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# PECULIARITIES OF SPECTROSCOPY OF THERMAL PLASMA WITH COPPER AND MOLYBDENUM VAPOUR ADMIXTURES

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**Abstract.** This study presents an investigation of arc discharge plasma generated between asymmetric pair of single-component copper and molybdenum electrodes. Optical emission spectra were registered in absolute intensity units with spatial resolution from the midsection of the arc column. Simultaneously laser absorption spectroscopy was carried out as well in order to determine radial distribution of optical thickness at the center of Cu I 510.5 nm spectral line. Particular attention was paid to assessing the influence of self-absorption effects, which can significantly distort the intensity of strong spectral transitions and lead to an underestimation of the spectral line intensity and, consequently, to a significant error in determining the temperature and number densities of metal atoms.

**Keywords:** Thermal plasma, optical emission spectroscopy, laser absorption spectroscopy, self-absorption, asymmetric electrodes.

## 1. Introduction

Spectroscopic diagnostics are indispensable for understanding the physical properties of plasma, particularly with metal vapor admixtures. Such plasmas are of significant interest in the context of material processing, arc erosion studies, and the development of functional coatings for advanced engineering applications. Among the available diagnostic techniques, Optical Emission Spectroscopy (OES) and Laser Absorption Spectroscopy (LAS) are among the most widely used [1, 2] due to their high sensitivity, non-intrusive nature, and ability to provide real-time spatially resolved data on plasma parameters.

OES is extensively employed to determine key plasma characteristics such as excitation temperature, electron density, and species concentration by analyzing the spontaneous emission from excited atomic or molecular states. However, its accuracy depends on several assumptions-most notably, local thermodynamic equilibrium (LTE) and the optical transparency of the spectral lines of the plasma. Violations of these assumptions can introduce significant errors into the analysis [3, 4].

LAS, in contrast, measures the absorption of the intensity of laser beam as it passes through the plasma and provides direct information about the population of specific energy levels – typically ground or lower energy levels – without being affected by self-absorption [5]. LAS is particularly useful for validating and complementing emission-based diagnostics, especially in non-equilibrium or edge regions of the plasma where emission is weak and OES becomes less reliable [6].

One of the most critical factors limiting the accuracy of OES is self-absorption – a phenomenon in which emitted photons are reabsorbed by atoms of the same species in lower energy states along the optical path [4]. This leads to underestimation of spectral line intensities and distortion of line shapes, resulting in inaccurate determination of excitation temperature and number density. For instance, Stark broadening, widely used to infer electron density, can be significantly affected by self-absorption, causing overestimated FWHM values and, consequently, inaccurate electron density calculations. Although self-reversal in spectral line profiles is a clear indication of self-absorption, it is not always observable in experimental spectra, necessitating the development of indirect methods for self-absorption identification and correction [4].

The choice of spectral lines for diagnostics is particularly crucial in plasma with metal vapors, such as copper and molybdenum. In this study, molybdenum lines were selected for detailed analysis due to molybdenum's growing relevance as a material for plasma-viewing mirrors in fusion devices, including ITER [7, 8]. In such systems, the monitoring by OES methods of molybdenum vapor admixtures [9] may be key to maintaining the functionality of such mirrors.

This work focuses on identifying and analyzing the effects of self-absorption in molybdenum spectral lines observed in arc plasma with copper and molybdenum vapor admixtures. By employing both LAS and OES in a synchronized setup, the study aims to determine accurate plasma parameters and identify self-absorption effects in emission spectra, which is essential for reliable diagnostics of plasma with metal vapors admixtures.

## 2. Experimental setup

The plasma of DC arc discharge between asymmetric pair of rod electrodes (6 mm in diameter) was investigated at an arc current of 3.5 A. The cathode (made

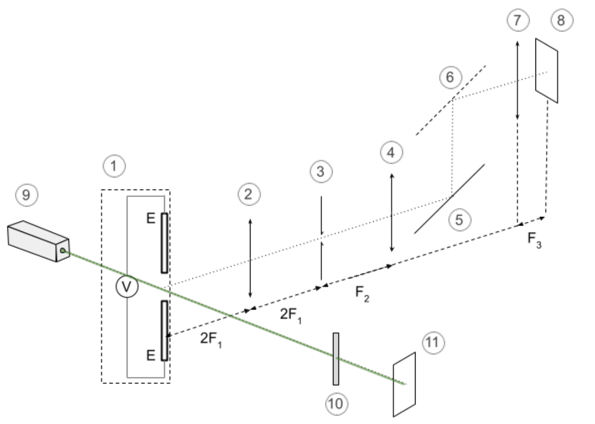


*Figure 1. Scheme of the combined simultaneous plasma emission and absorption registration [10]. The scheme consists of: 1 – vertically-oriented electrodes E with a power source V; 2 – lens with a focal length $F_1$ = 200 mm; 3 – horizontal entrance slit of the spectrograph; 4 – collimator with a focal length $F_2$ = 150 mm; 5 – mirror; 6 – diffraction grating; 7 – lens with a focal length $F_3$ = 50 mm; 8 – registration device; 9 – probing laser; 10 – neutral density filter; 11 – registration device synchronised with 8.*

of single-component copper) was mounted on the top and the anode (made of single-component molybdenum) was mounted on the bottom. The discharge gap was maintained at 8 mm. Discharge gap was blown by argon flow, which minimize the influence of the air atmosphere. The synchronous combination of laser absorption spectroscopy (LAS) and optical emission spectroscopy (OES) was used in accordance with the scheme of the experimental setup shown in Figure 1. The registration scheme and experimental setup are described in detail in [10].

In this work, plasma parameters such as radial distributions of plasma temperature and number densities of radiating admixtures of electrode-origin atoms are investigated. To determine these parameters, the Boltzmann plot technique based on the absolute emission intensities of spectral lines is used as described in [11]. Table 1 shows 28 Mo I and 5 Cu I spectral lines, which were identified on the emission spectrum and used in further steps of the investigation. The energy of the upper $E_k$ and the lower $E_i$ levels and spectroscopic data (product of statistical weight on oscillator strength $g_i f_{ik}$) of the corresponding spectral transitions are shown in Table 1 as well. The spectroscopic data for Cu I spectral lines were carefully selected previously [12], while those for Mo I were taken partially from [13] and NIST database [14].

| № | $\lambda$, nm | $E_i$, eV | $E_k$, eV | $g_i f_{ik}$ |
|---|---|---|---|---|
| 1 | Mo I 438.2 | 2.0809 | 4.9098 | 1.0965 |
| 2 | Mo I 443.5 | 2.0765 | 4.8713 | 0.6668 |
| 3 | Mo I 461.0 | 2.2601 | 4.9489 | 0.2355 |
| 4 | Mo I 466.3 | 1.4703 | 4.1286 | 0.0329 |
| 5 | Mo I 467.2 | 2.6462 | 5.2993 | 0.1820 |
| 6 | Mo I 470.7 | 2.5972 | 5.2304 | 1.0965 |
| 7 | Mo I 473.1 | 2.6227 | 5.2424 | 1.6596 |
| 8 | Mo I 475.0 | 2.5231 | 5.1324 | 0.1202 |
| 9 | Mo I 476.0 | 2.6462 | 5.2501 | 2.0606 |
| 10 | Mo I 481.9 | 2.6462 | 5.2182 | 0.8492 |
| 11 | Mo I 483.1 | 2.6227 | 5.1887 | 0.9977 |
| 12 | Mo I 486.8 | 2.5972 | 5.1434 | 0.5534 |
| 13 | Mo I 495.1 | 2.2601 | 4.7638 | 0.0968 |
| 14 | Mo I 495.8 | 2.2759 | 4.7761 | 0.1178 |
| 15 | Mo I 497.9 | 1.3351 | 3.8245 | 0.0257 |
| 16 | Mo I 536.1 | 3.2633 | 5.5756 | 2.9512 |
| 17 | Mo I 550.7 | 1.3351 | 3.5861 | 1.1482 |
| 18 | Mo I 553.3 | 1.3351 | 3.5753 | 0.8531 |
| 19 | Mo I 557.0 | 1.3351 | 3.5602 | 0.4603 |
| 20 | Mo I 563.3 | 1.3596 | 3.5602 | 0.0485 |
| 21 | Mo I 565.0 | 1.3815 | 3.5753 | 0.0359 |
| 22 | Mo I 568.9 | 1.3815 | 3.5602 | 0.0995 |
| 23 | Mo I 572.3 | 1.4202 | 3.5861 | 0.0316 |
| 24 | Mo I 575.1 | 1.4202 | 3.5753 | 0.0968 |
| 25 | Mo I 579.2 | 1.4202 | 3.5602 | 0.0899 |
| 26 | Mo I 585.8 | 1.4703 | 3.5861 | 0.1012 |
| 27 | Mo I 588.8 | 1.4703 | 3.5753 | 0.169 |
| 28 | Mo I 603.1 | 1.5307 | 3.5861 | 0.2999 |
| 29 | Cu I 510.5 | 1.3890 | 3.8170 | 0.0197 |
| 30 | Cu I 515.3 | 3.7859 | 6.1916 | 1.6466 |
| 31 | Cu I 521.8 | 3.8167 | 6.1924 | 1.9717 |
| 32 | Cu I 570.0 | 1.6422 | 3.8170 | 0.0057 |
| 33 | Cu I 578.2 | 1.6422 | 3.7862 | 0.0130 |

*Table 1. Spectral lines used for determining plasma parameters.*

## 3. Results and Discussions

The typical Boltzmann plot based on the absolute intensities of Mo I spectral lines is constructed for axial radial point of plasma channel ($r = 0$ mm) as shown in Figure 2. Signatures of points on the plot, responsible for specific spectral lines, correspond to the number of the spectral line in the Table 1. In turn, the radial distributions of plasma temperature determined by the Boltzmann plot technique based on the emission intensity of both Mo I ($T_{\mathrm{Mo}}$) and Cu I ($T_{\mathrm{Cu}}$) spectral lines in ten radial points of the plasma channel are shown in Figure 3.

One can see that the points in Figure 2 corresponding to the spectral lines Mo I 550.7 (17), 553.3 (18), 557.0 (19) and 603.1 (28) nm do not coincide significantly with the fitting line. As can be seen from Figure 3, indeed, the plasma temperature determined based on the emission intensity of Mo I spectral lines is higher in comparison with that determined based on the Cu I spectral lines, which violates our assumption about the realization of the local thermodynamic equilibrium (LTE) in such plasma [12, 13]. Obviously, taking into account the above-mentioned Mo I spectral lines leads to the overestimating plasma temperature. It can be assumed that underestimation of the spec-

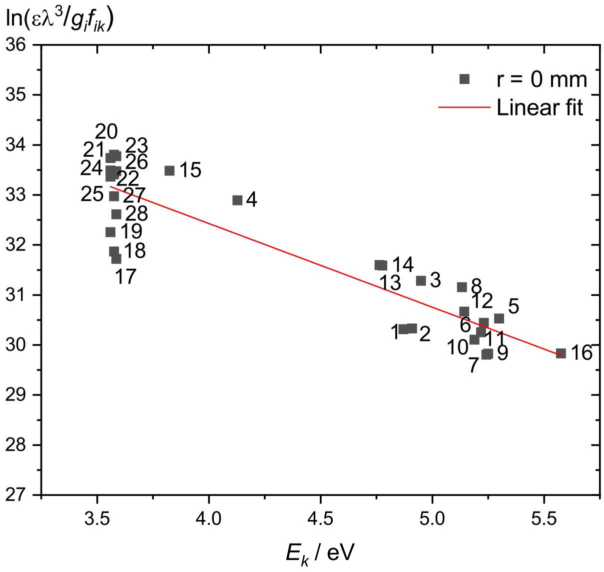


*Figure 2. Typical Boltzmann plot based on the absolute intensities of Mo I spectral lines, constructed for axial radial point of plasma channel ($r = 0$ mm).*

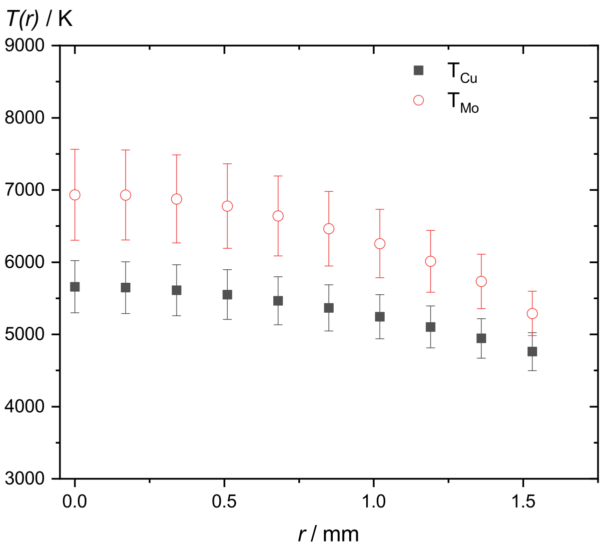


*Figure 3. Radial distributions of plasma temperature obtained based on emission intensity of Mo I and Cu I spectral lines.*

tral lines intensity is caused by the self-absorption of these spectral lines. First, the lower level energies of these spectral transitions are quite low, which in turn means a relatively high population of these levels. Second, $g_i f_{ik}$ value of these lines is also relatively high. All these factors together may indicate the presence of the self-absorption of spectral lines.

In the next step, spectral lines that may exhibit self-absorption were excluded from the determination of plasma temperature by the Boltzmann plot technique (see Figure 4). The corrected radial distribution of plasma temperature determined without taking into account the self-absorbed lines is shown in Figure 5.

Figure 5 shows that the exclusion of some molybdenum spectral lines with possible self-absorption leads

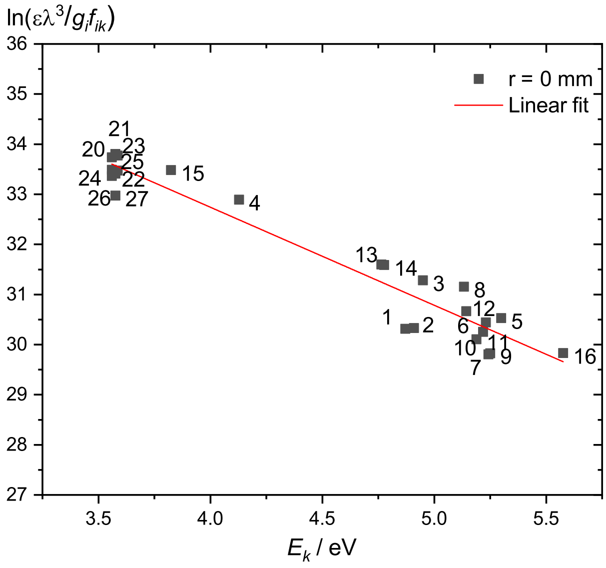


*Figure 4. Typical Boltzmann plot without self-absorbed Mo I spectral lines, constructed for axial radial point of plasma channel ($r = 0$ mm).*

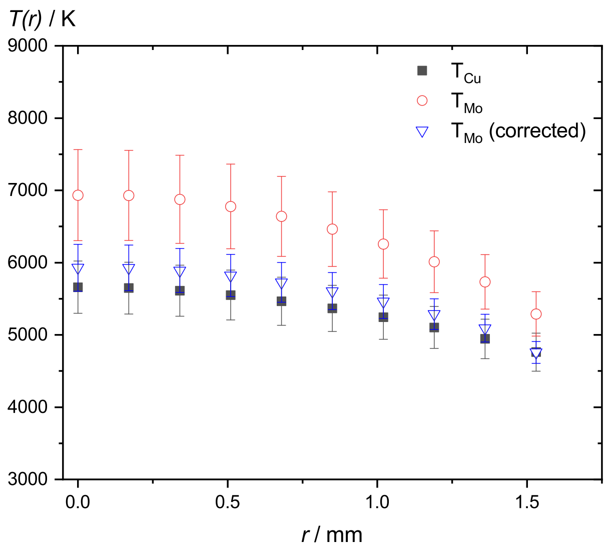


*Figure 5. Radial distributions of plasma temperature, determined based on Cu I spectral lines, all Mo I spectral lines and excluding self-absorbed Mo I spectral lines (corrected).*

to a decrease in the temperature by 10% coinciding with the temperature determined based on the copper spectral lines, which agrees well with the assumption of the realization of LTE in such a plasma. In turn, Figure 6 shows the radial distributions of number densities of molybdenum atoms $n_{Mo}$ obtained from Boltzmann plots with self-absorbed spectral lines (Figure 2) and without (Figure 4). One can see that taking into account the self-absorbed lines leads to a significant underestimation of number density of atoms (by a factor of approximately 3 for a temperature change within a frame of 10%).

To quantify the self-absorption of spectral lines in the investigated plasma the self-absorption coefficient

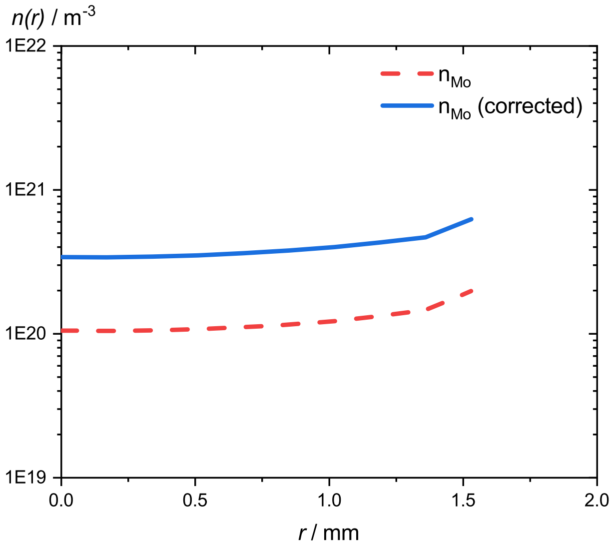


*Figure 6. Radial distributions of number densities of molybdenum atoms obtained from Boltzmann plots with self-absorbed spectral lines and without.*

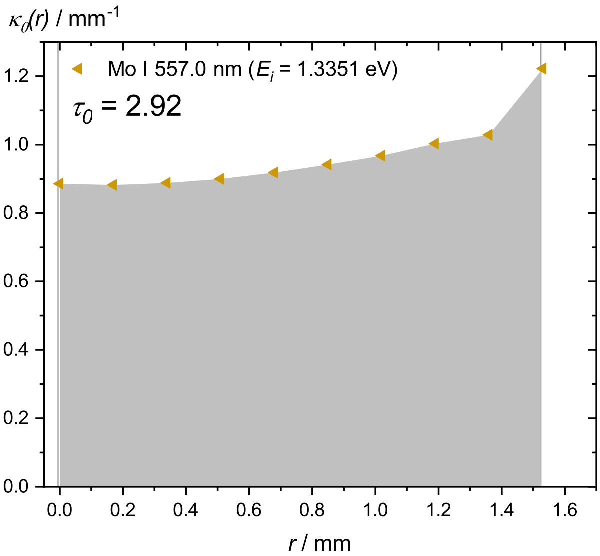


*Figure 7. Radial distribution of absorption coefficient in the center of Mo I 557.0 nm spectral lines obtained based on corresponding population density.*

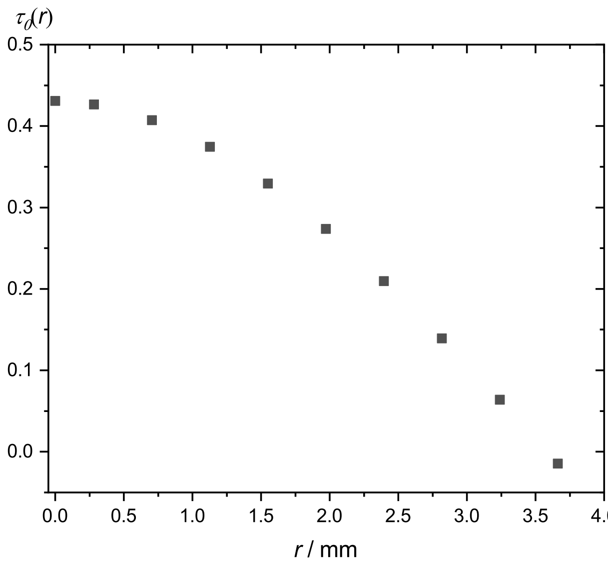


*Figure 8. Spatial distribution of the optical thickness at the center of Cu I 510.5 nm spectral line obtained by LAS.*

$SA$ was calculated [4]. Thus the degree of the self-absorption can be calculated as follows:

$$P = 1 - SA = 1 - \frac{1 - e^{-\tau_0}}{\tau_0} \qquad (1)$$

where $\tau_0$ is the optical thickness at the center of spectral line. In turn, having a radial distribution of the absorption coefficient at the center of spectral line $\kappa_0$, one can determine $\tau_0$ in the center of the arc discharge as follows:

$$\tau_0 = 2\int_0^{r_0} \kappa_0(r)\,\mathrm{d}r. \qquad (2)$$

This absorption coefficient is known from classical electrodynamics [5]:

$$\kappa_0(r) \;=\; \sqrt{\frac{\ln(2)}{\pi}}\frac{\lambda_0^2}{\Delta\lambda_D(r_0)}\frac{e^2}{2mc^2\epsilon_0}n_i(r)f_{ik} \qquad (3)$$

where $\lambda_0$ is the center of the spectral line, $e$ is the elementary charge, $m$ is the electron mass, $c$ is the speed of light, $\epsilon_0$ is the vacuum permittivity, $n_i$ is the population density of the excited level with energy $E_i$, $\Delta\lambda_D$ is the full-width at half maximum (FWHM) of the spectral line profile broadening due to Doppler effect. Term $\sqrt{\frac{\ln(2)}{\pi}}$ in (3) is responsible for Gaussian shape of the spectral line profile [15].

It is assumed that the spectral lines of molybdenum have a Gaussian contour due to broadening by Doppler effect. The broadening coefficients of molybdenum spectral lines due to the Stark effect have been calculated in work [16]. It is shown that electron density $n_e$ in the plasma of the order of $10^{23}$ m$^{-3}$ and at temperature of 13 000 K, the FWHM of spectral lines is of the order of 0.015 nm. For typical values of $n_e$ in this type of discharge at arc current of 3.5 A ($10^{21}$ m$^{-3}$ [12]), the Stark width will be of the order of 0.00015 nm. The estimation of the Doppler width of the spectral lines by the equation used in the work [10] showed that its value is of the order of 0.0025 nm, which allows one to neglect the contribution of the Stark effect to the broadening of the spectral lines. Nevertheless, it should be noted that for a more accurate estimation it is necessary to use the normalized profile of the Voigt function to take into account both of these broadening effects.

In turn, the population densities of the lower levels of all investigated molybdenum spectral lines were calculated from the Boltzmann distribution [11] based on the corrected temperature and number density of molybdenum atom obtained by Boltzmann plots (Fig-

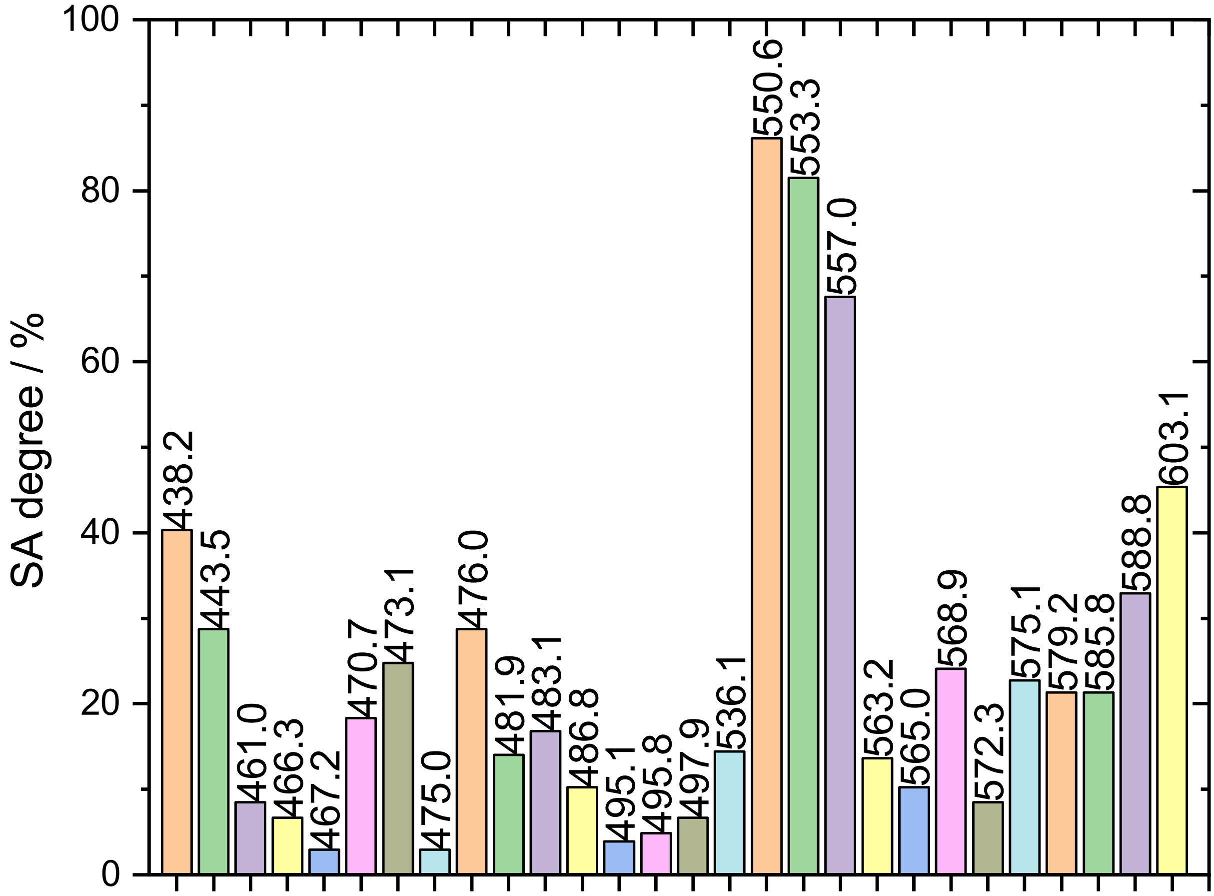


*Figure 9. Degree of the self-absorption of Mo I spectral lines.*

ure 4). Thus, the absorption coefficient in the spectral line center can be obtained according to (3). Typical absorption coefficient of Mo I 557.0 nm spectral lines with region of integration (gray region) and obtained $\tau_0$ in the center of arc discharge are shown in Figure 7.

Moreover, $\tau_0$ can be determined experimentally from the Beer-Lambert law using LAS, as shown in the work [10]. In this work, a synchronous combination of LAS and OES was used, which made it possible to study not only the plasma emission, but also the absorption of the Cu I 510.5 nm spectral line simultaneously. The spatial distribution of the optical thickness in the center of the Cu 510.5 nm spectral line is shown in the Figure 8.

One can see, that the optical thickness of Cu I 510.5 nm spectral line obtained experimentally in the center of arc discharge by LAS (see first dot in Figure 8) is significantly less compared to the thickness of Mo I 557.0 nm spectral line (Figure 7) calculated by (8) (0.43 and 2.92, respectively). From this one can conclude that the degree of self-absorption of the spectral lines of copper is several times less than that of molybdenum.

At the next step, the radial distributions of absorption coefficients and, accordingly, the optical thickness of each molybdenum spectral line under study were calculated using (8). The probabilities of self-absorption of Mo I spectral lines presented in Table 1 were calculated by equation (1). The calculation results are shown in Figure 9.

It can be concluded from Figure 9 that the first assumption concerns the self-absorption of the Mo I 550.7, 553.3. 557.0, and 603.1 nm spectral lines are correct. Moreover, it is observed that in addition to the above-mentioned lines, the Mo I 438.2, 443.5, 473.1, 476.0. 568.9, 575.1, and 588.8 nm spectral lines demonstrate a high tendency to self-absorption (more than 20%). Thus, these spectral lines should not be taken into account when determining the parameters of plasma with molybdenum vapor admixtures at an arc current of 3.5 A. On the contrary, the other molybdenum spectral lines can be recommended for determining the plasma parameters at such discharge parameters. It is worth noting, however, that the estimates provided concern only a part of the plasma channel observed along the arc diameter. For a complete estimate, it is necessary to calculate the spatial distributions of the optical thickness of the plasma for each spectral line, after which the intensity can be adjusted using SA.

## 4. Conclusions

The plasma of an arc discharge at a current of 3.5 A between an asymmetric pair of single-component copper and molybdenum electrodes in an argon flow was investigated. Particular attention was paid to the assessment of the degree of self-absorption of the spectral lines of molybdenum along diametrical line of sight of arc discharge column.

The assessment was carried out using experimentally obtained plasma parameters, in particular, the radial distributions of plasma temperature and number density of radiating metal atoms of electrode origin. Based on these parameters, the populations density of the lower energy levels of all spectral transitions (identified in this experiment) were calculated. In addition, the synchronous combination of LAS and OES made it possible to obtain the experimentally obtained optical thickness of Cu I 510.5 nm spectral line, which in turn confirms the correctness of the temperature determination using the Boltzmann plot technique based on the Cu I spectral lines.

It was found that the spectral lines Mo I 550.7, 553.3, 557.0 and 603.1 nm are subject to significant self-absorption along diametrical line of sight of arc discharge column (86%, 82%, 68% and 45%, respectively). Removing these lines from the determination of the plasma temperature leads to a coincidence (within 5% error) of the radial distributions of the plasma temperature determined by the Boltzmann plot technique based on the absolute emission intensity of Cu I and Mo I spectral lines. This coincidence indicates the validity of the assumption concerning the realization of local thermodynamic equilibrium in such plasma.

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