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A Mass Spectrum Analysis of the Products of Ionization by Electron Impact in Nitrogen, Acetylene, Nitric Oxide, Cyanogen and Carbon Monoxide

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A *mass spectrograph*, designed for the identification of the products of ionization and dissociation by electron impacts in molecular gases is described.

Ionization potential of nitrogen. A direct comparison in a nitrogen-argon mixture showed that the ionization potential of nitrogen is at least 0.04 volt less than that of argon. The ionization potential is therefore not greater than 15.65 volts, though it may be lower by as much as 0.1 volt.

Analysis of ionization and dissociation products in C_2H_2, NO, and C_2N_2. The ions formed by electron impacts in these gases together with their appearance potentials in volts are as follows:

Ion	$C_2H_2^+$	C_2H^+	C_2^+	CH^+	C^+	H^+
App. pot.	11.2	17.8	23.8	22.2	24.5	21.7, 25.6
Est. error	±0.1	±0.2	±0.3	±0.5	±1.0	±1.0 ±1.0

Ion	NO^+	N^+	NO^{++}
App. pot.	9.5	22.0	44
Est. error	±0.1	±0.5	±1.0

Ion	$C_2N_2^+$	C_2N^+	CN^+	C_2^+
App. pot.	14.1	19.8	21.3	18.6
Est. error	±0.1	±0.5	±0.3	±0.5

Negative O^- ions appear in NO as reported by Tate and Smith. An ion of mass 27 found in C_2H_2 is ascribed to $C^{12}C^{13}H_2$. The abundance ratio C^{13} : C^{12} was calculated to be 1 : 100.

I. THE MASS SPECTROGRAPH

IN THE studies here to be described of the effects of electron impacts in various gases a mass spectrograph was used to identify the ionized products of the impacts.

The mass spectrograph which is shown diagrammatically in Figs. 1 and 2 is similar to that described by Bleakney.[1] Since many of the gases to be studied are dissociated at the hot filament it was necessary to shut off the filament, except for the first small diaphragm in the cylinder A, in a separate compartment provided with a separate pump. The scheme is shown in Fig. 1. Since the pressure is kept lower on the filament side of A than in the main tube the products of dissociation were kept from diffusing into the region where impact ionization and dissociation were being studied.

A magnetic field of about 900 gauss parallel to the axis of the tube was provided by a large solenoid surrounding the tube and coaxial with it. This field served the double purpose of maintaining the electron beam from the filament in line and of providing the magnetic field for the analyzer.

Electrons from the tungsten filament F are accelerated by a constant drawing out potential between F and A. S_1 is at the same potential as A. A variable potential V_a is applied between the filament F and the slits S_2, S_3 and S_4 which are all at ground potential. The electrons with energy of approximately V_a electron-volts then enter the region between the plates P_1 and P_2 which form part of the analyzer shown in end section in Fig. 2. Here a few of them suffer impacts with the gas molecules but the majority go straight through to the electron trap which is, in

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[1] W. Bleakney, Phys. Rev. **40**, 496 (1932).

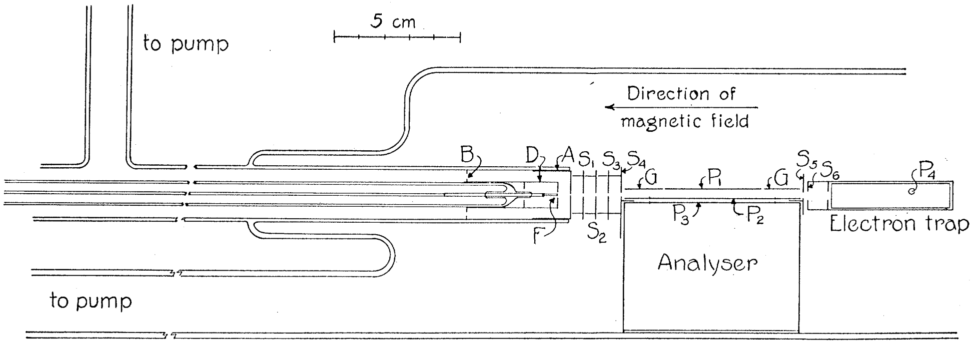

FIG. 1. Diagram of the apparatus as viewed from the side.

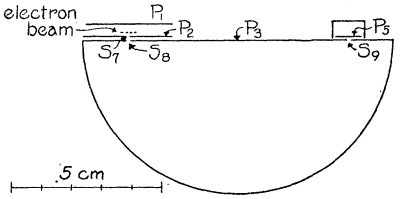

FIG. 2. Diagram as viewed from the end with electron gun removed. S_1, S_2, S_3 and S_4—1×6 mm; S_7—0.2×50 mm; S_8 and S_9—0.155×50 mm.

turn, connected with a galvanometer. The pressure of the gases to be studied is so low (10^{-4} to 10^{-6} mm Hg) that a very small fraction of the electrons experience single impacts, and multiple impacts are negligible.

The ions produced in the region between P_1 and P_2 are drawn downward by a small potential V_0 (about 2 volts) applied between P_1 and P_2. This potential is so applied that the space through which the electron beam passes is maintained at ground potential. There is a long slit in P_2 (Fig. 2) through which a narrow sheet of ions may pass. These are further accelerated by a variable potential V_1 between P_2 and P_3, are bent around in the magnetic field and pass through the slit S_9 to the collector P_5. The current to P_5 is measured with a Compton electrometer or vacuum tube amplifier. The resolving power of the analyzer (ratio of $\Delta(m/e)$ to (m/e) is about 1/40).

All of the metal parts of the spectrograph are of tantalum or tungsten with Pyrex insulation. The tube is mounted in an electric furnace which in turn is mounted in the center of a water-cooled solenoid.

The tube was evacuated and baked at a temperature of about 400°C, for many hours and the baking process was repeated at frequent intervals. The spectrograph itself forms a good ionization gauge. The residual pressure, before admitting the gas to be studied, was less than 10^{-7} mm Hg. The gases were admitted through a long capillary and allowed to flow continuously out through the pumps.

In making an m/e analysis of the ions their velocity was varied by varying V_1 in steps of 0.1 or 0.05 volt and the current to P_5 plotted as a function of V_1 (see Fig. 3, for example). When the appearance potential of a particular type of ion is to be determined V_1 is set for the collection of that ion and the electron velocity varied by varying V_a. The ion current is then plotted as a function of V_a. This type of curve is shown in Fig. 4.

II. IONIZATION POTENTIAL OF NITROGEN

The precise value of the ionization potential of the nitrogen molecule has for several years been a matter of some concern both to those interested in electron collision phenomena and to band spectroscopists. Determinations of the threshold energies electrons must have in order that they be capable of producing ions in a gas are subject always to uncertainties introduced by the shape of the ionization curves near the threshold. These uncertainties have two causes: the first a lack of sharpness in the velocity distribution of the electrons themselves and the second a lack of knowledge about the actual probability-of-ionization as a function of velocity in the neighborhood of the threshold.

The first cause of uncertainty can be removed by an independent determination of the velocity distribution but the second is more refractory and is particularly troublesome in the case of molecules for which the sharpness of onset of ionization depends on the shapes of the potential-energy curves for the molecule and molecular ion and the relative positions of their minima with respect to internuclear separations. The result is that the estimate of ionization potential will depend on the sensitiveness of the measuring instruments and any value so obtained usually represents an upper limit.

The present determination of the ionization potential of nitrogen was made by using a mixture of nitrogen and argon in the mass spectrograph and by measuring simultaneously the number of N_2^+ and of A^+ ions collected for a number of electron energies near the threshold energy. The advantage of using argon as a calibrating gas is that its ionization potential differs from that of nitrogen by only about 0.1 volt yet the mass spectrograph permits a complete separation of the A^+ and N_2^+ ions and a determination of their relative abundance.

This method of estimating the ionization potential of nitrogen eliminates all uncertainty relative to contact potentials and velocity distribu-

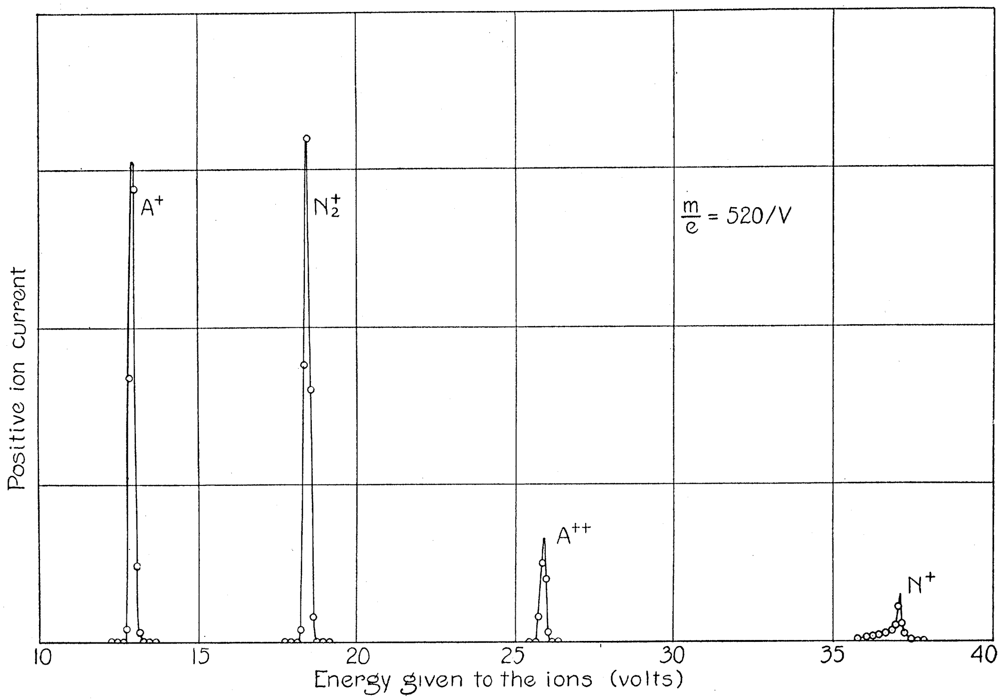

FIG. 3. Mass spectrum of the products of ionization in a mixture of argon and nitrogen. Electron energy $V_a = 100$ EV. $H = 900$ gauss.

tion of electrons. There remains only the uncertainty about the relative behavior of the ionization-probability curves for argon and nitrogen. It is probable that the onset of ionization in argon is somewhat sharper than in nitrogen.

The mass spectrum of an argon-nitrogen mixture is shown in Fig. 3. The heights of the A^+ and of the N_2^+ peaks are plotted against electron velocity in Fig. 4. It will be seen that the ionization potential of nitrogen is a little lower than that of argon. Twelve curves of the sort shown in Fig. 4 give for the difference in ionization potentials an average value of 0.04 volt. The mean deviation from this average was 0.04 volt. If we assume that the ionization-potential of argon is 15.69 volts, the apparent value for nitrogen is 15.65 volts. We believe that the true ionization potential is certainly not greater than this by more than 0.02 volt but may be less by perhaps 0.10 volt.

In Table I are given the values of previous measurements of the ionization potential of nitrogen. The fact that electron impact measurements lead to upper limits is indicated by the

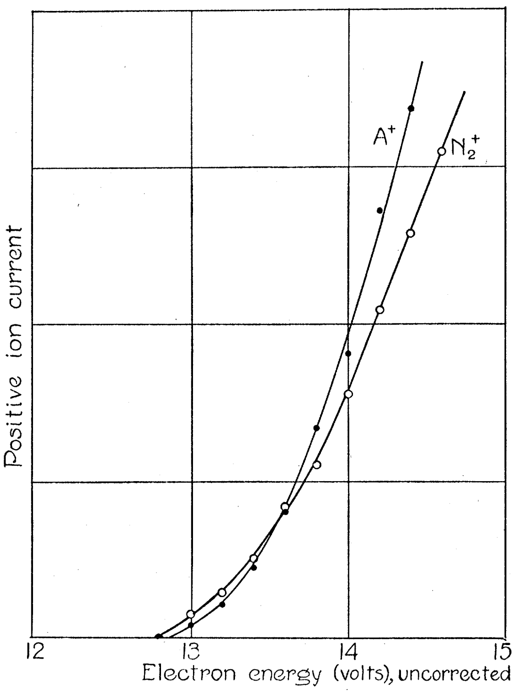

FIG. 4. Typical ionization curves showing positive ion current as a function of the electron energy (uncorrected).

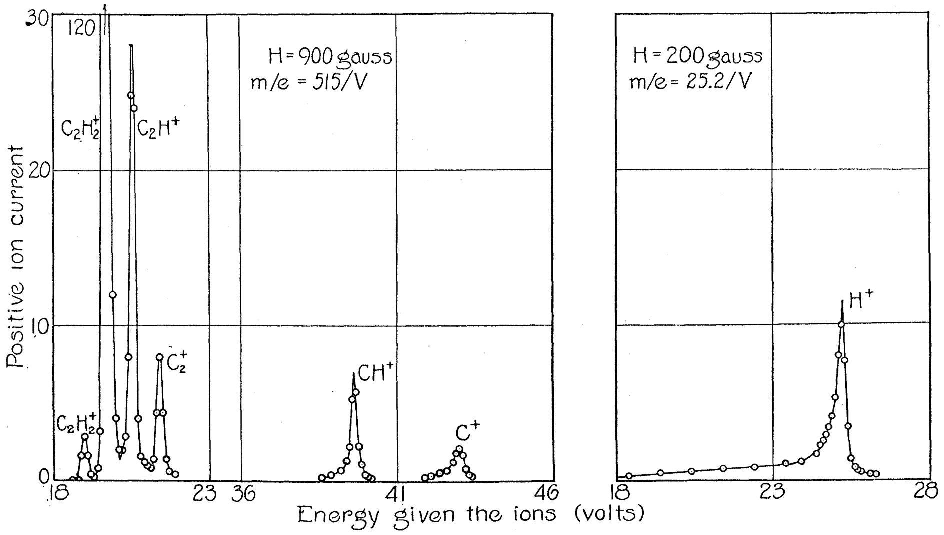

FIG. 5. Mass spectrum of the products of ionization in acetylene. Electron energy $V_a = 100$ EV.

way in which, as the experimental technique is refined the values given become lower and lower.

TABLE I. *Observed ionization potential for molecular nitrogen.*

I.P. (volts)	OBSERVER	REFERENCE
18	Davis and Goucher	Phys. Rev. **13**, 1 (1919)
18	Smyth	Phys. Rev. **14**, 409 (1919)
16.9	Mohler and Foote	Phys. Rev. **15**, 555 (1920)
17.2	Stead and Gosling	Phil. Mag. **40**, 413 (1920)
15.8	Found	Phys. Rev. **16**, 41 (1920)
16.95	Brandt	Zeits. f. Physik **8**, 32 (1921)
15.8	Boucher	Phys. Rev. **19**, 189 (1922)
16.2	Duffendack	Phys. Rev. **20**, 665 (1922)
16.3	Mackay	Phys. Rev. **24**, 319 (1924)
15.8	Turner and Samson	Phys. Rev. **34**, 747 (1929)
15.8	Vaughan	Phys. Rev. **38**, 1687 (1931)
15.7	Tate and Smith	Phys. Rev. **39**, 270 (1932)
15.65	Tate, Smith and Vaughan	This paper.

Recently Mulliken[2] concludes from Hopfield's[3] study of a Rydberg series of absorption bands that 15.51 volts is a minimum value for the ionization potential of nitrogen. We can therefore assert with some confidence that the ionization potential lies somewhere between 15.51 and 15.65 volts.

As a matter of general interest we looked for negative ions of nitrogen but found none at any velocity of impact.

III. PRODUCTS OF IONIZATION AND DISSOCIATION PRODUCED BY ELECTRON IMPACT IN ACETYLENE, NITRIC OXIDE, CYANOGEN AND CARBON MONOXIDE

A. Acetylene

The gas was prepared by repeated fractional distillation of the commercial product. The measurements were made with the acetylene at a pressure of about 10^{-5} mm Hg. The mass spectrum of the products of ionization and dissociation are shown in Fig. 5. Eisenhut and Conrad[4] found the same primary ions. The appearance potentials and estimated accuracy are obtained from curves of the type shown in Fig. 6 and are as follows:

Ion	$C_2H_2^+$	C_2H^+	C_2^+	CH^+	C^+	H^+	
App. pot. (volts)	11.2	17.8	23.8	22.2	24.5	21.7	25.6
Est. error	±0.1	±0.2	±0.3	±0.5	±1.0	±1.0	±1.0

It will be noted that the peaks for the C^+, CH^+ and H^+ ions trail out to the left. This is due to the fact that in the dissociation process the ions pick up kinetic energy. The energy lost by the electron at impact is greater by several electron volts than the sum of the ionization potential and the heat of dissociation and the difference appears as kinetic energy of the dissociation products. This

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[2] R. S. Mulliken, Phys. Rev. **46**, 144 (1934).

[3] J. J. Hopfield, Phys. Rev. **36**, 789 (1930).

[4] O. Eisenhut and R. Conrad, Zeits. f. Elektrochemie **36**, 654 (1930).

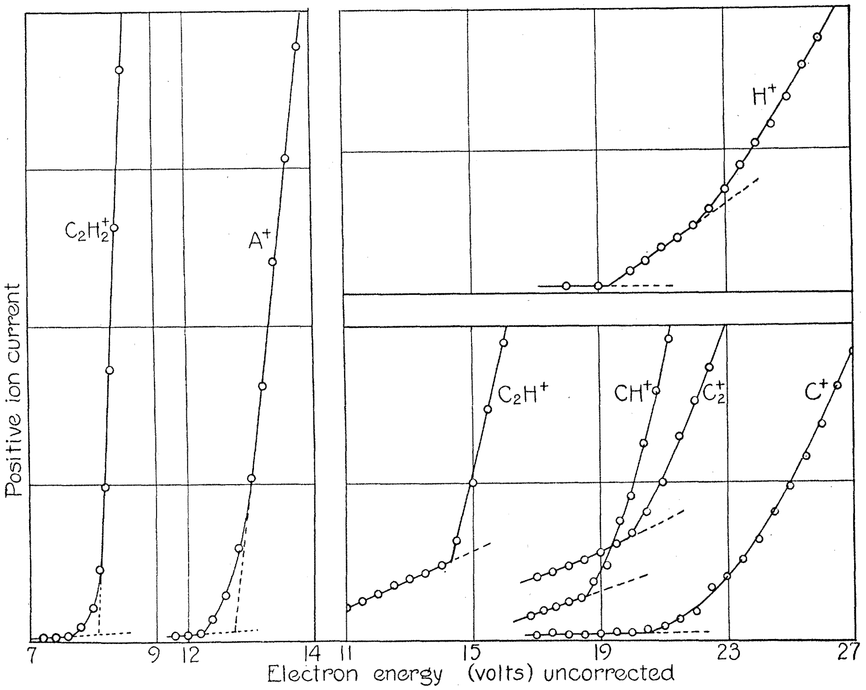

FIG. 6. Typical ionization potential curves in acetylene.

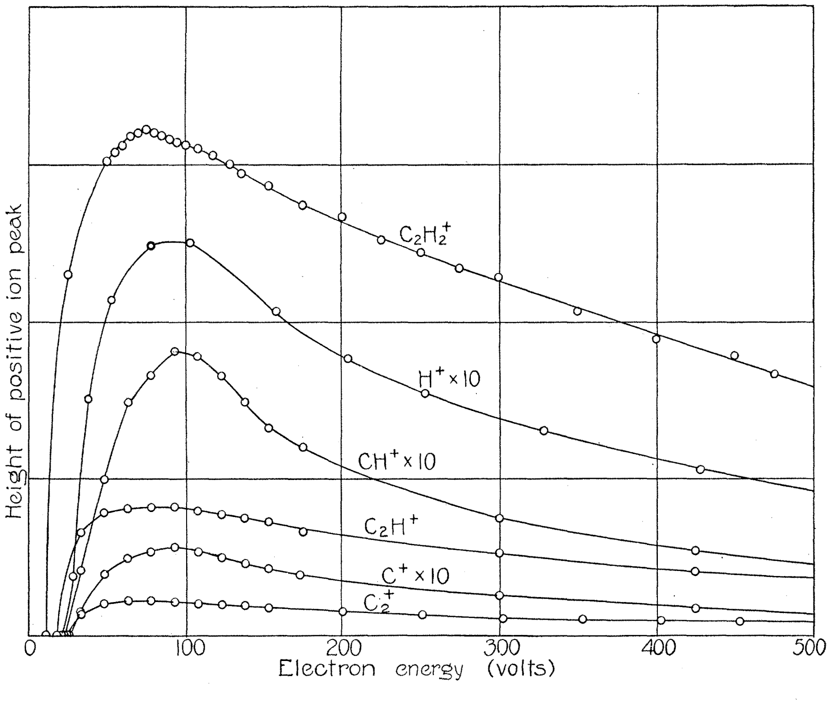

FIG. 7. Heights of ion peaks as a function of the electron energy in acetylene.

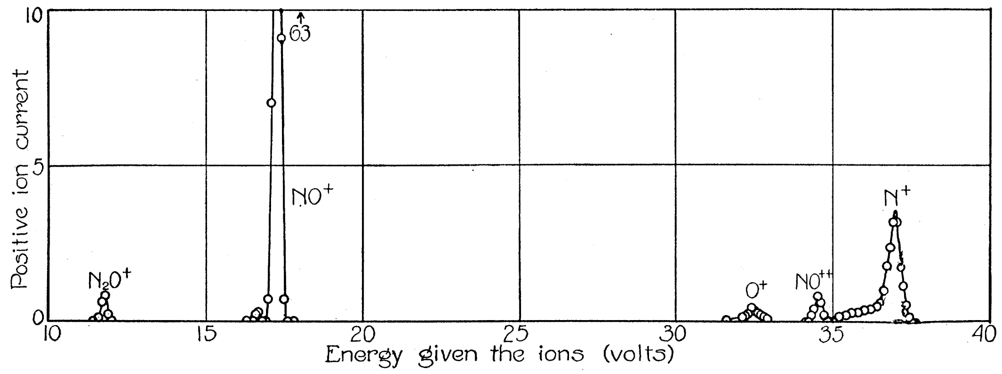

FIG. 8. Mass spectrum of the products of ionization in nitric oxide. Electron energy $V_a = 100$ EV.

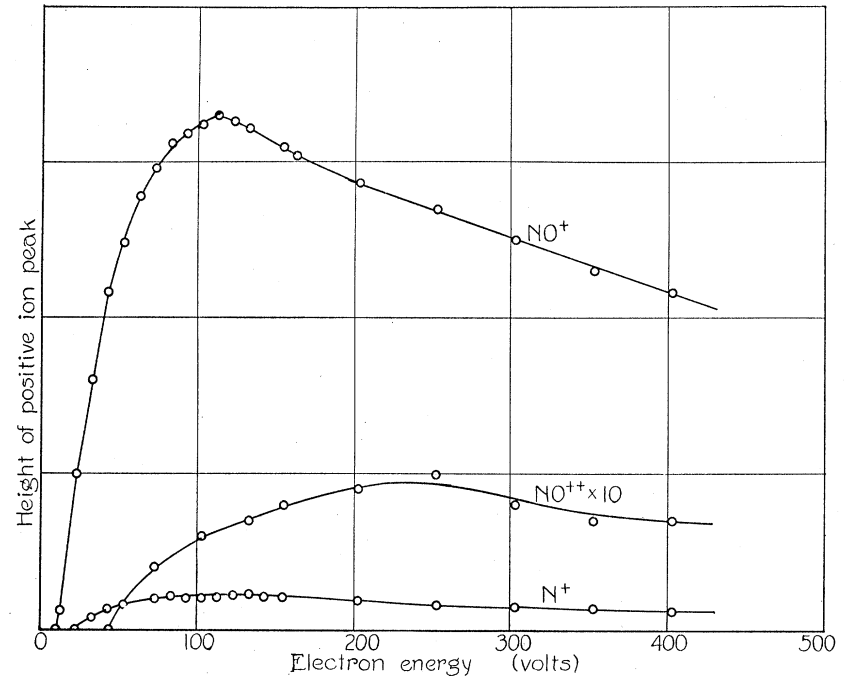

FIG. 9. Heights of the ion peaks as a function of the electron energy in nitric oxide.

effect will be the more marked the smaller the mass of the ion relative to the molecule. The C^+ and CH^+ ions have as much as 1.5 EV kinetic energy while the H^+ ion has up to 6 EV. Fig. 7 shows the heights of the various peaks (probability of formation) as functions of the electron energy in volts. No negative ions were observed.

There are two peaks labeled $C_2H_2^+$. The one on the left ($m/e = 27$) is presumably $(C^{12}C^{13}H_2)^+$. This ion appears at the same electron velocity as the ion of mass 26 and the relative heights of the two peaks remain the same as the electron velocity is varied. The relative abundance of C^{13} to C^{12} is approximately 1 part in 100. Jenkins and Ornstein[5] have reported a value of 1 part in 106. A more recent and refined determination[6] gives 1 part in 91.6. Aston[7] has found a ratio of 1 part in 140.

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[5] F. A. Jenkins and S. S. Ornstein, Proc. Acad. Sci. Amsterdam **35**, 1212 (1932).

[6] A. L. Vaughan, J. H. Williams and J. T. Tate, Phys. Rev. **46**, 327 (1934).

[7] F. W. Aston, Proc. Roy. Soc. **A149**, 396 (1935).

B. Nitric oxide

The sample was prepared by the action of HNO_3 on Cu. The NO was passed through water to remove any NO_2, dried over solid NaOH, collected over liquid air, and purified by repeated fractional distillation. After all these precautions there still remained approximately one percent of N_2O as determined by the mass spectrograph. Fig. 8 shows the mass spectrum. Fig. 9 is the height of the peaks plotted as a function of the electron energy in volts. The negative ions found by Tate and Smith[8] showed up strongly and were identified as O^- ions. The results are given in the following table.

Ion	NO^+	N^+	NO^{++}
App. pot. (volts)	9.5	22.0	44
Error (volts)	±0.1	±0.5	±0.1

A very faint trace of O^+ ions appeared at 21 volts. The ionization potential of NO is taken as 9.5 volts from the work of Tate and Smith[8] and this value was used to calibrate the scale.

In Fig. 8 there is an ion having an m/e value of 31. This peak seems to bear a constant relation to the NO^+ peak of about 1/2 to 1/3 percent independent of electron velocity and is probably due to the N^{15} isotope. A more careful study[6] of this has given a ratio of N^{14}/N^{15} of 265.

C. Cyanogen

The sample of C_2N_2 was obtained from the Department of Chemistry. The results may be compared to those of Dorsch and Kallman.[9]

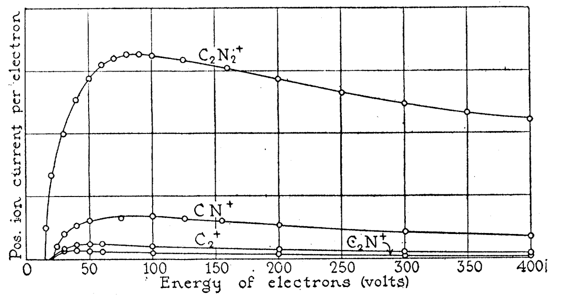

FIG. 10. Heights of the ion peaks as a function of the electron energy in cyanogen.

Ion		$C_2N_2^+$	CN^+	C_2^+	C^+	C_2N^+
App. pot. (volts)	Authors	14.1	21.3	18.6		19.8
	Dorsch and Kallman	13.5	18	17	22.5	

Fig. 10 shows the heights of the peaks as a function of the electron velocity in volts. C^+ and N^+ peaks were found, but their origin was uncertain since the sample of cyanogen contained small amounts of CO and N_2 as impurities.

D. Carbon monoxide

The work on carbon monoxide agrees with that published by Vaughan.[10] The O^+ ion which was masked by H_2O^+ in that work appears here but is very small. It appears at 27±1 volts and is only about 10 percent as plentiful as the C^+ ion at 100 volts electron velocity.

The authors are very grateful to C. H. Dane, E. F. Greinke and William B. Haliday for their help and cooperation. The senior author wishes to express his appreciation to the Graduate School of the University for a grant from the Fluid Research Funds.

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

[9] K. E. Dorsch and H. Kallman, Zeits. f. Physik **60**, 376 (1930).

[10] A. L. Vaughan, Phys. Rev. **38**, 1687 (1931).