OCTOBER 1, 1931 PHYSICAL REVIEW VOLUME 38

THE ROTATIONAL ANALYSIS OF THE FIRST NEGATIVE GROUP OF OXYGEN (O_2^+) BANDS

By Daniel S. Stevens

Ryerson Physical Laboratory, University of Chicago

(Received August 24, 1931)

Abstract

The ultraviolet O_2^+ bands have been produced by a hollow cathode discharge, or with greater intensity from a mixture of helium with a small amount of oxygen in a large discharge tube. Photographs were taken in the second order of a 21 foot Rowland grating (dispersion = 1.32A/mm). The following bands were used for a rotational analysis: 1–8; 0–8; 1–9; 0–9. As was expected, since NO and O_2^+ have the same number of electrons, these bands correspond to a $^2\Pi \rightarrow {}^2\Pi$ transition like the double headed β bands of NO. The lower $^2\Pi$ is case a as in NO. Unlike the case of NO, however, the upper $^2\Pi$ is case b. The lower $^2\Pi$ is regular, with a doublet separation A'' (corresponding to zero rotation) of 195 cm^{-1}. In the upper $^2\Pi$ the value of the spin-orbital coupling coefficient A' is $+8.2$. Each band consists of eight branches (four P and four R), the Q branches apparently being too weak to appear on the plates. This is in agreement with theory. Λ-type doubling is negligible in the upper $^2\Pi$ but is present in the lower $^2\Pi$ state. Alternate levels in each successive Λ-type doublet are missing. This is as prediced by the quantum theory of homopolar molecules, since it is known that the nuclear spin of the oxygen atom is zero. The probable electronic configuration of the upper $^2\Pi$ state is given as $\cdots 2p\pi^3\, 3d\pi^2$, and that of the lower $^2\Pi$ state as $\cdots 2p\pi^4\, 3d\pi$. The constants of the molecule in the two electronic states are given by: $B' = 1.048 - 0.014\, v'$; $B'' = 1.610 - 0.009\, v''$; $r_e' = 1.41 \times 10^{-8}$ cm; $r_e'' = 1.14 \times 10^{-8}$ cm; $A' = +8.2$ cm^{-1}; $A'' = +195$ cm^{-1}.

Introduction

A SYSTEM of double headed bands lying in the region $\lambda\lambda$4400–2000 can be obtained[1] by passing a discharge through pure oxygen. These bands are called the first negative group of oxygen and are attributed to O_2^+. From the type of transition and the molecular constants determined by the present rotational analysis there can be no doubt that O_2^+ is actually the emitter.

The vibrational analysis of these bands has been recently investigated by Ellsworth and Hopfield.[2] It seems probable that the v'' numbering as given by these investigators should be increased by two units. This was pointed out by Mulliken[3] from the intensity distribution in the band system. Stueckelberg[4] has shown that such a revised v'' numbering is the most probable from the Franck-Condon principle of transition probabilities. Ellsworth and Hopfield also found evidence on their plates of band progressions to lower final vibrational states than the level they called $v'' = 0$. For these reasons the bands which were used in the present rotational analysis have been called 1–8;

---

[1] J. Stark, Ann. d. Physik **43,** 319 (1914); R. C. Johnson, Proc. Roy. Soc. **A105,** 683 (1924).

[2] V. Ellsworth and J. Hopfield, Phys. Rev. **29,** 79 (1927).

[3] R. S. Mulliken, Phys. Rev. **32,** 213 (1928).

[4] E. C. G. Stueckelberg, Phys. Rev. **34,** 66 (1929).

0–8; 1–9; 0–9; although they were designated by Ellsworth and Hopfield as 1–6; 0–6; 1–7; 0–7.

Since NO and O_2^+ have the same number of electrons it would be expected that their band systems would be similar. The beta bands of NO and the first negative group of O_2^+ bands lie in the same spectral region and are similar in appearance, (both are double headed and degrade toward the red). The NO beta bands have been analyzed[5] and found to be $^2\Pi \rightarrow {}^2\Pi$, both states being

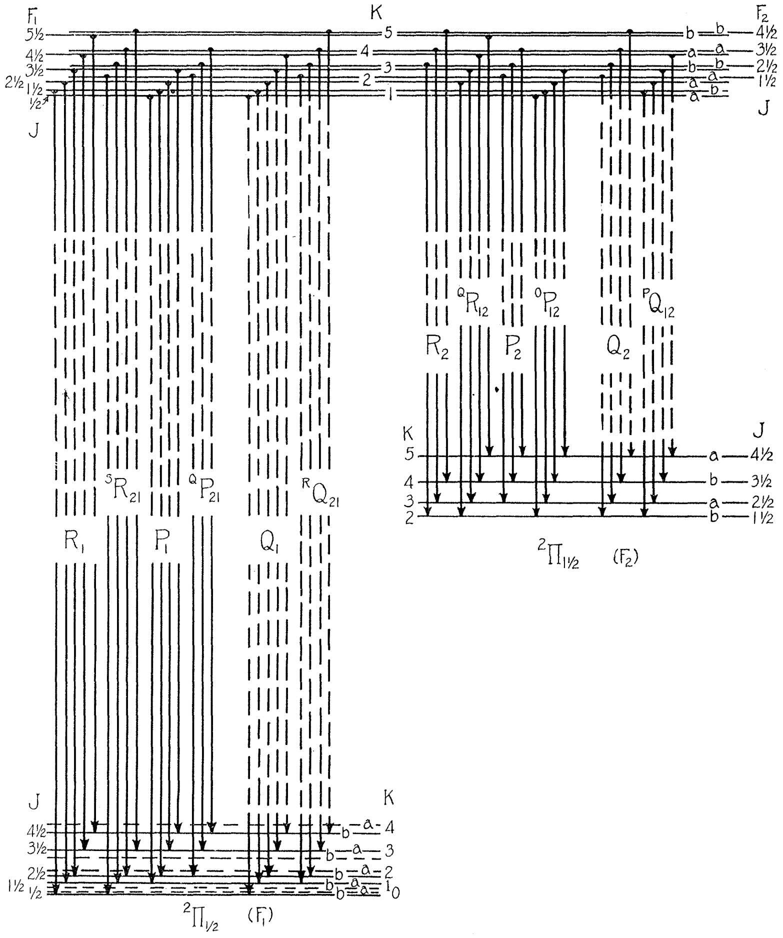

Fig. 1. First few rotational terms for the initial state $v'=0$ and final state $v''=9$ of the first negative group of oxygen (O_2^+) bands. The possible transitions are grouped into branches. The Q branches (shown dashed) were not found in the bands. The other branches were all definitely located and established the case b $^2\Pi \rightarrow$case a $^2\Pi$ nature of transition. All the rotational levels are drawn to the same scale except that the Λ-type doubling is magnified 50X. Even then, it shows only in the lower $^2\Pi_{\frac{1}{2}}$ state. The levels shown dashed do not exist physically (cf. section on Λ-type doubling). The a and b classification on the levels shown in full is in all cases for the level actually present.

---

[5] F. A. Jenkins, H. A. Barton and R. S. Mulliken, Phys. Rev. **30**, 150–174 (1927); **30**, 175–188 (1927).

case *a*. For each of the two heads there is a strong *R* and a strong *P* branch, also a very weak *Q* branch. It was expected that the first negative group of O_2^+ bands would have a similar structure. But four strong branches were found in each head of each band. This situation can be accounted for[6] if the transition is from a case *b* state to a case *a* state rather than between two case *a* states.

In transitions between two case *a* states, there are the selection rules $\Delta\Sigma = 0$ and $\Delta J = 0, \pm 1$. In case *b*, Σ is no longer a quantum number,[7] and the selection rule $\Delta\Sigma = 0$ no longer holds in case *b*→case *a* transitions but the selection rule $\Delta J = 0, \pm 1$ still holds. The various branches[8] which can appear in a $^2\Pi$ case $b \rightarrow$ $^2\Pi$ case *a* transition are shown by Fig. 1.

The *Q* branches, which are shown with broken lines in the figure, were too weak to be found in the bands. The other branches, however, have all been definitely located and establish the case *b*→case *a* type of transition. The "main" *R* and *P* branches (R_1 and P_1; R_2 and P_2) are of about equal intensity and have their maximum at about $J = 20\frac{1}{2}$. The "satellite" branches ($^SR_{21}$ and $^QP_{21}$; $^QR_{12}$ and $^OP_{12}$) are somewhat weaker than the main branches.

EXPERIMENTAL PROCEDURE

The bands were produced in a hollow cathode discharge. The tube was similar to that described by Frerichs.[9] It was, however, found advantageous to construct the cathode with a block of tin instead of the aluminum used by Frerichs. Cooling coils were embedded in the tin so that a large current (1.5 amp.) could be passed through the cathode for many hours (50–100). Some bands due to the cathode material appeared on the high frequency side of the 1–8 and 0–8 O_2^+ bands, but those foreign bands did not interfere with the analysis. The bands were photographed in the second order of a 21 foot Rowland grating giving a dispersion of 1.32 A/mm.

Recently Drs. S. M. Naudé and W. Weizel, while photographing the visible O_2^+ bands in this laboratory, have found a more intense source of O_2^+ spectra by using helium with a small amount of oxygen in a discharge tube similar to that described by Naudé and Christy.[10] They have kindly furnished me with a plate taken in the same region as mine. By means of this plate it was possible to show that there were no errors due to the presence of the tin bands. Only a few faint lines of the tin bands had appeared inside the heads of the 1–8 and 0–8 bands of O_2^+.

DATA AND RESULTS

Due to the presence of many branches the appearance of the bands was rather complex and many of the lines were blends. This was especially true

---

[6] Cf. R. S. Mulliken, Reviews of Modern Physics **3**, 128–146 (1931).

[7] For a discussion of cases *a* and *b* cf. R. S. Mulliken, Reviews of Modern Physics **2**, 105–108 (1930).

[8] For the nomenclature of the branches, cf. R. S. Mulliken, Reviews of Modern Physics **3**, 119 (1931).

[9] R. Frerichs, Zeits. f. Physik **35**, 683 (1926).

[10] S. M. Naudé, and A. Christy, Phys. Rev. **37**, 492 (1931).

TABLE I. *Wave number and intensity data for the 0−8; 1−8; 0−9; 1−9 bands of the first negative group of oxygen* (O_2^+) *bands. The first six numbers represent the wave number of a given line, the next figure in bold-face type gives the number of times the line was used in the scheme of analysis and the last figure is an estimate of the relative intensity of the line. The letter d means that the line appeared diffuse and A means atomic line.*

1−8 Band, First head

$J''+\frac{1}{2}$	$^{S}R_{21}$	$^{Q}P_{21}$	R_1	P_1
1	28620.6**4**4		28613.7**3**3*d*	
2	21.3**4**4		13.0**3**3*d*	28605.9**2**1
3	21.2**4**4	28607.3**1**1	11.3**1**1	00.4**1**1
4	20.7**4**4	02.4**3**6	09.1**2**2	28594.1**1**1
5	19.2**2**2	28597.2**3**6	05.8**2**1	87.2**1**2
6	16.7**1**2*d*	89.9**3**10	01.1**3**6	78.4**1**2*d*
7	13.5**3**3*d*	82.6**2**5	28596.3**3**6	69.2**1**1
8	09.2**2**2	73.8**2**4	89.1**3**10	58.5**1**2
9	03.7**3**6	64.6**2**4	82.6**2**5	47.5**1**3
10	28597.0**3**6	53.9**2**5	73.6**2**4	34.3**1**3
11	89.9**3**10	42.8**2**7	64.5**2**4	21.6**1**4
12	81.0**1**2	29.8**2**6	53.5**2**5	06.4**1**4
13	72.1**1**1	16.7**2**8	42.7**2**7	28491.2**1**5*d*
14	61.3**1**4	01.9**2**8	29.8**2**6	74.2**1**5
15	50.1**1**4	28486.7**2**5*d*	16.8**2**8	57.2**1**5
16	37.5**1**5	69.8**2**7	02.1**2**8	38.3**1**6
17	24.5**1**3	52.6**2**10	28487.1**2**5*d*	19.3**2**4
18	09.6**1**3	33.7**2**8	70.2**2**7	28398.3**2**6
19	28494.8**1**4	14.7**4**4	53.6**2**10	77.3**1**5
20	77.6**1**4	28393.5**1**4	34.4**2**8	54.1**1**5
21	61.0**1**4	72.4**1**2	15.4**4**4	31.3**1**5
22	41.9**1**3	49.2**1**2	28394.4**3**6	06.0**1**5
23	23.4**2**2*d*	26.1**1**2	73.6**1**2	28280.9**1**5
24	02.0**4**8*d*	01.2**1**2	50.5**1**2	53.9**2**6*d*
25	28381.1**2**4*d*	28276.1**2**4	27.7**1**2	27.0**1**5
26	58.0**2**5	49.0**1**1	02.5**1**2	28197.7**2**5*d*
27	35.7**1**1	22.3**1**1	28277.7**2**4	68.9**3**7*d*
28	10.6**1**2	28193.3**1**1	49.9**1**2	37.7**1**5
29	28285.3**1**1	64.2**1**1		06.9**1**5
30	57.6**2**3	33.7**1**1		28073.1**1**4*d*
31	30.5**1**1			40.8**2**5*d*
32	01.4**1**2			05.4**1**5
33	28173.7**1**2			27970.7**1**5
34				33.1**1**5
35				27896.5**1**4

1−8 Band, Second head

$J''+\frac{1}{2}$	R_2	P_2	$^{Q}R_{12}$	$^{O}P_{12}$
2	28429.4**2**1		28420.6**2**2	28413.2**2**2
3	29.5**2**1	28415.3**4**4	19.3**2**4	08.4**2**4
4	28.2**1**1	10.9**2**1	17.5**1**1	02.3**4**8*d*
5	26.5**1**1	04.9**1**1	13.2**2**2	28394.4**3**6
6	24.1**2**2*d*	28398.3**2**6	08.4**2**4	85.5**2**6*d*
7	20.6**2**2	90.3**1**1	02.3**4**8*d*	75.8**2**4
8	15.3**4**4	81.1**2**4	28396.1**1**1	64.7**2**6*d*
9	09.7**2**1	69.7**2**6	88.4**1**3*d*	53.1**2**4
10	02.3**4**8*d*	59.3**1**3	79.4**1**4	39.9**1**2
11	28394.4**3**6	47.0**1**2	69.6**2**6	26.1**2**2
12	85.5**2**6*d*	34.1**1**2	58.1**2**5	10.6**2**2
13	75.8**2**4	20.0**1**2	46.4**1**2	28294.8**1**2
14	64.7**2**6*d*	04.5**1**2	33.1**1**2	77.4**2**4
15	52.7**2**4	28288.6**1**3	19.1**1**2	59.2**1**3
16	38.9**1**2	71.2**1**4	03.8**1**3	39.9**1**3
17	25.2**1**2	53.1**2**6	28287.7**1**3	19.6**1**4
18	09.6**1**3	33.5**1**5	70.2**1**2	28198.1**2**5
19	28293.5**1**3	13.4**1**5	52.1**1**2	76.0**1**2*d*
20	76.1**2**4	28191.0**1**2	32.4**1**2	52.5**1**4
21	57.6**1**3	69.5**3**7*d*	12.3**1**2	28.2**1**4
22	37.9**1**4	45.7**1**5	28190.7**1**2	02.3**1**4*d*
23	17.8**1**4	21.7**1**5	68.1**3**7*d*	28076.0**1**5
24	28195.9**1**4	28095.5**1**6	44.6**1**3	48.3**2**8*d*
25	73.7**2**4	69.0**2**5*d*	20.3**1**2	19.8**1**4
26	49.9**1**5	41.1**2**5*d*	28094.2**1**2	27989.8**1**5
27	25.6**1**5	12.9**2**6	67.7**1**2	59.7**1**4
28	28099.2**1**5	27982.2**2**7	39.7**1**2	27.2**1**4
29	74.2**2**8*d*	52.3**2**6	13.0**2**6	
30	45.9**1**5		27982.7**2**7	
31	18.0**1**2		52.3**2**6	
32	27987.6**1**1		19.8**1**2	
33	57.1**1**1			
34	24.1**1**1			
35	27892.1**1**2*d*			

TABLE I. (*Cont.*)

0–8 Band, First head

$J''+\frac{1}{2}$	${}^{S}R_{21}$	${}^{Q}P_{21}$	R_1	P_1
1	27747.311		27740.121	
2	48.725		40.121	27732.712
3	49.825	27735.411	39.224	28.124
4	49.925	31.028*d*	37.411	22.423*d*
5	48.825	25.923	34.225	14.815
6	46.214*d*	19.225*d*	30.828*d*	07.315
7	43.616*d*	12.211	25.823	27698.212
8	39.224	03.511	19.125*d*	87.412
9	34.525	27694.624	13.026*d*	76.914
10	28.124	84.224	04.726	64.612
11	21.723*d*	73.413	27696.013	51.812
12	13.026*d*	61.013*d*	85.413	37.312
13	04.726	48.313	74.914	22.5210
14	27694.624	34.014	62.714	06.228
15	84.224	19.114	50.217	27589.426
16	72.014	03.015	35.917	71.025
17	59.814	27586.713	21.7210	52.637
18	45.814	68.213	05.928	32.1510*d*
19	31.717	50.024	27589.426	11.715
20	15.514	29.713	71.025	27489.635
21	27599.314	09.636	52.937	67.114
22	81.515*d*	27487.111	32.8510*d*	42.813
23	63.514	65.124	12.814	18.613
24	43.511	41.422	27490.713	27392.513
25	23.525	16.911	68.715	66.515
26	01.418	27390.711	44.712	38.112
27	27479.324	64.912	20.714	10.524
28	55.813	37.524	27394.813	27280.113
29	32.012	09.122	68.825	50.422
30	05.724*d*	27278.711	40.911	18.122
31	27380.212	49.022	13.411	27186.635
32	52.011	18.022	27283.424	52.422
33	25.014	27186.635	53.413	
34	27294.711	52.422	21.712	
35	65.011	18.713	27190.212	
36	33.311		56.511	
37	02.011		23.111	

0–8 Band, Second head

$J''+\frac{1}{2}$	R_2	P_2	${}^{Q}R_{12}$	${}^{O}P_{12}$
2	27557.921		27549.434	27542.311
3	58.211	27543.711	47.911	36.911
4	57.421	38.923*d*	45.522	30.313
5	55.811	33.1410*d*	42.321	23.225
6	53.037	26.135	37.711	14.513
7	49.734	18.623	32.8410*d*	05.113
8	45.122	09.836	26.135	27494.213
9	40.323*d*	00.325	18.623	82.714
10	33.1410*d*	27489.635	09.436	69.914
11	26.135	78.117	00.325	56.414
12	17.413	65.124	27489.635	41.422
13	08.312	51.711	78.724	25.915*d*
14	27497.612	37.027	65.712	09.116*d*
15	86.712	21.525	52.512	27391.613
16	73.712	04.514	37.527	72.714
17	60.413	27387.213	22.125	53.213
18	45.713	68.313	05.724*d*	32.315
19	30.415*d*	48.813	27388.216	10.524
20	13.614	27.913	69.325	27287.816
21	27396.412	06.413	50.112	64.116
22	77.713	27283.424	29.311	39.114
23	58.413	60.123	08.012	13.714
24	37.524	35.113	27285.012	27186.635
25	16.313	10.014	61.823	59.313
26	27293.414	27182.714	36.614*d*	30.214
27	70.311	55.514	11.512	01.214
28	45.214	26.314	27184.211	
29	20.015	27097.214	57.412	
30	27193.012		27.912	
31	65.912		27099.013	
32	36.813			
33	07.714			

TABLE I. (*Cont.*)
1 – 9 Band, First head

$J''+\frac{1}{2}$	${}^SR_{21}$	${}^QP_{21}$	R_1	P_1
1	26972.326		26965.721	
2	74.224		65.721	26959.111
3	75.911	26961.611	64.628	53.926
4	74.811	57.316	63.114	49.211
5	73.924	52.128	60.426	41.712
6	72.126	45.928*d*	56.012	33.713
7	69.612*d*	38.9310	51.928	25.31*A*
8	64.728	30.3310	45.928*d*	14.813
9	60.426	21.214	38.9310	04.013
10	53.826	10.714	30.3310	26891.413
11	47.315	00.014	22.014	78.713
12	38.9310	26887.514	11.713	64.413
13	30.3310	74.914	01.313	49.613
14	20.114	60.516	26888.914	33.311
15	09.615	46.114	76.515	16.715
16	26897.715	29.514	62.216	26798.416
17	85.314	12.913	48.015	79.738
18	71.015	26795.014	31.615	59.4410
19	56.815	76.736	15.415	38.938
20	40.315	56.314	26796.915	16.6410
21	24.815	36.312	78.938	26694.926
22	06.513	14.113*d*	49.4410	70.524
23	26788.513*d*	26692.112	39.038	46.415
24	68.024	67.512	16.6410	20.3310
25	48.413	43.812	26694.926	26594.225
26	26.114	17.514	70.524	66.224
27	04.314*d*	26591.812	46.415	38.323
28	26680.318	63.525	20.2310	08.125
29	56.726*d*	35.536*d*	26594.225	78.425
30	30.113	05.711	66.824	
31	04.327*d*		38.323	
32	26576.3310		08.125	
33	49.215*d*		26478.425	
34	19.227			
35	26489.415			

1 – 9 Band, Second head

$J''+\frac{1}{2}$	R_2	P_2	${}^QR_{12}$	${}^OP_{12}$
2	26785.035		26776.736	26769.711
3	85.335	26771.639	75.711	65.025
4	84.435	66.523*d*	72.839	58.211
5	82.612	60.7110	69.424	50.813*d*
6	79.938	53.7310	65.125	42.513
7	76.836	46.411	59.6410	33.01*A*
8	71.639	37.126	52.7310	22.214
9	66.723*d*	27.826	45.613*d*	10.715
10	60.4410	17.0410	37.126	26697.814
11	53.0310	05.727	27.626	84.316
12	44.212	26692.928	17.3410	69.614
13	34.838	79.628	05.827	54.114
14	24.314	64.62*A*	26693.128	37.517
15	13.014	49.126	79.628	20.1310
16	00.113	32.424*d*	64.72*A*	01.115
17	26687.015	15.028	49.626	26581.515
18	72.015	26596.025	32.624*d*	60.616
19	56.726	76.6310	15.128	39.218
20	39.917	55.613	26596.725	16.217
21	22.617	34.236	77.1310	26492.617
22	04.127*d*	11.218	56.912	68.015
23	26584.417	26488.115	35.236	
24	63.515	63.113		
25	42.216			
26	19.227			
27	26495.917			
28	71.117			

TABLE I. (*Cont.*)
0−9 Band, Second head

$J''+\frac{1}{2}$	R_2	P_2	$^QR_{12}$	$^OP_{12}$
2	25913.538		25905.012	25898.523
3	14.238	25899.611	03.912	93.325
4	13.738	95.122	01.712	86.612
5	12.327	89.224	25898.523	79.313
6	09.525*d*	82.824	94.122	71.113
7	06.712	75.83*A*	89.224	61.515*d*
8	02.412	67.037	82.824	51.517
9	25897.3210	57.537	75.83*A*	40.016
10	91.314	46.925	67.637	27.616
11	84.614	36.125	58.614	14.516
12	76.63*A*	23.815	48.528*d*	00.316
13	67.637	11.015	37.714	25785.115
14	57.537	25796.616	25.628	68.716
15	46.925	81.816	12.928	51.72*A*
16	34.716	65.328*d*	25798.616	33.548*d*
17	22.116	48.716*d*	84.037	14.727
18	08.018	30.518*d*	67.814	25694.627
19	25793.517	11.818	51.32*A*	73.712
20	77.517	25691.718	33.548*d*	51.425
21	61.117	71.017	14.727	28.716
22	43.218	48.917	25694.627	04.716
23	24.918	26.6110	74.312	25580.116
24	04.818	02.519	52.311	53.62*A*
25	25684.618	25578.117	30.228	
26	62.718	52.118	06.213	
27	40.718*d*		25582.013	
28	16.718		56.02*A*	
29	25592.718			
30	66.818			
31	40.918			

0−9 Band, First head

$J''+\frac{1}{2}$	$^SR_{21}$	$^QP_{21}$	R_1	P_1
1	26102.426		26095.048	
2	04.326		95.548	26088.411*d*
3	05.228	26091.137	95.148	84.226
4	05.528	86.624	93.411*d*	78.427
5	04.526	81.9210*d*	90.837	71.126
6	02.326	75.113	86.624	63.228*d*
7	26099.814	68.115*d*	81.9210*d*	54.312
8	95.548	59.918	76.014	44.411
9	91.237	51.517*d*	69.515	33.424
10	85.226	41.115	61.416	21.525
11	79.127	30.716	53.427*d*	09.112
12	71.126	18.716	43.326	25995.012
13	63.228*d*	06.728	33.424	80.715
14	53.227*d*	25992.615	21.525	64.716
15	43.626	78.528*d*	09.716	48.715
16	31.914	62.926	25996.016	30.717
17	20.413	47.015	82.317	13.028
18	06.928	29.315	66.718	25893.325
19	25993.515	11.827	51.218	73.713
20	78.128*d*	25892.213	33.918	52.213
21	62.926	73.013	16.518	30.628*d*
22	45.613	51.526	25897.3310	07.226
23	28.613	30.228*d*	78.115	25784.037
24	09.525*d*	07.026	56.937	58.728*d*
25	25890.612	25784.237	35.725	33.548*d*
26	69.612	59.128*d*	12.929	06.314
27	48.828*d*	34.348*d*	25790.316	25679.514
28	25.628	07.011	65.328	50.313
29	03.512	25680.411	40.813	21.913
30	25778.612	51.425	13.613	25590.814
31	54.211	23.111	25687.316	60.314
32	27.413	25592.2210	58.517	
33	01.111	62.011	30.228	
34	25672.512		25599.513	
35	44.415		69.614	
36	13.711		36.913	

near the heads, where the assignment of lines was difficult. In the second head of each band the branches were better separated. The structure of the bands was determined by locating first the branches in the second head and from them calculating the positions of the rotational levels of the upper electronic state. Knowing these levels and one or two branches in the first head, the remaining branches in the first head could be calculated. The wave numbers of the lines which form the various branches are given in Table I.

DETERMINATION OF THE Δ_2F'S

By reference to Fig. 1, it will be seen that various internal combinations can be obtained in each band. For the first heads of the bands, the relations for the lower $^2\Pi$ are:

$$^{S}R_{21}(J-1) - {}^{Q}P_{21}(J+1) = R_1(J-1) - P_1(J+1)$$
$$= F_1''(J+1) - F_1''(J-1) \equiv \Delta_2F_1''(J) \quad (1)$$

and for the second heads:

$$^{Q}R_{12}(J-1) - {}^{O}P_{12}(J+1) = R_2(J-1) - P_2(J+1)$$
$$= F_2''(J+1) - F_2''(J-1) \equiv \Delta_2F_2''(J). \quad (2)$$

Similar relations that give the Δ_2F's of the upper electronic state are:

$$^{S}R_{21}(J) - {}^{Q}P_{21}(J) = R_2(J) - P_2(J) = \Delta_2F_2'(J) \quad (3)$$
$$R_1(J) - P_1(J) = {}^{Q}R_{12}(J) - {}^{O}P_{12}(J) = \Delta_2F_1'(J). \quad (4)$$

All of these Δ_2F's are listed in Tables II and III. The vibrational quantum numbers of the four bands used in the analysis were such that the rotational levels associated with two adjacent vibrational levels ($v'=0, 1$; $v''=8, 9$) of both the upper and lower electronic states were obtained. Furthermore every Δ_2F in both the upper and lower states is determined independently four times by the differences of four pairs of lines. In the following tables data are given only for the vibrational states $v'=0$ and $v''=9$. Similar data for the vibrational states $v'=1$ and $v''=8$ may readily be obtained from the wave numbers of Table I.

After a series of lines had been located in a band it was not possible to tell immediately what branch it corresponded to. The combination relations just given were used to determine the proper designations of the series. The combinations between the series were first obtained. Then by reference to Fig. 1 it will be seen that for a given J value any member of the $^{S}R_{21}$ branch would have a larger wave number than the corresponding member of the R_1 branch. Exactly the same relation held between the $^{Q}P_{21}$ branch and the P_1 branch.

VALUES OF THE CONSTANTS B, D AND A

The terms of the upper $^2\Pi$ state can be represented accurately by Hill and Van Vleck's equation (see Eq. (9) following). This state, however, is so close to Hund's case b that the terms, except for the lowest K values, can also be represented by the following equation:[7]

TABLE II. *The first set of data gives the values of* $\Delta_2F_1''(J)$ *for the 9 vibrational state obtained from Eq. (1). The second set of data gives the values of* $\Delta_2F_2''(J)$ *for the 9 vibrational state obtained from Eq. (2). The J values have been omitted from the column headings so that* R_1-P_1 *really stands for* $R_1(J-1)-P_1(J-1)$. *Other column headings are exactly similar.*

$\Delta_2F_1''(J)$						$\Delta_2F_2''(J)$					
	0−9 Band		1−9 Band				0−9 Band		1−9 Band		
$J+\frac{1}{2}$	${}^SR_{21}-{}^QP_{21}$	R_1-P_1	${}^SR_{21}-{}^QP_{21}$	R_1-P_1	*av.*	$J+\frac{1}{2}$	R_2-P_2	${}^QR_{12}-{}^OP_{12}$	R_2-P_2	${}^QR_{12}-{}^OP_{12}$	*av.*
2	11.3	10.8	10.7	13.4	11.6	3	18.4	18.4	18.5	18.5	18.5
3	17.7	17.1	16.9	16.5	17.1	4	25.0	24.6	24.6	24.9	24.8
4	23.3	24.0	23.8	22.9	23.5	5	30.9	30.6	30.7	30.3	30.8
5	30.4	30.2	28.9	29.4	29.7	6	36.5	37.0	36.2	36.4	36.5
6	36.4	36.5	35.0	35.1	35.8	7	42.5	42.6	42.8	42.9	42.7
7	42.4	42.2	41.8	41.2	41.4	8	49.2	49.2	49.0	48.9	49.0
8	48.3	48.5	48.4	47.9	48.3	9	55.5	55.2	54.6	54.9	55.1
9	54.4	54.5	54.0	54.5	54.4	10	61.2	61.3	61.0	61.3	61.2
10	60.5	60.4	60.4	60.2	60.4	11	67.5	67.3	67.5	67.5	67.5
11	66.5	66.4	66.3	65.9	66.3	12	73.6	73.5	73.4	73.5	73.5
12	72.4	72.7	72.4	72.4	72.5	13	80.0	79.8	79.6	79.8	79.8
13	78.5	78.6	78.4	78.4	78.5	14	85.8	86.0	85.7	85.7	85.8
14	84.7	84.7	84.2	84.6	84.6	15	92.2	92.1	91.9	92.0	92.2
15	90.3	90.8	90.6	90.5	90.6	16	98.2	98.2	98.0	98.1	98.1
16	96.6	96.7	96.7	96.8	96.7	17	104.2	104.6	104.1	104.1	104.3
17	102.6	102.7	102.7	102.8	102.7	18	110.3	110.3	110.4	110.4	110.4
18	108.6	108.6	108.6	109.1	108.7	19	116.3	116.4	116.4	116.4	116.4
19	114.7	114.5	114.7	115.0	114.7	20	122.5	122.6	122.5	122.5	122.5
20	120.5	120.6	120.5	120.5	120.5	21	128.6	128.8	128.7	128.7	128.7
21	126.6	126.7	126.2	126.4	126.6	22	134.5	134.6	134.5		134.5
22	132.7	132.5	132.7	132.5	132.6	23	140.7	141.0	141.0		140.9
23	138.6	138.6	139.0	139.1	138.8	24	146.8				146.8
24	144.4	144.6	144.7	144.8	144.6	25	152.7				152.7
25	150.4	150.6	150.5	150.4	150.6						
26	156.3	156.2	156.6	156.6	156.4						
27	162.7	162.6	162.6	162.4	162.6						
28	168.4	168.4	168.8	168.0	168.4						
29	174.2	174.5	174.6		174.3						
30	180.4	180.5			180.5						
31	186.4				186.4						
32	192.2				192.2						

TABLE III. *The first set of data gives the values of* $\Delta_2F_1'(K=J-\frac{1}{2})$ *for the 0 vibrational state obtained from Eq. (4). The second set of data gives the values of* $\Delta_2F_2'(K=J+\frac{1}{2})$ *for the 0 vibrational state obtained from Eq. (3). The J values have been omitted from the column headings so that* R_1-P_1 *really stands for* $R_1(J)-P_1(J)$. *Other column headings are exactly similar.*

	$\Delta_2F_1'(K=J-\frac{1}{2})$						$\Delta_2F_2'(K=J+\frac{1}{2})$				
	0−8 Band		0−9 Band				0−8 Band		0−9 Band		
$J+\frac{1}{2}$	R_1-P_1	${}^QR_{12}-{}^OP_{12}$	R_1-P_1	${}^QR_{12}-{}^OP_{12}$	*av.*	$J+\frac{1}{2}$	${}^SR_{21}-{}^QP_{21}$	R_2-P_2	${}^SR_{21}-{}^QP_{21}$	R_2-P_2	*av.*
2	7.4	7.1	7.1	6.5	7.0	3	14.4	14.5	14.1	14.6	14.4
3	11.1	11.0	10.9	10.6	10.9	4	18.9	18.5	18.9	18.6	18.7
4	15.0	15.2	15.0	15.1	15.1	5	22.9	22.7	22.6	23.1	22.8
5	19.7	19.1	19.7	19.2	19.4	6	27.0	26.9	27.2	26.7	26.9
6	23.5	23.2	23.4	23.0	23.3	7	31.4	31.1	31.7	30.9	31.1
7	27.7	27.7	27.6	27.7	27.7	8	35.4	35.3	35.6	35.4	35.4
8	31.7	31.9	31.6	31.3	31.8	9	39.1	40.0	39.7	39.8	39.6
9	36.1	35.9	36.1	35.8	36.0	10	43.9	43.5	44.1	44.4	44.0
10	40.1	39.5	39.9	40.0	39.9	11	48.3	48.0	48.4	48.5	48.4
11	44.2	43.9	44.3	44.1	44.1	12	52.0	52.3	52.4	52.8	52.4
12	48.1	48.2	48.3	48.2	48.2	13	56.4	56.6	56.5	56.6	56.5
13	52.4	52.8	52.7	52.6	52.6	14	60.6	60.6	60.6	60.9	60.7
14	56.5	56.6	56.8	56.9	56.7	15	65.1	65.2	65.1	65.1	65.1
15	60.8	60.9	61.0	61.2	61.0	16	69.0	69.2	69.0	69.4	69.2
16	64.9	64.8	65.3	65.1	65.0	17	73.1	73.2	73.4	73.4	73.3
17	69.1	68.9	69.3	69.3	69.2	18	77.6	77.4	77.6	77.5	77.5
18	73.8	73.4	73.4	73.2	73.4	19	81.7	81.6	81.7	81.7	81.7
19	77.7	77.7	77.5	77.6	77.6	20	85.8	85.7	85.9	85.8	85.8
20	81.4	81.5	81.7	82.1	81.9	21	89.7	90.0	89.9	90.1	90.0
21	85.8	86.0	85.9	86.0	85.9	22	94.4	94.3	94.1	94.3	94.3
22	90.0	90.2	90.1	89.9	90.0	23	98.4	98.3	98.4	98.3	98.3
23	94.2	94.3	94.1	94.2	94.2	24	102.1	102.4	102.5	102.3	102.3
24	98.2	98.4	98.2	98.7	98.4	25	106.6	106.3	106.4	106.5	106.4
25	102.2	102.5	102.2		102.3	26	110.7	110.7	110.5	110.6	110.6
26	106.6	106.4	106.6		106.5	27	114.4	114.8	114.5		114.6
27	110.2	110.3	110.8		110.4	28	118.3	118.9	118.6		118.6
28	114.7		115.0		114.8	29	122.9	122.8	123.1		122.9
29	118.4		118.9		118.7	30	127.0		127.2		127.1
30	122.8		122.8		122.8	31	131.2		131.1		131.2
31	126.8		127.0		126.9	32	134.0		135.2		135.2
32	131.0				131.0	33	138.4		139.1		139.1
						34	142.3				142.3
						35	146.3				146.3

$$T = T_0^e + G(v) + B_v[K(K+1) - \Lambda^2 + \overline{G^2}] + f(K, J-K) + \phi_i(K, J) + D_v K^2(K+1)^2 + \cdots \quad (5)$$

The lower $^2\Pi$ state is co close to Hund's case a that the terms can be represented by the following equation:[7]

$$T = T_0^e + G(v) + A\Lambda\Sigma + B_v^*[J(J+1) - \Omega^2 + \overline{G^2} + S_{perp}{}^2] + \phi_i(\Sigma, J) + D_v J^2(J+1)^2 + \cdots \quad (6)$$

By use of Eq. (5), the Δ_2F's of the upper $^2\Pi$ state should be given very closely by the relation:

$$\Delta_2F'(K) = 2B_v(2K+1) \quad (7)$$

From Eq. (6), the Δ_2F's of the lower $^2\Pi$ state should be given by:

$$\Delta_2F''(J) = 2B_v^*(2J+1). \quad (8)$$

The use of these simplified expressions for the Δ_2F's can be justified except for the lowest values of K of the upper $^2\Pi$ state and for the highest values of the rotational quantum number in either electronic state. In both Eqs. (5) and (6), the ϕ function represents the Λ-type doubling. In the upper electronic state the Λ-type doubling is experimentally found to be negligible. There is Λ-type doubling in the lower electronic state, but the rate of change of the ϕ function with J is so small that it does not affect the Δ_2F's. The same argument can be applied to the other neglected terms which are either constant or change very slowly with respect to J. The last statement holds for the term involving D for rotational quantum numbers less than 15. For values above this number, the Δ_2F's are increasingly less than those given by Eqs. (7) and (8), since D is inherently negative. $[D = -4B_e^3/\omega_e^2]$. From this relation, for the upper electronic state $D' = 5.6\times10^{-6}$ and for the lower electronic state $D'' = 4.6\times10^{-6}$. D values calculated from the departure of the Δ_2F's from a straight line agree with these fairly well. This would be expected for the upper electronic state which is case b but not necessarily for the lower case a electronic state.

TABLE IV. *B values.*

	upper $^2\Pi$	
	$v'=0$	$v'=1$
$B(F_1)$	1.050	1.030
$B(F_2)$	1.047	1.037
$B(av)$	1.048	1.034
	lower $^2\Pi$	
	$v''=8$	$v''=9$
$B^*(F_1)$	1.525	1.520
$B^*(F_2)$	1.550	1.538
$B(av)$	1.538	1.529

Considering Eqs. (7) and (8), it is seen that they predict a linear relation between the $\Delta_2 F$'s and the rotational quantum numbers; the slope of the line in each case being $4B$. The plot of the actual $\Delta_2 F$'s in each case lay on a straight line for moderate values of the rotational quantum number, and the slope of the line was used to obtain the B values listed in Table IV. Since K has integral values and J half-integral values for these states, it would be expected that the intercept of the line on the axis of rotational quantum numbers would be close to a whole number for the upper $^2\Pi$ state and close to a half-number for the lower $^2\Pi$ state. This was found to be the case.

Since the upper $^2\Pi$ in case b, B_v should have practically the same value for the F_1 and F_2 sets of rotational levels. This was observed. For the lower $^2\Pi$ state, which is case a, the observed B_v's are called B_v^* since they are not true B_v values. The values of B_v^* differ for the F_1 and F_2 sets of levels as follows:[11]

$$B_v^* = B_v(1 \pm B_v/A\Lambda)$$

with $\pm B_v/\mathrm{A}$ according as $\Sigma = \pm \frac{1}{2}$

From the above equation the difference between the B_v^* values for the F_2 and F_1 sets of levels of the lower $^2\Pi$ state should be ≈ 0.023. This is close to the observed values. The true B_v is obtained by taking the average of $B_v^*(F_1)$ and $B_v^*(F_2)$.

B_v is related to other molecular constants[12] by the equations:

$$B_v = B_e - \alpha(v + \tfrac{1}{2}) = B_0 - \alpha v,$$
$$B_e = h/8\pi^2 \mu c r_e^2 = 27.70 \times 10^{-40}/\mu r_e^2.$$

Values of some of these constants are given in Table VII.

The value of A'', the parameter governing the doublet separation of the lower $^2\Pi$ state, can be calculated from Eq. (6). This is done by taking the difference between a line in the first head and a line in the second head which come from the same upper level and end on lower levels of the same J value. An expression for this term difference involving A'' may be obtained from Eq. (6). The smallest J values, for which the data were considered most reliable, were chosen to calculate A''. The result was $A'' = 195$ cm^{-1}.

The value of A' for the upper $^2\Pi$ state can be determined by the use of Hill and Van Vleck's formula:[13]

$$T = T_0^e + G(v) + B_v\{(J + \tfrac{1}{2})^2 - \Lambda^2 \pm \tfrac{1}{2}[4(J + \tfrac{1}{2})^2 - 4A\Lambda^2/B_v + A^2\Lambda^2/B_v^2]^{1/2} + \overline{G^2}\} + \phi_i(J) + \cdots \quad (9)$$

This equation is quadratic in A and gives two possible values, i.e., for the upper electronic state $A' = +8.2$ or -4.0. One can decide between these

---

[11] For a discussion of B^* cf. R. S. Mulliken, Reviews of Modern Physics **2,** 113 (1930); **3,** 110 (1931).

[12] Cf. R. S. Mulliken, Reviews of Modern Physics **2,** 65–67 (1930).

[3] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32,** 261–2 (1928).

two values in the following way. Either A' value will give the same term value for all rotational levels except the lowest ($J=\frac{1}{2}$). Also for every J value except the lowest, there are two rotational levels, one of which can be classified as an F_1 level and the other level as belonging to the F_2 set. There is only one level for $J=\frac{1}{2}$.[14] According as A' is positive or negative the position of this level should from the theory be such that it would be naturally classified with the F_1 set or with the F_2 set of levels.

By reference to Fig. 1 it will be seen that one more line near the origin would be added to the P_1 and ${}^OP_{12}$ branches than to the ${}^QP_{21}$ and P_2 branches if the level $J=\frac{1}{2}$ belongs to the F_1 set of levels. The converse will be true if this level belongs to the F_2 group of levels. In most of the bands it was not possible to decide definitely between the two possible positions of the level $J=\frac{1}{2}$. In four instances, however, it appeared that this level belonged to the F_1 set of levels rather than to the F_2 set, thus indicating that $A'=+8.2$. [The first line of each of the following branches appears to come from the level $J=\frac{1}{2}$: P_1 of the 0–9 and 1–9 bands, ${}^OP_{12}$ of the 1–9 band. On the other hand a line from this level appeared to be definitely absent in the case of P_2 branch of the 1–8 band.]

CALCULATION OF THE Δ_1F'S OF THE UPPER $^2\Pi$ STATE

Since there were no Q branches present, it was impossible to obtain the Δ_1F's directly by combinations between the lines. In the upper electronic state for each value of K there is an F_2 level with $J=K-\frac{1}{2}$, slightly above an F_1 level with $J=K+\frac{1}{2}$. The relative position of the F_2 and F_1 levels is a function of A/B_v.[15] The separation of these two levels for a given value of K will be called the spin-doubling distance (ϵ_K) since it is due to the two orientations of the spin vector with respect to K.

For moderate and large values of K the spin-doubling distance changes very slowly with K, so it can be obtained with sufficient accuracy from the lines in the following way. By reference to Fig. 1 it is seen that:

$$\begin{aligned} {}^SR_{21}(J-1) - R_1(J-1) &= {}^QP_{21}(J+1) - P_1(J+1) \\ &= R_2(J-1) - {}^QR_{12}(J-1) \\ &= P_2(J+1) - {}^OP_{12}(J+1) \\ &= \Delta_1F_1'(J+\tfrac{1}{2}) + \epsilon_{K=J+1/2}. \end{aligned} \tag{10}$$

[For definition of Δ_1F cf. end of next section on p. 1309] From Eq. (10):

$$\Delta_1F_1'(J+\tfrac{1}{2}) + \epsilon_{K=J+1/2} + \Delta_1F_1'(J-\tfrac{1}{2}) + \epsilon_{K=J-1/2} = \Delta_2F_1'(J) + 2\epsilon_{K=J}. \tag{11}$$

In the right hand member of Eq. (11) the sum of the two ϵ terms corresponding to $K=J-\frac{1}{2}$ and $K=J+\frac{1}{2}$ is practically the same as twice the value which ϵ_K would have for a hypothetical intermediate level with $K=J$.

Values of ϵ are readily calculated from Eq. (11) since the $\Delta_2F'_1(J)$ terms can be obtained directly from the line differences according to Eq. (4), or by

---

[14] Cf. R. S. Mulliken, Reviews of Modern Physics **2**, 109 (1930).

[15] Cf. R. S. Mulliken, Reviews of Modern Physics **2**, 114 (1930).

reference to Table III. Fig. 2 is a plot of ϵ against K. The solid line shows the values obtained by Hill and Van Vleck's formula and the circles are the values obtained from the lines by the method outlined. For the lowest K values many of the lines were not resolved. The lowest term differences, that were considered most reliable, were used to determine the constants in Hill and Van Vleck's equation, and then the position of the lowest rotational levels was calculated. The first members of the branches could then be located. The first values of ϵ in Fig. 2 are from these blended lines.

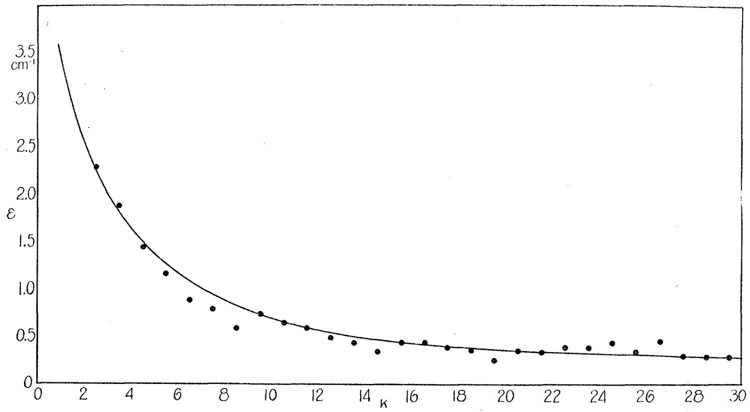

Fig. 2. A graph of ϵ_K (the spin-doubling distance) for the upper $^2\Pi$ state against K. The solid line is drawn from values obtained from Hill and Van Vleck's equation. The circles are values obtained from the lines according to Eq. (11).

The quantities given by Eq. (10) are listed in columns 2 through 10 of Table V. By subtracting the ϵ's from these quantities the Δ_1F's of the upper $^2\Pi$ state are obtained. These are listed in columns 11 and 12 of Table V.

CALCULATION OF THE Δ_1F^*'S OF THE LOWER $^2\Pi$ STATE

The Δ_1F^*'s of this state were obtained in a similar manner. The Δ_1F^*'s of the vibrational state $v''=9$ as listed in Table VI will be taken as an example. In columns 2 and 6 is listed the difference:

$$^{S}R_{21}(J) - R_1(J+1)$$

and in columns 4 and 8

$$^{Q}P_{21}(J) - P_1(J+1)$$

These columns are labelled uncorrected since they must be corrected by subtracting the proper ϵ_K (already obtained, cf. Fig. 2) from each difference to obtain the $\Delta_1F_1^*$ of the lower state. This will be seen by reference to Fig. 1. It will be noted that the ϵ_K to be subtracted from any one member of columns 2 and 6 is for a K value two units greater than the ϵ_K to be subtracted from the corresponding member of columns 4 and 8. These two values of ϵ are practically the same for moderate and high values of K but not so for low values of K (cf. Fig. 2). The columns labelled uncorrected have the appear-

TABLE V. *Values of* $\Delta_1F_1'(K=J)$ *and* $\Delta_1F_2'(K=J)$ *for the 0 vibrational state obtained from Eqs. (10) and (11). The J values have been omitted from the column headings, so that;* (1) ${}^SR_{21}-R_1$ *stands for* ${}^SR_{21}(J-1)-R_1(J-1)$; $R_2-{}^QR_{12}$ *stands for* $R_2(J-1)-{}^QR_{12}(J-1)$; *and* (2) ${}^QP_{21}-P_1$ *stands for* ${}^QP_{21}(J+1)-P_1(J+1)$; $P_2-{}^OP_{12}$ *stands for* $P_2(J+1)-{}^OP_{12}(J+1)$.

	0−8 Band				0−9 Band						
$J+\frac{1}{2}$	${}^SR_{21}-R_1$	${}^QP_{21}-P_1$	$R_2-{}^QR_{12}$	$P_2-{}^OP_{12}$	${}^SR_{21}-R_1$	${}^QP_{21}-P_1$	$R_2-{}^QR_{12}$	$P_2-{}^OP_{12}$	*av.*	$\Delta_1F_2'(K\equiv J)$ $=av-\epsilon_{K=J-\frac{1}{2}}$	$\Delta_1F_1'(K\equiv J)$ $=av-\epsilon_{K=J+\frac{1}{2}}$
1	7.2	7.3		6.8	7.4	6.9		6.3	7.0	3.6	4.5
2	8.6	8.6	8.5	8.6	8.8	8.2	8.5	8.5	8.5	6.0	6.5
3	10.6	11.1	10.3	9.9	10.1	10.8	10.3	9.9	10.4	8.4	8.7
4	12.5	11.9	11.9	11.6	12.1	11.9	12.0	11.7	11.9	10.2	10.4
5	14.6	14.0	13.5	13.5	13.7	13.8	13.8	14.3	13.9	12.4	12.7
6	15.4	16.1	15.3	15.6	15.7	15.5	15.4	15.5	15.6	14.4	14.6
7	17.8	17.7	16.9	17.6	17.9	18.1	17.5	17.5	17.6	16.6	16.6
8	20.1	19.6	19.0	19.7	19.5	19.6	19.6	19.3	19.6	18.6	18.8
9	21.5	21.6	21.7	21.7	21.7	21.6	21.5	21.6	21.8	21.0	21.1
10	23.4	23.7	23.7	23.7	23.8	23.7	23.7	23.5	23.6	22.9	22.9
11	25.7	25.8	25.8	25.8	25.7	26.0	26.0	25.9	25.8	25.1	25.2
12	27.6	27.8	27.8	27.9	27.8	27.9	28.1	27.9	27.8	27.2	27.2
13	29.8	29.7	29.6	29.9	29.8	29.8	29.9	30.1	29.8	29.2	29.3
14	31.9	32.0	31.9	31.8	31.7	32.2	31.9	31.8	31.9	31.4	31.4
15	34.0	34.1	34.2	34.0	33.9	34.0	34.0	34.0	34.0	33.5	33.6
16	36.1	36.1	36.2	36.0	35.9	36.0	36.1	35.9	36.0	35.6	35.6
17	38.1	38.3	38.3	38.2	38.1	38.1	38.1	38.1	38.2	37.8	37.8
18	39.9	40.1	40.0	40.1	40.2	40.0	40.2	40.3	40.1	39.7	39.7
19	42.3	42.5	42.2	42.3	42.3	42.4	42.2	42.3	42.3	41.9	41.9
20	44.5	44.3	44.3	44.3	44.2	44.3	44.0	44.2	44.3	43.9	43.9
21	46.4	46.5	46.3	46.4	46.4	46.2	46.4	46.5	46.4	46.2	46.0
22	48.7	48.9	48.4	48.5	48.3	48.3	48.6	48.9	48.6	48.2	48.2
23	50.7	50.4	50.4	50.7	50.5	50.7	50.6		50.6	50.2	50.2
24	52.8	52.6	52.5	52.5	52.6	52.8	52.5		52.6	52.2	52.3
25	54.8	54.4	54.5	54.3	54.9	54.8	54.4		54.6	54.3	54.3
26	56.7	57.4	56.8		56.7	56.7	56.5		56.8	56.5	56.5
27	58.6	58.7	58.8		58.5	58.5	58.7		58.6	58.3	58.3
28	61.0	60.6	61.0		60.3	60.6	60.7		60.7	60.4	60.5
29	63.2	62.4	62.6		62.7	62.8			62.7	62.5	62.5
30	64.8	65.6	65.1		65.0				65.1	64.9	64.9
31	66.8		66.9		66.9				66.9	66.7	66.7
32	68.6				68.9				68.8	68.6	68.6
33	71.6				70.9				71.2	71.0	71.0
34	73.0				73.0				73.0	72.8	72.8

TABLE VI. *The values of* $\Delta_1 F_1''^*(J+\frac{1}{2})$ *for the 9 vibrational state.*

	0−9 Band				1−9 Band				
$J+\frac{1}{2}$	$R_{21}(J)-R_1(J+1)-\epsilon_{K=J+1\frac{1}{2}}$ uncorr.	corr.	${}^QP_{21}(J)-P_1(J+1)-\epsilon_{K=J-\frac{1}{2}}$ uncorr.	corr.	$R_{21}(J)-R_1(J+1)-\epsilon_{K=J+1\frac{1}{2}}$ uncorr.	corr.	${}^QP_{21}(J)-P_1(J+1)-\epsilon_{K=J-\frac{1}{2}}$ uncorr.	corr.	$\Delta_1 F_1''^*(J+\frac{1}{2})$ av. of corr.
1	6.9	4.4			6.6	4.1			4.3
2	9.2	7.2			9.6	7.6			7.4
3	11.8	10.1	12.7	10.2	12.8	11.1	12.4	9.9	10.3
4	14.7	13.2	15.5	13.5	14.4	12.9	15.6	13.6	13.3
5	17.9	16.7	18.7	17.0	17.9	16.7	18.4	16.7	16.7
6	20.4	19.4	20.8	19.3	20.2	19.2	20.6	19.1	19.3
7	23.8	22.8	23.7	22.5	23.7	22.7	24.1	22.9	22.7
8	26.0	25.2	26.5	25.5	25.8	25.0	26.3	25.3	25.2
9	29.8	29.1	30.0	29.0	30.1	29.4	29.8	28.8	29.1
10	31.8	31.1	32.0	31.2	31.8	31.1	32.0	31.2	31.1
11	35.8	35.2	35.7	35.0	35.6	35.0	35.6	34.9	35.0
12	37.7	37.1	38.0	37.3	37.6	37.0	37.9	37.2	37.1
13	41.7	41.2	42.0	41.4	41.4	40.9	41.6	41.0	41.2
14	43.5	43.0	43.9	43.3	43.6	43.1	43.8	43.2	43.1
15	47.6	47.2	47.8	47.3	47.4	47.0	47.7	47.2	47.2
16	49.6	49.1	49.9	49.4	49.7	49.3	49.8	49.3	49.3
17	53.7	53.3	53.7	53.3	53.7	53.3	53.5	53.1	53.3
18	55.7	55.3	55.6	55.2	55.6	55.1	56.1	55.7	55.3
19	59.6	59.2	59.6	59.2	59.9	59.5	60.1	59.7	59.5
20	61.6	61.4	61.6	61.2	61.4	61.0	61.4	61.0	61.2
21	65.6	65.2	65.8	65.4	65.4	65.0	65.8	65.4	65.3
22	67.5	67.1	67.5	67.1	67.5	67.1	67.7	67.3	67.1
23	71.7	71.3	71.5	71.1	71.9	71.5	71.8	71.4	71.3
24	73.8	73.5	73.5	73.1	73.1	72.8	73.3	72.9	73.1
25	77.7	77.4	77.9	77.5	77.9	77.7	77.6	77.2	77.4
26	79.3	79.0	79.6	79.3	79.7	79.4	79.2	78.9	79.2
27	83.5	83.2	84.0	83.7	84.1	83.8	83.7	83.4	83.4
28	84.8	84.6	85.1	84.8	86.1	85.9	85.1	84.8	84.8
29	89.9	89.7	89.6	89.3	89.9	89.7			89.6
30	91.3	91.1	91.1	90.8	91.8	91.6			91.1
31	95.7	95.5			96.2	96.0			95.7
32	97.2	97.0			97.9	97.7			97.3
33	101.6	101.4							101.4
34	102.9	102.7							102.7
35	107.5	107.3							107.3

TABLE VI (*Continued*). *The values of* $\Delta_1 F_2''^*(J+\frac{1}{2})$ *for the 9 vibrational state*

$J+\frac{1}{2}$	0–9 Band $R_2(J)-{}^QR_{12}(J+1)$ uncorr.	$-\epsilon_{K=J+1\frac{1}{2}}$ corr.	$P_2(J)-P_{12}(J+1)$ uncorr.	$-\epsilon_{K=J-\frac{1}{2}}$ corr.	1–9 Band $R_2(J)-{}^QR_{12}(J+1)$ uncorr.	$-\epsilon_{K=J+1\frac{1}{2}}$ corr.	$P_2(J)-{}^QP_{12}(J+1)$ uncorr.	$-\epsilon_{K=J-\frac{1}{2}}$ corr.	$\Delta_1 F_2''^*(J+\frac{1}{2})$ av. of corr.
2	9.6	7.6			9.3	7.3			7.5
3	12.5	10.8	13.0	10.5	12.5	11.8	13.4	10.9	11.0
4	15.2	13.7	15.8	13.8	15.0	13.5	15.7	13.7	13.7
5	18.2	17.0	18.1	16.4	17.5	16.3	18.2	16.5	16.4
6	20.3	19.3	21.3	19.8	20.3	19.3	20.7	19.2	19.4
7	23.9	22.9	24.3	23.1	24.1	23.1	24.2	23.0	23.0
8	26.6	25.8	27.0	26.0	26.0	25.2	26.4	25.4	25.6
9	29.7	29.0	29.9	28.9	29.6	28.9	30.0	29.0	29.0
10	32.7	32.0	32.4	31.6	32.8	32.1	32.7	31.9	31.9
11	36.1	35.5	35.8	35.1	35.7	35.1	36.1	35.4	35.3
12	38.9	38.3	38.7	38.0	38.4	37.8	38.8	38.1	38.0
13	42.0	41.5	42.3	41.7	41.7	41.2	42.1	41.5	41.5
14	44.6	44.1	44.9	44.3	44.7	44.2	44.5	43.9	44.1
15	48.3	47.9	48.3	47.8	48.3	47.9	48.0	47.5	47.8
16	50.7	50.3	50.6	50.1	50.5	50.1	50.9	50.4	50.3
17	54.3	53.9	54.1	53.7	54.4	54.0	54.4	54.0	53.9
18	56.7	56.3	56.8	56.4	56.9	56.5	56.8	56.4	56.4
19	60.0	59.6	60.4	60.0	60.0	59.6	60.4	60.4	60.0
20	62.8	62.4	63.0	62.6	62.8	62.4	63.0	62.6	62.5
21	66.5	66.1	66.3	65.9	65.7	65.3	66.2	65.8	65.8
22	68.9	68.5	68.8	68.4	68.9	68.5			68.5
23	72.6	72.2	73.0	72.6	74.3	73.9			72.6
24	74.6	74.3							74.3
25	78.4	78.1							78.1
26	80.7	80.4							80.4
27	84.7	84.4							84.4

ance of giving combination agreements except near the origin and this caused considerable confusion before the branches had been classified.

It should be noted that the quantities above called $\Delta_1 F$ or $\Delta_1 F^*$ are not "true" $\Delta_1 F$'s, because of the existence of Λ-type doubling. As explained in the following section on Λ-type doubling, each rotational level has an *a* and *b* component. A "true" $\Delta_1 F(J+\frac{1}{2})$ would be the distance from the *a* or *b* component of the *J* level to the *a* or *b* component respectively of the $J+1$ levels. In the case of $O_2{}^+$, however, alternate levels in the successive Λ-type doublets are missing. Because of this the quantity which has physical existence is the distance from the *a* level of *J* to the *b* level of $J+1$ (cf. Fig. 3), or from the *b* level of *J* to the *a* level of $J+1$. This quantity, for the lower

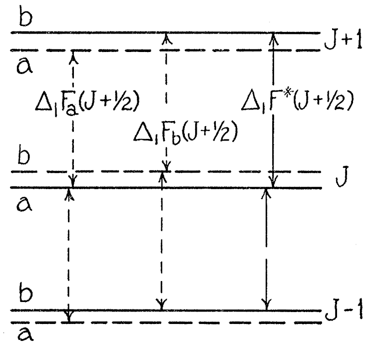

Fig. 3. The relation of the $\Delta_1 F^*$'s to the $\Delta_1 F$'s.

$^2\Pi$ state, will be denoted as $\Delta_1 F''^*$. In the upper $^2\Pi$ state this distinction will not be made since the Λ-type doubling in this state cannot be detected experimentally. This means that a $\Delta_1 F_1{}'^*$ is identical within experimental error with a "true" $\Delta_1 F'$.

Λ-TYPE DOUBLING

For an electronic state with $\Lambda > 0$, the rotational levels are double, one level of the doublet being classified as an *a* level and the other as a *b* level.[16] However $O_2{}^+$ is a homonuclear molecule and the angular momentum (*I*) of the oxygen atom is zero,[17] as is known from the atmospheric oxygen bands. This means that alternate levels in the successive Λ-type doublets should be missing (cf. Fig. 3).

Alternate levels were actually observed to be missing. This is shown by the fact that the number of lines in any one series was the same as though there were no Λ-type doubling. But the lines were staggered since each rotational level was in effect slightly displaced, i.e., every other line was of slightly greater or smaller wave number than if there had been no Λ-type doubling. The staggering was made evident by plotting successive differences

---

[16] For a discussion of the nomenclature of these levels cf. R. S. Mulliken, Reviews of Modern Physics **3,** 93 (1931).

[17] For a discussion of homonuclear molecules cf. R. S. Mulliken, Reviews of Modern Physics **3,** 146 (1931).

of the lines of a branch against an arbitrary number. A straight line could be drawn between the points such that alternate points lay on opposite sides of this line. If there had been no Λ-type doubling the points would all have been on this line.

The Λ-type doubling should also appear in a plot of the $\Delta_1 F^*$'s. This causes the $\Delta_1 F^*$'s to stagger similarly to the series discussed above. The amount of this staggering is equal to the width of the Λ-type doublet, i.e., the distance which there would be between an *a* and *b* level of the same *J* value if both levels physically existed in the case of O_2^+.

When the $\Delta_1 F^*$'s were plotted it was found that there was Λ-type doubling in the lower $^2\Pi$ state, but not an appreciable amount in the upper $^2\Pi$ state. The Λ-type doublet widths are shown by Fig. 4. The following theoretical relations are expected:[18]

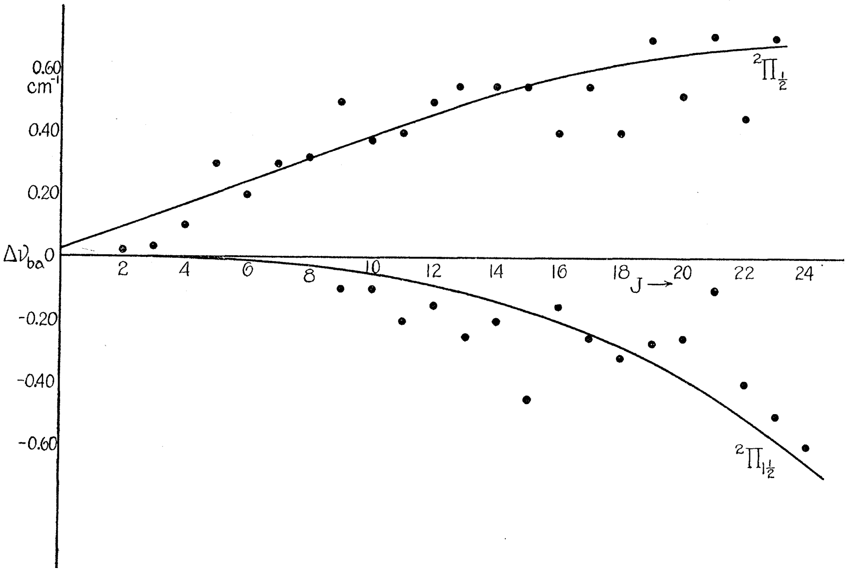

Fig. 4. Comparison of experimentally observed Λ-type doublet widths with the theoretical curves of Eqs. (12) and (13). The value of p was obtained from the slope of the initial portion of the curve through the points of the lower $^2\Pi_{\frac{1}{2}}$ state.

For a case *a* $^2\Pi_{\frac{1}{2}}$ state

$$\Delta\nu_{ba} = p(J + \tfrac{1}{2}). \tag{12}$$

For a case *a* $^2\Pi_{1\frac{1}{2}}$ state

$$\Delta\nu_{ba} = [p/Y^2 + 2q/Y](J - \tfrac{1}{2})(J + \tfrac{1}{2})(J + 3/2). \tag{13}$$

These relations represent the data fairly well and give $p = 0.036$, $q = 0.0027$.

There are reasons for believing that the upper electronic state of O_2^+ is $^2\Pi_u$ and the lower state $^2\Pi_g$. If this is true, then since for oxygen the complete ψ is Sy and for an atom with $I = 0$ ψ_{nu} is s, only—rotational levels can

---

[18] R. S. Mulliken and A. Christy, Phys. Rev. **38**, 94 (1931).

exist in the upper $^2\Pi$ state and +rotational levels in the lower $^2\Pi$ state.[17] If these conditions are correct, then the designations *a* and *b* as assigned here correspond respectively to the *c* and *d* classes of rotational levels.[16]

From an examination of the staggering of the $\Delta_1F''^*$'s in the lower $^2\Pi_{\frac{1}{2}}$ state, it is found that those $\Delta_1F''^*$ (N)'s, where $N=J+\frac{1}{2}$, for which N is an odd integer have slightly larger values than they would have if there were no Λ-type doubling. Also those $\Delta_1F''^*(N)$'s, for which N is an even integer have slightly smaller values than they would have if there were no Λ-type doubling. This means that for the lower $^2\Pi_{\frac{1}{2}}$ state the *a* levels are above the *b* levels in each Λ-type doublet. For the lower $^2\Pi_{1\frac{1}{2}}$ state the reverse is true, i.e., the *b* levels are above the *a* levels. This difference is in agreement with theory.[18]

CONCLUSION

A possible explanation why the upper $^2\Pi$ is case *b* can be found by considering the probable electron configuration[19] of this state. The electronic configuration of normal O_2^+ has been designated as $1s\sigma^2\ 2p\sigma^2\ 2s\sigma^2\ 3p\sigma^2\ 3d\sigma^2\ 2p\pi^4\ 3d\pi^2$. The removal of a $3d\pi$ electron probably gives the lower $^2\Pi$ state of O_2^+ with the electronic configuration $\cdots 3d\sigma^2\ 2p\pi^4\ 3d\pi$. The removal of a $2p\pi$ electron would give the electronic configuration $\cdots 3d\sigma^2\ 2p\pi^3\ 3d\pi^2$. Such a configuration would give several electronic states one of which is a $^2\Pi$ state that would be expected to have a small coupling of the spin with the electric axis, corresponding to the upper $^2\Pi$ case *b* state.

TABLE VII. *Values of the molecular constants.*

upper $^2\Pi$	lower $^2\Pi$
$A'=+8.2$ cm^{-1}	$A''=+195$ cm^{-1}
$B'=1.048-0.014v'$	$B''=1.610-0.009v''$
(observed $v'=0, 1$)	(observed $v''=8, 9$)
D' (cal.) $=5.6\times10^{-6}$	D'' (cal.) $=4.6\times10^{-6}$
D' (obs.) $\approx 5\times10^{-6}$	$r_e''=1.14\times10^{-8}$ cm
$r_e'=1.41\times10^{-8}$ cm	$p=0.036$
	$q=0.0027$

In conclusion I wish to thank Professor R. S. Mulliken for proposing the problem and for his many valuable suggestions; also Dr. A. Christy for his interest and advice during the investigation.

---

[19] Cf. R. S. Mulliken, Phys. Rev. **37**, 1711 A (1931).