Further Studies in the Spectrum of the OH Molecule: A New (2,2) Band; Satellite Series in λ3122; Λ-Type Doubling and Electronic Spin Doubling

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The investigations begun in the neighborhood of the (0′,1″) band at λ3428 (cf. reference 4) have been extended to include the bands of the (0,0) and (1′,0″) sequences. Approximately 400 lines were observed in this region of the spectrum, of which 120 are reported for the first time. All but 18 of these have been successfully assigned. The assignments include the identification of a new (2,2) band with its principal head at λ3185; the identification of $^{RR}R_{21}$ and of $^{PP}P_{12}$ satellite branches of the (1,1) band; complete assignments of the regular R-branches of the (1,1) and (2′,1″) bands; and extensions of nearly all the remaining branches of the bands which appear in this region. The new data are also utilized to obtain Λ-doublets and spin doublets to $K=35$ for the 0″ level and to somewhat smaller values of K for the 1″ and 2″ levels. The experimental results are compared with equations in the literature. Molecular constants derived from the new (2,2) band are in good agreement with those derived from the (1′,2″) band.

INTRODUCTION

THE spectrum of the neutral OH molecule is of considerable interest both from a theoretical standpoint, because of its more than usual complexity[2] for a diatomic molecule, and from a practical standpoint because of its importance in the interpretation of numerous photochemical reactions and in the determination of certain chemical equilibria. Yet, in spite of its importance and of its early investigation[3] only a few bands are known and the assignments in them are incomplete.

In an earlier paper[4] we described the results of our investigations on the "water vapor" bands in the region between λ3429 and λ3570, which is the neighborhood of the (0′,1″) band. Those results included, among other things, the identification of the (1′,2″) band, with its principal head at λ3484, and permitted the formulation of the vibrational energy equation for the normal state of OH. The present paper describes the results of a similar investigation in the neighborhood of the (0,0) and (1,1) bands with principal heads at λ3064 and λ3122, and in certain other regions of the spectrum.

EXPERIMENTAL PROCEDURE

The method of excitation was similar to that described by J, D and W, and the same spectrograph was employed, a Hilger E 185 with quartz prisms. Exposure times were eight hours (λ3064 region) and twelve hours (λ2811 region), with a slit width of 0.001 mm. We also made some exposures with a new type of source, by substituting commercial 3 percent hydrogen peroxide solution for the distilled water. Oxygen was bubbled through this solution, as with the former procedure. Although the initial 3 percent solution yielded results no different from those with ordinary water, as the hydrogen peroxide became more concentrated by the process of distillation[5] during a series of exposures, the OH spectrum was noticeably intensified without a corresponding intensification of the residual background.

PLATE MEASUREMENTS

Tables I–VI contain *all new* lines which appeared on our plates in the regions under

[1] Dawson, Du Pont Fellow in Chemistry, 1932–33.

[2] Some of the factors responsible for this are: a large magnetic coupling energy leading to an inverted multiplet; an unusually large Λ-type doubling; the presence of numerous satellite branches; a nearly complete transformation from Hund's case (a) to Hund's case (b); etc.

[3] For a fairly complete bibliography of the earlier work on this spectrum, cf. reference 4.

[4] Johnston, Dawson and Walker, Phys. Rev. **43**, 473 (1933). We will henceforth refer to this paper as J, D and W.

[5] Water is the more volatile constituent. By continued distillation a residue with about 70 percent H_2O_2 remains.

investigation, with the possible exception of approximately 15 very faint markings which appeared adjacent to the strongest lines of λ3064 and which we attributed to some characteristic of the optical system.[6] These very faint markings did not appear in the correct positions for either isotope lines or for satellite lines. Furthermore, they resemble in appearance similar markings which were observed adjacent to over exposed iron lines.

The lines were measured with a Gaertner comparator and were calibrated against iron lines which were photographed before and after each OH exposure. Two independent readings were made on each line. Our measurements of 200 lines in λλ3064 and 3122 agreed with the measurements of Grebe and Holtz[7] to within an average 0.01A and our measurements of 135 lines in λλ2811 and 2875 checked the measurements of Watson[8] to within an average 0.001A. However,

TABLE I. *The (2,2) band, λ3185.*

K	λ air	Intensity	$\nu_{vac.}$	λ air	Intensity	$\nu_{vac.}$
	R_1				R_2	
1	3189.64	0	31342.5	3202.76	7*t*	31214.1
2	3188.04	7*t*	31358.2	3199.50	7*q*	31245.9
3	3186.95	2*t*	31368.9	3196.18	2	31278.3
4	3186.00	7*hq*	31378.3	3193.85	2	31301.2
5	3185.27	2*t*	31385.4	3192.37	7*t*	31315.7
6	3184.75	2*t*	31390.6	3191.28	0*t*	31326.4
7	3184.75	2*t*	31390.6	3190.15	0*t*	31337.5
8	3185.27	2*t*	31385.4	3190.15	0*t*	31337.5
9	3185.75	2	31380.7	3190.79	7*t*	31331.2
10	3186.95	2*t*	31368.9	3191.28	0*t*	31326.4
11				3192.76	7*t*	31312.2
	Q_1				Q_2	
1	3195.88	4	31281.3	3208.71	4	31155.8
2	3197.56	7	31264.9	3208.48	4*dq*	31158.5
3	3199.50	7*t*	31245.9	3208.48	4*dq*	31158.5
4	3201.53	9	31226.1	3209.41	7*q*	31149.4
5	3203.94	9*hq*	31202.6	3210.80	7*t*	31136.0
6	3206.57	2	31177.0	3212.65	4*t*	31118.0
7	3209.41	7*q*	31149.4	3215.04	4	31094.9
8	3212.65	4*t*	31118.0	3217.94	4	31066.9
9	3216.57	4	31080.1	3221.25	2	31034.9
10	3221.04	2	31036.9	3224.94	2	30999.4
11	3225.21	7*dq*	30996.8	3229.13	2	30959.2
12	3229.94	7*ht*	30951.4	3233.68	7*dq*	30915.6
13	3235.22	7*dq*	30900.9	3238.24	2	30872.1
14	3241.10	2	30844.9			
	P_1				P_2	
1	3199.09	7*ht*	31249.9			
2	3203.94	9*hq*	31202.6	3214.81	4	31097.1
3	3208.48	4*dq*	31158.5	3217.82	4	31068.1
4	3214.04	4	31104.6	3222.05	2	31027.2
5	3219.48	7	31051.9	3226.45	7*t*	30984.9
6	3225.21	4*dq*	30996.8	3231.29	2	30938.5
7	3231.53	2*t*	30936.2	3236.96	4	30884.3
8	3237.60	4	30878.2	3242.84	2	30828.3
9	3244.34	7*q*	30814.1	3249.18	4	30767.2
10	3251.25	4	30748.6	3256.04	2	30703.4
11	3258.83	2	30677.1	3263.12	2	30636.7
12	3266.68	0	30603.3	3270.74	2	30565.3
13	3274.25	4*t*	30532.6	3277.88	0	30498.8
					$^PQ_{12}$	
1				3211.99	2	31124.4

[6] Cf. Shenstone, Phys. Rev. **34**, 726 (1929).

[7] Grebe and Holtz, Ann. d. Physik **39**, 1243 (1912).

[8] Watson, Astrophys. J. **60**, 145 (1924).

TABLE II. *R-branches and satellite branches in the (1,1) band, λ3122.*

K	λ air	Intensity	$\nu_{vac.}$	Calculated $\nu_{vac.}$	K	λ air	Intensity	$\nu_{vac.}$	Calculated $\nu_{vac.}$
		R_1					R_2		
1	3128.23	4*hq*	31957.8	31957.6	1	3140.44	2*t*	31833.4	
2	3126.64	4*dt*	31974.5	31973.6	2	3136.85	7*dt*	31869.9	31867.9
3	3125.28	4	31987.9	31987.7	3	3133.96	2	31899.2	31898.9
4	3123.90	9*t*	32002.0	32001.3	4	3131.44	4*t*	31924.9	31924.5
5	3122.96	4*t*	32011.7*	32011.3	5	3129.49	7*t*	31944.9*	31944.6
6	3122.24	4	32019.1*	32020.0	6	3128.04	2	31959.7*	31959.8
7	3121.62	4*hq*	32025.4*	32024.4	7	3127.02	4	31970.1*	31969.8
8	3121.62	4*hq*	32025.4*	32025.7	8	3126.48	4	31976.0*	31975.8
9	3121.62	4*hq*	32025.4*	32023.0	9	3126.34	4	31977.6*	31977.0
10	3122.49	9*dq*	32016.5*	32017.0	10	3126.64	4	31974.5*	31974.4
11	3123.43	4	32006.9*	32007.4	11	3127.32	4	31967.1*	31966.8
12	3124.63	2	31994.6	31993.2	12	3128.55	2*ht*	31954.5	31954.8
13	3126.64	4*dt*	31974.5	31974.0	13	3130.23	7*t*	31937.2	31938.4
14	3128.77	2	31952.3	31952.7	14	3132.16	2	31917.6	31918.0
15	3131.44	4	31924.9	31925.5	15	3134.61	7*ht*	31892.6	31892.7
16	3134.33	7*ht*	31895.5	31894.2	16	3137.69	7*dq*	31861.3	31861.3
					17	3141.16	4	31826.2	31826.2
					18	3145.12	0	31786.1	31786.0
		$^{P}Q_{12}$					$^{PP}P_{12}$		
1	3150.33	2	31733.5		2	3156.14	7*t*	31675.1	
					3	3162.16	4	31610.4	31608.9
		$^{RR}R_{21}$			4	3169.64	7*t*	31540.3	31540.0
					5	3177.30	4	31464.2	31464.6
1	3118.88	0	32053.5	32054.3	6	3185.27	2*t*	31385.4	31385.1
2	3114.25	0	32101.2	32101.1	7	3193.85	2*t*	31301.2	31301.8
3	3108.81	0	32157.3	32157.7	8	3202.76	7*t*	31214.1	31215.0
4	3104.79	0	32199.0	32198.7	9	3211.99	2*t*	31124.4	31124.6
5	3101.01	0	32238.2	32238.2					
6	3096.82	9*t*	32281.8	32281.5					

TABLE III. *Extensions in the (0,0) band, λ3064.*

K	λ air	Intensity	$\nu_{vac.}$	Calculated $\nu_{vac.}$	K	λ air	Intensity	$\nu_{vac.}$	Calculated $\nu_{vac.}$
		R_1					R_2		
22	3096.08	9*t*	32289.5		22	3098.56	11*t*	32263.7	
23	3101.67	2	32231.3		23	3104.34	4	32203.6	
24	3107.86	0	32167.2		24	3110.55	2	32139.4	
25	3114.70	7*dt*	32096.5		25	3117.11	7*ht*	32070.9	
26	3121.62	4*hq*	32025.4						
		$^{RR}R_{21}$					$^{PP}P_{12}$		
19	3024.25	2	33056.4	33056.9	15	3216.12	2	31084.5	31084.7
20	3026.16	2	33035.6	33034.8	16	3229.13	2	30974.5	30975.5
21	3028.78	0	33007.0	33007.4	17	3239.19	2	30863.1	30863.5
22	3031.88	0	32973.3	32972.9	18	3251.25	4*t*	30748.6	30749.2
23	3035.53	0	32933.6	32932.9	19	3263.58	0	30632.4	30632.4
24	3039.90	0	32886.3	32885.4	20	3276.26	7*t*	30513.9	30513.6
25	3044.81	0	32833.3		21	3289.56	0	30392.2	30392.1
26	3050.24	0	32774.8		22	3302.74	0*t*	30268.7	30268.8
					23	3316.68	0*t*	30142.0	30143.4
					24	3330.91	0	30013.2	30013.2
					25	3345.33	0	29883.9	29883.9

TABLE IV. *Extensions in the (1,0) band, λ2811.*

K	λ air	Intensity	$\nu_{vac.}$	Calculated $\nu_{vac.}$	K	λ air	Intensity	$\nu_{vac.}$	Calculated $\nu_{vac.}$
		P_1					P_2		
22	2979.93	2	33548.0		22	2982.39	2	33520.4	
23	2992.31	1	33409.3		23	2994.80	1	33381.5	
24	3005.99	0	33265.5		24	3007.74	0	33237.9	
		R_1					R_2		
19	2850.02	8*t*	35077.1	35075.3	19	2852.60	10*t*	35045.4	35046.4
20	2856.55	2	34997.0	34996.7	20	2858.91	4	34968.1	34967.9
21	2863.70	8*t*	34909.6	34911.6	21	2865.66	7*ht*	34885.8	34882.7
22	2871.08	0	34819.9	34820.2	22	2873.38	2	34792.0	34790.5
		Q_1					Q_2		
22	2926.87	4*t*	34156.3	34156.7	23	2939.16	2	34013.4	34013.5
23	2937.20	1	34036.1	34037.4	24	2950.01	1	33888.3	33889.1
24	2948.05	0*dt*	33910.8	33912.1					

TABLE V. *Extensions in the (2,1) band, λ2875.*

K	λ air	Intensity	$\nu_{vac.}$	Calculated $\nu_{vac.}$	K	λ air	Intensity	$\nu_{vac.}$	Calculated $\nu_{vac.}$
		P_1					P_2		
11	2941.23	2	33989.5		12	2952.32	2	33861.8	
12	2949.11	1	33898.6		13	2960.46	1	33768.7	
13	2957.33	1	33804.5		14	2969.09	0	33670.6	
14	2966.05	0	33705.1		15	2978.18	0	33567.8	
		R_1					R_2		
1	2877.22	2	34745.6	34744.5	1	2887.99	7*t*	34616.1	34617.5
2	2876.34	4*t*	34756.3	34756.0	2	2885.10	4	34650.7	34650.7
3	2875.67	5*ht*	34764.4*	34763.1	3	2883.06	4	34675.3	34674.2
4	2875.51	6	34766.3	34765.8	4	2881.61	6*t*	34692.7	34690.1
5	2875.27	6	34769.2	34768.9	5	2880.81	6*t*	34702.4	34702.1
6	2875.67	5*ht*	34764.4*	34764.5	6	2880.53	5	34705.7	34705.4
7	2876.34	4*t*	34756.3	34756.3	7	2880.81	6*t*	34702.4	34702.5
8	2877.49	2	34742.4	34742.4	8	2881.61	6*t*	34692.7	34693.4
9	2878.88	7*t*	34725.6	34723.6	9	2882.82	6*t*	34678.2	34678.4
10	2881.14	2	34698.4	34698.4	10	2884.83	4*ht*	34654.0	34656.1
11	2883.65	6*t*	34668.2	34667.8	11	2886.98	2	34628.2	34628.4
12	2886.69	2	34631.7	34630.9	12	2889.78	0	34594.5	34594.1
		Q_1					Q_2		
11	2913.77	2	34309.8	34309.5	11	2916.92	2*t*	34272.7	34273.1
12	2919.21	4*t*	34245.9	34244.7	12	2922.14	2	34211.5	34211.6
13	2925.06	1	34177.4	34176.5	13	2927.89	1	34144.4	34144.2
14	2931.39	1	34103.5	34103.3	14	2934.24	0	34070.4	34071.2
15	2938.09	5*t*	34025.8		15	2940.90	0	33993.3	33993.5
					16	2948.05	0*dt*	33910.8	

TABLE VI. *Unassigned lines in the region between λ2780 and λ3429.*

λ air	Intensity	$\nu_{vac.}$	λ air	Intensity	$\nu_{vac.}$
2820.04	1	35449.8	3131.80	4	31921.2
2906.01	1	34401.4	3153.89	2	31696.7
2917.21	2	34269.4	3172.02	2	31516.5
2926.40	1	34161.8	3172.23	2	31514.4
2934.10	0	34072.0	3176.70	2	31470.1
2937.73	0	34029.9	3204.62	0	31196.0
2942.68	0	33972.7	3229.63	0	30954.4
2967.30	1	33690.9	3232.61	0	30925.9
3077.64	2	32483.0	3240.34	2	30852.1
3105.12	0	32195.5	3242.09	0	30835.5
3111.14	0*d*	32133.3	3265.94	2	30611.2
3116.30	2	32080.1	3274.98	0	30525.8
3125.64	4	31984.2	3341.39	0	29919.1

the wave-lengths of individual lines were not ordinarily reproducible to much better than 0.05A (=0.4 cm^{-1}). The symbols in the "intensity" columns and the asterisks have the significance assigned them in the paper by J, D and W, and are on the same scale of intensities (i.e., lines of apparently equal intensity in λ3064 and λ3484, for instance, bear the same intensity rating).

THE (2,2) BAND, λ3185

A Fortrat diagram of the region of the spectrum encompassed by the intense (0,0) band (λ3064) is shown in Fig. 1, where the principal *P*, *Q* and *R*-branches are represented by full lines and the ${}^{PP}P_{12}$ and ${}^{RR}R_{21}$-branches by broken lines. The circles represent new lines, or in some instances reassignments, which are recorded in Tables I, II and III. Portions of the branches from which circles are omitted were experimentally observed but are recorded, and correctly assigned, in earlier literature.[3, 15]

The most interesting feature of this diagram is the new (2,2) band,[9] with its principal head at λ3185, for which we observed the six principal branches. Our assignments are confirmed by the application of the combination principle as

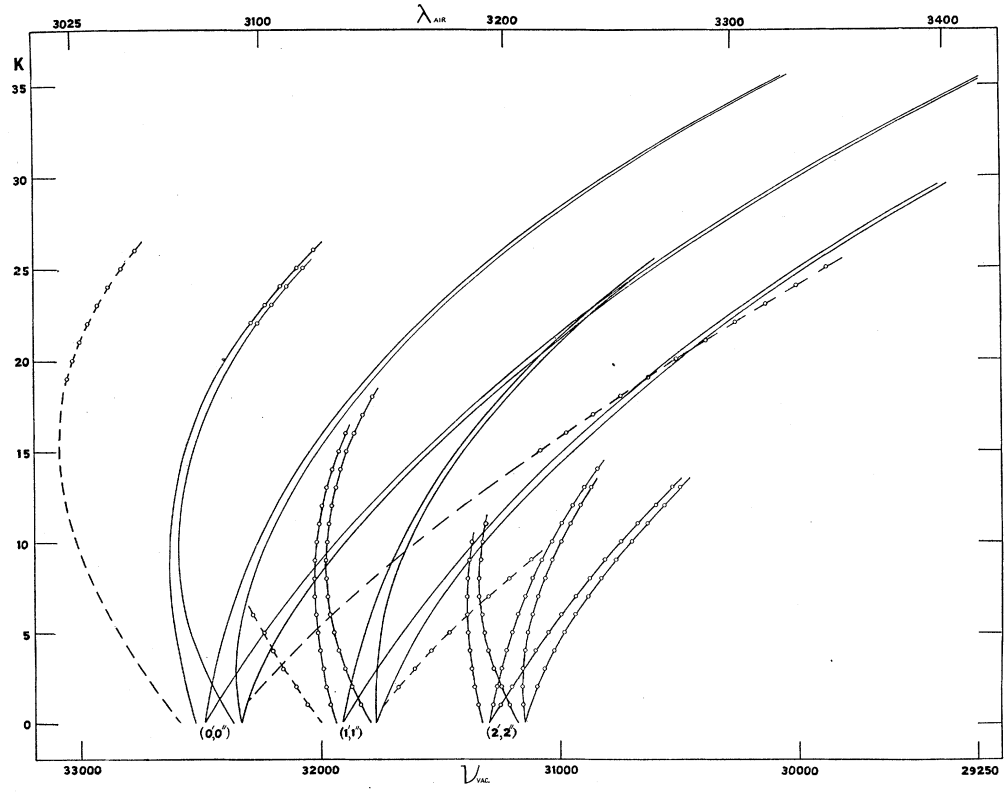

FIG. 1. Fortrat diagrams for λλλ3064, 3122 and 3185. Open circles are lines assigned in this research; full lines, *P*, *Q* and *R*-branches; broken lines, ${}^{RR}R_{21}$ and ${}^{PP}P_{12}$-branches.

[9] Johnston and Dawson, Phys. Rev. **43**, 580 (1933).

TABLE VII.[10] *Application of the combination principle to the upper state of the (2,2) band.*

K	$R_{12}(K)-P_{12}(K)=\Delta_2F_{12}'(K)$			$R_1(K)-Q_1(K)\cong\Delta_1F_1'(K+\frac{1}{2})$			$R_2(K)-Q_2(K)\cong\Delta_1F_2'(K+\frac{1}{2})$		
	(2,0)	(2,1)	(2,2)	(2,0)	(2,1)	(2,2)	(2,0)	(2,1)	(2,2)
1	90.7	90.6	91.2	61.3	61.3	61.2	60.8	58.7	58.3
2	152.3	152.5	152.2	92.2	91.8	93.3	90.9	91.0	87.4
3	212.6	213.8	210.3	121.5	123.5	123.0	121.3	121.4	119.8
4	271.3	272.8	273.9	150.2	150.2	152.2	151.6	152.1	151.8
5	333.6	333.9	332.2	183.0	183.5	182.8	181.5	181.9	179.7
6	392.6	392.7	390.9	212.9	212.4	213.6	211.4	211.2	208.4
7	(451.8)	451.8	453.8	242.8	242.9	241.2	240.8	240.8	242.6
8	509.8	509.5	508.2	272.1	272.5	267.4	270.4	270.5	270.6
9	567.4	568.3	565.3	301.6	303.4	300.6	299.2	300.3	296.3
10	623.1	622.6	621.7	330.1	326.5	332.0	327.5	325.7	327.0

TABLE VIII. *Application of the combination principle to the lower state of the (2,2) band.*

	$R_{12}(K-1)-P_{12}(K+1)$				$R_{12}(K-1)-Q_{12}(K)$			
K	Δ_2F_{12}''		B_2''		Δ_1F_{12}''		B_2''	
	(1,2)	(2,2)	(1,2)	(2,2)	(1,2)	(2,2)	(1,2)	(2,2)
2	167.8	170.0	17.21	17.43	68.4	66.5	17.63	17.15
3	235.4	236.3	17.16	17.22	100.0	99.8	17.03	17.00
4	305.0	304.1	17.25	17.20	135.9	135.7	17.30	17.28
5	374.0	372.6	17.30	17.24	170.6	169.9	17.35	17.28
6	440.6	440.7	17.27	17.27	203.0	202.0	17.22	17.13
7	506.3	507.7	17.22	17.27	236.7	234.9	17.24	17.11
8	573.4	574.0	17.25	17.28	268.4	269.6	17.14	17.21
9					301.9	301.3	17.19	17.16
10					335.0	334.6	17.23	17.21
11					366.7	365.1	17.22	17.14

shown in Table VII, for the upper level, and in Table VIII for the lower level. The treatment of the data in making the calculations of ΔF's and of B_2'' in these tables is identical with that employed for the (1′, 2″) band by J, D and W. The weighted average of B_2'', computed from the data of λ3185 is 17.217 which compares very favorably with the value 17.216 computed from the rotational structure of λ3484.

Null lines calculated from Eqs. (12a) and (12b) of J, D and W are

$$\nu_{01}=31{,}273.5\ \text{cm}^{-1};\quad \nu_{02}=31{,}135.1\ \text{cm}^{-1}.$$

The expected positions of the null lines, calculated from the vibrational constants in Table XII of J, D and W are 31,272.8 cm^{-1} and 31,133.6 cm^{-1}, respectively. The agreement is within the limits of error.

[10] For the (2′,0″) band we employed the data of Jack (Proc. Roy. Soc. **A115**, 373 (1927)) and for the (2′,1″) band, the data of Watson[8] for the P and Q-branches and the data of Table IV for the R-branches.

THE (1,1) BAND, λ3122

The stronger lines which appear near the heads of the R_1 and R_2-branches of λ3122 were measured by Grebe and Holtz[7] and assigned by Heurlinger[11] and by Fortrat.[12] However, many of the assignments appear to be incorrect and since we have also considerably extended the data of these branches we publish them completely in Table II, with the older assignments corrected where necessary. The calculated frequencies, which guided us in our assignments, were computed from the relationships

$$R_1(K)=P_1(K)-\Delta_2F_1'(K) \qquad (1a)$$

$$R_2(K)=P_2(K)-\Delta_2F_2'(K). \qquad (1b)$$

The (Δ_2F')'s were calculated from the data of the (1′,0″) band by the use of Eqs. (2a, b) of J, D and W. Inasmuch as our assignments differ considerably from those of Heurlinger and of Fortrat

[11] Heurlinger, *Dissertation*, Lund (1918).

[12] Fortrat, J. Phys. Radium **5**, 20 (1924).

we have further confirmed our own set of assignments by other combination relationships. Comparison of $(\Delta_1 F')$'s with those of the (1′,0″) band, by $(R-Q)$ combinations is given in Table IX. The agreement leaves little doubt as to the correctness of our assignments.

TABLE IX. $\Delta_1 F'$ *Combination differences in the (1,1) band.*

	$R_1(K)-Q_1(K)$		$R_2(K)-Q_2(K)$	
K	(1,1)	(1,0)	(1,1)	(1,0)
1	64.5	64.6		64.7
2	97.7	96.6	98.5	96.0
3	128.4	128.7	127.8	128.2
4	161.7	161.1	160.4	160.0
5	192.9	192.8	192.0	191.9
6	224.3	225.3	223.2	223.5
7	257.6	256.4	254.6	254.5
8	287.3	287.5	285.4	285.1
9	318.2	318.5	316.2	315.8
10	348.3	348.8	346.2	346.3
11	378.6	379.2	375.9	375.9
12	409.4	408.2	404.4	405.6
13	436.2	436.6	432.1	433.8
14	456.2	465.5	461.6	461.9
15	492.0	492.8	489.6	489.4
16	521.0	520.0	515.5	515.9
17			541.7	542.0
18			567.2	567.3

Table II also includes 14 assignments in the weak ${}^{RR}R_{21}$ and ${}^{PP}P_{12}$ satellite branches of λ3122. Although this is the first evidence of the existence of these branches in λ3122, they have been observed previously[13] for λλλλ3064, 2811, 2608 and 3428. The calculated values were obtained from the relationships[14]

$$ {}^{RR}R_{21}(K) = Q_1(K) + R_1(K+1) - P_1(K+1) - 0.216(K+2), \quad (2a) $$

$$ {}^{PP}P_{12}(K) = Q_2(K) - R_2(K-1) + P_2(K-1) + 0.216(K-2). \quad (2b) $$

THE (0,0) BAND, λ3064

Shaw[15] recently reported 63 new assignments in the P and Q-branches of λ3064. With the exception of one or two of the weakest lines reported by Shaw we have confirmed these by our own measurements. In addition we have been able to extend the R-branches and the satellite ${}^{RR}R_{21}$ and ${}^{PP}P_{12}$ to the extent of some 28 assignments, almost entirely with new lines. These are listed in Table III. The calculated lines in the satellite series were computed by Eqs. (2a, b).

THE (1′,0″) AND (2′,1″) BANDS, λλ2811 AND 2875

Several new lines, which proved to be extensions of the regular P, Q and R-branches of λ2811 and of λ2875, were observed and are tabulated in Tables IV and V. In particular, the R-branches of λ2875 were extended in both directions from the heads and, in some instances, we found it necessary to change assignments of the few lines of these branches which are now in the literature. Accordingly we publish the data for these branches, complete. The calculated positions of regular R-branch lines were computed by Eqs. (1a,b), with $(\Delta_2 F')$'s obtained from the data of the (2′,0″) band[10] while the calculated Q-branch lines were obtained from the relationships

$$ Q_i(K) = P_i(K) + [Q_i(K) - P_i(K)]_{v'}; \quad i = 1, 2. \quad (3) $$

The bracketed expression represents the $(Q-P)$ combination for another band with the *same* upper vibrational quantum number. For the (1′,0″) band we employed the data of the (1,1) band to evaluate this term and for the (2′,1″) band we employed the data of the (2′,0″) band. Eq. (3) involves the assumption that the Λ-type doublet intervals are independent of v''. By comparison among the stronger bands we find that this assumption is in error to the extent of only 0.1 or 0.2 cm^{-1} for the range of rotational quantum numbers encompassed in Tables IV and V.

We observed no new lines in the ${}^{RR}R_{21}$ and ${}^{PP}P_{12}$ satellite branches of λ2811 and were unable to detect these branches in λ2875 although we made a special effort to bring them out.

UNASSIGNED LINES

Lines which we identified but were unable to assign are recorded in Table VI. Including the 4 unassigned lines in the neighborhood of the (0′,1″) sequence which were reported by J, D and W, there now exist a total of 30 unassigned lines between the head of the (1′,0″) band at λ2811 and the tail of the (1′,2″) band out to λ3570. The total number of lines which we ob-

[13] Watson, reference 8; Jack, reference 10; Almy, Phys. Rev. **35**, 1495 (1930), and Almy and Rahrer, Phys. Rev. **38**, 1816 (1931).

[14] Cf. Mulliken, Phys. Rev. **32**, 388 (1928).

[15] R. M. Shaw, Astrophys. J. **76**, 202 (1932).

served within this region of the spectrum was 780. Considering the complexity and overlapping of the various branches and various bands we regard this as very satisfactory. Substantially all of the unassigned lines are very weak and some of them may be optical effects. It is probable that only a few, if any, of them belong to the "water vapor" bands.

Band Intensities

The relative intensities of the bands of the OH system are shown in Table X. The intensity ratings are based on an empirical scale as the bands appear to the eye. The numbers in parentheses are the numbers of lines observed in the Q-branches of the respective bands, and parallel the visual ratings. It is apparent that the locus of maximum intensities runs close to the diagonal of the table. Probably a more significant comparison would be in the lengths of exposure necessary to bring out a definite number of the stronger lines. Put on this basis and compared as to the time necessary to bring out about the fifty strongest lines of the respective bands, the (0,0), (1′,0″) and (0′,1″) bands rate in the proportions 50 : 4 : 1.

Table X. *Relative intensities of the bands of OH.*

	$v''=0$	1	2
$v'=0$	10 (35)	6 (28)	
1	6 (25)	6 (25)	2 (19)
2	2 (17)	2 (15)	2 (14)

An effort was made to bring out the (0′,2″), (3′,2″) and (3′,3″) bands but, so far, we have been unsuccessful in accomplishing this.

Λ-Doubling in the OH Bands

The question of Λ-doubling has been discussed, from a theoretical standpoint, by Van Vleck[16] who concludes that for a $^2\Pi$ term the magnitudes of the doublets should be given by the expressions

$$\delta_1=\delta_2=(C_1-C_2)K(K+1) \qquad (4a)$$

for a case (b) molecule, and

$$\delta_1=a(j+\tfrac{1}{2});\quad \delta_2=0 \qquad (4b)$$

for a case (a) molecule, where C_1, C_2 and a are constants which can be calculated from other molecular constants.[17] Mulliken,[14, 18] has given empirical equations for the Λ-doublets in OH, based on the data then available on the (0,0) and (1′,0″) bands. These are

$$\delta_1=0.04j^2=0.04(K+\tfrac{1}{2})^2, \qquad (5a)$$

$$\delta_2=0.03j^2=0.03(K-\tfrac{1}{2})^2. \qquad (5b)$$

In form, Mulliken's equations resemble that of Van Vleck for a case (b) molecule although the constants differ from the theoretical value by a factor of ten.

The new data make it possible to test these relationships for much higher values of the rotational quantum number. It is necessary to compute the values of the doublets indirectly since a direct evaluation of the individual doublets requires the use of very weak satellite branches[19] for which the data are unreliable. Accordingly we have employed the following relationship, which is that used by Mulliken,

$$\begin{aligned}&[R_i(K)-Q_i(K+1)]-[Q_i(K)-P_i(K+1)]\\&=[F_{iA}''(K)+F_{iA}''(K+1)]\\&\quad-[F_{iB}''(K)+F_{iB}''(K+1)]\\&=\delta_i(K)+\delta_i(K+1)\cong 2\delta_i(K+\tfrac{1}{2});\quad i=1,\,2. \qquad (6)\end{aligned}$$

Values of δ_1 and δ_2 calculated by this method are given in Table XI for the $v''=0,1$ and 2 levels, respectively, with all the data now available.[20] The values given by Mulliken's formulae (5a,b) are also included in Table XI. It is apparent that,

[16] Van Vleck, Phys. Rev. **33**, 467 (1929).

[17] $(C_1-C_2)=4B^2/\nu$ where ν is the frequency of the electronic transition. For OH, which behaves as a case (b) molecule except at low quantum numbers, this gives $(C_1-C_2)=3.4\times10^{-3}$.

[18] Mulliken, Phys. Rev. **33**, 507 (1929).

[19] $\delta_1=Q_{1A1B}-Q_1$; $\delta_2=Q_{2A2B}-Q_2$. The nomenclature is that of Mulliken.[14]

[20] The following data were used:
$v''=0$: (0,0) band—data of Fortrat and this research.
(1′,0″) band—data of Watson, and this research.
(2′,0″) band—data of Jack.
$v''=1$: (0′,1″) band—data of J, D and W.
(1,1) band—data of Fortrat and this research.
(2′,1″) band—data of Watson and this research.
$v''=2$: (1′,2″) band—data of J, D and W.
(2,2) band—data of this research.

TABLE XI.[21] Λ-*Doublets in the OH bands.*

K	$\delta_1(K+\frac{1}{2})$											Eq. (5a)
	$v''=0$				$v''=1$				$v''=2$			
	(0,0)	(1,0)	(2,0)	Aver.	(0,1)	(1,1)	(2,1)	Aver.	(1,2)	(2,2)	Aver.	
1	0.07	0.18	0.43	0.33	0.2	0.3	0.3	0.3	0.1	(−0.6)	0.1	0.16
2	0.37	0.25	0.58	0.40	−0.1	0.5	0.7	0.4	(1.5)	(3.0)		0.36
3	0.54	0.58	0.64	0.59	0.4	0.3	1.0	0.6	1.0	0.8	0.9	0.64
4	1.00	0.98	(−0.21)	0.99	0.6	1.2	(−0.1)	0.9	(3.0)	0.8	0.8	1.00
5	1.47	1.22	1.51	1.40	1.5	1.3	1.7	1.5	1.6	1.3	1.5	1.44
6	2.10	2.13	1.95	2.07	1.8	1.8	1.8	1.8	2.2	0.2	1.2	1.96
7	2.66	2.72	2.45	2.61	2.3	3.3	2.8	2.5	2.1	(0.7)	2.1	2.56
8	3.43	3.47	3.12	3.34	3.6	3.2	3.3	3.4	2.9	(0.7)	2.9	3.24
9	4.34	4.22	4.30	4.29	3.5	5.8	3.4	4.2	4.2	6.2	5.2	4.00
10	5.12	5.08	5.18	5.13	4.6	4.8	(3.1)	4.7		6.2	6.2	4.84
11	6.21	6.08	6.26	6.18	7.4	5.6	5.6	6.3				5.76
12	6.93	7.13		7.03	6.5	7.3	6.5	6.8				6.76
13	7.89	7.58		7.74	6.4	7.4		6.9				7.84
14	8.94	8.94		8.94	7.7	8.7		8.2				9.00
15	10.04	10.01		10.03	9.0	9.5		9.3				10.24
16	11.07	11.42		11.25	9.5	11.4		10.5				11.56
17	12.06	12.48		12.27								12.96
18	13.02	13.70		13.36								14.44
19	14.52	15.46		14.99								16.00
20	15.93	16.66		16.30								17.64
21	17.0	14.07		15.54								19.36
22	17.8	17.55		17.68								21.16
23	19.5			19.5								23.04
24	20.8			20.8								25.00
25	21.6			21.6								27.04
26	25.1			25.1								29.16

K	$\delta_2(K+\frac{1}{2})$											Eq. (5b)
	$v''=0$				$v''=1$				$v''=2$			
	(0,0)	(1,0)	(2,0)	Aver.	(0,1)	(1,1)	(2,1)	Aver.	(1,2)	(2,2)	Aver.	
1	−0.21	−0.01	−0.06	−0.11	−0.6	+0.7	−1.3	−0.4	+1.2	−1.6	−0.2	
2	−0.32	−0.19	−0.24	−0.25	−0.3	−0.4	−0.7	−0.5	−0.3	−1.5	−0.9	
3	−0.20	−0.18	+0.14	−0.08	+0.1	+0.1	−0.2	0.0	−0.2	−1.2	−0.7	
4	−0.02	−0.11	+0.20	+0.03	+0.1	+0.2	0.0	+0.1	−0.4	+0.4	0.0	0.48
5	+0.20	+0.22	+0.24	+0.22	+0.9	+0.5	+0.1	+0.5	+0.3	+0.1	+0.2	0.75
6	0.39	0.58	0.47	0.45	−0.2	+1.4	+0.2	+0.5	(0.0)	(−1.1)		1.08
7	0.94	0.63		0.79	+0.7	+1.3	+1.1	+1.0	+1.2	+2.0	+1.6	1.47
8	1.39	1.17	1.60	1.39	1.6	1.9	1.8	+1.8	(−0.4)	+1.5	+1.5	1.92
9	1.42	2.28	1.84	1.85	1.7	2.4	2.5	2.2		(+0.2)		2.43
10	1.92	2.58	2.28	2.26	1.7	3.1	1.6	2.1		+1.6	+1.6	3.00
11	2.46	3.53	2.64	2.88	2.9	3.5	2.9	3.1		+1.4	+1.4	3.63
12	3.26	4.30		3.78	4.1	3.9	3.7	3.9				4.32
13	3.92	4.64		4.28	5.7	5.3		5.5				5.07
14	4.68	5.35		5.02	6.8	7.0		6.9				5.88
15	5.65	6.63		6.14	6.5	7.1		6.8				6.75
16	6.42	7.40		6.91	9.3	8.3		8.8				7.68
17	7.21	8.54		7.88		8.9		8.9				8.67
18	8.13	9.62		8.88								9.72
19	9.26	10.49		9.88								10.83
20	11.49	11.28		11.39								12.00
21	12.92	13.63		13.28								13.23
22	14.3	13.62		13.96								14.52
23	14.6			14.61								15.87
24	15.7			15.7								17.28
25	17.3			17.3								18.75

[21] Figures in parentheses have been omitted in taking averages.

although Mulliken's formulae hold nearly to ($K=20$), which was about the limit of the data available at the time of Mulliken's work, it fails rapidly at the higher quantum numbers.

In order to make use of the data to still higher quantum numbers ($K=35$) we may employ a second indirect method, which solves for the *differences* between δ_1 and δ_2 without the need of R-branch lines. Thus, if we express the doublet separations in the excited $^2\Sigma$ state by the equation of Mulliken with the constant of Almy[13]

$$F_1'(K)-F_2'(K)=0.216K \tag{7}$$

we may write

$$\{[P_1(K)-P_2(K)]-0.216(K-1)\} - \{[Q_1(K)-Q_2(K)]-0.216(K)\} = \delta_1(K)-\delta_2(K). \tag{8}$$

The results of this calculation are shown graphically in Fig. 2, for the $v''=0$, 1 and 2 levels. In obtaining these values we have averaged the calculations for the several bands as given in reference 20. The broken line was constructed by the use of Mulliken's formulae (5a,b). From Fig. 2 it appears that the Λ-doublets, or at least their differences vary directly with K and not with $(K+1/2)^2$. This is inconsistent with the results to be expected from Van Vleck's theoretical treatment.

The Spin Doublets in the OH Bands

The electronic spin doublets in the OH bands have been considered by Kemble[22] and by Hill and Van Vleck.[23] The latter authors, whose

[22] Kemble, Phys. Rev. **30**, 387 (1927).
[23] Hill and Van Vleck, Phys. Rev. **32**, 250 (1928).

TABLE XII. *Electronic doublets in the OH bands.*

K	$v''=0$												
	R Doublets			P Doublets			Q Doublets			Average		Δ	
	(0,0)	(1,0)	(2,0)	(0,0)	(1,0)	(2,0)	(0,0)	(1,0)	(2,0)	R and P	Q	Obs.	Calc.
1	126.18	126.38	126.14	126.66	126.73	124.94	126.22	126.62	125.93	126.17	126.26	126.22	
2	104.08	103.82	103.91	103.97	104.12	103.67	103.38	103.51	102.00	103.93	102.96	103.45	
3	87.30	87.01	86.18	87.09	87.02	86.82	86.69	86.47	86.14	86.90	86.43	86.72	
4	74.42	74.36	71.90	74.46	74.36	75.95	73.62	73.39	73.45	74.94	73.47	74.21	
5	65.80	64.03	63.77	64.70	64.54	64.24	63.58	63.34	62.50	64.51	63.14	63.83	63.60
6	57.22	57.23	56.95	57.07	57.06	56.90	55.74	55.74	55.64	57.07	55.71	56.39	
7	51.17	51.44	51.27	51.50	51.09	51.16	49.56	49.47	49.51	51.27	49.52	50.40	
8	46.48	46.55	46.87	46.37	41.42	45.88	44.54	44.21	44.40	45.26	44.38	44.82	
9	42.65	42.76	42.80	42.65	42.52	42.19	40.50	40.26	40.59	42.59	40.45	41.52	
10	39.36	39.34	39.29	39.68	39.40	39.64	37.00	37.02	36.94	39.45	36.99	38.22	36.75
11	37.09	37.19	36.80	36.88	36.77	36.69	34.14	34.10	33.43	36.90	33.89	35.40	
12	34.61	34.02	34.00	34.61	33.67	34.65	31.66	31.59	30.79	34.26	31.35	32.81	
13	32.76	32.11		32.77	32.66	32.34	29.61	29.44	28.58	32.55	29.21	30.88	
14	30.97	30.91		30.99	30.84	30.92	26.73	27.62	28.36	30.93	27.57	29.25	
15	29.64	29.20		29.58	29.93	29.27	26.25	26.03	25.88	29.52	26.05	27.79	25.50
16	28.51	28.43		28.50	28.14	27.73	24.66	24.54	24.37	28.26	24.52	26.39	
17	27.28	26.93		27.28	27.23		23.42	23.08	21.09	27.18	23.53	25.36	
18	25.64	25.91		26.28	26.17		22.28	22.15		26.00	22.22	24.11	
19	25.45	27.46		25.53	25.53		21.38	21.13		25.74	21.26	23.50	
20	24.60	24.35		24.76	24.61		20.46	19.98		24.58	20.17	22.38	19.46
21	23.99	22.11		24.04	23.68		19.65	22.08		23.46	20.87	22.17	
22		22.93		23.50	23.10		18.68	18.83		23.18	18.76	20.97	
23				22.89	23.07		18.03	17.76		22.98	17.89	20.44	
24				22.46	22.55		17.26	17.29		22.51	17.28	19.90	
25				22.38			16.71			22.38	16.71	19.55	15.71
26				21.39			16.04			21.39	16.04	18.72	
27				21.23			15.44			21.23	15.44	18.34	
28				20.96			14.25			20.96	14.25	17.61	
29				20.47			14.47			20.47	14.47	17.47	
30				19.92			14.39			19.92	14.39	17.16	13.17
31				19.65			16.12			19.65	16.12	17.89	
32				19.33			13.25			19.33	13.25	16.29	
33				19.15			12.76			19.15	12.76	15.96	
34				18.85			12.43			18.85	12.43	15.64	
35				19.45			12.88			19.45	12.88	16.17	11.33

TABLE XII. (*Continued.*)

K	$v''=1$												
	R Doublets			P Doublets			Q Doublets			Average		Δ	
	(0,1)	(1,1)	(2,1)	(0,1)	(1,1)	(2,1)	(0,1)	(1,1)	(2,1)	R and P	Q	Obs.	Calc.
1	126.8	124.0	127.2			127.0	126.7		126.6	126.3	126.7	126.5	
2	104.2	103.9	105.7	105.4	105.4	105.0	104.1	105.0	104.4	104.9	104.5	104.7	
3	88.7	87.8	88.2	87.8	88.0	88.5	87.6	87.5	86.4	86.8	87.2	87.0	
4	75.4	76.0	72.6	74.8	75.7	75.2	74.8	74.9	74.6	75.0	74.8	74.9	
5	65.9	65.5	65.5	65.9	65.9	66.0	65.6	64.8	64.1	65.8	64.8	65.3	65.14
6	59.2	57.9	57.2	57.9	58.6	58.0	57.1	57.0	56.2	58.1	56.8	57.5	
7	51.8	53.6	52.2	52.5	53.6	52.5	50.6	50.8	50.3	52.7	50.6	51.7	
8	49.5	47.5	47.8	48.0	47.9	47.5	46.0	45.8	46.0	48.0	45.9	47.0	
9	44.0	35.6	45.2	43.9	43.5	43.4	43.4	41.4	42.3	44.3	42.4	43.4	
10	39.9	39.8	42.0	40.5	40.3	40.3	37.6	37.7	41.4	40.5	38.9	39.7	37.85
11	37.6	37.2	37.4	37.9	37.6	37.2	35.3	34.8	34.7	37.5	34.9	36.2	
12	35.3	37.3	34.4	37.5	35.2	34.4	32.9	32.5	31.8	35.7	32.4	34.1	
13	31.0	34.3		33.2	33.1	33.2	30.7	30.4	30.2	33.0	30.4	31.7	
14	29.8	30.0		30.0	31.4	31.6	28.7	28.1	30.1	30.9	29.0	30.0	
15	29.5	29.0		29.0	30.0		28.1	26.6	29.3	29.3	28.0	28.7	26.31
16	26.3	30.8		30.8	28.9		27.2	25.2		29.2	26.2	27.7	
17	(28.0)	25.9		25.9	27.5		24.6	24.1		26.7	24.4	25.6	
18	26.0				26.8		23.1	23.2		26.4	23.2	24.8	
19	25.5				26.7		21.7	21.6		26.1	21.7	23.9	
20	24.7				25.4		21.1	20.8		25.1	21.0	23.1	20.08
21	25.2				24.3		19.8	18.5		24.7	19.2	22.0	
22	23.4				23.8		19.0	16.8		23.6	17.9	20.8	
23	19.3				22.8		18.2	18.7		21.1	18.5	19.8	
24	22.4				22.7		17.1	18.8		22.6	18.0	20.3	
25	21.8				21.1		16.9			21.4	16.9	19.2	16.23
26	21.4				21.1		16.9			21.2	16.9	19.1	
27	23.1				21.1		13.2			22.1	13.2	17.7	
28					20.9					20.9			
29					20.3					20.3			

K	$v''=2$									
	(1,2)	(2,2)	(1,2)	(2,2)	(1,2)	(2,2)	R and P	Q	Obs.	Calc.
1	126.1	128.0		125.5	126.5	125.3	126.5	125.9	126.2	
2	109.9	101.6	106.4	105.3	107.2	106.0	105.8	106.6	106.2	
3	90.0	89.7	90.7	91.2	88.8	86.7	90.4	87.8	89.1	
4	78.6	76.0	76.1	76.7	74.9	75.8	76.9	75.4	76.2	
5	66.9	68.4	68.3	66.1	65.3	65.5	67.8	65.4	66.6	66.58
6	60.5	62.2	58.9	57.2	57.9	57.7	59.7	57.8	58.8	
7	52.8	51.4	53.7	50.6	52.2	53.0	52.1	52.6	52.4	
8	47.2	46.0	47.5	48.4	46.4	48.2	47.3	47.3	47.3	
9	44.9	47.3	48.2	45.2	42.3	43.3	46.4	42.8	44.6	
10	44.2	41.4		43.3	39.2	35.3	42.2	37.4	39.8	38.91
11	40.7			38.2	36.2	35.2	39.5	35.7	37.6	
12	35.4			35.6	34.0	33.2	35.5	33.6	34.6	
13	35.2			31.2	30.7		33.2	30.7	32.0	
14	32.7				30.7		32.7	30.7	31.7	
15	30.9				28.7		30.9	28.7	29.8	27.09
16	29.9				27.1		29.9	27.1	28.5	
17					25.6					
18					23.8					
19					23.0					

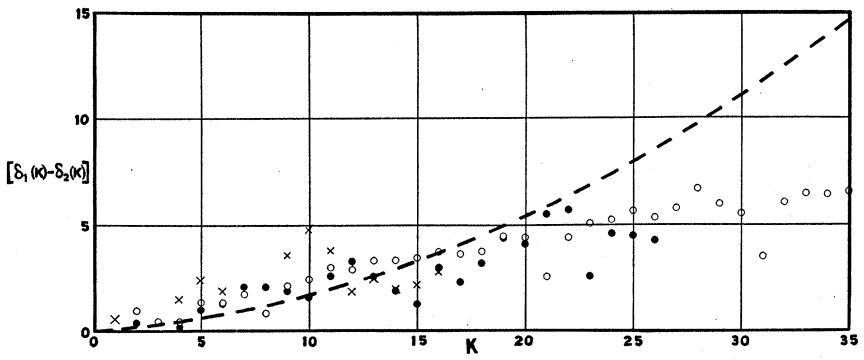

FIG. 2. Λ-doublet differences in F_1 and F_2 states of OH. Open circles, $v''=0$ level; closed circles, $v''=1$ level; crosses, $v''=2$ level. The broken line is Mulliken's formulae (see Eqs. (5a, b)).

treatment is somewhat more exact than that of Kemble, give an equation for the doublets which may be put in the form

$$\Delta = F''_{2AB}(K) - F''_{1AB}(K) = B[\{4(K+\tfrac{1}{2})^2 + (A/B)(A/B-4)\Lambda^2\}^{\frac{1}{2}} - (2K+1)], \quad (9)$$

where the (F''_{AB})'s represent the midpoints of the Λ-doublets and the other symbols have the significance given by J, D and W. The doublets may also be evaluated from the experimental data by the relationships

$$[F''2_A(K) - F''_{1A}(K)] = [Q_1(K) - Q_2(K)] - 0.216K, \quad (10a)$$

$$[F''_{2B}(K) - F''_{1B}(K)] = [P_1(K) - P_2(K)] - 0.216(K-1), \quad (10b)$$

$$= [R_1(K) - R_2(K)] - 0.216(K+1), \quad (10c)$$

$$F''_{2AB}(K) - F''_{1AB}(K) = \tfrac{1}{2}[F''_{2A}(K) - F''_{1A}(K)] + \tfrac{1}{2}[F''_{2B}(K) - F''_{1B}(K)]. \quad (10d)$$

These relationships have been calculated for all of the bands and are recorded in Table XII which also shows values of Δ calculated by Eq. (9) for every fifth value of K, by using the values of the constants given in J, D and W. It is evident that Eq. (9) fails to reproduce the data within the limits of experimental accuracy beyond about $K=10$.