

Progress of Laboratory Aeronomy and Airglow Research in India during the Last Fifty Years: Part I—Low-energy Proton-induced Spectra of Atmospheric Gases

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Laboratory aeronomy research deals with collisions of low energy protons and atmospheric gases. Such collisions lead to excitation of gases. The proton source and the spectrograph used are described. The characteristic features of spectra are analyzed in detail and explanations are offered for their excitations.

1 Introduction

Inelastic collision between ions and neutral atoms and molecules has been the subject of study for a considerable period of time and a large amount of information on excitation, dissociation, charge exchange and ionization produced by ion bombardments has been collected. Information on such collisions is useful in understanding the physics of upper atmosphere and for the advancement of technology of heavy-particle accelerators, high-temperature plasma, mass spectrometry and radiation chemistry.

Ghosh *et al.*¹⁻⁶ carried out excitation of spectra by low energy (560 eV-1.7 keV) proton bombardment. These investigations are described in the following sections and are summarized in Table 1. The target gases were N₂, air, Ar, (Ar, O₂) mixture, and CO₂. Spectroscopic, photometric and microphotometric studies were made. For the target gases N₂ and air, it was observed that in the above energy range, the nature of the excited spectra was independent of the proton energy and that a distinct change in the spectral intensity was recorded with the variation of target gas pressure.

For Ar, it was observed that for the above energy range and pressure 5-30 mTorr, only Ar I lines were excited and that the intensity varied linearly with pressure. Besides its intrinsic interest, the investigation can enable us to provide a buffer gas which could be used for studying the spectra of certain planetary and cometary gases excited by low-energy proton bombardment.

Bombardment of N₂ by 0.5-1.7 keV protons revealed the presence of 1 PG and 2 PG systems of N₂, 1 NG system of N₂⁺ and H α and H β lines in the spectral region 2900-7000 Å.

While investigating the spectra of air³ excited by

proton bombardment, it was observed that the H α , H β lines, the 1 PG and 2 PG systems of N₂ and the 1 NG system of O₂⁺ and N₂⁺ were excited. The 1 NG system of O₂⁺ and the 1 PG system of N₂ overlapped in the red spectral region. Due to the low dispersion of a medium quartz spectrograph used in the investigation, the identification of the 1 NG system of O₂⁺ was difficult. It was, therefore, felt that it is desirable to investigate the excitation of O₂ by low-energy protons. Due to the high chemical reactivity of hydrogen and oxygen, O₂ was bombarded in an inert atmosphere of argon by low energy protons. Argon whose spectrum was previously studied and found to consist of Ar lines, was selected because its spectrum is different from that of O₂. The 1 NG system of O₂⁺ and strong Balmer lines were excited. Relative intensities of H α and H β lines for different proton energies were calculated.

2 Experimental Arrangement

Ghosh *et al.*¹⁻⁶ adopted a dynamical flow method for the investigation of excitation of spectra of gases by proton bombardment. It may be remembered that since the reaction between ions and molecules is very rapid, the state of the reaction and the non-equilibrium distribution of molecules vary rapidly with time. Therefore, a particular state of reaction is difficult to observe in a static system. On the other hand, in a dynamical flow system, by suitable adjustment of the flow of the gas to be bombarded by the ion, the desired state of the reaction can be made steady in a particular portion of the collision chamber⁵.

The experimental system was connected to a high vacuum system consisting of an Edwards Speedvac F-203 oil diffusion pump and a Cenco Hyvac-14 rotary pump (Fig. 1). A pressure of $(1-1.5) \times 10^{-5}$ Torr was maintained in the experimental system and was measured by an Edward ionization gauge, IG-2AH. The diffusion pump was continuously cooled by

Table 1—Characteristics of Spectra Excited by Proton Bombardment¹⁻⁶

Bombarded gas	Pressure	(Proton energy, 0.56-1.7 keV)	
		Spectra excited	Remarks
N ₂	A few tens mTorr	1 PG and 2 PG systems of N ₂ , 1 NG system of N ₂ ⁺ , H α and H β lines	The nature of the excited spectra is independent of proton energy. A distinct change in the spectral intensity was recorded with the variation of target gas pressure. The 1 NG system of N₂⁺ and Balmer lines may be excited by a charge exchange process: $\text{H}^+ + \text{N}_2 \rightarrow \text{N}_2^+ + \text{H}$ $\text{N}_2^+ \rightarrow \text{N}_2 + h\nu \text{ (1 NG system of N}_2^+)$ $\text{H}^* \rightarrow \text{H} + h\nu \text{ (Balmer lines)}$ 1 PG and 2 PG systems of N₂ can be excited by (1) the fast H-atoms produced by charge exchange and/or (2) secondary electrons produced by the bombardment of metallic surface of the collision chamber by ion beam. Thus $(1) \begin{cases} \text{H}^+ + \text{N}_2 \rightarrow \text{N}_2^+ + \text{H} \\ \text{H} + \text{N}_2 \rightarrow \text{N}_2^+ + \text{H} \end{cases}$ and $(2) \text{e} + \text{N}_2 \rightarrow \text{e} + \text{N}_2^+$
Air	A few mTorr	1 PG and 2 PG systems of N ₂ , 1 NG systems of N ₂ ⁺ and O ₂ ⁺ , H α and H β lines	The excited spectra are independent of proton energy. The spectral intensity varies with the target gas pressure. 1 NG system of N₂⁺, Hα, Hβ lines and 1 PG and 2 PG systems of N₂ may be excited by the same processes as for the excitation of these lines and bands by bombardment of N₂ by proton. The 1 NG system of O₂⁺ and also Balmer lines may be excited. Thus $\text{H}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{H}^*$ $\text{O}_2^+ \rightarrow \text{O}_2 + h\nu \text{ (1 NG system of O}_2^+)$ $\text{H}^* \rightarrow \text{H} + h\nu$
Ar	A few mTorr	Only Ar I lines are excited	The spectra do not reveal any appreciable change in their character with proton energy. Ar I line intensities vary linearly with pressure. Ar I lines may be excited by the following process: $\text{H}^+ + \text{Ar} \rightarrow \text{H}^+ + \text{Ar}^*$
(Ar, O ₂) mixture	do	Ar I lines, 1 NG systems of N ₂ ⁺ and O ₂ ⁺ , 1 PG and 2 PG systems of N ₂ and Balmer lines of H atoms	These lines and bands are excited by processes given above.
CO ₂	do	Angström and 3 PG systems of CO, comet tail bands of CO ⁺ and Balmer lines of H atoms	The collisional processes which may produce these emissions are: $(1) \text{H}^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{H}^* \text{ (charge exchange)}$ $\text{H}^* \rightarrow \text{H} + h\nu \text{ (Balmer lines)}$ $(2) \text{H}^+ + \text{CO}_2 \rightarrow \text{H}^+ + \text{CO}^+ + \text{O}$ (Dissociation with excitation) $\text{CO}^+ \rightarrow \text{CO} + h\nu$ (Angström and 3 PG systems of CO) $(3) \text{H}^+ + \text{CO}_2 \rightarrow \text{H}^+ + \text{CO}^{++} + \text{O}$ (Dissociation with charge exchange) $\text{CO}^{++} \rightarrow \text{CO}^+ + h\nu$ (Comet tail bands of CO⁺) $\text{H}^* \rightarrow \text{H} + h\nu \text{ (Balmer lines)}$

Voltas 'Tushar' water cooler having a temperature range 7-11°C, which was controlled automatically.

Protons were obtained from a Moak, Reese and Good⁷ RF ion source, henceforth referred to as M.R.G. source (Fig. 2). They were produced by passing an RF discharge in a pyrex glass envelope from a 100 MHz oscillator with a 60 W output. H₂ gas

(oxygen content not exceeding 0.5%), after passing through a heated palladium tube, was allowed to leak to the source through a small hole in the 2 S aluminium proton base. The M.R.G. ion source is capable of giving a proton current of the order of a few milliamperes. The current was composed of H⁺ (92%), H₂⁺ (6.4%) and H₃⁺ (1.6%).

To extract protons, the outlet in the aluminium base was surrounded by a quartz sleeve. For the collimation of the beam, dc current was passed through a coil placed at the base of the source. H_2 was

introduced through a Hoke needle valve into the discharge tube by heating the palladium tube. The flow of H_2 and the dc current through the coil were adjusted to obtain a well-focussed proton beam. The

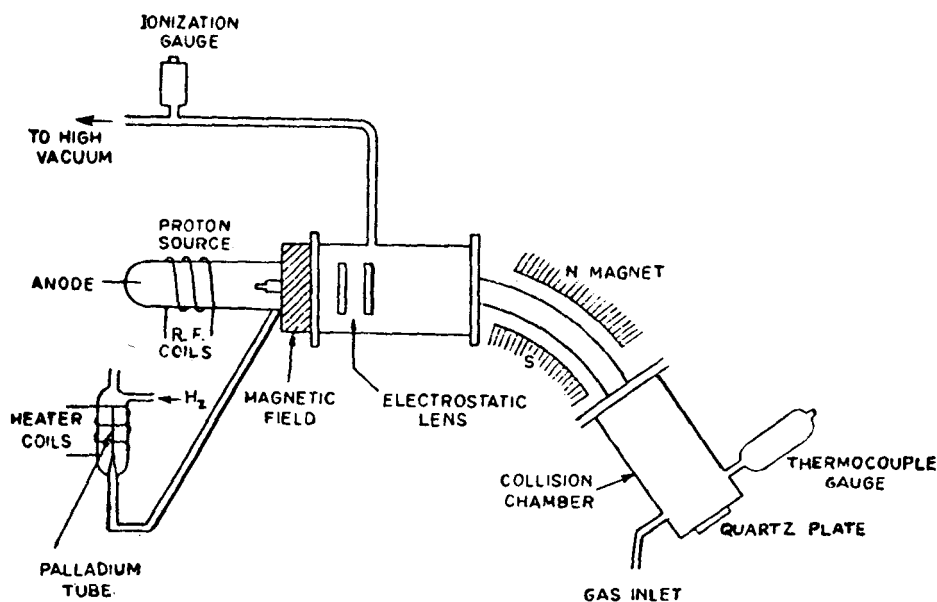


Fig. 1—Experimental set-up for exciting spectra of gases by proton bombardment

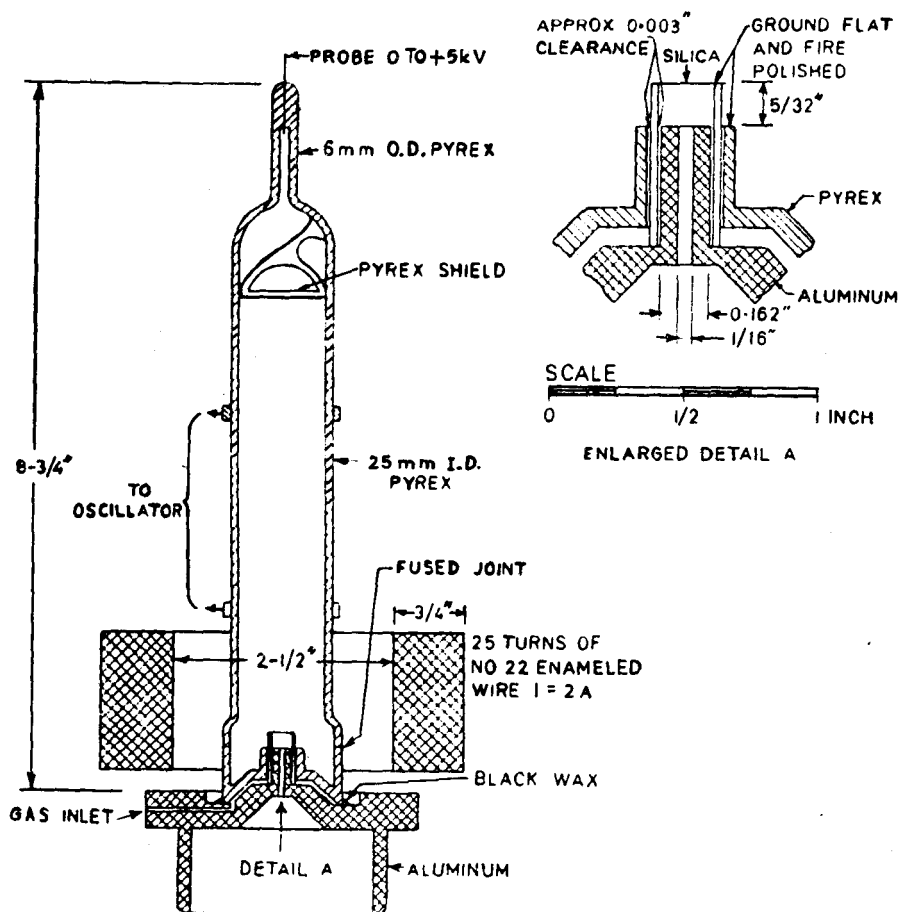


Fig. 2—M.R.G. ion source

proton beam was found to be pencil-like when a dc current of about 2 A and 24 V was passed through the coil. The beam after emerging from the exit hole of the base entered the collision chamber, which was also made of pyrex glass, through a hole in the brass plate. The plate supported the proton source on one side and the collision chamber on the other.

The anode of the proton source was kept at a positive potential with respect to the chamber (the aluminium base) and was grounded. The voltage was supplied by a 10 kV dc power supply having separately wound primary and secondary for ac voltage input.

Tank N_2 of 99.5% purity was leaked into the collision chamber through a needle valve. For the target gas air, before introducing it into the system, it was purified for carbon dioxide, water vapour and dust by passing it through a tower of wet cotton, a bottle containing distilled water, two bottles of conc. sulphuric acid, a tube containing soda asbestos and a U-tube containing silica gel. The pressure at the input was measured by an M.R.G. thermocouple gauge.

When Ar and (Ar, O_2) mixture were the target gases, they were leaked into the collision chamber through a needle valve. O_2 was 99.5% pure. Different mixtures of argon and O_2 were obtained by controlling the output pressure of the two gas tanks which were connected to the input valve through a Y-joint of pyrex glass. The pressure at the input was measured by an M.R.G. thermocouple gauge.

The following procedure was adopted for exciting the target gas by proton impact. After obtaining a well-focussed proton beam in the collision chamber, the target gas was introduced into the system through the needle valve. A bright glow was observed. Its brightness was increased to the maximum (by visual estimate) by adjusting the flow of target gas. Once the

maximum intensity of the glow was obtained, it remained constant for a considerable period of time.

3 Experimental Details and Results

3.1 Spectroscopic Studies

The spectra were taken with a Hilger Watts (E 498-306 59223 medium quartz) spectrograph using Kodak 103 F and Ilford HP3 plates. As the collision chamber was made of glass, only the spectra above 2900 Å could be photographed.

Figs 3 and 4 show the spectrum of N_2 and air under different physical conditions. It can be seen that for N_2 in the spectral region 2900-7000 Å, 1 PG and 2 PG systems of N_2 , 1 NG system of N_2^+ and $H\alpha$ and $H\beta$ lines were emitted. For air, in addition to the above, the spectrum contained a few bands of 1 NG system of O_2^+ . As the dispersion of the medium quartz spectrograph is low for higher wavelength regions, the identification of 1 PG system of N_2 , 1 NG system of O_2^+ and the $H\alpha$ line was uncertain.

The nature of the spectra of N_2 and air did not change as the energy of the bombarding protons was increased from 560 to 1700 eV. However, marked change in the intensity of all systems was recorded with the increase of pressure from 5 to 30 mTorr and a slight change in the intensity was observed as the energy of the protons was varied from 560 to 1700 eV.

Figs 5 and 6 show the spectra of Ar and (Ar, O_2) mixture respectively. It can be seen that within the spectral region of 3000-7000 Å, only Ar lines were excited when Ar was bombarded; and Ar I lines, Balmer lines and the 1 NG system of O_2^+ were excited when the mixture of Ar and O_2 was bombarded. Since N_2 bands were easily excited by proton bombardment, to avoid the predominance of these bands due to N_2

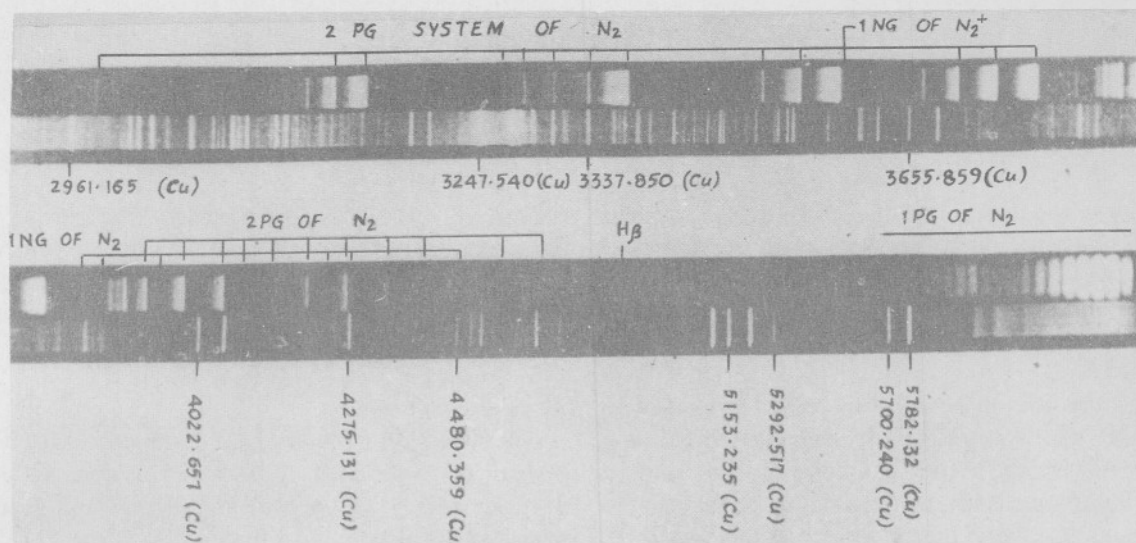


Fig. 3—Spectrum of N_2 excited by 560 eV protons with Cu spectrum (N_2 pressure, 40 mTorr; exposure, 2 hr 45 min)

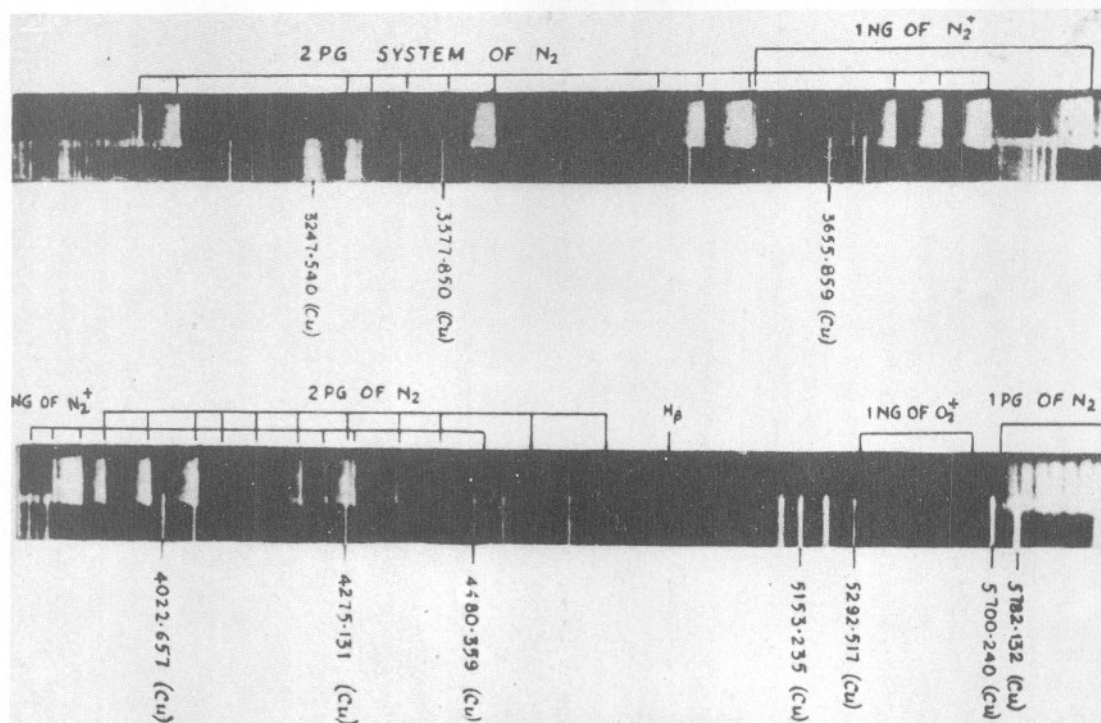


Fig. 4—Spectrum of air excited by 560 eV protons with Cu spectrum (Air pressure, 6 m Torr; exposure 1 hr 30 min)

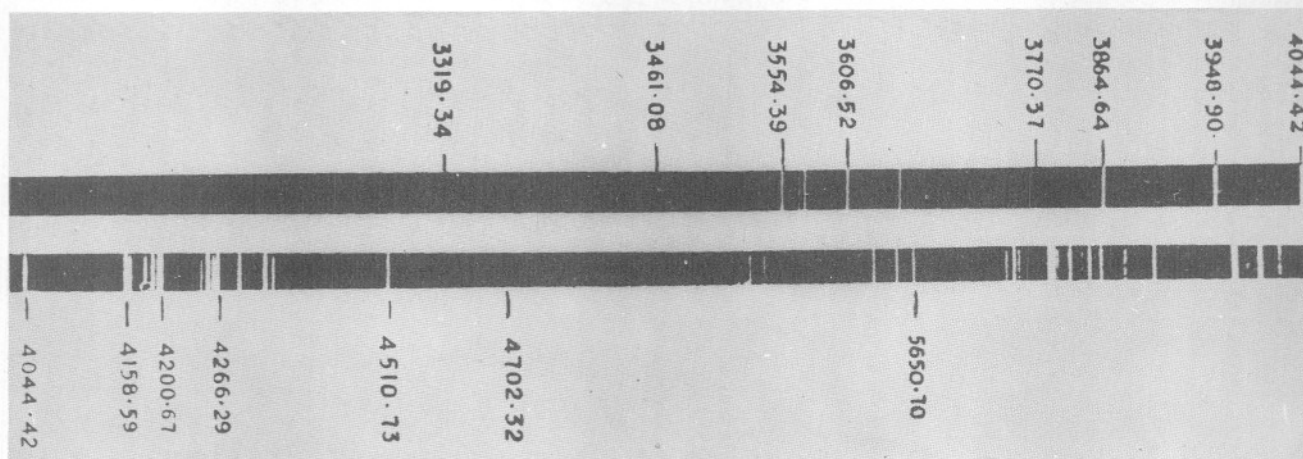


Fig. 5—Spectrum of argon bombarded by 560 eV protons (Argon pressure, 11 m Torr; exposure, 1 hr)

impurity in the oxygen tank and also due to intrinsic leakage of air into the collision chamber, the spectra of the oxygen-argon mixtures were kept underexposed. These spectra showed faintly the 1 NG system of N_2^+ , and the 1 PG and 2 PG systems of N_2 in the background.

When the proton energy was varied from 560 to 1700 eV, the spectra of Ar did not reveal any appreciable change in their character. Ar lines showed only a slight increase in their intensities. In the mixture of Ar and O_2 , when the oxygen content was raised, keeping the total pressure of the mixture constant, the

intensity of the O_2^+ bands increased. The intensity of the $H\alpha$ line also increased as the oxygen content was increased. If a fixed proportion of oxygen and argon was kept in the mixture, the intensities of the O_2^+ bands and the $H\alpha$ line increased with pressure.

3.2 Photometric Studies

From the glow of N_2 and air, certain bands of 2 PG system of N_2 (3159.3, 2271.3, 2576 and 4200 Å), 3914.4 Å of 1 NG system of N_2^+ (Figs 3 and 4) were selected by a Baush and Lomb monochromator. The intensity was recorded by a photomultiplier tube

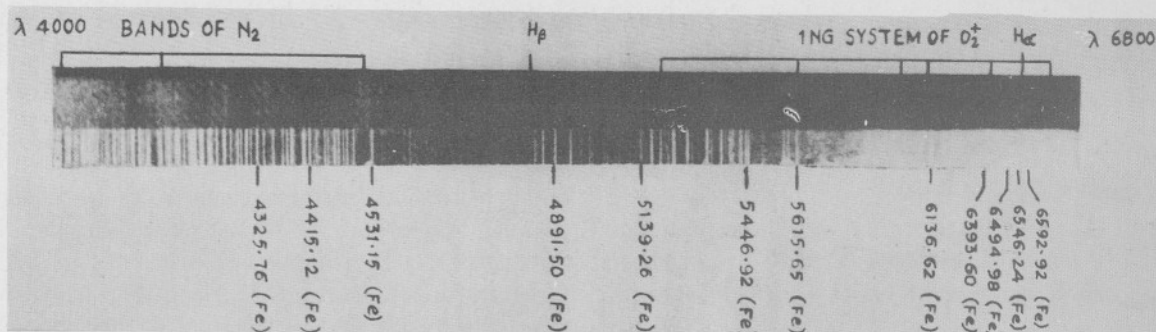


Fig. 6—Spectrum of (Ar, O₂) mixture in 1:5 proportion excited by 840 eV protons with Fe-arc spectrum
(Total pressure of (Ar, O₂) mixture, 10 mTorr; exposure, 1 hr 15 min)

(RCA 1P21) to which a Leeds and Northrup Speedomax recorder was connected. At a fixed energy of protons, the variation in the intensity of bands with the pressure of the target gas was recorded. Fig. 7 shows that the intensity of the 2PG system rises quadratically and that of 1 NG system linearly with the increase of N₂ and air pressure.

The photometric study of argon lines at 3606.5 and 4333.5 Å was also carried out by the same apparatus. It was observed that for a fixed energy of protons, the intensity of line rises linearly with the pressure (Fig. 7).

3.3 Microphotometric Studies

The intensities of the various emissions in the spectra of N₂ and air were measured by a Hilger and Watts microphotometer No. L459.301/57 coupled to a Minneapolis Honeywell recorder (Model 153 × 17V-X-30R). These plates were scanned from 2950 to 6500 Å by a servomotor rated for a speed of 0.75 mm/min.

It was observed that in the spectra of both N₂ and air, the intensities of 1 PG and 2 PG systems of N₂ were higher compared to those obtained by other investigators. Again, when the energy of the bombarding protons was raised from 560 to 1700 eV, the intensity of nitrogen bands showed slight increase in the spectra of both N₂ and air, while that of 1 NG system of O₂⁺ in spectra of air varied inversely with the energy.

It was observed that the intensity of Ar I lines increased with proton energy, while that of the 1 NG system of O₂⁺ and the Hα lines decreased with proton energy. When the contents of oxygen and argon were in 1:1 proportion, the 1 NG system of O₂⁺ and the Hα line were more intense than those obtained with mixtures in 1:3 and 1:5 proportions.

4 Discussion

The spectra were excited by low energy (0.56–1.7 keV) proton bombardment. Previously such excitations were carried out from a few keV to MeV proton energy. The mechanism for the excitation of

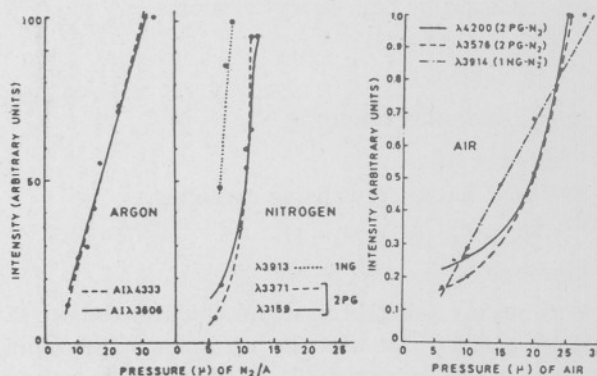


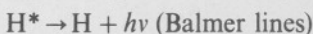
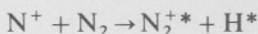
Fig. 7—Variation of light intensity with N₂, argon and air pressure

spectra for N₂ and air, Ar, (Ar, O₂) mixture and CO₂ as target gases may be as follows:

(1) 1 NG system of N₂⁺ (Fig. 7): It indicates that the system is excited by a single collisional process. Therefore, this system can be excited by (i) Charge exchange or (ii) Direct ionization.

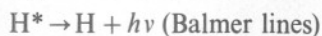
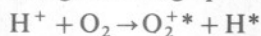
Of the two processes, the charge exchange is favoured for two reasons: (a) charge exchange cross-sections are high at low energy, (b) when N₂ and air are bombarded by protons, in addition to 1 NG system of N₂⁺, Balmer lines of H atoms are excited. The latter can be excited only by a charge exchange process.

The 1 NG system of N₂⁺ and the Balmer lines of H are therefore excited by the following processes:



(2) 1 NG system of O₂⁺: According to Stier and Barnett⁸, at 5 keV proton energy, the charge exchange cross-section for O₂ is eight times the ionization cross-section. The former falls and the latter rises as the energy of the bombarding protons is increased. By extrapolating the charge exchange and ionization cross-section versus energy curves of Stier and Barnett to the proton energy 0.56–1.7 keV, it will be seen that the charge exchange cross-section is more than one order higher than the ionization cross-section. This

suggests that 1NG system of O_2^+ is excited by the charge exchange process, i.e.

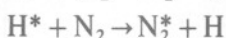
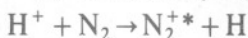


(3) 1 PG and 2 PG systems of N_2 : The excitation of 1 PG ($B^3\pi - A^3\Sigma^+$) and 2 PG ($C^3\pi_u - B^3\pi_g$) systems of N_2 can be attributed to any of the following reactions:

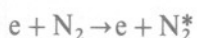
(i) Direct excitation



(ii) Collision by high energy H atoms



(iii) Collision by electrons



(iv) Very low-energy charge exchange



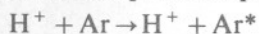
With regard to the direct excitation [reaction (i)], it may be pointed out that the variation of the light intensity of 2 PG system of N_2 depends on the square of target gas pressure (Fig. 7), indicating that a product of the primary collision interacts with a second N_2 molecules. Again, the excitation of this system from the ground state is due to an intercombination transition. Therefore, this system is to be excited by electron exchange, which cannot occur by proton bombardment. Hence reaction (i) will not be effective.

The 1 PG and 2 PG systems of N_2 can be excited by reaction (ii). The fast H atom produced by charge

exchange collides with nitrogen molecules and excite them to $^3\pi$ state. They then radiate 1 PG and 2 PG systems of N_2 . The reaction (iii) necessitates the presence of electrons which may be obtained as low energy secondary electrons produced by the bombardment of metallic surface of the collision chamber by ion beam. The excitation of 1 PG and 2 PG systems of N_2 by reaction (iii) is supported by the experimental observations of Hayakawa *et al.*⁹ who have observed the 2 PG system of N_2 by employing low energy electrons. The 1 PG and 2 PG systems of N_2 can also be excited by reaction (iv). The kinetic energy (K.E.) distribution of ground state of N_2 ions formed in charge transfer may well extend to several electron volts. Very low energy charge transfer yielding excited states via curve-crossing has been observed by Lipples *et al.*¹⁰ for (Ar^+ , He) reactions.

It has been observed that 1NG system of N_2^+ is easily excited by bombardment of energetic particles. Hence one may expect that, during the above reaction, N_2^+ rather than N_2 will be in excited state. Again, the K.E. required for excitation of such system is quite high. For these reasons, the probability of this reaction will be expected to be low.

(4) Ar lines: Collisions of protons with Ar atoms in the energy range 0.56-1.7 keV have produced only Ar I lines. The probable process of excitation is:



The photometric studies of Ar I lines 3606.5 and 4333.5 Å reveal that the intensity variation of these lines with argon pressure is linear, indicating that the excitations of Ar I lines result from a single collisional process (direct excitation).

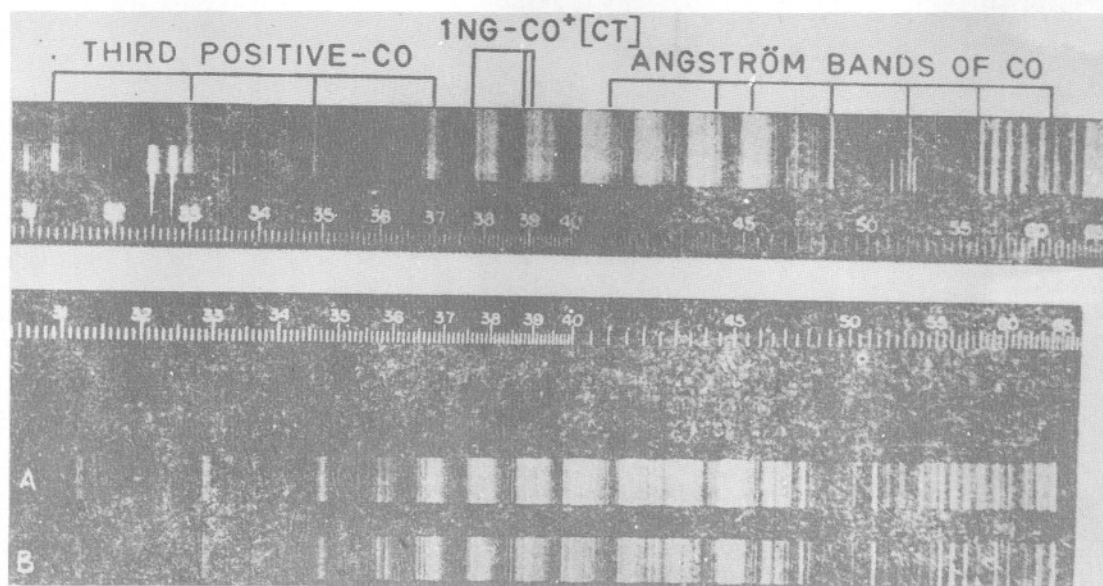


Fig. 8—Spectrum of CO_2 excited by 0.5-2 keV proton bombardment

At low energies, charge exchange has a high probability. Its cross-section for (H^+ , Ar) collision is maximum at about 1.6 keV proton energy¹¹. However, at low proton energies, charge exchange accompanied by excitation has a low probability. This is observed by Stedeford and Hasted¹² who found that the cross-section is small for the formation of atomic hydrogen in the 2S or higher states by collision of proton with Kr, Xe and Ar. Therefore, the absence of Ar II and H I lines in the spectra of Ar observed by Ghosh *et al.*⁴ may be due to low cross-sections of charge exchange accompanied by excitation whereas the excitation energies of both H and Ar^+ are high.

From the above discussion, it may be concluded that the spectral features of N_2 , air, Ar excited by low energy proton bombardment¹⁻³ can be explained by applying collisional processes, in particular, charge exchange, ionization and excitation processes. Similarly, the spectra of (Ar, O_2) mixture and CO_2 excited by low energy protons⁴⁻⁶ can be explained. The spectrum of CO_2 consists of Ångstrom and 3PG systems of CO, comet tail bands of CO^+ and Balmer

lines of H atoms (Fig. 8). Their excitation mechanisms are given in Table 1.

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