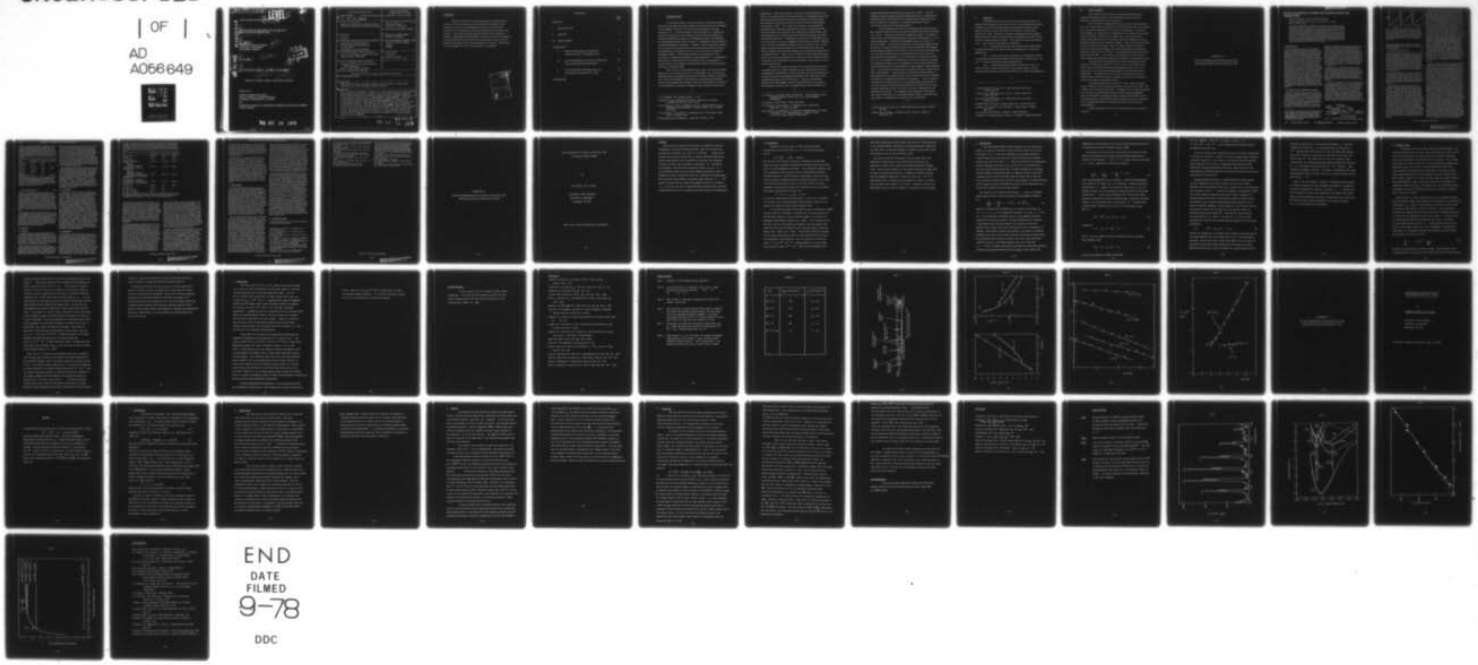
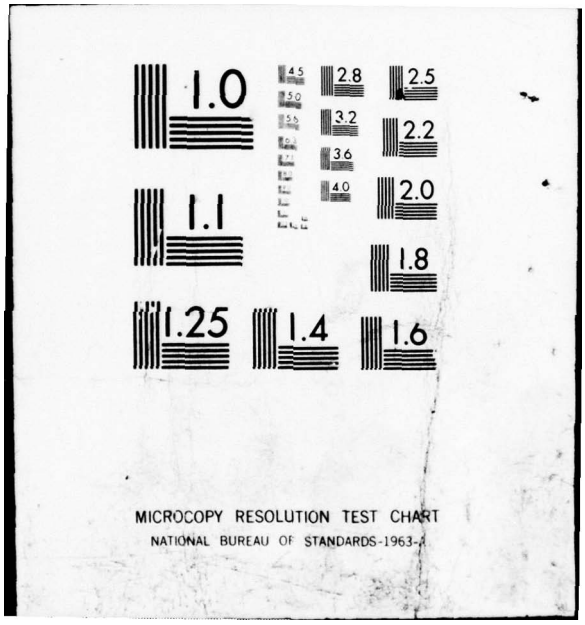
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(6) BINARY POSITIVE ION-NEGATIVE ION MUTUAL NEUTRALIZATION REACTIONS

(10) David Smith
Department of Space Research
University of Birmingham
Birmingham, England

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(11) 31 May 1978

(12) 56p.

(9) Interim Scientific Report, 1 Apr 1977 - 31 Mar 1978

(16) 2303 (17) G1

Approved for public release; distribution unlimited

Prepared for

UNITED STATES AIR FORCE
Air Force Office of Scientific Research
Building 410, Bolling AFB, DC 20332

and

EUROPEAN OFFICE OF AEROSPACE RESEARCH AND DEVELOPMENT
London, England

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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. Report Number AFGL TR-78-0162 / 2. Govt Accession No.	3. Recipient's Catalog Number
4. Title (and Subtitle) BINARY POSITIVE ION-NEGATIVE ION MUTUAL NEUTRALIZATION REACTIONS	5. Type of Report & Period Covered Interim scientific 77 Apr 01 - 78 Mar 31
	6. Performing Org. Report Number -
7. Author(s) D. Smith	8. Contract or Grant Number AFOSR-77-3260A
9. Performing Organization Name and Address Department of Space Research The University of Birmingham P. O. Box 363 Birmingham B15 2TT England	10. Program Element, Project, Task Area & Work Unit Numbers 61102F 2303G1
11. Controlling Office Name and Address Air Force Geophysics Laboratory/LKB Hanscom AFB, MA 01731	12. Report Date 31 May 78
	13. Number of Pages 52
14. Monitoring Agency Name and Address European Office of Aerospace Research and Development Box 14, FPO, New York 09510	15.
16. & 17. Distribution Statement Approved for public release; distribution unlimited.	
18. Supplementary Notes	
19. Key Words Mutual neutralization, flowing afterglow, thermal plasma, atomic ions, molecular ions, clustered ions, emission spectra.	

20. Abstract

The results are described of a study of the rate coefficients at thermal energies of several binary positive ion-negative ion mutual neutralization reactions. This includes reactions of the simpler molecular ions e. g. $NO^+ + NO_2^-$ and those of the so-called cluster ions e. g. $H_3O^+(H_2O)_n + NO_3^-(HNO_3)_m$. The ionic recombination coefficients for all of these molecular ion reactions are similar being within the range $(4\text{-}10) \times 10^{-8}\ cm^3 s^{-1}$ in general accordance with theoretical predictions. The variation with temperature of two simple ion reactions have also been obtained and varies as $T^{-1/2}$, again in line with the theory. For several atomic ion reactions e. g. $Ar^+ + Cl^-$, is much smaller than for reactions involving molecular ions. A spectroscopic study of one reaction ($NO^+ + NO_2^-$) has been carried out and data on the product neutral states have been obtained.

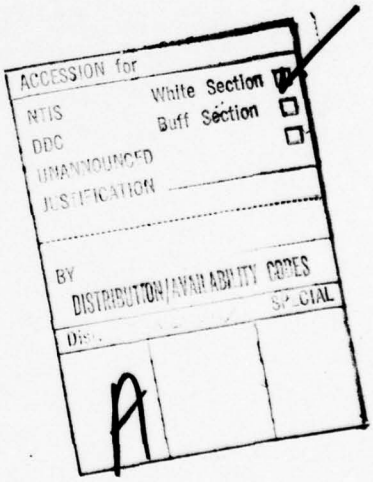
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PREFACE

This work is part of a larger programme of ionic reaction studies at thermal energies which includes determinations of ion-molecule reaction rate coefficients and product ion distributions, electron-ion recombination coefficients and electron attachment coefficients. The work is largely supported by the Science Research Council. Substantial contributions to the effort in the ionic recombination work described in this report have been made by each of the co-authors of the papers which form Appendices A, B and C, these being Dr. N. G. Adams, Dr. M. J. Church and Dr. T. M. Miller.



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I INTRODUCTION

The extensive study of reaction kinetics at thermal energies in partially ionized gases has been largely directed towards such processes as ion-molecule reactions, electron-ion recombination, Penning ionization, etc. The determination of binary positive ion-negative ion mutual neutralization (recombination) rates at thermal energies has relatively speaking been ignored, presumably because of the difficulty in establishing suitable interactive media in association with satisfactory ion density diagnostic techniques. However, loss of ionization in gases which contain electronegative species may ultimately result from ionic recombination, as is expected to be the case in the lower ionosphere (Ferguson, 1967). The earliest studies of this phenomenon were carried out in weakly ionized gases at high pressures ($\sim$ 1 atmosphere) and as such are concerned with termolecular ionic recombination. A brief review of this subject has been given by Sayers (1962) and more recently by Flannery (1972).

Prior to the work described in this report, the only determined approach to the study of binary ionic recombination was carried out by Peterson and his colleagues at the Stanford Research Institute (Peterson, 1971; Aberth and Peterson, 1970) using the merged beams technique, and they have studied several atomic and molecular positive and negative ion recombination reactions including several reactions of ionospheric

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E. E. Ferguson, Rev. Geophys. (1967), 5, 305

J. Sayers, Atomic Molecular Processes, (1962) Ed. D. R. Bates, Academic Press, New York, p. 272

M. R. Flannery, in M. C. R. McDowell and E. W. McDaniel (Eds). Case Studies in Atomic Collision Physics (1972), Vol. 2, Wiley, New York

J. R. Peterson, W. H. Aberth, J. T. Moseley and J. R. Sheridan, Phys. Rev. A, (1971) 3, 1651

W. H. Aberth and J. R. Peterson, Phys. Rev. (1970) 1, 158

significance. This work has been reviewed in detail by Moseley et al (1975). In parallel with the experimental work, the Stanford group have also pursued an associated theoretical programme directed towards the calculation of ionic recombination rates and their energy dependences (Olson, 1972). For atomic ion reactions, their theoretical estimates are in substantial agreement with their merged beam data, but for molecular ion reactions their experimental recombination coefficients appear to be significantly and irreconcilably higher than their theoretical predictions. Although the reasons for the discrepancy are not as yet clear, it has been suggested by Peterson et al (1971), (Bennett et al, 1974) that the molecular negative ions in the beam may, in some cases, be electronically excited which would effectively reduce the electron affinity of the molecular species and consequently increase the recombination rate. Also it is in the nature of the merged beams technique that an energy extrapolation is required in order to obtain thermal energy data and it is possible that this procedure could result in erroneous low energy data.

Not all of the above criticism of the merged beams data could be substantiated and a different approach to the measurement of ionic recombination coefficients at thermal energies was clearly desirable to increase the body of knowledge and perhaps to cast some light on the merged beams data vis à vis the theory. Thus we developed the experiment in Birmingham, which we demonstrated to be capable of providing data on binary ionic recombination for mass identified and

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J. T. Moseley, R. E. Olson and J. R. Peterson. Case Studies in Atomic Collision Physics, (1975) Vol. 5, p. 1, North Holland, Amsterdam

R. E. Olson, J. Chem. Phys. (1972), 56, 2979

J. R. Peterson, W. H. Aberth, J. T. Moseley and J. R. Sheridan, Phys. Rev. A. (1971), 3, 1651

R. H. Bennett, D. L. Huestis, J. T. Moseley, D. Mukherjee, R. E. Olson, S. W. Benson, J. R. Peterson and F. T. Smith, (1974), A. F. C. R. L. Rept. AFCRL-TR-74-0417

energy relaxed ionic species (Smith and Church, 1976a). The data obtained to date (see below) indicates significantly lower recombination coefficients than those obtained in the merged beams experiment and, where comparison is possible, in acceptable agreement with the theoretical estimates of the Stanford group.

The Birmingham data have been obtained using a flowing afterglow apparatus which has been described in detail in the literature (Smith et al, 1975). Plasma is produced in a glass flow tube ($\sim$1 m long) by a microwave cavity discharge through a mixture of helium gas ($\sim$1 torr) and to this plasma, a reactant electronegative gas (e. g. NO_2 at $\sim$ 1 mtorr) is added. The gas is constrained to flow along the glass tube by the action of a large mechanical pump and thus distributes thermalised plasma along the length of the tube and remote from the active discharge. At a particular distance from the discharge (which can be varied by adjusting the partial pressure of the reactant gas, the gas flow velocity, etc.), an ion-ion plasma is established in which the major loss process for ionization is binary ionic recombination, if the ionization density is sufficiently high and if the gas pressure is high enough to inhibit diffusive loss. Such plasmas are ideal interactive media in which to study binary ionic recombination. Downstream of the flowing afterglow plasma, a mass spectrometer sampling orifice probe is located in order to identify the positive and negative ions present in the plasma. Thus a collision dominated ion-ion plasma (due to the relatively high gas pressure) is created in which the ions are mass identified and in which ionic recombination loss along the axis of the flow tube can be established as the dominant loss process. The Langmuir probe diagnostic technique is then used to determine the ion density gradient along the flow tube axis from which a recombination coefficient can be determined.

D. Smith and M. J. Church, Int. J. Mass. Spectrom. Ion. Phys. , (1976a) 19, 185

D. Smith, N. G. Adams, A. G. Dean and M. J. Church, J. Phys. D. , (1975), 8, 141

II RESULTS

During the year prior to the award of the present Grant, we exploited the technique to determine the ionic recombination coefficients at 300 K of several molecular positive and negative ions (Smith and Church, 1976a), several reactions of the so-called "cluster ions" (Smith et al, 1976), reactions in plasmas containing SF_6 (Church and Smith 1977) and a study of the temperature dependence of the $NO^+ + NO_2^-$ reaction (Smith and Church 1976b). The present Grant was awarded to extend this work and to date this has resulted in

(i) a detailed study of the ionic recombination coefficients of simple molecular ions and of cluster ions (Smith et al, 1978a and Appendix A),

(ii) a study of the ionic recombination coefficients at 300 K of reactions between atomic positive ions and atomic negative ions, e. g. $Ar^+ + F^-$ (Church and Smith 1978 and Appendix B),

(iii) a spectroscopic study of the reaction $NO^- + NO_2^-$ at 300 K in order to obtain information on the neutral products of this reaction and their states of excitation (Smith et al, 1978b and Appendix C).

D. Smith and M. J. Church, Int. J. Mass. Spectrom. Ion. Phys., (1976a) 19, 185

D. Smith, N. G. Adams and M. J. Church., Planet. Space Sci., (1976), 24, 697

M. J. Church and D. Smith, Int. J. Mass Spectrom. Ion Phys., (1977), 23, 137

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D. Smith, M. J. Church and T. M. Miller, J. Chem. Phys., (1978a), 68, 1224

M. J. Church and D. Smith, J. Phys. D. (1978) submitted

D. Smith, N. G. Adams and M. J. Church, J. Phys. B. (1978b) submitted

III CONCLUSIONS

The results of these studies are presented in detail in the respective Appendices and so only a brief description of the most important conclusions will be presented here.

Both the absolute magnitudes and the temperature variations of the ionic recombination coefficients for the simple molecular ion reactions are in acceptable agreement with theoretical predictions. Somewhat surprisingly, the recombination coefficients for the cluster ion reactions are very similar to those for the simpler ions, even when both the positive and negative ions are quite large clusters (although the corresponding cross sections are somewhat larger). Thus, all the data obtained to date for molecular species, albeit for negative ions formed from species of high electron affinity, have ionic recombination coefficients within the range $(4-10) \times 10^{-8} cm^3 s^{-1}$ for temperatures within the limited range 180 K to 530 K. This result if confirmed by a more extensive study will greatly simplify calculations of atmospheric deionization rates.

The atomic ion studies indicate that ionic recombination coefficients for reactions such as $Ar^+ + Cl^-$ are very much smaller (by at least a factor of ten) than those involving molecular ions, in fact, so small that we were only able to obtain upper-limit estimates of their magnitudes. This general result is again in accord with theoretical expectations for these rare gas ion-halogen ion reactions and will be of interest to workers in gas laser studies.

The spectroscopic study of the $NO^+ + NO_2^-$ reaction at 300 K clearly indicates that the reaction proceeds via an electron transfer from the NO_2^- into an excited state of NO. It appears that the neutral products of the reaction are ground state molecule NO_2 and the excited state molecule NO ($A^2\Sigma^+$) although the higher energy $C^2\Pi$ and $D^2\Sigma^+$ states cannot positively be ruled out. This study represents our first contribution to the challenging problem of identifying the neutral states of ionic recombination.

These programmes will be continued during the second year of the grant.

APPENDIX A

MUTUAL NEUTRALIZATION OF SIMPLE AND CLUSTERED POSITIVE AND NEGATIVE IONS

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Mutual neutralization of simple and clustered positive and negative ions[a)]

David Smith, Michael J. Church, and Thomas M. Miller[b)]

Department of Space Research, University of Birmingham, Birmingham B15 2TT, England
(Received 14 September 1977)

Measurements are reported of the rate coefficients, α, for several ion–ion mutual neutralization reactions principally involving NH_4^+ ions and their ammonia clusters $NH_4^+ \cdot (NH_3)_{1,2,3}$ with several different negative ions. The data were obtained utilizing an ion–ion flowing afterglow plasma combined with Langmuir probe diagnostics. Most of the measurements were obtained at 300 K although the $NH_4^+ + Cl^-$ reaction has also been studied at 220 and 430 K. Both the absolute magnitude of α and its temperature variation are shown to be in acceptable agreement with theoretical predictions. The α for the cluster ion reactions are very similar to those for the simpler ions, even when both positive and negative ions are large clusters, although an increase in the mean reaction cross section for the cluster ion reactions is discernible. All the α measured to date for both simple and cluster ion reactions, albeit for species of high electron affinity and over the limited temperature range of 180 to 530 K, are within the range $(4–10)\times10^{-8}$ cm^3 s^{-1}, more marked variations occurring with temperature than with ionic mass.

I. INTRODUCTION

We have studied the binary mutual neutralization ("ionic recombination") of some clustered positive and negative ions at thermal energies in a flowing afterglow. Previously we have published ion–ion neutralization coefficients for relatively simple positive and negative ions[1,2] and also for a few clustered species, notably the water cluster ion $H_3O^+ \cdot (H_2O)_3$.[3] Studies of ionic recombination of clustered as opposed to simple ions has fundamental importance since the neutralization mechanisms may vary.[4,5] Also since cluster ions dominate the charged species in the lower atmosphere[6] this work provides ionic recombination coefficients for ionospheric and stratospheric modelling. We have discussed this in a previous publication.[7] The new data presented here are mainly concerned with the neutralization reactions of $NH_4^+ \cdot (NH_3)_n$ ions ($n = 0$ to 3) and now a significant body of data is available on both "simple" ion and cluster ion neutralization rate coefficients, sufficient to allow valid comparisons to be made. Neutralization data on positive ion clusters of ammonia are especially relevant to stratospheric and tropospheric deionization since it has been suggested that these species will dominate in these regions.[8]

II. APPARATUS AND EXPERIMENTAL METHOD

The flowing afterglow apparatus has been described in detail in our previous publications.[9,10] Recently some minor changes have been made in the pumping systems and in the Pyrex flow tube; a schematic of the present configuration is shown in Fig. 1. Flowing afterglows are created by a microwave discharge in helium carrier gas at pressures ranging from about 0.5 to 1.0 Torr. An electron attaching gas is added either upstream or downstream of the discharge and some distance downstream of the addition point the electron density has decreased to a sufficiently small value that a transition from electron–ion to ion–ion plasma takes place.[1] A small cylindrical Langmuir probe movable axially along the entire length of the flow tube (with its current collecting tip positioned on axis) is used to determine both positive and negative ion densities from the probe current–voltage characteristics obtained under orbital-limited conditions,[11] providing the masses of the positive and negative ions are known. The positive and negative ions are sampled downstream with a quadrupole mass spectrometer.

Conditions may be created such that binary mutual neutralization is the dominant loss process, this requiring ion densities $\sim10^{10}$ cm^{-3} and pressures sufficiently large that ambipolar diffusion of the ions is relatively slow. Under such conditions a plot of reciprocal ion density versus afterglow time (obtained by measuring the plasma flow velocity[10]) yields the recombination coefficient, α.

In the present experiments Cl^- ions were produced by adding Cl_2 gas and NO_2^- ions were produced using NO_2 gas (containing HNO_3 as an impurity). At increased NO_2 concentrations, reactions of NO_2^- with this impurity produced NO_3^- and eventually the cluster ions $NO_3^- \cdot HNO_3$ and $NO_3^- \cdot (HNO_3)_2$.[12] The positive ion clusters $NH_4^+ \cdot (NH_3)_n$ were created by adding various concentrations of NH_3 to the afterglow downstream of the Cl_2 or NO_2 addition point. At small ammonia concentrations NH_4^+ was dominant at the mass spectrometer sampling orifice whereas at higher concentrations the cluster $NH_4^+ \cdot (NH_3)_2$

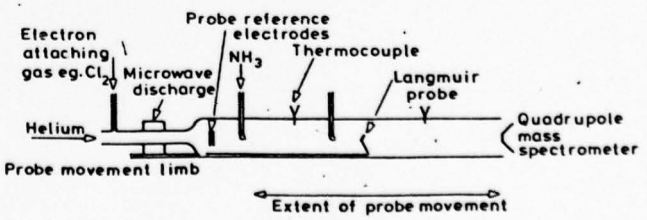


FIG. 1. Schematic diagram of the flowing afterglow apparatus.

[a)]This work has been supported by the Science Research Council, and by the U. S. Air Force under Grant No. AFOSR-77-3260. TMM has been supported by the Defense Nuclear Agency through the U. S. Air Force Geophysical Laboratory.
[b)]Permanent address: Stanford Research Institute 106B, Menlo Park, California 94025.

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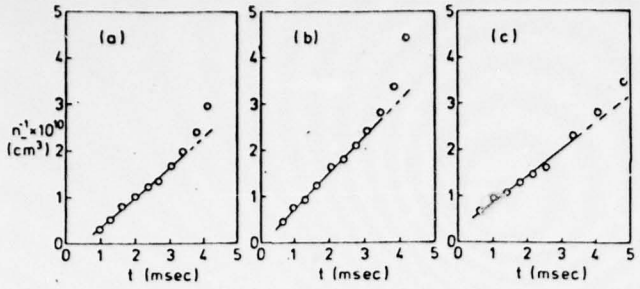


FIG. 2. Reciprocal negative ion density vs afterglow time, at 300 K. The slopes of the linear portions of the data are equal to the ion–ion neutralization rate coefficients for three cases: (a) simple ions, $NH_4^+ + Cl^-$; (b) clustered positive ions, $NH_4^+ \cdot (NH_3)_2 + Cl^-$; and (c) a mixture of both positive and negative ion types, [NH_4^+, NO^+, NO_2^+, $NH_4^+ \cdot NH_3$, $NH_4^+ \cdot (NH_3)_2$] + [NO_3^-, $NO_3^- \cdot HNO_3$, $NO_3^- \cdot (HNO_3)_2$]. The time scale has an arbitrary zero.

could be made dominant or a mixture of the clusters $NH_4^+ \cdot (NH_3)_2$ and $NH_4^+ \cdot (NH_3)_3$ generated. The sequence of clustering equilibria

$$NH_4^+ \cdot (NH_3)_n + NH_3 \rightleftharpoons NH_4^+ \cdot (NH_3)_{n+1} \qquad (1)$$

has been studied by Kebarle and co-workers.[13,14] Since the mass spectrometer is remote from the upstream regions of the reaction zone careful interpretation of the data is necessary to ensure that these mass spectrometer data sensibly reflect the ionic composition of the plasma upstream. Additional information concerning the ionic composition upstream may be obtained from the probe data which provides mass ratios m^-/m^+ of the ions as a function of axial position,[1] which indicates whether there is a change in the ion types with axial position in the plasma.

Typical plots of reciprocal ion density vs afterglow time are shown in Fig. 2. The slopes give the ion–ion neutralization rate coefficients (cm^3 s^{-1}) in each case. At late afterglow times a departure from linearity can be seen as the ion density falls to the point where ambipolar diffusion contributes significantly to the loss of ionization.[1]

In Fig. 2(a) data are shown for the decay of an ion–ion afterglow plasma consisting of the "simple" ions $NH_4^+ + Cl^-$. The data are shown for the decay of the Cl^- ion density, but equivalent results were obtained with the NH_4^+ density data. The ion densities shown range from 4×10^{10} to 3×10^9 cm^{-3}. For this experiment the Cl_2 concentration was kept sufficiently low such that the negative ions were all Cl^-. The NH_3 concentration was adjusted so that all positive ions were rapidly converted to NH_4^+ but such that not more than a few percent of the $NH_4^+ \cdot NH_3$ cluster ions were observed downstream in the mass spectrometer. This ensures that insignificant concentrations of cluster ions exist in the upstream reaction zone. The linear portion of the data of Fig. 2(a) yields a neutralization rate of 6.3×10^{-8} cm^3 s^{-1} at 300 K. The linearity of this plot over a density range greater than two half-lives (> factor of 4) means that the neutralization rate coefficient may be obtained with some confidence.[15]

In Fig. 2(b) data are shown for the decay of a plasma in which the cluster ion $NH_4^+ \cdot (NH_3)_2$ was the dominant positive ion, and Cl^- was the only negative ion. Density data for Cl^- were used to determine the neutralization rate coefficient because there was no uncertainty in this ion mass throughout the reaction zone. For this experiment the NH_3 concentration was set so that ~95% of the positive ions observed with the mass spectrometer were $NH_4^+ \cdot (NH_3)_2$. Insight into the ion composition along the flow tube could be gained by varying the NH_3 concentration while watching the positive-ion mass spectrum. Mindful that the mass spectrometer sampling is at the terminus of the flow tube, the NH_3 concentration was set on the high side of the value needed to produce maximum $NH_4^+ \cdot (NH_3)_2$ current. The mass ratios m^-/m^+ given by the probe also indicated no apparent changes in the ionic composition along the afterglow. The problem of probe hysteresis[16] is aggravated at high NH_3 concentrations because of contamination of the surface of the probe. (In fact, a white deposit formed on all surfaces within the flow tube during the experiments. Presumably it was NH_4Cl created by wall recombination of the ions. This deposit was removed at the beginning of each data run by baking the flow tube at ~500 K.) Probe hysteresis can be minimized by heating the probe (by electron bombardment) when necessary, but nevertheless the data tended to suffer statistically when high NH_3 concentrations were used. A neutralization rate coefficient of 7.9×10^{-8} cm^3 s^{-1} was obtained from the density data in Fig. 2(b).

In several instances we have obtained data for plasmas in which no one positive or negative ion type could be called dominant. An average neutralization rate coefficient could be determined provided that the reciprocal ion density varied linearly with afterglow time, within the scatter in the data. Such an average neutralization coefficient is a useful result because there is no other way at present of obtaining information on the ion–ion neutralization of most of the larger cluster ions. Our procedure seems valid in view of the linearity of the reciprocal density plots and in view of the fact that all of the neutralization rate coefficients measured to date fall in a fairly narrow range of values. In most cases reported here, the identity of the negative ion is unambiguous and an average neutralization rate is readily obtained from the negative ion density data, even if the positive ion component of the plasma consists of different ion types. In three cases, however, the negative ions were also produced in clustered form to determine if the neutralization rates were affected by having both the positive and negative ions clustered. Fig. 2(c) gives an example of the data in a complex case where the positive ions were a mixture of NH_4^+ (16), NO^+ (16), NO_2^+ (19), $NH_4^+ \cdot (NH_3)$ (23), and $NH_4^+ \cdot (NH_3)_2$ (26), while the negative ions were a mixture of NO_3^- (19), $NO_3^- \cdot HNO_3$ (38), and $NO_3^- \cdot (HNO_3)_2$ (43), (as given by the mass spectrometer operated at low resolution), percentages in parentheses. The Langmuir probe characteristic gives the sum of the individual positive ion currents, or negative ion currents, the ion currents being proportional to the inverse square root of the ion mass in each case.[11] That is, an effective mass m_{eff} can be defined by

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TABLE I. Ion–ion netralization rate coefficients α measured at 300 K with the flowing afterglow for "simple" ions. An average cross section $\bar{\sigma}$ has been calculated in each case by dividing α by the mean relative velocity between the ions at 300 K. In cases where more than one measurement was made, the average value is given. In the last reaction listed, the fractional concentrations are given in parentheses for the positive ions.

Ions	$\alpha \times 10^8$ cm^3 s^{-1}	$\bar{\sigma} \times 10^{12}$ cm^2	Reference
$CCl_3^+ + Cl^-$	4.5 ± 0.5	0.93	1
$CClF_2^+ + Cl^-$	4.1 ± 0.4	0.84	1
$NH_4^+ + Cl^-$	6.7 ± 0.7[a]	0.93	present
$NO^+ + NO_2^-$	6.4 ± 0.7[b]	1.09	1
$NO^+ + NO_3^-$	5.7 ± 0.6	1.02	1
NO^+ (0.7), NH_4^+ (0.3) $+ NO_2^-$	6.3 ± 0.7	0.97	present

[a]The rate coefficients measured at other temperatures are: 8.3 ± 1.0 (220 K) and $5.6^{+0.3}_{-0.6}$ (430 K), in units of 10^{-8} cm^3 s^{-1}.
[b]At 296 K. The rate coefficients measured at other temperatures are: 8.4 ± 1.0 (185 K), 6.4 ± 0.8 (420 K), and 5.8 ± 0.6 (530 K), in units of 10^{-8} cm^3 s^{-1} (Ref. 7).

$$m_{eff}^{-1/2} = f_1 m_1^{-1/2} + f_2 m_2^{-1/2} + \cdots , \quad (2)$$

where f_i is the fraction of a given ion present in the plasma and is determined by the mass spectrometer, and m_i its mass, so that the total ion density is readily determined from the probe characteristic according to orbital-limited probe theory. The mass ratios m^-/m^+ determined with the probe are in good agreement with the ratio m_{eff}^-/m_{eff}^+ determined from the mass spectrometer data thus giving experimental support to the above procedure. An average neutralization rate of 5.8×10^{-8} cm^3 s^{-1} is indicated by the slope of the reciprocal density plot.

The majority of results were obtained at 300 K. Two rate coefficients were measured at ~200 K by surrounding the flow tube with solid CO_2 and precooling the helium carrier gas. Measurements have also been made at temperatures up to ~550 K by surrounding the flow tube with an oven. Temperatures were measured using two thermocouples positioned in the flowing gas near to the flow tube walls at two axial positions.

III. RESULTS

A. Simple ions

The measured ion–ion neutralization coefficients α for "simple" ions (as opposed to clustered ions) at 300 K are listed in Table I. In each case we have also listed an average cross section $\bar{\sigma}$ which is simply $\alpha/\bar{v}_r$, where $\bar{v}_r$ is the mean relative velocity of approach between two thermal ions. The velocity $\bar{v}_r$ is given by $\bar{v}_r = (8kT/\pi\mu)^{1/2}$, where μ is the reduced mass of the ion pair.[17]

Much of the data in Table I have been previously reported, and these are indicated. We have listed in Table I only those reactions involving Cl^-, NO_2^-, and NO_3^-, appropriate for comparisons with the cluster ion measurements to be presented below. We have not listed our results at temperatures other than 300 K since most of the measurements were made at room temperature. However, it is relevant to mention that our previous $NO^+ + NO_2^-$ data[7] span the temperature range 185–530 K and the neutralization rate coefficients are consistent with a $T^{-1/2}$ temperature dependence as predicted by theory[18] (for $T \lesssim 10^3$ K). In the current set of measurements, we have obtained neutralization rate coefficients for $NH_4^+ + Cl^-$ at 220, 300, and 430 K. These results are listed in Table I and a footnote to Table I; again the measured neutralization rate coefficients are consistent with a $T^{-1/2}$ temperature dependence.

One notes from Table I that the range of values for the mutual neutralization rates of "simple" ions is narrow, and likewise the average cross sections. Theoretical work[18] has shown that not much variation is expected in the cross sections for reactions involving species of high electron affinity (E.A. $\gtrsim$ 2 eV). Here, we are working with Cl(E.A. = 3.6 eV), NO_2(E.A. = 2.3 eV), and NO_3(E.A. = 3.9 eV). Although no calculations have been made for most of the specific reactions studied, the measured neutralization rate coefficients are in general agreement with the magnitudes obtained theoretically for other reactions.[18]

B. Clustered ions

In Table II we present the results for clustered ion species at 300 K. From the measured rate coefficients α we have again calculated mean cross sections $\bar{\sigma}$ by dividing α by the mean relative velocity between ion pairs, $\bar{v}_r$. Where there were mixtures of ion types we give an average α and a range of $\bar{\sigma}$ values on the assumption that the individual rate coefficients of the simultaneous reactions between all combinations of positive and negative ions are identical. The $\bar{\sigma}$ are useful in comparisons with the $\bar{\sigma}$ for simple ions (Table I), but the comparisons are strictly speaking valid only if the energy dependence of the cross section is the same for both simple and unclustered ions.[17] As was observed for simple ions, the range of values of α for the cluster ions in Table II is small. However, the general trend within these data is of a significantly increased cross section for cluster ions compared with unclustered ions, but only by about 50% on average. The increased values of $\bar{\sigma}$ for clustered species are, of course, a reflection of the similarity of the measure rate coefficients between the clustered and unclustered systems, but we feel that the increase in $\bar{\sigma}$ is indeed noteworthy.

IV. DISCUSSION

The process of mutual neutralization of simple positive and negative ions is relatively well understood compared with the neutralization of clustered ions. For simple atomic species the neutralization may be viewed as a Coulomb interaction between the ions which leads to electron transfer, converting the initial ionic states into neutral product states. Since the reactions are exoergic by several eV there will be a number of excited neutral product states that are accessible, and electron transfer can take place where any of these excited neutral potential curves cross the ionic potential curve ("curve crossings"). The electron transfer probability

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TABLE II. Ion–ion neutralization rate coefficients α measured at 300 K with the flowing afterglow for clustered ions. An average cross section $\bar{\sigma}$ has been calculated in each case by dividing α by the mean relative velocity between the ions at 300 K. Where mixtures of ion types were present, the fraction of each as measured downstream at the mass spectrometer is given. In cases where more than one measurement was made, the average value is listed.

Ions	$\alpha \times 10^8$ cm^3 s^{-1}	$\bar{\sigma} \times 10^{12}$ cm^2	Reference
$NH_4^+ \cdot (NH_3)_2 + Cl^-$	7.9 ± 1.0	1.45	present
$NH_4^+ \cdot (NH_3)_2 + NO_2^-$	4.9 ± 0.6	0.94	present
$NH_4^+ \cdot (NH_3)_2(0.67)$, $NH_4^+ \cdot (NH_3)_3(0.33)$ + NO_2^-	5.5 ± 0.6	1.08–1.15	present
$NH_4^+(0.31)$, $NO^+(0.25)$, $NH_4^+ \cdot NH_3(0.25)$, $NH_4^+ \cdot (NH_3)_2(0.19)$ + $NO_2^-(0.47)$, $NO_3^-(0.53)$	9.6 ± 1.3	1.37–2.03	present
$NH_4^+(0.16)$, $NO^+(0.16)$, $NO_2^+(0.19)$, $NH_4^+ \cdot NH_3(0.23)$, $NH_4^+ \cdot (NH_3)_2(0.26)$ + $NO_3^-(0.19)$, $NO_3^- \cdot HNO_3(0.38)$, $NO_3^- \cdot (HNO_3)_2(0.43)$	5.8 ± 0.9	0.86–1.47	present
$NH_4^+ \cdot NH_3(0.27)$, $NH_4^+ \cdot (NH_3)_2(0.33)$, $NH_4^+ \cdot (NH_3)_3(0.40)$ + $NO_3^-(0.30)$, $NO_3^- \cdot HNO_3(0.33)$, $NO_3^- \cdot (HNO_3)_2(0.37)$	6.1 ± 1.0	1.15–1.73	present
$H_3O^+ \cdot (H_2O)_3 + Cl^-$	4.8 ± 0.6	0.93	present
$H_3O^+ \cdot (H_2O)_3 + NO_3^-$	5.5 ± 1.0	1.27	1
$H_3O^+ \cdot (H_2O)_3 + NO_3^- \cdot HNO_3$	5.7 ± 1.0	1.54	1
$NO^+ \cdot (NO_2)_2 + NO_3^- \cdot (HNO_3)_3$	3.5[a]	1.2[a]	1

[a]This reaction was studied at 182 K; however, the values of α and $\bar{\sigma}$ given above have been extrapolated to 300 K (assuming $\alpha \sim T^{-1/2}$ and $\bar{\sigma} \sim T^{-1}$), to facilitate comparisons.

may be calculated by the Landau–Zener method. For molecular ions the number of curve crossings becomes very large and Olson[18] has given an "absorbing sphere" model of the interaction where the accessible product states are treated as a continuum. This theory has been used by Olson to calculate rate coefficients for a number of reactions, and his values tend to be within a factor of two of our experimental values for the simple ion reactions. Furthermore, neutralization rate coefficients that we have measured at different temperatures (185–530 K) display the theoretically predicted temperature dependence.

For the neutralization of clustered ions, it has been suggested that the addition of polar molecules to a core ion will modify the neutralization process.[4,5] It is expected that the effect of building clusters will be to impede the normal process of neutralization by electron transfer, since clustering to both positive and negative ions will make the ionic states more stable with respect to the neutral states (by as much as 1 eV per water molecule, for example). For a negative ion the binding energy of the polar molecule to the core ion tends to increase the electron affinity, while for a positive ion clustering effectively reduces the ionization potential. For the smaller water clusters in particular, F. T. Smith[19] has suggested that there may be unfavorable Franck–Condon factors for the electron transfer, as well. As more polar molecules are added the ionic cluster states become more and more stable until eventually electron transfer may become endoergic. For clusters larger than some critical size, Bennett *et al.*[4] and Huestis *et al.*[5] propose a mechanism of neutralization by coalescence of the positive and negative ions into a larger neutral entity. (For water clusters, it is possible that as few as six water molecules bound to both the positive and negative core ions could lead to a stable ionic state of the coalesced molecule.) They envisage that during the Coulomb interaction there is "tidal excitation" of rotational and vibrational modes in the bonds between the polar molecules and the core ions, resulting in an initially unbound orbit being converted into a bound orbit. Once the orbit is bound the ions eventually coalesce but charge separation is maintained.

In order to estimate the order of magnitude of the rate coefficient for this process two models have been proposed which should give approximate lower and upper bounds for α.[4] It is suggested that the model of a hard sphere collision between positive and negative ions should give the lower bound. The upper bound was estimated on a tentative description of the tidal excitation process. These preliminary estimates of the rate of this coalescence set the approximate lower bound $\simeq 5 \times 10^{-8} (300/T)^{1/2} (6/\bar{n})^{1/6}$ cm^3 s^{-1} and the upper bound $\simeq 5 \times 10^{-7} (300/T) (6/\bar{n})^{1/2}$ cm^3 s^{-1} for water cluster ions (of $\bar{n} \geq 6$), where $\bar{n}$ is the average hydration number. The lower limit for α is actually consistent with our ex-

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perimental results, although our ions are of smaller $\bar{n}$. The slow decrease of α with $\bar{n}$ that is predicted is interesting since our data suggest that any variation of α with $\bar{n}$ is, in fact, small. Certainly there would have to be a dramatic increase in α between $\bar{n} \sim 3$ and $\bar{n} \sim 6$ if experimental data were to approach the upper limit theoretical prediction.

Consideration of our experimental data in terms of these theoretical ideas shows that at least up to $\bar{n} = 3$ there is no marked change in α due to clustering although the cross sections are somewhat increased. Thus it can be said that our cluster ion reactions probably fall in the class of reactions describable by the absorbing sphere model, and it is not possible to point to effects special to clustered ions. However, some of the systems we have studied may be likely candidates for a "coalescence" neutralization process despite their relatively low $\bar{n}$ values. The ions $NO_3^- \cdot (HNO_3)_n$ which we have studied are more strongly bound than some other cluster ions,[12,20] and thus only a few nitric acid units should be required to favor the "coalescence" neutralization.

V. CONCLUSIONS

The most striking feature of the data is the small spread in the rate coefficients obtained at 300 K for all the neutralization reactions, including the simple monatomic, diatomic, and triatomic positive and negative ions and the much larger polyatomic cluster ions. It is gratifying that the magnitudes of the coefficients are in good agreement (about a factor of 2) with the absorbing sphere calculations of the rate coefficients for simple ion reactions. The theory also predicts, as we observe, only small differences in α for reactions of species with relatively large electron affinities ($\gtrsim 2$ eV). This agreement between experiment and theory is further reinforced by our experimental data on the temperature variation of α for the two reactions $NO^+ + NO_2^-$ and $NH_4^+ + Cl^-$ which are consistent with the theoretically predicted variation at low temperatures (i.e., $\alpha \sim T^{-1/2}$).

That the magnitudes of α for the cluster ion reactions are so similar to those for the simple ions, even when both the positive and negative ions are clustered, is very interesting. The electron affinities of the clusters we have investigated are also high and on the basis of the absorbing sphere model it would not be expected that appreciable differences between the theoretical values of α for these moderately large clusters and those for their core ions would result, despite the larger ionic mass; again, this is substantiated by our experiments. Unfortunately, it seems unlikely that we will be able to investigate the variation with temperature of α for a given cluster ion reaction, because of the rapid change with temperature of the three-body ion–molecule reaction rates which result in the production of the cluster ions. Thus we are not able to justify further the premise that the absorbing sphere model is applicable to moderate size cluster ions. However, the limited evidence we have[7] does at least indicate that the reaction cross sections for neutralization of the cluster ions increases with decreasing temperature. A detailed theoretical treatment of cluster ion neutralization rate coefficients is likely to be prohibitively difficult, but the crude estimates made to date[4,5] for larger clusters ($\bar{n} \gtrsim 6$) give lower limit magnitudes which are remarkably close to our values (measured for somewhat smaller clusters, $\bar{n} \leq 3$), and only a weak dependence on the degree of clustering, $\bar{n}$. On the basis of all the available experimental and theoretical evidence one is tempted to conclude that no great differences should be expected in the neutralization coefficients from those given in Table II even for larger clusters. Indeed, it appears that the ion temperatures are more important in determining the α for cluster ion neutralizations than are the sizes of the ions. If finally substantiated, this conclusion will greatly simplify the problem of calculating deionization rates in the Earth's atmosphere (a modellist's dream!).

Several experimental objectives remain. It is most desirable that measurements are made involving negative ions formed from species of low electron affinity such as O atoms and O_2 molecules, as a further critical test of the theory, which predicts an increase of about a factor of 2 in α at 300 K above those predicted for the higher affinity species. The precision of the afterglow experiment is quite adequate to distinguish such small differences; the problem is in creating high density ion–ion plasmas in which these low affinity species are dominant. Attempts should also be made to determine α for cluster ions ($\bar{n} > 6$) in order to assist theorists in this most difficult area. It is also most desirable to measure the neutralization rates coefficients for atomic ion systems such as $Xe^+ + Cl^-$, since detailed curve-crossing calculations may be made for these and thus valuable comparisons of our experimental data could be made with theory, and also with measurements made using the merged beams technique.[18] Knowledge of the rare-gas/halide neutralization rate coefficients is particularly important in the modeling of excimer laser systems.[21] We would also like to study the reaction $K^+ + Cl^-$ which appears theoretically to be exceptional,[22] having a neutralization rate coefficient 100 times smaller than our typical values.

VI. ACKNOWLEDGMENT

We wish to thank Mr. Peter Lisin for his assistance in data acquisition and analysis.

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APPENDIX B

IONIC RECOMBINATION OF ATOMIC AND MOLECULAR IONS IN FLOWING AFTERGLOW PLASMAS

Ionic Recombination of Atomic and Molecular Ions in Flowing Afterglow Plasmas

by

M.J. Church and D. Smith

Department of Space Research,
University of Birmingham,
Birmingham B15 2TT

Short title: Ionic Recombination in Afterglows

Abstract

Measurements are reported of the decay of ionization in positive ion/negative ion flowing afterglow plasmas. When one or both of the ion species is molecular, e.g. $Cl_2^+ + Cl^-$ or $NO^+ + NO_2^-$, conditions of pressure and ionization density can be readily established under which mutual neutralization (ionic recombination) dominates over ambipolar diffusion and hence the recombination coefficient α_i can readily be determined. When both ionic species are atomic, e.g. $Ar^+ + F^-$, the recombination rate is so slow that ambipolar diffusion is seen to dominate over ionic recombination under the conditions of the experiment, and it has only been possible to determine upper limits for α_i. The results indicate that for several rare gas/halide atomic ion reactions α_i is at least one order of magnitude smaller than for those reactions involving molecular ions, in general accord with theoretical expectations.

1. Introduction

During the last two years we have measured the mutual neutralization rate coefficients, α_i, for many binary reactions such as

$$NO^+ + NO_2^- \longrightarrow \text{products} \qquad (1)$$

The data have been obtained in positive ion/negative ion collision-dominated flowing afterglow plasmas (Smith and Church 1976) and as such relate to truly thermalized conditions. Our measurements represent the only comprehensive data obtained so far for thermalized conditions, although previously a detailed study at suprathermal energies was made using the merged ion beams technique (reviewed by Moseley et al., 1975). A clear distinction should be made at the onset between the binary (two-body) neutralization process under discussion here and the ternary (three-body) neutralization process, viz:

$$A^+ + B^- + M \longrightarrow C + D + M \qquad (2)$$

in which the chemically-passive third body M acts only to stabilize the reaction, this process dominating de-ionization in positive ion/negative ion plasmas at high pressures (Mahan, 1972).

Our interest in mutual neutralization (ionic recombination) stemmed initially from our involvement in aeronomy and so the data obtained so far have been largely for those reactions thought to be important in atmospheric de-ionization (Smith et al., 1976). This invariably means that one or both of the positive and negative ions are molecular and indeed both are often "clustered" ions, (e.g. $H_3O^+.(H_2O)_n$) (Smith and Church, 1977; Smith et al., 1978). This previous study has revealed that the rate coefficients at 300K for these neutralization reactions show remarkably little variation; all are large and lie within the range $(4 - 8) \times 10^{-8}$ cm^3 s^{-1}, being equivalent to a mean thermal cross section of about 10^{-12} cm^2. This is quite consistent with

theoretical predictions, and the large cross section is essentially due to the strong Coulombic attraction of the reacting species coupled with the large number of "pseudo-crossings" of potential curves which result when molecular ions are involved (Olson, 1972).

When both the positive and negative ions are atomic then, from theoretical considerations, the neutralization coefficients are expected to be small (Olson, 1977) since many fewer pseudo-crossings occur. Thus the major objective of the present study was to obtain data on atomic ion mutual neutralization. Largely for practical purposes the rare gas/halide systems were chosen for study, e.g. $Ar^+ + F^-$; additionally there is interest in such systems in relation to excimer laser operation (e.g. Mangano et al., 1977). During the course of the measurements some new data on molecular ion systems were also obtained.

2. Experimental

The experimental apparatus and technique have been reported in detail in a previous publication (Smith and Church, 1976) and will only be alluded to here. A microwave discharge is established upstream in a fast flowing carrier gas producing a spatially-distributed afterglow plasma in the flow tube (Fig. 1). A small concentration of an appropriate electron attaching gas (such as F_2, Cl_2, NO_2 etc.) is introduced into the carrier gas (usually helium) and a positive ion/negative ion flowing afterglow plasma is established which is completely devoid of electrons. A Langmuir probe, which can be moved along the centre axis of the flow tube, is used to determine the positive ion and negative ion number densities in the plasma and a mass spectrometer positioned at the downstream end of the flow tube identifies the ion types present.

The reduction in ion density with distance z along the afterglow plasma column is due to ion-ion recombination and ambipolar diffusion, i.e.

$$v_p \frac{dn_i}{dz} = \frac{dn_i}{dt} = - \alpha_i n_i^2 + D_a \nabla^2 n_i \qquad (3)$$

where n_i is the positive ion density (n_+) or negative ion density (n_-) ($n_i = n_+ = n_-$), v_p is the plasma flow velocity, t is time, α_i is the ion - ion recombination coefficient and D_a is the ambipolar diffusion coefficient in the ion-ion plasma. The prime objective is to establish a sufficiently high ionization density of the desired positive and negative ions to ensure that loss of ionization by ionic recombination is dominant. This clearly requires that diffusive loss should be relatively unimportant and this in turn requires that the carrier gas pressure should be sufficiently high to inhibit diffusive loss (for a given achievable ionization density). The highest pressure that can be tolerated ($\sim$ 1 - 2 Torr) is largely determined by the onset of ion/neutral collisions within the space-charge sheath around the Langmuir probe, which would

complicate the interpretation of the probe characteristics from which the ion densities are obtained (Clements and Smy, 1969)

For reactions involving at least one molecular ion species, we have found that recombination-controlled flowing afterglow plasmas can be created for ion densities $\sim 10^{10}$ cm $^{-3}$ at helium carrier gas pressures of $\sim$ 1 Torr. Equation (3) then has the solution

$$\frac{1}{(n_i)_t} - \frac{1}{(n_i)_o} = \frac{\alpha_i z}{v_p} = \alpha_i t \qquad (4)$$

and so from measurements of n_i at several z , coupled with measurements of v_p (Adams et al., 1975), α_i can be obtained. A typical reciprocal density plot of n_i against time is shown in Fig. 2a for a Cl_2^+ / Cl^- afterglow plasma. The ion-ion plasma is readily obtained by introducing chlorine gas ($\sim$ 1 mTorr partial pressure) into the flow tube either upstream or downstream of the microwave discharge. Inevitably, molecular positive ions are produced when a molecular gas is introduced into a helium plasma containing helium ions, He^+, and metastable atoms, He^m, viz

$$He^+ , He^m + Cl_2 \longrightarrow Cl^+ , Cl_2^+ \qquad (5)$$

followed by

$$Cl^+ + Cl_2 \longrightarrow Cl_2^+ + Cl \qquad (6)$$

The Cl^- ions are formed in electron collisions with Cl_2 molecules (see Caledonia, 1975)

$$Cl_2 + e^- \longrightarrow Cl^- + Cl \qquad (7)$$

and an ion-ion plasma is rapidly established.

For the reaction $Cl_2^+ + Cl^-$ we obtain a value of α_i of 5.0×10^{-8} cm^3 s^{-1}, quite consistent with values previously obtained for molecular ions.

At low ion densities the recombination process contributes decreasingly to the loss of ionization ($\alpha_i n_i^2 \rightarrow 0$) and the plasma becomes diffusion controlled. Equation 3 then reduces to the familiar diffusion equation which means that in the limit of fundamental mode diffusion the ion density will decrease exponentially with time. This will also be the case when α_i is sufficiently small as is predicted for atomic ion reactions (see Section 1 and Section 4).

Afterglow plasmas consisting of a single species of atomic positive ion and a single species of atomic negative ion are not so readily generated, and the procedure we have used to achieve this is best described with reference to Fig. 1. A microwave discharge is established in helium and a short distance downstream the afterglow plasma is exposed to a second microwave field which is sufficiently intense to enhance greatly the diffusive loss of plasma electrons (and positive ions) but not to produce electrical breakdown. By this means all of the positive ions and electrons are removed from the carrier gas and only the long-lived metastable helium atoms (mainly 2^3S with some 2^1S) pass along the flow tube (Smith et al., 1975). A rare gas (Ar, Kr or Xe) is then introduced into the flow and undergoes Penning ionization with the helium metastables:

$$\text{e.g.} \qquad He^m + Xe \rightarrow Xe^+ + e + He \qquad (8)$$

Finally, the halogen gas is introduced which results in the production of the atomic negative ions (via reactions such as (7)) from the Penning electrons. We have been able to study those systems for which the rare gas positive ions cannot charge transfer with the halogen to produce molecular positive ions so that the plasma only contains atomic positive

and atomic negative ions. For several such plasmas, n_i has been measured as a function of z as described above, but the plots of n_i^{-1} against time in all cases do not have the linear form expected when ionic recombination dominates the ionization loss process. The data for the $Xe^+ + Cl^-$ plasma shown in Fig. 2a is typical, being characteristic of a diffusion-dominated afterglow plasma and indicating an α_i much smaller than that for the $Cl_2^+ + Cl^-$ reaction. That diffusion is dominant in the $Xe^+ + Cl^-$ plasma is indicated by the linear semilogarithmic plot of the data (Fig. 2b), in marked contrast with the data for $Cl_2^+ + Cl^-$.

Hence it was not feasible to operate at sufficiently high pressures in atomic ion plasmas such that diffusion was negligible in comparison with ionic recombination, because of the small α_i. However, use could be made of a carrier gas through which ions diffuse only slowly. Argon is the only practical alternative to helium and this we have used for the first time in the investigation of one atomic ion system ($Ar^+ + F^-$) as discussed in the following.

3. Summary of Data

In all except one of the atomic positive ion/atomic negative ion reactions studied, helium was used as the carrier gas and in each case the ion-ion afterglow plasma was clearly diffusion controlled, indicating small ionic recombination coefficients for the reactions. Fig. 3 shows the positive ion number density decay curves obtained which indicate that within the scatter of the data n_+ decays exponentially with time, a clear indication of diffusive loss of ionization. The slopes of these linear plots provide values for the ambipolar diffusion coefficients of the ion pairs (Smith et al., 1975), and these data are listed in Table 1. Other measurements of $D_a p_o$ for these ion pairs are not available for comparison; however the $D_a p_o$ values obtained here are within 10% of those calculated on the basis of published mobility data (McDaniel and Mason, 1973; Dotan et al., 1977).

That diffusion so clearly dominates the loss of ionization along the flowing afterglow plasma column prevents the determination of recombination coefficients α_i. However we have adopted a procedure by which we have estimated the upper limits to α_i given in Table 1. This has involved estimating the maximum value which α_i could take for observable departures to result from the exponential decay curves of Fig. 3 (consistent with any such departures which may be hidden in the scatter of the data). For sufficiently small values of α_i, recombination would have little effect on the spatial distribution of ion density which would closely approximate to a fundamental diffusion mode (McDaniel and Mason, 1973). Then equation (3) may be re-written

$$\frac{dn_i}{dt} = - \alpha_i n_i^2 - \frac{D_a n_i}{\Lambda^2} \qquad (9)$$

where Λ is the characteristic diffusion length. From solutions of this equation, families of decay curves were constructed for each ion pair using

several relatively small values of α_i and the appropriate D_a value from Table 1. These decay curves were then compared with the experimental data to assess the upper limits of α_i . This procedure indicates (Table 1.) that the atomic ion recombination coefficients at 300K are at least an order of magnitude less than those for reactions involving molecular ions. So that closer limits could be placed on α_i , we have used argon as a carrier gas, in which the diffusion coefficients are much smaller than in helium (McDaniel and Mason, 1973). To check that the flow dynamics were properly understood in argon carrier gas we decided first to re-measure α_i for $NO^+ + NO_2^-$, (reaction (1)), which previously we have studied in detail in helium carrier gas and hence for which α_i is well established. This was accomplished by introducing a small amount of NO_2 upstream of the microwave discharge in the argon carrier gas so that an NO^+ / NO_2^- plasma was readily established. Fig.4 shows the reciprocal ion density plot for the system; from the slope of the line an α_i of $7.0 \pm 1.0 \times 10^{-8}$ cm^3 s^{-1} at 300K was derived, in very good agreement with the value obtained in the helium carrier gas ($6.4 \pm 0.7 \times 10^{-8}$ cm^3 s^{-1}, Smith and Church, 1976). The departure from linearity at early afterglow times is due to the flow of argon not being fully developed (Adams et al., 1975).

Next, the $Ar^+ + F^-$ reaction was investigated by simply introducing into the pure argon afterglow a small amount of fluorine downstream of the microwave discharge. The F^- is readily formed (by a reaction similar to (7)) but charge transfer between the Ar^+ ions and F_2 is endothermic at thermal energies so the plasma created contains only Ar^+ and F^- ions. The dramatic difference between the reciprocal density plot obtained in this plasma compared with that obtained in the plasma containing the molecular ions $NO^+ + NO_2^-$ shown in Fig. 4 illustrates forcibly the much slower rate of loss of ion density in the atomic ion plasma. Diffusion is again dominant as may be seen from the data for this reaction

in Fig. 3, however the much smaller diffusive loss rate results in a closer estimate to α_i than that obtained in helium (Table 1).

Unfortunately the other rare gas positive ion/ halide negative ion reactions cannot be studied using argon carrier gas, since Ar^+ charge transfers with chlorine producing Cl_2^+ and use of the Penning ionization technique is not possible because the relatively low energy of Ar^m atoms prevents them from ionizing Kr or Xe. The use of argon carrier gas at higher pressures than in the experiment discussed above (0.3 Torr) would of course further improve the prospects of studying slow recombination processes. Modifications to the flow systems are required before this can be carried out.

4. Conclusions

The data indicate that α_i for the atomic ion reactions studied are at least one order of magnitude less than those typical of reactions involving molecular ions at the same temperature (300K). For the $Ar^+ + F^-$ reaction which we were able to study in argon carrier gas, α_i is seen to be $\lesssim 2 \times 10^{-9}$ cm^3 s^{-1}, approaching two orders of magnitude smaller than the largest value we have obtained at 300K for a molecular ion reaction, i.e. 9.5×10^{-8} cm^3 s^{-1} for $O_2^+ + CO_3^-$ (previously unpublished). Although we know of no calculations of α_i for the particular atomic ion reactions listed in Table 1, the small values are consistent with theoretical expectations for such systems. Indeed it is possible that the actual rates are considerably smaller than our upper limits because in these systems very few product states are available, i.e. there are very few or no favourable pseudocrossings.

Olson (1977) has calculated the recombination coefficients and temperature dependences for the reactions $Na^+ + Cl^-$ and $K^+ + Cl^-$. The values at 300K are 9.3×10^{-9} cm^3 s^{-1} and 1.8×10^{-10} cm^3 s^{-1} respectively. Experimental support for Olson's theoretical values of α_i for the alkali - halide reactions has been obtained by Burdett and Hayhurst (1977) (see also Hayhurst and Sugden, 1967) in their higher temperature studies of flame plasmas. The relatively small values of α_i for these reactions above illustrate not only the general point that an atomic positive ion and an atomic negative ion will neutralize slowly relative to a reaction in which one ion is molecular, but also that there is expected to be a much wider variation in α_i for atomic systems than for molecular systems. Thus it is unwise to generalize further on atomic ion recombination coefficients, and each reaction needs individual consideration.

Accurate experimental determination of the rare gas/halide atomic ion recombination coefficients at room temperature is clearly very difficult

and for reactions with $\alpha_i \lesssim 10^{-9}$ cm^3 s^{-1}, prohibitively so using our flowing afterglow technique. For such slow reactions, reliance will for the time being have to be placed on theory.

Acknowledgements.

We are grateful to Dr. N.G. Adams for many fruitful discussions. This work has been supported by grants from the Science Research Council and from the United States Air Force under Grant No. AFOSR - 77 - 3260.

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Figure Captions

Fig. 1 Schematic of the flowing afterglow apparatus

Fig. 2a Reciprocal positive ion densities versus time at $\sim 300K$ for afterglow plasmas of the ions $Cl_2^+ + Cl^-$ and $Xe^+ + Cl^-$

Fig. 2b Data of Fig. 2a replotted as logarithms of positive ion density versus time.

Fig. 3 Log of positive ion number density versus time at $\sim 300K$ for the atomic ion afterglow plasmas studied. The lower three curves are displaced vertically downwards by one decade for clarity. The data for $Ar^+ + F^-$ (Ar) were obtained in argon carrier gas, all other data were obtained in helium.

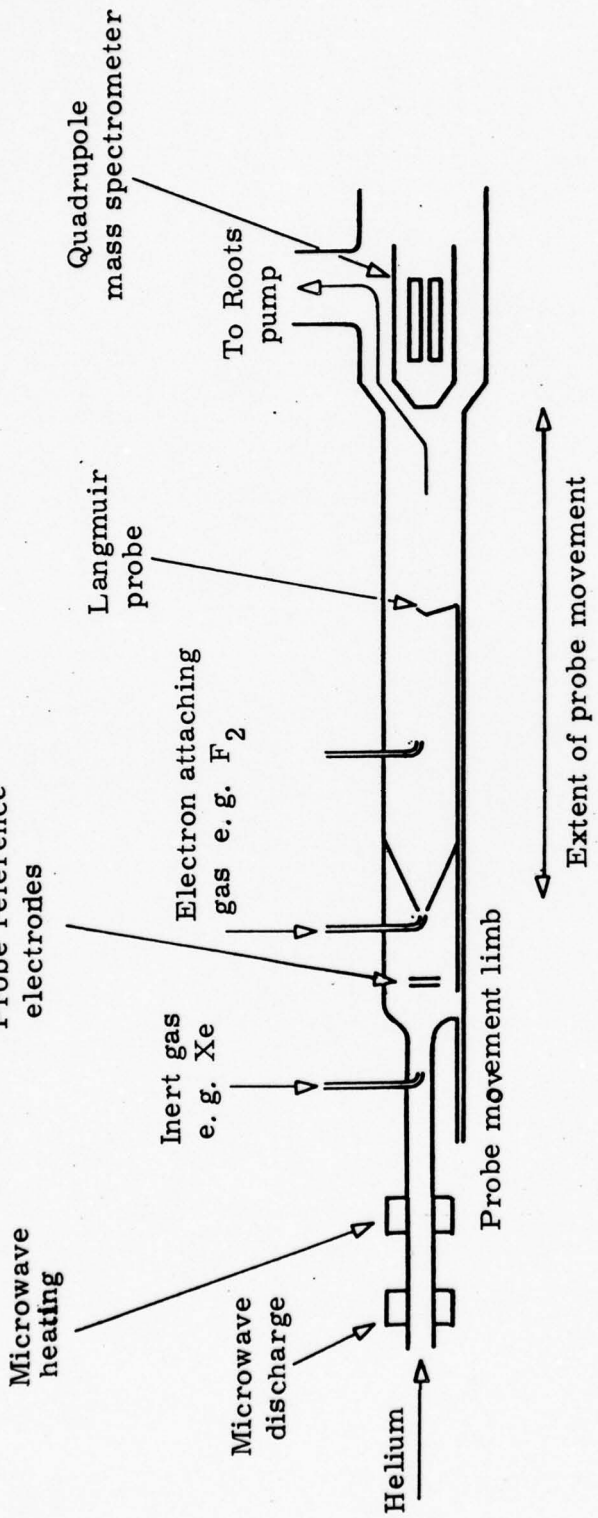
Fig. 4 Reciprocal ion density plots obtained in argon carrier gas at $\sim 300K$ contrasting the behaviour of the molecular ions $NO^+ + NO_2^-$ with the atomic ions $Ar^+ + F^-$

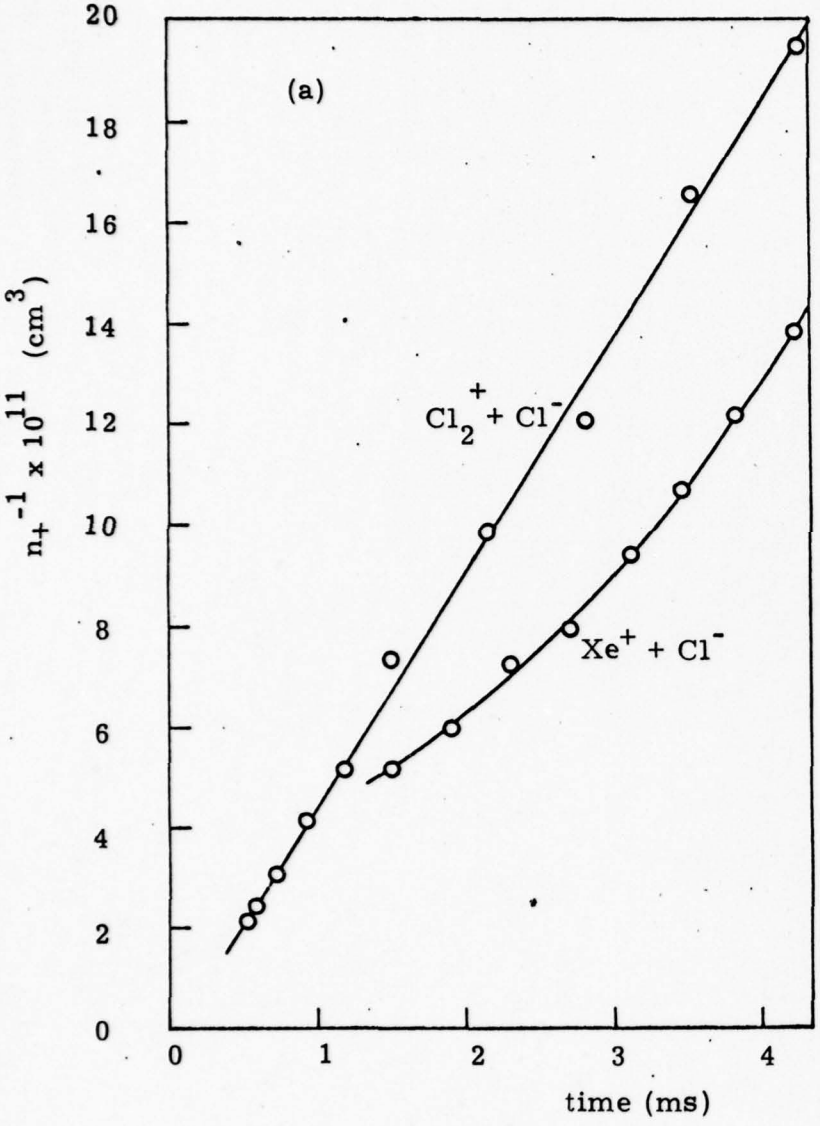
Table 1 Upper limits of α_i for the atomic ion systems investigated experimentally and the values of $D_a p_o$ derived from the exponential decays of Fig. 3. The system marked * was studied in argon carrier gas, all others were in helium.

TABLE 1.

Ions	$D_a p_o$ (cm^2 Torr s^{-1})	$\alpha_i \times 10^8$ ($cm^3\ s^{-1}$)
$Xe^+ + Cl^-$	362	$\leq$ 0.5
$Xe^+ + F^-$	415	$\leq$ 0.5
$Kr^+ + F^-$	460	$\leq$ 0.5
$Ar^+ + F^-$	365	$\leq$ 1.0
$^*Ar^+ + F^-$ (Ar)	23	$\leq$ 0.2

FIG. 1.


Quadrupole mass spectrometer
To Roots pump
Langmuir probe
Electron attaching gas e.g. F_2
Probe reference electrodes
Inert gas e.g. Xe
Microwave heating
Microwave discharge
Helium
Probe movement limb
Extent of probe movement


(a)
$n_+^{-1} \times 10^{11}$ (cm^3)
20
18
16
14
12
10
8
6
4
2
0
$Cl_2^+ + Cl^-$
$Xe^+ + Cl^-$
0
1
2
3
4
time (ms)

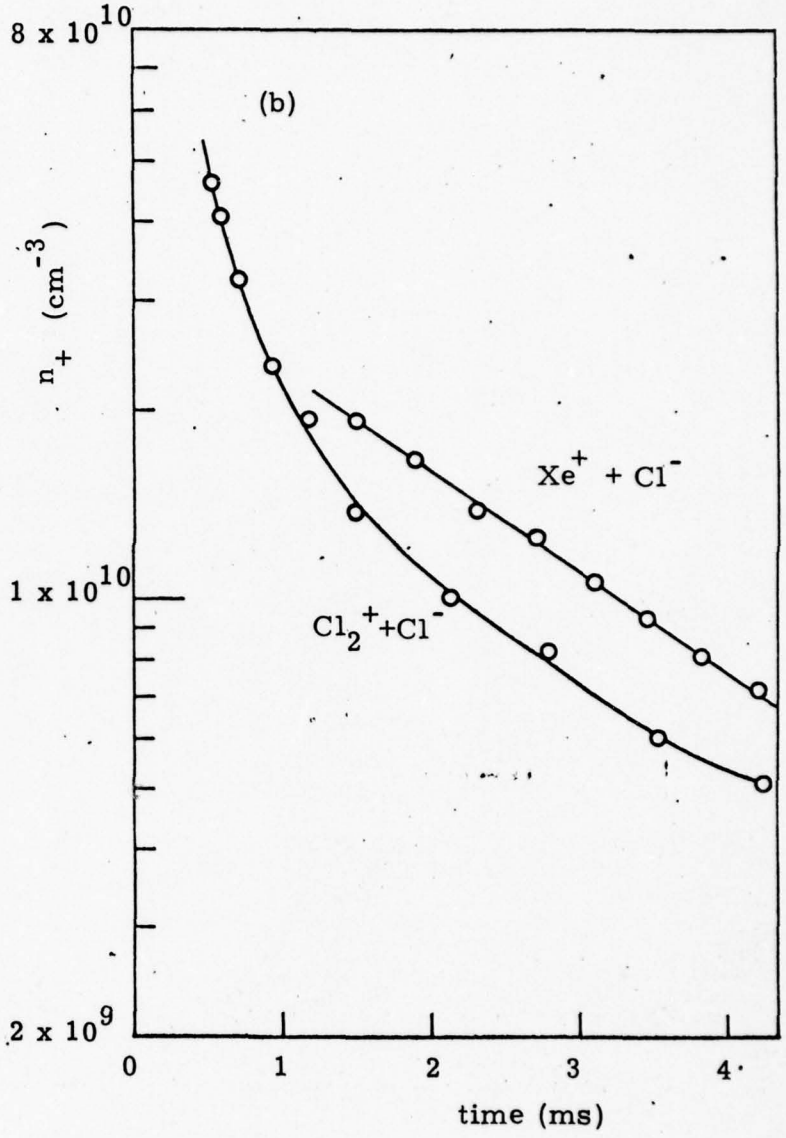

(b)
n_+ (cm^{-3})
8×10^{10}
1×10^{10}
2×10^9
$Xe^+ + Cl^-$
$Cl_2^+ + Cl^-$
0
1
2
3
4
time (ms)

FIG. 2

FIG. 3

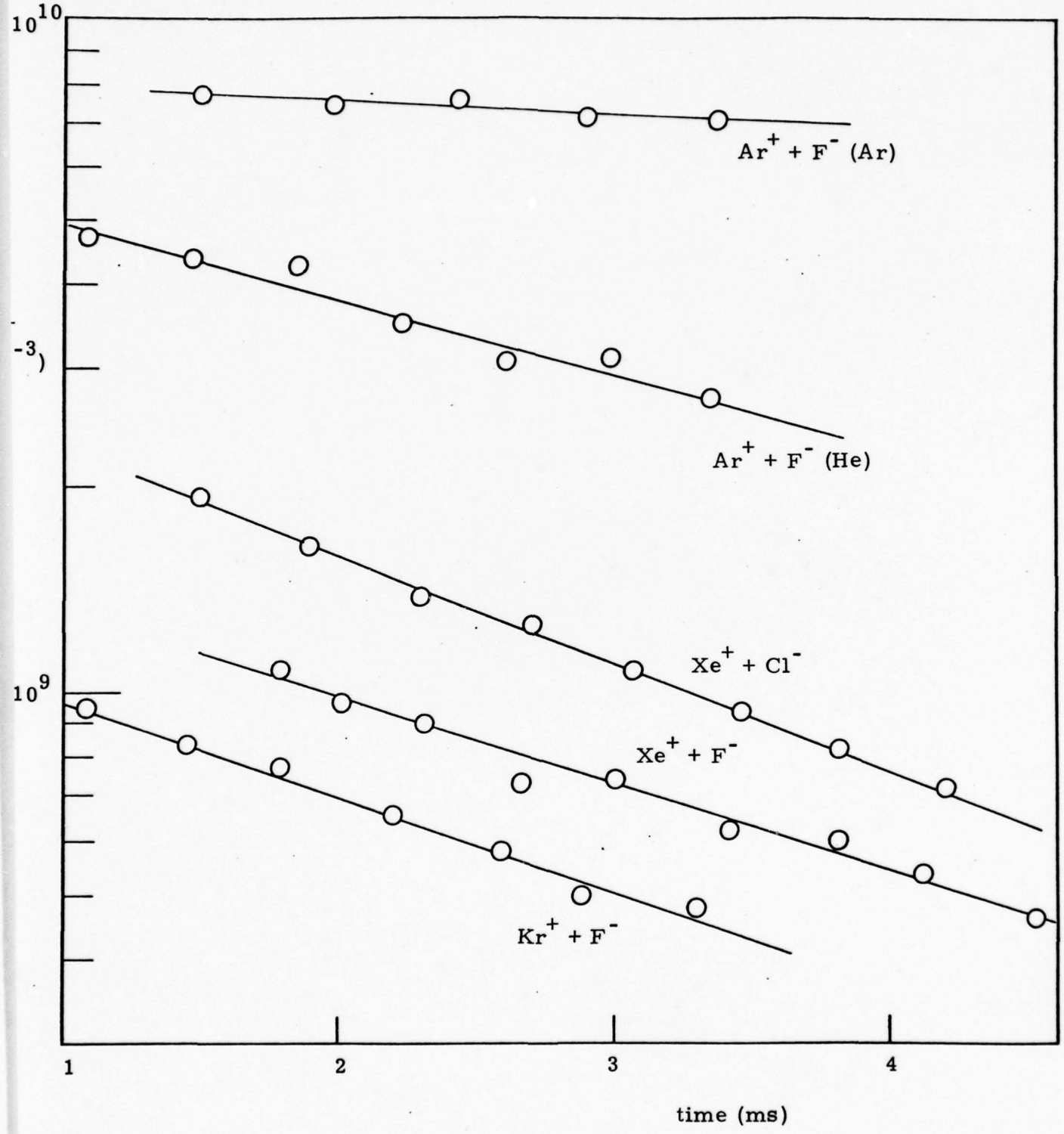
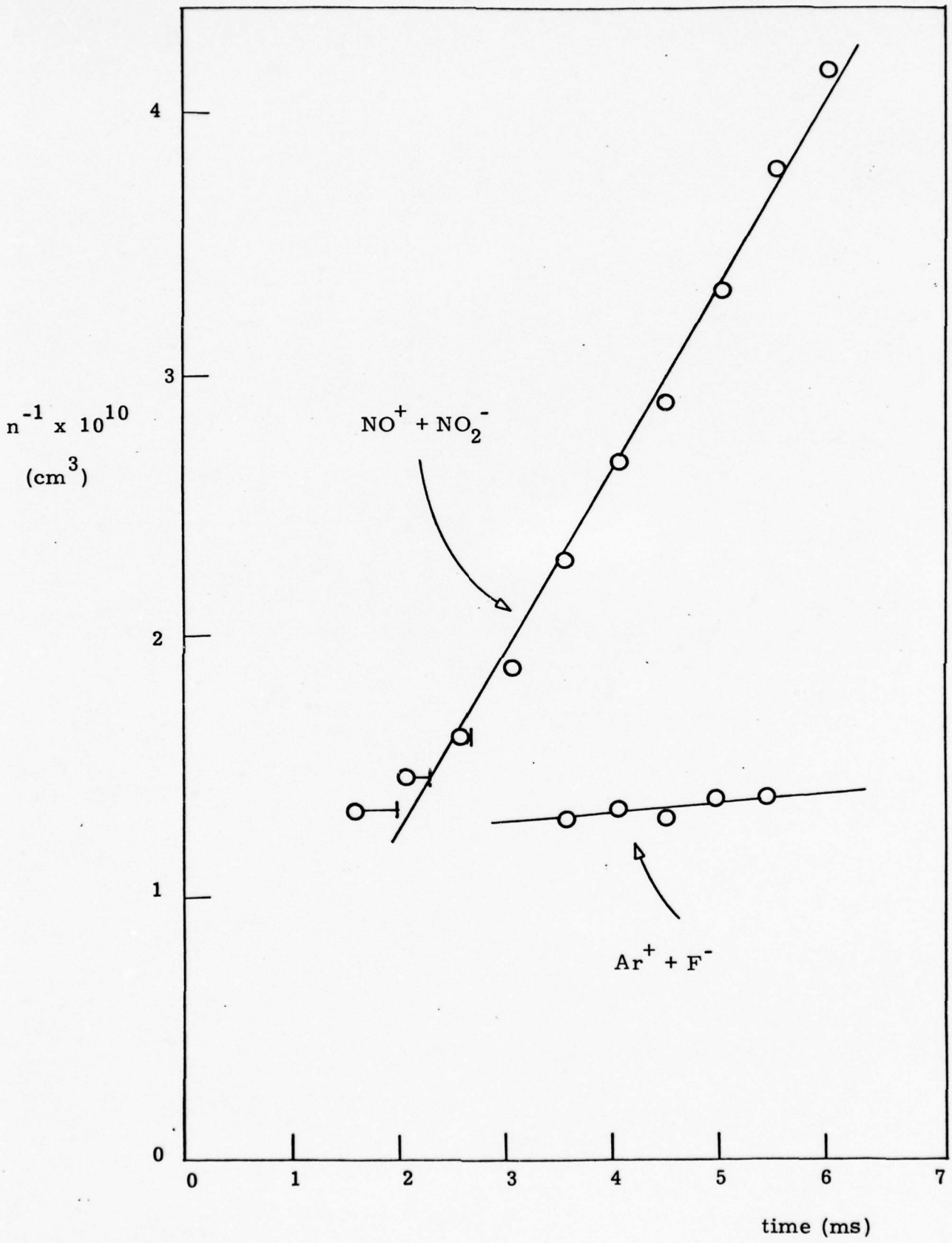


FIG. 4



APPENDIX C

ON THE EMISSION OF RADIATION FROM THE NEUTRALIZATION REACTION $NO^+ + NO_2^-$

ON THE EMISSION OF RADIATION FROM THE NEUTRALIZATION REACTION $NO^+ + NO_2^-$

by

D.SMITH, N.G.ADAMS and M.J.CHURCH

Department of Space Research,

University of Birmingham,

Birmingham, B15 2TT.

Short Title: Radiation from the $NO^+ + NO_2^-$ reaction.

Abstract

A spectroscopic study has been made of the ion-ion neutralization reaction

$$NO^+ + NO_2^- \longrightarrow \text{neutral products}$$

in the wavelength range 180nm to 600nm. This was accomplished by observing the radiation emitted from a flowing afterglow plasma in which the dominant loss process for ionization was the above neutralization reaction. The only significant radiation observed was identified as the γ - bands of NO and it is deduced that the neutralization reaction proceeds via a long-range electron transfer from the NO_2^- into the $A^2\Sigma^+$ state of NO, although population of the $C^2\Pi$ and the $D^2\Sigma^+$ states cannot be ruled out.

1. Introduction

Following our development of the flowing afterglow/Langmuir probe combination to measure binary positive ion/negative ion recombination rate coefficients, α_i , at thermal energies (Smith and Church, 1976) we have measured α_i for several "simple ion" reactions, e.g.

$$NO^+ + NO_2^- \longrightarrow \text{products} \qquad (1)$$

and several "cluster ion" reactions (Smith et al., 1976; Smith et al., 1978), e.g.

$$H_3O^+(H_2O)_3 + NO_3^- \cdot HNO_3 \longrightarrow \text{products} \qquad (2)$$

Such reactions are considered to control deionization in the Earth's lower atmosphere.

Reaction (1) has received special attention since laboratory plasma conditions are established relatively easily for its study (Section 2) and this has enabled α_i to be obtained over a limited temperature range ($\sim$ 200K - 550K) α_i being seen to vary approximately as $T^{-\frac{1}{2}}$ in accordance with theoretical predictions (Olson, 1972; Smith and Church, 1977). The accumulated data of our previous experiments represent a quite comprehensive study of binary mutual neutralization rate coefficients at thermal energies and include reactions involving only atomic ions. (Church and Smith, 1978) e.g.

$$Ar^+ + F^- \longrightarrow \text{products} \qquad (3)$$

These are seen to be very slow reactions relative to those involving molecular ions such as reactions (1) and (2).

We have now turned our attention to the more challenging problem of identifying the neutral products of these reactions and their states of excitation, so that the partition of energy in the reaction products can be investigated and the nature of the interaction can be more accurately described. In this short paper we report the results of a brief spectroscopic study of reaction (1)

2. Experimental

The apparatus has been described in detail in the references cited above and so it will only be alluded to here. The ionic recombination reactions are studied by creating positive ion/negative ion flowing afterglow plasmas in a glass flow tube approximately 1 metre long and 8 cm in diameter. The ion number density in the plasma can be determined at all points on the axis of the flow tube using a movable Langmuir probe. For the particular case under study here, the NO^+/NO_2^- plasma was generated by adding a small amount of commercial NO_2 (partial pressure ~1 mTorr) into the helium carrier gas (at ~ 1 Torr) upstream of a microwave cavity which is used to establish an electrical discharge in the gas mixture. A short distance downstream of the discharge an NO^+/NO_2^- plasma is established which is completely devoid of electrons. Mass spectrometric sampling of the plasma is routinely carried out to establish its ion content (Smith and Church, 1976).

For these spectroscopic studies a quartz window was attached to the Pyrex glass flow tube (via a graded seal) at a position about 25 cm downstream from the discharge and the radiation emitted from the ion-ion plasma was viewed with a grating monochromator (Monospek 600) together with a cooled photomultiplier (EMI 6256 S with a type S cathode). With this combination we were able to explore the wavelength range 180 nm to 600 nm (~7 to 2eV photon energy). Quartz lenses were used in an attempt to focus the radiation from the plasma onto the entrance slit of the monochromator. However in a plasma column in which recombination is the dominant loss process for ionization (and in which, therefore, ambipolar diffusion has been minimized by operating at a sufficiently high gas pressure) then the ion density is approximately independent of radial position and hence a uniformly distributed source of radiation results.

Thus, although sharp focusing could not be achieved, the absence of ionization density gradients ensures that the Langmuir probe measurement of ionization density at the central axis of the afterglow plasma is simply related to the total column density of radiation emitting plasma as viewed by the monochromator. If the spatial distribution of ionization density departs from this simple case, this is manifest in the amount of radiation collected by the monochromator (Section 3)

3. Results

The spectral data was obtained by scanning the monochromator over the available spectral range and by accumulating the photon pulses into a multichannel analyser. Typically, the background in the detection system was equivalent to about 2 photons per second. The spectrum obtained was remarkably simple; only the NO γ-bands ($A^2\Sigma \rightarrow X^2\Pi$ transitions). could be recognized within the complete wavelength range accessible in the experiment. As can be seen from Fig 1 the signal-to- noise ratio is good, the intensity of the major peaks in the spectrum being greater than 100 times the background.

The origin of the spectrumcan be seen with reference to the potential curves of Fig 2 (due to Gilmore, 1965). The emitted radiation is almost entirely due to transitions between the ground vibrational level of the electronically excited A state in NO (i.e. $A^2\Sigma^+$ ($v'=0$)) to the vibrational/rotational manifold of the ground electronic state (i.e. $X^2\Pi(v''=0,1,2...)$), although relatively weak bands can be ascribed to transitions between the $v'=1$ and 2 levels of the A state and the X state manifold. The relative intensities of the bands originating from $v'=0$ transitions to the ground state manifold ($v''=0,1,2,3$ etc) are in close agreement with those expected using the Franck-Condon factors (F.C.F.) for these transitions (Jain and Sahni, 1968). The F.C.F. for transitions from $v' = 1,2,3$ to $v''=0,1,2,3$ are appreciable, yet the observed emissions are weak, indicating that either vibrational states other than $v' = 0$ in the A state are not significantly populated in the aftermath of the positive ion - negative ion neutralization reaction or collisional quenching of higher vibrational levels is occurring (see Section 4).

In order to ensure that the emitted radiation was originating from the ion-ion reaction and that appreciable amounts were not resulting from photoexcitation of the neutral NO in the plasma by radiation from the upstream gas discharge, followed by fluorescence of the NO, the intensity

within the γ-bands was monitored as a function of the ion density, $n_{+,-}$, in the plasma. $n_{+,-}$ was readily varied by changing the helium carrier gas pressure (or to some extent the intensity of the microwave discharge). Fig. 3 shows a typical plot of the radiation intensity against $n^2_{+,-}$ The linearity of the plot confirms that the radiation does indeed originate from the neutralization reaction (since $\frac{dn}{dt}_{+,-} = -\alpha_i n^2_{+,-}$ when ionic recombination is the dominant loss process for ionization). The discernible departure from linearity of the plot at low $n^2_{+,-}$ and hence at low helium pressures is due to the increasing contribution of ambipolar diffusion to the loss of ionization with the accompanying approach towards a fundamental mode Bessel function radial ionization density distribution. This then means that the ionization density as measured by the Langmuir probe at the centre of the plasma is no longer simply proportional to the ionization density averaged along a radius of the flow tube as is the case for the recombination controlled plasma, and so the probe overestimates the average ionization density.

4. Discussion

That the observed radiation largely originates from NO in the $A^2\Sigma (v'=0)$ state does not necessarily mean that this state is preferentially populated immediately after the neutralization reaction. Other states indicated in Fig. 2 are energetically accessible as can be seen from the following consideration of the energetics of the reaction.

We assume that the reactant ions are in their ground vibronic states. This is a reasonable assumption in view of the possible mechanisms by which NO_2^- is formed i.e. via the production of O^- by electron collisions with NO_2 in the gas discharge followed by the charge transfer reaction $O^- + NO_2 \rightarrow NO_2^- + O$ or possibly from HNO_3 impurity in the NO_2 via the reaction, HNO_3 + e (thermal) $\rightarrow NO_2^-$ + OH (Fehsenfeld et al, 1975). Also although NO^+ has two long-lived metastable electronic states, any that are formed in the collisions of electrons with NO_2 in the discharge will be largely collisionally quenched by the electrons in the upstream electron-positive ion plasma. Thus the maximum amount of energy available for excitation after the reaction.

$$NO^+ (X^1\Sigma^+) + NO_2^- (^1A_1) \rightarrow NO (X^2\Pi_r) + NO_2 (\tilde{X}^2A_1)$$

is equal to the difference in the ionization potential of NO (9.25 eV) and the electron affinity of NO_2 (2.28 eV), i.e. 6.97eV. Because the positive and negative ions are accelerated towards each other due to the Coulomb force then an amount of potential energy is transformed into kinetic energy. However in principle this energy is still available to be converted to internal energy. The actual amount of energy available depends on the distance apart at which the electron transfer from the NO_2^- to the NO^+ occurs. (i.e. curve crossing). The potentials at large separation for some possible neutral product states ($(NO)^*$ and NO_2) referred to the NO and NO_2 ground states as the zero of potential and the attractive Coulomb curve for the NO^+ and NO_2^- ground states are shown in Fig.4. It can be seen that the potential curves of the reactant and the likely product states cross at intermolecular distances within the range 10 - 50 Å.

Thus the electron transfer occurs at these relatively large distance for which distortions in the energy levels of the individual interacting species are not significant.

At these distances the available kinetic energy due to the acceleration is within the approximate range 1.4 to 0.3 eV. However it is likely that for electron transfer at these distances, the kinetic energy will largely remains with the product neutrals $(NO)^*$ and NO_2, but this is by no means certain and thus reflects the uncertainty indicated above in the total amount of energy available for internal excitation of the products.

Thus it can be seen with reference to Fig.2 that several electronic states could be populated during the reaction. These include the $a^4\Pi_i$, $b^4\Sigma^-$ and $B^2\Pi_i$ states, each of which have a significantly greater N-O internuclear separation than the ground state of NO^+ and so we consider it unlikely that these states will be populated significantly in the rapid electron transfer at relatively large inter-molecular distance (as corroborating evidence the $B^2\Pi_r \rightarrow X^2\Pi_r$, β-bands were not observed) The electron will most probably enter an electronic energy level in NO whose internuclear separation is similar to that of the NO^+ ground state (a Franck-Condon interaction) producing $(NO)^*$. Therefore $(NO)^*$ could be either the $A^2\Sigma^+$, $C^2\Pi$ or the $D^2\Sigma^+$ states each of which is energetically accessible and none of these three can be ruled out. Indeed it is possible that all three states are populated in varying degrees. Population of the $A^2\Sigma^+$ state is possible up to $v=5$ and although as mentioned above significant emissions are not observed from $A^2\Sigma^+$ $(v>0)$ (in spite of favourable F.C.F.) this could be due to the collisional quenching of the higher vibrational levels by helium atoms, since the radiative lifetime of the $A^2\Sigma^+$ state (2×10^{-6} s, Nicholls, 1964) is comparable to the mean free time for $(NO)^*$/He collisions. That the NO δ-bands ($C^2\Pi \rightarrow X^2\Pi_r$ transitions) were not obvious in the emission spectrum implies that the $C^2\Pi$ state was not significantly populated.

However the $C^2\Pi \rightarrow A^2\Sigma^+$ transitions are allowed and thus provide a mechanism for depopulating the C state. Unfortunately these latter emissions are in the near infra-red and as such are inaccessible to our techniques at present. That the ϵ-bands ($D^2\Sigma^+ \rightarrow X^2\Pi_r$ transition) are also absent from the spectrum similarly does not positively rule out the population of the $D^2\Sigma^+$ state, although only the v=0 and 1 levels are accessible and if any vibrational excitation of the NO_2 ground electronic state occurs in the neutralization process, then both the C and D states essentially become inaccessible energetically. Electronic states of NO_2 are accessible (for NO in the ground state) but no characteristic spectra were observed which if present would have been detected in our experiment.

In summary, the present data are consistent with the model that the NO^+/NO_2^- reaction results either in excitation of NO predominantly in the lower vibrational levels of the A state (v = 0 to 5) which is then collisionally quenched or possibly in the C and D states which then radiatively decay to the A state followed by $A \rightarrow X$ de-excitation and emission of the γ - bands. Observation of the $C \rightarrow A$ and the $D \rightarrow A$ systems in the near infra-red would clarify the situation.

Acknowledgements

This work has been supported by grants from the Science Research Council and from the United States Air Force under Grant No. AFOSR-77-3260.

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Smith D., Church M.J. and Miller T.M. 1978 J.Chem. Phys. 68 1224 - 1229

Figure Captions

Fig.1 Emitted spectrum of an NO^+/NO^-_2 flowing afterglow plasma at 300K. showing the double headed γ-band system of NO. The helium carrier gas pressure was 0.56 Torr. Transitions between the individual vibrational levels are indicated as $v' - v''$.

Fig.2 Partial potential curves for NO from Gilmore (1965).

Fig.3 Plot of the intensity of emitted radiation from the NO^+/NO^-_2 plasma as a function of the (ion number density)^2. This data refers to a wavelength appropriate to the $A^2\Sigma^+$ ($v' = 0$) to $X^2\Pi_r$ ($v'' = 1$) transition (236.3 nm).

Fig.4 The potentials of some possible neutral product states ($(NO)^*$ and NO_2) referred to the NO and NO_2 ground states as the zero of potential and the attractive Coulomb curve of the NO^+ and NO^-_2 ground state ions (only the $v = 0$ vibrational levels are shown). The arrows indicate the inter-molecular separations of the curve crossings.

FIG. 1

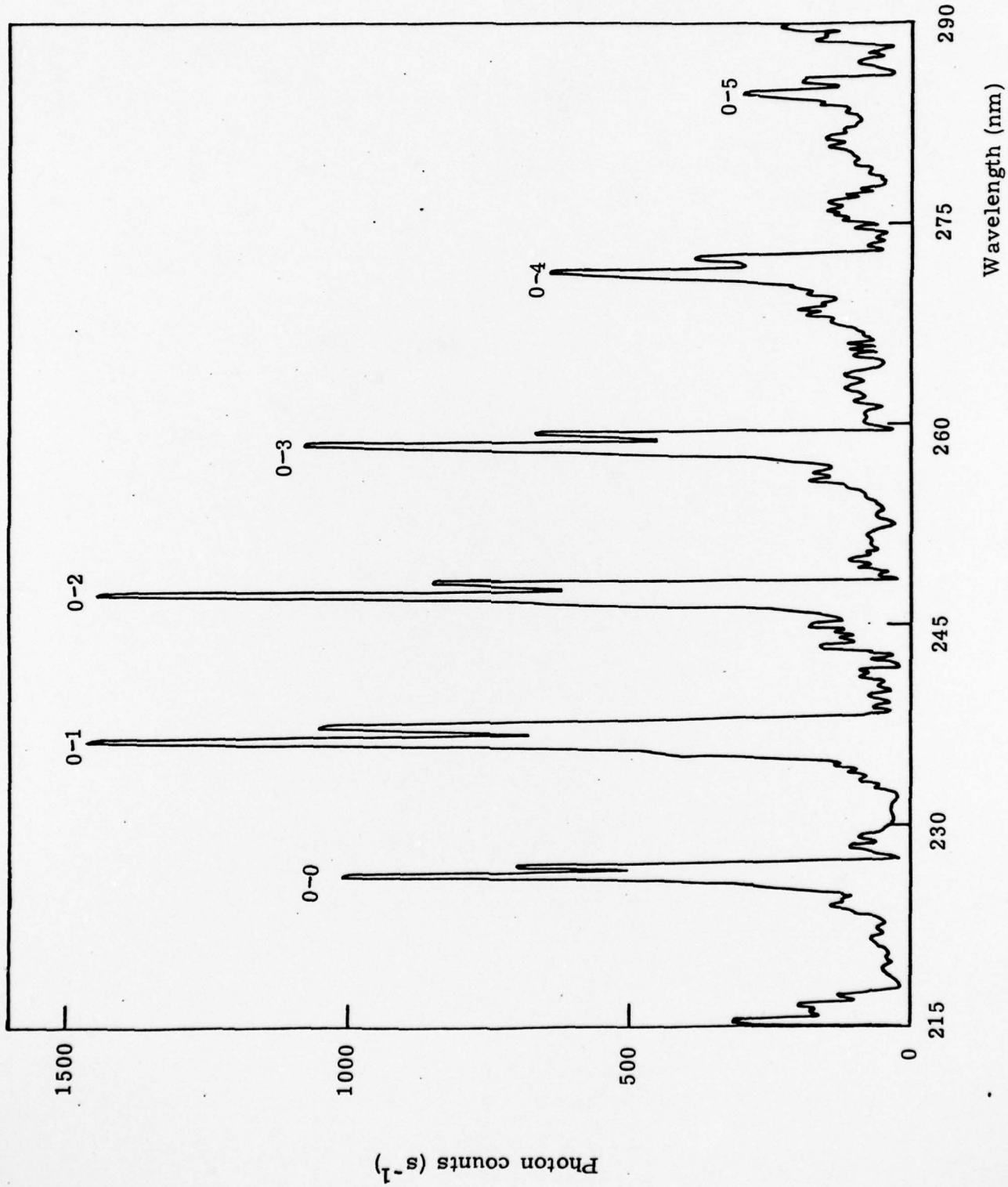

Photon counts (s^{-1})
1500
1000
500
0
215
230
245
260
275
290
Wavelength (nm)
0-0
0-1
0-2
0-3
0-4
0-5

FIG. 2

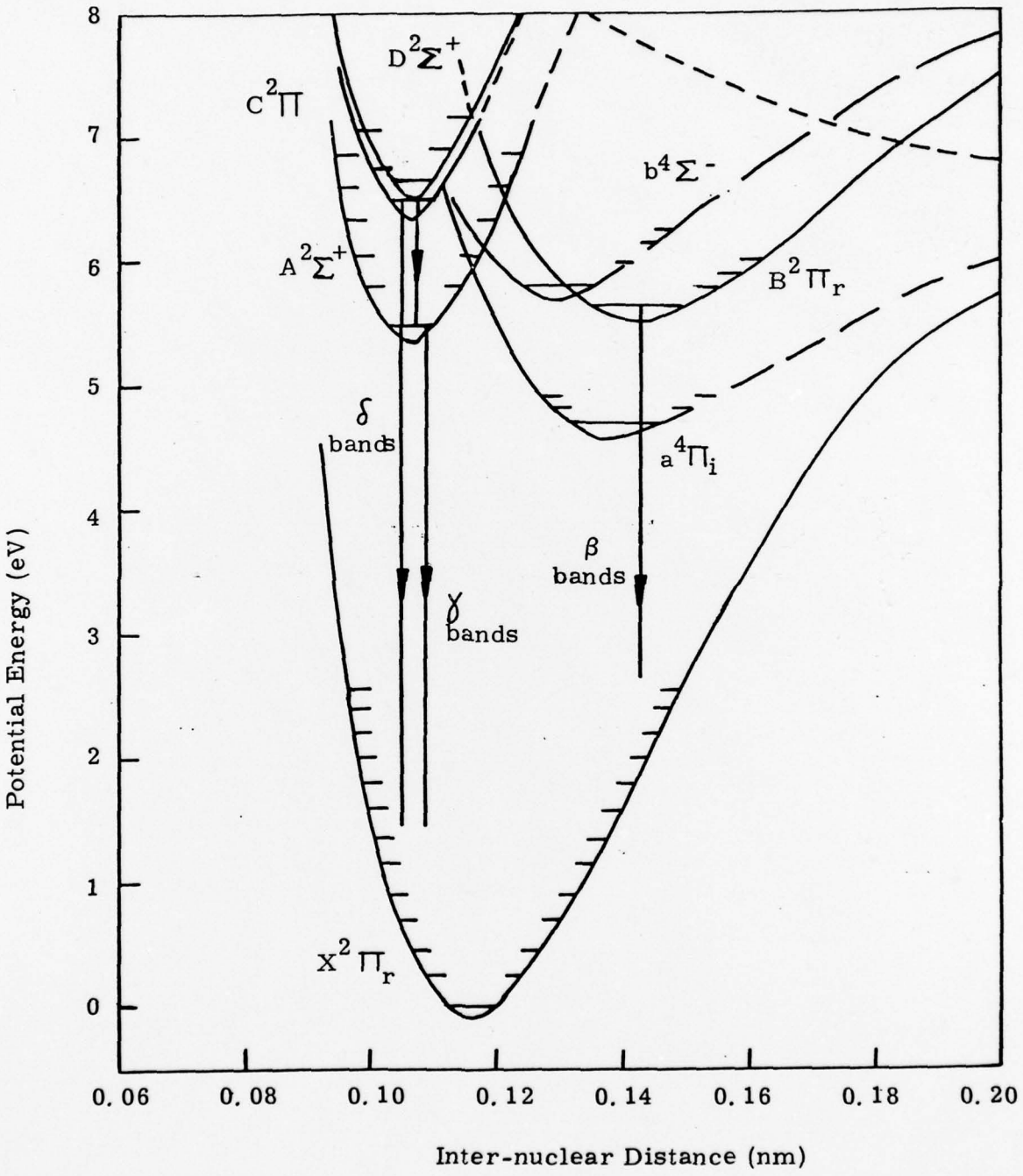

Potential Energy (eV)
Inter-nuclear Distance (nm)
0
1
2
3
4
5
6
7
8
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
$C^2\Pi$
$D^2\Sigma^+$
$b^4\Sigma^-$
$A^2\Sigma^+$
$B^2\Pi_r$
$a^4\Pi_i$
$X^2\Pi_r$
δ bands
γ bands
β bands

FIG. 3

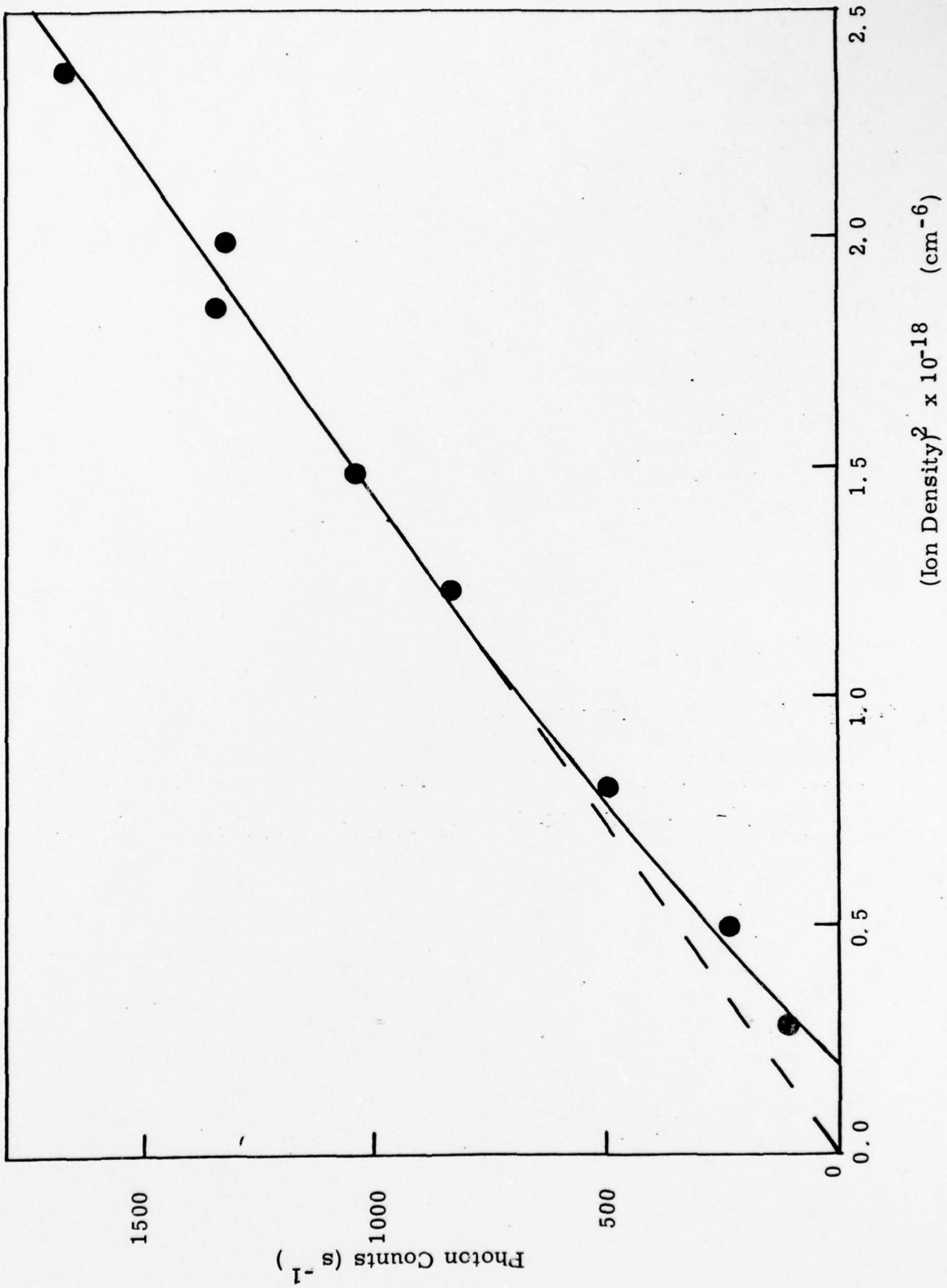
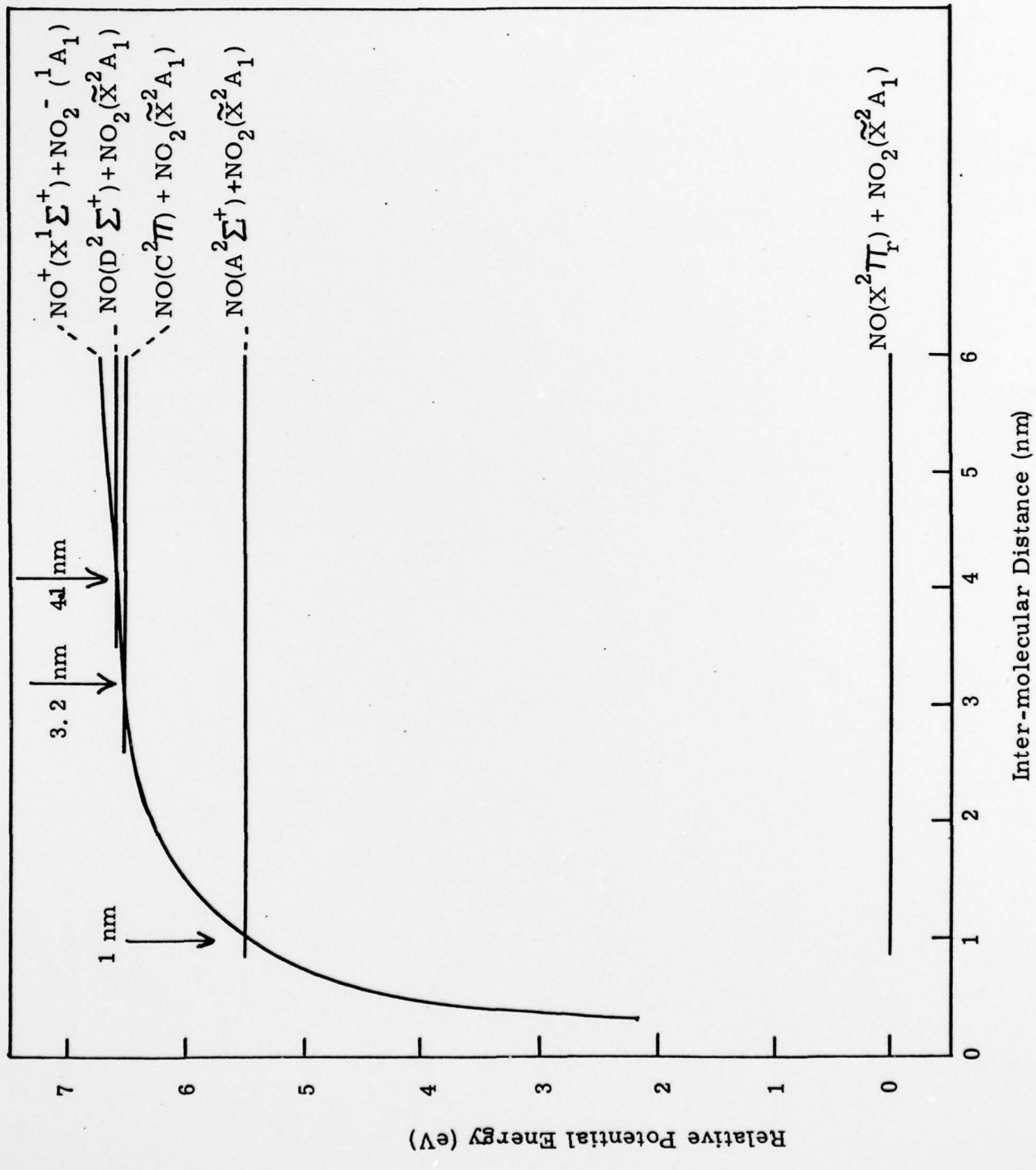

Photon Counts (s^{-1})
0
500
1000
1500
0.0
0.5
1.0
1.5
2.0
2.5
(Ion Density)^2 x 10^{-18} (cm^{-6})

FIG. 4


Relative Potential Energy (eV)
Inter-molecular Distance (nm)
$NO^+(X^1\Sigma^+) + NO_2^-(^1A_1)$
$NO(D^2\Sigma^+) + NO_2(\tilde{X}^2A_1)$
$NO(C^2\Pi) + NO_2(\tilde{X}^2A_1)$
$NO(A^2\Sigma^+) + NO_2(\tilde{X}^2A_1)$
$NO(X^2\Pi_r) + NO_2(\tilde{X}^2A_1)$
1 nm
3.2 nm
4.1 nm
0
1
2
3
4
5
6
7

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