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T- and H- forms of dc oxygen discharge at medium pressures: spectroscopic study

Abstract: The active DC glow discharge sustained in the pure oxygen can be employed in various technological applications, such as thin layer deposition or sterilization. Considering applied pressures of hundreds of Pascals, two different forms of the positive column of the discharge can co-exist: T- and H-form. These forms are commonly distinguished according to the values of the axial electric field strength: values in the H-form are generally one order of magnitude higher compared to the T-form. However, electric measurement itself may often affect the discharge plasma. Optical emission spectroscopy as a non-invasive diagnostic was therefore employed as an alternate characterization of both forms.

We found that the H- and T-forms can be clearly recognized by values of intensities of particular oxygen spectral lines. This characterization enabled us to observe transition between the both particular forms when spatial distribution measurements were employed. Moreover, transition in the rotational temperature $T_{\text{rot}}$ was also observed.

Keywords: oxygen glow discharge, T- and H- forms of positive column, optical emission spectroscopy

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1 Introduction

Oxygen discharges in various configurations can be utilized for various applications such as thin layer deposition or sterilization [1,2]. Therefore they have been subject of both experimental and numerical studies for pressures varying from low values to atmospheric [3-5]. In the case of DC glow discharge in oxygen for medium pressures of hundreds of Pascals, two different forms of positive column can be formed, which can co-exist simultaneously in different parts along the discharge tube depending on the pressure and discharge current. Both forms are historically defined according to the gradient of the electric potential, i.e. according to the values of the axial electric field strength $E$. We distinguish the high-gradient H-form and the low-gradient T-form. The H-form corresponds to the standard positive column of the discharges sustained in molecular gases, with values of $E$ typically kilovolts per meter, while the low-gradient T-form with values of $E$ reaching hundreds of volts per meter starts to appear for higher pressures and lower discharge currents [6-8].

The range of existence of both forms with respect to discharge parameters has been studied by various authors. These results were influenced especially by the purity of the gas used, by the vacuum purity of the experimental system, as well as the presence of other gases in oxygen mixtures [9-11].

However, the main drawback of studying both forms is the fact that their direct determination by measuring the values of $E$ can itself cause instabilities which affect the properties of the discharge plasma. Moreover, measuring the values of $E$ (i.e. application of external voltage to a pair of measuring probes) often leads to significant changes in the region where both H-form and T-form can co-exist. The goal is to find another physical parameter to distinguish the two particular forms without affecting the discharge.

Optical emission spectroscopy seems to be a convenient method. We have already studied differences in behaviour of the rotational temperature $T_{\text{rot}}$ determined from the emission spectra of oxygen molecules, with respect to both particular forms [12]. $T_{\text{rot}}$ was found systematically higher in the H-form and our measurements were supplemented with axial electric field strength measurements. Several authors have suggested that the T-form is characterized by a higher $[O]$
to $[O_2]$ concentration ratio [13]. We therefore also decided to study the intensities of atomic oxygen emission lines.

The above-mentioned studies typically investigated plasma parameters at fixed positions corresponding to regions of H- and T-form existence, while varying the discharge conditions (pressure and discharge current. In order to also study the transition between the two forms, spectroscopic measurements with the recording optical system movable between the regions of existence of both particular forms were performed, while discharge conditions were kept constant.

The main aim of our contribution is therefore to present results of measurements of variations of atomic emission lines with respect to the existence of the H-form and T-form of the discharge. The transition between the two forms is also investigated in the context of rotational temperature.

2 Experimental

The DC glow oxygen discharge was studied in an U-shaped discharge tube made of silica. The central part of the tube with inner diameter approximately 22 mm was 390 mm long and was equipped with two pairs of cylindrical platinum probes (5 mm long, 0.1 mm in diameter) used for measurements of axial electric field strength. Each pair was located about 50 mm from the cathode and anode, respectively. The distance between the probes in the pair was approximately 15 mm, and the two pairs were positioned about 210 mm from each other.

Prior to each measurement, the tube was placed in an electric furnace, heated up to 420°C and pumped using a turbomolecular pump pre-pumped by a diaphragm pump for several hours in order to eliminate impurities that could affect the discharge plasma. The pressure in the vacuum system measured after this procedure using a PKR 261 (Pfeiffer Vacuum) compact full range gauge was better than $5 \times 10^{-5}$ Pa.

The discharge was generated using a Glassman HV EQ series high-voltage power supply connected in current-controlled mode.

The emission spectra were detected perpendicular to the optical axis. The emitted radiation was recorded using optical fibre (0.2 mm in diameter), which was positioned perpendicular to the positive column at several positions related to the regions of existence of the particular forms. In order to investigate the spatial dependence of the emission spectra, the fibre was equipped with a rectangular diaphragm (width of 1.0 mm) and was attached to the movable holder. This holder enabled us to shift the fibre along the tube and was also equipped with the fixed meter so that the actual position of the fibre could be easily determined. As can be seen in Fig. 1, the position of the rightmost probe in the anode pair of probes corresponds to a value of 32 mm on the fixed meter, whereas the left probe in the cathode pair corresponds to 246 mm.

Spectra of emitted radiation were analysed by means of a Jobin Yvon-Spex Triax 550 monochromator (focal length 550 mm) using planar grating with 1200 grooves/mm (declared spectral resolution 0.024 nm for 546.07 nm). The monochromator was equipped with a thermo-electrically cooled MTE CCD 1024x256-16 detector linked to a CCD 3000 controller connected to a PC.

The experimental system is schematically shown in Fig. 1. Our measurements were realized in spectrally pure oxygen of Linde production (declared purity better than 10 ppm) for pressures of 650–1250 Pa and for discharge currents of 10–40 mA.

3 Results and Discussion

The high-gradient H-form was only observed in the positive column of the discharge for pressures below 550 Pa,
which was verified by measurements of axial electric field strength $E$ on both cathode and anode probe pairs [14]. For higher pressures, the T-form started to appear at the anode side of the discharge tube. Our measurements were performed for discharge conditions under which both forms were simultaneously present in the positive column of the discharge without being affected by electric measurements.

At first, the electric field strength $E$ was determined by means of the double-probe compensation method [15]. The measurements were performed using both pairs of probes in order to determine the regions of existence of the T- and H-forms. Results are presented in Fig. 2.

Differences in magnitude can be seen especially for the measurements on the pair of probes closer to the anode. Different occurrences of the H- and T-form at the anode and cathode side, respectively, are a result of the different spatial distribution of the particular forms in the positive column. The T-form, which appears at the anode side, spreads towards the cathode side with increasing pressure and decreasing discharge current. At a pressure of 1250 Pa, standing striations were observed in the anode region of the positive column. These striations caused a random increase of the local electric field strength $E$. Therefore corresponding values of $E$ in Fig. 2 cannot be considered as reliable.

These measurements were taken as reference for the characterization of the positive column and were combined with recordings of emission spectra at two fixed positions – between the probes and electrode – for both the cathode and anode sides of the discharge tube (Fig. 1). Since most significant spectral lines in the DC glow discharge in oxygen under medium pressures can be found within the spectral region 700-900 nm [10], the lines at 777.2 nm (transition $3p^3P \rightarrow 3s^3S^0$) and 844.6 nm (transition $3p^3P \rightarrow 3s^3S^0$) were analysed. Examples of the emission spectra can be seen in Fig. 3.

We concentrated on the relative intensity of the above-mentioned lines. It has been found that the H-form is characterized by similar values of the intensities of 777.2 nm and 844.6 nm lines, while the intensity of the 777.2 nm line is always higher than the 844.6 nm line in the T-form, as seen in Fig. 4. The observed difference in the 777.2 nm to 844.6 nm intensity ratio is significant.

In order to investigate the spatial dependence of emission spectra, the fiber holder was moved between electrode pairs. We have focused on the transition between both forms of the discharge. Results are shown in Fig. 5, where the transition region between the forms can be clearly seen as a region where the relative intensity $I_{777.2}/I_{844.6}$ drops from about 1.8 in the T-form to about 1.0 in the H-form. The width of the transition region can be estimated approximately as 20 mm and its position depends on the pressure and slightly also on the discharge current. For these measurements, the discharge current was set between 25 mA and 40 mA so the discharge was stable without striations. Measurements within the range 180-200 mm were limited by the discharge tube holder which prevented proper detection of the spectra at these positions.

This observed difference in the emission suggests that there are substantially different plasma-chemical reactions occurring in the respective forms and enables us to deduce changes in relative concentration of corresponding particles. Appropriate models of the H-form were presented e.g. in [16,17,4], but a model of the T-form is still lacking, presumably because of its inutility.

Figure 2: Axial electric field strength measured both on anode (a) and cathode (b) pairs of probes with respect to pressure and discharge current. Low-gradient T-form appeared for higher pressures and lower discharge currents. Values for $p = 1250$ Pa may be unreliable due to presence of striations.
and lack of experimental data. However, the observed difference in the relative intensity ratio $I_{777}/I_{845}$ seems to be an applicable and repeatable parameter to distinguish both particular forms.

The longitudinal profile of the rotational temperature of oxygen was also investigated. The rotational temperature $T_{rot}$ was determined by means of a Boltzmann plot from the so-called Atmospheric band ($\Lambda$-band) of molecular oxygen with head at $759.4 \text{ nm}$, with corresponding transitions $O_2 (b^3 \Pi_g^+ , v = 0) \rightarrow O_2 (X^3 \Sigma_g^-, v = 0)$. The detailed procedure can be found for example in [18]. Results comparing measurements for four different pressures are shown in Fig. 6 (with the same scaling of the x-axis as used in Fig. 5). The transition between the forms can be clearly seen. The rise in temperature confirms our previous measurements with substantially higher temperature for the H-form [12].
4 Conclusions

We performed spectral measurements in the DC glow oxygen discharge for such discharge conditions, under which both T- and H-forms of the discharge were simultaneously present in the positive column. It was found that both forms can be distinguished by different values of atomic oxygen intensity lines, particularly by the 777.2 nm and 844.6 nm intensity ratio. Optical emission spectroscopy therefore enables us to determine particular form of the positive column of the discharge without need to perform measurements of axial electric field strength E.

The 777.2 nm to 844.6 nm intensity ratio was therefore employed for observation of transition between T- and H-form during spatially resolved measurements. Transition in the rotational temperature $T_{rot}$ was also observed.

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Figure 6: Longitudinal profile of the rotational temperature $T_{rot}$ of oxygen molecules.