A HOLLOW CATHODE DISCHARGE SOURCE FOR SPECTRA OF IONIZED MOLECULES

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Paul Tak-shing Chan

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This is to certify that the

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A HOLLOW CATHODE DISCHARGE SOURCE

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Paul Tak-shing Chan

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C. W. Hause

Major professor

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A HOLLOW CATHODE DISCHARGE SOURCE FOR SPECTRA OF IONIZED MOLECULES

by

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A THESIS

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I. Introduction

Since the turn of the last centry, investigation of molecular spectra has become more and more important. For from it, one can understand more about the structure of the molecules, electron distribution, nature of the binding of the molecules, etc.

A part of the above problem is the development of light sources which give controlled excitation and emit radiation suitable for high resolution work.

Among the several light sources devised which are useful in the field of high resolution spectroscopy and capable of controlled excitation, the hollow cathode discharge tube is the simplest in design and most efficient in operation.

The majority of hollow cathode sources are designed to excite the solid materials w ith which the cathode is impregnated. A variation in design is introduced here, such that a permanent gas can be excited. A rather intensive study of the molecular radiations emitted by the source was made with small quantities of NO (nitric oxide) admitted to the system.

II. Hollow Cathode Source

A. Introductory

The hollow cathode source is essentially a modified Geissler tube — a source in which an electrical discharge is maintained in a gas at low pressure. It is simple in design and easy to operate. It was first developed by Paschen.[1] He found that if the cathode was made hollow, as the discharge pressure was reduced, the negative glow retreated into the cathode cavity. When a pressure such that the mean free path of the electron is approximately the same as the diameter of the hollow cathode was attained, the negative glow became most intense. However, due to the high temperature, the Doppler boardening[2,3] of the spectral lines became very serious. Schuler[4] redesigned the tube by removing the cathode to the exterior where drastic cooling could be employed. As a result, this defect is almost completely eliminated. Hence, from this source, sharp and intense spectral lines can be obtained.

B. Mechanism of the Discharge

In the hollow cathode source, an inert gas,[5] such as helium, argon, etc., is passed through the tube at a reduced pressure. When a potential is applied between the anode and cathode, a typical gaseous discharge takes place. As the operational conditions of the gas pressure and the applied voltage are adjusted, the positive glow disappears and the negative glow recedes inside the cathode and becomes very in-

tense. The positive ions of the gas, say helium, formed in the discharge are urged by the field toward the cathode and sputter any material there. Since a gaseous sample is intended for investigation, a special design and suitable constructional material for the cathode are necessary. This material must have the minimum or the least sputterring factor so that the spectrum for investigation will not be complicated by it. Aluminum is suitable for this purpose.

Due to the mechanism of the discharge, large numbers of the helium atoms are excited to a metastable energy state and possess 19.7 ev (argon, 11.5 ev). Upon collisions with the sample gas molecules, the energy of the metastable helium atoms is transformed into the potential energy of excitation for the sample gas molecules. Hence the characteristic emission spectrum of the latter is observed when the excited molecules return to lower energy states. Since the metastable helium atoms lose their energy by radiationless transitions, the helium spectrum, although observed, is very weak.

C. General Design[6]

Fig. 1 shows the cross section of a hollow cathode source for exciting the gaseous sample. The main body of the tube is made of brass. It consists of two sections which are insulated by a rubber gasket on the edge and a pyrex tubing inside. They are held together by the external atmospheric pressure. One section incorporates the anode and the other the cathode. They are made of hard aluminum. The position

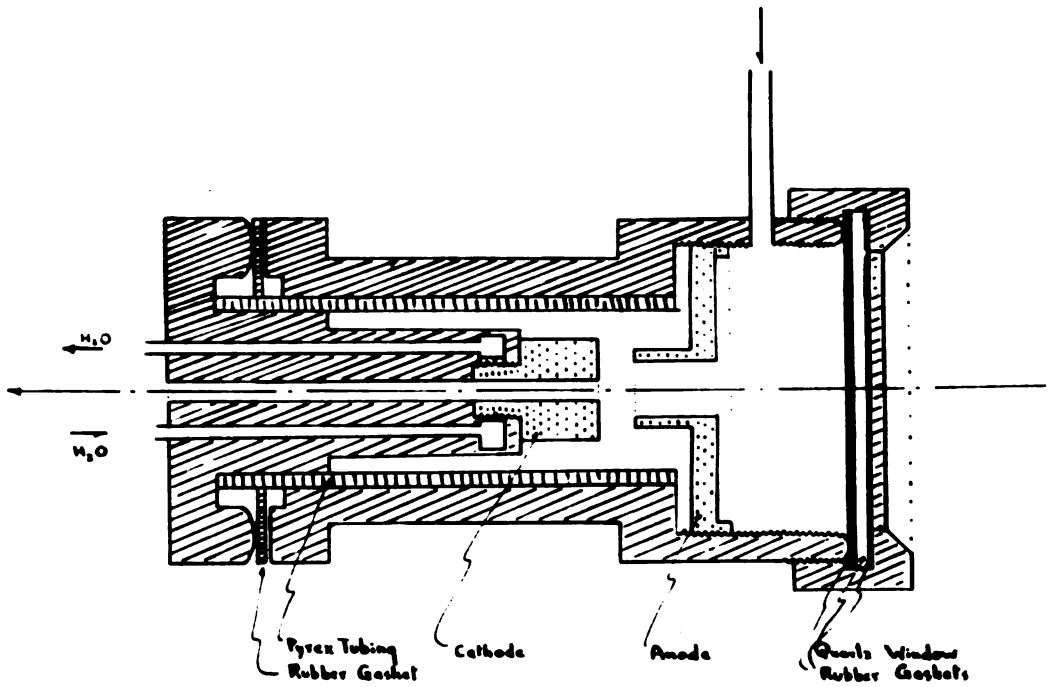


Fig. 1 Cross section of a Hollow Cathode Discharge Tube

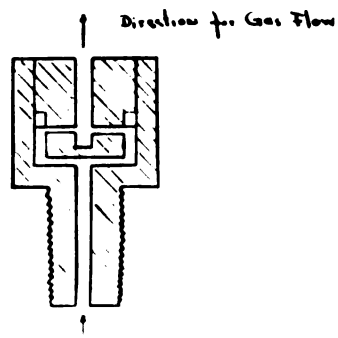


Fig 2 Cross section of a Hollow Cathode for Investigating Solids

of the anode is adjustable such that the maxium intensity of the discharge can be utilized. The cathode is removeable. Hence its design can be easily altered. Fig. 2 is a design of a cathode for exciting solids. The cathode is imbedded in a cavity where water is circulated. A quartz window with rubber gaskets at one end allows the radiation to be observed. An inlet for the carrier gas and the gaseous sample is placed in front of the anode, while the outlet is at the back of the cathode. In this way all the gas molecules pass through the cathode and have the maxium opportunity for excitation.

D. Gas and Power Supplies

The key problem of this subject is to control the flow of the gaseous sample, NO, and the carrier gas, helium, so that a certain pressure and a desirable mixture of helium and NO can be obtained in the hollow cathode. Hence leak valves with controlable devices are necessary.

A cylinder of helium at 1,700 psi furnishes the supply of carrier gas for the source. This pressure is reduced to 4 psi by a Purox reduction valve. Again this pressure is reduced by means of two tapered leak valves, one at the inlet and the other at the outlet of the system. The tapered leak valve consists of a male taper which may be seated snugly or loosely into a corresponding female taper as indicated in Fig. 3. Therefore the flow of gas can be adjusted. An O-Ring furnishes the seal. A Hg manometer is placed by the inlet of the hollow cathode discharge tube to indicate the

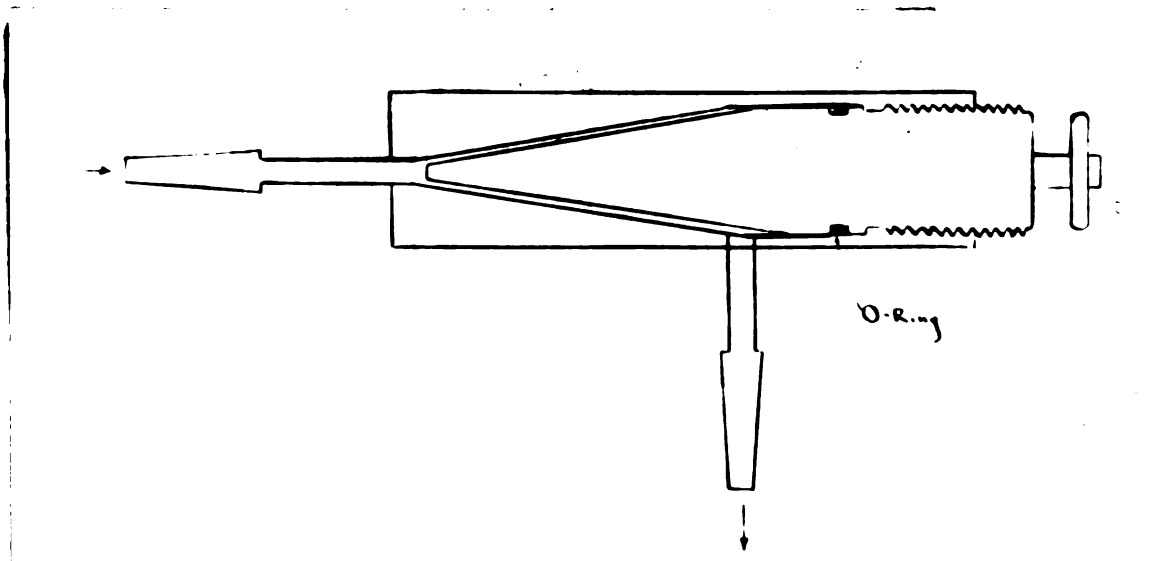


Fig. 3 Cross section of a Tapered Leak Valve

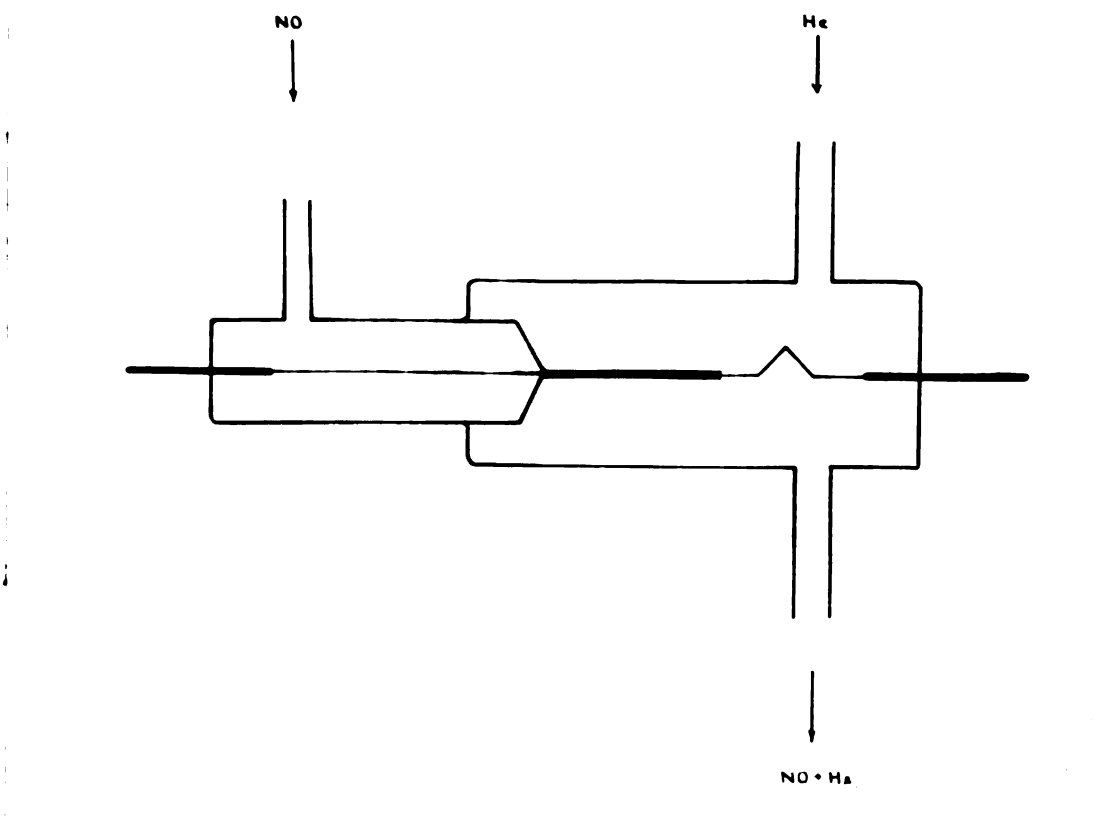


Fig. 4 Cross Section of a Micro-Leak Valve

pressure in the tube.

The helium gas after release from the cylinder, is passed through a carbon trap which is submerged in a dry ice and acetone bath in order to absorb the impurities.

Since only a small portion of NO is used in the hollow cathode, a very sensitive type of leak valve is needed in order to control the flow of NO to a minute amount. From the suggestion of John J. Hopfield,[7] a glass variable micro-leak valve is built as indicated in Fig. 4. A capillary tube which has been drawn to approximately the size of a .018 inch platium wire, is joined to a 12 mm pyrex tube and then fused into a 15 mm pyrex tube. The platium wire is put inside the capillary with tungsten wires as leads. A loop in the platium wire is to prevent the strain on the glass envelope due to the thermo-expansion of the wires. When a current is passed through the platium wire, the wire is heated and expands, and has a tendency to fill up the space within the capillary. Hence, the flow of NO is decreased. The range of applied current can be from zero to eight amperes without fear of damaging the device. That rate flow is dependent upon the pressures at the reservoir of NO and at the hollow cathode, and the rate of evacuation of the gases. From experimental results, the rate flow is as follows:

Pressure at		Applied Current at the Micro-Leak Valve (ampere)	Rate flow of NO (micron per sec.)
Reservoir of NO (mm of Hg)	Hollow Cathode (mm of Hg)		
35	4	0	17
15	5	4	2

The No is supplied by the Matheson Co. in a cylinder. A small quantity is fed into a two liter pyrex flask. The pressure is indicated by a Hg manometer. The gas is allowed to pass through the micro-leak valve and enters the hollow cathode for excitation.

The power supply for the discharge tube is from a 2,300 volt, 1.2 kw filtered full wave rectifier. The circuit diagram is shown in Fig. 5. A resistance of 2,700 ohms is

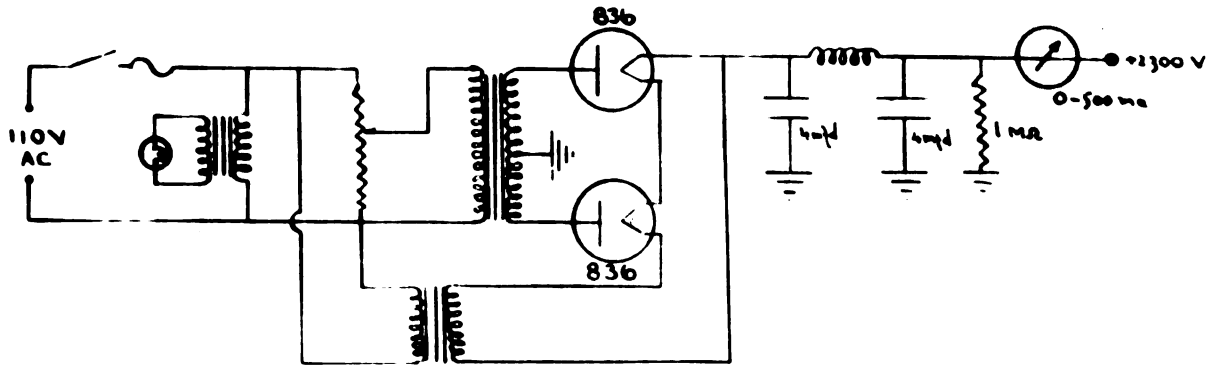


Fig. 5 Circuit Diagram of the Power Supply

placed in series with the discharge tube in order to facilitate starting the discharge and also to stabilize the current during operation. For, at the beginning, the resistance of the discharge tube is very high, hence the applied potential is entirely across the electrodes. When the discharge commences, the resistance of the tube decreases to approximately 800 ohms. As a result, almost three quarter of the applied potential is across the ballast resistance. Therefore, a small fluctuation of the tube resistance does not effect the constant flow of

current.

The applied potential for the micro-leak valve is taken from a 12 volt DC voltage supply and is regulated by a 2.8 ohm rheostat.

The schematic diagram of the gas flow is represented by Fig. 6. The helium gas after passing through the reduction valves and the carbon trap, mixes with the NO at the outlet of the micro-leak valve and enters together with the NO into the hollow cathode. From there this mixture passes through another leak valve, comes to a two-liter pyrex flask, and finally is pumped by a Cenco Megavac rotary oil pump into the air. The flask serves to stabilize the pressure of the system.

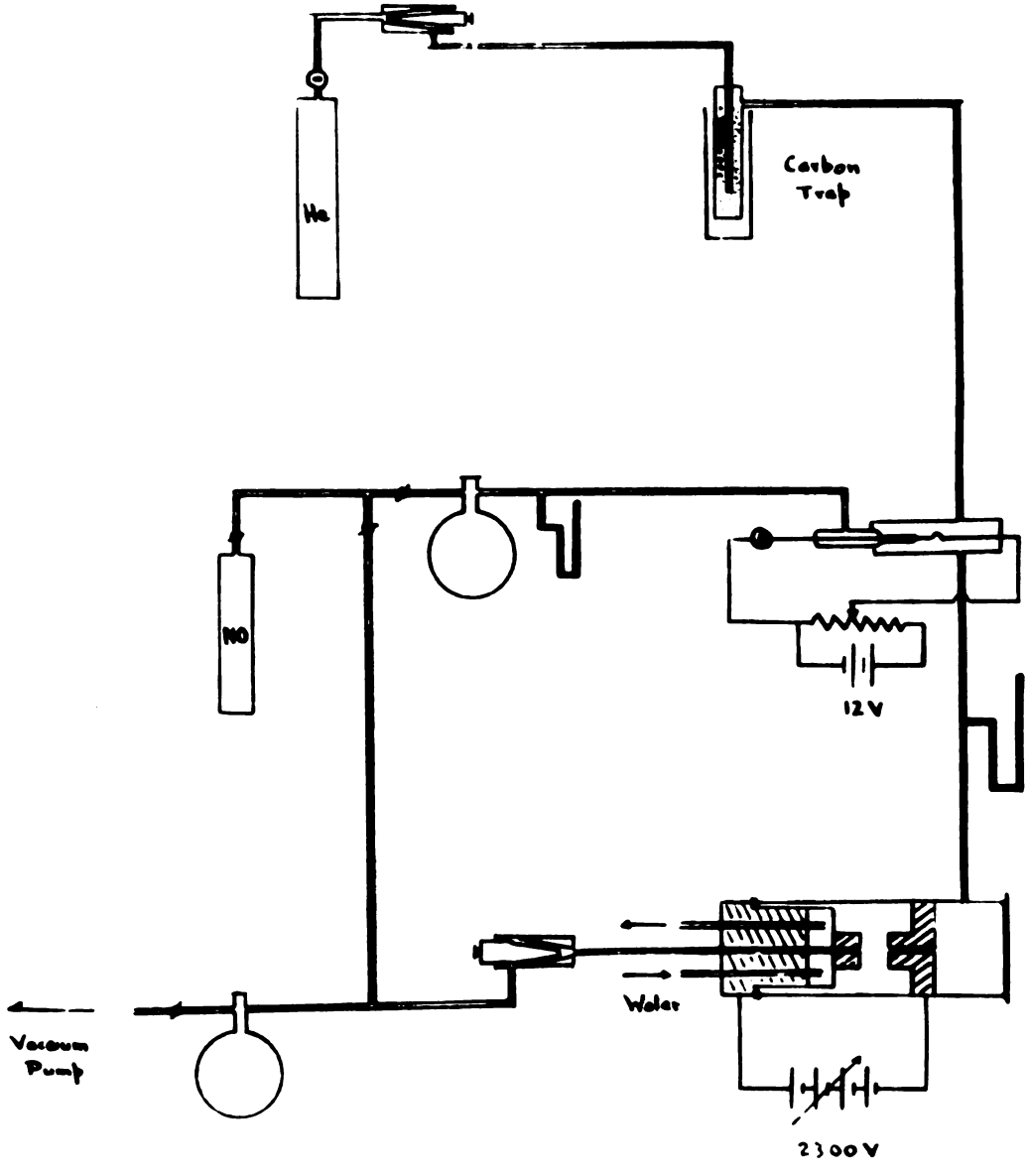
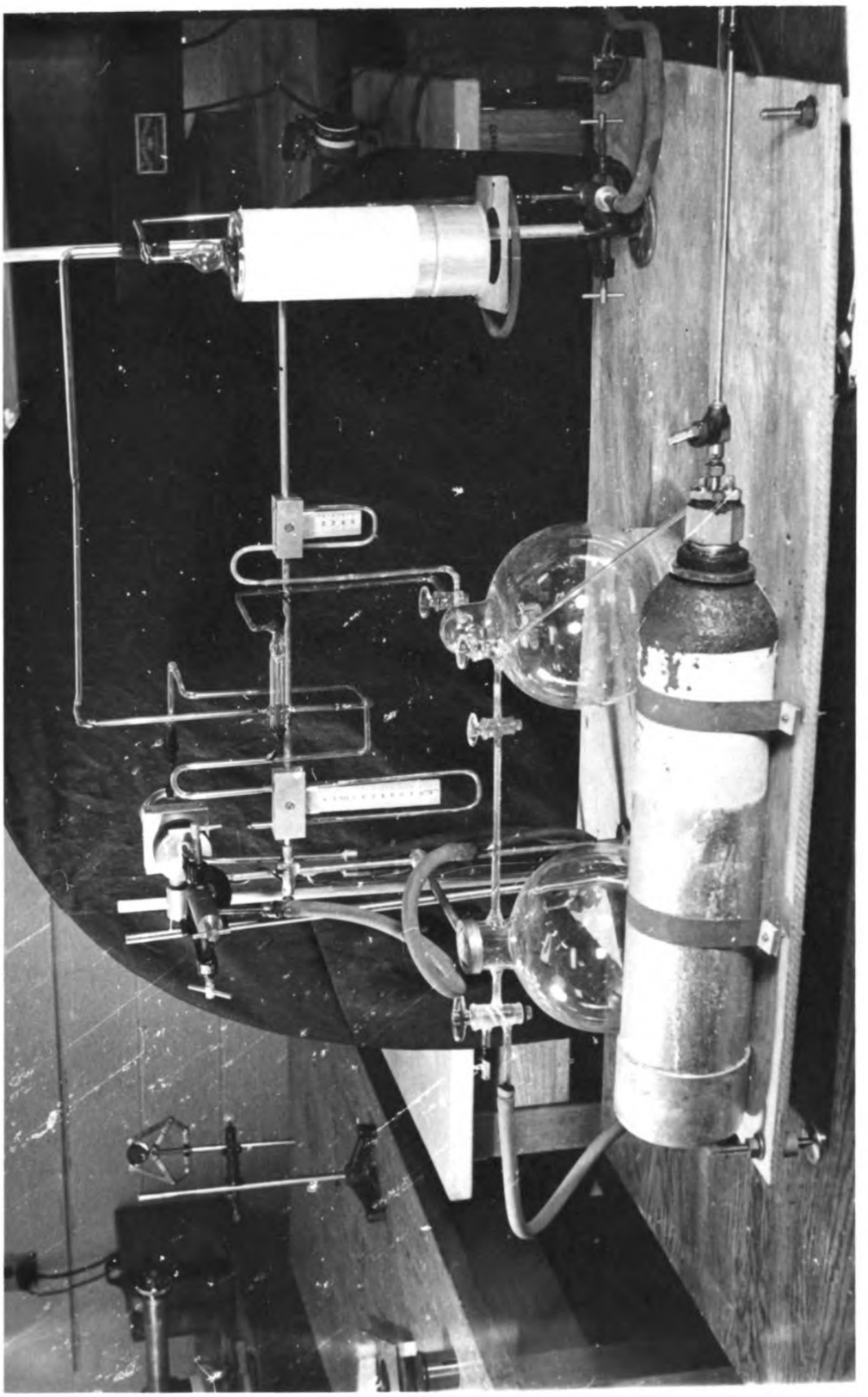


Fig. 6 Schematic Diagram of the Gas Flow



III. Ionized Spectrum of NO

A. Introductory

In order to perdict what may occur when NO is introduced into the hollow cathode discharge, some knowledge of the electronic configuration of the molecule and those molecules which may be formed is desireable.

When the NO is introduced, the molecules may be dissociated or ionized and N_2, N_2^+, NO^+, O_2, or O_2^+ formed. Of course these formations are dependent on the energies available in the discharge and the stability of the molecules. The energy available is closely controlled in the hollow cathode being largely the energy of the metastable states of the carrier gas. The latter is dependent on the nature of the molecules. If the situation is favorable for a particular molecule, its spectrum will appear and be intensified, otherwise it will be depressed or even absent.

B. Electronic Configurations and Allowed Energy Transitions

Molecular spectra of N_2, N_2^+, O_2, O_2^+, and NO in emission have been studied quite extensively. The most prominent band systems attributed to each of them are as follows:

N_2:[8] The electronic configuration is

$$(1s\sigma_g)^2(1s\sigma_u)^2(2s\sigma_g)^2(2s\sigma_u)^2(2p\pi_u)^4(2p\sigma_g)^2$$

The best established electronic levels for nitrogen in order of energy from the ground state are $X^1\Sigma$, $A^3\Sigma$, $a^1\pi$, $B^3\pi$, $C^3\pi$, $D^3\Sigma$. The observed band systems are:

First Positive System:[9]

Occurrence: In the positive column of the dis-

charge tubes containing nitrogen. The bands appear very readily.

Appearance: Degraded to the violet. Under small dispersion the appearance is of waves of regularly spaced triple-headed bands strongest in the orange, the red and the yellow green. Under large dispersion the rotation structure is seen to be complex, and there are several heads to each band.

Range: 10,000 - 5,000 A.

Transition: $B\,^3\Pi \longrightarrow A\,^3\Sigma$

Excitation potential: 7.4 ev.

Second Positive System:[10]

Occurrence: In the positive column of discharge tubes containing nitrogen or air and in arcs at low pressure. The bands appear very readily and are of frequent occurrence as an impurity.

Appearance: Degraded to shorter wave lengths. Closed triple-headed bands forming fairly obvious sequences.

Range: 4,900 - 2,800 A.

Transition: $C\,^3\Pi \longrightarrow B\,^3\Pi$

Excitation potential: 11 ev.

N_2^+: [8,11] The electronic configuration is:

$(1s\,\sigma_g)^2(1s\,\sigma_u)^2(2s\sigma_g)^2(2s\sigma_u)^2(2p\,\pi_u)^4(2p\sigma_g)$

The ground state is $^2\Sigma$, and the only observed transition is $A^2\Sigma \rightarrow X^2\Sigma$ in discharge tubes at very low pressure or at moderate pressure in presence of excess helium in hollow cathode. The strong bands are degraded to the violet, but a few weak bands are degraded to the red. The bands entend from 5,000 to 3,200 A. The excitation potential is 18.74 ev.

NO:[8] The electronic configuration is:

$$(1s\sigma)^2(1s\sigma)^2(2s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^4(2p\pi)$$

The ground state is $^2\pi$.

β System:[12]

Occurrence: In discharge tube containing oxygen and nitrogen, and in nitrogen after-glow, and especially strong when excess oxygen is introduced into active nitrogen.

Appearance: Double-headed and degraded to the red.

Range: 5,300 - 2,300 A.

Transition: $B^2\pi \rightarrow X^2\pi$

Excitation potential: 5.6 ev.

γ System:[13]

Occurrence: In discharge tube containing nitrogen and oxygen, in active nitrogen and in flames containing NO.

Appearance: Double double-headed bands and degraded to the violet.

Range: 3,500 - 1,600 A.

Transition: $A^2\Sigma \rightarrow X^2\pi$

Excitation potential: 5.48 ev.

O_2:[8,14] The electronic configuration of O_2 is:

$$(1s\sigma_g)^2(1s\sigma_u)^2(2s\sigma_g)^2(2s\sigma_u)^2(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g)^2$$

The ground state is $^3\Sigma$. The neutral oxygen molecule does not readily show an emission spectrum. However, an emission spectrum of oxygen ($B^3\Sigma \rightarrow X^3\Sigma$) was observed by Schumann, and Runge in the region 4,400 -3,100 A.

O_2^+: [8] The electronic configuration is:

$$(1s\sigma_g)^2(1s\sigma_u)^2(2s\sigma_g)^2(2s\sigma_u)^2(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g)$$

The ground state is $^2\pi$. There are two systems of bands attributed to the ionized oxygen molecules, the First Negative bands[15] from the red to the green, and the Second Negative bands[16] in the ultra-violet.

C. The Unknown Spectrum of NO^+

So far the spectrum of ionized nitric oxide molecules has not been observed. A search for this spectrum has been carried on here. The predictions for the unknown are based upon the iso-electronic relationship.

The electronic configuration of the NO^+ molecule is:

$$(1s\sigma)^2(1s\sigma)^2(2s\sigma)^2(2s\sigma)^2(2p\pi)^4(2p\sigma)^2$$

Since this is similar to that of the neutral nitrogen molecule, then one would expect that the electronic states and the band spectrum should be resemble those of the neutral nitrogen molecule.

There are two possibilities for the formation of the NO^+ molecules from the NO in the hollow cathode discharge:- (1) directly from the neutral NO molecules through ionization, or (2) by combining $N^+ + O \rightarrow NO^+$, or $N + O^+ \rightarrow NO^+$, after collisions of second kind.

(1) Now if the former did happen, then the ionization potential of NO is of importance. From the limit of Ryberg Series in band spectra, the molecular ionization potential of N_2 has been obtained:[17]

N_2 15.581 ev.

The only information available for NO is from electron impact experiments[18] which gives an ionization potential of 9.5 ev. Since the energy from the metastable helium is 19.7 ev, then there will be 10 to 11 ev available to excite the NO^+ molecules.

(2) If the formation of the NO^+ molecule is from collisions of the second kind, that means after the dissociation of NO, the neutral nitrogen atom or the neutral oxygen atom one or both excited, collides with the metastable, energetic helium atom. During the collision, the excitation energy of the latter is transformed into the potential energy for the former and, as a result, becomes ionized. Now, if the ionized nitrogen or oxygen atom combines with the neutral oxygen or nitrogen atom, respectively, then the ionized nitric oxide molecule is formed. Although this type of formation seems improbable, NO is observed in discharge tubes containing N_2 and O_2 as was mentioned and AlH^+ was obtained with

good intensity from a hollow cathode source with aluminum cathode and helium as the carrier gas when Hg was introduced as an impurity.[19]

IV. Experimental

A. Optical System

In order to search for the spectrum of the ionized nitric oxide molecules, various conditions for the hollow cathode discharge are examined first by observing visually with a constant deviation spectrometer, and then photographing with a littrow spectrograph with quartz optical train.

Fig. 7 is a photograph of the optical system with the spectrometer and the littrow spectrograph in position.

Kodak Spectroscopic plates III F and Kodak Spectrum Analysis No. 1 plates were used. The plates were developed in D-19 for 4 minutes and fixed in D-76.

B. Results

Two conditions of the hollow cathode discharge were investigated. One is with excess NO and the other with a trace of NO. The operational conditions are as follows:

Operational Condition		Excess NO	Trace of NO
Operation-current for discharge		200 ma	200 ma
Pressure:			
NO & He		4 mm	5 mm
NO		32 mm	15 mm
Leak-valve current		0 amp	4 amp
Slit	Time exposure		
2mm	Range 1	12 min. (Fe: 15 sec)	25 min. (Fe: 15 sec)
2mm	Range 2	30 min. (Fe: 15 sec)	1 hr. (Fe: 15 sec)
3mm	Range 3	2 hrs. (Fe:150 sec)	2 hrs. (Fe:150 sec)

Samples of the spectra obtained with these conditions are shown

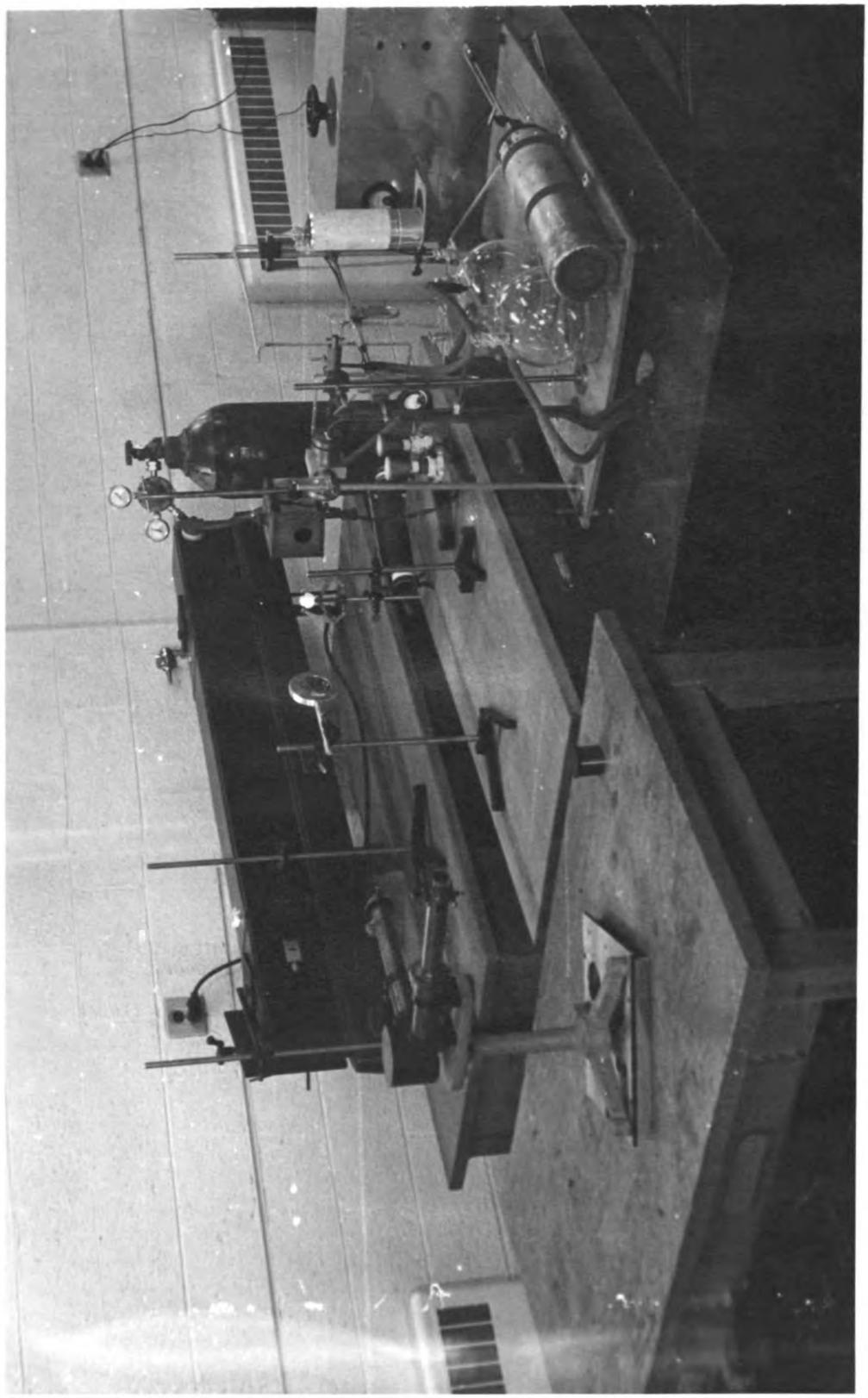


Fig. 7

in Fig. 8 I, II, and III with (a) representing the case having excess NO and (b) for the case having a trace of NO. Their identifications are made by the relative position of the Fe spectrum.

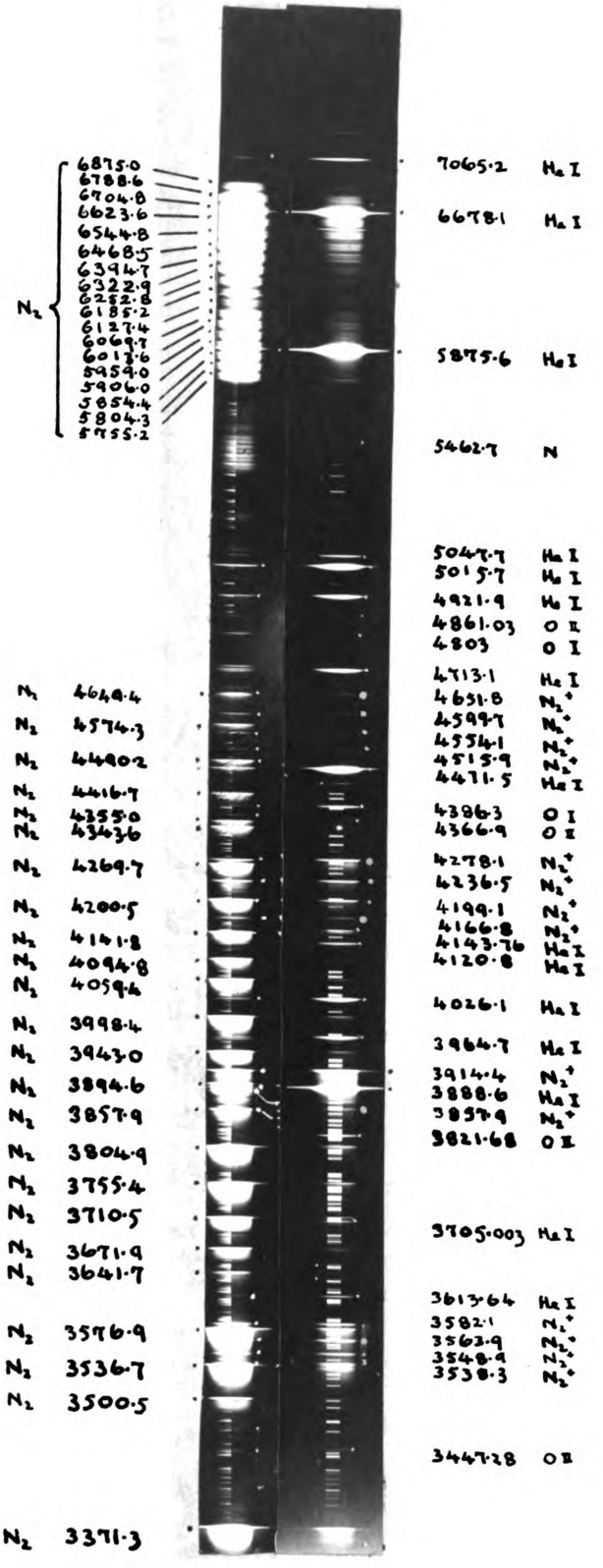


Fig. 8.1 Spectra of NO — Range 1

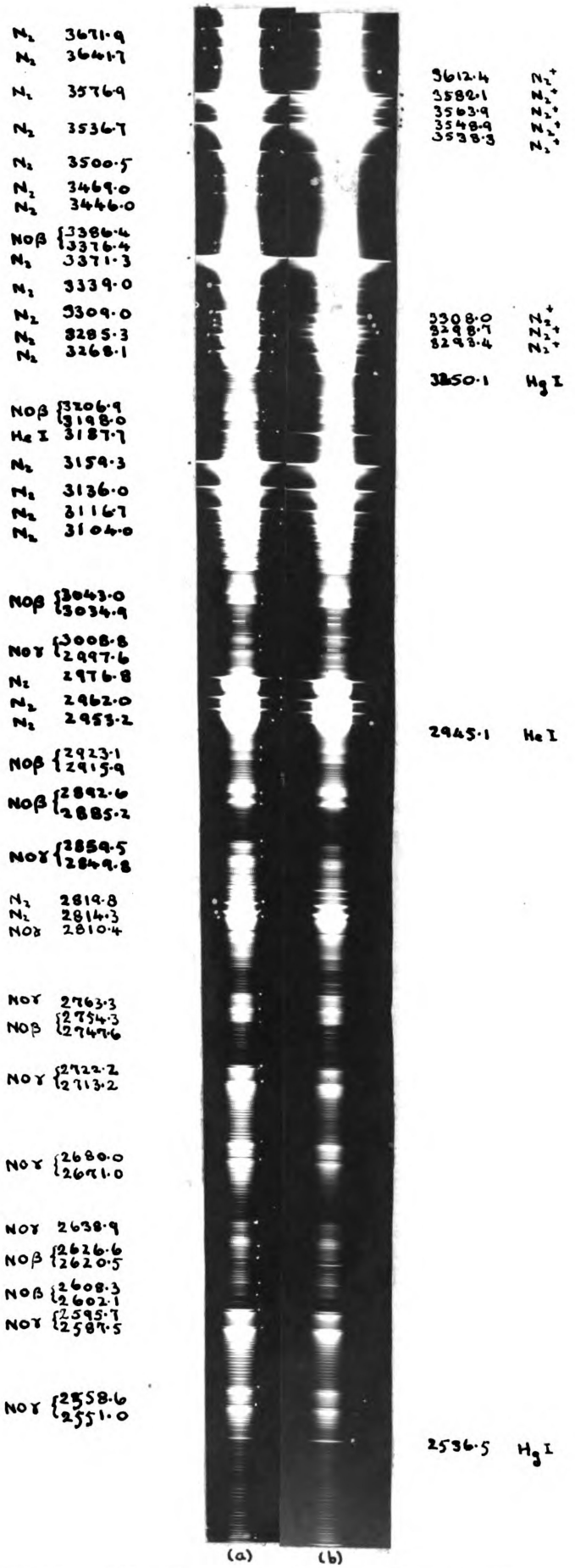


Fig. 8. II Spectra of NO — Range 2

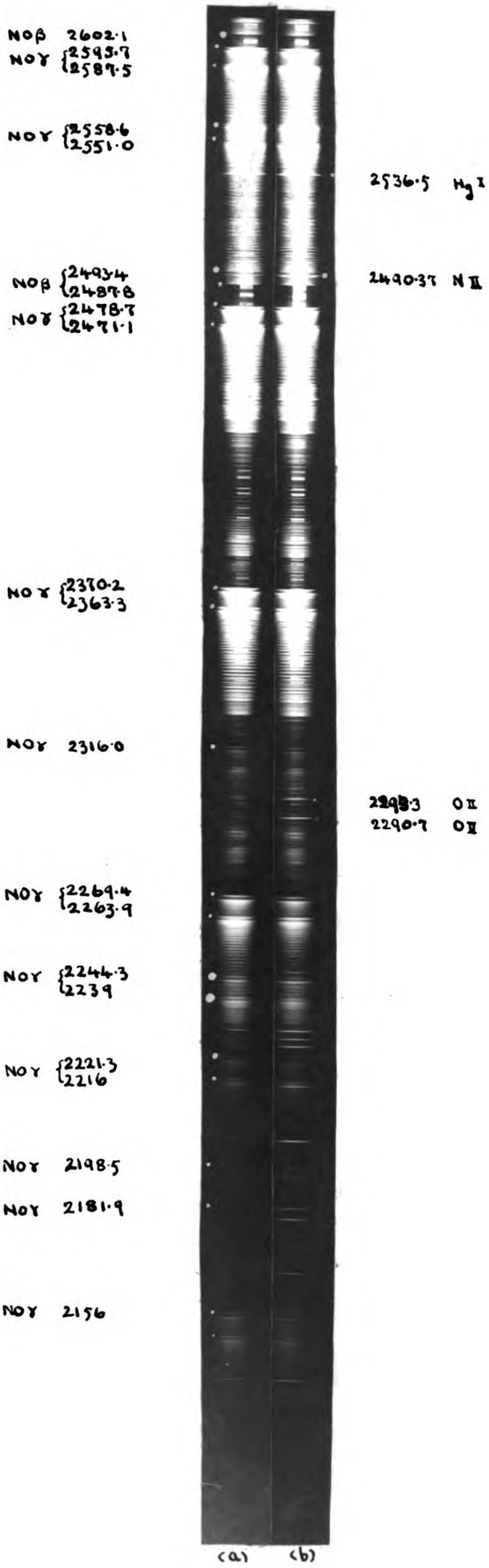


Fig. 8. III Spectra of NO — Range 3

V. Conclusion

The aim of this project is to design and construct a hollow cathode source which gives controlled excitation for the spectra of ionized molecules. This purpose has been fulfilled satisfactorily as indicated by the spectra shown in Fig. 8 I, II and III.

In case (a), the spectrum of N_2 is prominent, because with excess NO, the energy of the metastable helium atom is distributed to either ionization or decomposition of the NO molecules. As a result, NO^+, N and O are formed. The nitrogen atoms combine to form N_2, and oxygen atoms, O_2.

In case (b), the spectrum of N_2^+ is prominent, because with a trace of NO, only a minute amount of N and O is formed. With excess metastable helium atoms accumulating about the cathode, N_2^+ can be readily formed by collisions of the second kind.

After a careful search through the spectra shown in Fig. 8 I, II, and III, no evidance for the presence of the spectrum of NO^+ has been found. Of course this does not mean that there has been no formation of the NO^+ molecules in the discharge. According to the previous discussion (Section III C, p. 14), the formation of the NO^+ molecules are quite possible. Firstly, the available energy is more than enough for the ionization of NO. Secondly, from the presence of O^+, it will be logical to believe that there are N and N^+ also. Thus

NO^+ could be formed, and the abundance of N_2 and N_2^+ can not apparently be accounted for on the basis of impurities. Hence, we can sum up by saying that the prominent transitions of NO^+ are most probably in the extreme ultra-violet or extreme infra-red which cannot be detected with our spectrograph.

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