THE EMISSION BAND SPECTRUM OF Cl_2^+

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Introduction

During the course of an attempt to excite the band spectrum of CbCl in a high frequency discharge through $CbCl_5$ vapour, the author has obtained an extensive band spectrum of chlorine, part of which has been analysed and attributed to the Cl_2^+ molecule by Elliott and Cameron (1937 and 1938). Of about 90 bands recorded by them in the visible region, 45 bands were arranged into two sub-systems on the basis of a $^2\Pi - ^2\Pi$ electronic transition. Though they confess that their vibrational arrays of both the systems were rather meagre, their assignment of vibrational quantum numbers was extensively supported by the observed chlorine isotope effect in both the systems. Further confirmation of the vibrational assignment was obtained by the rotational analysis of some of the bands belonging to a common level in a progression. In conclusion, Elliott and Cameron suggest that the remaining unclassified bands might belong to another doublet system or that the whole spectrum might consist of four sub-systems arising from a $^4\Delta - ^4\Delta$ transition. In view of this, the author felt that there is need for further investigation on the emission spectrum of chlorine.

Description and analysis of the bands

Owing to the free decomposition of the $CbCl_5$ into free chlorine and other products, the set-up of a high frequency discharge through low-pressure vapour proved a suitable method of excitation. The spectrum was photographed both

Table I

Vibrational analysis of Sub-system I of Cl_2^+ bands

v' \ v''	0	1	2	3	4	5	6	7
0		20120·7		18859·2				
1	21324·7							
2	21872·7		20595·0*	19971·7	19349·7			
3			21139·3	20509·2				
4		22302·4	21668·7	21040·9	20418·9		19192·3	18587·7
5	23457·7	22820·5	22186·2	21559·0		20320·8		
6	23967·1	23327·7	22694·0		21440·4	20827·9		
7			23184·6	22556·9	21936·2		20713·5	
8	24947·9	24308·4						20595·0*
9		24788·3	24148·2		22893·7			
10	25883·5	25242·2	24600·6		23354·7			

* Occurs twice in the system.

TABLE II

Isotopic Separations of the new Cl_2^+ bands

Wave-number.	Classification.	Isotopic separations.	
		Calc.	Obs.
20509·2 20514·7 i	3, 3	3·7	5·5
20595·0	2, 2	2·7	*
21132·6 i 21139·3	3, 2	4·6	6·7
21315·1 i 21324·7	1, 0	7·1	9·6
21433·5 i 21440·4	6, 4	6·9	6·9
21919·9 i 21936·2	7, 4	12·7	16·3
22168·5 i 22186·2	5, 2	17·3	17·7
22537·0 i 22556·9	7, 3	20·9	19·9
22868·0 i 22893·7	9, 4	23·5	25·7
23155·6 i 23184·6	7, 2	29·3	29·0
23327·4 i 23354·7	10, 4	28·3	27·3
23420·9 i 23457·7	5, 0	34·7	36·8
24554·1 i 24600·6	10, 2	45·1	46·5
24735·1 i 24788·3	9, 1	48·7	53·2
25184·4 i 25242·2	10, 1	53·6	57·8

* Too small to be measured accurately.

on a Fuess Glass Instrument and on the higher dispersion of a three prism Glass Littrow spectrograph. Plate II(*a*) and II(*b*) which are reproductions of plates taken on the latter, show the well-resolved rotational structure of most of the bands. For a detailed rotational analysis of the bands, still higher dispersion such as the first order of a 10 ft. grating is necessary. However, the dispersion of the Glass Littrow instrument was quite sufficient for a vibrational analysis of the bands.

A close scrutiny of the reproductions shown here with those published by Elliott and Cameron (1937) revealed the existence of many bands newly obtained

in the present investigation. Owing to the fact that the development of the vibrational schemes given by them is rather meagre, the author's first attempt was to see whether these new bands could form part of the two sub-systems. It was found that 30 new bands could be fitted into the vibrational scheme of sub-system I as shown in Table I. Half of these bands were due to the less abundant molecule $Cl^{35}Cl^{37}+$. The correctness of the assignment is proved not only by the fit of the bands in the band head formula

$$\nu = 20797{\cdot}3+[572{\cdot}3\,(v'+\tfrac{1}{2})-5{\cdot}32\,(v'+\tfrac{1}{2})^2-0{\cdot}013\,(v'+\tfrac{1}{2})^3] \\ -[645{\cdot}3\,(v''+\tfrac{1}{2})-2{\cdot}91(v''+\tfrac{1}{2})^2]$$

but also by the extensive agreement between the calculated and observed isotopic separations shown in Table II. Some of the prominent isotopic pairs newly assigned were shown in the reproductions II(a) and II(b). No new bands belonging to sub-system II were observed.

The intensity distribution in the bands (including those analysed in the present work) on a scale of 10 is shown in Table III. It can be seen that the distribution corresponds to a Franck-Condon parabola type to be expected for a system with such ω_e values as given above.

TABLE III

Intensity Distribution in Sub-system I

	0	1	2	3	4	5	6	7
0	..	2	..	3	..	..	..	..
1	8	..	..	..	..	..	..	..
2	4	..	6	4	2	..	..	..
3	..	..	5	4	..	..	..	..
4	..	2	7	8	4	..	1	1
5	4	8	6	5	..	4	..	..
6	3	7	6	..	6	7	..	..
7	..	..	5	6	6	..	5	..
8	3	4	..	..	..	..	..	6
9	..	6	7	..	2	..	..	..
10	3	5	4	..	7	..	..	..

For establishing the electronic transition of both the sub-systems a detailed study of the rotational analysis of some of the new bands using the higher dispersion of a 10 ft. grating is necessary. An attempt should also be made to interpret the origin of the large number of unclassified bands some of which are very intense. They may probably belong to the neutral molecule Cl_2. Further study of the spectrum in the visible and the near infra-red is still in progress.

The emission spectrum of bromine was also photographed in the visible region and further study in the near infra-red is in progress.

ABSTRACT

The emission spectrum of chlorine has been excited in a high frequency discharge tube containing a small quantity of $CbCl_5$ using a three prism glass littrow spectrograph. An examination of the spectrum revealed the existence of about 30 new bands attributable to Cl_2^+ in addition to those reported earlier by Elliott and Cameron. A vibrational analysis of these bands has shown that they belong to sub-system I of Cl_2^+ bands analysed by them on the basis of a $^2\Pi$-$^2\Pi$ transition. About 15 bands have been newly classified, the remaining being the isotopic heads due to the less abundant molecule $Cl^{35}Cl^{37}+$.

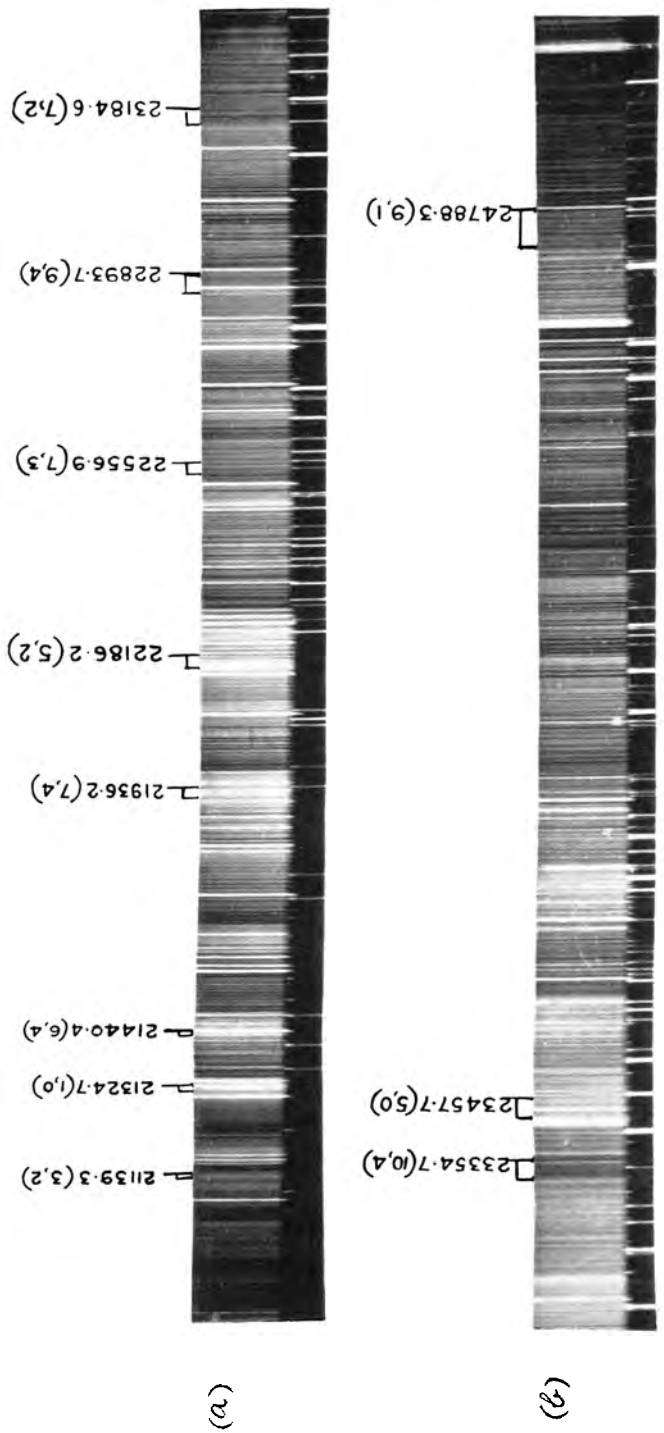

PLATE I. C^{+}_{2} emission bands: showing some of the newly analysed isotopic pairs. (Shorter limbs represent C^{13}_{6} C^{13}+ heads).

The vibrational assignment of each one of the bands is well supported by the observed isotope effect.

Further work to know the origin of the remaining unclassified bands in the emission spectrum of chlorine is in progress.

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