THE EMISSION SPECTRUM OF CHLORINE (Cl_2^+)

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Plate X

ABSTRACT. The emission spectrum of chlorine as excited in a high frequency discharge from a 100 watt oscillator, is photographed in the visible region on Fuess and Hilger glass Littrow spectrographs. Photographs of the spectra reveal many more new bands, especially on the longer wavelength side. New vibrational analysis for these bands has been proposed. Most of the bands have been arranged into three systems designated as Systems I, II, III, having the vibrational frequencies of the upper and lower states approximately in the ratio of 1 : 2. The following vibrational constants are derived.

	ν_e	ω_e'	$x_e'\omega_e'$	ω_e''	$x_e''\omega_e''$
System—I	20448.0	350.0	2.0	656.0	4.6
System—II	20736.0	375.0	2.6	656.0	4.7
System—III	20569.0	347.5	2.0	655.0	5.5

The occurrence of a fourth system consisting of the remaining unclassified bands is also suggested. From the equality of the vibrational constants of the lower states of Systems—I and II, it is concluded that they have a common lower level. The vibrational analysis of these emission bands is well supported by the observed chlorine isotope effect.

INTRODUCTION

In addition to its atomic line spectrum, chlorine has long since been known to emit a larger number of red degraded bands extending from λ6400 to λ3400. Ota and Uchida (1928) were the first to arrange them tentatively into three systems on the basis of their measurements of these emission bands. Later, Elliot and Cameron (to be referred to as EC) (1937) considered that some of the progressions in the vibrational schemes of Ota and Uchida are not genuine for want of sufficient accuracy in their measurement of band heads. These latter authors reinvestigated the spectrum under improved experimental conditions of excitation and were able to get more accurate measurements of band heads. They proposed the analysis of the bands as belonging to two sub-systems I and II having a common lower state, probably the ground state of the molecule. They suggested that the transition involved is, in all probability, a $^2\Pi$—$^2\Pi$, from a rotational analysis of some of the bands belonging to both the systems. They further claim that although their vibrational schemes are rather meagre, their vibrational assignments are well supported by the observed chlorine isotope effect and also from the rotational analysis of some of the bands. Because of the large number of unclassified bands in the spectrum, they, however, did not rule out the possibility of a quartet system arising from the transition ${}^4\Delta$—${}^4\Delta$.

However, there are certain inconsistencies in EC's analysis of these emission bands, some of which have been pointed out by Howell (1953).

(a) The intensity distribution of the bands in each of the systems is inconsistent with the values of ω'_e and ω''_e as derived from the analysis. Further, large number of gaps in the vibrational arrays suggest a fundamental weakness in their schemes. Also a large number of bands remain unclassified.

(b) The value of the energy of dissociation of the ground state common to both the systems, derived from the Birge Sponer extrapolation method, is obtained as 4.4 ev. as against 2.23 ev. indirectly obtained from the values of the ionisation potentials I of Cl and Cl_2 and the dissociation energy D of Cl_2. Because the ionisation potentials of Cl and Cl_2 and the dissociation energy of Cl_2 are now well established and known to be extremely reliable, Howell considers that the above discrepancy should rather be attributed to the incorrectness of the analysis of the bands proposed by EC.

(c) The derived values of B_e and ω_e' from EC's analysis are not consistent with each other. For different band systems of a molecule, the ratio B_e/ω_e should be approximately constant. For the neutral halogen molecules the ratio B_e^2/ω_e is found to be constant. From the derived values of B_e and ω_e of the upper and lower states, it can be seen that the constancy of the ratio B_e^2/ω_e fails badly.

On the basis of electron configurations and predicted term types for Cl_2^+, (Mulliken, 1934), the ground state electron configuration of Cl^+_2 is now accepted as

$$(\sigma+\sigma,\ \sigma_g)^2\ (\pi+\pi,\ \pi_u)^4\ (\pi-\pi,\ \pi_g)^3 \ldots\ldots {}^2\Pi_{3/2g},\ {}^2\Pi_{1/2g} \qquad \ldots\ (1)$$

The first two excited electron configurations are respectively

$$\sigma_g^2\ \pi_u^3\ \pi_g^4 \ldots\ldots\ldots\ {}^2\Pi_{3/2u},\ {}^2\Pi_{1/2u} \qquad \ldots\ (2)$$

and

$$\sigma_g\pi_u^4\ \pi_g^4 \ldots\ldots\ {}^2\Sigma_g^+ \qquad \ldots\ (3)$$

As can be seen from the configurations (2) and (3) an electron goes from a bonding orbital to an antibonding orbital. This means that the vibrational frequency of these excited states should be considerably reduced relative to that of the ground state. The derived ω_e' and ω_e'' values from EC's analysis are in disagreement with the above theoretical prediction. Further, according to the vibrational analysis proposed by the authors (1955) for similar bands in the case of bromine, the vibrational frequency of the upper state of both the systems are considerably lowered relative to the vibrational frequency of the ground state viz., ($\omega_e'' = 376$ common to both the systems, $\omega_e' = 190$ and 152 for systems I and II).

In view of the above discrepancies in the EC's analysis of the emission bands of Cl_2^+, and also the results of our investigation on similar emission bands in the case of bromine molecule, it is thought desirable to reinvestigate the visible emission band spectrum of chlorine. The experimental results and the details of the vibrational analysis are described in the following pages. A preliminary report of the details of the analysis has already appeared in *Current Science* (1956).

EXPERIMENTAL

In the present work the spectrum of Cl_2^+ is excited, as in the case of bromine, in an electrodeless discharge from a high frequency high power oscillator of 16 Mcs. frequency and about 150 watt output power. The discharge tube made of pyrex glass of length 30 cm. and diameter 18 cm. has two side tubes along its length which contain small quantities of cupric chloride. One end of the tube is cemented with a glass or quartz window by means of shellac, while the other end is drawn into an adopter for connecting to a system of high vacuum pumps through a liquid air trap. Chlorine is generated by electrical heating of cupric chloride contained in the side tubes of the discharge tube. An Edwards Speedivac oil diffusion pump of single stage backed by a Cenco Hyvac pump provides a system to maintain chlorine at low pressures in the discharge tube. The pressure is also regulated by adjusting the current in the circuit of the heating coil. The current is so adjusted that a bluish emission free from any traces of usual impurities is observed in the discharge column.

Hilger three prism glass Littrow and Fuess spectrographs are used to photograph the spectra on Ilford Special Rapid Panchromatic plates. About four to five hours on the Littrow instrument, and one and a half to two hours on the latter instrument are found necessary to give rise to intense spectra. The spectra recorded on the Littrow spectrograph reveal, owing to the high dispersion, an open rotational structure of the bands. For the vibrational analysis of the bands, measurements of band heads are taken on plates recorded on Fuess instrument having a smaller dispersion. Measurements of band heads are taken on a good number of plates and it is found that they agree within one cm^{-1}.

RESULTS

Table I records the band head data and their quantum assignment in the different systems. The isotopes of the neighbouring bands are marked by the letter (i) in the assignment columns.

TABLE I

Authors		E C		Assignment		
Wave-length	Wave-number	Wave-number	Int.	System I v', v''	System II v', v''	System III v', v''
6434.3	15537		1			
6410.1	15596		1			
6402 8	15614		1			
6366.3	15703		1			
6344.0	15759		1			
6335.2	15780		1			
6323.6	15809		2	3, 9		
6281.2	15916		2			
6267.0	15952		2			
6254.9	15983		2			
6244.7	16009		2			
6230.6	16045		2			
6219.4	16074		2			
6210.2	16098		3			
6201.9	16120		3			
6192.8	16143		3	4, 9		
6171.8	16198		2	i		
6149.2	16258		3			
6094.4	16404		3			
6070.0	16470		3	5, 9		
6051.8	16519		1	i		
6036.0	16563		2			
6026.6	16588		4			
6019.9	16607		4			3, 8
6013.6	16624		4	2, 7		
6003.6	16654		4			
5995.6	16674		4	i		
5981.1	16715		4	4, 8		
5964.4	16761		4	i		
5945.0	16816		4			
5934.4	16863		4			
5905.2	16929		3			
5894.5	16960		3	3, 7		
5865 0	17046		5	5, 8		
5850.8	17087		3	i		
5821.9	17172		4			3, 7
5805.5	17220		3	2, 6		i
5792.8	17258		3	i		
5779.8	17297		4	4, 7		
5767.1	17335		3	i		
5750.2	17386		2			
5738.0	17423		2			
5720.8	17475		4	—		
5706.0	17521		4			
5693.7	17558		5	3, 6		
5682.2	17594		4	i		
5676.7	17611		2			
5670.5	17630		4	5, 7		
5654.2	17681		4			
5645.3	17709		3			

TABLE I (contd.)

Authors		E C		Assignment		
Wave-length	Wave-number	Wave-number	Int	System I v', v''	System II v', v''	System III v', v''
5632.5	17749		2			3, 6
5616.6	17799		2			
5607.2	17829		2			
5603.8	17840		3		6, 8	
5587.0	17894		3	4, 6		
5582.6	17908		4			
5577.4	17924		1	i		
5545.4	18028		2			
5538.4	18051		3			
5519.1	18114		4			
5503.9	18164		4			6, 7
5494.2	18196		2			i
5479.4	18245		4			
5469.6	18278		3	7, 7		
5460.9	18307		2	i		
5442.7	18368		2			
5432.9	18401	18401.4	4			5, 6
5423.7	18432	18431.9	4			i
5396.9	18524	18522.0	6			
		18541.8				
5389.6	18549	18546.9	5	6, 6		
5382.6	18573		2	i		
5375.5	18598	18598.2	3	8, 7		
5368.0	18624		2			
5349.2	18689		2			
5337.4	18730		2			
5330.8	18754		3			
5324.6	18775	18777.3	3			
5318.5	18797		3			
5314.3	18812		2			
5310.1	18827		4	5, 5	9, 8	
5305.0	18845		3	i		
5302.3	18854	18858.6	3		i	
5297.4	18872	18873.4	5	7, 6		
5291.4	18893		2	i		
5264.5	18990		6			5, 5
5259.0	19010		4		6, 6	i
5255.3	19023	19024.3	2			
5244.6	19062	19061.2	2			
5238.4	19084		2		8, 7	
5230.6	19113		4			
5223.7	19138	19137.9	4			
5219.4	19154	19152.8	4	6, 5	10, 8	
5212.0	19181	19182.6	3			
5209.1	19192	19192.6	3	8, 6		
5202.4	19217		3			
5189.3	19265		3			4, 4
5184.2	19284		3			i
5175.6	19316	19311.8	4			6, 5
5171.0	19333		4			i

TABLE 1 (contd.)

Authors Wave-length	 Wave-number	E C Wave-number	Int.	 System I v', v''	Assignment System II v', v''	 System III v', v''
5167.9	19345	19349.4	3		7, 6	
5163.3	19362	19358 1	3		i	
5158 5	19380	19380.0	3			
5153.7	19398	19396.5	3			
5150.0	19412		4		9, 7	
5145.7	19428		2		i	
5136.4	19463	19463 1	3			
5132.5	19478	19479.7	4	7, 5		
5126.0	19503	19500 4	3			
5121.1	19522	19518 3	3			
5102 4	19593		2			5. 4
5099 3	19606		1			i
5094.9	19622	19624.0	2			
5080 8	19676	19676 1	7		8, 6	
5077 1	19691	19691 8	4		i	
5071 3	19713		3			
5065 4	19736		4		10, 7	
5059.8	19758	19758.8	5			
5049 6	19798	19800 3	2	8, 5		
		19816 0				
5023 4	19901	19903 2	4			
5020.1	19914	19913 3	6			
5010 5	19952		2			6, 4
5005.4	19973	19972.0	2			
5002 8	19983	19983.6	4			
4997.8	20003		1		9, 6	
4977 9	20083	20083.0	4			
4969.5	20117	20118.4	2	9, 5		
4940 7	20234	20228.2	4			7, 4
4924.6	20301	20300.1	5			
4918.1	20327	20323 8	2		10, 6	
4903.9	20386	20383 5	3			
4897 2	20414	20416.0	4	8,4		
4882.6	20475		2			
4870 5	20526	20524 1	6			6, 3
4852 5	20602	20595 6	5		9, 5	
4837.3	20667	20668 2	5			
4826.3	20714	20711.3	5	7, 3		
4822.5	20730		2	9, 4		
4818.3	20748		2			
4799.4	20830	20828 6	5			
4795.0	20849	20852.3	8			7,3
4786.7	20885	20885.5	4			
4777 2	20927	20927.2	5		10, 5	
4704.2	20984		4			
4751.0	21041	21041.7	8	10, 4		
4732.4	21125	21121.6	7			
4726.2	21153		7			6, 2

TABLE I (contd.)

Authors		E C		Assignment		
Wave-length	Wave-number	Wave-number	Int.	System 1 v', v''	System II v', v''	System III v', v''
4723.9	21163	21161 1	4			
4715.2	21202	21201.5	7			
4711.0	21221	21222.0	5			
4705.4	21246		3		11, 5	
4684.7	21340	21339 7	6	i		
4682.5	21349	21349.8	8	11, 4		
4677.1	21375		3			
4655.1	21476	21476.3	8			7, 2
4646.6	21515	21513 5	2			
4637.2	21559	21559.1	3		12, 5	
4616.3	21656	21659.0	6	i		
4613.6	21669	21668.7	6	10, 3		
4592.1	21770		2			i
4589 1	21785	21,783.0	4			8, 2
4579.4	21831	21831.5	5			
4571 3	21869	21872 2	1			
4552.6	21959	21959 0	7	i		
4549 1	21976	21976 4	8	11,3		
4521 1	22112	22111.5	4			
4509.7	22168	22168 5	6			
4506 2	22185	22186 2	6			
4491.3	22259	22260.3	4	i		
4487.0	22280	22277 3	5	12, 3 i		
4482.8	22301	22301.0	2	10,2		
4465 1	22390		3			10, 2
4462 8	22401	22402 7	2			
4459.2	22419		2			
4447.9	22476		3			
4442 4	22504	22504 5	5			
4437.6	22528	22529 3	3			
4433.7	22548		3			
4426 7	22584	22585 7	4	i		
4421 5	22610	22609 3	5	11, 2		
4410 4	22667	22671.5	4			i
4405 4	22694	22696.3	5			11, 2
4399.5	22724		2			
4385.6	22795	22793 0	3			
4381 2	22818	22819 7	3			
4371 3	22870		3			
4368 2	22886	22886.0	2	i		
4363.0	22914	22912.7	3	12, 2		
4358.9	22935		2			
4353.9	22061	22961.2	5			i
4348.5	22990	22990.0	3			12, 2
4341.3	23028		1			
4334 3	23065		2		i	
4330.6	23085		3		13, 3	.
4322.2	23130	23130.3	3	i		
4316 2	23162	23163.4	5	15, 3		
4309.0	23200	23200 9	3			
		23264.9				

TABLE 1 (contd.)

Authors		E C		Assignmentœ		
Wave-length	Wave-number	Wave-number	Int.	System I v', v''	System II v', v''	System III v', v''
4201.5	23295	23295.5	3			i
4285.6	23327	23327.4	4			11, 1
4278.2	23368		3			
4273 0	23396		3			
4264.1	23445	23444.7	2			
4259.5	23470	23474.0	2	i		
4252.9	23507	23509 9	4	14, 2		
4238.6	23586	23586 6	3			i
4231.7	23624	23624.2	4			12, 1
4207.4	23761	23762.0	2			
4201.6	23794	23797.2	6	i		
4194.4	23835	23833.3	6	13, 1		
4185 4	23886	23887 8	4			i
4178 7	23925	23925.2	5			13, 1
4177 6	23930		3		i	
4171 7	23964	23964.4	4		16, 3	
4148 2	24100	24102 3	5	i		
4140.5	24145	24147.3	6	14, 1		
4127 6	24220	24215.2	4			i
4119.8	24266	24265 9	6		i	12, 0
4112.7	24308	24308 7	5		15, 2	
4107.5	24339		2			
4091.3	24435	24425 4	3	i		
4083 3	24485	24484 8	4	13, 0		
4078.3	24513		2		i	i
4071 6	24553	24551.7	4		i	
4070.1	24562		3			13, 0
4064 4	24597	24596.9	5		16, 2	
4041.7	24735	24735.1	4	i		
4033.0	24788	24788.3	5	14, 0		
4024.2	24843		2			
4015.1	24899	24896 0	3		i	
4007.2	24948	24948 1	3		15, 1	
3979 7	25120	25122.6	3			
3969.8	25183	25180.3	4		i	
3961.5	25236	25236.2	5		16, 1	
3940.5	25370	25365.4	4		i	
3932.0	25425	25426.3	5		19, 2	
3926 3	25462		4		i	
3917.7	25518	25526.5	5		17, 1	
3890.0	25700	25699.8	4			
3881.3	25757	25757.3	5			
3871.7	25821	25819.9	4		i	
3862.6	25882	25882.4	5		16, 0	
3829.7	26104		4		i	
3820.7	20166		5		17, 0	

TABLE II

Vibrational scheme for System I

v' \ v''	0		1		2		3		4		5		6		7		8		9
2													17220* 338	596	16624* 336				
3													17558* 336	598	16960* 337				15809* 334
4													17894*	597	17297* 333	582	16715* 331	572	16143* 327
5											18827* 327				17630*	584	17046*	576	16470*
6											19154 324	605	18549 323						
7							20714		X		19478 320	606	18872 320	593	18279* 319				
8									20414 316	616	19798 319	606	19192	594	18598				
9									20730* 311	613	20117								
10					22301 309	632	21669 307	628	21041 308										
11					22610 304	634	21976 304	627	21349										
12					22914	634	22280												
13	24485 303	650	23835 310																
14	24788	643	24145	638	23507														

Note. Bands marked with "*" are newly obtained in the present work.
The place marked (X) is superposed by atomic line.

TABLE III

Vibrational scheme for System II

v' \ v''	0		1		2		3	4		5		6		7		8
6												19010* 335				17840*
7												19345 331				
8												19676 327	592	19084* 328		
9										20602 325	599	20003* 324	591	19412* 324	585	18827* 327
10										20927 319	600	20327	591	19736*	582	19154
11										21246* 313						
12								22168	609	21559						
13							23085*									
14								X								
15			24948 288	640	24308 289											
16	25882 284	646	25236 282	639	24597	633	23964									
17	26166*	648	25518													
18																
19					25425											

Note. The place marked (X) is superposed by atomic line.
Bands marked with "*" are newly obtained in the present work.

TABLE IV

Vibrational scheme for System III

v'' v'	0		1		2		3		4		5		6		7		8
3													17749*	577	17172*	565	16607*
4									19265* 328				X				
5									19593* 321	603	18990* 326	589	18401				
6					21153* 323	627	20526 323	612	19914 320	598	19316		X		18164*		
7					21476 309	627	20849	615	20234								
8					21785												
9					X												
10			X		22390* 304												
11			23327 297	633	22694 296												
12	24266 296	642	23624 301	634	22990												
13	24562*	637	23925														

Note. Bands marked with "*" are newly obtained in the present work.
The places marked (X) are superposed by atomic lines.

Photographs of the spectra of Cl^+_2 recorded on Fuess instrument are reproduced in Plate X. The spectrum extends from λ 6500 to λ 3400. All the bands are clearly red degraded. However, owing to the fall in intensity of the bands below λ 3800, they are not shown in the plate. The plate reveals a large number of additional bands, especially in the longer wavelength region of the spectrum which are not reported by EC. The bands which are bracketted in the plate are the isotope components belonging to the various systems.

VIBRATIONAL ANALYSIS

In the present investigations on the emission spectrum of chlorine, many more new bands especially in the region above λ 5200, and some additional bands in the central region of the spectrum have been obtained. This can be seen in Table I in which the measurements by authors are given in column one, while in column two those reported by EC are given for comparison. In view of this additional data obtained by the authors, it is considered worthwhile to attempt to analyse the bands in the light of the above predictions that were discussed for Cl^+_2. After a number of attempts, the following analysis seems to be a plausible one for the visible emission bands of Cl^+_2.

A prominent feature of the band spectrum is the presence of double headed bands especially on the short wave length side and in the central region. EC have indentified most of these double headed bands as due to the isotopic molecules $(Cl^{35}\,Cl^{35})^+$, $(Cl^{35}\,Cl^{37})^+$, from intensity considerations and also from a detailed study of the rotational analysis of some of the bands. The identification of these double heads as due to isotopes by EC is considered reliable.

With the ratio of the vibrational frequencies ω'_e and ω''_e being roughly 1/2, most of the bands could be arranged into three different systems designated here as Systems I, II, and III respectively. The location of the system origins and the assignments of the vibrational quantum numbers are made on the basis of the observed isotope separations in each case.

System I

System I consists of prominent double headed bands reported by EC. A few additional bands marked with * in its vibrational scheme, displayed in Table II are also found to belong to the same system. About 70 bands including isotopes are assigned to this system.

System II

The vibrational analysis of this system is presented in Table III. About half of the bands assigned in this scheme are those that are newly recorded in the present emission plates. About 50 bands including isotopic heads are assigned to this system.

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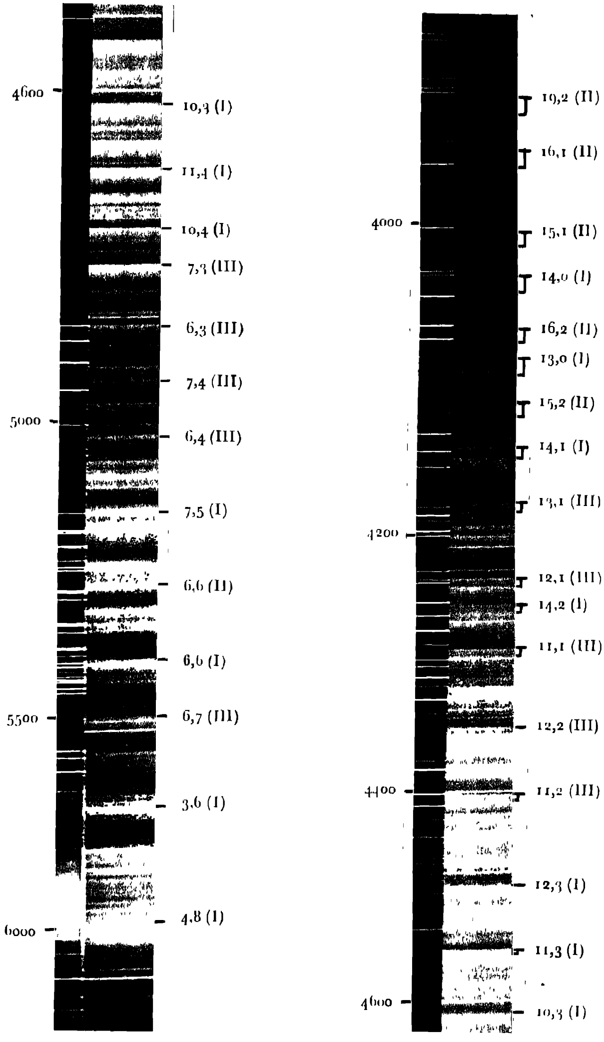
PLATE X



Emission spectrum of chlorine (Cl_2^+)

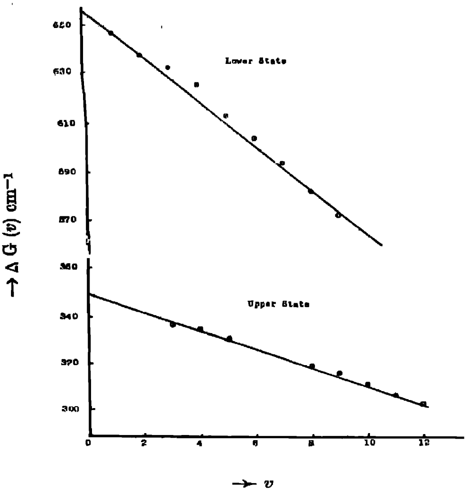


Fig. 1. System I

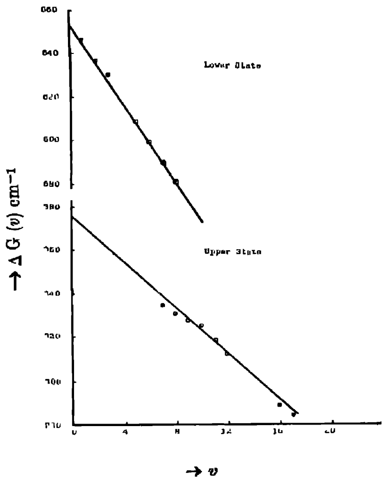


Fig. 2. System II

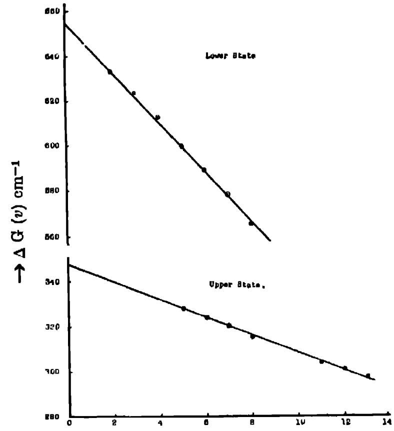


Fig. 3. System III

System III

The analysis of this system as shown in Table IV contains half of the bands that are newly recorded. About 50 bands including the isotopic components are found to belong to this system.

If linear curves are drawn by plotting the usual $\Delta G(v)-v$ values, the following vibrational constants for the above three systems, have been derived. The $\Delta G(v)-v$ curves are shown in figures 1, 2 and 3 for the three systems respectively.

Vibrational constants

	ν_e	ω_e'	$x_e\omega_e$	ω_e	$x_e\omega_e$
System I	20448.0	350.0	2.0	656.0	4.6
System II	20736.0	375.0	2.6	656.0	4.7
System III	20569.0	347.5	2.0	655.0	5.5

In addition to the bands assigned to the above three systems, there are some bands lying above λ 4400 and extending upto λ 6500 which could not be fitted into any one of these vibrational schemes. A recurring wave number interval of about 640 cm^{-1} among these bands suggests the possibility of yet another system in this region. No analysis could be presented for this system as its development is inadequate.

TABLE V

Isotope effect of chlorine

(Cl^{35}Cl^{35})$^+$ v' v''	(Cl^{35}Cl^{37})$^+$ Calculated Separation	Observed Separation
	SYSTEM I	
14, 0	53.2	53
13, 0	49.9	50
14, 1	44.6	45
13, 1	41.8	41
14, 2	36.2	37
12, 2	29.5	28
11, 2	26.1	26
10, 2	22.6	21
12, 3	21.3	21
11, 3	17.9	17
10, 3	14.4	13
11, 4	9.9	9
5, 5	20.4	18
7, 6	20.0	21
6, 6	23.9	24
4, 6	32.0	30
3, 6	36.2	36
2, 6	40.5	38
7, 7	27.2	29
4, 7	39.2	38
2, 7	47.7	50
5, 8	42.0	41
4, 8	46.1	46
5, 9	48.7	49
4, 9	52.8	55
	SYSTEM II	
17, 0	63.3	62
16, 0	60.6	61
17, 1	54.7	56
16, 1	52.0	53
15, 1	49.1	49
19, 2	53.4	55
16, 2	43.6	44
15, 2	40.7	42
16, 3	35.4	34
8, 6	14.5	15
7, 6	18.4	17
9, 7	17.8	16
9, 8	24.7	27
	SYSTEM III	
13, 0	49.5	49
12, 0	46.2	46
13, 1	40.9	39
12, 1	37.6	38
11, 1	34.2	32
12, 2	29.3	29
11, 2	25.9	27
10, 2	22.4	*
8, 2	15.0	15
7, 2	11.2	*
5, 4	12.6	13
5, 5	20.1	20
6, 5	16.1	17
5, 6	27.3	27
6, 7	30.1	32
3, 7	44.0	48
3, 8	49.2	47

Note: The places marked (*) are superposed by atomic lines.

REMARKS

The following points which arise from the vibrational analysis of the emission spectrum of Cl_2^+ are in accordance with the theoretical predictions for Cl_2^+.

The intensity distribution in each of the above analysed systems is of an open Franck-Condon parabola type, that could be normally expected when the two frequencies ω_e' and ω_e'' are approximately in the ratio of 1 : 2.

From the equality of the vibrational constants of the lower states of systems I and II, it may be concluded that the two systems, as in the case of bromine, may have a common lower state, which is most probably the normal state of the molecule Cl_2^+. Using Birge Sponer extrapolation method, the dissociation energy of the ground state is obtained as 2.8 e.v. This value, although an approximate one, comes nearer the indirectly determined value 2.23 ev. for the ground state of Cl_2^+.

As shown in Table V the observed isotope separations agree closely with those calculated from the formula for a large number of bands in all the three systems.

$$\nu^i-\nu = (\rho-1)[\omega_e'(v'+1/2)-\omega_e''(v''+1/2)]$$
$$-(\rho^2-1)[x_e'\omega_e'(v'+1/2)^2-x_e''\omega_e''(v''+1/2)^2]$$

ν^i is the wavenumber of the band head due to the less abundant molecule $(Cl^{35}\,Cl^{37})^+$, the more abundant molecule being $(Cl^{35}\,Cl^{35})^+$. For bands for which $\nu > \nu_e$ the interval $\nu^i-\nu$ is negative and for those for which $\nu < \nu_e$ the interval is positive. For the sake of convenience, the positive and negative signs are omitted in Table V. Because of the presence of four overlapping systems in the same region, a few of the isotope components of the bands belonging to one system coincide in position with those of the main bands belonging to one of the other systems.

If the emission bands of bromine reported earlier by the author are regarded as due to Br_2^+, a value of $\omega_e''(Br_2^+)/\omega_e''(Br_2)$ is obtained as 1.16. This is found to be equal to the ratio $\omega_e''(Cl_2^+)/\omega_e''(Cl_2)$ for each of the systems.

For the halogens the ratio B^2/ω_e is found to be approximately a constant for a pair of electronic states belonging to a system. Using the values of rotational constants B' and B'' obtained by EC it is found that the values of B^2/ω_e to be approximately constant for each of the above systems.

The rotational constants B_v' and B_v'' derived by EC from the combination relations are utilised by the authors to check the quantum assignments of band heads in the three systems. It is found that in each of these present systems, bands belonging to the same vibrational level (upper or lower) have the same values of B_v' or B_v'' respectively. This feature is shown in Table VI.

TABLE VI
Rotational constants

Band head	Assignment	B_v'	B_v''	Previous assignment
		SYSTEM—I		
21669*	10, 3	0.1753	0.2658	4, 2 (I)
21042*	10, 4	0.1770	0.2655	4, 3 (I)
21976	11, 3	0.1735	0.2650	5, 2 (II)
21350	11, 4	0.1733	0.2635	5, 3 (II)
		SYSTEM—II		
24948	15, 1	0.1645	0.2688	8, 0 (I)
25236*	16, 1	0.1668	0.2688	9, 0(II)
24308	16, 2	0.1640	0.2669	8,1 (I)
24597	16, 2	0.1660	0.2668	9, 1 (I)
25882*	16, 0	0.1615	0.2693	10, 0 (I)
26166*	17, 0	0.1598	0.2663	11, 0 (II)
		SYSTEM—III		
23327	11, 1	0.1693	0.2668	6, 1 (I)
23624	12, 1	0.1695	0.2665	7, 1 (II)
23924	13, 1	0.1658	0.2669	Unclassified
21476*	7, 2	0.1758	0.2640	Unclassified
22693	11, 2	0.1695	0.2655	6, 2 (I)
22990	12, 2	0.1698	0.2650	7, 2 (II)

The rotational constants for the bands marked with (*) are not accurate as was reported by EC.

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