SINGLET ELECTRONIC STATES OF THE *TiO* MOLECULE

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ABSTRACT

Rotational analyses of the bands in the spectrum of the *TiO* molecule at 8859 A and 5597 A have made it possible to identify the corresponding electronic transitions as $^1\Pi - {}^1\Delta$ and $^1\Phi - {}^1\Delta$, respectively. The two transitions have a common lower state. The resulting rotational constants are presented in Table 3. It is shown that the two bands are the (0–0) bands of the respective systems. Additional bands of the two systems are listed in Tables 5 and 6. The excitation energies, ν_{00}, of the $^1\Pi$- and $^1\Phi$-states are 11,272.77 and 17,840.60 cm^{-1}, above the $^1\Delta$-state, respectively.

A. INTRODUCTION

Up to the present time, three band systems have been identified in the spectrum of the *TiO* molecule: (1) the α-system ($^3\Pi - {}^3\Pi$) in the blue-green region, analyzed by Christy;[1] (2) the β-system in the yellow; and (3) the γ-system in the infrared. A vibrational analysis carried out by Lowater[2] showed that the γ-system was associated with a $^3\Sigma - {}^3\Pi$ transition, the lower ($^3\Pi$) state being the same as the lower state of the α-system. The β-system consists of a single sequence of bands degraded to the red, with the head of the most intense band at 5597 A. Each band in the sequence has an intense Q head and a weaker R head. From the appearance of the bands Lowater has suggested that they constitute the main sequence of a $^1\Pi - {}^1\Sigma$ transition, the most intense band at 5597 A being the (0–0) band. All three of these band systems are present in the spectra of M-type stars.

The γ-system has been found by Wurm and Meister[3] to extend to 8646 A. They have also found a large number of additional bands extending to 11,238 A. Recently, Kiess[4] reported on a series of improved measurements of the heads of a number of these bands, extending to 9602 A. The most intense of these new bands are also found in the spectra of M-type stars.[5] Of particular interest is a sequence of intense bands, starting at 8859 A and degrading to the red.

No positive identifications of any of the bands beyond 8646 A have been made up to the present time, although some suggestions have been offered. Dobronravin[6] has attempted to place the sequence at 8859 A, together with others in the same region of the spectrum, into a new triplet system ($^3\Sigma - {}^3\Pi$), with the same lower state as the α-system, while Wurm and Meister have suggested that this sequence might be associated with a singlet system. This latter suggestion raises an interesting possibility. The sequence of bands at 8859 A has a general appearance which is quite similar to that of the β-system. Furthermore, just as in the case of the β-system, no additional sequences of comparable intensity and appearance are found in the same region of the spectrum. Therefore, if the suggestion of Wurm and Meister is valid, it is likely that the 8859 A sequence is a main sequence of a new singlet transition, with the (0–0) band at 8859 A. Both the 8859 A

[1] Andrew Christy, *Phys. Rev.*, **33**, 701, 1929.

[2] F. Lowater, *Proc. Phys. Soc. London*, **41**, 557, 1927.

[3] Karl Wurm and H. J. Meister, *Zs. f. Ap.*, **13**, 199, 1936.

[4] C. C. Kiess. Paper read before the American Astronomical Society, Pasadena, Calif., 1948.

[5] See, e.g., Paul W. Merrill, *Ap. J.*, **79**, 183, 1934.

[6] P. P. Dobronravin, *C.R. Acad. Sci. U.S.S.R.*, **17**, 399, 1937.

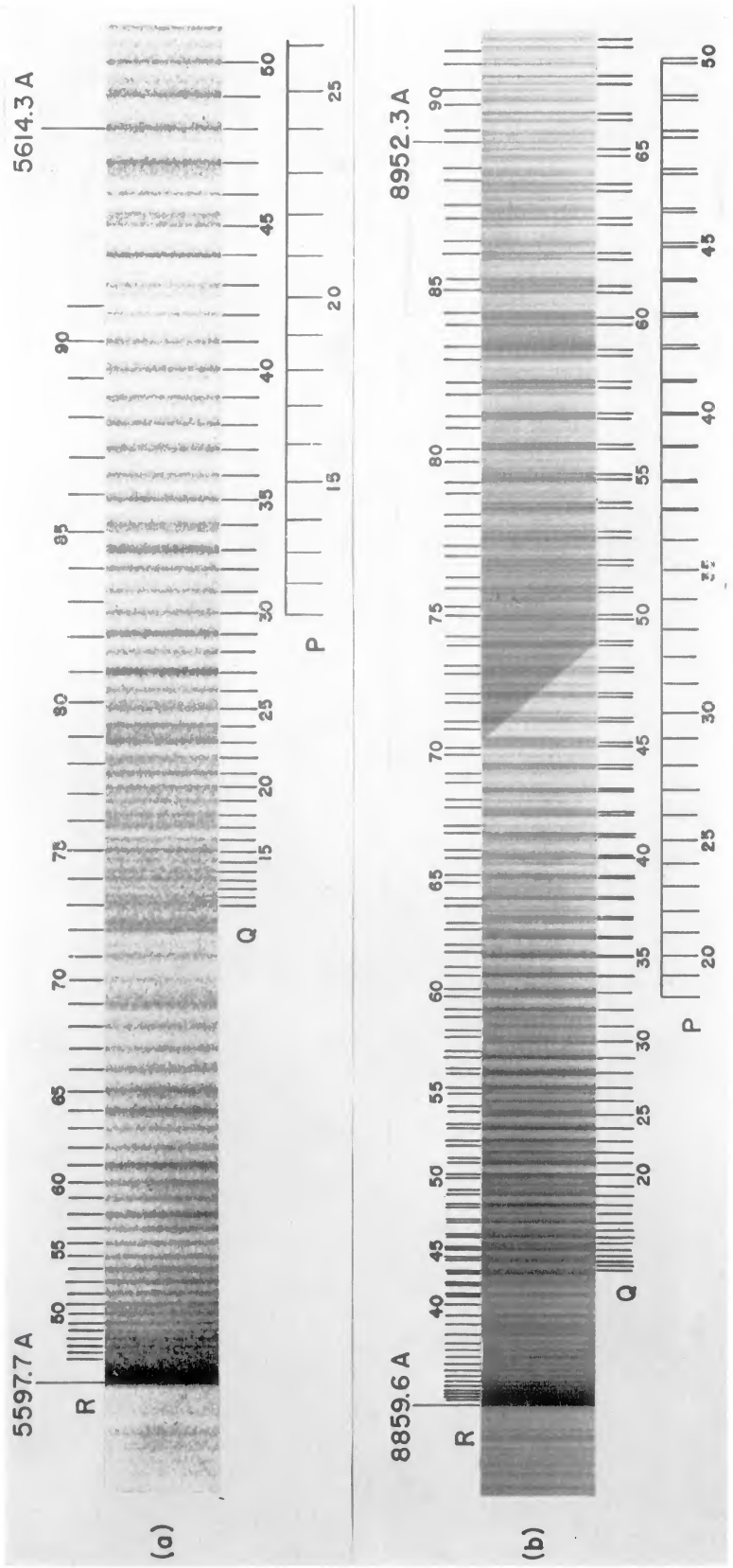

FIG. 1.—The spectra of two singlet bands of *TiO*. *a*, the (0, 0) band of the $^1\Phi - {}^1\Delta$ system at 5597 A; *b*, the (0, 0) band of the $^1\Pi - {}^1\Delta$ system at 8859 A. In each spectrum the leading lines show the positions of the lines in each of the three branches.

band and the 5597 A band are present in absorption in the spectra of M-type stars, so that their lower states are certainly not greatly different in energy. Indeed, the possibility exists that the two bands have a lower state in common..

It is important to show which of the two suggestions mentioned above is correct. This may be done by carrying out a rotational analysis of the band at 8859 A. A comparison of combination differences with those of the α-system would then show whether or not the suggestion of Dobronravin is correct. Also, by carrying out a rotational analysis of the 5597 A band, a similar comparison of the combination differences of the 8859 A band and the 5597 A band would show whether these two bands have a state in common.

These two investigations were accordingly undertaken, in the hope that they would result in the determination of the transition associated with the sequence at 8859 A.

B. EXPERIMENTAL

The source that was used to produce the spectrum of *TiO* was a high-tension a.c. arc. The arc consisted of two carbon electrodes, with a piece of titanium metal in a depression in the top of the lower electrode. The arc was connected directly to the secondary of a 4800-volt, 5-kva transformer. A 7-ohm resistance was placed in series with the 220-volt primary of the transformer. It was found, quite by accident, that, if an ordinary Bunsen flame fed with natural gas was played on the burning arc from the side and the spectrum taken of the extremity of the bow formed by the arc as a result of the blast of the burner, the atomic lines of titanium were considerably reduced in intensity, while the spectrum of the oxide was greatly enhanced. This technique was followed in obtaining all the exposures used in this study.

The spectrograms were taken with the 21-foot grating spectrograph. The 5597 A band was photographed in the second order with a dispersion of 1.25 A per millimeter. Exposure times ranged from 20 seconds to 1 minute with 103*a*-F emulsions. The 8859 A band was photographed in the first order, with a dispersion of 2.5 A per millimeter. Using sensitized I-N plates, the exposure times that were required ranged up to 25 minutes in duration.

C. ROTATIONAL ANALYSIS OF THE 8859 A BAND

The measurements made of the 8859 A and 5597 A bands are presented in Tables 1 and 2, respectively. The method used to obtain the correct J values of the 5597 A band will be described later. In the case of the 8859 A band the analysis was carried out in the following manner: As can be seen in Figure 1, the band degrades to the red, has an intense Q branch, and weaker R and P branches. No difficulty was experienced in obtaining the correct rotational numbering. In the case of the Q and P branches, this was obtained immediately, since only short extrapolations to the band origin were required. In the case of the R branch, lines with low J were masked by the more intense lines in the part of the branch returning from the head, so the following procedure was used to obtain the J values. It will be noticed in Figure 1 that each of the branches experiences a splitting into two components for large J. When the magnitude of the doubling in the Q and P branches was plotted against $J(J + 1)$, the plot presented in Figure 2 was obtained. The points exhibited considerable scatter, but a straight line through the origin represented the observations quite well. This shows that the splitting is caused by Λ-type doubling and not by spin doubling, because in the latter case a plot of splitting versus J would be a straight line through the origin. Furthermore, for a given J, the doubling is the same for the Q and P branches, within the error of observation. Therefore, as will be shown in greater detail later, one of the two electronic levels involved in the transition must have negligible Λ-type doubling. This circumstance makes it possible to use the Q and P

TABLE 1

WAVE NUMBERS OF THE LINES IN THE 8859 A BAND

J	$R_{ab}(J)$	$R_{ba}(J)$	$Q_a(J)$	$Q_b(J)$	$P_{ab}(J)$	$P_{ba}(J)$
7.....			11271.49 cm^{-1}			
8.....			271.06			
9.....			270.67			
10.....			270.13			
11.....			269.60			
12.....			268.96			
13.....			268.37			
14.....			267.67			
15.....			267.01			
16.....			266.19			
17.....			265.36			
18.....			264.46			
19.....			263.58		11244.09 cm^{-1}	
20.....			262.56		242.14	
21.....			261.51		240.11	
22.....			260.51		238.01	
23.....			259.43		235.89	
24.....			258.28		233.70	
25.....	11283.62 cm^{-1}		257.05		231.47	
26.....	283.37		255.76		229.13	
27.....	283.06		254.48		226.74	
28.....	282.71		253.12		224.52	
29.....	282.34		251.65		222.03	
30.....	281.90		250.24		219.63	
31.....	281.40		248.73		217.06	
32.....	280.85		247.22		214.46	
33.....	280.31		245.60		211.88	
34.....	279.61		11243.88	11244.09	11209.12	11209.32
35.....	278.98		242.14	242.33	11206.53	
36.....	278.13		240.38	240.59	203.79	
37.....	277.35		238.56	238.79	11200.81	11201.03
38.....	276.52		236.69	236.96	198.10	198.42
39.....	275.74		234.76	235.06	194.89	195.38
40.....	11274.66	11274.95	232.84	233.16	192.06	192.37
41.....	273.69	273.95	230.86	231.13	189.04	189.26
42.....	272.62	272.89	228.81	229.13	185.92	186.31
43.....	271.49	271.82	226.74	226.98	182.86	183.19
44.....	270.41	270.67	224.52	224.88	179.72	180.02
45.....	269.28	269.60	222.34	222.68	176.49	176.82
46.....	267.99	268.37	220.09	220.44	173.30	173.60
47.....	266.66	267.01	217.80	218.16	169.93	170.27
48.....	265.36	265.71	215.46	215.83	166.53	166.94
49.....	263.92	264.26	213.06	213.44	163.19	163.54
50.....	262.56	262.91	210.63	211.02	159.75	160.20
51.....	261.05	261.51	208.11	208.54	156.20	156.57
52.....	259.43	259.89	205.58	206.02	152.65	153.07
53.....	257.86	258.28	202.97	203.42	149.12	149.50
54.....	256.22	256.68	200.34	200.81	145.48	145.88
55.....	254.48	255.02	197.63	198.10	141.73	142.20
56.....	252.73	253.31	194.89	195.38	138.04	138.48
57.....	250.99	251.65	192.06	192.61	134.22	134.72
58.....	249.14	249.75	189.26	189.77	130.31	130.89
59.....	247.22	247.79	186.31	186.87	126.49	127.00
60.....	245.23	246.08	183.38	183.96	122.59	123.10
61.....	243.27	243.88	180.38	180.95	118.52	119.13
62.....	241.22	241.82	177.36	177.96	114.49	115.05
63.....	239.14	239.76	174.22	174.85	110.37	110.99
64.....	236.96	237.60	171.08	171.73	106.11	106.80

TABLE 1—*Continued*

J	$R_{ab}(J)$	$R_{ba}(J)$	$Q_a(J)$	$Q_b(J)$	$P_{ab}(J)$	$P_{ba}(J)$
65.....	11234.76 cm^{-1}	11235.43 cm^{-1}	11167.90 cm^{-1}	11168.55 cm^{-1}		
66.....	232.48	233.16	164.65	165.35		
67.....	230.18	230.86	161.34	162.03		
68.....	227.85	228.53	158.00	158.69		
69.....	225.39	226.19	154.62	155.34		
70.....	222.95	223.74	151.14	151.89		
71.....	220.44	221.20	147.65	148.44		
72.....	217.80	218.65	144.18	144.87		
73.....	.....	216.15	140.52	141.31		
74.....	212.58	213.44	136.87	137.67		
75.....	209.86	210.63	133.18	133.99		
76.....	207.08	208.11	129.42	130.31		
77.....	204.32	205.14	125.60	126.49		
78.....	201.34	202.34	121.75	122.59		
79.....	198.42	199.35	117.79	118.75		
80.....	195.38	196.44	113.86	114.79		
81.....	192.37	193.37	109.85	110.77		
82.....	189.26	190.30	105.77	106.80		
83.....	185.92	187.30				
84.....	182.86	183.96				
85.....	179.72	180.75				
86.....	176.14	177.36				
87.....	172.98	174.22				
88.....	169.63	170.77				
89.....	166.19	167.29				
90.....	162.54	163.88				
91.....	159.04	160.20				
92.....	155.34	156.57				
93.....	151.89	153.07				

branches to derive two sets of combination differences, $\Delta_1F_r''(J)$ and $\Delta_1F_v''(J)$, using the equations

$$\Delta_1F_r''(J) = Q_r(J) - P_r(J+1),$$

$$\Delta_1F_v''(J) = Q_v(J) - P_v(J+1),$$

where the subscripts r and v refer to the components of each doublet to long and short wave lengths, respectively. The combination differences $\Delta_1F_r''(J)$ and $\Delta_1F_v''(J)$ derived in this way were then used to compute an R branch. It was found that the computed and observed R branches agreed within the error of measurement, so that the corresponding numbering could be assigned to the observed R branch. The doublet splitting of the R branch is also plotted in Figure 2. The resulting points fall on the same straight line as do the Q and P branches. The final rotational numbering of the three branches is included in Table 1.

As mentioned above, for a given J the doublings of the R and P branches are the same as that of the Q branch, within the accuracy of the measurements. Now, if both the upper and the lower states involved in the transition exhibited Λ-type doubling of comparable magnitude, then the doublet separation, in the case of the Q branch, would be equal to the sum of the Λ-type doublings of the corresponding upper and lower rotational levels, and equal to their difference in the case of the R and P branches. The fact that the R and P branches exhibit the same amount of splitting as does the Q branch shows that one of the electronic states must have negligible Λ-type doubling, as compared with that of the other state. Furthermore, the presence of a strong Q branch shows that $\Delta\Lambda$

between the upper and lower state must be ± 1. These two facts together show that the transition is between a Π- and a Δ-state, since a Δ-state usually has a negligibly small Λ-type doubling as compared with that of a Π-state.

Without further information it cannot be ascertained whether the Π-state is the upper or the lower state. The relative intensities of the R and P branches cannot be used, since the I-N emulsion changes rapidly in sensitivity through this region of the spectrum. The two possibilities are illustrated in Figure 3, which shows the nomenclature to be used in the two cases. For simplicity, singlet states are shown in Figure 3. A similar nomenclature can be used in the case of a sub-band of a triplet system. Since it is impossible to apply the criteria proposed by Mulliken[7] for designating the two series into which the

TABLE 2

WAVE NUMBERS OF THE LINES IN THE 5597 A BAND

J	$R(J)$	$Q(J)$	$P(J)$	J	$R(J)$	$Q(J)$	$P(J)$
9...		17839.28 cm^{-1}		51...	17856.30 cm^{-1}	17802.39 cm^{-1}	
10...		838.98		52...	855.85	800.86	
11...		838.61	17826.93 cm^{-1}	53...	855.37	99.35	
12...		838.24	825.66	54...	854.84	797.81	
13...		837.85	824.27	55...	854.32	796.26	
14...		837.47	822.89	56...	853.73	794.68	
15...		837.02	821.44	57...	853.13	793.06	
16...		836.53	819.84	58...	852.52	791.35	
17...		836.02	818.33	59...	851.85	789.75	
18...		835.51	816.75	60...	851.15	787.96	
19...		834.94	815.15	61...	850.44	786.28	
20...		834.34	813.43	62...	849.69	784.50	
21...		833.78	811.89	63...	848.87	782.72	
22...		833.11	810.14	64...	848.11	780.85	
23...		832.41	808.30	65...	847.28	779.05	
24...		831.69	806.61	66. .	846.35	777.18	
25...		830.99	804.97	67...	845.46	775.21	
26...		830.21	803.06	68...	844.53	773.27	
27. .		829.42	801.36	69...	843.59	771.28	
28		828.58	799.35	70...	842.56	769.26	
29.		827.84	797.57	71...	841.56	767.27	
30.		826.93	795.60	72...	840.47	765.20	
31.		826.04	793.69	73...	839.28	763.08	
32...		825.10	791.84	74...	838.24	760.93	
33...		824.27	789.75	5...	837.02		
34. .		823.20	787.74	76...	835. 3		
35		822.17	785.76	77 ..	834.60		
36.		821.14	783.62	78...	833.34		
37..		820.08	781.59	79...	832.00		
38...		819.01	779.45	80...	830.69		
39...		817.87	777.18	81...	829.42		
40...		816.75	775.21	82...	827.84		
41...		815.56	772.89	83...	826.47		
42...		814.35	770.66	84...	825.10		
43...		813.12	768.42	85...	823.48		
44. .		811.89	766.13	86...	821.91		
45...	17858.41 cm^{-1}	810.61	763.87	87...	820.40		
46...	858.15	809.29	761.56	88...	818.70		
47...	857.82	807.97		89...	817.10		
48...	857.47	806.61		90...	815.56		
49...	857.12	805.19		91...	813.99		
50...	856.75	803.78					

[7] Robert S. Mulliken, *Rev. Mod. Phys.*, **3**, 89, 1937.

rotational levels of the Π-state are split as *c* or *d* levels, the temporary symbols *a* and *b* must be used. The lower series is designated by the symbol *a* and the upper series by the symbol *b*. For the Δ-state these two series are superimposed.

The first few members of each of the six branches are shown in Figure 3. In the case of a Π — Δ transition, the violet components of the doublet are $R_{ba}(J)$, $Q_b(J)$, and $P_{ba}(J)$, and the red components $R_{ab}(J)$, $Q_a(J)$, and $P_{ab}(J)$. The violet components all arise from the *b* series, and the red components from the *a* series. An analogous situation arises in the case of a Δ — Π transition.

In the case of a Π — Δ transition, the combination differences $\Delta_2F_a'(J)$ and $\Delta_2F_a''(J)$ are found by combining the $R_{ab}(J)$ and $P_{ab}(J)$ components of the doublets, and, similarly, the $R_{ba}(J)$ and $P_{ba}(J)$ components are to be combined to find the differences $\Delta_2F_b'(J)$ and $\Delta_2F_b''(J)$. Similar relationships can be derived in the case of a Δ — Π transition.

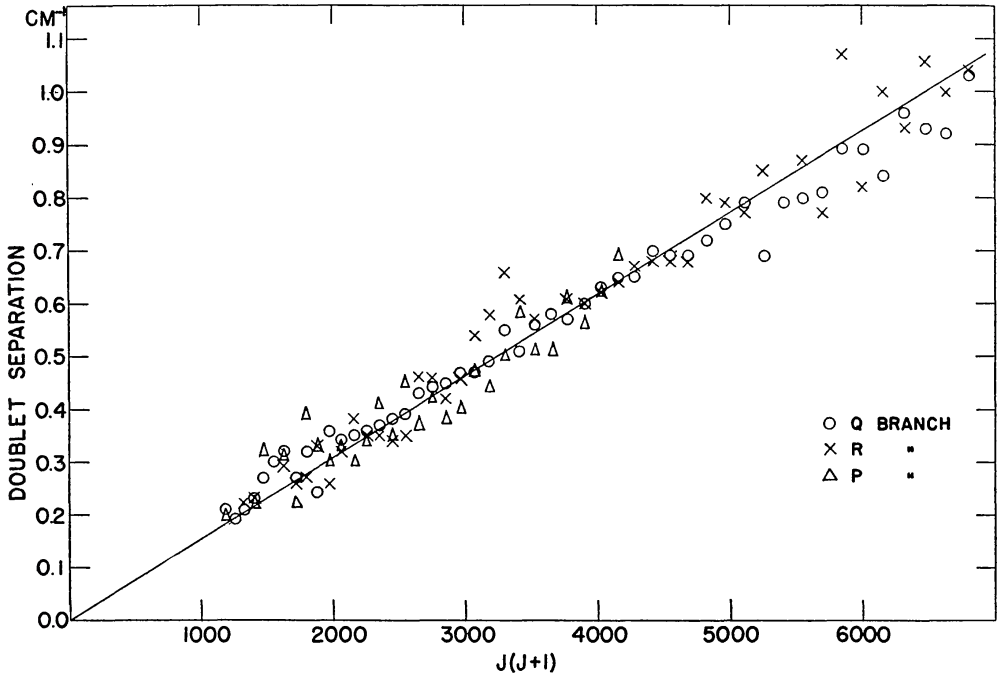

FIG. 2.—Doublet separations of the lines of the 8859 A band

The usual methods were used to derive the approximate rotational constants $\overline{B}'$, $\overline{B}''$, $\overline{D}'$, and $\overline{D}''$; the band origin, ν_0; and the differences $(B' - B'')$ and $(D' - D'')$, from which more accurate constants could be derived. The details will not be presented here.[8] The differences $(B' - B'')$ and $(D' - D'')$ between the rotational constants B_a', B_b', D_a', and D_b' of the upper state and B_a'', B_b'', D_a'', and D_b'' of the lower state could be determined quite accurately. However, on account of the observational scatter of the measurements, the determination of the approximate constants could not be carried out accurately enough to make it possible to decide from this one band whether the Δ-state was the upper or the lower state. Both interpretations led to a set of rotational constants which represented the observations equally well. It will be shown later, however, that it can be ascertained that the Δ-state is the lower state, so that the band is associated with a Π — Δ transition. With this interpretation, it was possible to derive the constants found in the second and third columns of Table 3. In the case of the Π-state, the constant

[8] See, e.g., G. Herzberg, *Molecular Spectra and Molecular Structure*, I (New York: Prentice-Hall Book Co., Inc., 1939), 183 ff.

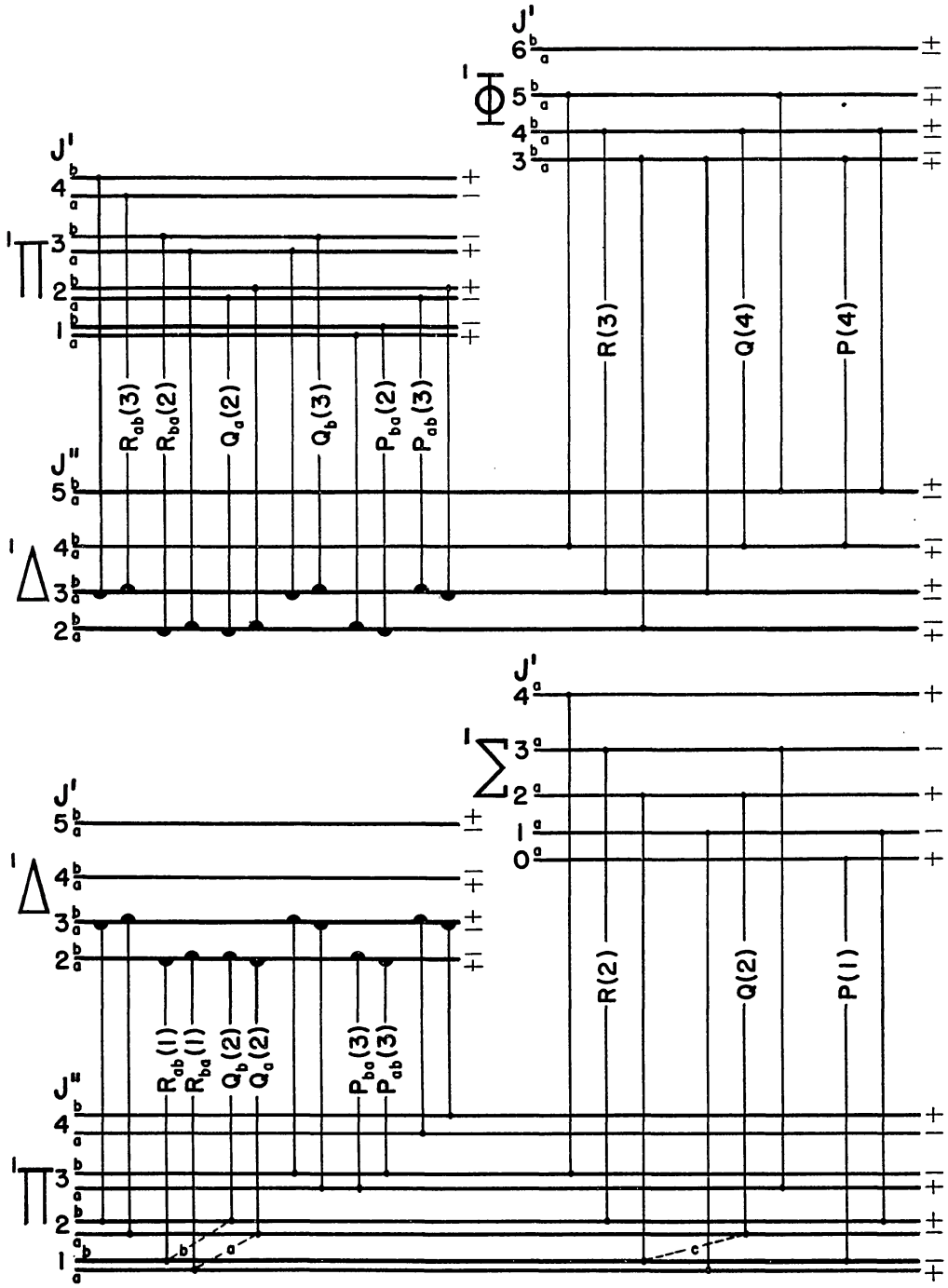

FIG. 3.—*Above*, permitted rotational transitions in the case of a $^1\Pi - {}^1\Delta$ and a $^1\Phi - {}^1\Delta$ transition; *below*, permitted rotational transitions in the case of a $^1\Delta - {}^1\Pi$ and a $^1\Sigma - {}^1\Pi$ transition.

B in Table 3 is the mean of B_a and B_b, and the Λ-type doubling constant, q, is the difference $(B_b - B_a)$.

D. COMPARISON OF THE 8859 A BAND AND THE α-SYSTEM

The combination differences $\Delta_2F(J)$ of the 8859 A band were compared with those obtained from the published measurements on the α-system made by Christy. No agreement could be found with any of the three sub-bands of each of the (0–0), (1–0), and (0–1) bands. Also, the constants given in Table 3 are different from those computed for the α-system by Budó,[9] in a rediscussion of Christy's measurements. These constants are: $B_0'' = 0.5340$, $B_1'' = 0.5309$, $B_0' = 0.4884$, and $B_1' = 0.4855$ cm^{-1}. The differences are larger than the errors in the determinations.

Thus it can be said definitely that the 8859 A band does not have a state in common with a substate of the α-system, so that the suggestion made by Dobronravin, which was mentioned in the introduction, is untenable. This does not exclude the possibility that the 8859 A band is a sub-band of a $^3\Sigma - {}^3\Pi$ transition to a lower state which is quite different from the lower state of the α-system. However, if the 8859 A band is such a sub-

TABLE 3

MOLECULAR CONSTANTS OF THE SINGLET STATES OF *TiO*

Electronic State	$^1\Pi$	$^1\Delta$	$^1\Phi$
B_0	0.5120_0 cm^{-1}	0.5362_0 cm^{-1}	0.5211_5 cm^{-1}
D_0	$0.63_3\times10^{-6}$ cm^{-1}	$0.59_4\times10^{-6}$ cm^{-1}	0.30×10^{-6} cm^{-1}
H_0	.....	.....	2.76×10^{-11} cm^{-1}
r_0	1.6567_0 A	1.6188_8 A	1.6420_9 A
q_0	0.00016 cm^{-1}	.....	.....
Excitation energy, ν_{00}	11,272.77 cm^{-1}	.....	17,840.60 cm^{-1}

band, one should expect the other two sub-bands of the triplet system to appear in its neighborhood in the spectrum and to be of comparable intensity. Such bands are not found. It should be mentioned that Dobronravin did, indeed, call attention to this anomalous intensity distribution, but he did not consider that it invalidated his suggestion.

E. COMPARISON OF THE 8859 A BAND AND THE 5597 A BAND

As was pointed out in the introduction, if the 8859 A band is a member of a singlet system, then there is a possibility that it would have a lower electronic state, in common with the 5597 A band.

The suggestion was tested by making another comparison of combination differences. The usual methods were used to find the rotational numbering of the branches of the 5597 A band. It was then found that there does exist a close agreement between corresponding combination differences of the lower states of the 8859 A band and the 5597 A band. A partial list in Table 4 illustrates the agreement that was found.

The relationships illustrated in Table 4 have an important implication when the types of electronic states involved in the two transitions are considered. As can be seen from the table, the combination differences $\Delta_1F''(J)$ of the 5597 A band agree with the differences $\Delta_1F_v''(J)$ and $\Delta_1F_r''(J)$ of the 8859 A band. These latter two quantities were defined above in Section C. Now it was also shown in Section C that the lower state of the 8859 A band must be either a Π- or a Δ-state. It is now possible to state definitely that the lower state must be a Δ-state, since otherwise the particular relationships illustrated in Table 4

[9] A. Budó, *Zs. f. Phys.*, **98**, 437, 1936.

would not be found. This can be demonstrated by a process of elimination, as follows: Assume for a moment that the lower state of the 8859 A band is a Π-state, as illustrated in the lower part of Figure 3. The difference $R_v(J) - Q_v(J+1)$ then is the difference between two successive rotational levels in the a series, shown by the dotted line a in the figure, and, similarly, the difference $R_r(J) - Q_r(J+1)$ is the difference between two successive levels in the b series, shown by the dotted line b. Now the 5597 A band has an intense Q branch, so that if its lower state is a Π-state, its upper state must be a Σ- or a Δ-state. However, the upper state cannot be a Σ-state, since the resulting combination

TABLE 4

COMPARISON OF COMBINATION DIFFERENCES OF THE 5597 A BAND AND THE 8859 A BAND

J	5597 A Band	8859 A Band			
	$\Delta_1F''(J) = R(J)-Q(J+1)$	$\Delta_1F''(J)=R(J)-Q(J+1)$		$\Delta_1F''(J)=Q(J)-P(J+1)$	
		$\Delta_1F''_v(J)$	$\Delta_1F''_r(J)$	$\Delta_1F''_v(J)$	$\Delta_1F''_r(J)$
46	50.18 cm^{-1}	50.21 cm^{-1}	50.19 cm^{-1}	50.17 cm^{-1}	50.16 cm^{-1}
47	51.21	51.18	51.20	51.22	51.27
48	52.28	52.27	52.30	52.29	52.27
49	53.34	53.24	53.29	53.24	53.31
50	54.36	54.37	54.45	54.45	54.43
51	55.44	55.49	55.47	55.47	55.46
52	56.50	56.47	56.46	56.52	56.46
53	57.56	57.47	57.52	57.54	57.49
54	58.58	58.58	58.59	58.61	58.61
55	59.64	59.64	59.59	59.62	59.59
56	60.67	60.70	60.67	60.66	60.67
57	61.78	61.88	61.73	61.72	61.75
58	62.77	62.88	62.83	62.77	62.77
59	63.89	63.83	63.84	63.77	63.72
60	64.87	65.13	64.85	64.83	64.86
61	65.94	65.92	65.91	65.90	65.89
62	66.97	66.97	67.00	66.97	66.99
63	68.02	68.03	68.06	68.05	68.11
64	69.06	69.05	69.06		
65	70.10	70.08	70.11		
66	71.14	71.13	71.14		
67	72.19	72.17	72.18		
68	73.25	73.19	73.23		
69	74.33	74.30	74.25		
70	75.29	75.30	75.30		
71	76.36	76.33	76.26		

differences, $\Delta_1F''(J)$, would be differences between an a sublevel of a given rotational level and the b sublevel of the neighboring rotational level, or vice versa, as shown by the dotted line c in the lower part of Figure 3. This is not what is actually observed. On the other hand, the upper state of the 5597 A band cannot be a Δ-state, since such a state would have a negligibly small Λ-type doubling, so that the resulting spectrum would exhibit a doubling similar to that observed in the 8859 A band. It can be seen from Figure 1 that this is not the case. These objections eliminate the possibility that the 8859 A band is associated with a Δ — Π transition.

As can be seen from the upper part of Figure 3, no similar objection can be raised against the assumption that the 8859 A band is part of a Π — Δ band system, the lower state being the one held in common with the 5597 A band.

Corresponding to the identification of the lower state of the 5597 A band as a Δ-state, it is quite definite that the upper state is a Φ-state, in view of the fact that the R branch of this band is more intense than the P branch and also that this upper state must exhibit negligible Λ-type doubling. Both these considerations would seem to eliminate a Π-state as the upper state, although there is a possibility, as has been pointed out by Herzberg,[10] that the Π-state involved in the 8859 A band might have an abnormally large Λ-type doubling as the result of perturbations caused by a close Σ-state. However, the observed intensities of the R and P branches would still favor a Φ-state as the upper state.

As far as the multiplicities of the electronic states involved in these transitions are concerned, the appearance of the bands and the sequences associated with them favor the interpretation that they are singlet states. There is no evidence to indicate that the bands are sub-bands of triplet transitions. This is especially true of the sequence at 5597 A, which is not complicated by the superposition of any extraneous bands.

The results of this section may be summarized by stating that it has been shown that the 8859 A band is associated with a $^1\Pi - {}^1\Delta$ transition, and the 5597 A band, at the head of the β-system, with a $^1\Phi - {}^1\Delta$ transition, the $^1\Delta$-state being common to both systems. As mentioned in the introduction, Lowater has suggested that the β-system is associated with a $^1\Pi - {}^1\Sigma$ transition. The general appearance of the bands of this system would indeed suggest a $^1\Pi - {}^1\Sigma$ transition as the most probable. It is only the fact that another band system has been found to have an electronic state in common with the β-system that makes it possible to be more definite in the identification.

F. THE ROTATIONAL CONSTANTS OF THE $^1\Phi$ STATE

Since the upper ($^1\Phi$) state of the 5597 A band has been shown to have negligible Λ-type doubling, it is permissible to use the combination differences $\Delta_1F'(J)$ to obtain the rotational constants. These combination differences can be derived from the R, Q, and P branches of Table 2 through the use of the equations:

$$\Delta_1F'(J) = R(J) - Q(J) = Q(J+1) - P(J+1).$$

By inserting these combination differences into the usual equation,

$$\frac{\Delta_1F'(J)}{J+1} = 2B' - 4D'(J+1)^2,$$

and plotting the left side of the equation against $(J+1)^2$, we obtain a straight line. The constant B' can then be derived from the intercept and the constant D' from the slope of the straight line. When this procedure was followed, the following constants were obtained: $B' = 0.5222$ cm^{-1} and $D' = 0.61 \times 10^{-6}$ cm^{-1}. These constants can be regarded as only provisional, in view of the scatter of the points on the plot.

The next step was to find the band origin, ν_0. To do this, the measured positions of the lines of the Q branch were introduced into the equation

$$Q(J) - \overline{(B' - B'')}\,J(J+1) = \nu_0 + (B' - B'')_{\text{corr}}\,J(J+1),$$

where, as usual, the difference $\overline{(B' - B'')}$ is the difference between the provisional rotational constants and $(B' - B'')_{\text{corr}}$ is the correction to be applied to $\overline{(B' - B'')}$. When the left side of this equation is plotted against $J(J+1)$, the curve shown in Figure 4 was obtained.

The curve in Figure 4 is quite anomalous. Normally, the plotted points would define either a straight line or a curve which deviated from a straight line only for large values

[10] Private communication.

of J, the deviation being explainable by the fact that the approximate equation that is used does not take into account the influence of centrifugal force on the magnitude of the rotational quanta. But the points in Figure 4 exhibit a double curvature, with a point of inflection. The best that could be done was to draw as smooth a curve as possible through the observed points and determine the band origin from the point where this curve intersected the ordinate. In this way it was found that the origin was located at 17,840.60 cm^{-1}.

The anomaly mentioned above may be illustrated in another way. The rotational quanta $F'(J)$ of the upper state can be found from the lines in the three branches, through the use of the following equations:

$$F'(J+1) = R(J) - \nu_0 + F''(J)$$

$$F'(J) = Q(J) - \nu_0 + F''(J),$$

$$F'(J-1) = P(J) - \nu_0 + F''(J),$$

all the quantities on the right sides of these equations being known. The quanta $F''(J)$ can be computed from the rotational constants of the $^1\Delta$-state, and the band origin has been found above.

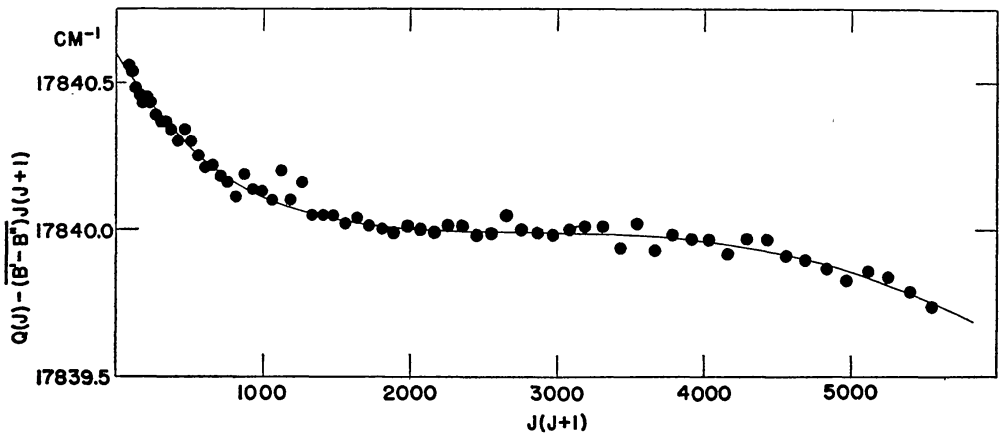

FIG. 4.—Determination of the origin of the 5597 A band. The quantities $Q(J) - \overline{(B' - B'')}J$ (J+ 1) are plotted as ordinates and $J(J + 1)$ as abscissae.

If the quanta $F'(J)$ found in this way are then introduced into the usual equation,

$$\frac{F'(J)}{J(J+1)} = B' - D'J(J+1),$$

and the left side of the equation plotted against $J(J + 1)$, the curve shown in Figure 5 is obtained. Normally, this curve is a straight line, whereas in Figure 5 the plot shows a definite downward curvature. The curvature is greatest for small values of $J(J + 1)$, while for large values of $J(J + 1)$ the curve approaches a straight line.

The most likely explanation for this curvature is that additional rotational terms are required in the equation for $F'(J)$. Accordingly, the following equation was used:

$$F'(J) = B'J(J+1) - D'J^2(J+1)^2 - H'J^3(J+1)^3.$$

By the use of graphical methods, the constants in the fourth column of Table 3 were obtained.

The constants found in this way were then used, together with those of the $^1\Delta$-state, to compute the wave numbers of the lines in the three branches. The differences (O − C) between the computed and observed wave numbers are plotted in Figure 6. It can be seen that, to about $J = 60$, the differences are small, but, nevertheless, systematic. Beyond $J = 60$, the differences are much larger. These differences could be reduced still more by adding more terms to the equation for $F'(J)$ used above, but several would have to be added to make the differences (O − C) as small as the error of measurement over the whole range of J values.

G. ADDITIONAL BANDS OF THE $^1\Pi - {}^1\Delta$ AND $^1\Phi - {}^1\Delta$ SYSTEMS

a) THE $^1\Pi - {}^1\Delta$ SYSTEM

Among the bands found by Wurm and Meister and Kiess in the neighborhood of the 8859 A band, there are three which form, together with the 8859 A band, a definite sequence. The three bands are on the long-wave-length side of the 8859 A band, their separations are the same, within the error of measurement, and there is a regular decrease in

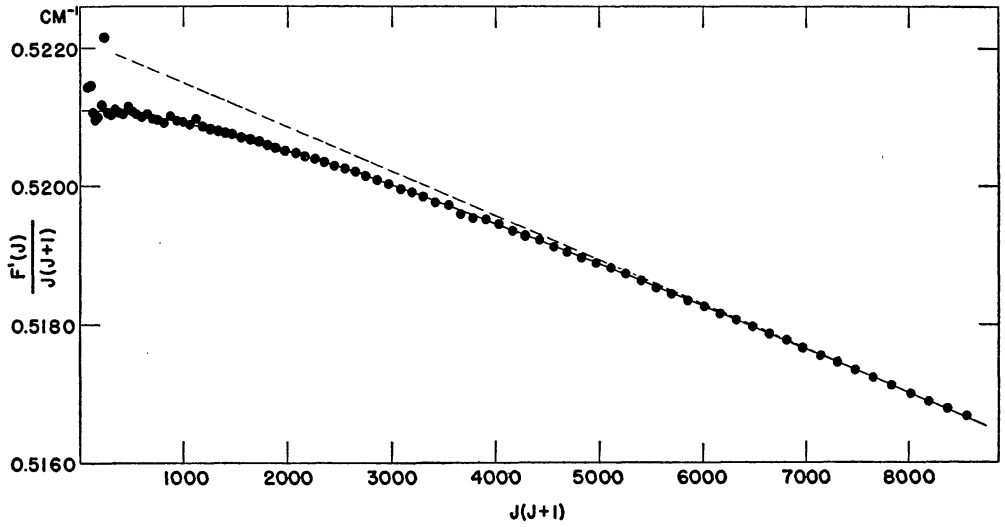

FIG. 5.—The quantities $[F'(J)]/[J(J+1)]$ of the 5597 A band plotted against $J(J+1)$

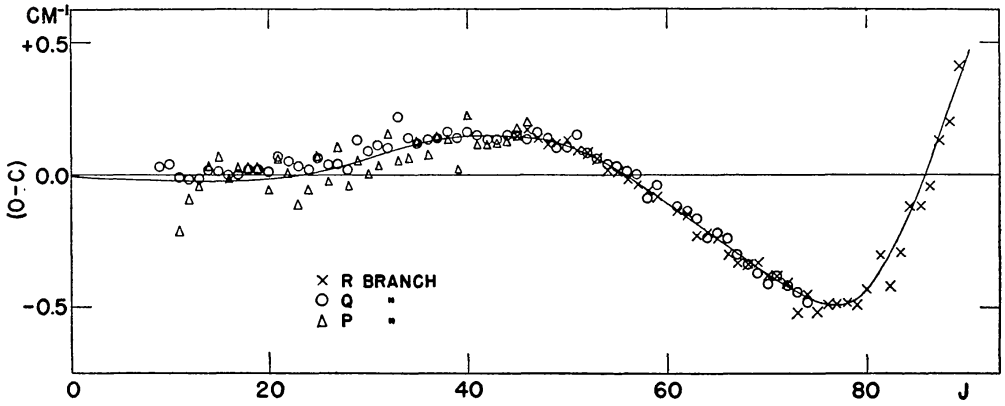

FIG. 6.—The differences (O − C) between the observed and the computed wave numbers of the lines of the 5597 A band.

intensity from one to the next. They are all degraded to the red. The most intense of the three bands, at 8937 A, has an observable Q branch, whose head is 15.5 cm^{-1} from the head of the R branch. This compares favorably with the analogous separation in the 8859 A band (11.3 cm^{-1}), when one considers that the Q head is quite weak, making accurate measurement impossible. Thus it is probable that these three bands, together with the 8859 A band, form a sequence of the $^1\Pi - {}^1\Delta$ system.

One may determine approximately where additional sequences of this band system should be located in the spectrum. As is well known, there is an approximate proportionality between the magnitudes of the rotational and vibrational constants for a given electronic state of a given molecule. Thus, since the rotational constants B of the $^1\Pi$- and $^1\Delta$-states are approximately the same as the rotational constants of the lower ($^3\Pi$) state of the a-system ($B''_0 = 0.5340$ cm^{-1}), then the vibrational constants, ω_e, should be approximately the same also, or about 1000 cm^{-1}. Therefore, in angstroms, one might expect additional sequences to appear at about 8139 A and 9721 A. The spectrum in the neighborhoods of both these wave lengths is very complex, and it is possible that some of the fainter band heads may be members of the $^1\Pi - {}^1\Delta$ system. This cannot be determined definitely, however, until better observational material is available. However, it

TABLE 5

BANDS OF THE $^1\Pi - {}^1\Delta$ SYSTEM

V', V''	λ_{air}		ν_{vac}	Int.	$\Delta\nu_{head}$
0, 0	8859.64 A	R	11,284.04 cm^{-1}	50	.....
	8868.49	Q	11,272.77	10	98.1 cm^{-1}
1, 1	8937.38	R	11,185.9	15	.....
	8949.8	Q	11,170.4	3	95.9
2, 2	9014.6	R	11,090.0	2	.....
					97.4
3, 3	9094.5	R	10,992.6	2	.....

is certain that no additional sequences are present which are similar in intensity to the 8859 A sequence. Therefore, it is highly probable that the 8859 A sequence is the main sequence of the $^1\Pi - {}^1\Delta$ system and that the 8859 A band is the (0–0) band. One may, accordingly, assign vibrational quantum numbers to the other members of the sequence, as shown in Table 5. Except for the 8859 A band, the measurements presented in Table 5 are those of Kiess,[11] as are also all the estimates of relative intensity. In the last column is shown the separation of successive band heads in wave numbers. These are all the bands which may be definitely assigned to the $^1\Pi - {}^1\Delta$ system at the present time, although, as mentioned above, additional work on the fainter bands in the spectrum will probably yield additional members.

b) THE $^1\Phi - {}^1\Delta$ SYSTEM

As was first pointed out by Lowater, a series of bands extending from the 5597 A band to longer wave lengths are undoubtedly further members of the same band system, since they constitute a sequence, with the 5597 A band at its head. Up to the present time, no additional sequences of this system have been found. By an argument similar to the one

[11] The author wishes to acknowledge the generosity of Dr. Kiess for permitting the use of these unpublished measurements.

used above in the case of the $^1\Pi - {}^1\Delta$ system, it is highly probable that this sequence at 5597 A is the main sequence of the $^1\Phi - {}^1\Delta$ system and that the 5597 A band is the (0–0) band of the system. This is in agreement with the suggestion made by Lowater. For the sake of completeness, Table 6 has been included here. All the measurements and identi-

TABLE 6

BANDS OF THE $^1\Phi - {}^1\Delta$ SYSTEM

V', V''	λ_{air}		ν_{vac}	Int.	$\Delta\nu_{head}$
0, 0	5597.68 A	*R*	17,859.60 cm^{-1}	8	.....
	5603.64	*Q*	17,840.60	3	101.3 cm^{-1}
1, 1	5629.28	*R*	17,759.3	7	.....
	5635.27	*Q*	17,740.4	2	101.2
2, 2	5661.55	*R*	17,658.1	7	.....
	5667.59	*Q*	17,639.3	2	101.9
3, 3	5694.42	*R*	17,556.2	4	.....
	5700.61	*Q*	17,537.1	2	101.2
4, 4	5727.43	*R*	17,455.0	3	.....
	5733.40	*Q*	17,436.8	2	.....

fications in Table 6 are those of Lowater, with the exception of the measurements of the heads of the (0–0) band, which have been taken from the present study.

I wish to acknowledge several helpful suggestions made by G. Herzberg during the course of this investigation and also his generosity in reading the manuscript.