Determination of Argon metastable density from relative emission intensity measurements combined with optical emission cross section data

S. Adams¹, J. Miles¹, A. Laber¹, V. Demidov², J. Williamson³, B. Tolson³

¹Propulsion Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH, USA
²UES Inc., Dayton, OH, USA
³Innovative Scientific Solutions Inc., Dayton, OH, USA

Abstract: Measurements of relative intensities of violet spectral lines within an argon pulsed discharge were applied to a model of excitation rates from the Ar ground and metastable states using previously published electron impact optical cross sections which yield the absolute argon metastable concentrations within the discharge for a known electric field.

Keywords: argon, metastable, spectroscopy, model

1. Introduction

The plasma diagnostic technique of optical emission spectroscopy can yield a variety of information depending on the resolution of measurement and the extent of supporting data that exists on the fundamental optical properties of the species of interest. On the most basic level, a simple knowledge of the spectral location of strong transition lines can yield information on the identity of plasma species and changing line intensities with time may indicate temporal changes in the density of the species. More advanced plasma diagnostics can be achieved when optical emission measurements are combined with available electron-impact cross sections, which can potentially yield many useful plasma parameters such as electron density, electron temperature, and gas temperature as well as absolute species concentration. In recent years, a considerable amount of data has been compiled for electron excitation of rare-gas atoms including Argon [1]. In particular for Ar, optical cross-sections have been measured for electron excitation from both the ground state and metastable states [2], representing direct and stepwise electron impact excitation respectively. Here, it is shown that simple measurements of specific relative spectral intensities under certain conditions allow calculations of absolute Ar metastable concentrations.

Comprehensive data has been previously compiled of electron excitation cross sections from the ground state and from the 1s₁ and 1s₅ metastable states of Ar into a limited number of excited states including the 2p and the 3p configurations [2,3]. This study focuses on modeling excitation into the ten levels of the 3p configuration from both the ground and metastable states and interpreting the resulting optical emission in the violet spectral region. Of particular utility to this analysis is the fact that the electron excitation pattern from the singlet ground state and the triplet metastable states is quite different between the various 10 levels of the 3p state (3p₁ to 3p₁₀). The result of this pattern is that the emission spectrum of 3p-1s transitions will display a unique intensity distribution depending on whether the 3p state is generated by direct electron excitation from the ground state, or stepwise excitation from one of the 1s metastable states [4]. An energy level diagram for Ar is shown in Fig. 1 which illustrates how this dual excitation phenomenon affects, for example, two particular emission lines in the violet, at 419.8 nm and 420 nm from the 3p₅ and 3p₉ levels respectively.

2. Theory and Model

The ground state of Ar has an electron configuration which is a closed shell with a total angular momentum value of J=0. The first excited state is a configuration consisting of four levels with J=1,0,1 and 2 (which are designated the 1s₂, 1s₁, 1s₄, and 1s₅ levels in Paschen’s notation). The J=1 levels (1s₂ and 1s₄) are short lived due to the dipole allowed transition to the ground state, but the J=0 and J=2 levels (1s₀ and 1s₅) are considered triplet spin state with dipole forbidden transitions to the singlet ground state and are thus considered metastable states, with long radiative lifetimes.

Fig. 1 Direct and stepwise excitation and emission in Ar
Fig. 1 displays the direct electron excitation from the ground state to the 3p manifold, which results in the population of both the 3p$_9$ and 3p$_{10}$ levels and emission at both 419.8 nm and 420 nm. The relative intensity of these emission lines due to direct electron excitation can be determined for a known electron energy distribution function, but in many cases the 420 nm/419.8 nm ratio is approximately equal. Also illustrated in Fig. 1 is stepwise excitation which occurs readily from the 1s$_2$ metastable state to the 3p$_9$ state, and in all cases results in a much stronger 420 nm emission compared to 419.8 nm. Thus, the relative amount of direct excitation and stepwise excitation occurring within an Ar discharge will strongly affect the 420 nm/419.8 nm emission ratio, along with the rest of the violet spectral line intensity distribution [5].

The available optical cross section data allow the entire violet emission spectrum to be predicted quite accurately for a known electron energy distribution function. In many Ar plasma situations it is found that the spectrum in the violet region contains significant contributions from both direct and stepwise excitation. This study has shown that a model combining the 3p excitation cross sections from both the ground state and metastable states can also accurately predict spectral distributions with contributions from both direct and stepwise excitation.

4. Results and Discussion

The optical emission in the 410 nm to 430 nm range from the Ar dc discharge included several Ar (3p$_i$→1s$_j$) transitions along with several emissions 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

$$I_{ij}(\lambda) \propto \left( k_{ij}^d + \frac{n_m}{n_g} k_{ij}^s \right) \delta(\lambda_{ij}) ,$$

where $I_{ij}(\lambda)$ is the emission intensity of the Ar($3p_i$→$1s_j$) 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 cm$^3$/s leading to Ar($3p_i$→$1s_j$) emission at wavelength $\lambda_{ij}$. The direct and stepwise electron impact excitation rates, $k_{ij}^d$ and $k_{ij}^s$, can be found by

$$k_{ij} = \int_{0}^{\infty} \sigma_{ij}(\varepsilon) \frac{2\varepsilon}{m} f(\varepsilon) d\varepsilon$$

where $\sigma_{ij}$ is the optical cross section, $m$ is the electron mass, $\varepsilon$ is the electron energy, and $f(\varepsilon)$ is the normalized Maxwell-Boltzmann electron energy distribution function (EEDF). For this study, published data sets were applied in the model for $\sigma_{ij}^d(\varepsilon)$ and $\sigma_{ij}^s(\varepsilon)$ representing the optical cross sections for direct and stepwise electron impact excitation from ground state and metastable Ar respectively and resulting in Ar ($3p_i$→$1s_j$) emission [1].

The model was applied to fit experimental optical emission spectra taken at various times within the Ar pulsed dc discharge. With the E/N measured experimentally, the only adjustable parameter in the fit was the charge to match the pressure-distance (pd) product corresponding to the minimum breakdown voltage in the Ar Paschen curve.
ratio of densities of Ar 1s metastables to ground state neutral Ar atoms \((n_m/n_g)\). Fig. 2 shows the experimental optical emission spectrum (solid line) taken early in the discharge, 1 \(\mu\)s into the pulse, where the electric field is relatively high during gas breakdown. As seen in this case, the model provided a reasonable fit to the experimental optical emission data with a measured \(E/N\) of 1500 Td and the \(n_m/n_g\) ratio set to 0.0%. Since we assumed the metastable density to be negligible this early in the discharge, the good fit with \(n_m/n_g = 0.0\) is a positive confirmation of our modeling accuracy. Note the two closely spaced lines near 420 nm, in which the ratio of the 420 nm to the 419.8 nm line is less than 1 with a value of approximately 0.7.

At 100 \(\mu\)s into the discharge, the applied pulse was ending and the electric field was decaying rapidly so that the \(E/N\) was difficult to measure. We assumed, though, that \(n_m/n_g\) had not changed significantly from the equilibrium concentration, and we used the model to fit the spectral data at the end of the pulse by allowing the \(E/N\) to vary. Fig. 4 shows the experimental data and modeled fit for the emission 100 \(\mu\)s into the pulse, when the metastable ratio was assumed to still be \(n_m/n_g = 0.010\). An \(E/N\) value of 220 Td provided the best fit to the experimental data. In this case, the ratio of the 420 nm line intensity to the 419.8 nm line was approximately 3, which was much greater than in the other cases.

The model was further used to calculate the 420 nm to 419.8 nm intensity ratio for a larger range of \(E/N\) and \(n_m/n_g\) values using the cross section data for 5 mTorr. The plot in Fig. 5 shows the results of this calculation. With this plot, given a measured \(E/N\) and a measured 420 nm to 419.8 nm intensity ratio, the ratio of the metastable to ground state density of Ar, and thus the absolute metastable concentration, could be easily predicted. The accuracy of a prediction in this plot depends in which region of the chart the parameters coincided, as some regions are more sensitive to the variation of parameters.
5. Summary

Information on absolute Ar metastable concentrations has been derived from measurements of relative intensities in the violet emission spectrum. The different patterns of excitation rates from the Ar ground and metastable states allow the emission rates due to the excitation from the various levels to be combined and generate a predicted spectrum. This diagnostic technique was applied to a pulsed dc Ar discharge where the E/N was measured or assumed and the resulting fit of the relative emission intensities provided a calculation of the absolute number density of Ar metastables. The generalized model was presented as a plot where the 420 nm to 419.8 nm line intensity ratio was predicted for a given E/N and metastable concentration using published electron impact cross sections for 5 mTorr of Ar.

References