Broadening of the Spectral Atomic Lines Analysis in High Density Argon Corona Plasma by Using Voigt Profile

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Abstract. Studies of spectrum emission from high density argon plasma corona has been done. The analysis of the broadening of spectral atomic lines of Ar-I profile has been curried out by using an empirical approximation based on a Voigt profile. Full-width at half-maximum (FWHM) of the spectral-lines of 763.5 nm has been determined from atmospheric pressure until liquid state. The study liquid argon was curried out in a variation of temperature from 87.5 K to 151.2 K and hydrostatics pressure from 2.1 MPa to 6.4 MPa. These pressure gives the densities \( N_\infty \) (i.e. density very far from ionization zone) a variation from \( 1.08 \times 10^{22} \) to \( 2.11 \times 10^{22} \) cm\(^{-3}\). FWHM of Voigt approximation \( W_v \) of the line 763,5 nm of Ar I for: the emission lamp very low pressure \( W_v = 0.160 \) nm and our corona discharge at a pressure of 3.5 MPa \( (W_v = 0.67 \) nm) and at a pressure of 9.5 MPa \( (W_v = 1.16 \) nm). In gas, corona plasma has been generated from 0.1 MPa to 9.5 MPa. We found that the broadening spectral line increase by increasing densities both for the spectral-lines of 763.5 nm and 696.5 nm. We concluded that broadening of spectrum cause of Van der Waals force.

1. Introduction

The applications of corona plasma technology have increased in different scientific and technological fields (gas purification, detoxification, medical, chemical analysis, ozone production, etc.) [1]. Nur et. al. detected ions wind phenomenon and measured mobilities of charges carrier in argon corona discharge from atmospheric pressure until liquid state [2]. In liquid and gaseous cryogenic helium experimental data on spectral shape of the line 706 nm emitted by corona discharge are published by Bonifaci et. al. [3]. The convolution of a Lorentz and a Gauss function, commonly known as the Voigt function, is important in many branches of physics, e.g., atomic and molecular spectroscopy, atmospheric radiated transfer, plasma physics, astrophysics, etc.[1] Plasma parameters can be studied by using atomic and molecular emission spectroscopy. In case of plasma corona Argon high density broadening of emission spectrum line are due to the Lorentzian (due to the pressure broadening) distributions, and the Gaussian (due to the Doppler broadening) [4]. In this case, its is necessary to lead to the Voigt profile function, which turns out to be the convolution of Lorentzian and...
Gaussian distributions. The van der Waals broadening is produced by the dipolar interaction between an excited atom (the emitter) and the dipole induced by it over a neutral perturbing atom in the ground state. Christova et al [5] analyzed of the profiles of the argon 696.5 nm spectral line excited in non-stationary wave-guided discharges. This group used 696.5 nm line to “measure” discharge temperature.

**Voigt Profile**

In general broadening line of atomic emission or rotational molecular emission can be identified by Full Width Half Maximum (FWHM). In 1968, Whiting has proposed an empirical analytical approximation Voigt profile until the second order [6]. This approximation has been used by Aeschliman et al [7], it gives satisfactory results and precise. It is well known that the voigt profile, which corresponds to the composition of two types of Lorentzian and Gaussian enlargement, would provide a distribution of intensity, observed experimentally, an atomic line or rotational line molecular. This profile is written as follows [7]:

\[
I_{\lambda} = \frac{2}{\pi} \frac{\lambda_0}{W_g} \int_{-\infty}^{\infty} \exp \left\{ -\frac{2.772\lambda_0^2}{W_g} \left( \frac{v}{c} \right)^2 \right\} d\left( \frac{v}{c} \right) \frac{1}{1 + \frac{4}{W_l^2} \left( \frac{\lambda - \lambda_0}{\lambda_0} \right)^2} \left( \frac{v}{c} \right)^2
\]

(1)

Or most of the symbols are defined in Figure 1. \( I_{\lambda_{0}} \) is a fictitious maximum intensity of a line corresponding to a pure thermic enlargement, c is the velocity of light, \( v \) is the velocity integrated over all molecules that contribute to intensity of \( \lambda \).

The Voigt profile consists of two types of profile, given by the equations:

**Gaussian profile**

\[
I_{\lambda} = I_{\lambda_0} \exp \left\{ -2.772 \left( \frac{\lambda - \lambda_0}{W_g} \right) \right\}
\]

(2)

**The Lorentzian-type profile**

\[
I_{\lambda} = I_{\lambda_0} \frac{1}{1 + 4 \left( \frac{\lambda - \lambda_0}{W_l} \right)^2}
\]

(3)

In 1968, Whiting [6] has proposed an empirical analytical approximation Voigt profile until the second order. This approximation has been used by Aeschliman et al [7], it gives satisfactory results and precise. The empirical formula is written for voigt profile after Whiting [6]:

\[
I_{\lambda} = \frac{2}{\pi} \frac{\lambda_0}{W_g} \int_{-\infty}^{\infty} \exp \left\{ -\frac{2.772\lambda_0^2}{W_g} \left( \frac{v}{c} \right)^2 \right\} d\left( \frac{v}{c} \right) \frac{1}{1 + \frac{4}{W_l^2} \left( \frac{\lambda - \lambda_0}{\lambda_0} \right)^2} \left( \frac{v}{c} \right)^2
\]
\[
\frac{I_\lambda}{I_{\lambda_0}} = \left(1 - \frac{W_i}{W_v}\right) \exp\left[-2.772 \frac{(\lambda - \lambda_0)}{W_v}\right] + \left(\frac{W_i}{W_v}\right) \frac{1}{1 + \frac{\left(\frac{(\lambda - \lambda_0)}{W_v}\right)^2}{4}} \\
+ 0.016 \left(1 - \frac{W_i}{W_v}\right) \left(\frac{W_i}{W_v}\right) \exp\left[-0.4 \frac{\left(\frac{(\lambda - \lambda_0)}{W_v}\right)^{2.25}}{10 + \left(\frac{(\lambda - \lambda_0)}{W_v}\right)^{2.25}}\right]
\]  

(4)

\[\frac{I_\lambda}{I_{\lambda_0}}\] is the normalized intensity of line \(\frac{(\lambda - \lambda_0)}{W_v}\) is the wavelength normalized and \(W_g, W_v, W_i\) are respectively the widths at mid-height of Gauss, Lorentz and Voigt.

In this paper, the broadening of the spectrum will be discussed of the corona plasma emission wavelength of argon for 763.5 nm and 696.5 nm. Gas pressure ranging from 1 bar to 100 bars. We present also the broadening of argon micro-plasma spectrum that was formed in the argon liquid. Measurements of the line profiles atomic transitions were analyzed assuming the combined effects of Lorentzian (pressure) and Gaussian (kinetic) contributions which can be most conveniently superimposed using the Voigt profile.
2. Method

Experimental system for this research is shown in Figure 1. Spectroscopy equipment consisted of the lens Spectrosil B which serves to focus the light emission from the plasma into the slit (25 mm) of a spectrograph with medium resolution HRS Jobin-Yvon. The corona discharge reactor can be moved towards the vertical and horizontal position. By this movement, the slit can be placed at specific locations of the emissions. Spectrograph with a focal length of 600 mm equipped with a number of gratings 1200 grooves per mm, and connected with a photodiode detector or CCD (model LN/CCD-512 SF & SB, Princeton Instruments, Inc.). The detector is connected to an EG & G Optical Multichannel Analyzer (OMA) which has a spectral range between 200-850 nm (model 1460 EG & G Princeton Applied Research). To reduce the parasitic beam, detector was cooled at a temperature of -40°C.

![Figure 2. Scheme series of experiments](image)

Simultaneously performed well gas discharge current measurements in the reactor with an electrometer Keithley (model 610C), and voltage can be read directly from a DC generator RHSR/20PN60 Spellman. In addition to the above, the light emission was also detected through the help photo-multiplicator (Dario 56AVP model) which has a spectral response between 300 and 650 nm. Current pulse was detected with a Tektronix oscilloscope (model 7633)

3. Results and Discussion

3.1. Characterization of Current-Voltage and Ozone concentration

The analysis of the atomic lines of Ar-I profile has been done by using an empirical approximation based on a Voigt profile, proposed by Whiting [5]. This approximation is given by equation (4). Full width half maximum of the spectral-lines has been determined from atmospheric pressure until liquid state. The study argon liquid was curried out in a variation of temperature from 87.5 K to 151.2 K and hydrostatics pressure from 2.1 MPa to 6.4 MPa. These pressure gives the density \(N_\infty\) (i.e. density very far from ionization zone) a variation from \(1.08 \times 10^{22}\) to \(2.11 \times 10^{22}\) cm\(^{-3}\). The figure 3 shows the
experimental profiles and Voigt approximation of the line 763.5 nm of 'Ar I for: the emission lamp very low pressure (W_I = 0.157 et W_V = 0.160 nm) and our corona discharge at a pressure of 3.5 MPa (W_I = 0.32 et W_V = 0.67 nm) and at a pressure of 9.5 MPa (W_I = 1.06 et W_V = 1.16 nm).

There are different causes of spectral-line broadening. In our case, we suppose that the plasma take in place in the surrounding of the active electrode, dense enough and its temperature is not excessively high. Broadening due to the thermic agitation effect (Doppler effect) can be ignored. It rest now broadening collisions (pressure effect) that are several phenomena: Stark effect, energy transfer by resonance, and, broadening by Van der Waals force. According to Griem [8], Stark effect is more important that the level of atom emitter is high. In this study, the emitter levels of the spectral-lines analyzed are not enough high cause its represent of the 4p and 4p' forward 4s and 4s' transitions. In addition, in our case, the current of the discharge is not very high (several 100 µA) and in consequent, the glow discharge can be considered as a plasma with weak ionization degree where the electron density N_e is weak enough. This leads us to consider that the line broadening 4s-4p by the Stark effect is negligible compared to other effects (resonance and/or Van der Waals). Muñoz, et al, [9] used the Van der Waals broadening of spectral atomic lines to measure the gas temperature of an argon–helium microwave plasma at atmospheric pressure. In our case, we work in the high density argon gas and argon liquid, we certain that broadening of spectral lines were due to Van der Waals force.

3.2 Broadening of the line 696.5 nm and line 763.5 nm of Ar-I

In the figure 4 we plotted the broadening depending on the density of the fluid (N_in) for line spectrum of 763.5 nm and figure 5 for line spectrum od 696.3 nm. However, the density must be considered is the actual density (N_p) of the medium plasma (ie the ionization zone which emits light). Effect in determining the temperature T_p (plasma temperature) which is certainly higher than the temperature T_in, the middle distance of the tip and the pressure P_in in the plasma produced by a glow discharge is equal to either continue the test pressure P_in gas or hydrostatic pressure applied to the liquid. Our work was
to estimate the temperature $T_p$ of the bright area to calculate $N_p$. To strengthen our hypothesis, we discussed the work of Aeschliman et al [7]. In this work on the broadening and displacement of argon spectral line showed that the Stark effect is completely negligible. Konjevic (1999) explained that Van der Waals broadening results from the dipole interaction of an excited atom with the induced dipole of a neutral ground-state atom of density $N_\infty$; it is really our condition of experiment in high density gas and liquid state [10]. According to [11] in microplasma van der Waals contributions were the most important effects in the spectral line broadening. The Voigt full-widths at half-maximum (FWHM) normally combination between Gaussian and Lorentzian, and we used Whiting’s [6] empirical analytical approximation Voigt profile until the second order (equation 4). We found that this formula gives satisfactory results and precise. An observed line generally has a Voigt profile and its FWHM can be measured directly.

In liquid argon, there appears a correlation between enlargement and the hydrostatic pressure applied to the liquid. Unfortunately, we have not made sufficient steps by varying the hydrostatic pressure at different temperatures of tests to quantify this result. More systematic studies of this phenomenon should be undertaken. For now, we can only say that the atoms emit light are not in the condensed phase for the following reasons. There are atomic emission lines of $\text{Ar-I}$. Hydrostatic pressure plays an important role on the line broadening that this expansion does not correspond to that seen with trials in the gas at the same pressure $P_\infty$. For example in the liquid, $P_\infty = 2.1 \text{ MPa}$ and $T_\infty = 87 \text{ K}$, the expansion observed for the line at $696.5 \text{ nm}$ is equivalent to that measured in the tests in the gas at $P_\infty = 89 \text{ MPa}$ and $T_\infty = 300 \text{ K}$.
4. Conclusion

In this work, we have shown that Voigt approximation can be used for measuring broadening of the spectrum line emissio by plasma corona generated from gas state to liquid state in Agron. We found that the broadening spectral line increase by increasing densities both for the spectral-lines of 763.5 nm and 696.5 nm. We concluded that broadening of spectrum cause of Van der Waals force. Plasma corona cence generated in the liquid state in a variation of temperature from 87.5 K to 151.2 K and hydrostatics pressure from 2.1 MPa to 6.4 MPa or densities $N_{\infty}$ (i.e. density very far from ionization zone) a variation from $1.08 \times 10^{22}$ to $2.11 \times 10^{22}$ cm$^{-3}$. In liquid argon, there appears a correlation between enlargement and the hydrostatic pressure applied to the liquid. Unfortunately, we have not made sufficient steps by varying the hydrostatic pressure at different temperatures of tests to quantify this result. More systematic studies of this phenomenon should be undertaken.

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