"A SPECTROSCOPIC STUDY OF AN UNCONDENSED SPARK BETWEEN COPPER ELECTRODES IN THREE DIFFERENT CASES AT VARIOUS PRESSURES"

BY JAGDEO SINGH AND SREE RAMULU

(Plate X)

ABSTRACT. A detailed study of the nature of the spectra at various portions of the spark in illuminating gas air and carbon dioxide at various pressures, the spark being excited by a large induction coil, is described.

The following are some of the more important observations and results obtained:—

(*a*) Most of the lines are due to the material of the electrode. They are prominent at higher pressures and decrease in intensity as the pressure decreases. At a pressure of 10 cms. practically all of them disappear. Even at higher pressures, where the lines are prominent, they are more concentrated at the two ends of the spark.

(*b*) Bands are practically absent from the atmospheric pressure up to 30 cms. of mercury. They appear at this pressure and gain in intensity as the pressure is further reduced. The optimum pressure at which the bands are developed with the greatest intensity shows practically no variation from gas to gas.

(*c*) A study of the bands due to CN and NO indicates that the formation of these molecules and their excitation to give their characteristic spectra is influenced by the neighbouring gases.

(*d*) It seems likely that the effective temperature of the spark is not constant throughout its length, the middle portion being cooler than the end portion. This statement requires confirmation by accurate methods of evaluating temperatures.

(*e*) One particular line, belonging to ionised oxygen exhibits a strong effect of pressure broadening in the illuminating gas.

INTRODUCTION

The selective excitation of lines and bands in spectroscopy has been studied in a number of cases. It mainly falls in three groups: (1) The effect of foreign gases on the nature of spectrum of a substance, (2) The method of excitation and (3) The effect of pressure. There are various cases of the first type specially in a discharge tube as for example (*a*) the behaviour of first positive nitrogen (Jevons, 1932) bands in the presence of high pressure inert gases, (*b*) the production of negative nitrogen (Jevons, *loc. cit.*) bands in high pressure helium containing a trace of nitrogen, (*c*) the intense development of the Swan band (Jevons, *loc. cit.*) system by a trace of carbon in high pressure helium or argon; (*d*) the development of Cameron bands (Jevons, *loc. cit.*) by a trace of cabon in high pressure neon; (*e*) the isolation of the high pressure carbon and the triplet carbon band systems under similar conditions; (*f*) the behaviour of mercury vapour (Wood, 1924) in the presence of foreign gases as revealed by Wood's investigations on mercury vapour in the presence of nitrogen at a pressure of 2 m.m. Kaplan (1930) observes that CO is more effective in quenching λ 2536 line than N_2.

Coming to the second case we have various methods of excitation as for example electro-luminescence, photo-luminescence, chemi-luminescence, thermo-luminescence, etc. In electroluminescence again there are many classes: *e.g.*, high frequency discharge, spark discharge, arc-discharge, etc. In a variety of cases the high frequency (Brasfeld, 1929) discharge gives rise to an intensity distribution different from that obtained from other types of excitation of spectra. In hydrogen (Asundi and Ors. 1942) it has been found that the primary spectrum is stronger than the secondary spectrum when excited by an ordinary induction coil and the secondary spectrum is stronger than the line spectrum when excited by the H.F. discharge. It has been found by Notingham that the relative intensities of the lines in the spectrum of the arc depends upon the current strength and in the case of the spark on the size and shape of the electrodes too. Peters and Mankoff found that in the case of low voltage arc using cathode layer, the line spectra of most elements are from 10 to 100 times stronger immediately in front of the cathode than in the arc gas column, this effect being stronger for elements of the first three groups of the periodic table. It has been found that the self induction and the capacity in the circuit cause considerable changes in the excitation of spectra. The introduction of an auxiliary spark gap in series with the analysis spark has three effects: (1) general increase in intensity. (2) selective increase in intensity and (3) stabilization of the spark. Lastly the investigations of Newmann on the arc discharge in gases and mixed gases at various pressures are among other sources of data on selective excitation. A detailed study of this nature of the uncondensed spark spectra of three gases namely the illuminating gas, the carbon dioxide and the air has been presented in this paper.

EXPERIMENTAL ARRANGEMENT AND PROCEDURE

The uncondensed spark was maintained in a glass tube of nearly 3 cms. in diameter which had copper electrodes fitted to it with sealing wax. The glass tube was blown in the form of a bulb in the middle where the spark used to occur and the whole thing was kept inside a water tight wooden trough such that the two side tubes and the front end of the tube with quartz window projected outside the trough. The inlet and outlet tubes were bent so that they might rest on the top of the trough when the tube was kept in position. A continuous flow of water through the wooden trough was arranged, care being taken to see that the water level in the trough was always 2 or 3 cms. above the main body of the discharge tube. This arrangement was made to avoid the discharge tube from being cracked by the heat of the spark. Two copper electrodes were inserted inside the tubes. They were completely insulated by rubber except at either ends, so that there might not be any sparking between the electrodes and the side tubes. The outer tube was connected to the Cenco-high-vacuum pump to exhaust the gas inside through a two-way glass tube, the other end of which was connected to a mercury manometer which could record pressures from 1 cm. of mercury up to the atmospheric pressure. All the joints were made air-tight with sealing wax. The tube was washed many times by the gas before the spark was passed. The discharge tube which was ultimately adopted is shown in Fig. 1.

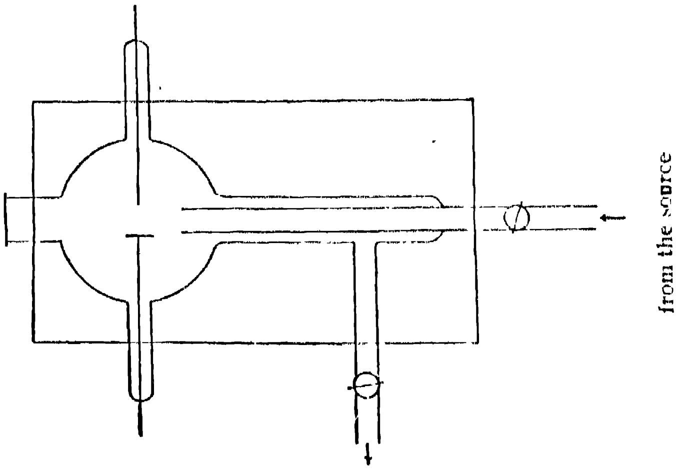


FIG. 1

A large induction coil of 10 in. spark-length was used so that a very high voltage was impressed. The current from the 220 D.C. mains regulated through a rheostat was supplied to a mercury interrupter whose base was 15 cms. in diameter. The interrupted current (6 to 9 amp) passed through the primary ends of the induction coil, the secondary ends of which were connected to the two electrodes of the experimental discharge tube. The interrupter used to stop functioning after some time and then the mercury was cleaned and replaced. Sometimes shaking the interrupter also helped in this direction.

The illuminating gas used was obtained from the main laboratory supply and had the constitution of 48% nitrogen, 12% oxygen, 24% methane, 4% hydrogen and 12% unsaturated hydro-carbons ; carbon dioxide was produced by the action of dilute hydrochloric acid on marble in a Woulf's bottle. In this way the spark discharge between copper electrodes in illuminating gas, carbon dioxide and air at the pressures 2, 5, 10, 20, 30. 40, 50, 60 and 75 cms of mercury was studied from the three parts of the spark, namely the central portion ; the stationary spot at the cathode and the moving spot at the other end of the spark and these are denoted by a, b, c respectively in the spectrograms (Plate IX).

A Hilger small quartz spectograph was used for photographing the spectra. Ilford H. P. 2 plates were used and the time of exposure in all cases was 10 minutes. Spectogram (1) and (2) are taken with the illuminating gas at the pressures of 40, 30, 20, 10, 10, 5 and 2 cms. of mercury. Spectogram (3) is taken the pressure of 40, 30, 20, and 10 cms. and plates (4) and (5) are taken with air at carbon dioxide at the pressures of 75, 60, 50, 40, 40, 30, 20 and 10 cms. of mercury. In all these a, b, c are marked for the three spots.

RESULTS AND DISCUSSIONS

The intensity of bands and lines has been estimated visually from the blackening on the plates without taking into account many other well-known factors such as the sensitivity of the plate, etc. modifying the blackening. Because of this fact much importance has not been attached to the observations of the individual bands, but only systems of bands as a whole are taken into account. This is summarised in Table I.

The spectra of the spark in various gases have been found to show widely different intensity distribution in the case of bands, lines and continuum present. As will be seen from Table I, pressure has a marked effect on the excitation of bands, the lines and the continuous spectra also. Various portions of the spark give rise to widely different spectra. The nature of spectra appears to be dependent mainly upon three factors, namely (1) the gas in which the spark is excited ; (2) the pressure of the gas and (3) the portion of the spark photographed.

The present investigation, however, confines itself only to the mention of some very striking differences and it is believed that for such observations, the visually estimated intensities can be relied upon :

(1) *Bands.*—The observation in the case of first negative nitrogen, second positive nitrogen, cyanogen violet, NOγ and OH are summarised in the Table I.

(2) *Lines.*—From the Spectograms we see that the lines present are almost all those of the Cu electrodes. They are intense at higher pressures and decrease in intensity as the pressure decreases, so much so that in air a pressure of 10 cms. of mercury all the lines except the two strongest copper lines at λλ 3247, 3274 have disappeared completely. Same is found to be the case in carbon dioxide and illuminating gas. Further in general the lines when present are more prominent at the two ends of the spark and weak at the central portion of the spark. This is true for all the three gases investigated.

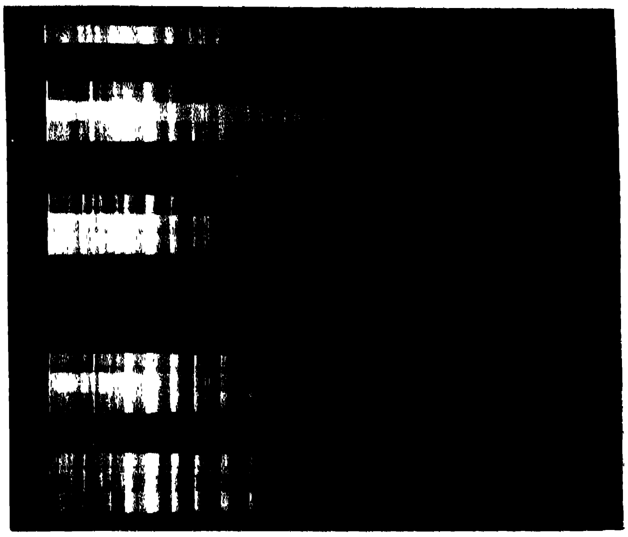
(3) The continuous spectrum is present with weak intensity only in the case of the illuminating gas.

Thus from the results given above we can conclude that the various lines present except a very few, namely carbon line at λ2478 and some oxygen lines, are all due to the material of the electrodes of the spark. It can be seen that the lines are more prominent at the atmospheric pressure and decrease in intensity as the pressure of the gas surrounding decreases and nearly disappear at a pressure of 10 cms. of mercury. This is true in the case of almost all the three gases investigated. On the other hand the bands show variations in intensity in the reverse direction. They are absent at the atmospheric pressure and as the pressure decreases they make their appearance at a particular pressure which we may say is the characteristic of the system excited as well as of the gas surrounding the spark. At pressures lower than this optimum pressure the system may become weak as has been found firstly in the case of first negative nitrogen bands excited in the illuminating gas (41% of N_2), where they become prominent at a pressure of 10 cms. and become weaker at still lower pressures, or the system

Pressures in cms. of Hg

SPECTROGRAM 1

40
40
30
20
10

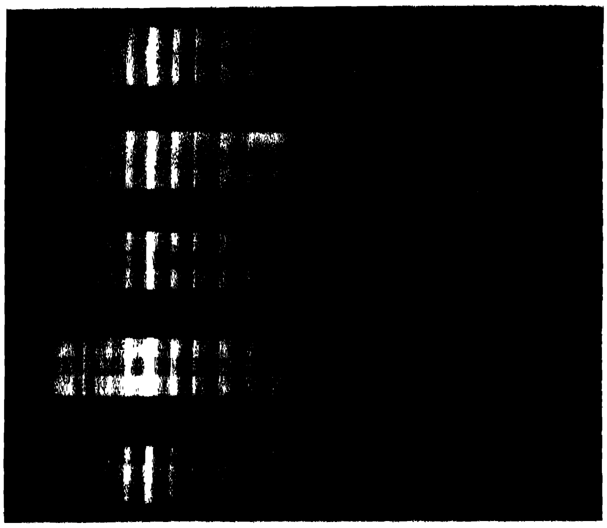


a b c (Central Cathode)

Pressures in cms. of Hg

SPECTROGRAM 2

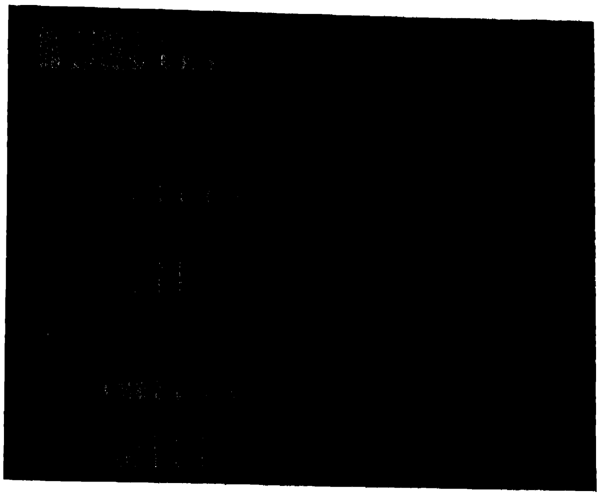
10
5
2
2



a b c (Central Cathode)

Pressures in cms of Hg

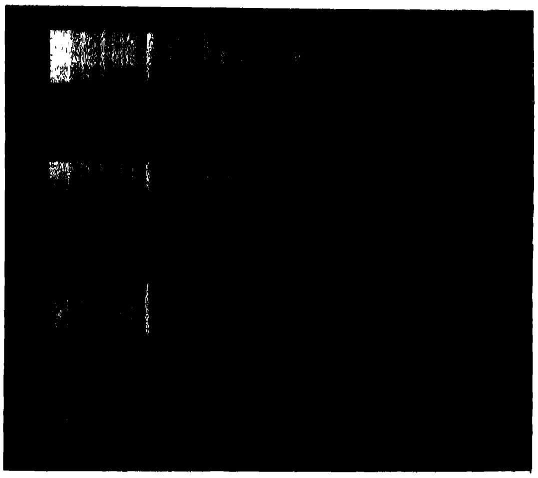
SPECTROGRAM Air ↓



40, 30, 20, 10

a, b, c (Central Cathode)

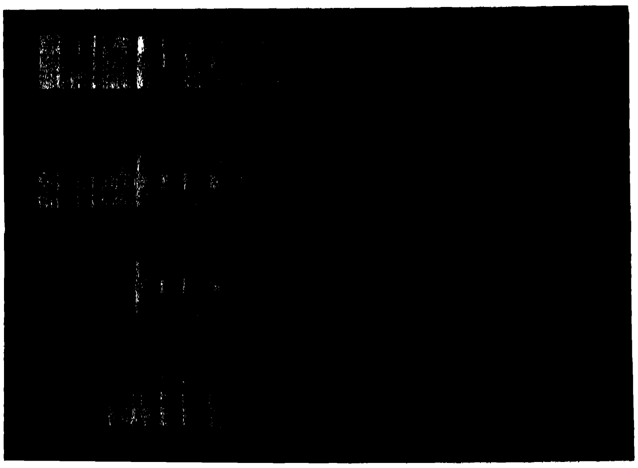
SPECTROGRAM 4. CO_2 ↓



75, 60, 50, 40

a, b, c (Central Cathode)

SPECTROGRAM 5. CO_2 ↓



40, 30, 20, 10

a, b, c (Central Cathode)

may become strong at pressures lower than the characteristic pressures for excitation as has been found in the case of second positive nitrogen bands developed in air when they appear at a pressure of 40 cms. and become stronger at still lower pressure or the system may remain with the same intensity at pressures lower than the characteristic pressure as has been found in the case of cyanogen violet system developed both in the case of CO_2 and illuminating gas but not in air. So we can generalise and say that under the conditions of the present experiments it is possible to excite the molecules of the surrounding gas in the spark discharge between the electrodes almost free from the characteristic lines of the electrodes. This happens when the pressure of the surrounding gas is near about 10 cms. of mercury. There appears to be a very slight variation in this pressure depending upon the nature of the gas.

We wish to point out another striking peculiarity. The first negative nitrogen bands as produced in the illuminating gas and in air are present only at the stationery spot of the spark in the illuminating gas while in the case of the air they are strong at the moving spot of the spark. It is difficult to understand this phenomenon. It would be very interesting if a more detailed investigation of this particular phenomenon is undertaken employing accurate methods of intensity measurements.

Another interesting observation concerns NOγ bands. Since nitric oxide is not present as such in any of the three gases, the presence of these bands is indicative of the conditions suitable for their development. Again the NOγ (Bair, 1920) bands are particularly weak in the illuminating gas, which contains as has been mentioned above a fairly large amount of nitrogen and oxygen. These bands are strong both in air and CO_2 in the latter of which nitrogen and oxygen can only be in small amounts as impurities. This is rather interesting when we contrast it with the complete absence of cyanogen bands in air, which must presumably contain traces of carbon. Probably it will be correct to say that whereas for the production of NOγ bands traces of nitrogen and oxygen if avilable in the presence of other gases are more favourable, a much higher concentration of carbon is necessary for the development of cyanogen bands in the presence of other gases. In this respect, however, Newmann (1929) has obtained cyanogen bands when an intermittent arc discharge is passed through hydrogen at a pressure of 10^{-3} mm. in the presence of helium and neon, where also therefore carbon and nitrogen must have been present only as impurities in small quantities. Newmann explains the presence of these bands as due to the effect of temperature being responsible for the production and excitation of CN bands. This is in contradiction to the observation made here. The effective temperature is roughly of the same order of magnitudes in both cases. Hence the absence of CN bands in the sparks in air is not explained on the temperature hypothesis. We have to conclude that the presence of helium and neon is responsible for the production of these bands in Newmann's experiment.

TABLE I

System of bands.	Illuminating gas (investigated at prs. 40-2 cms.)		Air (investigated at prs. 40-10 cms.)		Carbon dioxide (investigatsd at pressures 75-10 cms)	
	At different pressures	At various portions of the spark	At different pressures	At various portions of the spark.	At different pressures	At various portions of the spark
First negative nitrogen bands	Completely absent at pressures higher than 10 cms. They also decrease in intensity at still lower pressures.	Present only at the stationary spot of the spark (one end of the spark commonly known as the cathode.	They appear at all pressures and increase in intensity as the pressure decreases, but the change is not so well marked.	The system as a whole is very strong at the moving spot of the spark (may be called anode)	Appear at all pressures but become weak as the pressure decreases.	Equally intense at all portions of the spark.
Second positive nitrogen bands	Appear at all pressures become more intense as the pressure decrease.	Equally strong at all portions of the spark, but with this difference that at pressures lower than 10 cms. they are slightly less intense at the stationary spot.	Appear at all pressures and become prominent as the pressure decreases, the effect being marked this system is more prevalent in air than in illuminating gas at all pressures.	Less intense at the central portion of the spark.	Become prominent at pressure = 30 cms. the system as a whole increases in intensity as the pressure decreases. The increment being gradual and marked so much so that the 0, 0 band which is absent at pressure = 75 cms. makes its appearance at pressure = 10 cms. with intensity = 10	Intense at the stationary spot and weak equally both at the moving spot and the central portion of the spark.

TABLE I—(contd.)

System of bands.	Illuminating gas (investigated at prs. 40-2 cms.)		Air (investigated at prs. 40-10 cms.)		Carbon dioxide (investigated at pressures 75-10 cms.)	
	At different pressures	At various portions of the spark	At different pressures	At various portions of the spark.	At different pressures	At various portions of the spark
Cyanogen violet system.	Make their appearance at all prassures and do not show much variation with pressure.	Equally strong at all portions of the spark.	Completely absent at all pressures.	Completely absent at all portions of the spark.	The system as a whole appear even at pressure=75 cms. and shows practically no variation with the pressure.	The various portions of the spark are giving rise to the same intensity distribution.
$NO\gamma$ bands.	Very weak at all prestures.	Equally weak at all portions of the spark.	Make their appearance at all pressures and increase in intensity as the pressure decreases	At pressure=10 cms., they are very weak at the stationary spot, but at higher pressures equally intense at all portions of the spark.	Become prominent at pressure=20 cms.	Equally intense at all portions of the spark
OH bands	Make their appearance at pressure—20 cms, becoming stronger at still lower pressures.	Weak at the cathode.	The system is more prominent in air than in the illuminating gas at all pressures. Makes its appearance at pressure=40 cms.	At pressures=40 cms. and 30 cms. equally strong at all portions. At pressure=20 cms. were at the moving spot and at pressure=10 cms. weak at the stationary spot.	Make their appearance at pressure=20 cms. and increase in intensity as the pressure decreases.	equally strong at all portions of the spark.

From the observations of the intensity distribution of nitrogen bands obtained by the spark in air Tawde (1934) evaluated a temperature of 7200°K. The present experiments do not allow us to evaluate the effective temperature with any confidence. But it is interesting that values obtained by using the visually estimated rough intensities for the band heads, are of the same order of magnitude as that obtained by accurate measurements of intensity. Thus for the spark in air at a pressure of 20 cms. a temperature of 8160°K is derived as the mean of the values for the three parts of the spark. In general we find that at the same pressure in different gases the temperature is the lowest in the illuminating gas, whereas in air and carbon dioxide they are of higher magnitude, but roughly coincident with the values obtained by previous workers. Also the middle portion of the spark gives a temperature lower than the two ends of the spark. No quantitative significance can obviously be attached to the values thus obtained but from the right order of magnitude it seems likely that the differences in temperature along the length of the sparks are real. It would be interesting to test this by accurate methods of intensity measurements.

There is one particular line which has been marked in the Spectrogram 1 as O^+. This is one of the three or four lines of ionised oxygen which lie at about λ 4870A. This line is very broad and appears as a band at a pressure of 40 cms. It gradually becomes less broad with decrease in pressure and at 10 cms. it is almost sharp like a line. This line is, therefore, pressure sensitive. It, however, is present in the spark spectra of illuminating gas and absent in other spectra.

In conclusion the results show that it is not improbable to arrange the conditions of the spark in various media in such a way that not the lines characteristic of the electrodes but the bands characteristic of the molecules of the vapour can be excited. This observation is rather interesting and further work will show whether the method cannot be employed to bring about an excitation of multiatomic molecules.

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REFERENCES

Asundi, Singh and Singh, 1942, *Proc. Ind. Sci. Cong*, 35.
Bair, 1920, *Astro. Phy. Jour.*, **52**, 301.
Brasefield, 1929, *P.R.*, **34**, 431.
Jevons, 1932, Report on Band Spectra.
Kaplan, 1930, *P.R.*, **35**, 788.
Newmann, 1929, *Phil. mag.* **7**, 1084.
Tawde, 1934, *Proc. Phy. Soc.*, **46**, 333.
Wood, 1924, *P.R.S.*, **106**, 679.