A BAND OF UNUSUAL STRUCTURE PROBABLY DUE TO A HIGHLY UNSTABLE CALCIUM HYDRIDE MOLECULE

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Abstract

In the spectrum of the calcium arc in hydrogen at low pressure (best 3-20 mm) an isolated band occurs in association with the lines of neutral calcium. The wide spacing of the lines and the absence of appreciable isotope effect practically assure its hydride origin. The simple structure indicates a diatomic molecule. Reproductions and measurements of the lines are given. The band appears to consist of a P and an R branch with a single missing line in the middle. The two branches do not form a single series. From the abnormally weak central lines, the intensity of each branch rises to a maximum, then begins to fall slowly, until the lines are cut off sharply at the tenth line in the R and the eleventh in the P branch. These two lines both show a perturbation of -0.60 wave-number units. Assuming that these last perturbed lines have a common *initial* state, the band is analyzed in accordance with Kratzer's theory, applicable to molecules which have net electronic angular momentum in the plane of molecular rotation. For the initial state, the energy may be expressed by: $E'/hc = C + 28,353.38 + 0.039 (j' - \frac{3}{4}) + 4.798 (j' - \frac{3}{4})^2 - 0.000900$ $(j'-3_4)^4$; for the final state, by $E''/hc = C - 0.043 (j''-1_2) + 4.232$ $(j''-\frac{1}{2})^2-0.000192$ $(j''-\frac{1}{2})^4$, where j is the rotational quantum number. The last line in each branch corresponds to j' = 11. This limitation of the j'values, and the limitation to the value 0 of the vibrational quantum numbers n' and n'', indicated by the isolated character of the band, are explained as due to extreme molecular instability, such that the force holding the Ca and H atoms together begins to fall off very rapidly with distance if the atoms depart somewhat from their (rotationless) equilibrium position. Such a rapid falling off is possible only for a non-polar molecule. The emitting molecule is probably, then, a compound of hydrogen with an excited (not ionized) calcium atom, which may be of an unstable H₂-like type analogous to the emitters of the Zn, Cd, Hg, Cu, Mg and other hydride bands.

THE band discussed in this paper was called to the writer's attention by Professor F. A. Saunders, who had noticed that it occasionally appeared in the Ca arc at low pressure. The band, which is shaded toward high frequencies and whose head lies at λ 3533.6 A, is characterized by an unusual structure which indicated that its interpretation in the light of the quantum theory of band spectra might be of interest. Professor Saunders very kindly placed his plates at the writer's disposal for this purpose.

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Measurements

The measurements given below were made chiefly on a grating plate which was very kindly lent by Professor Henry Crew of Northwestern University. This plate, which has a dispersion of 2.9 A/mm, shows the band extremely well, except for the central weak lines. Fig. 1 is an enlarged reproduction from the plate, which is one of those take**n** by Crew and McCauley² in their work on the wave-lengths of the Ca lines in the vacuum arc.

Apparently the only reference in the literature to the band under discussion is the following from Crew and McCauley's paper, p. 38: "In addition to bands already studied by Olmsted³ and Eagle,⁴ the arc spectrum of calcium at reduced pressure shows several bands which make



Fig. 1. The band lines are all marked, beginning at the left with R (10), with full lines. The argon lines λ 3509.79 and 3511.11 are marked by dotted lines. The perturbation of the last line on the right, P (12), is distinctly visible; that of R (10) is less noticeable, although equally large.

their appearance only during the first half hour of exposure with fresh calcium electrodes. These lie in the region $\lambda 6700-7000$ and at $\lambda 3500$, and present a structure of fairly sharp lines with no continuous background. The origin of these bands we have left undetermined."

In order to determine which of the very weak central lines of Fig. 1 belonged to the band, and whether other weak band-lines might be present, a large number of photographs were taken by the writer with a Hilger quartz spectrograph (type C). A much enlarged reproduction of one of these is given in Fig. 2. The exposure was about 2 min., with the Ca arc running in an exhausted globe to which well-dried hydrogen at about 15 mm pressure had just been admitted. In general, best results were

² H. Crew and G. V. McCauley, Astrophys. J. 39, 29 (1914)

^a C. Olmsted, Astrophys. J. 29, 66 (1908)-Ca hydride bands.

⁴ A. Eagle, Astrophys. J. 30, 231 (1909)—Ca, Sr, and Ba hydride bands.

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obtained with a hydrogen pressure of 3-20 mm. The band was always present under these conditions, but became weaker or disappeared when the hydrogen was pumped out. The band was found to be absent from the spectrum of the Mg arc in hydrogen. It appears to be entirely isolated; a search for other related bands in neighboring regions of the spectrum proved fruitless.

Table I gives the results of measurements on the band lines.⁵ In addition to the lines recorded in the table, there are numerous very weak lines throughout the region occupied by the band, but probably unrelated to it. There is also a very weak line (int. 00) which always appears at λ 3526.02 (ν =28.352.5); this is exceedingly weak on some of



Fig. 2. The first line at the left is argon λ 3509.79, then come R (10), R (9), etc., to the faint line R (1). After a gap at the missing line P (1), the lines P (2), P (3), and P (4) can be distinguished.

the photographs, such as that from which Fig. 1 was made. This line might be denoted R(0), since its position agrees with that to be expected tor an R branch line immediately preceding R(1); nevertheless it seems unlikely that it belongs to the band. There are also the lines $\lambda 3511.115$ (int. 0, grating, Fig. 1; 00, prism) and $\lambda 3509.79$ (int. 0, grating, Fig. 1; 1, prism, Fig. 2), and other weaker lines at $\lambda 3508.17$ (int. 000, prism), etc. The former two lines are apparently the lines $\lambda 3511.11$ and $\lambda 3509.79$ of the argon "blue" spectrum. That these lines do not belong to the band

⁶ These were made with reference to the strong Ca lines for which the best values of Crew and McCauley are λ 3474.611 and λ 3474.774, and with the help of additional (Fe) comparison lines.

is shown by their varying intensity with respect to the band lines on different photographs, although $\lambda 3509.79$ showed a remarkable constancy of relative intensity throughout the prism photographs, suggesting the possibility that the band might be due to a compound of a hydrogen and an excited argon atom. The spectrum of the discharge, either condensed or uncondensed, through various mixtures of argon and hydrogen at low pressure, failed, however, to show the band.

TABLE	I
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Line	Rotational transition*	Int.	Wave-length (I.A.)	Wave-number	Obscalc.†
R(10)	$10\frac{1}{4} \rightarrow 9\frac{1}{2}$	7	3511.779	28,467,48	-0.60
$\mathbf{R}(9)$	$9\frac{1}{4} \rightarrow 8\frac{1}{2}$	8	13.523	453.36	02
$\mathbf{R}(8)$	$8\frac{1}{4} \rightarrow 7\frac{1}{2}$	8	15.291	439.04	01
$\mathbf{R}(7)$	$7\frac{1}{4} \rightarrow 6\frac{1}{2}$	9	17.003	425.20	05
R (6)	$6\frac{1}{4} \rightarrow 5\frac{1}{2}$	8	18.621	412.13	+.02
$\mathbf{R}(5)$	$5\frac{1}{4} \rightarrow 4\frac{1}{2}$	7	20,145	399.83	+.08
R (4)	$4\frac{1}{4} \rightarrow 3\frac{1}{2}$	6	21.575	388.29	+ .01
$\mathbf{R}(3)$	$3\frac{1}{4} \rightarrow 2\frac{1}{2}$	4	22.886	377.73	04
$\mathbf{R}(2)$	$2\frac{1}{4} \rightarrow 1\frac{1}{2}$	1 +	24.056	368.31	+ .02
R(1)	$1\frac{1}{4} \rightarrow \frac{1}{2}$	0	25.099	359.91	+ .02
P (2)	$\frac{1}{4} \rightarrow 1\frac{1}{2}$	0	3527.06	344.1	-0.1
P(3)	$1\frac{1}{4} \rightarrow 2\frac{1}{2}$	0+	28.255	334.54	06
P(4)	$2\frac{1}{4} \rightarrow 3\frac{1}{2}$	2	29.304	326.12	+ .03
P(5)	$3\frac{1}{4} \rightarrow 4\frac{1}{2}$	4	30.231	318.69	+ .01
P(6)	$4\frac{1}{4} \rightarrow 5\frac{1}{2}$	6	31.023	312.34	.00
P(7)	$5\frac{1}{4} \rightarrow 6\frac{1}{2}$	7	31.683	307.05	+ .04
P(8)	$6\frac{1}{4} \rightarrow 7\frac{1}{2}$	9	32.234	302.63	+ .02
P(9)	$7\frac{1}{4} \rightarrow 8\frac{1}{2}$	9	32.686	299.01	04
P(10)	$8\frac{1}{4} \rightarrow 9\frac{1}{2}$	8	33.043	296.16	06
P(11)	$9\frac{1}{4} \rightarrow 10\frac{1}{2}$	8 —	33.309	294.03	+ .03
P(12)	$10\frac{1}{4} \rightarrow 11\frac{1}{2}$	7	33.608	291.63	-0.61

* Probable change of nuclear rotational quantum number m, where $m = j - \epsilon$. The corresponding j changes (j=total rotational quantum number) involve in each case the next higher *integer*.

† Calculated values obtained with help of Eqs. (8) and (9), below.

STRUCTURE OF BAND

In structure and intensity distribution the band considerably resembles ordinary bands having a single positive (R) and a single negative (P) branch, and a single missing line in the middle (Fig. 2). The resemblance is perhaps closest to the CuH bands.^{6,7} But there are marked differences

⁶ R. Frerichs, Zeit. f. Phys. 20, 185 (1923); E. Bengttson, Zeit. f. Phys. 20, 229 (1923). Frerichs favors hydride origin on account of large spacing of lines (cf. Kratzer, ref. 9, p. 102), but is not sure. He shows that the Zn bands are best developed in presence of hydrogen.

⁷ R. S. Mulliken, Nature, April 6, 1922. The hydride origin of the CuH bands is proved from Frerichs' data, which show the expected rotational isotope effect. (Cf. also R. Mecke and R. Frerichs, Naturwiss., Sept. 26, 1924.) Absence of appreciable isotope effects in Zn, Cd and Hg bands shows them also of hybride origin. The same argument applies to the Ag and Au bands. from the simple CuH type. (1) The lines of the two branches do not form a single series; nor are they displaced by 1/2 unit as in many of the He₂ bands.⁸ The first difference $\Delta \nu$ between adjacent lines does not approach equality from opposite directions for the two branches at the region of the missing line. Equality is already reached for the intervals P(3)-P(4)and R(2)-R(1); and the relative spacing of the two branches is reversed in the intermediate central region. (2) The central lines, especially from R(1) to P(3), are relatively much weaker than usual. (3) The second differences $\Delta(\Delta \nu)$, after getting gradually smaller, suddenly decrease greatly and change to a negative value at the last line in each branch; the lines R(10) and P(12) both show a marked perturbation, the frequency being lower than expected by the same amount (0.60 units) for both (Fig. 1). (4) Both branches are cut off abruptly at the perturbed lines R(10) and P(12), both of which are intense lines, lying in each case, in fact, just beyond the line of maximum intensity. This sudden cessation after an intense line appears to be without a parallel. There seems, however, to be an approach to a similar condition in some of the He₂ bands^{8,9} which, after a flat maximum of intensity, fade off very rapidly. and disappear near where $\Delta \nu$ reaches a maximum value. According to Birge, a similar sudden fading off apparently occurs in the CN bands beyond where $\Delta \nu$ reaches a maximum, but this is for lines of very high ordinal number; some of the phosphorus bands also attain a maximum $\Delta \nu$ before fading out.⁹—The He₂ bands, it may be noted, show a few large perturbations, but not, as here, at the last line of a series.

Before attempting to interpret the peculiarities just described the band will be analyzed and quantum numbers assigned. Since non-integral rotational quantum numbers seem to be involved, a brief discussion of these is called for.

THEORY OF NON-INTEGRAL ROTATIONAL QUANTUM NUMBERS

Kratzer has shown¹⁰ that the energy E^m associated with the rotational quantum number m in band spectra may in many cases be expressed in the form

$$E^{m}/hc = \left[Bm^{2} - \beta m^{4} + \cdots \right] + \left[2\delta m + \cdots \right].$$
⁽¹⁾

Here $\beta < \langle B \rangle$, and $\delta < B$, where B has the usual meaning; $m = j - \epsilon$, where j is a quantum number, assumed always integral, corresponding to the

⁸ W. E. Curtis, Proc. Roy. Soc. 101A, 38 (1922); Ibid, 103A, 315 (1923).

⁹ R. T. Birge, Astrophys. J. 46, 92 (1917).

¹⁰ A. Kratzer, Ann. der Phys. **71**, 72 (1923). Theory of electronic origin of fractional quantum numbers; application to CN, Zn, Cd, Hg bands; discussion of probable hydride origin of last three. The notation here used differs from that of Kratzer.

total angular momentum, while ϵ corresponds to the *resultant electronic* angular momentum in the direction of rotation, and *m* to the angular momentum of the *nuclei*. Theoretically, according to Kratzer, ϵ may have any value; in practice, such values as 0, $\pm 1/4$, and $\pm 1/2$ usually appear, so that *m* likewise is fractional.^{10,11,12,13} Kratzer finds that δ has the same sign as ϵ in the bands he has studied.^{10,12}

Eq. (1) can be written in the form :

$$E^{m}/hc = a + B(m+\rho)^2 - \beta m^4 + \cdots \qquad (2)$$

Like δ , ρ should be small: $\rho = \delta/B$; $a = \delta^2/B$. By study of combination relations involving higher power terms, etc., ρ can apparently be determined independently of ϵ in some cases.¹⁰ Contrary to expectation, large ρ 's, of the same order of magnitude as the ϵ 's, seem to occur in a few cases when this method is used.¹⁴ This Kratzer tentatively ascribed in one case¹² to the presence of an appreciable cubic term in the second member of Eq. (1). However this may be, the usual close approach of ρ to zero, when exact fractional values (in particular 1/2) are assigned to ϵ , strongly supports such an assignment.

It is important to note that in Kratzer's theory, R, P and Q branches correspond to transitions $\Delta j = \pm 1,0$, but *not* necessarily to $\Delta m = \pm 1,0$, since ϵ may change at the same time as j. The structure and appearance of a band depend, however, on the values of Δm , not of Δj .

For a molecule having electronic angular momentum $\sigma h/2\pi$ around the line joining the nuclei, Eq. (1) should be replaced¹⁵ by

$$E^{m}/hc = B(\sqrt{j^{2} - \sigma^{2}} - \epsilon)^{2} + \cdots$$
(3)

ANALYSIS OF BAND STRUCTURE

In the case of the present band, its isolated position and the absence of more than two branches make useless any attempt to determine separately ρ and ϵ of Eq. (2). If it were not for the perturbations (cf. Table I)

¹² He₂ bands, A. Kratzer, Zeit. f. Phys. 16, 353 (1923).

¹³ In the HCl bands (ref. 12), the HCu bands (ref. 6), and the CO bands (ref. 12), it appears that ϵ is restricted to the value $\pm \frac{1}{2}$, and $\delta = 0$, or very nearly so.

¹⁴ Thus in one of the He₂ bands (ref. 13), for the initial state of the molecule, $\epsilon' = 0.843$, $\epsilon' - \rho' = 0.2513$; for the final state, $\epsilon'' = -0.3775$, $\epsilon'' - \rho'' = -0.2478$. Also in Kratzer's analysis of the ZnH, CdH, and HgH bands, some similar discrepancies appear: HgH, $\epsilon' = \frac{1}{2}$, $\epsilon' - \rho' = 0.13$, 0.11; $\epsilon'' = \frac{1}{4}$, $\epsilon'' - \rho'' = 0.17$; CdH, $\epsilon' = 0$, $\epsilon' - \rho' = 0.02$, 0.00; $\epsilon'' = \frac{1}{2}$, $\epsilon'' - \rho'' = 0.47$; ZnH, $\epsilon' = \frac{1}{4}$, $\epsilon' - \rho' = 0.01$, 0.00; $\epsilon'' = \frac{1}{2}$, $\epsilon'' - \rho'' = 0.49$.

¹⁶ A. Kratzer, Naturwiss. 27, 581 (1923); H. A. Kramers and W. Pauli, Jr., Zeit. f. Phys. 13, 351 (1923).

¹¹ HCl bands: E. F. Barker, Astrophys. J. 58, 201 (1923); W. F. Colby, Astrophys. J. 58, 303 (1923); E. C. Kemble, Phys. Rev. 25, 19 (1925); CO bands, E. Hulthèn, Ann. der Phys. 16, 353 (1923).

of R(10) and P(12)—and the perturbations, consisting in complete absence, of all following lines—it would be impossible to make more than a guess as to which (if any) lines of the P and R branches have terms in common. The numerical equality of the perturbations of R(10) and P(12) shows, however, that these must have either a common initial or a common final state.

Since the initial electronic state of the molecule is presumably more unstable than the final state, the common perturbation of lines R(10) and P(12) may be assumed to indicate a common *initial* state for these lines.¹⁶ This assumption is justified (1) by the following consideration of the intensity distribution in the band,¹⁷ and (2) by the fact that the alternative assumption would give a *positive* coefficient for the fourth power term of Eq. (9) below; this would be contrary to theory and all previous experience.

In band spectra consisting of a positive (R) and a negative (P) branch, the usual rule is that lines at an equal distance from the null-line are nearly equal in intensity, but that the P branch lines are somewhat the stronger. For cases where $\epsilon = 1/2$, this means that the transitions $(j-1\rightarrow)$ j and $j \rightarrow (j-1)$ are nearly equal in intensity, but that this equality is modified by a tendency for $(j-1)\rightarrow j$ and $(j+1)\rightarrow j$ to be equal. This rule holds in the infra-red absorption bands¹⁸ of HF, HCl, and HBr and in the HCu and the violet CN emission bands.⁶

In all these cases as well as in the Zn, Cd, and Hg, etc., bands, the first line of the P branch corresponds, according to Kratzer's theory, to the *j* transition $1 \rightarrow 2$, and the first line of the R branch to $2 \rightarrow 1$, transitions involving the state j=0 being always absent. In the present band P(2) and R(1) should then correspond to the transitions $1 \rightarrow 2$ and $2 \rightarrow 1$, respectively.¹⁷ This assignment of *j* values is the only one—unless j=0be admitted or j=0,1 be both excluded—which is consistent with a common initial state for R(10) and P(12). With the numbering adopted, the lines $(j-1) \rightarrow j$ and $j \rightarrow (j-1)$ are, as in other bands with a P and an R

¹⁶ An additional assumption is also involved here, viz., that the lines of the P and R branches involve an *identical set* of final states. That this is not always true for different branches of a band is shown in Kratzer's work (refs. 11, 13). However, where P and R branches are alone involved, such an assumption has so far proved justified, and it gives a reasonable interpretation in the present case.

¹⁷ The doubtful line R(0) is here excluded. If R(0) were taken as $2\rightarrow 1$, neither a common initial nor a common final state of R(10) and P(12) would be possible. If P(2) were $1\rightarrow 2$, and a common *final* state for R(10) and P(12) were assumed, R(1) would correspond to $4\rightarrow 3$; $3\rightarrow 2$ would be represented only by the abnormally weak R(0), and $2\rightarrow 1$ would be absent. Admitting j=0 would not remove the objections to the assumption of a common final state or to the inclusion of R(0).

¹⁸ Cf. E. C. Kemble, ref. 12, for discussion of intensities in HCl.

branch only, nearly equal in intensity; but, contrary to the usual situation, the R branch lines, instead of the P branch lines, are now decidedly the stronger, i.e., there is a strong tendency for $j \rightarrow (j+1)$ and $j \rightarrow (j-1)$ to be equal in intensity (cf. Table I).

It is now possible to proceed to the determination of the spectral terms for the initial and final states of the molecule. Let the terms corresponding to the energy of the molecule in its *initial* and *final* states, respectively, be denoted by F'(m) and F''(m), where

 $F'(m) = C + \nu^{e} + E'(m) / hc ; F''(m) = C + E''(m) / hc$ (4)

Here C is an undeterminable additive constant, and ν^{ϵ} is a spectral term corresponding to the difference in electronic plus vibrational energy for the two states of the molecule. It is possible to obtain a set of values of $\Delta F(m) = F(m+2) - F(m)$ by taking the differences of the wave-numbers of lines having a common final term. Thus, $\Delta F'(m) = \nu[F'(m+2) - F''(m+1)] - \nu[F'(m) - F''(m+1)] = R(m+1) - P(m+1)$. Similarly, $\Delta F''(m) = \nu[F'(m+1) - F''(m)] - \nu[F'(m+1) - F''(m+2)] = R(m) - P(m+2)$. Corresponding relations obviously hold for $\Delta F'(j)$ and $\Delta F''(j)$. In Table II are recorded the values of $\Delta F'(j)$ and $\Delta F''(j)$, together with their first differences.

In Table II the values in parentheses may be expected to be unreliable on account of the weakness of the lines involved, while the values in

Lines used	$\Delta F'(j)$	First diff.	Lines used	$\Delta F^{\prime\prime}(j)$	First diff.
R(2) - P(2)	(24.2)	(10, 0)	R(1) - P(3)	(25.37)	(16.92)
R(3) - P(3)	43.19	(19.0)	R(2) - P(4)	42.19	(10.82)
R(4) - P(4)	62.17	18.90	R(3) - P(5)	59.04	16.03
R(5) - P(5)	81.14	18.65	R(4) - P(6)	75.95	16.83
R(6) - P(6)	99.79	18.36	R(5) - P(7)	92.78	16,72
R(7) - P(7)	118.15	18.26	R(6) - P(8)	109.50	16.69
$\mathbf{R}(8) - \mathbf{P}(8)$	136.41	17.94	$\mathbf{R}(7) - \mathbf{P}(9)$	126.19	16.69
R(9) - P(9)	154.35	[16.97]	R(8) - P(10)	142.88	16.45
K(10) - P(10)	[171.32]		R(9) = P(11) P(10) = P(12)	159.33	16.52
	Lines used R(2) - P(2) R(3) - P(3) R(4) - P(4) R(5) - P(5) R(6) - P(6) R(7) - P(7) R(8) - P(8) R(9) - P(9) R(10) - P(10)	Lines used $\Delta F'(j)$ $R(2) -P(2)$ (24.2) $R(3) -P(3)$ 43.19 $R(4) -P(4)$ 62.17 $R(5) -P(5)$ 81.14 $R(6) -P(6)$ 99.79 $R(7) -P(7)$ 118.15 $R(8) -P(8)$ 136.41 $R(9) -P(9)$ 154.35 $R(10) -P(10)$ $ 171.32 $	Lines used $\Delta F'(j)$ First diff. $R(2) -P(2)$ (24.2) (19.0) $R(3) -P(3)$ 43.19 18.98 $R(4) -P(4)$ 62.17 18.97 $R(5) -P(5)$ 81.14 18.65 $R(6) -P(6)$ 99.7918.36 $R(7) -P(7)$ 118.1518.26 $R(8) -P(8)$ 136.4117.94 $R(9) -P(9)$ 154.35[16.97] $R(10) -P(10)$ [171.32]	Lines used $\Delta F'(j)$ First diff.Lines used $R(2) - P(2)$ (24.2) (19.0) $R(1) - P(3)$ $R(3) - P(3)$ 43.19 18.98 $R(2) - P(4)$ $R(4) - P(4)$ 62.17 18.97 $R(3) - P(5)$ $R(5) - P(5)$ 81.14 18.65 $R(4) - P(6)$ $R(6) - P(6)$ 99.79 18.36 $R(5) - P(7)$ $R(7) - P(7)$ 118.15 18.26 $R(6) - P(8)$ $R(8) - P(8)$ 136.41 17.94 $R(7) - P(9)$ $R(10) - P(10)$ $ 171.32 $ $ 16.97 $ $R(9) - P(11)$ $R(10) - P(12)$ $R(10) - P(12)$ $R(10) - P(12)$	Lines used $\Delta F'(j)$ First diff.Lines used $\Delta F''(j)$ $R(2) - P(2)$ (24.2) (19.0) $R(1) - P(3)$ (25.37) $R(3) - P(3)$ 43.19 18.98 $R(2) - P(4)$ 42.19 $R(4) - P(4)$ 62.17 18.97 $R(3) - P(5)$ 59.04 $R(5) - P(5)$ 81.14 18.65 $R(4) - P(6)$ 75.95 $R(6) - P(6)$ 99.79 18.36 $R(5) - P(7)$ 92.78 $R(7) - P(7)$ 118.15 18.26 $R(6) - P(8)$ 109.50 $R(8) - P(8)$ 136.41 17.94 $R(8) - P(10)$ 142.88 $R(10) - P(10)$ $ 171.32 $ $ 16.97 $ $R(9) - P(11)$ 159.33 $R(10) - P(12)$ 175.85

TABLE II

brackets are affected by the perturbation of the initial state j' = 11. The remaining values were used to obtain the empirical equations

$$\Delta F'(j) = 4.312 + 19.650j' - 0.112j'^2 \tag{5}$$

$$\Delta F^{\prime\prime}(j) = 8.176 + 17.067 j^{\prime\prime} - 0.030 j^{\prime\prime 2}.$$
 (6)

Cubic terms in j should also be involved (cf. Eq. 7) but the data are not sufficiently accurate for their independent determination.

The theoretical expression for $\Delta F(m)$ deducible from Eq. (1) is

$$\Delta F(m) = [4B + 4\delta - 16\beta] + [4B - 32\beta]m - 24\beta m^2 - 8\beta m^3.$$
(7)

If δ is small, as would be expected, the constant term and the coefficient of *m* should be nearly equal. This near-equality can be obtained in Eq. (5) by putting m'=j'-3/4, i.e., $\epsilon = +3/4$, and in Eq. (6) by putting m''=j''-1/2, i.e., $\epsilon = +1/2$. The theoretical $\Delta F'(m)$ and $\Delta F''(m)$ expressions of the form of Eq. (7), after making the indicated substitution for *m* and expanding, may now be used in a re-analysis of the data of Table II, so as to obtain the coefficients *B*, δ , and β of Eqs. (1) and (7). Knowing these, the expressions for E'(m) and E''(m) of Eqs. (1) and (4) can be written down. Now $R(m) = F'(m+1) - F''(m) = \nu^{e} + (1/hc)$ [E'(m+1) - E''(m)], by Eq. (4); and $P(m) = F'(m-1) - F''(m) = \nu^{e} + (1/hc)$ [E'(m-1) - E''(m)]. From these relations and the data of Table I, ν^{e} can be determined. The final results are

$$F'(m) = C + 28, 353.385 + 0.0392(j - 3/4) + 4.7985(j - 3/4)^{2} - 0.000900(j - 3/4)^{4}$$
(8)

$$F''(m) = C - 0.0434(j - 1/2) + 4.2315(j - 1/2)^2 - 0.000192(j - 1/2)^4 \quad (9)$$

The "Obs.—calc." values of Table I show that these equations hold within experimental error—which is greatest for the central weak lines—except for the perturbation of -0.60 units which is common to the lines R(10) and P(12).¹⁹

The smallness of the values of δ in Eqs. (8) and (9), in spite of the large m^4 coefficients and other indications of great instability, is notable. For any choice of ϵ values differing much from that used, both δ 's would be large. The δ 's correspond to $\rho' = 0.008$ and $\rho'' = -0.010$ (see Eq. (2) for meaning of ρ); this seems to justify the assumption of the ϵ values

 $\begin{array}{l} F'(m) = C + 28,353.496 - 0.285 \ (j - \frac{3}{4}) + 4.9265 \ (j - \frac{3}{4})^2 - 0.01867 \ (j - \frac{3}{4})^3 \\ F''(m) = C - 0.178 \ (j - \frac{1}{2}) + 4.2743 \ (j - \frac{1}{2})^2 - 0.0050 \ (j - \frac{1}{2})^3 \end{array} \tag{8'}$

¹⁹ If one assumed in Eq. (1) an m^3 term instead of an m^4 term, the data could be represented about as well as before (i.e., with about the same average difference "Obs.-calc." in Table I) by the equations:

The coefficients of m, m^2 , and m^3 here may be obtained by the use of Eqs. (5) and (6), after making appropriate m transformations, etc. Eqs. (8') and (9') lack the theoretical foundation of Eqs. (8) and (9); it is interesting to note that the δ 's are now much larger than before, and furthermore are negative, contrary to Kratzer's findings for ϵ positive. This last is of course also true for δ'' of Eq. (9), which, however, is much smaller than here. Eqs. (8') and (9') give a perturbation of -0.81 units for lines R(10) and P(12).

3/4 and 1/2, and to indicate that these fractional values have a real meaning.²¹

The presence of a σ as in Eq. (3) is not indicated by the data, but the central lines, where its effect would be greatest, are too weak for certainty. The absence of a Q branch, however, tends to indicate that $\sigma = 0$.

Intensity distribution. A study of a number of the arc photographs (cf. Fig. 2) indicates that the strongest lines are R(8) and P(9), for both of which $m' = 8\frac{1}{4}$ for the initial state of the molecule. According to the equation $T = (1.431)(2B)m^2_{max}$, this would correspond,²² for an equilibrium thermal distribution of the m' values, to a temperature of 680°C. This would seem too low for the Ca arc, unless the band is emitted at the outer mantle of the flame. However, the m' distribution may, as presumably in many cases of electronic excitation, be very far from that corresponding to thermal equilibrium. In the present case it would seem that the lowest values of m' are strongly disfavored in the formation of CaH molecules, while m' values above $10\frac{1}{4}$ are absolutely disfavored, probably because such molecules are incapable of existence.

NATURE OF EMITTER AND RELATION TO OTHER EMITTERS

With the information now available, it becomes very probable that the emitter of the band belongs to a class of unstable diatomic hydrides of which the emitters of the ZnH, CdH, and HgH bands are examples. These are characterized¹¹ by a variety of values of $\epsilon(0, \pm \frac{1}{4}, \pm \frac{1}{2})$, large values of *B* (between 5 and 7.5), and large values of β . The CuH bands (B = about 6, $\epsilon = \frac{1}{2}$), as well as the analogous AgH and AuH bands, also appear to belong in this class.^{6,7,23} The Mg hydride bands (B = about 5)^{24,25} the red Ca hydride bands,^{3,4} and the Ba and Sr hydride bands,⁴ and others (Al, etc.)²³ probably also belong here,²⁶ although possibly some of these are due to triatomic hydrides MH₂.

²¹ According to Kratzer's interpretation of δ , one might expect it to be large for an extremely unstable molecule like that here involved, if ever. Its actual small value here (in agreement with the small values for HCl, HCu, CO (ref. 14) CN, CdH (ref. 15), etc.) thus tends to cast suspicion on the very large δ 's found by Kratzer for the HgH bands (both states of the molecule) and the ZnH bands (initial state). Of course in the present case the δ 's could be made large by a different choice of the ϵ 's.

²² E. C. Kemble, Phys. Rev. **8**, 689 (1916); T. Heurlinger, Dissertation Lund (1918), p. 65-6; R. T. Birge, Astrophys. J. **55**, 273 (1922).

²³ CuH, also Ag, Al, Mg, Zn, Na hydride bands, O. H. Basquin, Astrophys. J. 14, 1 (1901); AuH bands, E. Bengttson, Arkiv. f. Mat. Astron. och. Fysik 18, No. 27, 1 (1924); AgH bands, E. Bengttson and E. Svensson, Compt. Rend. 180, 274 (1925).

²⁴ A. Fowler, Phil. Trans. Roy. Soc. 209A, 447 (1909); etc.

²⁵ T. Heurlinger, Diss. Lund, 1918.

²⁶ The ultraviolet "water vapor" tands, which resemble the Mg hydride bands,²⁵ may analogously be due to OH; see W. W. Watson, Astrophys. J. **60**, 145 (1924); H. Witt, Zeit. f. Phys. **28**, 249 (1924).

The unstable character of the binding in these hydrides is indicated (cf. Kratzer, ref. 11, p. 102) by the *relatively* low values of *B*, as compared with the values for the infra-red bands of the more stable molecules HF, HCl, HBr (B = 20,10.5, 8.4, respectively). The CaH band has the smallest values of B and in its initial state the largest value of β (among known bands only the He₂ bands show larger values of β) of any of the bands of its class that have been analyzed. This indicates an unusually high degree of instability, which is supported by the other peculiarities of the band. The following values of the internuclear distance, calculated from the values of B'' for the less excited states of the respective molecules, are of interest in this connection: ClH, $r_0 = 1.27 \times 10^{-8}$; ZnH, 1.60×10^{-8} ; CaH, 2.00×10^{-8} cm. The difference between ZnH and CaH may, however, be due, in part at least, to the probably larger size of the Ca atom.

The hydride origin of the class of bands under discussion is attested by several facts. First, there is the high value of B, higher than for such compounds as N₂, CN, and CO ($B \sim 2$), which can hardly be accounted for in a compound of a heavy atom like Ca, Cu, Zn, Cd, Hg, etc., except by a hydride.10 Second, the absence of an appreciable isotope effect in the band spectra of most of these compounds can be explained only by hydride origin.⁷ According to Dempster,²⁶ it is probable that Ca has in addition to the chief isotope of atomic weight 40, a small amount of 44. If so, CaH is the only Ca compound for which the rotational isotope effect could escape detection on the grating plate used. The rotational isotopic displacement²⁷ would be -0.22 per cent for (Ca⁴⁴H, Ca⁴⁰H), but -2.6 per cent for (Ca⁴⁴O, Ca⁴⁰O). For the line R(10) the displacement, which would be a maximum for either compound, would be 0.03 A toward the red for CaH-probably too small to be detected-but 0.38 A for CaO. It would be progressively less for other lines nearer the band origin.²⁷ Since no displaced lines were observed, only CaH seems to be possible if Ca⁴⁴ exists in appreciable amounts.

The frequent occurrence of the present band and others of its class in the vacuum arc and in vacuum discharge tubes may probably be ascribed to the presence of traces of moisture.²⁸ In every case where the

²⁶ A. J. Dempster, Phys. Rev. 19, 431 (1922).

²⁷ R. S. Mulliken, Phys. Rev. **25**, 119, Feb. 1925. There might also be a vibrational isotope effect, but this would probably be very small (see below, also ref. 31).

²⁸ Red Ca hydride bands, refs. 2 (see quotation in text), 3, 4; also A. S. King, Astrophys. J. **29**, 190 (1909); **43**, 341 (1916); also J. Barnes, Astrophys. J. **30**, 14 (1909); **31**, 175 (1910). Mg hydride bands, ref. 21; also A. Fowler and H. Payn, Roy. Soc. Proc. **72A**, 253 (1903); E. E. Brooks, Roy. Soc. Proc. **80A**, 218 (1908); Astrophys. J. **29**, 177 (1909); A. S. King, Astrophys. J. **43**, 341 (1916). Ba and Sr hydrides, ref. 4. CuH, ZnH, etc., refs. 6, 23.

experiment has been tried, the addition of hydrogen as such has favored the production of such bands.^{28,29} Of particular interest is Compton and Turner's recent work²⁹ on the HgH bands, in which they find the bands only in regions of the discharge where excited Hg atoms are being produced, and with intensity proportional to the hydrogen pressure. It may be that the emitters of this entire class of bands are compounds of an excited metal atom with a hydrogen atom. An excited atom of Zn, Cd, Hg, or of Mg, Ca, Sr, or Ba, with one of its valence electrons removed to an outer orbit, should resemble a hydrogen atom and tend to form with another excited atom of its own kind or with a H or H-like atom, a molecule analogous to H₂. A probably similar compound of excited hydrogen-like atoms^{30,27} is the He₂ molecule.³¹ The absorption band spectra of the alkali metals indicate that these, being already hydrogenlike, can form diatomic molecules with little or no excitation. In the case of the present CaH band it was noted that the band was most intense where the lines of neutral Ca were strong, but that it was not correlated with the Ca⁺ lines. This indicates that it may be due to a compound of an excited, but not of an ionized, Ca atom.

INTERPRETATION OF LIMITATION OF ROTATIONAL AND VIBRATIONAL QUANTUM NUMBERS

Besides the large value of r_0 , the isolated character of the band and the sudden cessation of the series of m' values at $10\frac{1}{4}$ indicate extreme molecular instability. They also indicate (see below) a non-polar molecule, in agreement with the suggestions made above.

The absence of related bands is best explained by ascribing the band to a vibrational transition $(0 \rightarrow 0)$, with the supposition that the molecule is too unstable, even in its final state, to exist, in appreciable amounts at any rate, with any vibrational energy.³² Kratzer has recently pointed out³³ that the vibrational quantum number *n* can have no theoretical

²⁹ K. T. Compton and L. A. Turner, Phil. Mag. **48**, 360 (1924); Compton, Turner, and W. H. McCurdy, Phys. Rev. **24**, 608 (1924). E. Hulthèn (Compt. Rend. **179**, 528, 1924) also finds hydrogen to have a favorable effect.

³⁰ W. Lenz, Verh. d. Deutsch. Phys. Ges. **21**, 632 (1919) first suggested the resemblance of excited He to H atoms.

³¹ In connection with He₂, Hg₂, etc. see also J. Franck and W. Grotrian, Zeit. f. Phys. **4**, 89 (1921); in regard to Hg₂, see also ref. 30.

²² See ref. 28 in regard to the possibility that the lowest values of the vibrational quantum numbers may not be zero, but e.g. sometimes $\frac{1}{2}$.

³³ A. Kratzer, Zeit. f. Phys. **26**, 40 (1924); P. Tartakowsky had previously concluded (Zeit. f. Phys. **24**, 98, 1924), but on an erroneous basis according to Kratzer, that a maximum value of n is to be expected in general.

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maximum value for molecules for which the law of force $F = \sum a/r^n$ contains terms with $n \leq 3$. The vibrational energy, however, should have a maximum value equal to an energy of dissociation. In practice there is evidence that n may sometimes have a limiting maximum value; e.g., n'_{max} is equal to 0 in the fourth positive nitrogen bands, 4 in the second positive bands,³⁴ and 0 in CaH. In other cases—in particular that of the visible absorption spectrum of I_2 —n' may reach very large values, corresponding to more and more closely spaced bands which, in the case cited, become lost in a region of apparently continuous absorption which probably means that actual dissociation of the molecule is reached or at least closely approached.³⁵ For polar molecules, i.e. molecules which would dissociate into oppositely charged ions, the law of force should approach $F = a/r^2$ at large distance, so that for these an unlimited number of n values should be possible. For non-polar molecules it would seem that a maximum value of n is to be expected. In the case of the CaH molecule now under consideration, a non-polar binding is therefore indicated by the limitation of n' and n''; this may well be of a H₂-like type, as above suggested.

The non-occurrence of m' values above $10\frac{1}{4}$ is most reasonably interpreted in an analogous way. It can be shown that m can have an unlimited number of values only if the law of force between the nuclei approaches $F = a/r^n$, $n \leq 3$, for large distances. In other cases—including non-polar molecules (in the sense used above) only—m should have a maximum value, corresponding to a maximum angular momentum. For most molecules, m_{max} is apparently very large and so is usually not reached, on account of the insufficiently high temperature of the source of light. Its remarkably small value in the present case indicates an extremely unstable molecule.³⁶ Physically a qualitatively correct idea

³⁶ It is of course *possible* that there are a large number of m' values beyond 10¹₄, all represented by extremely weak lines because of the presumably very small energy interval between the energy of $m' = 10^{1}_{4}$ and that of dissociation. If such lines were present there would be a reversal of direction of the R branch with formation of a head, or "tail" (ref. 10), while in the P branch, the incipient head would be left uncompleted and the series continued with no reversal of direction. Another possible explanation of the absence of m' values greater than 10^{1}_{4} , might be instability of some electronic orbit beyond this critical point; or possibly the explanation lies in some peculiarity of the mechanism of formation.

³⁴ E. Hulthèn and G. Johansson, Zeit. f. Phys. 27, 308 (1924).

³⁶ The series of heads (cf. R. Mecke, Ann. der Phys. **71**, 104, 1923) converge toward about λ 4900 (equivalent to 2.52 v). This is suggestively close to Foote and Mohler's resonance potential at 2.34 v. It is greater than the chemical heat of dissociation, equivalent to 1.37 v. The visible absorption spectra of Br₂ and Cl₂ are probably completely analogous to that of I₂. The absorption bands farther in the ultraviolet for I₂ and Br₂ probably involve an entirely different electron jump.

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is conveyed by stating that an attempt to increase m' by 1 unit above $10\frac{1}{4}$ would result in dissociation of the molecule by centrifugal action. The extremely high value of the coefficient of m^4 in Eq. (8) means³⁷ that the binding is very weak and that the molecule expands considerably with increasing m'; while the perturbation at $m' = 10\frac{1}{4}$ may well correspond to the sudden beginning of a rapid falling off in the force between the nuclei. This is completely in harmony, it will be noted, with the condition $n'_{max} = 0$. Somewhat similar explanations may apply to the sudden fading of the He₂ and CN bands (see earlier discussion under "Structure of Band") although in these the cessation of the lines is apparently not as abrupt as here. In the case of He₂, Curtis has in fact called attention to the expansion and possible ultimate instability of the molecule under centrifugal force.⁸

The CaH band here described may deserve further study if intense and pure exposures can be obtained under high dispersion. For this purpose, a quartz Ca arc lamp containing hydrogen and run at a sufficiently high temperature to prevent loss of hydrogen as solid CaH₂, would seem to be promising. Some of Professor Saunders' photographs were obtained with such a lamp, containing, however, only such hydrogen as was accidently present. It may be that the Ca hydride bands in the red^{2,3,4} are emitted by the molecule that emits the present band, but in a lower state of excitation.

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³⁷ For theoretical interpretation of this coefficient see A. Kratzer, Zeit. f. Phys. 3, 289 (1920).



Fig. 1. The band lines are all marked, beginning at the left with R (10), with full lines. The argon lines λ 3509.79 and 3511.11 are marked by dotted lines. The perturbation of the last line on the right, P (12), is distinctly visible; that of R (10) is less noticeable, although equally large.



Fig. 2. The first line at the left is argon λ 3509.79, then come R (10), R (9), etc., to the faint line R (1). After a gap at the missing line P (1), the lines P (2), P (3), and P (4) can be distinguished.