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Analysis of a New Band System of the C_2 Molecule

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The 0–3, 0–4, 0–5 and 0–6 bands of a new band system of the C_2 molecule are analyzed. The lower state, $^3\Pi$, is the same as the lower state of the Swan bands (in all probability the ground state). The upper state is a new $^3\Pi_g$ state. The rotational and vibrational constants of the upper and lower state are given in Table VII. While the constants for the upper state are entirely new those for the lower state (ground state) are considerably improved over those at present in the literature. The triplet splitting and staggering in the new bands is much larger than in the Swan system. In the $^3\Pi_0-{}^3\Pi_0$ component a reversal of the staggering is observed. The electron configuration of the new state is briefly discussed. Finally a number of other bands, very probably due to C_2, but not yet analyzed, are given.

A. Introduction

In recent years the spectrum and the structure of the C_2 molecule have received little attention. However, a more complete knowledge of this molecule would be of considerable interest both because of its chemical and its astrophysical importance.

We have therefore thought it worth while to re-investigate the spectrum of the C_2 molecule in order to find, if possible, new information about the structure of this molecule.

B. Experimental

A weakly condensed discharge was passed through an ordinary discharge tube (capillary of 5 mm diameter and 8 cm length) which was filled with helium of 2–5 cm pressure and was in connection with a side tube containing pure C_6H_6. In some experiments the tube was used without He while the C_6H_6 was streaming through rapidly. Solid carbon was of course quickly deposited on the walls of the discharge tube, so that for longer exposures it had to be cleaned several times.

The spectra were taken partly with a Hilger E3 and partly with a smaller spectrograph of higher light power which could be used both with quartz and with glass prism and lenses.

Under the best conditions the spectrum consisted only of the known bands of C_2 and CH and some unidentified bands but showed no trace of common impurities such as CN and CO. The absence of the strong violet CN bands, which, as is well known, occur so easily as impurities, was considered as a satisfactory proof that a pure spectrum, due solely to C_2 and CH, had been obtained and that the unidentified bands were due to C_2 or CH.

Among the new bands were two at 2855A and 2987A which were shaded to the red but did not show pronounced heads. These two bands were found to be identical with two bands previously obtained by one of us (H) with high dispersion (2.7A/mm, second order of a 3 m grating) under conditions which did not allow any definite conclusions about the carrier of these bands. They had been obtained, for instance, in an uncondensed discharge through argon containing a slight amount of CO_2. The new spectrograms seemed to show that they were due to C_2 (the fine structure being much too narrow for CH). This was unambiguously confirmed by the fine structure analysis which was consequently carried out with the older grating plates. In the course of the measurements two further bands having the same fine structure and therefore belonging to the same system were found on the grating plates. They were however badly overlapped by other bands and could only partly be measured.

C. Rotational Analysis of the New Bands

In Fig. 1 a spectrogram of part of the band at 2987A is reproduced. As can be seen by inspection six branches are present. It will be noticed that in every alternate group of six lines the spacing seems to be somewhat different from that in the intermediate groups.

If a quadratic formula, $\nu=a+bm+cm^2$, is roughly fitted to the component of lowest frequency of each group and the deviations from this formula are plotted it is immediately seen, as shown in Fig. 2, that in each of the six branches there is the "*staggering*" characteristic of $\Pi-\Pi$ transitions of molecules with equal nuclei of spin 0. Conversely this staggering forms an unambiguous proof that the emitter of the bands is a homonuclear molecule with nuclear spin $=0$, such as C_2 and O_2. Of these two, O_2 is excluded by the conditions of excitation as well as by the fine structure analysis (cf. below).

Since the magnitude of the staggering is different for the different branches the above mentioned alternation in the spacing of successive groups results.

The presence of *six branches*, each showing staggering, is only compatible with the assumption that the electron transition responsible for these bands is ${}^3\Pi-{}^3\Pi$, that is, the same type as for the well-known Swan bands of the C_2 molecule.[1] Indeed, as we shall show, the two systems have the lower electronic state, ${}^3\Pi$, in common.

In Tables I, II, III and IV the wave numbers of the lines of the four new bands are given. For the reasons given above the bands at 3129 and 3283A are only very incompletely measured whereas the bands at 2855 and 2987A have been measured down to fairly low J values. For still lower J values we have not been able to assign the lines unambiguously.

TABLE I. *Wave numbers of the lines in the (0–3) band. $\nu_0=35022.14$.*

J	${}^3\Pi_0-{}^3\Pi_0$		J	${}^3\Pi_1-{}^3\Pi_1$		J	${}^3\Pi_2-{}^3\Pi_2$	
	R_3 (J)	P_3 (J)		R_2 (J)	P_2 (J)		R_1 (J)	P_1 (J)
			5		34998.51			
			6		990.84	7		34998.51
			7		983.45	8	35025.23	990.01
7		34969.88	8		974.40	9	020.85	980.78
8	35005.25	960.21	9		965.48	10	015.74	970.92
9	000.68	951.26	10		954.56	11		960.21
10	34994.19	939.92	11	34998.51	944.33	12	003.11	948.84
11	988.04	929.06	12	990.84	931.91	13	34995.62	936.74
12	979.83	916.20	13	983.45	919.75	14	987.65	923.98
13	971.90	903.66	14	974.40	905.98	15	978.58	910.23
14	962.15	889.14	15	965.48	892.50	16	969.01	896.06
15	952.63	874.87	16	954.56	876.88	17	958.53	880.79
16	941.34	858.88	17	944.33	861.90	18	947.26	865.03
17	929.93	843.07	18	931.91	844.87	19	935.26	848.28
18	917.11	825.61	19	920.31 919.75	828.35	20	922.74	831.04
19	904.13	807.89	20	905.98	809.62	21	908.98	812.67
20	889.96	788.94	21	892.50	791.66 791.06	22	894.95	793.91
21	875.30	769.55	22	876.88	771.08	23	879.63	773.88
22	859.53	749.04	23	861.90	751.55	24	864.12	753.75
23	843.07	728.17	24	844.42	729.45	25	847.14	732.05
24	825.61	706.17	25	827.79	708.42	26	830.08	710.50
25	807.89	683.75	26	808.96	684.65	27	811.43	687.27
26	788.94	660.04	27	791.06	662.17	28	792.86	664.06
27	769.24	635.74	28	770.48	637.00	29	772.73	639.27
28	749.04	610.83	29	750.84	612.74	30	752.71	614.61
29	727.69	585.10	30	728.67	586.09	31	730.80	588.15
30	705.71	558.53	31	707.63	560.48	32	709.23	562.08
31	682.91	531.09	32	683.75	531.93	33	685.80	534.00
32	659.44	503.16	33	661.22	505.01	34	662.87	506.50
33	634.92	474.09	34	635.74	474.86	35	637.72	476.85
34	609.96	444.52	35	611.59	446.22	36	613.15	447.63
35	583.72		36	586.09		37	586.63	
36	557.38		37	558.96		38	560.48	
37	529.44		38	530.22		39	531.93	
38	501.63		39	503.16		40	504.49	
			40			41	474.09	
			41	444.52		42	445.43	

The *relative numbering* of the lines was found by a *perturbation* (splitting into two components) occurring in the center branches R_2 and P_2 of the two bands (see Fig. 2). The *absolute numbering* was found by the requirement that

$$\Delta_2F_i'(K)=R(K)-P(K)$$

and
$$\Delta_2F_i''(K)=R(K-1)-P(K+1)$$

plotted as a function of K should go through $-\frac{1}{2}$, at least for the center component.

Table V gives the Δ_2F_i' values of the two bands 0–3 and 0–4. They show as good an agreement as can be expected, thus giving a further check on

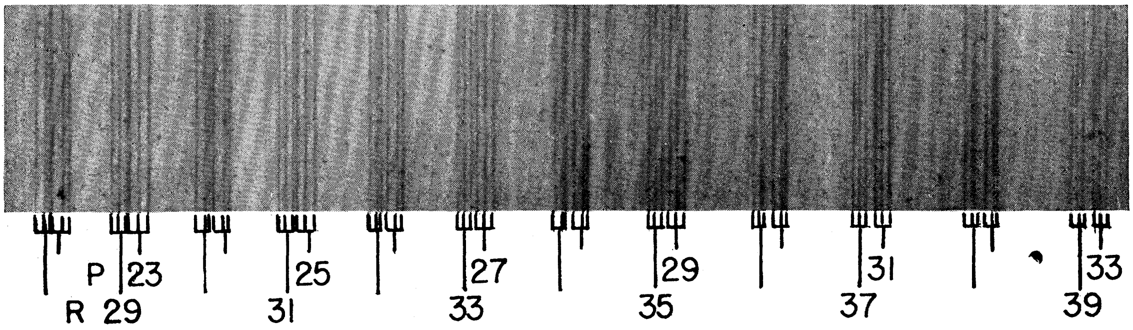

FIG. 1. Part of $0-4$ band.

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[1] The possibility of a ${}^1\Pi-{}^3\Pi$ transition, which might be considered since the triplet splitting in the upper state is unmeasurably small (see below), is ruled out because a perturbation in the upper state appears only in the P_2 and R_2 branches. (Cf. below.)

the analysis. As can be seen there is no systematic deviation between the Δ_2F_1', Δ_2F_2' and Δ_2F_3' values, indicating that the triplet splitting in the upper $^3\Pi$ state is very small for $K>7$.

The Δ_2F' values of the two incompletely measured bands (Tables III and IV), as far as they go, also coincide with the values in Table V. Therefore the upper state in all the bands is the same. Since no other bands have been found it must be the $v'=0$ state of the upper electronic level. Thus the four bands form a v'' *progression*, the v'' values being 3, 4, 5 and 6 as will be shown below.

The *rotational constants B and D* of the upper and lower states were determined according to the method given by Budó[2] for $^3\Pi$ states, i.e., from the average of the $\Delta_2F_i(J)$ values for $i=1$, 2, 3. The values obtained are given in Table VI. The accuracy of the B values for $v'=0$ and $v''=3$ and 4 is probably within 2 or 3 units of the last decimal place given, whereas for $v''=5$ and 6 an error of ± 0.0010 does not seem impossible due to the incompleteness of the data. Also for these latter an average D'' value from the other bands was adopted.

TABLE II. *Wave numbers of the lines in the (0–4) band. $\nu_0=33474.07$.*

J	$^3\Pi_0-{}^3\Pi_0$		J	$^3\Pi_1-{}^3\Pi_1$		J	$^3\Pi_2-{}^3\Pi_2$	
	R_3 (J)	P_3 (J)		R_2 (J)	P_2 (J)		R_1 (J)	P_1 (J)
						3		33476.67
			3	33479.67		4		471.30
			4	478.35	33457.28	5	33487.18	465.07
4		33442.67	5	476.67	451.07	6	484.93	458.54
5		437.62	6	473.99	443.99	7	481.87	451.07
6		429.90	7	471.30	436.15	8	478.35	442.67
7	33463.38	423.04	8	467.33	427.34	9	473.99	434.01
8	458.55	413.80	9	463.38	418.71	10	469.20	424.43
9	454.47	404.89	10	457.91	408.33	11	463.38	413.80
10	448.34	393.99	11	452.51	398.37	12	457.28	403.09
11	442.67	383.61	12	445.36	386.45	13	450.17	391.24
12	434.83	371.15	13	438.54	374.88	14	442.67	379.00
13	427.34	359.05	14	429.90	361.55	15	434.01	365.74
14	418.17	345.15	15	421.48	348.48	16	425.05	352.05
15	409.08	331.35	16	411.25	333.54	17	414.97	337.20
16	398.37	316.00	17	401.44	319.06	18	404.56	322.16
17	387.76	300.69	18	389.64	302.55	19	393.00	305.91
18	375.42	283.81	19	378.61 377.98	286.61	20	381.18	289.44
19	363.18	266.95	20	364.87	268.58	21	367.94	271.58
20	349.61	248.51	21	352.05	251.40 250.79	22	354.65	253.67
21	335.70	229.98	22	337.20	231.49	23	340.00	234.34
22	320.64	210.34	23	323.00	212.74	24	325.34	215.00
23	305.15	190.18	24	306.49	191.51	25	309.09	194.08
24	288.63	169.05	25	290.80	171.29	26	292.98	173.40
25	271.58	147.29	26	272.76	148.52	27	275.19	150.99
26	253.67	124.81	27	255.68	126.91	28	257.66	128.85
27	234.89	101.43	28	235.95	102.51	29	238.25	104.85
28	215.54	077.48	29	217.52	079.50	30	219.36	081.30
29	195.17	052.60	30	196.22	053.54	31	198.39	055.71
30	174.49	027.26	31	176.33	029.12	32	177.99	030.77
31	152.53	33000.75	32	153.49	001.62	33	155.46	003.65
32	130.31	32973.99	33	132.08	32975.80	34	133.71	32977.33
33	106.84	945.85	34	107.59	946.68	35	109.55	948.59
34	083.23	917.70	35	084.92	919.42	36	086.38	920.94
35	058.07	888.02	36	058.78	888.78	37	060.61	890.71
36	033.03	858.53	37	034.66	860.16	38	036.03	861.57
37	006.31	827.31	38	006.93	827.94	39	008.71	829.64
38	32979.78	796.25	39	32981.32	797.86	40	32982.74	799.19
39	951.44		40	952.06		41	953.78	
40	923.71		41	925.17		42	926.47	
41	893.60		42	894.23		43	895.86	
42	864.47		43	865.94		44	867.52	
43	832.84		44	833.36		45	834.86	
44	802.18		45	803.56		46	805.54	

TABLE III. *Wave numbers of the lines in the (0–5) band. $\nu_0=31949.59$.*

J	$^3\Pi_0-{}^3\Pi_0$		J	$^3\Pi\ -{}^3\Pi$		J	$^3\Pi_2-{}^3\Pi_2$	
	R_3 (J)	P_3 (J)		R_2 (J)	P_2 (J)		R_1 (J)	P_1 (J)
23		31675.70	24		31677.00	25		31679.66
24		655.58	25		657.83	26		660.03
25		634.50	26		635.65	27		638.20
26		613.07	27		615.26	28		617.28
27		590.55	28		591.59	29		593.91
28		567.73	29		569.79	30		571.65
29	31686.26	543.60	30	31687.28	544.68	31	31689.47	546.69
30	666.77	519.50	31	668.68	521.46	32	670.42	523.21
31	645.71	493.83	32	646.59	494.71	33	648.68	496.81
32	624.86	468.46	33	626.73	470.31	34	628.28	471.94
33	602.21	441.24	34	603.08	442.08	35	604.98	443.98
34	580.02	414.56	35	581.83	416.33	36	583.38	417.83
35	555.83	385.82	36	556.58	386.57	37	558.45	388.44
36	532.39	357.79	37	534.06	359.43	38	535.48	360.99
37	506.70	327.52	38	507.32	328.22	39	509.10	329.93
38	482.35	298.23	39	483.38	299.81	40	484.87	301.24
39	455.07		40	455.76		41	457.33	
40	429.83		41	430.57		42	431.84	
41	400.76		42	401.69		43	402.65	
42	374.33		43	375.10		44	376.26	

TABLE IV. *Wave numbers of the lines in the (0–6) band. $\nu_0=30448.19$.*

J	$^3\Pi_0-{}^3\Pi_0$		J	$^3\Pi_1-{}^3\Pi_1$		J	$^3\Pi_2-{}^3\Pi_2$	
	R_3 (J)	P_3 (J)		R_2 (J)	P_2 (J)		R_1 (J)	P_1 (J)
18		30270.44	19		30273.42	20		30276.23
19		254.94	20		256.71	21		259.76
20		237.99	21		240.93 240.25	22		243.10
21		220.99	22		222.56	23		225.41
22		202.81	23		205.20	24		207.49
23	30298.74	184.40	24	30300.65	185.73	25	30302.85	188.38
24	284.39	165.07	25	286.60	167.00	26	288.12	169.09
25	268.58	144.53	26	270.44	146.12	27	272.88	148.61
26	252.80	124.06	27	254.94	126.08	28	256.71	127.96
27	235.68	102.30	28	237.27	103.91	29	239.66	106.19
28	218.53	080.49	29	220.47	082.67	30	222.26	084.14
29	200.13	057.22	30	201.63	058.90	31	203.70	061.10
30	181.43	034.16	31	183.22	036.43	32	184.73	037.56
31			32	162.97	011.08	33	164.85	013.19
32	141.41		33	143.11		34	144.92	
33	120.88		34	121.46		35	123.52	
34	099.90		35	100.15		36	102.30	

In Table VI are also given the B and D values of the $v''=0$ and 1 states of the lower $^3\Pi$ state of the Swan system as given by Budó.[2] It is at once apparent that the B_0'' and B_1'' values of the Swan system and the B_3'', B_4'', B_5'' and B_6'' values of the new system form a single series. They can all be represented extremely well by the formula

$$B_v''=1.6320-0.01659(v''+\tfrac{1}{2})$$

with the residuals given in Table VI in the

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[2] A. Budó, Zeits. f. Physik **98**, 437 (1936).

TABLE V. *Combination differences of the upper state.* $\Delta_2F_i'(K)=R_i(K)-P_i(K)$.

	0 – 3 BAND			0 – 4 BAND		
K	$\Delta_2F_1'(K)$	$\Delta_2F_2'(K)$	$\Delta_2F_3'(K)$	$\Delta_2F_1'(K)$	$\Delta_2F_2'(K)$	$\Delta_2F_3'(K)$
4				22.11	21.07	
5				26.39	25.60	
6				30.80	30.00	
7	35.22			35.68	35.15	
8	40.07			39.98	39.99	40.34
9	44.82		45.04	44.76	44.67	44.75
10			49.42	49.59	49.59	49.58
11	54.27	54.18	54.27	54.19	54.15	54.35
12	58.88	58.93	58.98	58.93	58.91	59.06
13	63.67	63.70	63.63	63.66	63.66	63.69
14	68.35	68.42	68.24	68.27	68.35	68.28
15	72.95	72.98	73.01	73.00	73.01	73.02
16	77.74	77.68	77.76	77.77	77.71	77.74
17	82.23	82.43	81.46	82.40	82.38	82.37
18	86.98	87.04	86.86	87.09	87.09	87.07
19	91.70	$\begin{Bmatrix}91.40\\91.96\end{Bmatrix}$	91.50	91.75	$\begin{Bmatrix}91.37\\92.00\end{Bmatrix}$	91.60
20	96.31	96.36	96.24	96.36	96.29	96.23
21	101.04	$\begin{Bmatrix}100.84\\101.44\end{Bmatrix}$	101.02	100.99	$\begin{Bmatrix}100.65\\101.26\end{Bmatrix}$	101.10
22	105.75	105.80	105.75	105.67	105.72	105.72
23	110.37	110.35	110.49	110.34	110.26	110.30
24	115.09	114.97	114.90	115.01	114.98	114.97
25	119.58	119.37	119.44	119.58	119.52	119.58
26	124.16	124.31	124.14	124.20	124.23	124.29
27	128.80	128.89	128.90	128.81	128.77	128.86
28	133.46	133.48	133.50	133.40	133.44	133.46
29	138.10	138.10	138.21	138.06	138.02	138.06
30	142.65	142.58	142.59	142.68	142.68	142.57
31	147.15	147.15	147.18	147.22	147.21	147.23
32	151.80	151.82	151.82	151.81	151.87	151.77
33	156.37	156.21	156.28	156.38	156.28	156.32
34	160.87	160.88	160.83	160.95	160.91	161.00
35	165.52	165.37	165.44	165.44	165.51	165.53
36				169.90	170.00	170.05
37				174.46	174.49	174.51
38				179.07	179.00	179.01
39				183.55	183.46	183.53

TABLE VI. *Rotational constants of the upper and lower state.*

STATE	v	B (cm^{-1})	OBS.-CALC.	D (cm^{-1})	
lower $^3\Pi$	0	1.6239	+0.0002	$6.4\cdot10^{-6}$	from Budó[2]
	1	1.6068	−0.0003	$6.6\cdot10^{-6}$	
	2				
	3	1.5742	+0.0003	$6.8\cdot10^{-6}$	this paper
	4	1.5572	−0.0001	$6.6\cdot10^{-6}$	
	5	1.5408	+0.0005	$(6.6\cdot10^{-6})$	
	6	1.5233	−0.0009	$(6.6\cdot10^{-6})$	
upper $^3\Pi$	0	1.1804		$6.05\cdot10^{-6}$	

column obs.-calc. Since these residuals are within the accuracy of the determinations it follows conclusively that the *lower electronic state of these two systems is the same* and also that the vibrational numbering is correct. The same conclusion is obtained from the vibrational analysis (cf. below). Thus it is definitely proven that the *emitter of the new bands is the C_2 molecule.*

In the upper part of Table VII the *rotational constants B_e, B_0, α, D* and the *moments of inertia I_e, I_0* and the *nuclear distances r_e, r_0* for the upper and lower electronic states of the new bands are given. The I and r values have been calculated using Bearden's[3] values for e, h and N. We consider the values of the constants of the ground state to be improved over those at present in the literature while the constants for the upper state are of course entirely new.

In the new bands, as is usual in $^3\Pi-{}^3\Pi$ transitions,[4] the *triplet splitting* between the lines of equal K increases rapidly with decreasing K (see Fig. 2). It is about 4 to 5 times larger than in corresponding triplets of the 0–0 band of the Swan system, as can be seen from the data of Johnson[5] and Shea.[6] The line splitting is the difference (or possibly sum) of the term splitting in the upper and lower state. The individual term splitting can therefore not be determined accurately. But an approximate value for the term splitting can be obtained from the difference between Δ_2F_1, Δ_2F_2, Δ_2F_3 for equal K. The differences between the Δ_2F_i'' values of the 0–3 and 0–4 bands are are about equal to those for the 0–0 and 0–1 Swan bands. This is to be expected if, as shown above, the lower electronic state for the two systems is the same, since the multiplet splitting does not depend appreciably on the vibrational quantum number. The Δ_2F_i' values for equal K do not show any consistent difference (cf. Table V), indicating that the triplet splitting in the upper $^3\Pi$ state of the new bands is much smaller than in the ground state, whereas in the upper state of the Swan bands it is nearly as large as in the ground state. This explains why the triplet splitting in the new bands is so much larger than in the Swan bands.

The *staggering* (cf. Fig. 2) is also considerably larger for the new bands than for the Swan bands (about 3 to 5 times in the center branches). Again

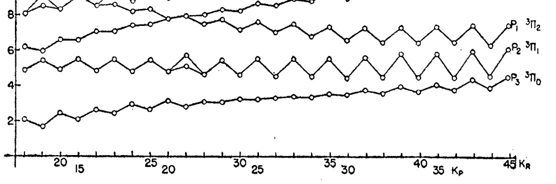

FIG. 2. Staggering and triplet splitting in the branches of the 0 – 4 band.

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[3] J. A. Bearden, Phys. Rev. **47**, 883 (1935).

[4] W. Jevons, *Report on Band Spectra of Diatomic Molecules.*

[5] R. C. Johnson, Phil. Trans. Roy. Soc. **226**, 157, 1926/27.

[6] J. D. Shea, Phys. Rev. **30**, 825 (1927).

TABLE VII. *Constants of the C_2 molecule.*

	LOWER $^3\Pi$ (GROUND) STATE	UPPER $^3\Pi$ STATE
B_e	1.6320 cm^{-1}	—
B_0	1.6237 "	1.1804 cm^{-1}
α	0.01659 "	—
D	$6.6\cdot10^{-6}$ "	$6.05\cdot10^{-6}$ "
I_e	$17.104\cdot10^{-40}$ g cm^2	—
I_0	$17.192\cdot10^{-40}$ "	$23.648\cdot10^{-40}$ g cm^2
r_e	1.3101A	—
r_0	1.3135A	1.5405A
Excitation energy	0	39806.70 cm^{-1}
ω_e	1641.70 cm^{-1}	—
ω_0	1629.99 "	1047 "
$\omega_e x_e=\omega_0 x_0$	11.71 "	

the staggering in the branches is equal to the difference (or possibly sum) of the Λ doubling in the upper and lower states. Therefore the latter cannot accurately be determined. But the fact that the Δ_2F'' values stagger appreciably whereas for the Δ_2F' values the staggering is just barely noticeable shows that the Λ doubling in the upper state of the new bands is much smaller than in the ground state. Thus most of the large staggering in the branches is due to the Λ doubling of the lower state. However, for the upper state of the Swan bands the Λ doubling is not very different from that in the ground state so that the staggering in the Swan bands is small.

As can be seen from Fig. 2, for large K values the staggering tends to be about the same for the three components. This is to be expected since both states are close to Hund's case (*b*) for large K values. However for small K values the staggering is largest for the $^3\Pi_0-{}^3\Pi_0$ component, smaller for $^3\Pi_1-{}^3\Pi_1$, and very small for $^3\Pi_2-{}^3\Pi_2$. In fact this is how the correlation of the branches to $^3\Pi_0$, $^3\Pi_1$, $^3\Pi_2$ was found (cf. Mulliken[7]).

Figure 2 shows further that for about $K'=25$ a *reversal of the staggering* in the P_3 and R_3 branches ($^3\Pi_0-{}^3\Pi_0$) occurs: for larger K values all the three lines in a group of equal K stagger in the same way whereas for smaller K the P_3 and R_3 lines stagger in the opposite direction to the corresponding lines of the P_1, P_2, R_1, R_2 branches. Since the Λ doubling in the upper state is small compared to that in the lower it follows that there is a reversal in the Λ doubling of the $^3\Pi_0$ component of the ground state. Such a reversal has been previously found by Funke[7a] for the $^3\Pi_0$ state of the NH molecule. Since there is no such reversal in the Swan bands one must conclude that for them both in the upper and lower state the Λ doubling reverses.

Finally it may be noted that, while for the Swan bands the lines with even K are shifted to higher frequencies, for the new bands the lines with odd K are shifted in that direction (except for the P_3, R_3 branches for $K<25$).

D. VIBRATIONAL ANALYSIS

The *zero lines* ν_0 of the bands are given in Table VIII. They were obtained in the following way: according to Budó's formulae one can easily see that $R_1(J)+R_2(J)+R_3(J)+P_1(J)+P_2(J)+P_3(J)=6\nu_0+6B'+6(B'-B'')\ J(J+1)$ apart from very small terms with higher powers of $J(J+1)$. Therefore, by plotting the sum $\Sigma R_i(J)+\Sigma P_i(J)$ against $J(J+1)$ very nearly a straight line is obtained whose intercept with the ordinate axis gives $6\nu_0+6B'$ and therewith ν_0.

TABLE VIII. *Zero lines ν_0 and vibrational quanta $\Delta G''$.*

$v'-v''$	ν_0	$\Delta G''$	OBS.–CALC. (Johnson's formula)
0−3	35022.14		
		1548.07	−0.12
0−4	33474.07		
		1524.48	−0.37
0−5	31949.59		
		1501.40	−0.11
0−6	30448.19		

The third column of Table VIII contains the *vibrational quanta* $\Delta G''$ of the lower state derived from the observed ν_0 values. In the next column are given the deviations of these observed $\Delta G''$ values from those following from Johnson's formula for the lower state of the Swan system:

$$\nu=19373.87+1773.42\ v'-19.35\ v'^2-(1629.88\ v''-11.67\ v''^2).$$

The deviations are of the same order as those of Johnson's own $\Delta G''$ values derived from the Swan bands. This is another conclusive proof that the lower state of the new bands is identical with that of the Swan bands, and also of the correctness of the vibrational numbering.

The slight systematic deviations from Johnson's formula for the higher v'' values available here can be used to improve the formula for the vibrational quanta of the lower state. We obtain

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[7] R. S. Mulliken, Rev. Mod. Phys. **3**, 89 (1931).

[7a] G. W. Funke, Zeits. f. Physik **96**, 787 (1935).

the following equation for the new bands.

$$\nu=39806.77-(1629.99\,v''-11.71\,v''^2).$$

This formula represents our zero lines within less than ± 0.10 cm^{-1}. The new vibrational term of the ground state $1629.99\,v''-11.71\,v''^2$, if introduced into the formula for the Swan system, gives just as good a representation of the Swan bands as the old formula.

The improved *vibrational constants* of the ground state of the C_2 molecule are given in the lower part of Table VII. An approximate value for the vibrational frequency ω' of the upper state is also given. It was obtained from the rotational constant D' and Kratzer's formula $D=4B^3/\omega^2$.

The absence of the 0–0, 0–1 and 0–2 bands of the new system is easily accounted for by the Franck-Condon principle, since the nuclear distance in the upper state is so much larger than in the lower. As can be seen by plotting the potential curves, the 0–5 or 0–6 band should be the most intense of the progression in agreement with visual estimates. Bands with higher v'' would be overlapped by the much stronger Deslandres and Swan systems and have not been observed.

E. ELECTRON CONFIGURATIONS

According to Mulliken the lower state of the Swan bands is $^3\Pi_u$ the upper state $^3\Pi_g$. The electron configurations are

$$(K)(K)\sigma_g{}^2(2s)\sigma_u{}^2(2s)\pi_u{}^3(2p)\sigma_g(2p)\ {}^3\Pi_u,$$
$$(K)(K)\sigma_g{}^2(2s)\sigma_u(2s)\pi_u{}^3(2p)\sigma_g{}^2(2p)\ {}^3\Pi_g.$$

The upper state of the new bands must also be $^3\Pi_g$. The first electron configuration, next to the above, that gives rise to a $^3\Pi_g$ state is

$$(K)(K)\sigma_g{}^2(2s)\sigma_u{}^2(2s)\pi_u{}^2(2p)\sigma_g(2p)\pi_g(2p).$$

In fact four different $^3\Pi_g$ terms arise from this configuration. The orbital $\pi_g(2p)$ is well known to be *strongly anti-bonding*. It is therefore significant and a strong argument in favor of our assignment that the upper state of the new bands has a considerably larger nuclear distance r_0 and a much smaller vibrational frequency ω_0 than the ground state (or the upper state of the Swan bands).

TABLE IX. *Other C_2 bands. R means "shaded to the red;" V means "shaded to the violet;" N means "headless band."*

	λ(A)	ν(cm^{-1})		λ(A)	ν(cm^{-1})
R	4996.74*	20007.5	*R*	3599.2	27776
R	4910.99*	20356.8	*R*	3560.7	28076
R	4836.13*	20671.9	*R*	3506.6	28510
R	4770.13*	20958.0	*R*	3434.0	29112
R	4496.9	22231	*R*	3384.4	29539
R	4339.6	23037	*V*	2421.5	41284
R	4324.4	23118	*N*	2313.7	43208
R	4147.8	24102	*V*	2218.5	45061
R	3688.7	27102	*V*	2216.6	45100
R	3670.8	27234	*V*	2143.0	46649
R	3618.0	27632			

F. OTHER C_2 BANDS

In addition to the new bands, discussed in detail above, a number of further bands have been found under the conditions of excitation given in section *A* which in all likelihood are also due to the C_2 molecule. In Table IX the wavelengths and wave numbers of these bands are collected together. Except for the band marked by *N*, band heads have been measured. For the headless band marked by *N* the intensity minimum of the center was measured. The bands marked by an asterisk have been measured on grating plates whereas the others have only been measured with small dispersion. The former have also been recorded by Johnson. Possibly they form the tail bands 13–12, 12–11, 11–10 and 10–9 of the $\Delta v=+1$ sequence of the Swan bands. Similarly the bands 3618.0 and 3599.2A very probably form the tail bands 6–5 and 5–4 of the Deslandres system. Thus far we have not been able to obtain a satisfactory vibrational analysis of the other bands of Table IX.

The strong headless band at 2313.7A has been observed by a number of investigators, but its fine structure has not yet been satisfactorily analyzed. According to Mulliken[8] it is a $^1\Sigma-{}^1\Sigma$ transition of the C_2 molecule while Hori[9] claims it to be due to a C_3 molecule. An incomplete fine structure analysis by L. Herzberg confirms Mulliken's interpretation. It is possible that the weak band at 2421.5A is the 0–1 band of the same system.

It will be shown in a later paper by one of us that the so-called high pressure bands of carbon[10] belong to the Swan system and do not have a new electronic state as the upper level.

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[8] R. S. Mulliken, Zeits. f. Electrochem. **36**, 603 (1930).

[9] T. Hori, Zeits. f. Physik **83**, 495 (1934).

[10] Cf. e.g. R. C. Johnson and R. K. Asundi, Proc. Roy. Soc. **124**, 668 (1929).

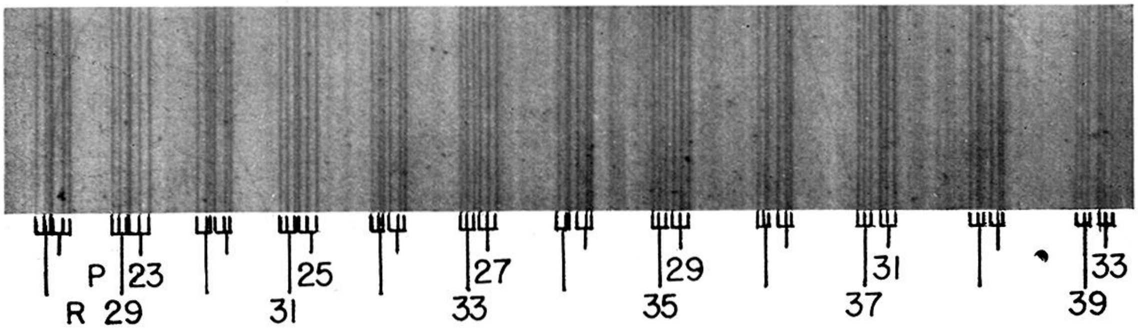

FIG. 1. Part of 0—4 band.