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AN EXPERIMENTAL INVESTIGATION OF THE EFFECTS OF RADIATION OF THE PROPOGATION OF ELECTROMAGNETIC SIGNALS IN AIR

THIRD QUARTERLY PROGRESS REPORT

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by

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I. INTRODUCTION

The present report covers work performed during the period 1 January to 31 March 1964. It begins with a description of several changes made in the optical spectrometer system and vacuum chamber. The results of mass spectrometer measurements on irradiated gases are included; of particular importance in these results is the identification of O_4^+ as the dominant positive ion in O_2 and 2-1, N_2-O_2 mixtures at least at pressures between 1 and 10 Torr. The results of electron loss rate measurements in N_2-O_2 mixtures is presented. The loss frequency in air at low electron densities is found to be $\nu_a = 1 \times 10^{-31} M^2 \text{ sec}^{-1}$, where M is the number of air molecules per cm^3, a factor of two lower than that reported in the previous quarter, apparently due to improved vacuum techniques. Some atmospheric processes are then mentioned, and the report closes with a discussion of work contemplated during the next quarterly period.

II. EXPERIMENTAL EQUIPMENT

A. Optical Window

The 1" pyrex viewing port used for the spectroscopic observations presented in the Second Quarterly Report was replaced with a 3-1/4" diameter pyrex optical window. This larger diameter permits the spectrometer to be placed up to 20" away from the window, allowing ample room to shield the multiplier, without the need for a lens (see calculations in Sec. Quarterly Report). Measurements of the emission from N_2-O_2 mixtures show roughly the same signal-to-noise ratio as did the earlier measurements with the lens and small port. There is reason to believe that the new window has in fact improved the signal-to-noise ratio by a factor of about 5, but quantitative estimates of this are difficult to make, for the following reasons:

First, the photomultiplier tube used for the earlier measurements was damaged during the modification work on the vacuum system. A photomultiplier of larger dark current than the earlier tube, and with unknown photoefficiency relative to it, has been used since the window was changed.

Second, the window had been darkened by F-center formation under continued bombardment of the cavity, so that its visible light transmission was below 50% of the initial value for the measurements made during this quarter.

Another result of the F-center production in the window, even more unfortunate than the darkening, is the gradual structural weakening of the pyrex as irradiation progresses. After about ten hours of cavity irradiation at 1.5 ma beam current the window cracked under atmospheric loading, and was no longer usable.

As a result of this radiation damage in pyrex, a new

fused quartz window will be put into service somewhat sooner than originally anticipated. Fused quartz has been chosen for the window material because of its excellent radiation resistance, broad wavelength transmission range, chemical inertness, and low price. It will be sealed to the cavity with a Viton-A C ring seal for at least initial experiments.

B. Lock-In Amplifier for Optical Spectrometer

The background noise from the photomultiplier in the absence of the electron beam and light signals is of the order of 10^{-9} amperes; an electron beam of 1 ma. raises this by about a factor of 5. The photocurrent from optical signals in the cavity is typically less than 5×10^{-10} amperes, about 10% of the background current. Under the assumption that the photomultiplier gain is 10^5, one finds for the statistical fluctuations in the background photocurrent the value 10^{-10} amperes, which is almost the same as the signal level quoted above. If in addition one includes the effect on the apparent signal intensity of variations in the background due to Van de Graaff instabilities, the prospects for quantitative intensity measurements seem gloomy.

In order to improve the signal-to-noise level in the recording system, the electrometer scheme was replaced by a synchronous detector, in the following way. A large chopper wheel, 12" in diameter, with 16 pairs of alternate teeth and spaces, is mounted in front of the entrance slit of the spectrometer. When driven by a 3600 rpm synchronous motor the chopper produces a 100% modulation of the light entering the spectrometer, at a frequency of 1 kcps. The background noise, which originates in the photomultiplier, is not modulated, so that an ac amplifier tuned to the chopping frequency will see all the light signal but only that portion of the noise spectrum lying in the bandpass of the amplifier. There are two methods which can now be

employed to reduce the noise component of the ac signal-plus-noise out of the amplifier. If the noise has a frequency dependence, one chooses a chopping frequency at which the noise level is low. The second method of noise reduction is to use as narrow a bandwidth as possible in the detecting system. A convenient technique for narrow-banding involves the use of a "lock-in" amplifier, or phase detector. A reference signal is derived from the modulation scheme which is unambiguously frequency and phase related to the chopper. The phase detector can be made to act like a fractional-cycle bandwidth amplifier with center frequency firmly locked to the signal frequency.

A phase detector was obtained from Princeton Applied Research Corporation and compared with the electrometer performance. There is a considerable reduction in the noise produced by the beam, although the improvement is not all that one could wish. A more sensitive photomultiplier and improved gamma shielding will go a long way toward remedying this.

Optical measurements had to be discontinued after the window was destroyed, but will be resumed during the next quarter.

C. Vacuum System

Several modifications were made to the vacuum system during the present quarterly period which have further reduced the ultimate system pressure. The large O-ring gaskets in the cavity and beam tube flanges have been replaced with Viton-A gaskets, which can be baked to 250°C. The channel between the two O-rings on the cavity flange which was formerly used for water cooling has been permanently connected to the forepump. The stainless tubulation in the gas filling system has been cleaned and shortened. The result of these measures has been the reduction of ultimate cavity pressure to 1.6×10^{-7} Torr.

III. MASS SPECTROMETER

At the beginning of this quarterly period, the mass spectrometer was attached to the rf cavity. Two modifications of the spectrometer were made at this time; the ion lens was aligned optically and the entrance aperture was replaced. An aperture diameter of .0135 inches was chosen, which enables the spectrometer to maintain a low internal pressure even with a cavity pressure of 10 Torrs. All of the studies planned for the near future will use gas pressures in the 1 Torr to 10 Torr range.

Typical majority ion currents entering the mass spectrometer in a steady-state experiment are of the order of 100 ions per second as calculated from the diffusion equation, which corresponds to a current of 1.7×10^{-17} amperes. If the mass spectrometer transmits 10% of the entering ions, and the electron multiplier has a gain of 10^6, then the currents measured at the output will be of the order of 10^{-12} amperes. The largest source of noise results from the bremsstrahlung generated by the electron beam from the Van de Graaff accelerator, which produces photoelectrons within the electron multiplier. In addition the gammas produce currents in any cables in the detecting system which are exposed to the gamma flux. With an electron beam of 1.5×10^{-3} amperes, the electron multiplier produces a noise current of 1.4×10^{-10} amperes (3.5 k.v. across the dynode string). This current is equivalent to 1000 input ions per second. The rms fluctuation of this input will produce an output fluctuation of 4×10^{-12} amperes. In fact, the observed fluctuation noise is about 5×10^{-12} amperes. Therefore, in the presence of the electron beam, a signal-to-noise ratio on the order of 1 to 1 can be expected and indeed is found.

Ions were observed in oxygen, in nitrogen, and in mixtures of oxygen and nitrogen when these gases were bombarded by 1.5 Mev

electrons. However, for all but a few ionic species, the signal-to-noise ratio was poor (on the order of 2 to 1). Furthermore, the resolution was poor (on the order of 30) so that positive identification was made for only a few ion species. Table I is a summary of the mass spectrometer data taken during this quarterly period. It is interesting to note that O_4^+ appears to be the predominant ion in all of the measurements made on pure O_2 and 1-2 O_2-N_2 mixtures. There is not enough data nor is it of sufficient quality to warrant further comment at this time.

The electron multiplier current was measured with an electrometer and recorded on a strip chart recorder. One experiment was performed using an ac amplifier and phase detector; for this measurement the voltage on one of the ion lenses was modulated sinusoidally using the reference voltage from an internal oscillator in the phase detector unit. This technique also yielded a signal-to-noise ratio of about 2 to 1, but can be expected to do better when the ion beam can be turned on and off at the reference frequency instead of being sine-modulated as described above. In the next quarter the phase detection technique will be studied further.

In order to improve the resolution of the spectrometer the entrance and exit apertures on the monopole itself will be made smaller. The optimum diameter of the injection aperture is $r_o/\left(\frac{m}{\Delta m}\right)^{\frac{1}{2}}$.

For a resolution of 100 and r_o of 1.5 cm, the optimum diameter is 1.5 mm. A larger diameter has been used in order to increase the transmission through the spectrometer. However, with improved detection, the improvement in resolution will allow a more positive identification of the ion mass despite the decrease in transmission. Of course the improvement in resolution will also separate adjacent mass peaks which now are unresolved.

TABLE I

Mass	Ion Identification	Relative Intensity	Sample Gas
18	H_2O^+	3	N_2 (contaminated)
28	N_2^+	4	at 4 Torrs pressure
36	$2H_2O^+$	2	"
42	N_3^+	2	"
46	NO_2	4	"
56	N_4^+	3	"
70	N_5^+	3	"
85	?	2	"
32	O_2^+	1-1/2	O_2 2 Torrs
48	O_3^+	2	"
64	O_4^+	18	"
32	O_2^+	3	"
48	O_3^+	20	"
56	N_4^+	3	"
64	O_4^+	75	"
80	O_5^+	13	"
85	?	5	"
28	N_2^+	3	2-1 Mixture N_2-O_2
42	N_3^+	7	Total pressure 7-1/2 Torrs
46	NO_2^+	2	"
48	O_3^+	2	"
56	N_4^+	5	"
64	O_4^+	8	"

TABLE I (continued)

Mass	Ion Identification	Relative Intensity	Sample Gas
48	O_3^+	5	O_2 4-1/2 Torrs
64	O_4^+	32	"
80	O_5^+	2	"

IV. IONIZATION MEASUREMENTS

A series of Steady-state measurements of electron densities as a function of pressure and beam current was performed on O_2 and various mixtures of N_2 and O_2 during the quarter. These measurements are of the same type as those described in earlier reports for O_2 and N_2-O_2 mixtures. Research grade gases in steel cylinders, supplied by the Matheson Corporation, were used for the experiments. The empty cavity pressure prior to filling with the gas was typically on the order of 2×10^{-7} Torr with the cavity open to the pumps. This is the best vacuum yet obtained, and is better than that reported in the last quarter by a factor of approximately three.

The electron densities measured in the N_2-O_2 mixtures are linear with beam current at least up to 50 μA over the pressure range investigated, but for higher currents they show a departure from linearity. This latter phenomenon has been discussed in the Final Report and is attributed to an additional significant electron removal process at the higher ionization densities, probably recombination with positive ions. As in earlier work, the slopes of the linear portions of these curves are plotted as a function of pressure.

Three curves are shown in Figure 1, one for pure O_2, and the other two for 1:1 and 4:1 mixtures of N_2 and O_2. A straight line of slope -1 on a semi-log plot is fitted to the data assuming a p^{-1} dependence as required at these pressures if three body attachment is the dominant process. A complete list of all the measurements taken during this quarter is given in Table I, along with estimates of the accuracies of the slopes based on the scatter of the points.

Figure 1 shows that the data are well approximated at the higher pressures by the straight lines, indicating that a p^2

electron loss process such as three-body attachment is in fact occurring. Two features should be noticed. First, the greater the concentration of N_2 in the gas mixture the higher the pressure at which the peak of the specific ionization occurs. This has also been indicated by some preliminary measurements in 2:1 and 3:1 gas mixtures, which are as yet too fragmentary to be included in the present report. Second, the peak of the oxygen curve seems to move to lower pressures than that described in the Final Report. Confirmation of this awaits an extension of measurements to lower pressures. The second observation suggests that the dominant electron removal process at low pressures is more nearly characterized by diffusion with a coefficient of $Dp = 110\ cm^{-2}sec^{-1}$ than by the value $3000\ cm^{2}sec^{-1}$ which was required to provide agreement with the original oxygen data. A comparison of the present data and that contained in the Final Report is shown in Figure 2. The value $Dp = 110\ cm^{+2}\ sec^{-1}$ is the coefficient expected in the ambipolar regime if the diffusing ion is O_2^+. In the Final Report, the apparent large diffusion coefficient was ascribed to electron attachment to beam-generated impurity molecules. The fact that the initial cleanliness of the cavity in the present experiments is a factor of 10 greater than that in the oxygen measurement described in the Final Report would seem to indicate that impurities in the cavity do in some way lead to an anomalously large low-pressure removal frequency.

If three body attachment is the dominant process at high pressures, as indeed indicated by all the data up to the present, then it will be of considerable importance in the delineation of gas processes occurring at these pressures in mixtures of O_2 and N_2 to consider very closely the role of the N_2 molecule in stabilizing the negative ion O_2^-. Assuming N_2 and O_2 are the only species present, the following reactions should occur:

$$O_2 + e^- + O_2 \longrightarrow O_2^- + O_2 \qquad (1)$$

$$O_2 + e^- + N_2 \longrightarrow O_2^- + N_2 \qquad (2)$$

Assuming that electrons are lost only as indicated by the above two equations, the steady-state plasma can be represented by the following equation:

$$k_n p_n i + k_o p_o i = \alpha p_o^2 n + \alpha p_o \xi p_n n \qquad (3)$$

where k_n, k_o are the ionization rate coefficients for N_2 and O_2; α is the attachment coefficient for O_2; p_n, p_o are the partial pressures in Torr of N_2 and O_2 in the gaseous mixture; and ξ is the coefficient which determines the efficiency of the N_2 molecule as a third body relative to the O_2 molecule (assumed to be of the order of a few percent). If we choose $p_o = 1$, then equation (3) becomes

$$k_N p_N i + k_o i = \alpha n + \alpha \xi p_n n \qquad (4)$$

or

$$n/i = \frac{k_n p_n + k_o}{\alpha(1 + \xi p_n)} \qquad (5)$$

where n/i is the slope of the linear plots of electron density versus beam current. For values of ξp_n much less than 1, equation (5) becomes

$$n/i \simeq \frac{k_n p_n}{\alpha} + \frac{k_o}{\alpha} \qquad (6)$$

For $\xi p_n \gg 1$, n/i approaches the assymptomatic value $\frac{k_n}{\alpha\xi}$. Hence assuming k_n, k_o, and α to be constant, a graph of n/i against p_n for small values of p_n should yield a straight line whose slope is k_n/α and whose intercept on the n/i axis is $k/o\ \alpha$. From the attachment coefficient α for O_2, values for k_o and k_n can be found from this plot, which, on substitution into equation (5) yields a value of ξ.

A plot of $n/_i$ against p_n is shown in Figure 3. The generally accepted value for the frequency of three body attachment of thermal electrons in pure oxygen is $2.2 \times 10^3 p^2$ sec^{-1}. Using this value of α, k_n and k_o were found to be 3.95×10^{11} pi electrons cm^{-3} sec^{-1} and 5.9×10^{11} pi electrons cm^{-3} sec^{-1}. The value of k_n is in almost exact agreement with that predicted in the Final Report from theoretical considerations based on data reported by Barber and by Jesse and Sadauskis.

From these values of k_n and k_o, a value of 0.06 was found for ξ. This value is estimated to have an accuracy of 50%, although subsequent data should improve this accuracy. It is, however, in agreement with the value of 0.05 reported by Stebbings and Van Lint[1]. In the next quarter, the measurements will be extended to higher partial pressures of N_2, in order to permit a more accurate estimate of ξ.

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(1) Report, DA-49-146XZ041 (1963) General Atomics, San Diego, Calif.

TABLE II

Run No.	Gas	Total Pressure in Torrs	Gas Mixture Ratio (N_2:O_2)	kc/μA Slope (n/i)	Estimated Accuracy
1.	O_2	1.02		2.70	±20%
	O_2+N_2	2.00	1:1	4.27	±20%
2.	O_2	0.5		5.18	±20%
	O_2+N_2	2.00	3:1	10.30	±5%
	O_2+N_2	1.00	3:1	16.50	±5%
3.	O_2+N_2	6.00	1:1	1.16	±30%
	O_2+N_2	3.00	1:1	2.48	±10%
	O_2+N_2	1.00	1:1	6.35	±10%
4.	O_2	0.2			
	O_2+N_2	1.45	1:1	5.13	±5%
	O_2+N_2	0.36	1:1	7.69	±5%
	O_2+N_2	0.36	1:1	7.30	±5%
5.	O_2	0.10		6.41	±5%
	O_2	0.05		4.84	±10%
6.	N_2+O_2	7.50	2:1	1.70	±5%
7.	N_2+O_2	0.65	2:1	14.65	±5%
8.	N_2+O_2	1.63	2:1	10.05	±5%
9.	N_2+O_2	1.13	3:1	17.0	±5%

TABLE II (continued)

Run No.	Gas	Total Pressure in Torrs	Gas Mixture Ratio (N_2:O_2)	kc/μA Slope ($n/_i$)	Estimated Accuracy
10	N_2+O_2	0.6	4:1	27.52	±5%
	N_2+O_2	1.0	4:1	28.10	±5%
	N_2+O_2	1.8	4:1	22.79	±5%
	N_2+O_2	2.0	4:1	17.52	±5%
	N_2+O_2	2.5	4:1	18.77	±5%
	N_2+O_2	2.6	4:1	13.4	±5%
	O_2+N_2	3.0	4:1	14.25	±5%
	O_2+N_2	3.5	4:1	13.68	±5%
	O_2+N_2	4.0	4:1	10.94	±5%

V. IMPLICATIONS FOR ATMOSPHERIC PROCESSES

Several experimental results obtained during the past two quarters should be reviewed at this time in terms of their possible importance in the understanding of atmospheric ionization processes.

The predominant electron loss process in room-temperature air at sufficiently low electron densities appears to be three-body attachment to neutral oxygen molecules. The negative ion formed in the attachment process has not yet been identified in this laboratory, but it is commonly believed to be O_2^-, which shall be assumed, for this discussion at least, to be correct. The coefficient assigned earlier [1] for the three-body attachment of thermal electrons to O_2, 2.2×10^{-30} cm^6/sec is still consistent with the measurements. In fact, the value for K_n, 4.0×10^7 electrons/cm^3-Torr μamp obtained in the N_2-O_2 mixture experiments is in excellent agreement with the prediction made in the earlier report [1] for ionization of N_2 by beam electrons based on measured energy deposition rates. Until better transient measurements of electron lifetimes are made, from which the attachment coefficients can be obtained directly, the value 2.2×10^{-30} cm^6/sec will be retained.

It is worth noting that our steady-state density measurements yield "linear" plots at low beam currents, the slopes of which cannot include more than a 5% contribution due to the presence of recombination. This is to be contrasted with the reported effect [2] of recombination on the apparent time constant of the exponential electron density decay in afterglows,

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(1) Final Technical Report R-146-8, 30 June 1963, The G. C. Dewey Corporation.

(2) V.A.J. Van Lint et al, Tech. Documentary Report RTD TDR-63-3076, General Atomics Division of General Dynamics, San Diego, Calif., December 1963

hence on the measured attachment coefficients.

The efficiency of N_2 relative to O_2 as a "third body" to stabilize the O_2^- ion formed in the attachment process has been found to be $\xi = 0.06 \pm 50\%$. This is, within experimental error, the commonly accepted value at 300°K. The best estimate of the attachment coefficient in room temperature air from our data is thus $(1.0 \pm 0.1) \times 10^{-31}$ M^2 sec^{-1}, where M is the number of air molecules per cm^3 (relative to the above value for the attachment coefficient in pure O_2). (The factor of two reduction in this number from the value quoted in the Second Quarterly Report must be attributed to improved cavity cleanliness.) This is the value currently recommended for ionospheric calculations[3].

A qualitative observation has been made which, if supported by future evidence, may significantly alter the models used for atmospheric calculation. This is the observation that in O_2 and 2:1 mixtures of N_2 - O_2 the dominant positive ion observed in the cavity is O_4^+, and only small peaks are observed from O_2^+, O_3^+, and O_5^+, as well as from the nitrogen oxides. If O_4^+ is in fact the predominant positive ion in the atmosphere, as is particularly likely at lower altitudes, then predictions of electron-ion and ion-ion recombination rates, which assume O_2^+ to be the positive ion, are irrelevant to atmospheric processes. Further investigation is needed to establish the origin of the O_4^+ peak in gas processes occurring in the cavity, and not to instrumental effects, before any extrapolation to the atmosphere can be made.

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(3) M.H. Bortner, "Chemical Kinetics of Atmospheric Deionization," AFCRL-63-848, General Electric Co., Space Sciences Laboratory, 1963.

VI. PLANS FOR THE NEXT QUARTER

During the next quarter, the measurements of electron attachment in N_2 - O_2 mixtures will be continued, and transient measurements will be resumed in order to provide independent quantitative information on production and loss frequencies. As time permits, the electron loss measurements will be extended to the region of recombination control. Mass spectroscopic studies of positive ions will be continued, and negative ion measurements attempted as well. The optical spectroscopic investigations will be resumed as soon as the new quartz window is installed.

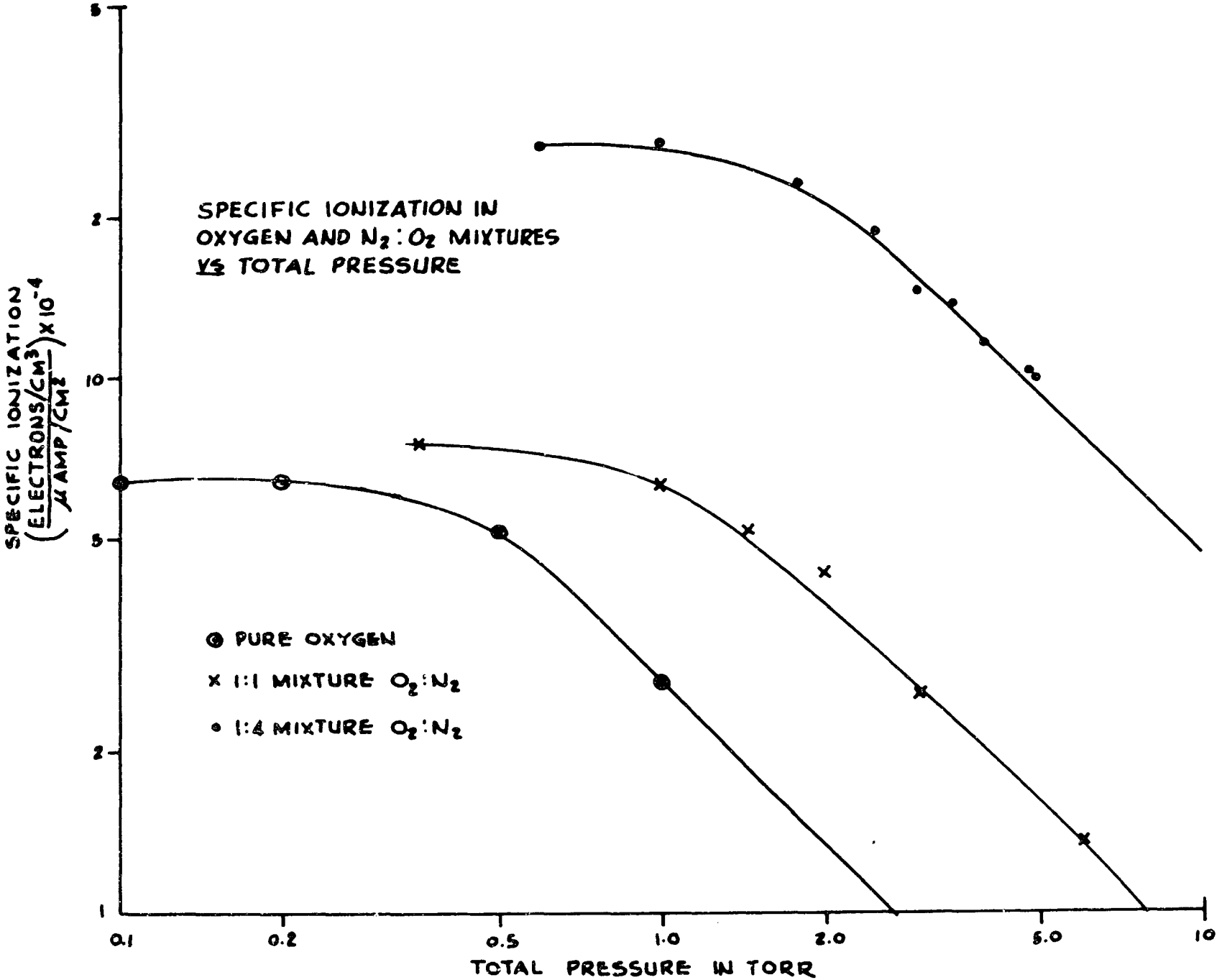
SPECIFIC IONIZATION IN
OXYGEN AND N_2 : O_2 MIXTURES
VS TOTAL PRESSURE
SPECIFIC IONIZATION $\left(\frac{\text{ELECTRONS/CM}^3}{\mu\text{AMP/CM}^2}\right) \times 10^{-4}$
5
2
10
5
2
1
PURE OXYGEN
1:1 MIXTURE O_2 : N_2
1:4 MIXTURE O_2 : N_2
0.1
0.2
0.5
1.0
2.0
5.0
10
TOTAL PRESSURE IN TORR

FIGURE 1

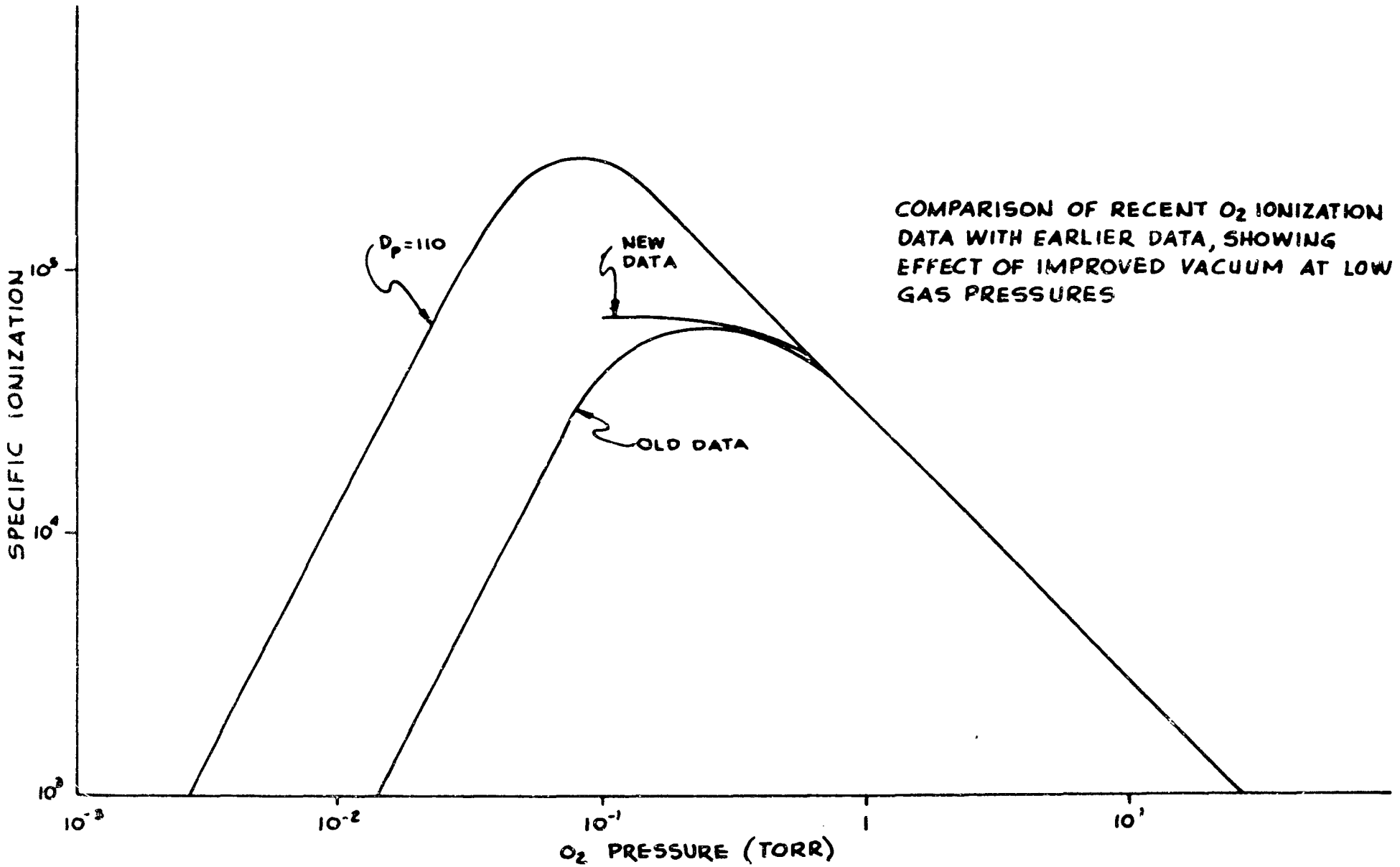
COMPARISON OF RECENT O_2 IONIZATION DATA WITH EARLIER DATA, SHOWING EFFECT OF IMPROVED VACUUM AT LOW GAS PRESSURES
D_p=110
NEW DATA
OLD DATA
SPECIFIC IONIZATION
10^5
10^4
10^3
10^{-3}
10^{-2}
10^{-1}
1
10^1
O_2 PRESSURE (TORR)

FIGURE 2

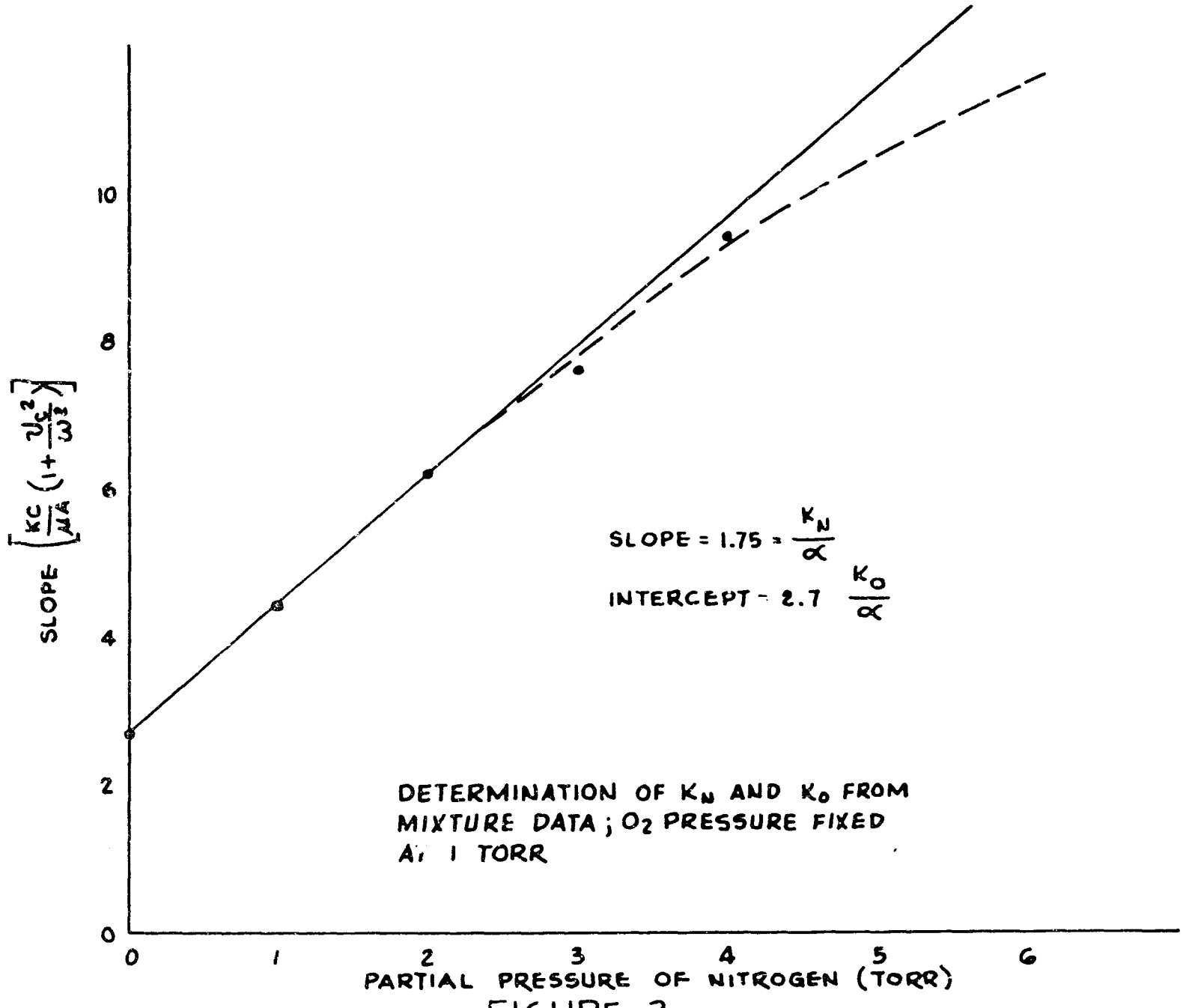
SLOPE $\left[\frac{KC}{\mu A}\left(1+\frac{\nu_c^2}{\omega^2}\right)\right]$
10
8
6
4
2
0
0
1
2
3
4
5
6
PARTIAL PRESSURE OF NITROGEN (TORR)
SLOPE = 1.75 = $\frac{K_N}{\alpha}$
INTERCEPT = 2.7 $\frac{K_O}{\alpha}$
DETERMINATION OF K_N AND K_O FROM MIXTURE DATA; O_2 PRESSURE FIXED AT 1 TORR

FIGURE 3