The Spectrum Lines of Oxygen and of Nitrogen in an Intense Electric Field.

By

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With respect to the Stark effect in nitrogen and oxygen, only a negative result on the band spectrum of nitrogen has been obtained by Stark; and, so far as the writer is aware, no effect of an electric field on the spectrum lines of these gases has hitherto been found. In the present investigation, the experimental arrangement used for photographing the spectrum and for exciting the discharge in the vacuum tube was essentially the same as that described in the former paper relating to the Stark effect in lithium[1]; and a three-prism-spectrograph was used throughout the present experiment. The vacuum tube used on this occasion was the same as that stated in the previous investigation on hydrogen and helium, and the cathode was inserted in a capillary tube of hard glass. For the cathode metal, aluminium was employed in the earlier part of the experiment, but afterward tantalum was adopted as being more satisfactory, for the sputtering was far less with tantalum than with aluminium, as was noted by Dr. Takamine and Mr. Kokubu[2] in their investigation on the Stark effect in helium and hydrogen.

The field strength was calculated by using the data given by Stark for the Balmer lines of hydrogen in the case of the "Grobzerlegung," assuming that the proportionality between the field intensity and the amount of separation holds good even up to the strong field that was used in the present investigation.

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1 Yoshida, Mem. Coll. Sci., Kyoto, **3**, 161, (1918).

2 Takamine and Kokubu, Proc. Tokyo Mathematico-Phys. Soc., **9**, 394, (1918).

Nitrogen.

By adopting a capillary tube of about one mm. in diameter, and increasing the field strength as much as possible, it was found that, when the gas in the tube was air, two spectrum lines at 4110.1 Å.U. and 4100.3 Å.U. were evidently displaced toward the violet side both in the parallel and in the perpendicular component. When the gas in the tube was replaced by oxygen or hydrogen, no trace of these two lines was detected, but when the tube was filled with nitrogen prepared chemically from sodium nitrite and ammonium sulphate, intense images of these two lines were observed on the photographic plate.

With the vacuum tube filled with nitrogen gas, Moissan and Deslandres[1] observed the five lines, 4151.7, 4143.7, 4110.0, 4108.0 and 4100.5 Å. U., and from their minute examination on the condition under which these lines appeared, they concluded that the lines were due to nitrogen or to an unknown gas whose chemical nature is similar to that of nitrogen.

Now in the present experiment, when the vacuum tube was filled with air or chemically prepared nitrogen, three lines at 4151.5, 4144.0 and 4108.3 Å.U. besides the two lines before mentioned were detected; and the order of their intensities were nearly similar to those given by Moissan and Deslandres. Consequently it may be concluded that the two spectrum lines under consideration are the same as those observed by Moissan and Deslandres at 4100.5 and 411.0 Å.U.

W. Hermann[2] and H. Wilsar[3] in their investigations on the Doppler effect of the canal rays of nitrogen, regarded these two spectrum lines under consideration as due to nitrogen. And there seems to be no contradiction in regarding the two spectrum lines at 4110 and 4100 Å.U. as those arising from nitrogen.

Some of the photographs obtained in the present experiment are represented in Fig. 1, Fig. 2, Plate I. The maximum electric field, in Fig. 1, calculated from the separation of H_γ was 7.6×10^4 volt/cm., and that in Fig. 2 calculated from the separation of H_β was 16.5×10^4 volt/cm. The dispersions on the photographic plate at Balmer lines of hydrogen, and the displacements of the lines 4100 and 4110 Å.U. in the field of 16.5 10^4 volt/cm are given in the Table 1 and Table 2.

1 Moissan and Deslandres, C.R., **126**, 1689, (1898).

2 Hermann, Phys. Z.S., **7**, 567, (1906).

3 Wilsar, Ann. d. Physik, **39**, 1251, (1912).

TABLE 1.

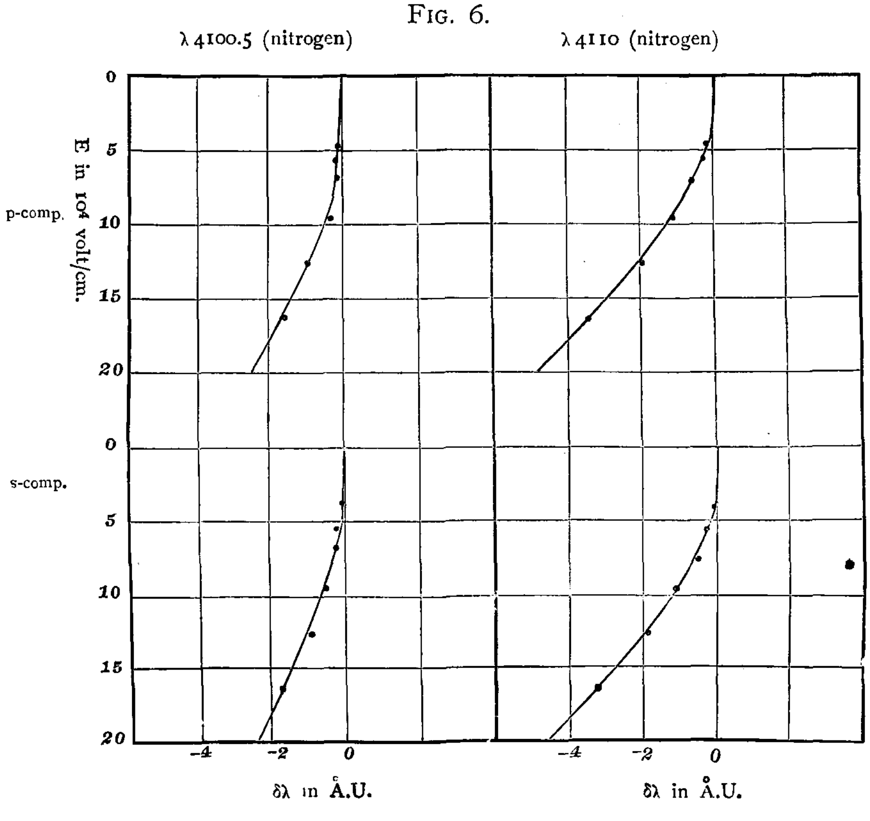
Balmer lines	4861	4341	4102
dispersion in Å.U. per mm.	60.0	39.0	28·0

TABLE 2.
Field-strength = 16.5×10^4 volt/cm.

	4100 Å.U.		4110 Å.U.	
	p-comp.	s-comp.	p-comp.	s-comp.
displacement in Å.U.	-1.7	-1.8	-3.5	-3.2

The details of the result of measurement are represented graphically in Fig. 6. Here it is worthy of note that, both in the line

FIG. 6.



4100 and in 4110 Å.U., the amount of displacement of the parallel and of the perpendicular components is equal in the limit of accuracy of measurement, the displacement of the line 4100 Å.U. being slighter than that of the other.

In a recently published paper on the Stark effect in Ca and Mg, Dr. Takamine and Mr. Kokubu[1] reported that the two lines at 4110.7 and 4110.3 Å.U. of unknown origin were displaced slightly toward the violet side in an intense electric field. Probably these will be the same as those described above.

Excluding the two lines above discussed, the other three observed by Moissan and Deslandres made also their appearance in the photograph as was stated before; but, so far as the present experiment is concerned, no effect of an electric field on these lines was detected.

In the region from 4000 to 5000 Å. U., many spectrum lines belonging to the negative band spectrum and the second positive band spectrum of nitrogen also appeared in the photograph, but no effect of an electric field was detected even in the strong field of 16.5×10^4 volt/cm.

Many other spectrum lines belonging to the line spectrum of nitrogen were also visible in the photograph, but, in the region from 4000 to 5000 Å.U., no positive result was obtained on any one of them.

Lastly, on testing the region of wave-lengths longer than 5000 Å.U., it was found that the two lines at 5553 and 5688 Å. U. were displaced evidently toward the red side, the displacement of each of these two lines being equal both in the parallel and in the perpendicular components. The amount of displacement of the former line was about 9 Å.U. in a field of 8.6×10^4 volt/cm., and that of the latter was about 4 Å.U. in the same field. Here it must be remarked that the wave lengths given above to the two spectrum lines now under consideration were not accurate, owing to the fact that the photographic images of these two lines were diffuse and the dispersion in this region was very small with the three-prism-spectrograph used in the present experiment. And, though it is very probable that these two lines are of nitrogen at 5551.0 and 5686.3 Å U., it is not, of course, definitely proven that these are really due to nitrogen and further study is necessary.

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1 Takamine and Kokubu, Mem. Coll. Sci., Kyoto, **3**, 173, (1918).

Oxygen.

In the present experiment, the spectrum lines belonging to the series spectrum and the spark spectrum or the elementary line spectrum of oxygen were examined. And some positive result was obtained on some of the series spectrum. Oxygen gas was generated by heating a mixture of potassium chlorate and manganese dioxide, then it was dried by phosphor pentoxide. For photographing the spectrum the three-prism-spectrograph described in the case of nitrogen was also used in this case for the spectrum region below H_β. For the region above H_β, the same spectrograph was so readjusted that it was in a state of minimum deviation at the green line of mercury. The dispersions of this readjusted spectrograph at various wave lengths are shown in the following table Table 3.

TABLE 3.

Spectrum lines	4861	4968.5	5019.5	5329.5	5436	6157	6455
dispersion in Å.U. per mm.	33	39	42	53	60	111	116

With this readjusted spectrograph and the former one used in the case of nitrogen, many spectrum lines belonging to the spark spectrum of oxygen were visible on the photographic plates, but no trace of displacement or separation of these lines was detected with a strong electric field of about 10×10^4 volt/cm.

The series spectrum lines which appeared in the photograph with an exposure of about six hours, are given in Table 4. In this table the notation T.N.I. represents triplet first subordinate series, and T.N.II triplet second subordinate series, and T.H. triplet principal series, and P.H. represents pair principal series.

TABLE 4.

notation	T.N.II	T.N.I	T.N.II	T.N.I	T.N.II	T.N.I	P.H.	T.H.
wave length measured	6455	6157	5436	5329.5	5019.5	4968.5	4368.0	3947.0
Runge and Paschen[1]	6456.287 54.756 53.900	6158.415 56.993 56.198	5437.041 35.968 35.371	5330.835 29.774 29.162	5020.31 19.52 18.96	4968.94 68.04 67.58	4368.466	3947.759 47.661 47.480

1 Runge and Paschen, Ann. d. Physik, **61**, 641, (1897).

Among these lines, the two 4368.0 and 3947.0 Å.U. which belong to the pair principal series and the triplet principal series respectively suffered no observable influence in a field of about 10×10^4 volt/cm. And on the line 6455 Å.U. which belongs to the second subordinate triplet series no measurable influence was detected in the field of 6.8×10^4 volt/cm. with the present experimental condition under which the dispersion at this line was small. All the other lines which belong to the first subordinate triplet series or to the second subordinate triplet series suffered a comparatively large influence, that on the lines of the first subordinate triplet series being larger than that on the others.

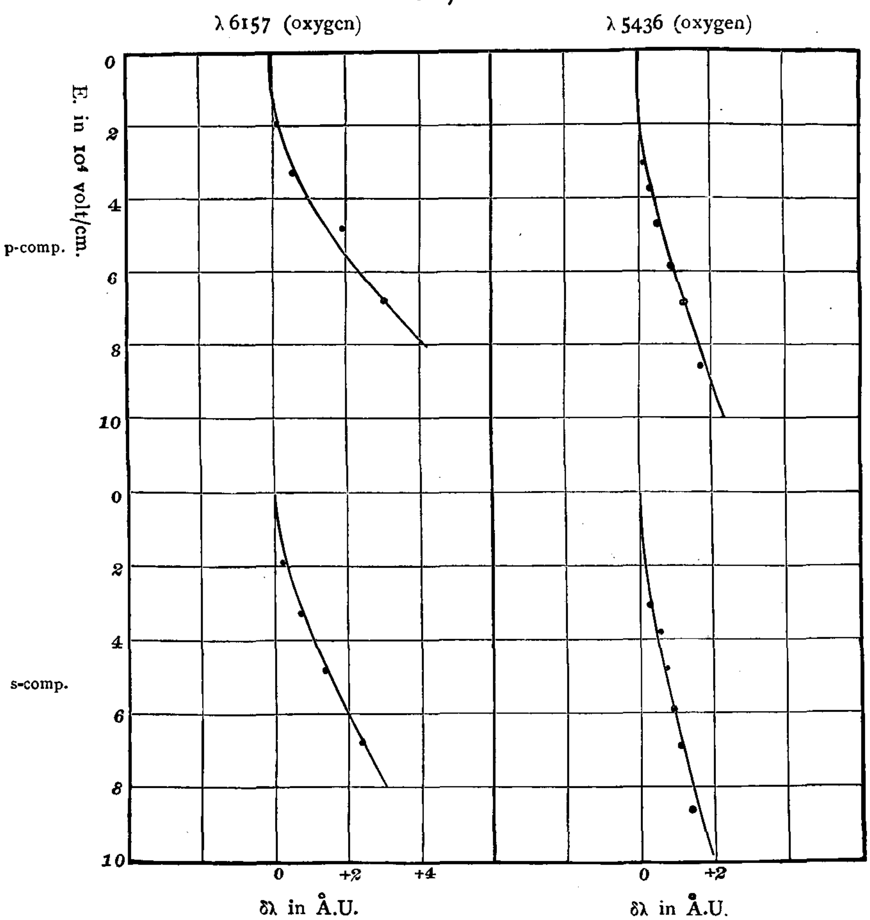
The photographs reproduced in Fig. 3, Fig. 4, Fig. 5, Plate I, represent the behaviors of these lines in the electric field. The maximum electric field in the case of Fig. 3 was 6.8×10^4 volt/cm. and that in the case of Fig. 4 was 8.6×10^4 volt/cm. and 8.2×10^4 volt/cm. in the case of Fig. 5. As the intensities of the series lines of oxygen were weak under the present experimental condition, an exposure of five or six hours was needed to obtain these photographs.

Here it must be remarked that, as the dispersion at these lines with the three-prism-spectrograph now used was small, these lines were not resolved as triplets; and therefore it was necessary in the following to regard these unresolved triplets as if they were simple spectrum lines.

Second Subordinate Triplet Series. Among the spectrum lines belonging to this series, the three lines denoted in Table 4 could be observed in the photograph as was shown in Fig. 3, Fig. 4, and Fig. 5, Plate I. And a positive result was obtained on the lines 5436 and 5019 Å.U. The behaviors of these lines in several electric fields are represented graphically in Fig. 7, and Fig. 9. As the field strength is increased gradually these two lines were displaced continuously toward the red side both in the parallel and perpendicular component, the amount of displacements of the parallel and of the perpendicular components being each equal in both cases. Considering the fact that the displacement of the line 5019 Å.U. is greater than that of the line 5436 Å.U., and that no effect was observed on the line 6455 Å.U., there seems to be no contradiction to conclude that the displacement of a line in this series is larger as the term number of the series increases. All these behaviors of the spectrum lines belonging to the second subordinate triplet series of oxygen are quite similar to those of the second subordinate series spectrum of helium and parhelium[1].

First Subordinate Triplet Series. Among the spectrum lines of this series, the three lines 6157, 5329.5 and 4968.5 Å.U. could be observed on the photographic plate, and a positive result was obtained on all these lines, as was seen in Fig. 3 and Fig. 5, Plate I. The effect of an electric field on the spectrum line 6157 Å.U. was the displacement toward the red side, and the result of the measurement is represented graphically in Fig. 7. Here the displacement of the parallel component is somewhat larger than that of the perpendicular

FIG 7.



1 Takamine and Yoshida, Mem. Coll. Sci., Kyoto, **2**, 325, (1917); and Takamine and Kokubu, Mem. Coll. Sci., Kyoto, **3**, 81, (1918).

one, but this may perhaps be due to an experimental error. For the dispersion at this line was very small with the present experimental arrangement, and the photographic image of this line was more intense and consequently appeared more broadened in the perpendicular component than in the parallel one. And therefore the displacements of the parallel and the perpendicular components may be regarded as of nearly equal amount.

Next the electric effect on the lines 4968.5 and 5329.5 Å.U. is shown in Fig. 5, Plate I, and the result of the measurement at the maximum electric field applied are tabulated in the following table Table 5.

TABLE 5.

4968.5 Å.U., field-strength $=8.16\times10^4$ volt/cm.

	p-comp.			s-comp.		
δλ in Å.U.	−15.6	+2.3	+15.9	+15 9	+2.8	+16.9
Intensity	1	1	1	2	2	2

5329.5 Å.U., field-strength $=8.16\times10^4$ volt/cm.

	p-comp.			s-comp.		
δλ in Å.U.	−30.0	−10.0	+10.8	−30.1	−11.6	+7.6
Intensity	1	4	8	2	5	10

The behaviors of these lines in several electric fields are represented graphically in Fig. 8, and Fig. 10. The lines 4968.5 and 5329.5 Å.U. were displaced toward the red side. And in the case of the former line, the amount of displacement of the parallel component is nearly equal to that of the perpendicular one. This is not the case on the line at 5329.5 Å.U., and the displacement of the parallel component is somewhat larger than that of the other. Judging from the fact that the photographic image of this line appeared more intense and consequently more broadened in the perpendicular component than in the parallel one, the inequality of the displacements of the two components may be ascribed to an experimental error. And consequently we may conclude that the displacements of the parallel and of the perpendicular components are nearly equal respectively in the case of the three spectrum lines before mentioned.

Next, in Fig. 5, Plate I, two spectrum lines will be seen, so to speak quite isolated, in the immediate violet side of the line 5329.5 Å.U.; also in the immediate violet side of 4968.5 Å.U., two very weak isolated lines are visible exactly in the corresponding position as before. The behavior of these lines in several electric fields are represented graphically in Fig. 8, and Fig. 10, in conjunction with those of 4968.5 and 5329.5 Å.U. In order to determine whether these isolated spectrum lines were due to oxygen or some other impurities, the writer examined it more closely. On measuring the wave lengths of all the spectrum lines which were seen on the photograph, it was found that, excepting the lines which are due to oxygen, most of the other lines are of hydrogen and nitrogen, and a few are of mercury and sodium. Of these four elements, the latter two have no spectrum lines in the neighbourhood of the isolated spectrum lines before mentioned. The other two elements, especially hydrogen, have some spectrum lines which might cause the appearance of the isolated spectrum lines before mentioned. As these weak lines of hydrogen or nitrogen, which might be considered as the continuation of the isolated spectrum lines in the region of no electric effect, was visible on the photograph, the writer experimented with hydrogen or nitrogen alone. And it was confirmed that none of the questionable spectrum lines of hydrogen and nitrogen showed any electrical effect. Consequently we may consider that the isolated spectrum lines before mentioned are due to oxygen.

With regard to the four isolated spectrum lines above discussed, it seems, to the writer, to be convenient to consider them as isolated components of the lines 5329.5 and 4968.5 Å.U., as in the case of helium[1] and lithium[2]. All these isolated components appeared on the immediate violet sides of the lines 4968.5 and 5329.5 Å.U., as in the case of other elements. Moreover the isolation of the isolated components of 4968.5 Å.U. is of smaller amount than that of the isolated components of 5329.5 Å.U. This is similar to the behavior of the

1 Takamine and Yoshida, Mem. Coll. Sci., Kyoto, **2**, 325, (1917); Takamine and Kokubu, Ibid, **3**, 81, (1918); Takamine and Kokubu, Proc. Tokyo Math. Phys. Soc., **9**, 394, (1918).

2 Yoshida, Mem. Coll. Sci., Kyoto **3**, 161, (1918).

isolated components of the spectrum lines of helium and parhelium[1], of which the isolation of an isolated component of a spectrum line of the first subordinate series become smaller as the term number of the series increases.

In the previous paper dealing with the Stark effect in lithium[2], it was stated that the lithium line 4602 Å.U. had a so-called isolated component on its immediate violet side, and the fact observed by Saunders[3] that this line became double when broadened was explained by the appearance of an isolated component of this spectrum line in an electric field. Recently Merton[4] investigated the broadening of helium lines by condensed spark discharges, and found a close agreement between the broadening and the electrical resolution of helium lines. Especially interesting is Merton's result, that the isolated components in the electrical resolution were observed in the broadened lines. In the present case, some isolated components of oxygen lines were found in an electric field as stated before; and an investigation on the broadening of oxygen lines will be of much interest.

Band Spectrum Lines of Oxygen. In the present experiment, only two negative band spectra at 563—555 $\mu\mu$ and 529—520 $\mu\mu$ of oxygen were visible on the photographic plate. The intensity of these band spectra was very much reduced in the Crookes' dark space where the electric field was much stronger than in the other portion of the discharge tube. Owing to their weak intensities the writer could not ascertain whether the wave lengths of the band spectrum lines of oxygen were affected by an electric field or not.

The intensities of the spectrum lines of the triplet series of oxygen increase, contrary to the case of band spectra, in the Crookes' dark space, and they become stronger continuously as we pass from the region of weaker electric field to the stronger one. Next with regard to the spark spectrum lines of oxygen, they behave similarly as the band spectrum of oxygen. But the diminution of the intensities of the spark lines in the Crookes dark space is slighter than in the other case.

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1 Takamine and Kokubu, Mem. Coll. Sci., Kyoto, **3**, 81, (1918).

2 Yoshida, loc. cit.

3 Saunders, Astrophys. J., **20**, 188, (1904).

4 Merton, Nature, **101**, 279, (1918).

Summary.

1. The Stark effect on the spectrum lines of nitrogen and oxygen was investigated, and a positive result was obtained on the lines at 4100 and 4110 Å.U. of nitrogen, and on some of the lines belonging to the first and second subordinate triplet series of oxygen.

2. Excepting a few ambiguous cases, the amount of the displacement or of the separation of each of all these lines is nearly equal respectively in both the parallel and the perpendicular components.

3. The behavior of the lines of the second subordinate triplet series of oxygen in the electric field is similar to that of the lines belonging to the second subordinate series of helium and parhelium.

4. The effect on the spectrum lines of the first subordinate triplet series of oxygen is larger than that on the second subordinate triplet series.

5. Each of the lines 5329.5 and 4968.5 Å.U. of the first subordinate triplet series have two isolated components respectively in its immediate violet side. The isolation of the said components become smaller as the term number of the series increases. This is exactly similar to that of the isolated components of helium and parhelium

In conclusion the writer's sincere thanks are due to Prof. T. Mizuno for his interest in the research.

Fig. 8.
λ 4968.5 (oxygen).

Fig. 9.
λ 5019 (oxygen).

Fig. 10.
λ 5330 (oxygen).

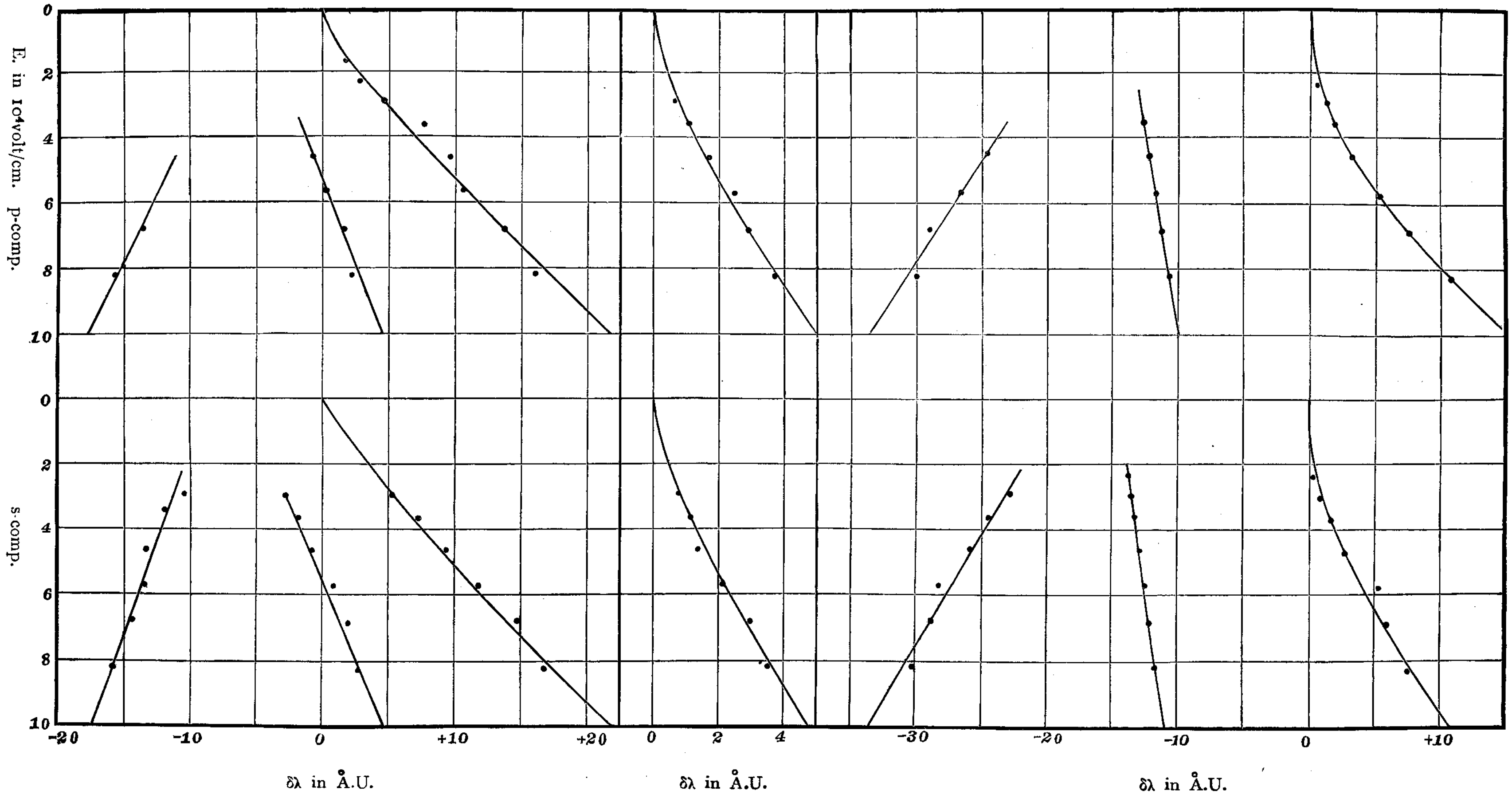
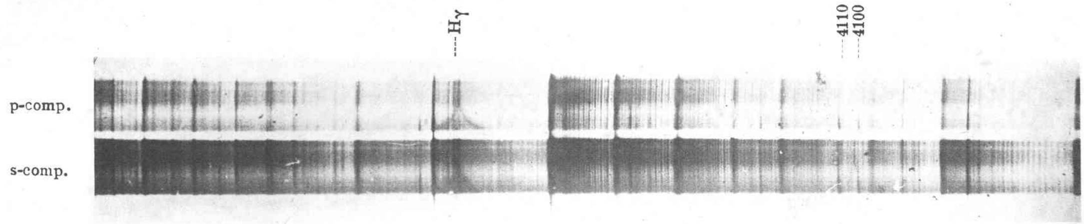
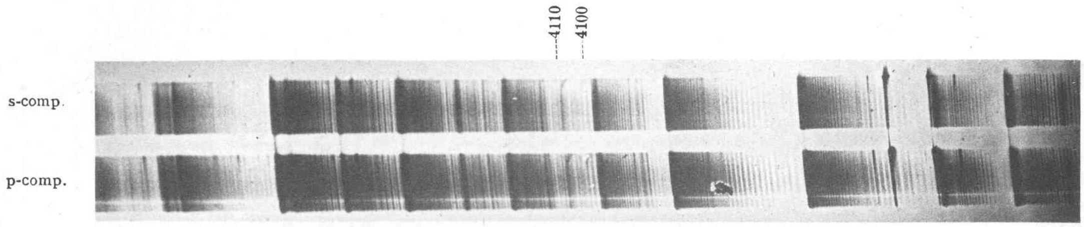


Fig. 1. Nitrogen



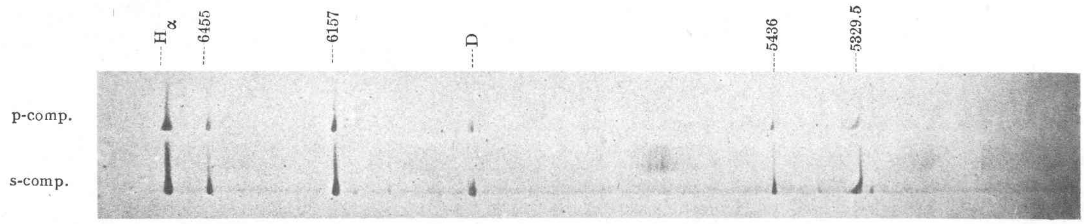
Magnification 7. $E_{max.} = 7.6 \times 10^4$ volt/cm.

Fig. 2. Nitrogen



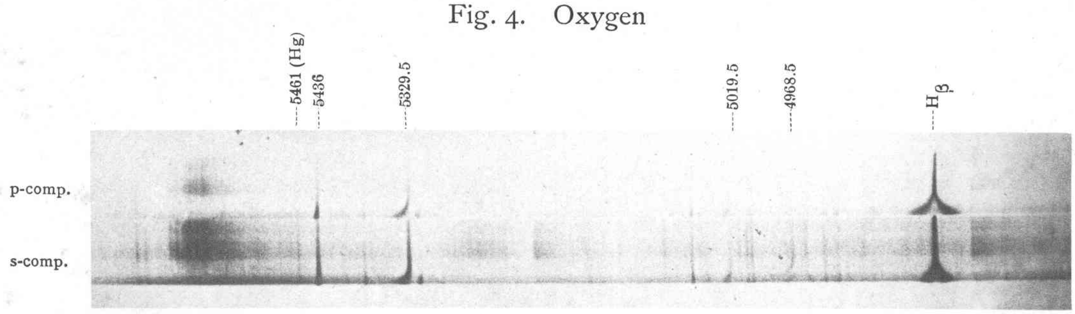
Magnification 6.7. $E_{max.} = 16.5 \times 10^4$ volt/cm.

Fig. 3. Oxygen



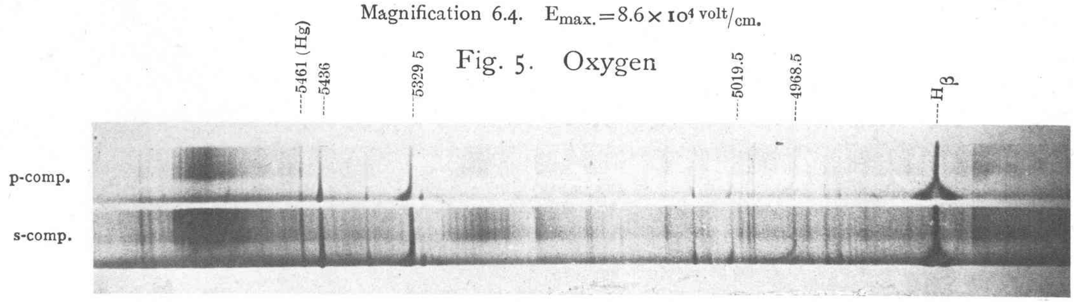
Magnification 6.1. $E_{max.} = 6.8 \times 10^4$ volt/cm.

Fig. 4. Oxygen



Magnification 6.4. $E_{max.} = 8.6 \times 10^4$ volt/cm.

Fig. 5. Oxygen



Magnification 6.4. $E_{max} = 8.2 \times 10^4$ volt/cm.