Emission spectrum of highly ionized argon in the 100 to 900 Å range

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Emission spectrum of highly ionized argon in the 100 to 900 Å range

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Résumé. — Nous avons étudié le spectre d'émission de gaz rares produit par une source à décharges. Nous avons relevé 70 raies nouvelles dans le spectre de l'argon, produites par des ions fortement ionisés, principalement Ar IV à Ar VIII. Ces raies n'ont pas pu être classifiées, mais sont probablement émises par des états excités de haute énergie potentielle.

Abstract. — We have studied the emission spectra of rare gases produced by a discharge light source. We report 70 new lines for the argon spectrum, related to highly ionized ions, mainly Ar IV to Ar VIII. The classification of these lines has not been possible here, but they are probably emitted by excited states of high potential energy.

1. Introduction.

The spectrum of argon in the extreme ultraviolet region was investigated thoroughly, more than fourty years ago, by Boyce [1] and by Phillips and Parker [2]. They measured and classified many lines, relative to highly ionized argon, in the spectra produced by electrical discharge in the argon gas. More recently, Schönheit [3] has studied the spectrum of another discharge light source and has reported more than one hundred new, unclassified lines of argon. In the last decade, the development of the beam foil technique [4-7] has allowed the degree of ionization of the atoms to be more easily identified and some new lines (sometimes those of Schönheit) have been identified and classified.

In an earlier paper [8], we reported a source of VUV radiation produced by electrical discharges in a rarefied gas, emitting a spectrum mainly composed of ionic lines of highly ionized elements.

We had attempted to identify the new lines but our wavelengths were not accurate enough (0.3 Å) and the method of identification had proven to be not very reliable [9]. In this paper, we will improve the precision of our wavelength determination and propose a better method to deduce the degree of ionization of the atoms from the variations of the intensities of the lines.

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2. Experimental device.

As described in our previous paper [8], the repetitive discharge of the 0.25 μF condenser takes place in a quartz capillary of 4 mm internal diameter and of 100 mm length. The optimal conditions for the emission of lines in the studied spectral range were achieved with an applied voltage of 9 kV and with a total pressure of the gas of 4×10^{-2} torr (5 Pa).

For analysis of the emitted spectrum, a grazing incidence (82°) monochromator type « Romand et Vodar », with a concave grating of 3 m curvature radius was used. The widths of the entrance and exit slits were fixed at 0.1 mm, which gives a 0.8 Å resolution in the spectral range 100-1 000 Å. The detection of the maxima in the spectrum is automatized. Unfortunately, the mechanical motion of the grating on the Rowland circle shows irreducible irregularities which scatter the measured wavelengths. By averaging several measurements on different spectra, the uncertainty has been reduced for most of the lines below 0.1 Å.

3. Selection of the argon lines.

The new lines of argon and krypton spectra are obtained by eliminating all known lines from the observed spectrum of the gas. An important problem arises from the presence of some extra lines irrespective of the gas that is introduced into the tube. These extra lines can be mistaken with the studied ones. These lines are emitted by elements vapourized from the capillary wall and from the electrodes. Actually, most of these extra lines have been attributed to oxygen and silicon ions. For this identification, we have used the compilation of lines of Kelly and Palumbo [10].

The easiest way to distinguish the extra lines from the studied lines is to change the gas introduced in the tube. If a line appears in the neon, argon and krypton spectra, it is clearly an extra line. In some cases, this test is rather ambiguous because the intensity of the extra lines can be very sensitive to the nature and the excitation level of the elements in the plasma. For instance, an oxygen ion easily excited by impact with a particular argon ion produces lines which may be seen only with the argon spectra and could be presumed wrongly to be a true argon line. For this reason, we have used a second test to identify the new lines.

Essentially, the second test may be described as follows. With a constant voltage applied to the tube, the intensity of the lines emitted by the gas introduced varies strongly [4, 5] with the pressure of this gas. As the pressure rises, we generally observe an initial increase in the intensity of the line followed by a decrease as the gas absorbs the emitted radiations. The position of the maxima in the intensity depends on the degree of ionization of the emitting ions and also on the wavelength of the line. The intensity of

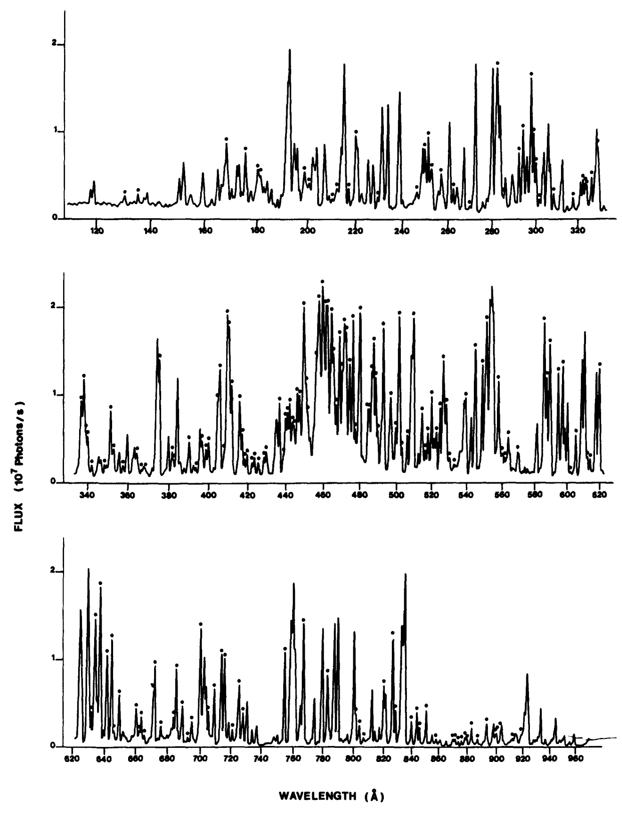

Fig. 1. — Spectrum emitted by our discharge source in the following condition : $V = 9$ kV, $p = 0.05$ torr. Black dots indicate the argon lines.

the extra lines seems to be nearly independent of the pressure of the gas and shows only decreasing curves.

We have thus recorded several spectra with different pressures. The study of the evolution of the intensity of each line with the pressure has been used to confirm the identification of the new lines.

4. Identification of the degrees of ionization.

It is well known [3] that the intensity of a line depends strongly upon the characteristics of the discharge, such as the applied voltage, the discharge current, the inductance of the electric circuit and the pressure of the gas. Owing to the fact that, for some close group of lines related to the same ion, the intensities of the lines change in a similar way as a function of the parameters of the discharge, the new lines can be identified by comparison with the known lines.

It follows from our previous work [8] that the intensities of the lines depend primarily on the pressure and the applied voltage and this dependence varies as a function of the wavelength of the considered lines. This means that the ratio of the intensities of a line for two different conditions can be taken as characteristic of the degree of ionization of the atom only if the effect of wavelength is taken into account.

For this study, we have recorded seven spectra under the following conditions of pressure and voltage :

$$p = 0.1 \text{ torr (13 Pa)}, \qquad V = 3, 6 \text{ and } 9 \text{ kV}$$
$$p = 0.03 \text{ torr (4 Pa)}, \qquad V = 6, 9, 12 \text{ and } 15 \text{ kV}$$

and have calculated for each lines, the different ratios :

$$\left(\frac{I_{6\,\mathrm{kV}}}{I_{9\,\mathrm{kV}}}\right)_{0.03}, \quad \left(\frac{I_{12\,\mathrm{kV}}}{I_{9\,\mathrm{kV}}}\right)_{0.03}, \quad \left(\frac{I_{15\,\mathrm{kV}}}{I_{9\,\mathrm{kV}}}\right)_{0.03},$$
$$\left(\frac{I_{3\,\mathrm{kV}}}{I_{6\,\mathrm{kV}}}\right)_{0.1}, \quad \left(\frac{I_{9\,\mathrm{kV}}}{I_{6\,\mathrm{kV}}}\right)_{0.1}.$$

The plot of these ratios *versus* λ for the classified lines shows smooth variations over the studied wavelength interval. The experimental ratios for the new lines of the spectrum can be then compared directly to these curves.

In order to facilitate the identifications of the new lines, we have used a different presentation for the ratio of the known lines, as reported in figure 2. The five different ratios mentioned above are smoothed and interpolated for a set of 10 arbitrary wavelengths, regularly spaced over the 200 to 900 Å interval. These interpolated ratios are then plotted on a log-scale in a number of graphs, which are shown together on figure 2 with the degree of ionization as abscissa and the wavelength as ordinate. For a new line, the reading of the degree of ionization of the emitting ion follows from the comparison of the experimental ratios plotted on same scale diagrams, with the schemes of figure 2.

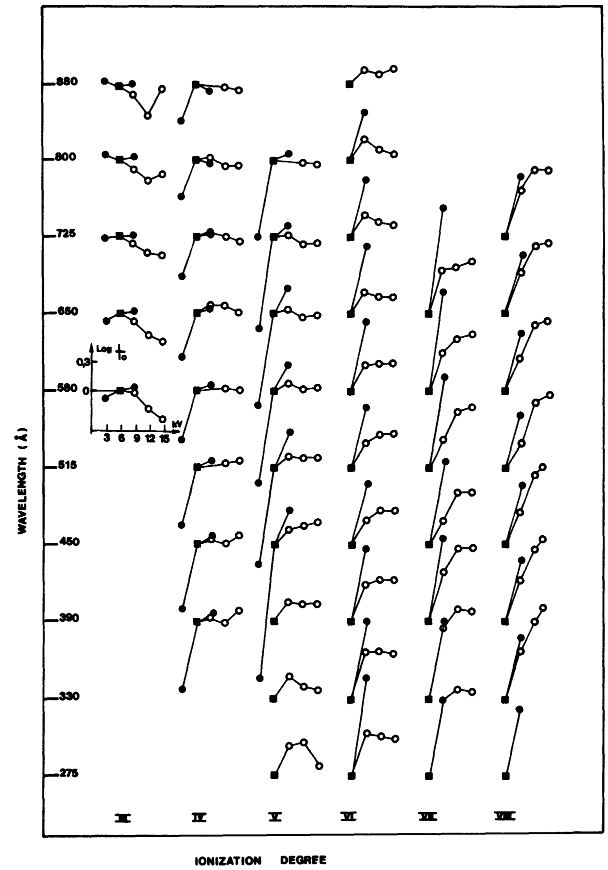

Fig. 2. — Diagram used for the determination of the degrees of ionization. In each sketch, the black square represents the intensity taken as reference ($V = 6$ kV, $p = 0.03$ or 0.1 torr), the black dots represent the intensities of the lines for a pressure of 0.03 torr and the circles for a pressure of 0.1 torr. Each of the sketches is drawn to the same scale as indicated in the insert.

5. Results and discussion.

The argon spectrum emitted by our source, in the 100 to 920 Å range, is composed of some 210 lines, and is reported in figure 1. We have determined, for about 140 of them, the degree of ionization of the ion, giving confirmation for 92 already classified lines and new identification for 46 lines. Most of these newly identified lines are related to the Ar V and Ar VI spectra.

The observed lines have been arranged according to the ionization degree of the ion and listed in table I. The small lines and the lines showing inconsistent behaviour have been listed separately in table II.

With an applied voltage of more than 3 kV, the strongest lines of the Ar II and Ar III spectra appear as very weak lines in our spectrum, which indicate that our discharge is relatively devoid of ions Ar^+ and Ar^{++}, for the range of voltage used (6-15 kV).

On the other hand, we observe no line of the Ar IX spectrum [11-14] which means that the impacts in the plasma are not sufficiently energetic to produce or excite Ar^{8+} ions.

The unidentified lines in table II may then probably be related to the Ar IV to Ar VIII spectra.

As can be seen in the different compilations of lines [10] and spectral terms [12, 13], the spectra of highly ionized argon is relatively less well known than those of the other atoms of the isoelectronic sequences. We have then deduced some new spectral terms of Ar IV to Ar VIII by interpolation from the neighbouring elements (silicon to titanium) in each isoelectronic sequence. No new definite classification could be proposed from this study. Actually, our spectrum does not seem to be convenient for further

Table I. — *Identified lines emitted by our discharge source. Majuscule letters S, D, T and Q refer to the singulet, doublet, triplet and quartet series of lines. Lines belonging to the same multiplet are noted with bracket. a : wavelength and classification given by Kelly and Palumbo* [10], *b : wavelength and classification given by Berry* et al. [5], *c : wavelength and classification given by Buchet-Poulizac* et al. [7], *d : wavelength given by Schönheit* [3], *e : wavelength and classification given by Fawcett* et al. [14].

Ar III			
λ_{exp}	$I_{rel.}$	λ_{ref}	comments
604.3	2	604.15	a
769.1	2	769.15	S - a
871.1	1	871.10	T - a
875.4	1	875.53	T - a
878.5	2	878.73	T - a
879.6	1	879.62	T - a
883.4	1	883.18	T - a
887.3	2	887.40	T - a

Ar IV			
λ_{exp}	$I_{rel.}$	λ_{ref}	comments
396.7	8	396.87	Q - a
398.6	7	398.55	Q - a
423.4	6	423.48	D - a
429.6	7	429.80	d
444.0	12		
452.7	14	452.92	Q - a
495.6	15	495.56	D - a
683.3	5	683.28	D - a
689.0	10	689.01	D - a
807.4	2	807.46	d
840.0	4	840.03	Q - a
843.7	8	843.77	T - a
850.4	10	850.60	Q - a
900.5	3	900.36	D - a
901.2	3	901.17	D - a

Table I *(continued)*.

AR V			
λ_{exp}	$I_{rel.}$	λ_{ref}	comments
262.2	8		
284.5	7		
317.6	4		
322.1	8	322.02	Q - e
323.2	7	323.15	Q - e
324.0	5	323.94	Q - e
326.2	8		
336.7	25	336.56	T - a
337.9	20	338.00	T - a
339.1	12	339.01	T - a
340.0	10	339.89	T - a
348.3	4		
351.0	15	350.88	S - a
400.0	7		
405.5	25	405.42	d
415.6	18	415.86	d
417.0	7	417.12	d
425.4	5		
436.4	25	436.67	S - a
445.8	20	445.99	T - a
446.9	40	446.95	T - a
449.0	50	449.06	T - a
460.9	50		
464.0	50	463.93	T - a
465.1	30	465.02	d
499.2	8		
502.4	7	502.42	d
505.4	8	505.45	d
513.9	12	513.91	I - a
517.2	8	517.25	I - a
522.1	10	522.09	T - a
524.2	17	524.19	T - a
527.6	15	527.69	T - a
558.5	20	558.48	S - a
570.4	5	570.61	I - a
705.5	8	705.35	T - a
709.0	15	709.20	T - a
715.7	15	715.64	T - a
720.9	3	720.94	d
725.0	13	725.11	S - a
822.1	8	822.16	T - a
827.1	16	827.05	T - a

AR VI			
λ_{exp}	$I_{rel.}$	λ_{ref}	comments
220.7	12	220.95	D - a
282.0	50	281.92	Q - a
292.1	40	292.15	D - a
294.0	25	294.05	D - a
298.8	20		
301.6	4		
329.4	16	329.48	Q - e
352.3	8		
375.1	15		
409.2	35	409.12	d
410.0	40	410.10	d
439.6	15		
440.6	18		
451.2	25		
455.8	35	455.81	Q - a
457.2	30	457.48	D - a
459.2	80	459.32	Q - a
466.9	25	466.93	Q - a
468.3	40	468.38	d
470.1	25		
470.8	40		
471.8	18		
476.9	10		
483.9	12		
484.6	12		
485.9	22	485.79	d
486.7	30	486.60	D - dc
488.1	22		
509.0	50	509.02	d
544.7	45	544.73	D - a
548.9	30	548.91	D - a
551.4	50	551.37	D - a
564.4	7		
587.0	18	587.01	Q - a
588.9	30	588.92	D - a
589.7	18	589.78	Q - a
594.0	20	594.10	Q - a
596.7	25	596.69	D - a
611.8	5		
613.3	3	613.40	d
618.8	20	618.63	D - cd
		619.04	
631.7	6	631.68	d
649.2	7	649.03	d
754.8	20	754.93	D - a
767.0	25	767.06	D - a
804.6	3	804.59	D - dc
893.9	3		
904.7	3	904.89	D - dc

AR VII			
λ_{exp}	$I_{rel.}$	λ_{ref}	comments
175.5	18	175.50	S - e
249.5	20	249.38	T - a
251.0	25	250.94	T - a
297.6	50	297.70	T - a
473.8	40	473.93	T - a
475.6	80	475.66	T - a
479.4	100	479.38	T - a
492.2	40	492.2	T - c
501.0	60	501.1	S - c
539.0	25	539.0	S - c
585.7	60	585.75	S - a
634.1	30	634.21	T - a
637.1	50	637.05	T - a
641.3	25	641.32	T - a
644.4	30	644.38	T - a
685.1	18	685.0	S - c
821.0	10	821.1	T - c
828.9	5	829.1	T - c

AR VIII			
λ_{exp}	$I_{rel.}$	λ_{ref}	comments
180.3	18	180.25	D - a
300.0	15		
519.4	35	519.43	D - a
526.4	55	526.46	D - a
700.3	45	700.40	D - a
714.0	30	713.99	D - a

Table II. — *Unidentified lines. The third column refers to probable degree of ionization of the emitting ion, as determined in our study of the intensities. (For the letters a, b, c, d, e, see caption of table I.)*

λ_{exp}	$I_{rel.}$	Deg	λ_{ref}	comments
130.2	6			
134.9	5		134.80	S VII - e
167.3	18			
168.7	10		168.60	T VII - b
180.1	10		180.07	D VI - a
198.9	10			
200.4	8			
210.5	4			
212.0	5			
217.1	8		217.31	T VII - b
229.3	6		229.44	D VIII - a
244.8	5			
245.9	5			
252.1	7	V ?	252.07	T V - e
256.8	16			
269.5	7			
308.4	8	VII-VIII		
309.4				
310.2				
342.0	3	V ?		
357.2	4	IV - V	357.21	
364.2	7	VII ?		
366.4	4			
368.5	4			
378.5	4			
381.6	5	VI ?		
382.4	7	VI ?		
387.5	2		387.45	S III - a
390.2	7			
393.6	3	IV ?		
402.5	2			
404.8	15	V ?		
407.8	8		407.87	D VIII - b
411.6	28	VII ?		
418.2	3			
419.6	3	V - VI		
422.3	4	IV ?		
428.4	4			
438.4	6		438.64	d
441.8	18	V - VI	441.83	d
443.2	17		443.40	D IV - a
461.5	100		461.23	T V - a
481.8	6		481.85	T III - a
489.2	10		489.08	
492.1		IV ?		
496.1	16	VI ?		
515.6	12		515.62	d
518.2				
529.4	4	IV ?		
532.3	4		532.41	T III - a
539.8	6	V ?	539.79	d
560.9	7		561.06	I IV - a
562.2	6	V ?	562.18	
568.0	3			
569.9				
603.2	2		603.26	d
645.8	3	V - VI		
652.7	2			
659.9	7	VIII ?	659.9	T VII - c
661.7	3	VI ?	661.9	T IX - b
663.0	4	VI ?		
665.0	2	VI ?	664.93	d
670.6	7		670.39	d
675.4	5	VII ?	675.28	d
692.4	2	III - IV		
694.9	5	VI ?	694.85	I IV - a
698.0	2		698.08	I IV - a
727.5	3		727.58	d
783.1	12	VI - VII	783.14	d D IV - c
794.6	1		794.53	d
799.1	1		798.92	
802.2	7		801.91	D IV - a
845.7	3	V ?	845.68	d
855.6	1		855.71	d
857.2	2			
869.6	1			
913.0	2		912.91	d

spectroscopic study because of the still low wavelength accuracy and because of the presence of more than one hundred extra lines which mask important portions of the spectrum.

6. Concluding remarks.

The extreme ultraviolet spectrum emitted by our source has shown numerous lines emitted by Ar^{3+} to Ar^{7+} ions. New lines are reported in this study, indicating that the spectra of these ions are still not completely known.

By using a method of determination, based on the study of the influence of the discharge parameters on the intensity of the lines, we could identify the degree of ionization of 46 new lines related mainly to Ar V and Ar VI spectra.

It is probably difficult to say why our source produces so many lines of the spectra of Ar^{4+} and Ar^{5+} ions, more numerous than previously reported by other authors, but two reasons can be proposed. First, our spectrum shows strong lines related to Ar^{7+} ions and these ions can produce a great variety of strongly excited ions of lower degrees of ionization by recombination. Second, our discharge is a very complex phenomenon. The dense plasma inside the discharge is always far from thermal equilibrium. This means that during the time of discharge, the physical parameters of the plasma (velocity and density of ion) are continuously changing, probably over several orders of magnitude. In this case, nearly all excited species can be produced, giving birth to the numerous observed lines.

References

[1] BOYCE, J. C., *Phys. Rev.* **48** (1935) 396.

[2] PHILLIPS, L. W. and PARKER, W. L., *Phys. Rev.* **60** (1941) 301.

[3] SCHÖNHEIT, E., *Optik* **23** (1965) 409.

[4] PINNINGTON, E. H., CURNUTTE, B. and DUFAY, M., *J. Opt. Soc. Amer.* **61** (1961) 978.

[5] BERRY, H. G., DESESQUELLES, J., TRYON, P., SCHNUR, P. and GABRIESLE, G., *Phys. Rev. A* **14** (1976) 1457.

[6] LIVINGSTON, A. E., PINNINGTON, E. H., IRWIN, D. J., KERNAHAN, J. A. and BROOKS, R. L., *J. Opt. Soc. Amer.* **71** (1981) 442.

[7] BUCHET-POULIZAC, M. C., BUCHET, J. P. and CEYZERIAT, P., *Nuclear Instrum. Meth.* **202** (1982) 13.

[8] GIRARD, S., LÉVÊQUE, G. and ROBIN, S., *J. Phys. E* **12** (1979) 719.

[9] GIRARD, S., Thèse Montpellier, unpublished (1981).

[10] KELLY, R. L. and PALUMBO, L. J., Atomic and Ionic Emission lines Below 2 000 Å, NRL Report 7599, Washington 1973.

[11] BERRY, H. G., DESESQUELLES, J., CHENG, K. T. and SCHECTMAN, R. M., *Phys. Rev. A* **18** (1978) 546.

[12] MOORE, C. E., U.S. Nat. Bur. Stand., *Atomic Energy Levels* I (1949), II (1952).

[13] STANLEY, S. and STONER, J. O., *Atomic Energy Level and Grotrian diagrams*, vol. II (North Holland Pub. Comp. Amsterdam) 1978.

[14] FAWCETT, B. C., RIDGELEY, A. and BROMAGE, G., *Physica Scripta* **18** (1978) 315.