Regular Article – Plasma Physics

On the use of Ar I 517.753 nm spectral line for electric field measurements in the cathode sheath of a Grimm-type glow discharge source

Nikodin V. Nedić[1], Nikola V. Ivanović[2,a] (iD), Ivan R. Videnović[1], and Djordje Spasojević[1]

[1] Faculty of Physics, University of Belgrade, P.O. Box 44, 11001 Belgrade, Serbia
[2] Faculty of Agriculture, University of Belgrade, Nemanjina 6, 11080 Belgrade, Serbia

Abstract. We present the results of the optical emission spectroscopy study of the Ar I 517.753 nm spectral line, observed at different positions in the cathode sheath of an abnormal DC Grimm-type glow discharge source operated in argon. The line profiles were recorded parallel to the cathode surface (side-on view), along the discharge axis from the cathode towards the negative glow. The spectra show a red line shift, which diminishes with the distance from the cathode surface and decreasing electric field. This allows experimental determination of the coefficient C in quadratic relation, $\Delta\nu = CE^2$, between the wavenumber Stark shifts, $\Delta\nu$, and electric field strength, E. The above relation is a low-field (up to 25 kV/cm) approximation of the quadratic dependence of the upper-level shift, measured for a large set of argon lines at high electric fields (up to 700 kV/cm) by Windholz (Phys Scr 21:67–74, 1980). One of these lines, Ar I 537.349 nm, is used here for independent measurement of the electric field E and correlated with the Ar I 517.753 nm upper-level wavenumber shift $\Delta\nu$ to obtain a line-specific coefficient C. In this way, the Ar I 517.753 nm spectral line complements the set of argon lines suitable for Stark spectroscopy diagnostics of the electric field distribution and cathode sheath length, the knowledge of which allows for a better understanding and description of the glow discharge processes through various theoretical models.

1 Introduction

Due to its high sputtering efficiency, argon is the most commonly used noble gas in glow discharge sources (GDS) for various applications such as in-depth analytical spectroscopy, thin film deposition, or plasma etching. The development of non-intrusive plasma diagnostic tools based on optical emission spectroscopy (OES) of argon spectral lines is, therefore, essential for understanding, modelling, and control of discharge conditions. The cathode sheath (CS), a tiny dark layer next to the cathode surface, appears vital for sustaining the glow discharge. This is the region where most of the externally applied voltage is consumed to generate a macroscopic electric field, which accelerates electrons towards the bright negative glow (NG) region and heavy species—ions and recombined fast neutrals—towards the cathode, resulting in sputtered cathode material and secondary electrons emission [1–4].

The influence of a strong DC electric field (up to 700 kV/cm) on argon energy levels through the Stark effect has been extensively investigated by Windholz [5] in visible and near UV spectral regions. The study showed that splitting and shifting of the spectral lines

depend on the upper-level wavenumber shifts $\Delta\nu$ which can be analytically expressed as

$$\Delta\nu = a_1 E^2/(a_2 - \Delta\nu), \qquad (1)$$

where E is the electric field strength and a_1 and a_2 are the line-specific numerical coefficients. It has been shown also [5] that a large majority of argon lines' upper-level terms exhibit shifts to the lower wavenumbers, resulting in red line shifts in the spectra.

Recent studies [6–9] of the Stark effect influence on argon spectral lines focused on lower E values (≈ 25 kV/cm) in experiments carried out in the CS of the micro-hollow and Grimm-type GDS. In a low-field approximation, Windholz's Eq. reduces to

$$\Delta\nu = (a_1/a_2)E^2 = CE^2. \qquad (2)$$

In Grimm GDS [7], two spectral lines of neutral argon, Ar I 518.775 nm and Ar I 522.127 nm, exhibiting blue and red wavelength shifts, respectively, were observed along the CS region. At typical field strengths in GDS, argon lines show small Stark shifts and difficulties in distinguishing Stark components, hence imposing a need for an appropriate model function to

ᵃ e-mail: nikolai@ff.bg.ac.rs (corresponding author)

extract the information on the field strength. A significant improvement in argon lines Stark spectroscopy in Grimm GDS was achieved by Vasiljević et al. [8], who detected both components of the Ar I 522.127 nm spectral line, allowing for the line-specific quadratic Stark shift coefficient C to be determined. The comparison of the obtained results with the low-field approximation of Windholz's measurements and analytical description [5] showed deviations of no more than 10–15%.

In a most recent investigation in the Grimm-type GDS [9], Nedić et al. have studied the correlation of the side-on measured neon and argon lines with the so-called end-on profiles, recorded from the end of the discharge, in line with the discharge axis and perpendicular to the cathode surface. For the studies in argon, they selected the lines from Windholz's set [5] that exhibit larger Stark shifts, so that the line components are well resolved and a simple peak separation technique can be used to measure the shifts and correlate them with the electric field strength.

In this paper, we aim to complement the set of argon lines with considerable Stark shifts that enable easy and accurate electric field measurements in the cathode sheath of a Grimm-type GDS. The line Ar I 517.753 nm appears to be a good candidate, which has not been studied earlier by Windholz [5], and its C coefficient is missing. The Ar I 517.753 nm Stark shifts are measured against the electric field, independently determined from the shifts of the Ar I 537.349 nm line, which belongs to Windholz's set [5] and has a known C value. Improving and broadening the cathode sheath electric field diagnostics in a glow discharge source is aimed to help better understanding of the discharge sustaining mechanism and the processes that take place in the CS region, e.g. charged particle's acceleration, their trajectories, kinetic energies, collisions with other particles, cathode material sputtering, etc.

2 Experimental

Our Grimm-type glow discharge source (Fig. 1) is laboratory made after Ferreira et al. design [10], modified and improved by Kuraica et al. [11]. It consists of a cylindrical hollow brass anode (30 mm long with 8.00 mm inner diameter) with a longitudinal slot (16 mm long and 1.5 mm wide) for side-on observations along the discharge axis. An exchangeable copper cathode (18 mm long and 7.40 mm in diameter) is affixed onto the water-cooled holder and partially inserted into the anode cylinder to enable side-on observations right away from the cathode surface. The entire source was mounted on a holder that enables fine translation along the discharge axis in 1/16 mm steps.

The GDS is differentially evacuated, both from the plasma chamber side and from the interelectrode gap, using a two-stage mechanical vacuum pump. The experiments were performed in 99.999% purity argon, sustained by a needle valve in the 5–10 mbar pressure range at a continuous gas flow rate of 300 cm3/min s.t.p. The

pressure values are taken as the average between the readings at the gas inlet and outlet. To run the discharge, a current-stabilized DC power supply (0–2 kV, 0–100 mA) and a ballast resistor of 5 kΩ are used.

The GDS side-on emission was focused with unity magnification by an achromatic lens (focal length 75.8 mm) onto the 20-µm-wide entrance slit (height restriction 2 mm) of the 2-m Ebert-type monochromator with 651 g/mm reflection grating blazed at 1050 nm. The OES system features the reciprocal dispersion of 0.37 nm/mm in the second diffraction order and introduces a Gaussian instrumental profile with the full width at half maximum (FWHM) of 0.012 nm. To prevent higher diffraction orders penetration, a 400–700 nm band-pass filter is placed between the lens and the entrance slit. The resolved light is detected by a thermoelectrically cooled Hamamatsu CCD camera ($T = -10$ °C, 2068×512 pixels, 12 µm pixel size, S10140/10141 series), A/D converted and digitally stored and processed.

3 Results

Figure 2 shows a typical set of OES side-on measurements of the Ar I 517.753 nm spectral line in the CS at three different positions (i.e. distances from the cathode surface) and one in the negative glow. Under our experimental conditions, the profiles of the Ar I 517.753 nm spectral lines recorded in the CS region consist of one unshifted and one shifted component. The shifted component is emitted under the influence of the electric field in the cathode sheath, while the unshifted component occurs as a consequence of the discharge partial protrusion through the anode slot, hence emitted from a zero-field region. The appearance of an unshifted field-free component, also noticed in previous studies in the same type of Grimm GDS in helium, neon, and argon [7–9, 12], enables us to perform fast and reliable measurements of Stark shifts and, thereby, the determination of the electric field strength. The values of the electric field depend on the distance d measured from the cathode towards the recording position. As indicated in Fig. 2, they decrease with the increase in d, starting from the maximum value attained near the cathode and falling to zero at the CS-NG boundary.

We used two techniques for measuring the Stark shifts of the Ar I 517.753 nm line. In the case of clear separation between the shifted and unshifted components, we measured directly peak-to-peak Stark wavelength shift (see Fig. 2a). However, for the profiles

Fig. 1 Schematics of the modified Grimm-type GDS with enlarged observation area
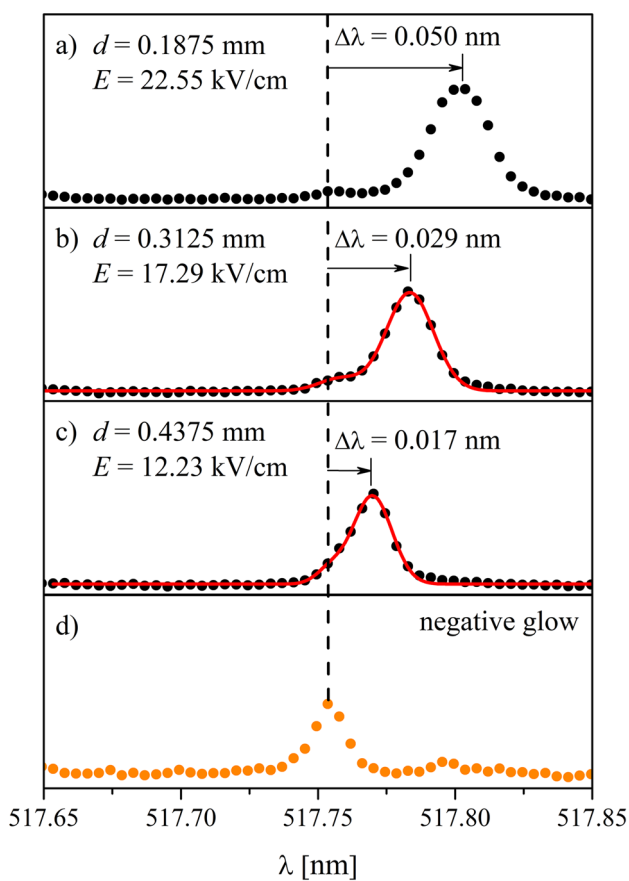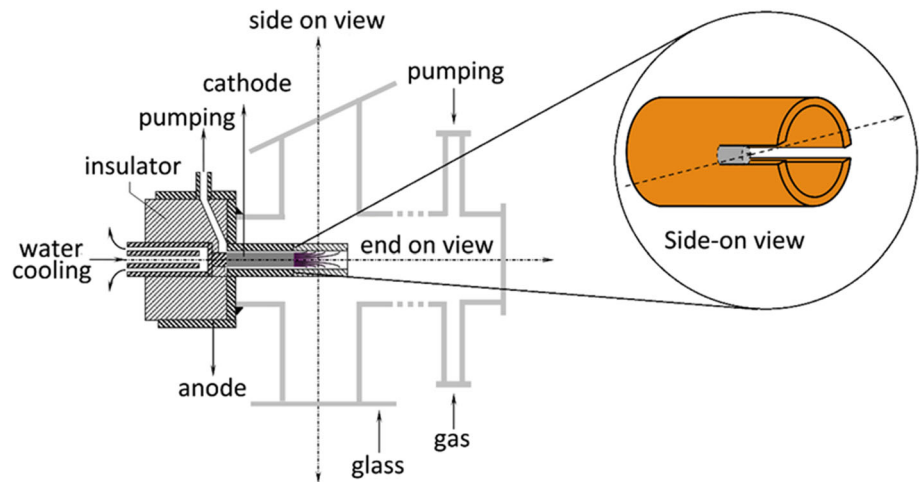

Fig. 2 The profiles of the Ar I 517.753 nm line recorded in the CS at different distances d from the cathode surface (**a**–**c**) and in the NG region (**d**). In legends, corresponding values of distances d, electric field strength E, and Stark shift $\Delta\lambda$ are provided. The dashed line indicates the location in the spectra of the unshifted peak originating from the protruded zero-field radiation, and the solid (red) lines in (**b**) and (**c**) show the best-fitting model function curves (3)
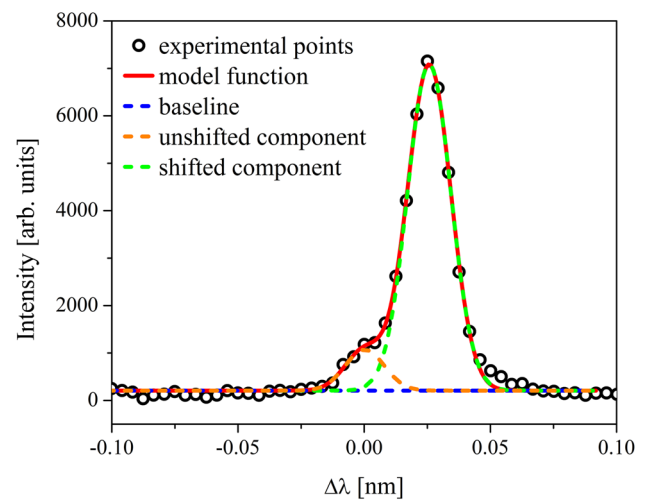

Fig. 3 Example of the Ar I 517.753 nm line experimental profile and its best fit (solid red line) using the model function (3)

recorded at low electric fields, the foregoing simple technique is not applicable because the components are not sufficiently resolved. In this case, as illustrated in Fig. 3, we estimated the Stark shift using the best fit of the experimental profiles by the model function:

$$I(\lambda; \lambda_S) = G(\lambda; H_S, \lambda_S, w_S) + G(\lambda; H_0, \lambda_0, w_0) + b, \quad (3)$$

comprised of the base-line level b and a sum of two Gaussians

$$G(\lambda; H, c, w) = H \exp\left[-\left(2\sqrt{2\ln 2}\,\frac{\lambda - c}{w}\right)^2\right], \quad (4)$$

depending on the wavelength λ as the independent variable and on Gaussian's height H, centre c, and FWHM w as the parameters. The first Gaussian in Eq. (3)
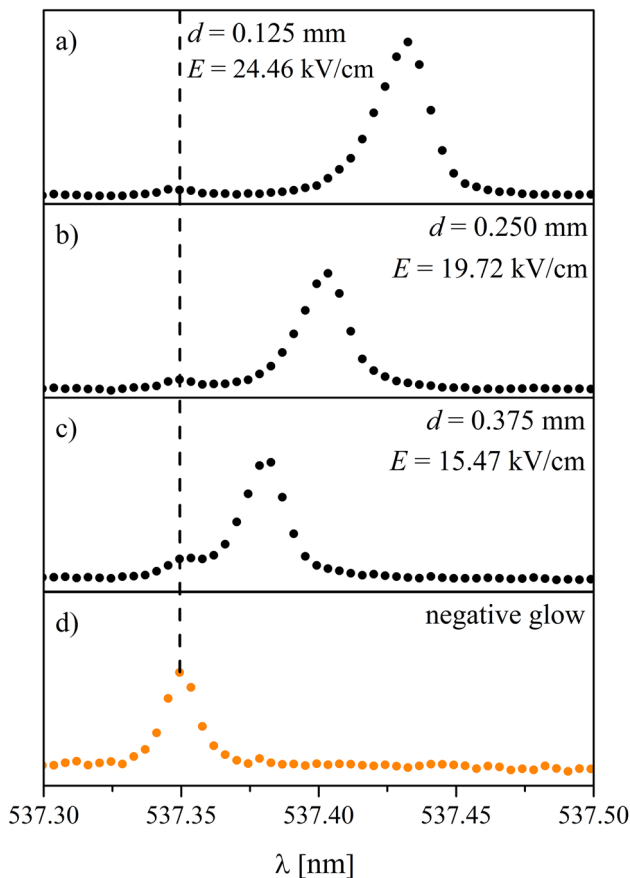
Fig. 4 The profiles of the Ar I 537.349 nm line recorded in the CS region at different distances d from the cathode surface (**a**–**c**) quoted in legends together with the corresponding values of electric field strength E. (**d**) The profile recorded in the NG region. The dashed line indicates the unshifted peak of the protruded zero-field radiation

Fig. 5 Comparison between the wide-range (1) and reduced, low electric field prediction (5) for the Stark wavelength shifts

describes the shifted component centred at the wavelength λ_S, while the second one describes the unshifted component with a fixed centre $\lambda_0 = 517.753$ nm. Although the model function (3) depends on six free fitting parameters, namely $H_S, \lambda_S, w_S, H_0, w_0$ and b, the only relevant one in the current context is λ_S. Its best-fit value gives the Stark shift of the line $\Delta\lambda = \lambda_S - \lambda_0$, estimated by the model function method that agrees with the peak-to-peak value whenever both methods are applicable.

Parallel with the Stark shifts determination for the Ar I 517.753 nm line, we measured the electric field strength using the side-on profiles of the Ar I 537.349 nm line, taken from the recordings at the same positions (see the examples in Fig. 4).

We estimated the values of the electric field strength following Windholz's study [5] in high electric fields of up to 700 kV/cm, where the coefficients correlating the wavenumber Stark shift $\Delta\nu$ and the electric field strength are presented in Table 3 for a large set of argon lines, including the Ar I 537.349 nm. Since the electric field strengths reached in our experimental conditions
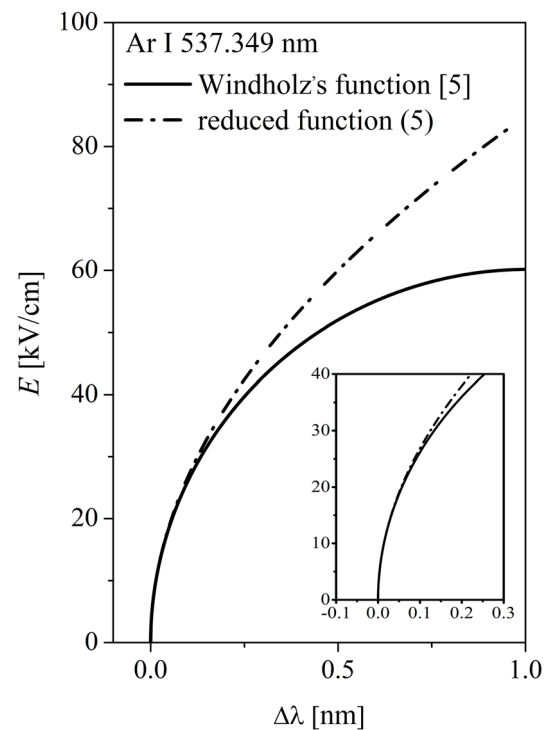
are much lower (< 30 kV/cm), we used the simplified quadratic formula equivalent to (2):

$$\Delta\lambda \approx -\lambda_0^2 \frac{a_1}{a_2} E^2 = -\lambda_0^2 C E^2, \tag{5}$$

where $a_1 = 0.335$ kV^{-2} and $a_2 = -69.63$ cm^{-1} are the corresponding coefficients [5] for the Ar I 537.349 nm line. Figure 5 illustrates that in the range of electric fields up to 30 kV/cm the approximation (5) is in reasonable agreement with the Windholz function (1) as a wide-range prediction for the wavelength shift [5].

Finally, by fitting our experimental data for the Ar I 517.753 nm spectral line to the formula (5) (see Fig. 6), we obtained the line-specific coefficient C of $-0.00371(6)$ cm/kV^2, which agrees well with the value quoted by Nedić et al. [9].

4 Summary and conclusion

We report the results of a study of the Ar I 517.753 nm spectral line Stark wavelength shifts observed in the electric field of the cathode sheath of an abnormal Grimm-type glow discharge in argon. For the electric fields above 15 kV/cm, the line profiles manifest a clear separation between the shifted and unshifted components, enabling simple measurements of the wavelength shift, whereas for lower fields the corresponding smaller
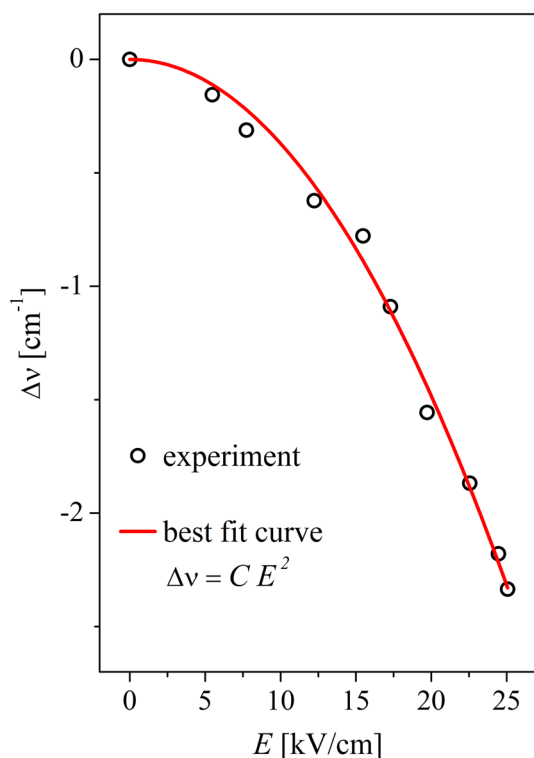
Fig. 6 Upper-level wavenumber shift of the Ar I 517.753 nm line versus electric field strength and the best-fit curve of type (5)

Stark shifts are determined by fitting the experimental profile to a suitable model function. The electric field is calculated independently from the measured Stark wavelength shifts of the Ar I 537.349 nm line. Based on these findings, the Stark shift coefficient for the Ar I 517.753 nm spectral line is obtained, which can be used for the measurements of electric fields up to 30 kV/cm in argon discharges.

Author contribution

NVN contributed to conceptualization, investigation, methodology, and writing—original draft. NVI contributed to conceptualization, investigation, methodology, and writing—original draft. IRV contributed to conceptualization, methodology, and writing—review and editing. DS contributed to conceptualization, methodology, writing—review and editing, and supervision.

Data Availability Statement The data sets supporting the conclusions of this article are available from the corresponding author upon reasonable request.

References

1. A. von Engel, *Ionized Gases* (Oxford Clarendon Press, Oxford, 1965)
2. B. Chapman, *Glow Discharge Processes: Sputtering and Plasma Etching* (Wiley, New York, 1980)
3. R.K. Marcus, J.A. Broeckaert, *Glow Discharge Plasmas in Analytical Spectroscopy* (Wiley, Chichester, 2003)
4. D.J. Spasojević, M. Cvejić, N.M. Šišović, N. Konjević, (2010) Simultaneous plasma and electric field diagnostics of microdischarge from hydrogen Balmer line shape. Appl. Phys. Lett. **96**, 241501 (2010). https://doi.org/10.1063/1.3449129
5. L. Windholz, Stark effect of Ar 1'- lines. Phys. Scr. **21**, 67–74 (1980)
6. M. Cvejić, D.J. Spasojević, N.M. Šišović, N. Konjević, A contribution to spectroscopic diagnostics and cathode sheath modeling of micro-hollow gas discharge in argon. J. Appl. Phys. **110**, 033305 (2011). https://doi.org/10.1063/1.3615962
7. G.L.J. Majstorović, N.V. Ivanović, N.M. Šišović, S. Djurović, N. Konjević, Ar I and Ne I spectral line shapes for an abnormal glow discharge diagnostics. Plasma Sources Sci. Technol. **22**, 045015 (2013)
8. M.M. Vasiljević, D.J. Spasojević, N.M. Šišović, N. Konjević, Stark effect of Ar I lines for electric field strength diagnostics in the cathode sheath of glow discharge. Europhys. Lett. **119**, 55001 (2017)
9. N.V. Nedić, N.V. Ivanović, I.R. Videnović, D.J. Spasojević, N. Konjević, Estimation of the maximum electric field strength in the cathode sheath of a Grimm-type glow discharge by end-on view optical emission spectroscopy in neon and argon. J. Anal. At. Spectrom. **37**, 1318–1326 (2022). https://doi.org/10.1039/D2JA00109H
10. N.P. Ferreira, H.G.C. Human, L.R.P. Butler, Distribution of metastable argon atoms in the modified Grimm-type electrical discharge. Spectrochim. Acta B **35**, 273–279 (1980)
11. M. Kuraica, N. Konjević, M. Platiša, D. Pantelić, Plasma diagnostics of the Grimm-type glowdischarge. Spectrochim. Acta Part B: At. Spectrosc. **47**(10), 1173–1186 (1992)
12. M.M. Kuraica, N. Konjević, I.R. Videnović, Spectroscopic study of the cathode fall region of Grimm-type glow discharge in helium. Spectrochim. Acta B **52**, 745–753 (1997). https://doi.org/10.1016/S0584-8547(96)01640-0