

Interpretation of the Spectra of CaF and SrF.

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[PLATES 13–15.]

Introduction.

The structure of the band spectra of the diatomic alkaline earth fluorides has been considered in the light of the quantum theory by Mecke,* Jevons,† Johnson,‡ and Jenkins.§ Because of the closeness of the rotational structure it has proved impossible to obtain sufficient resolution for the application of the combination principle to the individual band lines except for BeF, which molecule has the smallest moment of inertia (Jenkins, *loc. cit.*). With the heavier molecules, assignments of vibrational quantum numbers were made from the positions and intensities of the band heads, and designations of the electronic terms were given, based on the evident similarity of certain band systems in this group of molecules. The ${}^2\Pi \rightarrow {}^2\Sigma$ system, which lies in the ultra-violet for BeF and MgF, and in the visible for CaF, SrF and BaF, was shown in the case of BeF to possess the expected rotational structure. The system designated ${}^2\Sigma \rightarrow {}^2\Sigma$ by Johnson‡ is known only in CaF, SrF and BaF, and has a slightly higher frequency than ${}^2\Pi \rightarrow {}^2\Sigma$.

In the course of a search for isotope effects in the spectra of CaF and SrF I have obtained plates with the 21-foot concave grating showing the two systems mentioned above in both emission and absorption. For the absorption the method of Walters and Barratt|| was used. Although the study of these plates gave evidence of isotopes only in the case of SrF, certain observations on the modifications in structure between emission and absorption are important for the interpretation of the rotational structure of the bands of both molecules, a question which apparently can only be cleared up by indirect evidence of this kind.

* 'Z. Physik,' vol. 42, p. 390 (1927).

† 'Proc. Roy. Soc.,' A, vol. 122, p. 211 (1929).

‡ 'Proc. Roy. Soc.,' A, vol. 122, pp. 161, 189 (1929).

§ 'Phys. Rev.,' vol. 35, p. 315 (1930).

|| 'Proc. Roy. Soc.,' A, vol. 118, p. 120 (1928).

$^2\Pi \rightarrow ^2\Sigma$ Systems.

The two stronger heads of the (0, 0) band of this system lie at $\lambda\lambda$ 6037, 6064 for CaF and $\lambda\lambda$ 6512, 6633 for SrF. These are evidently the Q_2 and Q_{12} heads, in the notation of Mulliken.* The associated P_2 and P_{12} heads are well developed in emission, with intensities indicated by the vertical lines drawn below them in fig. 1. In absorption at 1100° C.– 1200° C. the P_{12} heads are

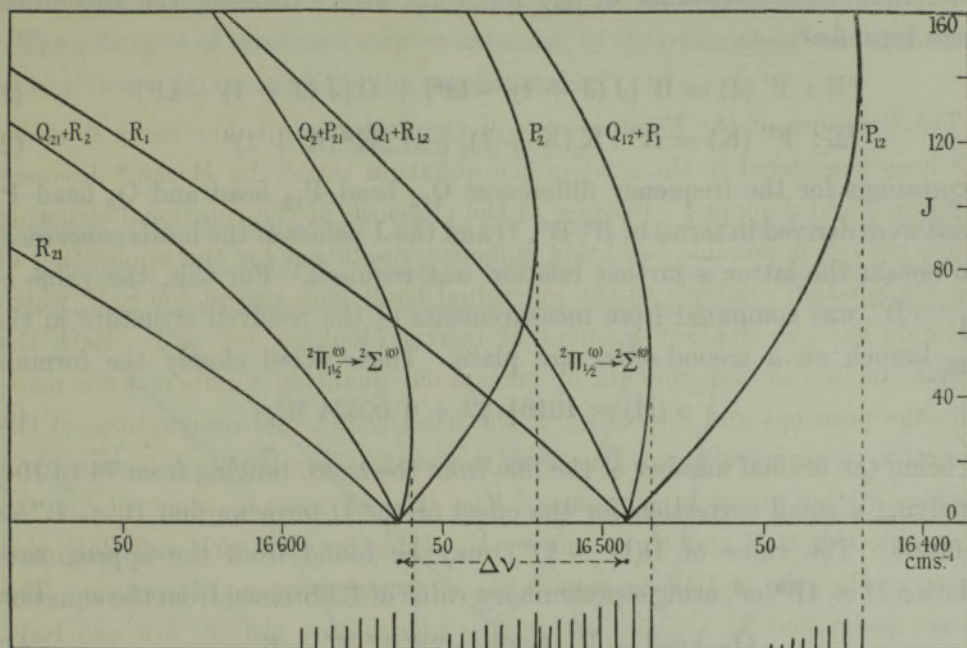


FIG. 1.—Fortrat diagram of $^2\Pi^{(0)} \rightarrow ^2\Sigma^{(0)}$ CaF band on basis of constants obtained from the analysis; the positions of the heads of the ($v' - v'' = 0$) sequence are shown on the bottom line.

entirely absent in the case of CaF (Plate 14, fig. 7, *a*) and are very faint in SrF (Plate 15, fig. 12, *a*) whilst the P_2 heads are much weaker in both cases. This is evidently a consequence of the extremely high values of the rotational quantum numbers at which these heads are formed, since in both cases structure lines can be seen extending towards the red from the Q_{12} head and fading out before they reach the position of the P_{12} head. This behaviour is consistent with the type of structure illustrated in fig. 1, which was drawn according to approximate constants obtained for CaF by a method described in the following paragraph. The change in the Boltzmann distribution from the arc to the absorption tube is adequate to account for these modifications if the rotational quantum numbers are as shown.

* 'Phys. Rev.', vol. 32, p. 411 (1928).

Qualitatively, it is to be expected that $J_{P \text{ head}}$ should be great, because of the near equality of the rotational constants in the ${}^2\Pi$ and ${}^2\Sigma$ states. The close spacing of successive bands of the sequences shows that the vibration frequencies are nearly the same in the two states ($\omega' \sim \omega''$), and when this is the case, the moments of inertia also differ only slightly, so that $B' \sim B''$. A more quantitative consideration has been made in the case of CaF by estimating these constants in the following way. Utilising the theoretical term formulæ*

$${}^2\Pi : F'(J) = B'[J(J+1) - \Omega^2] + D[J(J+1) - \Omega^2]^2 \quad (1)$$

$${}^2\Sigma : F''(K) = B'' \cdot K(K+1) + D \cdot K^2(K+1)^2 \quad (2)$$

expressions for the frequency differences $Q_{12} \text{ head} - P_{12} \text{ head}$ and $Q_2 \text{ head} - P_2 \text{ head}$ were derived in terms of B' , B'' , D and the J values of the heads concerned. To obtain the latter a further relation was required. For this, the value of $B'_1 - B''$ was computed from measurements of the resolved structure in the Q_{12} branch on a second-order arc plate. These fitted closely the formula

$$\nu(M) = 16484.92 + 0.00334 M^2, \quad (3)$$

M being the ordinal number of the line from the head, ranging from 74 to 104. Applying a small correction for the effect of the D term we find $B'_1 - B'' = 0.00306$. The value of $D(D' \sim D'')$ may be found from the approximate relation $D = 4B^3/\omega^2$, using a preliminary value of B obtained from the equation

$$Q_{12} \text{ head} - P_{12} \text{ head} = 2B'B''/B' - B'', \quad (4)$$

and the value of ω (583 cm.^{-1}) obtained by Johnson (*loc. cit.*) from the Q heads. Applying successive approximations, these estimates may be considerably improved. The final results of this calculation of constants for the $(0, 0)$ band of CaF were

${}^2\Pi_{1/2} \rightarrow {}^2\Sigma.$	${}^2\Pi_{11/2} \rightarrow {}^2\Sigma.$
$B'_1 = 0.3246 \text{ cm.}^{-1}$	$B'_2 = 0.3268 \text{ cm.}^{-1}$
$B'_1 - B'' = 0.00306 \text{ cm.}^{-1}$	$B'_2 - B'' = 0.00531 \text{ cm.}^{-1}$
$J_{Qh} = 52$	$J_{Qh} = 29$
$J_{Ph} = 137$	$J_{Ph} = 86$
$B'' = 0.3215 \text{ cm.}^{-1}$	
$D' = D'' = -0.38 \times 10^{-6} \text{ cm.}^{-1}.$	

The origins, ν_1^0 and ν_2^0 , of the ${}^2\Pi_{1/2} \rightarrow {}^2\Sigma$ and ${}^2\Pi_{11/2} \rightarrow {}^2\Sigma$ bands are found to be, respectively, 16493.6 and 16565.8 cm.^{-1} , giving as the doublet separation in

* R. S. Mulliken, 'Rev. Mod. Phys.', vol. 2, p. 60 (1930).

the Π state $\Delta v^0 = 72.2 \text{ cm.}^{-1}$. This may be compared with the separation of the Q heads, 75.03 cm.^{-1} , and of the P heads, 98.06 cm.^{-1} . The differences result from the inequality in the distance of the two Q heads from the origins (8.5 and 5.6 cm.^{-1}) and of the P heads (69.4 and 43.6 cm.^{-1}). The larger distance in each case refers to the ${}^2\Pi_{1/2} \rightarrow {}^2\Sigma$ component, and is a consequence of the requirement that $B_2 > B_1$, which invariably holds for case (a) doublet states where the difference in B arises from the rotational distortion.*

The estimates of constants may be extended to the other observed sequences, ($v' - v'' = -1$), by applying the empirical rule†

$$\frac{2xB^{(0)}}{\alpha} = 1.4 \pm 0.2 \quad (5)$$

to obtain α in the equation‡ $B^{(v)} = B^{(0)} - \alpha v$. One obtains $\alpha_1' = 0.0026$, $\alpha_2' = 0.0024$, $\alpha'' = 0.0020$. These values lead to a ready explanation of the

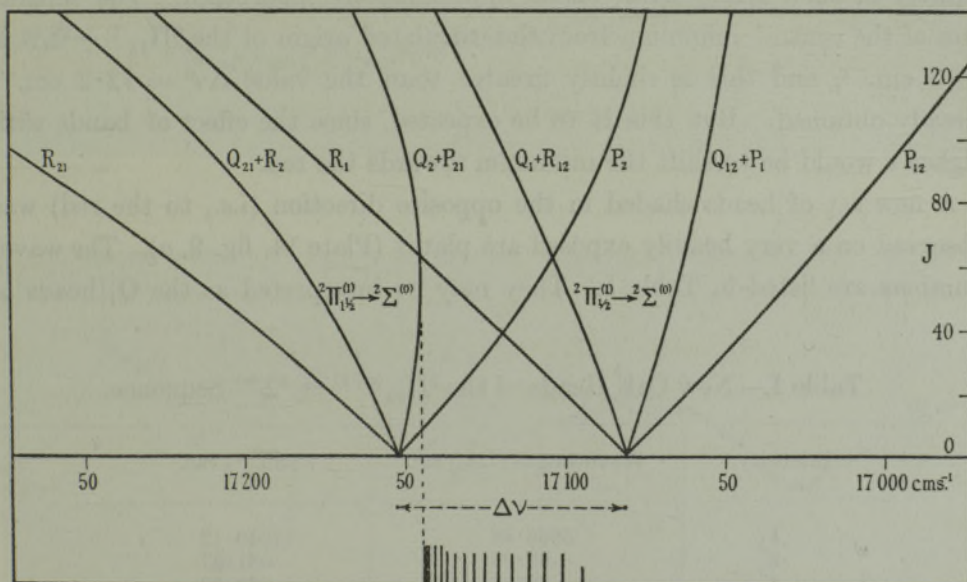


FIG. 2.—Fortrat diagram of ${}^2\Pi(1) \rightarrow {}^2\Sigma(0)$ CaF band based on constants obtained; the positions of the heads of the ($v' - v'' = +1$) sequence are shown on the bottom line.

* R. S. Mulliken, 'Phys. Rev.', vol. 32, p. 390 (1928).

† This rule was given by R. T. Birge at a meeting of the American Physical Society in Berkeley, 1928. Only an abstract of this paper has appeared—R. T. Birge, 'Phys. Rev.', vol. 31, p. 919, abstract 30 (1928).

‡ In general v is used as a subscript to B. In this case, however, it is more convenient to use it as a superscript in parentheses to avoid confusion. The use of v as a subscript is not an essential part of the standard notation, and it is more in conformity with the other notation employed here to use the subscripts to differentiate between the two values of B.

remarkable appearance of the ($v' - v'' = +1$) sequence (Plate 14, fig. 9, *b*). This contains only one series of heads, the Q_2 heads (see fig. 2), in which the earlier heads are in approximate coincidence. The absence of other series of heads follows from the result that $B_2^{(1)'} - B^{(0)''}$ is very small, and $B_1^{(1)'} - B^{(0)''}$ practically zero, thus requiring the heads to be formed at very high J values. That the ${}^2\Pi_{1/2} \rightarrow {}^2\Sigma$ component is really present, though no heads of any strength are visible, is indicated by a diffuse double maximum with its centre at 17076.6 cm.^{-1} , as measured on an emission plate. The microphotometer record of fig. 3 (Plate 13) makes this more apparent, and shows that its integrated intensity is at least as great as that of the ${}^2\Pi_{1/2} \rightarrow {}^2\Sigma$ component. The modification of this sequence in absorption is significant; the double maximum is still evident, but is shifted slightly to the violet. This is to be expected if the observed maxima are due to the integrated effect of a number of such symmetrical bands approximately superposed. The separation of the central minimum from the calculated origin of the ${}^2\Pi_{1/2}^{(1)} \rightarrow {}^2\Sigma^{(0)}$ is 78.5 cm.^{-1} , and this is slightly greater than the value $\Delta\nu^0 = 72.2 \text{ cm.}^{-1}$ already obtained. But this is to be expected, since the effect of bands with higher v would be to shift the minimum towards the red.

A new set of heads shaded in the opposite direction (*i.e.*, to the red) was observed on a very heavily exposed arc plate† (Plate 14, fig. 9, *a*). The wave-numbers are listed in Table I. They may be interpreted as the Q_1 heads of

Table I.—New CaF Heads of the ${}^2\Pi_{1/2}^{(v+1)} \rightarrow {}^2\Sigma^{(v)}$ Sequence.

Intensity.	Wave-length (I.A.) air.	$\nu \text{ (cm.}^{-1}\text{) vac.}$
1	5866.88	17040.12
2	69.93	031.27
1	72.86	022.77
2	76.03	013.59
2	79.17	004.50
2	82.38	16995.22
1	85.61	985.89
—	—	—*
0	92.37	966.41
—	—	—*
0—	99.46	946.02
0—	5903.16	935.40

* Masked by D-lines.

† This was one of a number of plates kindly lent for the purpose of this investigation by Dr. A. S. King, of the Mount Wilson Observatory.

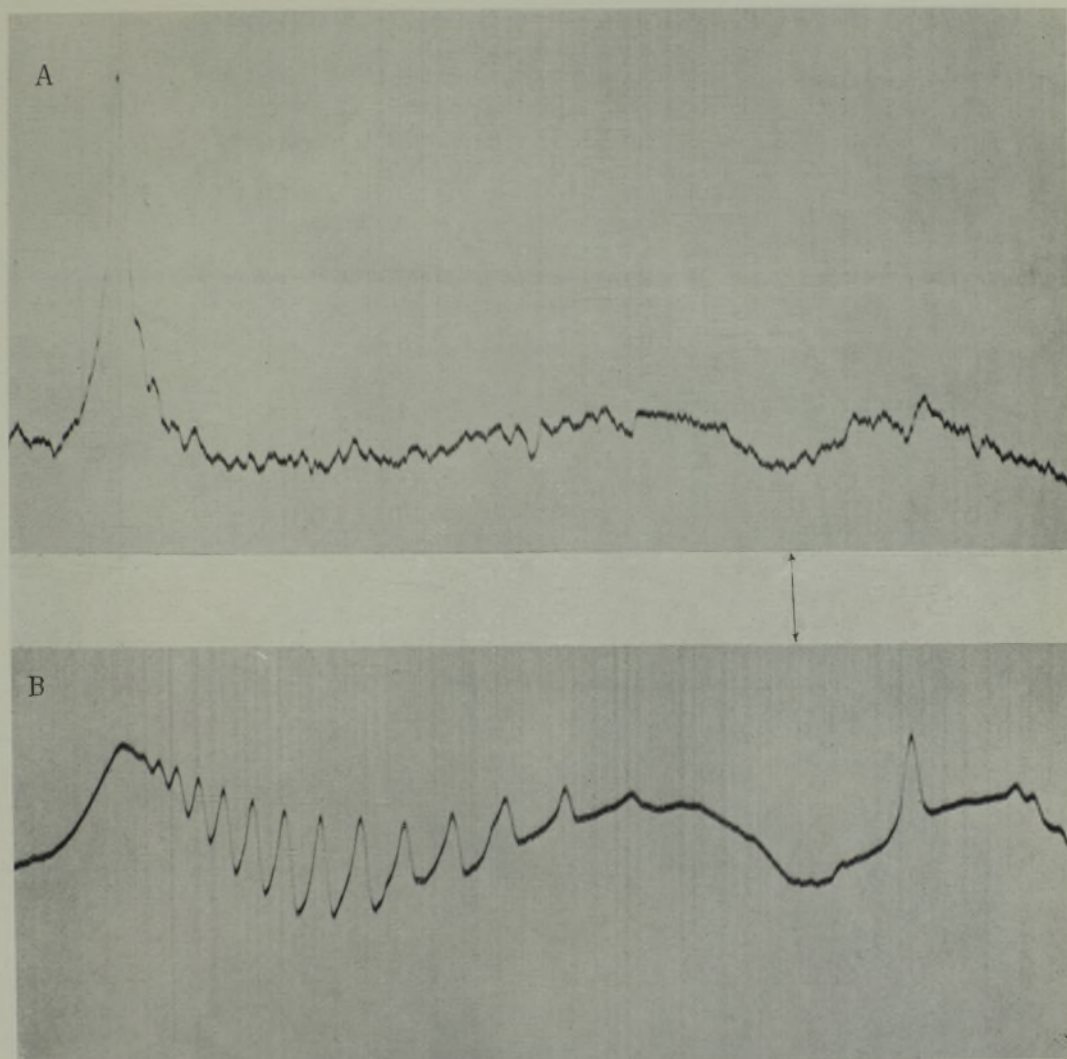


FIG. 3.—Microphotometric traces of the ${}^2\Pi(v+1) \rightarrow {}^2\Sigma(v)$ sequence of CaF. (A) In absorption.
(B) In emission.

bands with very high v . That they are shaded to the red follows from the reversal of sign of $B_1^{(v+1)' - B^{(v)'}}$ which probably takes place for high values of v . Similarly, the sudden breaking off of the sequence of Q_2 heads after that at $\lambda 5846$ does not require any assumption as to dissociation of the molecule, as made by Johnson (*loc. cit.*), but is a natural consequence of the fact that the heads are formed at higher and higher values of J as we proceed down the sequence, combined with the normal fall of intensity with increasing v .

The $(v' - v'' = -1)$ sequence behaves normally in absorption; the heads are formed at lower values of J than in the main sequence. The Q heads in this case are well separated, and measurements of their relative intensities in emission and absorption were made with the microphotometer. The results are given in Table II, using as a measure of the intensity the electrometer deflection when the head passes the microphotometer slit. As a result of the lower temperature in absorption a definite shift of intensity towards lower v 's is observed. The same effect is easily seen visually in the reproductions of the other two sequences.

Table II.—Microphotometer Deflections for Q Heads of $2\Pi^{(v)} \rightarrow 2\Sigma^{(v+1)}$ Sequence.

Band.	(0, 1).	(1, 2).	(2, 3).	(3, 4).	(4, 5).	(5, 6).	(6, 7).	(7, 8).	(8, 9).
Q_{12} head	$\lambda 6285.3$	$\lambda 6280.9$	$\lambda 6276.5$	$\lambda 6272.4$	$\lambda 6268.4$	$\lambda 6264.5$	$\lambda 6260.9$	$\lambda 6257.4$	$\lambda 6254.1$
Emission deflection	3.0	7.2	10.4	9.7	9.5	9.0	8.0	8.1	7.2
Absorption deflection	2.5	3.5	3.1	2.6	2.2	0.8	—	—	—
Q_2 head	$\lambda 6256.6$	$\lambda 6252.2$	$\lambda 6247.8$	$\lambda 6243.7$	$\lambda 6239.8$	$\lambda 6236.0$	$\lambda 6232.3$	$\lambda 6228.9$	$\lambda 6225.7$
Emission deflection	3.2	4.5	6.6	4.8	5.2	4.8	3.8	3.5	3.3
Absorption deflection	2.1	2.6	1.8	2.1	1.4	0.9	—	—	—

The large, and variable, distance from heads to origins—even for Q branches—indicated above, vitiate any attempt to apply the combination principle to measurements of the heads for determining the vibrational term differences, and renders very inexact any constants obtained therefrom. The assignments of v made by Johnson were chosen to make the discrepancies a minimum, but this method is not trustworthy in the present instance, and it seems best to base assignments of v on the intensity relations alone. Since the first few Q_2 heads of the $(v' - v'' = +1)$ sequence are superposed, the value of v must remain uncertain to one or two units. In the $(v' - v'' = -1)$ sequence the first P_{12} head was overlooked by Johnson, but appears clearly at $\lambda 6301.10$, $v = 15865.97$ on one of my heavily exposed arc plates (Plate 15, fig. 10). It is

definitely the first head of this sequence and hence belongs to the (0, 1) band. The assignment given by Johnson for these heads should be lowered by two units. The best values of the vibrational constants, in default of a complete correction of all heads to origins, are evidently obtained by combining the Q_2 heads in the ($v' - v'' = 0$) and ($v' - v'' = -1$) sequences, since the corrections involved here are the smallest.

The ${}^2\Pi \rightarrow {}^2\Sigma$ system of SrF (Plate 15, fig. 12) is somewhat more regular in its behaviour; apparently the constants B' and B'' are not so nearly equal in this case. No attempt has been made to estimate the rotational constants as was done for CaF, since the structure is finer and a sufficiently accurate determination of $B' - B''$ did not seem feasible. The separation of the ${}^2\Pi$ level is greater than for CaF, being approximately 277 cm.^{-1} , correcting the $Q_2 - Q_{12}$ separation of 279.2 cm.^{-1} by the same proportion as in CaF. In the ($v' - v'' = 0$) sequence both sets of P heads appear in absorption, though P_{12} is very faint and is seen only in the case of the (0, 0) band. The ($v' - v'' = +1$) sequence, in contrast to CaF, proceeds to the violet; in emission the Q heads are present for both components, the P_2 heads are faint whilst the P_{12} heads are not formed. In absorption the P heads were not detected, but two or three of the earlier members of both Q sequences are visible. The ($v' - v'' = -1$) sequence showed only the Q_2 heads in absorption, and by analogy with CaF this is to be expected because of the low J value of the head. The other heads would probably be observed if a higher density of the absorbing vapour were used, since this sequence is weak as a whole.

${}^2\Sigma \rightarrow {}^2\Sigma$ Systems.

The bands of this system have double heads and are shaded to the red, the (0, 0) heads falling at $\lambda\lambda$ 5293, 5291 for CaF and $\lambda\lambda$ 5779, 5772 for SrF. Only two sequences of heads occur in each case, these being the ($v' - v'' = 0$) and ($v' - v'' = +1$) sequences. The presence of double heads of wide separation in a ${}^2\Sigma \rightarrow {}^2\Sigma$ system is unusual, and the components are attributed by Johnson (*loc. cit.*) to R and Q branches. It is well known, however, that in bands having $\Lambda' = \Lambda'' = 0$ the Q branch is very weak, if present at all.* That the doubling is of a type which increases in magnitude with increasing J is definitely shown by the fact that in the ($v' - v'' = +1$) sequence the doublet separation of the heads is smaller than in the ($v' - v'' = 0$) sequence, whilst at the same time the heads must be formed at lower J's (since $B^{(1')} < B^{(0')} < B^{(0'')}$). It is therefore not analogous to the doubling in BeF, where just the opposite

* R. S. Mulliken, 'Phys. Rev.,' vol. 30, p. 138 (1927).

behaviour is found.* The only possibility of doubling in the branches of $^2\Sigma \rightarrow ^2\Sigma$ bands is the separation of the component levels $J = k \pm 1/2$, known as "p-type" doubling. Doubling of heads due to this cause is known, and in certain cases (such as HgH), the separation of the rotational levels may reach a considerable magnitude. We may note here that in the two cases under discussion this doubling must be confined chiefly to the upper state, since no evidence for a doubling of the heads was found in the $^2\Pi \rightarrow ^2\Sigma$ systems.

A very remarkable feature of this system is its appearance in absorption, as first shown by Walters and Barratt (*loc. cit.*). The whole appearance of the ($v' - v'' = 0$) sequence is altered, the clear succession of double heads being replaced by a broad region of fine-line absorption, with occasional accumulations of intensity apparently bearing no evident relation to the heads in emission. Seen under high dispersion, however, the absorption spectrum shows a definite correlation with the emission spectrum. In fact, over the region $\lambda\lambda$ 5310 to 5330 in CaF, there is an emission line in exact coincidence with every absorption line, and a similar effect occurs in SrF. An examination of the spacing of the rotational structure of this sequence in emission shows that most of the strong lines must belong to the (0, 0) band, which is therefore considerably stronger than the succeeding ones. The small decrement in intensity of the heads in passing down the sequence is probably due to two factors—first, to a spurious enhancement by overlying structure from the preceding bands, and second, to the fact that the value of J head decreases with increasing v . The latter is evidenced by the decreasing doublet separation. We would expect the predominance of the (0, 0) band to be even greater in absorption, an effect which has already been noted in the $^2\Pi \rightarrow ^2\Sigma$ system.

Other points of resemblance between the absorption and emission are: (1) the first pair of heads, belonging to the (0, 0) band, appear very faintly in absorption with CaF. With SrF only the second (low-frequency) component of the first pair is observed, and the same component of the second and third pairs is also faintly visible (Plate 15, fig. 13, *b*). (2) A pronounced minimum which occurs in the arc spectrum near the (3, 3) heads with a centre at λ 5308 for CaF, and at λ 5792 for SrF, becomes a very prominent feature of the absorption spectrum. In view of the fact that practically all of the intensity in absorption should be concentrated into the (0, 0) band, and that only P and R branches are expected, the simplest explanation of this minimum is that it represents the approximate position of the origin of the (0, 0) band. This would place the origin of this band $60\cdot7$ and $53\cdot8$ cm^{-1} from the two R heads

* W. Jevons, *loc. cit.*

in the case of CaF, and $59\cdot1$ and $36\cdot7$ cm^{-1} in SrF. These large separations of heads from origin are not unreasonable in view of the near equality of rotational constants in the upper and lower states; that the vibrational constants differ only slightly is again attested by the crowding of the bands into close sequences. Furthermore, the suppression of most of the heads in absorption is evidence for the formation of heads at very high rotational quantum numbers. An important piece of evidence for the double heads *both* being formed at high J 's is found in the fact that for CaF the components of the (0, 0) double head as seen in absorption, though faint, are still of almost equal intensity. If, as Johnson suggests, the second component were formed by a Q branch, this behaviour could not be explained, for the Q head should be greatly enhanced relative to the R at the lower temperature. As mentioned above, an effect of this sort does appear in SrF, but here the ρ -type doubling has become so large that the two R heads must turn at considerably different values of J .

Satisfactory confirmation of this interpretation of the structure is obtained by actual measurement of certain groups of fine lines which are clearly resolved on the absorption spectrograms of CaF. These groups are regularly spaced on either side of the origin, the spacing of the lines in each group, and of the groups themselves, increasing toward the red. Their probable origin is the

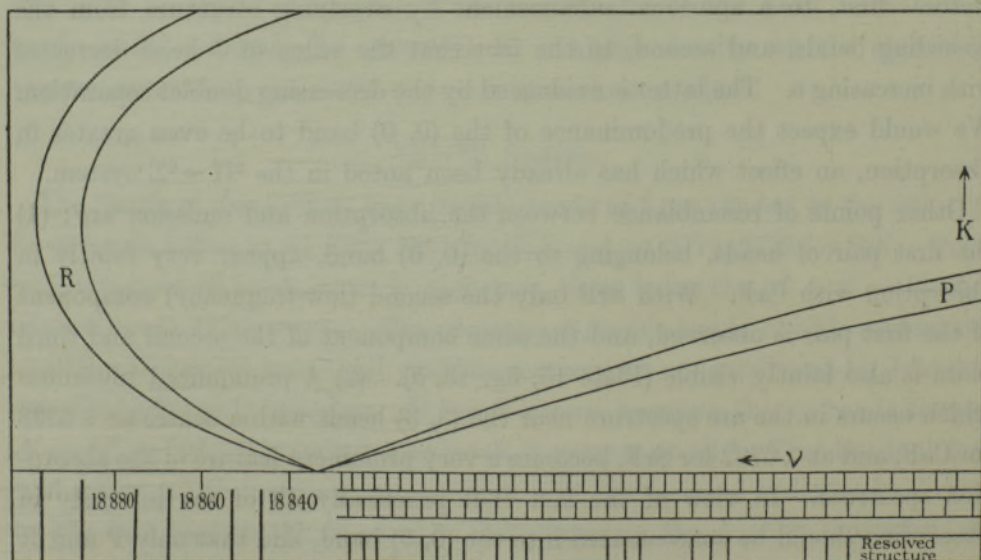


FIG. 4.—Diagrammatic representation of the $2\Sigma(0) \rightarrow 2\Sigma(0)$ CaF band. On the left side of the bottom line are plotted the heads of the earlier members of the $(v' - v'' = 0)$ sequence—this illustrates the appearance in emission. On the right is indicated the manner in which the two P branches of the (0, 0) band form groups of fine structure lines—this is typical of the appearance in absorption.

periodic coincidence and non-coincidence of the two series of lines with slightly different spacing which make up the two P and the two R branches, *i.e.*, the components of the ρ -type doublets (see fig. 4). Only the groups formed by the P branches were well resolved, and the measurements of these are given in Table III. In fig. 5 is plotted the mean separation in each group against

Table III.— $^2\Sigma^{(o)} \rightarrow ^2\Sigma^{(o)}$ P-branch Fine Structure Absorption Groups.

Centre of group.	Number of lines observed.	Mean separation.
cm. ⁻¹ .		cm. ⁻¹ .
18831.9	4	0.67
821.9	8	0.71
809.5	13	0.75
795.2	17	0.79
778.2	12	0.84
760.9	8	0.88

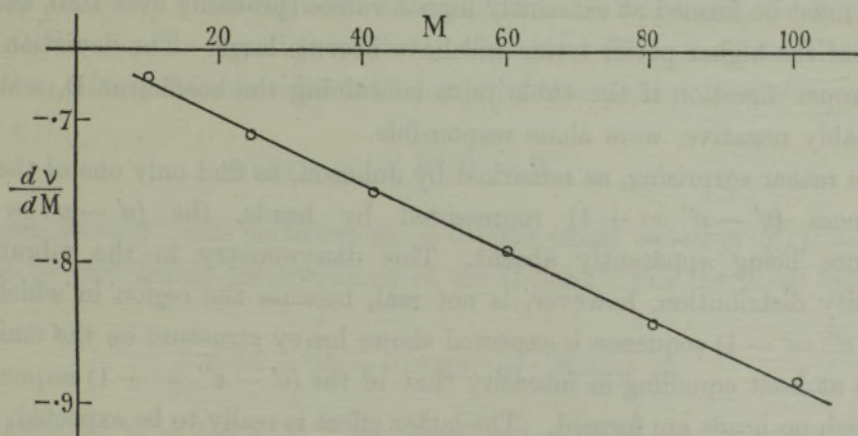


FIG. 5.—Plot of dv/dM against M for the P branches of the $^2\Sigma^{(o)} \rightarrow ^2\Sigma^{(o)}$ CaF band.

integral numbers M assigned in such a way that the frequencies of the lines in all the groups are a smooth function of M . (M thus represents the approximate rotational quantum number, apart from an unknown additive constant.)

By extrapolation of the spacing of these lines to the origin it is possible to determine the spacing at that particular point. However, owing to the uncertainty in M we plot the spacings against their frequencies and extrapolate to the known position of the origin, finding the spacing there to be 0.66 cm.^{-1} . This is in agreement with the expected spacing at the origin, which should be $B' + B''$. We have found, from the less refrangible system, that for the lower

$^2\Sigma$ state $B'' = 0.3215$. Furthermore, $B' - B''$ can be found from fig. 5; it is half the slope of the line (assumed straight) and amounts to -0.0012 . Hence $B' + B'' = 0.64 \text{ cm.}^{-1}$, and, the measured value being 0.66 cm.^{-1} , we thus have good support for our assignment of the position of the origin. Fine structure groups are also apparent in the corresponding SrF sequence in absorption (Plate 15, fig. 13, *b*). These are much more closely spaced, however, and contain fewer lines in each. This is to be expected, since the "beat frequency" should be greater, corresponding to the greater p -type doubling.

On the best second order CaF arc plate, 14 lines forming a regular series were resolved between the two R heads of the (0, 0) band. These fitted closely the formula

$$\nu(M) = 18894.73 - 0.00394 M^2, \quad (6)$$

where M represents the ordinal number of the line, counting from the head. That the coefficient of the quadratic term is considerably larger than the value of 2 ($B' - B''$) found above from the P branches is not surprising, because these heads must be formed at extremely high J values (probably over 100), and the effect of the higher power terms will have become large. The deviation is in the proper direction if the cubic term containing the coefficient D , which is invariably negative, were alone responsible.

It is rather surprising, as remarked by Johnson, to find only one of the side sequences ($v' - v'' = +1$) represented by heads, the ($v' - v'' = -1$) sequence being apparently absent. This dissymmetry in the vibrational intensity distribution, however, is not real, because the region in which the ($v' - v'' = -1$) sequence is expected shows heavy structure on the emission plates at least equalling in intensity that of the ($v' - v'' = +1$) sequence—although no heads are formed. The latter effect is really to be expected, since we have $B^{(0)'} < B^{(0)''}$, while $B^{(1)''} < B^{(0)''}$. Hence the value of $B^{(0)'} - B^{(1)''}$ must be small, all the values of α found earlier being of the same order of magnitude as the difference $B^{(0)''} - B^{(0)'}$.

With regard to the assignment of vibrational quantum numbers, we must again rely on intensity relations alone, in view of the large and variable contribution of the rotational energy change to the frequency of a band head. In SrF the allocation of v is straightforward—both the sequences ($v' - v'' = +1$) and ($v' - v'' = 0$) begin abruptly with the (1, 0) and (0, 0) heads respectively. In CaF, however, the designation by Johnson of the first band in the ($v' - v'' = +1$) sequence as (2, 1) certainly requires revision. On a very heavy exposure (Plate 15, fig. 11) it is clear that this band is the first member

of the sequence and hence should be denoted (1, 0). Although this makes the correspondence of the vibrational differences for the lower state with those derived from the Q heads of the ${}^2\Pi \rightarrow {}^2\Sigma$ system less exact, the deviation is, in the correct sense, being caused primarily by the smaller separation ν head- ν origin in the ${}^2\Sigma^{(\nu+1)} \rightarrow {}^2\Sigma^{(\nu)}$ sequence as compared with ${}^2\Sigma^{(\nu)} \rightarrow {}^2\Sigma^{(\nu)}$.

From the value of $B^{(0)''}$ already obtained, and the relation $B = h/8\pi^2 Ic$, we find the moment of inertia of CaF to be 86×10^{-40} g. cm.², and the inter-nuclear distance $r_0 = \sqrt{I_0/\mu}$ to be 2.0×10^{-8} cm. That no large error has been committed in determining these constants is proved by the application of an empirical rule, according to which the product

$$\omega r^3 = 3000 \text{ cm.}^{-1} \text{ \AA}^3 \quad (8)$$

for molecules in which the nuclei are nearly equal in mass, and somewhat greater for those in which the masses are unequal. An extreme case is that of the hydrides, where the product may be as high as 6000.* In the present case $\omega r^3 = 573 \times 2^3 \cong 4600$, a very reasonable result. This rule can be applied to show definitely that Johnson's interpretation of the double heads in the green CaF system as R and Q heads is untenable. Were the heads R and Q type then a fairly reliable value of B should be obtained by using the equation

$$\nu_{\text{R head}} - \nu^\circ = \bar{B}^2/B' - B'', \quad (9)$$

in which $B' - B''$ can be taken as -0.0039 (from equation (6)), and ν° should be very closely the frequency of the Q head. For the (0, 0) band we have

$$-6.55 = \bar{B}^2/-0.0039 \quad \text{or} \quad \bar{B} = 0.16.$$

This leads to $r_0 = 2.8 \times 10^{-8}$ cm., and $\omega r^3 = 12600$ —an impossibly high value. We may take this as effectively disposing of the possibility that the second heads are Q heads.

Isotope Effects.

Calcium has isotopes of mass-number 40 and 44, of which Ca^{44} comprises 2.7 per cent. of the whole, as calculated from the atomic weight 40.07 with allowance for the packing fraction and for the existence of the oxygen isotopes O^{17} and O^{18} .† The small abundance of the Ca^{44}F molecule would not prohibit its detection in the band spectrum, since recently isotopes present to the

* R. S. Mulliken, 'Rev. Mod. Phys.', vol. 2, p. 81 (1930).

† S. M. Naudé, 'Phys. Rev.', vol. 36, p. 333 (1930).

extent of less than 0.1 per cent. have been detected by this method.* Unfortunately, however, a computation of the positions where the Ca^{44}F heads should lie shows that in all cases they would fall in such places as to be completely masked by the band structure due to the stronger system of Ca^{40}F . Verification of the isotope effect in calcium will probably be more successful in the spectrum of some other molecule than the fluoride.

In the SrF bands the situation is more favourable. Here, again, two isotopes are known, Sr^{88} and Sr^{86} , of which Sr^{86} has an abundance of 14.5 per cent. Because of the small difference from unity of the isotope coefficient, $\rho = \sqrt{\mu_1/\mu_2} = 1.00207$, the detection of the isotope heads in the sequences $v' - v'' = 0$ is not possible. In the sequences ${}^2\Pi^{(v)} \rightarrow {}^2\Sigma^{(v+1)}$ and ${}^2\Sigma^{(v+1)} \rightarrow {}^2\Sigma^{(v)}$ the separations, as calculated from the simplified relation†

$$\nu_i - \nu = (\rho - 1)\nu_v \quad (10)$$

should be of the order of 1 cm.^{-1} , and we would thus expect the weaker Sr^{86}F heads to be resolved. In the first case four weak companion heads were identified on the arc plates accompanying the first four Q_2 heads, and having the proper separation. It is to be remarked, however, that these isotope heads have an unexpectedly great relative intensity, having regard to the calculated abundance, and that no companions could be detected for the corresponding Q_{12} heads. Hence no insistence is made that this effect is real here, although no alternative explanation of the extra heads is obvious.

In the ${}^2\Sigma^{(v+1)} \rightarrow {}^2\Sigma^{(v)}$ sequence of SrF the isotope effect is clearly marked (Plate 15, fig. 14). The heads of this sequence, with the exception of the first, are very close doublets, with a separation increasing towards the red. This is due to a somewhat fortuitous coincidence—the second R head of one band is nearly superposed on the first R head of the following band in the sequence. The coincidence is exact for the first two bands. In addition to these heads of the main band system of Sr^{88}F , there is present to the violet of each a corresponding faint head, which can be measured accurately and agrees exactly in position with that expected for Sr^{86}F . Only six heads could be measured, but the isotope heads are visible well beyond the (7, 6) band, although somewhat masked by the fine structure from the preceding bands. The isotope heads of the less refrangible component were not detected, but this was due to their being masked by the more refrangible heads. In Table IV the measured shifts

* H. D. Babcock, 'Proc. Nat. Acad. Sci.,' vol. 15, p. 471 (1929), estimates the abundance of $0^{18}/0^{18}$ to be 1250 : 1. The 0^{17} isotope is still less abundant than the 0^{18} isotope.

† F. W. Loomis, chap. V of "National Research Council Report on Molecular Spectra in Gases."

in cm.^{-1} are compared with those calculated by equation (10), using 17257 cm.^{-1} for the system-origin in computing ν_v . The isotope heads are indicated by dots in the enlargement (Plate 15, fig. 14). Finally, the plates show that no isotopes lighter than 86 can be present with an abundance of more than about $1/5$ of Sr^{86} itself.

Table IV.— Sr^{86}F Heads. ${}^2\Sigma^{(v+1)} \rightarrow {}^2\Sigma^{(v)}$ Sequence of SrF .

(v', v'')	Sr^{88}F	Sr^{86}F	Observed shift, cm.^{-1} .	Calculated shift, cm.^{-1} .
(1, 0)	17783.07	—	—	1.09
(2, 1)	771.28	17772.32	1.04	1.06
(3, 2)	759.56	760.48	0.92	1.04
(4, 3)	747.83	748.69	0.86	1.02
(5, 4)	735.97	736.91	0.94	0.99
(6, 5)	724.05	725.05	1.00	0.97
(7, 6)	712.02	712.93	0.91	0.94

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Summary.

(1) The designations ${}^2\Sigma \rightarrow {}^2\Sigma$ and ${}^2\Pi \rightarrow {}^2\Sigma$ for the more, and less, refrangible band systems of CaF and SrF are supported by a comparison of the spectra in absorption and emission under high dispersion.

(2) The different appearance of the bands in absorption and in the arc is shown in all cases to be a natural consequence of the difference in temperature, the main effects of lowering the temperature being (a) to shift the intensity toward lower vibrational quantum numbers in each sequence, (b) to lower the value of the rotational quantum number at which the intensity reaches a maximum in a given branch.

(3) Approximate values of the rotational constants of CaF are estimated by combining measurements of the fine structure with theoretical equations for the separations of the heads. For the lower ${}^2\Sigma$ state

$$I_0'' = 86 \times 10^{-40} \text{ g. cm.}^2, r_0'' = 2.0 \times 10^{-8} \text{ cm.}$$

(4) A re-interpretation of the heads in the ${}^2\Sigma \rightarrow {}^2\Sigma$ bands is proposed, in which the double heads are ascribed to two R branches resulting from a large ρ -type doubling.

(5) Discrepancies previously found in the vibrational constants, as well as the apparent absence of certain sequences, are shown to be consequences of the extremely large value of the rotational quantum number at which most of the heads are formed. Alterations in the previous assignment of vibrational quantum numbers in the sequences ${}^2\Pi^{(v)} \rightarrow {}^2\Sigma^{(v+1)}$ and ${}^2\Sigma^{(v+1)} \rightarrow {}^2\Sigma^{(v)}$ are made.

(6) The isotope effect for Sr^{88} , Sr^{86} is found in the ${}^2\Sigma^{(v+1)} \rightarrow {}^2\Sigma^{(v)}$ sequence of the SrF bands.

DESCRIPTION OF PLATES 14, 15.

FIG. 6.—Self-reversal of the $\text{CaF } {}^2\Pi^{(v)} \rightarrow {}^2\Sigma^{(v)}$ sequence.

FIG. 7.— $\text{CaF } {}^2\Pi^{(v)} \rightarrow {}^2\Sigma^{(v)}$ sequence, (a) in absorption, (b) in emission.

FIG. 8.—Light exposure of the $\text{CaF } {}^2\Pi^{(v)} \rightarrow {}^2\Sigma^{(v)}$ sequence in emission.

FIG. 9.— $\text{CaF } {}^2\Pi^{(v+1)} \rightarrow {}^2\Sigma^{(v)}$ sequence, (a) very heavy exposure showing new heads degraded to red, (b) normal exposure of the "tail" sequence.

FIG. 10.— P_{12} heads of the $\text{CaF } {}^2\Pi^{(v)} \rightarrow {}^2\Sigma^{(v+1)}$ sequence in emission.

FIG. 11.—First members of the $\text{CaF } {}^2\Sigma^{(v+1)} \rightarrow {}^2\Sigma^{(v)}$ sequence in emission.

FIG. 12.— $\text{SrF } {}^2\Pi^{(v)} \rightarrow {}^2\Sigma^{(v)}$ sequence, (a) in absorption, (b) in emission.

FIG. 13.— $\text{SrF } {}^2\Sigma^{(v)} \rightarrow {}^2\Sigma^{(v)}$ sequence, (a) in emission, (b) in absorption.

FIG. 14.— $\text{SrF } {}^2\Sigma^{(v+1)} \rightarrow {}^2\Sigma^{(v)}$ sequence in emission.

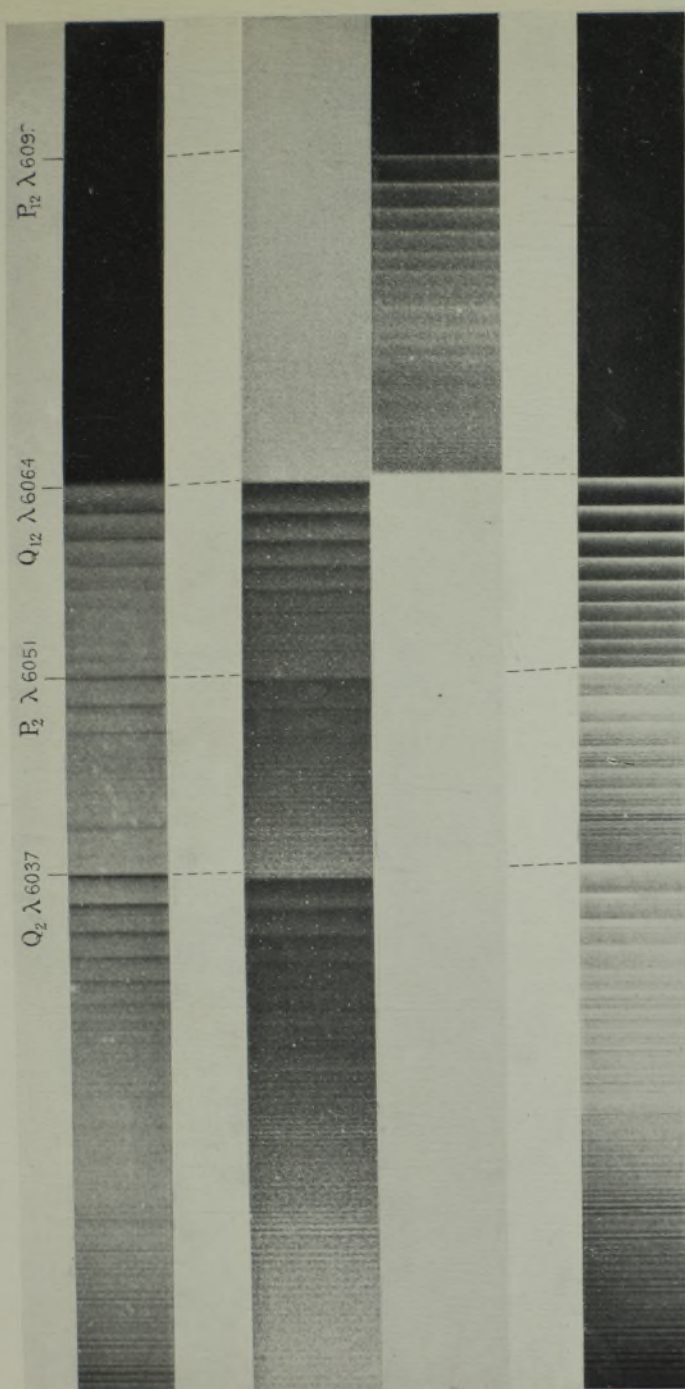


FIG. 6.

*a**b*

FIG. 7.

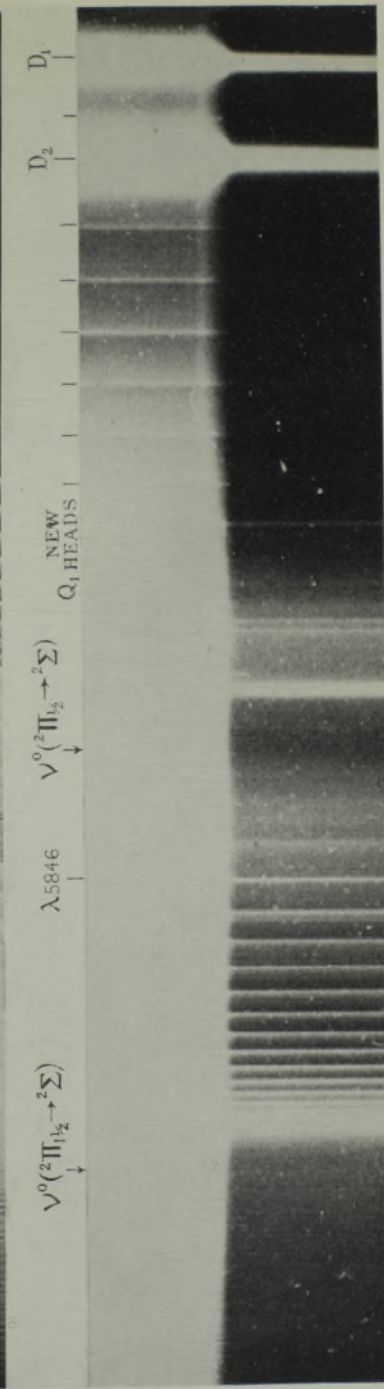


FIG. 8.

*a**b*

FIG. 9.

