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CANAL RAY* AND ELECTRON EXCITATION OF THE BAND SPECTRUM OF NITROGEN

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Abstract

The idea is suggested that the excitation of band spectra by canal ray* impact on the one hand, and by electron impact on the other, may give quite different intensity distributions. The results of three groups of experiments on the band spectra of nitrogen are presented.

In the first, the relative intensities of the lines in the 3914 negative band were studied. There seemed to be a small weakening of the lower rotational lines in the canal-ray excitation compared to electron excitation.

In the second, the relative intensities of the second positive group and of the negative group were observed in a canal-ray beam. The intensities of the transitions from high initial vibrational states were abnormally great. The variations in comparison plates taken by us and by others with various sources were so great that no satisfactory standard of comparison could be chosen as representing excitation purely by electron impact.

This suggested the third phase of the work, a study of the excitation by a beam of 700 volt electrons. This gave a most unusual distribution of intensity with nearly all the energy in the $0\rightarrow 0$ and $0\rightarrow 1$ bands of the negative group and a similar concentration in the second positive group.

Introduction

The theory of the relative intensities of the lines in a band and the bands in a system has been rather fully developed.[1] There is no need to reproduce it here in detail but we may recall one guiding principle, that due to Franck and Condon. According to this notion an electron striking a molecule can alter only the electronic configuration without having any direct effect on the vibration or rotation of the nuclei.

Initially, the authors were interested in a case where this principle certainly should not apply, namely, excitation by canal ray* impact. In such a case the impacting ion might be expected to transfer both angular and vibrational momentum to the molecule being excited and consequently to produce a different distribution of intensity from that observed with pure

* The term "canal ray" is used throughout this paper to include both the positive ions and high speed neutralized molecules that emerge behind the perforated cathode of a discharge. It seems better to restrict the term positive ray to ionized molecules.

[1] See Mulliken, Revs. of Modern Phys. **2**, 79 (1930) and references cited there.

electron excitation. It might be expected, therefore, that, in a given band, the higher rotational members of all branches would be relatively stronger than when excitation was by electron impact and, similarly, that, in a given system, the bands corresponding to higher initial vibrational states should be relatively stronger than when excitation was by electron impact. A search for such effects was undertaken.

The bands of nitrogen were chosen for examination because more is known about them than about the bands of any other gas of equal experimental convenience. There have, of course, been many studies of the excitation of spectra by canal rays and in particular the bands of nitrogen have been studied. But the point of view was so different from our present one that no very satisfactory evidence on intensity distribution is available. Detailed discussion of previous work will be more intelligible later on in connection with our own results.

But the earlier work did suggest what we found to be the case, namely that the intensities are not strikingly different from those usually published and ascribed to pure electron excitation. It became necessary therefore to examine these "electron excitation experiments," considering carefully the evidence on relative intensities and their variation with varying conditions of source. For example, Birge gives a set of intensity estimates on the second positive nitrogen bands. He says[2] this illustrates "the most common type of intensity distribution." Yet in a footnote he says "the relative intensity of the bands in this system is very sensitive to changes in self-induction, capacity and other experimental conditions. Hence it is very difficult to give a normal intensity distribution." Yet he does treat this particular distribution as the "normal" intensity distribution and proceeds on this basis. For the sake of convenience we will also speak of this particular distribution as "normal." Birge has apparently studied deviations from this "normal" intensity considerably but his only reference[3] is to a fifteen line abstract and we can find no complete account of his investigations. Fortunately, other authors are not so hesitant about publishing their results and theories, imperfect though they be. Herzberg[4,5] in a series of papers has given an excellent account of the variations of intensity distribution in the nitrogen bands under different conditions of excitation and the factors to be considered in accounting for the observations theoretically. However, in all his experiments he used an electrodeless discharge so that it is difficult to say exactly what the conditions of excitation were. Apparently the only experiments where the excitation was certainly by single electron impact were those whose object was to determine the critical potentials of various band systems.[6] Consequently the electron speeds used were low.

Both in Birge's "normal" case and in those reported by Herzberg the intensity distribution is of the type predicted by theory. That is, if the

[2] Birge, Molecular Spectra in Gases, Bull. Nat. Res. Council, **57,** 135 (1926).
[3] Birge, Phys. Rev. **25,** 240, 1925.
[4] Herzberg, Ann. d. Physik, **86,** 189 (1928).
[5] Herzberg, Zeits. f. Physik **49,** 761 (1928).
[6] See references 16, 17, 18.

system is arranged in a square array with the bands of the same initial vibration state all in the same row and the bands of the same final state all in the same column (See Tables I to IV), the most intense bands lie on a parabola whose vertex is toward the $0\rightarrow 0$ band and whose shape depends on the nuclear binding in the initial and final electronic states. The distributions differ only in rate of falling off of intensity with increasing distance from the vertex of the parabola. This is just the kind of effect we may expect from canal-ray excitation. It is clear, therefore, that control experiments with electrons must be made before any conclusions can be drawn from those on canal rays. Furthermore experiments with electrons are of importance for direct comparison with theory. This, then, became the secondary object of our work.

Though our experiments have suffered many interruptions and are by no means complete, we believe them of sufficient importance to report. We feel this the more strongly because we are convinced that progress in this field has been retarded by the substitution of abstracts, footnotes and "private communication" for frank and full publication.

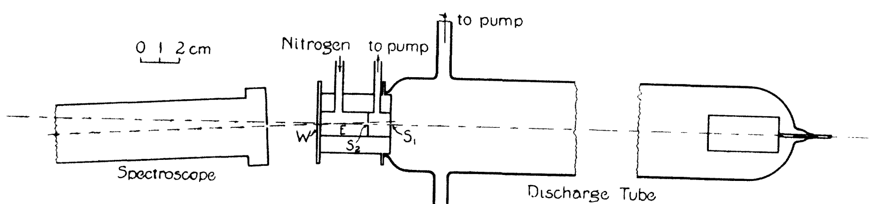


Fig. 1. Schematic diagram of canal ray apparatus.

Canal Ray Excitation

First experiments

At the Chicago meeting of the Physical Society last November we reported[7] the results of shooting canal rays from a mixture of nitrogen and mercury into an atmosphere of nitrogen. The apparatus, Fig. 1 and Fig. 2 (a), consisted of a cylindrical discharge tube into the end of which a brass water-cooled cathode was sealed with wax. The slits S_1 and S_2 behind each other in the cathode defined a canal-ray beam which shot into the space E in front of the quartz window, W. Nitrogen generated from ammonia and bromine and stored over P_2O_5 flowed continually into the chamber E and out through the slits and the evacuation tube between the slits. The discharge contained mercury at approximately room temperature and a certain amount of nitrogen that diffused through the slits. The discharge was run with a 15,000 volt transformer and with a kenotron in circuit for rectification. Pressure and voltage conditions were varied until a fairly intense canal ray beam appeared; the pressure of nitrogen finally used was of the order of 0.04 mm in the space E. In these early experiments there was sometimes a certain amount of secondary discharge within the cathode. In taking photographs the spectroscope was set at a slight angle to the beam as shown in Fig. 1. This angle had to be very small to get good intensity yet large enough so

[7] Smyth and Arnott, Phys. Rev. **35**, 126, 1930.

that no light came through the slits S_1 and S_2 into the spectroscope. The difficulty of this adjustment and the occasional secondary discharge made these preliminary results less reliable than later ones since the spectrum photographed may not have been entirely due to canal-ray excitation.

Photographs were made first with a constant deviation small glass Hilger instrument and then with a small one-meter concave grating. The plates made with the prism spectroscope covered the region from about 4900 to 3900A.U. with sufficient intensity and resolving power for the study of the bands of the second positive and the negative groups which lie in this region. The lines in the bands were not resolved but in the stronger bands the positive (R) and negative (P) branches were separated. In the grating spectra, in the second order, all the lines of the R and some of those in the P branch were resolved. In both cases very long exposures of the order of 30 to 80 hours were required to bring out any considerable intensity. Ilford Panchromatic plates were used with the prism spectrograph and Eastman Panchromatic films with the grating.

The first photographs taken with the prism instrument showed both negatve and second positive bands present with the 4278 and 3914 negative bands predominating. The relative intensity of the bands seemed approximately "normal" but there appeared to be an abnormal separation of the positive and negative branches. These facts suggested that the vibrational intensity might be the same as in electron excitation but that the lower rotational states were abnormally weak.

Attention was therefore concentrated on getting grating photographs and then making exact measurements on the relative intensities of the lines in the bands 3914 and 4278. Photographs were also made with an electrodeless discharge and compared with the canal-ray plate both visually and with a densitometer; the results of Fassbender[8] and of Ornstein and van Wijk[9] were also compared. The experimental result seems to be a small but definite weakening of the lower rotational transitions in the canal-ray plate. This was the stage of the work reported at Chicago. Since that time we have been more meticulous about our conditions of excitation and avoidance of light from the main tube, as we will describe presently. Unfortunately this made it impossible to get photographs with the grating even with exposures of as much as 72 hours and therefore no further quantitative evidence is available on the relative intensities of the lines in a single band.

Searching the older work, we find the published reproductions of Fulcher[10,12] and of Rau[11,12] have sufficient resolution to show the fine structure of the 4278 band. Fulcher's is the clearer picture and looks very much like ours, but the problem needs more accurate experimental work before any certain conclusion can be drawn.

[8] Fassbender, Zeits. f. Physik **30**, 73 (1924).

[9] Ornstein and van Wijk, Zeits. f. Physik **49**, 315 (1928).

[10] G. S. Fulcher, Astrophys. J. **35**, 101 (1912).

[11] H. Rau, Ann. d. Physik **73**, 266 (1924).

[12] Wien-Harms, Handbuch der Exp. Phys. XIV, p. 687, and p. 690.

Later experiments

A number of changes were now made in the apparatus. A General Electric high potential set made up of transformer, kenotrons, condensers and resistances and supposed to give a constant potential was substituted for the transformer. This meant that the canal rays would now be of nearly uniform energy instead of having energies ranging from zero to the maximum voltage of the secondary of the transformer. The other principal change was in the mounting of the discharge tube which was tilted until at an angle of about thirty degrees from horizontal. This made it possible to head the spectroscope directly at the canal ray beam without its receiving any light through the slits S_1 and S_2 from the discharge tube. To prevent reflected light from getting into the spectroscope the inside of the cathode was painted black. There were some further minor modifications in the cathode which need not be described. The new set-up is shown in Fig. 2 (b).

This new outfit ran very much more smoothly than the old as long as no more than a few milliamperes were drawn from the high potential set.

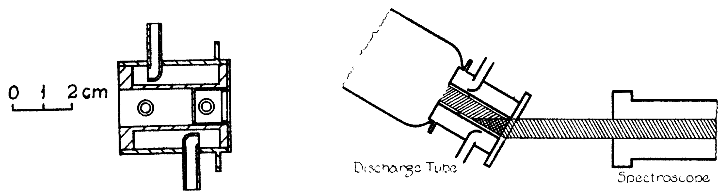


Fig. 2. (a) Details of water-cooled cathode. (b) Second arrangement of tube and spectroscope.

At such currents and with a voltage of 5000 it was possible to get a clearly defined beam which seemed just about as bright as the one we had been using. Nevertheless we were unable to get more then a few mercury lines on any spectra taken with the grating.

Returning to the small glass instrument several satisfactory spectra were obtained. They were very similar to those obtained before showing the same wide separation of positive and negative branches in the 4278 band, but showing a slightly higher intensity in the higher vibrational bands. It was obviously desirable to cover a greater range of the spectrum than was possible with this instrument so a Type E315 Quartz Hilger spectroscope was tried. The first photograph was a little overexposed but the second was very satisfactory. It was an exposure of fifty hours during which the tube ran perfectly steadily at a voltage of 5500 to 6000 with a pressure of 0.04 mm of nitrogen in the cathode and a sharply defined bluish canal-ray beam reaching without scattering to the quartz window.

This plate covered the spectrum range from $\lambda = 5790$ to $\lambda = 2100$, but above 4708 there was very little on it and the dispersion was small. Measurements and densitometer records were made of this entire plate. Besides the negative and second positive groups of bands it showed many mercury lines and many nitrogen spark lines. As impurities there were the resonance lines of Al and Cu and a few other Al lines. These might all be expected since the main part of the cathode was brass but with an aluminum disk over the front of it to reduce sputtering. Unexpected and unaccounted for were a

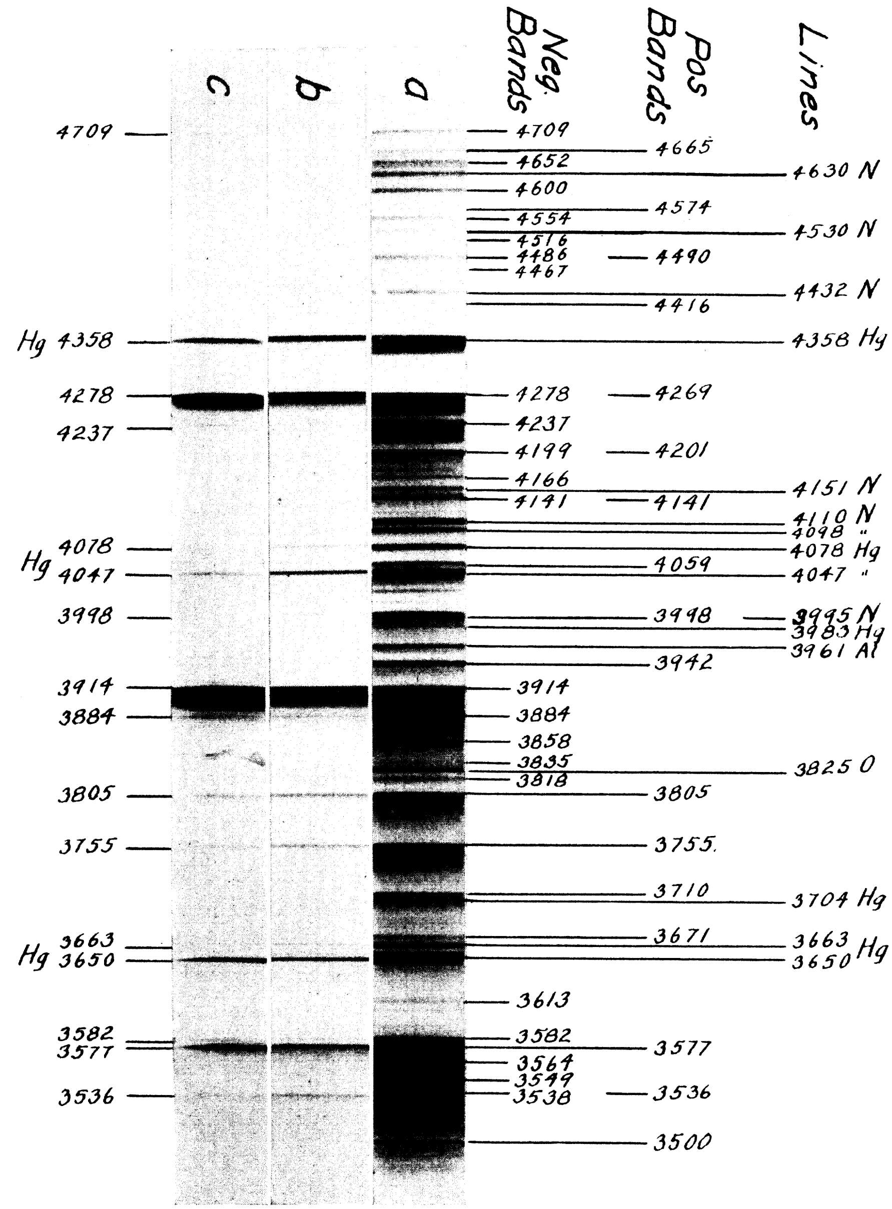


Fig. 3. Spectrograms taken with E315 quartz Hilger spectroscope. (a) Canal ray beam (5500 volts). (b) Discharge used as source of canal rays. (c) Electron beam (700 volts).

number of oxygen lines chiefly below 3000A.U. Finally there were a few faint bands in the neighborhood of 2500 which may have been the fourth positive group of nitrogen.

In Fig. 3 (a) a section of this plate is reproduced. The print is a little over exposed to show some of the fainter bands, in particular the one at 3613. From a study of this plate and the densitometer records of it, it was possible to estimate the intensity of most of the bands of both the second positive and the negative groups. In some cases the resolution was so poor that an estimate was dubious or impossible. This is indicated in the tables below which give the results of visual and densitometer estimates of the relative blackening of the photographic plate.

TABLE I. *Densities of second positive group. Canal-ray excitation plates.*

v' \ v''	0	1	2	3	4	5	6	7	8	9
0	3371 18	3577 11	3805 12	4059 8	4344 *	4666 4				
1	3159 15	3339 3	3536 6*	3755 12	3998 10*	4269 *	4574 00			
2	2977 12	3136 14	3309 6*	3500 4	3710 10	3942 9	4201 *	4490 4*		
3	2820 2*	2962 12	3116 10	3284 6	3469 1	3671 7	3894 *	4141 *	4416 1	
4		2814 4	2953 12	3104 7	3268 6	3446 0	3642 4	3857 *	4094 *	4356 *

* Wholly or partially obscured by another line or band.

Considering first the second positive group one could hardly ask for a more perfect parabolic intensity distribution. In general it agrees very well with the intensities given by Birge. One curious point is the extreme weakness of the 4574 band. This is confirmed by the other plates taken with this type of excitation in contrast to the comparison plates but we have no explanation for it. Looking for the effect we expected, an enhancement of the bands coming from the higher initial states of vibration, we find nothing very striking but a distinct tendency for the intensities in the 4th and 5th rows to be relatively stronger than in the figures published by Birge. They are also stronger than in our own comparison plates which will be discussed more fully below.

Turning to the negative bands, perhaps the most striking result is the presence of the "tail bands" first reported by Herzberg.[4] The strongest of these at 3613 is on the reproduction Fig. 3 (a) where it is hoped that the shading off to the red may be seen. It is very clear in the original. The band $4\rightarrow 0$ at 2885A.U. is also identifiable on our plate, observed for the first time so far as we know. The absence of the higher sequences is presumably due to the low sensitivity of the plate in the region where they lie but had they been present they would not have been resolved.

The general run of intensities is very similar indeed to that given by

Herzberg,[5] for the case of strong excitation. Possibly in our case there is a slightly greater intensity in the lower rows of the table corresponding to higher initial vibrational states but certainly this is not sufficiently marked to be a proof of the effect we are seeking.

TABLE II. *Densities of negative group. Canal-ray excitation plates.*

v' \ v''	0	1	2	3	4	5	6	7	8	9
0	3914 20	4278 15	4709 7							
1	3582 15	3884 12	4237 12	4652 7						
2	3308 7*	3564 12	3858 9	4199 10	4600 9					
3	3078 17	3299 8	3549 12	3835 6	4166 7	4554 6*				
4	(2885) (1)	3076 1*	3293 8	3538 10*	3818 8	4141 7*	4516 4			
5					3533 5*	(3807) *		4486 6*		
6									4467 5	
7										4459 *
8										
9										
10							2987 0	3174 0	3381 2	3613 7
11									3223 1	

* Partially or entirely obscured by other lines or bands. The band 14-10 at 3217 was also noted with intensity 0.

Nor does study of our own comparison plates strengthen our case. These were made with one spectroscope or the other with the following sources (a) a capillary Geissler tube discharge (b) the first transformer discharge used as a source of canal rays (c) an electrodeless discharge (d) the end of the positive column toward the cathode in the high voltage discharge finally used as canal-ray source. Of these comparisons the first three all gave about the same results, the second positive group, as in Birge's "normal" distribution, was somewhat weaker in the lower rows than in Table I, while the negative bands were also perhaps a little weaker in the high initial vibration bands. In the case of the (d) comparison, the intensities were entirely different. They are given in Table III and can be seen in Fig. 3 (b).

TABLE III. *Density distribution in high voltage discharge plates.*

Negative Bands

v' \ v''	0	1	2	3
0	15	12	8	
1	6	6	7	
2				1

Second Positive Bands

v' \ v''	0	1	2	3	4
0	15	14	10	2	
1	10	4	10	10	
2		4*		2	3

* Partially obscured by neighboring line.

Obviously this distribution has a relatively higher concentration in the lower vibrational bands than the canal-ray excitations given in Table I and II, or than in other comparison plates. It agrees quite well with Herzberg's "weak" excitation as far as the negative bands are concerned. He gives no intensities for the positive bands so comparison is not possible.

Originally we intended to study positive ion excitation and compare it with electron excitation. By this time we were pretty well convinced that we had no pure electron excitation spectra for comparison. Therefore we preceeded to get some.

ELECTRON EXCITATION

In making comparison plates with electron impact we wished to change conditions as little as possible and therefore used a tube, Fig. 4, very similar to that used for positive ions. However in order to reduce the length of exposure necessary, a filament source of electrons was used. As shown in

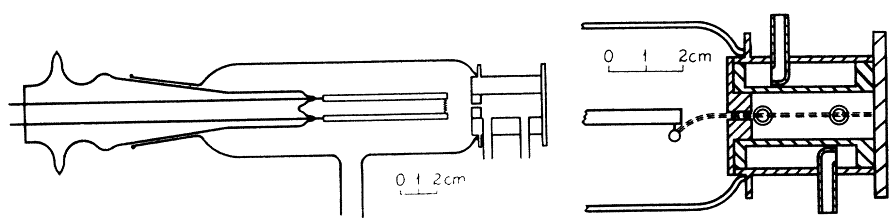


Fig. 4. (a) Schematic diagram of electron beam apparatus. (b) Details of filament, electron beam and water-cooled anode.

the figure the filament was mounted below the hole in the anode so that none of its light got into the excitation chamber. A small electromagnet was then used to bend some of the electrons into the path shown in Fig. 4. With a voltage of 700, a current to the anode of 70 milliamperes, a pressure of 0.06 mm in the excitation space and of 0.006 mm in the discharge tube a sharp luminous beam was obtained. Part of a spectrogram taken of this beam with the type E315 Quartz Hilger is given in Fig. 3(c). This was an exposure of two hours with an Eastman Speedway plate. The estimated densities of the negative and positive bands are given below in Table IV.

TABLE IV. *Density distribution with excitation by a Beam of 700 volt electrons.*

Negative Bands

v' \ v''	0	1	2	3
0	40	25	5	—
1	8	8	7	1
2				

Second Positive Bands

v' \ v''	0	1	2	3	4
0	12	14	8	1	
1	10	1	8	7	*
2	1	1	—	—	1

Clearly we have here an extreme concentration of intensity in the low initial vibration states.

General Discussion

Before making any attempt to interpret the results presented above they will be compared with previous work. First, as to the positive ray results, the photograph published by Stark and Hermann[13] shows the nitrogen canal-ray spectrum between 5500 and 3550A.U. Both the negative and positive bands are present and though the reproduction is not good enough to pick out many of the bands, there is at least no conspicuous departure from the intensity distributions of Tables I and II. A study of Fig. 4, in Fulcher's paper[10] gives a similar result. Again the reproduction given by Wilsar[14] shows the intensities of the first two sequences of the negative bands with intensities approximately like those of Table II. Doubtless a study of the original plates of these experimenters would yield really satisfactory intensity estimates. Dr. C. J. Brasefield has kindly turned over to us some early plates which he took in his work on canal rays in hydrogen[15] at a time when he was being troubled with nitrogen as an impurity. One of these plates shows eight members of the 4708 and four of the 4278 sequence of the negative bands. Their intensity is approximately as given in Table II and not at all like Table III or IV. Thus what evidence there is agrees with ours.

The question may be raised whether the excitation in all these experiments is actually by canal-ray impact. There are two other possibilities. The excitation of the N_2^+ ions might occur in the discharge before their passage through the cathode. This seems unlikely in view of the distance between the slit S_1 (Fig. 1) and the place where the spectrum is observed, the observations of Wien on the decay of the N_2^+ bands, and the pressure in the observation chamber. Or the excitation might be by secondary electrons. Considering the sharpness of the beam and the fact that it was observed nearly a centimeter beyond the last slit, this seems unlikely also.

Granted that the excitation is by canal-ray impact is the radiation observed from the canal ray or the molecule that is struck? If we are interested only in the conversion of kinetic energy of translation into energy of vibration or rotation this is not a fundamental question since it is immaterial which molecule is stationary. However, this question raises the point which was the

[13] Stark and Hermann, Phys. Zeits. **7**, 92 (1906).
[14] Wilsar, Ann. d. Physik **39**, 1251 (1912).
[15] Brasefield, Phys. Rev. **31**, 215 (1928).

chief concern of the previous papers we have been discussing, the Doppler effect. They all agree that there is no Doppler effect in the positive bands when they are observed in the canal-ray spectrum but there is not complete agreement on the negative bands. The consensus of opinion appears to be that it is either absent or very small.[11,12] In our experiments there was no sign of doubling in the bands, and as it was extremely unlikely that the shifted bands should be present without any trace of the unshifted we concluded that the Doppler effect was small or absent. But for some of the lines in the better resolved part of the spectrum there appeared to be both a shifted and an unshifted line of about the expected separation.

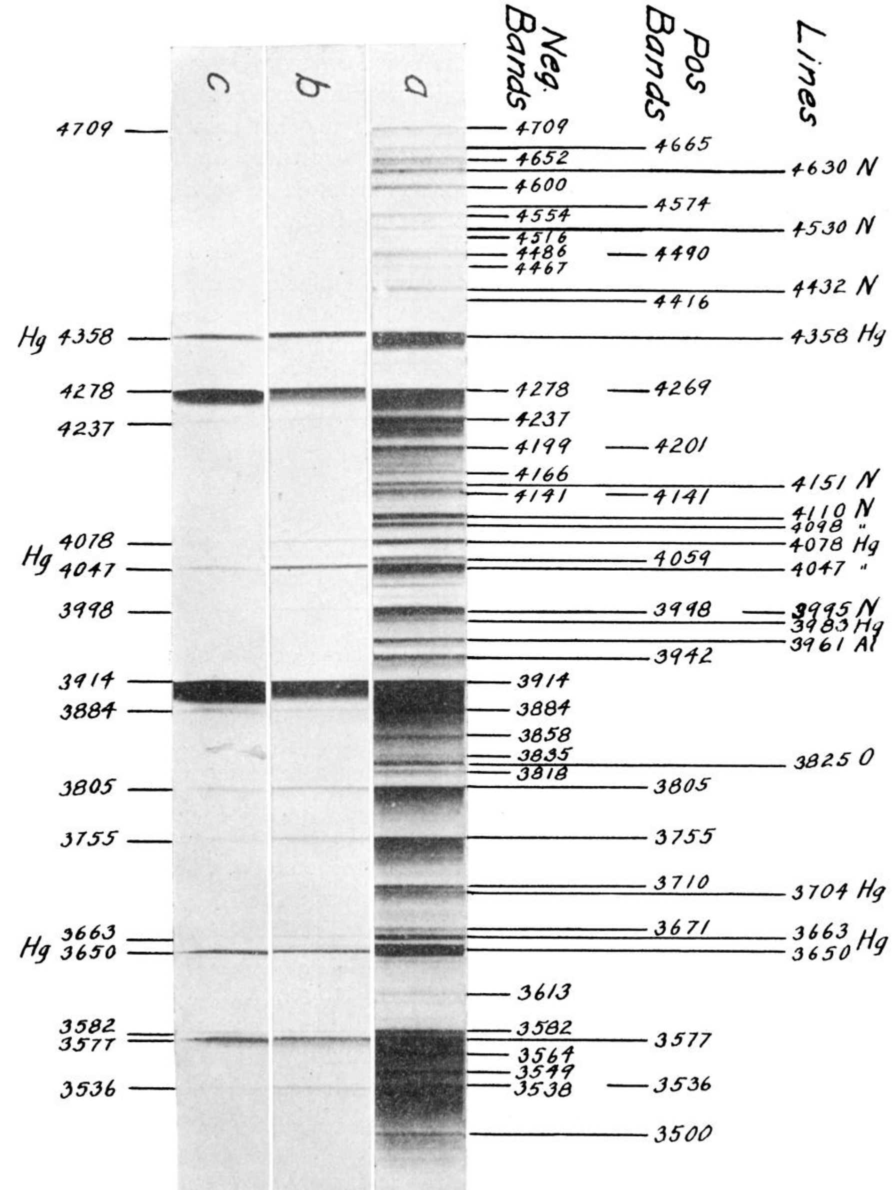
The conclusion is then that the intensities given in Tables I and II are confirmed by the older work and actually represent the excitation of band spectra by rapidly moving molecules of nitrogen or mercury. These molecules may or may not be charged.

Returning to the electron excitation, previous work needs to be considered. The remarkable fact is that there seems to be so little. Several authors have studied the excitation potentials of the various band systems of nitrogen[16,17,18] but of these apparently only Kneser worked with electron speeds as high as 100 volts, and made some slight study of the variation in the intensity of the different bands. His results, for both electrons of 100 volts and electrons of about 30 volts, are not very complete but as far as they go, show an intermediate intensity distribution between those of Tables I and II and those of Table III but nearer Table III. As far as one can judge from reproductions published in some of the other papers mentioned, Kneser's work is typical of the results with electron impact below 100 volts. Apparently no one has worked before with electron impact at higher voltages. Our photographs with 700 volts are a start and it is in this direction that we expect to continue our work next year.

Final Summary and Conclusion

Reviewing the whole situation we see that the parabolic intensity distribution is maintained under all types of excitation. It is presumably characteristic of the transition probabilities and therefore may be expected to be independent of excitation conditions. But the distribution along the parabola varies greatly. At one extreme with canal-ray excitation we have the intensity spread well out along the parabola toward higher quantum numbers. At the other extreme with high voltage electron excitation we have the intensity very much concentrated at the head of the parabola. This much is in accord with our original notion that the canal-ray impact may convey vibrational momentum and the electron impact may not. Intermediate types of distribution are obtained from impact of low velocity electrons and from various types of discharge. Surprisingly the electrodeless discharge supposed to be purely electronic in its excitation, gives the distribution most nearly like the canal-ray excitation. This is probably due to secondary effects which raise large numbers of the molecules into high vibration states.

[16] Turner and Samson, Phys. Rev. **34**, 747 (1929).
[17] Sponer, Zeits. f. Physik **34**, 622 (1925).
[18] Kneser, Ann. d. Physik **79**, 597 (1926) and others.



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