

INTENSITY VARIATIONS IN THE FIRST POSITIVE AND SECOND POSITIVE BANDS OF NITROGEN EXCITED BY HIGH FREQUENCY OSCILLATIONS

BY R. K. ASUNDI AND JAGDEO SINGH*

(Department of Physics, Benares Hindu University)

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INTRODUCTION

HIGH frequency oscillations have been used by many workers for the excitation of the spectra of atoms and molecules. Hulburt¹, before the theory of molecular spectra had developed, investigated the spectra of hydrogen, oxygen and air in the spectral region 3500–5000 Å, by exciting the gases by discharges of various frequencies, viz., 60, 3×10^5 , 10^6 and 0.43×10^7 cycles per second. The spectra were reported to be unmodified by the changes in frequency. In the case of hydrogen, the Balmer lines were faint and the spectrum consisted mainly of about 300 lines of the secondary spectrum and a faint continuum. Later, however, Brasefield² obtained some striking results in his investigations on the spectrum of hydrogen excited by h.f. discharge. These were followed by a study of the excitation functions of the lines of molecular hydrogen.³ For this purpose, the optical densities of the lines were measured under excitation by electron impact and plotted against the exciting voltages. In this way, Brasefield investigated a large number of lines of the $np^3\Pi \rightarrow 2s^3\Sigma$ systems and compared them with typical lines of the singlet systems. In each case a sharp distinction between the excitation function of the lines of singlet and triplet systems was found, the singlets being relatively more enhanced at electron energies much higher than the excitation potential while the triplets are strongest at energies very close to it. In this respect, the difference in the excitation functions is quite similar to that between the corresponding excitation functions for the mercury atom. Further work on hydrogen bands excited by h.f. discharge enabled Brasefield^{4,5} to correlate the frequency of discharge and its equivalent electron velocity and offer a simplified mechanism of h.f. discharge. He finds that his experimental results can be fully explained under the following assumptions:—

1. The electron velocities increase as the voltage between the electrodes is increased, the gas pressure and the frequency of oscillations being kept constant.

* At present Lecturer in Physics, Udai Pratap College, Benares.

2. For a given voltage between the electrodes, the electron velocity is greater the smaller the frequency of oscillations.

3. The electron velocity decreases as the pressure of the gas is increased.

It is to be remembered, however, that for the above assumptions to have theoretical justification, the main process of excitation should involve the emitters in the normal state only.

Similar results are obtained in the excitation by h.f. oscillations of the atomic spectrum of mercury.^{6,7} In this case, however, a more recent investigation⁸ indicates that the mechanism of excitation becomes complicated at higher pressures at which, therefore, the simple relation between the relative intensities of the singlet and triplet lines breaks down. Many other similar changes in intensity distribution in spectra excited by h.f. discharge have been observed in this laboratory and briefly reported.^{9,10,11} Working with a discharge tube containing a trace of air, it was observed that the colour of the discharge underwent a remarkable change when the frequency of the exciting oscillations was changed. The glow which was pinkish red at lower frequencies gave place to an orange yellow colour when the frequency of oscillations was increased. The change over from one colour to the other took place rather sharply at a frequency of exciting oscillations of 735*, below and above which it was red and yellow respectively. These variations have been studied spectroscopically in the visible region where the spectrum of the glow consists of the first positive and second positive band systems of nitrogen. A few suitable bands belonging to the first positive system and some to the second positive system were selected for a study of relative intensity changes depending upon the frequency of exciting oscillations. The results obtained are presented in this paper.

EXPERIMENTAL

In these experiments a glass discharge tube of the π type was used. It was about 20 cm. long and 1 cm. in diameter. Two bulbs containing P_2O_5 and crushed KOH were also sealed on to it. The discharge tube had internal electrodes of aluminium in its two vertical limbs. These however, were not used and the excitation was brought about by two external electrodes of tin foil wrapped round the horizontal part of the discharge tube and separated from each other by a distance of about 5 cm. The tube was provided with a quartz window which was attached to one of its ends by sealing wax. This, however, was not very necessary because there was no suitable spectro-

* Frequencies are expressed in kilocycles per second.

graph available which would photograph the visible and the ultra-violet regions of the spectrum with sufficient dispersion on one plate.

The source of h.f. oscillations was a modified Hartley circuit containing a Phillips triode valve T.C. 04|10 D 17 taking a filament current of 1 amp. and an anode potential of 340 volts. The frequencies of oscillations obtained varied between 600 and 1500 depending upon the variable condenser readings which were calibrated in terms of frequencies by means of an absorption frequency meter. The discharge tube was sealed onto an evacuating apparatus consisting of a high vacpump, a mercury manometer and a number of bulbs containing P_2O_5 , KOH and $CaCl_2$. The tube was thoroughly evacuated and freed from impurities of carbon after which a small amount of air was introduced by an artificial leak. The pressure in the tube was again adjusted by running the pump and when the discharge could be easily passed using the external electrodes, the tube was sealed off from the evacuating apparatus. The resolving instrument used was a Hilger constant deviation glass spectrograph. The discharge tube was set in proper collimation with the spectrograph and the light from the discharge tube was focussed by a lens onto the slit of the spectrograph. During each series of exposures, except for the lowering of the plate holder, no other part of the arrangement was touched, so that the collimation and the focussing lens were strictly undisturbed throughout the series of exposures. Ilford H.P. 2 (hypersensitive panchromatic) plates were used. An exposure time of 5 minutes was found suitable. Since the nitrogen bands could be easily identified by reference to a previously measured plate taken on the same setting of the spectrograph, no standard lines were found necessary and hence were not taken on the spectra.

Fig. 1 is typical of the plates obtained. It contains 14 spectra excited by various frequencies of oscillations which are marked on the plate. The last two exposures 13 and 14 differ only in the matter of time of exposure which for 14 is one minute. For all other exposures the exposure time is 5 m. The groups of first positive and second positive bands are indicated in Fig. 1. From this spectrogram exposures 5, 6, 7 and 12 were selected for a microphotometric study. They were run under a Zeiss recording microphotometer* and the four curves obtained are given in Figs. 2, 3, 4 and 5 which represent the exposure numbers 5, 6, 7 and 12 respectively. Of the first positive bands three at 5371, 5406, 5441 Å and of the second positive seven bands at 4355, 4417, 4490, 4649, 4724, 4815 and 4916 Å were chosen for study and these are indicated in Figs. 1 and 4.

* Courtesy of Prof. S. P. Prasad, Head of Physics Department, Science College, Patna.

From the microphotograms, the following values are calculated:—
 I_0 , the distance between the limits of clear background and complete darkness and I , the distance between the maximum of the peak and the limit of complete darkness (see Fig. 3). In cases where the fine structure of the preceding band is superposed on the band head, the blackening due to the superposed fine structure is taken into account in arriving at the true I value for the band head. In this way values of the optical density S are evaluated as $\log_{10} I_0/I$, for the three first positive and the seven second positive nitrogen bands in the four selected exposures and are given in Table I.

TABLE I
Optical Densities

Exp. No.	2nd positive bands at A							1st positive bands at A			Excitation Frequency
	4355	4417	4490	4649	4724	4815	4917	5371	5406	5441	
5	.33	.13	.24	.14	.13	.15	.11	.15	.17	.17	680
6	.28	.10	.29	.11	.11	.11	.09	.15	.15	.17	695
7	.28	.21	.29	.18	.13	.13	.12	.32	.32	.32	715
12	.13	.10	.18	.14	.07	.07	.08	.37	.36	.36	790

DISCUSSION

From the four curves it will be seen that for all the selected bands the density of blackening is neither very low nor has it reached the saturation limit. We are thus working on the straight line portion of the characteristic curves connecting the density and intensity for the photographic plate. In any case, if the wavelength of the radiation affecting the plate is also kept constant, that is to say, if we compare the density of the same band at various frequencies of excitation, since other factors (time of exposure, age and nature of plate, its subsequent treatment in developing, etc.) which govern the density are kept strictly the same, a change in density always means a corresponding change in intensity even though the converse may not hold (e.g., very low intensity or saturation limit).

Table I shows that the intensity of every single second positive band in general shows an increase at the three frequencies 715, 695 and 680 over its value at frequency 790. On the other hand, the reverse is true for every single first positive band. The average intensity of the first positive bands at frequency 790 is represented by $S = .36$. This reduces to .32 at frequency 715 and to .16 at frequencies 695 and 680. Thus the optical density of the bands is reduced to about half its value. On

the other hand, for the second positive bands the average value of S for frequency 790 is $\cdot 11$ and this increases to $\cdot 19$ at frequencies 715 and 680. There is a slight drop in density at frequency 695 but even then the value is greater than that at 790. We can thus conclude that the three bands of the first positive system decrease in intensity as the frequency of exciting oscillations is reduced from 790 to 680 while the seven bands of the second positive system exhibit exactly the opposite behaviour. The process of excitation being essentially one of electronic impact one would expect that similar effects will be exhibited by the rest of the bands of the two systems.

In this connection the experiments of Brasefield on the controlled excitation by electronic impact of molecular hydrogen and h.f. discharge in hydrogen are particularly informative. It will be quite interesting to see if his assumptions can help us to understand the changes in intensity observed. In the energy level diagram of nitrogen bands, the second positive system involves the transition $C^3\Pi_u \rightarrow B^3\Pi_g$. Its excitation potential which is represented by the position of the $C^3\Pi_u$ level is 10.98 e.v. Similarly the first positive bands arise out of the transition $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ and have an excitation potential of 7.32 e.v. which represents the position of the $B^3\Pi_g$ level.¹² If we make the plausible assumption that in the present experiments the changes in frequency do not bring about changes in the voltage across the electrodes to an appreciable extent then according to the assumption 2 of Brasefield, the second positive bands should be stronger at lower than at higher frequencies because then the equivalent e.v. will be the greater. Similarly the first positive bands should be stronger at higher frequencies than at lower ones. This is exactly what is observed.

But the fact that there is a frequency below which the glow is pinkish red and above which it is orange yellow still remains to be explained. This change in colour is presumably connected with the relative intensities of the two band systems. Such a behaviour strongly suggests that here we are concerned with a well-known phenomenon observed in experiments on the controlled excitation of spectra, we mean the dependence of excitation function of an energy level of atoms or molecules on the velocity of the colliding electron, reference to which we have already made. For such experiments it is of course necessary that all the emitters must be excited from the normal state, so that indirect excitation be negligible. The phenomenon is particularly striking for even electron-emitters which give rise to singlet and triplet electronic states. In the present case, however, we are concerned not with a singlet and a triplet state but with two systems each of which is a triplet. The excitation functions of some of the bands of the second positive system

have been investigated by Langstroth.¹³ All the three bands investigated show that their excitation function is that typical of the triplet states. Though the intensity of the maxima for the three bands is not the same it may be noted that the position of the maximum is nearly the same namely about 17 e.v. The excitation function of the first positive bands has been investigated by Bernard and Fouilloure.¹⁴ In this case also the nature of the curve is the same, but the maximum intensity occurs for a velocity of 13.5 e.v. of the colliding electrons. Since the two curves, the one typical of the second positive bands and the other typical of the first positive bands, will intersect each other at a point for which the velocity of the electrons will be about 15 e.v., this will be the transition electron velocity below which the first positive bands will be stronger than the second positive bands and above which the reverse will be true. The colour changes observed in the present experiments therefore indicate that this transition velocity for electrons is reached when the frequency of exciting oscillations is about 735. The fact that such a correlation is at all possible further indicates that in the present experiments the excitation involves molecules from their normal state.

SUMMARY

A discharge tube containing air at low pressure is excited by h.f. frequency oscillations from a modified Hartley circuit. It is observed that there is a critical frequency of exciting oscillations, namely 735 k.c./sec. below which the colour of the discharge is pinkish red and above which the colour is orange yellow. The spectrum of the discharge in the visible region consists of the first positive and second positive bands of nitrogen. A study of some of these bands as regards their intensity variation depending upon the frequency of exciting oscillations is made. It is found that the first positive bands at 5371, 5406 and 5441 Å decrease in intensity as the frequency of exciting oscillations is reduced from 790 to 680 k.c./sec. The second positive bands at 4355, 4417, 4490, 4649, 4724, 4815 and 4917 Å on the other hand, increase in intensity under the same conditions. The results are in harmony with the theoretical conceptions, regarding such phenomena and allow us to conclude that in the present experiments an energy of 15 e.v. is available for excitation when oscillations of frequency 735 k.c./sec. are used.

REFERENCES

1. E. O. Hulburt .. *Phys. Rev.*, 1922, **20**, 127.
2. C. J. Bresefield .. *Ibid.*, 1929, **33**, 925.
3. ————— .. *Ibid.*, 1929, **34**, 431.
4. ————— .. *Ibid.*, 1930, **35**, 92 and 122.
5. ————— .. *Ibid.*, 1930, **35**, 1073.
6. S. Tolansky .. *Proc. Phys. Soc. London*, 1930, **42**, 556 ; 1931, **43**, 545.
7. D. D. Pant .. *M.Sc. Thesis*, Benares Hindu University, 1942.
8. N. L. Singh .. *D.Sc. Thesis*, Benares Hindu University, 1944.
9. R. K. Asundi, N. L. Singh and J. Singh .. *Proc. Ind. Sci. Cong.*, 1942, **3**, 35.
10. ———, ——— and D. D. Pant .. *Ibid.*, 1942, **3**, 35.
11. ——— and N. L. Singh .. *Nature*, 1942, **150**, 123.
12. H. Spöner .. *Molekuel Spektren*, 1935.
13. G. O. Langstroth .. *Proc. Roy. Soc. London*, 1935, **150 A**, 71.
14. R. Barnard and R. Fouilloure .. *Comp. Rend.*, 1939, **209**, 647.