DECEMBER, 1927 *PHYSICAL REVIEW* *VOLUME 30*

THE STRUCTURE OF THE SWAN BANDS

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ABSTRACT

Frequency of the lines of the Swan spectrum.—Data obtained by Leinen, Komp, Hindrichs and Johnson have been used in a detailed quantum analysis of the Swan bands. The very recent data by Johnson have been employed only in the study of the multiplicity of the lines. Tables of the frequencies of the lines and their combination differences are given for the (0, 0), (0, 1), (1, 0), (1, 1) and (1, 2) bands.

Quantum analysis of the Swan spectrum.—Quantum numbers have been assigned to all lines of the R and P branches of the above bands. The Q branch is not observed in these bands. The combination principle is verified in the case of all the above bands. A new method for obtaining accurate numerical values of the constants of the rotational energy function, $E=B_0m^2+D_0m^4+F_0m^6+H_0m^8+\cdots$, has been developed, assuming the theoretical relations between rotational and vibrational constants recently derived by Kratzer, Kemble, and Birge. The so-called method of zero sums has been re-formulated for rapid use in band spectra computations.

Molecular constants of the carrier.—The moment of inertia of the Swan band carrier for infinitely small vibration is found to be 15.84×10^{-40} gm cm^2 for the initial state in the emission process, and 17.03×10^{-40} gm cm^2 for the final state, with a probable error of less than 0.1 percent. The constants of an assumed law of force of the form $F=k_1(r-r_0)+k_2(r-r_0)^2+k_3(r-r_0)^3+\cdots$ are evaluated.

Multiplicity of the lines.—For small values of j the R branches consist of triplets, the P branches of doublets, the separation decreasing as j increases. Empirical formulas for this separation as a function of j are given. The separation for corresponding j values in the various bands shows interesting numerical relations. The well-known "staggering" of alternate lines has been investigated quantitatively for the (0, 0) band, and can be explained by the assumption of a double moment of inertia, either in the initial or final state, in agreement with Mulliken's prediction of σ-type doubling for these bands. The necessary difference of the two values of the moment of inertia is 0.012 percent. The molecule $C^- - C^-$ is suggested as the probable carrier of the Swan bands, provided such a doubly charged molecule can exist.

INTRODUCTION

THIS paper[1] deals with the analysis, on the basis of quantum theory, of the Swan bands resulting from the vibrational quantum transitions (0,0) (λ5165), (0,1) (λ5635), (1,0) (λ4737), (1,1) (λ5129) and (1,2) (λ5585). Certain theoretical relations have been tested, and the more important constants for the carrier have been evaluated with a high degree of accuracy.

The so-called Swan bands were first observed by Wollaston[2] in 1802, but the bands were not described until Swan[3] investigated them in 1857. The bands, which are quite complex, occur in the visible portion of the spectrum.

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[1] Preliminary results of this investigation have been reported to the American Physical Society in the following abstracts: Phys. Rev. **25,** 716 (1925) Abstract 9; Phys. Rev. **27,** 245 (1926) Abstract 14.

[2] Wollaston, Trans. Roy. Soc. London, **11,** 365 (1802).

[3] Swan, Trans. Roy. Soc. Edinburgh, **21,** III, 411 (1857).

Although the existence of these bands has been known for more than a century, the molecule to which they are due is still in doubt.[4,5,6] The molecule undoubtedly contains at least two carbon atoms. Whether or not one or more hydrogen atoms are also present has not been decided. These bands are observed in the Bunsen flame, in stars of spectral types *R* and *N*, in comets,[7] in the carbon arc, in vacuum tubes with carbon electrodes containing an inert gas at low pressures,[6] and in the furnace spectra of King.

Excellent photographs of these bands have been published by Johnson.[6] Cut (b) in the frontispiece of the Bulletin of the National Research Council, Vol. XI, Part 3, December 1926, entitled "Molecular Spectra in Gases," was prepared by the writer from an enlargement made from a plate taken by Birge with the large concave grating at the University of Wisconsin. This cut is of the (0,0) and (1,1) bands, the lines of the (0,0) band being labeled with their correct quantum numbers.

The Swan system consists of five sequences[8,9] of bands with the head of the first band of each sequence in the vicinity of the following wave-lengths: $\lambda\lambda$6191 (0,2), 5635 (0,1), 5165 (0,0), 4737 (1,0) and 4381 (2,0). These correspond to the sequences $n''-n'=+2, +1, 0, -1$ and -2. Thus in the $+1$ sequence the λ5635 band is produced by a transition in emission from the vibrational state $n'=0$ to the vibrational state $n''=1$.

TABLE I

Schematic representation of the Swan bands.

n'	$n''=0$	1	2	3	4	5	6
0	5165	5635	6188				
1	4737	5129	5585	6120			
2	4381	4716	5096	5541	6060		
3		4371	4698		5502	6005	
4			4364	4683		5473	5958
5					4673		

Table I contains the vibration quantum number assignments of the Swan bands. It is the same as that given by Mecke[10] and Birge.[11] Each band corresponds in emission to a transition from the vibration state n', given at the left of the row in which a particular band occurs, to the vibration state n'', given at the top of the column.

[4] Watts, Phil. Mag. (6) **28**, 117 (1924).

[5] Kayser, Handbuch der Spectroscopie, Vol. V, 226 (1910) and Vol. VII, 139 (1924).

[6] Johnson, Trans. Roy. Soc. London **A227**, 157 (1927).

[7] Wright, Lick. Obs. Bull. **7**, 8 (1912) See also Fig. 171 p. 435 Vol. I, Russell, Dugan and Stewart, Astronomy, (1926).

[8] For an introduction to the quantum theory of band spectra see Sommerfeld, Atombau, 4th edition, Chapter 9.

[9] For a more detailed account see the Report of the National Research Council on Molecular Spectra in Gases, 1926. The nomenclature of this paper is the same as that in the report of the National Research Council, and reference will be made to it as "Report."

[10] Mecke, Phys. Zeits. **26**, 217 (1925).

[11] Birge, Phys. Rev. **23**, 294 (1924).

The structure of the Swan bands has been investigated by Thiele,[12] Leinen,[13] Heurlinger,[14] and others.[5,6] The individual lines of the various bands can be arranged in ten series, such that the second frequency difference of the lines in each series is approximately a constant. These series can be conveniently considered as two sets of doublets and two sets of triplets. The two sets of doublets (and similarly for the triplets) are found by taking alternate lines of what seems at first to be a single doublet series. The basis of this division lies in the fact that if it is not made, the second differences show a systematic irregularity due apparently to a slight mutual displacement of alternate lines. Leinen, Thiele and other early investigators made the division into ten series. Heurlinger assumed only five series, which he interpreted on the quantum theory as a doublet P branch and a triplet R branch. It has recently become evident that the band series of homopolar molecules as a rule consist of lines which alternate in intensity,[15] and the application of this rule suggests that the true interpretation of the Swan bands is to assume two P branches (each composed of doublets), and two R branches (each composed of triplets). Each P or R branch consists of alternate strong and extremely weak lines, and the two P branches (similarly the two R branches) interlace in such a fashion that the faint lines of one almost coincide with the strong lines of the other. In the tables, the lines of each band are listed in order, as if there were only one doublet P and one triplet R branch, merely for convenience.

Several investigators have measured the wave-lengths of the lines in different portions of the Swan spectrum. Only the measurements giving the wave-lengths to 0.001A were used in this work. Hindrichs,[16] about 1904, measured the lines of the bands in the $n''-n'=-1$ sequence. These measurements, although made under fairly high dispersion, do not seem to be as accurate as those of later investigators. Leinen[13] measured the lines of the $n''-n'=0$ sequence, the measurements being published in 1905. He used an electric arc as source, and lists but two heads, the (0,0) and (1,1). Komp,[17] about 1911, measured the lines of the $n''-n'=+1$ sequence. Since the work reported in this paper was completed, a paper by Johnson[6] has appeared which gives accurate measurements of the lines of many of the Swan bands, including several which are not considered in the present paper. His data were obtained, for the most part, under low temperature conditions, and give only lines which are relatively near the head. Combining these measurements with the older ones would produce little if any change in the results already obtained before Johnson's paper appeared, and accordingly this has not been done.

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[12] Thiele, Astrophys. J. **8,** 1 (1898).

[13] Leinen, Zeits. f. wiss. Phot. **3,** 137 (1905).

[14] Heurlinger, Untersuchungen über die Struktur der Bandenspektra, Dissertation, Lund (1918).

[15] Report, Chapter IV, Section 5e, p. 200 et seq.

[16] Hindrichs, Ueber Messungen und Gesetzmassigkeiten in der Vierten Kohlebande. Bonn Diss. (1904).

[17] Komp, Zeits. f. wiss. Phot. **10,** 117 (1911–12).

THE COMBINATION PRINCIPLE AND ITS VERIFICATION

The lines of the three possible branches, P, Q, and R of the usual quantum theory, are defined as follows:

$$P_j=\nu_0+F_{j-1}'-F_j'' \tag{1a}$$

$$Q_j=\nu_0+F_j'-F_j'' \tag{1b}$$

$$R_j=\nu_0+F_{j+1}'-F_j'' \tag{1c}$$

In these equations F_j is the "term" value (i.e., the energy divided by hc) expressed as a function of j, the resultant angular momentum of the molecule in $h/2\pi$ units, ν_0 is the frequency of the origin. The Q branch is not observed in the Swan bands. From experimental data it is possible to evaluate only m, the angular momentum due to the rotation of the nuclei. Assuming for the present that m and j are parallel, one may write $m=j-\epsilon$, where j is assumed to be an integer. However, it is possible that j may be a half-integer, and in order to distinguish this case, we write $m=k-\alpha$, where k is an exact half-integer.[18] For the sake of convenience, a line will always be referred to in terms of its j for the final state, as shown by Eqs. (1a)–(1c).

In the particular case of the Swan bands m is known to be approximately a half-integer, and hence if the resultant angular momentum is integral, ϵ is approximately one half. If the resultant angular momentum is half-integral, then α is nearly zero.

From Eqs. (1a) and (1c) it follows that

$$R_j-P_j=F_{j+1}'-F_{j-1}'=2\Delta F_j' \tag{2a}$$

$$R_{j-1}-P_{j+1}=F_{j+1}''-F_{j-1}''=2\Delta F_j'' \tag{2b}$$

In these equations $F_{j+1}-F_{j-1}$ is defined as being equal to $2\Delta F_j$.[19] Eqs. (2a) and (2b) are the essential equations in a test of the combination principle. Thus Eq. (2a) indicates that although both R_j and P_j are functions of the initial and final states, their difference is a function of the initial state only. If now the values of $2\Delta F_j'$ are evaluated from the observed lines in two different bands of an n'' progression (i.e., having the same initial vibration state) these values should be identical within the limits of experimental error. This relation should hold whether the lines are perturbed or not. The same argument applies to the values of $2\Delta F_j''$ for the various bands of an n' progression. This identity of the values of $2\Delta F_j$ for different bands is known as the combination principle. In the case of bands in which a Q branch is observed, additional combinations are possible. In all bands thus far analyzed, perturbations have been found to occur in pairs, and each pair of perturbed lines may be explained as due to an irregularity in one energy level, usually in the initial state. Thus if F_j' is greater than expected by any

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[18] ϵ (or α) is thus interpreted as a measure of the angular momentum due to electronic motion. The more recent interpretation of the new wave mechanics is not pertinent in the present investigation.

[19] By this definition of $2\Delta F_j$, it follows that $2dF/dj=2\Delta F_j$ to a high degree of approximation. (Report, Chap. IV, Eq. (78).).

given amount, the R_{j-1} and P_{j+1} lines will both be displaced to the violet by this same amount. This fact is very useful, as it definitely fixes the relative values of j for the R and P lines, provided perturbations exist. Perturbations do exist in the Swan bands, and with these as a basis, the writer has assigned relative values of j to all the series lines of the (0,0), (0,1), (1,0), (1,1) and (1,2) bands. Then by the use of Eqs. (2a) and (2b) the values of $2\Delta F_j'$ and $2\Delta F_j''$ have been evaluated. The equalities predicted by the combination principle were then found to exist, thus proving that the previous assignment of vibration quantum numbers is correct. The series and the corresponding values of the combination differences are given in Tables II to VI. In these tables the measurements for each band are listed

TABLE II

Frequencies of the lines of the (0,0) band, and their combination differences.

j	R^r	R^c	R^v	P^r	P^v	$2\Delta F'^r$	$2\Delta F'^v$	$2\Delta F''^r$	$2\Delta F''^v$
1									
2									
3		19389.05							
4		393.16							
5		397.83							
6	19400.88	402.53							
7	406.31	407.55							
8	411.42	412.80	19414.52						
9	417.22	418.30	419.80						
10	422.83	424.01	425.33						
11	429.03	429.95	431.13						
12	435.13	436.15	437.13						
13	441.77	442.57	443.50						
14	448.29	449.19	449.93					87.16	87.30
15	455.38	456.13	456.89	19354.61	19355.27	100.77	100.86	93.68	93.92
16	462.41	463.22	463.88	354.61	355.27	107.80	107.95	100.11	100.28
17	469.93	470.64	471.28	355.27	355.85	114.66	114.79	106.56	106.82
18	477.41	478.18	478.70	355.85	356.40	121.56	121.78	113.53	113.27
19	485.25	486.07	486.64	356.40	357.37	128.85	128.70	119.55	119.73
20	493.40	494.08	494.64	357.86	358.45	135.63	135.63		126.13
21	501.85	502.43	502.95		359.94		142.49	132.47	132.62
22	510.28	510.92	511.26	360.93	361.46	149.35	149.46	139.01	139.00
23	519.22	519.81	520.22	362.84	363.43	156.38	156.38	145.44	145.48
24	528.05	528.73	528.90	364.84	365.44	163.21	163.29	151.81	151.86
25	537.52	538.07	538.42	367.41	367.95	170.11	170.12	158.17	158.34
26	546.82	547.49	547.49	369.88	370.39	176.94	177.10	164.63	164.67
27	556.77	557.32	557.62	372.89	373.40	183.88	183.92	171.20	171.16
28	566.51	567.22	567.22	375.62	376.33	190.99	190.89	177.41	177.46
29	577.05	577.41	577.72	379.36	379.86	197.69	197.55	183.72	183.94
30	587.18	587.84	587.84	382.79	383.28	204.39	204.56	190.25	190.14
31	598.11	598.72	598.87	386.80	387.27	211.31	211.45	196.48	196.70
32	608.76	609.38	609.38	390.70	391.14	218.06	218.24	202.89	203.05
33	620.23	620.79	620.79	395.22	395.67	225.01	225.12	209.20	209.35
34	631.27		631.85	399.56	400.03	231.71	231.82	215.59	215.76
35	634.24		643.80	404.64	405.03	238.60	238.77	221.84	221.99
36	654.71		655.26	409.43	409.86	245.28	245.40	228.28	228.40
37	667.13		667.72	414.96	415.40	252.17	252.32	234.51	234.62
38	679.09		679.62	420.20	420.64	258.89	258.98	240.85	241.01
39	691.98		692.56	426.28	426.71	265.70	265.85	247.09	247.20
40	704.39		704.88	432.00	432.42	272.39	272.46	253.39	253.57
41	717.69		718.27	438.59	438.99	279.10	279.28	259.61	259.70
42	730.54		731.03	444.78	445.18	285.76	285.85	265.88	266.00
43	744.43		744.90	451.81	452.27	292.62	292.63	272.06	272.14
44	757.65		758.12	458.48	458.89	299.17	299.23	278.37	278.43
45	772.06		772.31	466.06	466.47	306.00	305.84	284.46	284.58
46	785.64		786.12	473.19	473.54	312.45	312.58	290.84	290.68
47				481.22	481.63			296.84	296.92
48	814.80		814.96	488.80	489.20	326.00	325.76		
49	830.19		830.19					309.12	309.28
50	844.39		844.74	505.68	505.68	338.71	339.06	315.30	315.30
51	860.26		860.75	514.89	514.89	345.27	345.86	321.40	321.49
52	875.09		875.44	522.99	523.25	352.10	352.19	327.58	327.77
53	891.42		891.81	532.68	532.98	358.74	358.83	333.62	333.68
54	906.64		907.01	541.47	541.76	365.17	365.25	339.82	339.78
55	923.44		923.86	551.60	552.03	371.84	371.83	345.63	345.82
56	939.04		939.43	561.01	561.19	378.03	378.24	351.87	351.91
57	956.32		956.71	571.57	571.95	384.75	384.76	357.63	357.78
58	972.43		972.76	581.41	581.65	391.02	391.11	363.78	363.83
59	990.15		990.52	592.54	592.88	397.61	397.64	369.71	370.04
60	20006.94		20006.94	602.72	602.72	404.22	404.22	375.75	375.80

TABLE II (cont.)

Frequencies of the lines of the (0,0) band, and their combination differences.

j	R^r	R^c	R^v	P^r	P^v	$2\Delta F'^r$	$2\Delta F'^v$	$2\Delta F''^r$	$2\Delta F''^v$
61	20024.83		20025.21	19614.40	19614.72	410.43	410.49	381.95	381.70
62	041.24		041.97	624.99	625.24	416.25	416.73	387.64	387.70
63	060.45		060.66	637.19	637.51	423.26	423.15	393.02	393.53
64	077.87		077.87	648.22	648.44	429.65	429.43	399.64	399.41
65	096.70		097.07	660.81	661.25	435.89	435.82	405.49	405.29
66	114.33		114.56	672.38	672.58	441.95	441.98	411.12	411.20
67	133.91		134.20	685.58	685.87	448.33	448.33	416.95	416.86
68	152.13		152.13	697.38	697.70	454.75	454.43	422.81	422.78
69	171.95		171.95	711.10	711.42	460.85	460.53	428.51	428.51
70	190.52		190.52	723.62	723.62	466.68	466.90	434.31	434.31
71	210.85		211.11	737.64	737.64	473.21	473.47	439.94	439.92
72	229.55		229.55	750.36	750.60	479.19	478.95	445.50	445.76
73	250.50		250.73	765.35	765.35	485.15	485.38	451.27	451.27
74	269.71			778.28	778.28	491.43		456.92	457.15
75	291.09			793.58	793.58	497.51		462.38	
76	310.50			807.33		503.17		468.36	
77	332.49			822.73		509.76		473.99	
78	352.17			836.51		515.66		479.70	
79	374.44			852.79		521.65		485.23	
80	394.76			866.94		527.82		490.69	
81	417.36			883.75		533.61		496.46	
82	437.76			898.30		539.46		501.88	
83	460.79			915.48		545.31		507.21	
84	481.62			930.51		551.11		512.59	
85	505.29			948.20		557.09		518.29	
86	526.27			963.33		562.94		523.55	
87	550.37			981.74		568.63		528.74	
88	571.48			997.53		573.95		534.24	
89	596.15			20016.13		580.02		539.20	
90	617.85			032.28		585.57		544.85	
91	642.61			051.30		591.31		550.06	
92	664.65			067.79		596.86		555.35	
93	689.79			087.26		602.53		560.38	
94	712.21			104.27		607.94		565.64	
95	737.74			124.15		613.59		570.83	
96	760.43			141.38		619.05		576.08	
97	786.39			161.66		624.73		581.13	
98	809.27			179.30		629.97		586.25	
99	835.54			200.14		635.40		591.25	
100	858.73			218.02		640.71		597.03	
101	885.25			238.51		646.74		601.21	
102	908.85			257.52		651.33		607.54	
103	935.93			277.71		658.22		611.24	
104	959.61			297.61		662.00		616.14	
105	986.85			319.79		667.06		620.87	
106	21010.84			338.74		672.10		625.95	
107	038.40			360.90		677.50		630.69	
108	062.63			380.15		682.48		635.89	
109	090.50			402.51		687.99		639.90	
110				422.73				644.82	
111				445.68					
112				465.56					
113				488.71					
114				509.21					
115				532.37					
116				553.31					
117				576.71					
118				598.06					
119				622.57					
120				645.17					
121				667.69					

TABLE III

Frequencies of the lines of the (0,1) band, and their combination differences.

j	R^r	R^c	R^v	P^r	P^v	$2\Delta F'^r$	$2\Delta F'^v$	$2\Delta F''^r$	$2\Delta F''^v$
1									
2									
3									
4									
5									
6			17787.48						
7			792.30						
8			797.57						
9		17801.65	803.14						
10		807.59	808.93						
11		813.89	815.09						
12		820.45	821.44						

TABLE III (cont.)

Frequencies of the lines of the (0,1) band, and their combination differences.

j	R^r	R^c	R^v	P^r	P^v	$2\Delta F'^r$	$2\Delta F'^v$	$2\Delta F''^r$	$2\Delta F''^v$
13		17827.30	17828.18						
14		834.31	835.16						
15		841.68	842.47						
16	17848.39	849.33	849.98	17740.70		107.69			99.28
17	856.57	857.27	857.87	741.74	17742.40	114.83	114.87	105.47	105.61
18	864.42	865.34	865.91	742.92	743.72	121.50	121.62	112.02	112.08
19	873.19	873.83	874.41	744.55	745.19	128.64	128.64	118.13	118.44
20	881.49	882.52	882.97	746.29	746.90	135.20	135.62	124.74	142.76
21	890.90	891.56	892.02	748.45	749.07	142.45	142.49	130.82	131.24
22	900.03	900.56	901.06	750.67	751.28	149.36	149.28	137.49	137.59
23	909.60	910.30	910.73	753.41	753.97	156.19	156.33	143.86	143.78
24	919.32	920.28	920.28	756.17	756.78	163.15	163.50	150.15	150.25
25	929.58	930.12	930.52	759.45	760.05	170.13	170.47	156.54	156.91
26	939.30	940.61	940.61	762.78	763.37	176.52	177.24	163.02	162.97
27	950.49	951.05	951.43	766.56	767.15	183.93	183.90	168.84	169.54
28	961.16		961.94	770.46	771.07	190.70	190.87	175.60	175.58
29	972.54		973.23	774.89	775.47	197.65	197.76	181.83	182.06
30	983.53		984.35	779.33	779.88	204.20	204.47	188.22	188.39
31	995.39		996.31	784.32	784.84	211.07	211.47	194.23	194.58
32	18007.30		18008.00	789.30	789.77	218.00	218.23	200.61	200.97
33	019.81		020.44	794.78	795.34	225.03	225.10	206.95	207.16
34	031.95		032.64	800.35	800.84	231.60	231.80	213.44	213.46
35	044.97		045.63	806.37	806.98	238.60	238.65	219.47	219.67
36	057.66		058.35	812.48	812.97	245.38	245.38	225.78	226.01
37	071.17		071.91	819.19	819.62	251.98	252.29	231.95	232.13
38	084.54		085.15	825.71	826.22	258.83	258.93	238.22	238.46
39	098.33		099.20	832.95	833.45	265.38	265.75	244.45	244.63
40	112.44		112.92	840.09	840.52	272.35	272.40	250.43	250.81
41	127.05		127.58	847.90	848.39	279.15	279.19	256.97	256.95
42	141.22		141.75	855.47	855.97	285.75	285.78	263.12	263.16
43	156.42		156.94	863.93	864.42	292.49	292.52	269.18	269.24
44	171.16		171.61	872.04	872.51	299.12	299.10	275.40	275.45
45	186.94		187.46	881.02	881.49	305.92	305.97	281.49	281.47
46	202.16		202.63	889.67	890.14	312.49	312.49	287.75	287.87
47				899.19	899.59			293.71	293.79
48	233.89		234.52	908.45	908.84	325.46	325.68		
49			251.23					306.09	305.98
50			267.56	927.80	928.54		339.02		311.93
51	284.64		285.18		939.30		345.88		318.02
52	301.14		301.64		949.54		352.10	324.15	324.02
53	318.93		319.64	960.49	961.16	358.44	358.48	330.02	330.07
54			336.69	971.12	971.57		365.12	335.89	336.11
55	354.74		355.29	983.04	983.53	371.70	371.76		341.92
56	372.36		372.78	994.33	994.77	378.03	378.01	348.00	347.99
57	391.41		391.85	18006.74	18007.30	384.67	384.55	353.92	353.93
58	409.45		409.90	018.44	018.85	391.01	391.05	359.97	359.90
59	429.03		429.48	031.44	031.95	397.59	397.53		365.81
60	447.68		448.07		044.09		403.98	371.83	371.82
61	467.64		468.03	057.20	057.66	410.44	410.37		377.63
62	486.67		487.02		070.44		416.58		383.49
63	507.14		507.62		084.54		423.08		389.36
64	526.68		527.04		097.66		429.38		395.18
65	547.90		548.27		112.44		435.83		400.83
66			568.10		126.21		441.89		406.52
67			590.14		141.75		448.39		412.29
68			610.20		155.81		454.39		418.53
69			632.11		171.61		460.50		424.00
70			653.09		186.20		466.89		429.48
71			675.93		202.63		473.30		435.15
72			697.03		217.94		479.09		441.41
73			720.34		234.52		485.82		446.44
74			742.02		250.59		491.43		452.18
75			765.86		268.16		497.70		457.38
76			787.41		284.64		502.77		463.52
77			812.13		302.34		509.79		468.48
78			834.40		318.93		515.47		474.92
79			859.34		337.21		522.13		479.66
80			882.25		354.74		527.51		485.42
81			907.48		373.92		533.56		490.84
82			930.72		391.41		539.31		496.29
83			956.50		411.19		545.31		501.69
84			980.14		429.03		551.11		507.15
85			19006.87		449.35		557.52		512.18
86			030.43		467.96		562.47		518.08
87			057.35		488.79		568.56		522.81
88			081.77		507.62		574.15		526.36
89					528.99				533.87
90					547.90				

successively. For the (1,0) band, Johnson's data have been substituted for the much poorer data of Hindrich's which were originally used. In this band, as well as in the (1,2) band, the series assignments have been carried to

TABLE IV

Frequencies of the lines of the (1,0) band, and their combination differences.

j	R^r	R^c	R^v	P^r	P^v	$2\Delta F'^{r}$	$2\Delta F'^{v}$	$2\Delta F''^{r}$	$2\Delta F''^{v}$
1									
2	21135.36	21138.65	21142.55						
3	139.86	142.55	145.99						
4	144.86	146.50	149.64						
5	149.13	150.90	153.63						
6	153.63	155.38	157.74						
7	158.82	160.16	162.18						
8	163.71	165.07	166.83						
9	169.10	170.22	171.75						
10	174.34	175.51	176.85						
11	180.09	181.05	182.25						
12	185.69	186.72	187.76						
13	191.86	192.64	193.62						
14	197.77	198.71	199.54						
15	204.24	205.04	205.89						
16	210.54	211.41	212.26						100.32
17	217.47	218.13	218.81		21104.72		113.41		106.69
18	224.20	224.99	225.53		104.72		120.27	113.32	112.98
19	231.49	232.11	232.73	21104.15	105.15	126.77	126.96	119.48	119.84
20	238.61	239.36	239.80	104.72	105.15	133.89	134.21	126.34	126.24
21	246.24	246.92	247.34	105.15	105.87	141.09	141.05	132.47	132.75
22	253.71	254.42	254.82	106.14	106.61	147.57	147.81	139.24	138.96
23	261.78	262.40	262.82	107.00	107.96	154.78	154.44	145.36	145.23
24	269.62	270.30	270.62	108.35	109.19	161.27	161.11	152.09	151.77
25	278.11	278.75	279.04	109.69	110.63	168.42	168.12	158.17	158.09
26	286.49	286.95	287.23	111.45	112.21	175.04	174.74	164.82	164.70
27	295.08	295.68	297.06	113.29	114.05	181.79	181.63	171.07	170.93
28	303.86	304.35	304.77	115.42	116.02	188.44	188.33	177.28	177.57
29	312.44		313.50	117.80	118.11	195.64	195.39	183.90	183.86
30	321.93		322.86	119.96	120.49	201.97	202.37	189.68	190.29
31	330.22		330.89	122.76	123.21	207.46	207.68	196.45	196.84
32	341.35		341.83	125.48	126.02	215.87	215.81	202.94	203.24
33	351.67		352.32	127.28	127.65	224.39	224.67	209.56	209.54
34	360.82		361.31	131.79	132.29	229.03	229.02	215.96	215.95
35	371.25		371.83	135.71	136.37	235.54	235.46	221.76	222.25
36	381.40		381.77	139.06	139.33	242.34	242.44	228.02	228.12
37	393.12		393.91	143.23	143.71	249.89	250.20	234.49	234.50
38	402.52		403.10	146.91	147.27	255.61	255.83	240.97	
39	413.85		414.10	152.15		261.70		247.02	247.14
40	424.80		425.22	155.50	155.96	269.47	269.26	253.16	253.02
41	436.44		437.26	160.69	161.08	275.75	276.18	259.93	259.84

TABLE V

Frequencies of the lines of the (1,1) band, and their combination differences.

j	R^r	R^c	R^v	P^r	P^v	$2\Delta F'^{r}$	$2\Delta F'^{v}$	$2\Delta F''^{r}$	$2\Delta F''^{v}$
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14	19582.91	19583.58	19584.57						
15	589.26	590.41	591.26					92.87	92.57
16	596.50	597.38	598.11	19490.04	19491.01	106.46	106.37	98.66	99.40
17	603.86	604.60	605.36	490.60	491.01	113.26	113.59	105.49	105.78
18	611.07	612.02	612.41	491.01	491.60	120.06	120.42	111.90	111.72
19	619.09	619.74	620.23	491.96	492.88	127.13	126.86	118.19	118.62
20	626.57	627.55	627.98	492.88	493.40	133.69	134.15	125.01	125.10
21	635.13	635.75	636.35	494.08	494.64	141.05	141.11	131.03	131.38
22	643.24	643.80	643.80	495.54	496.17	147.70	147.63	137.53	137.57
23	652.08	652.69	653.09	497.60	498.18	154.48	154.51	143.59	143.63
24	660.81	661.25	661.25	499.65	500.17	161.16	161.08	150.23	150.26
25	669.97	670.61	670.93	501.85	502.43	168.12	168.18	156.63	156.46
26	679.09	679.62	679.62	504.18	504.79	174.91	174.83	163.05	163.12
27	688.75	689.38	689.59	506.92	507.49	181.83	181.89	169.38	169.34
28	698.34	698.92	699.20	509.71	510.28	188.63	188.64	175.63	175.77
29	708.42	708.96	709.19	513.12	513.61	195.30	195.35	182.01	182.00
30	718.27	719.12	719.12	516.33	516.92	201.94	202.20	188.61	188.56
31	727.59	728.12	728.12	519.81	520.40	207.78	207.72	194.37	194.69
32	739.47	740.06	740.06	523.90	524.43	215.57	215.63	199.54	199.39
33	751.43	751.75	751.75	528.05	528.73	223.38	223.02	206.79	207.08

TABLE V (cont.)

Frequencies of the lines of the (1,1) band, and their combination differences.

j	R^r	R^c	R^v	P^r	P^v	$2\Delta F'^r$	$2\Delta F'^v$	$2\Delta F''^r$	$2\Delta F''^v$
34	19761.51	19761.95	19761.95	19532.98	19533.48	228.83	228.53	213.91	213.68
35	773.12	773.59	773.95	537.52	538.07	235.60	235.52	219.75	219.79
36	784.33		784.90	541.47	541.76	242.57	242.57	225.63	225.87
37	797.15		797.68	547.49	547.72	249.66	249.96	232.30	232.30
38	807.93		808.48	551.60	552.03	255.90	256.45	238.47	238.49
39	820.63		821.13	558.68	559.19	261.95	261.94	244.77	244.71
40	832.50		832.96	563.16	563.77	269.34	269.19	250.19	250.93
41	845.61		846.21	569.76	570.20	275.85	276.01	256.92	256.94
42	857.96		858.55	575.58	576.02	282.38	282.53	263.16	263.30
43	871.65		872.14	582.45	582.91	289.20	289.23	269.20	269.29
44	883.75		884.74	588.76	589.26	294.99	295.48	275.54	275.64
45	898.30		898.83	596.11	596.50	302.19	302.33	281.36	282.02
46	911.43		911.91	602.39	602.72	308.71	309.17	287.90	287.76
47	926.00		926.50	610.40	611.07	315.60	315.43	293.72	293.83
48	939.43		939.77	617.71	618.08	321.72	321.69	299.96	299.93
49	954.48		954.99	626.04	626.57	328.44	328.42	305.89	305.89
50	968.44		968.79	633.54	633.88	334.90	334.91	312.07	312.16
51	983.73		984.20	642.41	642.83	341.32	341.37	318.12	318.06
52	998.50		998.58	650.32	650.73	348.18	347.85	324.12	324.12
53	20014.11		20015.24	659.61	660.08	354.50	355.16	330.78	330.15
54	028.71		029.06	667.72	668.43	360.99	360.63	336.28	337.02
55	044.98		045.41	677.83	678.22	367.15	367.19	342.13	342.11
56	060.45		060.66	686.58	686.95	373.87	373.71	347.60	347.71
57	077.87		077.87	697.38	697.70	380.49	380.17	354.27	354.13
58	092.14		092.54	706.18	706.53	385.96	386.01	360.86	360.65
59	109.02		109.33	717.01	717.22	392.01	392.11	365.34	365.74
60	125.35		125.63	726.80	726.80	398.55	398.83	371.54	371.69
61	143.28		143.78	737.48	737.64	405.80	406.14	377.64	377.70
62	159.79		159.79	747.71	747.93	412.08	411.86	383.60	384.10
63	176.40		176.78	759.68	759.68	416.72	417.10	389.69	389.69
64	193.78		193.78	770.10	770.10	423.68	423.68	393.74	394.12
65	212.27		212.71	782.66	782.66	429.61	430.05	400.94	400.56
66	229.55		229.55	792.84	793.22	436.71	436.33	406.24	406.68
67	248.38		248.38	806.03	806.03	442.35	442.35	413.09	412.73
68	265.27		265.52	816.46	816.82	448.81	448.70	418.19	418.19
69	285.04			830.19	830.19	454.85	454.85	423.92	423.94
70	302.47			841.35	841.58	461.12	460.89	430.00	429.69
71	322.37			855.04	855.35	467.33	467.02	435.53	
72	339.97			866.94		473.03		441.02	
73	360.90			881.35		479.55		446.58	
74	378.64			893.39		485.25		452.75	
75	394.92			908.15		486.77		457.81	
76	417.36			920.83		496.53		459.30	
77	437.76			935.62		502.14		469.16	
78	457.25			948.20		509.05		474.43	
79	479.05			963.33		515.72		479.84	
80	497.77			977.41		520.36		485.45	
81	518.98			993.60		525.38		490.83	
82	538.94			20006.94		532.00			
83	561.25								
84	580.85								
85	603.39								
86	623.21								
87	646.36								
88	666.32								
89	689.79								
90	710.11								
91	734.21								
92	754.35								
93	778.38								
94	799.03								
95	823.49								
96	844.53								
97	868.96								
98	890.51								
99	915.03								
100	935.93								
101	959.61								

somewhat larger values of j than given in Tables II to VI but seem too uncertain to warrant publication.

In all cases the values of $2\Delta F^r$ have been obtained by the use of red component of the P and R branches. The values of $2\Delta F^v$, however, have been obtained from the violet component of the P branch and the central component of the R branch, where it exists, otherwise from the violet component. This has been done because, as is shown later in the paper, the violet component of the P branch corresponds to the central component of the R

TABLE VI

Frequencies of the lines of the (1,2) band, and their combination differences.

j	R^r	R^c	R^v	P^r	P^v	$2\Delta F'^r$	$2\Delta F'^v$	$2\Delta F''^r$	$2\Delta F''^v$
1									
2									
3									
4									
5									
5									
6									
7									
8									
9									
10			17967.21						
11			973.23						
12	17977.30	17978.39	979.47						
13	984.35	985.18	986.09					78.73	78.80
14	991.10	992.02	992.92	17898.57	17899.59	92.43	92.43	85.16	85.15
15	998.46	999.29	18000.12	899.19	900.03	99.27	99.26	91.51	91.46
16	18005.88	18006.74	007.30	899.59	900.56	106.29	106.18	97.90	98.21
17	013.79	014.52	015.24	900.56	901.08	113.23	113.44	104.80	104.69
18	021.68	022.49	023.09	901.08	902.05	120.60	120.44	110.68	110.76
19	030.10	030.82	031.44	903.11	903.76	126.99	127.06	118.08	117.27
20	038.56	039.29	039.83	904.60	905.32	133.96	133.97	123.49	123.50
21	047.56	048.19	048.66	906.61	907.32	140.95	140.87	129.72	129.69
22	056.39	057.20	057.66	908.84	909.60	147.53	147.60	136.18	136.17
23	065.95	066.49	066.94	911.38	912.02	154.57	154.47	142.32	142.28
24	075.31	076.02	076.40	914.07	914.92	161.24	161.10	148.74	148.71
25	085.15	085.91	086.28	917.21	917.78	167.94	168.13	155.03	155.07
26	095.31	095.96	096.27	920.28	920.95	175.03	175.01	161.09	161.25
27	105.77	106.32	106.70	924.06	924.66	181.71	181.66	167.51	167.42
28	116.29	117.05	117.05	927.80	928.54	188.49	188.51	173.80	173.77
29	127.05		127.58	931.97	932.55	195.08	195.03	180.00	180.15
30	138.32		139.03	936.29	936.90	202.03	202.13	186.44	186.14
31	150.03		150.94	940.61	941.44	209.42	209.50	192.43	192.59
32	161.37		162.05	945.89	946.44	215.48	215.61	199.98	199.51
33	173.59		174.29	951.05	951.43	222.52	222.86	204.87	205.00
34	185.56		186.20	956.50	957.05	229.06	229.15	211.07	211.02
35	198.37		199.06	962.52	963.27	235.83	235.79	217.27	217.53
36	210.75		211.33	968.29	968.67	242.46	242.66	223.57	223.72
37	224.02		224.70	974.80	975.34	249.22	249.36	229.71	229.86
38	236.78		237.36	981.04	981.47	255.74	255.89	225.29	235.97
39	250.59		251.23	988.73	988.73	261.86	262.50	242.01	241.97
40	263.86		264.36	994.77	995.39	269.09	268.97	248.10	248.25
41	278.33		278.94	18002.49	18002.98	275.84	275.96	254.18	254.23
42	292.04		292.71	009.68	010.13	282.36	282.58	260.46	260.50
43	306.91		307.54	017.87	018.44	289.04	289.10	266.37	266.43
44	321.20		321.77	025.67	026.28	295.53	295.49	272.43	272.57
45	336.69		337.21	034.48	034.97	302.21	302.24	278.55	278.54
46	351.34		351.88	042.65	043.23	308.69	308.65	284.10	283.86

branch. The combination principle is tested by comparing the values of $2\Delta F_j'$ for all bands having the same initial vibration state, and the values of $2\Delta F_j''$ for all bands having the same final vibration state. In general the discrepancies are less than about 0.15 cm^{-1} and fall within the limits of experimental error.

THE DETERMINATION OF THE CONSTANTS OF THE MOLECULAR CARRIER

Birge[20] and others have recently developed the quantum theory, with certain assumptions, to such a point that it is now possible to determine certain constants for the molecule giving rise to a band spectrum with a comparatively high degree of accuracy. The first assumption is that the law of force between the two nuclei of the molecule can be represented by:

$$F(\text{dynes}) = k_1(r-r_0)+k_2(r-r_0)^2+k_3(r-r_0)^3+\cdots \tag{3}$$

The second important assumption is that the values of the energy levels can be represented by an expression of the form[21]:

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[20] Birge, Nature **116**, 783 (1925); Phys. Rev. **27**, 245 (1926); Report, Chap. IV.

[21] Birge, Report, pp. 173–175, 234–237.

$$E/hc=(E^n+E_m)/hc=E^nhc+B_nm^2+D_nm^4+F_nm^6+H_nm^8+\cdots. \qquad (4)$$

where $m=j-\epsilon=k-\alpha$ and E^n is the energy due to vibration. Kemble,[22] considering only the first three terms on the right of Eq. (4), has obtained expressions for B_0, B_1, D_0 and D_1. The relations are simplified if the case of the non-vibrating molecule is considered, i.e., if $n=0$. Neglecting the electronic energy, as is done in Eq. (4), one can write:

$$E_m/hc=F_m=B_0m^2+D_0m^4+F_0m^6+H_0m^8+\cdots. \qquad (5)$$

The constants of the molecule referred to above are the values of k_1, k_2, and k_3 of Eq. (3) and the value of B_0 of Eq. (5). The moment of inertia I_0 of the molecule is determined from B_0, since $B_0=h/8\pi^2I_0$.

Expressions for the values of the k_1, k_2, k_3, etc., which will be called here the k_i (i taking on the values 1, 2, 3, $\cdots$), can be developed for the cases of a molecule rotating, but having only infinitesimal vibration, and of a molecule vibrating, but having only infinitesimal rotation. The expressions for the k_i for the first case involve only quantities which can be derived from rotational data alone. The expressions for the k_i for the second case involve the values of B_0 and B_1, which must be determined from rotational data, in addition to quantities which can be determined from vibrational data.[23]

In the actual determination of the constants it is better in view of the relative accuracy of the two types of data to eliminate the k_i from the expressions for the k_i derived for the two cases considered. The following relations are then obtained:

$$D_0=-4B_0^3/(\omega^{0^2}) \qquad (6)$$

$$F_0=(2-\alpha\omega^0/6B_0^2)D_0^2/B_0 \qquad (7)$$

$$H_0=3F_0D_0/B_0-5D_0^3/B_0^2+F_0^2/D_0-8D_0^2x/3\omega^0 \qquad (8)$$

where ω^0 is the limiting frequency of vibration for infinitesimal amplitude, $\alpha=B_0-B_1$, and $x=(\omega^0-\omega^1)/2\omega^0$, ω^1 being the frequency of vibration for the state $n=1$. Eq. (6) is due to Kratzer,[24] Kemble,[22] and others, while Eqs. (7) and (8) are due to Birge.[25] Kemble, using only terms inclusive of D_n in Eq. (4) has derived a theoretical expression for β'' in

$$D_n=D_0+\beta''n \qquad (9)$$

This is as far as usable theoretical relations had been developed at the time the present investigation was carried on.

Since the expression for the frequency of the lines of a band involve the values of the rotational energy for both the initial and final states, Eqs. (1a) and (1c), it is inconvenient to make use of these expressions. The combination differences, however, Eqs. (2a) and (2b), involve only the energy values

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[22] Kemble, J. Optical Soc. Am. **12,** 1 (1926).

[23] Birge, Report, p. 235 et. seq.

[24] Kratzer, Zeits. f. Physik **3,** 289 (1920).

[25] Birge, Report, p. 237; Nature, **116,** 783 (1925).

for a single state. Substituting Eq. (5) in either Eq. (2a) or (2b) there results:

$$2\Delta F_j = 4B_0 m + 8D_0 m^3 + 12F_0 m^5 + 16H_0 m^7 + \cdots \tag{10}$$

Eqs. (6) to (8) are expressions for D_0, F_0 and H_0 in terms of quantities derivable from vibrational data, but each of these are functions of B_0. As B_0 is not accurately known at first, Eq. (10) can most conveniently be solved by the method of successive approximations.

In the case of the Swan bands m is not an exact half-integer, and it is therefore necessary to determine α (or ϵ) at the same time that B_0 is determined. In the course of the investigation it was found that α itself is a function of k of the form

$$\alpha = \alpha_0 + \zeta_0 k^2 + \theta_0 k^4 + \cdots \tag{11}$$

with an analogous expression for ϵ. This is not without precedent, as Birge[26] found it necessary to use a variable α in the case of the CuH bands. In the case of the Swan bands it was found necessary to include only the first two terms of Eq. (11).

The method of calculation actually used will now be briefly outlined. The quantities which are derivable from vibrational data are assumed to be accurately known, due to the fact that the percent error in their determination is very small It is then necessary to express Eq. (10) as a function of the unknowns, which are B_0, B_1 and α (or ϵ). The resultant expression is unwieldy and the method of successive approximations is used.

Let B_s be an assumed value of B_0, i.e., an approximate value of B_0 determined in any suitable manner. With this value of B_0 approximate values of D_0, F_0, and H_0 are calculated, these being denoted by D_s, F_s, and H_s. Approximate values of $2\Delta F_j$ may then be calculated by means of Eq. (10) using the values of B_s, D_s, F_s and H_s. Residuals are then formed, in the sense of observed value of $2\Delta F_j$ minus the calculated value. Corrections to the value of B_s are then determined from these residuals in the following manner. The variation of Eq. (10) with respect to the quantities which are variable is

$$\begin{aligned}\delta 2\Delta F_j = {} & 4m\delta B_0 + 8m^3\frac{\partial D_0}{\partial B_0}\delta B_0 + 12m^5\frac{\partial F_0}{\partial B_0}\delta B_0 + 12m^5\frac{\partial F_0}{\partial B_1}\delta B_1 \\ & + 16m^7\frac{\partial H_0}{\partial B_0}\delta B_0 + 16m^7\frac{\partial H_0}{\partial B_1}\delta B_1 + \cdots \end{aligned} \tag{12}$$

B_1 differs but little from B_0 and hence B_s may be used as an approximate value of B_1. The variation of $2\Delta F_j$ is, except for terms of higher order than the first, the residual found by means of the approximate values of the constants. If α (or ϵ) is to be determined it may be included in Eq. (12) and evaluated along with the δB_0 and δB_1. In the actual case of the Swan bands it was also necessary to include a term due to ζ_0 of Eq. (11). Sub-

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[26] Birge, Report, pp. 174–175, 236. See also Kemble, Report, p. 346.

stituting $k-\alpha$ for m in Eq. (12) and for α its expanded form in Eq. (11), one has

$$\delta 2\Delta F_j = a+\delta B_0\left(4k+8k^3\frac{\partial D_0}{\partial B_0}+12k^5\frac{\partial F_0}{\partial B_0}+16k^7\frac{\partial H_0}{\partial B_0}\right)+ck^2$$
$$+\delta B_1\left(12k^5\frac{\partial F_0}{\partial B_1}+16\,k^7\frac{\partial H_0}{\partial B_1}\right)+\cdots \tag{13}$$

where $a=-4B_0\alpha_0+\cdots$ and $c=-12B_0\zeta_0-24D_0\alpha_0+\cdots$.

The most probable values of the unknowns in Eq. (13) are given by the method of least squares. However, as no rapid method of least squares has been formulated to cover such a case as this the labor involved is excessive. After much consideration it was decided to solve Eq. (13) by the method introduced into modern literature by Norman Campbell under the name of "Zero Sums."[27] The method of zero sums consists of dividing the observational equations up into as many groups as there are unknowns, and then adding the observational equations of each group. One then has as many simultaneous equations ("normal" equations) as there are unknowns, and the solution is made in any convenient way. This method, when applied to Eq. (13) reduces enormously the amount of work necessary. Let one consider a rational integral function where values of the dependent variable are given for equidistant values of the independent variable, and make a change of variable, if need be, so that the independent variable has successive values which differ by unity, but which are not necessarily integral. The observational equations of any one of the "Zero Sums" groups may then be represented by

$$y_x = a_0+a_1(x_c+r)+a_2(x_c+r)^2+a_3(x_c+r)^3+\cdots \tag{14}$$

in which r is either an integer or a half-integer, depending upon whether there is an odd or even number of observations in the group, and varies from $-u$ to $+u$, where $u=(n-1)/2$, n being the number of observations in the group. x_c is the central or average value of the independent variable for the group. If now the average of n consecutive observational equations be taken, there results, by application of the binomial expansion,

$$(1/n)\sum_{r=-u}^{r=+u} y_x = a_0+a_1Z_1+a_2Z_2+a_3Z_3+\cdots \tag{15}$$

where, if $A=\frac{n^2-1}{12}$; $B=\frac{3n^2-7}{20}A$; $C=\frac{3n^4-18n^2+31}{112}A$

$$\begin{array}{lll} Z_0=1 & Z_3=x_c^3+3Ax_c & Z_6=x_c^6+15Ax_c^4+15Bx_c^2+C \\ Z_1=x_c & Z_4=x_c^4+6Ax_c^2+B & Z_7=x_c^7+21Ax_c^5+35Bx_c^3+7Cx_c \\ Z_2=x_c^2+A & Z_5=x_c^5+10Ax_c^3+5Bx_c & \end{array} \tag{16}$$

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[27] Campbell, Phil. Mag. (6) **39,** 177 (1920). The writer believes this method to be essentially the same as that given by Tobias Mayer in 1748. See Whittaker and Robinson, Calculus of Observations, p. 258.

Eq. (15) is rigorous, but the left hand side in practice contains the algebraic sum of the errors, divided by n, and will therefore be referred to as a normal place.

Now Eq. (15) may be applied to both Eq. (10) and Eq. (13) Thus it is not necessary to calculate the individual residuals, but the algebraic sum of the residuals may be computed at once by the application of Eq. (15). The original values of $2\Delta F_j$ are divided into as many groups as there are unknowns, and the sums of the $2\Delta F_j$ are found for each group. From this point until the approximations are finished it is not necessary to deal with the individual values. In the actual work on the Swan bands an equation, analogous to Eq. (13), was set up for the vibrational state $n=1$. The inclusion of the data for the vibration state $n=1$ practically doubled the number of observational equations, but only increased the number of unknowns from four to six, the two additional unknowns being the values of a and c of Eq. (13) for the state $n=1$. In the present investigation about one hundred and seventy values of $2\Delta F_j$ were available.

The various constants discussed above were evaluated, with the results which follow. The constants for the vibration state $n=1$ are not listed, as the theoretical basis upon which they were computed is not sufficiently well founded to warrant their publication.

Initial State	*Final State*
$\alpha'=0.0487-7.36\times10^{-6}k^2$	$\alpha''=0.0324-2.55\times10^{-6}k^2$
$B_0'=1.7495$ cm^{-1}	$B_0''=1.6260$ cm^{-1}
$D_0'=6.8673\times10^{-6}$ cm^{-1}	$D_0''=-6.5040\times10^{-6}$ cm^{-1}
$F_0'=0.9068\times10^{-11}$ cm^{-1}	$F_0''=1.2365\times10^{-11}$ cm^{-1}
$H_0'=-3.14\times10^{-16}$ cm^{-1}	$H_0''=-1.64\times10^{-16}$ cm^{-1}
$B_0'-B_1'=0.01730$ cm^{-1}	$B_0''-B_1''=0.01487$ cm^{-1}
$I_0'=15.84\times10^{-40}$ gm cm^2	$I_0''=17.03\times10^{-40}$ gm cm^2
$r_0'=1.265\times10^{-8}$ cm	$r_0''=1.311\times10^{-8}$ cm
$k_1'=10.92\times10^5$ dyne cm^{-1}	$k_1''=9.28\times10^5$ dyne cm^{-1}
$k_2'=-3.44\times10^{14}$ dyne cm^{-2}	$k_2''=-2.68\times10^{14}$ dyne cm^{-2}
$k_3'=2.75\times10^{22}$ dyne cm^{-3}	$k_3''=2.25\times10^{22}$ dyne cm^{-3}

The above values are obtained from the central component of the R branch and the violet component of the P branch. The value of B_0 is believed to be within 0.10 percent of the true value. α_0 is difficult to determine, and the error in its determination may be as high as ten percent. ζ_0 is believed to be accurate to at least five percent. The value of I_0 has essentially the same accuracy as B_0. Fig. 1 gives the residuals of $2\Delta F_j$. In this figure, in order to eliminate somewhat the rather large individual errors of the observations, the residuals are grouped in sets of five, and the average of each set plotted, except for the first and last points on the curve, where the mean of a smaller number of residuals is used. If there is a trend present, it is believed to be so small as not appreciably to affect the constants.

Johnson's published values of I_0' and I_0'' are 16.236×10^{-40} and 17.410×10^{-40}, and while he does not claim for these values an accuracy greater than 0.5 percent, they differ from the present values by over two percent. His values of the moment of inertia, as well as the numbering of the lines, were determined by a graphical method proposed some years ago by Birge. His procedure, while very rapid, is rather indeterminate for complex bands such as those studied here, and has since been superseded by more definite and precise methods,[28] the most accurate of which is that used in the present investigation. Any one of the new methods indicates that Johnson's numbering of j' and j'' is too large by one unit. This incorrect numbering accounts entirely for the above discrepancy. Fig. 2 is a plot of the first differences of $2\Delta F_j''$ for the (0,0) band. The circles are the values determined from Leinen's data, and the filled in circles are the values given by Johnson. A curve passed through these points and extrapolated back to $m=0$ (or $j=0.5$ approximately) gives the value of $4B_0$, since from Eq. (10) we obtain, to a high degree of approximation,

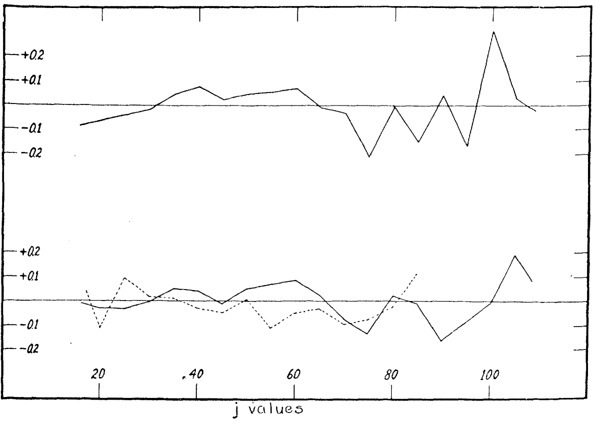

Fig. 1. Mean Residuals of $2\Delta F$. Upper: $2\Delta F''$ (0, 0) band. Lower: $2\Delta F'$, solid line (0,0) band, dotted line (0, 1) band.

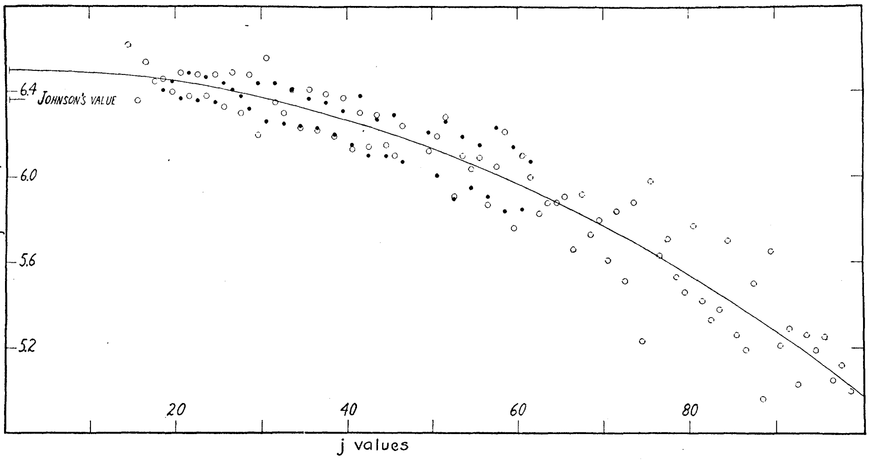

Fig. 2. Values of $2\Delta^2F_j''$ for the (0, 0) band. Open circles from Leinen's data, solid circles from Johnson's data. Abscissae are j values, ordinates cm⁻¹.

$$2\Delta^2F_j = 4B_0 + 24D_0m^2 + \cdots \tag{17}$$

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[28] See Report, pp. 169–175.

The theoretical curve resulting from the constants determined by the writer has been drawn on the figure, as well as the value of $4B_0$ given by Johnson. It is quite apparent that his value is too small. Precisely similar relations hold for the initial state.

In order to determine the frequencies of the origin of the various bands, the contribution due to rotation was calculated and then subtracted from the frequencies of the R and P lines, as indicated in the following equations.

$$\nu_0 = R_j - (F_{j+1}' - F_j'') \tag{18a}$$

$$\nu_0 = P_j - (F_{j-1}' - F_j'') \tag{18b}$$

The following values have been calculated for the frequency of the origin:

(0,0) band, 19379.20 ± 0.2 cm^{-1}
(0,1) band, 17761.10 ± 0.2 cm^{-1}
(1,1) band, 19513.50 ± 0.4 cm^{-1}
(1,0) band, 21131.60 ± 0.5 cm^{-1}

These values are for the mean of the red and violet components. They differ slightly from the values of the origin determined by Johnson, whose values are for the central component. Until a satisfactory explanation of the triplet separation has been developed any value for the origin is somewhat meaningless.

Multiplicity of the Lines

The interpretation of the separation of the components of the doublets and triplets is, to say the least, difficult. Mulliken's interpretation[29] is probably correct, but expressions based upon this interpretation for the separation have not yet been published in sufficient detail to use.[30] None of the other theoretical expressions thus far derived seem to apply in the case of the Swan bands. The R branch consists of triplets for small values of j, and the triplet separations decrease as j increases. In the vicinity of $j=30$ the central component approaches so close to the violet component that it is no longer possible to resolve these two components. In the vicinity of $j=70$ the separation between the resulting two components has become so small that it is no longer possible to resolve them. In the case of the P branch the lines can be carried back only to $j=16$ approximately, but even at this point, with an arc as source, there is no evidence of a triplet structure. Johnson, using a tube fitted with carbon electrodes and filled with argon at 30 mm pressure, has obtained a triplet P branch. Fig. 3 is a plot of the separations of the various components of the (0,0) band, Johnson's data being used. In this figure the lines of the R branch are indicated by the large circles, and the lines of the P branch by the smaller filled-in circles. The vertical axis represents the mean position of the red and violet components of the R branch. The red components of the P branch have been made to coincide,

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[29] Mulliken, Phys. Rev. **29**, 637 (1927).

[30] Kemble and Jenkins, Phys. Rev. **29**, 607 (1927), Abstract 8; See also Phys. Rev. **30**, 171 (1927).

arbitrarily, with the red components of the *R* branch. It is apparent from the plot that the violet component of the *P* branch coincides with the central component of the *R* branch, while the central component of the *P* branch falls between the red and central components of the *R* branch. Now the central component is observed by Johnson only when using the vacuum tube as a source. There is no evidence whatsoever of a central component when the arc is used as a source. It is therefore evident that these *P* lines do not correspond to the central component of the *R* branch, and their true explanation should be a matter of some interest.

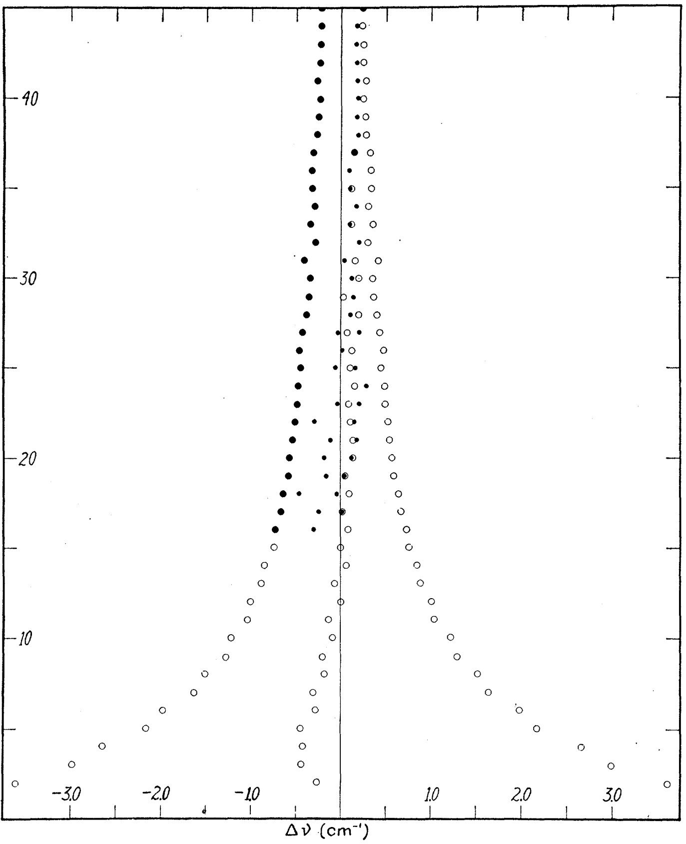

Fig. 3. Component separations of the *R* and *P* branches of the (0, 0) band. Large circles represent lines of the *R* branch with the mean position of the red and violet components taken as the vertical axis. For the *P* branch the red component is plotted arbitrarily in coincidence with the red component of the *R* branch, such points being indicated by filling in the large circles. The smaller filled-in circles then represent the position of the violet and (in a few cases) central component of the *P* branch.

Heurlinger[14] concluded that the separations were a function of m^{-1}. That this is the case is clearly brought out by the fact that the separation of the red and violet components of the *R* branch can be represented within the limits of experimental error from about $j=10$ to $j=70$ by the very simple expression $R^v-R^r=c/k$, where c is a constant and $k=j-0.5$. In the region $j=2$ to $j=10$ the separation may be represented by the addition of a term of the form Ae^{-dk}, where A and d are constants. These expressions are, of course, empirical, and are not suggested as a basis for an interpretation of the separation. Any expression which can be made use of theoretically must involve the j for both the initial and final states of the molecule. The basis of this statement lies in the following observed relations, which seem to be true, on the average, except for the R lines for which $j=2$:

$$\begin{aligned}(R^v-R^r)_{(1,0)}-(R^v-R^r)_{(0,0)}&=(R^v-R^r)_{(1,1)}-(R^v-R^r)_{(0,1)}\\&=(R^v-R^r)_{(1,2)}-(R^v-R^r)_{(0,2)}\end{aligned}\tag{19a}$$

$$(R^v-R^r)_{(0,1)}-(R^v-R^r)_{(0,0)}=(R^v-R^r)_{(1,1)}-(R^v-R^r)_{(1,0)}\tag{19b}$$

$$(R^v-R^r)_{(1,1)}>(R^v-R^r)_{(1,0)}>(R^v-R^r)_{(0,1)}>(R^v-R^r)_{(0,0)}\tag{19c}$$

Eq. (19a) is a function of the initial state, and Eq. (19b) is a function of the final state. The differences involved in Eqs. (19a) and (19b) are all quite small, of the order of the experimental error, and at the same time are one-half, or less, the resolving power of the grating used. The necessity of exempting the lines R_2, in the above relations, suggests that Johnson may be in error in his assignment of these particular lines.

In the early portion of this paper a slight mutual displacement of alternate observed lines was discussed. This will now be taken up quantitatively, and, for convenience, the amount of the displacement will be denoted by the term "stagger" and the phenomenon itself as "staggering." Fig. 4 shows the amount of staggering, for the (0,0) band, of the violet component of the P branch and of the central component of the R branch to $j=36$, and of the violet component of the R branch from $j=37$ to $j=100$. Johnson's data were used from $j=0$ to $j=47$, and Leinen's from $j=48$ to $j=100$. The amount of staggering was determined by forming a table of differences, using alternate lines, and then interpolating to halves by means of the formula[31]:

$$f_{0.5}=f_0+\tfrac{1}{2}f_{0.5}'-(f_0''+f_1'')/16+\cdots\tag{20}$$

Curves plotted for the staggering of the various branches indicate that in the vicinity of the origin the stagger is zero for all branches except for the red component of the R branch, the stagger near the origin for this component being about 0.2 cm^{-1}. This seems to be real. In Fig. 4 the stagger of the P branch is indicated by the small filled-in circles, while that of the R branch is indicated by the larger open circles. The dotted curve was plotted from values of $S=1.967\times10^{-4}j^2$. If this is interpreted as due to a change in the moment of inertia of the molecule, a corrective term should be added, due to the effect of this change in B_0 on the value of D_0. The solid curve of Fig. 4 was plotted from values of $S=1.967\times10^{-4}j^2-2.36\times10^{-9}j^4$, where the coefficient of j^4 is the change in D_0 produced by a change in B_0 of 1.967×10^{-4}. It is made on the assumption that the final state alone is double, although the assumption that the initial state is double is equally tenable. If the

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[31] See, for example, S. Newcomb's Logarithmic Tables, p. 64, Section 29.

initial state alone is double then the coefficient of j^4 would be a trifle less. Mulliken[29] has predicted that the staggering in the Swan bands is due to a so-called rotational doubling (σ-type doubling). Such rotational doubling can be considered as the effect of a double moment of inertia. Thus Mulliken's prediction is verified in the case of the Swan bands, the two moments of inertia, if the final state alone is concerned, differing by 0.012 percent.

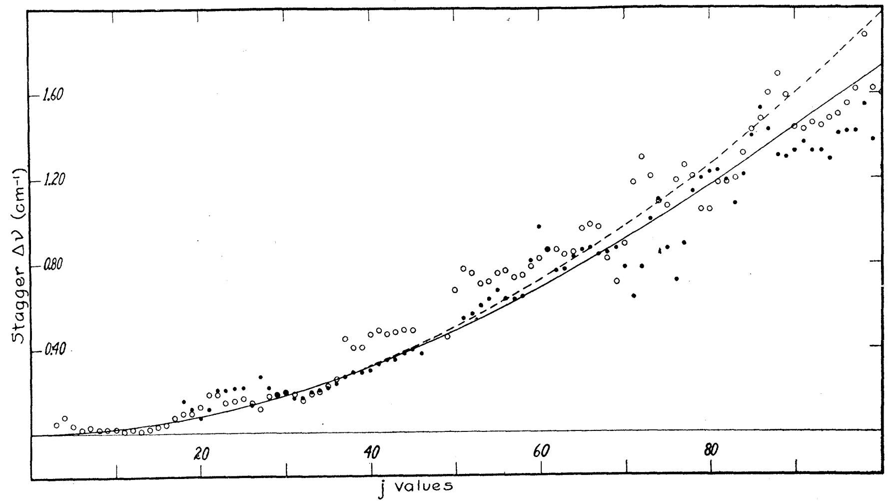

Fig. 4. "Staggering" for the (0, 0) band. Open circles refer to the R branch, filled-in circles to the P branch. Dotted curve, $S=\Delta Bj^2$; Solid curve, $S=\Delta Bj^2+\Delta Dj^4$.

In regard to Johnson's suggestion that the Swan bands may be due to CH-HC (acetylene), the writer wishes to point out that the Swan bands have never been produced in absorption in acetylene, nor in any cold gas. Combination bands, having the same vibrational energy changes as the Swan bands, have not been observed. The writer, from a consideration of these facts, and from the sources of the Swan bands, believes that the carrier is either C-C or, if such a compound is possible, $C^{-}-C^{-}$ [4,32]. Except for the fact that it is without precedent, the doubly negatively charged molecule would be preferable in that it has the same number of electrons as N_2, and the second positive group of nitrogen is known to be quite similar to the Swan spectrum. On the tetrahedron model of the chemist, with electrons occurring in pairs in the vicinity of the vertices of the tetrahedron, this assumption gives a structure which would seem to be stable.

In conclusion I wish to extend thanks to Professor R. T. Birge, under whose guidance the present work was done, for his many helpful suggestions, and to Dr. A. S. King of Mt. Wilson Observatory for his kindness in providing me with enlargements of furnace spectrograms.

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August 29, 1927.

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[32] J. J. Thomson, Nature **86**, 466 (1911).