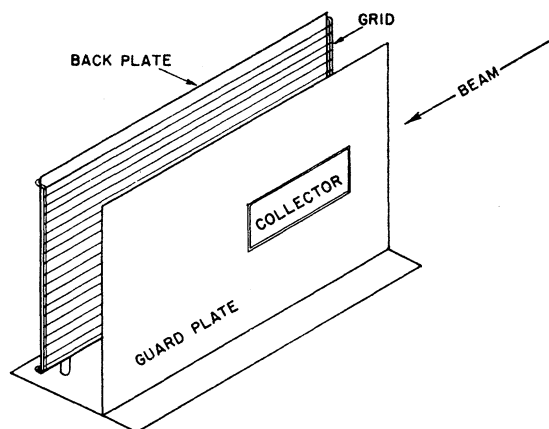


FIG. 3. Ion chamber electrode arrangement.

tered out of the beam. A potential difference of 30 V was maintained between the back plate and grid. This prevented secondary electrons arising at the back plate from reaching the collector. The guard plate insured a uniform field over the collection region and a well-defined collection length. The collector was 10×4 cm, and was spaced 4 cm from the grid. The grid was spaced 1 cm from the back plate. All electrode surfaces were plated with gold.

The electrode assembly was contained in a chamber evacuated by means of CO_2 -acetone trapped oil diffusion pump. A 4-in. diam disk perforated with forty 0.12-in. holes was placed between the chamber and pump to cut down the pumping speed and remove large pressure gradients in the ion chamber. (The entire region between the ion source and neutralization chamber was evacuated by means of a titanium gettering pump. The only connection between the beam vacuum system and the ionization chamber vacuum system was the 3-mm exit aperture from the neutralization chamber, Fig. 2.) This arrangement was used in order that the ionization chamber pressure could be controlled independently of the neutralization chamber pressure. Furthermore, when a target gas other than nitrogen was used, it was essential to keep the target gas as pure as possible. This necessitated continually pumping out the nitrogen which entered the ionization chamber from the neutralization chamber.

Target gas was admitted to the ionization chamber through an aperture pointed so that the gas in the interaction region had diffused off the chamber walls. In this way the pressure gradient in the interaction region was kept small. The pressure calibration was made with a McLeod gauge whose aperture looked into the interaction region. Relative pressure measurements were made with a Bayard-Alpert type ionization gauge operated at low emission (40 μ amp). The ionization gauge readings were linear with McLeod gauge readings over the pressure range 6×10^{-5} to 6×10^{-4} mm Hg. A CO_2 -acetone cold trap was always used between the

McLeod gauge and ionization chamber in order to exclude mercury vapor from the chamber.

Electron Collection and Current Measurement

The electron collecting field was maintained between the grid and the collector and guard plate. The distance between was 4 cm. The collector and guard plate were held at ground (chamber) potential, with the grid being made negative. Since ionization electrons are expected to have kinetic energies less than a few tens of electron volts,² a negative potential of a few hundred volts on the grid should have sufficed to repel the ionization electrons to the collector. Relatively few positive ions then reached the collector, since their energies would have had to be quite high and their directions correct to overcome the field.

The collector plate was connected to a Cary vibrating reed electrometer driving a strip-chart recorder. It was possible to measure reliably currents smaller than 10^{-16} amp when charging times of 100 sec were used.

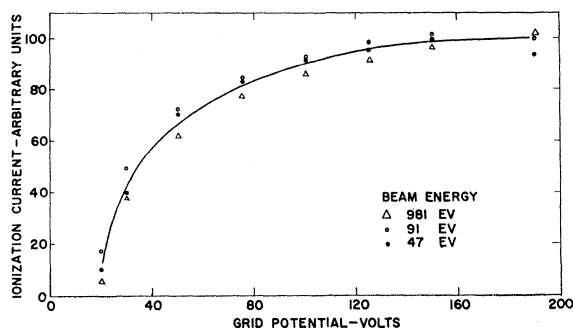


FIG. 4. Collector current saturation curves.

Figure 4 shows the collector current as a function of negative grid potential for several beam energies. The curves have been normalized to equal values at high grid potentials. Reasonable saturation was obtained below 200 v. The back plate was maintained 30 v positive with respect to the grid during these measurements.

It may be noted that at grid potentials less than 20 v, the current to the collector became positive. This is explained by the emission of secondary electrons from the collector due to the impact of scattered molecules. At small collecting fields the secondary electrons were able to escape from the collector, while at greater fields they were returned.

At the pressures employed, the process of electron multiplication made a negligible contribution to the electron current.

The ionization measurements were always made with the grid at a potential of -95 v in order to reduce grid microphonic noise input to the electrometer. The final results have been increased 10% to effectively increase

the ionization current to the saturation value (see Fig. 4).

SECONDARY ELECTRON EFFECTS

In order to be certain that the collector current corresponded to ionization electrons rather than secondary electrons, it was necessary to make measurements which indicated the magnitude of the secondary electron effects. These measurements are discussed in the following paragraphs.

Pressure Saturation Curves

The first measurement consisted of varying only the ionization chamber pressure P while keeping the ion and molecular beams constant. Under these conditions the ionization current was proportional to the pressure. (Other possible sources of current also proportional to P will be discussed further on.) In contrast, a constant current was produced by any secondary electrons arriving at or leaving the collector due to impact of direct beam molecules or photons on the electrode surfaces. Photons, for example, may have been produced when the ion beam was deflected onto the ion collector (Fig. 2). In obtaining the ionization cross section σ_i from the data, collector current was divided by the pressure P . Ionization thus led to a constant value for σ_i , while the secondary effects mentioned were indicated by a $1/P$ dependence. Figure 5 shows the results of this measurement for three beam energies. It may be seen that such secondary effects were indeed present and obscured the measurement of σ_i at low pressures.

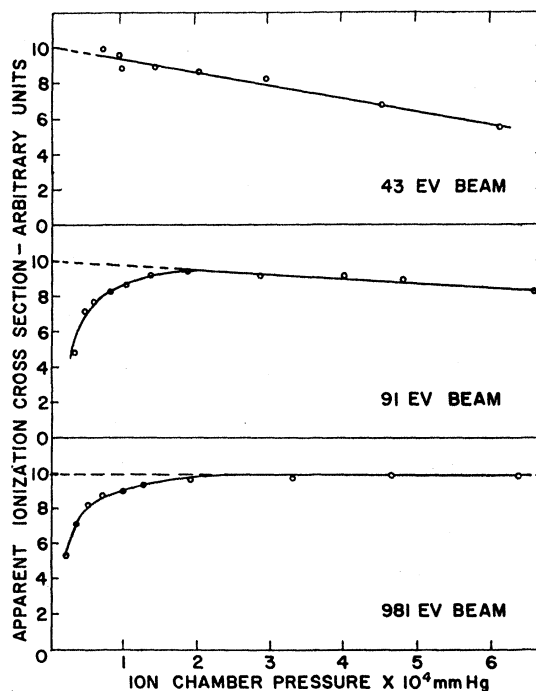


FIG. 5. Pressure saturation curves.

² H. W. Berry, Phys. Rev. **121**, 1714 (1961).

However, in each case pressures were easily reached at which a constant or slowly decreasing value for σ_i was obtained. A slow exponential decrease with P (almost linear over the range of interest) must be expected due to gas scattering of the molecular beam in the ion chamber. The gas scattering effect as seen here was a function of both the ordinary scattering cross section and the ionization cross section. A molecule could be scattered, for example, but still produce ionization at a rate characteristic of its energy after scattering. Since the ordinary scattering cross section decreases as the energy increases and since the ionization cross section becomes less energy dependent at higher energies, it is not surprising to find gas scattering most important at low energies.

A slight modification of this technique was employed to include the secondary current due to molecules which arose from partial neutralization of the ion beam in the region of the ion collector. In this measurement no neutralizing gas was admitted to the neutralization chamber directly. The pressure of the gas in the neutralization chamber was then proportional to the pressure P in the ion chamber. The molecular beam B was therefore proportional to P (so long as β was small and i_1 was constant) and the ionization current was proportional to P^2 . Any molecules arising from neutralization of ions directed toward the electrodes yielded a secondary electron current proportional to P . In obtaining σ_i under these conditions, the collector current was effectively divided by P^2 . Again the secondary effects had a $1/P$ dependence. The shape of the curves so obtained were very similar to Fig. 5, again indicating that these secondary effects were negligible at higher pressures. There were additional secondary currents which always had the same pressure dependence as the ionization current, and those will be discussed in the next section.

Pressures of about 1.5×10^{-4} mm Hg were used when obtaining the ionization cross section data. A 7% correction was made to the final data in order to extrapolate to approximately zero pressure.

Efficiency of the Grid

Secondary electrons arising from the impact of gas-scattered molecules on electrode surfaces gave rise to a current which had the same pressure dependence as the ionization current. It was therefore not possible to separate this secondary current by varying the pressure. The magnitude of this particular effect was determined in the following manner.

If no grid had been present, secondary electrons arising at the back plate due to the impact of gas-scattered molecules would have been accelerated to the collector and would have been indistinguishable from ionization electrons. The grid was added to eliminate this effect. By making the grid sufficiently negative, it was possible to return the secondary electrons to the back plate. However, the grid itself presented a nonzero

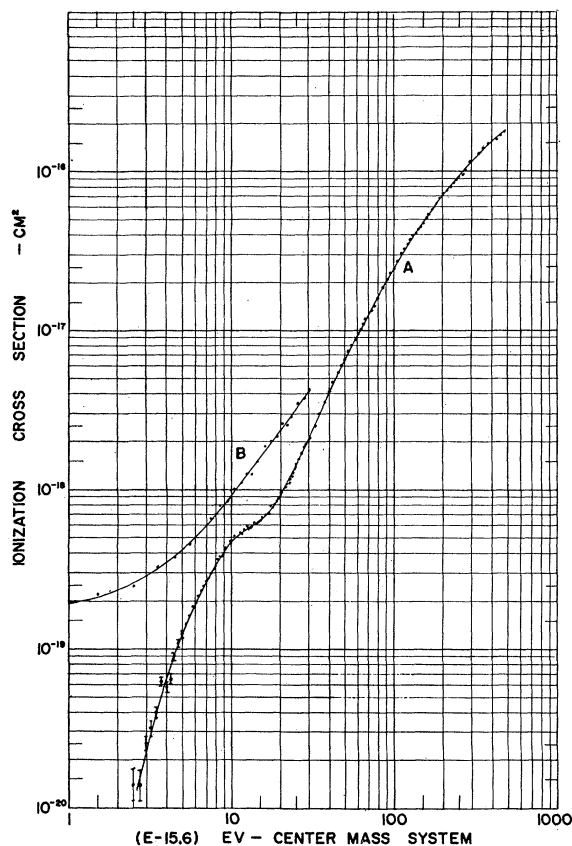


FIG. 6. Curve A: N_2 - N_2 ionization cross section. Curve B: Experimental check. See text.

area to scattered molecules, and secondary electrons arising at the grid could reach the collector. The grid wires constituted about one percent of the total grid area as seen by scattered molecules. With the grid in operation, the secondary current should therefore have been about one percent of the current present without the grid. Measurements were made with the grid 0, 30, and 50 v negative with respect to the back plate (grid-to-collector potential difference -95 v). At zero difference in potential, the secondary current should have been about a factor of 100 greater than when the grid was repelling the secondaries arising at the back plate.

Figure 6, curve B, shows the results of the measurement made with zero potential difference between the grid and back plate. It may be compared to the final results, curve A, made with the grid 30 v negative with respect to the back plate. (The 50-v measurements varied less than 2% from those at 30 v.) The ionization current as given by curve A was subtracted from the collector current in obtaining curve B. It is seen that the secondary current for zero potential difference was only a few times greater than the ionization current. The secondary current with the grid 30 v negative was therefore negligible in comparison to the ionization current. Furthermore, the difference in the shapes of

the two curves indicates that two different processes were being studied.

In addition to the tests already discussed, changes in electrode orientation were made to further check for possible sources of error. The beam producing apparatus was rotated 90° with respect to the ion chamber plates with no significant change in the final results. The equipment was completely disassembled and realigned several times during the course of the investigation.

As a final check, preliminary measurements of the N₂-O₂ ionization cross section were made (O₂ as the target gas). Ionization was observed at a lower center of mass energy, corresponding to the lower ionization threshold for O₂. Furthermore, no structure was evident in the cross section vs energy curve. (It is expected that the N₂-O₂ data will be reported in a later paper.)

RESULTS

Figure 6, curve A, shows the final results. Cross section values were obtained from

$$\sigma_i = 3.05 \times 10^{-20} (i/PB) \text{ cm}^2,$$

where i is collector current in units of 10^{-16} amp, P the ion chamber pressure in units of 10^{-4} mm Hg, and B the neutral beam equivalent current in units of 10^{-10} amp. The collector length was 10 cm and the temperature was 22°C. The collector current values were corrected for saturation and pressure effects as indicated in the preceding sections.

The energy scale for Fig. 6 is the energy in the center-of-mass system minus 15.6 ev. This corresponds to excess energy with respect to the energy threshold for production of N₂⁺. It should be noted that σ_i corresponds to the total ionization cross section up to 15.6 ev on this scale, since up to this point only one electron may be produced per event. At higher energies σ_i

becomes the apparent total ionization cross section,³ since more than one electron may be produced per event.

The error flags at the low end of the curve indicate random errors in σ_i and are due mostly to uncertainties in i . Beam energy uncertainty also becomes important near threshold, and is estimated to be ± 0.25 ev (c.m. system). At higher energies the random uncertainties are a few percent.

The largest systematic uncertainty in σ_i was due to the molecular beam intensity B , which was known to within $\pm 20\%$.¹ The pressure uncertainty was less than $\pm 10\%$. Other uncertainties should not have been over a few percent, so it is reasonable to assign the results an absolute uncertainty of $\pm 25\%$.

Little was known about the internal energy state of the beam molecules, or about the magnitude of the effect excited states might have on the ionization cross section near threshold.

Structure was quite evident near the middle of the cross section-vs-energy curve. A satisfactory explanation for this structure has not been given as yet, although the energy at which the structure occurred might suggest dissociation effects. The possibility for ionization of both colliding molecules occurred above 31.2 ev in the c.m. system and might explain structure in that region. The production of N₃⁺ and N₄⁺ may also have been a factor. It therefore appears that an explanation must await a more detailed study of the ionizing events, including energy and mass spectrometric analysis of the resulting ions.

ACKNOWLEDGMENT

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³ H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952).