Stark broadening and regularities of prominent spectral lines of multiply ionized chlorine and fluorine

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(Received 29 September 1987)

Stark widths of six Cl II, eight Cl III, three Cl IV, and two F III spectral lines and Stark shifts of six Cl II and eight Cl III spectral lines have been measured in a linear-pinch discharge plasma and compared with available experimental and theoretical data. The electron density determined by single-wavelength laser interferometry using the visible 632.8-nm transition of a He-Ne laser was 1.97×10^{23} m^{-3}. The electron temperature of 27 000 K was determined from the Boltzmann slope of several Cl II spectral lines and from the intensity ratios of several Cl II to Cl III spectral lines. Since the majority of Cl II, Cl III, and Cl IV spectral lines investigated originate from 4*s*-4*p* transition arrays, the Stark-width (w) dependence on the upper-level ionization potential (I) of corresponding lines has been established and discussed both within one stage of ionization of chlorine and within several stages of ionization of chlorine and fluorine (including neutral chlorine and fluorine). Simultaneously, the Stark-width dependence was found on the net charge (z) of the emitter core acting upon the optical electron undergoing transition. Similarly, Stark-width data obtained for F III spectral lines originating from the 3*s*-3*p* transition array, together with other authors' experimental and theoretical data of F I, F II, and F III spectral lines originating from the same transition arrays, were used to discuss the features of these dependences. The dependences are of the forms $w=AI^{-a}$ (within one ionization stage of chlorine or fluorine) and $w=Bz^2I^{-b}$ (among several ionization stages of chlorine or fluorine), where A, a, B, and b are constants independent of the ionization potential. The trends obtained were used to predict the Stark width of uninvestigated spectral lines originating from the given 4*s*-4*p* (chlorine) and 3*s*-3*p* (fluorine) transitions with an accuracy better than 30%.

I. INTRODUCTION

Several papers[1–4] deal with Stark-width and shift measurements of singly-ionized-chlorine spectral lines. However, only one[5] experimental study of the Stark broadening of singly-ionized-fluorine and doubly-ionized-chlorine spectral lines has apparently been published. The published experimental data were discussed and compared with existing theoretical results in the critical reviews,[6,7] and it was concluded that, in general, the agreement is very good among different experiments (within ±20%). However, the agreement between any particular experimental (Stark-width measurements) and the corresponding theory[8–11] is as follows: with Griem's theoretical results,[8] within ±20%; with the modified semiclassical and the semiempirical theoretical approach,[9–11] within ±60%. There are no published experimental data on the Stark broadening of F III and Cl IV spectral lines. The aim of this work was to provide more Stark-width and shift experimental data of prominent Cl II, Cl III, Cl IV, and F III spectral lines and to compare them with the existing experimental and theoretical data. The emphasis is on the Stark-width (w) dependence on the upper-level ionization potential (I) of a particular spectral line originating from the same transition array (4*s*-4*p* and 3*s*-3*p* in chlorine and fluorine, respectively) (i) within one ionization stage and (ii) among different ionization stages, including the influence of net core charge (z) of the emitter acting upon the electron undergoing optical transition.

Recently, interest has grown in the Stark-width dependence on the upper-level ionization potential and also dependence on the net core charge of the emitter.[12,13] Since the majority of the spectral lines investigated up till now (experimentally or theoretically) of Cl I (Refs. 8 and 10), Cl II (Refs. 1–4), Cl III, and Cl IV and F I (Ref. 14), F II (Ref. 5), and F III originate from 4*s*-4*p* and 3*s*-3*p* transition arrays, respectively, it was possible to establish the above-mentioned dependences in more detail. It has been found that the dependences are of the form

$$w=AI^{-a}\,, \tag{1}$$

within one stage of ionization, and

$$w=Bz^2I^{-b}\,, \tag{2}$$

among different stages of ionization. The constants A, B, a, and b are independent of the upper-level ionization potential I and the net core charge of the emitter z. The general forms of the dependences obtained are similar to those obtained previously in the case of multiply-ionized-nitrogen[12] and -oxygen[13] spectral lines. They were used to predict Stark-width values for several experimentally investigated spectral lines for which there are no other calculations. The overall agreement of such predictions with experimentally obtained values is within ±30%. This can be regarded as a very good agreement, since the accuracy of any theoretical Stark-width calculations in the case of multiply ionized spectral lines is of the same order.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The recording of line profiles was done using a plasma source and spectroscopic setup schematically presented in Fig. 1 of Ref. 15. The working gas was dichlorodifluoromethane of 113 Pa pressure. The same technique and procedure were used also in spectral-line profile measurements described elsewhere.[12–15] The only difference is in the value of the discharge-current maximum ($I_{max}=7.5$ kA) and circuit period ($T=2.7$ μs).

Radiation emitted by the linear-pinch discharge in dichlorodifluoromethane was observed end on and recorded shot by shot using a photomultiplier (RCA 1P28 or EMI 9789 QB), and grating monochromator (Zeiss PGS-2, inverse linear dispersion in first order 0.735 nm/mm and in double pass 0.367 nm/mm). The instrumental half-width at half maximum was 0.004 and 0.002 nm, respectively. Another monochromator (Zeiss SPM-1) with photomultiplier (RCA 1P28) was used simultaneously to monitor the continuum radiation from the same part of the plasma to check the reproducibility. Special care was taken to minimize the influence of self-absorption on the Stark-width measurements. Optical depth was checked by measuring line-intensity ratios within a multiplet and comparing them with the calculated ones using data taken from Wiese *et al.*[16,17] The agreement obtained is within ±6%.

The measured line profiles were of Voigt type, as a result of convolution of Lorentzian-Stark, Gaussian-Doppler, and instrumental profiles. van der Waals and resonance broadening were found to be negligible. Standard deconvolution procedure[18] was used in order to separate the Stark component. The Stark shift was determined using the procedure described elsewhere.[4]

The electron temperature of 27 000 K±10% was determined from (i) the Boltzmann slope of several Cl II spectral lines (481.01, 522.13, 434.36, 476.87, and 391.39 nm with corresponding upper-level energy interval of 5.5 eV) and (ii) from intensity ratios of several Cl II to Cl III spectral lines. The necessary atomic data are taken from Wiese *et al.*[17] Electron density of 1.97×10^{23} m^{-3}±7% was determined by single-wavelength laser interferometry using the visible ($\lambda=632.8$ nm) transition of a He-Ne laser.

III. RESULTS AND DISCUSSION

Experimentally obtained Stark half widths at half maximum (HWHM) (w_m) and Stark shifts (d) of the investigated Cl II, Cl III, Cl IV, and F III spectral lines are given in Tables I, II, and III, together with other authors' experimental and theoretical data, and our predicted data on the basis of the established trends within one ionization stage (w_{p1}) and among several stages of ionization (w_{p2}). In Tables I, II, and III, corresponding electron densities and temperatures are also included. Estimated errors of our experimental data given in Tables I, II, and III are as follows: electron density, ±7%; electron temperature, ±10%; line HWHM, ±15%, and Stark shift, ±30%. Agreement between Griem's[8] semiclassical theoretical results and our experimental data is very good (within ±20% for Cl II spectral lines and 25% for Cl III spectral lines). Direct comparison between our and other authors' experimental data[1–3] for Cl II spectral lines is not possible due to different electron temperatures at which the data were recorded. Figure 1 is given as a demonstration of the very good agreement of the majority of the experimental data with Griem's theory.[8] We

TABLE I. Stark HWHM's w_m for Cl II: our experimental results and the results of other authors (Refs. 1–3); and the ratios of measured w_m to the theoretical results of Griem (Ref. 8). The electron density and temperature, multiplet numbers, and wavelengths are also given. w_{p2}'s are the predicted values according to Eq. (6).

Emitter ion	Transition array	Multiplet (No.)	Wavelength (nm)	T (10^4 K)	N (10^{23} m^{-3})	w_m (10^{-1} nm)	w_m/w_G	w_{p2} (10^{-1} nm)	Ref.
Cl II	$3p^34s-3p^34S^\circ 4p$	$^5S^\circ-{}^5P$ (1)	481.01	2.70	1.97	0.327	0.81	0.435	[a]
				1.33–1.78	2.64–4.27	0.605–0.855	1.00–0.92		2
				1.86	0.68	0.130	0.88		3
				1.15	1.0	0.45	1.87		1
		$^3S^\circ-{}^3P$ (3)	522.13	2.70	1.97	0.383	0.77	0.619	[a]
				1.86	0.68	0.155	0.83		3
	$3p^34s'-3p^32D^\circ 4p'$	$^3D^\circ-{}^3D$ (16)	507.82	2.70	1.97	0.497			[a]
				1.47–1.78	3.72–4.27	1.080–1.695			2
				1.45–1.86	0.50–0.68	0.14–0.17			3
		$^3D^\circ-{}^3P$ (19)	434.36	2.70	1.97	0.328			[a]
				1.45–1.86	0.50–0.68	0.115–0.130			3
	$3p^34s''-3p^32P^\circ 4p''$	$^3P^\circ-{}^3D$ (40)	476.87	2.70	1.97	0.308			[a]
				1.45–1.86	0.50–0.68	0.105–0.120			3
	$3p^34p'-3p^32D^\circ 4d'$	$^3F-{}^3F^\circ$ (68)	391.39	2.70	1.97	0.480			[a]
				1.45–1.86	0.50–0.68	0.135–0.175			3

[a]This work.

TABLE II. Comparison of measured w_m and calculated Stark HWHM's of Cl III, Cl IV, and F III spectral lines. The electron density and temperature, multiplet numbers, and wavelengths are given. Ratios of the measured to the theoretical results of Dimitrijević and Konjević (Refs. 9–11) are given [w_G according to Griem's theory (Ref. 8); w_{GM}, according to the modified semiclassical approach; and w_{SEM}, according to the modified semiempirical method]. Predicted values: w_{p1}'s are the predicted values calculated using Eq. (4); and w_{p2}'s are the predicted values calculated using Eqs. (6) and (7) for chlorine and fluorine, respectively.

Emitter ion	Transition array	Multiplet (No.)	Wavelength (nm)	T (10^4 K)	N (10^{23} m^{-3})	w_m (10^{-1} nm)	w_m/w_G	w_m/w_{SEM}	w_m/w_{GM}	w_{p1} (10^{-1} nm)	w_{p2} (10^{-1} nm)	Ref.
Cl III	$3p^2 4s$ –	^4P–$^4P^\circ$	328.34	2.70	1.97	0.218	1.07	1.47	1.51	0.198	0.175	a
	$3p^2\,^3P\,^4P$	(2)		2.42	0.58	0.048	0.78	1.07	1.12			5
			328.98	2.70	1.97	0.213	1.07	1.47	1.51	0.198	0.175	a
				2.42	0.58	0.048	0.78	1.07	1.12			5
		^4P–$^4S^\circ$	319.14	2.70	1.97	0.192	1.02	1.42	1.45	0.189	0.169	a
		(3)		2.42	0.58	0.048	0.81	1.10	1.16			5
			313.93	2.70	1.97	0.181	0.97	1.34	1.37	0.183	0.163	a
		^2P–$^2P^\circ$	332.06	2.70	1.97	0.231	1.11	1.59	1.56	0.211	0.191	a
		(6)	325.93	2.70	1.97	0.231	1.11	1.59	1.56	0.203	0.184	a
	$3p^2 3d'$ –	^2F–$^2D^\circ$	460.82	2.70	1.97	0.365						a
	$3p^2\,^1D\,4p'$	(13)										
	$3p^2 4s'$ –	^2D–$^2P^\circ$	296.56	2.70	1.97	0.160	0.93	1.31	1.33			a
	$3p^2\,^1D\,4p$	(11*UV*)										
Cl IV	$3p4s$ –	$^3P^\circ$–^3D	307.67	2.70	1.97	0.100	0.79	1.04	1.21		0.138	a
	$3p\,^2P^\circ\,4p$		306.31	2.70	1.97	0.104	0.82	1.07	1.26		0.137	a
		$^3P^\circ$–^3P	278.24	2.70	1.97	0.098	0.95	1.25	1.47		0.117	a
F III	$2p^2 3s$ –	^4P–$^4D^\circ$	311.36	2.70	1.97	0.092	0.97	1.14	1.23		0.092	a
	$2p^2\,^3P\,3p$	(1)										
	$2p^2 3p'$ –	$^2P^\circ$–^2D	315.44	2.70	1.97	0.115						a
	$2p^2\,^1D\,3d'$	(4)										

[a] This work.

TABLE III. Measured Stark shifts d_m of Cl II and Cl III spectral lines of corresponding electron temperatures normalized to the electron density of $N=10^{23}$ m^{-3}.

Emitter ion	Transition array	Multiplet (No.)	Wavelength (nm)	T (10^4 K)	d_m (10^{-1} nm)	Ref.
Cl II	$3p^3 4s-$	$^5S^\circ-{}^5P$	481.01	2.70	−0.02	[a]
	$3p^3\,{}^4S^\circ 4p$	(1)		1.86	0.00	4
		$^3S^\circ-{}^3P$	522.13	2.70	−0.02	[a]
		(3)		1.86	0.00	4
	$3p^3 4s'-$	$^3D^\circ-{}^3D$	507.82	2.70	0.00	[a]
	$3p^3\,{}^2D^\circ 4p'$	(16)		1.86	0.00	4
		$^3D^\circ-{}^3P$	434.36	2.70	0.04	[a]
		(19)		1.86	0.12	4
	$3p^3 4s''-$	$^3P^\circ-{}^3D$	476.87	2.70	0.00	[a]
	$3p^3\,{}^2P^\circ 4p''$	(40)		1.86	0.00	4
	$3p^3 4p'-$	$^3F-{}^3F^\circ$	391.39	2.70	0.12	[a]
	$3p^3\,{}^2D^\circ 4d'$	(68)		1.86	0.21	4
Cl III	$3p^2 4s-$	$^4P-{}^4P^\circ$	328.34	2.70	0.00	[a]
	$3p^2\,{}^3P\,4p$	(2)	328.98	2.70	0.01	[a]
		$^4P-{}^4S^\circ$	319.14	2.70	0.00	[a]
		(3)	313.93	2.70	0.00	[a]
		$^2P-{}^2P^\circ$	332.06	2.70	0.00	[a]
		(6)	325.93	2.70	0.00	[a]
	$3p^2 4d'-$	$^4F-{}^4D^\circ$	460.82	2.70	0.02	[a]
	$3p^2\,{}^1D\,4p'$	(13)				
	$3p^2 4s'-$	$^2D-{}^2P^\circ$	296.56	2.70	−0.02	[a]
	$3p^2\,{}^1D\,4p$	(11*UV*)				

[a]This work.

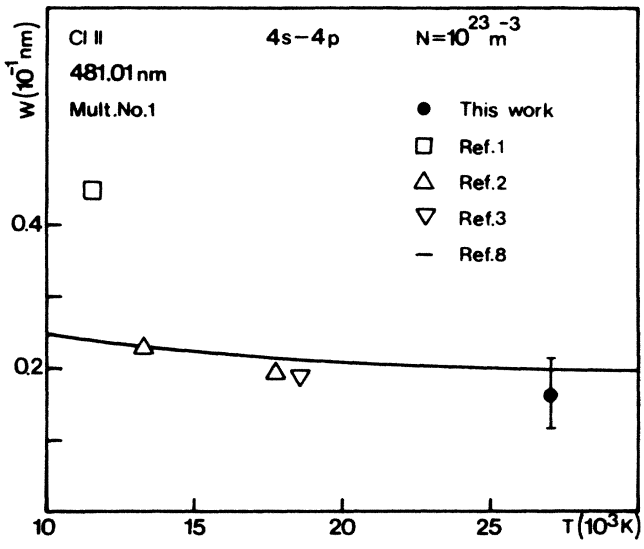

FIG. 1. Stark HWHM's of Cl II 481.01-nm spectral line vs electron temperatures at electron density $N=10^{23}$ m^{-3}: ●, our experimental data; □, Bengtson (Ref. 1); △, Konjević *et al.* (Ref. 2); ▽, Konjević *et al.* (Ref. 3); and ——, Griem (Ref. 8).

found also a very good agreement between our experimental data for Cl III spectral lines and the measurements done by Platiša *et al.*[5] Agreement of our Stark-width experimental data with modified semiclassical and semiempirical calculations[9–11] is within ±30% and ±40%, respectively, for the majority of investigated chlorine and fluorine spectral lines. Agreement of our Cl III Stark-width data with those obtained by Platiša *et al.*[5] is within ±15% (after correction for temperature). The predicted values w_{p1} (obtained from the trend within one ionization stage of chlorine or fluorine) and w_{p2} (obtained from the overall trend within several ionization stages of chlorine or fluorine) are also given in Tables I and II. They agree with our experimental data within ±30%. The agreement of our Stark-shift data with the existing experimental results[4] is within the experimental error of ±30%.

IV. REGULARITIES WITHIN ONE AND SEVERAL STAGES OF IONIZATION

The Stark HWHM experimental data that we obtained, and the corresponding experimental and theoretical data of other authors, were used to prove the validity

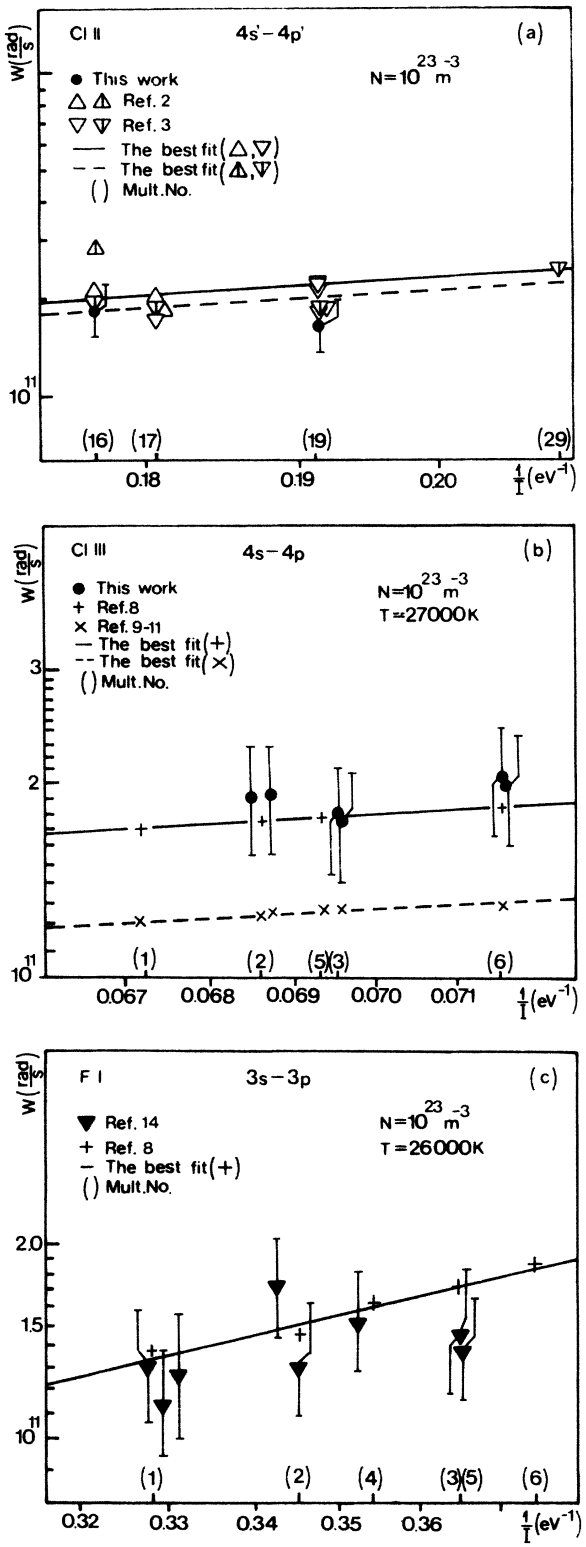

FIG. 2. Stark HWHM (w) vs inverse value of the upper-level ionization potential (I) for the following transition arrays: (a) Cl II $4s'$-$4p'$; (b) Cl III $4s$-$4p$; and (c) F I $3p$-$3p$ at different temperatures for $N=10^{23}$ m^{-3} electron density: ●, our experimental data at 27 000 K; △ and ▲, Konjević *et al.* (Ref. 2) at 14 700 K and 17 800 K, respectively; ▽ and ▼, Konjević *et al.* (Ref. 3) at 14 500 K and 18 600 K, respectively; ▼, Purić *et al.* (Ref. 14) at 26 000 K; +, Griem's theory (Ref. 8); ×, Dimitrijević and Konjević (Refs. 9–11), with appropriate best fits.

of Eqs. (1) and (2). In the case of the Cl II $4s'$-$4p'$ transition array, we have found the following relation between Stark width w and corresponding upper-level ionization potential I of a particular transition:

$$w=1.96\times10^{12}I^{-1.32}\ \text{(for 14 600 K)}, \tag{3a}$$

$$w=1.62\times10^{12}I^{-1.27}\ \text{(for 18 200 K)} \tag{3b}$$

[see Fig. 2(a)]. Although the results used in the figure are given at different temperatures, the agreement with Eqs.

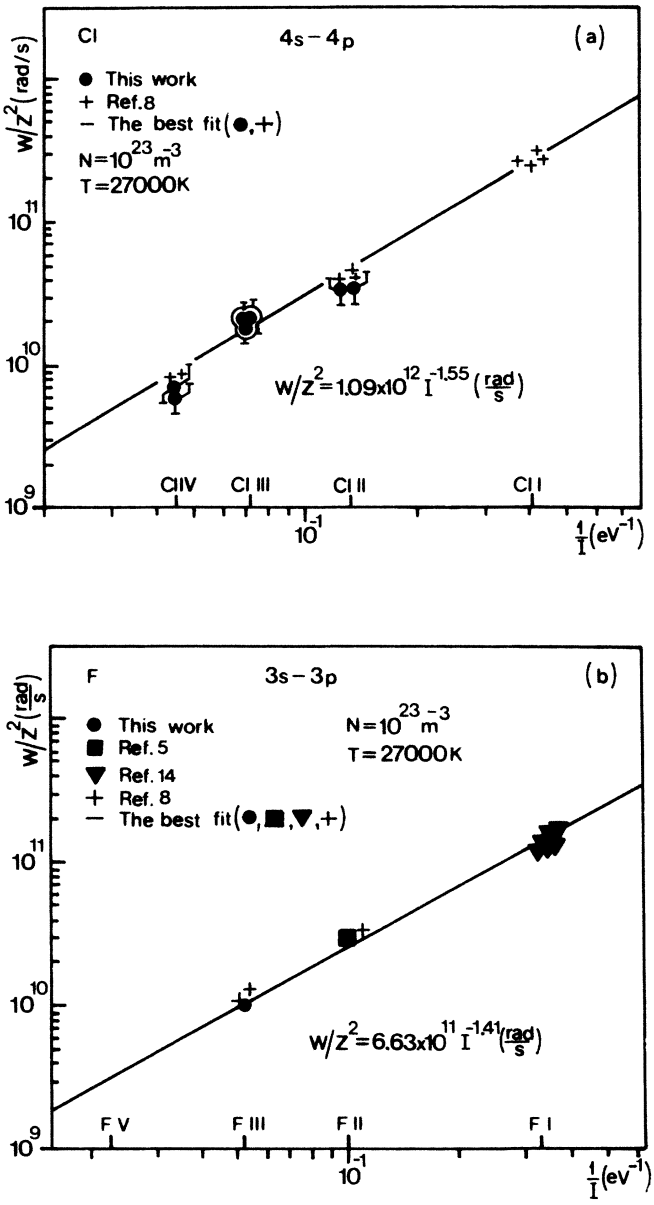

FIG. 3. Reduced HWHM (w/z^2) vs inverse value of the upper-level ionization potential (I) for (a) Cl I, Cl II, Cl III, and Cl IV, $4s$-$4p$; and (b) F I, F II, and F III $3s$-$3p$ transition arrays at electron temperature $T=27\,000$ K and electron density $N=10^{23}$ m^{-3}: ●, our results; ■, Platiša *et al.* (Ref. 5) (24 200 K); ▼, Purić *et al.* (Ref. 14) (26 000 K), and +, Griem's theory (Ref. 8) (27 000 K), with appropriate best fits.

(3a) and (3b) is within ±20% with the exception of the results given by Bengtson.[1] Similar dependence has been obtained for the Cl III $4s$-$4p$ transition array using Griem's theoretical results.[8] In this case,

$$w = 2.91 \times 10^{12} I^{-1.05} \quad \text{(for 27 000 K)} \tag{4}$$

[see Fig. 2(b)]. The agreement between our experimental results and the semiclassical calculation[8] is within 15%, which lies within experimental error. The modified semiclassical and semiempirical calculations done by Dimitrijević and Konjević[9–11] follow the trend given by Eq. (4) within 60%.

For the F I $3s$-$3p$ transition array we have used Griem's[8] theoretical results and the experimental data of Purić *et al.*[14] in order to get the corresponding dependence. It was found that, for this case,

$$w = 1.87 \times 10^{12} I^{-2.35} \quad \text{(for26 000 K)} \tag{5}$$

[presented in Fig. 2(c)]. The experimental results follow Eq. (5) within ±30%. In Eqs. (3)–(5), the ionization potential I has to be taken in eV in order to get w in rad/s.

The obtained Eqs. (4) and (5) are of the same form as Eq. (1). The corresponding correlation factors are better than 0.90. These equations were used to predict Stark-width values (w_{p1}) for the lines uninvestigated so far (theoretically or experimentally) but belonging to the same transition array. Such predictions agree with the measured value within ±30%, which can be regarded as very good, since the experimental errors are up to ±15%, and the uncertainty of the majority of theoretical approaches is within ±30%.

Simultaneous dependence of the Stark HWHM w (rad/s) on the net charge of the corresponding emitter core z and the upper-level ionization potential I are

$$w = 1.09 \times 10^{12} z^2 I^{-1.55} \tag{6}$$

for Cl I, Cl II, Cl III, and Cl IV $4s$-$4p$ transition arrays [presented in Fig. 3(a)], and

$$w = 6.63 \times 10^{11} z^2 I^{-1.41} \tag{7}$$

for F I, F II, and F III $3s$-$3p$ transition arrays [presented in Fig. 3(b)]. The corresponding correlation factors are better than 0.98.

Equations (6) and (7) were used to predict Stark-width values (w_{p2}) for several spectral lines belonging to the investigated transition arrays of given ionization stages of chlorine and fluorine. The predictions obtained agree with the measured values within ±30%. We have calculated, for instance, the Stark HWHM value for the Cl VII 218.98 nm spectral line ($4s^2\,S$–$4p^2\,P^\circ$ transition) according to the modified semiempirical method of Dimitrijević and Konjević[9–11], and found $w_{DM} = 0.0028$ nm. However, using the relation given by Eq. (6) for the same Cl VII line, one obtains $w_{p2} = 0.0030$ nm, which is almost equal to w_{DM}. Similarly, the prediction obtained for the F V 245.42-nm spectral line ($3s^2\,S$–$^1S3p^2\,P^\circ$ transition) on the basis of Eq. (7) is $w_{p2} = 0.0025$ nm; the calculated value according to the above-mentioned modified semiempirical method[9–11] is $w_{DM} = 0.0019$ nm, which agrees with the predicted value within 33%.

V. CONCLUSION

On the basis of the considerations given above, one can draw the following conclusions.

(a) Good agreement exists between our own and previous experiments,[2–4] as well as with Griem's[8] semiclassical theory (within ±25%). The agreement with the results of Platiša *et al.*[5] is within ±40%, although the temperatures are slightly different.

(b) The agreement with the modified semiclassical and semiempirical approaches of Dimitrijević and Konjević[9–11] is within 50% for the majority of the spectral lines investigated (the theory underestimates HWHM).

(c) Predictions using Eqs. (3)–(7) agree with our experimental data within ±30%.

It is very encouraging that the general validity of Eqs. (1) and (2) in the case of Stark-width data for the lines from several ionization stages of chlorine and fluorine is similar to the result found by us in the case of nitrogen[12] and oxygen[13] spectral lines.

One may expect in general that the form of the simultaneous dependence of the Stark width on the upper-level ionization potential of the corresponding spectral line, and on the net core charge of the emitter core acting on the electron undergoing transition within a particular transition array of several ionization stages, is independent of the specific emitter cores.

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