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STARK BROADENING AND SHIFT OF NEUTRAL COPPER SPECTRAL LINES

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Stark broadening parameters for the spectral lines of several CuI multiplets were calculated. Comparison with experimental Stark widths and shifts shows, in some cases, a very large discrepancy. The analysis of the experimental results indicates to the possible causes of the discrepancy between theory and experiment.

1. Introduction

Stark broadening and shift of spectral lines of neutral, non-hydrogenic atoms has been the subject of numerous experimental[1-3] and theoretical studies (see e. g. Ref. 1). The primary aim of these studies is to understand the proccesses of interaction of neutral emitters with charge particles in plasmas what is, obviously, not an easy task. At the present moment, experiments agree with comprehensive semiclassical calculations by Benett and Griem[1,4] in average within ±20 to 30%[1-3]. The exception are the results for HeI where the agreement between theory[1,4] and experiments (see e. g. Refs. 1—3) is in the range of ±10 to 15%[1-3]. Similar results of comparison with the experiments were achieved with other two versions of semiclassical approach[5]. Unfortunately semiclassical evaluation of the Stark broadening parameters requires elaborate calculations even for a single line. Recently, Dimitrijević and Konjević[6] offered simple formulae for estimating Stark widths and shifts of neutral atom lines based on the method of Freudenstein and Cooper[7] and GBKO semiclassical theory[8]. This simple method has been recently[9] tested for the evaluation of widths or shifts and the obtained results agreed in average with sophisticated semiclassical calculations[1,4] within ±30%.

From the point of view of applications reliable Stark broadening data are important for radiative transfer calculations, and diagnostics of both laboratory and astrophysical plasmas. For laboratory plasma diagnostics Stark broadening data for some elements are of particular importance. Here we shall mention helium, nitrogen, oxigen, argon, silicon and copper. Some of these elements like helium, nitrogen and argon, are used as a working gas in various plasma devices; others like oxigen are present as a reacting gas, and silicon and oxigen come into the plasma from the glass walls of the plasma container. Copper is usually introduced into plasma by evaporation of electrodes which are frequently made of copper or its alloys. While Stark broadening of prominent HeI, NI, OI and ArI lines has been studied extensively (see e. g. Refs. 1—3), for neutral copper only few experimental results of modest accuracy were reported10,11). In several papers the results of theoretical calculations of quadratic Stark constants for neutral copper lines have been published10,12–13) and these data in conjuction with Lindholm's formula (see e. g. Ref. 14) can be used for the estimation of electron impact Stark widths and shifts. Recently, Stark widths and shifts of a number of copper lines have been measured15) in a low pressure pulsed arc, and we shall use these data together with preceding results10,11) to compare with the results of our calculations. Comparison with other theoretical results10,12,13) will be also performed.

2. *Theory*

Detailed derivation of the used formulae for the evaluation of electron impact broadening and shift of neutral copper could be found elsewhere6,7) and, here, minimum details will be given for completeness.

After Freudenstein and Cooper7) electron impact half halfwidth w_e (s^{-1}) at electron density N(cm^{-3}) and temperatpure T(K) is calculated from the following equation:

$$w_e \cong \left(\frac{32}{27}\right)^{1/2} N\pi \left(\frac{\hbar a_0}{m}\right) \left(\frac{E_H}{kT}\right)^{1/2} R_i^2 f_w (\eta_{ii'} \vec{R}_{ii'}). \tag{1}$$

Dimitrijević and Konjević6) derived after Ref. 7 another formula used here for the evaluation of widths and shifts of non-hydrogenic atom lines which has the following form:

$$w_e + id_e \cong 1.089\pi \left(\frac{\hbar a_0}{m}\right) \left(\frac{E_H}{kT}\right)^{1/2} N \{\sum_{i'} \vec{R}^2_{ii'} [f_w(\eta_{ii'} \vec{R}_{ii'}) - i\varepsilon_{ii'} f_d(\eta_{ii'} \vec{R}_{ii'})] +$$

$$+ \sum_{f'} \vec{R}^2_{ff'} [f_w(\eta_{ff'} \vec{R}_{ff'}) + i\varepsilon_{ff'} f_d(\eta_{ff'} \vec{R}_{ff'})]\}. \tag{2}$$

In Eqs. (1) and (2) $\vec{R}^2_{jj'}$ is the square of the coordinate operator matrix element, i and f denote initial and final states, while i' and f' are the corresponding perturbing states within the dipole approximation; $\varepsilon_{jj'} = (E_j - E_{j'})/|E_j - E_{j'}|$ are the energy levels of the corresponding states. f_w and f_d are given by the following equations:

$$f_w(x) = e^{-1.33x} \ln\left(1 + \frac{2.27}{x}\right) + \frac{0.487x}{0.153 + x^{5/3}} + \frac{x}{7.93 + x^3}$$

$$f_d(x) = 1.571 e^{-2.487x} + \frac{1.295x}{0.415 + x^{5/3}} + \frac{0.713}{8.139 + x^3}$$

where $x = \eta_{jj'} \vec{R}_{jj'}$ and $\eta_{jj'} = |E_j - E_{j'}|/3kT$. Within the Coulomb approximation[16] $\vec{R}^2_{jj'}$ for a dipole transition of a neutral atom, is given by

$$\vec{R}^2_{jj'} \approx \left(\frac{3n_{l_>}}{2}\right) \frac{l_>}{2l+1} (n^2_{l_>} - l^2_>)\, \varphi^2 \tag{3}$$

where l is the orbital quantum number of the valent electron, $l_>$ is the larger of l_j and $l_{j'}$ and $n_{l_>}$ is the effective quantum number with larger orbital quantum number which is, for the neutrals, calculated from

$$n^2_j = \frac{E_H}{E_\infty - E_j}. \tag{4}$$

In Eq. (4) E_H is the hydrogen ionization energy and E_∞ is the appropriate series limit; φ is the correction factor tabulated in Ref. 17.

Since ion broadening can not be neglected for neutral atom lines the ion broadening parameter A is calculated for each CuI multiplet using Eq. (224) from Ref. 1.

For the evaluation of Stark broadening parameters of CuI lines the data for atomic energy levels and ionization potential are taken from Ref. 18.

3. Results and discussion

Results obtained from Eq. (2) for electron impact half-halfwidth w_e (nm) and shift d_e (nm) for several CuI multiplets at $N = 1 \times 10^{16}$ cm^{-3} and $T = 5000$, 10000, 20000 and 30000 K are given in Table 1 together with corresponding ion broadening parameter A. In this table average wavelength for the multiplet is given. Data for w_e and d_e at required wavelengths within multiplet is simple to evaluate since both quantities, w_e and d_e, are proportional to λ^2. For calculation of Stark halfwidth w_{tot} and shift d_{tot} of CuI lines from data in Table 1 one can use approximate formulae[1]

$$w_{tot} \cong 2\,[1 + 1.75\, 10^{-4} N^{1/4} A\, (1 - 0.068 N^{1/6} T^{-1/2})]\, 10^{-16} w_e N_e \tag{5}$$

$$d_{tot} \cong [\mathrm{d} \pm 2.0\, 10^{-4} N^{1/4} A\, w_e\, (1 - 0.068 N^{1/6} T^{-1/2})]\, 10^{-16} N_e \tag{6}$$

where w_e, d_e and A are electron impact half-halfwidth, shift and ion broadening parameters, respectively, all of them taken at $N = 1 \times 10^{16}$ cm^{-3} and at required electron temperature T (K); N is the electron density (cm^{-3}) at which w_{tot} and d_{tot} are to be calculated. There are certain restrictions to the applicability of Eqs. (4) and (5) and they are[1)]

$$B = 8.99\,10^{-2}\,N^{1/6} \lesssim 0.8 \tag{7}$$

$$0.05 \lesssim A \lesssim 0.5 \tag{8}$$

Whenever conditions (7) and (8) are not fulfilled one should use the procedure described in Ref. 1. Apart from basic spectroscopic data for each multiplet, in Table 1 are also given the values for $3kT/2\Delta E$ which represent the ratio of thermal

TABLE 1.

Transition	T (K)	w_e (nm)	d_e (nm)	A
$4s^2\ ^2D - 4p^2P^0$	5000	0.00082	−0.00003	0.010
$\lambda = 535.29$	10000	0.00106	−0.00009	0.008
$\Delta S/S = -053$	20000	0.00131	−0.00013	0.007
$3kT/2\Delta E = 0.56$	30000	0.00144	−0.00015	0.007
$4s^2P^0 - 5s^2S$	5000	0.0083	0.0098	0.045
$\lambda = 804.09$	10000	0.0110	0.0112	0.037
$\Delta S/S = -0.17$	20000	0.0139	0.0115	0.031
$3kT/2\Delta E = 1.11$	30000	0.0158	0.0111	0.028
$4p^2P^0 - 6s^2S$	5000	0.0147	0.0146	0.086
$\lambda = 451.51$	10000	0.0192	0.0152	0.071
$\Delta S/S = -0.04$	20000	0.0240	0.0142	0.060
$3kT/2\Delta E = 3.45$	30000	0.0265	0.0129	0.055
$4p^2P^0 - 4d^2D$	5000	0.0156	−0.0059	0.061
$\lambda = 519.82$	10000	0.0160	−0.0034	0.059
$\Delta S/S = -042$	20000	0.0156	−0.0019	0.060
$3kT/2\Delta E = 12.52$	30000	0.0150	−0.0014	0.062
$4p^2P^0 - 5d^2D$	5000	0.0853	0.0078	0.242
$\lambda = 405.03$	10000	0.0795	0.0052	0.255
$\Delta S/S = -0.16$	20000	0.0710	0.0042	0.278
$3kT/2\Delta E = 182.14$	30000	0.0652	0.0037	0.296
$4p'^4P^0 - 5s'^4D$	5000	0.00138	0.00217	0.047
$\lambda = 427.51$	10000	0.00184	0.00247	0.038
$\Delta S/S = -0.24$	20000	0.00236	0.00253	0.031
$3kT/2\Delta E = 0.94$	30000	0.00269	0.00244	0.028
$4p'^4F^0 - 5s'^4D$	5000	0.00163	0.00247	0.046
$\lambda = 461.00$	10000	0.00217	0.00282	0.037
$\Delta S/S = -0.24$	20000	0.00278	0.00289	0.031
$3kT/2\Delta E = 0.94$	30000	0.00318	0.00279	0.028

Electron impact half-halfwidths w_e, shifts d_e and ion broadening parameter A at electron density $N = 1 \times 10^{16}$ cm^{-3} for several CuI multiplets. w_e and d_e are calculated fiom Eq. (2) while ion broadening parameter A is evaluated from Eq. (224) Ref. 1.

energy of electron at $T = 10000$ K and energy difference to the nearest perturbing level. In the same column for each multiplet the ratio $\Delta S/S$ is given. This ratio is a measure of completeness of the set of perturbing levels in respect to the sums of dipole matrix elements R^2_{jj} and it is calculated from the following relation[20)]

$$\frac{\Delta S}{S} = \frac{\sum_{i'} \vec{R}^2_{ii'} + \sum_{f'} \vec{R}^2_{ff'} - R^2_{ii} - R^2_{ff}}{R^2_{ii} + R^2_{ff}}$$

where

$$R^2_{jj} = \frac{n_j^2}{2} \left[5n_j^2 + 1 - 3l_j (l_j + 1)\right]$$

and n_j is the corresponding effective principal quantum number. For a complete set of perturbing levels $\Delta S/S = 0$.

In Tables 2 and 3 are given experimental and theoretical results for widths and shifts of CuI lines. In Refs. 10 and 11 instead of actually measured Stark line widths quadratic Stark constants C_4 are given. These constants were derived[10,11)] from the widths of CuI lines using a well known Lindholm's formula (see e. g. Ref. 14)

$$2w_e\,(\mathrm{s}^{-1}) = 11.37\, v^{1/3}\, C_4^{2/3} N \tag{9}$$

where v is the mean velocity of electrons. In this case it would be more correct to replace $2w_e$ in Eq. (9) by w_{tot} since experimental widths include the contribution of ion broadening. Thus for the evaluation of w_{tot} at $N = 1 \times 10^{17}\,\mathrm{cm}^{-3}$ and $T = 10000$ K from experimental C_4 constants Eq. (9) is applied. Whenever theoretical C_4 constants from Refs. 10, 12 and 13 are used, first the electron impact half-halfwidth w_e at $N = 1 \times 10^{16}\,\mathrm{cm}^{-3}$ and $T = 10000$ K is calculated, and then Eq. (6) is used to evaluate w_{tot}. For these calculations the ion broadening parameter from Table 1 is used. However, it should be pointed out that, with exception of $4p\,^2P^0 - 5d\,^2D$ multiplet, the contribution of ion broadening never exceeded 10% from the total line width and therefore it is irrelevant for the explanation of large discrepancies between various theoretical calculations and experiments.

Comparison of experimental widths in Table 2 shows large discrepancies. Here we should draw attention to the fact that experimental results in Ref. 10 were obtain from a spacially and temporally inhomogenous plasma source — D. C. low current are in water. The electrodes were made of brass, and copper was introduced into the plasma by evaporation of electrodes. Spectra were recorded on the photographic plates and in this experimental arrangement the authors[10)] could not correct variations of intensities produced by wandering of the arc in water. Furthermore they did not performe Abeling procedure to determine radial distribution of line intensities, and therefore their C_4 constants represent some kind of average value which can not be used with confidence. Although in Ref. 11 a much more sophisticated technique is used for the analysis of spectra from a free burning arc between copper electrodes the reported results for C_4 constants of CuI lines can not be considered reliable since plasma electron density was derived only from the widths of CuI 453.08 and 448.04 nm lines using theoretical

TABLE 2.

Transition	Wavelength (nm)	STARK WIDTHS IN (nm) UNITS AT $N = 1 \times 10^{17}$ cm^{-3} AND $T = 10000$ K							
		EXPERIMENT			THEORY				
		Ref. (10)	Ref. (11)	Ref. (15)	Ref. (10)	Ref. (12)	Ref. (13)	Eq. (1)	Eq. (2)
$4s^2\,{}^2D - 4p\,{}^2P^0$	510.554			0.043			0.0026	0.016	0.021
	570.024			—			0.0032	0.020	0.026
	578.213			0.072			0.0034	0.021	0.027
$4p\,{}^2P^0 - 5s\,{}^2S$	793.313			0.320			0.043	0.161	0.226
	809.263			0.293			0.045	0.168	0.235
$4p\,{}^2P^0 - 6s\,{}^2S$	448.035	0.043		0.240	0.122		0.067	0.323	0.422
	453.078	0.044		0.221	0.125		0.068	0.331	0.432
$4p\,{}^2P^0 - 4d\,{}^2D$	515.324		0.088	0.190		0.065	0.063	0.576	0.346
	521.820			0.220		0.046		0.591	0.355
	522.007			0.220		0.054		0.591	0.355
$4p\,{}^2P^0 - 5d\,{}^2D$	402.263			0.431	0.767	0.650	0.640	2.760*	2.096*
	406.264			0.419		0.643		2.672*	2.139*
$4p'\,{}^4P^0 - 5s'\,{}^4D$	427.511		0.022	0.080				0.036	0.039
$4p'\,{}^4F^0 - 5s'\,{}^4D$	453.970			0.180				0.040	0.045
	458.697			0.140				0.041	0.045
	465.112		0.109	0.087				0.042	0.047

Experimental and theoretical results for the Stark widths of CuI lines normalized at $N = 1 \times 10^{17}$ cm^{-3} and $T = 10000$ K. Results denoted by asterix are corrected for Debye shielding (see Appendix IV in Ref. 1).

values of Stark constants10). This plasma diagnostic method can not be considered reliable enough as it will be seen from the discussion of theoretical results. Therefore, we shall concentrate our further discussion to the newest experiment15) performed in a low pressure pulsed arc with optical multichannel analyser and laser interferometry for electron density measurement.

Intercomparison of older theoretical results10,12,13) in Table 2 shows reasonable agreement. However, Lindholm's formula Eq. (9), used for the evaluation of Stark line widths in Table 2 is of very limited accuracy and its insufficiency was one of the reasons for the development of modern Stark broadening theory (see e. g. Ref. 19). Thus, for the comparison with the experiment in Table 2 we shall use approaches by Freudenstein and Cooper7), Eq. (1) and by Dimitrijević and Konjević16), Eq. (2), derived both from modern semiclassical GBKO8) theory. The agreement between the results from Eq. (1) and (2) in Table 2 is well within ±40% what can be considered good for two simplified approaches for the evaluation of Stark widths. Nevertheless, irrespective of discrepancy between the results of Eqs. (1) and (2), both sets of results show that Stark widths within multiplet are the same within several percent, and that the Stark widths increase with the increase of principal quantum number along the spectral series (see e. g. results for $4p\ ^2P^0 - 5s\ ^2S$ and $4p\ ^2P^0 - 6s\ ^2S$ in Table 2). Both these findings have been confirmed by a recent analysis of experimental data21). There are some exceptions of these rules when close perturbing levels to the upper (or lower)

TABLE 3.

Transition	Wavelength (nm)	Stark shifts (nm)	$N = 1 \times 10^{17}$ cm^{-3}, $T = 10000$ K
		exp. Ref. 15	Eq. (2)
$4s^2\ ^2D - 4p\,^2P^0$	510.554	0.0067	−0.0010
	570.024	—	−0.0012
	578.213	0.0076	−0.0012
$4p\,^2P^0 - 5s\,^2S$	793.313	0.071	0.116
	809.263	0.057	0.121
$4p\,^2P^0 - 6s\,^2S$	448.035	—	0.175
	453.078	0.057	0.179
$4p\,^2P^0 - 4d\,^2D$	515.324	−0.027	−0.043*
	521.820	−0.030	−0.044*
	522.007	−0.030	−0.044*
$4p\,^2P^0 - 5d\,^2D$	402.263	0.195	0.498*
	406.264	0.174	0.508*
$4p'\,^4P^0 - 5s'\,^4D$	427.511	0.030	0.026
$4p'\,^4F^0 - 5s'\,^4D$	453.970	0.019	0.029
	458.697	—	0.029
	465.112	0.0135	0.030

Experimental and theoretical results for the Stark shifts of CuI lines normalized at $N = 1 \times 10^{17}$ cm^{-3} and $T = 10000$ K. Results denoted by asterix are corrected for Debye shielding (see Appendix IV in Ref. 1).

level of the considered transition exists, but this is not the case for the most of CuI lines in Table 2. Only for the multiplet $4p^2P^0 - 5d^2D$ perturbing level $4f^2F^0$ is very close to the upper level, $\Delta E \cong 38\ \mathrm{cm}^{-1}$, and some larger differences between Stark width within multiplet may appear. Here we did not go into details to calculate this difference since it is irrelevant for the explanation of huge discrepancy between experiment[15] and theoretical results from Eqs. (1) and (2) in Table 2.

On the basis of the analysis of experimental apparatus and procedure in Ref. 15 we could not trace causes of the existing discrepancy between experiment[15] and our calculations. However, large variations of the experimental Stark widths[15] within multiplet (see results for multiplets $4s^2D - 4p^2P^0$ and $4p'^4F^0 - 5s'^4D$ in Table 2) usually indicate to the presence of strong, uncorrected selfabsorption of lines which may influence Stark width measurments (see e. g. Ref. 22). Furthermore, unexpected decrease of the Stark widths along spectral series $4p^2P^0 - 5s^2S$ and $4p^2P^0 - 6s^2S$ and large difference between widths of lines from $4p'\ ^4P^0 - 5s'\ ^4D$ and $4p'\ ^4F^0 - 5s'\ ^4D$ multiplet which should be approximately the same (contribution of lower level broadening to the total line width is usually small) are, most probably, caused by uncorrected selfabsorption and/or plasma inhomogeneity. Finally, if one compares the experiment and theory in Table 3, in average better agreement is found. This is an additional indication that undetected selfabsorption of lines was present in this experiment. Namely, shift measurements are less influenced by line selfabsorption and therefore the agreement with the theory is better.

4. Conclusions

In this paper we report results of Stark width and shift calculations for the lines of several CuI multiplets. Comparison with experimental data[15] showed sometimes a very large discrepancy well outside of estimated errors for both experiment and the theory. The analysis of experimental data indicates that uncorrected selfabsorption and/or plasma inhomogeneity may be present during line shape measurements in Ref. 15. Therefore we suggest a new experiment with reliable control of copper atoms in plasma, while on the other hand the results of sophisticated semiclassical calculations (see e. g. Ref. 1) would be of importance for accurate plasma diagnostics.

We believe that our results for electron impact widths and shifts in Table 1 are accurate within ±40% what is satisfactory for most of plasma diagnostic applications.

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ŠTARKOVO ŠIRENJE I POMERAJ SPEKTRALNIH LINIJA NEUTRALNOG BAKRA

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Originalan naučni rad

U radu su dati rezultati proračuna parametara Štarkovog širenja spektralnih linija nekoliko multipleta CuI. Poređenje ovih rezultata sa eksperimentalno određenim vrednostima u nekim slučajevima pokazuje veliko neslaganje. Analiza eksperimentalnih rezultata ukazuje na moguće uzroke neslaganja teorije i eksperimenta.