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NON-HYDROGENIC SPECTRAL LINE SHAPES FOR ELECTRON DENSITY DIAGNOSTICS OF ICP

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Abstract. On the basis of the analysis of the results reported in two recent experimental papers we draw attention to some experimental difficulties in electron density determination from the shapes and shifts of non-hydrogenic spectral lines in atmospheric pressure inductively coupled plasmas.

1. INTRODUCTION

For a number of years broadening and shifting of spectral lines is used as a basis of an important non-interfering plasma diagnostic technique. In the early sixties, a number of attempts have been made to improve and to check experimentally existing theories of spectral line broadening by plasmas. Most of these early works were concerned with the Stark broadening of hydrogen lines. Due to the large, linear Stark effect in hydrogen, these lines are very useful for low electron density plasma diagnostic purposes. However, it is not always convenient to seed plasma with hydrogen, and sometimes this is not possible. Furthermore, these broad lines in some cases interfere with other neighboring lines so it is difficult to determine their shape correctly. Therefore, from the early starts of this field of research and applications, there was an interest for the plasma broadening of isolated non-hydrogenic lines of neutral atoms and positive ions whose widths and shifts are result of quadratic Stark effect. The main drawbacks for the application of these lines for diagnostics of inductively coupled plasmas (ICPs) are small, difficult to measure, Stark widths and shifts induced by relatively low density of charged particles, $N \approx 10^{15}$ cm^{-3}. With the development of modern spectroscopic instrumentation (Fourier transform spectrometers, piezoelectrically scanning Fabry-Perot interferometers) and laser spectroscopy techniques, shapes and shifts of these lines may become an important source of information for plasma diagnostic purposes. Since atomic lines are usually broader than ionic lines and thus more practical for diagnostics of ICPs, we shall here confine our further discussion to atoms. However, this does not exclude completely the application of some ionic lines for ICP diagnostics. Namely, plasma broadened line widths and shifts depend (apart from plasma electron density and temperature) also upon disposition of energy levels of the emitter, so for some singly charged ion lines the influence of charged particles may be large enough for ICP diagnostics.

First semiclassical calculations of Stark broadening parameters for isolated non-hydrogenic atomic lines were carried out by Griem and coworkers (Griem *et al.*, 1962; Griem, 1962; Griem, 1964). After some improvements of the theory, the new comprehensive calculations of Stark broadening parameters of neutral helium through calcium and cesium spectral lines were published (Griem, 1974). Later on these calculations were extended to some elements heavier than calcium (Dimitrijević and Konjević, 1983).

Parallel with the development of the theory of Stark broadening, numerous experiments were performed to provide new plasma broadening data and to test theoretical predictions. The aim of this paper is to draw attention to some difficulties one may encounter when one uses non-hydrogenic spectral line shapes and shifts for the diagnostics of an atmospheric

pressure ICP. The experimental data for this analysis are taken from plasma emission experiment by Manning *et al.* (1990, 1991).

2. RESULTS AND DISCUSSION

In the ICP emission experiment (Manning *et al.*, 1990, 1991), the Los Alamos Fourier Transform Spectrometer (LAFTS) is used for a precision study of small spectral line shifts and widths of Ar I, Fe I, Ba II, Ca II and Sr II, lines in a 27.12 MHz RF Plasma Therm ICP (1.1, 1.5 and 1.9 kW). For all studies, the viewing height above coils was 12 mm. The gas flow rates were 12 l/min (outer), 0.8 l/min (intermediate) and 0.8 l/min (nebulizer). The hydrogen H_β line is used to estimate the electron density in the analytical zone viewed by the LAFTS. These electron densities are applied only to the analytical zone which was used to study Fe, Ba, Ca and Sr emission lines. The Ar emission, however, does not predominantly occur from the analytical zone but rather from the outer tangential flow zone. No electron densities were reported for the latter zone. Doppler temperatures were calculated from Gaussian part of the Voigt fit of ICP emission lines. The electron temperatures were not reported. The Abel inversion procedure was not applied to retrieve local line emission profiles.

After first theoretical estimate of the magnitude of Stark broadening parameters, Ba II, Ca II and Sr II spectral lines are excluded from further consideration as potential candidates for plasma diagnostics of ICP. For typical conditions of ICP, $N_e = (1\text{-}3)\cdot 10^{15}$ cm^{-3}, Stark shifts of these lines are very small (several times 10^{-4} nm), see Table 8 in Manning *et al.* (1990), what makes them presently impractical for plasma diagnostic purposes. Furthermore, large spread of the theoretical and experimental results of Stark broadening data for these lines (see e.g. Konjević and Wiese (1990) and references therein) introduces large uncertainty in plasma diagnostics. So we concentrate to Ar I and Fe I lines only.

For further analysis of Ar I we selected lines from (Manning *et al.*, 1990, 1991) with available theoretical data (Griem, 1974) which can be used for N_e evaluation. Here, we assumed electron temperature $T_e = T_g$ so gas temperatures (T_g) from Manning *et al.* (1990, 1991) are taken throughout these calculations. The assumption of Saha equilibrium in atmospheric pressure ICP may be easily justified for this purpose. Stark broadening parameters weakly depend upon T_e and the differences T_e - T_g of 1000-2000 K, typically measured in ICP (see e.g. Hanselman *et al.* (1994) and De Regt *et al.* (1996)), produce negligible influence to N_e diagnostics.

Further, the calculations of Van der Waals widths, w_V, and shifts, d_V, using Griem's estimate for w_V (Griem, 1964) and relationship $d_V = 2/3 w_V$, respectively, are performed also. For these calculations we take T_g as measured in Manning *et al.* (1990), while density of argon atoms in the ground state, N_a, is evaluated from $p = N_a k T_g$. The same values of N_a are used for evaluation of resonance broadening, w_R, using the formula derived by Ali and Griem (1966). All necessary atomic data for these calculations are taken from Wiese *et al.* (1959).

The results of above calculations, for the 1.1 kW RF power input, are given together with experimental data in Table 1. The order of appearance of spectral lines and relevant results is in accordance with their line strength values S; the data in the table start with the line having smallest and end up with the largest S value. In Table 1, w_m and d_m are measured half width of the Lorentzian part of line profile and measured line shift, respectively (Manning *et al.*, 1990, 1991); N_e^w is the electron density derived from the residual width $w_S = w_m - (w_V + w_R)$, which is the part of line width induced by Stark effect, while N_e^d is the

electron density derived from Stark shift $d_S = d_m - d_V$. Similar calculations have been performed for the RF power inputs of 1.5 and 1.9 kW.

Table 1. The data of Ar I lines at 1.1 kW RF power input. In this table w_m is measured half width of the Lorentzian part of line profile; w_V and w_R are calculated Van der Waals and resonance broadening half widths, respectively. N_e^w is electron density derived from the Stark width; d_m and d_V are measured and calculated Van der Waals shifts, respectively, while N_e^d is the electron density derived from Stark shift. w_m/d_m is measured total width-to-shift ratio and S is the line strength of observed Ar I lines.

λ (nm)	w_m (0.1 nm)	w_V (0.1 nm)	w_R (0.1 nm)	N_e^w (10^{15} cm^{-3})	d_m (0.1 nm)	d_V (0.1 nm)	N_e^d (10^{15} cm^{-3})	w_m/d_m	S (a.u.)
360.65	0.070	0.031	0.005	0.45	0.0408	0.0209	0.48	1.72	0.019
355.43	0.067	0.030	-	0.82	0.0436	0.0197	1.06	1.54	0.032
451.07	0.051	0.031	0.030	-	0.0240	0.0205	0.19	2.12	0.056
427.22	0.042	0.027	0.007	0.49	0.0191	0.0177	0.15	2.20	0.097
419.83	0.049	0.027	0.006	0.57	0.0219	0.0178	0.26	2.25	0.101
420.07	0.078	0.025	-	2.78	0.0188	0.0169	0.20	4.13	0.264
922.45	0.128	0.049	0.127	-	0.0161	0.0324	-	7.93	11.4
794.82	0.051	0.041	-	1.24	0.0160	0.0270	-	3.15	14.6
810.37	0.066	0.039	0.024	0.28	0.0142	0.0261	-	4.16	21.8
842.46	0.071	0.041	0.026	0.69	0.0011	0.0270	-	62.50	34.4
840.82	0.119	0.040	0.106	-	0.0108	0.0269	-	10.97	35.8
811.53	0.079	0.038	-	4.72	0.0072	0.0251	-	10.90	68.0

It is interesting to notice that in a number of cases it was not possible to evaluate electron density. This happened whenever $w_V + w_R > w_m$ or $d_V > d_m$. The latter may occur as a consequence of the error in w_m and d_m measurements, or it may be caused by the uncertainty in estimation of w_V, w_R and d_V. Here, one should bear in mind that equations (Griem, 1964; Ali and Griem, 1966) used for evaluation of these quantities, are approximate ones and their accuracy is in the range of ±100% or in some cases even worse.

If one compares w_m/d_m values along the Table 1, an increase of this ratio with S may be noticed. This is in particular clear for the strong IR lines in Table 1. Typical theoretical ratio of Stark width-to-shift for all investigated Ar I lines is about 1.5. The same ratio is for Van der Waals broadening. So only resonance broadening may increase width-to-shift ratio. With exception of 922.7 nm line, contribution of resonance broadening is small, see Table 1, and in some cases does not exist at all. Therefore, the contribution of resonance broadening cannot explain large ratios of w_m/d_m. The broadening of spectral lines in these cases may be explained only by radiative transfer effect (self-absorption), which does not influence shift measurements except when line with small shift becomes very broad so experimental measurements of d have large uncertainty. No test for optical thickness of measured line profiles is reported in Manning *et al.* (1990, 1991).

If one takes results for electron densities derived from Stark widths, N_e^w, for the first five lines in Table 1 ($w_m/d_m < 2.25$) and results for N_e^d, derived from Stark shifts of first six lines (self-absorption does not affect shift measurements), the reasonable consistency of data for different RF power inputs is found, see Table 2. Here, one should notice that shifts are measured more accurately than widths (Manning *et al.*, 1990, 1991). To derive Lorentzian

width, it is necessary to perform deconvolution of measured profile. Furthermore, to derive Stark width it is necessary to subtract Van der Waals broadening, w_V, and, if present, resonance width, w_R. The whole procedure introduces combined experimental and theoretical uncertainty in the final result for N_e^w. In case of shifts one has to subtract Van der Waals shift only. Nevertheless, the results for N_e derived from measured widths and shifts show reasonable mutual consistency. In spite of a fortuitous agreement of N_e results derived from the 810.5 nm and 842.7 nm with those of Ar blue lines, see Tables 1 and 2, the experimental widths of IR Ar I lines, due to large self-absorption, cannot be used with confidence for N_e determination.

Table 2. The average electron densities for various RF input powers using N_e^w and N_e^d values.

RF power (kW)	N_e^w (10^{15} cm^{-3})	N_e^d (10^{15} cm^{-3})
1.1	0.6	0.4
1.5	1.1	1.6
1.9	2.3	2.0

Therefore, from the above analysis of the emission experiments (Manning *et al.*, 1990, 1991), one may conclude that strong IR Ar I lines are not best candidates for plasma diagnostics of ICP. It is much better to use weaker Ar I lines with large Stark broadening parameters so Van der Waals broadening is small or negligible. Another attractive alternative would be to seed plasma with elements convenient for plasma diagnostics. Here, our choice is limited by available theoretical calculations of Stark broadening parameters.

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