The Alkaline Earth Halide Spectra and their Origin.

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[PLATE 2.]

It has been known since the early days of spectroscopy that there is a group of band spectra associated with the halogen salts of the alkaline earths. Probably the first distinction between the oxide and chloride bands of these elements was made by Lecoq de Boisbaudran* when he observed relative intensity fluctuations between two band systems on introducing hydrochloric acid vapour into a flame charged with calcium chloride. The system intensified by the acid vapour he attributed to the chloride. The other halides were also found to yield characteristic spectra. Since their discovery they have been the subject of only one publication of any real note. Olmsted† made a careful study of these spectra as they are found under flame excitation, and his catalogue of bands contains the only reliable data concerning these spectra which is available. An exception must be made of the fluoride spectra, which have been closely studied by Dufour, Datta, and others.

The origin of the present investigation of these bands was the discovery that it is possible to observe them, very conveniently, in absorption against a continuous background spectrum. In the course of attempts to find band spectra of the alkaline earth metals (corresponding to those of the alkali metals) a pair of bands at about λ 6200 was observed in the absorption spectrum of a column of calcium vapour at temperatures of 900° C. and upwards. On measurement, these bands, which are reproduced in Plate 2, figs. 1, 2 and 5, were found to coincide with two prominent calcium chloride bands. Ordinary commercial calcium had been used for the experiments, and on analysis approximately 0·05 per cent. of chloride was found in it.‡ It seemed evident that the development of the bands was due to this impurity in the metal, and the matter was clinched by adding a trace of bromide to the metal before heating, when the calcium bromide bands in the red also appeared prominently in absorption.

* ' Compt. Rend.,' vol. 69, p. 445 (1869).

† ' Z. Wiss. Photographie,' vol. 4, p. 255 (1906).

‡ Eagle (' Astrophys. J.,' vol. 30, p. 231 (1909)) observed the chloride bands in the arc spectrum of commercial calcium, and attributed them to chloride present as impurity.

We have since found that this method (of heating excess of the metal with the halogen salt) is a general one for obtaining all the members of this class of spectra in absorption—from magnesium, calcium, strontium, and barium, in combination with fluorine, chlorine, bromine or iodine. The method has obvious advantages over the previous practice of obtaining the bands in emission. Such emission sources are usually faint, and the photographic exposures required are excessive, while if the absorption method is employed the exposure can be made as short as may be desired merely by increasing the intensity of the continuous background. Another great advantage is that the spectra are obtained free from the oxide bands, or from any other interfering spectra. The bands, and especially the fainter ones, can thus be ascribed to their respective molecules with much more certainty than has previously been possible. We have therefore re-examined each of these spectra in absorption, with results that will be found in the catalogue of band heads given later in the paper. It is of interest that Liveing and Dewar* recorded the appearance of the green bands of barium chloride in absorption, when the salt was heated with reducing agents to high temperatures. The observation was only incidental, and they did not pursue the matter any further.

The observation that these bands can be obtained in absorption in this manner is of importance in other directions, as it throws light upon the nature of the " carriers " of the spectra. The only explanation, as we shall see, of the absorption phenomenon, is that the bands originate not from the normal halide molecules such as $CaCl_2$ or BaI_2, but from subhalide molecules $CaCl$, BaI, etc. Molecules of this type must persist in the vapour state at the temperature of the experiments. On the chemical side, there have already been several reported preparations of these subsalts in the solid state, and these statements have been followed by some polemical discussion. The claims for the existence of such compounds are completely vindicated, we believe, by the present observations.

It will be more convenient to discuss these conclusions fully, subsequent to an account of the experimental methods employed.

Experimental.

Apparatus.—The absorption spectra observed were those of a column of vapour about a foot long, maintained in a steel tube of $1\frac{1}{4}$ inch diameter. The tube was heated in a nichrome wound electric furnace, and the temperatures found to be necessary in practice were as high as can be obtained with such a

* ' Collected Papers,' p. 22.

winding—1,000° to 1200° C. The bands appear at lower temperatures, say 900° C., but they are not then sufficiently intense for satisfactory photography. The ends of the steel tube projected several inches from the furnace and were water-cooled by copper spirals, so that quartz windows could be affixed. For convenience, the windows were first attached to brass plates, and these were screwed to flanges soldered on the ends of the furnace tube, a washer of greased rubber making an airtight joint between the plate and the flange. A side tube was also let into the furnace tube near one end, for the removal or admission of gases.

Modifications were made in this simple system to smooth the running of the experiments. The charge of metal, etc., was not placed directly into the furnace tube but into an inner iron sheath which was withdrawn and cleaned each time. This addition prolonged the life of the main tube and kept it in much better condition. One of the chief experimental difficulties, and one which caused much delay, was the gradual distillation of the charge from the heated portion of the tube on to the end windows. These frequently became too opaque for observation just at the critical part of an experiment. This trouble was removed entirely by arranging behind each window an internal shutter which was only pulled down during exposures. The disposition of these shutters and of the rest of the apparatus will be evident from the diagram.
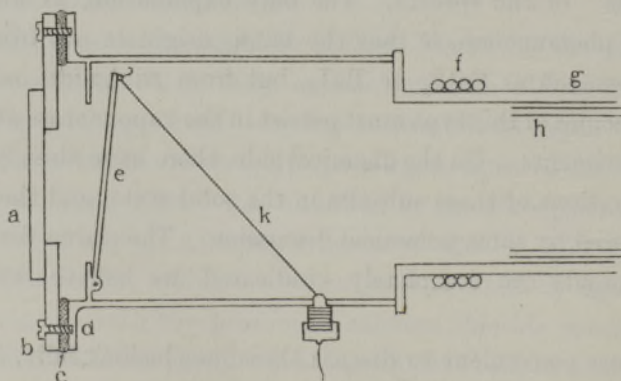
a, Quartz window; b, Brass plate; c, Rubber washer; d, Flange; e, Internal shutter; f, Copper spiral; g, Furnace tube; h, Inner sheath; k, Operating wire for shutter.

The shutter was hinged at one end, and a wire attached to the other, passing out through a packing gland. Normally the shutter closed the tube, and was kept in place by a spring. On pulling the wire the shutter was lowered, and the system was ready for observations.

The continuous background spectrum was provided by a 500-c.p. " Pointo-

lite " lamp, down to $\lambda\,3800$ (and with long exposures to $\lambda\,3100$). For shorter wave-lengths the positive crater of a carbon arc was used as a source, enabling us to photograph down to $\lambda\,2300$ or $\lambda\,2200$, and this was the limit of the observations. The spectrographs were a constant deviation instrument for the visible region, and a Hilger " E_3 " quartz spectrograph for the ultra-violet.

Preparation of Sub-halide Vapours.—In studying the calcium spectra, the sub-halide vapours were invariably obtained by heating a mixture of calcium turnings and a powdered and dehydrated calcium halide salt. This was the obvious procedure in view of the original observations, and it was found to work very well. The magnesium halide spectra were obtained in an analogous manner. It had been anticipated that to prepare the sub-halide vapours of strontium and barium it would be necessary to isolate the metals themselves, and then to mix them with the normal salts, but this proved to be superfluous. The vapours of these salts can be obtained quite readily by heating a mixture of calcium metal and the strontium or barium normal halides. The various calcium halide bands, of course, also appear in the absorption spectrum of the vapour, but these can easily be identified after a little experience. Further, by regulating the temperature it is possible to minimise the admixture of calcium subhalide vapour with the others, as the strontium and barium compounds seem to be more volatile. One slight difficulty arises from the hygroscopic nature of the normal salts. The water they soon absorb from the atmosphere is sufficient to cover the surface of the admixed metal with an oxide layer, through which it is most difficult to distil the underlying metal at the temperatures employed. It was sometimes found preferable therefore to heat the metal alone in the tube until it was volatilising freely, and then to admit free halogen in small quantity through the side tube, so that the subhalide was prepared *in situ.*

Some of the experiments were carried out with the tube evacuated, but more usually an atmosphere of dry hydrogen or argon was introduced, to slow up distillation of the charge to the cooler ends of the tube. Evacuation had no visible effect on the appearance of the spectra, with one important exception— the CaF band at $\lambda\,5292$. The behaviour of this band is fully described in another section. Perhaps owing to some chemical reaction, a hydrogen atmosphere had a distinct influence in making the spectra—and presumably the subhalides themselves—difficult to obtain. Argon was therefore always used when it was available. It may be mentioned that Guntz[*] states that hydrogen reduces the subsalts when these are in the solid state. We are also

* ' Bull. Soc. Chim.,' vol. 35 (6), p. 709 (1924).

in agreement with his observations that the ease of preparation of these salts increases with the atomic weight of the halogen component. The fluorides proved to be by far the most difficult vapours to obtain, and required a higher temperature than any of the others.

The Origin of the Alkaline Earth Halide Bands.

We may now consider the bearing of these experiments upon the origin of the spectra. There can be no doubt from the conditions under which the bands can be excited that they originate from molecules containing both alkaline earth and halogen atoms. The point upon which no experimental evidence has previously borne is whether these molecules are those of the normal halides, such as $CaCl_2$ or of a subhalide such as CaCl, or—just possibly— Ca_2Cl_2. The present observations eliminate two of these possibilities with some degree of certainty, and show that the carriers of the spectra are subhalide molecules of the simple type MX, where M stands for an alkaline earth and X for a halogen atom.

We have made many attempts to observe the spectra by heating the normal halides alone in the furnace, but always with a negative result, even on reaching furnace temperatures well in excess of those normally employed. Further it must be remembered that many of the normal salts are very involatile and have quite negligible vapour pressures at 1000° C., a temperature which is quite sufficient for the development of the bands when other conditions are satisfactory. We can therefore rule out the possibility that the normal halides themselves can show the absorption phenomena which we have recorded. The metal vapours by themselves have no band absorption spectra in the wavelength region under examination, but only a line absorption, details of which we have given elsewhere.* Commercial calcium, it is true, always gives the chloride bands on heating, but this can be traced to chloride present as an impurity, and the bromide, etc., bands are invariably absent from its absorption spectrum. It is only when the two materials, free metal and normal salt are present in the charge that the bands are developed, and so long as this condition is satisfied they always appear. The only explanation of this fact is that these two constituents of the charge must react to give a new type of halide molecule which contains a greater proportion of metal than the original normal salt, and which is also more volatile.

On theoretical grounds, both chemical and spectroscopic, by far the most

* Walters and Barratt, ' Phil. Mag.' (3), p. 991 (1927).

probable formula for these molecules is the simple MX type. The foregoing experiments by themselves do not rule out such molecules as M_2X or M_2X_2, but other experimental facts render such possibilities quite negligible. We have carried out many trials in which several alkaline earths and halogens were present together in the tube, and we have always found that the spectra were strictly additive : that is to say, there has never been any suspicion of spectra due to such mixed molecules as $CaSrCl$, or Ca_2ClBr, which might be expected if the carriers of the spectra were other than the simple diatomic molecules of the MX type.

These conclusions are in gratifying agreement with the theoretical predictions of R. S. Mulliken* on the origin of these and similar spectra. Such bands, it is held, would not be expected from a " complete " molecule such as $CaCl_2$, but are much more likely to be due to a molecule $CaCl$, containing an unsatisfied valency electron.

Further experiments may now be mentioned which, taken by themselves, would not present a very cogent argument for the subhalide origin of the spectra, but which receive a ready explanation in terms of it. It is well known that if chloroform or other vapour of high chlorine content—or chlorine itself—is introduced into a flame tinged with the familiar sodium yellow this colouration is immediately destroyed. The generally accepted explanation is that the excess of chlorine combines with the free sodium atoms, and therefore prevents the emission of the D lines. We have found that calcium, strontium, etc., flames can be made to exhibit similar, but rather more complex changes. A flame fed with a spray of a solution of any calcium salt is tinged with the usual calcium reddish colour, and this on examination with the spectroscope is seen to be due to the oxide bands in the red and green. If cotton wool soaked in chloroform is brought moderately near the air inlet of the burner, the colour of the flame changes slightly, and at the same time the oxide bands become extremely faint, and are replaced by the chloride bands in the orange. Finally, when even more chlorine is introduced into the flame by the near approach of the chloroform, the flame becomes " colourless " and neither oxide nor chloride bands can be distinguished. Parallel observations can be made by introducing bromine, or a volatile iodine compound such as ethyl iodide, into the flame. On the subhalide theory the explanation is as follows. The oxide bands show so long as no halogen, or only a little, is present ; with more, the chances of a CaX molecule being formed become greater, and the halide bands appear. With excess of halogen present most of the calcium atoms are present

* ' Phys. Rev.,' vol. 26, pp. 29–32 (1925).

as normal halide molecules, and the flame ceases to radiate either oxide or halide bands.

Wave-lengths, etc., of the Alkaline Earth Halide Bands.

The bands are likely to be of some theoretical interest now that they are known to be associated with an unusually simple type of molecule. Molecules of the type MX, according to current views of atomic structure, must contain a " completed " halogen atom, bound to an alkaline earth atom which still possesses one free " valency " electron. It has already been pointed out by Mulliken (*loc. cit.*) and by R. Mecke[*] that such a system resembles in some respects an atom of an alkali metal. It is not surprising that the resemblance extends to the spectra and that doublet bands are a characteristic of the halide spectra, just as doublet principal series are found with the alkali metals. In the early stages of this work we had some hope that the resemblance might extend further, and that a careful examination of the visible and ultra-violet bands of any one of these molecules might reveal a number of heads arranged according to the Rydberg series spectrum law. Such regularities would not have been new in kind, as they have already been found in the helium band spectrum by Fowler and in the secondary spectrum of hydrogen by Richardson. No such bands could be traced from the older emission data, but it was hoped that the higher members of such a band series, if it existed, would be more prominent in absorption than in emission, as are, for example, the higher members of the sodium principal series. In the event, the greater sensitivity of the absorption method certainly asserted itself by enabling us to detect new groups of bands in the ultra-violet, but these do not appear to be arranged according to the series law. We therefore conclude that the various groups of bands in each of these spectra do not correspond to successive members of a single atomic line series, but rather to the first members only of several such series.

All these molecules, except the magnesium halides, have band groups in the visible region. In general, the group of longest wave-lengths in each spectrum consists of bands degraded to the short wave-length side. The next group— usually in the near ultra-violet—is degraded to the long wave-length side. When other groups were found in absorption the direction of degradation alternated from one group to the next. The barium halide bands appear to be exceptional, but in all probability the first group of bands belonging to these molecules lies in the infra red, out of the range of observation. In all cases the first, or visible,

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[*] ' Naturwiss.,' vol. 13, p. 755 (1925), and ' Z. f. Physik,' vol. 42, p. 390 (1927).

group was found to be of far greater intensity than the others, some of which were only observed with difficulty, and with unusually dense vapour in the absorbing column. In the accompanying plate, several of the absorption spectra have been reproduced.

With the object of simplifying future work on this subject, in which instruments of higher dispersion than ours will probably be used, we have re-examined all these band spectra by the new absorption method, and we have catalogued below the band heads which can safely be ascribed to each of the various molecules. The possible wave-length accuracy of the measurements is not high, and in most cases we have given the wave-lengths only to the nearest Ångström unit. Visual intensity estimates have been given for each groups of bands, and the degradation to the " long " or " short " wave-length side is indicated. A few bands had no definite degradation. Some of the bands which were exceptionally weak, and others, with ill-defined heads, could not be measured satisfactorily. These are marked with an asterisk. It has not been thought necessary to give a bibliography of each spectrum, as these are available in Kayser's " Handbuch."

The wave-length limit of observation was curtailed for certain spectra by the inveterate appearance of clouds in the absorbing column, and we have therefore given this limit for each spectrum individually.

CaF Bands.

Limit of observations, λ 2250.   (See Plate 2, fig. 5.)

λ Air.	ν Vac.	Int.	Degr.
6064·3	16485	8	Long
6051·0	16522	5	,,
6035·8	16566	8	,,
5851	17086	0	,,
5835	17133	0	,,
5292	18891	10	,,

A group of bands were noticed at λ 2330, near the observation limit, but they were not developed suitably for measurement. A discussion of the behaviour of the λ 5292 band, and measurements on it with higher dispersion, will be found in a later paragraph.

CaCl Bands.

Limit of observations, λ 2500.   (See Plate 2, figs, 1, 2, 5.)

λ Air.	ν Vac.	Int.	Degr.
6350	15743	0	Short
6310	15843	0	,,
6210	16098	10	,,
6191	16148	5	,,
6183	16169	10	,,
6075	16456	2	,,
6068	16475	2	,,
6045	16538	2	,,
5934	16847	7	,,
5810	17207	1	,,
3994	25030	0	Long
3985	25087	0	,,
3969	25188	0	,,
3948	25322	0	,,
3937	25393	0	,,
3923	25483	0	,,
3907	25588	1	,,
3896	25660	1	,,
3889	25706	3	,,
3877	25786	5	,,
3827	26123	3	,,
3821	26164	2	,,
3816	26191	9	,,
3774	26489	3	,,
3768	26532	2	,,
3763	26567	10	,,
3727	26823	3	,,
3722	26859	2	,,
3717	26896	8	,,
3694	27063	2	,,
3683	27144	2	,,
3671	17233	2	,,
3238	30874	0	Short
3220	31047	0	,,
3186	31378	0	,,
3182	31477	0	,,
2918	34260	0	,,

CaBr Bands.

Limit of observations, λ 2200.   (See Plate 2, fig. 3.)

λ Air.	ν Vac.	Int.	Degr.
$\Big\{$ 6390·6	15643	0	Short
6363·8	15709	0	,,
$\Big\{$ 6285·0	15906	0	,,
6277·5	15925	. 10	,,
6258·0	15975	0	,,
6252·7	15988	10	,,
6211·6	16094	0	,,
6168·5	16207	0	,,
6145·6	16267	0	,,
6106·6	16371	5	,,
6004·3	16651	0	,,
3996	25018	0	Long
3960	25245	0	,,
3950	25309	4	,,
3917	25522	4	,,
3910	25568	0	,,
2967	33694	0	Short
2952	33865	0	,,
2945	33946	0	,,
2910	34354	0	,,
2890	34592	0	,,

We believe a further group of bands exists at about λ 2300, but these were always too indistinct for measurement.

CaI Bands.

Limit of observations, λ 2900.   (See Plate 2, fig. 4.)

λ Air.	ν Vac.	Int.	Degr.
⌈ 6609*	15126	0	Short
{ 6578*	15198	0	,,
⌊ 6557*	15246	0	,,
⌈ 6509·3	15358	1	,,
{ 6486·9	15413	1	,,
⌊ 6460·1	15475	1	,,
⌈ 6414·3	15586	10	,,
{ 6390·3	15645	10	,,
⌊ 6363·6	15711	6	,,
⌈ 6314·6	15833	8	,,
{ 6293·0	15863	6	,,
⌊ 6268·4	15949	8	,,
4334	23067	1	Long
4289	23309	5	,,
4255	23495	1	,,
4248	23534	0	,,
4211	23740	2	,,
3266	30609	0	Short
3215	31095	3	,,
3186	31378	3	,,
3158	31656	1	,,
3127	31970	1	,,

SrF Bands.

Limit of observations, λ 2950.   (See Plate 2, fig. 5.)

λ Air.	ν Vac.	Int.	Degr.
6635·7	15066	10	Short
6514·9	15345	10	,,
5772·8	17318	7	Long

A very faint band was registered on some plates at λ 3646.

SrCl Bands.

Limit of observations, λ 2300.   (See Plate 2, fig. 2.)

λ Air.	ν Vac.	Int.	Degr.
6879	14533	3	Short
6745	14822	10	,,
6614	15115	10	,,
6478	15432	3	,,
6360	15719	10	,,
6237	16029	2	,,
6220	16072	2	,,
4006	24955	2	Long
3982	25106	2	,,
3959	25252	10	,,
3935	25406	10	,,
3916	25529	0	,,
3892	25686	0	,,

SrBr Bands.

Limit of observations, λ 3000.

λ Air.	ν Vac.	Int.	Degr.
6924	14438	0	Short
6800·2	14701	10	,,
6666·6	14996	10	,,
6514·7	15345	5	,,
4186*	23882	0	Long
4146	24113	4	,,
4129	24212	1	,,
4108	24336	9	,,
4090	24443	3	,,
4073	24545	2	,,
4053	24666	10	,,
4019	24875	2	,,
3992*	25043	0	,,
3945	25341	5	,,
3909	25575	5	,,

SrI Bands.

Limit of observations, λ 2400.

λ Air.	ν Vac.	Int.	Degr.
7094·0	14092	2	Short
7011·0	14259	10	,,
6930·2	14425	10	,,
6847·7	14599	10	,,
6767·8	14772	10	,,
6691·5	14941	8	,,
6662·3	15005	8	,,
6177·3	16184	4	,,
4482	22305	0	Long
4447	22481	4	,,
4412	22659	10	,,
4381	22819	1	,,
4339	23040	2	,,
4307	23211	6	,,
4276	23380	1	,,
3439*	29070	0	Short
3406*	29351	0	,,
3378*	29595	0	,,

BaF Bands.

Limit of observations, λ 2800.

λ Air.	ν Vac.	Int.	Degr.
7358	13587	10	Long
7117	14047	10	,,
6911	14466	10	,,
5119*	19529	0	,,
4995·4	20013	2	,,
4988·3	20041	2	,,
4948·5	20202	4	,,
4939·9	20237	4	,,
3497	28588	0	,,
3458	28910	0	,,
3419	29240	0	,,
3401	29394	0	,,
3372	29647	0	,,
3365	29709	0	,,
3347	29869	0	,,
3330	30021	0	,,
3311	30193	0	,,

BaCl Bands.

Limit of observations, λ 2200. (See Plate 2, fig. 1.)

λ Air.	ν Vac.	Int.	Degr.
5322	18785	1	Short
5241·9	19072	10	Long
5213·9	19174	0	Short
5166·6	19350	2	Long
5136·0	19465	10	,,
5066·6	19731	0	Short

BaBr Bands.

Limit of observations, λ 2600. (See Plate 2, fig. 3—The two bands marked *
are due to BaCl.)

λ Air.	ν Vac.	Int.	Degr.
5417	18455	7	No head
5361	18648	10	,,
5303	18852	6	,,
5261	19002	4	,,
5206	19203	10	,,
5153	19400	5	,,
5101	19598	0	,,

BaI Bands.

Limit of observations, λ 3000.

λ Air.	ν Vac.	Int.	Degr.
5609·5	17822	10	Short
5381·7	18576	10	,,
5260*	19006	0	?
5160*	19374	0	?
3830	26102	1	Short
3804	26280	2	,,
3778	26461	3	,,
3756	26616	3	,,
3736	26759	1	,,

MgF Bands.
Limit of observations, λ 2800.

λ Air.	ν Vac.	Int.	Degr.
3659	27322	3	Long
3637	27487	0	,,
3619	27624	3	,,
3592	27832	2	,,
3563	28058	4	,,
3527	28344	4	,,
3497	28596	8	,,
3478	28744	1	,,
3462	28876	10	,,
3419	29240	10	,,
3401	29395	1	,,
3388	29507	0	,,
3382	29560	8	,,
3364	29718	3	,,
3345	29887	6	,,
3329	30030	4	,,
3314	30166	1	,,
3309	30212	3	,,
3294	30349	1	,,
3276	30516	0	,,
3261	30656	0	,,

MgCl Bands.
Limit of observations, λ 2700.

λ Air.	ν Vac.	Int.	Degr.
3779	26454	0	?
3776	26475	10	Short
3748	26673	10	,,
3708*	26961	0	,,
3687*	27114	0	,,

The band at λ 3779 was so narrow that it had the appearance of a sharp line.

MgBr Bands.
Limit of observations, λ 3000.

λ Air.	ν Vac.	Int.	Degr.
3934*	25412	0	Short
3918*	25516	2	,,
3881	25759	10	?
3864	25872	10	Short
3841*	26027	0	,,
3821	26164	2	?
3819	26177	2	Short

3881 and 3821 were so narrow as to appear to be sharp line absorptions.

MgI Bands.

Limit of observations, λ 3000.

λ Air.	ν Vac.	Int.	Degr.
4110	24324	10	Short
4027	24825	1	,,
4001	24987	1	Long
3983	25099	10	Short
3951	25303	10	Long
3927	25457	2	,,
3902	25620	2	,,
3657	27337	1	Short
3628	27555	1	,,
3602	27754	1	,,
3432	29129	0	,,
3405	29360	0	,,
3396	29438	0	,,
3380	29577	0	,,
3358	29711	0	,,

The Structure of the CaF *Band,* λ 5292, *in Absorption.*

We have compared many of the bands obtained in absorption by the methods described in preceding sections, with the corresponding emission spectra from flames and arcs, and in general we have been unable to detect any differences in their structure or intensity distribution. The calcium fluoride band at λ 5292 provided a notable exception. This band has been fully described by Datta[*] and observed in emission it has a very simple structure, consisting of a number of doublet lines with a separation of about 2 Å., which conform to a Deslandres formula. It was immediately evident, even under the small dispersion of the constant deviation instrument, that the structure of the absorption band was very different. It covered the same wave-length range, but there were many more lines developed within that range, and the intensity distribution had no relation to that of the emission band. With the very kind assistance of Prof. T. R. Merton we were afterwards able to examine the behaviour of this band under much higher dispersion. Photographs of the spectrum, in emission and absorption were taken in his laboratory with a Littrow spectrograph fitted with a glass prism which gave a dispersion of 5 Å. per millimetre in the region of λ 5300. The differences of structure suspected under small dispersion were found to be real. An enlarged reproduction of the band in arc emission and in absorption is given in the Plate 2, fig. 6.

The appearance of the band is so changed under the two conditions that

[*] ' Roy. Soc. Proc.,' A, vol. 99, p. 436 (1921).

evidence may be required that we are really dealing with the same band, and not merely with a coincidence in the position of two distinct bands of different "carriers." In the first place, the band cannot be obtained in either form unless calcium and fluorine are present. Also some of the lines in the emission band (including the two of shortest wave-length) coincide with lines in the absorption band; and finally parallel changes were seen, under small dispersion, in the SrF band at λ 5773, which vastly diminishes the chances of a mere coincidence.

The table appended to this section gives the wave-lengths of over 80 absorption lines in this CaF band, and also the wave-lengths of the few emission lines in the same region, calculated from Datta's formula in the paper previously quoted. The relative wave-lengths of the absorption lines are probably accurate to a few hundredths of an Ångström unit, but the absolute errors may be greater, as only one plate was available for measurement.

We are unable to assign any certain cause for this radical difference in the structure of the band in emission and absorption. The pairs in the emission band presumably correspond to molecular vibrational changes, and the closely packed absorption lines to rotational changes in the same molecule. It may be mentioned that, on strong plates the emission spectrum has a faint background of fine structure also, but this does not correspond in any way with the absorption lines. The most usual cause of intensity modifications in a band spectrum is a temperature effect, and the conditions of experiment were certainly such as to render operative any influence of this nature. The temperature in the absorbing column must have been very much less than that in the arc which produced the emission bands. The data we present in this paper are not sufficient to settle this point satisfactorily, but we do not believe that temperature differences—though doubtless these produce some modification—will prove a complete explanation of the changes.

There is one consideration which suggests that pressure may have an important bearing on the matter. While the absorption spectrum was being examined with the high dispersion spectrograph it was found that the fine structure of the band, here recorded, was only developed when the furnace tube had been evacuated of foreign gas. When hydrogen or argon were admitted, the absorption merged into two continuous regions separated by a rift at about λ 5303. Now if a photograph of the emission band is examined it will be found that there is always a weak continuous background in evidence, and that this has the characteristic rift at the same wave-length. It therefore seems possible that the fine structure of this CaF band only appears under suitable conditions

of pressure, and that it is usually represented only by a weak continuous spectrum.

Absorption Lines in the CaF Band, λ 5292.

λ Vac.	ν Vac.	Int.	λ Vac.	ν Vac.	Int.	λ Vac.	ν Vac.	Int.
5292·52	18894·59	1	5310·85	18829·37	1	5325·19	18778·67	1
5294·36	18888·02	2	5311·38	18827·49	1	5325·47	18777·68	1
5296·20	18881·46	0	5311·66	18826·50	1	5325·65	18777·05	1
5296·54	18880·29	1	5311·95	18825·47	1	5325·95	18775·99	1
5296·97	18878·71	2	5312·17	18824·69	1	5326·17	18775·21	2
5297·49	18876·85	2	5313·21	18821·01	3	5326·42	18774·33	1
5297·94	18875·26	3	5313·79	18818·95	1	5326·89	18772·67	8d
5298·84	18872·05	4	5314·16	18817·68	2	5327·52	18770·45	5
5299·60	18869·34	2	5314·73	18815·63	3	5328·19	18768·09	1
5300·12	18867·49	2	5315·32	18813·54	3d	5328·56	18766·79	3
5300·95	18864·54	5d	5316·07	18810·88	2	5329·34	18764·04	2
5302·12	18860·38	5	5316·45	18809·54	0	5329·64	18762·99	1
5302·86	18857·74	4	5316·89	18807·98	2	5329·89	18762·11	1
5303·55	18855·29	6	5317·36	18806·32	1	5330·11	18761·33	1
5304·24	18852·84	4	5318·05	18803·88	7d	5330·39	18760·35	2
5304·68	18851·27	3	5318·56	18802·08	0	5330·92	18758·48	0
5305·10	18849·78	2	5319·31	18799·43	3	5331·16	18757·64	1
5305·74	18847·51	3	5319·66	18798·19	2	5331·90	18755·04	4d
5305·94	18846·80	8	5320·16	18796·42	1	5332·88	18751·59	1
5306·29	18845·55	10	5320·85	18793·98	0	5333·71	18748·67	2
5306·56	18844·59	4	5321·27	18792·50	1	5334·02	18747·58	1
5307·31	18841·93	4	5321·52	18791·62	3	5334·55	18745·72	1
5307·70	18840·55	3	5321·96	18790·06	7	5334·82	18744·77	1
5308·02	18839·41	4	5322·24	18789·08	10	5336·22	18739·85	1
5308·52	18837·64	2	5323·02	18786·32	1	5336·55	18738·69	1
5309·19	18835·26	2	5323·51	18784·59	1	5336·90	18737·46	0
5309·51	18834·12	3	5323·76	18783·71	0	5337·22	18736·34	0
5310·25	18831·50	7	5324·01	18782·83	4			
5310·48	18830·68	7	5324·53	18781·00	0			

Emission Lines in the same Band.

5292–5	5298·2	5304·1	5310·1	5316·1	5322·1	5328·3	5334·6
94·4	5300·1	06·0	11·9	17·8	23·9	30·1	36·3

NOTE.—The lines marked (*d*) are unresolved complex lines.

Summary.

1. Alkaline earth subhalide molecules of the type MX exist in the vapour state at 1000° C. in equilibrium with the metal and the normal salts.

2. The alkaline earth halide spectra are the resonance spectra of these molecules, and they are readily observed in absorption through a column of the vapour.

3. The bands in each halide spectrum have been examined by the absorption methods, and new groups have been found in the ultra-violet.

4. The CaF band, λ 5292, has been examined under a dispersion of 5 Å. per millimetre. The structure of the band is very different in emission and absorption. The fine structure of the absorption band only appears at reduced pressures.