

being

$$H' = H_f' + H_m' + H_{\text{int}}',$$

where

$$H_f' = 2\pi c^2 P'^2 + (\omega^2/8\pi c^2) Q'^2,$$

$$H_m' = (1/2m) p'^2 + \varphi(\mathbf{q}') + 2\pi e^2 u^2 q'^2,$$

$$H_{\text{int}}' = 4\pi c \mathbf{u} \cdot (e \mathbf{q}') P' = 4\pi c \mathbf{u} \cdot \boldsymbol{\gamma} P'.$$

We see that the transformed Hamiltonian refers to the molecules only in terms of the (transformed) phenomenological variables.

So far there has been no approximation. The approximation consists of identifying H_f' and H_m' as the field and molecular energy, respectively. Such an approximation is justified for sufficiently weak coupling.

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Electron Impact Ionization of Atomic Nitrogen*

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The total cross sections for the ionization of atomic nitrogen by electron impact have been measured between 25 and 750 eV using a modulated molecular beam technique. The neutral beam source was a pulsed dc discharge which dissociated about 20% of the molecules. The number of ions formed in a region defined by the intersection of an electron beam and the modulated molecular beam was compared with the number of ions formed when the neutral beam was partially dissociated. All ions were collected, including those energetic ones formed in the dissociative ionization of molecular nitrogen. The degree of dissociation was measured with a mass spectrometer. From the data, the ratios of the atomic to the molecular ionization cross sections were obtained. The absolute atomic values were calculated by multiplying these ratios by the molecular ionization cross sections measured by Tate and Smith. The atomic cross sections are lower than those calculated by Seaton.

INTRODUCTION

MODULATED molecular beam techniques have been extensively used to study chemically unstable atoms. In particular, many collision properties of atomic hydrogen and of atomic oxygen have been measured, while those of atomic nitrogen have been neglected primarily because of the greater difficulty of dissociating the molecule. We have produced a nitrogen beam in which about 20% of the molecules were dissociated, and have applied it to measure the electron impact ionization cross section of atomic nitrogen between 25 and 750 eV.

EXPERIMENTAL

The method was similar to that previously used to obtain the ionization cross sections for H and O.¹ Since the radio-frequency discharge used in those experiments would not significantly dissociate nitrogen, a new source was required. In addition, a different ionizer was required for some of the data. A schematic arrangement of the apparatus is shown in Fig. 1.

The atomic nitrogen source, a pulsed dc discharge, is shown schematically in Fig. 2. The tube is of Pyrex and the electrodes are aluminum. The beam source was a slit fixed to the tip of the exit tube which was 2 cm in

length. The beam thus originated from the afterglow in the exit tube and not from the discharge column. The slit was sufficiently narrow to satisfy effusive flow conditions. Typically, the discharge operated at 1.6 kV and 50 mA, with a nitrogen pressure of about 0.2 mm Hg. The current pulse, similar in shape to a one-cycle damped sine wave, had a duration of about 26 μ sec. The positive and negative peak currents were about 750 and 350 A, respectively. Although the interval between

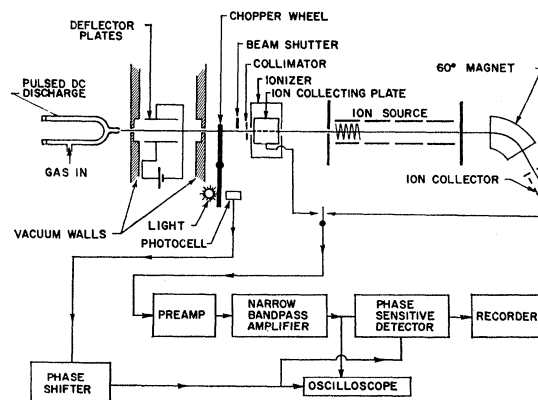


Fig. 1. Experimental arrangement for the ionization of atomic nitrogen by electron impact. A magnetically collimated electron beam intercepts the modulated neutral beam within the ionizer. The ions formed are collected and the resultant ac signal is measured by the electronic system. The mass spectrometer is used to determine the degree of dissociation of the nitrogen beam.

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¹ E. W. Rothe, L. L. Marino, R. H. Neynaber, and S. M. Trujillo, *Phys. Rev.* **125**, 582 (1962).

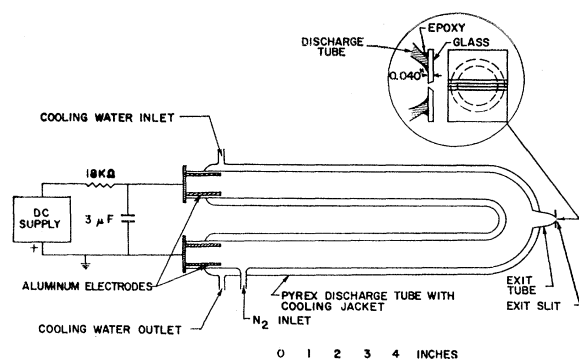


FIG. 2. Diagram of atomic nitrogen source. Two different exit slits were used for the ionization experiment. The dimensions were 0.0015×0.1 and 0.003×0.1 in.

pulses (about 66 msec) may cause a slight time dependence of the degree of dissociation, it can be shown that no error is introduced in our results by using the time-averaged value that is measured with the mass spectrometer.

There is evidence that the only active species present in appreciable concentration in the low-pressure afterglow of nitrogen is the ground-state nitrogen atom. Atoms in the 4S ground state were observed in magnetic resonance² and mass spectrometric³ experiments, but no atoms in the metastable 2D and 2P states were detected. Tanaka *et al.*⁴ investigated species present in nitrogen afterglows by an optical absorption technique and found that the concentration of atoms in the 2D and 2P states was several orders of magnitude lower than that of the ground state. In addition, metastable molecules were not detected in two mass spectrometric experiments.^{3,5} In each of these investigations a pulsed dc discharge source was employed and the search for metastable particles was made in a side tube. In the present source the

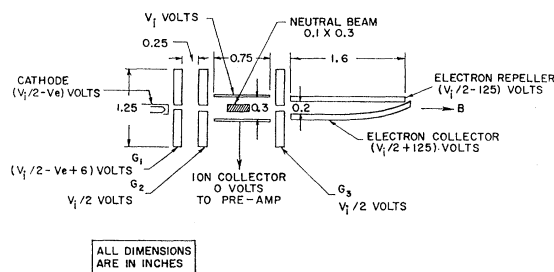


FIG. 3. Diagram of ionizer 2. The dimensions of the slits in G_1 , G_2 , and G_3 are, respectively, 0.03×0.5 , 0.06×0.75 , and 0.06×0.75 in. The long dimension of each slit is into the paper. The ion collection plates are 1.0 in. long in a direction normal to the paper.

² M. A. Heald and R. Beringer, *Phys. Rev.* **96**, 645 (1954).

³ J. Berkowitz, W. A. Chupka, and G. B. Kistiakowsky, *J. Chem. Phys.* **25**, 457 (1956).

⁴ Y. Tanaka, A. S. Jursa, F. J. LeBlanc, and E. C. Y. Inn, *J. Planet. Space Sci.* **1**, 7 (1959).

⁵ D. S. Jackson and H. I. Schiff, *J. Chem. Phys.* **23**, 2333 (1955).

shorter exit tube was less favorable for the decay of metastables. However, they still had a good chance to strike the wall with resulting de-excitation before passing into the neutral beam. It appears unlikely that significant concentrations of metastable atoms and molecules existed in the neutral beam.

The cross sections were measured using two different ionizers. Some data were obtained using the ionizer previously employed to measure the ionization cross sections of atomic hydrogen and atomic oxygen.¹ This purely electrostatic ionizer (hereafter referred to as ionizer 1) was unreliable below about 125 eV, largely because the small electron current resulted in poor signal-to-noise ratios. In addition, at even lower energies the ion collection field would have led to significant uncertainty in the electron energy and would have deflected the electron beam away from the collector. Another ionizer (hereafter referred to as ionizer 2), whose major feature was the magnetic collimation of the im-

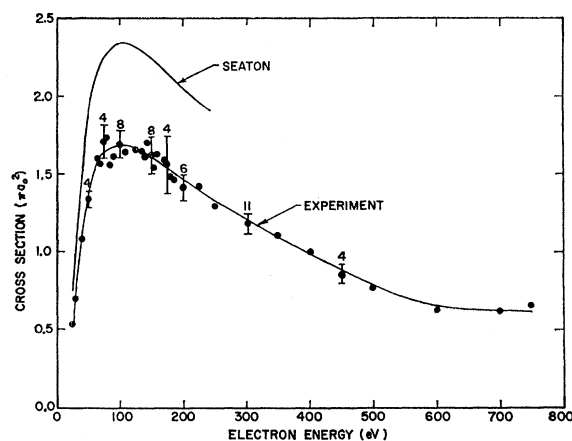


FIG. 4. Cross sections for ionization of atomic nitrogen by electron impact.

pact electrons, was constructed and is shown in Fig. 3. It was adapted from a gun described by Tate and Smith.^{6,7} The electron beam was ribbon shaped so that a large electron current would pass through the neutral beam. The electrodes were made of copper and were supported by quartz rods. Electrons, originating from a long oxide-coated cathode, were extracted through a slit in G_1 , which was maintained at a fixed potential with respect to the cathode. The electrons were accelerated to the desired energy between slits in G_1 and G_2 . This arrangement yielded an electron beam whose magnitude was independent of its energy. Electron currents between 90 and $180 \mu A$ were used. A magnetic field of about 400 G was applied parallel to the electron beam. The beam was defined by the magnetic field, rather than by the slits, and no electron current greater than $0.5 \mu A$ was detected at G_2 , G_3 , or on the ion col-

⁶ P. T. Smith, *Phys. Rev.* **36**, 1293 (1930); **37**, 808 (1931).

⁷ J. T. Tate and P. T. Smith, *Phys. Rev.* **39**, 270 (1932).

lector. Accordingly, no secondary electrons with incorrect energies were created. Another benefit of the magnetic field was to prevent scattered electrons, or electrons produced by ionization of the neutral beam, from reaching the ion collector. The potentials on the electron collector and repeller, as well as the magnetic field, prevented any electrons from leaving the electron collector region. The neutral beam intersected the electron beam between G_2 and G_3 , and the resulting ions were collected by the application of a potential V_i , which was usually about 30 V, to the ion collector. Ion saturation experiments indicated that all ions were collected, including energetic ones formed by dissociative ionization. Because the magnetic field ensured an electron beam that is of small height which is in the middle of the interaction region, the ion collection field caused only a small uncertainty in the electron energy, i.e., less than 3 eV for a 30-V ion collection potential. The height of the neutral beam was made sufficiently large to ensure that the entire electron beam passed through the neutral beam.

In order to eliminate surface charging, the ionizer was surrounded by a stainless steel oven which allowed it to be degassed at 475°C; after degassing it was normally operated at about 350°C. The magnetic field was provided by a solenoid which was placed around the ionizer and oven. The solenoid was embedded in an epoxy resin to prevent outgassing and was water cooled to protect the windings from the heat of the oven.

The ion signal was found to be a linear function of the electron current in the current and energy ranges of interest. This implies that there was no significant distortion of energy due to space charge.

A measurement of the relative ionization cross section as a function of electron energy between 25 and 550 eV was made for molecular nitrogen. The results were in good agreement with those obtained by Tate and Smith,⁷ e.g., the ratio of the cross section at 550 eV to that at 100 eV agreed with the Tate and Smith ratio to within 3%. These relative cross sections as well as the argon ion appearance potential, as extrapolated from measurements of the ionization cross section, indicated that the measured energies were correct to within 1.5 eV.

The procedure for obtaining the atomic cross sections was similar to that described for H and O.¹ At a given energy, total ion signals were measured when the neutral beam was molecular and again when the beam was partially dissociated. The degree of dissociation was measured with a mass spectrometer. From the data the ratios of the total atomic to the total molecular ionization cross sections were computed. The atomic cross sections were calculated from these ratios and the known molecular values.⁷

DISCUSSION OF RESULTS

The results are presented in Fig. 4. The points shown are averages of cross sections obtained at a given energy. At several energies digits above brackets indicate the number of cross sections used to obtain the average. At energies where there are no digits the number of cross sections employed in the average is less than four. A bracket indicates the root mean square deviation from the average and represents a reasonable estimate of the experimental error. No distinction is made between points obtained with ionizers 1 and 2. All data below 150 eV were taken with ionizer 2, but at higher energies the number of points obtained with each ionizer was approximately equal. At a given energy, the two ionizers gave the same results within the precision of the experiment. The curve was considered to be the best fit to the points when they were properly weighted.

Also shown in Fig. 4 are cross sections calculated by Seaton for single ionization of atomic nitrogen.⁸ These were obtained using the Bethe approximation for the relation between the electron impact ionization cross section and the photo-ionization cross section. The experimental cross sections include single and multiple ionization although the contribution of the latter is expected to be small. These measured cross sections should then represent an upper limit for single ionization. They are actually about 25% lower than Seaton's values. Better agreement was found in the case of the ionization of atomic oxygen.^{1,9}

⁸ M. J. Seaton, Phys. Rev. **113**, 814 (1959).

⁹ W. L. Fite and R. T. Brackmann, Phys. Rev. **113**, 815 (1959).