Stark-broadened hydrogen line profiles predicted by the model microfield method for calculating electron number densities

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Abstract

This report is the first account on the application of theoretical Stark-broadening profiles predicted by the model microfield method (MMM) to estimate electron number density ($n_e$) in several laboratory plasmas. The determination of $n_e$ is accomplished by least-squares fitting of the entire emission profile or the wing portions of the emission profile of the $\text{H}_\beta$ line (486.13 nm) to the theoretical Stark-broadened profiles. Experimental profiles obtained for the $\text{H}_\beta$ line from argon and helium inductively coupled plasmas (ICP), a glow discharge, and a high-voltage spark are used to test the new MMM profiles. Results are contrasted with data predicted by the traditional ‘Unified Theory’. Compared to the ‘Unified Theory’, the MMM profiles are more accurate in the line center and span over a wide range of temperature (2500–80 000 K) and electron number densities ($1 \times 10^{10}$–$1 \times 10^{17}$ cm$^{-3}$). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Model microfield method; Electron number density; Stark-broadened profiles; Unified Theory; Inductively coupled plasmas; Helium ICP

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1. Introduction

The determination of electron number densities \( n_e \) is important for understanding fundamental characteristics of plasma sources and for developing new analytical techniques [1–32]. Among various techniques used in plasma spectrometry, Stark broadening is the most popular approach for \( n_e \) estimation because of independence from local thermal equilibrium (LTE), absence of perturbation to the plasma, relative simplicity of the procedure, accessibility to suitable optical instruments in most laboratories, and the availability of theoretical Stark-broadening line profiles for emission lines of hydrogen, helium, and argon [33–36]. The computation of the shapes of hydrogen lines, based on the ‘Unified Theory’ of Vidal et al. [37], provides the well-known VCS tables which until recently were the most accurate. Using this technique, electron number densities are determined by either comparing the full width at half maximum (FWHM) or the entire observed profile (or the wing portion) with the theoretical profiles. The most recent algorithms for the calculation of \( n_e \), based on VCS tabulations, is described elsewhere [1].

In the ‘Unified Theory’ and in most theoretical approaches, the plasma ions are considered static during the radiative process. However, experiments in 1972 revealed that the static assumption is invalid, at least in the line center [38]. Clearly, the line shape may change with various masses of perturbing ions. For astrophysical conditions, the dominant ionic species are protons. In contrast, for laboratory plasmas, hydrogen is introduced in traces in helium or argon plasma gases or with the analysis sample. Accordingly, the hydrogen line shapes are affected by \( \text{Ar}^+ \) and \( \text{He}^+ \) perturbers (atomic mass \( m_e \)). The effect of the mass of the perturbing ions on the line shape is described by the reduced mass, i.e. \( m_e/(m_e + l) \), which varies from 0.5 for protons up to nearly unity for \( \text{Ar}^+ \) ions. The theoretical treatment of this subject is presented elsewhere [39].

Recently, Stehle and Hutcheon [40,41] tabulated Stark-broadening profiles for H lines calculated from the model microfield method (MMM) [42–44]. Using this method, the dynamical interaction between the perturbing electrons and ions can be considered. Therefore, the calculated line profiles are more accurate, especially at the line center. In this paper, new theoretical tabulations derived from the MMM are used to calculate \( n_e \) of several discharges: an argon inductively coupled plasma (Ar ICP); a helium ICP (He ICP); a direct current glow discharge; and a high-voltage spark [5]. To the best of our knowledge, this is the first study that uses the new theoretical tables for the determination of \( n_e \) in analytical discharges [45]. The effective \( n_e \) was calculated with MMM and VCS derivations using a modified version of an algorithm described elsewhere [1].

2. Experimental

The \( \text{H}_\beta \) profiles obtained from four different discharges were used to evaluate the MMM tabulations in comparison to VCS derivation. The sources cover electron number densities in the range of \( \sim 10^{13}–10^{17} \text{ cm}^{-3} \) [1]. None of the data presented here were Abel inverted. The aim is to illustrate improved fit offered by MMM vs. VCS tabulation, rather than focusing on well-established plasma inhomogeneity vs. radius or possible self-absorption in the line center [33]. These data must be treated with caution because spatially resolved \( n_e \)-values are not presented. Two line profiles were obtained for dry argon and helium ICP discharges operated at 1.1 and 1.4 kW, respectively. These were collected with a high-resolution Fourier transform spectrometer (FTS) facility at Los Alamos, NM, USA (now at National Institute of Standards and Technologies, NIST, Gaithersburg, MD, USA). The experimental conditions for the spectrometer and the ICP system are detailed elsewhere [46–48]. For the calculation of \( n_e \), instrumental broadening was ignored because of the high-resolution (\( \sim 0.058 \text{ cm}^{-1} \)) of the spectrometer. The spectral profiles consist of 10 coadded interferograms.

The third \( \text{H}_\beta \) profile was obtained by M.R. Winchester, of NIST, for a direct current glow discharge using a high-resolution (\( \sim 0.031 \text{ cm}^{-1} \))
FTS (Chelsea Instruments Ltd., London, England) [49,50]. The discharge was maintained at 6 torr of argon spiked with hydrogen to a final concentration of 0.5%, and operated at 500 V and a current of 43 mA. The spectral profile consists of 60 coadded interferograms.

The H$_\beta$ profile for a 5.8-kV high-voltage spark discharge in argon gas was provided by Bye and Scheeline [5]. These data were registered at 57 $\mu$s into the discharge using a 2-m monochromator charge coupled detector (CCD) (wavelength resolution of 0.005 nm). Two CCD frames were necessary to capture the complete H$_\beta$ profile. The frames were linked and normalized with a linear model to compensate for the quantum efficiency variation over the profile [5]. With this method of data collection, the central dip of H$_\beta$ contains more error because it includes data from the edges of the detector. The spectral interferences due to electrode materials and Ar (II) on the H$_\beta$ profile have been subtracted [5].

3. Results and discussion

3.1. The calculation algorithm

The calculation algorithm used in this paper is similar to the previous one [1]. However, a new calculation route (Fig. 1) was applied to simplify the process for the operator. The final version of the code will be described in a subsequent paper.
3.2. Theoretical data derived from the MMM method

The Stark-broadened line profiles for the Lyman and Balmer series of hydrogen lines have been presented under the conditions of stellar atmospheres and envelopes [40,41]. Among these hydrogen lines, Hα, Hβ, and Hγ are the most useful lines for analytical plasmas. Because the MMM method models the ion dynamic effects, the line shapes also vary with the masses of perturbing ions. This effect is illustrated in Fig. 2 for the Hβ line shape predicted in hydrogen, helium, and argon plasmas at 10000 K with an \( n_e \)-value of \( 1 \times 10^{15} \) cm\(^{-3} \). Because the profile variations with the detuning are symmetrical about the line centers, only half of the profiles are displayed for comparison with the VCS profile obtained from the ‘Unified Theory’. These data

![Graph showing theoretical Stark-broadening profiles](image)

Fig. 2. Comparison of theoretical Stark-broadening profiles (\( n_e = 10^{15} \) cm\(^{-3} \), \( T_e = 10000 \) K Doppler effect is not included). (a) Area normalized; (b) height normalized.
clearly illustrate that the ‘Unified Theory’ predicts a greater central dip for the H_B line than the MMM method, and consequently, the latter offers better agreement to the experimental profiles. Since the interactions between ions are considered, the line shapes also change for different perturbing ions in the MMM method. Heavier ions create deeper dips for the H_B line, therefore a greater dip is predicted for argon plasmas compared to helium plasmas.

The plots shown in Fig. 2a,b are normalized to peak areas and peak heights, respectively. Note that the normalization method affects the relative shapes of the profiles. Both normalization methods have been used in n_e-estimation programs [1–4]. In our view, area normalization provides results that are more accurate. We should also stress that defining baseline has been always difficult because of the broad width of the H_B line. For consistency, the baselines in the experimental profiles are typically defined at 2–3% of the peak height.

The MMM tabulated data included in this paper covers the electron density ranging from \(1 \times 10^{10}\) to \(1 \times 10^{17}\) cm\(^{-3}\) at 2500–80 000 K. Extensive calculations covering up to \(3.2 \times 10^{19}\) cm\(^{-3}\) and \(1.3 \times 10^{6}\) K are available [40], but not included in our program, since temperatures greater than 80 000 K do not prevail in analytical plasmas.

3.3. Electron number density in Ar ICP

The experimental H_B profile for a 1.1-kW wet Ar ICP is shown in Fig. 3a along with the best-fitted theoretical profiles derived from VCS and MMM. The MMM data represents the theoretical profiles for proton perturbers. Contribution due to Doppler broadening in the experimental profile was accounted for at a translational temperature \(T_{\text{trans}}\) of 5000 K. For this calculation an electron temperature \(T_e\) of 10 000 K was used [1]. The best-fitted curves are shown when the entire profiles are considered in \(n_e\) calculation. The estimated \(n_e\)-values are \(1.13 \times 10^{15}\) and \(1.22 \times 10^{15}\) cm\(^{-3}\) with residuals of \(6.89 \times 10^{-4}\) and \(1.04 \times 10^{-4}\) for the ‘Unified Theory’ and MMM method, respectively. Clearly, the MMM profile provides an enhanced fit to the experimental profile over the VCS profile. However, even with the MMM, the predicted central dip is still significantly larger than the one obtained experimentally. Therefore, deletion of some central points is still necessary to improve the accuracy.

Fig. 4 shows the effect of central points on \(n_e\) values and on the sum of squares of the residuals using VCS and MMM theoretical profiles, as data points are gradually removed from the line core. As more center points are neglected, an improved fit to the experimental profile is obtained for both VCS and MMM tabulations. This is indicated by: (1) the lower residual for the last iteration; and (2) reduced fluctuations in \(n_e\) as more points are neglected from the line center. The deletion of data points from the central dip increases the calculated \(n_e\)-values for the ‘Unified Theory’ [1] and MMM. Since the predicted dip for the MMM is shallower, the changes in \(n_e\) and residuals are much smaller than when the VCS profiles are used.

The \(n_e\)-values predicted by both theories correlate well by comparing the wing portion of the profiles. A systematic increase in the calculated \(n_e\)-values is observed after neglecting 10–15 central points. Fig. 3b shows the best-fitted profiles when 20 points were neglected in the calculation. For this comparison, only the experimental portion outside of the boxed area is considered for the calculation. Note that the profiles (Fig. 3b) derived by the MMM and VCS tabulations are much broader than the experimental profile, leading to a higher \(n_e\)-value. As points are gradually removed, focusing solely on the wing portion, the estimated theoretical profiles became slightly broader. In this example, removal of 20 points from the line core results in the comparison of profile wings located well below the corresponding Stark halfwidth (FWHM) region [51]. It is thus difficult to apply a straightforward criterion for neglecting the number of points from the line center, particularly because the residuals are lower. In our view, the deletion of central data points should be limited to the central dip (for this particular example, approx. four points for the half profile) to minimize contributions from background noise and to have sufficient data.
Fig. 3. (a) Best-fitted theoretical profiles and experimental profile of H$_\beta$ for a dry 1.1-kW Ar ICP. (b) Best-fit when 20 points (from the half-profile) are neglected from the line core. Boxed area represents portion not compared in the calculation.

points for the comparison in the wing portions. For this particular example, the central dip is approximately four points (0.04 nm) of the half profile, which corresponds to $\sim 7\%$ of the total portion being compared.

3.4. Electron number density in He ICP

Calculations were performed for the experimental data obtained with a He ICP, using the ‘Unified Theory’ and MMM tabulations. Typically, the $n_e$-value of He ICP is 10–25 times lower in comparison to Ar ICP under analytical conditions [1,2,32]. Fig. 5 shows the experimental H$_\beta$ profile obtained for a dry 1.1-kW He ICP and the best-fitted theoretical profiles using a $T_e$ and $T_{\text{trans}}$ of 10 000 and 2500 K, respectively. The calculated $n_e$-values are $3.80 \times 10^{13}$ and $4.81 \times 10^{13}$ cm$^{-3}$ with residuals of $1.05 \times 10^{-4}$ and $1.97 \times 10^{-5}$ for the VCS and MMM tabulations, respectively. As
in the case of the argon plasma, the theoretical profile derived from the ‘Unified Theory’ has a much more pronounced central dip. With the MMM profile, an improved fit is found as indicated by the residuals, which is lower by approximately an order in magnitude. Again, a systematic increase in the $n_e$-value is observed as more points are deleted. A plot of the profiles show that the theoretical results become broader as more points from the center are omitted in the calculation. In contrast to the results obtained for the Ar ICP, the calculated values are always higher than those
obtained with VCS profiles as more points are removed from the line center (Fig. 6a). However, there is less variation in the \( n_e \)-values for the MMM when the first few central points are removed. The \( n_e \)-values calculated can differ by approximately 17% when the entire profiles were compared to less than 2% (after the first 20 points have been removed).

### 3.5. Electron number density in a direct current glow discharge

The \( \text{H}_\beta \) profile obtained with a low-pressure direct current glow discharge is shown in Fig. 7. In general, optical methods are not often used for the determination of electron number densities in glow discharge sources [4,11,52–54]. In this example, the selection of an electron and gas kinetic temperature is not explicit due to the distinct regions and electron populations occurring in the glow discharge [6,8,18,27,54]. Furthermore, the dependence of electron temperature on the discharge current and pressure varies depending on source geometries and discharge gases used [6]. In this study (Fig. 7), the calculated \( n_e \)-values were \( 4.22 \times 10^{13} \) and \( 5.89 \times 10^{13} \) \( \text{cm}^{-3} \) with residuals of \( 2.89 \times 10^{-4} \) and \( 6.02 \times 10^{-6} \) for the VCS and MMM tabulations, respectively, assuming a \( T_e \) and \( T_{\text{trans}} \) of 10000 K (\( \sim 0.9 \) eV) and 500 K, respectively. These values are representative of data reported for glow discharges operated under similar conditions [4,11,18,27]. The relatively low \( T_e \) value used represents the less energetic, thermalized electrons. For a \( T_e \) of 80000 K (\( \sim 6.9 \) eV), an \( n_e \)-value of \( 9.0 \times 10^{13} \) \( \text{cm}^{-3} \) is calculated from MMM tabulation, which is lower by less than a factor of 2 compared to the \( n_e \)-value obtained at 10000 K. The disparity between the \( n_e \)-values due to different \( T_e \) values is less critical compared to the \( n_e \)-values that would be obtained using another measurement technique (which may differ by up to several orders of magnitude). Fang and Marcus encourage the use of Langmuir probes for measuring fundamental characteristics [54]. Typically, \( n_e \)-values obtained using the Stark broadening of the hydrogen line are higher (\( \sim 10^{12}–10^{14} \) \( \text{cm}^{-3} \)) than those reported using other techniques (\( \sim 10^9–10^{11} \) \( \text{cm}^{-3} \)), such as Langmuir probe measurements [6,8,54]. Nonetheless, the effective \( n_e \)-values obtained in this study are in good agreement with those obtained by optical methods reported previously [4,11,52,53].

![Fig. 5. Best-fitted theoretical profiles and experimental profile of H\( \beta \) for a dry 1.4-kW He ICP.](image-url)
3.6. Electron number density in a high-voltage spark source

It is prudent to test the MMM vs. VCS tabulations for analytical discharges that have relatively high electron number densities ($>10^{15}$ cm$^{-3}$). For this purpose, the $H_β$ line obtained for a 5.8-kV high-voltage spark, recorded at 57 μs into the discharge [5], was used to estimate $n_e$-values. The estimate was performed at a $T_e$ of 20000 K and without taking into account Doppler or instrumental broadening since at high electron number densities the $H_β$ line is broadened.
number density ($\sim 10^{17} \text{ cm}^{-3}$), such broadenings have little effect on $n_e$ [1]. Comparison of the entire experimental profile to the VCS profile illustrates that central dip and the top of the peak (Fig. 8a) are both significantly overestimated. While the MMM profile offers a better fit, the central dip is still overestimated. For the boxed area in Fig. 8b neglecting six points from the half-profiles provides an improved fit in the wings, especially for the VCS profile at the top of the peak. When six points are removed, the $n_e$ determined using MMM and VCS are $7.11 \times 10^{16}$ and $7.54 \times 10^{16} \text{ cm}^{-3}$, respectively, with residuals of $7.12 \times 10^{-6}$ and $1.14 \times 10^{-5}$, respectively. The residuals for the calculation when no points are removed were larger: $2.21 \times 10^{-5}$ and $1.01 \times 10^{-4}$ for the MMM and VCS, respectively.

4. Conclusion

New theoretical Stark-broadening data derived from the MMM method are used to calculate $n_e$-values in Ar ICP, He ICP, glow discharge, and a HV spark. The new theoretical data are better approximates to the experimental data in the center of the profiles in comparison to ‘Unified Theory’. Less fluctuation is observed for $n_e$-values estimated using MMM. The MMM derived $n_e$-values may differ by up to 20% from those obtained by the ‘Unified Theory’ when the entire profiles are compared, but the difference is much less (typically 2–6%) if the central portion of the line is neglected.

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Fig. 8. (a) Best-fitted theoretical profiles and experimental profile of Hα for a 5.8-kV high-voltage spark. (b) Best-fit when six points are neglected from the line core. Boxed area represents portion not compared in the calculation.

References


