Band Systems of MgCl, CaCl and SrCl

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A vibrational analysis has been made of band systems due to MgCl, CaCl and SrCl. There are two systems due to MgCl with $\nu_E{}^*=26{,}441.5$, $\omega'=474.8$ and $\omega''=447.4$ for the more intense system and $\nu_E=25{,}887.2$, $\omega'=466.9$ and $\omega''=447.4$ for the less intense system. CaCl has three extensive systems with $\nu_E=16{,}093.5$, $\omega'=367.1$, $\omega''=364.5$; $\nu_E=16{,}850.6$, $\omega'=361.0$, $\omega''=364.0$; $\nu_E=26{,}498.9$, $\omega'=336.0$, $\omega''=368.3$, respectively. There are also three weakly developed systems. Two strong systems of SrCl are observed with the respective constants $\nu_E=15{,}716.9$, $\omega'=306.3$, $\omega''=301.6$ and $\nu_E=25{,}245.5$, $\omega'=280.4$, $\omega''=300.6$. SrCl has three poorly defined systems as well. The isotope effect due to Cl^{35} and Cl^{37} is observed in all transitions.

The rotational structure is partially resolved for most systems, and in the ultraviolet CaCl bands sufficiently to estimate that $B'=0.24$ and $B''=0.26$. The electronic states and dissociation products are discussed. All values are expressed in cm^{-1}.

Introduction

The existence of many of the bands whose analysis is recorded here, has been known for a considerable time. Olmsted[1] photographed a number of them and Mecke[2] using his data made an analysis of certain of these. Walters and Barratt[3] photographed the bands of MgCl, CaCl and SrCl in absorption using a prism instrument, but made no attempt at analysis. Hedfeld[4] has analyzed the visible CaCl and SrCl bands using spectrograms taken in the first order of a twelve-foot grating.

No analysis has been reported previously of the MgCl bands. While analyzing these it seemed worth while to investigate the bands of CaCl and SrCl as well, improving the measurements and thereby the accuracy of the analyses.

Experimental Procedure

The SrCl, CaCl and MgCl bands were excited by means of an arc between a water-cooled nickel anode and a copper cathode in the form of a cup, the cup containing the anhydrous chloride whose diatomic spectrum it was desired to investigate. The arc current varied from 5–8 amperes with a 220 volt d.c. main. The arc was operated in a bulb containing helium, nitrogen or hydrogen at a pressure of 5–10 cm of mercury. Hydrogen was found to be the most suitable gas. The majority of the spectrograms were taken in the first and second orders of the twenty-one foot grating of Yale University, which is in a stigmatic mounting, giving a dispersion in the second order ranging from 2.2A/mm to a 2.5A/mm depending on the spectral region. Certain plates of CaCl were taken in the second order of the twenty-one foot grating of Columbia University which is in an astigmatic mounting and whose dispersion for the region and order investigated is 1.3A/mm.

The visible bands were photographed on Eastman hypersensitive panchromatic plates with the addition that the red SrCl band was also photographed on Eastman I-C plates. The ultraviolet bands were photographed on either Eastman 33 or Eastman 40 plates. The exposure times were of the order of fifteen minutes for the visible bands and several hours for the ultraviolet bands. An iron comparison spectrum was placed on each spectrogram.

The spectrograms were measured on the comparator of New York University, and I wish to thank Professor E. O. Salant for the opportunity of using it.

MgCl Bands

The existence of bands in the ultraviolet due to MgCl was reported by Olmsted.[1] The bands have two heads and degrade to the violet. We can therefore assign them as the P_1 and P_2 heads of a $^2\Sigma-{}^2\Sigma$ or a $^2\Pi-{}^2\Pi$ transition. The $\Delta v=0$, ±1, ±2 sequences are observed. The positions of the heads of the $MgCl^{35}$ band are

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* $\nu_E=\nu_{\text{head}}^{(-1/2,-1/2)}$

[1] C. M. Olmsted, Zeits. f. wiss. Phot. **4**, 255, 293 (1906).

[2] R. Mecke, Zeits. f. Physik **42**, 390 (1927).

[3] O. H. Walters and S. Barratt, Proc. Roy. Soc. **A118**, 120 (1928).

[4] K. Hedfeld, Zeits. f. Physik **68**, 610 (1931).

TABLE I. *Vibrational assignments of the P_1 and P_2 heads of MgCl.*

$v'-v''$	+1		0		−1		−2	
v''	P_2	P_1	P_2	P_1	P_2	P_1	P_2	P_1
0	26963.4	26958.0	26477.6	26455.0				
1	84.0		516.3	503.2	26033.6	26019.4		
2	27003.9	98.3	40.7	33.1	75.1	57.3		
3	23.0	27016.9	65.5	57.8	103.3		25643.3	25625.7
4	40.5	35.1	87.5	81.3	28.2	118.4	66.6	58.0
5	56.8	50.7	609.2	604.7	49.4		87.3	
6	75.3	68.8	27.3					
7	91.5		45.6					
8	104.8	99.0						

given in Table I, the $\Delta v=+2$ sequence being omitted as these bands were too weak for accurate measurements. From the $\Delta G(v)$ values given in Table II the following equation is set up:

$$\nu=26441.5+[474.8(v'+\tfrac{1}{2})-2.5(v'+\tfrac{1}{2})^2]$$
$$-[447.4(v''+\tfrac{1}{2})-1.6(v''+\tfrac{1}{2})^2].$$

A noticeable feature of these bands is the fact that bands involving the $v'=0$ level are markedly shifted from their normal position. This is doubtless due to a perturbation which has a maximum value at the head of the band. Further perturbations though not of the same magnitude exist in the $v'=7$ level and possibly $v'=8$ as well. Bands due to $MgCl^{37}$ are observed in the appropriate positions.

Besides the bands comprising this system, three others of quite appreciable intensity were observed whose frequencies are: 25,896.1 cm^{-1}, 25,915.1 cm^{-1} and 25,932.8 cm^{-1}. The assumption can be made that they are the (0,0), (1,1) and (2,2) bands, respectively, of a weaker MgCl system. Assuming that the final state is common to both systems we can fit them to the equation

$$\nu=25,887.2+[466.9(v'+\tfrac{1}{2})-2.3(v'+\tfrac{1}{2})^2]$$
$$-[447.4(v''+\tfrac{1}{2})-1.6(v''+\tfrac{1}{2})^2].$$

The bands observed by Querbach[5] in the region of 7800–8100A, which he thought might be attributed to MgCl, were sought by using Eastman I-N plates but the bands were not observed.

TABLE II. *Average $\Delta G(v)$ values for the X and B states of MgCl.*

v	0	1	2	3	4	5	6	7
X	445.6	442.3	438.0	435.9	431.3	429.5	429.7	
B	484.3	467.2	462.7	458.4	453.0	447.6	448.1	445.9

CaCl BANDS

CaCl has a number of band systems and of these three are well developed. Two systems in the red are observed with the $\Delta v=0, \pm 1$ sequences and one system in the ultraviolet with the $\Delta v=0, \pm 1, \pm 2, \pm 3$ sequences. The band system furthest to the red degrades to the violet and has four heads. Hence it is a $^2\Sigma$, $^2\Pi$ transition and the head-forming branches are the P_1, Q_1, P_2 and Q_2 branches. Table III lists the heads of this system due to $CaCl^{35}$. Several bands not recorded by Hedfeld[4] are observed in the $\Delta v=\pm 1$ sequences and therefore his (v', v'') assignments must be increased. Table IV contains the average $\Delta G(v)$ values for both Q branches. The equations obtained for the Q heads are:

$$\nu=16,093.5+[367.1(v'+\tfrac{1}{2})-0.91(v'+\tfrac{1}{2})^2]$$
$$-[364.5(v''+\tfrac{1}{2})-0.80(v''+\tfrac{1}{2})^2],$$
$$\nu=16,164.0+[355.3(v'+\tfrac{1}{2})-0.45(v'+\tfrac{1}{2})^2]$$
$$-[352.6(v''+\tfrac{1}{2})-0.33(v''+\tfrac{1}{2})^2].$$

Besides this system there is another system in the red as reported by Hedfeld, and our measurements agree with his for the most part. Each band has but a single head and hence we are led to assume that the system is a $^2\Sigma-{}^2\Sigma$ or a $^2\Pi-{}^2\Pi$ system with the same doublet splitting in both states. As the bands degrade to the violet, the heads are due to the P_1 and P_2 branches. The positions of the heads are recorded

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[5] J. Querbach, Zeits. f. Physik **60**, 109 (1931).

TABLE III. *Vibrational assignments of the P and Q heads of the A − X $CaCl^{35}$ bands.* The subscripts should be interchanged for this and subsequent band systems if the lower state is a $^2\Pi$ state instead of a $^2\Sigma$ state.

$v'-v''$	+1			0				−1			
v''	Q_1	P_2	Q_2	P_1	Q_1	P_2	Q_2	P_1	Q_1	P_2	Q_2
0	16452.0	16493.8	16509.9	16062.5	16094.8	16141.8	16164.3				
1	54.2	98.7	13.7	64.1	97.3	44.1	66.9	15704.7	15722.1	15782.0	15803.2
2	56.4	502.4	16.7	65.9	99.6	46.4	69.3	10.5	27.8	87.2	08.2
3	58.2	05.9	19.6	67.5	101.8	47.3	71.3	15.3	33.1	91.7	12.8
4	59.7		21.9	68.6	03.8		73.2	19.9	38.4	96.2	17.5
5	60.7		24.3	69.5	05.6		74.8	24.3	43.3	800.6	21.7
6	61.6		26.3	70.1	07.0		76.1	27.8	48.3	04.5	25.4
7	62.1		28.1		08.2		76.8	32.1	52.2	08.2	
8			29.5				78.1	35.6	56.3		
9			30.8				78.8	42.0	60.1		
10			31.7						63.7		
11			32.4						66.9		
12									69.9		
13									72.6		
14									75.0		
15									77.3		

TABLE IV. *Average ΔG(v) values for the Q heads of the A − X $CaCl^{35}$ transition.*

	X		A	
v	Q_1	Q_2	Q_1	Q_2
0	363.7	352.1	366.2	354.7
1	362.1	351.6	364.1	354.0
2	360.6	350.9	362.8	353.0
3	358.9	350.1	360.9	352.2
4	357.3	349.3	359.1	350.9
5	355.5	348.8	357.0	350.1
6	354.1		355.3	

in Table V for $CaCl^{35}$. In Table VI are given the values of $\Delta G(v)$ from which the following equation is derived for the heads:

$$\nu = 16{,}850.6 + [361.0(v'+\tfrac{1}{2}) - 1.2(v'+\tfrac{1}{2})^2] - [364.0(v''+\tfrac{1}{2}) - 1.0(v''+\tfrac{1}{2})^2].$$

In the ultraviolet there is a system of CaCl bands observed by Olmsted.[1] These bands exhibit four heads degrading to the red. These must be the R_1, Q_1, R_2 and Q_2 heads of a transition between a $^2\Sigma$ and a $^2\Pi$ state. The vibrational assignments for these bands are given in Table VII for the $CaCl^{35}$ molecule. The $\Delta G(v)$ values are recorded in Table VIII. By means of these we arrive at the following equation to represent the stronger Q heads

$$\nu = 26{,}498.9 + [336.0(v'+\tfrac{1}{2}) - 1.4(v'+\tfrac{1}{2})^2] - [368.3(v''+\tfrac{1}{2}) - 1.5(v''+\tfrac{1}{2})^2].$$

TABLE V. *Vibrational assignments of the P heads of the B − X $CaCl^{35}$ bands.*

$v'-v''$	+1	0	−1
v''	P	P	P
0	17207.0	16847.5	
1	00.0	43.3	
2	192.6	39.7	
3	84.6	35.7	16478.9
4	77.3	31.3	75.2
5	68.0	26.6	71.6
6	58.6	21.5	67.4
7		16.2	
8		10.5	
9		04.5	
10		798.0	
11		91.4	
12		84.2	
13		76.6	
14		68.5	
15		59.3	
16		51.5	

TABLE VI. *Average ΔG(v) values for the B − X $CaCl^{35}$ bands.*

v	0	1	2	3	4	5
X			358.9	356.9	355.3	352.9
B			354.9	352.5	350.5	347.8

The most interesting feature of these bands is that the rotational structure is particularly open. In fact as will be discussed later estimates can be made of B' and B''.

Table VII. *Vibrational assignments of the R and Q heads of the C—X* $CaCl^{35}$ *bands.*

v'	v''	0	1	2	3	4	5	6
0	R_2	26563.5						
	Q_2	26558.8	26191.8					
	R_1	26486.5						
	Q_1	26482.8	26115.4	25750.5				
1	R_2							
	Q_2	26893.4		26161.1	25793.6			
	R_1	26820.9				25368.8		
	Q_1	26816.4	26451.0	26084.5	25715.6	25364.2		
2	R_2		26856.7					
	Q_2	27216.6	26852.3					
	R_1		26785.2					
	Q_1	27141.1	26780.7	26419.7	26059.3	25694.1	25330.6	
3	R_2		27185.9	26820.9				
	Q_2		27183.8	26816.4				
	R_1	27460.1	27111.4					
	Q_1	27457.4	27108.7			26024.5	25667.0	
4	R_2							
	Q_2							
	R_1							
	Q_1			27073.1	26718.4		26003.7	25636.1
5	R_2							
	Q_2							
	R_1							
	Q_1				27040.8			
6	R_2							
	Q_2							
	R_1				27358.3			
	Q_1				27354.7			

Besides these well-developed systems there are several fragmentary systems. Walters and Barratt[3] observed CaCl bands in the ultraviolet beyond the system last mentioned. These bands were very weak in absorption and such was found to be the case in emission. Table IX gives the position of what is apparently the $\Delta v=0$ sequence of a group of single-headed bands arising from a $^2\Sigma-{}^2\Sigma$ or a $^2\Pi-{}^2\Pi$ transition with the same or negligible separations of the substates. For $v=2$, 8, 9 and 10, two heads are observed. This is probably due to perturbations in the upper state. There are a few additional weak bands in the region from 31,000 cm^{-1} to 33,000 cm^{-1} but not sufficient to form any definite sequence.

In the neighborhood of the red bands, there are two groups of weak bands comprising portions of two additional systems. One group apparently consists of two branches of a single sequence. The positions of these bands are given

Table VIII. *Average* $\Delta G(v)$ *values for the C—X* $CaCl^{35}$ *transition.*

v	0	1	2	3
X	360.6	364.1	361.3	358.4
C	334.4	332.2	326.7	

Table IX. *Vibrational assignments of the far ultraviolet* $CaCl^{35}$ *bands.* An atomic line partially obscures the (6,6) head.

v		
0	33685.6	
1	78.3	
2	68.2	64.9
3	52.7	
4	43.1	
5	31.7	
6	20.3	
7	07.7	
8	595.2	90.3
9	85.5	81.6
10	65.2	58.2
11	52.3	

TABLE X. *Additional weak bands of CaCl.*

16392.3	16408.9	15646.9
93.2	09.8	47.4
94.2	11.1	48.0
96.0	13.0	48.7
97.5	15.0	49.7
	16.7	50.6
	18.9	
	20.8	

in Table X. The small separation between the heads of the sequence shows that the ω values of the states involved are quite comparable. Another group of bands of similar spacing is also observed and likewise recorded in Table X. However these two groups cannot be related to one another except as the components of a $^2\Sigma$, $^2\Pi$ transition, for the separation between the two lowest bands bars the possibility of their being different sequences of the same system.

SRCL BANDS

SrCl gives rise to two intense band systems one in the red and one in the ultraviolet. The red bands for which the $\Delta v=0$, $\pm 1+2$ sequences are observed, exhibit four heads, P_1, Q_1, P_2 and Q_2. Table XI lists the bands of this system due to SrCl^{35}. From the $\Delta G(v)$ values in Table XII, we obtain the following equations for the heads of the Q branches:

$$\nu=15{,}109.5+[302.6(v'+\tfrac{1}{2})-0.82(v'+\tfrac{1}{2})^2]-[296.7(v''+\tfrac{1}{2})-0.93(v''+\tfrac{1}{2})^2],$$

$$\nu=15{,}716.9+[306.3(v'+\tfrac{1}{2})-0.76(v'+\tfrac{1}{2})^2]-[301.6(v''+\tfrac{1}{2})-0.63(v''+\tfrac{1}{2})^2].$$

The ultraviolet bands contain some members of the $\Delta v=2$ sequence as well as the $\Delta v=0$, ± 1 sequences. These bands degrade to the red and the four R_1, Q_1, R_2 and Q_2 branches form heads. These are listed in Table XIII for SrCl^{35} and the $\Delta G(v)$ values in Table XIV. The following equations may be deduced for the Q heads:

$$\nu=25{,}245.5+[280.4(v'+\tfrac{1}{2})-0.56(v'+\tfrac{1}{2})^2]-[300.6(v''+\tfrac{1}{2})-0.78(v''+\tfrac{1}{2})^2],$$

$$\nu=25{,}401.7+[279.3(v'+\tfrac{1}{2})-0.80(v'+\tfrac{1}{2})^2]-[298.9(v''+\tfrac{1}{2})-1.3(v''+\tfrac{1}{2})^2].$$

In addition to these bands several fragmentary systems are observed in the region of the red transition. These scattered sequences are apparently portions of three additional band systems. The positions of the various heads are given in Table XV for the best developed group.

TABLE XI. *Vibrational assignments of the $A-X$ SrCl^{35} bands.* As remarked above, the subscripts must be interchanged if the ground state is the $^2\Pi$ state.

$v'-v''$	+1		0		−1		−2
v''	Q_1	Q_2	Q_1	Q_2	Q_1	Q_2	Q_1
0	15420.6	16028.6	15115.3	15721.6			
1	25.1	30.4	22.5	26.5	14821.8	15422.1	
2	29.6	32.9	29.3	30.8	28.7	27.1	14529.2
3	33.8	34.6	36.0	35.1	35.6	31.8	38.9
4	39.8	36.5	42.6	39.0	42.7	36.5	48.1
5	42.4	38.4	48.9	43.1	49.4	41.0	56.4
6		39.9	55.6	46.9	55.9	45.2	
7		41.5		50.3	62.5	50.1	70.0
8		43.0				55.2	
9						59.2	
	P_1	P_2	P_1	P_2	P_1	P_2	
0	15401.5	16007.6	15101.2	15712.8			
1	06.4	09.9	07.2	17.3	14797.7	15401.5	
2	11.2	12.7		21.6	804.6	06.4	
3	16.0	15.0		25.6	11.8	11.2	
4		17.0		29.6	18.6	16.0	
5		18.8		33.4			
6		20.4		37.2			
7		22.0					

TABLE XII. *Average $\Delta G(v)$ values for the Q heads of the $A-X$ $SrCl^{35}$ transition.*

	X		A	
v	Q_1	Q_2	Q_1	Q_2
0	300.8	295.8	305.8	301.8
1	299.5	294.1	303.8	300.0
2	298.4	292.4	302.7	298.4
3	297.1	290.3	301.0	296.9
4	295.7		299.8	
5	294.7		298.5	
6	293.2		296.6	

Here we appear to have two sequences of a system, presumably the $\Delta v=0, -1$ sequences, which forms but one head. Besides these there are two groups, listed in Table XV, which cannot be correlated with each other or with the stronger group. One of these groups is single-headed and the other double-headed. The positions of the bands, the magnitudes of the separations between the bands of a sequence or the increase or decrease in the values of these separations prohibit the correlation of these groups either with one another or with the strong band system in this region. The fact that Walters and Barratt failed to observe them in absorption may be due to their low intensity or to the fact that the lower state of these bands is not the ground state of the SrCl molecule.

CaCl ROTATIONAL STRUCTURE

With few exceptions all the bands whose analysis is given above exhibit partially resolved rotational structure. In the near ultraviolet CaCl system, the rotational structure was more completely resolved than in any of the other band systems. The rotational structure of the (0,0) band was especially noticeable as the two P branches are completely resolved to the origin which is quite remarkable for a molecule both of whose atoms have atomic weights of this magnitude. A number of weak lines associated with the P_1 and P_2 lines of high J value are of the appropriate intensity for lines due to $CaCl^{37}$

TABLE XIII. *Vibrational assignments of the $B-X$ $SrCl^{35}$ bands with subscripts provisionally indicated.*

$v'-v''$	+1		0		−1		−2
v''	Q_2	Q_1	Q_2	Q_1	Q_2	Q_1	Q_2
0	25673.5	25514.8	25392.0	25235.5			
1	52.7	494.1	72.8	15.3	25097.3	24934.8	
2	30.9	72.4			80.7	16.4	
3	12.0	52.1			57.2	898.9	
4		32.2			40.5	80.7	
5					22.6	63.1	24747.6
6						45.7	32.8
7							17.9
8							03.1
9							689.0
10							74.5
11							60.5
12							46.6
	R_2	R_1	R_2	R_1	R_2	R_1	R_2
0	25678.5	25520.6	25396.9	25240.2			
1	58.5	498.7	78.1	20.3	25102.5	24940.5	
2	37.8	77.2			085.8	22.2	
3	16.8	55.6			63.3	04.1	
4					46.2	886.0	
5					30.1	68.5	24754.4
6					13.1	50.7	
7							
8							
9							
10							681.6

TABLE XIV. *Average $\Delta G(v)$ values for the Q heads of the $B-X$ $SrCl^{35}$ transition.*

	X		B	
v	Q_1	Q_2	Q_1	Q_2
0	297.7	300.1	278.5	279.9
1	292.1	299.0	279.9	278.8

and they are in the appropriate position for these lines. The P_1 and P_2 lines for both $CaCl^{35}$ and $CaCl^{37}$ are given in Table XVI. The fact that the bands have four heads indicates that they are due to a transition between a $^2\Sigma$ and a $^2\Pi$ state. We may estimate the values of B' and B'' in the following manner. For such a transition, the separation of the P lines near the origin is approximately $B'+B''$. The separations of the heads of the R branches from their respective origins is given by the expression

$$\nu(R_{\text{head}}) = -(B'+B'')^2/4(B'-B'').$$

By means of these two relationships we can deduce that:

$B''=0.26$ cm^{-1}
$I''=106(10)^{-40}$ g cm
$r''=1.86(10)^{-8}$ cm
$\omega r^3=2340$ cm^2

$B'=0.24$ cm^{-1}
$I'=115(10)^{-40}$ g cm
$r'=1.93(10)^{-8}$ cm
$\omega r^3=2430$ cm^2.

The values of B'' and B' are the average of the values obtained from the sub-ones and the sub-twos. An approximate value of A can be secured from the separation of the lowest P lines, assuming negligible splitting in the $^2\Sigma$ state. On this basis A is 77.4 cm^{-1}. Hence $Y=|A|/B$ is 310 and we see that the $^2\Pi$ state is close to case a.

ELECTRONIC STATES

In Table XVII the following constants: ν_E, A^*, ω_h, $x_h\omega_h$, r, D and $\nu_E+D'-D''$ are collected for the various alkaline-earth chlorides. A^* represents the separation of the two substates as determined from the separation of the two (0,0) bands and is not the true A value unless one of the electronic states involved has negligible doubling. The values of r are estimated from the empirical relationship that ωr_e^3 is approximately 3000. The values of Fredrickson and Hogan[6] for BeCl are included in this table as are the values of the writer[7] for BaCl. The bands of BeCl previously reported in an abstract[8] have since been found to be spurious. From the work of Walters and Barratt we know that the bands,

TABLE XV. *Additional weak bands of SrCl.* The two missing heads in the first sequence are due to superposed atomic lines. The first two sequences may be correlated with the v numbering shown.

$v'-v''$	+1	0			
v''	P	P	P	P	P
0	16164.5	15470.8	16469.4	16475.1	16846.9
1	67.0	75.3	50.5	55.2	43.4
2	69.4	79.4	31.8	34.7	39.7
3	71.8	83.3	14.5	17.0	35.3
4	73.2	86.9	398.3	02.6	31.1
5	74.9	90.5	85.3	389.7	26.0
6	76.1	94.1			21.2
7		97.7			15.5
8		501.0			10.0
9		04.1			804.0
10					797.7
11		10.4			90.9
12		14.1			
13		16.8			
14		19.7			
15		22.6			
16					
17		27.7			
18		30.5			

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[6] W. R. Fredrickson and M. E. Hogan, Jr., Phys. Rev. **46**, 454 (1934).

[7] A. E. Parker, Phys. Rev. **46**, 31 (1934).

[8] A. E. Parker, Phys. Rev. **45**, 752 (1934).

TABLE XVI. *Rotational assignments of the P lines of the (0,0) band of the near ultraviolet C−X CaCl system.* M is used as the quantum number since the proper J values cannot be determined.

	P_1		P_2	
M	$CaCl^{35}$	$CaCl^{37}$	$CaCl^{35}$	$CaCl^{37}$
0	26473.43		26550.76	
1	72.91		50.26	
2	72.38		49.72	
3	71.80		49.12	
4	71.09		48.55	
5	70.36		47.93	
6	69.68		47.35	
7	68.92		46.72	
8	68.27		46.09	
9	67.58		45.40	
10	66.80		44.69	
11	65.97		43.97	
12	65.30		43.23	
13	64.37		42.47	
14	63.50		41.71	
15	62.72		40.99	
16	61.74		40.17	
17	60.95		39.35	
18	58.86		38.51	
19	57.91		37.65	
20	57.19		36.78	
21	56.17		35.88	
22	55.23		34.98	
23	54.08		34.01	
24	53.02		33.10	
25	52.01		32.15	
26	50.95		31.21	
27	49.65		30.20	
28	48.28	26450.17	29.16	
29	47.19	48.74	28.18	
30	46.34		27.11	
31	45.27		26.08	
32	44.12		24.94	
33	42.87		23.87	
34	41.56		22.72	
35	26440.30	26442.08	26521.58	
36	39.08		20.46	
37	37.84		19.29	
38	36.60		18.08	
39	35.19		16.86	
40	33.83		15.55	
41	32.46		14.36	
42	31.04		13.07	
43	29.66	31.79	11.78	
44	28.18	30.31	10.52	
45	26.74	28.84	09.13	
46	25.32	27.37	07.91	
47	23.77	25.87	06.59	
48	22.27	24.43	05.12	
49	20.75		03.78	26505.82
50	19.22	21.52	02.32	04.38
51			00.92	
52			499.55	00.55
53			97.97	
54			96.43	498.56
55			95.00	97.09
56			93.48	95.58
57			92.11	
58			90.42	
59			88.87	91.18
60			87.08	89.57
61			85.81	88.13
62			84.08	
63			82.40	
64			80.75	
65			79.22	
66			77.60	
67			76.15	78.09
68			74.69	76.71
69			72.91	75.62

other than BeCl, involve the ground state of the molecule as they appear in absorption. Now Hedfeld has advanced the hypothesis that the ground state is a $^2\Pi$ state, on the basis of a comparable doublet separation of certain of the bands of particular molecules. This agreement is found in the case of only one chloride, CaCl, as is readily seen from Table XVII. BeCl and SrCl are represented by transitions between $^2\Sigma$ states and $^2\Pi$ states and it is impossible to decide which of these is the ground state. The bands of MgCl are either $^2\Sigma-{}^2\Sigma$ or $^2\Pi-{}^2\Pi$ transitions and here too no decision may be reached. In the case of BaCl which was discussed previously[7] the assignment of the lower state as a $^2\Sigma$ state may be made on the basis of the fact that the ultraviolet bands are a single-headed transition and hence are either a $^2\Sigma-{}^2\Sigma$ or a $^2\Pi-{}^2\Pi$ transition. If the latter is the case it would be extremely fortuitous if the A constants of the two states were identical as would be necessary for the production of a single-headed band system. However negligible spin-doubling of the $^2\Sigma$ states is to be expected and on this basis the assignments in reference 7 were made. The approximate agreement of the doublet separation of the ultraviolet CaCl bands and the $A-X$ red CaCl bands makes Hedfeld's hypothesis feasible for this molecule. But the single-headed $B-X$ CaCl bands must then be explained as a $^2\Pi-{}^2\Pi$ transition with identical A values for the two states which seems dubious.

TABLE XVII. *Constants of the alkaline-earth chlorides.* All values are expressed in cm^{-1} with the exceptions that r is expressed in Angstroms and that the atomic excitation, $\nu_E+D'-D''$ is also given in volts. A* represents the doublet separation of the bands.

	State	ν_E	A^*	ω_h	$x_h\omega_h$	r	D	$\nu_E+D'-D''$	
	A	27970.5		824.2	6.0	1.5	28,100	21,000	2.59
BeCl	X			846.6	5.1	1.5	35,100		
	B	26441.5	22.6	474.8	2.5	1.9	23,000	18,200	2.25
	A	25887.2		466.9	2.3	1.9	21,700	16,300	2.02
MgCl	X			447.4	1.6	1.9	31,300		
	D	33689		357					
	C	26498.9	76.0	336.0	1.4	2.1	20,200	23,600	2.91
	B	16850.6		361.0	1.2	2.0	27,400	11,600	1.45
	A	16093.5	70.5	367.1	0.91	2.0	37,000	11,800	1.46
				368.3	1.5	2.0	23,100		
				364.0	1.0	2.0	32,600		
CaCl	X			364.5	0.80	2.0	41,300		
	B	25245.5	156.3	280.4	0.56	2.2	22,500	18,800	2.32
	A	15716.9	607.4	306.3	0.76	2.1	30,800	7,400	0.91
				300.6	0.78	2.1	28,900		
SrCl	X			301.6	0.63	2.1	39,100		
	C	27097.3		311.5	0.93	2.1	25,500	34,600	4.27
	B	25496.9		304.6	1.04	2.1	22,300	29,800	3.68
	A	19450.1	387.2	285.0	0.79	2.2	15,800	16,800	2.08
				278.8	0.75	2.2			
				279.1	0.78	2.2			
BaCl	X			280.5	0.80	2.2	18,000		

DISSOCIATION PRODUCTS

The question of dissociation products is one of particular interest. The molecules whose constants are listed in Table XVII are all alkaline-earth chlorides. The lowest states of the Cl atom are the $(3p)^5\,{}^2P_{1/2,\,3/2}$ levels whose separation is 0.11 volt. The next lowest state of Cl is 9 volts higher. So we see that the atomic excitation differences, given by $\nu_E+D'-D''$ in Table XVII represent the excitation of the alkaline-earth atom. Now the accurate determination of this quantity depends on several facts. First there is the question of the effect of higher power terms in the expression for $G(v)$ which will certainly cause a decrease in D. This effect is to some extent minimized as the decrease in both states may make the relative change smaller. This might be expected to be the case for states such as those under consideration here. Then there is the question of the accuracy of the determination of $x_h\omega_h$. The dissociation energy is quite sensitive to small changes in $x_h\omega_h$ and so our values of the atomic excitation will be in error from this cause as well. Hence definite assignments of dissociation products cannot be made but estimates may be given.

Fredrickson and Hogan have correlated the excitation of the Be atom resulting from the dissociation of the two states of BeCl with the $(2s)(2p)\,{}^1P$ and $(2s)(3d)\,{}^1D$ levels of Be. These levels are separated by 2.70 volts. But this assignment is open to considerable question as they have since informed me by private communication. For equally good agreement between atomic and molecular values may be obtained by using the separation of the $(2s)^2\,{}^1S$ and $(2s)(2p)\,{}^3P$ states which is 2.70 volts or the separation of the $(2s)(2p)\,{}^3P$ and $(2s)(2p)\,{}^1P$ states which is 2.54 volts.

For the MgCl molecule it seems probable that the two excited states give rise to the same dissociation products. The best agreement with atomic spectra is the separation of the $(3s)(3p)\,{}^3P$ and the $(3s)(3p)\,{}^1P$ which lies 1.63 volts above it. The ground state of Mg is a $(3s)^2\,{}^1S$ state and it lies 2.69 volts below the $(3s)(3p)\,{}^3P$ state. It seems more probable that the molecular value is too high as a greater effect is to be expected for the higher order terms in the $G(v)$ equation for the excited state than for the ground state. Hence it seems probable that the first of the two possibilities is the correct one.

In the case of CaCl and of SrCl, no definite assignments may be made, while for BaCl this has been discussed previously[7] with the conclusion that the ground state of BaCl does not dissociate into a Ba atom in its ground state and that the probable products of the X and A states of BaCl are, respectively, $(6s)(5d)\,{}^1D$ and $(6s)(6d)\,{}^1D$ states of Ba.

For both MgCl and BaCl it seems likely that the ground state gives rise upon dissociation to an excited Mg and Ba atom, respectively. From the spectra of CaH, SrH and BaH, we know that the dissociation of these molecules gives rise to an excited atom. And by analogy we may assume that the same is true for CaCl and SrCl. Finally we may arrive at the conclusion that an atom in a ground $(ns)^2\,{}^1S$ state will not in general form a stable molecule. This fact has been previously discussed by Lessheim and Samuels[9] and others.

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[9] H. Lessheim and R. Samuels, Zeits. f. Physik **84**, 637 (1933).

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The Band Spectra of the Hydrides of Lithium

Part I: Li$^{(7)}$D

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The ${}^1\Sigma\rightarrow{}^1\Sigma$ spectrum of LiD has been photographed in absorption in the second order of a 21-foot grating giving a dispersion of 1A/mm. The spectrum is a headless concourse of lines stretching from λ3200 to λ4300A. About 80 percent of the lines (over 1400 in all) have been measured and assigned to 35 two-branch bands. The initial and final double differences, Δ_2F_v' and Δ_2F_v'', for Li$^{(7)}$D have been represented as functions of J by a semigraphical method; these represent the observed data on the average to within ± 0.023 cm^{-1} for the upper state and ± 0.019 cm^{-1} for the ground state. This gives $B_e'=1.6060$, $D_e'=4.8\times 10^{-4}$, $B_e''=4.2338$ and $D_e''=2.756\times 10^{-4}$. By using the rotational constants so determined the origins of the bands involved were computed and the values of $\Delta G'(v+\frac{1}{2})$ and $\Delta G''(v+\frac{1}{2})$ represented by least-square expressions in $(v+\frac{1}{2})$. The $\Delta G'$-values require a fifth degree polynomial while the $\Delta G''$ values are represented closely by a cubic. The corresponding expression for the origins of the whole system represents the data with an average deviation of ± 0.04 cm^{-1}. Here $\omega_e'=183.12$, $\omega_e'x_e'=-12.741$, $\omega_e''=1055.12$, and $x_e''\omega_e''=13.228$, with the electronic origin at $\nu_e=26{,}512.05$. The corresponding vibrational constants for Li$^{(7)}$H are computed from the simple isotope theory and although they differ considerably from the results of Nakamura, represent the isotope shifts within the rather large uncertainty involved. The question of possible l-uncoupling is examined and no *conclusive evidence is found for an appreciable l-uncoupling in either state of Li$^{(7)}$D.* This is contrary to the accepted interpretation of the anomalies of the spectrum.

INTRODUCTION

The spectra of the hydrides of the alkali metals are of unique interest among diatomic spectra because of the presence of certain anomalies. If we represent the total energy, E/hc (in inverse cm), of a rotating vibrator in the usual notation[1]

$$E/h_c=\nu_e+G(v)+F_v(J),\tag{1}$$

where

$$G(v)=\omega_v(v+\tfrac{1}{2})=\{\omega_e-x_e\omega_e(v+\tfrac{1}{2})+y_e\omega_e(v+\tfrac{1}{2})^2+z_e\omega_e(v+\tfrac{1}{2})^3+\cdots\}(v+\tfrac{1}{2})\tag{2}$$

and

$$F_v(J)=B_vJ(J+1)+D_vJ^2(J+1)^2+H_vJ^3(J+1)^3+\cdots.\tag{3}$$

Then in a normal band spectrum certain general-

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[1] Jevons, *Report on Band Spectra*, Cambridge, 1932. Here, to avoid confusion the coefficient of $J^3(J+1)^3$ in Eq. (3) has been written H_v instead of F_v.