

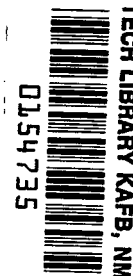
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# MASS SPECTRA OF POSITIVE AND NEGATIVE IONS IN NITROUS AND NITRIC OXIDES

*by C. S. Harden and E. E. Muschlitz, Jr.*

Prepared under Grant No. NsG-67-60 by  
UNIVERSITY OF FLORIDA  
Gainesville, Fla.

*for*

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SUMMARY

Using a high resolution mass spectrometer containing an electron impact ion source, the mass spectra of positive and negative ions in  $N_2O$  and  $NO$  have been studied for possible gas phase ion-molecule reactions. Over a pressure range of 0.05 to 0.5 microns Hg, as measured by a Pirani gauge in the ion source, no such reactions were observed.

The formation of  $NO^-$  by electron impact in  $NO$  was found to be second order pressure dependent at low pressures and first order at higher pressures. Initial electron attachment followed by collision stabilization is proposed as the mechanism for the process. The formation of  $NO^-$  ions from  $N_2O$  molecules was found to deviate slightly from a first order pressure dependence toward second order. It is suggested that the ion is initially formed in an excited energy state and that a second collision is required for the release of its excess energy. An intense peak at mass 26 was observed in the negative ion spectra of both  $N_2O$  and  $NO$ . It is suggested that this peak is due to  $CN^-$  which is produced in a surface reaction involving  $N^+$  ions and adsorbed hydrocarbons. The intensity is markedly reduced upon cleaning the source electrodes.

INTRODUCTION

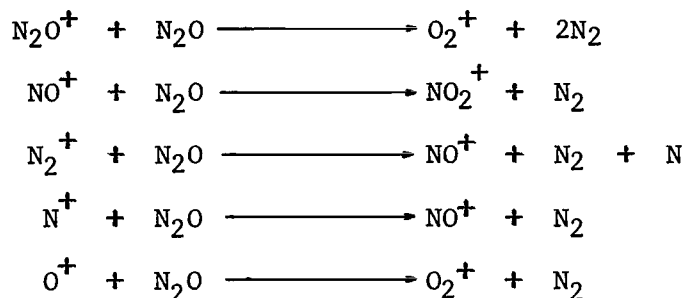
Positive Ion Formation

The study of gas phase reactions between ions and neutral molecules has been greatly aided by the observation of secondary reactions in the ion source of a mass spectrometer. These processes were observed by the early workers in the field of mass spectrometry (ref. 1) but were considered as nuisances in the development of their machines which were primarily used for measuring nuclear packing fractions and isotopic abundance ratios.

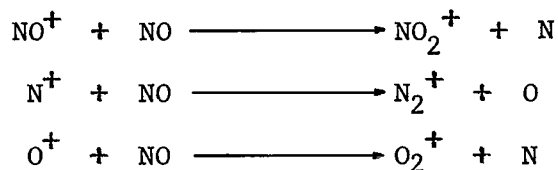
The number of secondary ions that are produced as a result of an ion-molecule reaction will be proportional to the number of primary ions traversing a gas filled region and to the number of neutral molecules occupying the region. Hence, the ratio of the number of secondary ions collected to the number of primary ions collected (assuming the same collection efficiency for both ions) will be proportional to the pressure of neutral molecules in the

ion source. In general, the desired information concerning such reactions is obtained from measuring the secondary to primary ion ratio as a function of pressure.

In this work, the mass spectra of the positive and negative ions produced by electron impact in nitrous oxide and nitric oxide are investigated for ion-molecule reactions. Curran and Fox (ref. 2) show that  $N_2O^+$ ,  $NO^+$ ,  $N_2^+$ ,  $N^+$ , and  $O^+$  are produced as primary ions in  $N_2O$ . Hence, there are a number of equations that may be written for possible gas phase reactions in  $N_2O$ . A few of these are:

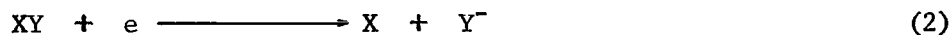


Cloutier and Schiff (ref. 3) found that  $NO^+$ ,  $N^+$ , and  $O^+$  are primary ions produced in  $NO$  as a result of electron bombardment. Some of the equations that can be written for possible ion-molecule reactions in  $NO$  are:



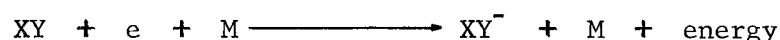
#### Negative Ion Formation

Negative ion formation arising from collisions of electrons with molecules comes about by three processes, namely



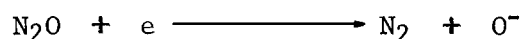
Process (1) occurs by attachment of an electron to a neutral molecule  $XY$  leaving the molecule in a vibrationally excited energy state. Unless this excess energy can be eliminated by collision with a third body the molecule will dissociate or emit a photon. If the third body is an atom, the energy will appear in an increase of translational energy; if it is a molecule, the energy can also appear as vibrational excitation. The over-all effect of the

attachment process obeys a three body equation



Biondi (ref. 4) has discussed a number of studies of this attachment process in  $O_2$ . At low pressure or low concentration of M, the number of  $O_2^-$  ions formed by this process should be a function of the square of the pressure. At high concentrations of M where chances of third body collision are good, the formation process should be linear with pressure. The reasons for this will be explained later by considering a similar process.

A dissociative attachment process, reaction (2) occurs when the energy of the incident electron is such that, when captured, it ruptures the X-Y bond and is attached to the Y fragment. This process, in general, occurs over a narrow range of electron energies. Curran and Fox (ref. 2) observe that the reaction



occurs over a range of electron energies of about zero to four electron volts. According to Cloutier and Schiff (ref. 3) the range of electron energies over which the reaction



occurs is about seven to eleven eV. In cases where  $Y^-$  is polyatomic, vibrational excitation could occur and a third body collision may be necessary for stabilization of the ion. Thus, such an instance would involve a second order pressure dependence at low pressures and a first order dependence at higher pressures.

Case (3) may occur as the result of an electron striking a molecule, exciting it to an unstable state which dissociates spontaneously into positive and negative ions. In this case the electron is not captured but merely acts as a source of energy needed to cause the electronic transitions necessary for such a dissociation.

Hagstrum and Tate (ref. 5) have shown by mass spectrometric methods that in  $O_2$ , CO, and NO,  $O^-$  is produced both by a dissociative capture process and by dissociation of the molecules into positive and negative ions. In all three molecules the appearance potential of  $O^-$  by the latter process is in the neighborhood of 20 eV.

In the work of Curran and Fox (ref. 2) and of Cloutier and Schiff (ref. 3) on  $N_2O$  and NO respectively only  $O^-$  is reported as appearing in the negative ion mass spectra of the gases. Knox and Burt (ref. 6) also found only  $O^-$  in the two gases. However, Rudolph, Melton, and Begun (ref. 7) report the formation of  $NO^-$  in both gases. They suggest that secondary processes are partially responsible for its formation. In part, this work is an attempt to carry the study of the formation of  $NO^-$  in  $N_2O$  and NO to higher pressures than were used by Rudolph, et al.

## Surface Phenomena

In 1936, Arnot and Milligan (ref. 8) reported experimental evidence which indicated that a positive ion, upon collision with a metal surface, may capture two electrons to form a negative ion. They found that when  $\text{Hg}^+$  ions of about 200 eV energy impinge upon nickel or tungsten surfaces the chance of producing  $\text{Hg}^-$  ions is about 1 in  $10^4$ . Similarly,  $\text{H}_2^+$  ions were found to produce  $\text{H}^-$  ions. They found that the negative ions were produced irrespective of whether the surfaces were hot or cold. In 1935 (ref. 9), it had been observed experimentally that negative ions are formed on a surface from which atoms or molecules are evaporated. Zandberg and Ionov (ref. 10) give an extensive review of the formation of positive and negative ions at a hot surface by surface ionization.

Arnot (ref. 8) proposed the following mechanism for the formation of a negative atomic ion from a positive atomic ion striking a metal surface. The positive ion first captures an electron from the surface placing the atom into an excited state. The excited atom then captures an electron from the surface and becomes a negative ion. This double capture process will be energetically favorable provided the sum of the ionization potential and the electron affinity of the incident atom is greater than twice the work function of the surface. Smith (ref. 11) worked out the quantum mechanical details of this process and found good agreement between theory and experimental results.

By using an apparatus which could be thoroughly degassed, Sloan and Press (ref. 12) were unable to find  $\text{Hg}^-$  ions being produced as a result of bombarding a nickel surface with  $\text{Hg}^+$  ions. Arnot and Beckett (ref. 13) found that the negative ion spectra produced by  $\text{Ar}^+$ ,  $\text{N}_2^+$ , and  $\text{Hg}^+$  striking a filament that had not been degassed to contain the same peaks, including ions of masses 12, 16, 24, 29, 32, 38, 44, and 51. The ions of mass 16 and 32 were identified as  $\text{O}^-$  and  $\text{O}_2^-$  while mass 24 may have been  $\text{C}_2^-$ . These ions were produced from gases adsorbed on the surface reacting with the bombarding ions of adequate energy. These peaks were removed by degassing the filament.

In experiments involving the efficiency of ionization by electron bombardment in several gases, Marmet and Morrison (ref. 14) explained the time varying nature of their data by considering that ionization at metal surfaces in their apparatus contributed to the spectra.

The final part of this work deals with the study of a negative ion in the spectra of  $\text{N}_2\text{O}$  and  $\text{NO}$  which seems to arise in much the same manner as the ions observed by Arnot and co-workers (ref. 8,13).



## EXPERIMENTAL

### Apparatus

Mass spectrometer and ion source. The mass spectrometer used in this work is a first order direction focusing instrument with 60-degree, 12-inch radius-of-curvature magnetic deflection. It is schematically illustrated in Figure 1. The ion source which was designed by S. O. Colgate (ref. 15) is contained in sections 1 and 2. Differential pumping on the filament is provided through section 6. Section 3 is the analyzer region, section 5 is the deflecting magnet, and section 4 houses a Nuclide Analysis 16-stage electron multiplier, Model EM-1. The electron multiplier is connected to a Cary, Model 31, vibrating reed electrometer. The instrument is evacuated through tubes P<sub>1</sub>, P<sub>2</sub>, and P<sub>3</sub> from sections 2, 3, and 6. Each of these tubes is connected through a liquid nitrogen trap to a mercury diffusion pump having a pumping speed of 80 liters per second. The diffusion pumps are connected to a Welch mechanical pump with a pumping speed of 375 liters per minute.

A schematic diagram of the ion source is shown in Figure 2. In this diagram F denotes the filament which is a thoria coated iridium strip, A is the anode, G<sub>1</sub> and G<sub>2</sub> are electron beam focusing electrodes, R is the repeller, T is the electron trap, and J<sub>1</sub> through J<sub>6</sub> are ion accelerating and focusing electrodes. The ion source contains a Pirani gauge, P, which permits direct pressure measurements in the ionization chamber, I. The temperature of the gas in the ionization chamber is controlled by circulating silicone oil from a constant temperature bath through a brass block which houses the chamber. The Pirani gauge is calibrated against a McLeod gauge.

Gas handling system. The gases used in this work are obtained from Matheson Company. The nitrous oxide has a minimum purity of 98 per cent with the principal impurity being air. Minimum purity of the nitric oxide is 99 per cent, the major impurities being carbon dioxide and nitrogen.

A diagram of the gas handling and pumping system is shown in Figure 3. Part of the system is designed for handling corrosive gases, such as NO. The nitrous oxide storage and purification system consists of a high pressure sample cylinder, a Matheson needle valve, V<sub>12</sub>, eight glass stopcocks, V<sub>1</sub>, V<sub>5</sub> through V<sub>11</sub>, two glass freeze bulbs, B<sub>1</sub> and B<sub>2</sub>, a mercury manometer, and a 12-liter glass storage bottle. This system is evacuated by a mercury diffusion pump, D.P. 1, connected to a Welch mechanical pump. The nitric oxide storage system consists of a high pressure sample cylinder, a Matheson needle valve, V<sub>4</sub>, a high pressure gauge, G<sub>2</sub>, a stainless steel storage tank, T, a Marsh absolute pressure gauge, G<sub>1</sub>, and a 3/8-inch composition seat Henry valve, V<sub>3</sub>. The leak system has one 3/8-inch Henry valve, V<sub>13</sub>, two 1/4-inch Hoke valves, V<sub>14</sub> and V<sub>16</sub>, and a stainless steel bellows type leak valve, L<sub>1</sub>, having a stem taper of 1000:1. The rest of the leak system is used for atmospheric gases. The nitric oxide storage system and the leak system are evacuated by a Consolidated Vacuum Corporation oil diffusion pump, D.P. 2, connected to a Cenco mechanical pump. The vacuum in the NO storage system and in the leak system is

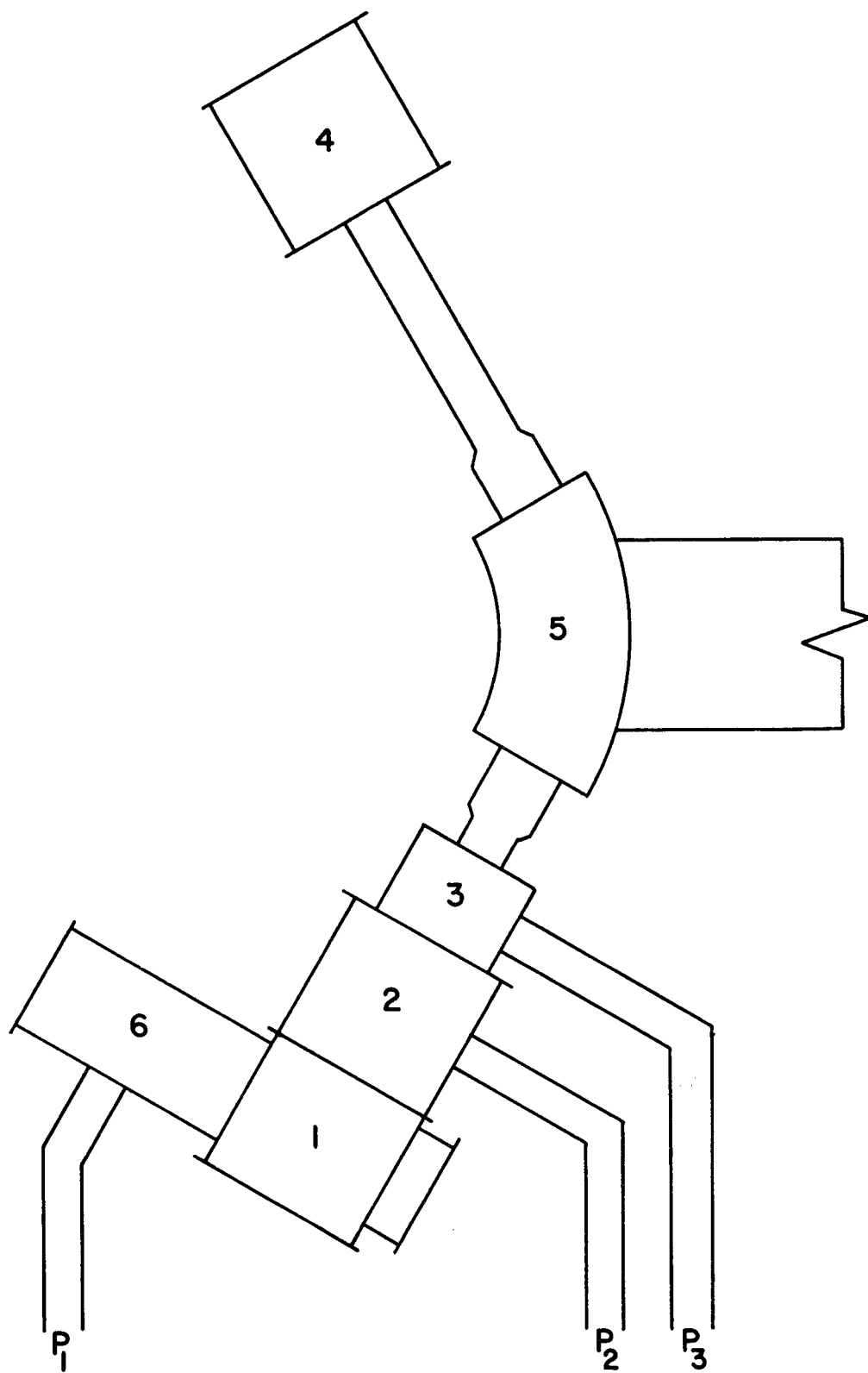
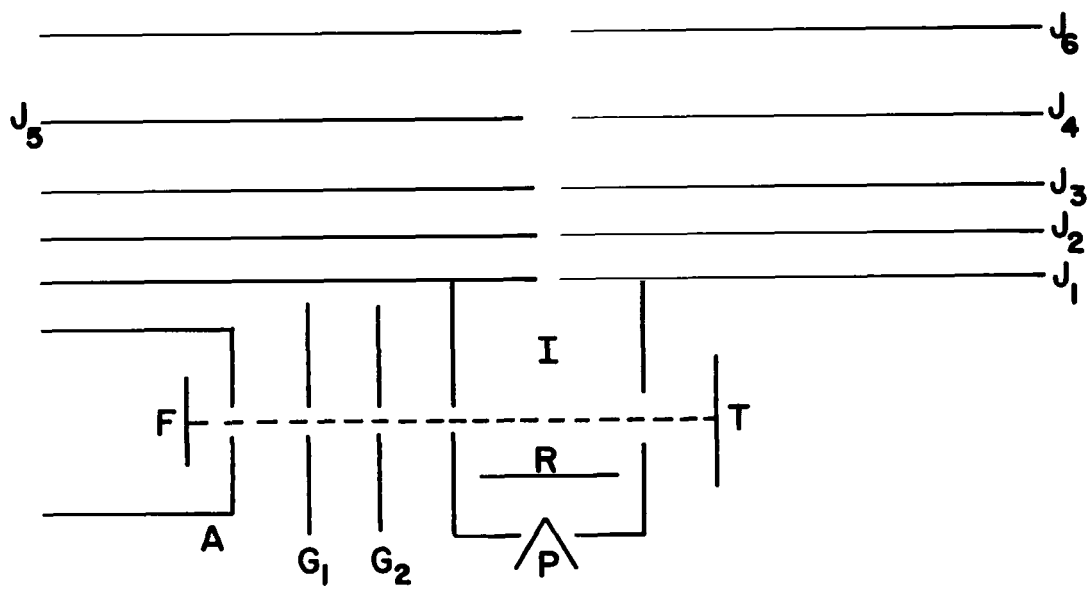
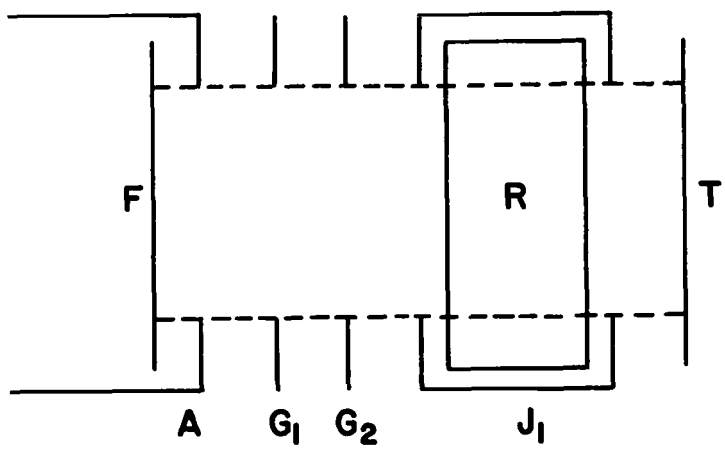


Fig. 1.-Schematic diagram of the mass spectrometer.



SIDE VIEW



TOP VIEW

Fig. 2.-Schematic diagram of the ion source.

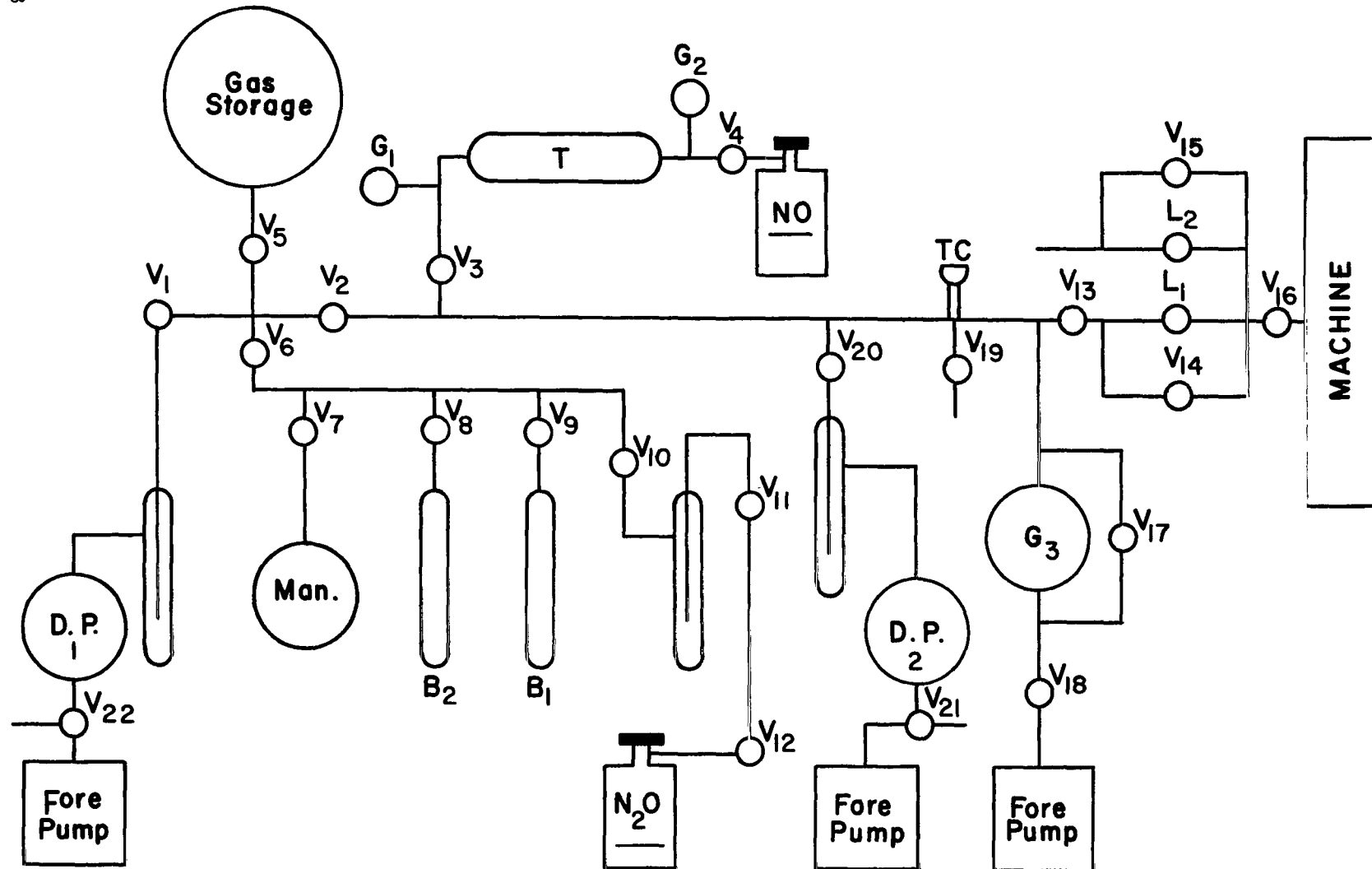


Fig. 3.-Gas handling system

checked by a Consolidated Electrodynamics Corporation thermocouple gauge. Gauge G<sub>3</sub> is a Wallace and Tiernan differential pressure gauge for measuring pressures greater than one mm Hg.

### Procedure

N<sub>2</sub>O purification. To evacuate the N<sub>2</sub>O purification system, valves V<sub>2</sub> and V<sub>5</sub> are closed, valves V<sub>1</sub>, V<sub>6</sub>, V<sub>7</sub>, V<sub>8</sub>, V<sub>9</sub>, V<sub>10</sub>, V<sub>11</sub>, are opened and D.P. 1 is turned on. The system is flushed twice with N<sub>2</sub>O and evacuated again. V<sub>6</sub> and V<sub>8</sub> are then closed. N<sub>2</sub>O is leaked into the system to a pressure of approximately one atmosphere through a dry ice trap and frozen out into B<sub>1</sub> by means of a liquid nitrogen bath. Any residual gases are pumped away. The liquid nitrogen bath is removed to allow about one-fourth of the frozen material to vaporize. Then V<sub>9</sub> is closed, the liquid nitrogen bath replaced around B<sub>1</sub>, and that portion of the gas pumped away. V<sub>9</sub> is then opened and the liquid nitrogen removed from B<sub>1</sub> until approximately one-half of the original sample has vaporized. This portion of gas is frozen out into B<sub>2</sub>. The remainder of the original sample is discarded. This procedure is repeated several times. Then the gas is transferred from B<sub>2</sub> to the gas storage bottle where it is frozen out into a cold trap and pumped on for about two hours to remove any residual N<sub>2</sub> or O<sub>2</sub> that may be present. The purity of the gas is estimated to be better than 99.5 per cent.

Measurements of mass spectra. For the positive ion measurements, the energy of the ionizing electrons is 70 electron volts, the trap voltage is five volts positive with respect to J<sub>1</sub>, and the ion accelerating potential is 5,000 volts. The electron energy for the negative ion studies is 30 eV, the trap voltage is adjusted for maximum trap current, and the ion accelerating potential is 6,500 volts. The repeller voltage, in most cases, is plus or minus 20 volts with respect to J<sub>1</sub> depending on whether positive ions or negative ions are being observed. The spectra were observed by sweeping the magnetic field at approximately one mass unit every 30 seconds. When obtaining the ratios of mass 30 to mass 16 and of mass 26 to mass 16 in the negative ion spectra, the desired peak is swept at the speed given above and the field is changed manually to a point where the next peak of interest can be swept without a great deal of time lapse between peaks. In all cases, the mass spectrometer is focused for maximum intensity of the primary ion of interest. The peak heights are recorded on a Varian type G-11 recorder.

The masses are determined by the use of a Harvey-Wells NMR Precision Gaussmeter. The gaussmeter is calibrated against peaks of known mass.

The temperature of the gas in the ionization chamber is 40 degrees Centigrade for all the gases used.

## RESULTS

### Positive Ions

As was stated in the Introduction, the primary positive ions in  $N_2O$  are  $N_2O^+$  ( $m/e = 44$ ),  $NO^+$  ( $m/e = 30$ ),  $N_2^+$  ( $m/e = 28$ ),  $O^+$  ( $m/e = 16$ ), and  $N^+$  ( $m/e = 14$ ). The primary ions in  $NO$  are  $NO^+$ ,  $N^+$ , and  $O^+$ . In  $N_2O$ , excluding the primary ions, peaks were observed at  $m/e$  of 46, 45, 32, 31, 29, 18, and 15. It is obvious that these peaks can be attributed to isotopes of the primary ions. However, in order to determine whether any of these peaks are due to secondary reactions, the ratios of their intensities to the primary ion of which they are probable isotopes were taken as a function of pressure. The same was done for peaks occurring at  $m/e$  of 44, 32, 31, 24, 18, and 15 in the  $NO$  spectrum. No pressure dependence was noted for any of these ratios over the pressure range 0-0.5 microns. With the exception of masses 44 and 28 in  $NO$ , all the ratios were very nearly the same as those calculated from the abundances of naturally occurring  $N^{15}$  and  $O^{18}$  isotopes of nitrogen and oxygen (ref. 16). These peaks may be attributed to small  $CO_2$  and  $N_2$  impurities in the nitric oxide.

### Negative Ions

In the negative ion spectrum of both  $N_2O$  and  $NO$ , peaks were observed at masses 16, 26, and 30. Mass 16 is attributed to  $O^-$  and mass 30 to  $NO^-$  in both gases. The ratios of masses 26 and 30 to mass 16 were measured as a function of pressure.

A plot of  $I_{NO^-}/I_{O^-}$  versus pressure (Figure 4) in  $N_2O$  gives a straight line with a very small slope. A plot of  $I_{30}/I_{16}$  versus pressure in  $NO$  (Figure 5), which includes a point from the work of Rudolph, Melton, and Begun (ref. 7), shows a pressure dependence at low pressure and an independence with pressure at higher pressures.

Plots of  $I_{26}/I_{O^-}$  versus pressure in  $N_2O$  and  $NO$  (Figures 6 and 7) give a slope of zero, within experimental error, indicating that the number of mass 26 ions being produced is proportional to the number of some primary ion being produced as a result of electron bombardment. This also indicates that the mass 26 ion does not result from a gas phase reaction. It appears that this peak is due to  $CN^-$ . The only other negative ion of mass 26 which could conceivably be present is  $C_2H_2^-$ .  $C_2H_2^-$  is reported by Melton and Rudolph (ref. 17) as being present in the spectra of methane, ethane, acetylene, n-butane, and several alcohols. In most cases the number of  $C_2H_2^-$  present in the negative ion spectra of these substances is less than 0.1 per cent of the total number of negative ions. In ethane,  $C_2H_2^-$  makes up about 2 per cent of the negative ions and in n-butane, about 3 per cent. Therefore, since the mass 26 peak is so small in the negative ion spectra of hydrocarbons, it probably would not appear here. A small peak was found at mass 27 in both gases. An isotopic analysis was performed on the ion and the ratio of the intensities of mass 27 to

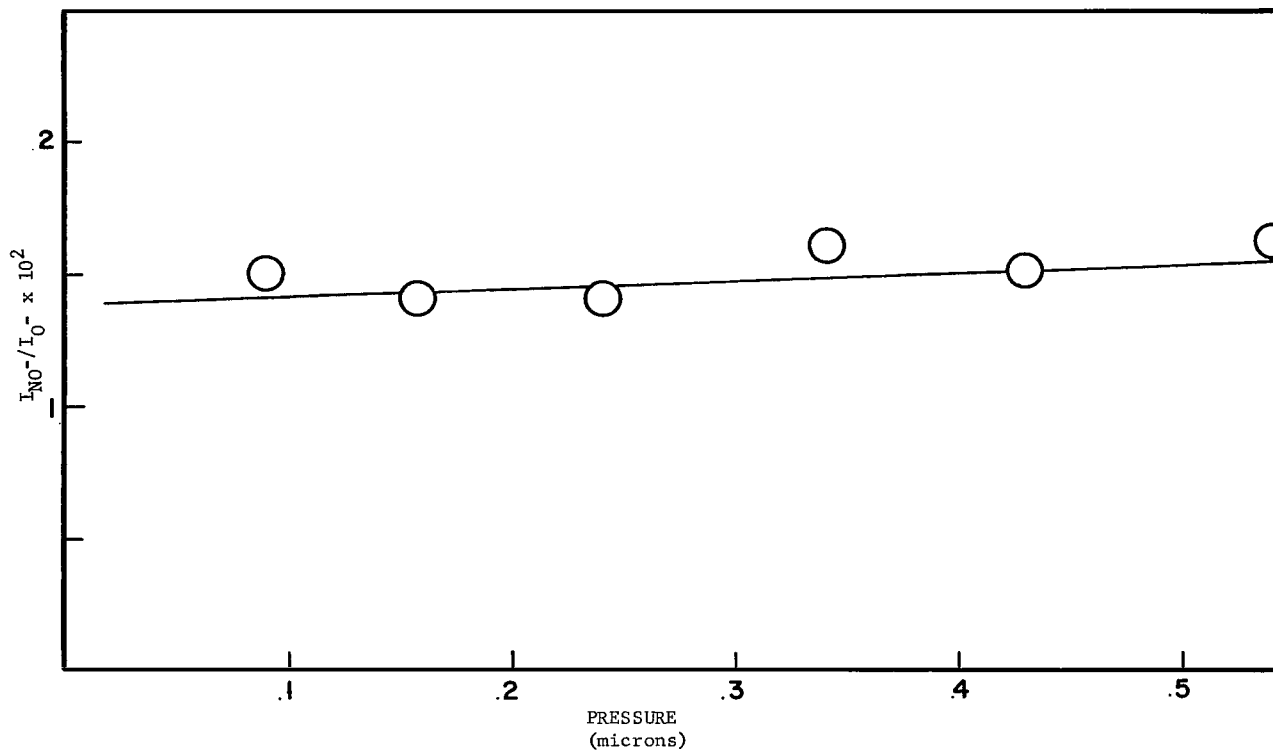


Fig. 4.- $I_{NO^-}/I_{O^-}$  versus pressure of nitrous oxide.

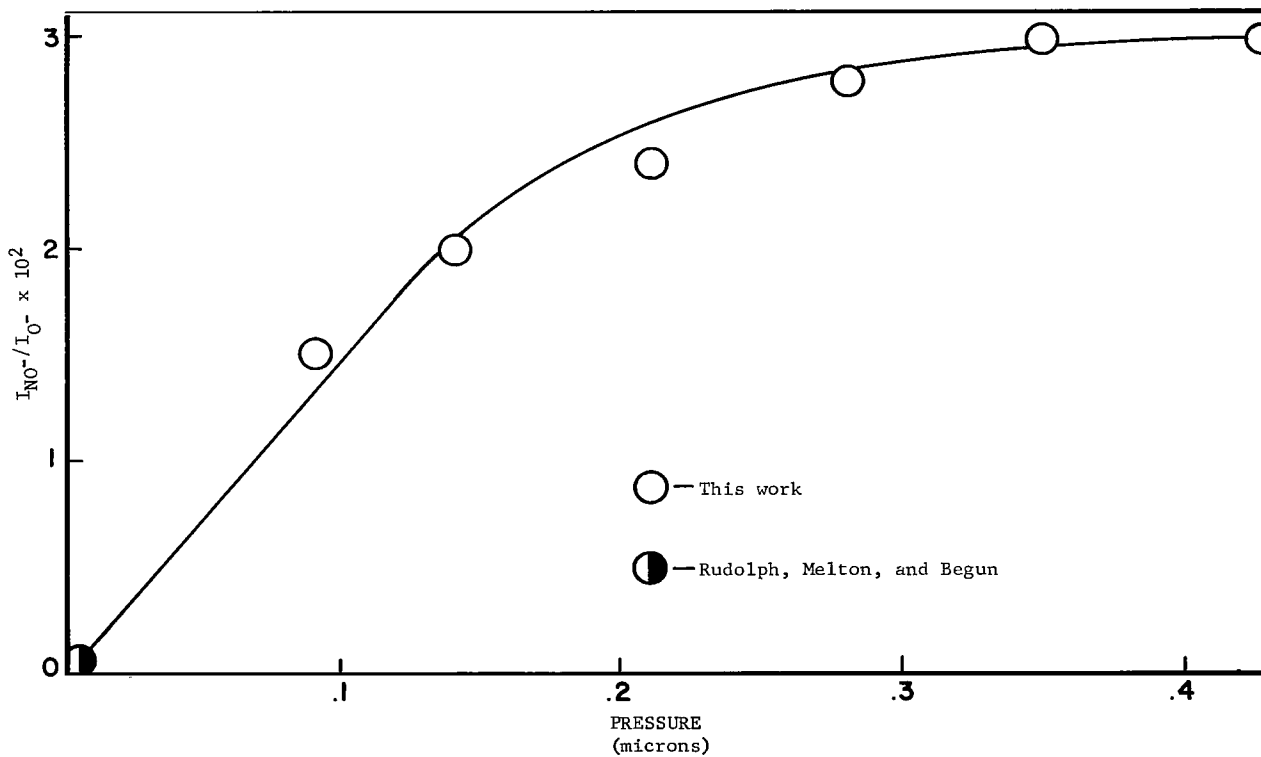


Fig. 5.- $I_{NO^-}/I_{O^-}$  versus pressure of nitric oxide.

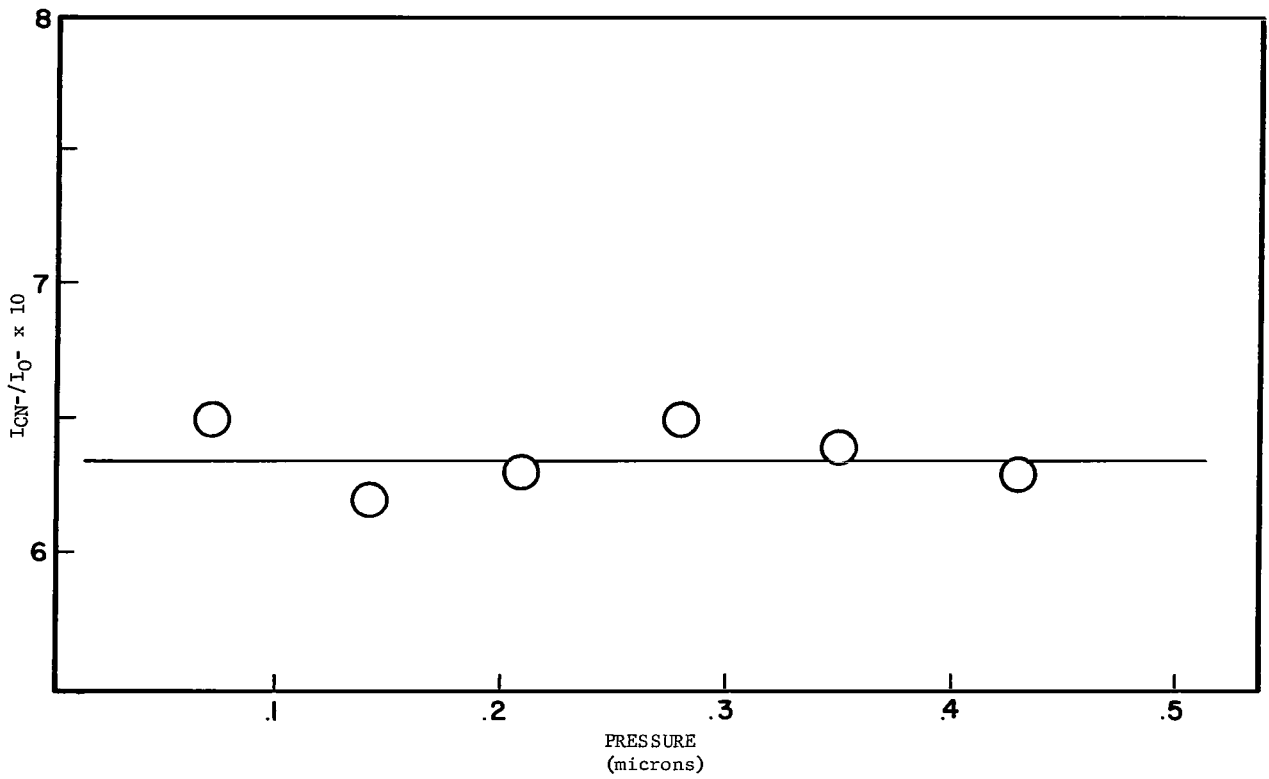


Fig. 6.- $I_{CN^-}/I_0^-$  versus pressure of nitric oxide.

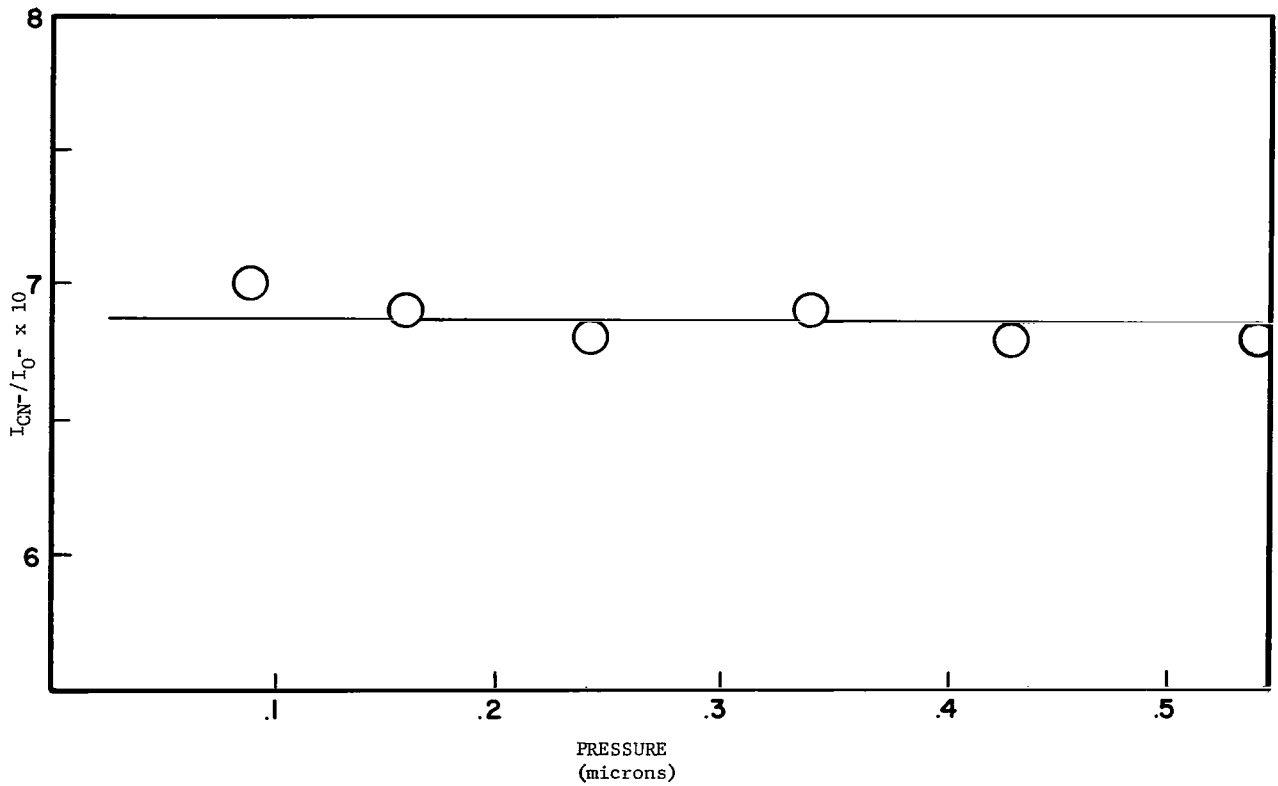


Fig. 7.- $I_{CN^-}/I_0^-$  versus pressure of nitrous oxide.



mass 26 is 0.014. This is almost exactly the ratio which is to be expected from the  $(C^{13}N^{14})^-$  and  $(C^{12}N^{15})^-$  contributions to  $CN^-$  (0.0147) (ref. 16). The naturally occurring abundance of  $(C^{13}C^{12}H_2)^-$  in  $C_2H_2^-$  is 2.2 per cent (ref. 16). To be sure that the mass 26 ion was not formed by an ion-molecule reaction involving a  $CO_2$  impurity, which is about 0.6 per cent in the NO sample used, a mixture of 98 per cent NO and 2 per cent  $CO_2$  was introduced into the machine.  $I_{CN^-}/I_{O^-}$  was then measured as a function of pressure. The ratio was found to be unchanged and constant with pressure.

The appearance potential of  $CN^-$  was measured in NO (Figure 8) and found to be 19 eV. This is nearly the same as the value of 19.5 eV for the appearance potential of  $N^+$  in NO reported by Cloutier and Schiff (ref. 3). This observation suggested that the precursor of the  $CN^-$  ion was  $N^+$ . To verify this, pure  $N_2$  was introduced into the machine and the mass 26 peak reappeared. Its appearance potential was measured (Figure 9) and found to be 15 eV with a discontinuity in the curve at 28 eV. The energy scale for the electrons was not calibrated, therefore the experimental error in determining these appearance potentials may be in the neighborhood of plus or minus two or three electron volts. Hence, the values determined here are the same as the reported appearance potentials of 15.6 eV for  $N_2^+$  and 24.3 eV for  $N^+$  in nitrogen (ref. 18) within the experimental error.

The  $I_{CN^-}/I_{O^-}$  ratio was measured as a function of repeller voltage and found to be independent of this voltage and therefore independent of the energy of the positive ions striking the repeller.

One explanation for the formation of  $CN^-$  in  $N_2O$ , NO, and  $N_2$  is that  $N^+$  and  $N_2^+$  from these gases could be reacting on the repeller plate with hydrocarbons that had been adsorbed there in previous experiments using this ion-source. An attempt was made to clean the repeller plate by running a high voltage discharge from it for 30 minutes in an atmosphere of oxygen. This would bring about the formation of  $CO_2$  from the hydrocarbons which could be frozen out in the liquid nitrogen traps. When this had been done a vacuum run was made to determine the background of  $O^-$ . The  $O^-$  peak was less than 0.1 per cent of the  $O^-$  peak in NO. The  $I_{CN^-}/I_{O^-}$  ratio was found to be about one-half of that obtained before the clean-up procedure and did not vary with pressure.

## CONCLUSIONS

### Positive Ion Studies

In the positive ion spectra of both  $N_2O$  and NO, no ion-molecule reactions are observed. In  $N_2O$ , plots of  $I_{46}/I_{44}$  and  $I_{32}/I_{30}$  versus pressure substantiate the fact that  $NO_2^+$  and  $O_2^+$  are not produced to any appreciable extent as a result of secondary reactions in this gas. It has been shown that the peaks at masses 46 and 32 are due to an isotope of oxygen in  $N_2O^+$  and  $NO^+$  respectively. Plots of  $I_{44}/I_{30}$ ,  $I_{28}/I_{30}$ , and  $I_{32}/I_{30}$  versus pressure of NO verify that mass 44 ( $CO_2^+$ ) and mass 28 ( $N_2^+$ ) are impurities in the gas and that mass 32 is not due to  $O_2^+$  but to the  $O^{18}$  isotope of oxygen in  $NO^+$ .

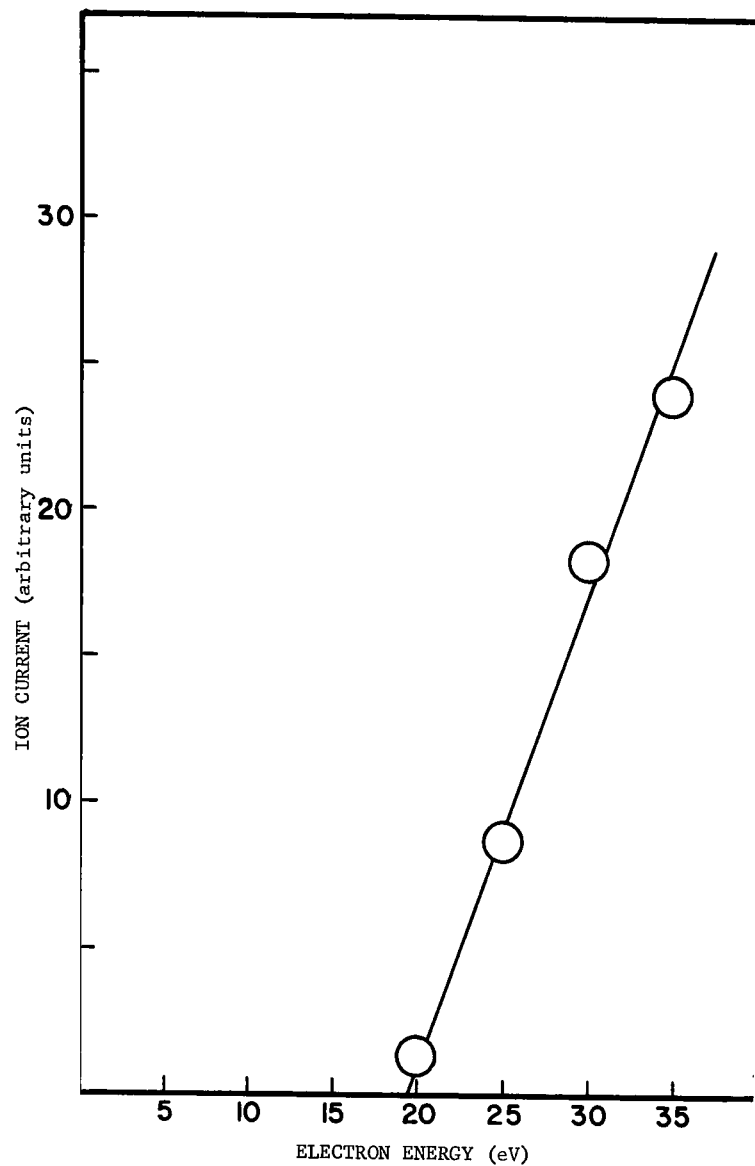


Fig. 8.-Appearance potential of mass 26 negative ion in nitric oxide.

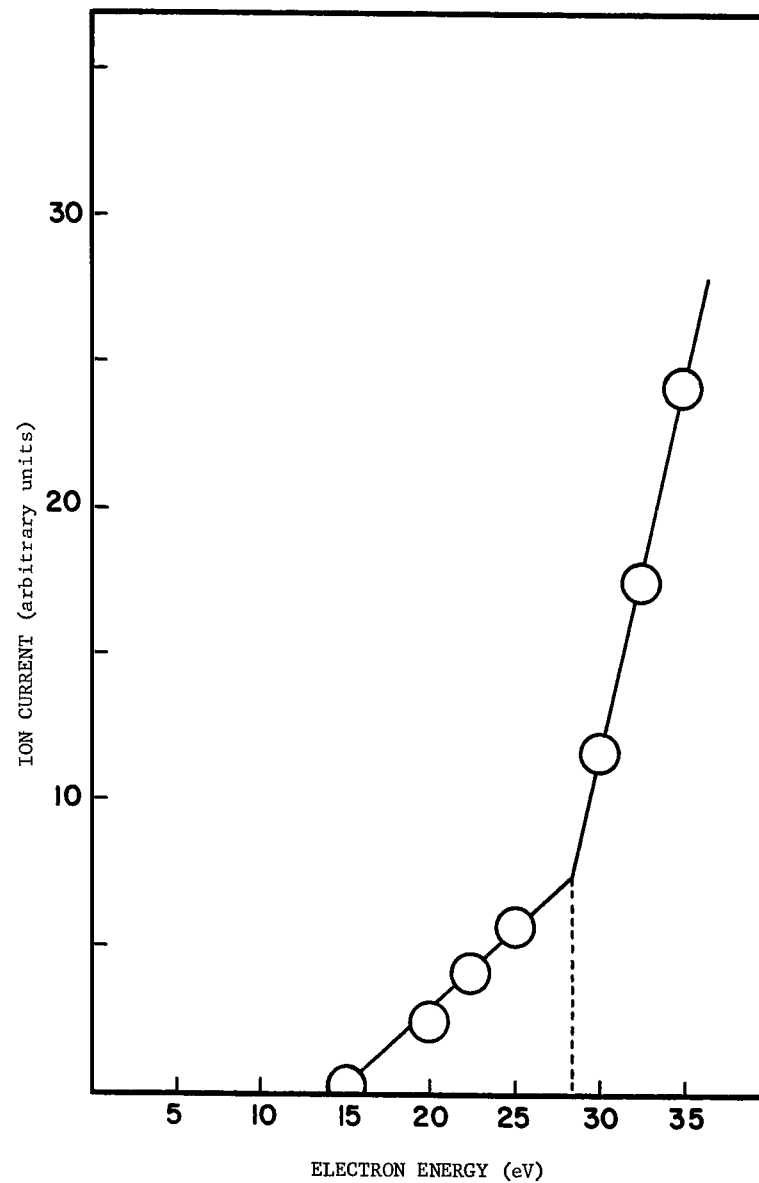
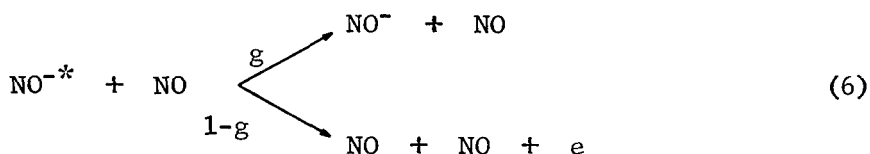
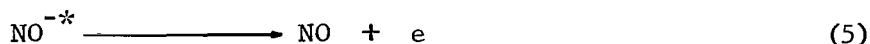
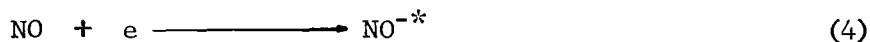


Fig. 9.-Appearance potential of mass 26 negative ion in nitrogen.

If any ion-molecule reactions are occurring in these gases, the sensitivity of the apparatus is such that the cross-sections must be less than  $0.01 \times 10^{-16}$  cm.<sup>2</sup>

### Negative Ion Studies

The dependence upon pressure of the formation of  $\text{NO}^-$  from  $\text{NO}$  molecules is second order at low pressures and first order at higher pressures. In terms of the measured quantities, the ratio of the  $\text{NO}^-$  to  $\text{O}^-$  ion intensities is first order pressure dependent at low pressures and independent of pressure at higher pressures. This is due to the  $\text{O}^-$  ion intensity being directly proportional to pressure. Using a point taken from the work of Rudolph, Melton, and Begun and the data obtained in this work, a plot of  $I_{\text{NO}^-}/I_{\text{O}^-}$  versus pressure of  $\text{NO}$  was made. The plot shows that the ratio increases up to a pressure of about 0.1 microns Hg. At this point the ratio starts to become independent of pressure and at about a pressure of about 0.3 to 0.4 microns Hg the slope goes to zero. These results may indicate that  $\text{NO}^-$  ions are produced by electron bombardment in  $\text{NO}$  as highly excited ions requiring subsequent collisions for stabilization. The following mechanism is proposed for such a process.



Where  $\text{NO}^{-*}$  denotes the excited state of the  $\text{NO}^-$  ion. An expression for the pressure dependence of the  $\text{NO}^-$  formation may be derived in the following manner.

Let  $(I_{\text{NO}^{-*}})_0$  be the number of  $\text{NO}^{-*}$  ions produced per second as the electron beam travels a distance  $l_e$  through the gas. Then

$$(I_{\text{NO}^{-*}})_0 = I_e N p \sigma_1 l_e \quad (7)$$

$(I_{\text{NO}^{-*}})_0$  is the initial intensity of the  $\text{NO}^{-*}$  ions,  $N$  is the number of molecules per unit volume at one torr pressure,  $p$  is the pressure of the gas in torr,  $\sigma_1$  is the cross section for reaction (4), and  $l_e$  is the length of the electron beam in the ionization chamber. As the  $\text{NO}^{-*}$  ions are accelerated toward the exit slit of the ionization chamber  $(I_{\text{NO}^{-*}})_0$  is diminished due to reactions (5) and (6). The intensity of  $\text{NO}^{-*}$  ions after having traveled a distance  $l$  through the neutral molecules is

$$(I_{\text{NO}^{-*}})_1 = (I_{\text{NO}^{-*}})_0 \exp[-(K + \sigma_2 N p)l] \quad (8)$$

where the constant  $K$  determines the loss of excited ions by reaction (5) and

$\sigma_2$  is the sum of the cross sections for the disappearance of  $\text{NO}^{-*}$  ions by reactions (6). Since  $\text{NO}^-$  ions are produced only as a result of the first of reactions (6), the  $\text{NO}^-$  ion intensity will be only a fraction of the attenuation of the  $\text{NO}^{-*}$  intensity. The attenuation of  $I_{\text{NO}^{-*}}$  is

$$(I_{\text{NO}^{-*}})_0 - (I_{\text{NO}^{-*}})_1 = (I_{\text{NO}^{-*}})_0 \left\{ 1 - \exp[-(K + \sigma_2 N_p)l] \right\} \quad (9)$$

and

$$I_{\text{NO}^-} = g \left[ \frac{\sigma_2 N_p}{\sigma_2 N_p + K} \right] (I_{\text{NO}^{-*}})_0 \left\{ 1 - \exp[-(K + \sigma_2 N_p)l] \right\} \quad (10)$$

Here,  $\left[ \frac{\sigma_2 N_p}{\sigma_2 N_p + K} \right]$  is the fraction of  $\text{NO}^{-*}$  ions disappearing due to both of reactions (6) and  $g$  is the fraction disappearing due to the first of reactions (6). Substituting (7) into (10) gives

$$I_{\text{NO}^-} = g \left[ \frac{\sigma_2 N_p}{\sigma_2 N_p + K} \right] I_{eNp} \sigma_1 l_e \left\{ 1 - \exp[-(K + \sigma_2 N_p)l] \right\} \quad (11)$$

$\text{O}^-$  ions are produced by electron bombardment as primary ions in  $\text{NO}$ , hence their formation provides a convenient means of measuring the pressure dependence of the  $\text{NO}^-$  ion formation. The intensity of the  $\text{O}^-$  ions is

$$I_{\text{O}^-} = I_e \sigma_0 N_p l_e \quad (12)$$

where  $\sigma_0$  is the cross section for the  $\text{O}^-$  formation process. Dividing (11) by (12) gives

$$I_{\text{NO}^-}/I_{\text{O}^-} = g \left( \frac{\sigma_1}{\sigma_0} \right) \left[ \frac{\sigma_2 N_p}{\sigma_2 N_p + K} \right] \left\{ 1 - \exp[-(K + \sigma_2 N_p)l] \right\} \quad (13)$$

The constant  $K$  may be expressed as  $1/\tau v$ , where  $\tau$  is the lifetime of the excited ion and  $v$  its average velocity.

At low pressures where the probability of  $\text{NO}^{-*}$  ions being involved in stabilization collisions is small,  $\sigma_2 N_p$  becomes small with respect to  $K$ , and

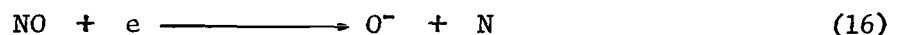
$$I_{\text{NO}^-}/I_{\text{O}^-} = g \left( \frac{\sigma_1}{\sigma_0} \right) \left( \frac{\sigma_2 N_p}{K} \right) [1 - \exp(-Kl)] \quad (14)$$

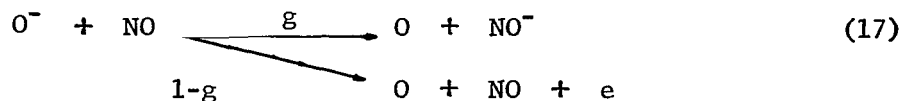
Hence at low pressures the ratio of the  $\text{NO}^-$  to  $\text{O}^-$  intensities is directly proportional to the pressure or the  $\text{NO}^-$  intensity is proportional to the square of the pressure. At high pressure where  $\sigma_2 N_p \gg K$ , equation (13) reduces to

$$I_{\text{NO}^-}/I_{\text{O}^-} = g \left( \frac{\sigma_1}{\sigma_0} \right) \quad (15)$$

Hence, at high pressures where the chances of stabilization collisions are good, the ratio is independent of pressure and the  $\text{NO}^-$  intensity is first order pressure dependent. This mechanism is analogous to that for the formation of  $\text{O}_2^-$  from  $\text{O}_2$  by electron impact (ref. 4,19).

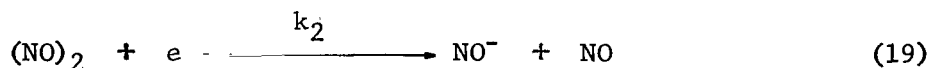
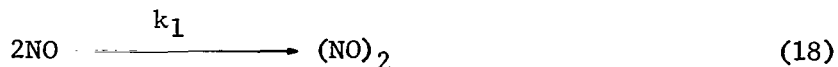
It should be pointed out that another possible mechanism is qualitatively satisfactory:





Equation (13) will still apply if  $K$  is put equal to zero and  $\sigma_1 = \sigma_0$ . In this case  $\sigma_2$  would represent the sum of the cross sections for the two processes in equation (17). The data can be fit within the experimental error only by taking a large value for  $\sigma_2$  of about  $3,000 \text{ \AA}^2$  with  $K = 1$ . This is not too unreasonable on the basis of the collision stabilization mechanism, equations (4) - (6), since  $g$  may be small, i.e., the cross section for destruction of the excited  $\text{NO}^-$  on collision may be much larger than the cross section for stabilization. Although the cross sections for electron detachment from negative ions in their ground state are not large (ref. 20), the cross section for a highly excited ion may be very large. With  $K = 0$  for the charge transfer mechanism above, a much larger value of  $\sigma_2$  is required.

Bradbury (ref. 21) has proposed that the  $\text{NO}^-$  formation comes about by a dissociative capture process via the reaction mechanism



It can be shown that this proposal is inconsistent with the observed data. The equilibrium constant for reaction (17) is given by

$$K = \frac{P_{(\text{NO})_2}}{P_{\text{NO}}^2} \quad (20)$$

where  $P_{\text{NO}}$  and  $P_{(\text{NO})_2}$  are the partial pressures of  $\text{NO}$  and  $(\text{NO})_2$  respectively. The total pressure,  $P$ , of the two gases is

$$P = P_{\text{NO}} + P_{(\text{NO})_2} \quad (21)$$

The rate of formation,  $R$ , of  $\text{NO}^-$  will be

$$R = k_2 P_{(\text{NO})_2} \quad (22)$$

$$= k_2 K P_{\text{NO}}^2 \quad (23)$$

Substituting (20) into (21) and (22) gives

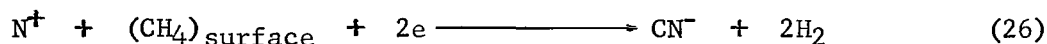
$$R = k_2 (P - P_{\text{NO}}) \quad (24)$$

$$= k_2 K (P - P_{(\text{NO})_2})^2 \quad (25)$$

In order for the  $\text{NO}^-$  formation to be first order pressure dependent the partial pressure of  $(\text{NO})_2$  will have to be very nearly equal to the total pressure or the partial pressure of  $\text{NO}$  will have to be negligible. This is shown by equations (24) and (25). Calculations by Johnston and Weimer (ref. 22) show that the degree of association in  $\text{NO}$  to form the dimer is about 0.2 per cent at a temperature of 193 degrees Kelvin and 160 atmospheres pressure. Thus, at the temperature of the gas here (313 degrees K), the total pressure would have to be far in excess of 160 atmospheres in order for the partial pressure of  $(\text{NO})_2$  to approach the measured pressure. Therefore, the reaction mechanism proposed by Bradbury is not the correct one. Every indication seems to point to reactions (4), (5), and (6) as the correct mechanism for the formation of  $\text{NO}^-$  from  $\text{NO}$ .

Over the range of pressures used in this experiment, the formation of  $\text{NO}^-$  from  $\text{N}_2\text{O}$  seems to be very slightly dependent upon the pressure. Rudolph, Melton, and Begun (ref. 7) find that  $\text{NO}^-$  formation departs from linearity with pressure at a pressure of about  $8 \times 10^{-6}$  mm Hg and indicate that its formation is partially due to an ion-molecule reaction and partially due to dissociative attachment. The slope of the plot of  $I_{30}/I_{16}$  versus pressure from their data comes out to be about one order of magnitude greater than the slope obtained in this work at higher pressures. This indicates that the pressure dependence of the ratio may be due in part to an  $\text{NO}^-$  ion being formed by dissociative attachment in an excited state which needs a third body collision for stabilization.

It has been mentioned earlier in this report that the mass 26 ion observed in the negative ion spectra of  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{N}_2$  appears to be due to  $\text{CN}^-$ . A possible explanation of the phenomenon is that the ion is formed on the surface of the repeller (R in Figure 2) by a reaction of the following type



Some other hydrocarbon may be involved, and the formation of  $\text{H}_2$  is surmised. The positive ion is formed in the electron beam and accelerated toward the repeller which is at a negative potential with respect to the ionization chamber. Upon striking the surface the ion is neutralized by an electron from the metal to atomic nitrogen which reacts with an adsorbed molecule to form  $\text{CN}$ . An electron from the metal surface is then attached to the  $\text{CN}$  molecule to form  $\text{CN}^-$  which is accelerated away from the surface. The efficiency of the process is about  $10^{-3}$  per cent. This is in the neighborhood of some of the efficiencies of processes observed by Arnot and his co-workers (ref. 8,13). The major difference between this process and those is that the energy of the incident positive ions is less than 20 eV whereas, the positive ion energies in Arnot's work were, in general, in excess of 200 eV. The  $\text{CN}^-$  ions continued to appear when the incident ions had energies in the neighborhood of zero eV, and their abundance, relative to that of  $\text{O}^-$ , was constant. This observation suggests that the process does not require any kinetic energy from the incident ions. Marmet and Morrison (ref. 14) have shown that it is possible for ions to become trapped on the walls of the ionization chamber and remain there for as long as several seconds. Hence, there arises the possibility that the  $\text{CN}^-$  ions may be produced

on the ionization chamber walls as well as on the repeller plate if the reaction does not require any kinetic energy from the positive ions. That such a process may occur is not surprising when one stops to consider the number of molecules that may be adsorbed. If the walls adsorb a monolayer of molecules there will be approximately  $10^4$  times more molecules on the walls than in the volume of about one cc between the walls at a pressure of 0.1 microns Hg.

The fact that the relative abundance of  $CN^-$  to  $O^-$  decreased by one-half by cleaning the repeller suggests that the reaction occurs at the surface of the repeller. Of course, the clean-up procedure could have cleaned the walls of the ionization chamber also.

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