

RÔLE OF ARGON IN THE DEVELOPMENT OF SOME BAND SYSTEMS OF NITROGEN

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1. INTRODUCTION

Conflicting views have been expressed regarding the probable cause of the observed differences in the intensity distribution in the spectrum of molecular nitrogen in air and in pure nitrogen. While Tawde and Patankar (1944, 1947) considered argon, the major rare gas constituent of air, as chiefly responsible for the effect, Gaydon (1944, 1948*b*) thought that 20% oxygen content of the atmosphere was the probable cause. Tawde and Korgaokar (1954) attempted to resolve this conflict by making a systematic study of the effect on spectra, of adding oxygen in gradually increasing proportions to pure nitrogen; but they could not include, within their scope of work, the effect of argon. This part of investigation was, therefore, undertaken by us in the same laboratory, almost simultaneously, and the present paper is an attempt to place on record the observations and conclusions therefrom.

The actual problem involved in the study is to follow quantitatively the intensity changes in bands of 1(*P*) and 2(*P*) systems of nitrogen with increasing admixture of argon in pure nitrogen excited in a discharge and to compare the same with those obtainable in a discharge through pure nitrogen and through atmospheric air. Observations were made on the following three definite mixtures of argon with nitrogen:

- I. Trace of argon in pure nitrogen (1% mixture).
- II. Argon and nitrogen in equal proportions (50% mixture).
- III. Excess of argon in nitrogen (99% mixture).

As a complementary part of these three conditions, observations on two further conditions, viz. (i) in pure nitrogen and (ii) in atmospheric air, were necessary. The data for these were utilized from the earlier work of Tawde and Patankar and of Tawde and Korgaokar respectively in this laboratory under similar conditions. This work therefore forms a logical sequence to the problem investigated by Tawde and Korgaokar.

2. EXPERIMENTAL

The electrical excitation of the spectra, the gas-filling system, the vacuum system, the discharge tube and the technique used for the intensity measurements were similar to those used by Tawde and Korgaokar (1954). The systems and the assembly were so designed as to allow nitrogen and argon to leak into the discharge tube at the desired partial pressure of each constituent and the total pressure of the mixture of the two gases. The pressures were measured by a dibutyl phthalate manometer. The total pressure maintained was the same, viz. 1.5 mm. of Hg., as that taken by Tawde and Korgaokar in the earlier experiments with oxygen effect. The electrical parameters and pressure were maintained constant throughout the observations on any given mixture condition. Two spectral instruments were used for the study, viz. (i) the Fuess medium quartz spectrograph for the ultra-violet region (dispersion $\sim 13 \text{ \AA}$ at $\lambda 3000 \text{ \AA}$ and 46 \AA at $\lambda 4600 \text{ \AA}$), and (ii) the Hilger glass prism infra-red spectrograph for the visible region (dispersion

$\sim 11 \text{ \AA}$ at $\lambda 4200 \text{ \AA}$ and 44 \AA at $\lambda 6000 \text{ \AA}$). About thirty-five bands of $2(P)$ and fifteen bands of $1(P)$ system were accessible for measurement of intensity.

As only the comparative aspects of the spectra under different conditions were involved in the investigations, only the peak intensity values have been used to represent band intensities. Correlations and final results of such values have been arrived at by two independent sets of plates. In the $2(P)$ system, intensity measurements in bands of (3, 0) sequence could not be made as the radiation from the standard lamp used did not reach 2800 \AA . Neglect of these is not likely to affect the overall picture and especially the comparative study involved in the work. The mean error in the estimation of intensities ranges from 5 to 8% for different bands. This accuracy is, however, considered to be much better than that involved in taking intensities as directly proportional to blackening densities.

3. RESULTS

The intensity values (I) of all the recordable bands of the two systems have been measured for each of the three mixtures and brought on a common scale with (0, 0) band of the $2(P)$ system as 1,000 units. All these data were read and examined together with data on two other conditions, viz. for pure nitrogen from the work of Tawde and Patankar (1944) and for air from the work of Tawde and Korgaokar (1954). All these readings form the five sets of observations for the critical study of the problems outlined. In all 150 band heads had to be subjected to measurement.

From the observed values of intensity (I), the quantity $(I/\nu^4) v'v''$ for each band has been computed in order to arrive at the total population rates ($\Sigma I/\nu^4$) for each of the two systems, corresponding to all the five cases mentioned. If the relative weight of populations in $1(P)$ system with respect to $2(P)$ system is expressed in terms of the ratio $(\Sigma I/\nu^4) 1(P)/(\Sigma I/\nu^4) 2(P)$ of the population rates, it is possible to calculate this ratio from the knowledge of $(I/\nu^4) v'v''$ and hence of $(\Sigma I/\nu^4)$. These ratios have been derived for all the five cases and recorded in column 4 of Table I, side by side, with the quantities $(\Sigma I/\nu^4) 1(P)$ and $(\Sigma I/\nu^4) 2(P)$ in other columns.

TABLE I

Discharge gas	$2(P)$ system ($\Sigma I/\nu^4$)	$1(P)$ system ($\Sigma I/\nu^4$)	Ratio $\frac{(\Sigma I/\nu^4) 1(P)}{(\Sigma I/\nu^4) 2(P)}$
O Nitrogen (T & P) ..	669.0	19.9	3.0×10^{-2}
I A trace of argon in nitrogen ..	664.0	12.7	1.9×10^{-2}
II Equal amounts of each (50:50) ..	639.0	8.8	1.4×10^{-2}
III A trace of nitrogen in argon ..	605.0	5.4	0.9×10^{-2}
IV (a) Air (T & K) ..	585.0	7.9	1.4×10^{-2}
(b) $N_2 + O_2$ } (T & K) 80:20 } ..	537.0	8.7	1.6×10^{-2}

Note :

- (1) T & P = Tawde and Patankar (1944).
- (2) T & K = Tawde and Korgaonkar (1954).
- (3) The data under IV(b) for N_2/O_2 mixture from the work of Tawde and Korgaonkar (1954) has also been included along with that in air, as it corresponds to proportion of these gases in air and will be referred to in discussion part.

The actual measure of the effect caused by particular admixture of argon with pure nitrogen can be obtained by referring any measured intensity value for that mixture to the corresponding intensity value for pure nitrogen condition as reference scale. Thus, if I is the intensity of a band in the mixture and I_N that in pure nitrogen, then the ratio I/I_N is taken as the measure of the argon effect on the band. The value unity of this ratio can be taken as absence of any effect by argon, the one less than unity as suppression, while that greater than unity as enhancement. These I/I_N ratios are calculated for the measured bands in each of the systems 1(P) and 2(P). From this, a mean value $(I/I_N)_{v'}$ of this ratio for bands arising at any v' level in the upper electronic levels B and C of nitrogen molecule, corresponding to the 1(P) and 2(P) systems respectively, has been derived. These results for the three argon-nitrogen mixtures are recorded in Table II. The variation of $(I/I_N)_{v'}$ with v' for the two systems is represented graphically in Figs. 1 and 2 from mixture to mixture.

TABLE II
Mean values $(I/I_N)_{v'}$

$B^3\Pi_g$ state 1(P) system	Argon-nitrogen mixture			$C^3\Pi_u$ state 2(P) system	Argon-nitrogen mixture		
	I	II	III		I	II	III
$v' = 5$	0.84	0.56	0.24	$v' = 0$	1.08	0.99	0.93
6	0.51	0.34	0.21	1	0.99	0.91	0.79
7	0.55	0.41	0.22	2	0.87	0.71	0.59
8	0.76	0.56	0.43	3	0.80	0.77	0.64
9	0.61	0.47	0.32	4	0.73	0.52	0.47
10	0.77	0.64	0.32
11	0.86	0.58	0.32
12	0.89	0.57	0.28

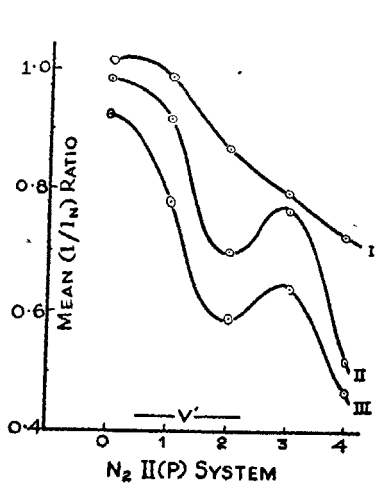


FIG. 1

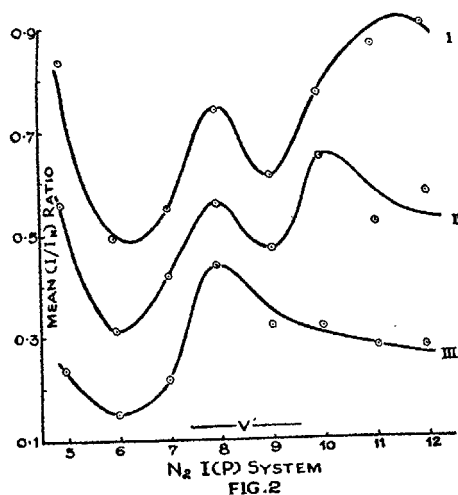


FIG. 2

4. CONCLUSIONS

- (i) Both the band systems persist to varying extents in the discharges in spite of very great dilution by argon.

(ii) The results of Table I indicate that with increasing argon content, the 1(*P*) system is increasingly weakened more than 2(*P*) system (cf. Table I).

(iii) In the general character of weakening outlined in (i) and (ii) above, individual bands or groups of bands in each system exhibit some peculiar features (cf. Figs. 1 and 2).

(iv) The following are the individual peculiarities in the systems:—

(a) *The 2(P) system*

With slight trace of argon in nitrogen (Curve I, Fig. 1) the bands associated with $v' \sim 0$ and 1 enhance to a slight extent over those in pure nitrogen, while others go down rapidly. Further increase of inert gas, even to very large excess of it, brings about a slow suppression in these progressions ($v' \sim 0, 1$) and a more rapid one at $v' \sim 2$ and $v' \sim 4$ and above. This behaviour gives an appearance of persistence or selectivity of bands associated with $v' \sim 0, 1$ and $v' \sim 3$ (Curves II and III, Fig. 1).

(b) *The 1(P) system*

The increasing argon content brings about intensity reduction which is more or less selective among the observed v' -progressions depending upon the argon proportion. In mixture I (1% argon), the selectivity is at $v' \sim 5, v' \sim 8$ and at $v' \sim 11, 12$, indicating the persistence of bands belonging to those progressions. With further increase of argon in the mixture, while the general reduction of intensity goes on, the selectivity of bands at $v' \sim 5, 8$ is maintained and the one at $v' \sim 11, 12$ shifts to $v' \sim 10$ (cf. Mixture II Curve, Fig. 2). With argon in considerable excess, the selectivity at $v' \sim 10$ disappears completely, leaving only the remaining two progressions to persist over others (cf. Mixture III Curve, Fig. 2).

5. DISCUSSION

A. General

It is possible for us now to discuss the relative rôles of oxygen and argon of air in producing the observed intensity changes in 1(*P*) and 2(*P*) systems of nitrogen. From Table I we have:

	Pure <i>nitrogen</i>	<i>Air</i>	20% oxygen + 80% <i>nitrogen</i>	Traces of argon in <i>nitrogen</i>
Relative weight ($\Sigma I/v^4$) 1(<i>P</i>) ($\Sigma I/v^4$) 2(<i>P</i>)	3×10^{-2}	1.4×10^{-2}	1.6×10^{-2}	1.9×10^{-2}

These results show that there is relative suppression of 1(*P*) system with respect to 2(*P*) system brought about by admixtures of oxygen and of argon. The relative suppression in air discharge cannot be attributed to any one of the two gases acting alone. It could be a contribution by both, though oxygen seems to play a more predominant part. The effective relative suppression of 1(*P*) system by oxygen appears to be 1.2 times that by argon. Here the nitrogen with trace of argon or with 20% oxygen admixture are considered as limiting conditions, equivalent to air discharge. Actually the reduction in air is much less. It is 1.14 times that by oxygen and 1.4 times that by argon. The fact that the reduction is not brought

to the level of air discharge by argon (trace) or oxygen (20%), acting either singly or together additively, suggests that the reduction effect is due to both acting as a unit. The observations, however, suggest that relatively the greater difference in colour of the air discharge from that of pure nitrogen discharge is brought about more by predominating oxygen proportion in agreement with the view of Gaydon (1944, 1948a) than by argon (trace) as indicated by Tawde and Patankar (1944, 1947). These aspects are discussed in the following sections in terms of the observed relative features and their probable mechanism.

B. Relative features : 1(P) and 2(P) systems

We now consider the possible mechanism that may cause the 1(P) system to be relatively suppressed with respect to the 2(P) system as a result of the admixture of argon. For this, we discuss the same possible mechanisms as have been considered by Tawde and Korgaokar (1954) in connection with their study on similar suppression produced by oxygen. These are:

- (a) Selective enhancement of $C^3\Pi_u$ state by changes in electron energies, if the excitation is chiefly by electrons.
- (b) Selective excitation of $C^3\Pi_u$ state, through inelastic collisions involving the metastables.
- (c) The depletion of $B^3\Pi_g$ state by radiationless transfer.
- (d) The formation of active nitrogen in the discharge tube in presence of argon gas.

We shall now deal with each of these mechanisms in the sequence stated.

(a) Electronic excitation

It has been shown by various workers that in the positive column, the electrons have Maxwellian distribution of energy and it is possible to assign a temperature T_e , representing the mean energy of electrons. T_e depends upon the nature of the gas, i.e. its critical potentials, etc., and also its pressure. Assuming that the mean free path of the electrons is small as compared with the size of the tube, and that no cumulative ionization takes place in the positive column, T_e could be worked out from the relation of Engel and Steenbeck (1934) from a knowledge of the characteristic constants of the gas, its pressure and the parameters of the discharge tube.

As the Engel and Steenbeck relation holds good for pure gases only, we may assume nitrogen and argon as the two extremes and their mixture as the intermediate between them and calculate the electron temperature from it, using the following constants and experimental parameters: p , the pressure of the gas = 1.5 mm. of Hg.; R , the radius of the discharge tube = 3.5 mm.; v_j , the ionization potential = 15.5 e.v. for nitrogen and 15.70 e.v. for argon.

The constant $C = 3.5 \times 10^{-2}$ c.g.s. units for N_2 .

The constant $C = 5.3 \times 10^{-2}$ c.g.s. units for A .

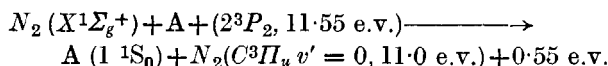
The electron temperatures thus determined come out to be $T_e = 1.92 \times 10^4$ °K, equivalent mean electron energy is 2.49 e.v. for nitrogen, and $T_e = 1.76 \times 10^4$ °K, equivalent mean electron energy is 2.48 e.v. for argon. Thus, on the above assumption, the electron energies should show a tendency to fall with increasing admixture of argon. This will cause reduction in the intensity of those bands, which originate from higher energy levels. In the present case, $C^3\Pi_u$ state being the higher of the two states involved, should weaken causing relatively greater suppression of 2(P) system as compared with the 1(P) system. This, however, is contrary to the experimental findings. Hence the possibility of preferential excitation of $C^3\Pi_u$ state by direct electron impacts with N_2 molecule in the ground state in the presence of argon may be ruled out.

(b) *Selective excitation of $C^3\Pi_u$ state through collision with metastable atoms and molecules*

It is known that argon atom has metastable states 3P_2 and 3P_1 with energies of 11.55 e.v. and 11.65 e.v. respectively and its ionization potential is 15.70 e.v. Nitrogen molecule, on the other hand, has one triplet metastable state ($A^3\Sigma^+_u$) at 6.20 e.v. and some singlet metastable states, designated as $X^1\Sigma_g^+$ ($v > 0$), $a^1\Pi_g^+$, $a'^1\Sigma_u^-$ and w , with energies ranging up to 9.3 e.v. for the last named. Its ionization potential is 15.58 e.v.

These metastable atoms and molecules may, therefore, be expected to play an important part in the energy exchanges occurring in the discharge. Many of the spectral phenomena resulting from the influence of foreign gases have been successfully explained with the help of inelastic collision processes, involving the metastables, provided the resonance rule and the Wigner's multiplicity rule are not violated.

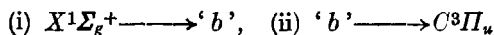
In A- N_2 mixtures, metastable argon atom can act as energy carriers to cause excitation of the nitrogen molecule in the ground state ($X^1\Sigma_g$) through collisions of the second kind. In a discharge tube containing argon atoms, the percentage of metastable and ionized atoms will be larger, the higher pressure of the gas and the more energetic the discharge. Thus, the metastable atom of argon in 3P_2 state (11.55 e.v. energy) may give up this energy to a nitrogen molecule and excite it to $C^3\Pi_u$ state ($v' = 0$, 11.0 e.v.) as follows:—



This reaction has reasonable probability of occurrence from the view-point of both the 'Resonance rule' as well as the 'Wigner's rule', provided it is assumed that 0.55 e.v. is distributed as translational energies of the components of the system. The possibility of such a reaction is indicated from our observations, as seen from the selectivity of $v' = 0, 1$ in Fig. 1.

The above mechanism is also supported by the results of Bernard (1939) which indicate that nitrogen molecules are excited by metastables of rare gas and that the transfer of energy is only possible between a metastable level of the rare gas and the neighbouring level of N_2 molecule. Such transfer of energy is accompanied by intense perturbations in the molecular band spectrum corresponding to that energy.

Another possible mode of excitation is as suggested by Nicholls (1948, 1951, 1954) involving the use of metastable molecules of N_2 in the singlet states and the collisions of slow electrons with them. Nicholls, while studying the spectrum of argon-nitrogen mixture (at $p \sim 600$ mm. in a high voltage arc source), has considered the indirect excitation mechanism in two steps. In the first step, energetic electrons in the arc source excite levels of some of the upper singlet states, such as a $^1\Pi_g$ or levels 'b' between 12 and 15 volts above $X^1\Sigma_g^+$. In view of high percentage of argon in the bulb, no collisional de-excitation of the levels of these states is possible, except near 11.5 e.v.—a level corresponding to the first excitation potential of argon. In the second step suggested by Nicholls each of the high energy electrons, which cause the primary excitation in a high pressure source, readily becomes part of the body of copious slow electrons. These slow electrons, it is suggested, are responsible for the multiplicity change, necessary to excite the triplet states $C^3\Pi_u$ and $B^3\Pi_g$ from the singlet levels by collision. The two steps of the indirect mechanism are represented in brief as



Thus, it may be supposed that the molecule initially excited to low vibrational levels of a singlet state of long life-time will, in second collision with slow electrons, populate the adjacent low vibrational levels of $B^3\Pi_g$ state, the radiation from these

levels will give rise to the observed $1(P)$ bands. Some levels of $a' \ ^1\Sigma_u$ and w states are adjacent to $C^3\Pi_u$ levels. Collisions of slow electrons with molecules in the singlet states could then readily cause the inter-combination transition thus populating the triplet levels.

Further, the collisions between the metastable molecules in a' and w levels, near to and higher than 11.5 e.v., and the argon atoms will result in radiationless transfer of the molecule from these levels. Thus, one could expect that any a' or w levels suitable for transfer to $C^3\Pi_u$ state ($v' = 1, 2, 3, 4$ levels) would be preferentially depopulated by collisions with argon atoms whose gas kinetic frequency can be of the order of 10^8 per second. Also if any $C^3\Pi_u$ ($v' = 1, 2, 3, 4$) levels were populated by a direct process from the ground state ($X^1\Sigma_g$), though there would be competition in the depopulation of the levels by radiation transfer, and the collisions of the second kind with argon atoms, there will result some radiation from these levels on account of the fact that by no means all the gas kinetic collisions are to produce a de-excitation.

On the basis of this mechanism, we should expect the predominance of bands of the $2(P)$ system originating from $v' \sim 0$ and 1 levels, and their relative weakening at $v' \sim 2, 3$, and 4. Though there is good evidence for this from the present observations, we cannot be certain about the predisposing indirect excitation mechanism suggested by Nicholls, in view of the relatively low pressures in our experiments as against high pressures, said to be favouring it.

Thus it is evident that the preferential excitation of $C^3\Pi_u$ state may come about through any of the processes discussed above, acting either singly or jointly.

(c) *Depletion of population in $B^3\Pi_g$ stated by radiationless transfer*

The energy of excitation of N_2 in $B^3\Pi_g$ state is 7.2 e.v. Depletion of N_2 in the $B^3\Pi_g$ state by normal argon atoms is not likely, but one may consider the possibility of collisions of N_2 with either (i) a metastable argon atom (11.55 e.v.) or (ii) argon ions. A collision of N_2 ($B^3\Pi_g$) with metastable argon atom (11.55 e.v.) may result in an ionized molecule in an excited state $A' \ ^2\Sigma_u^+$ ($v = 0, 1, 2$) which should yield bands of N_2^+ (a negative system of N_2). But this is less probable on account of the violation of Wigner's spin rule. We could not detect presence of even the strongest bands of N_2^+ (first negative bands) on our plates, which suggests that the depletion of population of N_2 in $B^3\Pi_g$ state is not very likely.

(d) *Active nitrogen hypothesis*

A collision of ion of argon with N_2 in $B^3\Pi_g$ state may result in causing the N_2 molecule to dissociate into N and N^+ atoms, involving about 22 e.v. of energy which is slightly less than the energy of the two colliding partners (argon ion 15.7 e.v. and N_2 ($B^3\Pi_g$), 7.2 e.v. = 22.9 e.v.). For this hypothesis to be tenable, we must have some evidence of the production of atomic nitrogen in neutral and ionized states. Mitra's theory of active nitrogen, as reformulated by him recently (Mitra, 1953), can be said to substantiate this reaction. According to it, the active substance in a glowing gas (Lewis-Rayleigh afterglow effect) is a mixture of nitrogen atoms in ground state 4S and in the metastable states 2D and 2P (the latter only in small proportion), produced by dissociative recombination of N_2^+ and an electron, under strong electric discharge, or under other suitable conditions. This mode of production of N atoms provided a link between metastable atomic theory and the ionic theory as was suggested by Mitra (1953) previously. N_2^+ and electron (e) are, as it were, the parent bodies of the active substance, though they themselves are not so directly.

There is support for the above reaction from nitrogen discharge spectra under the influence of argon, but is verifiable only for condition I of the mixture, i.e. with

a trace of argon in nitrogen. The spectra show selective effect in bands of v' -progression originating at $v' = 10, 11$ and 12 in $1(P)$ system, characteristic of the afterglow spectra of active nitrogen observed by Fowler and Strutt (1911). The selective effect goes down with increasing argon content which shows that only a trace of argon is favourable for it. This also receives support from the earlier findings of Tawde and Patankar (1944) on nitrogen spectra in air. The selective effect then is also confined to the bands indicated above and it has been attributed to the formation of active nitrogen under the influence of minute argon content of air.

Thus, on this basis of the atomic theory of active nitrogen, argon in trace appears to be conducive to production of active species, and more of it to annihilate or to destroy the afterglow characteristics. The comparison of the observed spectral behaviour of discharge mixture I with II and III brings this out well in the present experiments.

Having discussed so far the relative suppression of one system as a whole with respect to the other in the light of the three mechanisms, we now proceed to examine the individual features in each of the two systems separately.

C. Individual features

(a) The $2(P)$ system

The results of the present experiments on this system indicate a shift of the intensity from higher vibrational states ($v' = 3, 4$) to lower states ($v' = 0, 1$) as the argon content is increased. This may follow from the mechanism suggested by Janin (1946) based on the redistribution of energy between vibrational and rotational states. According to this a part of the vibrational energy is transferred to rotational states through collisions of unexcited atoms of the rare gas with the excited nitrogen molecule in the $C^3\Pi_u$ state. Janin concludes the operation of such a process from his observations on A- N_2 mixtures, wherein he finds evidence for molecules being drained from $v' = 3, K = 2, 3$ to reinforce the level $v' = 0, K = 36$. Thus, the observed reinforcement of population in the lower ($v' = 0$ and 1) levels along with the depletion in $v' = 2, 3$ and 4 in these experiments may be attributed to the preferential excitation of $C^3\Pi_u$ state due to perturbation by argon. This change in population in the v' levels is expected to cause a decrease of the effective vibrational temperature, derived on the basis of Maxwell-Boltzman distribution law. From Table III it appears that the temperature decreases as the argon content is increased

TABLE III
Vibrational temperatures

Mixture → Argon/Nitrogen	I	II	III
Temperature in °K ..	4800	3900	4000

up to 50% and is not affected later on. These values are much below the effective vibrational temperature of $6200^\circ K$ obtained in pure nitrogen by Korgaokar. This observation lends further support to the view stated above in terms of Janin's hypothesis. However, the evidence given above provides only a partial verification of Janin's mechanism, as we have no knowledge whether the shift of vibrational energy from higher to lower quanta has caused a shift of corresponding rotational energy from lower to higher states. For a complete confirmation of this view-point,

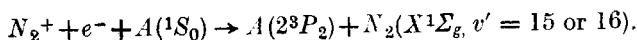
it would be desirable to obtain data simultaneously on intensities of rotational structure of the system with and without argon under the conditions of the experiment.

(b) *The 1(P) system*

We have to look here for the causes of selective enhancement of bands at $v' \sim 5$ and $v' \sim 11$, and also the relatively greater enhancement for the latter together with a persistent one at $v' \sim 8$. There is also the shift of prominence at $v' \sim 11$ with increasing argon content towards lower quantum numbers. Except for the shift at $v' \sim 11$, the features indicated above are more or less in accordance with the results of Tawde and Patankar (1944) in the discharge in air. They have attributed these phenomena to the formation of active nitrogen under the influence of small argon content. The fact that here too they come up with small admixture of argon with nitrogen is a point in favour of their suggestion.

As regards the shift of enhancement as $v' \sim 11$ to lower quantum numbers, it is not unexpected as Rayleigh (1923) also observed it in his experiments on the after-glow spectrum of nitrogen in different rare gas-nitrogen mixtures. A similar behaviour was observed by Johnson (1924). The shift was predicted by Okubo and Hamada (1932) and was later confirmed by them experimentally (1934). Their view is that where a suitable quantity of foreign gas (here argon) is mixed with nitrogen or where nitrogen is at a relatively high pressure, the molecules in $v' = 7, 8$ level of the $A^3\Sigma_u^+$ metastable state, because of their long life-time, will suffer many collisions with other neutral molecules or atoms of the foreign gas, before they make transition to $B^3\Pi_g$ state. This will effectively reduce their energy and cause them to go to the levels lower than $v' \sim 11$ and $v' \sim 6$ in $B^3\Pi_g$ state. As a result one should expect the intensity to shift from $v' \sim 11$ to $v' \sim 10, 9, 8$ etc. and from $v' \sim 6, 5$ to $v' \sim 5, 4, 3$ etc. as seen from the shift of the maximum at $v' \sim 11$ in Fig. 2 with increasing argon content. The present experimental condition, viz. the increasing argon content, in the mixture provides suitable quantity of argon for the shift to occur and thus favours Okudo and Hamada's mechanism. Similar shift for the small maximum at $v' \sim 6, 5$ to lower values of v' is not verifiable in these experiments as the bands below $v' \sim 5$ were not accessible. There is, however, a trend for such a shift from the nature of the curves. This latter point needs to be confirmed by estimating the bands below $v' \sim 5$.

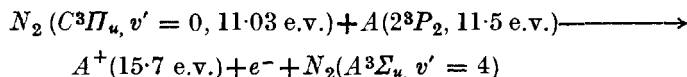
However, Okudo and Hamada's theory does not predict the most marked prominence at $v' \sim 8$. This is explainable from Janin's considerations, involving the operation of Franck-Condon principle. Janin considers a triple collision to take place between ionized nitrogen molecule, an electron and an unexcited argon atom producing a metastable atom and a normal nitrogen molecule in the ground state ($X^1\Sigma_g, v' = 15$ or 16). The reaction can be represented as



The energy of ionization (15.58 e.v.) of nitrogen molecule is liberated and utilized partly to raise argon atom to a metastable state (11.55 e.v.) and the rest of it is utilized to cause nitrogen molecule to come to the vibrational level $v' = 15$ or 16 in $X^1\Sigma_g$ state, corresponding to the energy of 3.96 or 4.19 e.v. While in this state ($X^1\Sigma_g, v' = 15$ or 16), a collision with energetic electron will carry the molecule to the excited state of $B^3\Pi_g$. If then the transition occurs according to Franck-Condon principle as shown by Okubo and Hamada (1932), the molecule will have greater probability for vibrational level $v' \sim 8$ in this $B^3\Pi_g$ state characterized by the same inter-nuclear distance as that of $v' \sim 15$ or 16 in the $X^1\Sigma_g$ state. Thus, in emission of 1(P) system, the preferential high population of molecules in levels $v' \sim 8$ will contribute a relatively greater intensity for bands arising from that level.

An alternative mechanism also leads to the identical result. The basic assumption for the mechanism is the observed phenomena of selective excitation of bands

of $v' = 0$ progression in $2(P)$ system. This means $C^3\Pi_u (v' = 0)$ molecules are relatively more numerous. These molecules suffering collisions of the second kind with metastable argon atoms are likely to descend to $A^3\Sigma_u^+$ state ($v' = 4$) according to the reaction given by Janin (1946),



and it represents a very close energy balance. The $A^3\Pi_u$ state, being a metastable state, is likely to raise the molecule by collision with electrons (slow ones) to higher electronic states of $B^3\Pi_g$ in which case, as a result of Franck-Condon principle, there is greater probability for them to go to level $v' \sim 8$. Investigations of Janin show that the above selective action is favoured more and more with (i) increasing total pressure of argon-nitrogen mixtures and (ii) also with increasing content of argon in low and high pressure of mixtures. The present experiments are confined to the latter case, i.e. condition (ii) above, and give results that seem to fit in well with Janin's predictions.

The work was carried out at the Spectroscopy Laboratory of the Institute of Science, Bombay, during the years 1950-52. One of the authors (D. D. Desai) records his appreciation of the helpful co-operation rendered by his colleague workers in the laboratory, Dr. K. S. Korgaokar and Dr. G. K. Mehta, during the progress of the investigations.

SUMMARY

The spectrum of nitrogen in the discharge through air is characteristically different from that in pure nitrogen. The rôle of argon content of air in causing this characteristic difference has been studied systematically by observing the spectra of graded mixtures of pure nitrogen with argon. These are compared with the spectra of pure nitrogen and of atmospheric air. The experimental method consisted in measuring quantitatively the intensity distributions in $1(P)$ and $2(P)$ systems relative to each other and also among the vibrational bands in each of them individually.

Critical analysis of the effect of oxygen admixture, as studied earlier by Tawde and Korgaokar, as against the effect of admixture of argon has been made in the light of the results and conclusions arrived at from this investigation. It appears that the two gases play a similar rôle but oxygen seems to exert a more predominant influence.

In other directions, the way in which argon would cause the suppression of one system with respect to the other has been examined in terms of the possible energy exchanges between argon and nitrogen in the discharge mixtures.

Further, the intensity distributions among vibrational levels of the two systems individually have given some peculiar features of selective enhancement, which have been critically discussed.

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