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THE ARC SPECTRA OF IODINE, BROMINE, AND CHLORINE IN THE SCHUMANN REGION

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Abstract

The arc spectra of Cl, Br, and I have been investigated in the region between 2050 and 1230 A. U. Wave-length tables are given. 1396.5 and 1633.6 A. U. are the wave-lengths of the lines of longest wave-length of Cl and Br, respectively, and correspond to the previously known 2062.1 line of I. Doublet differences of 881, 3685, 7600 wave number units are found between lines of Cl, Br, and I spectra respectively and are thought to be the separations of the two levels of normal doublet p states of the atoms. The probable resonance lines are of wave-lengths 1379.6, 1540.8 and 1782.9 A. U. corresponding to radiating potentials of 8.95, 8.01, and 6.92 volts. No band spectrum of HCl appeared in the region investigated although the excitation was probably favorable for its production.

SEVERAL investigators[1,2,3] have observed four very intense spectrum lines, emitted by mildly excited iodine vapor, in the region of the shortest wave-lengths which can be photographed with a quartz spectrograph. Their great intensity and the conditions for their excitation[3] suggested that these lines were probably arc lines arising from transitions between low energy levels of the atom, and that more strong lines which might show simple spectrum relationships would be found in the Schumann region. The study of this region of the spectrum was made possible by Professor T. Lyman who very kindly permitted me to use his vacuum spectrograph.

APPARATUS AND METHODS

The vacuum spectrograph has been fully described elsewhere.[4] The grating was one of 1 meter focus with 15,000 lines to the inch, ruled by Professor R. W. Wood at Johns Hopkins University. Experience has shown it to give spectra nearly free from ghosts of the Lyman type. A fluorite plate was placed over the slit to prevent the halogen vapors from entering the body of the spectrograph, consequently the shortest wave-length which could be measured was about 1230 A.U. The grating was so set that the longest wave-length observed was 2050 A. U. The

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[1] E. B. Ludlam and W. West, Proc. Roy. Soc. Edinburgh **44 II,** 185 (1923–24).

[2] C. Füchtbauer and E. Holm, Phys. Zeits. **26,** 345 (1925).

[3] R. S. Mulliken and L. A. Turner, Phys. Rev. **25,** 886 (1925).

[4] T. Lyman, Astrophys. J. **50,** 1 (1924).

spectra were photographed in the first order, the dispersion being 16.84 A. U. per millimeter.

The discharge tube had tungsten wire electrodes and an internal capillary tube placed close to the slit (Fig. 1). For nearly all of the exposures a continuous current of 10–15 milliamperes supplied by an arrangement of a transformer, kenetron rectifiers, and a large condenser, was used. This type of apparatus favors the production of spectra requiring only moderate excitation, as has been found in work with other elements. That such is the case was shown in these experiments with iodine by the great intensity of the band spectrum in the visible region as observed through the outer end of the discharge tube. Furthermore, three of the lines previously known to be excited strongly by active nitrogen and in a carbon arc,[3] were among the strongest of the lines obtained with the continuous current. Consequently, the spectra produced with this excitation have been designated as arc spectra. Different spectra were observed when an ordinary condensed spark discharge was used.

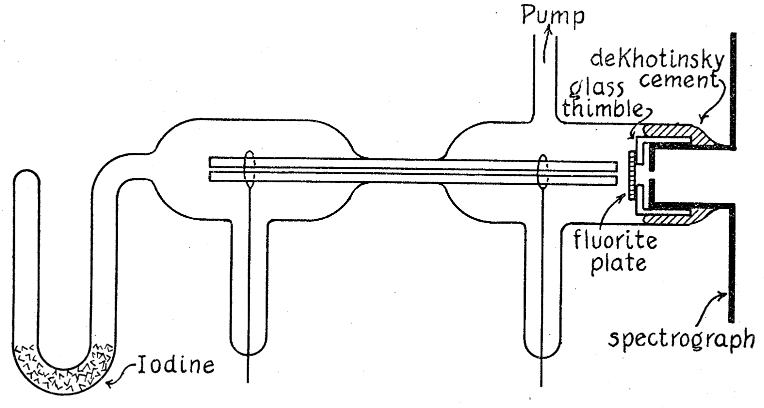

Fig. 1. The discharge tube.

Great difficulty was experienced with the frequent appearance, on the fluorite window, of thin films which were opaque to the light of short wave-lengths. The presence of a small amount of air or water vapor would cause the rapid appearance of such a film. The deKhotinsky cement, used to fasten the discharge tube to the spectrograph, was acted on by the halogen vapors and may have been a further source of impurities which caused these films. The region of the tube surrounding the positive electrode quickly became coated with a dark deposit but no such deposit formed around the negative electrode. Accordingly the electrode nearest the window was always made negative. It was found that the window would remain clean if the discharge tube were connected to the pump continuously through a liquid air trap. It was expected that these various impurities would give spectrum lines of their own but that such lines would be found in both the iodine and bromine spectra.

The standards of measurement used were lines of the many-line spectrum of hydrogen measured by Lyman[5] and the iodine line at 1876.40 measured by R. S. Mulliken and the author.[3] The wave-lengths of these hydrogen lines were originally estimated to be correct to within 0.3 A.U. but subsequent work has shown them to be considerably more accurate. The wave-lengths of the lines of the halogens should be accurate to 0.2 A.U.

IODINE

For obtaining the iodine spectra an appendix containing ordinary resublimed iodine was attached to one end of the discharge tube. It was kept in melting ice. The other end of the discharge tube was continuously connected to the pump through a liquid air trap. There was, therefore, a pressure gradient in the iodine vapor through the system, the maximum pressure being 0.03 mm. The flow of the iodine vapor tended to sweep out impurities. When the discharge tube was closed off from the liquid air trap the CO bands came out strongly and some of the strongest iodine lines were tremendously reduced in intensity. Others of the strong lines were apparently unaffected. The lines which show this reduction markedly are indicated in the list of lines of Table 1. This effect did not occur when the discharge was passed through a mixture of hydrogen and iodine. A few spectra were obtained with a different discharge tube having large external tinfoil electrodes, excited by the transformer alone. The spectra thus obtained were practically the same as those given by the continuous current discharge but of lower intensity. One exposure was obtained by passing a condensed spark discharge from a small transformer through the tube with the internal electrodes. In this exposure the fluorite window was quickly coated over but several strong new lines appeared on the plate. None of the most intense arc lines was present, however. The three lines marked with an asterisk in Table 1 were present in this spark exposure with moderate intensity, much less than that of several other new lines, however. No attempt was made to measure the wave-lengths of the spark lines because of the lack of a comparison spectrum for fixing the position of these lines with respect to the standards. Table 1 gives

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[5] T. Lyman, Memoirs Am. Acad. Arts and Sci., **XIII, III** (1906). Also "The Spectroscopy of the Extreme Ultraviolet."

TABLE I

Iodine

Intensity	Wave-length	Wave-number	Intensity	Wave-length	Wave-number
10	†2062.1	48494	5	1390.9	71897
7	1876.4	53293	3	1383.4	72286
9	1844.5	54216	0	1382.3	72342
10	+1830.4	54632	3	1368.3	73084
7	1799.2	55581	2	1367.7	73114
00	1789.6	55879	0	1366.6	73173
9	+1782.9	56089	5	1361.2	73465
8	1702.3	58744	3	1358.1	73631
1	1675.4	59690	6	1355.5	73775
7	+1642.5	60885	00	1354.3	73841
7	1641.1	60934	00	1352.4	73942
1	1639.2	61005	1	1350.3	74055
6	+1617.9	61809	1	1349.0	74128
6	1593.8	62742	1	1343.7	74420
1	1582.8	63179	2	1340.9	74579
1	1545.9	64685	0	1339.9	74631
4	+1526.6	65505	6	1336.7	74810
7	1518.3	65863	2	1330.4	75167
9	1514.8	66014	3	(1317.7)	75893
3	1507.3	66342	1	1314.1	76099
5	1493.2	66971	0	1313.6	76124
1	1486.1	67289	1	1303.2	76735
00	1466.7	68179	2	*1300.6	76888
5	1466.0	68210	0	1296.6	77127
6	1459.2	68528	1	1291.4	77437
6	+1458.2	68579	1	1289.6	77541
4	1457.6	68606	2	*(1286.3)	77742
4	1453.4	68806	0	1277.4	78281
5	1446.5	69131	2	*1275.7	78386
0	1429.7	69947	2	(1259.4)	79400
8	1425.7	70143	3	1234.2	81024
4	1421.6	70345			
3	1400.2	71421			
00	1395.0	71685			
2	1393.3	71769			

† This line lies outside of the region here investigated but previous work shows it to belong to this group. Its intensity is therefore uncertain, but is certainly much greater than that of 1876.4

+ Greatly reduced in intensity when the CO bands appear.

( ) Coincide with lines obtained with bromine.

* Possibly spark lines.

the estimated photographic intensities, the wave-lengths, and the wave-numbers of the arc lines.

BROMINE

Pure Kahlbaum bromine was placed in a small bulb which was connected to the discharge tube through a very fine capillary tube. As before, the discharge tube was connected continuously to the pump through a liquid air trap. The proper size of capillary to reduce the bromine pressure to the right amount was found by trial. The pressure was further adjusted by altering the temperature of the bulb and capillary so that a current of 10 milliamperes would flow through the tube when the conditions of excitation were the same as with the iodine. No attempt was made to measure the bromine pressure in the tube. If it were changed much either way the discharge would not pass. One spectrum was obtained with the condensed spark discharge. As with iodine, the strong lines of the spark spectrum were new ones. The strong arc lines appeared faintly. Table 2 gives the intensities, wave-lengths, and wave-numbers for the arc lines.

TABLE II

Bromine

Intensity	Wave-length	Wave-number	Intensity	Wave-length	Wave-number
10	1633.6	61214	0	1400.8	71387
8	1582.4	63194	0	1397.5	71558
6	1576.5	63432	0	1394.5	71710
9	1575.0	63492	0	1391.3	71875
6	1540.8	64902	8	1384.6	72224
7	1531.9	65277	1	[1379.6]	72485
8	1488.6	67176	0	[1363.5]	73341
0	1484.0	67383	0	[1351.7]	73981
2	1477.1	67699	1	[1347.3]	74224
0	1468.2	68111	0	[1335.6]	74869
0	1466.4	68192	6	(1317.8)	75884
4	1463.4	68336	5	1316.9	75937
0	1459.9	68498	5	1310.0	76335
1	1457.0	68633	1	(1286.4)	77735
3	1449.9	68968	2	1279.7	78145
0	1442.3	69335	1	1266.3	78969
0	1435.8	69646	1	1261.8	79253
2	1423.0	70276	2	(1259.4)	79406
2	1416.5	70597			
1	1411.5	70847	1	1255.9	79621
1	1410.1	70915	4	1251.8	79886
0	1407.1	71070	0	1249.7	80017
0	1405.1	71167	2	1244.0	80384
0	1403.6	71243	5	1232.5	81137

( ) Coincide with lines obtained with iodine.
[ ] Coincide with lines obtained with chlorine.

CHLORINE

It was not convenient to prepare and handle pure chlorine gas so the chlorine spectrum was obtained by the use of compounds. One set of exposures was made to a continuous current discharge in hydrogen chloride gas. The hydrogen chloride was generated by warming a mixture of potassium acid sulphate and sodium chloride, and was dried by passing it over phosphorous pentoxide. Its pressure was governed by the amount of warming and the adjustment of a stopcock. As with bromine the pressure was adjusted until it gave a discharge which behaved satisfactorily. The spectrum consisted of the many-line spectrum of hydrogen and seven strong lines. These same seven strong lines were the only prominent feature of a spectrum obtained from carbon tetrachloride which was used with a bulb and capillary in the same way as bromine. Consequently, the seven lines are ascribed to chlorine, the common element. Table 3 gives the data for these lines. Two of them agree within the limits of error with the two lines of wave-lengths 1351.6 and 1347.2 A.U. found by Millikan,[6] along with many other lines, in the hot-spark spectrum of chlorine.

TABLE III

Chlorine

Intensity	Wave-length	Wave-number
3	1396.5	71607
4	1389.9	71946
5	(1379.6)	72484
5	(1363.5)	73342
3	(1351.7)	73979
5	(1347.2)	74225
2	(1335.8)	74863

( ) Coincide with lines obtained with bromine.

It is of interest to note that there was no trace of a band spectrum which could be ascribed to the HCl molecule, although the excitation was probably most favorable for its production, if there is such a spectrum. Barker and Duffendack[7] found no band spectrum of HCl between 6000 and 2000 A.U. The present work places the lower limits at 1230 A.U. Apparently there is no electron transition in the HCl molecule of energy value between 2 and 10 volts. The non-existence of this band spectrum is in accord with Mulliken's[8] ideas concerning the instability of energized polar molecules.

IMPURITIES

It is not certain that all of the lines listed in the above tables actually belong to the elements to which they are ascribed because some of them may have been emitted by the impurities unavoidably present. Since the substances used were quite pure they must have resulted principally from contamination from the electrodes and the deKhotinsky cement. Any lines emitted by such impurities should appear in the spectra of all three elements. Three of the less intense lines which are common to the

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[6] R. A. Millikan, Phys. Rev. **23**, 1 (1924).

[7] E. F. Barker and O. S. Duffendack, Phys. Rev. **26**, 339 (1925).

[8] R. S. Mulliken, Phys. Rev. **26**, 29 (1925).

iodine and bromine spectra may be of this sort. The exposures made with the chlorine compounds were shorter so that these lines might not have shown on the plate even if present. The longest exposures were made with iodine so it may be that some of the weakest lines in its spectrum are those of such impurities but that they are not found in the bromine spectra because the exposures were too short to bring them out. Carbon and oxygen are probable impurities but their principal arc lines are not present. Five of the strong chlorine lines appear faintly in the bromine spectrum with the same relative intensities, indicating that the bromine used contained a small amount of chlorine. It is impossible, of course, to eliminate lines produced by an impurity present with only one of the halogens.

DISCUSSION

The most striking characteristic of these spectra is the progression of the long wave-length limits of the spectra towards longer wave-lengths with increasing atomic number. The minimum possible values of the radiating potentials, corresponding to the lines of longest wave-length, are thus fixed at 8.9, 7.6, and 6.0 volts for chlorine, bromine, and iodine, respectively. There are no indications of the convergence of iodine lines to a limit near 1400 A.U., the value corresponding to Smyth and Compton's[9] determination of the ionization potential of atomic iodine.

It was established by Paschen that the lines of the neon spectrum converge to two limits differing by 782 wave number units and Grotrian[10] showed the identity of these limits with the L x-ray absorption limits of the relativity doublet. Apparently the Ne^+ ion can exist in two different states differing in energy by an amount corresponding to the 782 wave number units. One would expect the neutral fluorine atom, having the same electron structure, to exist in two such states. The same should apply to the other halogen atoms which all presumably have similar outer structures. This is in accord with Pauli's[11] conclusion that the normal state of an atom lacking one electron from a completed group has the same multiplicity and inner quantum numbers as an atom having one extra electron of the same azimuthal quantum number. The normal state of these atoms should thus be a doublet p state. If it is double (or, to put it another way, if there is an excited state close to the normal one) the energy difference between the two states should show itself as a frequently recurring doublet difference between lines of these spectra.

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[9] H. D. Smyth and K. T. Compton, Phys. Rev. **16,** 501 (1920).

[10] W. Grotrian, Zeits. für Physik, **8,** 116 (1921).

[11] W. Pauli, Zeits. für Physik **31,** 765 (1925).

Each pair of lines corresponding to transitions from a given initial level to these two final levels should have this doublet difference.

The following differences, which are equal within the limits of the experimental error, are found between the wave numbers of the iodine lines. The estimated intensities are given in parentheses.

(9) 56089 − (10) 48494 = 7595
(7) 60885 − (7) 53293 = 7592
(6) 61809 − (9) 54216 = 7593
(1) 63179 − (8) 55881 = 7596
(3) 66342 − (8) 58744 = 7598
(6) 68528 − (7) 60934 = 7594
(4) 70345 − (6) 62742 = 7603
(3) 72286 − (1) 64685 = 7601
(5) 73465 − (7) 65863 = 7602
(00) 73942 − (3) 66342 = 7600
(2) 74579 − (5) 66971 = 7608
(0) 76124 − (6) 68528 = 7596

The fact that two of the lines appear twice indicates that some of these differences are the same purely by chance. On the other hand, the inclusion of so many of the strong lines is a point in favor of the reality and significance of this difference. Other recurring differences have been found but no other which groups as many lines or includes nearly as many of the strong lines of the spectrum.

Two such differences are found with the bromine lines. The wave numbers are as follows.

(9) 63492 − (10) 61214 = 2278
(10) 67176 − (6) 64902 = 2274
(0) 69646 − (0) 67383 = 2273
(1) 70915 − (1) 68633 = 2282
(0) 71243 − (2) 68968 = 2275
(1) 80017 − (2) 77735 = 2282

(6) 64902 − (10) 61214 = 3688
(8) 67176 − (9) 63492 = 3684
(3) 68968 − (7) 65277 = 3691
(0) 71387 − (2) 67699 = 3688
(0) 71875 − (0) 68192 = 3682
(1) 79621 − (5) 75937 = 3684
(1) 80017 − (5) 76335 = 3682

The second difference of 3685 units is more probably the significant one because it includes more of the strong lines.

Six of the chlorine lines can be grouped into three pairs as follows.

(5) 72484 − (3) 71607 = 877
(5) 74225 − (5) 73342 = 883
(2) 74863 − (3) 73979 = 884

More accurate wave-length determinations must be had before a final decision can be made as to the reality of these recurring differences. Nevertheless, it seems highly improbable that the results with iodine and chlorine, at least, can be a matter of chance. If these three differences of 881, 3685, and 7600 units are the differences between the energies of the two lowest states of the respective atoms the resonance lines are those of wave-lengths 1379.6, 1540.8 and 1782.9 A.U. and the radiating potentials 8.95, 8.01, and 6.92 volts for chlorine, bromine and iodine, respectively. The reasons for believing the resonance line of iodine to be other than the 2062.1 line have been discussed elsewhere.[12] The 2062.1 and 1782.9 lines are the pair of longest wave-length which have the doublet difference.

In a recent paper Dymond[13] has shown that experiments on the fluorescence of molecular iodine indicate that the iodine atom has an excited state 1.1 volts above the normal state. The frequency difference of 7600 wave number units found here corresponds to an energy of 0.94 volts. It agrees very well with a value of 0.9 volt calculated by Franck by extrapolation from the neon frequency difference, to which Dymond briefly refers. Dymond's value is in error by the same amount as the value for the heat of dissociation of molecular iodine of 1.4 volts, which he uses. The discrepancy may be due to an error in this quantity, which is a difficult one to determine accurately, although it seems rather large to be accounted for in this way.

Hopfield[14] has shown that the normal level of the oxygen atom and of the sulfur atom is triple and Pauli[11] has given theoretical reasons for expecting it to be quintuple. We should expect a halogen ion of similar electron structure to have that same multiplicity. If so, the arc spectra of these elements must have lines converging to either three or five different limits (just as the neon spectrum converges to two limits). The great complexity of these spectra is thus quite easily understandable.

It might also be noted that if the normal state of the halogen atom is double one would expect to find two electron affinity spectra for each element, with the doublet difference between them. The one of shorter wave-length would appear only under conditions where a considerable

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[12] Louis A. Turner and K. T. Compton, Phys. Rev. **25,** 791 (1925).

[13] E. G. Dymond, Zeits. für Physik **34,** 553 (1925).

[14] J. J. Hopfield, Phys. Rev. **21,** 710 (1923); Nature **112,** 437 (1923).

fraction of the atoms was in the higher of the two low states. So far as I am aware, such a doubling has never been noted in connection with the spectra ascribed to the electron affinity process.

I am greatly indebted to Professor Lyman for allowing me to use his spectrograph, and to his laboratory assistant, Mr. H. W. Leighton, for great help in performing the experiments. I also wish to thank Professor Lyman and Professor F. A. Saunders for their interest in this work and their helpful suggestions.

This work was done at the end of my year as National Research Fellow at Harvard University. I wish to take this opportunity to express my indebtedness to the National Research Council for making this year possible, and to thank all the members of the Physics Department of Harvard University for their courtesy and helpfulness which made it most profitable and pleasant.

Palmer Physical Laboratory,
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Note added with proof April 6, 1926:

These p_1-p_2 differences of 881, 3685, and 7600 wave number units, expressed in volts, are 0.11, 0.45, and 0.94 volts. They are in good agreement with the values 0.1, 0.5, and 0.9 predicted by Franck,[15] by extrapolation from the Ne^+ doublet difference. They also agree fairly well with the values calculated by Franck,[15] and by Wolf,[16] from the wave-lengths of the edges of the continuous absorption regions and heats of dissociation of the halogen molecules. Granting the correctness of the theoretical explanation of these continuous bands given by Dymond, Franck, and Wolf, accurate determinations of their wave-lengths combined with these doublet differences will give the most accurate values for the heats of dissociation of these molecules. The heat of dissociation of the iodine molecule so determined from Dymond's measurement of the edge of the band is $2.47-0.94=1.53$ volts, or 35.3 kg cal. per gram mol.

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[15] J. Franck. Address given before the Faraday Society. To appear in the Transactions of that society.

[16] K. L. Wolf, Zeits. f. Physik **35**, 490 (1926).