THE BAND SYSTEMS AND STRUCTURE OF CaCl.

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Introduction.

THE emission bands due to CaCl have been known for a long time. Olmsted[1] tabulated a number of bands in the ultra-violet while Meisenbach[2] measured under low dispersion, a number of bands in the orange and red regions. The present writer had photographed the visible spectrum as produced in the carbon arc fed with calcium chloride, in the first order of the 21 ft. Rowland concave grating in King's College, London. Before the work on the bands was complete, however, Hedfeld[3] presented data of these same bands which were obtained by him under various conditions of excitation and photographed in the first order of a 3·5 metre concave grating. He analysed the bands into two distinct systems and though he did not develop the usual equations for them, it was clear that his analysis was in the main correct. Recently, fresh interest in these bands was stimulated by a paper of Lessheim and Samuel[4] in which, among other things, they show that in the case of a number of molecules, *e.g.*, MgF, CaF, SrF, the excited $^2\Pi$ term showing an energy of dissociation bigger than in the ground state, involves the anomalous term due to the simultaneous excitation of both the outside *s*-electrons of the atom. The CdF spectrum[5] also indicated a similar behaviour. It was therefore thought desirable to undertake a detailed vibrational analysis of the CaCl bands. A preliminary report of the results obtained has been already published[6] and details are presented in this paper.

Experimental Data.

The present measurements of the band heads agree almost completely with those of Hedfeld. Following Jevons,[7] we shall denote the two sets of bands as the red doublet and the orange systems. The individual bands in both systems degrade towards the shorter waves. In the orange system, however, the sequences degrade towards the red. These and other physical peculiarities of the bands are also described by Hedfeld. In the former system each band consists of two Q and two P heads. Bands comprising the $\Delta v=0$ and -1 sequences only have been utilised in the present analysis. Hedfeld has included some bands which are classified as the $\Delta v = +1$ sequence. All these bands are very faint and diffuse. Some of them, however, were also obtained on my plates. It was ultimately found that they come up more intensely along with more bands in the CaO arc and it is therefore quite likely that they are not due to CaCl but to CaO. On this basis they seem to be the $\Delta v=0$ sequence of a transition $^3\Pi-{}^3\Sigma$, in the CaO molecule giving three P and three Q heads for each band. They are provisionally so arranged in Table I which gives the wave-numbers *in vacuo* of the various heads indicated.

TABLE I.

$v'-v''$	P_1	Q_1	P_2	Q_2	P_3	Q_3
0—0	16393·6	16409·3	16414·2	16426·1	16453·0	16469·3
1—1	94·8	11·5	16·0	28·9	56·9	70·3
2—2	96·4	13·7	17·8	30·9	59·9	71·8
3—3	97·9	15·2	20·0	32·1	62·5	73·7
4—4		17·2			64·3	75·5
5—5						77·3
6—6						79·0

Investigation on these bands is in progress and results will be presented in a future paper.

The orange system shows double-headed bands, the doublet structure being very probably due to two P heads arising out of ρ-type doubling as is observed in analogous systems of CaF, SrF, CdF, etc.[8] The data of Hedfeld do not contain most of these subsidiary heads and therefore for the analysis of these bands the data obtained by the present author have been used. Hedfeld has tabulated three heads each of o intensity as forming the $\Delta v=-1$ sequence. These heads do not appear on the present plates and are not taken into consideration. It has been possible to identify the isotopic heads due to the $Ca^{40}Cl^{37}$ molecule and thus obtain the correct assignment of vibrational quantum numbers. In analogy with homologous molecules and from theoretical considerations, the red doublet bands are evidently due to $^2\Pi\rightarrow{}^2\Sigma$ and the orange to $^2\Sigma\rightarrow{}^2\Sigma$ transitions in the CaCl molecule.

Analysis.

Table II gives the initial and final vibrational term differences for the Q_1 heads of the red doublet system.

TABLE II.

v	Initial ($\Delta G'$)	Final ($\Delta G''$)
0	362·3	359·6
1	360·3	357·6
2	358·3	356·1
3	355·8	353·8
4	353·3	351·6
5	351·1	349·6
6	348·7	347·4
7	346·6	345·5
8	344·7	343·8

With these differences the following equation† representing the band heads was derived by the method of least squares.[9]

$$\nu Q_{1\,\text{heads}} = 16094{\cdot}6 + (363{\cdot}76v' - 1{\cdot}16v'^2 + 0{\cdot}0012v'^3)$$
$$-(360{\cdot}81v'' - 1{\cdot}01v''^2 - 0{\cdot}001v''^3) \quad \ldots \quad \ldots \quad \ldots \quad (I)$$

Table III gives the observed minus calculated values according to this equation.

The Orange System.

This also consists of two sequences $\Delta v = 0$ and $+1$. Each band shows the ρ-type doubling so that the heads should in reality appear double. But here the separation between the P_1 and P_2 heads is bigger than the distance between successive members of the sequence so that the satellite accompanying each band is not necessarily its P_2 head. As a matter of fact, the P_2 heads of each band actually lie very near to the P_1 head of the band preceding it in the sequence. These facts are clearly disclosed by the microphotometer plates Figs. 1 and 2 of the $\Delta v = 0$ and $+1$ sequences respectively. Fig. 2 also shows the isotopic heads due to the $Ca^{40}Cl^{37}$ molecule. Table IV gives the wave-numbers *in vacuo* of the band heads arranged into sequences.

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† This and also equation (II) can be easily transformed to meet the requirements of the new quantum theory, when necessary.

TABLE III.

v'–v''	Observed ν, cm.$^{-1}$	Calculated ν, cm.$^{-1}$	O–C
0–0	16094·6	16094·60	0·00
1–1	16097·3	16097·40	−0·10
2–2	16100·0	16099·91	+0·09
3–3	16102·2	16102·16	+0·04
4–4	16104·2	16104·14	+0·06
5–5	16105·9	16105·88	+0·02
6–6	16107·4	16107·38	+0·02
7–7	16108·7	16108·65	+0·05
8–8	16109·8	16109·62	+0·18
9–9	16110·7	16110·60	+0·10
0–1	15735·0	15734·80	+0·20
1–2	15739·7	15739·62	+0·08
2–3	15743·9	15744·18	−0·28
3–4	15748·4	15748·45	−0·05
4–5	15752·6	15752·49	+0·11
5–6	15756·3	15756·27	+0·03
6–7	15760·0	15759·82	+0·18
7–8	15763·2	15763·16	+0·04
8–9	15766·0	15766·30	−0·30
9–10	15769·0	15769·05	−0·05
10–11	15771·5	15772·13	−0·63
11–12	15773·7	15774·12	−0·42

TABLE IV.

v'–v''	P_1	P_2	v'–v''	P_1	P_2
0–0	16847·6	..	1–0	17207·4	..
1–1	844·1	..	2–1	200·2	..
2–2	840·1	16843·4	3–2	192·8	17201·3
3–3	836·2	839·8	4–3	184·9	193·8
4–4	831·5	835·9	5–4	177·6	185·8
5–5	826·9	831·8	6–5	168·2	178·8
6–6	821·7	827·3	7–6	158·8	172·0
7–7	816·4	822·3	8–7	150·3	163·1
8–8	810·7	817·2	9–8		154·7
9–9	804·7	811·7			
10–10	798·3	805·9			
11–11	791·6				
12–12	784·2				
13–13	777·0				
14–14	768·7				

For purposes of calculation the P_1 heads which stand out more prominently have been utilised. The following equation representing these heads was deduced as in the red doublet sequence.

$$\nu P_1 \text{ heads} = 16847\cdot6 + (361\cdot38v' - 1\cdot68v'^2 - 0\cdot015v'^3)$$
$$-(364\cdot51v'' - 1\cdot46v''^2 - 0\cdot020v''^3) \quad .. \quad .. \quad .. \quad \text{(II)}$$

Table V contains O – C values according to this equation.

Discussion.

In analogy with similar molecules the ground state of CaCl is undoubtedly a $^2\Sigma$ level. This, it is assumed, is the level involved in the red doublet system. The lower $^2\Sigma$ of the orange system is probably identical with it. The vibrational functions of the two levels are, however, not identical and the value 1·5 volts (see Table VI) for the dissociation energy which is less than half

TABLE V.

$v'-v''$	O–C	$v'-v''$	O–C
0–0	0·00	1–0	+0·12
1–1	−0·15	2–1	−0·29
2–2	−0·40	3–2	−0·39
3–3	−0·16	4–3	−0·53
4–4	+0·77	5–4	+1·53
5–5	+2·08	6–5	+1·84
6–6	−0·28	7–6	−0·81
7–7	−0·52	8–7	+0·03
8–8	−0·34		
9–9	−0·45		
10–10	−1·00		
11–11	−1·60		
12–12	−2·50		
13–13	−3·71		
14–14	−5·68		

the value for the $^2\Sigma$ state of the other system, appears to indicate as already pointed out,[6] that it is a different level, presumably an excited state of the molecule. Still, it must be remembered that the orange system has only P heads and the distance of the origin from the heads is large and probably not constant for all bands, while the equation for the other system is derived from Q heads. Hence the discrepancies need not be over-emphasized. Of course P heads could equally be used in the red doublet system but as is known from other similar cases[5] the agreement is not expected to be better. On the other hand, if this discrepancy is assumed real, and the $^2\Sigma$ lower state of the orange system is not identical with the $^2\Sigma$ lower state of the red doublet system which is also the ground level of the molecule, the following appears to be the only plausible explanation. If we assume that the final stage of the orange system arises out of the same constituent atoms as the $^2\Sigma$ state of the red doublet system but is an excited state of the molecule, then the upper level of these bands will be situated at about 4 volts above the ground level of the molecule and will have the same frequency of vibration as that of the initial state of this system. Such an explanation, though by no means improbable, appears to have no experimental evidence. The only other level known in the CaCl molecule lies at 3·28 volts with a frequency of vibration of about 330 cm.$^{-1}$ The Olmsted bands that originate in this level are weak and there is no trace of even these on the present plates; presumably also not on Hedfeld's.

Energies of Dissociation.

As is well known, extrapolation of the vibrational levels accompanying the electronic term of a molecule is one of the methods of evaluating the energy of dissociation of the molecule in that state. The limitations of this method are well known. There are also other methods,[10] mostly graphical, of utilising the more commonly observed non-regular vibrational levels to derive this important information about the molecule. Here, however, such an elaboration is not undertaken and the values of dissociation energy (D) in volts obtained by the usual extrapolation in which also the coefficient of v^3 is included, are given in Table VI in which also the vibrational function G(v) and the difference in energy (W) in volts, of the products of dissociation, are tabulated.

TABLE VI.

Red doublet system

Level	G(v)	D	W
Upper A $^2\Pi$	$363{\cdot}76v'-1{\cdot}16v'^2+0{\cdot}0012v'^3$	4·6	3·1
Lower X $^2\Sigma$	$360{\cdot}81v''-1{\cdot}01v''^2-0{\cdot}0010v''^3$	3·5	0

Orange system

Level	G(v)	D	W
Upper $^2\Sigma$	$361{\cdot}38v'-1{\cdot}68v'^2-0{\cdot}015v'^3$	1·5	2·1
Lower $^2\Sigma$	$364{\cdot}51v''-1{\cdot}46v''^2-0{\cdot}020v''^3$	1·5	0

It is clearly seen that the energy of dissociation is not the same for the lower levels assumed identical, of the two systems of bands. This is so because of the discrepancies already pointed out especially in the unharmonic constant, but after all it may be genuine. Though not so glaring, however, similar discordant results are already met with especially in other alkaline earth halides.[4] In the absence of any experimental evidence to the contrary, we have to assume that the discrepancy is not genuine, and that the two levels are identical. However, more reliance has to be placed on the values obtained by the use of Q heads both for the vibrational function and the dissociation energy. The value 3·5 volts is of the right order of magnitude for the dissociation energy of the normal state of the molecule, the corresponding values similarly calculated for BeF, MgF, CaF and SrF being 5·4, 3·7, 3·8 and 3·1 respectively. The energies of dissociation in the orange system are however assumed to be relatively correct with respect to each other.

Structure of the Molecule.

Quite empirically, these values can be correlated with the atomic states of the dissociation products equally well in two different ways. In the first place, a little calculation[11] will show that it is possible to get a correlation like the following:

Ground $^2\Sigma$ from Ca $(4s^2\ {}^1S_0)$ + Cl $(2p^5\ {}^2P^0{}_{3/2})$.
Excited $^2\Sigma$ from Ca $(4s\ 4p\ {}^3P^0{}_0)$ + Cl $(2p^5\ {}^2P^0{}_{3/2})$.
Excited $^2\Pi$ from Ca $(4s\ 4p\ {}^1P^0{}_1)$ + Cl $({}^2p^5\ {}^2P^0{}_{3/2})$.

But as we know to-day, this is rather fortuitous. The Ca atom in its ground state has a closed s^2 group of electrons which normally acts repulsively and therefore cannot link itself with a halogen atom which has five p-electrons, for the formation of a molecule unless through the operation of Hund's q-functions.[12] In other words, for such a linkage to occur it is essential that the wave-function of the s-electrons hybridises, that is to say, the electron acquires the properties of a p-electron and will then enter the common molecular orbital with the true p-electron of the halogen. It is shown that such hybridisation of s-functions does not take place in BeO or in CO_2.[13] It is therefore improbable in view of the absence of perturbations, in the observed bands, that such a linkage occurs for the formation of the CaCl molecule. It is also clear that this fortuitous coincidence arises from the fact that the Ca atom possesses already a number of terms near its ground level. Similar fortuitous coincidences can at once be predicted also for molecules formed by similar atoms. But if we pass on for instance to Cd (*i.e.*, an atom in the subgroup), we find that in CdF[5] such a correlation is entirely impossible. In this case the energy difference between the $^1S_0$ ground level of the atom and the first excited term $(^3P^0{}_0)$ is so big that it is nearly double the observed excitation energy of the products of dissociation of the molecule. Also in BeF and MgF such a correlation is not possible; the bond energies in the molecules are strong and the term difference $^3P-^1S$ of the metal atoms comparatively small; the energies of excitation of the products of dissociation are about 30 to 40% higher than the energy of the resonance line of the atoms. Thus this type of hybridisation is not brought about at least in these molecules. Similar remarks apply to CO_2.

The second correlation which avoids these difficulties is the following. The normal state of the molecule arises out of Ca $(4s\,4p\ ^3P^0_0)$ + Cl $(^2p^5\ ^2P^0_{3/2})$. In this state, the molecule has a dissociation energy of 3·5 volts. In the excited $^2\Pi$ level which lies at 1·99 volts, the dissociation energy increases to 4·6 volts. Therefore the energy difference between the products of dissociation is $4{\cdot}6+1{\cdot}99-3{\cdot}5=3{\cdot}1$ volts. Actually in Ca we have the anomalous term $(4p^2)\ ^3P_0$, 2·87 volts above the $(4s\,4p)\ ^3P^0_0$ term. The agreement can be said to be satisfactory. It may be pointed out however that the anomalous term $(3d\,4p)\ ^3D_0$ which is 2·84 volts above the $^3P^0_0$ term fits equally well. In any case, this correlation definitely proves that in this as in similar other molecules,[4] the term with a dissociation energy higher than in the ground level, always arises out of an *anomalous* term. The upper $^2\Sigma$ level is, as is shown by the orange system at 2·1 volts with a dissociation energy of 1·5 volts. The lower level $^2\Sigma$ of this system also yields the same dissociation energy. (As explained above, values deduced from the same band system are comparatively more reliable for the two levels.) Thus the difference in energy of the products of dissociation in the two states is $1{\cdot}5+2{\cdot}1-1{\cdot}5=2{\cdot}1$ volts. The term $(4s\,5s)\ ^3S_1$ in Ca lies 2·04 volts above $(4s\,4p)\ ^3P^0_0$. The agreement is remarkably good. Here, the only existing linkage is due to the 5*s* electron of Ca and one of the *p*-electrons of Cl. With due reservation then, we may say that the existence of the molecule in this state indicates that these two electrons possess bonding power or enter the same molecular orbital even if their wave-functions, here the *s*- and *p*-functions respectively, are not identical.

Note :—

Since the above was written, there came to hand a paper[14] which partly deals with the band systems of the CaCl molecule. In this paper the author has proposed that the $v'\,v''$ assignment given by Hedfeld for the red doublet system which is also accepted here, should be increased on account of some more band heads observed by him. But it seems very likely that the whole of the $\Delta v = +1$ sequence and the bands at 15722·1 and 15727·8 cm.$^{-1}$ recorded there, are part of the CaO spectrum mentioned above. So also are certainly the weak bands recorded in Table X of his paper. Evidently the bands beginning from 15646·9 cm.$^{-1}$ are part of the $\Delta v = -1$ sequence of the above system of the CaO molecule. In view of this we do not propose to change the $v' v''$ assignment given here. The Olmsted bands are also newly recorded but on the whole they are rather fragmentary and the discrepancy between the constants for the final state of these bands and those for the ground level need not be seriously emphasised so that we assume that their final state is identical with the ground level of the molecule.

But it is interesting to find that a new band system originating at about 33686 cm.$^{-1}$ has been recorded. The data are meagre, only the o – o sequence being found. Some of these band heads show a doubling presumably of the ρ-type observed in the orange system. They are probably due to the transition from a $^2\Sigma$ level at 33686 cm.$^{-1}$ to the ground level of the molecule. If so, they throw considerable light on the question of the identity of the lower $^2\Sigma$ level of the orange system and the ground level of the molecule. It has been already pointed out above that the discrepancies in the constants of these two levels are rather glaring and a tentative explanation attributing the orange system to a transition from the upper excited $^2\Sigma$ level at about 4 volts to another lower but excited $^2\Sigma$ level situated at about 2 volts from the ground level of the molecule was put forward. Such an explanation was discounted in view of the absence of any trace of such a level at 4 volts. These new bands however definitely show that the explanation given is correct and that in reality the lower $^2\Sigma$ state of the

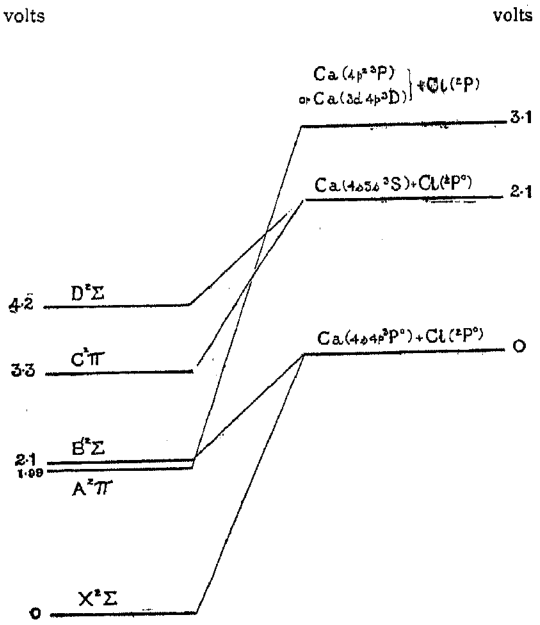

Fig. 3.

orange bands is not identical with the ground level of the molecule. On this basis we are now in a position to understand the spectrum and structure of CaCl in a more satisfactory way. We now know, therefore, *five* electronic levels of the CaCl molecule. Of these, X $^2\Sigma$, A $^2\Pi$ and C $^2\Pi$, have been correctly described already in literature. D $^2\Sigma$ is a new level discovered by Parker. The level till now recognised as B $^2\Sigma$, however, has no existence. Instead of this, the level B^1 $^2\Sigma$ which happens to have almost an identical excitation energy but differs from it widely in its constants and properties is newly located. This level is the final state of the orange system which has the new D $^2\Sigma$ for its initial state. Extrapolating for the energy of dissociation of the initial state of Olmsted bands and using the already calculated values of the dissociation energy in the various states of the molecule, we correlate them with the products of dissociation in Fig. 3, which is self-explanatory and which vindicates completely the structure of the molecule already described above.

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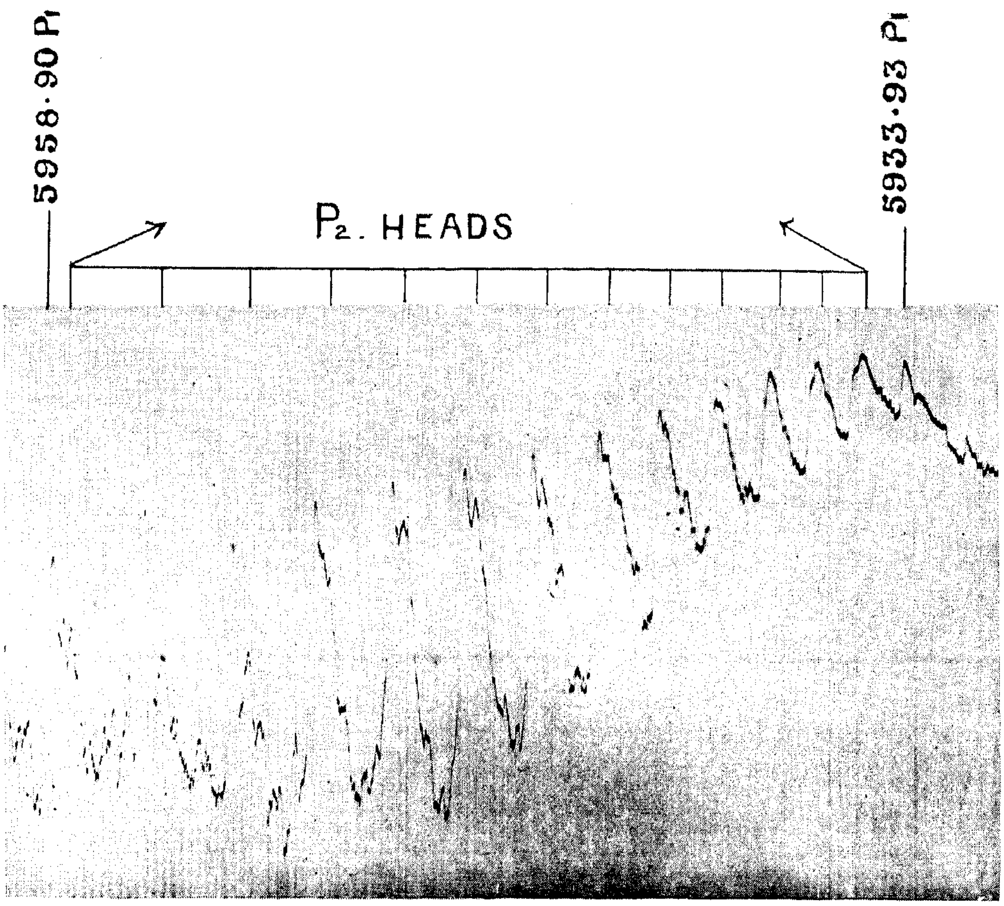
5958·90 P_1
P_2. HEADS
5933·93 P_1

Fig. 1.

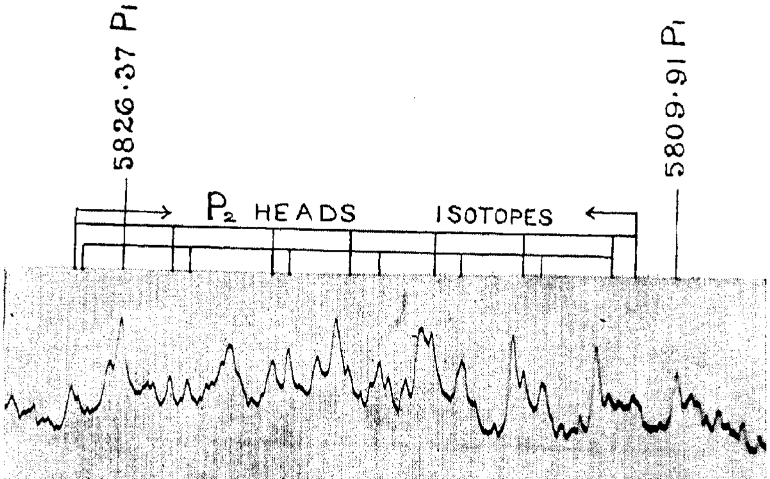
5826·37 P_1
P_2 HEADS
ISOTOPES
5809·91 P_1

Fig. 2.