EXTREME ULTRA-VIOLET SPECTRUM OF ARGON EXCITED BY CONTROLLED ELECTRON IMPACTS

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ABSTRACT

Excitation of extreme ultra-violet spectrum of argon.—Circulating purified argon was excited by electrons from a Wehnelt cathode at various voltages up to 150 volts, with gas pressures of about 0.05 mm and currents of about 100 ma. Such excitation has been shown to arise from single rather than multiple electron impacts. The spectrum was photographed with the aid of a high vacuum spectrograph equipped with a glass grating. 88 lines, all believed due to argon, have been found in the wavelength region 1066 to 461. 20 of these belong to the known arc spectrum. Of the remaining 68 spark lines, 44 have not previously been reported. We fail to excite previously known A III lines, so that we attribute our 68 spark lines to A II.

Analysis of the argon spectrum.—37 spark lines have been classified. 12 of these classifications have been checked by numerous combinations involving lines in the near visible region (6883–2300). Tables of lines, terms and combinations are given. Three series of two members each give the series limit as 223, 363, so that the ionization potential is 27.82 ± 0.05 volts. Adding the first ionization potential 15.69 volts gives 43.51 volts as the minimum potential for double ionization. These refer to ionization to the $^3P_2$ limit, the lowest energy state of A III. A tentative term value of -33230 (relative to $^3P_2$) is given to the higher ^1D limit.

THE extreme ultra-violet spectrum of argon has been the subject of several investigations. First came the discovery of the resonance lines 1067 and 1048 by Lyman and Saunders,[1] and its verification by Hertz and Abbink.[2] Next came the discovery by Saunders[3] of 19 lines in the range 1067–849 and the identification of some of them as A I combinations between the low $3p^1S_0$ term and higher terms identified by Meissner[4] in his analysis of the near-visible spectrum. Dorgelo and Abbink[5] then carried out an exhaustive study of the extreme ultra-violet argon spectrum in arcs, glow discharges and condensed sparks at various pressures and voltages, and discovered some 40 new lines between 1067 and 519. They classified these lines as *arc* or *spark* according to their behavior under various conditions of excitation, and identified the term combinations responsible for 21 of the A I lines. They pointed out that the strong lines 932 and 920, and also two other pair of lines have nearly the wave number difference (about 1431) predicted by Meissner as the fundamental difference to be expected in the A II spectrum. One sextet, between 887 and 871, also found by Hopfield and Dieke,[6] has such a structure as to lead to its classification by

[1] Lyman and Saunders, Nature, **116**, 358 (1925).
[2] Hertz and Abbink, Die Naturwissenschaften, **14**, 648 (1926).
[3] Saunders, Proc. Nat. Acad. Sc., **12**, 556 (1926).
[4] Meissner, Zeits. f. Physik, **37**, 238 (1926); **39**, 172 (1926); **40**, 839 (1927).
[5] Dorgelo and Abbink, Zeits. f. Physik, **41**, 753 (1927).
[6] Hopfield and Dieke, Phys. Rev., **27**, 638 (1926).

by the latter authors as belonging to A III. Finally, Saunders[7] has investigated the way in which intensities of lines, relative to the resonance pair of A I, vary with excitation conditions, and has arrived at conclusions regarding arc or spark classification which are in some respects different from those of Dorgelo and Abbink, and has pointed out the peculiar intensity of the pair 932, 920 which are strong under apparent arc conditions although listed by Dorgelo and Abbink as spark lines.

Recent work with neon[8] showed us that spectral excitation by electrons from a hot cathode, in gas at low pressure, is peculiarly effective in exciting the first spark spectrum and in permitting use of highly purified gas. We therefore used this apparatus, which has been described elsewhere,[9] to investigate argon. The argon was purified by preliminary long arcing over a misch metal cathode, and this purification process was continued during all

TABLE I. $I(90)$ is intensity in pure argon at 90 volts; $I(110)$ is intensity in argon-helium mixture at 110 volts Lines marked* are arc lines which have been classified by Saunders and by Dorgelo and Abbink. For significance of "?" see text. Terms followed by (^1S) or (^1D) go to these limits: all others go to ^3P limit. +line covered by He. $A_1=3p^2P_1$; $A_2=3p^2P_2$

λ	$I(90)$	$I(110)$	ν	Classification
1066.72	15	15	93745*	
1048.28	25	25	95394*	
1031.41	—	2	96954	
958.34	1d	–	104347	
931.97	7	7	107300	$A_1-sp^6\,{}^2S_1$
919.69	9	8	108732	$A_2-sp^6\,{}^2S_1$
894.27	4	–	111823*	
879.88	3	1	113652*	
878.68	–	1	113807	
876.00	4	1	114155*	
869.70	2	0	114982*	
866.77	4	2	115371*	
842.78	2	–	118655*	
834.45	6	2	119839*	
826.39	2	0	121008*	
825.42	1	0	121150*	
820.22	0	–	121918*	
816.32	4	2	122501*	
806.62	2d	1	123974*	
801.41	1	–	124780	
797.78	0	–	125348	
795.70	?	–	125675	
769 37	?	1	129976—arc limit	
762.37	2	–	131170	$A_1-3d^4D_2$
754.99	4	–	132452	$A_2-3d^4D_3$
755.21	–	0	132413	
748.39	1	–	133620	$A_1-4s^4P_2'$
745.22	8	3d	134189	$A_2-4s^4P_3'$; $A_1-4s^4P_1'$
740.45	5	2	135053	$A_2-4s^4P_2'$
731.10	3	1	136780	$A_1-4s^2P_2'$
725.73	5	3	137792	$A_1-4s^2P_1'$
723.54	6	5	138209	$A_2-4s^2P_2'$
718.29	4	2	139219	$A_2-4s^2P_1'$
704.72	3	0	141900	$A_1-3d^4P_2'$?
699.00	4	1	143062	$A_2-3d^4P_3'$; $A_1-3d^4P_1'$
698.19	2	–	143227	$A_1-3d^2P_1'$?
697.82	1	–	143303	$A_2-3d^4P_2'$?
693.55	4	0	144186	$A_1-3d^2P_2'$?
691.29	1.5	–	144657	$A_2-3d^2P_1'$?
686.73	2	–	145618	$A_2-3d^2P_2'$?
679.59	6	4	147148	
678.17	4	0	147456	
676.48	5	1	147824	$\left.\begin{matrix}A_1\\A_2\end{matrix}\right\}-3d\,(^4F',{}^2F',\ D)$
673.13	0	–	148560	
672.03	6	4	148803	
671.21	6	3	148985	
666.23	5	2	150098	
664.84	2	0	150412	
662.11	6	3	151032	
637.52	–	1	156858	
612.59	4	2	163241	
603.11	2	2	165817	$A_1-3d(^1D)^2S_1$?
597.92	3	3	167246	$A_2-3d(^1D)\,^2S_1$?
584.53	1.5	+	171078	$A_2-3d(^1D)\,^2F_3'$?
583.65	3	+	171335	$A_1-3d(^1D)\,^2D_2$?
580.47	5	3	172264	$A_2-3d(^1D)\,^2D_3$?
578.81	1.5	1	172768	$A_2-3d(^1D)\,^2D_2$?
578.34	1.5	1	172909	$A_1-3d(^1D)\,^2P_2'$?
576.93	2	2	173331	$A_1-3d(^1D)\,^2P_1'$?
573.55	4	3	174353	$A_2-3d(^1D)\,^2P_2'$?
572.20	1	1	174764	$A_2-3d(^1D)\,^2P_1'$?
560.38	3	2	178450	
557.01	3	2	179530	
548.92	1	–	182176	$A_2-5s^4P_2'$
547.54	4	4	182635	$A_1-4s(^1D)\,^2D_2$?
546.36	2	1	183038	$A_2-5s^2P_2'$
543.96	1	1	183837	$A_2-4d^4D_3$
543.33	5	5	184050	$A_2-4s(^1D)\,^2D_3$?
538.47	–	0	185711	
537.18	1	+	186157	
530.65	1	1	188448	
526.54	0	–	189919	
524.83	3	3	190538	
522.93	2	3	191231	$A_1-3d(^1S)\,^2D_2$?
519.47	4	4	192504	$A_2-3d(^1S)\,^2D_3$?
514.43	1	0	194390	$A_1-4s(^1S)\,^2S_1$?
512.72	–	0	195038	
510.68	3	1	195817	$A_2-4s(^1S)\,^2S_1$?
503.78	0	–	198499	
502.20	0	–	199124	
491.09	0	–	203629	
490.76	2	3	203766	
489.26	0	1	204390	
488.88	2d	2	204549	
487.27	2	3	205225	
475.79	–	1d	210177	
464.20	–	1d	215424	$A_1-4d(^1D)\,^2P'_{12}$, $4d(^1D)\,^2D_2$?
461.11	–	1d	216868	$A_2-4d(^1D)\,^2P'_{12}$, $4d(^1D)\,^2D_{23}$?

[7] Saunders, Proc. Nat. Acad. Sc., **13,** 596 (1927).

[8] Russell, Compton and Boyce, Proc. Nat. Acad. Sc., **14,** 280 (1928).

[9] Compton and Boyce, J. Frank. Inst., **205,** 497 (1928).

the exposures by forcing the circulating gas through the purifying bulb. Spectra of pure argon and of argon plus helium were photographed. The helium spark lines 303.81 and 256.33 (first, second and third orders) were used as primary standards and the arc lines 584.44, 537.12, 522.29, 515.70, 512.18, 510.07 508.72 (first and second orders) and 507.80, 507.13 (first order) as secondary standards of wave-length, thus giving calibration points all over the region of the spectrum investigated. Table I gives a list of the argon lines, their wave numbers, their intensities and their partial classification. At the shorter wave-lengths our measurements deviate slightly from those of Dorgelo and Abbink,[5] but we believe our values to be the better because of the wealth of helium standards used in this region.

The term arrangement of A II is similar to that of Ne II reported previously by us,[9] except for one important difference. In Ne II, only terms involving a displaced s electron exist in the group of next higher energy above the fundamental $2p^2P_{12}$ state. In A II on account of the additional completed outer shell of electrons, both $4s$ and $3d$ excited electron configurations exist at about the same levels above the fundamental $3p^2P_{12}$ state, so that the structure of the spectrum is very much more complicated than that of Ne II. Furthermore, a great part of the near-visible spectrum, most urgently needed for analysis, lies in regions which have not as yet been investigated or in which observations have not been made with sufficient precision.

With the wave-lengths of Table I, and the near-visible wave-lengths from Kayser's Handbuch, Vol. V and from L. Bloch, E. Bloch and G. Dejardin,[10] we have found about 150 combinations and thus identified a few of the A II terms. While this work was in progress, de Bruin[11] published a preliminary paper on the analysis of the near-visible spectrum, and we have used his results to correct our original mistake identification of some of the low s^4P terms. We have, in addition, found higher s^4P and d^4P terms, as well as s^2P terms, which permit three independent and consistent estimates of the ionization potential (to the p^3P_2 limit).

The following types of terms are predicted by the Hund theory. Fundamental terms $3p^2P_{21}$. Terms associated with $^3P_{210}$ limit: $s^4P'_{321}$, $p^4S'_2$, p^4P_{321}, $p^4D'_{4321}$, $d^4P'_{321}$, d^4D_{4321}, $d^4F'_{5432}$, $s^2P'_{21}$, $p^2S'_1$, p^2P_{21}, $p^2D'_{32}$, $d^2P'_{21}$, d^2D_{32}, $d^2F'_{43}$. Terms with ^1D limit: s^2D_{32}, p^2P_{21}, $p^2D'_{32}$, $p^2F'_{43}$, d^2S_1, $d^2P'_{21}$, d^2D_{32}, $d^2F'_{43}$, d^2G_{54}. Terms with ^1S limit: s^2S_1, p^2P_{21}, d^2D_{32}.

In Tables I and II the identifications *not* questioned are very likely correct, being checked by numerous intercombinations between higher terms. Those identifications marked "?" are suggested only as strongly indicated by the general spectral scheme of terms, intensities and frequency differences predicted by the Hund theory. In the absence of data permitting an adequate check by combinations which would be in the near infra-red or in the ultra-voilet beyond 2300, these identifications are only tentatively presented.

[10] L. Bloch, E. Bloch and G. Dejardin, Ann. de Physique **2,** 480 (1924).
[11] de Bruin, Zeits. f. Physik **48,** 62 (1928).

TABLE II. *Terms referred to $^3P_2$ limit as zero.*

Quartets	Term			Diff.
	to ^3P limit			
$3d$	D_4	91070.0	a	153.5
	D_3	90916.5	b	149.5
	D_2	90767.0	c	107.0
	D_1	90660.0	d	
$4s$	P_3'	89156.0	e	844.9
	P_2'	88311.1	f	515.7
	P_1'	87795.4	g	
$3d$	P_3'	80301	h?	241
	P_2'	80060	i?	
	P_1'	—		
$4p$	P_3	68354.4	s	308.0
	P_2	68046.4	t	356.8
	P_1	67689.6	u	
$4p$	D_4'	61163.4	v	439.3
	D_3'	65724.1	w	493.9
	D_2'	65230.2	x	260.3
	D_1'	64969.9	y	
$4p$	S_2'	62348.8	z	
$5s$	P_3'	41803.5	j	627.8
	P_2'	41175.7	k	729.1
	P_1'	40446.6	l	
$4d$	D_4	49722.6	m	122.3
	D_3	49600.3	n	188.3
	D_2	49412.0	o	206.2
	D_1	49205.8	p	

Other Limits

$^3P_1-1110$ } from triplet PP' group of A III (Ref. 6, 7)
$^3P_0-1573$ }

^1D -33230

^1S $-$?

Doublets	Term			Diff.
	to ^3P limit			
$3p$	P_2	223363	W	1430
	P_1	221933	X	
$4s$	P_2'	85153.6	A	1014.6
	P_1'	84139.0	B	
$3d$	P_1'	78705	C?	-960
	P_2'	77745	D?	
$3d$	D_3	73265	E?	314
	D_2	72951	F?	
$3d$	F_3'	72331	G?	
$4p$	D_3'	64667.6	Y	663.7
	D_2'	64003.9	Z	
$5s$	P_2'	40307.4	I	808.9
	P_1'	39498.5	J	
sp^2	$^2S_1$	114633		
	to ^1D limit			
$3d$	S_1	56117	K?	
$3d$	F_3'	52285	L?	
$3d$	D_3	51099	M?	503
	D_2	50596	N?	
$3d$	P_2'	49017	O?	417
	P_1'	48600	P?	
$4s$	D_3	39313	Q?	15
	D_2	39298	R?	
$4d$	P_2', P_1'	6502	S?	
	to ^1S limit			
$3d$	D_3	30859	T?	158
	D_2	30701	U?	
$4s$	S_1	27545	V?	

Table II gives the spectral terms and Table III indicates the combinations which have been identified. We have also found a number of additionial combinations which we are as yet unable to identify.

TABLE III. *A II Combinations* (*o found by de Bruin*).

	W	*X*	*Y*	*Z*	*s*	*t*	*u*	*v*	*w*	*x*	*y*	*z*
a			x		o			o	o			
b	x		x	x	o	o		o	o	o		
c		x	x	x	o	o	o		o	o	o	
d						o	o			o	o	
e	x		x	x	o	o		o	o	o		o
f	x	x	x	x	o	o	o		o	o	o	o
g				x		o	o			o	o	o
h	x											
i	x	x										
j				x	x	x		x	x			x
k	x		x		x	x	x		x	x		x
l						x	x			x	x	x
m					x			x	x			
n	x		x		x	x		x	x	x		
o			x	x	x	x	x		x	x	x	
p						x	x			x	x	

W	*X*	*Y*	*Z*	*s*	*t*	*u*	*v*	*w*	*x*	*y*	*z*	
x	x	x	x					x			x	*A*
x	x		x						x			*B*
x	x											*C*
x	x											*D*
x												*E*
x	x											*F*
x												*G*
x		x	x	x					x		x	*I*
			x		x				x	x	x	*J*
x	x											*K*
x												*L*
x												*M*
x	x											*N*
x	x											*O*
x	x											*P*
x												*Q*
	x											*R*
x	x											*S*
x												*T*
	x											*U*
x	x											*V*

The following brief outline is given of the reasons for the questionable identifications. Lines 698, 693, 691, 686 form a characteristic doublet PP' group with the fundamental 1431 frequency difference, but with intensities which suggest inversion of the upper pair of terms. The position of these lines is such that they come from the set of terms belonging to the ${}^3P$ limit. The only unfilled place for a PP' group in the Hund scheme is a $d^2P'_{12}$ combination with the fundamental p^2P_{12} terms. Furthermore, the corresponding pair of terms in Ne II has actually been found to be inverted. Thus we feel reasonably sure of this identification. The three lines 704, 699, 697 form a group of slightly lower frequency than the above group. Since we always find quartet terms a little lower than doublet terms of the same type, we naturally classify these lines as arising from d^4P' terms, which is supported by the fact that intensities and separations are consistent with this view.

Just to the high frequency side of these lines is a group of seven strong and two faint lines. There can be no doubt that these include the lines from the remaining $3d$ terms (^2D, $^4F'$, $^2F'$), but there is little evidence on which to base a classification, so that they are not given individual identification in the Tables. The only accurate 1431 frequency difference is between lines 671 and 664. These, together with 666 might arise from $3d^2D$, or with 662 might arise from inverted $3d^2D$ terms. $3d^2F$ would give only one line, and $3d^4F$ would give three lines. Possibly 679 and 673 belong to this latter system, but their frequency difference seems to depart more from 1431 than we should expect. Further spectroscopic work in the near-infra-red is needed to complete the classification of this group of lines.

After a considerable gap there next comes a group of fairly strong lines between 612 and 572. These are of too low frequency to be second members of any series going to the ^3P limit and too high to be first members of such series: furthermore all possible first members have already been accounted for. Thus they must be the first members of series associated with the higher limits ^1D or ^1S. These lines are therefore ascribed to series with ^1D limit, since these would be expected to be lower in frequency than series belonging to ^1S, and since the structure of the group can be explained only in this way. Lines 603, 597 have the right separation and intensities to indicate their origin in $3d^2S_1$. Lines 578, 576, 573, 572 for a doublet PP' group, which can only arise from the term $3d^2P'$. Lines 583, 578 have the 1431 separation and, with the intervening stronger line 580, form a perfect multiplet if ascribed to the $3d^2D$ terms. The isolated remaining line 584 can be only one thing, $3p^2P_2-3d^2F_3'$. These identifications take care unambigously of all $3d$ electron terms. The lines from the expected $4s^2D$ terms are almost certainly the strong pair 547, 543, which come among the second members of the ^3P limit series, but are very much stronger. We should expect three lines, the one of shorter wave-length being weakest and the next, close to it, being strongest. We find only two, and their separation is only 1415. This suggests that the weakest line was too weak to detect, and that the terms $4s^2D_2$ and $4s^2D_3$ are only about 15 frequency units apart. The two shortest lines found, 464, 461, come just right to be the second members of the series $3p^2P_{12}-m\ d^2P'_{12}$, if the quantum defect for a d electron is the same for this series as for the d electron series going to the ^3P limit. This identification is therefore likely, and enables the ^1D limit to be calculated as -33230.

Finally the remaining strong group 524 to 510 must by exclusion, and by position and structure, be the first members of the two series going to the ^1S limit. The pair 514, 510 have close to the 1431 frequency difference and are believed to arise from the $4s^2S_1$ term. The pair 522, 519 are probably the two strong members of the triplet group due to $3d^2D$.

There remain, unexplained, a fairly strong isolated line 612, a pair 560, 557 of separation 1080, a distinctive group 490, 489, 488, 487 which looks like a PP' group but is yet not quite right, and several other faint lines. None of these has been reported for any other element, and we have not found them in working with helium or neon. Neither do we find *any* known line of any other element on our plates. Consequently we believe them to be argon lines. They may belong to A III, but we do not find any trace of the A III sextet already found by Hopfield, Dieke and Saunders. In fact we have made several attempts, by using high voltage and long exposure, to excite these A III lines by single electron impact, but without success. Similarly our source apparently gives no N III or Ne III, so that we have come tentatively to the conclusion that single electron impacts do not excite the second spark spectrum, even though the voltage is ample. We are thus without a clue as to the origin of these remaining lines.

The ionization potential corresponding to the $s^2p^4\ {}^3P_2$ limit, and giving the low state of A III, is 27.82 ± 0.05 volts (223,363 frequency units). This limit falls between the approximate "Rydberg" limits calculated from the s and d electron series respectively, since the Ritz correction term is opposite in sign in the two cases. Since the first ionization potential is 15.69 volts, the minimum potential for double ionization is 43.51 volts, in good agreement with the experimental value of 45.3 ± 1.5 volts found by Barton[12] and somewhat higher than values predicted from indirect evidence.[13]

The peculiar intensity of the pair 931,919 noted by Saunders[7] is due to its peculiar mode of excitation, which is by ionization involving the removal of an s electron. It is also interesting to notice that Mohler[13] did not find photoelectric ionization of argon at a voltage corresponding to the excitation of this pair, although he found strong ionization by the corresponding pair in neon.[9] The explanation of this is that this pair in argon is of longer wave-length than the arc limit, whereas in neon it is of shorter wave-length.

We are glad to acknowledge the valuable suggestions and assistance of our colleague, Professor Shenstone.

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June 2, 1928.

[12] Barton, Phys. Rev., **25,** 469 (1925).
[13] Mohler, Phys. Rev., **28,** 46 (1926).