Large Displacements of the Spectral Lines of Chlorine.

By

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In the course of an investigation of the spectrum of chlorine to classify the lines into arc and spark types, certain lines were found to suffer large displacements when the methods of the excitation were varied. This peculiar phenomenon attracted my interest, and the behaviour of lines in the region from λ 5457 to λ 2577 was investigated.

The study was carried out with the following two spectrographs:—

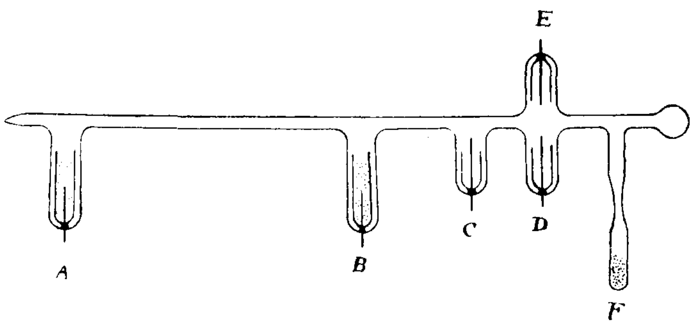
1. A five-prism spectrograph. This was constructed with five 60° glass prisms made by Hilger (length of the base 64 mm.), and an achromatic camera lens of 53 cm. focus. All the optical system of the instrument was placed in a wooden box, temperature of the enclosure being kept constant to within 0·1° C by an alcohol thermostat. This spectrograph was used to study the lines lying between λ 4585 and λ 3833, the dispersion on the photographic plate being about 0·085 mm. per 1 Å at λ 4570 and 0·266 mm. at λ 3833.

2. A concave grating of three meter focus. This was employed in the region from λ 5457 to λ 4585 and from λ 3833 to the ultra-violet, spectrograms being taken in the first order, and the dispersion was constant (0·181 mm. per 1 Å.) in the whole region investigated.

The vacuum tube used in this experiment was constructed in the following way:— A certain quantity of well-dried sodium chloride was put in a small glass cup having a platinum wire sealed in one end, and this was again sealed in an outer tube. Two tubes of such construction were connected to a main tube of about 3 mm. diameter, and 30 cm. in length, one end of which was blown out into a fine bulb. Besides these, another side tube containing a small quantity of well-dried cupric chloride was connected to the main discharge tube. During the evacuation of the tube, the glass walls were well heated, and a condensed electric discharge was sent through. After this treatment, the side tube containing the cupric chloride was properly heated and chlorine gas was driven out, and this was again evacuated to a suitable pressure. The tube was then sealed off from the pump when the discharge became bright. The tube thus prepared was excited by an electric discharge from a condenser of the capacity of about 0·008 μF charged by a 20 cm. induction coil. The image of an end-on emission from the tube was projected by an achromatic lens on the slit of the spectrograph, and the spectrum was photographed.

Next, a pair of carbon electrodes were seated in a suitable tube of fussed quartz filled with the chlorine gas at the pressure of one atmosphere, and the spark between the electrodes was produced in the gas by the discharge from the same condenser charged by a Thorderson transformer of 3/4 kVA giving 10,000 volts in the secondary. The spectrum of this spark was also photographed on one plate just below that of the Geissler tube. The plate thus obtained is reproduced in Fig. 1, (a) representing spectrum of Geissler discharge and (b) that of spark. Thus, it is observed that lines $\lambda\lambda$ 4573, 4570, 4277, 4271, 4254, 4241, 4236, 4234, etc. in the latter spectrum shift towards the red side as compared with the corresponding ones in the former.

Fig. 2.



It was also found that successive stages of these displcements were obtained when the pressure of the gas in the tube was varied gradually. The form of the tube employed is shown in Fig. 2. To the part of AB of the tube descrived above, another tube CDEF was connected, the distances between the electrodes B and C, C and D and D and E being 8, 2 and 0·4 cm. respectively, and the tube F containing a small quantity of cupric chloride.

First, the tube was well evacuated and an end-on emission from the tube produced by an electric discharge between A and B was photographed. Next, chlorine gas was so driven out by heating the cupric chloride that an electric discharge between B and C became very bright, and the light was photographed. This process was repeated, the pressure of the chlorine gas being increased step by step, and the spectra of the discharges between B and C, C and D and D and E were photographed one above the other on one plate. In these discharges, the condenser was charged by the 20 cm. induction coil, but it is obvious that the current desities were not the same. The plate thus obtained is reproduced in Fig. 3, in which I and V are due to the A-B discharge, and II, III and IV to the B-C, C-D and D-E discharge respectively. Unfortunately the pressures corresponding to each discharge were not measured, but the pressure in which V was taken was nearly of one atmosphere, because when the tube was broken in a pail of water after the experiment has finished, only a small quantity of water entered the tube.

The displacements of the lines in the spectrum of the spark were determined in comparison to the corresponding lines in the spectrum of the Geissler tube, the wave-lengths of the latter were taken from the tables given by Eder and Valenta[1] and Jevons[2]. In this measurement, the cross wires of a traveling microscope were set at the supposed centre of gravity of the line. But great difficulty was experienced in determining the centres of gravity on account of the diffuseness of the lines. Hence high accuracy of the readings could not be expected. The shifts from the non-shifted lines thus determined are given in Tables I, II and III.

Table I. Lines of the First Type—Arc Lines.

Wave-lengths of Non-shifted Lines	Shifted Lines			Eder-Valenta's Classification	Joseph Lunt's Classification
	Displacements of Centres of Gravity	Positions of Violet Edges	Breadths		
4661·38	0·35	−0·09	1·28	c	...
24·23	0·36	...	...	b	...
01·19	0·33	−0·12	1·63	a	...
4526·44	0·50	−0·09	1·65	a	...
4491·25	0·32	...	...	b	...
75·498	0·53	−0·21	1·04	c	...
69·569	0·40	...	...	c	...
46·096	0·38	...	...	c	...
38·735	0·30	...	...	c	...
03·610	0·34	...	...	c	...

1 Kayser, Handbuch der Spektroscopie. **5**, p. 307.
2 Proc. Roy. Soc., **103**, 193 (1923).

Table I. Lines of the First Type—Arc Lines. (Continued.)

Wave-lengths of Non-shifted Lines	Shifted Lines			Eder–Valenta's Classification	Joseph Lunt's Classification
	Displacements of Centres of Gravity	Positions of Violet Edges	Breadths		
4390·566	0·33	...	...	b	...
89·949	...	...	...	b	...
87·730	0·28 (?)	...	...	...	...
80·075	0·36	...	...	b	...
69·676	0·32	...	...	b	...
63·475	0·37	...	...	b	...
23·523	0·35	−0·15	1·26	c	...
4280·615	...	...	...	...	...
64·740	...	...	...	c	...
26·580	0·36	...	...	c	...
09·866	0·23 (?)	...	...	...	...

Table II. Lines of the Second Type—Spark Lines.

Wave-lengths of Non-shifted Lines	Shifted Lines			Eder-Valenta's Classification	Joseph Lunt's Classification
	Displacements of Centres of Gravity	Positions of Violet Edges	Breadths		
5457·28	0·48*	...	...	a	...
56·391	0·46*	...	...	a	...
44·412	0·50*	...	...	a	...
43·587	0·48*	...	...	a	...
23·441	0·50*	−0·36	1·68	a	...
5392·300	0·13	...	...	b	...
5285·8	0·15	...	...	...	...
21·48	0·17	...	...	b	...
18·07	0·18	−0·44	1·44	a	...
5113·3	0·15	...	...	...	...
03·18	0·14	...	...	b	...
5099·36	0·15	...	...	...	...
78·361	0·18	...	...	a	...
4995·7	0·36*	...	...	...	...
70·3	0·38*	...	...	...	...
27·3	0·41*	...	...	...	...
24·90	0·42*	...	...	...	...
17·870	0·14	...	...	b	...
04·905	0·15	...	...	a	...
4896·905	0·15	−0·65	1·82	...	...
19·628	0·15	−0·70	1·97	b	...
10·194	0·14	−1·45	3·12	b	...

Table II. Lines of the Second Type—Spark Lines. (Continued.)

Wave-lengths of Non-shifted Lines	Shifted Lines: Displacements of Centres of Gravity	Shifted Lines: Positions of Violet Edges	Shifted Lines: Breadths	Eder-Valenta's Classification	Joseph Lunt's Classification
4794·665	0·15	−1·57	3·46	b	...
85·41	0·14	...	...	...	...
81·49	0·15	...	...	c	...
79·06	0·14	...	...	c	...
71·22	0·20	...	...	...	...
68·80	0·16	...	...	c	...
55·9	0·36*	...	...	...	...
40·505	0·15	...	...	a	...
4585·05	0·29	...	...	...	...
37·0	0·67*	...	...	...	...
19·4	0·46*	...	...	...	...
04·50	0·45*	...	...	...	...
4497·45	0·66*	...	...	...	...
90·16	0·10	...	...	...	...
4399·373	0·18	...	...	b	...
73·119	0·10	...	...	b	...
43·822	0·15	−2·65	5·90	...	2
36·371	0·15	−0·75	1·82	c	2
33·125	0·11	...	...	...	...
09·189	0·24	...	...	b	2
07·593	0·25	...	...	c	2
04·211	0·25	−0·64	1·57	c	2
4291·861	0·20	−0·68	1·50	c	2
59·628	0·27	...	...	c	2
08·160	0·20 (?)	...	...	a	...
4158·021	0·22 (?)	...	...	b	2
32·680	0·27	...	...	a	...
04·965	0·36*	...	...	...	...
3991·625	0·19	...	...	b	...
82·060	0·27	...	...	...	...
61·770	0·26	...	...	...	...
55·582	0·27	...	...	..	...
3781·378	0·34*	...	...	c	...
74·324	0·18	...	...	...	...
73·813	0·18	...	...	...	...
69·187	0·16	...	...	...	...
68·228	0·16	...	...	...	...
67·647	0·17	...	...	...	...

Table II. Lines of the Second Type—Spark Lines. (Continued.)

Wave-lengths of Non-shifted Lines	Shifted Lines			Eder-Valenta's Classification	Joseph Lunt's Classification
	Displacements of Centres of Gravity	Positions of Violet Edges	Breadths		
3750·102	0·16	...	...	c	...
48·594	0·17	...	...	...	...
3673·9	0·18	...	...	...	...
63·948	0·18	...	...	c	...
59·913	0·17	...	...	c	...
58·499	0·18	...	...	c	...
50·243	0·18	...	...	c	...
3353·30	0·16	...	...	c	...
33·58	0·18	...	...	...	...
29·06	0·15	...	...	b	...
20·51	0·21	...	...	...	...
16·78	0·15	...	...	...	...
15·40	0·16	...	...	b	...
07·86	0·17	...	...	b	...
06·38	0·17	...	...	b	...
3283·32	0·15	...	...	...	...
76·72	0·15	...	...	...	...
59·24	0·18	...	...	...	...
47·52	0·16	...	...	...	...
44·36	0·16	...	...	...	...
3191·40	0·17	...	...	...	...
39·28	0·16	...	...	...	...
3092·14	0·15	...	...	...	...
71·31	0·13	...	...	...	...
2965·50	0·15	..	...	...	...
2691·49	0·18	...	...	...	...
88·03	0·14	...	...	...	...
85·40	0·15	...	...	...	...
76·92	0·14	...	...	...	...
65·52	0·15	...	...	...	...
61·56	0·14	...	...	...	...
58·74	0·13	...	...	...	...
24·72	0·16	...	...	...	...
20·08	0·15	...	...	...	...
16·99	0·13	...	...	...	...
03·50	0·16	...	...	...	...
2580·69	0·14	...	...	...	...
77·13	0·16	...	...	...	...

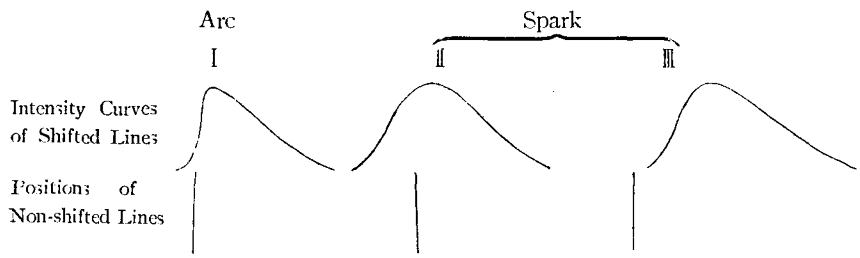
N. B. Lines marked with * suffered somewhat larger shifts than the other lines of the same type.

Table III. Lines of the Third Type—Spark Lines.

Wave-lengths of Non-shifted Lines	Shifted Lines			Eder-Valenta's Classification	Joseph Lunt's Classification
	Displacements of Centres of Gravity	Positions of Violet Edges	Breadths		
4572·79	1·81(?)	...	...	b	...
70·16	1·71(?)	...	...	...	...
4276·628	2·06	+0·53	3·37	a	1
70·725	2·10	+0·48	3·24	...	1
61·350	1·76(?)	...	...	b	1
53·532	1·85	+0·35	3·15	a	1
41·435	1·80	+0·45	3·02	a	1
35·608	1·72(?)	..	...	a	1
34·137	1·67(?)	...	...	a	1
25·139	1·93(?)	...	...	...	...
4147·203	...	...	...	a	...
24·153	0·83	...	...	...	...
3917·721	0·81	...	...	c	3
16·832	0·85	...	...	c	3
14·055	0·85	...	...	a	3
3884·045	0·88	...	...	b	3
68·844	0·89	...	...	c	3
61·008	0·88	+0·27	4·20	c	3
54·000	0·86	...	...	b	3
51·531	0·88	...	...	c	3
51·165	0·87	...	...	c	3
45·825	0·84	...	...	c	3
45·545	0·87	...	...	c	3
43·390	0·90	...	...	c	3
33·502	0·89	+0·14	2·82	a	3
29·550	...	...	...	...	...
27·802	0·89	...	...	...	3
20·404	0·88	...	...	...	3
10·215	1·14	...	...	b	...
09·697	1·11	...	...	...	3
05·384	1·12	+0·15	2·62	...	3
3725·912	0·88	...	...	...	...
3689·1	0·86	...	...	...	...
24·3	0·87	...	...	...	...
3576·211	0·83	...	...	...	...
68·03	0·87	...	...	b	...

The modes of the broadening of the affected lines may be classified into three types. The typical lines of the first type are λλ 4661, 4601, 4526, 4475, 4380, 4370, 4324, etc. All these lines are considered to be perhaps arc lines as the result of another experiment. The centres of gravity of these lines were shifted slightly to the red side. The lines are fairly sharp on the violet edge, but very diffuse on the other as shown diagrammatically by I in Fig. 4. The lines belonging to the second type are λλ 4820, 4810, 4795, 4344, 4336, 4304, 4292, 4133, etc., which are regarded as spark lines. They show no obvious displacements on mere inspection, the amount of the shifts of them being the smallest. The wings developed symmetrically on both sides as indicated in Fig. 4, II. The lines of the third type are λλ 4573, 4570, 4277, 4271, 4254, 4241, 3851, 3846, 3843, etc., and are worthy of special attention. These lines are considered to be spark lines, but they behave differently from the lines of the second type. The lines of this type lying in blue and violet were displaced about 2 Å towards the red side, while those in the ultra-violet region suffered a shift of about one half of the former. Even their violet edges are seen apparently displaced from the positions of the non-shifted lines, developing diffuser wings on the red sides as illustrated by Fig. 4, III.

Fig. 4.



Now, Eder and Valenta[1] determined the wave-lengths of chlorine lines emitted from tubes containing the gas at the pressures of 10-20 mm., 30-40 mm. and 70-100 mm. of mercury and observed the fact that, with the increase in the pressure, some of the lines became broadened especially towards the red side, some to both sides, while others remained sharp. In the above tables, such lines are indicated by a, b and c respectively. Some of them behaved similarly to ours, but many lines not.

Recently, Joseph Lunt[2] observed that certain lines of chlorine were subjected to large shifts when a condensed discharge was sent through a

1 Loc. cit.

2 Month. Not. Roy. Astronom. Soc., **85**, 148 (1924).

Geissler tube containing germanium tetrachloride or tin tetrachloride. He divided such lines into three classes. The first and second classes lie in the neighbourhood of Hγ, lines of the first showing a large displacement of about 0·8 Å, while the second only 0·1 Å. The lines belonging to the third class were found in the ultra-violet region, and suffered a shift of about 0·4 Å. In my tables, the lines thus classified by him are indicated by 1, 2 and 3 respectively. The lines of 1 and 3 are included in our Type III, and those of 2 correspond to Type II.

He considered that these large displacements of lines were caused solely by the changes in the temperature of the gas. But it seems to us that this phenomenon might be explained as the Stark broadening due to the field of ions in the large current flowing through the gas, as the current density in the case of the Geissler tube discharge was about 1·5 m. amp. per square mm., while in the spark discharge in chlorine gas at an atmospheric pressure, this was about 120 m. amp. per square mm.

Summary

1. Certain lines in the spectrum of chlorine were found to shift when the pressure of chlorine gas increased.

2. These lines were classified into three types, some of the lines belonging to one class suffering a shift of about 2 Å towards the red side.

The writer's sincere thanks are due to Professor M. Kimura for his kind guidance.

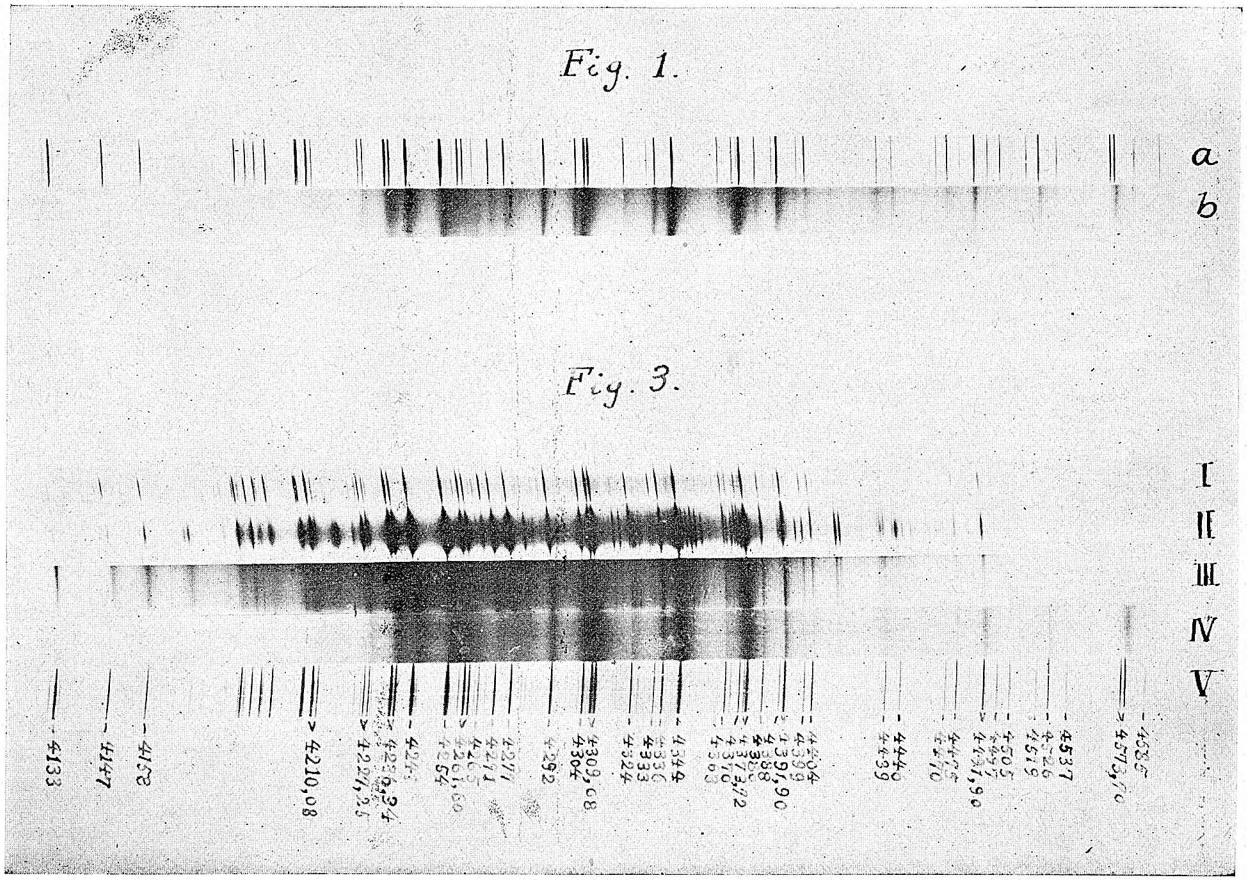


Fig. 1.
a
b
Fig. 3.
I
II
III
IV
V