AUGUST 1, 1929 *PHYSICAL REVIEW* *VOLUME 34*

THE EXCITATION OF THE ARC SPECTRUM OF NITROGEN

By O. S. Duffendack and R. A. Wolfe
University of Michigan

(Received April 24, 1929)

Abstract

The arc spectrum of nitrogen has been quite completely excited and measured in the region 8800–3400A with a low voltage arc in a mixture of helium and nitrogen. The process of excitation is probably a two step process: the first being the dissociation of nitrogen molecules into neutral atoms by impacts of the second kind with metastable helium atoms and the second, being the excitation of neutral nitrogen atoms by second impacts with metastable helium atoms. A complete list of wavelengths is given and the classifications of the lines designated as far as they are known. A considerable number of new lines have been classified.

Historical

Due to the great stability of the nitrogen molecule the usual methods of excitation yield band spectra, attributed to the neutral or ionized nitrogen molecule, and a line spectrum attributed to ionized atoms. When dissociation is produced in electric discharges through nitrogen only a very small percentage of neutral atoms are formed, the greater portion being ionized. For this reason the usual methods of excitation have not yielded the arc spectrum because the light emitted by the neutral atoms must have been extremely feeble.

Several different methods have been used to obtain portions of the nitrogen arc spectrum. The results obtained have been to a certain extent uncertain. While working with a nitrogen filled canal ray tube Hardtke[1] noticed a few lines in the glow back of the cathode which he attributed to the neutral nitrogen atom. They were not separated from the spark lines, were very uncertain, and were measured only approximately. A little later Merril[2] and Kiess[3] published lines observed in the near infra-red which they obtained from nitrogen filled discharge tubes. The same lines were also obtained by them while observing the spectra of arcs and sparks in air between metallic electrodes.

The next work on the arc spectrum of nitrogen was done by Merton and Pilley[4] who used a Geissler tube discharge through a mixture containing an excess of helium and a trace of nitrogen. The first three lines which they observed in the far red corresponded to three lines observed by Merril[2] and by Kiess.[3] This fact alone led to a preliminary analysis of the spectrum by Kiess.[5]

---

[1] Hardtke, Ann. d. Physik **56**, 363 (1918).

[2] Merril, Astrophys. J. **51**, 236 (1920).

[3] Keiss, Publ. Amer. Astron. Soc. **4**, 170, 363 (1923).

[4] Merton and Pilley, Roy. Soc. Proc. **A107** 411 (1925)

[5] Keiss, J.O.S.A. **11**, 1 (1925).

At nearly the same time Fowler[6] published an analysis of the spark spectrum of nitrogen which contained none of these previously observed lines.

The method used by Merton and Pilley presented certain difficulties in the removal of foreign gases and the control of the nitrogen pressure because it was difficult to regulate the amount of nitrogen introduced. They had no means of measuring the amount and even a slight excess prevented the development of the arc lines. After the foreign gases were removed and the nitrogen was admitted the tubes were operated for some time during which the nitrogen gradually "cleaned up" in the discharge. Photographs were taken at intervals and some of them showed the nitrogen arc lines. Thus it was difficult to duplicate the conditions most favorable to the excitation of the spectrum. Long exposures were necessary and the disappearance of the gas made it impossible to obtain many exposures from a single tube.

Merton and Pilley[4] account for the emission of the nitrogen arc spectrum by assuming that the helium atoms act as "safety valves" which blow off when they are struck by electrons possessing 20.5 volts of energy. This would set an upper limit to the amount of energy that an electron would proabably attain. If we assume that the amount of energy necessary to excite the arc lines is less than 20.5 volts and to excite the spark lines more than this amount then it would appear that the above method would bring about the complete isolation of the nitrogen arc lines.

A second explanation, advanced by K. T. Compton,[7] is that the nitrogen molecules are dissociated into neutral atoms by impacts of the second kind with metastable helium atoms possessing 20.5 volts of energy. According to this view the helium atoms in the tube are raised to their 20.5 volt level by direct electron impacts. These metastable helium atoms may collide with neutral nitrogen molecules and dissociate them.

In order to observe the arc spectrum a considerable concentration of neutral nitrogen atoms is necessary. This would necessitate a large electron current through the gas in order to obtain a high concentration of excited helium atoms. In low voltage arcs in helium, a high concentration of helium atoms in a metastable state, has been demonstrated. This would result in a high concentration of neutral nitrogen atoms. The concentration of both would, therefore, be proportional to the electron current through the tube.

If a low partial pressure of nitrogen were not used the electrons would make inelastic collisions with the nitrogen molecules and cause the emission of the band spectra. With a high accelerating voltage the nitrogen molecules would be dissociated into ionized atoms by the inelastic collisions and cause the emission of the spark spectrum.

In view of the above suggestions it seems logical to expect that a low voltage arc should be a suitable means of exciting the arc spectrum of nitrogen. This method would enable one to obtain the high concentration of metastable helium atoms and at the same time sufficient ionization to permit large electron currents through the gas. Moreover there must exist uniquely

---

[6] Fowler, Roy. Soc. Proc. **A107,** 31 (1925).

[7] Compton, Phil. Mag. **50,** 512 (1925).

favorable pressures of the helium and the nitrogen to obtain the best results. The apparatus used with the low voltage arc give one a ready means of studying such conditions, since the partial pressures of both gases can be varied at will.

EXPERIMENTAL

A low voltage arc discharge tube of the conventional design was used in this investigation. The light emitted by the discharge was photographed through a quartz window. Three liquid air traps were connected close to the discharge tube, the center one containing charcoal. The evacuating system consisted of a double stage mercury pump backed by a Cenco Hyvac pump. The pressure inside the system was determined by a McLeod gauge. For purifying and reclaiming the helium a separate system was sealed on consisting of a charcoal trap, a Geissler tube containing magnesium, and a Toepler pump. Bulbs were provided for storing the purified helium and nitrogen.

After the entire system had been completely freed of foreign gases the helium was introduced. It was allowed to stand for an hour or more in contact with the charcoal, in the first trap, immersed in liquid air. At the same time a heavy discharge was passed through the Geissler tube containing magnesium. The gas was then pumped through a second charcoal trap, a second Geissler tube and "getter" and into a storage bulb. After the helium had passed three times through this purifying process it became very pure and at high pressures showed only a faint trace of hydrogen, the only impurity.

The nitrogen was generated outside the system. A chemically pure solution of sodium nitrite was added drop by drop to a similar solution of ammonium chloride while at the same time the latter solution was gently warmed. The gas so produced was passed through a concentrated solution of potassium hydroxide to absorb the carbon dioxide, then over phosphorus pentoxide to absorb the water vapor, and lastly through copper turnings, heated to 550°C, to remove the oxygen. The nitrogen so generated failed spectroscopically to show any trace of an impurity.

Before the purified gases were introduced into the system the tungsten filaments and discharge tube were freed of gases in the usual manner. Mercury vapor was removed with liquid air traps. The optimum pressures for the helium and the nitrogen were then determined.

It should be remembered in this connection that a high current density was expected to be most favorable to the production of atomic nitrogen. With this in view various helium pressures, ranging from a fraction of a millimeter to 30 millimeters, were tried. At low pressures not enough positive ions were formed to neutralize the space charge around the cathode and the current was space charge limited. At high pressures too high a voltage was required to produce the desired current. At a pressure of 11 millimeters, large currents, as high as 10 amperes at 90 to 100 volts, could be maintained through the tube, and this was selected as the most desirable helium pressure. With helium at this pressure in the discharge tube, nitrogen was added in small amounts until the arc lines became most prominent. A slight excess of nitrogen brought out the negative bands strongly, covering up the arc lines. A higher percentage of dissociation was probably attained at extremely low nitrogen pressures but the feebleness of the emitted radiation made detection difficult. Best results seemed to be obtained when the negative bands were present with feeble intensity. The amount of nitrogen introduced varied in different spectral regions. In that portion of the visible region from 3400A to 6000A a partial pressure of about 0.01 millimeter was used. In the region around 8700A pressures as high as 0.1 millimeter were found to be most suitable.

As the discharge was run the nitrogen cleaned up quite rapidly on the filament, forming a brownish-black deposit, presumably of tungsten nitride. The nitrogen absorbed by the charcoal served as a reservoir and kept the partial pressure of the nitrogen in the mixture practically constant.

After the optimum pressures had been determined the usual method of procedure was as follows: Pure helium, at a pressure of about 11 millimeters, was introduced into the system. A potential difference of 90-100 volts was then then impressed upon the electrodes and the discharge started. Spectrograms were taken of the helium to determine its purity and to locate the helium band lines. The correct amount of nitrogen was then added and spectrograms taken under exactly similar conditions showing the nitrogen arc lines.

The Nitrogen Arc Spectrum

Theoretically a high current density is required for the formation of the nitrogen arc spectrum according to the explanation given by K. T. Compton[7] of this type of discharge. The first part of the work was done using a current of approximately 60 milliamperes through the tube. With such a small current the arc lines could not be detected even though a rapid spectrograph was employed and a high speed plate used. The current density could be increased readily enough by increasing the filament temperature, but such an increase in temperature quickly produced a "flare" condition. In order to limit the current through the tube a relay was placed in the plate circuit and set to operate at 250 milliamperes. This interruption of the arc prevented flare conditions and at the same time allowed the necessary current density. Although the relay interrupted the plate circuit when the meter indicated 250 milliamperes, the current through the tube was much in excess of this.

When the interrupted arc was used the region between the filament and plate showed the following characteristics: Spectrograms taken from a region direcly off of the filament showed well developed helium line and band spectra. Traces of nitrogen band edges were also present. Spectrograms taken from a region about 5 millimeters from the filament showed entirely different phenomena. At this point the helium lines were much weakened, the helium bands had in most cases completely disappeared, the nitrogen bands were slightly stronger, and a well developed arc spectrum of nitrogen appeared. This region was used in obtaining all the plates showing the arc lines. Spectrograms taken from a region just in front of the plate gave very few arc lines. The nitrogen bands and helium lines were very strong in this region and helium bands were again present. The light photographed in this case came from a group of small tufts on the plate.

Determination of Wave-Lengths

The measurements were made from fine grained plates with a precision comparator. High magnification was used and the settings made as nearly as possible on the centers of the lines. Measurements were repeated on the same line to insure as great accuracy as possible. International iron lines were used for comparison.

Three different spectrographs were used during the investigation. For use in detecting faint radiations a two prism glass spectrograph and a Hilger E2 quartz spectrograph were used. The plates from which the lines were measured were taken with a Hilger E1 spectrograph. For work from 3200A to 5000A it was equipped with a quartz prism and lens. For work above 5000A it was equipped with a glass prism and lens. With the quartz prism the dispersion varied from 8A per millimeter at 3400A to 20A per millimeter at 5000A. Using the glass prism the dispersion varied from 4A per millimeter at 4000A to 25A per millimeter at 7000A.

In the lower part of the visible region the lines obtained by using the glass prism were sonewhat fuzzy and plates taken with the quartz system were measured. The upper glass region gave lines which were clear and sharp.

The length of exposures necessary varied with the region of the spectrum and the type of plate used. Using the quartz system, in the visible region, spectrograms could be obtained on fast plates in one hour. Strong lines were easily photographed in 10 minutes. With fine grained plates exposures of two hours were made in the same region. With the glass system and spectrum plates, exposures of 3 hours were needed in the region from 5000A-7000A. In the glass region from 7000A-8860A Eastman Neocyanine plates were used. Exposures of six hours were found necessary here.

Results

The measurements contained in the table were obtained as explained above. The lines listed from 3400A-5000A are believed to be correct to at least 0.03 of an angstrom unit with the exception of those lines which are marked with an intensity of 00 or with a ? mark. An accuracy of at least 0.05A is believed to exist from 5000A-6900A and 0.1A from 6900A out to the longest measured wave-length. All of the lines have been measured on at least two different plates and most of them on three plates. Average values are given but only those values were averaged that agreed within the above mentioned limits of accuracy. In case of doubt the line was remeasured. Shifts of spectral lines due to temperature changes were not noticed; due, no doubt, to the comparatively short exposures necessary. A few lines were confused with nitrogen band structure and are so marked. Diffuse lines are also indicated. The intensities listed are eye intensities. They are average intensities as judged from different plates, and different length exposures.

As will be noticed from the table several of the lines reported by Merton and Pilley[4] have not been observed. Changes in intensity have been noticed and as a rule are toward greater intensity. This increased intensity resulted, no doubt, from the high current density which was maintained through the tube. Two or three lines reported by them as having considerable intensity could not be found, although a careful search was made on a large number of plates. The measured values in the table agree in most cases, within the limits of error, with Merton and Pilley's values. Hardtke[1] made no attempt to measure accurately the lines he observed. Several of the lines reported by Hardtke and not reported by Merton and Pilley have been found, but all such seem to have low intensity.

Due to the greater intensity of the source used spectrograms could be obtained on shorter exposures than with Geissler tubes. This prevented temperature shifts with the resulting broadening of the lines. Because of small dispersion the lines in the region around 8500A have been reported to only one decimal place. These lines were all found by Kiess. It is thought that more lines should be observed in the region around 6900A but plates sensitive in this region could not be found and the lines were not observed. Lines due to helium bands and nitrogen bands have been eliminated and no spark lines were obtained.

CONCLUSION

The writers believe that the present method shows marked superiority over the previous methods used in the excitation of the arc spectrum of nitrogen. The relative ease with which the helium can be purified and the ability to control the gas pressures seem to be distinct advantages. Since the work was done with a comparatively low pressure of helium fewer helium bands were formed, as they are generally recognized as high pressure bands. While photographing the arc spectrum they usually completely disappeared.

It should be mentioned at this point that Duffendack[8] and Duncan[9] failed to excite the nitrogen arc lines by using direct electron impacts with 20.5 volt electrons. This would seem to exclude the possibility that 20.5 volts of energy constitutes the best excitation voltage for the arc lines. It is probable, however, that the above writers might have observed arc lines in the region of longer wave-lengths.

When the nitrogen arc lines were obtained most readily the tungsten filament decomposed rapidly forming a brownish-black deposit on the leads. As normal nitrogen does not react with tungsten, the abnormal wasting of the filament suggests that active nitrogen was present. Under these conditions even strong spark lines were missing so its seems reasonable to suppose that the active nitrogen was due to neutral atomic nitrogen and not to ionized nitrogen atoms. Moreover, low voltage arcs in pure nitrogen do not-show an abnormal wasting away of the filament. When an excess of nitrogen was mixed with the helium, and the mixture excited, the tungsten leads functioned normally. Thus the active nitrogen must have been due to neutral atoms.

Merton and Pilley reported 114 lines. Of these 28 were reported by Hardtke. Hardtke reported 15 lines not found by Merton and Pilley. We have found 230 lines. All but 7 of the lines reported by Merton and Pilley

---

[8] Duffendack, Phys. Rev. **20**, 665 (1922).

[9] Duncan, Astrophys. J. **62**, 145 (1925).

have been found and 13 additional lines reported by Hardtke and not found by Merton and Pilley. Two of Hardtke's lines remain unverified. Kiess reported 21 lines, three of which were observed by Merton and Pilley. All of these lines have been observed. This leaves in addition 90 lines not previously reported. Since these results were reported at the Chicago meeting of the American Physical Society[10] Ryde has reported a considerable number of the same lines.[11]

The excitation of the arc lines of nitrogen in our discharge, and likewise in Merton and Pilley's, is probably a two step process. The first step is undoubtedly the dissociation of a nitrogen molecule into two neutral atoms. The dissociation of a molecule into a normal atom and an atom excited to one of the initial levels involved in the lines here reported is impossible by this process because an excited helium atom does not possess sufficient energy to do this. The lowest value of the heat of dissociation of a normal nitrogen molecule for which there is any basis[12] is 9.1 volts and the lowest initial level of the lines reported is that of the $3p^4D_{\frac{1}{2}}$ which has an excitation potential of 11.7 volts. Hence 20.8 volts energy is required to dissociate a nitrogen molecule and excite the lines originating in the *lowest* term while a metastable helium atom possesses not more than 20.5 volts energy.

The question then arises as to what is the second step in the excitation process. Two possibilities at once suggest themselves; an electron impact, and a second impact of the second kind. The electron current density in the region of the discharge under consideration was fairly large and the electrons possessed in general, sufficient energy to excite the lines. But the concentration of nitrogen atoms must have been very small; because, in the first place the partial pressure of the nitrogen was usually about 0.01 mm and never more than 0.1 mm and in the second place not all of the nitrogen in this region was atomic. The excitation of the negative bands of nitrogen, belonging to the nigrogen molecule ion, revealed the presence of molecular nitrogen and their intensity leads us to believe that probably not over half the nitrogen in this region was dissociated. As only 0.1 percent to 1 percent of the gas mixture was nitrogen, only one electron impact in a thousand or at most one in a hundred could have involved a nitrogen atom or molecule. Therefore, if the lines were excited by electron impacts, their intensities would be expected to be very low compared with the intensities of the helium lines. While in general the nitrogen lines were weaker than the helium lines, the difference in their intensities was not great.

Another reason for believing that the nitrogen lines were not excited by electron impacts is that the neutral or positive bands of nitrogen were lacking. Since molecular nitrogen must have been present in a concentration at least comparable with that of atomic nitrogen, as revealed by the negative bands in the spectrum, one must account for the failure of the positive bands to appear. The excitation potentials of the positive bands[9] are of the same order as of the arc lines and hence should have been excited by the same stream of electrons. But the positive bands were absent while the negative

---

[10] Duffendack and Wolfe, Phys. Rev. **29**, 209 (1927).

[11] Ryde, Roy. Soc. Proc. **A117**, 164 (1927).

[12] Kaplan, Phys. Rev. **33**, 638 (1929).

bands of higher excitation potentials appeared. The presence of the negative bands and absence of the positive bands leads us to suspect that nitrogen molecules were simultaneously ionized and excited by impacts with metastable helium atoms or helium ions. A similar excitation of the negative bands of carbon monoxide has been observed by Duffendack and Smith[13] in a mixture with helium. Their investigation shows that excitation of negative bands by this process is very great compared with that of the positive and negative bands by electron impacts when helium is the preponderant element of the gas mixture. The reason that the positive nitrogen bands are not excited by metastable helium atoms is that their excitation potentials are considerably below those of the helium atom, whereas the difference between the excitation potentials of the negative bands and the helium atom is less than one volt. Hence the probability that the negative bands would be excited instead of the positive bands is very great. The conclusion from this reasoning is that the nitrogen arc lines were probably not excited by electron impacts and hence must have resulted from second impacts of the second kind with metastable helium atoms.

The view that the nitrogen arc lines were excited by impacts of the second kind with metastable helium atoms aids in an accounting for some of the unclassified lines of the accompanying list. A study of the table shows that there are two important groups yet to be classified, one in the region of 4700A and the other in the region below 4350A. The former group comes at the place where lines for the transition $4p^2(P, D)$ to $3s^2\,P$ would be expected from a consideration of the terms now known with certainty. There is, however, no place for the group in the region below 4350A in the spectrum built on the terms listed in the accompanying paper by Dr. Ingram. But it can be predicted from the Hund theory that there are other terms in the N I spectrum. A series of doublet terms converging at the metastable ^1D term of N II should be fairly important and all of these except the first ones will have negative values and hence high excitation potentials. It would seem quite probable that the unclassified lines in the region below 4350A may belong to the doublet terms of this series. Metastable helium atoms have sufficient energy for their excitation.

Some explanation is needed with regard to the following table. The wavelengths given in the first column are our measurements except for those marked #. Lines marked thus were not found on our plates or were obscured by nearby helium lines or band structure. The intensities given are estimated relative eye intensities as determined from several plates. The letters in the third column indicate other observers who found the same line. The classifications in the last column are those previously published except those marked* which are new. The new classifications are due mainly to Dr. Ingram and the reasons for the assignments are discussed in his paper, which follows. The table has been made as complete as possible for the convenience of those interested in this spectrum.

We wish to acknowledge our indebtedness to the U. S. Bureau of Mines for helium used in this investigation.

---

[13] Duffendack and Smith, Phys. Rev. **34**, 68 (1929).

TABLE I.

Wave-lengths. (I.A.)	Intensity.	Wave-numbers (vacuum)	Other observers	Classification
8729.1	1	11452.79	C	$3s^4P_{1\frac{1}{2}}-3p^4D_{\frac{1}{2}}$
8719.0	2	11466.06	C	$3s^4P_{2\frac{1}{2}}-3p^4D_{2\frac{1}{2}}$
8711.9	2	11475.42	C	$3s^4P_{1\frac{1}{2}}-3p^4D_{1\frac{1}{2}}$
8703.4	2	11486.60	C	$3s^4P_{\frac{1}{2}}-3p^3D_{\frac{1}{2}}$
8686.4	3	11509.11	C	$3s^4P_{\frac{1}{2}}-3p^4D_{1\frac{1}{2}}$
8683.6	4	11512.79	C	$3s^4P_{1\frac{1}{2}}-3p^4D_{2\frac{1}{2}}$
8680.3	5	11517.18	C	$3s^4P_{2\frac{1}{2}}-3p^4D_{3\frac{1}{2}}$
8656.3	2	11549.18	C	$3s^2P_{1\frac{1}{2}}-3p^2P_{\frac{1}{2}}$
8629.5	4	11585.00	C	$3s^2P_{1\frac{1}{2}}-3p^2P_{1\frac{1}{2}}$
8594.3	3	11632.42	C	$3s^2P_{\frac{1}{2}}-3p^2P_{\frac{1}{2}}$
8568.1	2	11668.00	C	$3s^2P_{\frac{1}{2}}-3p^2P_{1\frac{1}{2}}$
8242.5	4	12128.94	C	$3s^4P_{2\frac{1}{2}}-3p^4P_{1\frac{1}{2}}$
8223.3	5	12157.28	C	$3s^4P_{1\frac{1}{2}}-3p^4P_{\frac{1}{2}}$
8216.45	7	12167.36	C	$3s^4P_{2\frac{1}{2}}-3p^4P_{2\frac{1}{2}}$
8210.9	3	12175.59	C	$3s^4P_{1\frac{1}{2}}-3p^4P_{1\frac{1}{2}}$
8200.6	1	12190.89	C	$3s^4P_{\frac{1}{2}}-3p^4P_{\frac{1}{2}}$
8188.2	5	12209.24	C	$3s^4P_{\frac{1}{2}}-3p^4P_{1\frac{1}{2}}$
8185.0	5	12214.11	C	$3s^4P_{1\frac{1}{2}}-3p^4P_{2\frac{1}{2}}$
7468.7	9	13385.54	C B	$3s^4P_{2\frac{1}{2}}-3p^4S_{1\frac{1}{2}}$
7442.6	9	13432.47	C B	$3s^4P_{1\frac{1}{2}}-3p^4S_{1\frac{1}{2}}$
7423.9	5	13466.32	C B	$3s^4P_{\frac{1}{2}}-3p^4S_{1\frac{1}{2}}$
6982.02	00	14318.56		$3p^4P_{1\frac{1}{2}}-5s^4P_{\frac{1}{2}}$*
6979.10	1	14324.55		$3p^4P_{2\frac{1}{2}}-5s^4P_{1\frac{1}{2}}$*
6951.50	1	14381.42		$3p^4P_{\frac{1}{2}}-5s^4P_{1\frac{1}{2}}$*
6945.22	4	14394.43	B	$3p^4P_{2\frac{1}{2}}-5s^4P_{2\frac{1}{2}}$
6926.90	1	14432.50	b	$3p^4P_{1\frac{1}{2}}-5s^4P_{2\frac{1}{2}}$
6874.30	1	14543.93	B	
6793.82	00d	14715.21		$3p^4P_{2\frac{1}{2}}-4d^4F_{3\frac{1}{2}}$*
6777.36	00d	14750.94		
6769.57	00d	14767.92		
6758.60	4	14791.89		$3p^4P_{1\frac{1}{2}}-4d^4D_{2\frac{1}{2}}$*
6752.40	4	14805.47		$3p^4P_{2\frac{1}{2}}-4d^4D_{3\frac{1}{2}}$*
6741.29	3	14829.87		$3p^4P_{1\frac{1}{2}}-4d^4P_{\frac{1}{2}}$*
6733.48	6	14847.07	B	$3p^4P_{\frac{1}{2}}-4d^4P_{\frac{1}{2}}$*
6723.12	9	14869.95	B	$3p^4P_{2\frac{1}{2}}-4d^4P_{2\frac{1}{2}}$*
6713.12	1	14892.10	B	
6708.81	4	14901.67	B	
6706.20	4	14907.47	B	$3p^4P_{1\frac{1}{2}}-4d^4P_{2\frac{1}{2}}$*
6666.75	0d	14995.68		$3p^2P_{1\frac{1}{2}}-5d^2P_{1\frac{1}{2}}$*
6656.61	1	15018.52	B	$3p^4D_{1\frac{1}{2}}-5s^4P_{\frac{1}{2}}$
6653.41	5	15025.75	B	$3p^4D_{2\frac{1}{2}}-5s^4P_{1\frac{1}{2}}$
6646.52	2	15041.32	B	$3p^4D_{\frac{1}{2}}-5s^4P_{\frac{1}{2}}$
6644.96	9	15044.85	B	$3p^4D_{3\frac{1}{2}}-5s^4P_{2\frac{1}{2}}$
6637.01	4	15062.87	B	$3p^4D_{1\frac{1}{2}}-5s^4P_{1\frac{1}{2}}$
6627.02	0	15085.58	B	$3p^4D_{\frac{1}{2}}-5s^4P_{1\frac{1}{2}}$
6622.53	3	15095.81	B	$3p^4D_{2\frac{1}{2}}-5s^4P_{2\frac{1}{2}}$
6612.63	00?	15118.41		
6606.77	00	15131.82		$3p^4D_{1\frac{1}{2}}-5s^4P_{2\frac{1}{2}}$?*
6580.70	0	15191.76		
6544.77	0d	15275.16		
6534.12	0d	15300.05		
6506.45	0	15365.13		$3p^4D_{3\frac{1}{2}}-4d^4F_{3\frac{1}{2}}$*
6499.52	3	15381.51	B	$3p^4D_{2\frac{1}{2}}-4d^4F_{2\frac{1}{2}}$
6491.28	3	15401.03	B	$3p^4D_{1\frac{1}{2}}-4d^4F_{1\frac{1}{2}}$
6484.88	9	15416.23	B	$3p^4D_{2\frac{1}{2}}-4d^4F_{3\frac{1}{2}}$
6483.75	3	15418.92	B	$3p^4D_{1\frac{1}{2}}-4d^4F_{2\frac{1}{2}}$
6482.74	9	15421.32	B	$3p^4D_{3\frac{1}{2}}-4d^4F_{4\frac{1}{2}}$
6481.73	2	15423.73	B	$3p^4D_{\frac{1}{2}}-4d^4F_{1\frac{1}{2}}$
6480.50	0	15426.65	B	$3p^4D_{1\frac{1}{2}}-4d^4D_{\frac{1}{2}}$
6471.03	1	15449.23	B	$3p^4D_{\frac{1}{2}}-4d^4D_{\frac{1}{2}}$
6468.32	4	15455.70	B	$\begin{cases}3p^4D_{3\frac{1}{2}}-4d^4D_{3\frac{1}{2}}\\3p^4D_{2\frac{1}{2}}-4d^4D_{2\frac{1}{2}}\end{cases}$
6462.83	0	15468.83	B	

TABLE I. (Continued)

Wave-lengths (I.A.)	Intensity	Wave-numbers (vacuum)	Other observers	Classification
6457.93	3	15480.57	B	$3p^4D_{1\frac{1}{2}}-4d^4D_{1\frac{1}{2}}$
6452.75	1	15493.00	B	$3p^4D_{1\frac{1}{2}}-4d^4D_{2\frac{1}{2}}$
6448.49	0	15503.23	B	$3p^4D_{\frac{1}{2}}-4d^4D_{1\frac{1}{2}}$
6441.70	5	15519.57	B	$3p^4D_{3\frac{1}{2}}-4d^4P_{2\frac{1}{2}}$
6440.95	3	15521.38	B	
6437.01	4	15530.88	B	$3p^4D_{1\frac{1}{2}}-4d^4P_{\frac{1}{2}}$*
6428.05	00	15552.53		$3p^4D_{\frac{1}{2}}-4d^4P_{\frac{1}{2}}$*
6422.93	3	15564.93		
6420.47	3	15570.89	B	$3p^4D_{2\frac{1}{2}}-4d^4P_{2\frac{1}{2}}$
6417.05	2	15579.19	B	
6411.53	0	15592.60		
6321.70	00	15814.17		$3p^4S_{1\frac{1}{2}}-6s^4P_{\frac{1}{2}}$*
6303.68	0	15859.37	B	$3p_4S_{1\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$
6298.30	0	15872.92		
6289.27	00	15895.71		
6285.78	1	15904.53	B	
6283.06	00	15911.42		
6279.42#	—	15920.63	B	
6275.43	1	15930.77	B	$3p^4S_{1\frac{1}{2}}-6s^4P_{2\frac{1}{2}}$
6272.83	1	15937.37	B	$3p^2D_{2\frac{1}{2}}-5d^2P_{1\frac{1}{2}}$*
6075.83	3	16454.11	B	
6017.70	2	16613.05	B	
6015.40	1	16619.41		
6008.48	10	16638.54	B	$3p^2S_{\frac{1}{2}}-4d^2P_{1\frac{1}{2}}$*
5999.47	6	16663.53	B	$3p^2S_{\frac{1}{2}}-4d^2P_{\frac{1}{2}}$*
5962.15	00	16767.84		
5941.94	0	16824.87		
5927.50	0	16865.86		
5856.23	1	17071.11		$3p^4P_{1\frac{1}{2}}-6s^4P_{\frac{1}{2}}$*
5854.16	2	17077.15		$3p^4P_{2\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$*
5841.01	2	17115.59		$3p^4P_{1\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$*
5834.71	1	17134.07	A	$3p^4P_{\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$*
5829.53	6	17149.30	B	$3p^4P_{2\frac{1}{2}}-6s^4P_{2\frac{1}{2}}$
5816.48	2	17187.78		$3p^4P_{1\frac{1}{2}}-6s^4P_{2\frac{1}{2}}$*
5793.51	1	17255.92		
5752.64	4	17378.52	B	$3p^4P_{2\frac{1}{2}}-5d^4P_{2\frac{1}{2}}$*
5747.36	2	17394.48		$3p^4S_{1\frac{1}{2}}-7s^4P_{2\frac{1}{2}}$*
5740.65	2	17414.81		
5735.63	1	17430.05		
5710.77#	–	17505.93	B	
5694.24	0	17556.75		
5686.19	0	17581.60	B	
5667.04	1	17641.01		
5648.68	0	17698.35		
5625.43	2	17771.50	B	$3p^4D_{1\frac{1}{2}}-6s^4P_{\frac{1}{2}}$
5623.20	4	17778.55	B	$3p^4D_{2\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$
5618.18	1	17794.44	B	$3p^4D_{\frac{1}{2}}-6s^4P_{\frac{1}{2}}$
5616.54	5	17799.63	B	$3p^4D_{3\frac{1}{2}}-6s^4P_{2\frac{1}{2}}$
5611.36	1	17816.06	B	$3p^4D_{1\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$
5604.28	0	17838.57		$3p^4D_{\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$*
5600.54	0	17850.48		$3p^4D_{2\frac{1}{2}}-6s^4P_{2\frac{1}{2}}$*
5567.63#	1	17955.97	B	
5564.37	9	17966.51	A B	$3p^4D_{2\frac{1}{2}}-5d^4F_{3\frac{1}{2}}$?*
5563.84#	3d	17968.21	B	
5560.37	9	17979.44	A B	$3p^4D_{3\frac{1}{2}}-5d^4F_{4\frac{1}{2}}$?*
5557.44	2	17988.92	B	
5551.34	0d	18008.68		
5548.18	00	18018.93		
5545.11	3	18028.91	A B	$3p^4D_{3\frac{1}{2}}-5d^4P_{2\frac{1}{2}}$*
5540.36	1	18044.37		
5535.37	1	18060.64		
5530.10	0d	18077.85		

TABLE I. (Continued)

Wave-lengths (I.A.)	Intensity	Wave-numbers (vacuum)	Other observers	Classification
5378.45	0	18587.56	B	$sp^4\,{}^4P_{\frac{1}{2}}-4p^4D_{\frac{1}{2}}*$
5372.66	3d	18607.59	A B	$sp^4\,{}^4P_{\frac{1}{2}}-4p\,{}^4D_{1\frac{1}{2}}*$
5371.10	1	18613.00		$3p^4P_{2\frac{1}{2}}-7s^4P_{2\frac{1}{2}}*$
5367.27	1	18626.28	A B	$sp^4\,{}^4P_{1\frac{1}{2}}-4p^4D_{1\frac{1}{2}}*$
5356.77	5	18662.78	A B	$sp^4\,{}^4P_{1\frac{1}{2}}-4p^4D_{2\frac{1}{2}}*$
5344.23	00	18706.58		$sp^4\,{}^4P_{2\frac{1}{2}}-4p^4D_{2\frac{1}{2}}*$
5334.42	1	18740.98		$3p^4P_{2\frac{1}{2}}-6d^4P_{2\frac{1}{2}}*$
5328.70	5	18761.10	A B	$sp^4\,{}^4P_{2\frac{1}{2}}-4p^4D_{3\frac{1}{2}}*$
5310.52	1	18825.32	B	$sp^4\,{}^4P_{\frac{1}{2}}-4p^4P_{1\frac{1}{2}}*$
5309.48	1	18829.01	A B	$sp^4\,{}^4P_{1\frac{1}{2}}-4p^4P_{\frac{1}{2}}*$
5292.75	0d	18888.53	A B	$\left\{\begin{array}{l}sp^4\,{}^4P_{2\frac{1}{2}}-4p^4P_{1\frac{1}{2}}*\\sp^4\,{}^4P_{1\frac{1}{2}}-4p^4P_{2\frac{1}{2}}*\end{array}\right.$
5281.18	3	18929.91	A B	$sp^4\,{}^4P_{2\frac{1}{2}}-4p^4P_{2\frac{1}{2}}*$
5201.71	2	19219.11	B	$3p^2S_{\frac{1}{2}}-5d^2P_{1\frac{1}{2}}*$
5200.00	0	19225.43		
5197.00#	00	19236.53	B	
5189.51	1	19264.29		$3p^4D_{3\frac{1}{2}}-7s^4P_{2\frac{1}{2}}?*$
5181.47	0	19294.18	A	$sp^4\,{}^4P_{1\frac{1}{2}}-4p\,{}^4S_{1\frac{1}{2}}*$
5179.61	00	19301.11		
5169.45	1	19339.05	A	$sp^4\,{}^4P_{2\frac{1}{2}}-4p^4S_{1\frac{1}{2}}*$
5162.78	1	19364.03		
4935.03	10	20257.68	A B	$3s^2P_{1\frac{1}{2}}-4p^2S_{\frac{1}{2}}$
4914.90	5	20340.63	A B	$3s^2P_{\frac{1}{2}}-4p^2S_{\frac{1}{2}}$
4886.30	2	20459.69		
4881.79	1	20478.58	B	
4868.92	00	20532.72	B	
4855.43#	0d	20589.77	B	
4847.38	2	20623.96		
4837.93	1	20664.24		
4831.16	1d	20693.20	B	
4753.13	2	21032.91	B	
4750.26	2	21045.62	B	
4744.04	3?	21073.20		
4742.90	2	21078.27	B	
4736.04	0	21108.80	B	
4734.20	0	21117.00		
4731.22	1	21130.30		
4685.74	3	21335.39		
4669.77	3	21408.36	A	
4660.05	2	21453.01	A	
4657.72	1	21463.74		
4656.65	1	21468.68		
4651.08	1	21494.39		
4625.61	1	21612.74		
4554.21	1	21951.57		
4553.38	1	21955.58		
4503.53	1	22198.60		
4502.27	2	22204.82		
4499.08	0	22220.56		
4497.45	1	22228.60		
4494.67	5	22242.35	B	
4492.40	7	22253.59	B	
4485.09	0	22289.86	A	
4466.56	0	22382.34	A	
4365.80	0	22898.90		
4358.27	10	22938.46	B	
4343.41	1	23016.94		
4336.48	5	23053.71	A B	
4324.89	0	23115.49	A	
4321.99	1	23131.01		
4317.70	5	23153.99	A B	
4313.11	4	23178.63	A B	
4305.46	6	23219.82	A B	

TABLE I. (Continued)

Wave-lengths (I.A.)	Intensity	Wave-numbers (vacuum)	Other observers	Classification
4284.92	2	23331.12	B	
4282.20#	1	23345.92	B	
4281.39	2	23350.35	B	
4253.28	4	23504.68	B	$3s^4P_{2\frac{1}{2}}-4p^4D_{3\frac{1}{2}}^*$
4236.04	0	23600.33		
4230.35	4	23632.07	B	$3s^4P_{2\frac{1}{2}}-4p^4P_{1\frac{1}{2}}^*$
4229.59	2	23636.32		
4224.74	4	23663.45	B	$3s^4P_{1\frac{1}{2}}-4p^4P_{\frac{1}{2}}^*$
4223.04	5	23672.98	A B	$3s^4P_{2\frac{1}{2}}-4p^4P_{2\frac{1}{2}}^*$
4220.79	2	23685.60		
4215.92	2	23712.96	A	$3s^4P_{\frac{1}{2}}-4p^4P_{1\frac{1}{2}}^*$
4214.73	5	23719.65		$3s^4P_{1\frac{1}{2}}-4p^4P_{2\frac{1}{2}}^*$
4213.0#	–	23729.4	A	
4209.05	1	23751.67		
4206.29	1	23767.26		
4205.65	2d	23770.86		
4193.49	3	23839.79	A	
4187.06	1d	23876.40	A	
4180.0#	–	23916.7	A	
4166.64	1	23993.41	A	
4164.74	0	24004.36		
4151.46	12	24081.15	A B	$3s^4P_{2\frac{1}{2}}-4p^4S_{1\frac{1}{2}}^*$
4145.78	2	24114.14	A	
		[24127.87]	obscured by helium	$3s^4P_{1\frac{1}{2}}-4p^4S_{1\frac{1}{2}}^*$
4137.63	7	24161.64	A B	$3s^4P_{\frac{1}{2}}-4p^4S_{1\frac{1}{2}}^*$
4129.16	1	24211.20		
4114.00	6	24300.41	A B	$3s^2P_{1\frac{1}{2}}-(^1D)3p\,^2D_{1\frac{1}{2}}$
4109.98	12	24324.18	A B	$3s^2P_{1\frac{1}{2}}-(^1D)3p\,^2D_{2\frac{1}{2}}$
4102.18	2	24370.43		
4099.94	9	24383.74	A B	$3s^2P_{\frac{1}{2}}-(^1D)3p\,^2D_{1\frac{1}{2}}$
4041.30	0	24737.55		
4037.35	1	24761.75	B	
4033.64	1	24784.53		
4019.10	0	24874.19		
4015.08	0	24899.09		
4010.99	2	24924.48	A B	
4001.65	1	24982.66		
3999.98	4	24993.08	B	
3994.86	3	25025.11		
3969.95	1	25182.14		
3957.20	3	25263.27	B	
3952.21	3	25295.17	B	
3869.10	4	25838.51	B	
3834.84	2	26069.34		
3834.24	4	26073.42	B	$3s^2P_{1\frac{1}{2}}-(^1D)3p^2P_{\frac{1}{2}}$
3830.39	9	26099.63	B	$3s^2P_{1\frac{1}{2}}-(^1D)3p^2P_{1\frac{1}{2}}$
3822.07	6	26156.44	B	$3s^2P_{\frac{1}{2}}-(^1D)3p^2P_{\frac{1}{2}}$
3818.27	2	26182.47	B	$3s^2P_{\frac{1}{2}}-(^1D)3p^2P_{1\frac{1}{2}}$
3687.88	2	27108.16		
3681.10	3	27158.09	B	
3650.19	5	27388.06	B	
3545.62	2	28195.79	B	
3532.65	4	28299.30	B	
3437.14	4	29085.64	B	
Classified lines measured by Ryde.				
5304.9	1	18845.3		$sp^4\,^4P_{1\frac{1}{2}}-4p^4P_{1\frac{1}{2}}^*$
5187.1	1	19273.2		$sp^4\,^4P_{\frac{1}{2}}-4p^4S_{1\frac{1}{2}}^*$
4254.7	4	23496.5		$\begin{cases}3s^4P_{1\frac{1}{2}}-4p^4D_{2\frac{1}{2}}^*\\3s^4P_{\frac{1}{2}}-4p^4D_{1\frac{1}{2}}^*\end{cases}$
4143.4	–	24127.87		$3s^4P_{1\frac{1}{2}}-4p^4S_{1\frac{1}{2}}^*$

A—Hardtke
B—Merton and Pilley
C—Kiess