Stark broadening and shift of singly and doubly ionized sulfur spectral lines

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Stark width and shift measurements of eight S II and one S III spectral line (of $4s$-$4p$, $4s'$-$4p'$, and $4p$-$4d$ transition arrays) have been performed for the electron density range 6.70×10^{22}–2.08×10^{23} m^{-3} and for an electron temperature range 27 000–40 000 K. Stark parameters of all these spectral lines, belonging mostly to higher multiplets, were measured in a linear low-pressure pulsed arc operating in SO_2. The obtained Stark width data were compared with the values calculated on the basis of various theoretical approaches and good agreement has been found. The existence of Stark width dependence on the upper-level ionization potential, for S II spectral lines belonging to the $4p$-$4d$ transition array, has also been proved.

I. INTRODUCTION

A number of experimental[1–5] and theoretical[6–8] papers have dealt with Stark broadening of S II and S III spectral lines. Experimental results of S II spectral lines belonging to lower multiplets were presented in Refs. 2–5 and for S III spectral lines in Ref. 1. No experimental results exist, known to the authors, for Stark shifts of S II and S III spectral lines.

The aim of this paper is to supply additional experimental data on S II and S III spectral lines originating from higher multiplets. This experimental study of linewidths and shifts of prominent S II and S III spectral lines is an extension of systematic studies of Stark widths and shifts and regularities of spectral lines of ionized atoms belonging to the second and third period of the Periodic system of the elements.[9–11]

We have measured Stark widths and shifts of 8 S II spectral lines (multiplet Nos. 14, 40, 44, 45, 49, 50, 56, and 59) and of one S III spectral line (multiplet No. 4). Except for the two lines at 452.495 and 433.271 nm belonging to the S II and S III spectra, respectively, all of the spectral lines were investigated for the first time. Measured Stark broadening parameters are compared with existing theoretical values and with our calculated values based on the semiempirical and modified semiempirical formulas.

Most of the investigated S II lines originate from the $4p$-$4d$ transition array. It is therefore possible to examine the Stark width dependence on the upper-level ionization potential I of the corresponding spectral line and the electron temperature T, as proposed in Refs. 9–12. The assumed functional dependence of the Stark width w (half-width at half intensity maximum, HWHM) is of the form

$$w = aT^{-1/2}I^{-b} , \quad (1)$$

where a and b are coefficients that are independent of ionization potential and the electron temperature for a given transition array at the given electron density. The established trend can be used to predict Stark HWHM of spectral lines that have not yet been measured.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

Details of the experimental apparatus were described in Ref. 12. A pulsed discharge occurred in a Pyrex discharge tube of 5-mm i.d., and had an effective plasma length of 7.4 cm. The tube had quartz windows. The gas was SO_2 at a filling pressure range 170–400 Pa. Spectroscopic observations of isolated spectral lines were made end on along the axis of the discharge tube. A capacitor of 0.3 μF was charged up to 14.6 kV and supplied discharge currents up to 6 kA. From the discharge current oscillograms some circuit characteristics have been evaluated as follows: circuit inductance of 1.13 μH, equivalent circuit resistance 0.53 Ω, and period 3.7 μs. For the spectroscopic study, a photomultiplier (EMI 9789QB) and a grating-spectrograph (Zeiss PGS-2, inverse linear dispersion 0.73 nm/mm) system were used. Scanning of the lines was done by using a shot-to-shot technique, which involved advancing the exit slit-photomultiplier combination in small (0.0073 nm) wavelength steps. Plasma reproducibility was monitored by the continuum and line radiation, as well as the discharge current. It was found to be within $\pm8\%$. Great care was taken to minimize the influence of self-absorption on Stark width determinations. The opacity was checked by measuring line-intensity ratios of the strongest lines within a multiplet. The values obtained are compared with calculated ratios of the products of the spontaneous emission probabilities and the corresponding statistical weights of the upper levels of the lines.[13] These ratios were found to differ by less than ±6%. The measured profiles were of the Voigt type due to the convolution of the Lorentzian Stark profile and the Gaussian profiles caused by Doppler and instrumental broadening. van der Waals and resonance broadening were found to be negligible. The instrumental HWHM was 0.007 nm in the first order. A standard deconvolution procedure was used, as described in Ref. 14.

The Stark shifts were measured relative to almost unshifted spectral lines emitted by the same plasma. The latter were observed at later times during plasma decay at considerably lower electron densities (the method has been described in Ref. 15).

The electron density was measured using a single wavelength He-Ne laser interferometer,[16] for the 632.8-nm transition in the visible spectrum, with an estimated error of ±7%. Peak densities were found to be 1.3×10^{23} and 2.4×10^{23} m^{-3} corresponding to two different initial gas pressures and discharge parameters.

In the case of $p=170$ Pa gas pressure, and $E=27$ J bank energy, the electron temperature was deduced from the slope of Boltzmann plot of six S II spectral lines (564.69, 416.27, 402.88, 426.78, 389.23, and 425.74 nm) with a corresponding upper-level energy interval of 4.16 eV. It was found that the electron temperature decayed slowly during the first 30 μs after the beginning of the discharge. The errors of these measurements are estimated to be within ±12%. Measured electron temperatures were 34 000 and 27 000 K corresponding to 5 and 10 μs

TABLE I. Stark HWHM w and shift d (in 10^{-1} nm). The values w_m and d_m are our data and experimental data of other authors taken from Refs. 3 and 1 for S II and S III, respectively, at given electron temperatures and densities. The ratios of measured w_m to theoretical w_{theor} values are given for S II, where single and double asterisks are the results of our calculations based on the formulas from Refs. 17 and 18; and S III, while MSE, SE, GM, and G are results from Ref. 7 based on the modified semiempirical, semiempirical, modified Griem's formula, and Griem's formula, respectively. The transition arrays, multiplet numbers, and wavelengths are also given. The positive shift is toward longer wavelengths.

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_{theor}	d_m (10^{-1} nm)	Ref.
S II	$3p^24s$-$3p^2(^3P)4p$	^2P-$^2D^\circ$ (14)	564.698	2.7	0.67	0.158	0.87* 1.01**		This work
				3.4	1.02	0.198	0.81* 0.94**		This work
				4.0	2.08			−0.06	This work
	$3p^24s'$-$3p^2(^1D)4p'$	^2D-$^2P^\circ$ (40)	452.495	2.7	0.67	0.186	1.60* 1.85**	−0.04	This work
				3.4	1.02	0.266	1.68* 1.95**		This work
				1.2	0.7	0.27	1.43* 1.71**		3
	$3p^24p$-$3p^2(^3P)4d$	$^4D^\circ$-^4F (44)	416.270	2.7	0.67	0.208		−0.04	This work
				3.4	1.02	0.268			This work
		$^4D^\circ$-^4D (45)	402.879	2.7	0.67	0.188		0.06	This work
				3.4	1.02	0.248			This work
		$^4P^\circ$-^4D (49)	426.780	2.7	0.67	0.229		0.04	This work
		$^4P^\circ$-^4P (50)	389.232	2.7	0.67	0.210		0.00	This work
		$^2D^\circ$-^2D (56)	361.692	2.7	0.67	0.220		0.05	This work
				3.4	1.02	0.271			This work
		$^4S^\circ$-^4P (59)	403.281	2.7	0.67			0.08	This work
				3.4	1.02	0.307	1.25* 1.31**		This work
S III	$3p4s$-$3p(^2P^0)4p$	$^3P^\circ$-^3D (4)	433.271	4.0	2.08	0.214	0.85 MSE 1.45 SE 0.80 GM 0.59 G	0.04	This work
				2.85	0.51	0.062	0.88 MSE 1.49 SE 0.90 GM 0.63 G		1

after the beginning of the discharge. All Strak parameters of spectral lines have been measured in this domain.

In the case of $p=400$ Pa and $E=32$ J the electron temperature was deduced from the intensity ratios of 433.27-nm S III spectral line to S II 564.69-nm spectral line, assuming the existence of local thermal equilibrium. The temperature was found to be 40 000 K with an estimated error of $\pm 14\%$ at 5 μs after the beginning of the discharge and decayed slowly during the first 20 μs.

III. RESULTS

A. Experiment

Experimentally determined Stark HWHM w_m and shift d_m of the S II and S III lines are given in Table I together with other experimental data,[1,3] theoretical values,[7] and our calculations based on Refs. 17 and 18 and the main plasma parameters, i.e., electron densities and temperatures. The estimated errors of our measured electron densities and temperatures presented in Table I are $\pm 7\%$ and $\pm 12\%$, respectively. The uncertainties in our experimentally measured Stark HWHM data presented in Table I are within $\pm 15\%$. The Stark shift data given in Table I are determined with absolute errors of ± 0.0018 nm at the given electron density and temperature.

B. Theory

Since there are no data available for all relevant perturbing energy levels of S II and S III spectral lines, the

TABLE II. Calculated Stark HWHM w (in 10^{-1} nm) at $N=1\times 10^{23}$ m^{-3} electron density. w_{MSE} and w_{SE} are our calculated values based on the modified semiempirical [Dimitrijević and Konjević (Ref. 17)] and semiempirical formulas [Griem (Ref. 18)], respectively, at a given electron temperature for the given transition array and average wavelengths $\bar{\lambda}$. ΔE is the energy difference to the nearest perturbing energy level that determines the critical electron temperature [see criterion (2)].

Emitter	Transition	T (K)	W_{MSE} (10^{-1} nm)	W_{SE} (10^{-1} nm)
S II	$4s\,^2P$-$4p\,^2D°$	10 000	0.895	0.766
	multiplet No. 14	15 000	0.731	0.625
	$\bar{\lambda}=565.36$	20 000	0.633	0.542
	$3kT/2\Delta E=0.81$	25 000	0.566	0.484
S II	$4s'\,^2D$-$4p'\,^2P°$	10 000	0.574	0.492
	multiplet No. 40	15 000	0.469	0.402
	$\bar{\lambda}=453.41$ nm	20 000	0.406	0.348
	$3kT/2\Delta E=0.50$	25 000	0.363	0.311
		30 000	0.331	0.284
		35 000	0.307	0.263
		40 000	0.287	0.246
S II	$4p\,^4D°$-$4d\,^4F$	10 000	0.721	0.739
	multiplet No. 44	15 000	0.589	0.603
	$\bar{\lambda}=415.96$ nm	20 000	0.510	0.522
	$3kT/2\Delta E=0.85$			
S II	$4p\,^4D°$-$4d\,^4D$	10 000	0.708	0.714
	multiplet No. 45	15 000	0.578	0.583
	$\bar{\lambda}=399.58$ nm	20 000	0.501	0.505
	$3kT/2\Delta E=0.92$			
S II	$4p\,^4P°$-$4d\,^4D$	10 000	0.835	0.837
	multiplet No. 49	15 000	0.682	0.683
	$\bar{\lambda}=428.66$ nm	20 000	0.591	0.592
	$3kT/2\Delta E=0.92$			
S II	$4p\,^4P°$-$4d\,^4P$	10 000	0.802	0.772
	multiplet No. 50	15 000	0.655	0.630
	$\bar{\lambda}=385.11$ nm			
	$3kT/2\Delta E=1.24$			
S II	$4p\,^2D°$-$4d\,^2D$	10 000	0.866	0.797
	multiplet No. 56	15 000	0.707	0.651
	$\bar{\lambda}=359.69$ nm			
	$3kT/2\Delta E=1.20$			
S II	$4p\,^4S°$-$4d\,^4P$	10 000	0.882	0.847
	multiplet No. 59	15 000	0.720	0.692
	$\bar{\lambda}=401.27$ nm	20 000	0.624	0.599
	$3kT/2\Delta E=0.59$	25 000	0.558	0.536
		30 000	0.509	0.489
		35 000	0.471	0.453

theoretical results of Stark parameters cannot be calculated with confidence. This is particularly true for the calculation of shifts. Total contribution, in calculating shifts, depends also on the position of each level. Thus omitting even a few perturbing levels could lead to incorrect values of Stark shifts and even change of the sign. This was the reason why the theoretical evaluation of Stark shifts has not been done.

For Stark width calculations we used simplified theoretical approaches, where the complete set of perturbing levels is not required. Stark widths of S II spectral lines have been calculated using modified semiempirical[17] and semiempirical[18] formulas. The values of widths calculated in this way were usually smaller than expected. All necessary data for these calculations were taken from Ref. 19.

Results of our calculations of Stark width of S II spectral lines for an electron density of $N=1\times10^{23}$ m^{-3} at different electron temperatures for average wavelength of multiplets are presented in Table II. Under our experimental conditions the contribution of ion broadening to the total linewidth can be neglected, since it is less than 1%. Measured Stark widths of S III spectral lines were compared with the theoretical values given in Ref. 7.

IV. DISCUSSION

The values in Table I are presented as the ratio between experimental w_m and theoretical w_{theor} HWHM values. Comparison of experimental data with the theoretical results, in the case of S II spectra, according to the approach in Ref. 17, could be done only if criterion

$$3kT/2\Delta E \leq 2 \quad (2)$$

is satisfied (ΔE is the energy difference to nearest perturbing level). The critical electron temperature, from this criterion, determines the range of applicability of the approximation. On the basis of this criterion only three S II spectral transitions could be compared. The semiempirical[18] and modified semiempirical[17] results are found to be systematically smaller than the experimental values. This discrepancy, however, does not exceed the estimated accuracy of applied theoretical approaches. Similar discrepancies exist also for the results given by Mar, Czernichowski, and Chapelle.[3]

Stark HWHM of multiplet No. 40, spectal line 452.49 nm, is presented graphically in Fig. 1 as a function of electron temperature for the electron density of $N=1\times10^{23}$ m^{-3}. In the case of this S II transition array the criterion (2) is satisfied up to 40 000 K electron temperature.

Our experimental results of Stark HWHM and those of Mar, Czernichowski, and Chapelle[3] are systematically larger in comparison to our calculated modified semiempirical (MSE) and semiempirical (SE) values on the basis of formulas taken from Refs. 17 and 18 by about 60% and 80%, respectively. Such discrepancies do not exceed an estimated accuracy, because of the uncertainties of the used approximative theoretical approaches and the measured Stark widths.

The lack of reliable theoretical data for Stark shifts made it impossible for us to compare our experimental results with the theory.

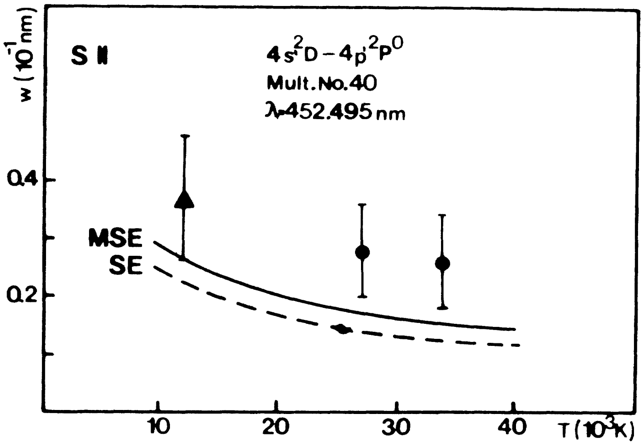

FIG. 1. Stark HWHM w (in 10^{-1} nm) of S II 452.495-nm spectral line vs electron temperature at the electron density of $N=1\times10^{23}$ m^{-3}; ●, our data, and ▲, experimental data of Mar, Czernichowski, and Chapelle (Ref. 3). The lines are our results of theoretical calculations based on the formulas by Dimitrijević and Konjević (Ref. 17) (MSE, solid line) and by Griem (Ref. 18) (SE, dashed line), respectively.

The experimental Stark HWHM of the S III spectral line has been compared with MSE and SE theoretical values given in Ref. 7 and with values G for Griem's formula and GM for modified Griem's formula calculated in

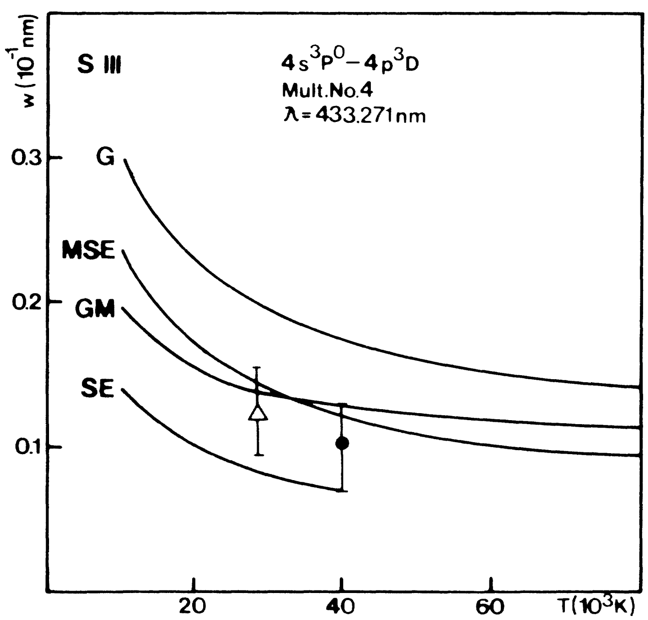

FIG. 2. Stark HWHM w (in 10^{-1} nm) of S III 433.271-nm spectral line vs electron temperature at the electron density of $N=1\times10^{23}$ m^{-3}; ●, our data, and Δ, experimental data of Platiša *et al.* (Ref. 1). The solid lines are theoretical values taken from Ref. 7 based on the modified semiempirical MSE and semiempirical formulae SE. G and GM represent the theoretical values calculated by Dimitrijević and Konjević (Ref. 7) on the basis of Eq. (526) from Ref. 6.

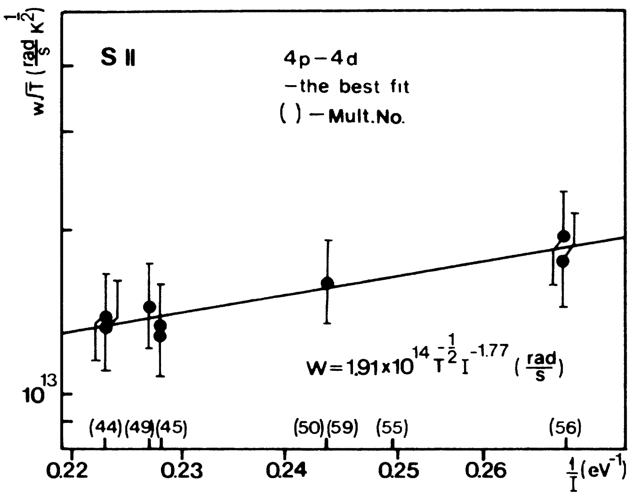

FIG. 3. Reduced Stark HWHM $wT^{1/2}$ (in rad $K^{1/2}$/s) vs the inverse values of the upper-level ionization potential I (in eV) for the S II 4*p*-4*d* transition array at an electron density of $N = 1\times10^{23}$ m^{-3}. ●, our experimental data at two different electron temperatures (see Table I).

Ref. 7 on the basis of Eq. (526) from Ref. 6. The ratio of experimental width to those theoretical values is also given in Table I. This ratio varies from −70% to +45% depending on the kind of theoretical approach and given electron temperature.

Stark HWHM of the 433.27-nm S III spectral line is presented graphically in Fig. 2 as a function of electron temperature for an electron density of $N = 1\times10^{23}$ m^{-3}. Our experimental results of Stark HWHM and those of Platiša *et al.*[1] are in good agreement with theoretical values calculated on the basis of MSE approaches and on the basis of modified Eq. (526) from Ref. 6 given in Ref. 7 like GM (see also Fig. 2).

V. REGULARITIES

It was pointed out by Wiese and Konjević[20] that all Stark widths for lines within a transition array should be nearly equal because of similar positions of their upper and lower energy levels. Our results for S II spectral lines from the 4*p*-4*d* array (see Table I) indeed verify this statement.

However, we have shown in a number of cases that the Stark width values obey certain trends within a particular transition array. For example, in the case of Ar II spectral lines from the 4*p*-4*d* array, in a broad range of the upper-level ionization potential (1.12 eV), the reduced Stark HWHM in log-log scale linearly depend on the inverse upper-level ionization potential (Fig. 2 in Ref. 21).

All our experimental data of the Stark HWHM for singly ionized sulfur spectral lines belonging to the 4*p*-4*d* transition array are satisfactorily fitted by Eq. (1) at an electron density of $N = 1\times10^{23}$ m^{-3}. Namely, for the 4*p*-4*d* transition array (multiplet Nos. 44, 45, 49, 50, 56, and 59 of the S II spectral lines), Eq. (1) has the form

$$w_{4p\text{-}4d} = 1.91\times10^{14} T^{-1/2} I^{-1.77}\ (\text{rad/s})\ . \qquad (3)$$

The corresponding correlation factor is 0.95. The numerical constants are valid for T in K and I in eV. It is evident from Fig. 3 that the reduced Stark HWHM ($wT^{1/2}$) on a log-log scale depends linearly on the inverse value of the upper-level ionization potential for the given transition.

By using Eq. (3), we may now predict Stark HWHM for spectral lines belong to the 4*p*-4*d* transition array of S II. The predicted value for 393.33 nm (multiplet No. 55) is 0.033 nm for $T = 27\,000$ K and $N = 1\times10^{23}$ m^{-3}, with an estimated error of ±25%.

VI. CONCLUSIONS

Stark widths and shifts of S II and S III spectral lines, belonging to higher multiplets, were measured in a linear, low-pressure, pulsed arc. Plasma was found to be optically thin even for the strongest spectral lines. Uncertainties of all the relevant parameters, which affect the Stark width and shift, were minimized within the error limits of such measurements.

Measured Stark widths of S II spectral lines were systematically larger than the theoretical values, calculated on the basis of modified semiempirical and semiempirical approaches. These discrepancies do not exceed the estimated accuracy, because of uncertainties of the used approximative theoretical approaches and the uncertainties of measured Stark widths.

Temperature dependence of Stark width of two (S II and S III) spectral lines is the same as given by the theory, in the temperature domain determined by the criterion (2).

Our and other authors' experimental results of Stark widths are in good agreement. Stark width dependence upon the corresponding upper-level ionization potential, for all S II spectral lines belonging to the 4*p*-4*d* transition array, follows a trend given by Eq. (1). The correlation factor for fitting to this trend is found to be 0.95.

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