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New Absorption Spectra of the Alkaline Earth Fluorides

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Investigation of the absorption spectra of the alkaline earth fluorides under high dispersion reveals several new band systems in the ultraviolet region as far as λ1950. Vibrational analyses of these systems give the vibration frequencies and electronic terms of one new state of MgF, three of CaF, four of SrF, and four of BaF. Some changes in the previous analyses of the $A\leftrightarrows X$ system of MgF and the $C\rightleftarrows X$ system of CaF are made. An increased binding in all of these higher energy states as indicated by the values of the constants is discussed with regard to the probable electron configurations.

THE electronic spectra of the diatomic alkaline earth fluorides, first photographed by Datta,[1] constitute one of the best examples of spectra of a series of homologous molecules. They have usually been observed in emission from the flame of a cored carbon arc, although, with the exception of BeF, the absorption spectra have also been observed for a limited range of wave-lengths.

In the search for new band spectra, absorption spectra have several advantages over arc spectra. Among these are the fact that the band heads are usually more pronounced, because of the lower temperature, and the fact that extraneous bands and lines due to impurities are much less troublesome. Moreover, the speed with which absorption spectra can be obtained is important. Although it is true that in absorption one observes only those bands whose lower electronic state is the normal state, such observations give additional information about the character of the excited states, since they must be among the types which can combine, according to the selection rules, with the normal state. No transitions between two excited states have so far been observed in the emission spectra of this group of molecules.

The present work was undertaken with a view to extending the observations on the absorption spectra of these fluorides from the resonance system to the limit of transmission of air in the ultraviolet.

At furnace temperatures below 1500°C only the known band systems were developed, but at higher temperatures twelve new higher energy states were revealed. Figure 1 shows the spectra under low dispersion. Table I summarizes the number of previously known and of newly discovered band systems of these molecules.

EXPERIMENTAL

The electric furnace, a carbon tube vacuum type, which has been previously described,[2] has a well-controlled temperature range between 900° and 2200°C. The fluoride vapors were produced by heating a small amount (∼10 g) of the salt at the center of the resistor tube in an atmosphere of nitrogen. A hydrogen lamp of the conventional design was used as the source, with which suitably exposed plates of the ultraviolet region as far as the O_2 bands at λ1950 were

TABLE I. *Band systems of the alkaline earth fluorides.*

MOLECULE	NUMBER OF SYSTEMS PREVIOUSLY KNOWN AND WAVE-LENGTH RANGE	NUMBER OF NEWLY DISCOVERED SYSTEMS AND WAVE-LENGTH RANGE
BeF	1, λλ2816–3393	0, ——
MgF	2, 3468–3686 2649–2742	1, λλ2249–2387
CaF	3, 6024–6301 5145–5421 3371–3525	3, 3081–3245 2754–3035 2554–2700
SrF	3, 6283–6870 5621–5852 3646–3795	4, 3345–3592 3052–3218 2916–3069 2775–2915
BaF	4, 7862–8738 6716–7734 4842–5139 4136–3650	4, 3475–3608 3278–3451 3069–3210_(2)

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[1] S. Datta, Proc. Roy. Soc. **A99**, 436 (1921).

[2] F. A. Jenkins and G. D. Rochester, Phys. Rev. **52**, 1135 (1937).

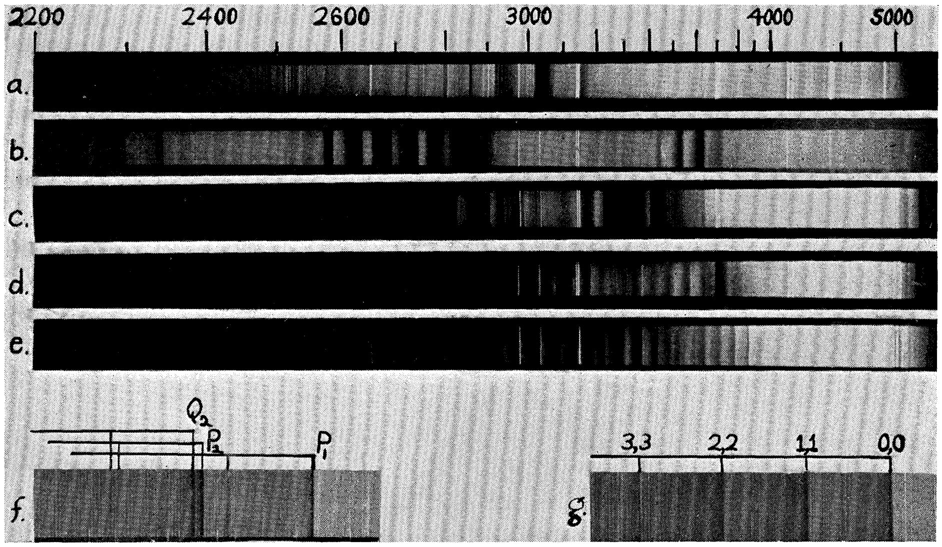

FIG. 1. Low dispersion spectra of (a) BeF, (b) MgF, (c) CaF, (d) SrF, (e) BaF. High dispersion spectra of (f) the $E^2\Pi$, $X^2\Sigma$ and (g) the $D^2\Sigma$, $X^2\Sigma$ systems of SrF.

obtained in 20 to 30 minutes. Exploratory work was done with a Hilger E-37 quartz spectrograph in the ultraviolet and with a Bausch and Lomb constant deviation spectroscope in the visible, furnace temperatures being increased by 100° increments beginning below the melting point. High dispersion spectrograms were obtained by means of the 30,000-lines-per-inch, 21-foot concave aluminum grating, with average dispersion of 1.3A/mm in the first order. This grating has the property of concentrating about 60 percent of the ultraviolet light ($\lambda 2536$) in the first order. Ilford Q-2 plates were used below $\lambda 2400$. Measurements of certain very weak or diffuse heads were made from microphotometer traces containing some standard iron lines.

OBSERVATIONAL DATA

1. BeF

A series of low dispersion spectrograms taken at gradually increasing temperatures showed that the $^2\Pi$, $^2\Sigma$ system, known from emission observations,[3–5] begins to be apparent at 1500°C and becomes rapidly stronger as the temperature rises. At the same time a continuous band, not observed below 1500° and whose maximum lies somewhere beyond the short wave-length limit of observation, extends to longer wave-lengths until at a temperature of 2000° it begins to overlap the 1,0 $^2\Pi$, $^2\Sigma$ band at $\lambda 2909$. The presence and behavior of this continuum is typical of all the molecules here investigated and indicates the existence of one or more repulsive electronic states well above the normal state. The plates showed no system of BeF except the $^2\Pi \leftarrow {}^2\Sigma$ down to the limit of observation ($\lambda 1950$). If such a system exists above $\lambda 1950$ it must be considerably weaker than the $A^2\Pi$, $X^2\Sigma$ system, and although it might appear at the highest temperatures, it would then be covered by the overlying continuum. A consideration of the trend of $B^2\Sigma$ states of the other alkaline earth fluorides indicates that for BeF the $B^2\Sigma \leftarrow X^2\Sigma$ system probably lies in the vacuum region.

The high dispersion spectrograms show the sequences $v'-v''=-1,\ 0,\ +1,\ +2$ of the $^2\Pi$, $^2\Sigma$ system with R_2, R_1 and Q_1 branches. In addition the 0,0 and 1,0 bands each possess a very weak branch forming heads at $\lambda 3001.86$ and $\lambda 2903.21$ respectively. An application of combination differences with the data of Jenkins[5] proves that these are the R_{21} branches, to be expected if the $^2\Pi$ state is not strictly a state with case (b) coupling. No trace of an isotope head due to Be^8F was found.

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[3] S. Datta, Proc. Roy. Soc. **A101**, 187 (1922).
[4] W. Jevons, Proc. Roy. Soc. **A122**, 211 (1929).
[5] F. A. Jenkins, Phys. Rev. **35**, 315 (1930).

TABLE II. *Wave number residuals* ($O-C$) *and estimated intensities of the band heads of the new systems. A dash indicates a band observed but too weak for measurement.* (P) *indicates a perturbation.*

v', v''	$O-C$	I
MgF, $C\leftarrow X$		
0,1	−1.0	2
1,2	−0.1	1
2,3	—	0
0,0	0.0	10
1,1	−0.6	5
2,2	—	0
1,0	−0.3	5
2,1	+0.5	4
3,2	−0.5	3
4,3	−0.2	1
5,4	—	0
2,0	−0.4	1
3,1	+0.7	2
4,2	−0.1	3
5,3	−0.2	2
6,4	—	0
CaF, $C\leftarrow X$		
0,2	−0.1	2
1,3	+0.2	3
2,4	−0.1	3
3,5	−0.2	2
4.6	+0.0	1
5,7	—	0
0,1	−0.2	7
1,2	+0.1	6
2,3	−0.5	5
3,4	+0.1	3
4,5	−0.1	1
0,0	0.0	10
1,1	+0.6	2
2,2	—	0
1,0	−0.2	5
2,1	−0.1	5
3,2	−0.7	3
4,3	−0.1	1
2,0	—	0
3,1	+0.1	1
4,2	−0.1	1
5,3	—	0
CaF, $D\leftarrow X$		
0,0	0.0	10
1,1	−0.2	8
2,2	+0.2	6
3,3	+0.7	2
1,0	+0.2	6
2,1	+0.2	8
3,2	0.0	9
4,3	0.0	8
5,4	0.0	7
6,5	−0.2	5
7,6	−0.1	2
8,7	+0.1	1
2,0	0.0	1
3,1	+0.1	5
4,2	0.0	7
5,3	−0.1	7
6.4	0.0	7
7,5	0.0	6
8,6	0.0	5
9,7	+0.1	4
10,8	−0.3	3
11,9	−0.1	2
12,10	−0.1	1
CaF, $E\leftarrow X$		
0,1	+0.2	4
1,2	+0.7	3
2,3	−0.3	1
0,0	0.0	10
1,1	+0.4	4
1,0	−0.5	8
2,1	+0.3	7
3,2	−1.0	4
4,3	−0.7	1
5,4	—	0
2,0	+0.8	4
3,1	−0.7	6
4,2	−0.8	7
5,3	−0.4	6
6,4	+0.1	3
7,5	—	0
4,1	−1.0	1
5,2	−0.6	2
6,3	−0.1	3
7,4	+0.1	3
8,5	+0.2	2
9,6	0.0	1
CaF, $F\leftarrow X$		
0,1	−0.5	6
1,2	+1.1	5
2,3	+0.6	3
0,0	0.0	10
1,1	−0.1	5
2,2	+0.1	1
1,0	+0.4	6
2,1	−0.6	5
3,2	−0.3	3
4,3	—	0
2,0	+0.4	1
3,1	0.0	2
4,2	+0.1	1
5,3	—	0
SrF, $D\leftarrow X$		
0,1	0.0	2
0,0	0.0	9
1,1	−0.1	10
2,2	−0.1	8
3,3	+0.3	6
4,4	−0.3	3
1,0	+0.1	4
2,1	−0.1	7
3,2	−0.3	7
4,3	+0.2	6
5,4	+0.1	5
6,5	−0.1	3
7,6	−0.3	2
8,7	−0.1	1
3,1	−0.7	2
4,2	0.0	3
5,3	0.0	4
6,4	0.0	4
7,5	−0.1	4
8,6	+0.3	3
9,7	+0.2	3
10,8	+0.2	2
11,9	0.0	2
12,10	−0.1	1
13,11	−0.4	1
SrF, $E\leftarrow X$		
0,1	−0.9	5
1,2	+0.1	2
0,0	0.0	10
1,1	−0.4	3
2,2	+0.1	1
1,0	−0.5	7
2,1	−0.6	6
3,2	+0.1	3
4,3	0.0	1
2,0	—	0
SrF, $F\leftarrow X$		
0,1	−0.1	6
1,2	−0.6	4
2,3	−0.3	2
3,4	—	0
0,0	0.0	8
1,1	−0.6	1
1,0	−0.3	10
2,1	+0.8	7
3,2	+0.7	3
4,3	+0.2	1
2,0	+0.2	5
3,1	+0.7	7
4,2	+0.3	6
5,3	+0.2	2
6,4	—	0
SrF, $G\leftarrow X$		
0,1	+0.4	4
0,0	0.0	10
1,0	−0.4	8
2,1	0.0	5
2,0	+0.4	6
3,1	−0.5	5
BaF, $E\leftarrow X$		
0,1	−0.3	3
0,0	0.0	10
1,1	−0.1	3
1,0	−0.3	5
2,1	−0.1	2
BaF, $F\leftarrow X$		
0,1	−0.3	4
1,2	−0.1	2
2,3	—	0
0,0	0.0	10
1,1	−3.9(P)	8
2,2	—	0
1,0	+0.2	7
2,1	+0.6	8
3,2	+0.5	6
4,3	+0.5	4
2,0	+0.1	2
3,1	−0.1	1
4,2	—	0
BaF, $H\leftarrow X$		
0,0	0.0	10
1,1	−0.5	6
2,2	−0.7	2
1,0	0.0	6
2,1	−0.2	7
3,2	+0.2	6
4,3	+0.2	4
5,4	+0.1	1
2,0	−0.9	2
3,1	−0.1	4
4,2	+0.1	5
5,3	0.0	3
6,4	+0.1	1

2. MgF

The known bands of the molecule MgF constitute a $^2\Pi$, $^2\Sigma$ system at λλ3470–3690 and a $^2\Sigma$, $^2\Sigma$ system at λλ2650–2740.[4, 6, 7] Both systems were developed with increasing intensities above 1350°C, and at 1800° a new system appeared extending from about λ2250 to λ2400. Good high dispersion plates were obtained with a furnace temperature of 1900°C, showing the new system as four sequences of single-headed bands degraded to shorter wave-lengths. In the 0,0 band the rotational structure is well enough resolved to show the presence of a P and an R branch only. Since the ground state is $^2\Sigma$, this proves that the new excited state is $^2\Sigma$ also. The twelve measured heads of this $C^2\Sigma\leftarrow X^2\Sigma$ system are given by the formula

$$\nu=42{,}528.0+821.9u'-4.82u'^2-717.1u''+3.67u''^2,$$

where $u=v+\frac{1}{2}$. The residuals (obs. − calc.) from the formula and the estimated intensities are given in Table II, which includes similar data for the new systems of the heavier molecules.

The system just described is not the one at λ2275 that Jenkins and Grinfeld mention as possibly due to MgF.[7] That single, closely spaced sequence of bands has appeared with more or less intensity not only on my MgF plates but also on the plates of BeF, BaF, SrF, and AlF. That it is actually due to the AlF molecule is readily seen by comparing its microphotometer trace given by Jenkins and Grinfeld with the reproduction of the $v'-v''=0$ sequence of AlF included in a recent paper by Rochester.[8]

The value of 717.1 cm⁻¹ for ω_e'' of the $C\leftarrow X$ system does not agree with the accepted value for the normal state, namely, 690.75 cm⁻¹. Investigation revealed that the previous vibrational analysis[6] of the $A^2\Pi$, $X^2\Sigma$ system was in error. A reassignment of vibrational quantum numbers, using Datta's measurements, gives for the Q_2 heads of that system,

$$\nu=27{,}847.4+746.0u'-3.97u'^2-718.2u''+4.02u''^2.$$

The three heads of each band are the Q_2, P_2 and

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[6] R. C. Johnson, Proc. Roy. Soc. **A122**, 189 (1929).

[7] F. A. Jenkins and R. Grinfeld, Phys. Rev. **45**, 229 (1934).

[8] G. D. Rochester, Phys. Rev. **56**, 305 (1939).

P_1 heads as pointed out by Jenkins and Grinfeld, who concluded that the $A^2\Pi$ state has a doublet separation of -34.3 cm^{-1}.

At the high temperatures employed, other sequences of the $B^2\Sigma \leftarrow X^2\Sigma$ system appear, namely $v'-v''=+2, -2, -3$. In the $+1$ and $+2$ sequences the isotope effect is clearly brought out in the appearance of well-developed heads due to $Mg^{25}F$ and $Mg^{26}F$. At about 1800°C a continuum appears at the short wave limit of observation and extends as far as λ2275 when the temperature is 2000°C.

3. CaF

Three band systems of this molecule are known in emission and absorption, involving the four states $X^2\Sigma$, $A^2\Pi$, $B^2\Sigma$, $C^2\Pi$, and lying in the red, green, and near ultraviolet respectively.[9, 10] They begin to appear at a furnace temperature of 1350°C along with a region of continuous absorption covering roughly 100A with its center at λ2180, which spreads until it reaches λ2500 at 2000°. At about 1700° other bands begin to appear in the ultraviolet, and at 2000° they cover the entire region λλ2500–3500.

High dispersion plates were taken of this region at temperatures of 1735°, 1835°, and 2000°C to bring out the weak and strong parts of the spectrum with intensities suitable for measurement. Nearly all the bands were readily grouped into four electronic systems. No evidence of an isotope effect was found in any of them. These systems, with the equations for the heads, are

$$\begin{aligned}
&C^2\Pi \leftarrow X^2\Sigma(Q_1) && \nu=30{,}255.9+481.7u'-2.02u'^2-588.2u''+2.75u''^2,\\
&D^2\Sigma \leftarrow X^2\Sigma && \nu=30{,}772.3+650.7u'-2.89u'^2-587.5u''+2.85u''^2,\\
&E^2\Sigma \leftarrow X^2\Sigma && \nu=34{,}135.2+646.3u'-3.24u'^2-587.8u''+2.90u''^2,\\
&F^2\Pi \leftarrow X^2\Sigma(P_1) && \nu=37{,}547.9+681.7u'-3.55u'^2-586.9u''+2.82u''^2.
\end{aligned}$$

The system $C^2\Pi \leftarrow X^2\Sigma$ is not new, but was observed in emission and measured by Datta.[1] Other investigators have failed to reproduce it because of its intrinsic weakness. Johnson[9] using Datta's measurements, and guided by the ground state constants already known from the other systems has attempted a vibrational analysis. The reason for the unsatisfactory nature of the results appears immediately from my high dispersion spectrograms. Datta's pictures did not reveal the two strongest and most important sequences, namely the 0 and $+1$ sequences with leading members at λ3305 and λ3254. With these added bands there is no ambiguity in making the v' and v'' assignments. The four observed heads are interpreted as R_{21}, R_2, R_1 and Q_1, and the formula has been calculated from the Q_1 heads. Table III lists the wave number separations of the other heads from the head given by the equation, as well as similar data for all of the other systems having multiple heads.

TABLE III. *Wave number separation of heads in the multiple-headed bands.*

v', v''	R_1-Q_1	R_2-Q_1	$R_{21}-Q_1$
	CaF, $C^2\Pi \leftarrow X^2\Sigma$		
0,2	—	29.7	—
1,3	12.0	28.9	—
2,4	12.2	30.3	—
0,1	10.8	29.5	45.5
1,2	10.3	29.2	—
2,3	10.7	29.8	—
3,4	10.8	30.2	—
0,0	10.2	29.3	43.0
1,1	9.7	28.6	—
1,0	8.0	28.7	41.3
2,1	7.3	28.4	40.7
3,2	8.5	28.1	—

v', v''	P_2-P_1	Q_2-P_1
	CaF, $F^2\Pi \leftarrow X^2\Sigma$	
0,1	2.1	11.8
0,0	2.0	11.2
1,0	2.1	12.4

v', v''	P_2-P_1	Q_2-P_1
	SrF, $E^2\Pi \leftarrow X^2\Sigma$	
0,1	80.7	86.1
1,2	78.0	—
0,0	80.4	86.1
1,1	79.4	85.2
2,2	—	—
1,0	79.8	85.8
2,1	79.7	—
3,2	—	—
2,0	80.0	—
	BaF, $F^2\Sigma \leftarrow X^2\Sigma$	
0,1	7.3	
1,2	—	
0,0	8.6	
1,1	6.8*	
1,0	9.8	
2,1	9.2	
3,2	9.4	
4,3	8.7	
2,0	11.0	

* Perturbation.

The system $D \leftarrow X$ and the considerably weaker $E \leftarrow X$ are quite certainly $^2\Sigma$, $^2\Sigma$ transitions. The bands are clearly of a single-headed type, and the rotational structure, where not confused by the structure of other bands of the sequence, apparently contains two branches only. Bands of both systems are degraded to shorter wavelengths. Superposed on part of the $E \leftarrow X$ system was another set of bands with well-resolved

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[9] R. C. Johnson, Proc. Roy. Soc. **A122**, 161 (1929).
[10] A. Harvey, Proc. Roy. Soc. **A133**, 336 (1931).

rotational structure, and with first differences for the lower and upper states of 837 cm^{-1} and 1002 cm^{-1} respectively. This is obviously not due to CaF. It may possibly be ascribed to CaO or CaN. Recent spectrograms of the absorption of CaO taken by Mr. R. E. Harrington fail to show it.

The $F \leftarrow X$ system consists of four sequences of bands of which at least the leading (and strongest) members possess three very closely grouped heads, the bands being again shaded toward the further ultraviolet. These are probably the P_1, P_2, and Q_2 heads of a $^2\Pi$, $^2\Sigma$ transition, similar to the BeF bands. The vibrational constants have been calculated from the leading (P_1) heads since in the weaker bands they alone were measurable. As to the doublet separation in the $^2\Pi$ state, one can only say that $2.0 < A < 11.7$ cm^{-1}, where the two limits are the P_1, P_2 and the P_1, Q_2 separations in the 0,0 band.

4. SrF

The known states of the SrF molecule are completely analogous to the first four of CaF, namely, a $^2\Sigma$ normal state, with $A^2\Pi$, $B^2\Sigma$, and $C^2\Pi$ excited states.[9, 10] Their energies, too, are comparable though somewhat depressed, as is expected in going to a heavier molecule of a homologous group. The visible systems, involving states A and B, were apparent at temperatures of 1200°C and up. The system $C \leftarrow X$ was developed at about 1480°, and from 1600° to 2000° four new band systems in the ultraviolet were observed, all shaded to shorter wave-lengths. Also present was a continuum extending from beyond the shortest wave-lengths to λ2500 at a furnace temperature of 2000°C. The band heads of the new systems can be represented by the equations

$$\begin{aligned}
D^2\Sigma \leftarrow X^2\Sigma \quad & \nu = 28{,}296.6 + 552.1u' - 2.15u'^2 - 501.3u'' + 2.19u''^2, \\
E^2\Pi \leftarrow X^2\Sigma(P_1) \quad & \nu = 31{,}528.7 + 564.4u' - 3.20u'^2 - 500.5u'' + 2.10u''^2, \\
F^2\Sigma \leftarrow X^2\Sigma \quad & \nu = 32{,}820.3 + 598.5u' - 3.42u'^2 - 502.0u'' + 2.45u''^2, \\
G^2\Pi \leftarrow X^2\Sigma \quad & \nu = 34{,}759.2 + 573.9u' - 1.28u'^2 - 501.9u'' + 2.13u''^2.
\end{aligned}$$

TABLE IV. *Wave numbers and intensities of band heads of the $G \leftarrow X$ system of* SrF. *(v', v'') assumed for calculation of vibrational constants.*

$v'-v''$	ν	I	$v'-v''$	ν	I
−1	34,298.2 (0,1)	4	+1	35,346.6	2
	34,302.0	1		35,359.4	5
	34,309.4	3		35,366.3 (1,0)	8
	34,320.0	3		35,373.8	6
	34,367.7	3		35,399.1	5
				35,408.5	2
0	34,767.1	3		35,421.2	5
	34,787.0	4		35,437.9 (2,1)	5
	34,795.4 (0,0)	10			
	34,810.1	3	+2	35,919.3	1
	34,818.4	3		35,935.9 (2,0)	6
				35,977.6	2
				35,991.1	3
				36,000.4	1
				36,003.7 (3,1)	5

The presence of sharp, single-headed bands, and the appearance of a P and an R branch only in certain of the stronger bands where resolution is sufficiently complete indicate that the systems $D \leftarrow X$ and $F \leftarrow X$ are $^2\Sigma$, $^2\Sigma$ transitions. These bands are similar to those of the $D \leftarrow X$ and $E \leftarrow X$ systems, respectively, of CaF in the number and length of the sequences, intensity distribution among the bands, and general appearance.

That the $E \leftarrow X$ system is a transition to a $^2\Pi$ state is shown by the fact that the strongest of the bands have three heads, two very close together and a third of considerably lower frequency. They are the Q_2, P_2, and P_1 heads, an interpretation indicated by the small, but nevertheless real, change in the $Q_2 - P_2$ separation wherever both heads were measurable. The direction of the change is that for $B' > B''$, which is the case here since the bands are degraded to the ultraviolet. The separation of the two components of the $^2\Pi$ state is probably rather near the difference of the heads Q_2 and P_1, or 86.1 cm^{-1}. The vibrational constants have been derived from the P_1 heads, since these are the most completely observed.

Inasmuch as the heads of the $G \leftarrow X$ system are definitely multiple, and because $\Delta\Lambda = 2$ is forbidden, the state G must be $^2\Pi$, but attempts to reconcile the number of and spacing between the observed heads with a $^2\Pi$, $^2\Sigma$ transition have been unsuccessful. The bands have three, four, or five apparently associated heads, whose positions and intensities are not explainable in the usual way. Furthermore, the separations are much too large to be due to isotopes. The most plausible explanation of the irregular arrangement of the heads is that the levels of this state suffer strong perturbations from a neighboring state. A v', v'' assignment was finally made by choosing certain of the thirty observed heads which yielded the proper ground state constants and a $\Delta G'(v+\frac{1}{2})$ that decreased regularly with increasing v'. The constants obtained in this way are probably good approximations to the actual values. Table IV lists the wave numbers and estimated intensities of all of the band heads of this system and indicates which were used in the calculation of the vibrational constants.

5. BaF

For this molecule, as for CaF and SrF, the known systems in the visible and near ultraviolet[11] were developed at the lower furnace temperatures, increased in strength as the temperature became greater, and at temperatures above 1800°C three groups of bands containing four new electronic systems were evident. The equations for the band heads are

$$\begin{array}{ll} E^2\Sigma\leftarrow X^2\Sigma & \nu=28{,}134.1+538.4u'-1.90u'^2-468.9u''+1.79u''^2, \\ F^2\Sigma\leftarrow X^2\Sigma & \nu=29{,}411.3+529.9u'-2.00u'^2-469.5u''+1.90u''^2, \\ G^2\Sigma\leftarrow X^2\Sigma & \nu=31{,}451.9+510.4u'-0.83u'^2-469.9u''+2.08u''^2, \\ H^2\Sigma\leftarrow X^2\Sigma & \text{only three heads observed.} \end{array}$$

Since it is similar but even weaker than the $E\leftarrow X$ system of CaF, the system $E\leftarrow X$ of BaF is probably a $^2\Sigma$, $^2\Sigma$ transition also. There is no evidence of multiple heads, but the branches in the bands cannot be distinguished because of the over-all low intensity.

The most noticeable feature of the $F\leftarrow X$ system is that its bands have double heads of about the same intensity. In general appearance it strongly resembles the red $B^2\Sigma\leftarrow X^2\Sigma$ system of BaF where the double heads are attributed to spin doubling.[11] A similar doubling of the heads is also found in both the CaF and SrF $B^2\Sigma\leftarrow X^2\Sigma$ systems.[10] Apparently closely associated with the main sequences 0 and +1 are two very faint sequences of bands, which were at first assumed to be the lower energy component of a $^2\Pi$, $^2\Sigma$ transition. A consideration of the intensity of the bands in the two sets, however, shows that this cannot be the case. Not only are the intensities of a different order of magnitude, but the relative intensity distributions among the bands of the two sets are unlike. Therefore, in view of the similarity of the strong bands to the red system, the upper state has been interpreted as a $^2\Sigma$ state, and its constants have been calculated from the higher frequency heads. First differences of the weak heads suggest that they are also due to BaF, if certain leading heads of the sequences are assumed to be too weak to be observed, indicating another electronic level, $\nu\approx 29{,}235$ cm^{-1}, with a vibration frequency nearly the same as that of the neighboring $F^2\Sigma$ state.

The bands in the region λλ3069–3210 apparently belong to a single electronic system, but a careful consideration of the position and intensities of the band heads indicates that they probably constitute two overlapping systems. The more extensive contains three sequences, the 0, +1, and +2, with no sign of a −1 sequence. The other system shows only the 0,1, 0,0, and 1,0 heads, the last two being of intensities equal to the corresponding bands in the more extensive system. If this were a $^2\Pi$, $^2\Sigma$ system, the appearance or nonappearance of certain of the heads in the different sequences might be explained by assuming certain relations between B' and B'', as is the case in the $A\leftarrow X$ system of SrF,[10] but the appearance of strong 0,0, 1,0 and 0,1 bands and the complete absence of other members of these sequences cannot be explained in this way. It seems more likely that two systems are present here, the upper states, probably $^2\Sigma$, lying only some 130 cm^{-1} apart. The heads of the less extensive system are at 31,136.8, 31,602.2 and 32,107.2 cm^{-1} which indicates that the ω_e values of the two new states are very nearly equal.

In addition to the systems described, a short wave-length continuum was present extending up to λ2450 with a furnace temperature of 2000°C. The spectrograms also contain the bands λλ3650–

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[11] F. A. Jenkins and A. Harvey, Phys. Rev. **39**, 922 (1931).

TABLE V. *Electronic terms and vibration frequencies for the alkaline earth fluorides.*

MOLECULE	STATE	T_e	ω_e
	$A^2\Pi$	33,241.8 33,225.4	1172.6
BeF	$X^2\Sigma$	0	1265.6
	$C^2\Sigma$	42,528.0	821.9
	$B^2\Sigma$	37,151.7	757.8
	$A^2\Pi$	27,847.4 27,813.1	746.0
MgF	$X^2\Sigma$	0	718.2
	$F^2\Pi$	37,547.9	681.7
	$E^2\Sigma$	34,135.2	646.3
	$D^2\Sigma$	30,772.3	650.7
	$C^2\Pi$	30,285.2 30,255.9	481.7
	$B^2\Sigma$	18,895.9 18,889.3	541.5
	$A^2\Pi$	16,557.2 16,482.1	593.4 591.9
CaF	$X^2\Sigma$	0	586.7
	$G^2\Pi$	34,759.2	573.9
	$F^2\Sigma$	32,820.3	598.5
	$E^2\Pi$	31,614.8 31,528.7	564.4
	$D^2\Sigma$	28,296.6	552.1
	$C^2\Pi$	27,041.3 26,977.8	452.5
	$B^2\Sigma$	17,301.9	488.9
	$A^2\Pi$	15,348.9 15,068.9	505.9 506.1
SrF	$X^2\Sigma$	0	500.1
	$H^2\Sigma$	31,582	509
	$G^2\Sigma$	31,451.9	510.4
	$F^2\Sigma$	29,411.3	529.9
	$E^2\Sigma$	28,134.1	538.4
	$D'^2\Sigma$	26,222.3	504.9
	$D^2\Sigma$	24,152.3	508.4
	$C^2\Pi$	20,197.2 19,998.2	456.0
	$B^2\Sigma$	14,064.4 14,070.6	424.4
	$A^2\Pi$	12,281.1 11,647.3	436.7 435.5
BaF	$X^2\Sigma$	0	468.9

4136 observed by Jenkins and Harvey, who concluded that they compose a single system whose upper state is a wide doublet of separation 2070 cm^{-1}. Despite the near equality of the vibration constants, it now seems more reasonable to interpret them as two distinct states, probably $^2\Sigma$. The wide separation, the differences in intensity and intensity distribution, and certain analogs such as the $D^2\Sigma$ and $E^2\Sigma$ states of CaF, all make this the more natural conclusion.

DISCUSSION

Table V gives the electronic energies and vibration frequencies of all the states now known for this group of molecules. Excluding BeF, where only one excited state is known, certain analogous states can readily be traced from molecule to molecule, particularly the first four excited states of CaF, SrF, and BaF. The analogy of the $D^2\Sigma$ and $E^2\Sigma$ states of CaF with the $D^2\Sigma$ and $D'^2\Sigma$ states of BaF is clear. The vibration frequencies of the first pair are nearly equal (651 and 646 cm^{-1}) and the same is true for the last pair (508 and 505 cm^{-1}). Other possible analogies, as well as some obvious discrepancies, may be detected. In general the expected decrease of excited state energies as one goes from lighter to heavier molecules of the group is observed, together with a diminution of the vibration frequencies.

Rather striking is the fact that all of the band systems involving states above $C^2\Pi$, thirteen in all for CaF, SrF and BaF, are without exception shaded toward shorter wave-lengths. This is also true of the two highest states of MgF. These excited states are, therefore, more tightly bound than the ground state. The outer electron configuration of the normal states of these molecules, like that of BeF, is in Mulliken's notation $z\sigma^2 y\sigma^2 w\pi^4 x\sigma$. Mulliken suggests that the first two excited states, $A^2\Pi$ and $B^2\Sigma$, arise from the excitation of a $w\pi$ and $y\sigma$ electron, respectively, into the $x\sigma$ orbit. The $C^2\Pi$ state is very likely due to the transition of the $x\sigma$ into the $v\pi$ orbit. It is reasonable to assume that the electronic states of higher energies are obtained from the normal state configuration by exciting the $x\sigma$ electron to σ and π orbits derived from atomic orbits of still higher total quantum number, leaving the closed shell configuration $z\sigma^2 y\sigma^2 w\pi^4$ undisturbed. The more highly excited the $x\sigma$ electron, the more nearly should the resulting state resemble the normal state of the ionized molecule (which it becomes in the limit). The spectra of the ionized molecules of this group are unknown, but the approximate magnitude of the binding can be determined by a consideration of the oxides, which are isoelectronic with the ions. For example, the vibration frequency of the normal state of CaO is 843 cm^{-1}.[12] A correction for the difference of reduced mass gives 790 cm^{-1} as an approximate estimate of the vibration frequency of CaF^+, indicating considerably stronger binding than in the CaF normal state ($\omega_e''=587\ \text{cm}^{-1}$). SrF and BaF give similar results. It seems reasonable, then, on the hypothesis that the excitation of the $x\sigma$ electron alone determines the higher energy states of this group of molecules, that those states should be more firmly bound than the normal state configuration.

The continua that appear at the ultraviolet limit of the spectrum in the case of every molecule investigated can be reasonably attributed each to its specific molecule. Some repulsive excited states of relatively high energy are theoretically predicted for most molecules, and only in absorption at high temperature can transitions involving such states be observed in many cases. Although the possibility exists that all the continua are due to some persistent impurity, the appearance of the λ2180 continuum of CaF is certainly characteristic, and probably the others are also.

In conclusion the writer wishes to thank Professor F. A. Jenkins, whose direction and criticism were of considerable assistance in this investigation.

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[12] P. H. Broderson, Zeits. f. Physik **104**, 135 (1936).

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On the Joint Action of Diffusion and Recombination of Ions

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The differential equation which describes the joint action of diffusion and recombination of ions is solved, for the one-dimensional case, by a method previously developed by the author. In Section I, the decay of a given initial distribution of ions is treated. The observable coefficient of recombination, as modified by diffusion, depends strongly in the initial stage on the given distribution. For later times it depends in a simple way on the density of ionization and the distance between the collecting plates. In Section II, the establishment of the steady state, with constant production of ions, is calculated. Diffusion introduces a linear term which may, for sufficiently small values of the ionic density and the electrode distance, mask the usual quadratic term. In Section III, it is shown that anomalies observed by Gardner in the recombination coefficient of oxygen and by Power in the establishment of the steady state in air are explained, without further assumptions, by diffusion to the walls.

INTRODUCTION

IN all measurements on recombination of ions diffusion plays a noticeable and often an important part. This holds whether the ionized volume extends to the collecting electrodes or not. For, in the former case, ions are lost to the electrodes and, in the latter case, the ionized volume increases by diffusion, thus affecting the apparent coefficient of recombination.

Langevin[1] was the first to recognize the importance of diffusion in measurements on recombination. As early as 1905 he solved the problem of the steady state created by a constant production of ions between parallel plates under the joint action of recombination and diffusion. His results do not seem to have found the attention which they deserve. In quite a number of cases where their application would have been of value they were replaced by less accurate computations. In more recent measurements on recombination, all observers had to correct their results for diffusion and did it somehow or other,[2] but none of the formulae used are adequate.

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[1] P. Langevin, J. de phys. (4) **4**, 322 (1905).

[2] A. D. Power, J. Frank. Inst. **196**, 327 (1923); L. C. Marshall, Phys. Rev. **34**, 618 (1929); O. Luhr, Phys. Rev. **35**, 1394 (1930); **36**, 24 (1930); P. Kraus, Ann. d. Physik **29**, 449 (1937); M. E. Gardner, Phys. Rev. **53**, 75 (1938); J. Sayers, Proc. Roy. Soc. **A169**, 83 (1938).

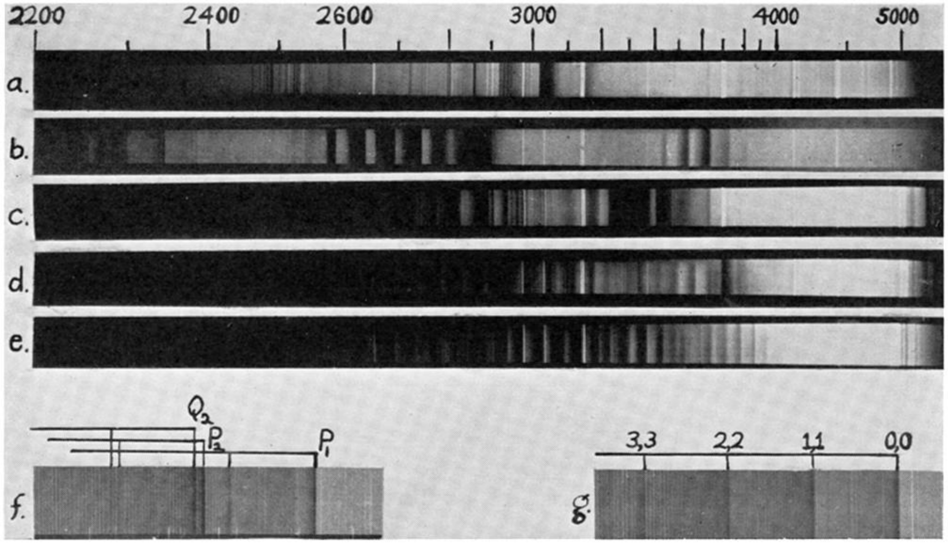

FIG. 1. Low dispersion spectra of (a) BeF, (b) MgF, (c) CaF, (d) SrF, (e) BaF. High dispersion spectra of (f) the $E^2\Pi$, $X^2\Sigma$ and (g) the $D^2\Sigma$, $X^2\Sigma$ systems of SrF.