Stark broadening and shift of singly ionized zinc and cadmium spectral lines

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The Stark width and shift of six Zn II and six Cd II spectral lines have been measured for the electron-density range of 1.0×10^{23}–1.23×10^{23} m^{-3} and for an electron-temperature range of 23 000–33 000 K in a pulsed linear arc plasma discharge in SF_6 and argon-helium mixture. Obtained Stark-width data were compared with the values calculated on the basis of various theoretical approaches.

I. INTRODUCTION

Only two papers, known to the authors, have dealt with investigations of Stark broadening of singly ionized zinc [1] and cadmium [2] spectral lines. No experimental results exist for Stark shifts of Zn II and Cd II lines.

The aim of this paper is to supply additional experimental data on Zn II and Cd II spectral lines in order to extend the systematic studies of Stark widths and shifts to the singly ionized heavy elements (tin [3] and mercury [4]).

We have measured Stark widths [half width at half maximum intensity (HWHM)] of six Zn II and six Cd II spectral lines. The lines 206.19, 747.88, 589.44, and 758.85 nm belonging to $4s$-$4p$, $4p$-$4s^2$, and $4d$-$4f$ transitions from Zn II spectra and lines 214.41, 441.56, and 274.86 nm belonging to $5s$-$5p$, $5p$-$5s^2$, and $5p$-$6s$ transitions from Cd II spectra, were investigated. Measured Stark HWHM are compared with our calculated values based on the semiempirical and modified semiempirical formulas. Existing experimental Stark HWHM data [1,2] were also compared with our calculated values.

II. APPARATUS AND PROCEDURE

The apparatus has been described elsewhere (Ref. [5]). A linear part of the pulsed discharge tube was of 5 mm i.d. and an effective plasma length was 7.5 cm. The tube had end-on quartz windows. Atoms are released by sputtering of zinc and cadmium deposited on the electrode surface that was close to the linear part of the discharge tube (see Fig. 1).

The working gas was continuously fed through one of the electrodes. We have chosen the gases that give a maximum amount of sputtered material. For this purpose the most convenient gas was SF_6 for both zinc and cadmium. A mixture of argon and helium was used only in the case of cadmium, for comparison reasons. Furthermore, SF_6 as a working gas in the spectra of F II, F III, S II, and S III left the observed lines of Zn II and Cd II isolated. Also, this gas conveniently prevented depositing of Zn and Cd on the quartz windows. The filling pressure was 130 Pa. Electrical parameters of the discharge circuit were adapted to requirements of the experiment, namely to ensure efficient release, transport, ionization, and excitation of the zinc and cadmium atoms. The discharge capacitor of 0.3 μF was charged to 31 J energy. We have determined the following values from the discharge-current oscillograms: circuit inductance is (4.10,4.36) μH, equivalent circuit resistance is (0,43,0.44) Ω, period is (7.0,7.2) μs, and the peak current is (3.58,3.48) kA for the case of zinc and cadmium, respectively. This kind of discharge ensured sufficient amount of impurity atoms in 20 μs after initiation of discharge while the plasma was still of comparatively high electron density for Stark-width studies. Spectroscopic observations of isolated spectral lines were made end-on along the axis of the discharge tube. The line profiles were recorded on a shot-by-shot basis using a Zeiss PGS-2 (inverse linear dispersion 0.73 nm/mm in the first order)

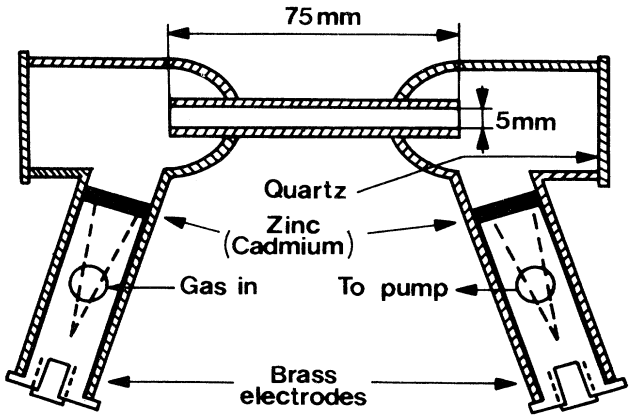

FIG. 1. Discharge tube.

spectrograph with an EMI 9789 QB and 9659 B calibrated photomultipliers. The exit slit of 10 μm with the photomultiplier was micrometrically traversed along the spectral plane in small (0.0073-nm) wavelength steps. Plasma reproducibility, found to be within 5%, was monitored by the F II and Ar II line radiation, as well as the discharge current. Reproducibility of Zn II and Cd II spectral line radiation intensities was 18%, which can be taken as acceptable, regarding the way the impurity atom was introduced. 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 (0.007 nm in the first order) broadening. Owing to the large masses of emitters (Zn II and Cd II) and comparatively small concentration the Doppler, van der Waals, and resonance broadening were found to be negligible. A standard deconvolution procedure was used, as described in Ref. [6]. The errors in our experimentally measured Stark HWHM data are within $\pm 20\%$. The Stark shifts were measured relative to the unshifted spectral lines emitted by the same plasma. The latter were observed at later times during plasma decay and at considerably lower electron densities [7]. The Stark-shift data are determined with absolute errors of ± 0.002 nm at the given temperature and density.

Electron temperature in the case of SF_6 carrier gas with Zn, as an impurity, was determined from the Boltzmann slope of eight F II spectral lines (384.71, 384.99, 410.92, 411.92, 354.18, 429.92, 320.27, and 350.56 nm with a corresponding upper-level energy interval of 5.4 eV) with the estimated errors of $\pm 13\%$. At 20 μs after the beginning of the discharge, when the properties were recorded, it was 33 000 K.

In the case of Cd II spectral lines study in SF_6 the electron temperature was determined from the Boltzmann slope of five S II spectra lines (564.70, 416.27, 426.78, 389.23, and 403.28 nm with a corresponding upper-level energy interval of 3.12 eV). At 20 μs after the beginning of the discharge the electron temperature was 23 000 K with the estimated errors of $\pm 12\%$. For discharge in the argon-helium mixture the electron temperature was deduced from the relative intensity ratio of the 331.12-nm Ar III spectral line to the Ar II 330.72-nm spectral line, assuming the existence of local thermodynamic equilibrium (LTE). At 20 μs after the beginning of the discharge the electron temperature was 30 000 K with the estimated errors of $\pm 14\%$.

The necessary atomic data were taken from Refs. [8] and [9]. The electron density was measured using a single wavelength He-Ne laser interferometer [10] for the 632.8-nm transition with an estimated error of $\pm 8\%$. At 20 μs after the beginning of the discharge the electron densities were 1.15×10^{23} m^{-3} (zinc in SF_6), 1.23×10^{23} m^{-3} (cadmium in SF_6), and 1.00×10^{23} m^{-3} (cadmium in an argon-helium mixture).

III. RESULTS

A. Experiment

Experimentally determined Stark HWHM w_m and shift d_m values of the Zn II and Cd II spectral lines are given in Table I at given electron temperature and density. Estimated uncertainties are $15\% < B \leq 30\%$,

TABLE I. Measured Stark HWHM (w_m) and shift (d_m) of Zn II and Cd II spectral lines at various electron temperatures T and densities N with estimated accuracy (Acc.) in percent. The transition arrays and wavelength are also given. Positive shifts are toward the red.

Emitter	Transition array	Wavelength (nm)	T (10^4 K)	N (10^{23} m^{-3})	w_m (10^{-1} nm)	Acc.	d_m (10^{-1} nm)	Acc.
Zn II	$4s\,^2S-4p\,^2P^\circ$	206.191	3.3	1.15	0.027	*D*	0.00	*D*
	$4p\,^2P^\circ-4s^2\,^2D$	589.435	3.3	1.15	0.264	*B*	0.054	*C*
		747.879	3.3	1.15	0.258	*B*		
	$4p\,^2P^\circ-5s\,^2S$	255.796	3.3	1.15	0.059	*C*	0.00	*D*
	$5s\,^2S-5p\,^2P^\circ$	758.848	3.3	1.15	0.256	*B*	0.066	*C*
	$4d\,^2D-4f\,^2F^\circ$	491.166	3.3	1.15	0.210	*B*	−0.048	*C*
Cd II	$5s\,^2S-5p\,^2P^\circ$	214.411	2.3	1.23	0.028	*D*	0.00	*D*
			3.0	1.00	0.021	*D*	0.00	*D*
		226.502	2.3	1.23	0.021	*D*	0.00	*D*
			3.0	1.00	0.020	*D*	0.00	*D*
	$5p\,^2P^\circ-5s^2\,^2D$	441.563	2.3	1.23	0.118	*B*	0.00	*D*
			3.0	1.00	0.069	*C*	0.00	*D*
	$5p\,^2P^\circ-6s\,^2S$	274.858	2.3	1.23	0.055	*C*	0.00	*D*
	$5p\,^2P^\circ-5d\,^2D$	219.456	2.3	1.23	0.056	*C*	0.00	*D*
		232.107	2.3	1.23	0.056	*C*	0.00	*D*

TABLE II. Calculated Stark HWHM (w) at $N=1\times10^{23}$ m^{-3} electron density. w_{SE}, w_{LTLSE}, and w_{LTLMSE} are our calculated values based on the semiempirical formula (SE) (Griem (Ref. [11]), low-temperature limit (LTL) approaches of the semiempirical LTLSE (Ref. [12]) formula and on the low-temperature limit approaches of the modified semiempirical, LTLMSE, formula (Dimitrijević and Konjević (Ref. [12])), respectively, at a given electron temperature T for the given transition array and average wavelength $\bar{\lambda}$. T_c is the critical electron temperature [see criterion (1)].

Emitter	Transition array	T (10^4 K)	w_{SE} (10^{-1} nm)	w_{LTLSE} (10^{-1} nm)	w_{LTLMSE} (10^{-1} nm)
Zn II	$4s^2S-4p^2P^\circ$	0.50	0.0213		
		1.00	0.0150	0.0149	0.0120
	$\bar{\lambda}=203.82$ nm	2.00	0.0106	0.0105	0.0084
	$T_c=36\,600$ K	3.00	0.0087	0.0086	0.0069
		4.00	0.0075	0.0075	0.0060
	$4p^2P^\circ-4s^{2\,2}D$	0.50	0.4326		
		1.00	0.3059	0.2975	0.4035
	$\bar{\lambda}=678.12$ nm	2.00	0.2296	0.2105	0.2855
	$T_c=28\,300$ K	3.00	0.2092	0.1720	0.2295
		4.00	0.2340		
	$4p^2P^\circ-5s^2S$	0.50	0.0966		
		1.00	0.0682	0.0700	0.0970
	$\bar{\lambda}=253.977$ nm	2.00	0.0562	0.0493	0.0684
	$T_c=25\,100$ K	3.00	0.0564	0.0404	0.0560
		4.00	0.0692		
	$5s^2S-5p^2P^\circ$	0.50	1.7234	1.7610	2.2420
		1.00	1.3206	1.2455	1.5855
	$\bar{\lambda}=763.815$ nm	2.00	1.2259		
	$T_c=8800$ K	3.00	1.3941		
		4.00	1.6151		
	$4d^2D-4f^2F^\circ$	0.50	1.3000		
		1.00	0.9640		
	$\bar{\lambda}=492.040$ nm	2.00	0.8383		
		3.00	0.8986		
		4.00	0.8825		
Cd II	$5s^2S-5p^2P^\circ$	0.50	0.0308		
		1.00	0.0218	0.0196	0.0167
	$\bar{\lambda}=218.38$ nm	2.00	0.0154	0.0138	0.0118
	$T_c=49\,300$ K	3.00	0.0126	0.0113	0.0096
		4.00	0.0112	0.0098	0.0084
	$5p^2P^\circ-5s^{2\,2}D$	0.50	0.1952		
		1.00	0.1380	0.1375	0.1900
	$\bar{\lambda}=388.77$ nm	2.00	0.0976	0.0970	0.1340
	$T_c=49\,300$ K	3.00	0.0852	0.0795	0.1095
		4.00	0.0825	0.0690	0.0950
	$5p^2P^\circ-6s^2S$	0.50	0.1262		
		1.00	0.0893	0.0880	0.1230
	$\bar{\lambda}=268.82$ nm	2.00	0.0755	0.0620	0.0870
	$T_c=23\,300$ K	3.00	0.0974		
		4.00	0.0904		
	$5p^2P^\circ-5d(^1S)^2D$	0.50	0.0795		
		1.00	0.0606	0.0540	0.0466
	$\bar{\lambda}=227.31$ nm	2.00	0.0526		
	$T_c=10\,300$ K	3.00	0.0584		
		4.00	0.0544		

$30\% < C \leq 50\%$, and $50\% < D \leq 75\%$.

Stark HWHM values for spectral lines 206.19 nm of Zn II and 214.41 and 226.50 nm from Cd II spectra were measured with larger error because of narrow experimental profile. In this case, contribution of the Lorentz fraction in the Voigt profile was small, comparable with the instrumental HWHM.

B. Theory

For calculation of Stark HWHM values we have used various theoretical approaches. In Table II calculated Stark HWHM values at various electron temperatures are listed as follows: w_{SE}, Griem's semiempirical (SE) formula (Ref. [11]); w_{LTLSE}, low-temperature limit of the semiempirical (LTLSE) formula [11] and w_{LTLMSE}, low-temperature limit of the modified semiempirical formula (LTLMSE) of Dimitrijević and Konjević (Ref. [12]). The results are valid for $N = 1 \times 10^{23}$ m^{-3} electron density.

Relevant atomic parameters were taken from Ref. [13]. In the case of the simplified semiempirical and simplified modified semiempirical formula (LTLSE and LTLMSE, respectively), the values w_{LTLSE} and w_{LTLMSE} were calculated for temperatures up to the critical value T_c, that follows from the approximation validity criterion, i.e.,

$$3kT_c/2\Delta E \leq 2 \quad (1)$$

(see Ref. [12]), where ΔE is the energy separation to the nearest perturbing level. Under our experimental conditions a contribution of the ion broadening to the total linewidth can be neglected.

IV. DISCUSSION

The values in Table III are presented as the ratios between experimental w_m and our calculated values w_{SE}, w_{LTLSE}, and w_{LTLMSE} based on the various theoretical approaches at given electron temperature and $N = 1 \times 10^{23}$ m^{-3} electron density.

In the case of calculations based on the simplified formulas such as LTLSE and LTLMSE, the ratios of Stark HWHM values are given only for those values of electron temperature that are smaller than critical (T_c), satisfying the criterion (1).

Agreement of our experimental values of Stark

TABLE III. Stark HWHM of Zn II and Cd II spectral lines. The values w_m are our and other authors' experimental [1,2] data. Ratios of measured w_m to theoretical values are given for the following theoretical results: w_{SE} are our calculations on the basis of the semiempirical [11] formula, w_{LTLSE} and w_{LTLMSE} are our calculations on the basis of the simplified (low-temperature limit, LTL) approaches of the semiempirical [11] and modified-semiempirical [12] formulas, respectively, at a given electron temperature T and $N = 1 \times 10^{23}$ m^{-3} electron density. Transition arrays and wavelengths are also given.

	Transition array	Wavelength (nm)	T (10^4 K)	w_m (10^{-1} nm)	$\frac{w_m}{w_{SE}}$	$\frac{w_m}{w_{LTLSE}}$	$\frac{w_m}{w_{LTLMSE}}$	Ref.
Zn II	$4s^2S-4p^2P^\circ$	206.191	3.3	0.023	2.80	2.80	3.49	This work
	$4p^2P^\circ-4s^{2\,2}D$	589.435	3.3	0.230	1.43			This work
		747.435	3.3	0.224	0.87			This work
	$4p^2P^\circ-5s^2S$	255.796	3.3	0.051	0.85			This work
			1.10	0.44	6.50	6.50	4.69	[1]
	$5s^2S-5p^2P^\circ$	758.848	3.3	0.223	0.16			This work
	$4d^2D-4f^2F^\circ$	491.166	3.3	0.183	0.20			This work
			1.10	1.225	1.33			[1]
Cd II	$5s^2S-5p^2P^\circ$	214.411	2.3	0.023	1.65	1.85	2.17	This work
			3.0	0.021	1.74	1.94	2.28	This work
		226.502	2.3	0.017	1.09	1.22	1.42	This work
			3.0	0.020	1.50	1.68	1.96	This work
			1.11	0.965	43.4	48.3	56.6	[2]
	$5p^2P^\circ-5s^{2\,2}D$	441.563	2.3	0.096	0.82	0.82	0.59	This work
			3.0	0.069	0.63	0.68	0.49	This work
	$5p^2P^\circ-6s^2S$	274.858	2.3	0.045	0.55	0.74	0.55	This work
	$5p^2P^\circ-5d^2D$	219.456	2.3	0.046	0.92			This work
			1.11	0.44	8.00			[2]
		232.107	2.3	0.046	0.81			This work
			1.11	0.25	4.06			[2]

HWHM is much better with the values calculated on the basis of semiempirical formulas [11]; this is remarkable in the case of Cd II. In the case of Zn II and Cd II, the ratios of experimental and theoretical values (SE approximation) lie in the interval 0.55–1.74. This is acceptable owing to experimental and theoretical limits. An exception is the 206.191-nm Zn II line, with a 2.8 ratio of the experimental to theoretical value. For the 758.848- and 491.166-nm lines from the Zn II spectrum of higher multiplets, the experimental value is as much as 6 times smaller than theoretically predicted.

Experimental values of Kusch and Oberschelp [1,2] for

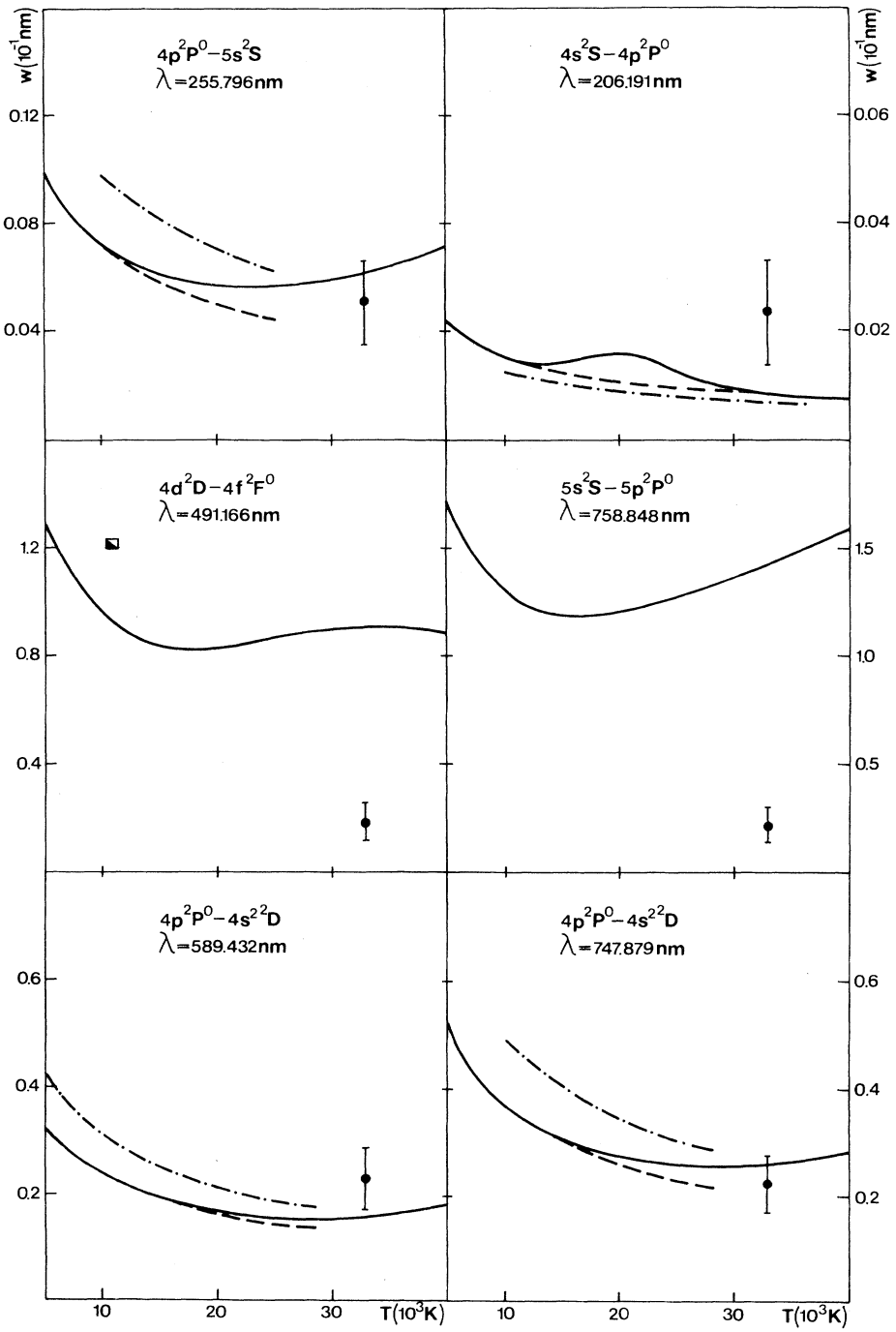

FIG. 2. Stark HWHM (w) of Zn II lines vs electron temperatures at $N=1\times10^{23}$ m^{-3} electron density: ●, our experimental data; ◪, Kusch and Oberschelp [1]; and (——), (— — —), and (—·—·—·), our calculated values based on the semiempirical [11], LTLSE [12], and LTLMSE [12] approaches, respectively.

lines belonging to Zn II and Cd II spectra are much larger than the values calculated by us. This is specially expressed for the resonant 226.502-nm line of Cd II where the ratio is 43. Due to the rather complex content of their plasma, this could be ascribed to a strong self-absorption. The only reasonable agreement was found for the 491.166-nm line of Zn II, with the ratio of 1.33.

In order to give an explicit presentation of the calculat-

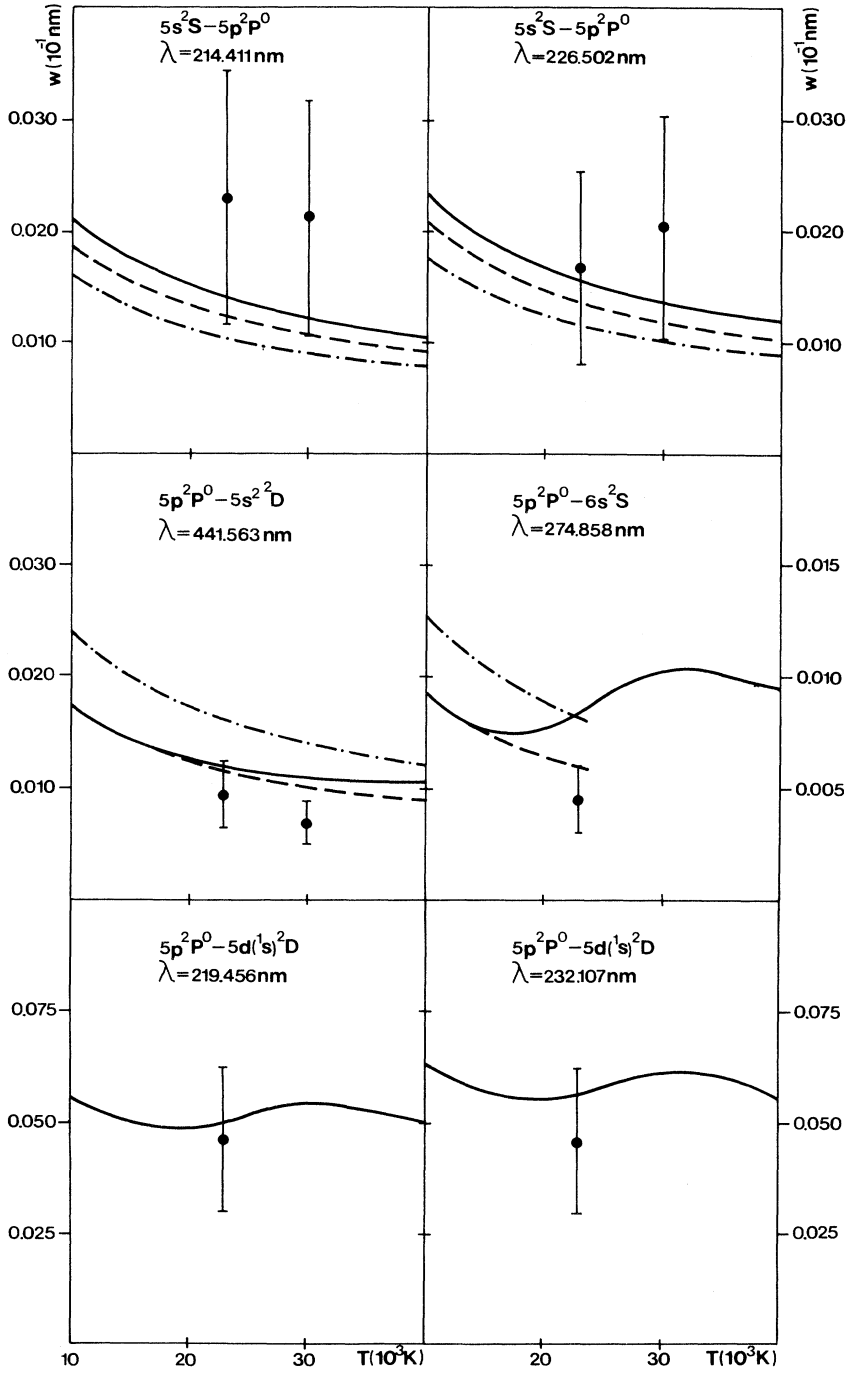

FIG. 3. Stark HWHM (w) of Cd II lines vs electron temperatures at $N = 1 \times 10^{23}$ m^{-3} electron density: ●, our experimental data; and (——), (— — —), and (—·—·—·), our calculated values based on the semiempirical [11], LTLSE [12], and LTLMSE [12] approaches, respectively.

ed values of Stark HWHM, we give in Figs. 2 and 3 values for Zn II and Cd II, respectively, based on SE, LTLSE, and LTLMSE approaches. The figures also contain ours and Kusch and Oberschelp's experimental values.

For 491.166- and 758.848-nm lines from the Zn II spectrum, the theoretical values LTLSE and LTLMSE were not calculated due to the small value of T_c.

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