Ambipolar Diffusion and Electron Attachment in Nitric Oxide in the Temperature Range 196 to 358°K†

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Ambipolar diffusion and electron attachment rates were measured in nitric oxide at pressures from 0.01 to 16 Torr and at temperatures from 196 to 358°K. The gas was photoionized by single pulses of ultraviolet radiation, at and near Lyman-α, from a hydrogen lamp. Pulse lengths ranged from 10 to 300 μsec and ionization levels were kept low to reduce electron-ion recombination. Rates for the latter process are reported in a separate paper. Electron loss rates were measured by a microwave-cavity method used to record the decay following a single ionizing pulse. Ion identification was made by a mass spectrometer which sampled the ions diffusing through a small hole in the wall of the microwave cavity. Ultrahigh-vacuum techniques were used in gas purification and in production and measurement of ionization. The diffusion results are to some extent consistent with the theory of diffusion of electrons and a single positive ion species in the presence of negative ions. The mass-spectrometer observations indicate that NO^+ is the dominant positive ion in photoionized NO at all pressures. The measured mobility of NO^+ for 298°K, referred to 0°C and 760 Torr, is 1.9 ± 0.2 cm^2 sec^{-1} V^{-1}, corresponding to a $D_a p$ of 83 ± 8 cm^2 Torr sec^{-1}. The mobility decreases slowly as the gas temperature is raised from 196 to 358°K. At gas densities near 10^{17} cm^{-3}, the attachment results are characteristic of a three-body process, but at higher densities there is an anomalous rise in the attachemnt coefficient. The apparent three-body attachment coefficients for densities near 10^{17} cm^{-3} are $6.8\pm0.7\times10^{-31}$ cm^6 sec^{-1} at 196°K, $2.2\pm0.2\times10^{-31}$ at 298°K, and $1.1\pm0.1\times10^{-31}$ at 358°K and exhibit approximately a T^{-3} temperature dependence. The principal negative ion observed with the mass spectrometer was NO_2^-, and no NO^- or $(NO)_2^-$ ions were detected. Direct attachment to NO_2, present as a minute impurity, seems unlikely; the NO_2^- ions may be formed by rapid charge transfer from a primary negative ion or by an attachment reaction involving rearrangement.

I. INTRODUCTION

IN recent years there has been great interest in deionization processes in the atmospheric gases. Many laboratory studies have been made of ion mobility, ion identity, ambipolar diffusion, electron attachment to form negative ions, electron-ion recombination, and ion-ion recombination. Much of this interest is due to the potential applicability of the results to studies of the ionosphere or to an artificially ionized atmosphere. A review of these and related topics has been made recently by Biondi.[1]

In ionized nitrogen, the ions N^+, N_2^+, N_3^+, and N_4^+ have been identified,[2] mobilities have been measured,[3] and recombination with electrons has been studied.[4,5] In oxygen, the ions O^+, O_2^+, O_3^+, O^-, O_2^-, and O_3^- have been studied.[4-9]

Interest in nitric oxide stems from the fact that NO^+ is an important ion in the lower ionosphere, although the neutral gas is present only as a minor constituent.

Some previous work was done in this laboratory on diffusion, attachment, and recombination in NO at 300°K,[10] and on electron recombination with NO^+ ions at 2900°K in shock-heated air.[11]

Ion mobilities have been determined in rare gases,[1] nitrogen,[3] and oxygen[6-9] by means of drift tubes, in which ion transit times are measured in uniform applied electric fields. Also, studies of ambipolar diffusion in an ionized gas in a microwave cavity or waveguide yield values of the diffusion rate coefficient which are directly related to ion mobilities.[12-16] Agreement between drift-tube and microwave results is good where direct comparison can be made.

Electron attachment to form negative ions has been studied in drift tubes[6-9] as well as by microwave methods.[10,17,18]

The present paper reports studies of ambipolar diffusion and electron attachment in nitric oxide at

† Work sponsored by the U. S. Air Force Special Weapons Center and the Lockheed Independent Research Program.

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[10] R. C. Gunton and E. C. Y. Inn, J. Chem. Phys. **35**, 1896 (1961).

[11] R. P. Stein, M. Scheibe, M. W. Syverson, T. M. Shaw, and R. C. Gunton, Phys. Fluids **7**, 1641 (1964).

[12] M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).

[13] A. V. Phelps and S. C. Brown, Phys. Rev. **86**, 102 (1952).

[14] H. J. Oskam, Philips Res. Rept. **13**, 401 (1958).

[15] A. C. Faire and K. S. W. Champion, Phys. Rev. **113**, 1 (1959).

[16] H. J. Oskam and V. R. Mittelstadt, Phys. Rev. **132**, 1435 (1963).

[17] P. J. Chantry, J. L. Wharmby and J. B. Hasted, *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases, Munich, 1961* (North-Holland Publishing Company, Amsterdam (1962), p. 630; M. J. Mulcahy, M. C. Sexton, and J. J. Lennon, *ibid.*, p. 612.

[18] V. A. J. van Lint, J. Parez, M. E. Wyatt, and L. K. Nichols, U. S. Air Force Weapons Laboratory Report RTD TDR-63-3076, December 1963, Kirtland Air Force Base, New Mexico (unpublished).

pressures from 0.01 to 16 Torr and at temperatures from 196 to 358°K. Ion identification was made with a mass spectrometer. Measurements of electron-ion recombination are reported in the accompanying paper.[19]

II. EXPERIMENTAL APPARATUS AND PROCEDURES

The general plan of the apparatus for the study of electron-loss processes is shown in Fig. 1. Nitric oxide gas, contained in one of two microwave cavities, was photoionized by a pulse of uv radiation from a hydrogen capillary lamp. The decay of electron density in the cavity was measured by a microwave interferometer.

Photoionization was used in an attempt to produce a simple ionized gas consisting largely of NO^+ ions, electrons, and NO molecules. The usual electrical discharge would cause excessive dissociation leading to the production of undesirable amounts of impurities such as NO_2. Both lamp and cavity had windows of lithium fluoride which transmits photons of energy less than about 11.3 eV (wavelength longer than 1100 Å). The ionization potential of NO is 9.3 eV (1340 Å)[20] and the dissociation energy is about 6.5 eV (1910 Å). The spectrum of the hydrogen lamp, as observed with a vacuum uv monochromator, contained lines at 1216 Å (Lyman-α), 1280 Å, and 1600 Å. An intense molecular continuum was also observed. Since radiation above the dissociation limit may produce undesired photodissociation, a 1-mm air path at atmospheric pressure was left between lamp and cavity windows to reduce this undesired radiation through absorption by oxygen bands. Further, to minimize the cumulative effects of repeated photoexcitation of the gas, determinations of electron loss rates were made by a technique in which the whole decay curve was obtained from a single ionizing pulse. Small cumulative effects were noted typically only after 100 to 1000 pulses; therefore, rate determinations for a sample of gas were made using fewer than 10 single pulses. The hydrogen lamp was driven with pulses ranging in length from 10 to 300 μsec by a high-voltage pulser.

The photoionized electrons are ejected with excess kinetic energy up to 2 eV which is dissipated in collisions with the gas, or by rapid diffusion of hot electrons to the walls, or both. Thermalization of electrons in NO is rapid because of excitation of rotational and vibrational transitions in inelastic collisions as well as transfer of energy in elastic collisions. Calculation of the thermalization time for a pressure of 1 Torr, using measured inelasticity factors,[21] indicates a value of about 2 μsec.
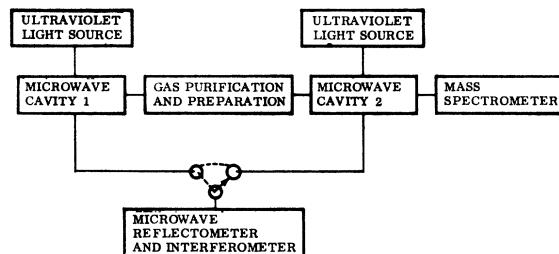

FIG. 1. Plan of the experimental apparatus.

The microwave cavities (Fig. 1) were constructed of type 304 stainless steel and designed to be bakeable to 350°C. They were electrically similar, having resonance frequencies near 9000 Mc/sec in the TM_{010} mode. Nitric oxide gas occupied the whole of the volume of each cavity. Cavity 1 was used for rate measurements with a static quantity of gas and was designed for operation in a liquid bath at temperatures ranging from 196 to 400°K. Further details of its construction are given in a separate paper.[22] Cavity 2, shown in Fig. 2, was designed for ion identification and was coupled to a mass spectrometer through a small hole of diameter 0.01 cm in one wall. The section of cavity wall containing the hole was insulated from the remainder of the cavity to permit application of a small pull-out voltage, typically 1 to 10 V.

The microwave cavity method used for measuring electron density during the decay period has been discussed in detail elsewhere.[23-25] A schematic diagram of the microwave system is shown in Fig. 3. The interferometer was used for the measurement of small electron densities, which produce small shifts of the cavity resonance frequency. It has been shown[25] that in the vicinity of resonance the change in phase angle of the reflection coefficient is very closely proportional to the change in cavity susceptance which, in turn, is proportional to average electron density in the cavity. The interferometer was adjusted to provide an output signal proportional to the change in phase of the reflection coefficient for small changes in phase and negligible change in amplitude. The interferometer signal was then nearly proportional to average electron density. This technique was checked by use of the repetitive method of Biondi[24] and proved feasible for electron densities less than about 10^9 cm^{-3}. For these low-electron densities the decay rates can be determined from a single ionizing pulse with an accuracy of about 5%. The ambipolar diffusion and attachment rates were measured using the interferometer.

The 10-stage rf mass spectrometer was similar to the one described by Redhead.[26] Ions emerging from the

[19] R. C. Gunton and T. M. Shaw, following paper, Phys. Rev. 140, 756 (1965).

[20] K. Watanabe, J. Chem. Phys. 22, 1564 (1954).

[21] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), p. 279. The computation used the data given for NO at a mean electron energy of 0.2 eV and a collision frequency inferred from the data on p. 206.

[22] T. M. Shaw, G. H. Brooks, and R. C. Gunton, Rev. Sci. Instr. 36, 478 (1965).

[23] H. J. Oskam, Philips Res. Rept. 13, 335 (1958).

[24] M. A. Biondi, Rev. Sci. Instr. 22, 500 (1951).

[25] S. C. Brown and D. J. Rose, J. Appl. Phys. 23, 711, 719, 1028 (1952).

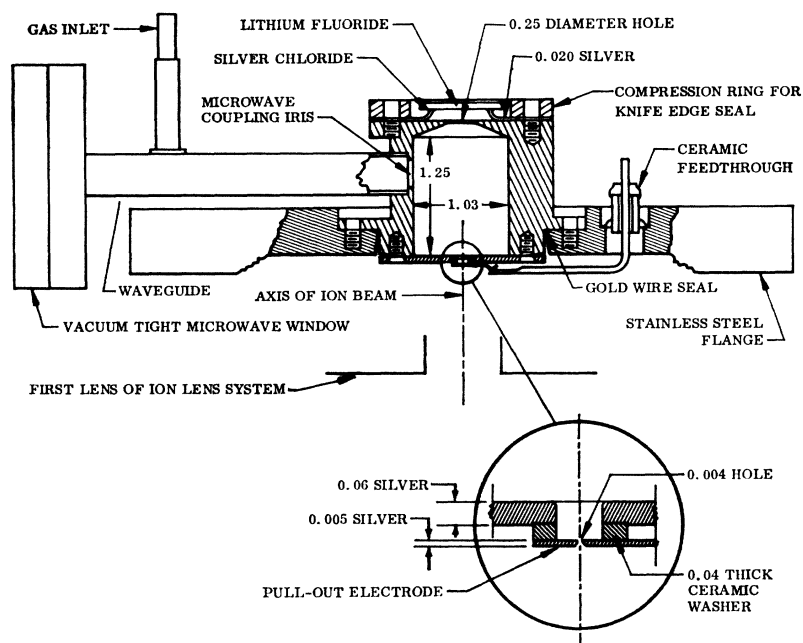[26] P. A. Redhead, Can. J. Phys. 30, 1 (1952).

FIG. 2. Details of construction of micro-
wave cavity 2 coupled to the mass spec-
trometer. All dimensions are in inches.

hole in the cavity wall were focused by an electrostatic
ion lens into the rf electrode system. At the output of
the rf accelerator section a retarding field was provided
to reject the low-energy portion of the ion beam and to
direct the beam through a slit onto the first dynode of
the ion multiplier detector. Between the slit and the
first dynode of the multiplier, an accelerating voltage of
1.5 to 3 kV was applied to insure adequate secondary
electron production at the first dynode.[27] The output
of the multiplier was coupled through a cathode follower
directly to an oscilloscope for a time-resolved display,
or to a lock-in amplifier, or to an amplifier and pulse
counter. The spectrometer had a range of 12 to 90 mass
units with a maximum resolution $m/\Delta m$ of 20. Circuits
were provided to permit analysis and detection of
either positive or negative ions.

FIG. 3. Schematic diagram of the microwave
reflectometer and interferometer.

[27] J. A. Allen, Proc. Inst. Radio Engrs. 38, 346 (1950).

The mass spectrometer vacuum system consisted of
a 750 liter sec^{-1} oil diffusion pump with a high-conduct-
ance zeolite trap. The computed pumping speed was
about 200 liters sec^{-1} at the ion sampling orifice between
the microwave cavity and the spectrometer. It was
possible to operate the mass spectrometer with cavity
pressures as high as 10 Torr.

The gas handling and vacuum system associated
with the two microwave cavities was a bakeable metal
and glass type, in which final purification of NO,
storage of purified gas, and pressure measurement were
conducted. Sputter ion pumps were used following an
initial pumpdown to about 10^{-6} Torr with a well-
trapped oil diffusion pump. Bakeout typically lasted
for 10 h at about 350°C,[28] after which the residual
pressure of the cold system was about 5×10^{-9} Torr
with a rate of rise less than 10^{-9} Torr min^{-1}. An auxiliary
unbaked glass system was used for preliminary puri-
fication of NO and for filling of the hydrogen lamps.
Pressure measurements were made by a means of a
bakeable null-type diaphragm manometer together
with a reference oil manometer and Alphatron. The
latter gages were calibrated with a mercury manometer.

The purification of NO gas involved a number of
steps. Gas of 99% stated purity from a steel cylinder
was passed through a trap in the glass system containing
zeolite cooled to −78°C. The zeolite which had been
previously outgassed by baking was effective in re-
moving NO_2 whose freezing point is −9°C at a pressure
of 760 Torr. The boiling and freezing points of NO at
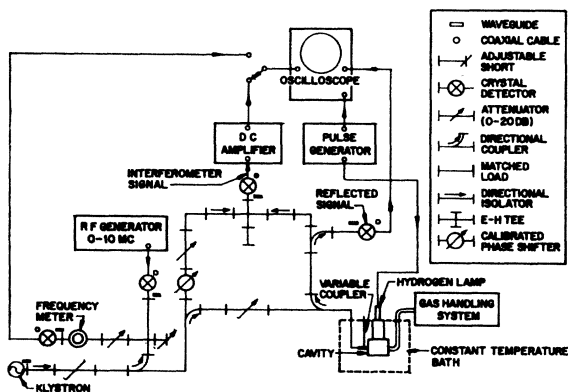760 Torr are −152 and −164°C, respectively. The NO

[28] The microwave window of cavity 2 on the mass spectrometer
had to be held at temperatures below 350°C by water cooling.
Cavity 1 was fully bakeable at 350°C.

was again passed through zeolite at $-78°C$ into the baked system where final purification was effected by repeated distillation at temperatures from -152 to $-196°C$.

Photoelectrons produced from the walls of the evacuated microwave cavity were observable with the interferometer during intense light pulses from the hydrogen lamp; however, the level of electron density from this source was always negligible relative to the electron density produced by photoionization of NO.

III. THE DECAY OF ELECTRON DENSITY

The principal processes determining the disappearance of electrons and ions in NO at the electron densities, gas densities, and gas temperatures of this experiment, are (a) ambipolar diffusion of charged particles to the wall followed by neutralization at the wall, (b) attachment of electrons to molecules to form negative ions, and (c) volume electron-ion and ion-ion recombination. In the measurements reported in this paper, electron and ion densities were kept low in order that the volume recombination processes should have only a small effect on the measured rates of diffusion and attachment. It is assumed that no mechanisms, such as the action of metastables, produce additional ionization after photoionization ceases.

The rate of decay of electron density in an ionized gas is given by[5]

$$\partial n_e/\partial t = D_a\nabla^2 n_e - \nu_a n_e - \alpha n_e n_+, \qquad (1)$$

where n_e is the electron density, D_a is the ambipolar diffusion coefficient, ν_a is the attachment frequency, α is the recombination coefficient, and n_+ is the positive ion density. The assumption is made that only one species of positive ion is present and the possible influence of negative ions on diffusion is neglected, for the moment. If the charged particles are distributed in the fundamental diffusion mode, the decay equation for the whole of the ionized gas neglecting recombination is

$$dn_0/dt = -(D_a/\Lambda_1^2)n_0 - \nu_a n_0, \qquad (2)$$

where n_0 is the electron density at a point in the distribution and Λ_1 is the characteristic diffusion length of the container for the mode. The coefficient D_a is given to good approximation by[23]

$$D_a = D_+[1 + (T_e/T_g)], \qquad (3)$$

where D_+ is the diffusion coefficient for positive ions, T_e is the electron temperature (Maxwellian distribution assumed), and T_g is the ion temperature, assumed equal to the gas temperature. If $T_e = T_g$, it may be shown that $D_a N$ is independent of gas density N for a given ion temperature T_g.[29] Positive ion mobility may be computed from the ambipolar diffusion coefficient by the

relation

$$\mu^+ = D_+e/(kT_g), \qquad (4)$$

where μ^+ is the positive ion mobility.

For a three-body attachment reaction of the type

$$e + M_1 + M_2 \rightarrow M_1^- + M_2, \qquad (5)$$
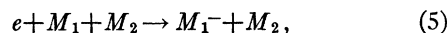
the attachment frequency ν_a may be expressed in the form

$$\nu_a = KN_1N_2, \qquad (6)$$

where M_1 is the attaching molecule of number density N_1, M_2 is a third body of density N_2, and K is the three-body attachment coefficient.

Equation (2) may be integrated to give

$$n_0(t) = n_0(0)e^{-t/\tau}, \qquad (7)$$

where the decay time constant τ is given by

$$1/\tau = (D_a/\Lambda_1^2) + \nu_a. \qquad (8)$$

Three regions of gas density may be distinguished here: a low-density region, an intermediate region, and a high-density region.

In the low-density region diffusion is dominant and a plot of $\ln n_e$ versus time is, according to Eq. (8), a straight line of slope $1/\tau$ very nearly equal to D_a/Λ_1^2. At early times, higher order diffusion modes may influence the slope of the decay curve; however, these modes decay fairly rapidly and make only a minor contribution after a decay time Λ_1^2/D_a. This point is discussed further in Sec. IV.

In the low-density region, the possible influence of negative ions on ambipolar diffusion must be considered. For the case of ambipolar diffusion of electrons with one type of positive ion and one type of negative ion, Oskam[23] shows that the ambipolar diffusion coefficients are

$$D_{a,e} \approx 2(1+\lambda)D_+, \qquad (9)$$

$$D_{a,-} \approx 2(1+\lambda)D_+D_-/D_e, \qquad (10)$$

$$D_{a,+} \approx 2D_+, \qquad (11)$$

where λ is the ratio of negative-ion density to electron density, $D_- = \mu^- kT_-/e$ and $D_e = \mu^e kT_e/e$, μ^- and μ^e are negative-ion and electron mobilities, T_- and T_e are negative-ion and electron temperatures. Equations (9), (10), and (11) are valid only if $T_e = T_g = T_- = T_+$, if the form of the spatial distribution of each type of charged particle is the same, if charge neutrality holds, and if λ is not much larger than unity. It may be noted from (10) that the diffusion rate for negative ions is small[30] because of the smallness of the ratio D_+/D_e, and from (9) that the diffusion rate for electrons depends on the ratio λ. Under these conditions the decay time constant for electrons τ may be expected to increase during the decay, if λ increases. For purposes of this study, the electron density decay rate is described with sufficient

[29] S. C. Brown, *Basic Data of Plasma Physics* (John Wiley and Sons, Inc., New York, 1959), p. 90.

[30] Similar conclusions are drawn from theory developed by M. A. Biondi, Phys. Rev. 109, 2005 (1958).

accuracy by (8) in which D_a is replaced by $D_{a,e}$ defined in (9). Complete theory has been given by Oskam[23] and Biondi.[30] The diffusion coefficient for positive ions according to (11) is unaffected by the partition of negative charge between electrons and negative ions.

In the low-density region diffusion cooling must also be considered, as Biondi[31] and Oskam and Mittelstadt[16] have pointed out for the rare gases. In the high gas-density region three-body attachment becomes dominant, and, from Eq. (8), $1/\tau$ becomes very nearly equal to ν_a. In the intermediate density region, diffusion and attachment have commensurate rates.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Typical decay curves for the electron density are shown in Fig. 4 for several pressures at a gas temperature of 358°K. Similar curves were obtained for gas temperatures of 196 and 298°K. Maximum initial electron densities for these observations were about 10^9 cm^{-3} and the effect of electron-ion recombination on the decay rates was less than an estimated 15% at the highest electron densities. Decay curves such as those of Fig. 4 may show evidence of curvature at early times because of recombination and higher mode diffusion.

As a check on the influence of higher diffusion modes, computations which considered diffusion loss only were made of the fundamental and higher mode content of the initial experimental electron distribution and of the decay of the modes using the method outlined by Oskam.[23] For this purpose, the initial distribution was
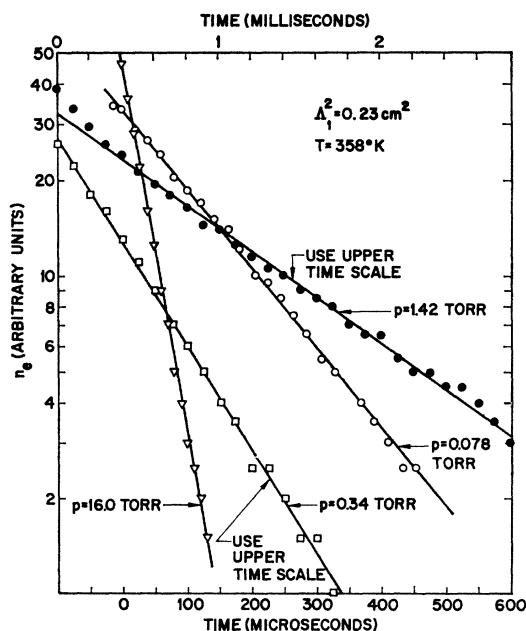

FIG. 4. The decay of electron density n_e with time following a photoionizing pulse for NO at four pressures at a temperature of 358°K. The pressures were measured at 298°K.
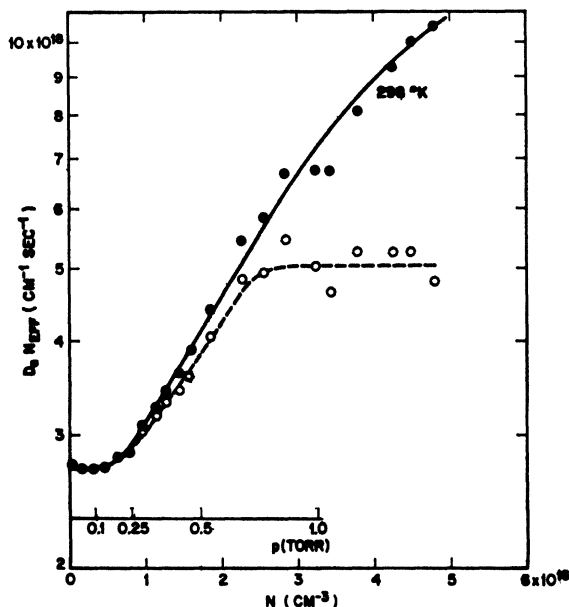
[31] M. A. Biondi, Phys. Rev. 93, 1136 (1954).

FIG. 5. A plot of $D_a N_{EFF}$ for 298°K as a function of N, the density of NO molecules. The data in solid circles were computed from $D_a N_{EFF}=N/\tau$ and include other electron loss processes as well as diffusion. The open circles show the results after correction to eliminate attachment loss.

determined with the aid of measurements of the distribution of radiation intensity from the hydrogen lamp.[19] For simplicity, the electron density was assumed proportional to the radiation intensity, although the assumption leads to an overestimate of the initial higher mode content.[32] Computations, using the measured electric field distribution in the cavity,[22] showed that the fundamental mode contributed 78% of the frequency shift initially and 96% after a time Λ_1^2/D_a.

Time constants τ of such decay curves as those of Fig. 4 were used together with gas densities to compute effective values of $D_a N$ defined as $D_a N_{EFF}=N/\tau$. The values for gas densities up to 5×10^{16} cm^{-3} and a temperature of 298°K are plotted in Fig. 5 as solid circles and include both diffusion and attachment loss. The method of correcting these data to eliminate attachment loss is described below. The decay rates for high gas density ($N>10^{17}$ cm^{-3}) were computed in terms of an effective attachment coefficient defined as $K=1/\tau N^2$ and are shown plotted against N^2 in Fig. 6. In that figure, the K values for lower densities and for $T_g=298°K$ are relatively constant. A constant value of K in such a plot is characteristic of 3-body attachment where both M_1 and M_2 of Eq. (6) are molecules of the parent gas. When the lower density K values are averaged and used together with Eqs. (6) and (8) to

[32] Diffusion during production leads to a smoothing of the distribution and a larger fundamental mode content. Consequently, at low gas densities, the higher mode effect is less than indicated by this computation. At high gas densities ($N>10^{17}$ cm^{-3}) the initial electron distribution is affected by appreciable absorption of the ionizing uv radiation by the gas; however, attachment so dominates the decays that the effect of higher mode diffusion is not observed.

correct the $D_a N_{EFF}$ values of Fig. 5, the corrected diffusion results are as shown in that figure with open circles. If, in turn, the upper density corrected diffusion values of Fig. 5 are used in an iterative procedure to correct the lower density K values of Fig. 6 for 298°K, those values become more nearly constant as indicated in Fig. 6. The data for gas temperatures of 196 and 358°K, similarly corrected, are shown as open symbols in Figs. 6 and 7.

Mass-spectrometer observations of the ionic composition of photoionized NO at 298°K showed that ions of mass 30 (NO$^+$) were present. The only other positive ion observed was of mass 60, most likely (NO)$_2{}^+$, whose signal in the pressure range 0.01 to 5 Torr was always less than 1% of that of NO$^+$ and independent of the magnitude of the pull-out voltage. The principal negative ion observed with the mass spectrometer in photoionized pure NO at all pressures from 0.01 to 5 Torr was mass 46(NO$_2{}^-$). Prior to these observations, the mass spectrometer and cavity were baked out as discussed in Sec. II. Traces of other negative ions were observed including masses 35 and 37, both probably Cl$^-$ originating from the AgCl used in cementing the bakeable LiF window and pull-out electrode insulator, but no evidence was obtained for the presence of NO$^-$ or (NO)$_2{}^-$. With regard to the source of the NO$_2{}^-$ ion, the NO purification procedure should reduce the NO$_2$ partial pressure to 10^{-6} Torr or less; however, even at such a low level of contamination, there may be sufficient NO$_2$ to produce the observed negative ion effects. Another possible source of NO$_2$ is photodissociation of NO by the ionizing light pulse, since the resulting O atoms can react very rapidly[33] with NO to form NO$_2$. Such an

FIG. 7. A plot of $D_a N_{EFF}$ for various temperatures as a function of N, the density of NO molecules. All of these data have been corrected to eliminate attachment loss.

effect is expected to be cumulative from pulse to pulse. However, cumulative effects were not observed after any of the first few pulses; consequently, the effects of photodissociation appeared to be small.

The ion signals were displayed on an oscilloscope for observation of their pressure dependences and their temporal behavior. For the low ionizing pulse intensities of this study, very few negative ions were observed at a pressure of 0.08 Torr (NO$_2{}^-$<1% of NO$^+$), and virtually none at lower pressures. The number of negative ions observed increased with pressure up to about 0.5 Torr then decreased slowly. The diffusion behavior predicted by Eqs. (9) to (11) was observed qualitatively; that is, during the decay negative ion signals remained small until the electron density, monitored with a simultaneous microwave probing signal, dropped to zero. Following electron disappearance, positive and negative ions were observed in approximately equal numbers for similar mass spectrometer and pull-out electrode voltage magnitudes.

The decay of the NO$^+$ signal was found to be slower than the decay of electron density. The ion signals exhibited a pulse structure due to single ions incident on the first dynode of the electron multiplier and quantitative measurements were made of NO$^+$ decay rates by pulse counting, through the use of an amplifier with a variable time gate and a counter connected to the multiplier output. The early decays for pressures of 0.08, 0.25, and 0.5 Torr were all approximately exponential with time constants of 310, 970, and 1900 μsec, respectively, within 10%. These time constants are larger than for the corresponding electron decays and if used directly to compute values of $D_{a,+}N$, all yield 1.92×10^{18} cm^{-1} sec^{-1}, within 10%. This value is 73% of the lowest $D_a N_{EFF}$ value of Fig. 5. Some understanding of this result may be gained by considering the pull-out electrode in this case as a negative probe for the collection of positive ions. Probe potential was 10 V.
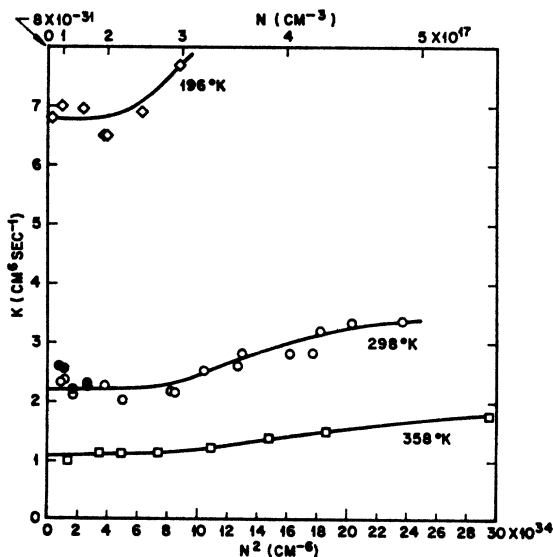

FIG. 6. A plot of the attachment coefficient, $K = 1/\tau N^2$, as a function of the square of NO molecule density for three temperatures. The data in solid circles for 298°K are uncorrected for diffusion loss. The data in open symbols for all temperatures have been corrected where necessary to eliminate diffusion loss.

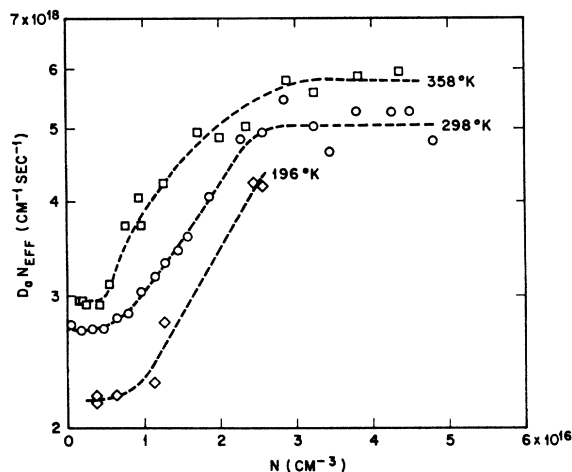[33] M. Nicolet, J. Geophys. Res. 70, 679 (1965).

In order to check the positive ion time constants, the time dependence of the current drawn to the pull-out electrode was observed and recorded on an oscilloscope. Agreement of the ion current decay time constants with the mass spectrometer decays was obtained, within 10%, for 0.08 and 0.25 Torr. The ion current for 0.5 Torr, at the low pulse levels used, was too small for such a measurement.

In this connection, the work of Schulz and Brown[34] on positive ion collection by a negative probe in a microwave cavity, while not directly applicable, seems pertinent. They studied the use of small cylindrical probes, developing the theory of such probes for various pressure regimes. The theory was found to predict well the observed dependence in hydrogen of probe current on probe voltage, pressure, and electron density. The latter was measured by a microwave technique and was assumed equal to the positive ion density. For a cylindrical probe the current was found to be proportional to $n_+{}^x$ where the exponent x varied from 0.80 to 0.58, depending on the number of ion-molecule collisions in the sheath. The current also decreased as pressure was increased.

In the present case, although the pull-out electrode is not a cylindrical probe, its complex electric field distribution may give it some of the characteristics of such a probe. If the assumption is made that the ion current drawn to the pull-out electrode is proportional to $n_+{}^x$, and if the decay is exponential, the time constant of the ion current is x^{-1} times the time constant of the positive ion decay. In the present case a value $x=0.73$ seems appropriate. These positive-ion-decay results further suggest that the diffusion decay of positive ions in range 0.08 to 0.5 Torr proceeds with a constant $D_{a_+}N$ although D_aN_{EFF} for electrons increases in the same pressure range. This result is in agreement with the prediction of Eq. (11).

The density dependence of the effective electron diffusion rate, shown in Figs. 5 and 7, may be attributed to an increase of λ with density because of increased attachment. The diffusion rate given by Eq. (9) depends on λ; that is, the observed diffusion rate for electrons is increased because of the presence of negative ions which diffuse very slowly. The predictions of Oskam and Biondi for diffusion, Eqs. (9) to (11), although verified qualitatively in most respects, were not tested quantitatively because of lack of knowledge of the number densities of negative ions during electron decay. Equations (9) and (10) suggest that the electron diffusion rate should increase with time during the decay due to an increase in λ. This effect was not observed for low ionizing pulse intensities but was observed in decays in NO following intense ionizing pulses at pressures in range 0.2 to 1 Torr.

Other phenomena which were considered in an attempt to explain the observed dependence of electron decay on gas density are not thought to be important.

For example, diffusion cooling[16,31] produces a density dependence of the diffusion rate but is probably not important in NO due to rapid thermalization of electrons in collision with NO molecules. Another possibility is a change of positive ion species leading to a change in ion mobility. Although the mass spectrometer observations indicate that NO^+ is the dominant positive ion at all pressures, it is possible that more $(NO)_2{}^+$ exists in the cavity than the trace observed with the mass spectrometer because such a complex ion may be loosely bound and the small number observed may be only the result of breakup in the mass spectrometer sampling process.

A test was made of the ability of the mass spectrometer to sample complex ions of low binding energy, such as $N_4{}^+$ from the plasma in the cavity. A small electron gun structure was sealed into the cavity in place of the LiF window and was located on the cavity axis near the pull-out electrode. When research grade N_2 at pressures up to 0.7 Torr was ionized by this gun, the ions N^+, $N_2{}^+$, $N_3{}^+$, and $N_4{}^+$ were observed, in relative abundances in qualitative agreement with the findings of Saporoschenko.[2] For $N_4{}^+$, which has a binding energy of 0.5 eV,[35] pull-out voltages greater than 1 V produced smaller signals, evidently due to breakup of the ion in the sampling process; whereas, for ions of large binding energy larger pull-out voltages produced larger ion signals. The system was thus able to detect complex ions with binding energies as low as 0.5 eV. Since the $(NO)_2{}^+$ peak in photoionized NO was not observed to increase with decreasing pullout voltages, we conclude that it was not the dominant ion and was not producing an apparent change in ion mobility.

Mobility values for the NO^+ ion in NO were computed from the low density ($N<0.5\times10^{16}$ cm^{-3}) values of D_aN_{EFF} and are shown in Fig. 8. At these gas densities, the negative ion influence was assumed negligible, since the number of negative ions observed was small or zero. The computed mobility for $T_g=298°K$ is 1.9 ± 0.2 cm^2 sec^{-1} V^{-1}, referred to a gas pressure of 760 Torr at 273°K and the corresponding D_ap is 83 ± 8 cm^2 Torr sec^{-1}. The mobilities for 196 and 358°K are 2.4 ± 0.2 and 1.8 ± 0.2 cm^2 sec^{-1} V^{-1}, respectively.

The error limits assigned to the mobility and D_ap values ($\pm10\%$) are an estimate of the maximum uncertainty associated with the determination of electron decay time constants and the measurement of pressure and temperature. As stated above, the microwave technique has produced mobilities in good agreement with the more direct measurements of drift tubes.[16] The mobilities from this study may be compared with the recent measurement of the mobility of NO^+ in N_2 by Young et al.[36] who obtained 3.3 ± 0.2 cm^2 sec^{-1} V^{-1} corresponding to 20°C and 760 Torr. The mobility of the NO^+ ion in the parent gas may be lower because of

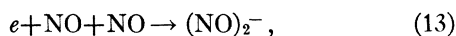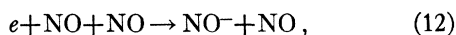[34] G. J. Schulz and S. C. Brown, Phys. Rev. 98, 1642 (1955).

[35] R. N. Varney, J. Chem. Phys. 31, 1314 (1959); 33, 1709 (1960).

[36] R. A. Young, C. R. Gatz, R. L. Sharpless, and C. M. Ablow, Phys. Rev. 138, A359 (1965).

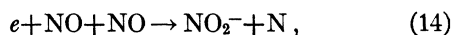the phenomenon of charge transfer as observed in other gases.[37]

The attachment results shown in Fig. 6 at gas densities near 10^{17} cm^{-3} are characteristic of a three-body attachment process for which the coefficients K are $6.8\pm0.7\times10^{-31}$ cm^6 sec^{-1} at 196°K, $2.2\pm0.2\times10^{-31}$ at 298°K and $1.1\pm0.1\times10^{-31}$ at 358°K. This process may be one of

$$e+NO+NO \rightarrow NO^-+NO, \qquad (12)$$

$$e+NO+NO \rightarrow (NO)_2^-, \qquad (13)$$

or

$$e+NO+NO \rightarrow NO_2^-+N, \qquad (14)$$

where (13) may represent an intermediate stage in (14). The anomalous rise in K value at higher densities is not in agreement with the behavior expected from (12), (13), or (14) and no explanation for it has been found. The mass spectrometer indicates that NO_2^- is the dominant negative ion and the rate K exhibits a strong temperature dependence, approximately T^{-3}. The attaching electrons should be thermalized since estimated cooling times are very short at the densities where attachment is dominant. In the early work of Bradbury[38] on attachment in NO, evidence for a three-body process was also obtained.

Direct attachment of electrons to an NO_2 impurity in the present case does not seem likely. Van Lint et al.,[18] have reported attachment in NO_2 ionized by 25-MeV electrons and have measured a very large three-body coefficient, approximately 1×10^{-26} cm^6 sec^{-1}. The attaching electrons were probably thermalized. In the present study, the NO_2 impurity content is estimated to be much less than the level of about 20 ppm required for direct attachment of thermal electrons to account for the measured attachment rates. In addition, direct attachment to NO_2 would not be expected to have the observed T^{-3} dependence, but rather a direct dependence, as observed in the attachment of low-energy electrons in O_2.[7,18]

The observation of NO_2^- and the temperature dependence are possibly consistent with reactions (12) or (13) followed by charge transfer to an NO_2 impurity, or with reaction (14). With regard to (13), it is known that NO has a tendency to form dimers in the gas phase with a binding energy computed[39] to be about 0.1 eV, and the gas phase is estimated to be 1% associated at the boiling point, 113°K. If the degree of association is extrapolated to the NO densities and temperatures of interest in the present study, the equilibrium numbers of $(NO)_2$ molecules are too small, less than 10^{12} cm^{-3}, to account for the observed attachment rates. However, collisions of NO molecules may produce large numbers of temporary loosely bound complexes, which may act as attaching centers. The numbers of such centers may be expected to vary inversely as some power of the temperature, and of
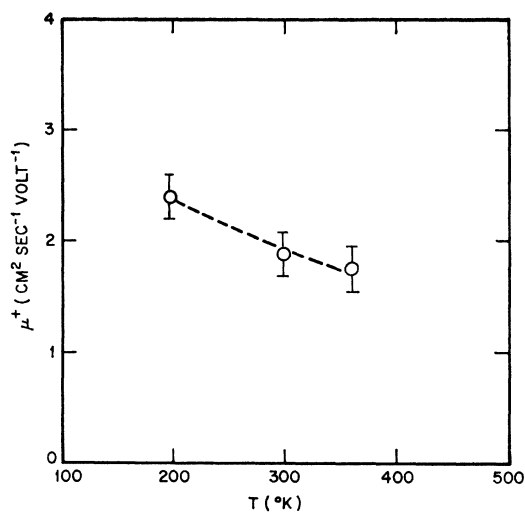
[37] Reference 29, p. 62.
[38] N. E. Bradbury, J. Chem. Phys. 2, 827 (1934).
[39] O. K. Rice, J. Chem. Phys. 4, 367 (1936).

FIG. 8. A plot of the mobility of the ion NO$^+$ in NO as a function of temperature.

course, the collisions of electrons with the centers are also temperature-dependent. In (13) the association and attachment energy must be dissipated in internal excitation of the complex ion, possibly in vibration and rotation, as Varney has suggested for the association energy of the complex positive ion, N_4^+.[35] The possibility that the NO_2^- ions observed may have been formed by charge transfer from a primary negative ion such as NO$^-$ or $(NO)_2^-$ to an NO_2 impurity molecule is suggested by the work of Curran[40] who has demonstrated that NO_2 has a very high electron affinity, probably greater than 3.8 eV, and large cross sections for charge transfer from negative ions such as Cl$^-$ and O$^-$. Finally, reaction (14) is probably exothermic by about 0.5 eV and although it requires a rearrangement, may have a rate high enough[41] to account for the experimental observations.

V. CONCLUSIONS

Ambipolar diffusion in photoionized NO is complicated by the presence of negative ions which increase the observed electron diffusion rate. The theory of the diffusion of electrons, positive ions and negative ions is in agreement with some of the observations. The dominant positive ion is NO$^+$ and its mobility may be inferred from electron diffusion at low pressures under conditions of small negative ion influence. The measured mobility of NO$^+$ decreases slowly as the gas temperature is raised from 196 to 358°K. Attachment, the dominant electron loss process at higher gas densities, exhibits approximately the density dependence expected for a three-body process, and has a strong T^{-3} temperature dependence. The principal negative ion observed is NO_2^-, which may be formed by charge transfer to a trace impurity from a primary negative ion or may be formed directly in a rearrangement reaction.

[40] R. K. Curran, Phys. Rev. 125, 910 (1962).
[41] Suggested by D. D. Briglia (private communication).