trolled, we can only state that the quantum efficiency lies between a few tenths and unity. Experiments currently planned using a new lamp design should permit a more precise definition of this efficiency.

Irradiations were carried out at a variety of pressures between 200 and 700 mm and, as anticipated, no pressure effect was observed since in this region the absorption is linear and the collision lifetime is many of orders of magnitude shorter than the lifetime for light emission.

In this work other reaction products such as carbon and carbon suboxide polymer, which should also have been formed, were not investigated. In the static system shown in Fig. 2 such products would have accumulated on the vessel walls and would have been very difficult to detect under the experimental conditions employed.

Conclusions

The iodine lamp has been shown to be very useful for the photochemical study of excited CO ($a^3\Pi$) molecules. The lamp provides specific excitation to the $a^3\Pi$ level in its lowest vibrational level. The high quantum efficiency for reaction to form CO_2 provides an explanation for the fact that the CAMERON bands are never observed in emission except at very low CO pressures.

Acknowledgement

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Production of the Oxygen 5577 Å Emission by Polonium-210 Alpha Radiation*

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Dedicated to Prof. Dr. W. GROTH *on his sixtieth birthday*

The production of the oxygen 5577 Å emission in purified nitrogen at atmospheric pressure by radiation with Po-210 alpha was studied spectroscopically. When the concentration of oxygen in the nitrogen was one part in ten thousand, the most intense emission observed was that of the forbidden atomic oxygen ($^1S \rightarrow {}^1D$) transition. This line emission at 5577 Å was seen to be associated with a continuum that extended from approximately 5600 to 5400 Å. To determine the reaction mechanism producing this emission, the effects of an electric field, temperature, and concentration of oxygen were examined. Several possible mechanisms are considered. The reaction producing oxygen atoms excited to the ^1S state which we found most favorable is shown below.

$$N^+ + O_2 \rightarrow NO^+ + O(^1S).$$

An understanding of the primary processes induced by ionizing radiation and of the reactions of the ions, atoms, and excited species formed are of paramount importance in radiation chemistry. An effective experimental approach to the problems in this field is to examine the emission spectra obtained by the irradiation of gaseous systems with the ionizing radiation of Po-210 alpha particles. It is the purpose of this paper to discuss an interesting observation which was made in an investigation of this type, namely, the presence of the forbidden auroral green line of atomic oxygen ($^1S \rightarrow {}^1D$) at 5577 Å in the spectra resulting from the irradiation of purified nitrogen containing small amounts of oxygen.

This auroral green line is observed when the oxygen concentration is about one part in ten thousand. The intensity of this line plus its associated continuum exceeds the intensity of any other spectra emitted under these conditions. Other than the associated presence of the 2972 Å ($^1S \rightarrow {}^3P$) line, no other lines of atomic oxygen (or atomic nitrogen) are seen.

The 5577 auroral green line is well-known from auroral and airglow studies in the upper atmosphere.

* This is an excerpt from a longer article to be published in Nukleonik, Springer-Verlag.

As early as 1931, CHAPMAN [1] suggested that the OI forbidden system was due to the three atom recombination of oxygen as follows:

$$O + O + O \rightarrow O_2 + O(^1S). \quad (1)$$

He also suggested the reaction:

$$N + N + O \rightarrow N_2 + O(^1S). \quad (2)$$

TANAKA and coworkers [2], working with a low pressure discharge in nitrogen at low temperatures, observed the OI 5577 Å line in the afterglow. NOXON [3] also used a discharge through nitrogen, but in a streaming system at one atmosphere pressure. He observed an afterglow which consisted of the first positive bands of nitrogen, the VEGARD–KAPLAN bands, the atomic nitrogen line ($^2P \rightarrow {}^4S$) at 3466 Å, and the atomic oxygen lines at 5577 Å (rather strong) and at 2972 Å (rather weak). NOXON did not determine precisely the minute concentration of oxygen in his nitrogen. He did notice, however, that he could get a greater intensity of the 5577 Å line if he prepared his nitrogen from sodium azide, and he estimated his oxygen concentration as 0.01% or less.

The production of the auroral green line in our experiments was achieved under different conditions from above, namely, nitrogen at atmospheric pressure and ionizing radiation. Under these conditions the mechanisms of equations (1) and (2) do not apply since concentration of atomic species are too small. It may be seen that the excitation of the $O(^1S)$ state of the oxygen atom may be achieved in different ways, but it will be observed only if the system does not quench the excited state.

Electric discharge techniques are highly developed and simpler experimentally then the techniques involved in the use of ionizing radiation. It might, therefore, seem wise to use discharge techniques and extrapolate the data to ionizing radiation conditions. This is not feasible because the impact of ionizing radiation particles (in this case alpha particles) is predominantly with uncharged and undissociated molecules, whereas in an electric discharge there is a high stationary state of ions and radicals which may become excited by electron impact. Therefore, ionizing radiation must be used and cannot be substituted to determine exactly the proceses that occur.

Experimental

In the irradiation experiments, a polonium-210 alpha source was used. The polonium is in elemental form deposited on the surface of a stainless steel disc one inch O. D. and one-quarter inch thick. A stainless steel window 0.00027 inches thick is placed over the polonium. This very thin window enables the alpha particles to pass through and excite and ionize the gas. A stainless steel wire grid was placed over this thin window for protection against rupture due to electrostatic force and arcing during the application of an electric field. The effective radiation acting on the gas as measured in these experiments using the principle of an ionization chamber is approximately only 1% of the initial factory calibrated activity of the polonium using calorimetry. Although a number of sources were used, the average thermally calibrated strength was about 5 curies. These sources were obtained from Mound Laboratories in Miamisburg, Ohio, a division of the Monsanto Company.

The cell (Fig. 1) containing the polonium source was designed so that the irradiated gas could be cooled with liquid oxygen. By cooling the gas, the concentration of condensible impurities such as moisture could

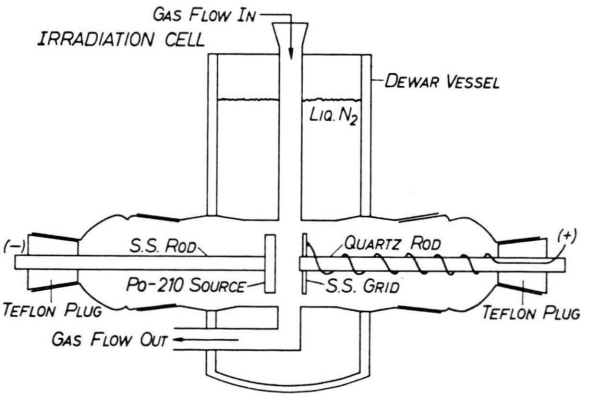

Fig. 1. Schematic of the irradiation cell.

be reduced. Furthermore, the volume of gas emitting light was reduced at these low temperatures due to the higher density of the gas. The temperature change due to the heat liberated by the radiation source is negligible. To facilitate handling of the polonium source during the insertion and removal process, the source was attached to a stainless steel rod held in a large glass joint by means of a Teflon plug. Similarly, a quartz rod with polished ends was inserted in the opposite end of the cell to conduct the weak light emitted during the irradiation to the slit of the emission spectrograph. Without the use of this quartz rod, the ex-

[1] S. CHAPMAN, Proc. Roy. Soc., Lond. A **132**, 353 [1931].
[2] U. TANAKA, F. LEBLANC, and A. JURSA, J. Chem. Phys. **30**, 1624 [1959].
[3] J. F. NOXON, J. Chem. Phys. **36**, 926 [1962].

posures, which averaged a few hours, would be orders of magnitude longer. A stainless steel grid was fitted over the quartz rod and wired to the outside of the cell. Using the source as the other electrode, electric fields as high as 5,000 volts per cm could be applied to the irradiated gas. The purpose of the electric field was to collect the ions formed during irradiation, and notice any effects on the species emitting the light. From the saturation ion current the absorbed energy could be directly determined, since 35 ev are absorbed per ion pair formed in pure nitrogen. Saturation currents varied from 15 to 150 microamps depending on the source used and the age of the source. The Po-210 decays to stable Pb-206 with a half life of 138.4 days.

Tank prepurified nitrogen was purchased from the Matheson Company, East Rutherford, New Jersey. The nitrogen was further purified by passage through two chromous chloride gas washing bottles followed by three liquid oxygen cold traps. After purification, the gas was injected into the cell containing the source. After passing through the cell the gas was bubbled through 15 mm of mercury to maintain a slight overpressure in the system and prevent impurities leaking in. Therefore, the pressure of the gas being irradiated was always kept at 15 mm above atmospheric pressure. The cell containing the source was kept in a dry box which was continually exhausted through filters into a hood. The entire physical arrangement is shown in Fig. 2. Mass spectrometric analysis (Consolidated Electrodynamics Corp. Model 21-130) was used to determine the concentration of impurities and added gases in the nitrogen. Concentrations of parts in ten thousand could be measured precisely.

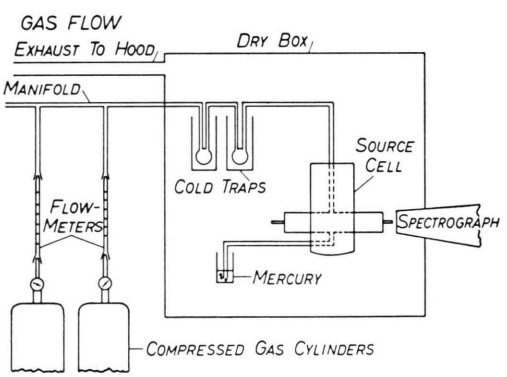

Fig. 2. Schematic of the experimental arrangement.

A HILGER–WATTS Medium Quartz Spectrograph, Model E-498, a HILGER–WATTS Medium Glass Spectrograph Model E-474, and a BAUSCH and LOMB 1.2 meter grating spectrograph were used in this work. The quartz spectrograph covered the range from 2000 Å to 10,000 Å. The glass spectrograph covered the range from 4000 Å to 15,000 Å. The grating spectrograph covered the range from 1850 Å to 7400 Å and was used when better resolution was necessary. Kodak spectroscopic plates and film were used.

Results

When tank nitrogen was passed through chromous chloride bubblers and a series of liquid oxygen cold traps, mass spectrometric analysis showed that the major impurity was still oxygen which was present in one part per ten thousand or slightly less. The predominant emissions observed when this purified nitrogen is irradiated with polonium alpha at room temperature are the oxygen auroral green ($^1S \rightarrow {}^1D$) emission and the nitrogen second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) system. The less intense spectra seen are the nitrogen first positive 0,0 Band ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$), the N_2^+ ($^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$), the NO γ ($A^2\Sigma^+ \rightarrow X^2\Pi$), the NO β ($B^2\Pi \rightarrow X^2\Pi$), a broad continuum from approximately 3700 Å → 4700 Å, Hg lines, and, from very small impurity concentrations, the CN violet and NH 3360 Å system. Long exposures have shown the nitrogen Gaydon green system also.

To determine the nature of the oxygen green ($^1S \rightarrow {}^1D$) emission, the grating spectrograph was used to obtain better resolution. Spectra 9 of Fig. 5 shows the sharp line of the OI ($^1S \rightarrow {}^1D$) transition to be superimposed on a continuum. Long exposures showed this continuum to extend from approximately 5600 Å → 5400 Å. Although the continuum extended to longer wavelengths than the 5577 Å line, it was primarily degraded to the U. V. The 2972 Å line ($^1S \rightarrow {}^3P$) is normally associated with the 5577 Å line at an intensity of about 8% of the 5577 Å line[4]. From long exposures we found the 2972 Å line to be present, but with intensity considerably less than 8% of the 5577 Å emission. (This agrees with NOXON's result at atmospheric pressure.) Since the transition ($^1S \rightarrow {}^1D$) at 5577 Å appeared with high intensity and the transition ($^1S \rightarrow {}^3P$) at 2972 Å could also be observed, we searched for the red lines ($^1D \rightarrow {}^3P$) at 6300 Å and 6364 Å which have an extremely low transition probability of 0.9×10^{-2} (Ref. [4]). Although long exposures and spectroscopic plates highly sensitive to the red were used, these lines were not observed indicating that the metastable ^1D state was quenched most likely by the small amounts of O_2 present. The metastable levels of the oxygen molecule in this region i. e. ($a^1\Delta_g$ and $b^1\Sigma_g^+$) could disactivate the ^1D atomic oxygen state. No other atomic oxygen lines or molecular oxygen bands were observed.

[4] J. W. CHAMBERLIN and A. B. MEINEL in Kuiper's The Solar System Vol. II, University of Chicago Press [1954].

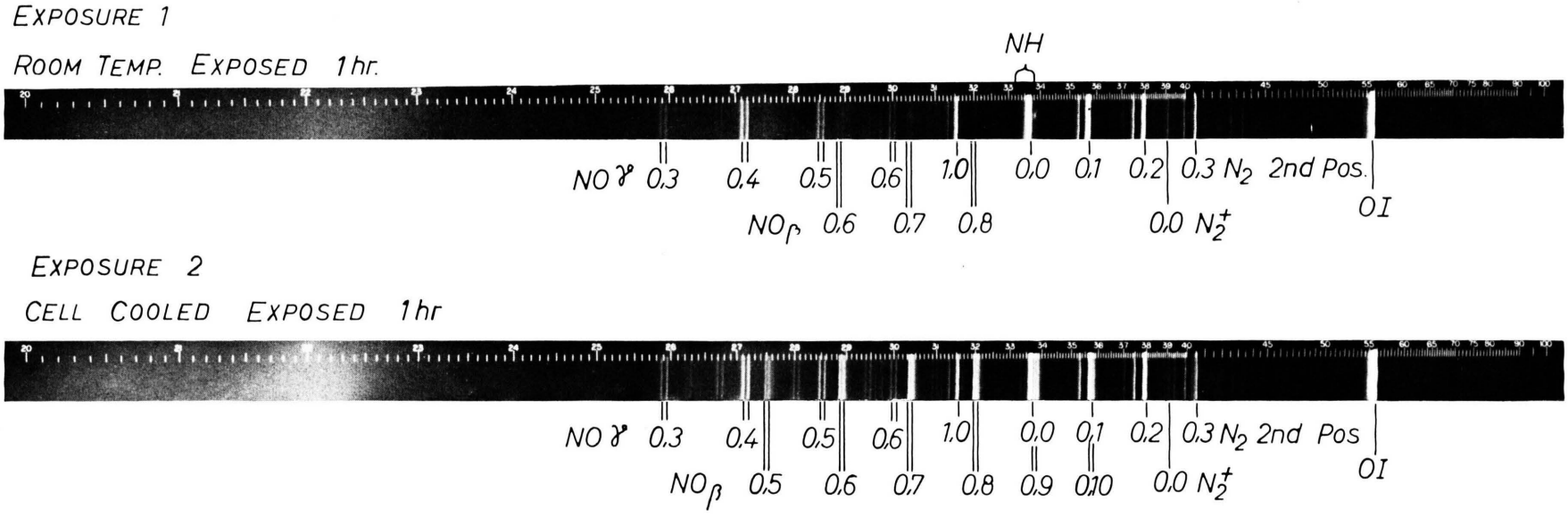

Fig. 3. Spectra of purified nitrogen at two temperatures; room temperature (25 °C) and liquid oxygen temperature (−183 °C) taken with a Hilger–Watts quartz prism spectrograph.

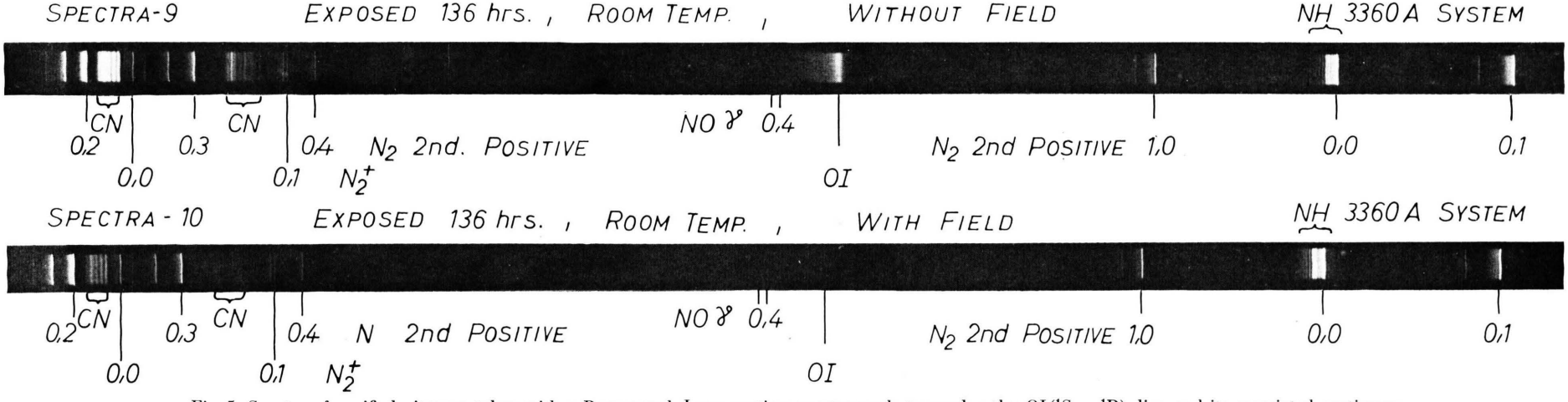

Fig. 5. Spectra of purified nitrogen taken with a Bausch and Lomb grating spectrograph to resolve the OI ($^1S \rightarrow {}^1D$) line and its associated continuum.

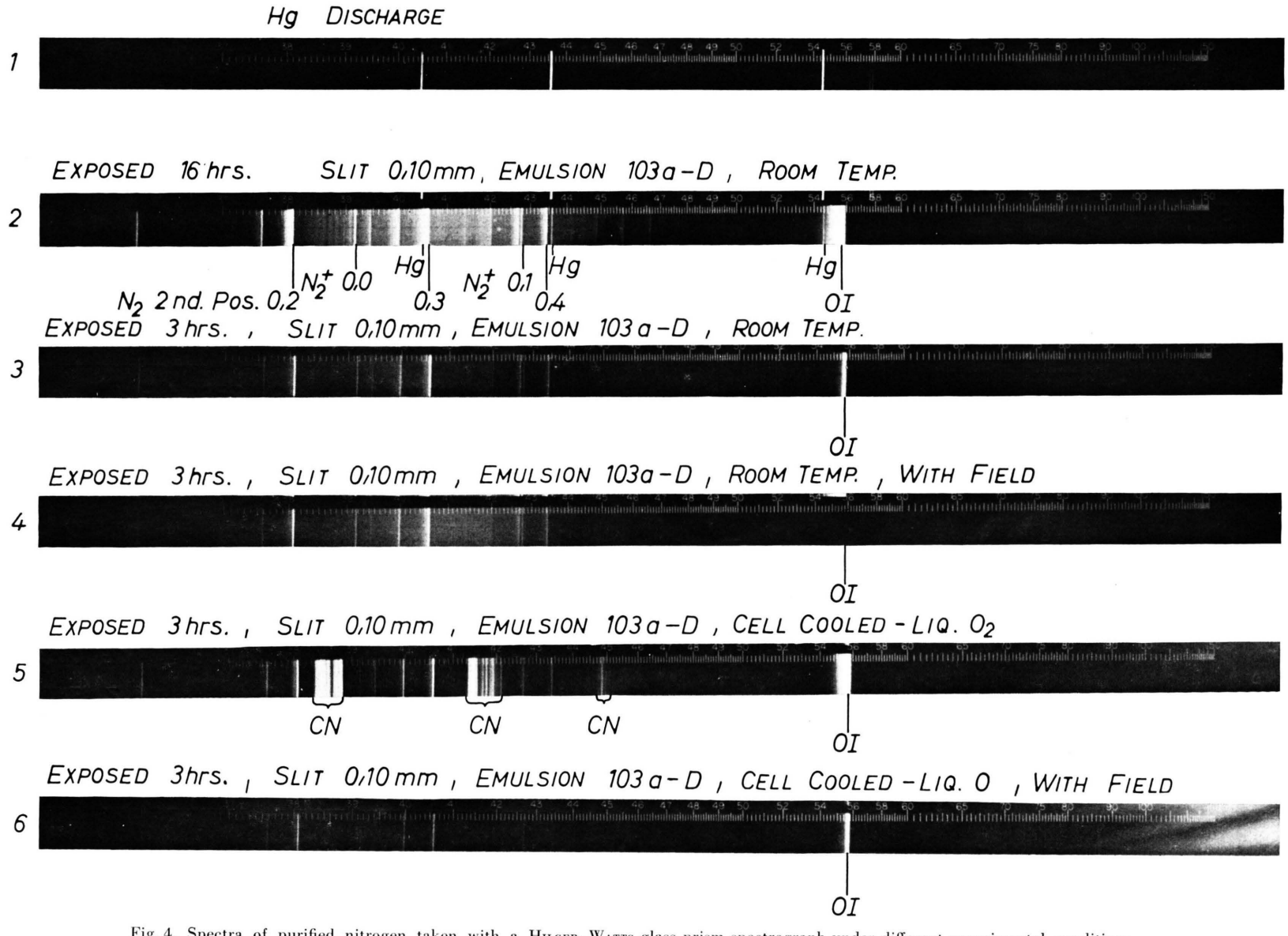

Fig. 4. Spectra of purified nitrogen taken with a HILGER–WATTS glass prism spectrograph under different experimental conditions.

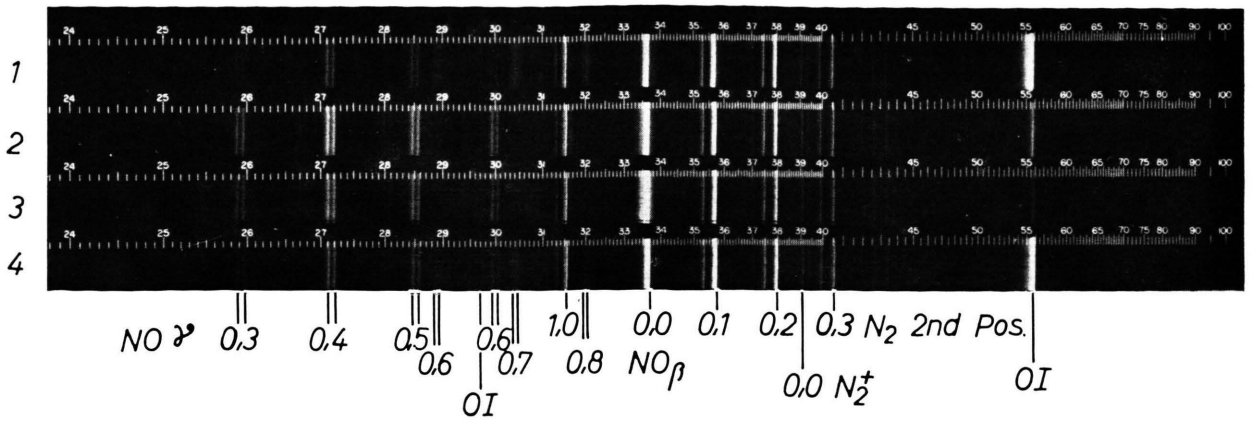

Fig. 6. Spectra of purified nitrogen taken with a HILGER–WATTS quartz prism spectrograph showing the effect of an electric field on the spectra. 1 Without field, 2 with field, source positive, 3 with field, source negative, 4 without field.

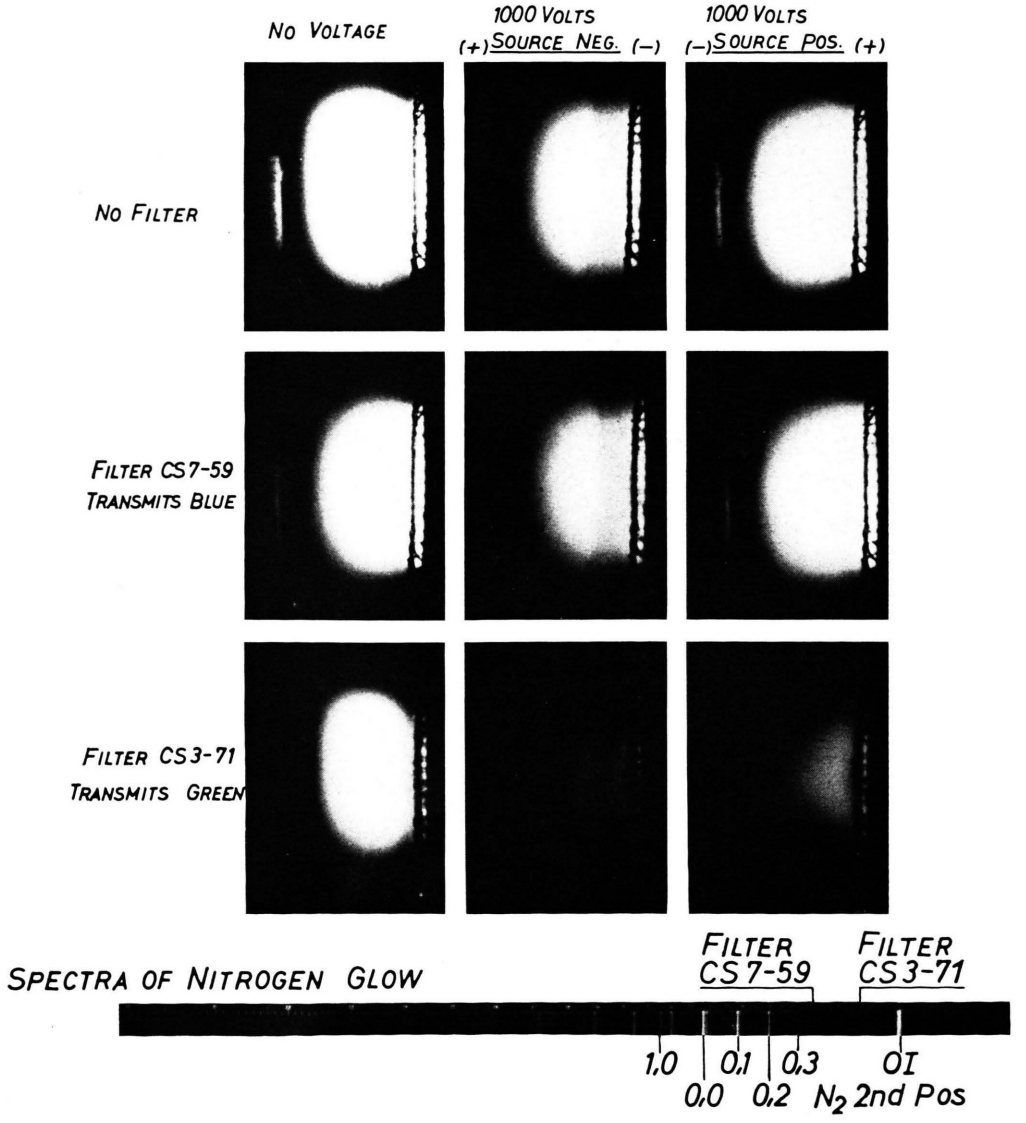

Fig. 7. Using filters and an electric field photographs were taken of the luminescence in nitrogen produced by the polonium alpha radiation.

Effect of Temperature

When the cell is cooled, with liquid oxygen, the oxygen ($^1S \rightarrow {}^1D$) emission (line and continuum) is generally increased in intensity by a factor of approximately 3. The intensity of the NO β and CN violet bands are enhanced also. This is rather striking since the concentration of possible impurities at liquid oxygen temperature is extremely small. The nitrogen second positive and NO γ systems are not effected. The $N_2^+(^2\Sigma^+)$, the NH 3360 Å systems, the Hg lines and the continuum from 3700 Å $\rightarrow$ 4700 Å are all completely quenched or reduced in intensity. Fig. 3 shows spectra of the purified nitrogen taken with the quartz HILGER. The effect of cooling the cell can be seen by comparing exposure 1 (room temperature) with exposure 2 ($-183\,^\circ$C). The spectra shown on Fig. 4 are of purified nitrogen taken with the glass HILGER. Exposures 3 and 5 are of the cell at room temperature and $-183\,^\circ$C respectively. In comparing Fig. 3 * and Fig. 4 it is seen that the CN system is very strong in Fig. 4 at $-183\,^\circ$C and is not seen in Fig. 3 at $-183\,^\circ$C. From the above, the three systems generally enhanced on cooling [the OI ($^1S \rightarrow {}^1D$), the CN violet, and the NO β] are very dependent on minute impurity concentrations.

Effect of Electric Field

Of major importance was the fact that certain light emitting species were substantially effected by the application of an electric field. If an ion mechanism causes the production of an excited species and the mechanism involves a particle which has a very small concentration, then the application of an electric field will rapidly remove the ions and the emission of this light emitting species should disappear or be considerably diminished. The electric field can also have the effect of accelerating electrons capable of exciting species to low energy levels. The OI ($^1S \rightarrow {}^1D$) 5577 Å line, its associated continuum and the OI ($^1D \rightarrow {}^3P$) 2972 Å line were seen to be substantially diminished or entirely quenched when an electric field was applied indicating than an ion mechanism is involved. The other species diminished by the electric field are the NO β and the CN violet. The nitrogen second positive band system was not affected by the electric field at room temperature, but, it was slightly decreased by the field when the cell was cooled. The $N_2^+(^2\Sigma^+)$ was not effected by the field at room temperature or when the cell was cooled. The NH 3360 Å system and the continuum from 3700 Å $\rightarrow$ 4700 Å were enhanced by the electric field at room temperature. The Hg line at 2536 Å was increased in intensity while the Hg lines at 5460 Å, 4358 Å, and 4046Å were decreased by the field at room temperature. The effects of the electric field on the NO γ emission were inconsistent. The effects of the electric field on the spectra can be seen in Figs. 4, 5 and 6.

In summation of the above; the predominant light emissions in purified nitrogen are the OI ($^1S \rightarrow {}^1D$) and the nitrogen second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$). The three systems completely quenched or substantially diminished by an electric field are the OI ($^1S \rightarrow {}^1D$), the CN violet, and the NO β. These are also the three systems intensified when the cell is cooled.

Effect of Oxygen Concentration

The OI emission was at its maximum when the oxygen concentration was at one part in ten thousand or slightly less. When the concentration of oxygen was increased by a small amount (to approximately 3 parts/10,000) the OI emission was completely quenched indicating that the oxygen interferes substantially in the light emitting mechanism. The OI emission intensity was also seen to decrease when the oxygen content was reduced into the region of parts per 100,000. The maximum NO γ emission was obtained when the oxygen concentration was approximately 5 parts per 10,000. The NO β emission was still seen when the oxygen concentration was in the region of one part per 10,000.

Photographs of Glow

Using a quartz cell and a quartz lensed camera, together with appropriate filters, photographs were taken of the glow area in front of the source (Fig. 7). With a green filter permitting only the transmission of the OI forbidden transition and associated continuum to reach the film, an oblate glow envelope was obtained. This OI green glow was not intense at the surface of the source. The glow envelope obtained for the nitrogen second positive emission (filter transmitting blue) was more half spherical and was intense at the surface of the

* Fig. 3—7 on pages 8 a, b, c.

source. When an electric field was applied the green (OI) glow was substantially removed. The nitrogen second positive envelope was seen to be divided into two sections by the field. When the field was increased and the source was negative the division between the sections moved away from the source. When the source was positive the curvature of the division reversed (not clearly seen in Fig. 8). Other photographs showed the NO γ emission envelope to be similar to the nitrogen second positive envelope. Further experimentation is required prior to a full discussion of these effects.

Discussion

In a system of pure nitrogen under ionizing radiation from polonium alpha particles, a complex series of reactions occur. For simplification, the major primary reactions are listed below with their relative abundance.

$$N_2 \begin{cases} \sim\!\!\rightarrow N_2^* & \sim 50\%, \quad (3) \\ \sim\!\!\rightarrow N_2^+ + e^- & \sim 45\%, \quad (4) \\ \sim\!\!\rightarrow N^+ + N + e^- & \sim 5\%. \quad (5) \end{cases}$$

Nitrogen atoms will be formed by the dissociation of the primarily excited molecules produced in reaction (3) and by ion recombination of ions produced in reaction (4). From the previous work [5] we have estimated the steady state concentration and lifetime of N_2^+ and atomic N as:

N_2^+	concentration	2.81×10^{10} particles/cm^3,
N_2^+	lifetime	3.57×10^{-4} seconds,
N	concentration	2.72×10^{13} particles/cm^3,
N	lifetime	0.087 seconds.

It should be pointed out that, in very pure nitrogen, N^+ can also be produced as a secondary ion by charge transfer as follows:

$$N_2^+ + N \rightarrow N_2 + N^+. \quad (6)$$

Thus, in our system considering the nitrogen only, the species present are: N_2, N_2^+, N and N^+.

When a concentration of one part in ten thousand of oxygen is introduced into the nitrogen, and the system irradiated with polonium alpha particles, a number of species of oxygen will be present in addition to the nitrogen species shown above. These are O_2, O_2^+, O, O^+ and negative ions (O_2^- and O^-). Because of the very low concentration of oxygen the primary formation of oxygen ions and radicals by interaction with alpha particles can be neglected. These species must be formed from secondary processes. Also, due to considerations of concentration, reaction rate, and temperature independence of the phenomenon, the reaction

$$N + O_2 \rightarrow NO + O \quad (7)$$

may be disregarded. N_2^+ can react with O_2 in ion neutral reactions:

$$N_2^+ + O_2 \rightarrow NO^+ + NO \quad (8)$$

or in charge transfer:

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+. \quad (9)$$

It has been shown that the heat of activation for the ion-neutral reaction is 7 kcal [6]. From studies made in this laboratory (to be published shortly), the charge transfer from N_2^+ to O_2 occurs very easily, however. From the O_2^+ oxygen atoms can be formed through the process of ion recombination:

$$O_2^+ + e^- \rightarrow O + O \quad (10)$$

or

$$O_2^+ + O_2^- \rightarrow O_2 + O + O \quad (11)$$

with reactions (10) and (11) being sufficiently exothermic to excite oxygen atoms to the ^1S state. In our system, the maximum G-value for oxygen atom formation by reactions (10) and (11) is of the same order of magnitude as that for nitrogen atom formation, thus the concentrations of oxygen atoms will be in the same order of magnitude as that of the nitrogen atoms. With these atoms in our system, it is possible to have the formation of N_2, O_2, and NO by atom recombination, which will proceed according to their rate constants [7]. O^+ is also derived as a secondary ion from the charge transfer process as:

$$N_2^+ + O \rightarrow N_2 + O^+. \quad (12)$$

The negative ions, O_2^- and O^- are formed from

$$O_2 + e^- \rightarrow O_2^-, \quad (13)$$

$$O + e^- \rightarrow O^- \quad (14)$$

and by electronic transfer.

[5] P. HARTECK, S. DONDES, and C. KUNZ, A Spectroscopic Study of the Alpha Ray Induced Luminescence in Gases, AEC Report NYO 10,691 [1963].

[6] S. Y. PSHEZHETSKY and M. T. DIMITRIEV, Dokl. Akad. Nauk SSR **103**, 647 [1955].

[7] P. HARTECK and R. REEVES, in Chemical Reactions in the Lower and Upper Atmosphere, Interscience Publishers [1961].

From the above, we now have the following species in our system: N_2, N_2^+, N, N^+, NO, O_2, O_2^+, O, O^+, O_2^-, O^-. The question therefore arises as to which species react to produce our O (^{1}S) forbidden transition. This auroral green emission is of high intensity and must therefore be initiated by a species formed at a high yield and by a process of high efficiency. Since 4.17 ev are required to excite the oxygen atom to the ^{1}S state and a few tenths of an ev are required for the excitation of the continuum, only those reactions can be considered which have sufficient energy to produce the observed results. Atom reactions can be disregarded since the O(^{1}S) line and continuum emission is substantially reduced by the application of an electric field. Therefore ion reactions can only be considered. The following ion reactions have sufficient energy to produce the ^{1}S state and the continuum:

$$N^+ + O_2 \rightarrow NO^+ + O(^1S) \quad 6.6 \text{ ev}, \qquad (15)$$

$$N + O_2^+ \rightarrow NO^+ + O(^1S) \quad 4.3 \text{ ev}, \qquad (16)$$

$$O^+ + NO \rightarrow NO^+ + O(^1S) \quad 4.3 \text{ ev}. \qquad (17)$$

In addition, ion recombination may excite the oxygen atom to the ^{1}S state through reactions of the type:

$$O_2^+ + e^- \rightarrow O + O(^1S), \qquad (10)$$

$$N_2^+ + O_2^- \rightarrow NO + N + O(^1S). \qquad (18)$$

It should be pointed out that it is very difficult to distinguish which of the reactions is operative. Reactions (15), (16) and (17) have the same products and reactions (16) and (17) have practically the same energy balance. It can only be through additional observations that one reaction can be favored over another.

Since the intensity of the O(^{1}S) emission increases when the temperature is lowered [8], all reactions involved in producing this emission cannot have a heat of activation of over one kcal. Reactions (10), (11) and (15) through (18) meet this requirement. The observation that the OI emission is quenched when the concentration of O_2 is 3 parts per 10,000 or greater, indicates a strong dependence upon the oxygen concentration. Except for NO, O_2 has the lowest ionization potential in the system. It is therefore possible for all species to transfer their charge to O_2. From this point of view, reactions (10), (11) and (16) should not be as sensitive to higher concentrations of O_2 as reactions (15) and (17).

From the above, it still would seem possible that more than one reaction could operate at the same time to produce the O(^{1}S) state. If this were the case, the relative intensity of the line and continuum would not remain constant under varying conditions. The observation that the line and continuum does indeed appear to have a constant relative intensity indicates that only one mechanism was operating to excite the O(^{1}S) state.

The observation that when the concentration of NO is 3 parts per 10,000 or greater the OI emission is quenched [5], tends to lessen the favorability of reaction (17). Also, the findings that the NO emission is at a maximum intensity when the O_2 is approximately 5 parts in ten thousand and that the OI emission is strongest when the NO emission is fading out, also tends to reduce the possibility of reaction (17).

Therefore, as the O_2 concentration increases, the charge transfer processes according to reaction (9) predominates and will tend to quench the OI emission, whereas the decrease of O_2 concentration (i. e. to 1/10,000) will favor reaction (6) followed by reaction (15) to give us our maximum intensity as observed. In a recent publication [9] the rate constant for (15) was estimated at 1×10^{-10} cm^3 sec^{-1}, indicating that these species will indeed interact according to (15) on practically every collision.

From the many considerations enumerated above, it would seem as if reaction:

$$N^+ + O_2 \rightarrow NO^+ + O(^1S) \quad 6.6 \text{ ev} \qquad (15)$$

produces the excitation of the 5577 Å OI line when nitrogen with one part in ten thousand concentration of oxygen is irradiated by polonium-210 alpha particles at one atmosphere pressure.

Conclusions

1. When very pure nitrogen with oxygen concentration of one part in ten thousand is irradiated with polonium alpha radiation, the predominant emission is the oxygen auroral (^{1}S $\rightarrow$ ^{1}D) green emission.

[8] The increase in intensity of the O(^{1}S) emission as the temperature is lowered may be due to the decrease of impurities which may quench the excited species.

[9] A. Galli, A. Giardini-Guidoni, and G. G. Volpi, J. Chem. Phys. **39**, 518 [1963].

This line emission is associated with a continuum. The high intensity of this emission requires that it be initiated by a species formed at a high yield and by a process of high efficiency.

2. The intensity of this emission increases when the temperature is lowered and therefore all reactions involved in producing this emission can not have a heat of activation over one kcal.

3. An electric field substantially quenches this light emission indicating that an ion mechanism is involved. There are several possible ion reactions or ion recombination reactions which could excite the oxygen atom to the ^1S state. All these reactions involve ions that must be formed by charge transfer or ion neutral reactions.

4. When the oxygen concentration is increased to 3 parts per ten thousand or over, the OI emission is completely quenched. This strong dependence on oxygen concentration can be understood if we assume that the oxygen molecule deactivates the $O(^1S)$ readily on collision, and in addition that N_2^+ transfers its charge to oxygen forming O_2^+ where the O_2^+ does not react to form the $O(^1S)$ state. It should also be mentioned that the OI ($^1S \rightarrow {}^1D$) emission is strongest when the NO emission is fading out. (The NO emission is at maximum intensity when the O_2 concentration is approximately 5 parts in ten thousand.)

5. It is possible that more than one reaction could operate at the same time to produce the $O(^1S)$ state. However, it is unlikely that the relative intensity of the line and continuum would remain constant under various conditions if this were the case. The line and continuum appeared to have a constant relative intensity to each other indicating that one mechanism operates to excite the $O(^1S)$ state.

We therefore conclude that there are many considerations which favor reaction (15) over reactions (10), (16), (17) and (18)

$$N^+ + O_2 \rightarrow NO^+ + O(^1S) \quad 6.6 \text{ ev.} \qquad (15)$$

Acknowledgement

We wish to acknowledge the assistance and cooperation of the Atomic Energy Commission under Contract AT(30-3)-321 in making this work possible. We also wish to acknowledge the assistance of Dr. L. G. Bassett in editing this paper.