Analysis of optical emission in the violet range from Argon pulsed ICP using Langmuir probe measurements and optical emission cross section data

S. Adams¹, J. Miles¹, L. Sobota¹, J. Caplinger¹, V. Demidov², J. Williamson²

¹Propulsion Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH, USA
²UES Inc., Dayton, OH, USA

Abstract: Spectral emission intensities from an inductively coupled plasma pulsed source in Argon were modeled using an electron energy distribution functions (EEDF) measured by Langmuir probe and published optical cross sections for electron impact. The emission spectra in the violet region were simulated and compared to experiments which clearly showed effects of electron impact excitation from the Ar ground state, or direct excitation, and electron impact excitation from an Ar metastable state, or step-wise excitation. The plasma source was coupled with a time-resolved Langmuir probe system for EEDF measurements and a spectrometer/intensified charge-coupled device (ICCD) detector for time-resolved emission spectroscopy. The spectrometer was tuned to the violet range (410-430 nm) for this study, which represented optical emission from the Ar 3p-1s transitions, produced from both direct and step-wise excitation to the Ar 3p manifold (Paschen’s notation). The model provided a good fit to the experimental spectra data by assigning a specific ratio of Ar metastables to ground state Ar atoms.

Keywords: Argon, optical emission, electron energy distribution, step-wise excitation

1. Introduction

Optical emission spectroscopy (OES) has historically been a valuable diagnostic in gas discharge research. The main objective of this effort was to apply OES to further the understanding of electron impact excitation within an inductively coupled plasma (ICP) radio frequency (rf) source with Ar gas at low pressure. The influence of the electron energy distribution function (EEDF) on the generation of excited species is examined through a combination of diagnostics including Langmuir probe measurements and moderately high-resolution time-resolved OES in the violet region.

Most previous efforts in Ar optical emission analyses have focused on the infrared optical emission, although there also exists reasonably intense violet emission in an Ar discharge that may have some analytical advantages. This work specifically focuses on the spectral analysis of the violet emission from an Ar discharge and its relationship to electron impact “direct excitation” from ground state Ar and “step-wise excitation” from Ar metastable states within an Ar discharge. Along with optical cross section data, knowledge of the electron energy distribution function (EEDF) for a particular discharge is also critical in analyzing Ar optical emission spectra. The EEDFs used in this effort were generated from experimental Langmuir probe measurements.

For the pulsed Ar ICP discharge investigated here, the time evolution of the emission spectrum was influenced by an evolving EEDF and/or by a changing density of Ar metastables during or after the pulsed discharge. The time periods considered in this study were (a) at the beginning of the pulse immediately after discharge initiation, (b) in the middle of the pulse during the discharge, and (c) after the end of the pulse in the afterglow. By collecting the optical emission spectra and Langmuir probe data within small gated time periods, the resulting spectra could be simulated and the corresponding degree of step-wise excitation during each of these three times analyzed.

2. Experimental Set-up and Modeling

The experiment centered on an rf-excited (13.56 MHz) ICP source, which has been described in detail previously [1]. The ICP system was a modified commercial ion-beam system built by Nordiko with the extraction grids removed allowing the plasma to diffuse freely from the source in a large volume chamber. The ICP source was run in pulsed mode with a 2 ms pulse duration at 100 Hz repetition rate. The chamber was equipped with a time-resolved Langmuir probe system (Scientific Systems’ Smart Probe) and a half-meter spectrometer/intensified charge-coupled device (ICCD) detector which allowed for time-resolved emission spectroscopy. The spectrometer collected emission from 410nm-430nm in this study. A diagram of the experimental set-up is shown in Figure 1. All data for this study were taken at an Ar pressure of 5 mTorr with the probe positioned 1 cm from the rf source window and the emission imaged from the same region.

Both the Langmuir probe and spectrometer/ICCD were gated for 5 μs time windows relative to specific trigger times. Probe and optical data representing the beginning of the pulse at time (a) was taken within the first 10 μs of the rf pulse, during which time the discharge was changing from a capacitively coupled mode to an inductively coupled mode. The data for time (b) was taken 1 ms after the start of the pulse and represented a period “during” the inductively coupled discharge. The data for time (c) was taken starting 10 μs after the end of the 2 ms rf pulse and represented the short afterglow period.
The optical emission in the 410 nm to 430 nm range from the Ar dc discharge included several Ar \((3p \rightarrow 1s)\) transitions along with several emission lines from Ar\(^+\) excited states. To model the relative intensities of these emission lines, rates were calculated for direct and stepwise electron impact excitation as well as electron impact ionization to Ar\(^+\), all leading to 410-430 nm emission. The expression relating the optical emission intensities to the excitation rates is given by

\[ I_{ij}(\lambda) \propto \left( \frac{n_m}{n_g} k_{ij}^d + k_{ij}^s \right) \delta(\lambda_{ij}) \tag{1} \]

where \( I_{ij}(\lambda) \) is the emission intensity of the Ar\((3p_{ij} \rightarrow 1s)\) transition, \( n_g \) and \( n_m \) are the ground and metastable state densities, \( k_{ij}^d \) and \( k_{ij}^s \) are the direct and stepwise excitation rates in \( \text{cm}^3/\text{s} \) leading to Ar\((3p_{ij} \rightarrow 1s)\) emission at wavelength \( \lambda_{ij} \). The direct and stepwise electron impact excitation rates, \( k_{ij}^d \) and \( k_{ij}^s \), are determined by

\[ k_{ij} = \int_0^\infty \sigma_{ij}(\epsilon) \sqrt{\frac{2\epsilon}{m}} f(\epsilon) \, d\epsilon \tag{2} \]

where \( \sigma_{ij} \) is the optical cross section, \( m \) is the electron mass, \( \epsilon \) is the electron energy, and \( f(\epsilon) \) is the normalized electron energy distribution function (EEDF). For this study, published data sets were applied in the model for \( \sigma_{ij}(\epsilon) \) and \( \sigma_{ij}(\epsilon) \) representing the optical cross sections for direct and stepwise electron impact excitation from ground and metastable state Ar respectively and resulting in Ar \((3p \rightarrow 1s)\) emission [2,3]. In addition published data for optical cross sections involving ion excitation, \( \sigma_{ij}^{ion}(\epsilon) \), were also applied in the model.

Figure 2 shows a comprehensive collection of optical cross sections with emission in the 410-430 nm region, where the red curves are for stepwise excitation, blue curves are for direct excitation and green curves are for ion excitation.

Figure 3 shows the normalized EEDF, or \( f(\epsilon) \), determined from Langmuir probe data, with \( f(\epsilon) \) calculated from the second derivative of the I-V curve. Where the noise in \( f(\epsilon) \) becomes excessive at higher electron energies, the “high energy” \( f(\epsilon) \) curve was extrapolated by adding the tail of either a Maxwellian or Druyvesteyn fit to the experimental \( f(\epsilon) \) at lower energies.

Using the experimental normalized EEDF and the published optical cross sections, the only fit parameter in simulating the relative emission spectra was the ratio of densities of the metastable to ground states of Ar, which is the ratio \( n_m/n_g \) in equation 1. Each of the simulated spectral lines was convolved with a Gaussian line function to approximately match the instrument lineshape of the experimental emission lines for a nice graphical comparison.

3. Results and Discussion

Langmuir probe data was taken for the select times of (a) early in the discharge, (b) during the discharge, and (c) immediately after the discharge. The EEDFs calculated from the probe data were found to become relatively noisy above threshold energies between 20-30 eV. To account for this, the high
energy data were replaced with extrapolated functions that gave the best fit at the lower energies, as explained earlier. The EEDFs for each time are shown in Figure 3 with the solid lines showing the experimentally determined function and the dashed lines showing the extrapolated high energy EEDF. The transition point between experimental data and extrapolation is identified by a slash. For time (a) and (c), Maxwellian distributions best fit the lower energy $f(e)$'s, thus Maxwellian high energy tails were added to each with the best fits corresponding to electron temperatures of 6 eV for time (a) and 2 eV for time (c). For times (b) the high energy tail was extrapolated from the best fit at lower energies, which was a Druyvesteyn distribution corresponding to an electron temperature of 8 eV.

Figure 4 shows the experimental (solid line) and simulated (dotted line) optical emission spectra in the violet region for time (a), early in the discharge. Two noticeable features in this early experimental spectrum is the presence of ion emission lines, albeit very weak, occurring at 422.8, 423.7, and 427.8 nm and the ratio of nearly 1 in the two strong emissions lines at 420.1 nm and 419.8 nm.

The best fit of the spectra at time (a) occurred with $n_m/n_e = 0$. The assignment of $n_m/n_e = 0$ made physical sense, since the density of metastables were expected to be minimal at very early times in the discharge. The emergence of ion emission lines in the spectrum was an artifact of the high average electron energy at time (a) and especially the extended high energy tail of the EEDF past the threshold of the ion emission cross sections. The ratio of the 420.1 nm to 419.8 nm line intensity was approximately 1:1 in both the experimental and simulated spectra, although the agreement is not exact. A 420.1 nm to 419.8 nm ratio of ~1:1 was indicative of an absence of step-wise excitation (i.e. very low metastable density) which was included in the model with the assignment of $n_m/n_e = 0$. Experimentally, it was found that the 419.8 nm line intensity was slightly, but reliably, greater than the 420.1 nm intensity, whereas the simulation showed the opposite, that the 420.1 nm line was slightly more intense than 419.8 nm. Substituting a Maxwellian EEDF with an even higher average energy would increase the simulated 419.8 nm intensity compared to 420.1 nm to match the data, but it would also increase the relative ion emission to levels beyond what is seen experimentally. Thus, the simulation using the experimental EEDF seems to represent the best overall fit.

Figure 5 shows the experimental and simulated optical emission spectra for time (b), which is representative of a “steady state” spectrum during the discharge. The most notable feature of the spectrum during this time period was the ratio of the 420.1 nm to 419.8 nm line pair, which in this discharge was approximately 2:1. The more intense 420.1 nm emission can be attributed to the presence of Ar 1s metastables and the resulting electron impact step-wise excitation [4,5]. The best fit of the
simulated spectrum to the experimental data occurred with the assignment of $n_m/n_g = 0.2 \pm 0.1\%$. This represents a reasonable density of Ar metastables, which could possibly be checked in a future effort by a diode laser absorption measurement.

Figure 6 shows the experimental and simulated optical emission spectra for time (c), which was taken 10 $\mu$s after the end of the 2 ms rf pulse and could be considered in the “afterglow” of the Ar discharge. The striking feature of this experimental spectrum is dominance of the 420.1 nm line intensity over the 419.8 nm, which shows a ratio of roughly 8:1. This ratio can be attributed to a removal of the rf excitation, a depletion of high energy electrons and a reduction in direct excitation, while step-wise excitation continued due to the persistence of lower energy electrons. Since the 420.1 nm step-wise cross section is consistently many times the magnitude of 419.8 nm step-wise cross section, the resulting larger line intensity ratio was certainly expected. The simulated spectrum from time (c) was generated by keeping the assignment of $n_m/n_g = 0.2\%$, as was found during the discharge, although the fit was not nearly as sensitive to the metastable ratio here, since the competing direct excitation rates were very low.

3. Conclusion
An investigation has been conducted of an rf ICP pulsed discharge in 5 mTorr Ar, where the violet optical emission was simulated using Langmuir probe measurements and previously published optical cross sections. The simulated spectra compared very favorably to experimental data and accurately predicted specific spectral features characteristic of either direct or step-wise electron excitation at various times relative to the rf pulse. For the best spectral fits, the ratio of the Ar metastable state compared to the ground state population was assigned to $n_m/n_g = 0\%$ very early in the discharge pulse. At a time 1 ms into the discharge pulse, the ratio was assigned to $n_m/n_g = 0.2\%$, which had reached a steady state value within the pulse. Immediately after the pulse, the ratio was assumed unchanged from the steady state value and again assigned to $n_m/n_g = 0.2\%$, which resulted in a good fit to the afterglow spectrum.

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References