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ON THE BAND SPECTRUM OF CALCIUM HYDRIDE

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Abstract

An arc of calcium burning in hydrogen at low pressure emits numerous bands in the region 6000–7000A. This spectrum was photographed at high dispersion and two groups of bands, shading toward the violet may be distinguished: the A groups with heads at λλ7035, 7028, 6921, 6903 and the B groups with heads at λλ6389, 6382. In addition to these, the arc emits an isolated C group—a single band in the ultra-violet at λ3533.6. This group is identical with a band of calcium hydride recently studied by R. S. Mulliken. The structures of A, B and C are very different. The A group forms a doublet system (A_1, A_2) of *P-Q-R* branches. The bands of the B group have a similar structure to that of the violet cyanogen bands, signified by doublet P_1, P_2 and R_1, R_2 branches. The C group consists of a single band having *P-R* branches. In all bands the series deviate largely from polynomials of second degree. Thus, in B and C there is a remarkable "red-shift" of high numbered lines, accompanied by a sharp cut-off in their intensity. From combinations found between the *P-R* branches, conclusions are reached regarding the spectral terms in CaH. The A, B and C groups have a common final (N) electronic term with a rotational doubling ($\epsilon_2 = \pm\frac{1}{2}$, $\sigma_2 = 0$). The initial state of A forms an electronic doublet (A_1, A_2) with the emission electron in a σ-orbit ($\epsilon_1 = 0$, $\sigma_1 > 0$), thus explaining the appearance of Q branches in A. In B (initial) there is again a rotational doubling ($\epsilon_1 = \pm\frac{1}{2}$, $\sigma = 0$). In C (initial) only one ϵ component is present ($\epsilon_1 = -\frac{1}{2}$, $\sigma_1 = 0$). The departure from half-integral quantum numbers in C is avoided by accepting a large Kratzer's linear term $2\delta j$. The nuclear spacings in the CaH molecule are not in correlation with their vibration frequencies, violating a rule by Birge and Mecke. A comparison of the A group with the spectra of ZnH, CdH and HgH shows several interesting parallels, confirming the theory of Mulliken regarding these spectra.

ALTHOUGH the band spectrum of calcium hydride, discussed in this paper, has previously been noted by several investigators, no serious effort has been made to resolve and to measure accurately the great number of lines in the region 6000 to 7000A. The main interest seems to have been centered in identifying these bands in the sun-spot spectrum and from this point of view we may mention the works of C. M. Olmsted[1] and A. Eagle.[2] Olmsted presented evidence that the calcium hydride bands at λλ6389, 6382 appear in the sun spectrum. Eagle photographed the spectra of calcium, strontium and barium hydride in the region 6000–7000A. From his photographs the homologous structure of all three spectra appears clearly.

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* International Education Board.

[1] C. M. Olmsted, Astrophys. J. **29**, 66 (1908).

[2] A. Eagle, Astrophys. J. **30**, 231 (1909).

In addition there is a single band of calcium hydride in ultra-violet at λ3533.6, consisting of a small number of lines but having a very unusual structure. This band has recently been investigated by R. S. Mulliken.[3]

SOME GENERAL REMARKS REGARDING THE HYDRIDE BAND SPECTRA

Before entering into a detailed discussion of the band-spectrum of calcium hydride some general properties in the spectra of hydrides and their relations to the periodic table of elements may here be discussed. At present we know something about the hydride spectra of Cu, Ag, Au, —Mg, Ca, Sr, Ba,—Zn, Cd, Hg,—B, Al,—C,—N, P,—O. From theoretical interpretations of several of these spectra (moments of inertia, isotope effects, etc.), it is most probable that they are all emitted by a dipole of the element and a hydrogen atom. Besides the wide spacing of lines, which is an essential property of all hydrides, there is a clear conformity in the structure of bands belonging to elements of the same column in the periodic table. This is best illustrated by the table below.

TABLE I

Correlations in hydride band spectra

Hydrides	Shading direction	Band structure	Electronic frequencies
Cu, Ag, Au	Red	P, R	24910, 29900, 27342 38230
Mg, Ca, Sr, Ba	Violet	$P_1P_2,\ Q_1Q_2,\ R_1R_2.$	19333.9 (Mg)....
Zn, Cd, Hg	"	$P^{(1)}P^{(2)}, Q^{(1)}Q^{(2)}, R^{(1)}R^{(2)}.$	23263.6 22278.0 24933.9 23594.0 23279.0 28617.1
B, Al	Red	P, Q, R	23477 (Al)
	Violet	$P_1{}^{(1)}P_2{}^{(1)}, P_1{}^{(2)}P_2{}^{(2)}, Q_1{}^{(1)}\ldots, R_1{}^{(1)}$..	23161
C	Red	$P_1P_2,\ Q_1Q_2,\ R_1R_2.$	25715
N, P	Red	$P_1P_2P_3,\ Q_1Q_2Q_3,\ R_1R_2R_3.$	29750 (N)
O	Red	$P_1P_2,\ Q_1Q_2,\ R_1R_2.$	32423

There is a remarkable alternation in the shading directions of bands belonging to the elements of the first columns. No pretentions are made, however, that this is a rule or that the notations regarding the band structures given in the table are complete. The spectrum of calcium hydride will illustrate these points.

SPECTRUM OF CALCIUM HYDRIDE

The calcium hydride bands in the region 6000–7000A form two groups of bands with more or less distinct heads at λλ7035, 7028, 6921, 6903 and λλ6389, 6382. The bands are all degraded toward the violet and though crowded with lines, are easily resolved under high dispersion.

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[3] R. S. Mulliken, Phys. Rev. **25**, 509 (1925).

As source a calcium arc burning in hydrogen at low pressure was used. The arc ran steadily at 6 amp., 220 v., d.c., with a hydrogen pressure of about 20 mm. Under these conditions, with an exposure of from two to six hours, the spectrum was well developed in the first and second

TABLE II

The lines of the A band of calcium hydride

j	P_1	P_2	Q_1	Q_2	R_1	R_2
0						
1			14399.92		14406.90	14470.58
2	14385.88		402.85		19.17	76.24
3	81.53	14428.52	05.77		31.15	82.45
4	76.94	17.51	08.62		42.79	89.14
5	71.95	06.71	11.45		54.10	96.10
6	66.80	396.46	14.30	14448.14	65.23	503.40
7	61.38	86.63	17.21	47.39	76.24	10.97
8	55.63	77.21	20.19	47.28	87.02	18.68
9	49.91	68.23	23.48	47.53	97.74	26.73
10	44.12	59.32	26.76	48.14	508.35	34.80
11	38.21	50.78	30.20	49.59	18.89	43.15
12	32.40	42.55	33.82	51.26	29.33	51.57
13	26.55	34.55	37.57	53.22	39.77	60.17
14	20.74	27.00	41.53	55.50	50.11	68.92
15	15.02	19.53	45.69	58.14	60.53	77.77
16	09.35	12.27	49.99	61.09	70.89	86.66
17	03.78	05.25	54.46	64.32	81.24	95.64
18	298.34	298.48	59.16	67.82	91.61	604.75
19	93.05	92.00	64.04	71.55	601.95	13.86
20	87.86	85.69	69.12	75.57	12.33	23.09
21	82.86	79.70	74.37	79.87	22.62	32.42
22	78.05	73.93	79.87	84.40	33.09	41.89
23	73.36	68.37	85.45	89.14	43.54	51.31
24	68.92	63.06	91.24	94.20	53.91	60.82
25	64.62	58.04	96.92	99.48	64.37	70.37
26	60.54	53.26	503.41	504.87	74.79	79.96
27	56.69	48.73	09.73	10.50	85.22	89.68
28	53.07	44.43	16.25	16.38	95.73	99.33
29	49.66	40.45	23.08	22.56	706.16	709.04
30	46.43	36.72	29.90	28.70	16.63	18.87
31	43.51	33.28	37.00	35.29	27.19	28.71
32	40.78	30.08	44.19	41.92	37.72	38.57
33	38.30	27.18	51.57	48.78	48.28	48.28
34	36.05	24.47	59.14	55.81	58.70	
35	34.09	22.06	66.55	62.93	69.25	
36	32.34	19.96	74.46	70.38	79.89	
37	30.93	18.12	82.43	77.77		
38	29.68	16.54	90.62	85.51		
39	28.70	15.29	98.69	93.26		
40	27.97	14.20	607.09	601.25		
41	27.44	13.55	15.46	09.34		
42	27.18	12.94	24.03	17.58		
43		12.78		25.86		

order of a large concave grating (dispersion, 2.6 and 1.3A/mm respectively). The spectrum extends on both sides of the 6000–7000A region. However, these faint bands showed such a complicated array of numerous lines that no attempt was made to analyze them. Apparently they correspond to excited vibration levels of the two main groups at 6000–7000A. When a small amount of air or moisture was present in the arc-bulb, a continuous background appeared in the region 6300–6100A, sometimes rising to a bright intensity, covering the sharp lines of the hydride bands. This background belongs probably to the CaO spectrum and was easily suppressed by a permanent flow of hydrogen through the bulb.

TABLE III

The lines of the A′ band of calcium hydride

j	P_1	P_2	Q_1	Q_2	R_1	R_2
0			14429.00			
1			32.04		14442.18	
2	14421.44		35.09		54.10	
3	17.21		38.00		65.94	
4	12.69		40.82		76.89	
5	07.94		43.54		88.28	
6	02.85	14432.66	46.31		98.64	14536.62
7	397.38	22.84	49.07		509.25	43.76
8	91.69	13.39	51.95	14483.25	19.56	51.09
9	85.88	04.37	54.87	83.02	29.90	58.69
10	80.01	395.49	57.93	83.02	39.94	66.74
11	74.07	86.89	61.09	83.25	50.11	74.46
12	68.06	78.75	64.32	83.98	60.17	82.49
13	62.13	70.72	67.82	85.03	70.02	90.62
14	56.25	62.94	71.55	86.46	80.02	98.97
15	50.42	55.63	75.34	88.28	89.96	607.35
16	44.71	48.25	79.24	90.42	99.88	15.85
17	39.14	41.24	83.50	93.00	609.84	24.44
18	33.70	34.55	87.81	95.58	19.73	33.09
19	28.40	27.98	92.25	98.64	29.68	41.89
20	23.28	21.75	96.92	501.83	39.73	50.79
21	18.24	15.70	501.83	05.47	49.74	59.73
22	13.38	09.94	06.73	09.24	59.73	68.63
23	08.67	04.31	11.95	13.31	69.70	77.64
24	04.31	299.08	17.45	17.60	79.74	86.68
25	299.99	93.86	23.08	22.16	89.68	95.73
26	95.87	89.06	28.70	26.73	99.70	704.95
27	92.00	84.33	34.44	31.82	709.74	14.12
28	88.39	80.11	40.57	37.00	19.83	23.38
29	84.85	76.07	46.81	42.30	29.86	32.64
30	81.68	72.18	53.12	48.06	39.91	41.89
31	78.57		59.60	53.63	49.93	51.15
32	75.87		66.35	59.60	59.89	
33	73.36		73.05	65.64		
34	70.88		80.02	71.95		

In order to simplify our notations in the following we will refer to the long wave-length bands at $\lambda 7000$ as the A-group and to the bands at $\lambda\lambda 6389$, 6382 as the B-group. The overlapping faint bands in A and B are called A′, B′, respectively. The isolated band at $\lambda 3533$ already analyzed by Mulliken we refer to as the C-group. The lines of A, A′,

TABLE IV

The lines of the B band of calcium hydride

j	P_1	P_2	R_1	R_2
0				15763.17
1		15745.12	15761.91	73.07
2	15745.12	37.87	70.73	83.20
3	36.53	30.86	79.91	93.75
4	28.43	24.11	89.51	804.58
5	20.70	17.78	99.54	15.73
6	13.48	11.81	809.93	27.21
7	06.72	06.23	20.65	38.99
8	00.33	01.00	31.70	51.08
9	694.40	696.17	43.11	63.42
10	88.83	91.69	54.82	76.04
11	83.59	87.60	66.81	88.93
12	78.90	83.84	78.99	902.04
13	74.47	80.48	91.45	15.38
14	70.32	77.42	904.14	28.97
15	66.69	74.70	17.08	42.76
16	63.35	72.32	30.09	56.76
17	60.34	70.42	43.47	70.84
18	57.64	68.65	56.99	85.12
19	55.26	67.18	70.53	99.49
20	53.23	66.15	84.30	16014.04
21	51.41	65.37	98.23	28.64
22	50.05	64.88	16012.17	43.35
23	49.02	64.55	26.25	58.11
24	48.09	64.55	40.39	72.94
25	47.34	64.88	54.61	87.74
26	47.00	65.37	68.82	102.62
27	47.00	66.15	83.12	17.41
28	47.11	67.18	97.33	32.25
29	47.52	68.28	111.52	46.92
30	48.09	69.64	25.68	61.65
31	48.86	71.18	39.74	76.13
32	49.82	72.81	53.75	90.53
33	50.92	74.59	67.63	
34	52.13	76.46	81.33	
35	53.52	78.48	94.83	
36	54.95	80.48		
37	56.49	82.61		
38	58.05	84.78		
39	59.63			
40	61.24			
41	62.81			

B, B′ are in Tables II to V arranged in series. This arrangement includes practically all lines measured (approximately 800) and is based on the rules holding for band series and on the combination principle applied to band spectra.

TABLE V

The lines of The B′ band of calcium hydride

j	P_1	P_2	R_1	R_2
0				
1			15745.87	
2	15729.45		54.45	
3	21.05		63.39	15778.05
4	13.11		72.77	88.33
5	05.61	15703.86	82.53	99.04
6	698.49	697.72	92.65	810.18
7	91.69	92.03	803.15	21.25
8	85.58	86.77	13.85	32.81
9	79.74	81.78	24.81	44.52
10	74.23	77.08	36.04	56.51
11	69.07	72.81	47.43	68.65
12	64.19	68.65	59.07	81.00
13	59.63	64.88	70.80	93.52
14	55.26	61.64	82.75	906.21
15	51.41	58.45	94.84	19.03
16	47.52	55.58	907.02	32.01
17	44.14	53.00	19.33	45.10
18	40.89	50.68	31.76	58.25
19	37.88	48.58	44.26	71.42
20	25.19	46.76	56.87	84.68
21	32.72	45.12	69.38	97.92
22	30.48	43.75	82.00	16011.17
23	28.40	42.53	94.65	24.38
24	26.54	41.50	16007.22	37.54
25	24.86	40.62	19.74	50.64
26	23.40	39.91	32.14	63.61
27	22.02	39.32	44.46	76.47
28	20.75	38.79	56.68	89.04
29	19.58	38.30	68.82	101.45
30	18.48	37.88	80.43	13.49
31	17.46	37.44	91.92	25.26
32	16.39	36.92	103.06	36.40
33	15.34	36.31	13.67	46.92
34	14.05	35.39		56.84
35	12.44			

BAND STRUCTURE

In Figs. 1 and 2 the groups B and A are graphically represented around their origins. The B group consists of two doublet branches P_1, P_2 and R_1, R_2, overlapped by a faint B′ band having a similar structure (P_1', P_2', R_1', R_2') to that of B, only shifted a little toward the red. The

P_1, P_2 branches of B converge into two distinct heads at λλ6382, 6389. The series of B and B′ may be represented by polynomials:

$$P(j)=\sum_{k=0}\pi_k j^k,\quad R(j)=\sum_{k=0}\rho_k j^k, \tag{1}$$

where k is a positive integer.

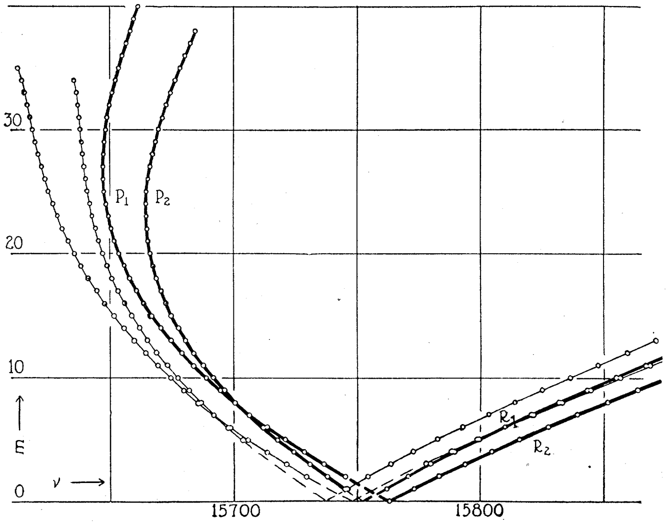

Fig. 1. Graphical representation of Group B bands.

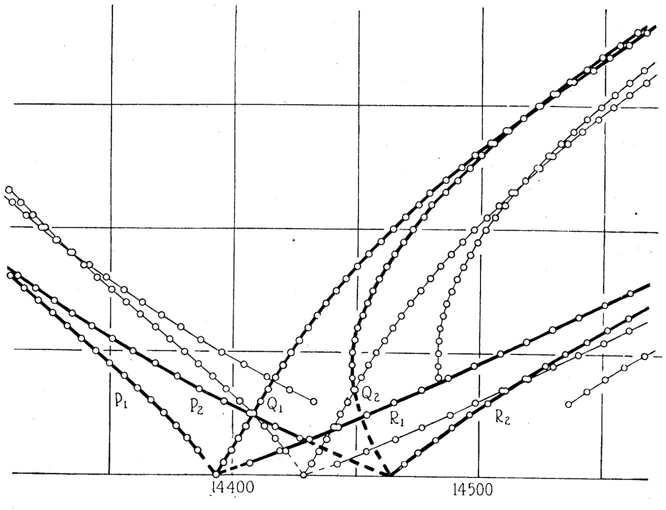

Fig. 2. Graphical representation of Group A bands.

According to the arrangement in the tables the lines $P_1(1)$, $P_1(0)$, $R_1(0)$ are missing in the P_1, R_1 series. In P_2, R_2 only $P_2(0)$ is missing.

The lines $P_1(2)$ and $P_2(1)$ coincide at 15745.12 but judged from the intensity of this line undoubtedly both are present. In the series of the B′ band there is a great number of additional lines missing. Considering the relative faintness of this band it seems probable that the restrictions for missing lines are the same here as in B. For small j values the series may be represented by polynomials of the second degree ($k=0$, 1, 2) but for high j numbers there is a remarkable "red-shift" indicating the presence of the coefficients $\rho_4, \rho_6, \cdots \pi_4, \pi_6$ in (1). This is best observed in the P_1, P_2 series of the B′ band, which do not converge into any heads, the spacing between the lines again increasing for the highest numbers observed. There is also an abrupt cut-off in the intensity of these series. Anomalies of this kind, but of still more prominent form, have already been noted by Mulliken[3] in the C group of this spectrum and by Erikson and Hulthèn[4] in the spectrum of AlH. One is inclined to attribute these properties to an extreme molecular instability.[3,4]

The A group (Fig. 2) may be considered as two bands, $A_1(P_1,Q_1,R_1)$ and $A_2(P_2,Q_2,R_2)$ having two different origins. As in B the A group is overlapped by the faint A′, having a similar structure to that of A though here shifted toward the violet. The boundaries in A have a very unusual shape. Thus in A_1 and A_1' the series for small j values develop as if the bands were going to "shade" toward the red (ρ_2, π_2 in (1) are negative). From about $j=8$ the influence of higher terms of (1) appear and turn their "shading" into the opposite direction.

In A_1 and A_1' the lines $P_1(1)$, $P_1(0)$ and $R_1(0)$ are missing, while the Q_1 branch can be traced down to its first line $Q_1(0)$. In A_2 and A_2' the Q_2 series vanish totally below $j=5$ and $j=6$ respectively. The absence of several lines around the band origin seems to be a common property for the short wave-length components in many spectra of doublet bands.[5]

As already mentioned the arrangements in Tables II to V are mainly based on the application of the combination principle to band spectra using simple assumptions regarding the nature of the emitter. Thus the lines are numbered according to the scheme:

$$\begin{aligned} P_i(j) &= \nu_0 + F(j-1,\, j_e') - f(j,\, j_e) \\ Q_i(j) &= \nu_0 + F(j,\, j_e') - f(j,\, j_e) \qquad (i=1,2) \qquad (2) \\ R_i(j) &= \nu_0 + F(j+1,\, j_e') - f(j,\, j_e) \end{aligned}$$

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[4] G. Erikson and E. Hulthèn, Zeits. f. Physik **34**, 775 (1925).

[5] Regarding the (C+H) spectrum see E. Hulthèn, diss. Lund, 1923, p. 43, 45 OH spectrum, W. W. Watson, Astrophys. J. **60**, 145 (1924). MgH spectrum, W. W. Watson and Ph. Rudnick, Astrophys. J. **63**, 20 (1926).

where j is the quantum numbers for the total angular momentum and j_e the one for the resultant electronic angular momentum of the molecule. j_e may be divided into a σ component along the figure-axis of the dipole and an ϵ component perpendicular thereto. Different values of j_e correspond to rotational doublets as P_1P_2 and R_1R_2 in the B-group.

In Tables VI and VII the final and initial terms of rotation are isolated, using the following abbreviations:

$$\begin{aligned} R_1(j-1)-P_i(j+1)&=F_i(j+1)-F_i(j-1)=\Delta F_i(j)\\ R_i(j)-P_i(j)&=f_i(j+1)-f_i(j-1)=\Delta f_i(j) \end{aligned} \tag{3}$$

TABLE VI

Values of the final and initial terms of rotation in the band spectra of calcium hydride

	A		B		C	A′		B′	
j	Δf_1	Δf_2	Δf_1	Δf_2	Δf	Δf_1	Δf_2	Δf_1	Δf_2
1				25.30	25.37				
2	25.37		25.37	42.21	42.19	24.97		24.82	
3	42.23		42.30	59.09	59.04	41.41		41.34	
4	59.20	75.74	59.21	75.97	75.95	58.00		57.78	74.19
5	75.99	92.68	76.03	92.77	92.78	74.04		74.28	90.61
6	92.72	109.47	92.82	109.50	109.50	90.90		90.84	107.01
7	109.60	126.19	109.60	126.21	126.19	106.95	123.23	107.07	123.41
8	126.33	142.74	126.25	142.82	142.88	123.37	139.39	123.41	139.47
9	142.90	159.36	142.87	159.39	159.33	139.55	155.60	139.62	155.73
10	159.53	175.95	159.52	175.82	175.85	155.83	171.80	155.74	171.71
11	175.95	192.25	175.92	192.20		171.88	187.99	171.85	187.86
12	192.24	208.60	192.34	208.45		187.98	203.74	187.80	203.77
13	208.59	224.57	208.67	224.62		203.92	219.55	203.81	219.36
14	224.75	240.64	224.76	240.68		219.60	234.99	219.39	235.07
15	240.76	256.65	240.79	256.65		235.31	250.72	235.23	250.63
16	256.75	272.52	256.74	272.34		250.82	266.11	250.70	266.03
17	272.55	288.18	272.45	288.11		266.18	281.30	266.13	281.33
18	288.19	303.64	288.21	303.66		281.44	296.46	281.45	296.52
19	303.75	319.06	303.76	318.97		296.45	311.34	296.57	311.49
20	319.09	334.16	319.12	334.12		311.44	326.19	311.54	326.30
21	334.28	349.16	334.25	349.16		326.35	340.85	326.39	340.93
22	349.26	364.05	349.21	364.09		341.07	355.42	340.98	355.39
23	364.17	378.83	364.08	378.80		355.42	369.55	355.46	369.67
24	378.92	393.27	378.91	393.23		369.71	383.78	369.79	383.76
25	393.37	407.56	393.39	407.57		383.87	397.62	383.82	397.63
26	407.68	421.64	407.61	421.59		397.68	411.40	397.72	411.32
27	421.72	435.53	421.71	435.44		411.31	424.84	411.39	424.82
28	435.56	449.23	435.60	449.13		424.89	438.05	424.88	438.17
29	449.30	462.61	449.24	462.61		438.15	451.20	438.20	451.16
30	462.65	475.76	462.66	475.74		464.04		451.36	464.01
31	475.85	488.79	475.86	488.84		476.57	476.61	464.04	476.57
32	488.89	501.53	488.82	501.54		489.01		476.58	488.95
33	501.67	514.10	501.62	514.07				489.01	501.01
34	514.19	526.22	514.11					501.23	513.49
35	526.36		526.38						
36	538.32		538.34						

Comparing the Δf of Table VI we find that they agree with each other for all groups, A, B, C. Consequently these groups are emitted by the same molecule and they have a common final state. Between Δf_1 and Δf_2 the following relation exists:

$$\Delta f_1(j+1) = \Delta f_2(j) + c$$

where c is a very small constant (about 0.09 cm^{-1}). In the C group, where no doubling appears, there is a close agreement between the values of Δf and those of Δf_2, which shows that they must be identical.

TABLE VII

Values of the final and initial terms of rotation in the band spectra of calcium hydride

	A		B		C	A′		B′	
j	ΔF_1	ΔF_2	ΔF_1	ΔF_2	ΔF	ΔF_1	ΔF_2	ΔF_1	ΔF_2
1				27.95	24.2				
2	33.29		25.61	45.33	43.19	32.66		25.00	
3	49.62		43.38	62.89	62.17	48.73		42.34	
4	65.85	71.63	61.08	80.47	81.14	64.20		59.66	
5	82.15	89.39	78.84	97.95	99.79	80.34		76.92	95.18
6	98.43	106.94	96.45	115.60	118.15	95.79		94.16	112.46
7	114.86	124.35	113.93	132.76	136.41	111.87		111.46	129.22
8	131.39	141.47	131.37	150.08	154.35	127.87	137.70	127.83	146.04
9	147.83	158.50	148.71	167.25	171.32	144.02	154.32	145.07	162.74
10	164.23	175.48	165.99	184.35		159.93	171.25	161.81	179.43
11	180.68	192.37	183.22	201.33		176.04	187.57	178.36	195.84
12	196.93	209.02	200.09	218.20		192.11	204.74	194.48	212.35
13	213.22	225.62	216.98	234.90		207.89	219.90	211.17	228.64
14	229.37	241.92	233.82	251.55		223.77	236.03	227.49	244.57
15	245.51	258.24	250.39	268.06		239.54	251.72	243.43	260.58
16	261.54	274.39	266.74	284.44		255.17	267.60	259.50	276.43
17	277.46	290.39	283.13	300.62		270.70	283.20	275.19	292.10
18	293.23	306.27	299.35	316.47		286.03	298.54	290.87	307.57
19	308.90	321.86	315.26	332.31		301.28	313.91	306.38	322.84
20	324.47	337.40	331.07	347.89		316.45	329.04	321.68	337.92
21	339.76	352.72	346.82	363.27		331.50	344.03	336.66	352.80
22	355.04	367.96	362.12	378.47		346.35	358.69	351.52	367.42
23	370.18	382.94	377.23	393.56		361.03	373.33	366.25	381.85
24	384.99	397.76	392.30	408.39		375.43	387.60	380.68	396.04
25	399.75	412.33	407.27	422.86		389.69	401.87	394.88	410.02
26	414.25	426.70	421.82	437.25		403.83	415.89	408.74	423.70
27	428.53	440.95	436.12	451.26		417.74	429.79	422.44	437.15
28	442.66	454.90	450.22	465.07		431.44	443.27	435.93	450.25
29	456.50	468.59	464.00	478.64		445.01	456.57	449.24	463.15
30	470.20	482.15	477.59	492.01		458.23	469.71	462.00	475.61
31	483.68	495.43	490.88	504.95		471.36		474.46	487.82
32	496.94	508.49	503.93	517.72		484.02		486.67	499.48
33	509.98	521.10	516.71					498.33	510.61
34	522.65		529.20						521.45
35	535.16		541.31						
36	547.55								

The Q series in the A group do not fit into any simple scheme like that of (2) and probably not to any inter-combination between the F_i and f_i terms. Thus the numeration given in the tables is doubtful regarding these series. As in the P and R branches of A also here the long wavelength component Q_1 is far more intense than Q_2 for small j numbers. It is also worth noticing that while in P and R the intensity of the lines at first slowly increase with their numeration, the lines of Q_1 almost at once gain their full strength.

In the B group our view of the structure seems to be complete and identical to that of the violet cyanogen bands. In order to explain the missing lines in these bands Kratzer[6] excludes all transmissions from, or to, any states of $j=0$. From this postulate he concludes that the lines $R_2(0)$ and $P_2(1)$ in the "false doublets" formed by $R_1(j)$, $R_2(j-1)$ and $P_1(j)$, $P_2(j-1)$ must be missing. This could not be controlled in the CN spectrum because of the small separation of the doublets around the 0 lines. In the B group of CaH, however, these doublets are easily separated down to their origin and, contrary to the predictions of Kratzer, $R_2(0)$ and $P_2(1)$ are distinctly present.

In our scheme the missing lines are explained by excluding only those values of j which render

$$m=j-\epsilon<0$$

m is the quantum number for the angular momentum of the nuclei. These properties are illustrated in Fig. 3.

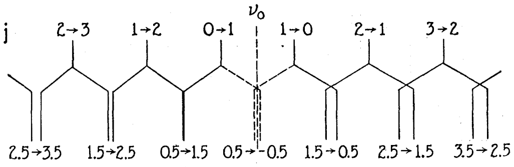

Fig. 3. Doublets separations in Group B bands.

In Fig. 4 the term structure for the entire spectrum is given by its electronic levels and additional vibration levels. While the N and B levels are noted as rotational doublets, we here refer to A_1, A_2 as an electronic doublet. These and other notations in the figure will be explained further down.

On the Nature of the Emitter

The theory of diatomic molecules, as developed by Kratzer,[6] Kramers and Pauli,[7] gives the following expression for the spectral term due to the rotation or precession:

$$F(j)=B((j^2-\sigma^2)^{\frac{1}{2}}\mp\epsilon)^2\pm2\delta((j^2-\sigma^2)^{\frac{1}{2}}\mp\epsilon)+\cdots \tag{4}$$

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[6] A. Kratzer, Ann. d. Physik **71**, 72 (1923).

Here j, σ and ϵ are the notations given above (3). The double sign of ϵ, introduced by Kratzer, indicates that the corresponding vector can stand parallel or anti-parallel to that of m. ϵ is generally supposed to be accompanied by a double-signed δ term, giving account of the influence of the molecular rotation upon the electronic system. Applying the theory to the empirical results in our Tables VI and VII we have:

$$\Delta F(j)=4B(j\mp\epsilon)\pm 2B\sigma^2\epsilon/(j^2-1)\pm 4\delta+\cdots$$

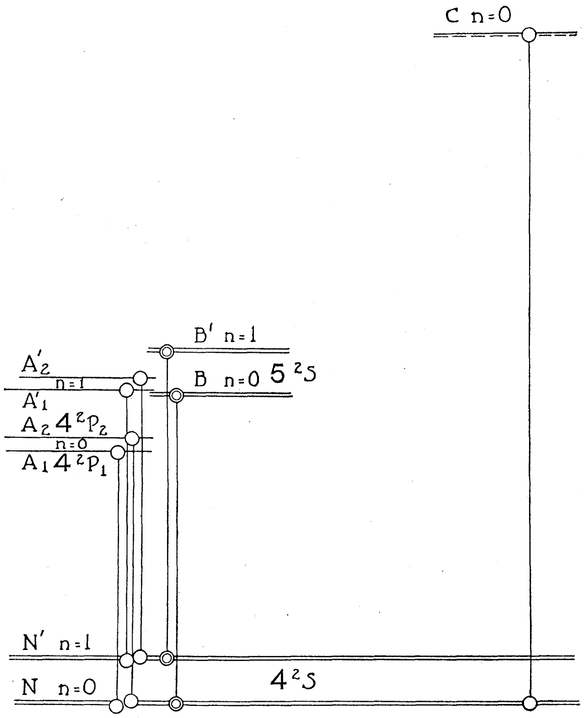

Fig. 4. The electronic levels in the CaH spectrum.

Obviously, as pointed out by several writers,[8] it is here impossible to distinguish between ϵ and δ unless σ is not present. Further, σ can not be detected unless ϵ is not present. Unhappily, the real support for the σ, except for the appearance of Q branches and the postulate for missing lines, is given by only the first lines in a band series, and as these are

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[7] H. A. Kramers and W. Pauli, Zeits. f. Physik **13**, 351 (1923).

[8] For a more complete discussion of the Kramers and Pauli formula see: R. S. Mulliken, Systematic Relations between Electronic Structure and Band-Spectrum Structure I, II, III, Proc. Nat. Acad. Sci. **12**, 144, 151, 338 (1926). In the following pages the writer in many cases follows the directions given in these very interesting papers.

mostly very faint or entirely missing, our knowledge about σ is very uncertain. ϵ and δ have to be considered from a theoretical point of view, ϵ usually assuming fractional values $\frac{1}{4}$, $\frac{1}{2}$, $\cdots$ and δ being generally very small. In Table VIII the constants of (4) are given as calculated from the $\Delta F(j)$ of Tables VI and VII.

The σ values of A_1, A_2 (1/2 and 3/2 respectively) are chosen on the basis of the missing lines $(j-j_e \geqq 0)$. It is difficult to state whether in these terms a small ϵ is present or not. In any case it is interesting that all through the terms of the table a *distinct* ϵ appears in connection with an *inconsiderable* σ and *vice versa.*[9] In the C group the value $\epsilon_1 = +\frac{3}{4}$ given by Mulliken[3] is changed into $\epsilon_1 = -\frac{1}{2}$ on account of the close agreement between its final term with that of $N_2(\epsilon_2 = -\frac{1}{2})$ and on adoption of half-quantum numbers for band spectra. Thus δ in C turns out very large. However, considering the extremely unstable C term, indicated by the spectrum, this is not discouraging. It is also worth while to notice that according to our table no intercombination of the type $\pm\epsilon_1 \rightarrow \epsilon_2 \mp$ occur. In the next to last column of the table the nuclear spacings r_0 corresponding to the different states of the molecule are given.

TABLE VIII

Values of the constants in Eq. (4) calculated from the values of $\Delta F(j)$ in Tables VI and VII

	B	ϵ	σ	δ	$r_0.10^8$	ν_0
N_1 N_2	4.225	$\pm\frac{1}{2}$	0	+0.011	2.01	
N_1' N_2'	4.125	$\pm\frac{1}{2}$	0	+0.011	2.03	
A_1	4.09	0	$\frac{1}{2}$	———	2.03	14392.30
A_2	4.49	0	$\frac{3}{2}$	———	1.94	14472.20
A_1'	4.01	0	$\frac{1}{2}$	———	2.05	
A_2'	4.38	0	$\frac{3}{2}$	———	1.97	
B_1 B_2	4.400	$\pm\frac{1}{2}$	0	−0.250	1.96	15753.84
B_1' B_2'	4.308	$\pm\frac{1}{2}$	0	−0.250	1.98	15738.08
C	4.912	$-\frac{1}{2}$	0	−1.04	1.88	28353.04

From the simple theory of band spectra (Heurlinger, Lenz) we know that bands shaded toward the violet correspond to an increase of the nuclear spacing for the end configuration in the molecule. It is therefore somewhat confusing that though all bands of the spectrum are shaded toward the violet r_0 is larger for A_1 than for N_1. The violet shading of A_1, however, as already mentioned, may be considered as an effect of the higher terms in (1) or in (4).

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[9] In the spectrum of HgH Mulliken (l.c.) finds a small $\sigma^2\epsilon$-term for the $^2P_1$, ^2S states. From a theoretical point of view, M. Born (Vorlesungen über Atom mechanik, Berlin, 1925, p. 140) excludes the simultaneous presence of σ and ϵ in (4).

In Fig. 4, A′, B′ have already been assigned as vibrational states ($n=1$) of N, A, B. This assumption is confirmed when we consider their r_0 values, which all show an increase compared to those of N, A, B. Theoretically this is explained by the unsymmetric character of the mutual force potential of the ions around their equilibrium position (r_0) in the molecule. The forces between the ions are indirectly measured by their vibration frequencies (ω) as these appear in band spectra and according to a rule by Birge[10] and Mecke[11] (based on a great number of spectra) the forces increase when r_0 decreases. Thus from the r_0 values of Table VIII we would expect

$$\omega_{A_1} < \omega_N < \omega_B < \omega_{A_2} < \omega_C$$

while the spectrum shows:

$$\omega_{A_1} = \omega_{A_2} > \omega_N > \omega_B$$

In the C term no vibrational state appears.[3] Considering the minimum nuclear spacing of this state in connection with its low degree of stability we may say that the CaH molecule acts throughout in opposition to the rule of Birge and Mecke.

ELECTRONIC LEVELS

According to the theory of the structure of molecules, as this has been developed recently by Birge, Mecke and Mulliken, the spectrum of a molecule agrees with that of the "corresponding atoms or molecules"—corresponding atoms and molecules having the same number of electrons in their coupled system. This comparison between the spectra of atoms and molecules has been worked out successfully for a number of diatomic molecules assigning their terms by S, P, D notations. In some cases a close agreement was found between the magnitudes and separations of the terms of corresponding atoms and molecules.

Here considering the elements in the second column of the periodic table, the spectra of ZnH, CdH, HgH show a doublet separation parallel to that of the $^3P_{1,2}$ of their metal atoms.[12] Applying the alternative and displacements laws as developed for band spectra, Mulliken[9] and Mecke[13] later on pointed out the parallel also existing between these separations and those of $^2P_{1,2}$ in Cu, Ag, Au—the corresponding atoms. It is now very satisfying, that the A group of CaH forms electronic doublets (A_1, A_2 and A_1', A_2') with separations roughly estimated to $\Delta\nu \backsim 80$ cm^{-1},

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[10] R. T. Birge, Phys. Rev. **25**, 240 (1925).

[11] R. Mecke, Zeits. f. Physik, **32**, 823 (1925).

[12] E. Hulthèn, Nature, Oct. 31 (1925).

[13] R. Mecke, Zeits. f. Physik, **36**, 795 (1926).

which are of the same magnitude as the $^2P_{1,2}$ of the potassium atom ($\Delta\nu = 57.90$ cm^{-1})—here the corresponding atom.

The A terms ($^2P_{1,2}$) of CaH may be pictured by an emission electron in a 4_2 orbit standing perpendicular (or nearly so) to the molecular figure axis. This explains the high stability of these states, a striking fact when we consider their various nuclear spacings.

The N level is assumed as the normal (^2S) level as indicated by the fact that it makes the final state for three different electronic transitions in the molecule. The failure of the CaH bands in absorption[14] is no serious argument against this assumption. Probably, the absorption of unstable molecules like those of MeH is a very complicated problem involving the stability and duration of the molecule. We know from the investigations of hydride spectra that the state of minimum energy does not necessarily mean a maximal nuclear stability (consider the spectra of CuH, HgH, AlH, OH).

In the N and B states the coupled electronic system of the molecule is assumed to be in the plane of the figure axis of the molecule ($\sigma = 0$), its angular momentum standing parallel as well as anti-parallel to the axis of rotation ($\epsilon = \pm\frac{1}{2}$). Because of these similarities between N and B they are both assigned ^2S levels (compare them with the terms of the violet CN bands). In the C state the electronic system again is of ϵ type ($\sigma = 0$) here however only the anti-parallel direction ($\epsilon = -\frac{1}{2}$) of its angular momentum is present. Whether this is an effect due to the highly unstable characteristics of C or not, we do not know. Bands analogous to those of B and C have not yet been found in the spectra of ZnH, CdH and HgH.

Finally it may be mentioned that the band spectrum of MgH (λ5211) apparently corresponds to the A group of CaH and thus should be assigned by a $^2P_{1,2} - {}^2S$ transition. Also here the doublet separation ($\Delta\nu \backsim 20$ cm^{-1}) roughly agrees with that of the corresponding Na atom ($^2P_{1,2} = 17$).

This work will be continued by an investigation on the spectra of strontium and barium hydride. The writer is indebted to the Director of this Laboratory, Professor H. M. Randall, for his very obliging and valuable interest in this work, and to the International Education Board for the award of a Fellowship.

Department of Physics,
University of Michigan
Sept. 30, 1926.

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[14] E. Hulthèn and R. V. Zumstein, Phys. Rev. **28**, 13 (1926).