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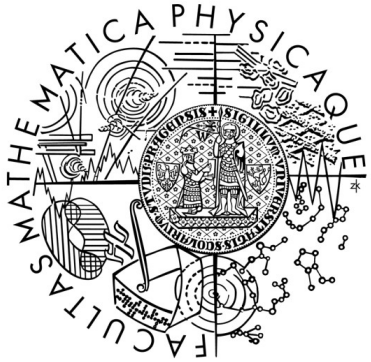

Lukáš Schmiedt

STUDY OF GLOW DISCHARGE IN OXYGEN AND ITS MIXTURES AT MEDIUM PRESSURES

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Study programme: Physics
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Prague, June 2016

Lukáš Schmiedt

Název práce:	Studium doutnavého výboje v kyslíku a jeho směsích za středních tlaků
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Abstrakt:

Stejnosměrný doutnavý výboj v kyslíku a jeho směsích s argonem byl pro tlaky v rozmezí 200 – 1750 Pa a pro výbojové proudy do 40 mA zkoumán ve dvou výbojových trubicích stejného tvaru, avšak z různého materiálu (křemen a Pyrex). Šlo především o studium emisních spekter a podélného elektrického pole, a to s přihlédnutím k možné existenci vysokogradientní a nízkogradientní formy kladného sloupce doutnavého výboje. Náš výzkum byl zaměřen zejména na kvalitativní analýzu odlišností emisních spekter v obou formách výboje a dále na možnosti stanovení rotační teploty kyslíkové molekuly za různých výbojových podmínek, především v závislosti na množství příměsi.

Klíčová slova: doutnavý výboj; kyslík; střední tlaky; emisní spektra

Title:	Study of Glow Discharge in Oxygen and its Mixtures at Medium Pressures
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Abstract:

The positive column of DC glow discharge sustained in oxygen and oxygen-argon mixtures has been studied in two discharge tubes of the same shape made from different materials (Silica and Pyrex glass) for total pressures 200 – 1750 Pa and discharge currents up to 40 mA. Parameters of the discharge – electric field strength and emission spectra – were studied with respect to existence of the low- and high-gradient forms of the positive column of the discharge. We have focused on the qualitative analysis of the differences in emission spectra for both particular forms, as well as on possibility of determination of the rotational temperature of oxygen molecule under various discharge conditions, particularly with respect to the relative amount of the admixture.

Keywords: glow discharge; oxygen; medium pressures; emission spectra

I would like to express my utmost gratitude to my supervisor, Věra Hrachová, for her support, counselling and all the opportunities she presented to me during my doctoral studies. I am grateful for her patience and clemency regarding my spirit, which has always been straddled between physics and music.

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The great deal of gratitude belongs to my wife for giving me a son, whose smile always brings me new energy, for her sympathy, patience, self-sacrifice and all her support, which enabled me to finish this work.

Contents

1. Preface

The main aim of this thesis is the experimental study of the oxygen DC glow discharge and its positive column at medium pressures by means of the optical emission spectroscopy and also probe methods. The influence of several factors (the presence of another gas, the material of the discharge tube …) will also be investigated.

Discharges sustained in molecular gases are used in still growing number of technological applications (e.g. plasmochemical reactors, gas lasers …). Study of processes in these discharges is therefore one of the dynamic branches of plasma physics. Knowledge of such basic parameters as active particles density, electron density, temperature, electrical field strength, etc., is necessary for understanding of processes governing the discharge.

The most of above-mentioned applications usually require low operating pressure. This fact makes experimental set up more complicated both technically and financially, because some kind of vacuum apparatus is needed. Moreover, pumping processes lengthen the time of preparation. Another problem appears at atmospheric pressures. Because of the short mean free path, some effects known in the low pressure discharges cannot be observed at pressures of atmospheric values (e.g. existence of metastable particles). The possible solution could be compromise between both low and high pressures, so-called „medium pressure range“, which means pressures about hundreds of Pa.

Among the most important technical gases belongs oxygen and its mixtures. Regarding the glow discharge and its regions, particularly the positive column of the discharge is a matter of concern, because it is a medium of production of atomic oxygen, which play crucial role as an active particle in various processes. Considering medium pressures, two forms of the positive column of the discharge can be observed. We distinguish the high-gradient H form and the low-gradient T form, which differ from each other in the value of the axial electrical field strength. A wide range of oxygen plasma applications (such as plasma etching, oxidation, thin layers deposition, sterilization …) makes knowledge of properties of both forms very important.

The submitted thesis is closely related to the previous experiments performed in our laboratory, which mainly concerned with the study of glow discharge in a mixture of molecular gases for various pressures of several hundreds of Pa. The aim of this work is to perform experimental study of DC glow discharge in oxygen extended also to the higher pressures.

The thesis is divided into six chapters. The introduction to the issue of the DC glow discharge sustained in oxygen and its binary mixtures with rare gases and a review of the corresponding literature will be presented in the second chapter following the preface. In older papers, non SI units can be found particularly for the pressure expression (millimetre of mercury, i.e. Torr) and author of presented thesis use them when citing instead of recalculating them into Pa. This chapter is enclosed by the particular objectives of the thesis. The third chapter deals with the used diagnostic methods. The experimental set-up is described in the forth chapter. Our results are presented in the fifth chapter, the sixth chapter is the final conclusion of the whole thesis. The thesis is enclosed by list of the references and list of abbreviations. Author's papers concerning this thesis are attached at the very end.

2. Introduction

The low temperature plasma of oxygen and its mixtures with rare or molecular gases (N_2, Cl_2, CF_4, SF_6 …) plays an important role in miscellaneous applications, e.g. plasma etching [1-4], plasma oxidation [5], thin layer deposition [6], formation of superconducting materials [7] and sterilization [8, 9]. The discharge sustained in mixtures of rare and molecular gases (for example O_2-Ne mixture, O_2-Ar mixture) can also be found in gas lasers [10].

Growing number of applications using oxygen discharge mixtures is reflected by both basic and application research. We will try to summarize the most important facts about glow discharge in pure oxygen and its mixtures with rare gases in following subsections. We will also deal with the surface interactions in special subsection. As it will be shown, these interactions can play very important role, especially in oxygen.

2.1 Glow Discharge Sustained in Pure Oxygen

Glow oxygen discharge is the discharge which can be sustained under wide pressure range. The typical structure of the glow discharge consists of cathode areas (Aston dark space, cathode glow, cathode dark space /also called Crookes dark space/, negative glow, Faraday space), positive column and anode area (anode glow and anode dark space) [11]. Spatial occupancy of the particular areas depends foremost on the size of discharge area (i.e. distance of the driving electrodes) and on the working pressure.

Considering low pressures, the glow oxygen discharge can exist in the form of the long (high) cathode fall with spatial domination of the cathode area at the expense of the positive column. The form with the long cathode fall can be also distinguished by the values of driving voltage for particular discharge current, which are of one order of magnitude higher compared to the standard form. Also the current-voltage characteristics is very steep in the form with long cathode fall. This behaviour is rather common also for glow discharges sustained in other gases [12].

With increasing pressure, the discharge exists in the standard form with widely spread diffusion-controlled positive column, which can transform to the contracted form for high pressures [11].

The glow discharge in oxygen is a complex medium containing both neutral and charged particles, i.e. atoms and molecules, both in ground and excited quantum states, then electrons and also positive and negative ions. Regarding atomic oxygen, it has been found that the degree of dissociation of the molecular oxygen increases with increasing current [13] and slightly decreases with pressure.

The investigation of the influence of the vacuum purity on the emission spectra of oxygen discharge was presented for example by Hrachová et al. [14]. The glow discharge was studied in a Pyrex discharge tube with 22 mm in diameter for pressures 66 – 300 Pa and discharge currents up to 40 mA. By different way of preparation, the different vacuum purity was reached before filling the working gas in and spectra recording. The important result was found: the better vacuum purity of the system, the lower degree of dissociation of molecular oxygen. Similar results for pressures 250 Pa and 330 Pa were obtained in [15].

Kylián [16] studied radial temperature profiles of the oxygen DC glow discharge in the same pressure range as [14] by means of emission spectroscopy. No radial variations of rotational and consequently gas temperature were observed.

To explain the experimental results, several theoretical models of pure oxygen discharge were created (e.g. [17]). The most complete model of positive column of the glow oxygen discharge was lately published by Gousset et al. [18]. This one-dimensional self-consistent model is based on the solution of Boltzmann's kinetic equation for electrons and set of balance equations for molecular oxygen O_2 in ground electronic state and excited states $O_2(a^1\Delta)$ and $O_2(a^1\Sigma)$, for atomic oxygen O, ozone O_3 and O^- ions. Interactions between electrons and vibrationally excited O_2 molecules in a ground quantum state were also taken into account. This model was able to determine transport parameters of electrons (mean value of energy, drift velocity) as well as dependence of reaction rate constants on the value of electrical field strength. Knowing these factors, it was also possible to specify importance of each single process for all species included (creation and extinction of particles) and to obtain values of their densities.

By this analysis, the dissociation of O_2 and $O_2(a^1\Delta)$ by impact of an electron was found to be the main process for creation of the atomic oxygen:

$$e + O_2 \rightarrow e + O + O, \qquad \text{(E 2.1)}$$

$$e + O_2(a^1\Delta) \rightarrow e + O + O. \qquad \text{(E 2.2)}$$

On the other hand, the surface reassociation was found as the most important process for the atomic oxygen extinction:

$$O + wall \rightarrow 1/2\, O_2. \qquad \text{(E 2.3)}$$

As it was stated above, the important part of oxygen discharge are negative oxygen ions (O^-, O_2^-, O_3^-). Their density can be even greater than electron density in some cases. High values of rate coefficient of the dissociative attachment of electrons by O_2 molecules or $O_2(a^1\Delta)$ metastables are the main reasons:

$$e + O_2 \rightarrow O^- + O, \qquad \text{(E 2.4)}$$

$$e + O_2(a^1\Delta) \rightarrow O^- + O. \qquad \text{(E 2.5)}$$

Three-body collision also plays an important role for values of reduced electric field strength over 5000 Vm^{-1}:

$$e + O_2 + O_2 \rightarrow O_2^- + O_2. \qquad \text{(E 2.6)}$$

The presence of negative ions in the discharge can affect discharge properties such as conductivity, electrical field strength and also ambipolar diffusion, which is the key process for the space distribution of particles created by the interactions with electrons. Study of radial distribution of charged particles is therefore one of the very important topics.

Sabadil [19] dealt with radial profiles of positive ion density, electron density and negative ion density. He started with equations for flows of the charged particles in the radial direction.

He also used the quasineutrality condition:

$$n_+ = n_e + n_{-,} \qquad \text{(E 2.7)}$$

where is n_+ positive molecular ion density, n_- is negative ion density and n_e is electron density. A constant value of neutral O atoms density along the whole diameter was supposed. Obtained numerical solutions of the set of differential equations were compared to the Bessel function of the zero order J_0 . The decrease of electron density n_e with the parameter ρ, which is defined as a relative distance from the discharge tube axis ($\rho = r/R$), was found. This decrease was quite small for small values of ρ, but it became very apparent at the $\rho = 0.95$.

Arutunyan et al. [13] described influence of the negative ions on the radial changes of electron density. Radial profiles of charged particles densities were connected with the ratio η of electron and negative ion density:

$$\eta = \frac{n_-}{n_e}. \qquad \text{(E 2.8)}$$

The radial distribution of electron density n_e was flat for the large values of η ($\eta \geq 10$), which means that electron density n_e along the whole radius of the discharge tube was equal to he value of n_e in the axis of the tube. However, the shape of the radial distribution of n_e became similar to the Bessel's one (E 2.11) for decreasing η, which is the standard situation for discharges without presence of negative ions.

The same experimental setting as in [13] was used by Amiryan et al. [20], who studied radial profiles of n_e and n_- in the positive column of pure oxygen discharge for pressure range 5 – 530 Pa. The radial profiles of n_e could be approximated with the Bessel function (E 2.11) for values of η (defined by E 2.8) about 3.5 – 4. The slower decrease of radial n_e distribution function was found for higher values of η, while steeper decrease was observed for lower values of η.

The radial distribution was also studied by Ferreira et al. in a general model of the positive column of the discharge in electronegative gas with respect to oxygen discharge [21, 22]. Three types of charged particles were considered in this model: electrons, positive ions and negative ions. Assuming constant space values of ionization frequency, electron attachment frequency and negative ion extinction frequency together with the quasineutrality condition (E 2.7), it was found that negative ions were more cumulated near the axis of the discharge tube with decreasing pressure.

2.1.1 T and H form of oxygen discharge

One of the important parameters of positive column is the axial electric field strength E, which corresponds to the energy dissipated to the discharge. Güntherschulze [23] studied the dependence of the axial electric field strength E on discharge current, mean free path (consequently pressure) and discharge tube radius for various gases in conical geometry. The following formula was obtained:

$$E = C \cdot \frac{l^{(m-1)}}{R^m}, \qquad \text{(E 2.9)}$$

where C is constant, l denotes mean free path of oxygen molecules and R is the discharge tube radius. The value of parameter m is to be set $m = 1$ for monoatomic gases while $m = \frac{1}{3}$ for polyatomic (molecular) gases. The equation (E 2.9) can be then rewritten as:

$$E = C \cdot l^{-\frac{2}{3}} \cdot R^{-\frac{1}{3}}, \qquad \text{(E 2.10)}$$

which can be applied to all polyatomic (molecular) gases independently on the discharge current.

Considering oxygen, measurements of Güntherschulze were realized in discharge tubes with radius of 4,1 mm, 15 mm and 45 mm, respectively, in pressure range 0,316 – 1,135 Torr and for discharge currents 25 and 50 mA. During the measurements, besides standard positive column with values of electric field strength

E of about 2000 V/m, corresponding to equation (E 2.8), another form of the oxygen discharge was observed under same conditions. This form was distinguished by the colour of emitted light as well as by values of the electric field strength *E* of about 650 V/m. For the widest discharge tube (radius 45 mm), only the form with lower values of *E* appeared independently on the discharge current. For the tube of 15 mm in radius, this form appeared after the discharge ignition but immediately transformed into the form with higher values of *E*. For the narrowest tube this form was not present at all.

This study was followed by Seeliger and Wichmann [24], who investigated the influence of the pressure and discharge current on the existence of the forms in the tubes 50 –120 cm long with the inner diameter of 10, 30 and 60 mm, respectively. Studied pressure range was 0.5 – 7 Torr and used discharge current was up to 250 mA. The observed difference in values of the axial electric field strength *E* was systematically about one order of magnitude. According to the values of *E* authors named the forms as follows: the high-gradient form with electrical field strength of about kVm^{-1} was called the H form and the low-gradient form with electrical field strength of about hundreds of Vm^{-1} was called the T form. It was found, that the low-gradient T form appeared at higher pressures and lower current densities compared to the high-gradient H form. Moreover, authors managed to set such values of pressure and discharge current, that the both forms existed simultaneously, each in different part of the discharge tube. Authors also analysed emission spectra at the visible range of the wavelengths. In the H form they found spectral lines corresponding to the transitions between quantum states of the neutral atomic oxygen, while the T form was characterized by the band of the so-called first negative system (see, e.g. [25]) corresponding to the deexcitation of the O_2^+ molecular excited states.

Seeliger then studied influence of the discharge tube material and purity of the inner wall on the transition between the both forms [26]. He found that the particular value of the discharge current corresponding to the transition between the both forms was higher, when the tube was heated up to 465 °C before the measurements, compared to the case when the tube was only being pumped.

Pekárek and Šícha [27] investigated the presence of ionization waves in the positive column for the pressure 2 Torr and discharge current 9,5 mA when the both forms were present in the positive column. They arrived at the conclusion that the positive column of the H form was homogeneous, while the ionization waves could be observed in the T form. Unlike striations, which are common in the rare gases or in hydrogen, however, the existence of the ionization waves in the T form of oxygen discharge was limited only to the certain distance from the cathode.

Sabadil [28] studied ionization waves both in the T form and in the H form. He found that the negative ionization waves in the T form had properties similar to the Gunn's instabilities observed in semiconductors [29].

Řezáčová studied the electron density in the both forms for pressures 2 – 7 Torr and discharge currents up to 40 mA by means of a microwave toroidal resonator [30]. The lower electron density was found in the H form than in the T form. Řezáčová also studied the electron density in both types of discharges, which differed in the cathode fall. The transition of the one type to another at the pressure of 0.35 Torr was observed. The electron density in both types was measured for discharge current of 21.5 mA, when gradient in the positive column was 9 $V.cm^{-1}$. The value of electron density in both types was found to be $n_e = 1.10^9\ cm^{-3}$, which was in good agreement with Drost et. al [31].

The mass analysis of positive ions both in the T and H forms of the glow discharge in pure oxygen was realized by Kerren [32] for the pressure 2,5 Torr and for the discharge current 10 mA by the use of the quadrupole mass spectrometer. The discharge tube used for the measurements was of the inner diameter of 33 mm. Positive ions O_2^+ and O^+ were found in the T form, while only O_2^+ ions were observed in the H form under the same conditions.

The mass spectrometer was used by Kocian and Mayor for analysis of oxygen atom, O^+ and O^- ions density in the both forms [33]. Authors used an oxygen-nitrogen mixture with 0.4 % of N_2. Plasma was generated in a Pyrex discharge tube with inner diameter of 60 mm by DC glow discharge in the pressure range 0,05 – 5 Torr with discharge currents 20 – 200 mA. The investigation was realized in a flowing regime. Authors found out that the degree of dissociation of the molecular oxygen decreased with increasing discharge current in the low-gradient T form, while the increase of

this degree of dissociation with increasing discharge current was observed in the high-gradient H form. It was also found that the density of O^- ions increased in the H form with discharge current, while O^+ ions density was very small in this form (for O^+ density and neutral atoms density ratio authors mentioned the value 0.001).

Vicharev et al. [34] tried to explain the existence of the H and T forms, using the plasma kinetic model. Authors assumed the existence of only neutral O_2 molecules, positive molecular O_2^+ ions, negative O^- ions and electrons in plasma. Solving the balance equations for the electron density n_e, negative ion density n_-, positive molecular ion density n_+ and the neutral molecule density n_g, authors obtained the dependence of the axial electrical field strength in the positive column of the discharge on the electron density. The cylindrical positive column of the discharge in diffusion regime was assumed for the simplicity. Moreover, the plasma heating process and the electron-positive ion recombination were neglected. From the system of the above mentioned balance equations authors also obtained radial profile of the electron density $n_e(r)$, which was described by the Bessel function of the zero order J_0:

$$n_e(r) = n_{e0} J_0(2{,}405 \frac{r}{R}), \qquad \text{(E 2.11)}$$

where n_{e0} denotes electron density in the axis of the discharge tube and R is the discharge tube radius.

Analysis of the current-voltage characteristics of the DC glow discharge and the loading line of the electrical circuit by Vicharev at al. [34] enabled to estimate the range of the discharge current in which the T form could exist. This range narrowed with the decreasing pressure.

The complex investigation of the glow discharge in oxygen with respect to existence of the H and T forms was presented by Dettmer [35], who experimentally studied and mathematically modelled oxygen discharge in the quartz discharge tube with inner diameter 19 mm and the anode-cathode distance of 505 mm. The measurements were realised in flowing regime for the pressures 1 – 10 Torr and for current densities up to 35 mA/cm^2. Moreover, a cooling system was utilized to maintain the discharge tube and the wall on the temperature near that of tap water.

The H form was present at high currents and low pressures, the T form at low currents and high pressures. The H form exhibited stable characteristics while the low-gradient T form was observed to be unstable, exhibiting periodic or aperiodic oscillatory behaviour. The periodic oscillations existed only at certain frequencies or modes, and the discharge impedance was the function of the frequency.

Mass spectra measurements indicated that the atomic oxygen density increased significantly when the discharge transitioned from the low to the high-gradient form. Solutions of the Boltzmann transport equation indicated that the electron energy distribution function exhibited a characteristic intermediate between the Maxwellian and Druyvesteyn.

Chemistry model results showed O_2^+ to be the dominant positive ion, and the O^- to be the dominant negative ion. The transition from the stable to unstable form was found to be related to the two criteria: the dominance of the derivative of the attachment coefficient with respect to *E/N* over that of the ionization coefficient, and the equivalence of the negative ion and electron number densities. The metastable O_2^* ($a^1\Delta$) was important in the discharge for two reasons. First, the two-step ionization was required together with the direct ionization to match the experimental electron density measurements. Also, the inclusion of the metastable molecule as the primary electron detacher was required to match the transition points determined by experiment with those determined from the model.

2.2 Glow Discharge in Oxygen Mixtures with the Rare Gases

The influence of the presence of the rare gases (He, Ne, Ar) on the properties of the oxygen glow discharge was widely discussed [36-41]. Spectrally pure oxygen produced by Veb Technische Gase Lepzig (VEB-Leipzig) was used in all of these studies. Diagnostic methods were also the same: probe and double-probe diagnostics. Besides these, the microwave toroidal resonator for the electron density measurements was employed.

The positive column of the discharge sustained in pure oxygen or its binary mixtures with the rare gases was studied by Hrachová [39] for current range 5 – 30 mA and the total pressure 800 Pa. The dependence of the existence of the both forms on discharge current was observed in the mixture containing 5 % or 20 % of

He. The T form was found only for 5 % of neon in oxygen-neon mixtures. The electron density n_e was determined in the both forms. The T form was characterized by the higher values of the electron density compared to the H form, both in pure oxygen and in its mixtures with He and Ne, for all experimental conditions under which the T form was detectable.

Study [40] described the dependence of the transition between the T and H form on discharge current and the neon concentration in O_2-Ne mixtures. Used pressure range was 67 – 800 Pa. The transition between the forms was observed for 5 % of neon in the mixture for pressure 800 Pa and current 5 mA only. Considering the pure oxygen, the transition was observed for pressure 530 Pa and current 10 mA, and for pressure 800 Pa and current 5 mA, respectively.

The influence of argon on the existence of the both forms was investigated [38] under the same pressure range as in [40]. The positive column of the glow discharge was studied also by means of optical emission spectroscopy. Spectra were detected in a perpendicular direction to the axis of the discharge tube in the range of wavelengths 360 – 700 nm. The emission spectra of the T form corresponded to the first negative system of molecular ion O_2^+, while in the H form also atomic oxygen spectral lines of 436,8 nm and 394,7 nm were found. These results corresponded to the results of Seeliger's investigation [26].

The probe diagnostics and optical emission spectroscopy were also used in [41] for investigation of oxygen and its mixtures with neon and argon, respectively, for pressures 530 Pa and 660 Pa. The discharge tube with the inner diameter of 31.8 mm was made of Pyrex glass. From the simple comparison of the amplitude of the positive and negative branches of the probe characteristics, respectively, measured in pure oxygen, it was possible to estimate qualitatively, that the greater amount of the negative oxygen ions O^- was present in the H form compared to the T form. This fact was also determined approximately from the radial dependence of the electron density in the both forms. Considering the emission spectra, the most intensive lines in pure oxygen were 777,6 nm and 844,7 nm lines, and then the head (759,4 nm) and the origin (761,9 nm) of the atmospheric A-band of molecular oxygen. The head of A-band was dominant in the both forms. For the pressure 660 Pa, the both forms existed even with 50 % of neon and argon in the mixture, respectively, while the

T form was detected only up to 20 % of admixture for 530 Pa. Moreover, different behaviour of the both forms was observed. The neon lines of low intensity were observed in the T form only in O_2-Ne mixtures, while in O_2-Ar mixtures intensive argon lines were observed in the both forms.

Important results were found in [37], where emission spectra from glow discharge in oxygen from two different producers were compared. The first one was the above-mentioned VEB-Leipzig, which produces oxygen labelled as „spectrally pure“. The second producer was Linde, which guarantees the purity of produced oxygen as 5.0. Spectral measurements didn't show any significant lines of the first negative system of molecular ion O_2^+ in oxygen produced by Linde. That was in the contrast with the results obtained from spectral measurements performed in oxygen produced by VEB-Leipzig. Moreover, presence of O_2^+ system was influenced by the presence of the admixture with energy levels close to the oxygen ones, for example adding of 5 % of argon into oxygen. Important role played especially nitrogen.

Dettmer [35] also studied the dependence of the point of transition between the forms and the electric impedance on the presence of admixture. While no affection by the argon addition to the oxygen discharge was observed, adding an electron-detaching gas, carbon monoxide, increased the low field impedance until the difference between the forms essentially ceased to exist.

Oxygen-argon mixtures were lately studied in our laboratory [42]. The mixtures were studied for the total pressure of 3 and 7 Torr. Our attention has been paid to dependence of axial electrical field strength on the amount of Ar in the mixture. Slight increase of the reduced electric field strength *E/p* was found in the mixture which contained 5 % of argon and then decrease of *E/p* with increasing argon ratio was observed for the pressure of 3 Torr. Considering 7 Torr, the maximum of reduced electric field strength *E/p* for 50 % of argon in the mixture and then its decrease with increasing argon ratio has been observed. The transition between the H and T form was observed for discharge currents 15 – 25 mA and for 5 % of argon in the mixture.

The plasma-solid interactions in mixtures of oxygen with rare gases were studied by several computer models (e.g. [43, 44]). In the both studies, the main aim was to study the sheath region and influence of plasma parameters on its formation.

It was found, that the presence of negative ions was influenced the sheath thickness [43]. Behaviour of electrons and negative ions in the sheath region also differed. The sheath thickness was also influenced by the pressure – its decrease with increasing pressure of the gas mixture was found [44].

2.3 Wall Interactions and their Influence on the Oxygen Discharge

The key role in discharges sustained in oxygen and its mixtures play also interactions between atoms or molecules of the substance and the wall of the discharge tube. The parameter, which describes wall interactions, is called wall interactions probability γ, and it is defined by

$$\Phi_{-} = (1-\gamma)\Phi_{+}, \qquad \text{(E 2.12)}$$

where Φ_+ is the flux of particles impacting the surface and Φ- flux of the particles reflected from the surface.

The coefficient γ for the particular interaction depends partly on the type and the number of impacting particles, and also on the surface properties and temperature. Especially the dependence on the surface properties causes significant differences in the measured values of the γ.

Considering the glow discharge in oxygen and its mixtures, the wall interactions are rather important especially for particles with relatively long life time, such as singlet oxygen, vibrationally and electronically excited molecules and metastable particles (O_2(a), O_2(b), ...). Interaction of these particles with the surface leads to their extinction (under certain conditions, this is the main extinction process), eventually to creation of new particles. Therefore, the wall interactions have a significant impact on the composition of the discharge mixture and consequently also on the properties of studied discharges.

One of the most important wall interactions in low-pressure discharges sustained in oxygen mixtures is the association of atomic oxygen on the surface:

$$O + wall \rightarrow \frac{1}{2} O_2 . \qquad \text{(E 2.13)}$$

This reaction is rather crucial because it is the main interaction leading to extinction of atomic singlet oxygen. Great attention is therefore paid to study of wall association of oxygen atoms (e.g. [18]).

The values of γ corresponding to equation E 2.13 for different types of discharges and wall materials are shown in Table 2.1. It can be seen, that values of γ can vary over several orders of magnitude depending on the type of discharge, the estimation method and also on the wall temperature [45, 46], on discharge conditions, such as pressure [47, 48], or on the presence of impurities in the discharge [26, 49]. It was found, for example, that introducing small amount of N_2 into the oxygen discharge led to decrease of probability γ of above mentioned interaction as a result of occupation of active places on the surface by atomic nitrogen [50].

Material	**γ .10^{-3}**	**Discharge**	**Estimation method**	**Ref**
Silica	0,51	microwave	NO_2 titration	[51]
Silica	0,4-0,086	pulsed glow	absorption spectroscopy	[52]
Silica	0,2-3,8	microwave	catalytical probe	[53]
Pyrex	5	active glow	absorption spectroscopy	[54]
Pyrex	2,4	pulsed glow	absorption spectroscopy	[55]
Pyrex	1	pulsed glow	emission spectroscopy	[56]
Pyrex	0,46	glow	O_3-method, Wrede-Harteck method	[45]
Pyrex	0,12	radiofrequency	catalytical probe	[57]
Pyrex	0,051-0,1	radiofrequency	NO titration	[58]

Table 2.1 *Probability of atomic oxygen association on the wall of the discharge tube.*

2.4 Objectives of the Thesis

As a general conclusion of the above presented review can be summarized, that the properties of the oxygen discharge can strongly depend on starting experimental conditions (e.g. purity of the experimental system or the working gas, steady or flowing regime, discharge tube material or radius, …). Even a small difference in such parameters can lead to significant affection of the discharge and its positive column, which can consequently make comparison of the results obtained by various authors rather complicated.

Regarding these facts, our goal is to study properties of the DC glow oxygen discharge for wide range of discharge conditions (pressure, discharge current) whilst having the basic experimental conditions (geometry, purity, …) kept constant. The main objectives of presented thesis are to study:

- properties of the DC glow oxygen discharge under various discharge conditions with respect to the existence of the H and T forms of the positive column of the discharge
- properties of the both forms with respect to appearance of the atomic oxygen
- effect of the presence of argon on the properties of the discharge
- influence of the discharge tube material

3. Diagnostics

In the presented thesis, two basic diagnostic methods were employed for determination of the parameters of studied discharges in oxygen and its mixtures: electric probe diagnostics and optical emission spectroscopy (OES).

Probe plasma diagnostics is one of the oldest and still most often used methods of determining the plasma parameters. Important advantage of probe diagnostics is especially a number of parameters which can be obtained by this method (eg. the concentration of charged particles, electron temperature, electron distribution function, plasma potential, electric field ...). On the other hand, the presence of probes in plasma can largely disturb studied plasma and can even lead to creation of inhomogeneities in the plasma. During our measurements, two electric probes were employed for determination of the electric field strength *E*.

Optical emission spectroscopy belongs to the diagnostic methods often used to study glow discharge due to plenty of plasma parameters, which can be determined (concentration of particles in basic and excited quantum states, vibrational and rotational temperature molecules, electron energy distribution function, ...). The most important advantage of this method is especially the fact that as a passive method of plasma diagnostics, unlike electric probes, it does not affect the studied plasma. In our study, OES was employed both for qualitative and quantitative analysis of the emission spectra.

Both methods are described in following subchapters in details.

3.1 Double-probe Method

The double-probe method was originally proposed for use in decaying plasma, in which the plasma potential varied in time, so it was difficult to maintain constant probe-plasma potential [11]. Because the current in a double probe is much lower than the electric current of a single probe, the affection of the plasma by the usage of this method is less effective.

Since the both probes are biased with respect to each other but insulated from the ground, the entire system „floats“ with the plasma and therefore follows the change of plasma potential.

The geometry is presented in Figure 3.1. Probes are located in plasma, which has the constant properties within the space between the probes. Voltage is applied between the probes, but the entire system is not connected to any electrode. That is the basic difference from the single probe method.

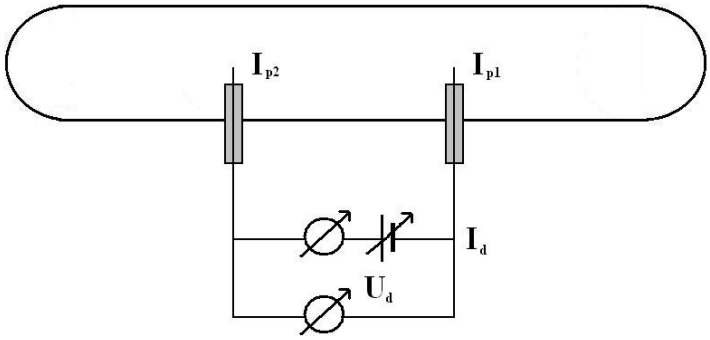


Figure 3.1 *Schematic drawing of double-probe diagnostics.*

3.1.1 Determination of Electric Field Strength

Double-probe method was; employed for determination of axial electric field strength. This method is based on the fact, that space potentials V_{S1} and V_{S2} at the points, where the probes are placed, are different. For both probes to float and probe currents to vanish, they must be placed at potential difference

$$\Delta V = V_{p1} - V_{p2} = V_{S1} - V_{S2}, \qquad \text{(E 3.1)}$$

where V_{p1} and V_{p2}, respectively, denotes the potential of particular probe with respect to the plasma. By setting the voltage to the value, when the probe current is zero, for electric field strength E between the probes we obtain

$$E = \frac{\Delta V}{d}, \qquad \text{(E 3.2)}$$

where d is the distance between two probes. However, the plasma potential cannot be found by the double-probe method in principle.

3.2 Optical Emission Spectroscopy

The optical emission spectroscopy was employed both for qualitative and quantitative analysis of studied discharges.

3.2.1 The Fundamentals of Quantitative Analysis

Optical emission spectroscopy is based on the detection and subsequent analysis of radiation emitted by the excited plasma particles (atoms, molecules, ions). Basic equation for optical emission spectroscopy is the relationship between the intensity of radiation emitted by the particle X during the transition from the excited *n*-state to the *m*-state and the concentration of the particles of excited *n*-state*:*

$$I_{mn} = A_{mn} \cdot h \cdot \nu_{mn} \cdot [X_n^*], \qquad \text{(E 3.3)}$$

where A_{mn} is the Einstein coefficient of spontaneous emission, h is Planck constant, ν_{mn} frequency of radiation corresponding to the transition between n and m levels, respectively, and $[X_n^*]$ concentration of particles X in quantum state n.

Equation E 3.3 enables the direct estimation of the concentration of particles in the excited *n*-state from the measured radiation intensity. If a system of particles is in thermal equilibrium, the population of particles X in quantum state n is related to the total concentration of particles X by the Boltzmann distribution. Equation E 3.3 is therefore fundamental also for the determination of another plasma parameters: the concentration of particles in ground quantum state, vibrational temperature and particularly rotational temperature of molecular species, as will be shown in the next chapter.

3.2.2 Temperature Determination

The optical emission spectroscopy can be employed for the estimation of the kinetic temperature of neutral particles. The method is based on the equilibrium between kinetic temperature and the rotational temperature of the molecules in the ground state. i.e. on the measurement of temperature determined from energy levels of rotationally excited states. Nevertheless, since the dipole-allowed transition

lifetime of the excited levels used to measure the rotational distribution is generally much shorter than the collision time in low pressure discharges, it is not possible to assume a priori that the rotational temperature corresponding to the rotational excitation is identical to the kinetic temperature. It is therefore necessary to verify whether this equilibrium is fulfilled. Considering oxygen discharge, this condition has already been discussed and verified by Touzeau et al. [59].

Assuming well-resolved rotational spectrum with energy levels governing by Boltzmann law, the intensity of single spectral line corresponding to the transition between J and J' rotational states can be written as:

$$I_{JJ'} = const \cdot \nu_{JJ'}{}^{4} \cdot S_J \cdot e^{-\frac{E_J}{k \cdot T_{rot}}}, \qquad \text{(E 3.4)}$$

where $\nu_{JJ'}$ is transition frequency, S_J Hönl-London factor [59], E_J is energy of J quantum state, k is Boltzmann constant and T_{rot} denotes rotational temperature. From so-called Boltzmann plot [59] (dependence of $\ln(\frac{I_{JJ'}}{S_J})$ on E_J) one can obtain so-called pyrometric line, whose slope determines rotational temperature T_{rot}:

$$\ln\left(\frac{I_{JJ'}}{\nu_{JJ'}{}^{4} \cdot S_J}\right) = const - \frac{E_J}{k \cdot T_{rot}}. \qquad \text{(E 3.5)}$$

4. Experimental

4.1 Discharge Tubes

The natural question of possible effect of discharge tube wall material on the discharge itself resulted in design of a pair of discharge tubes, which differed only by wall material. The same pair of discharge tubes was employed during our measurements.

The discharge was studied in two U-shaped discharge tubes made of Silica and Pyrex glass, respectively. Chemical composition of the both glass used can bee seen in Table 4.1.

Glass	Chemical composition	
Pyrex (Simax)	SiO_2	80 %
	B_2O_3	13.10 %
	Al_2O_3 + Fe O	2.25 %
	Na_2O	3.50 %
	K_2O	1.15 %
Silica	SiO_2	100 %

Table 4.1 *Material of used glass.*

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 (0.1 mm in diameter) used for measurements of axial electric field strength. Active part of the probes was about 5 mm long, the inactive part was covered with glass. 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. The tube is schematically shown in Figure 4.1.

Both the cathode and the anode part of the discharge tubes was equipped with a head-on planar window made from the same type of glass as the corresponding discharge tube. The advantage of this construction is basically the possibility of usage optical emission spectroscopy method to study the discharge parameters in the axial direction. Moreover, proposed shape of the tube shape factually eliminates the pollution of surface of the inner wall of the discharge tube by particles generated on electrodes by ion bombard.

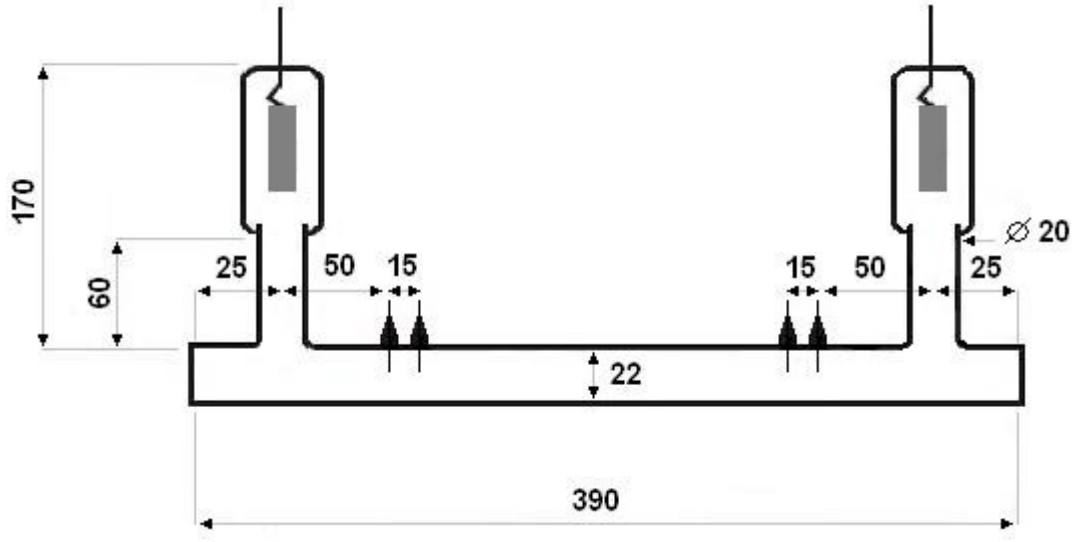


Figure 4.1 *Schematic drawing of the discharge tube.*

4.2 Vacuum System

Scheme of the pumping system employed for our measurements is shown in Figure 4.2. The system consisted of oil-free diaphragm pump Pfeiffer MVP T-015 with a base pressure of 350 Pa, serially connected to the turbomolecular pump Pfeiffer TMH 064. Fore-vacuum was measured by Pirani gauge VPR1. The pressure in the discharge tube was measured by compact Pirani-Penning gauge Pfeiffer PKR 261 with a measuring range 5.10^{-7} – 10^{6} Pa. The discharge tubes were placed in electric furnace and heated up to 420 °C for several hours before each measurement in order to avoid affecting the discharge plasma by presence of impurities. The pressure in vacuum system checked after this procedure was better than 5.10^{-5} Pa.

The filling part of the vacuum system enabled us to connect up to three glass reservoirs of studied gases through needle valves Balzers EVN 116. Opening of the glass bottles was realized by breaking the glass sealing with the help of the metal roller, covered by glass, which was externally controlled by the permanent magnet. In order to avoid eventual getting of splinters from a broken bottle sealing into the vacuum system, trash-traps by Vakuum Praha company were placed between the bottles and needle valves.

Pressure of the filling gas was measured by diaphragm gauge Balzers ACR 263. For studied pressures (hundreds of Pascals), the inaccuracies in the determination of a pressure achieved by this system was less than 1 %.

Our measurements were realized in spectral-pure oxygen of Linde production. The purity declared by producer is 5.0, which corresponds to less than 10 ppm of impurities.

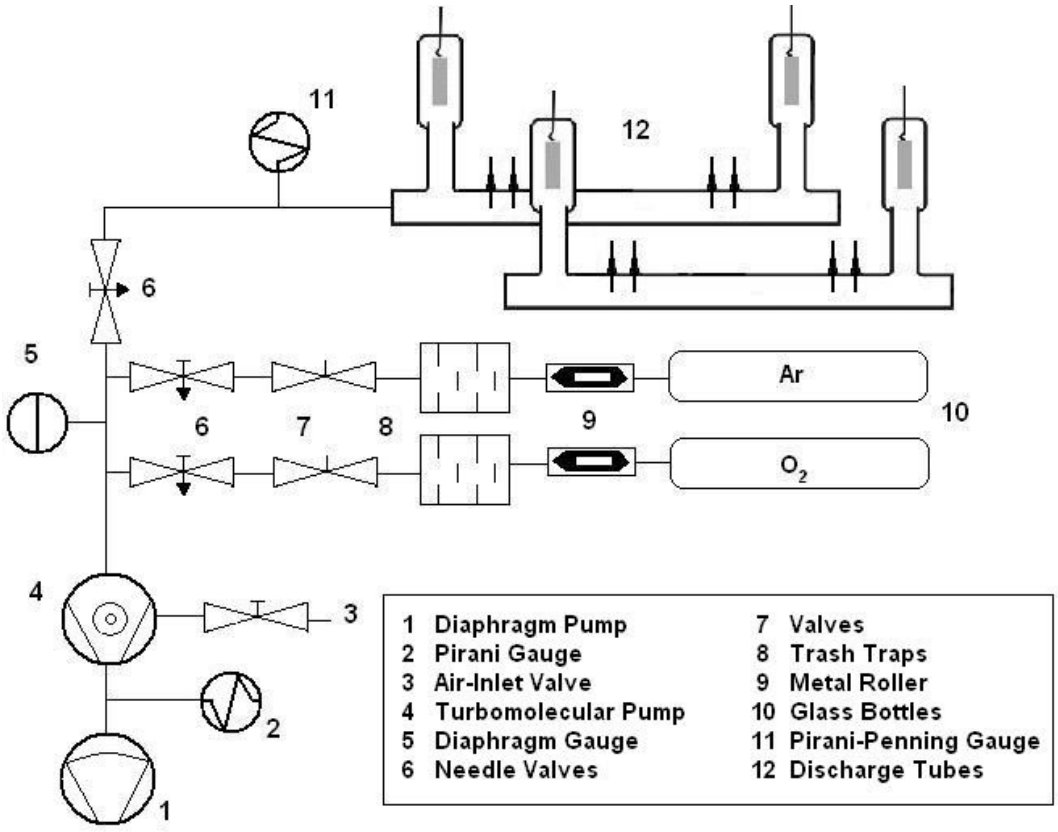


Figure 4.2 *Schematic drawing of the vacuum system.*

4.3 Electric and Optical Setup

The discharge was generated by high-voltage power supply Glassman HV of EQ series (0 – 10 kV, 0 – 120 mA). The power supply was operated in current-controlled mode.

The measurements of the axial electric field strength E were performed with two pairs of probes in order to compare properties of the discharge in two different parts of the discharge tube. Self-made block of batteries was used for the compensation of electric potential difference.

The emitted radiation was recorded using the optical fibre (0.2 mm in diameter), which could be positioned at several different positions. Considering the H form of the positive column present only, the optical fibre was positioned along the optical axis of the discharge tube. For both forms present in the discharge, the optical fibre was positioned perpendicularly to the positive column at several positions related to the regions of existence of the particular forms. The whole set up for the both configurations can be seen in Figure 4.3.

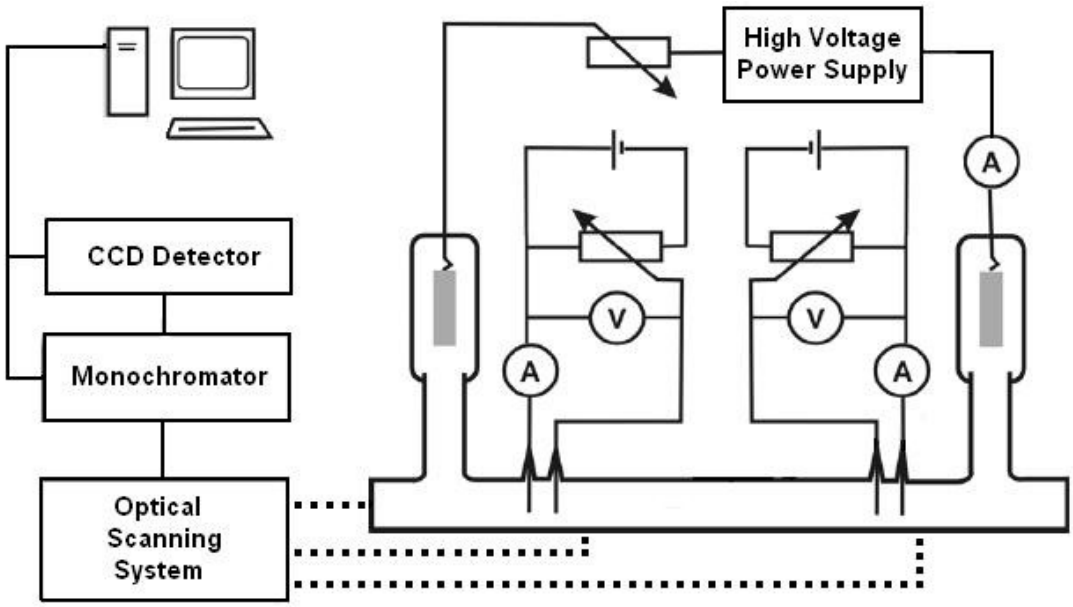


Figure 4.3 *Experimental set up for electric and optical measurements.*

Spectra of emitted radiation were analysed by means of monochromator Jobin Yvon-Spex Triax 550 (focal length 550 mm). The monochromator was equipped with three planar gratings (300, 1200 and 1800 grooves/mm, respectively). During our measurements, the planar grating with 1200 grooves/mm (declared spectral resolution 0.024 nm for 546.07 nm) was employed. The monochromator was equipped with thermo-electrically cooled MTE CCD 1024x256-16 detector linked to the CCD 3000 controller connected to the PC. This configuration enabled us to detect emission spectra in the range of 200 – 1050 nm.

4.3.1 Radial Measurements

Optical scanner of original construction was employed for studies of radial dependences of emitted spectra. The scanner consisted of two conical mirrors – one was fixed and the other was movable in the direction of the optical axis. Considering our arrangement, the entrance of the quartz fibre (diameter 0.2 mm) was placed into the focus plane of the achromatic objective (f´=240 mm), which replaces the field stop. The schematic drawing of the scanner can be seen in Figure 4.4. This system enabled us to detect the rays parallel to the optical axis in the form of hollow cylinder. The inner diameter of this cylinder was given by the shift between both mirrors, whereas outer diameter was adjusted by a diaphragm (1.5 mm and 1,8 mm, respectively).

The detailed description of the scanning system is presented e.g. in [60, 61]. The optical scanner was positioned in such a way, that the axis of the central part of the discharge tube corresponded to the axis of the scanner and intersected the apex of the positive mirror. The whole set up can be seen in Figure 4.5.

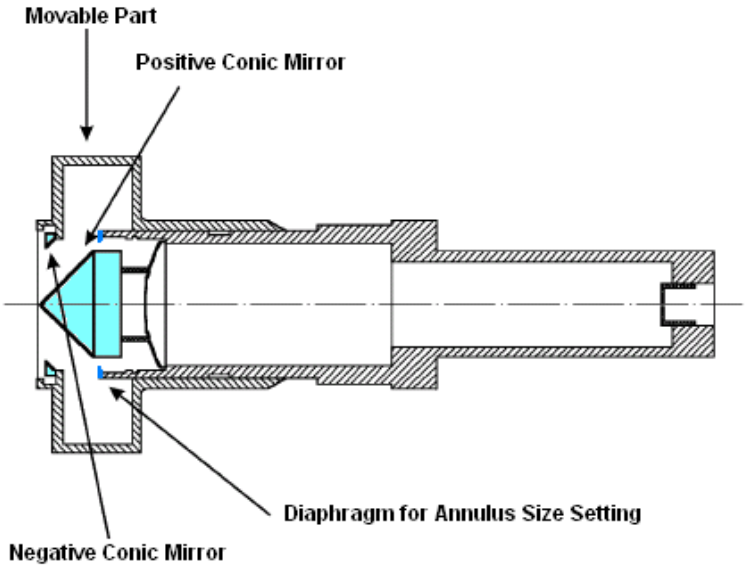


Figure 4.4 *Schematic drawing of optical scanner used for radial measurements.*

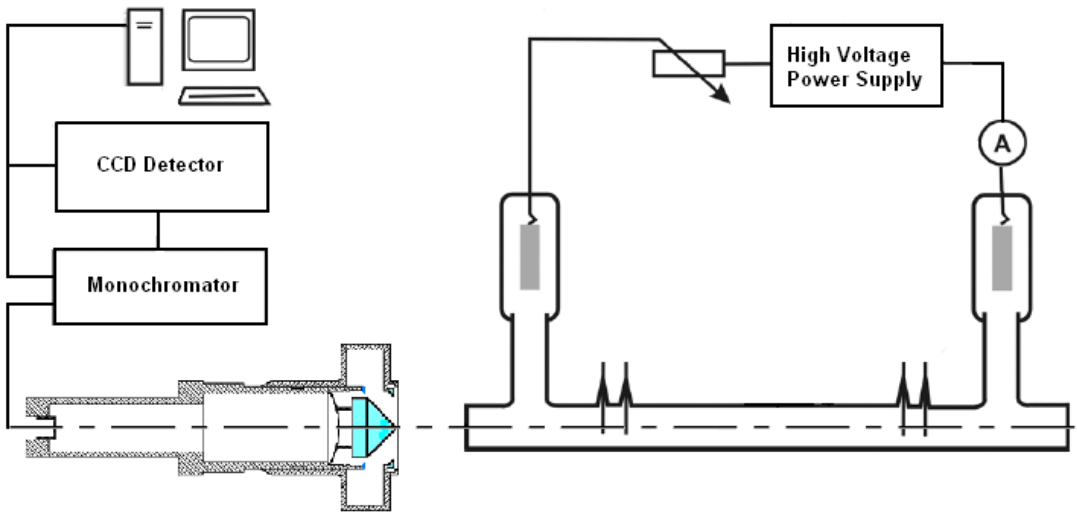


Figure 4.5 *Experimental set up for optical measurements in radial direction.*

5. Results and Discussion

The obtained results will be presented and discussed in the following chapters. The pure oxygen data will be shown first, followed by mixtures of oxygen with argon. As it was already mentioned in Chapter 4, two discharge tubes made of different materials were employed during our measurements. Generally, the presented results correspond to the measurements performed in the discharge tube made of Pyrex glass. The special subchapters will be devoted to the discussion of the results obtained in Silica, both for the pure oxygen and for oxygen-argon mixtures, respectively.

5.1 Discharge Sustained in Pure Oxygen

The DC glow discharge in pure oxygen was studied in the pressure range from 200 to 1750 Pa and for the discharge currents up to 40 mA. The discharge was maintained in steady regime. Therefore heating of the working gas due to power input led to increase of the measured pressure after the discharge ignition. The observed difference was about the units of Pa for the lowest studied pressures and it was increasing with increasing discharge current and filling pressure up to tens of Pa for the highest studied pressures. As it will be seen further, this behaviour is correlated to the increase of the power fed to the discharge. In order to keep the described pressure difference relatively small compared to the value of filling pressure, the values of studied pressures were chosen in such a way, that corresponding pressure increment did not overstep approximately 5 % of the value of the filling pressure. For this reason, the steps between studied pressures were not kept equidistant and they were increased with the increasing pressure.

5.1.1 Electric Characterization

First we have focused on the range of the existence of the particular forms, which are primarily defined according to the values of electric field strength E. For pressures up to approximately 500 Pa, we observed the uniform discharge, with the homogeneous H form of positive column spread in the whole central part of the

discharge tube. For higher pressures, T-form started to appear at the anode side of the discharge tube. We therefore observed different behaviour of E on the anode and cathode pair of probes, respectively.

Considering pressures about 500 – 700 Pa, the possibility of the appearance of the T form was dependent on the direction of the discharge current change. When the discharge was ignited with 10 mA of discharge current pre-set on the power supply, the both forms could be observed simultaneously, with the T form formed at the anode side of the tube. With increasing discharge current, the positive column switched to the H form in the whole central part of the tube. In contrast, with 40 mA of discharge current pre-set on the power supply before the discharge ignition, the positive column was entirely formed by the H form even when the discharge current was decreased to 10 mA. This behaviour correlates with the observed hysteresis in current dependence of transition between the both forms, measured by the pair of probes at the anode side for the pressures up to 850 Pa.

Considering the pressure of 1000 Pa, the T form of the positive column was observed at the anode side independently on the direction of the change of the discharge current, although the absolute values of E slightly differed.

These observations are summarized in following figures. The Figure 5.1 shows dependences of axial electric field strength E on the discharge current for the positive column of the discharge formed by the H form only. The measured values of E of the order of thousands of V/m represent typical values of electric field strength in the molecular gases. It can be also seen that axial electric field E increases with the pressure and slightly decreases with the discharge current. This behaviour is typical for the DC glow discharges and confirms that the H form corresponds to the standard form of the positive column of the DC glow discharge.

In Figures 5.2 and 5.3 can be seen the hysteresis in current dependence of axial electric field strength E with regards to transition between the both forms, which was observed at the anode side of the discharge tube for various pressures.

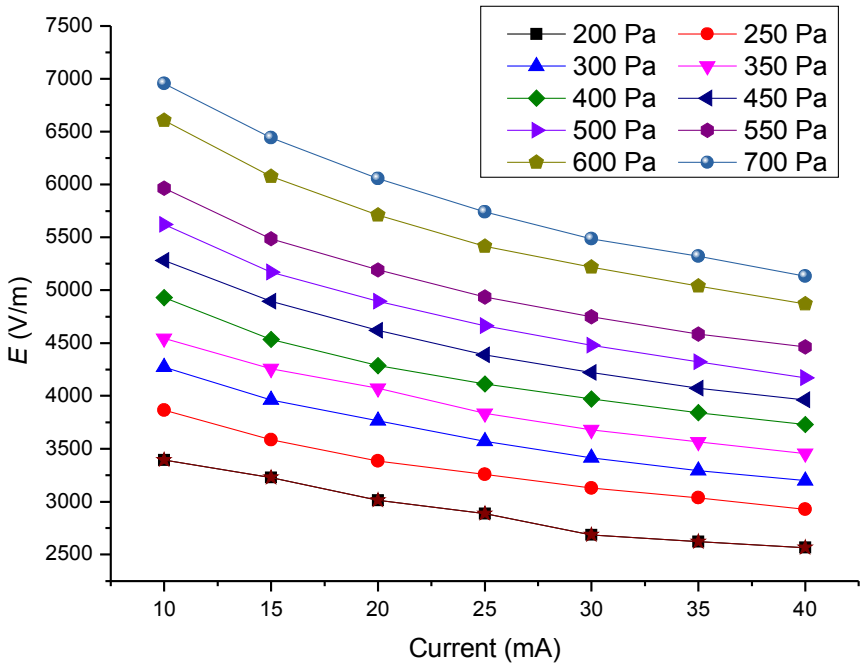


Figure 5.1 *Dependence of axial electric field strength E on the discharge current.*

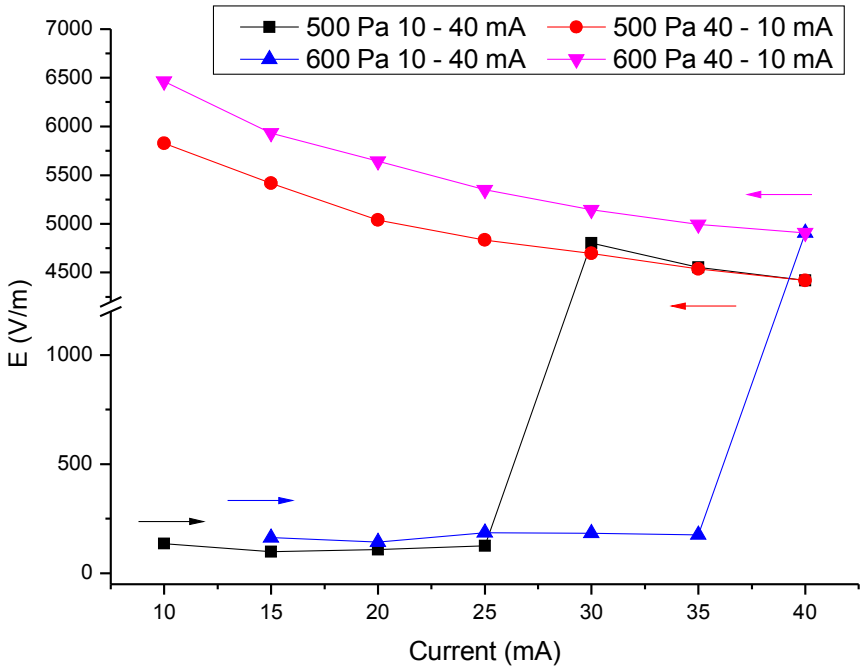


Figure 5.2 *The observed hysteresis in current dependence of axial electric field strength E with regards to transition between the both forms of the positive column (500 and 600 Pa, anode side of the tube).*

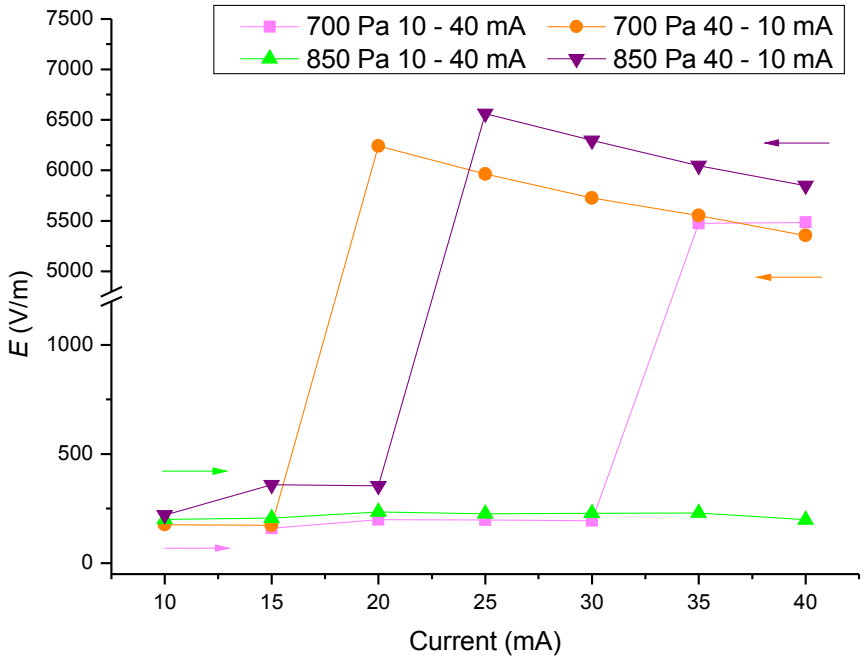
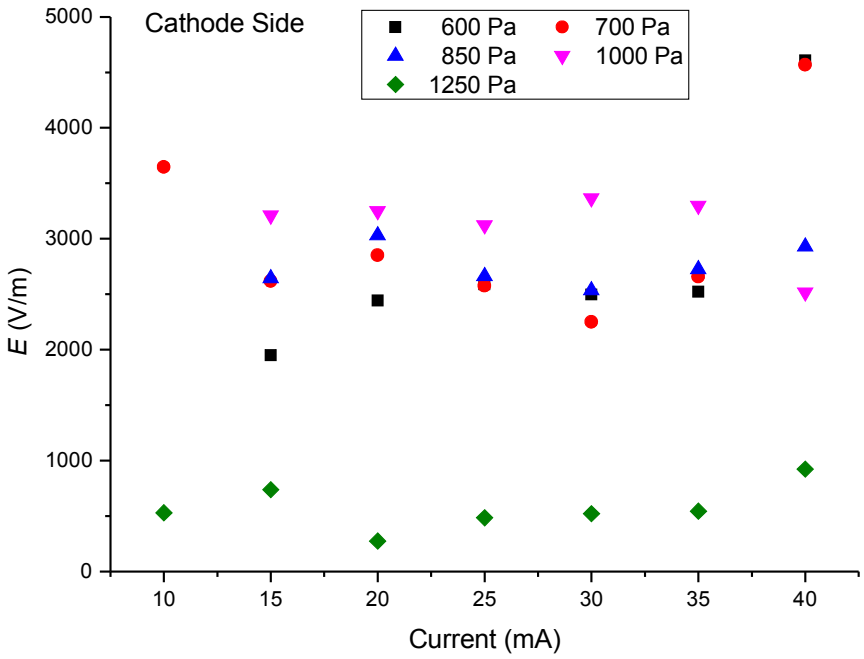


Figure 5.3 *The observed hysteresis in current dependence of axial electric field strength E with regards to transition between the both forms of the positive column (700 and 850 Pa, anode side of the tube).*

Considering the spatial distribution of the both forms, the T form always appeared at the anode side of the discharge tube. For particular pressure, the lower the discharge current was, the greater volume the T form occupied towards the cathode, where the H form was observed. However, the behaviour of electric field strength *E* measured through the pair of probes placed at the cathode side of the discharge tube did not obey behaviour observed in Figure 5.1. Although the absolute values of *E* reached thousands V/m, which would correspond to the H form, the decrease of *E* with increasing pressure was observed. We can therefore consider these results as reflection of the transition area. Similarly to the observations at the anode side for lower pressures, we could observe hysteresis in current dependence of transition between the both forms at the cathode side. This finally resulted in having the T form spread all over the central part of the discharge tube. This is documented in Figure 5.4, where the results obtained at the anode and cathode side are compared, respectively.



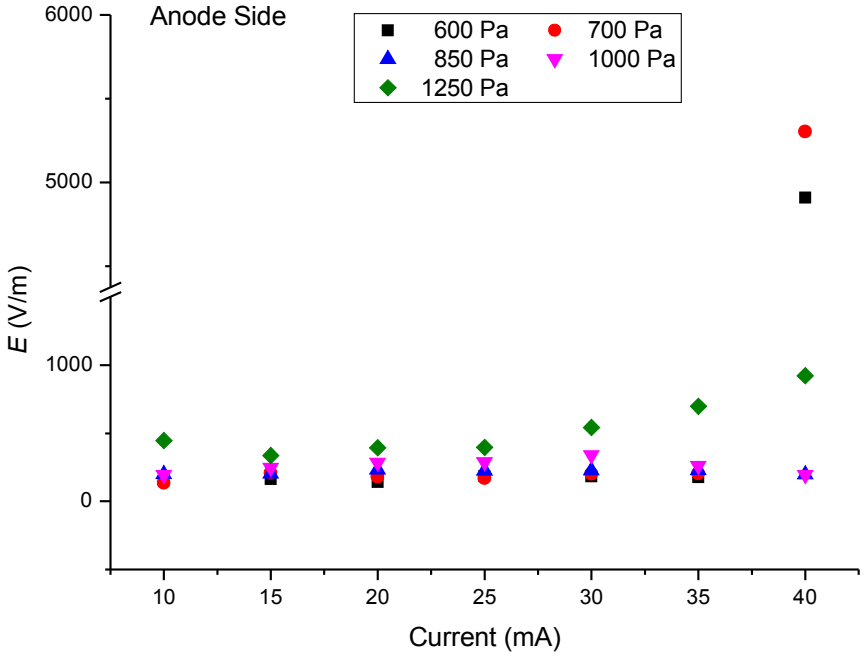


Figure 5.4 *Values of axial electric field strength measured both on cathode and anode pair of probes.*

Considering the highest studied pressures, the power supply enabled us to ignite discharge for up to 1750 Pa. The low-gradient form of the positive column was observed at the whole central part of the tube. The increase of E with the discharge current was also observed, which is in contrast to the behaviour observed in the H form (Figure 5.5). Moreover, the positive column became constricted, particularly for the lower discharge currents.

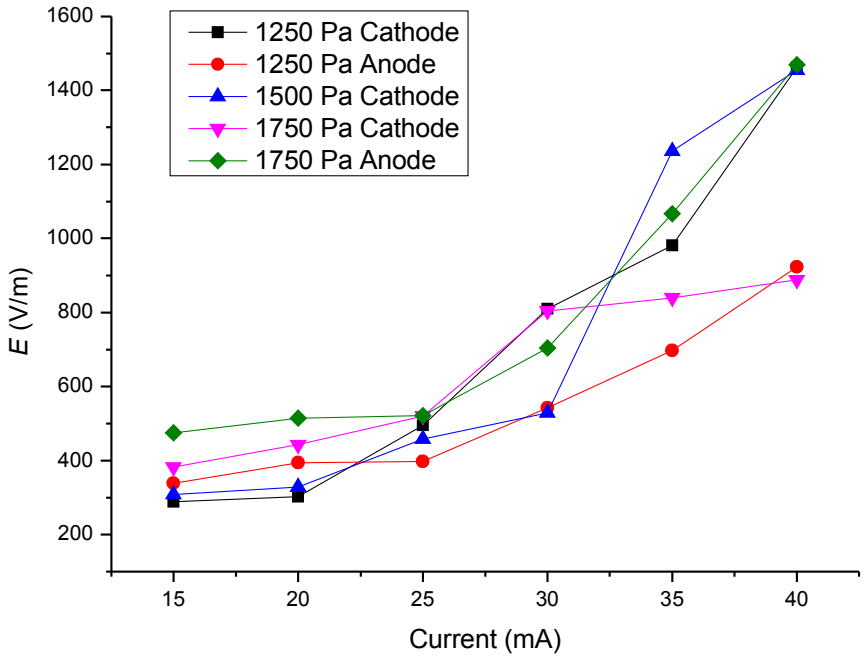


Figure 5.5 *Current dependence of axial electric field strength E measured for the hi pressure and discharge current.*

Finally, it need to be mentioned, that during our measurements we dealt with affection of the properties of the positive column by performing the measurements of electric field strength E itself. Measuring the values of E (i.e. application of the external voltage to the pair of measuring probes) often led to significant change of the region, where both H form and T form can co-exist, and also caused presence of instabilities which affect properties of the discharge plasma. However, all the spectral measurements, which are discussed in following chapters, were performed for undisturbed positive column only.

5.1.2. Emission Spectra

The emission spectra were detected in two different ways with regards to the existence of the particular forms of the discharge. Considering the uniform positive column of the discharge formed by the H form only, the spectra were detected in axial direction. This practically meant to study the mean value of intensity of radiation emitted in the direction of axis of the discharge tube. For the cases when the both forms were observed in the positive column, the emission spectra needed to be detected perpendicularly to the optical axis of the tube.

Regardless to the theoretical observable spectral range, which was mentionedin Chapter 4, due to the low spectral transmissivity of Pyrex glass in the near ultraviolet region as well as due to low spectral sensitivity of used CCD detector in near infrared region (less than 10 % for wavelengths over 950 nm), the emission spectra were detected in the range 350 – 900 nm.

5.1.2.1 Identification of the Spectra

Identification of the emitted spectra was performed by the help of spectral tables presented in [62, 63]. Considering discharge sustained in pure oxygen, the spectral lines corresponding to transitions between different quantum states of neutral oxygen atom O (ionisation energy 13,6 eV) or neutral molecule O_2 were observed during our measurements. Example of such spectrum is shown in Figure 5.6.

The spectral resolution of our experimental setup enabled us to to obtain atmospheric A-band with well-resolved ${}^{P}P$ and ${}^{P}Q$ branches corresponding to the rotational transitions of neutral molecule O_2 (head of the band at 759,4 nm). Also partially resolved atomic triplet (777,2 nm, 777,4 nm and 777,5 nm lines), to which will be referred to as “777,4 nm” triplet in following text, and atomic oxygen line 844,7 nm were observed. The 844,7 nm line also represents triplet [62], however it was unresolved in our case. The above mentioned lines and corresponding transitions are summarized in Table 5.1.

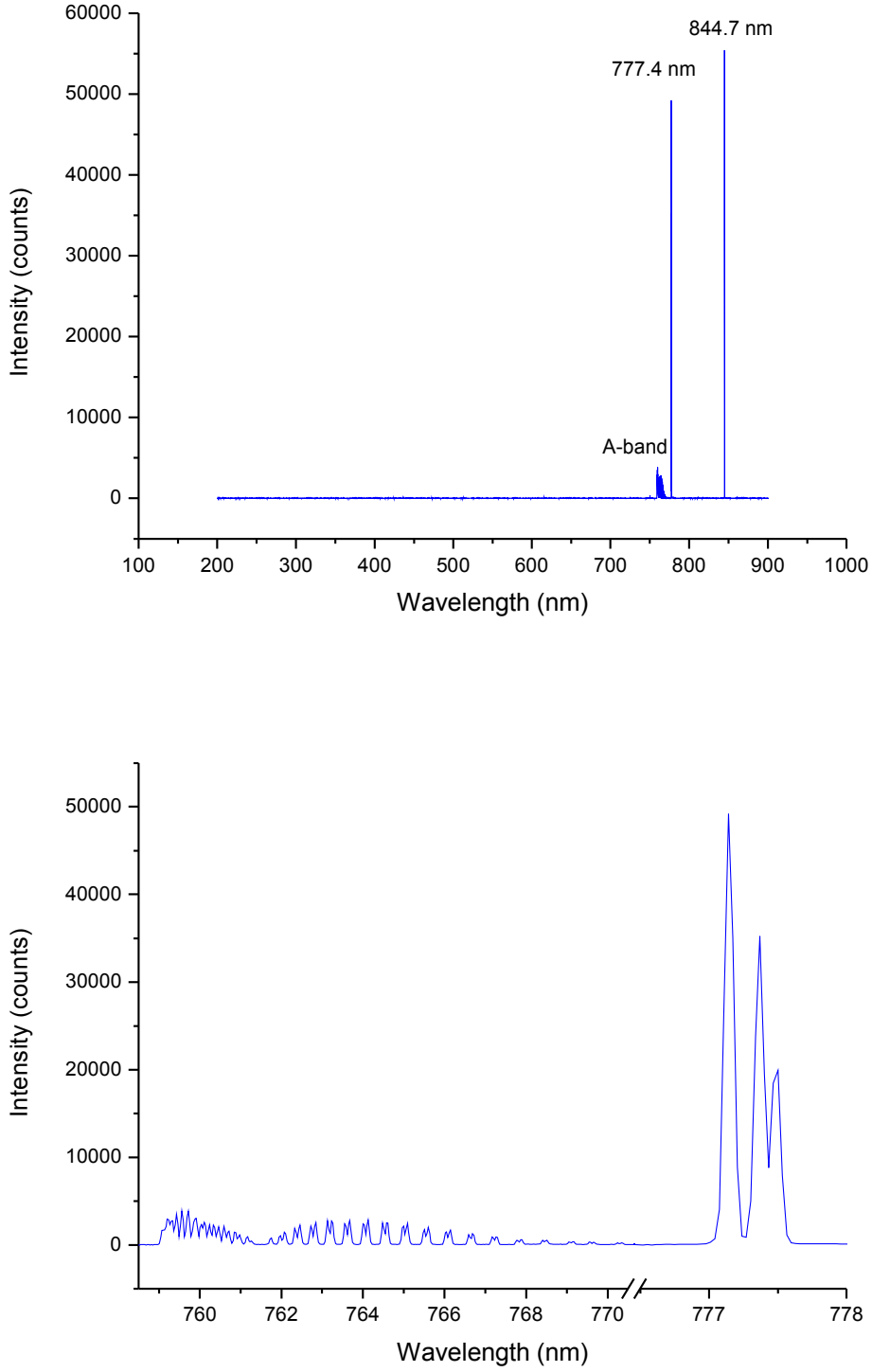


Figure 5.6 *Example of oxygen spectrum detected for 400 Pa and 40 mA (in the lower part can be seen atmospheric A-band and 777,4 nm triplet in details).*

Line	Transition
759,4 nm (A-band)	$b^1\Sigma^+_g, v=0 \rightarrow X^3\Sigma^-_g, v=0$
777,2 nm	$3p^5P,\ J=3 \rightarrow 3s^5S^0,\ J=2$
777,4 nm	$3p^5P,\ J=2 \rightarrow 3s^5S^0,\ J=2$
777,5 nm	$3p^5P,\ J=1 \rightarrow 3s^5S^0,\ J=2$
844,7 nm	$3p^3P \rightarrow 3s^3S^0$

Table 5.1 *Identification of studied oxygen spectra (J denotes the total electronic angular momenta and ν vibrational quantum number for the lower and upper levels, respectively).*

Considering the oxygen discharge plasma, the excited state related to 844,7 nm radiation is created by direct electron impact [64]:

$$e + O \rightarrow e + O^* . \qquad \text{(E 5.1)}$$

Similarly, the excited state related to 777,4 nm radiation is created from the ground state of oxygen atom O(^{3}P) by the direct electron impact [65]:

$$e + O(^3P) \rightarrow e + O(^5P), \qquad \text{(E 5.2)}$$

or by dissociative excitation of O_2 molecule by electron impact as well [45, 65]:

$$e + O_2 \rightarrow e + O^* + O . \qquad \text{(E 5.3)}$$

Aside from the above-mentioned lines, another spectral lines corresponding to transitions from excited states of atomic oxygen could be find in the spectra, i.e. 394,8 nm, 436,8 nm, 532,9 nm, 645,6 nm, 725,4 nm, or 882,0 nm, as well as the band of neutral molecule O_2 with head at 862,3 nm. However, these lines were not observable under all experimental conditions. They were detected particularly for the lower pressures and higher discharge currents and their maximal observed intensities reached values generally of two or three orders of magnitude lower compared to the intensities of 777,4 nm or 844,7 nm lines. We therefore did not considered these lines in our study and concentrated on emission spectra within the spectral range 755 – 845 nm.

5.1.2.2 Normalization

As it was mentioned in previous chapter, studied lines could be found in the spectral region 755 – 845 nm. In order to compensate linear decrease of spectral sensitivity of the CCD detector in this range of wavelengths, values of spectral sensitivity for wavelengths corresponding to studied lines were considered from the technical data provided by the manufacturer. The measured intensities of particular lines were then multiplied by the coefficient, which represents the inverse value of particular spectral sensitivity. One value of the coefficient was used for the whole A-band. We could afford this simplification due to relatively short interval of wavelengths detected in the spectra, which correspond to the A-band. Similar simplification was used for atomic triplet at 777,4 nm.

The width of the entrance slit of the monochromator was set to the value 0,05 mm for our measurements, except for the specific cases which will be mentioned later. The integration time, i.e. the time of the duration of having the shutter in front of the entrance slits opened, was variable in order to avoid saturation of the CCD detector system by the most intense lines. Measured values of intensities were then normalised with respect to integration time, i.e. divided by the value of integration time set during the particular measurement. Intensities of spectral lines were therefore estimated in counts per seconds, for which will be the abbreviation "cps" used in following text, including figures.

5.1.2.3 Characterization of the H form

At first, we concentrated on measurements performed for cases, when only H form of the positive column was observed in the discharge. The input of optical fibre was placed in a holder at the distance of 5 cm from the planar window and positioned to the optical axis of the central part of the discharge tube.

Current dependences of studied spectral lines for particular pressures are shown in Figures 5.7 - 5.9, respectively. The increase of all studied lines with increasing discharge current was observed. The curves for both 777,2 nm and 844,7 nm atomic oxygen lines has the similar shape, which can be considered as parabolic. The slight decrease with the increasing pressure was also observed, probably as a result of worse acceleration of exciting electrons along the shorter mean free path.

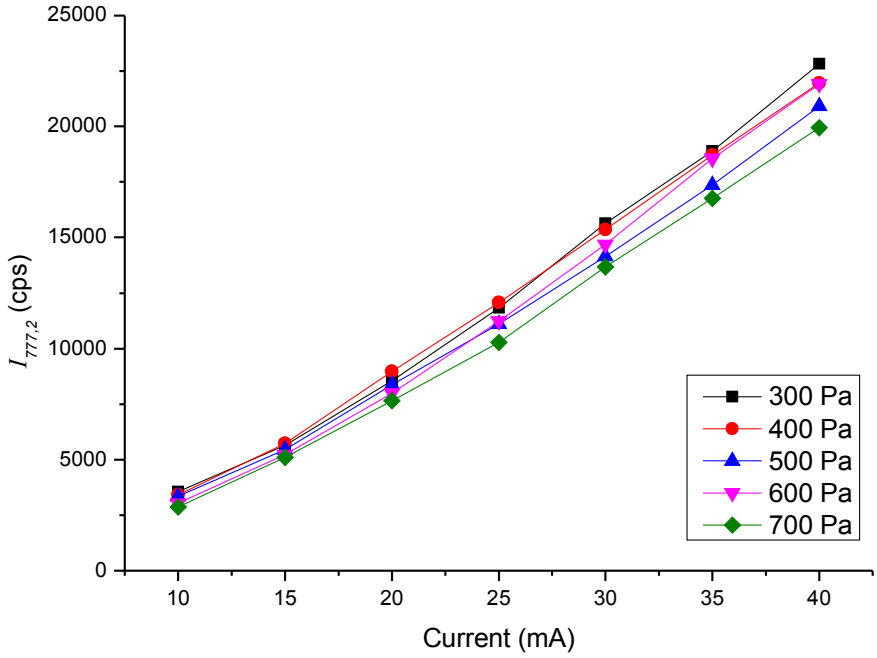


Figure 5.7 *Current dependence of 777,2 nm line for various pressures.*

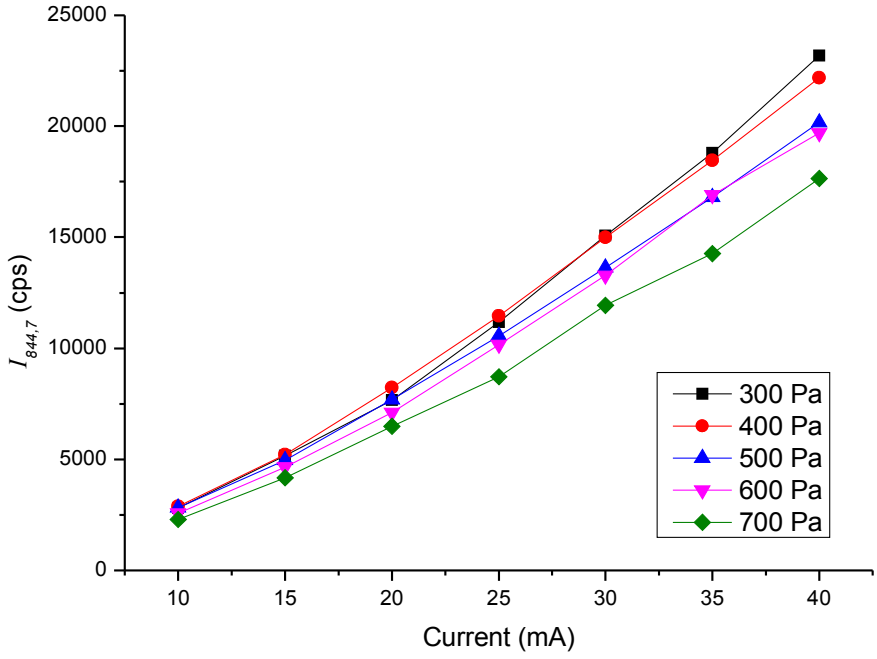


Figure 5.8 *Current dependence of 844,7 nm line for various pressures.*

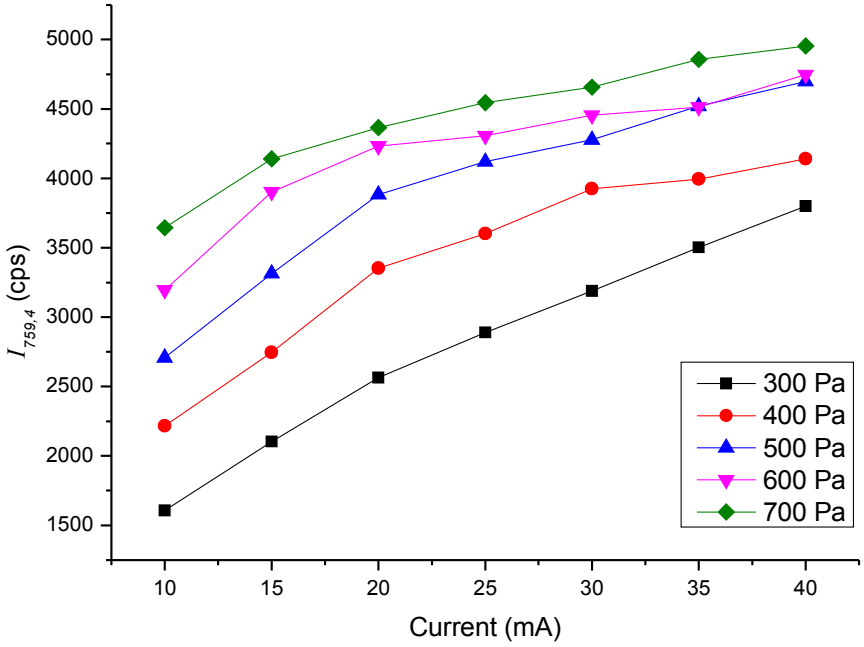


Figure 5.9 *Current dependence of 759,4 nm (head of A-band) line for various pressures.*

The shape increase of 759,4 nm (head of A-band) line can be considered as square root. The decrease of increments in the intensity of this line with increasing current could be probably explained by increased dissociation of oxygen molecule which might overbalance the excitation process. By increased dissociation could be also probably explained decrease of intensity of this line with decreasing pressure as a result of electron acceleration along the longer mean free path.

We also focused on the determination of rotational temperature T_{rot} of neutral O_2 particles from the atmospheric A-band. Sufficient spectral resolution enabled us to distinguish particular lines around the band origin at 761.9 nm. These lines form so-called ${}^{P}P$ and ${}^{P}Q$ branches of the band [63].

Good agreement between values of rotational temperature obtained from both specified bands was found [66] (A.1). Dependence of T_{rot} on variation of discharge parameters can be seen in Figure 5.10. As can be seen, the rotational temperature was increasing with increasing pressure and discharge current. Considering electric measurements mentioned in Chapter 5.1.1, this behaviour can be explained by increased power fed to the discharge.

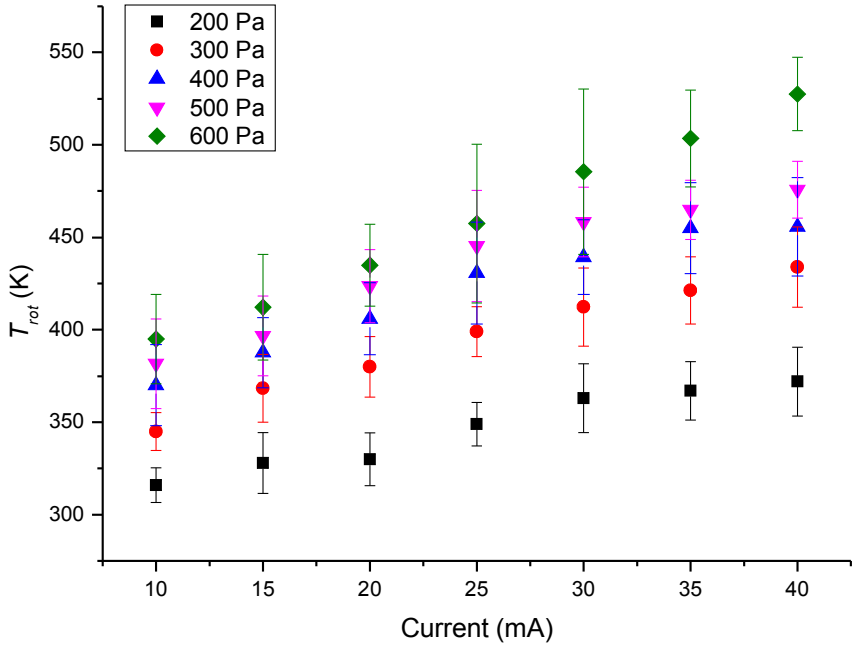


Figure 5.10 *Dependence of the rotational temperature T_{rot} on the pressure and discharge current.*

5.1.2.4 Radial profiles

The properties of a positive column of DC glow discharge, such as the rotational temperature, can also vary radially. Radial profiles of the rotational temperature of molecular oxygen were previously studied also in our laboratory by means of optical emission spectroscopy. In order to reach sufficient signal intensity, the spectral resolution of the optical system had to be decreased and numerical simulations were employed with flat profile of radial dependences of T_{rot} as the result [16]. Therefore, we tried to study radial distribution of rotational temperature T_{rot} derived by from the well-resolved atmospheric A-band of molecular oxygen.

The measurements were performed by the help of the apparatus described in chapter 4.5. Since the measurements were performed in axial direction on principle, we studied radial profiles of the emission spectra in the tube made of Pyrex glass for such conditions, under which only the high-gradient H form was present.

In order to be able to determine rotational temperature T_{rot} of molecular oxygen, we had to find balance between the level of intensity of the incoming signal and spectral resolution of the optical system. Usage of the above described optical scanner for radial measurements caused significant decrease of the intensity of detected radiation due to the decrease of volume from which emitted radiation was collected. With constant distance of the scanner from the plasma, given by construction of the experimental apparatus, it was necessary to enlarge entrance slit of monochromator or to use optical grating with low groove density.

Finally, grating with 1200 grooves/mm was employed and entrance slit of our monochromator was enlarged to 0.06 mm. Also the integration time of the optical detection system needed to be prolonged up to tens of seconds. This configuration enabled us to gain maximum possible intensity of incoming radiation with molecular A-band still well-resolved.

The measurements were performed with radial step corresponding to the width of the diaphragm. The results obtained for the radial step of 1,5 mm are shown in Figures 5.11 and 5.12. Figure 5.11 shows the radial profiles of the rotational temperature for two different pressures, while current dependence of rotational temperature is shown in Figure 5.12. The x-axis corresponds to the position of the radial scanner normalized with respect to the radius of the discharge tube. Each position of movable mirror is related to annulus, from which optical signal is detected. Values on the x-axis than represent r/R ratio, where r denotes position (mean radius) of annulus and R the radius of the discharge tube, respectively. This normalization was already used in our previous measurements.

As can be seen from both figures, radial profile of T_{rot} is flat independently on pressure and discharge current. Similar results were obtained under all studied conditions, which can be explained by the good thermal conductivity of the positive column of the glow discharge. This confirms experimentally previous results obtained in our laboratory, as well as the increase of the rotational temperature T_{rot} with increasing pressure and discharge current. Similar results were found for the width of the diaphragm of 1,8 mm [67] (A.4).

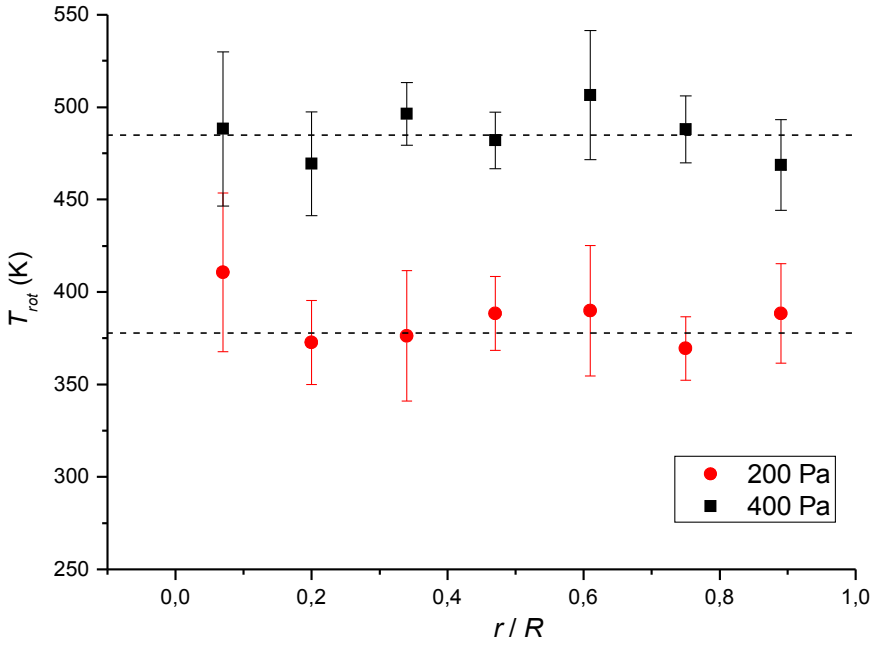


Figure 5.11 *Pressure dependence of rotational temperature T_{rot} (40 mA).*

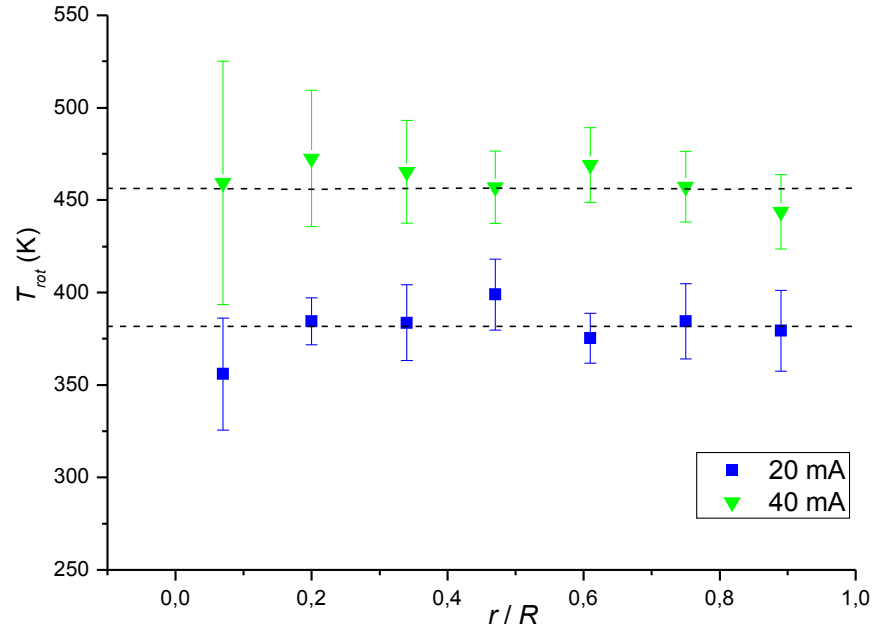


Figure 5.12 *Dependence of T_{rot} on the discharge current (300 Pa).*

Partial attention was paid to the spectral lines. In order to be able to compare radial dependences of intensities of studied spectral lines we had to take into account the area of annulus, from which optical signal is detected. The thickness of annulus corresponds to the thickness of diaphragm for annulus size setting and it was equal to the value of 1,5 mm. Measured values of intensities of spectral lines were divided by the area of particular annulus, so that we obtained normalized intensity I/S_r in each annulus [16, 68]. Example of radial profile for the 844,7 nm line can be seen in Figure 5.13. The maximum intensity in the centre of the tube and then decrease towards wall of the tube corresponds to the profile which he previously observed for $N_2(C)$ nitrogen bands [69]. Regardless to the radial dependences, the values of the studied atomic oxygen lines were approximately the same under all physical conditions, which corresponds to the fact, that H form of the discharge was established during our measurements.

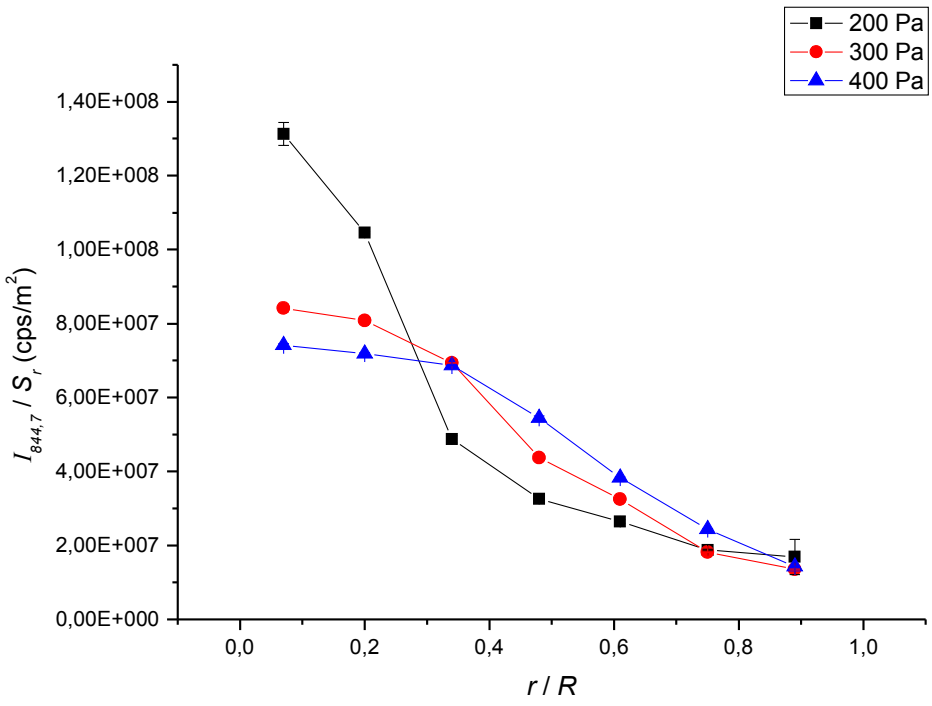


Figure 5.13 *Radial dependence of 844,7 nm atomic line normalized to the annulus area (40 mA).*

5.1.2.5 T and H Forms of the Discharge

As it was mentioned above, the measurements of electric field strength can affect discharge properties and therefore also range of existence of the both forms of the positive column of the discharge. We have therefore concentrated on spectral differences, which could help to the identification of the each particular form without need of the measurement of the electric field strength.

Generally, the emission spectra reflected the he variations of electric field strength. The T form was characterized by the weaker spectrum, i.e. by values of intensities, which were about one order of magnitude lower compared to the H form. The hysteresis could also be observed in transition between the both particular forms, as can be seen on example in Figure 5.14.

Due to lack of absolute calibration of our system, we concentrated on study of ratios of studied atomic lines and head of atmospheric A-band, in order to be able to compare spectra detected under various conditions. Examples of current and pressure dependences of these ratios, respectively, for the H form can be seen in Figures 5.15 and 5.16.

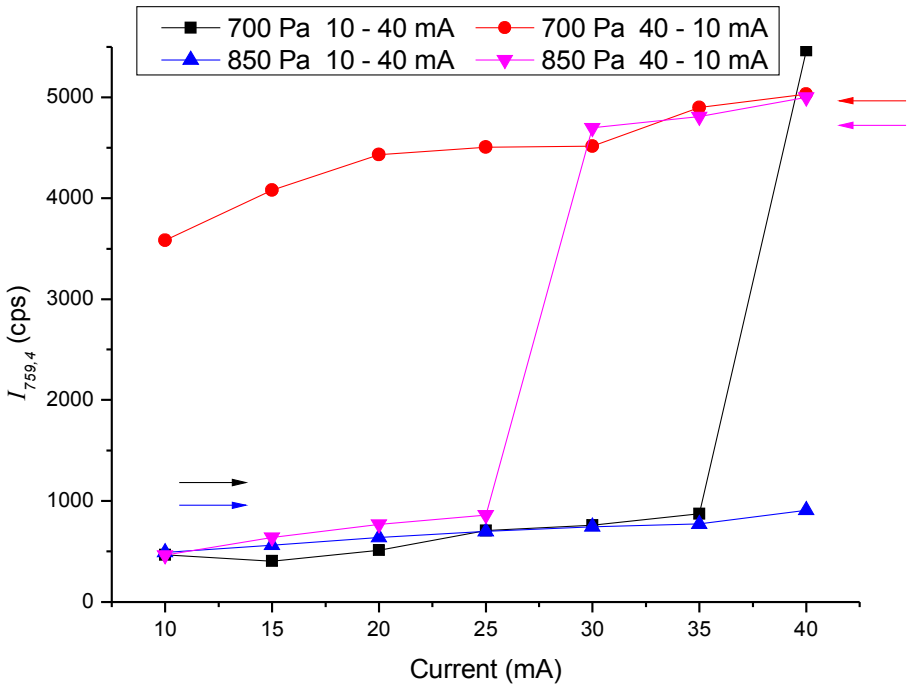


Figure 5.14 *Intensity of the head of A/band at 759,4 nm line correlation with transition between T and H forms, respectively.*

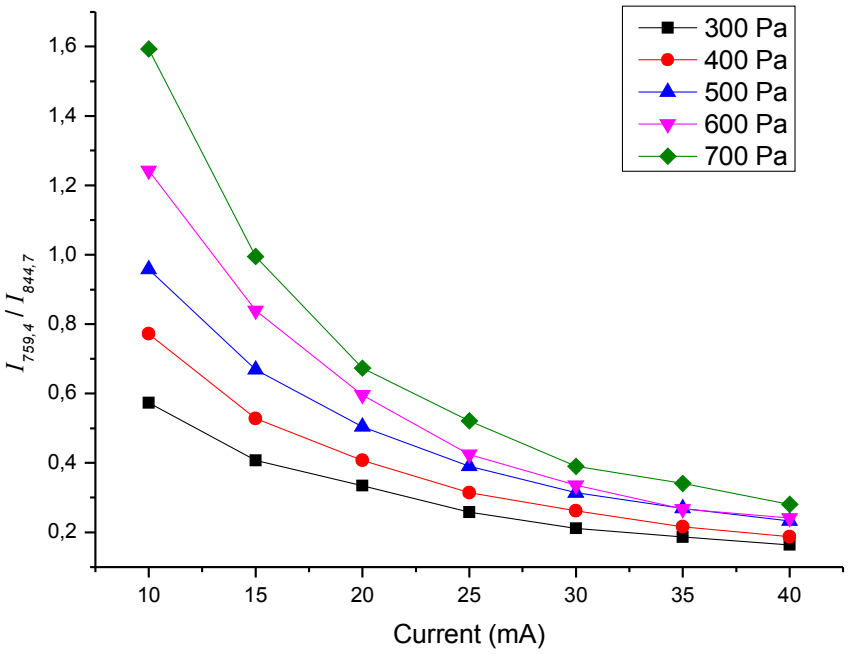


Figure 5.15 *Current dependence of the ratio of the 759,4 nm and 844,7 nm lines (H form).*

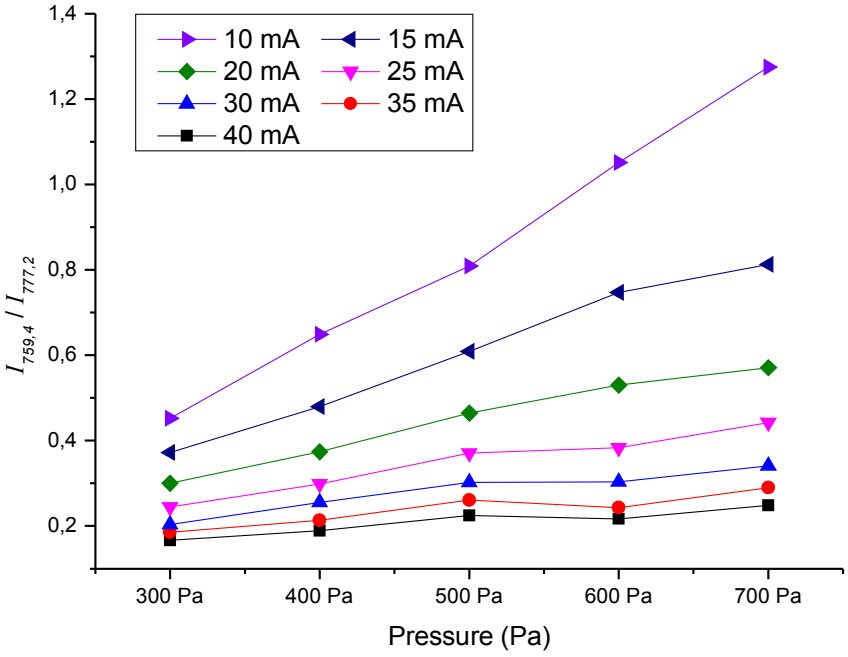


Figure 5.16 *Pressure dependence of the ratio of the 759,4 nm and 777,2 nm lines (H form).*

As can be seen from Figures 5.15 and 5.16, the relative intensity of the head of the A-band with respect to the both studied atomic oxygen lines was increasing with increasing pressure and with decreasing discharge current, which corresponded to the behaviour of the intensity of the particular lines.

Significant difference was observed particularly in the ratio of atomic oxygen lines. According to our results, the H form was characterized by similar values of intensities of 777,2 nm and 844,7 nm lines, as can be seen in Figure 5.17. Considering the T form, the 777,2 nm/844,7 nm intensity ratio was obviously increased. The difference became more apparent for the increased pressure. Comparison of the results obtained at the both anode and cathode side, respectively, is shown in Figure 5.18. The drop in the 777,2 nm/844,7 nm intensity ratio could be observed also when the fibre holder was moved between electrode pairs [70] (A.5).

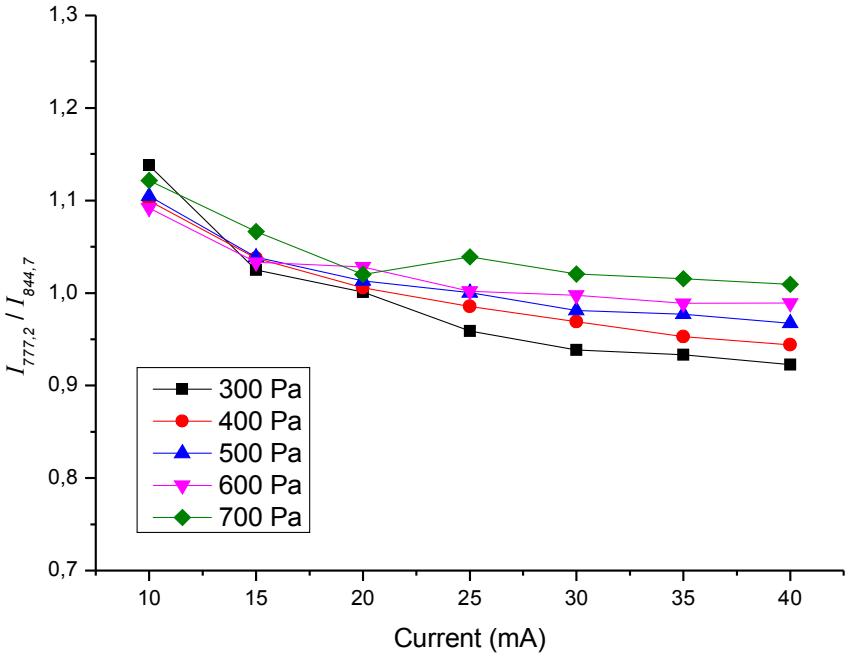


Figure 5.17 *Current dependence of the 777,2 nm/844,7 nm intensity ratio.(H form).*

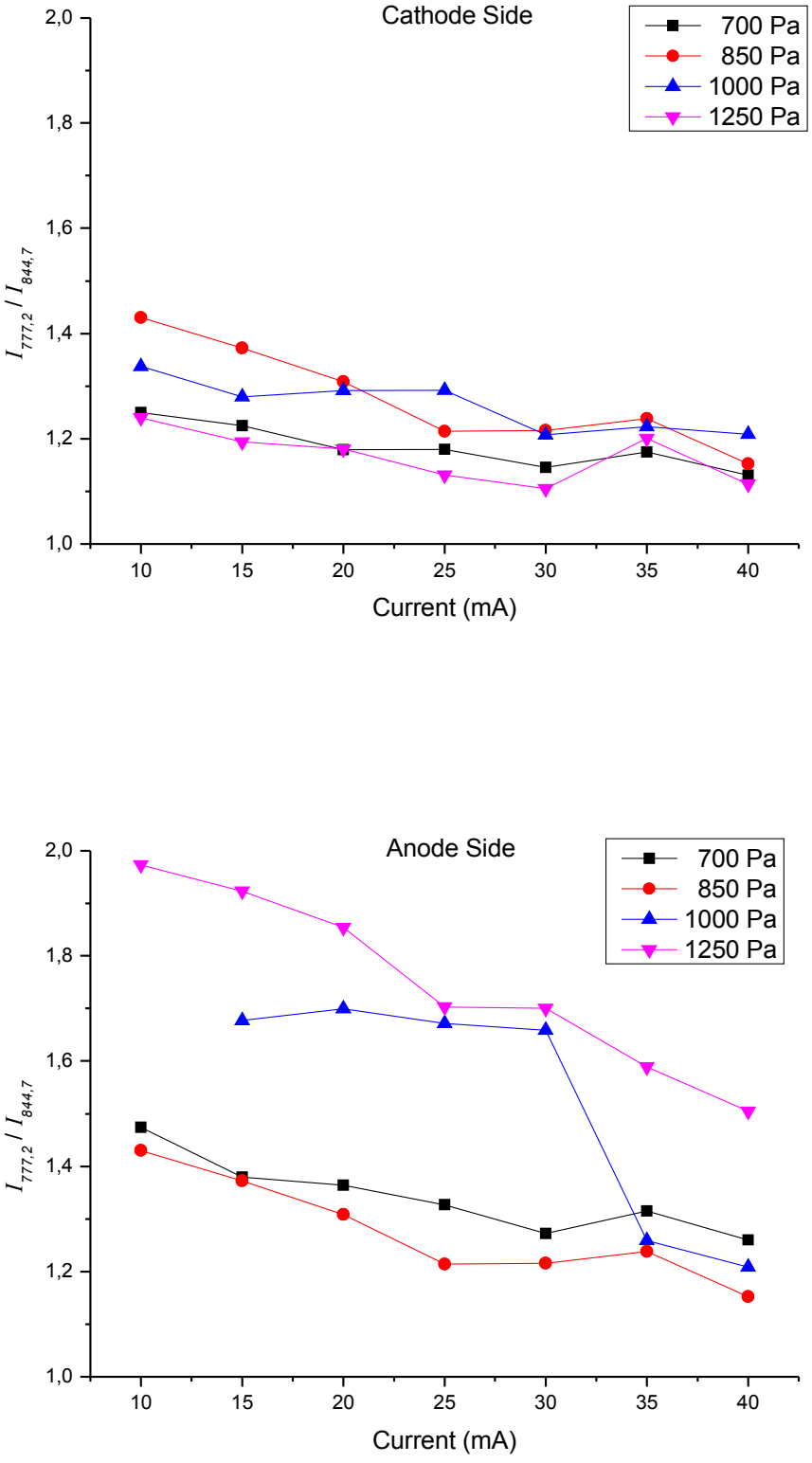


Figure 5.18 *777,2 nm/844,7 nm intensity ratio obtained at the both cathode and anode sides of the discharge tube.*

Considering the rotational temperature determined from the atmospheric A-band, the estimated values were also dependent on the particular form of the positive column. The increase of T_{rot} with the discharge current was found in the both forms (Figure 5.19). This is in good agreement with our previous results for lower pressures. Moreover, values of T_{rot} were higher in the H form, which could correspond to the energy gain from the electric field strength. This is shown in Figure 5.20, where the dependence of T_{rot} on the supplied power (electric field strength multiplied by discharge current) is presented. While a linear increase of rotational temperature with increasing power in the H form was observed, no obvious dependence was found for the T form [71] (A.3). However, the error of the estimation of the rotational temperature in the T form, considered as the standard deviation obtained from a large number of measurements, was is in our case up to 10 %, which was caused mostly by the weak spectra and therefore worse resolution of particular lines from the ^{P}P and ^{P}Q branches, respectively.

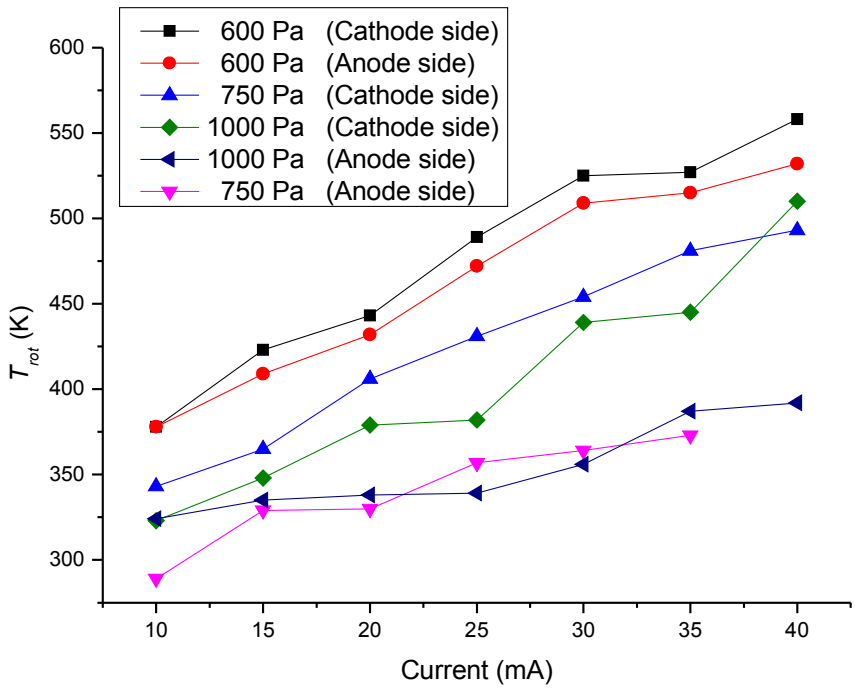


Figure 5.19 *Dependence of T_{rot} on the discharge current* [71] (A.3).

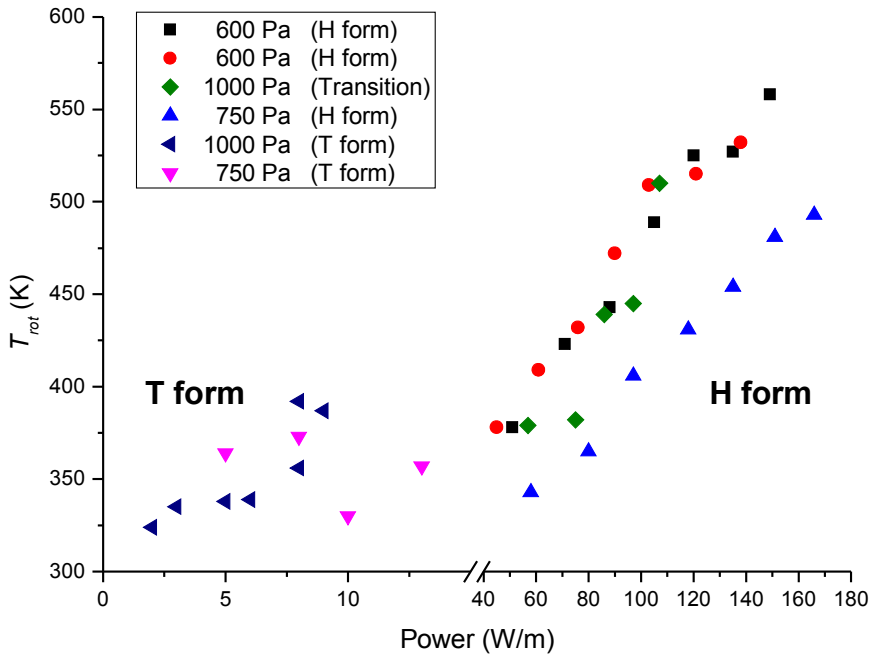


Figure 5.20 *Dependence of T_{rot} on the supplied power* [71] (A.3).

5.1.3 Measurements in the Discharge Tube Made of Silica

As it was mentioned at the beginning of the Chapter 5, the previous results were obtained in the discharge tube made of Pyrex glass. Results obtained in the discharge tube made of Silica as well as their comparison with the Pyrex glass will be discussed in this subchapter.

Considering the electric characterization, similar behaviour as for the Pyrex glass was observed. In Figure 5.21 are shown values of electric field strength E measured in the H form under different discharge conditions. Also the similar hysteresis in electric field strength as in the Pyrex discharge tube was observed in Silica, as can be seen in Figure 5.22.

Considering the spatial distribution of the both forms, the the T form also always appeared at the anode side of the discharge tube and for particular pressure spread towards the cathode with decreasing discharge current.

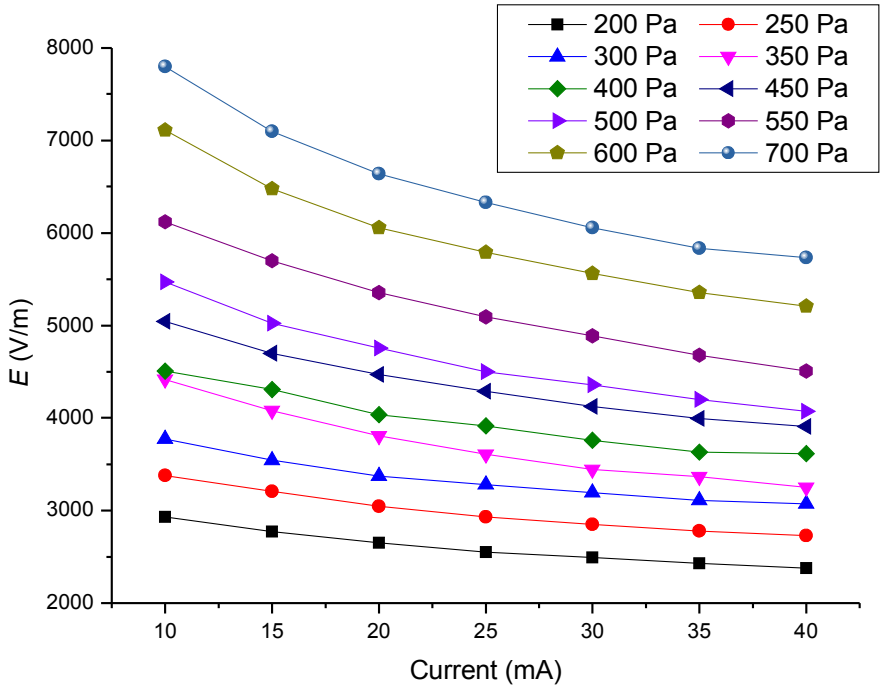


Figure 5.21 *Values of axial electric field strength E measured in Silica discharge tube for the H form only present.*

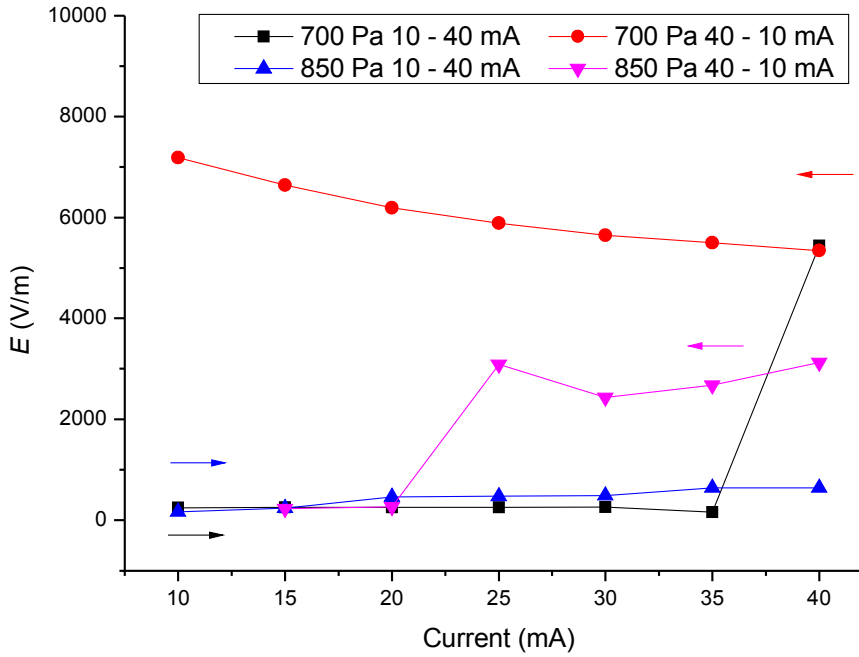


Figure 5.22 *The observed hysteresis in current dependence of axial electric field strength E with regards to transition between the both forms of the positive column (anode side of the tube).*

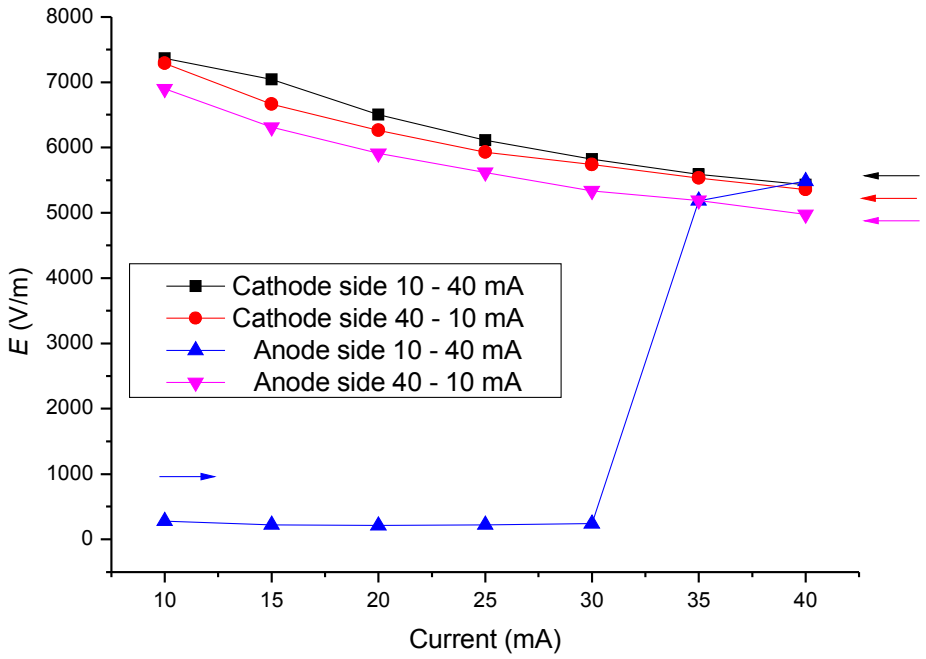
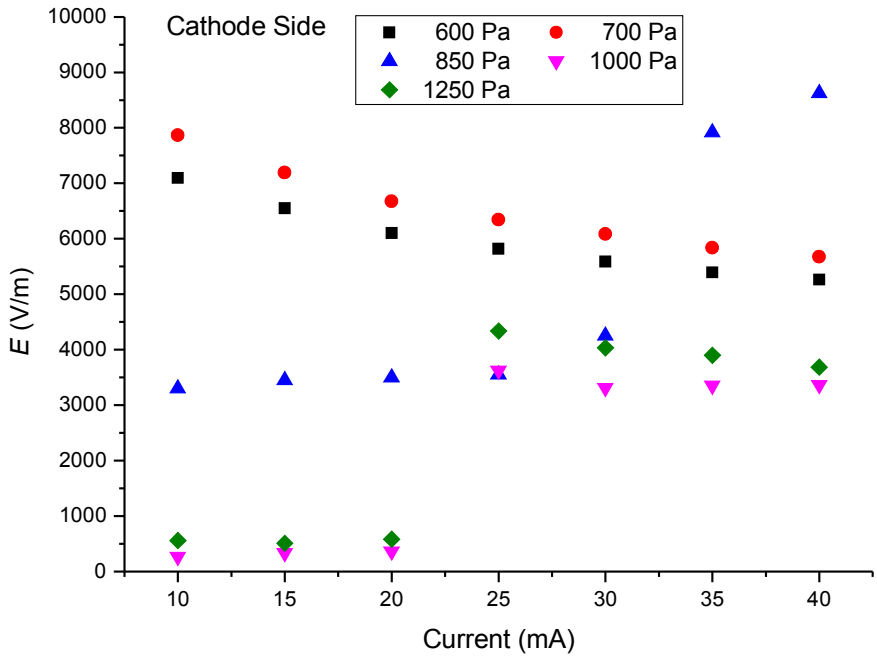


Figure 5.23 *The observation of hysteresis and appearance of the T form at 650 Pa.*

However, the region of existence of the T form was shifted to higher pressures compare to the measurements in Silica. Regardless the direction of the discharge current variation, we did not observed T form for pressures 500 and 600 Pa, respectively, and started to appear at 650 Pa (Figure 5.23).

At the pressure of 700 Pa, the H form only was observed at the cathode pair of probes. The "transition values" (as mentioned in Chapter 5.1.2.5) were observed for pressures 850 Pa and higher. T form was spread all over the central part of the discharge tube for the currents up to 20 mA even for the highest pressures, as can be seen in Figure 5.24, where the results obtained at the anode and cathode side are compared, respectively.

These results qualitatively confirm dependence of the range of the existence of the both particular forms, among the other parameters, also on the material of the discharge tube. We also note, that we didn't manage to ignite discharge for pressures higher than 1400 Pa in the Silica tube.



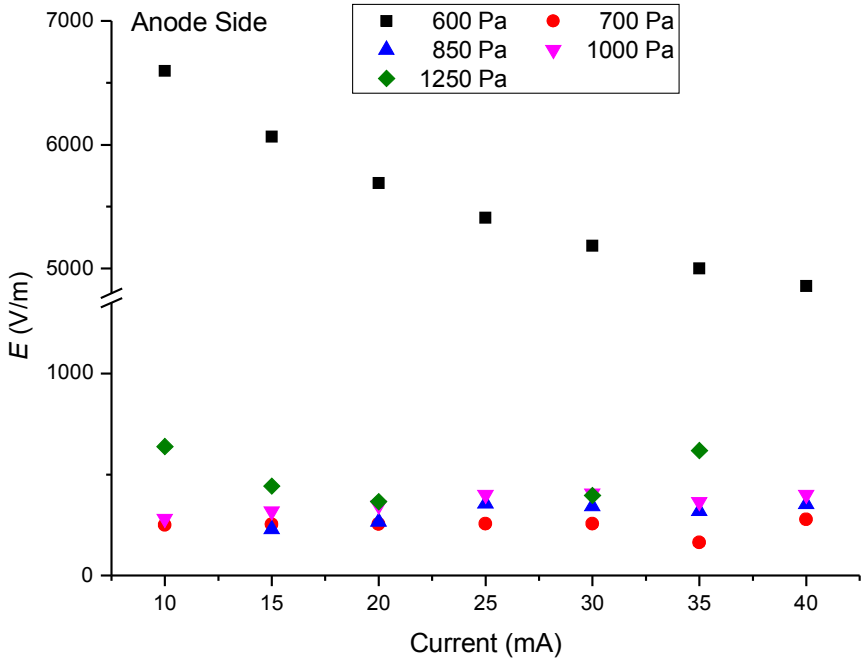


Figure 5.24 *Values of axial electric field strength measured both on cathode and anode pair of probes.*

Considering the emission spectra, the observed current dependences of intensities of studied lines were found to be similar to the case of the Pyrex discharge tubes, as it is documented on the example shown in Figure 5.25. The important difference was observed particularly in development of the whole atmospheric A-band. In comparison with Pyrex, the A-band was significantly weaker in Silica relatively to the atomic lines, which is documented in Figure 5.26 for relative intensity of 759,4 nm/844,7 nm lines. The observed behaviour reflects the importance of the wall interactions regarding the atomic oxygen production in the discharge.

In order to qualitatively describe differences in relative amount of the atomic and molecular oxygen, respectively, with respect to the discharge tube material, we measured intensity of the whole atmospheric A-band and compare it to the sum of intensities of studied atomic oxygen lines. The results can be seen in Figures 5.27 and 5.28, where current and pressure dependences of such ratio are shown, respectively.

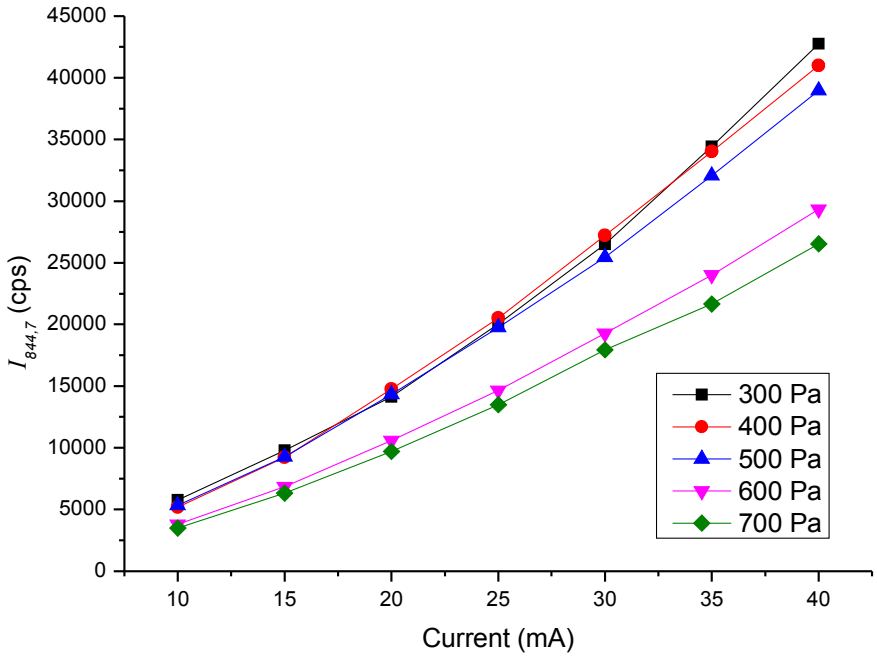


Figure 5.25 *Current dependence of 844,7 nm atomic line for various pressures.*

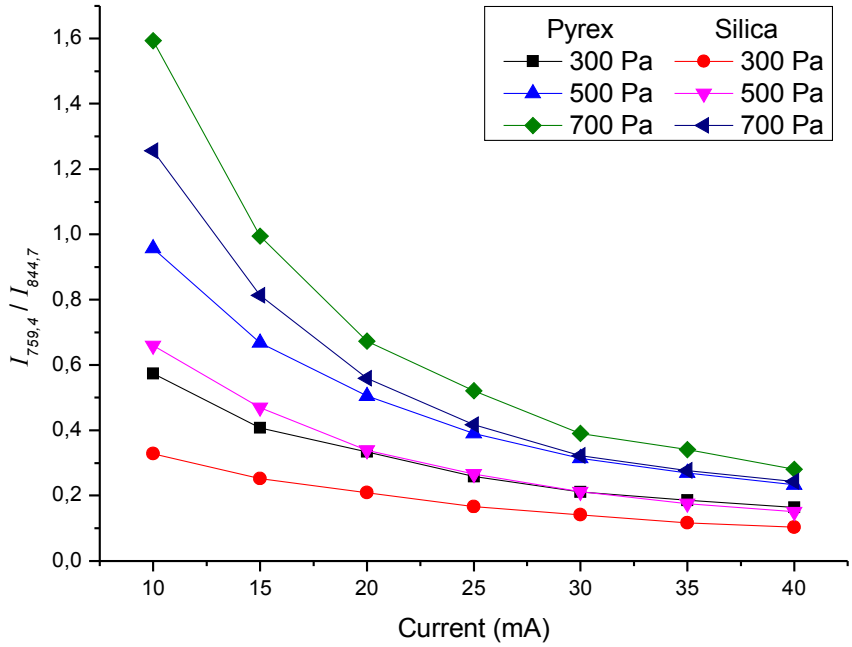


Figure 5.26 *Comparison of the 759,4 nm/844,7 nm lines intensity ratio for the both discharge tubes.*

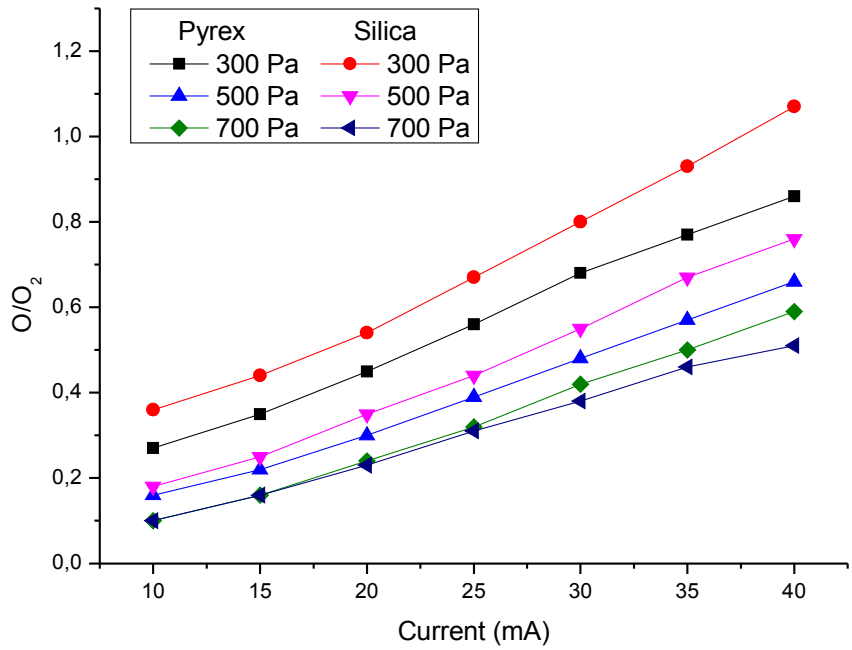


Figure 5.27 *Current dependence of relative amount of excited oxygen atoms and molecules with respect to the two different materials of the discharge tubes.*

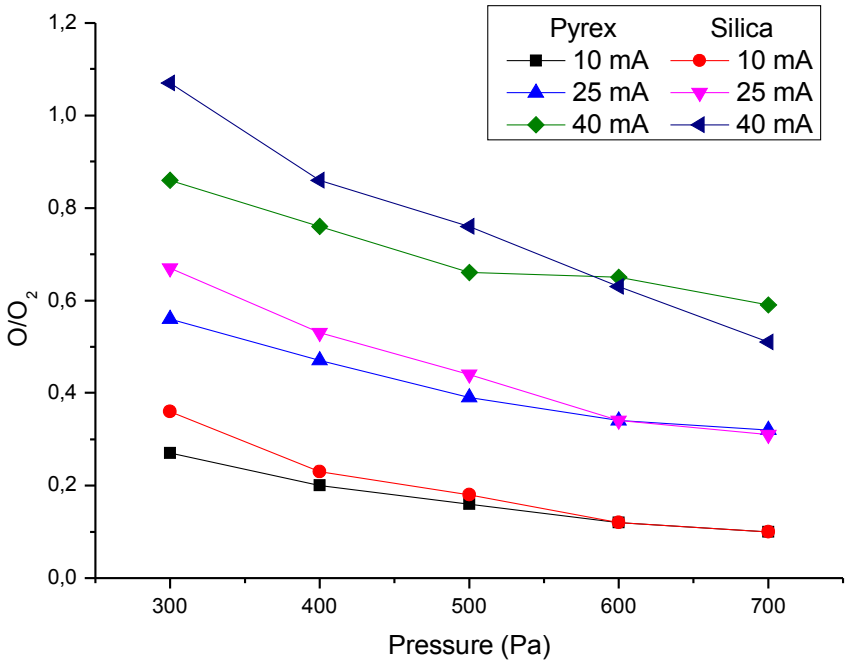


Figure 5.28 *Pressure dependence of relative amount of excited oxygen atoms and molecules with respect to the two different materials of the discharge tubes.*

From these figures can be seen, that the wall material affects the value of the intensities of the spectral lines of atomic oxygen and therefore also relative intensities of atomic oxygen lines with respect to the band. These relative intensities, which might be considered as a qualitative measure of balance between neutral oxygen atoms and molecules, were generally higher in the discharge tube made of Silica. Nevertheless, observed effect diminished with increasing pressure.

Considering the rotational temperature T_{rot}, differences were observed too. As can be seen in Figure 5.29, the rotational temperature T_{rot} seems to be higher in the Pyrex discharge tube than for Silica. This effect was observed over the whole range of parameters for which our measurements were made and corresponds to the previous measurements for the lower pressures. The difference could be probably explained by the different thermal conductivity of Pyrex glass (1.14 W/mK) and Silica (1.38 W/mK).

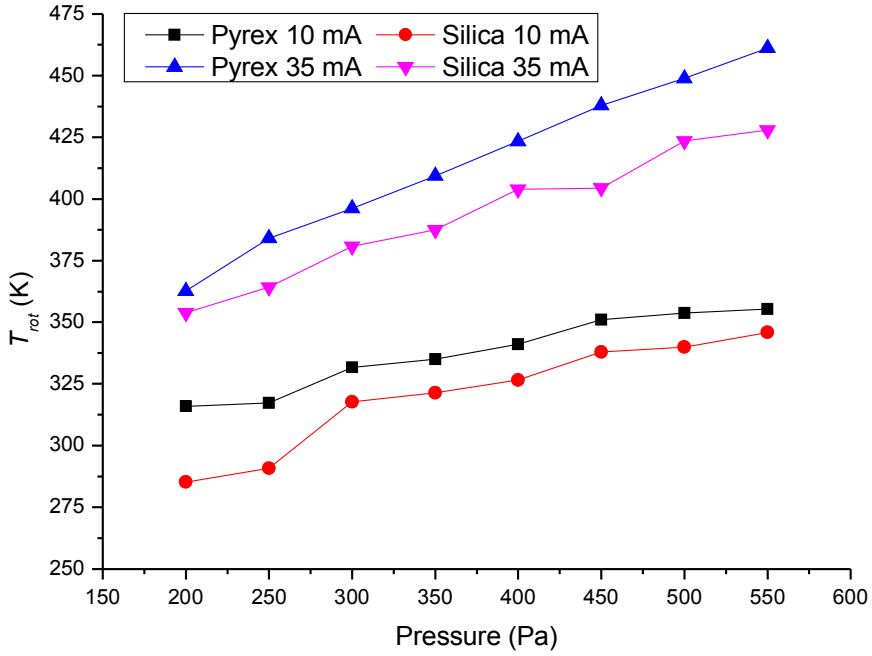


Figure 5.29 *Comparison of the pressure dependence of the* T_{rot} *for both discharge tubes* [66] (A.1).

5.2 Discharge Sustained in Mixtures of Oxygen with Argon

The investigation of properties of DC glow oxygen discharge sustained in oxygen-argon mixtures follows the previous measurements performed in our laboratory [41, 70]. The measurements were performed in Pyrex discharge tube, except for series of measurements, which will be described in special subchapter.

5.2.1 Pure Argon

Before introducing argon into the oxygen discharge, we briefly dealt also with the DC glow discharge sustained in pure argon. The argon discharge performed generally much intense emission compared to the discharge sustained in pure oxygen with the markedly observable ionization waves. The presence of these instabilities caused slight fluctuations of electric field strength E measured for the particular pressure and discharge current. These fluctuations usually did not exceed 5 % of measured value, which was obtained through averaging process that was performed by the measuring device. The curves of the measured electric field strength are shown in Figure 5.30. It can be seen, that the values of electric field strength correspond to the typical values for atomic gas, which means order of magnitude of hundreds of V/m. Despite the the above mentioned affection by instabilities, decrease of E with discharge current as well as increase of E with the pressure follows the standard behaviour of E in positive column of the DC glow discharge.

The example of detected emission spectra can be seen in Figure 5.31. Apart from a group of rather weak lines around 400 nm (e.g. 415,9 nm or 434,5 nm), the most intense lines could be observed within the spectral region 700 – 850 nm. These so-called persistent lines [62] correspond to the transitions between different quantum states of neutral Ar atom (ionisation energy 15,8 eV) and together with corresponding transitions are summarized in Table 5.2. Example of current dependences of intensities of particular lines are shown in Figure 5.32, where the increase of intensity with increasing discharge current can be seen.

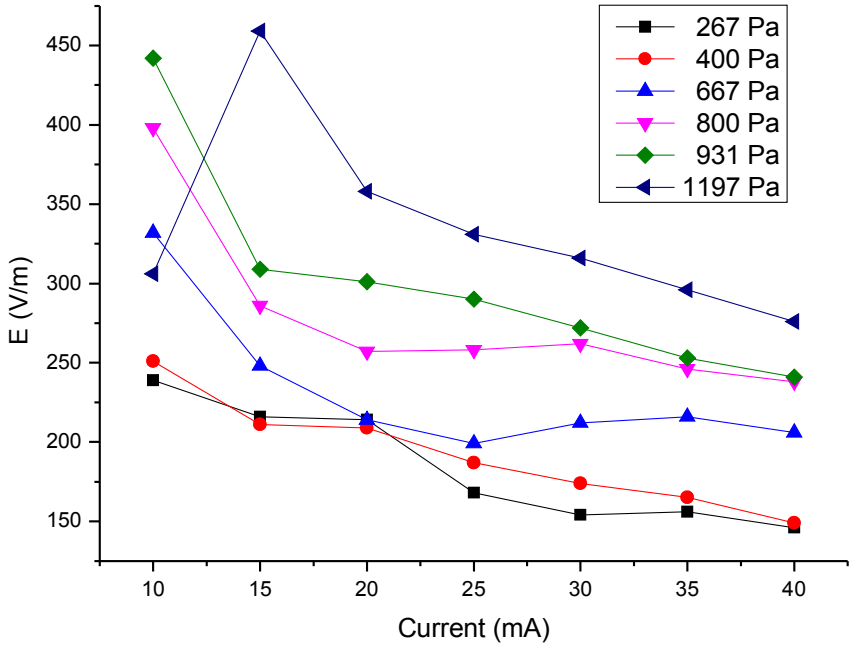


Figure 5.30 *Dependence of electric field strength E on discharge current for various pressures.*

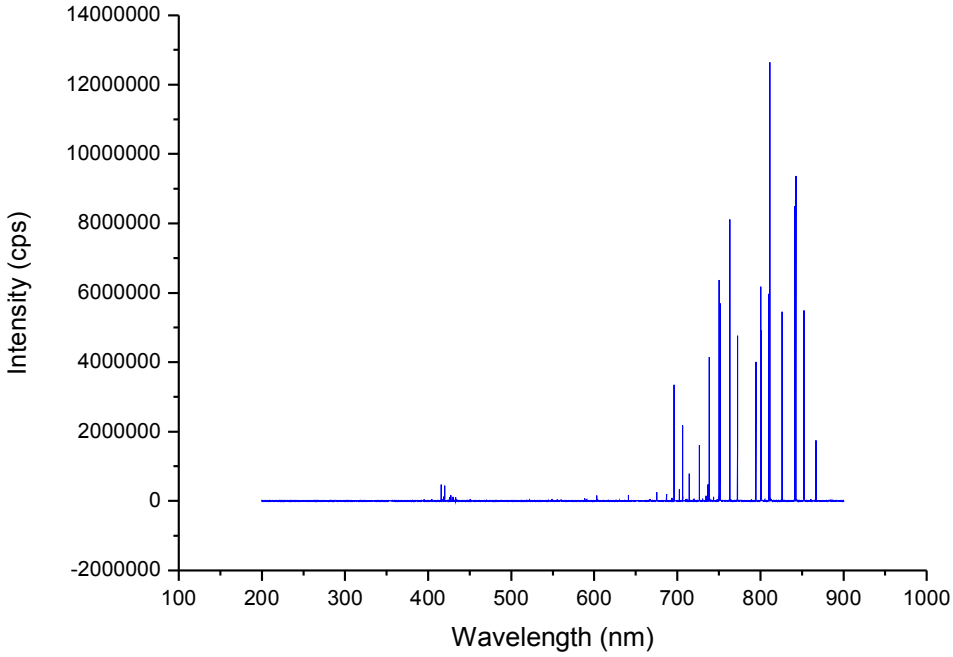


Figure 5.31 *Example of argon spectrum detected for 133 Pa and 30 mA.*

Line	Transition
706,7 nm	$4p\ ^2[3/2]\ ,\ J=2 \rightarrow 4s\ ^2[3/2]^0\ ,\ J=2$
750,4 nm	$4p\ ^2[1/2]\ ,\ J=0 \rightarrow 4s\ ^2[1/2]^0\ ,\ J=1$
763,5 nm	$4p\ ^2[3/2]\ ,\ J=2 \rightarrow 4s\ ^2[3/2]^0\ ,\ J=2$
794,8 nm	$4p\ ^2[3/2]\ ,\ J=1 \rightarrow 4s\ ^2[1/2]^0\ ,\ J=0$
800,6 nm	$4p\ ^2[3/2]\ ,\ J=2 \rightarrow 4s\ ^2[3/2]^0\ ,\ J=1$
801,5 nm	$4p\ ^2[5/2]\ ,\ J=2 \rightarrow 4s\ ^2[3/2]^0\ ,\ J=2$
810,4 nm	$4p\ ^2[3/2]\ ,\ J=1 \rightarrow 4s\ ^2[3/2]^0\ ,\ J=1$
811,5 nm	$4p\ ^2[5/2]\ ,\ J=3 \rightarrow 4s\ ^2[3/2]^0\ ,\ J=2$

Table 5.2 *Identification of argon spectra (J denotes the total electronic angular momenta for the lower and upper levels, respectively).*

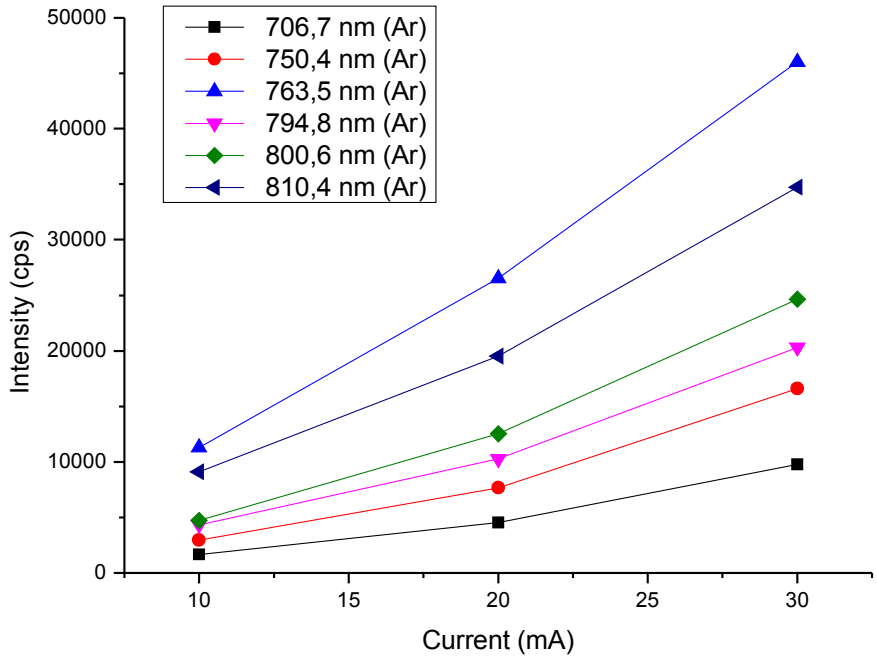


Figure 5.32 *Example of current dependence of intensities of particular neutral argon lines (1000 Pa).*

We also studied behaviour of 706,7 nm, 763,5 nm, 794,8 nm and 826,5 nm lines in two types of discharges under different experimental conditions. The linear increase with power fed to the discharge was observed as a result of more efficient excitation by electron impact [72].

5.2.2 Oxygen-argon Mixtures

The DC glow discharge in oxygen mixtures with argon was studied in for pressures up to 500 Pa, for discharge currents up to 40 mA and various Ar/O_2 ratios. The particular mixtures were prepared by introducing the admixture gas into the discharge tube up to the pressure corresponding to the demanded concentration ratio first, then the major gas was introduced up to the total studied pressure.

5.2.2.1 Electric Characterization

The variations of measured electric field strength E in dependence on pressure and discharge current for various mixture compositions are shown in Figures 5.33 and 5.34, respectively. The standard decrease of electric field strength with increasing pressure and discharge current was observed. Introduction of argon to the oxygen for Ar/O_2 ratio up to the 10 % had practically no effect on observed curves. The presence of argon in such concentrations could even caused slight increase of electric field strength, which was probably result of presence of argon instabilities. With further increase of Ar/O_2 ratio, the decrease of electric field strength can be clearly observed. This behaviour followed our previous measurements performed for 400 Pa [42].

The decrease can be explained by the replacement of the oxygen molecules by argon, which has generally lower values of E as an atomic gas. This decrease becomes more apparent with increasing pressure, which also corresponds to pressure dependence of electric field strength measured in pure argon and oxygen, respectively [73] (A.2).

From the measured values of electric field strength we can conclude, that under all experimental conditions only the H form of the positive column was present in the discharge. This observation was independent on the particular composition of the mixture.

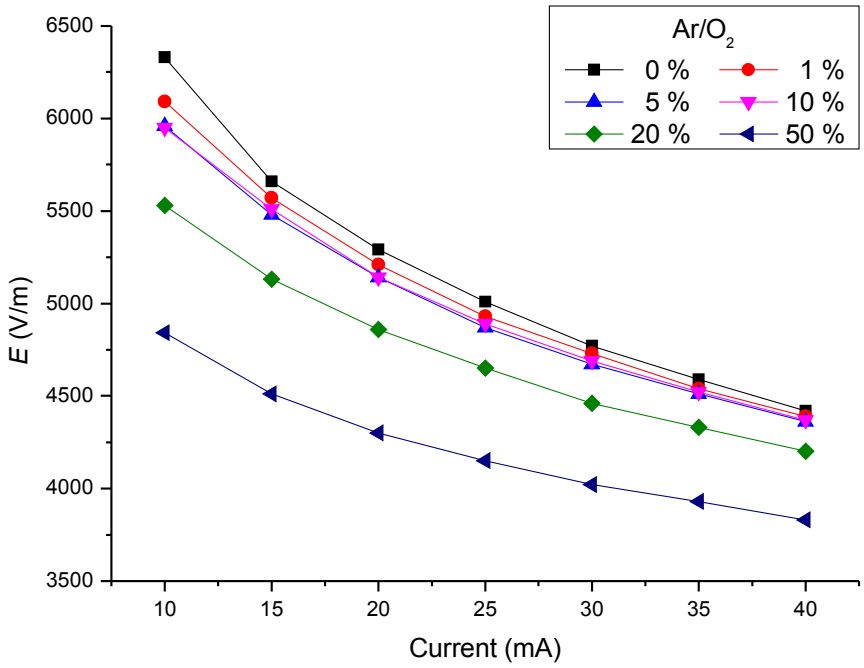


Figure 5.33 *Dependence of electric field strength E on discharge current for various Ar/O₂ mixtures (pressure 500 Pa)* [73](A.2).

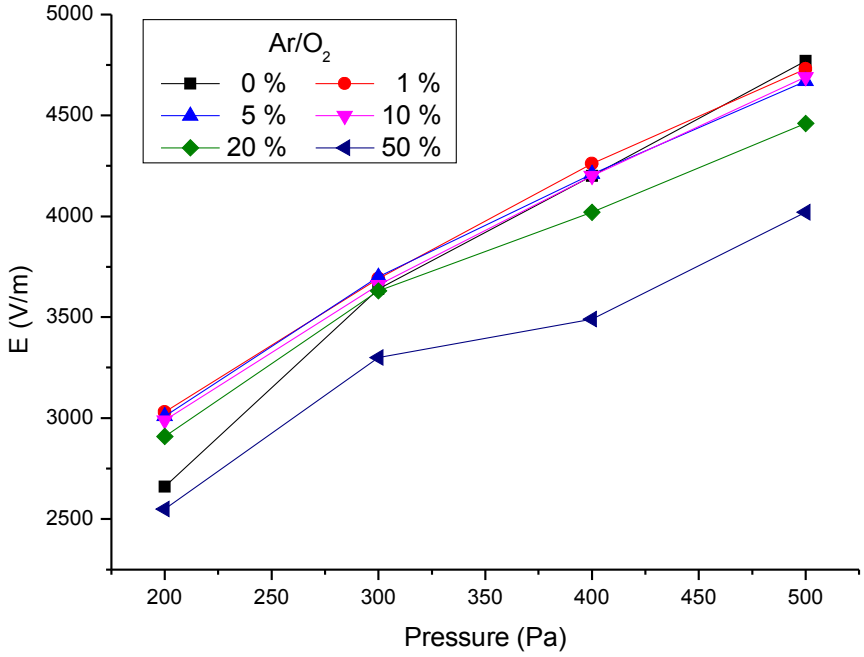


Figure 5.34 *Pressure dependence of electric field strength E for various Ar/O₂ mixtures (current 30 mA)* [73](A.2).

5.2.2.2 Emission Spectra

Considering the emission spectra, even for the smallest Ar/O_2 ratio of 1 % the argon lines were dominant in the detected spectra, which is documented by in Figure 5.35. The current dependences of particular spectral lines for the Ar/O_2 ratio of 1 % and for the two different pressures are shown in the Figure 5.36. The increase of all studied lines with the discharge current was observed. The increase can be considered as linear. Considering particular Ar/O_2 ratio, the slope of all of the curves was found to increase with increasing pressure. Moreover, the intensity of atomic oxygen lines increased more steeply both with pressure and discharge current compared to the argon lines for the particular Ar/O_2 ratio.

These effects can be explained by generally higher energy needed for excitation of upper state of argon atoms compared to the oxygen. The higher pressure corresponds to the shorter main free path for acceleration by electric field strength and therefore the excitation of argon atoms becomes more problematic.

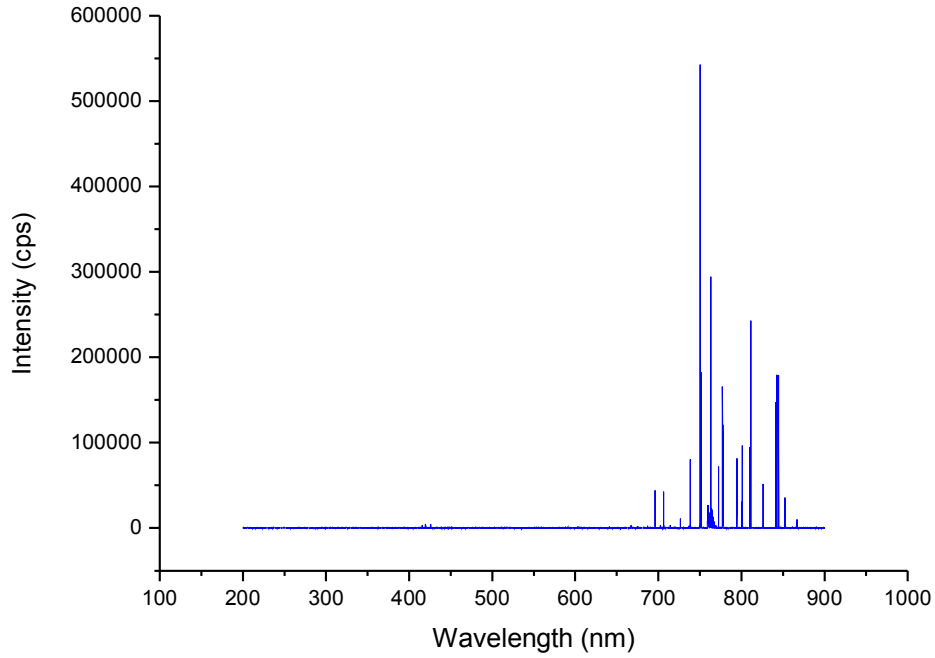
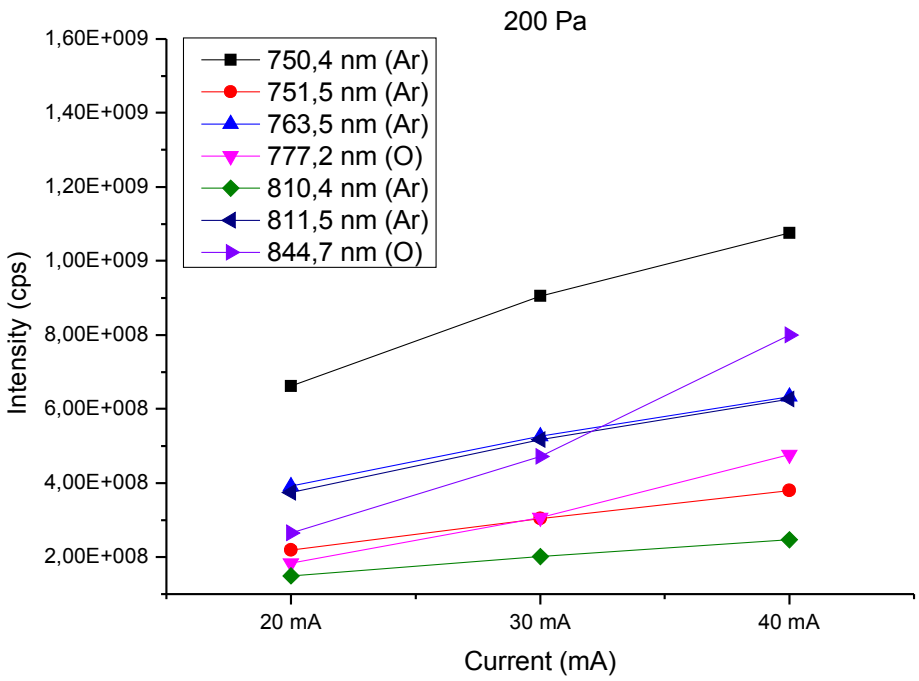


Figure 5.35 *Example of spectrum detected for 200 Pa, 30 mA and 1 % Ar in the mixture.*



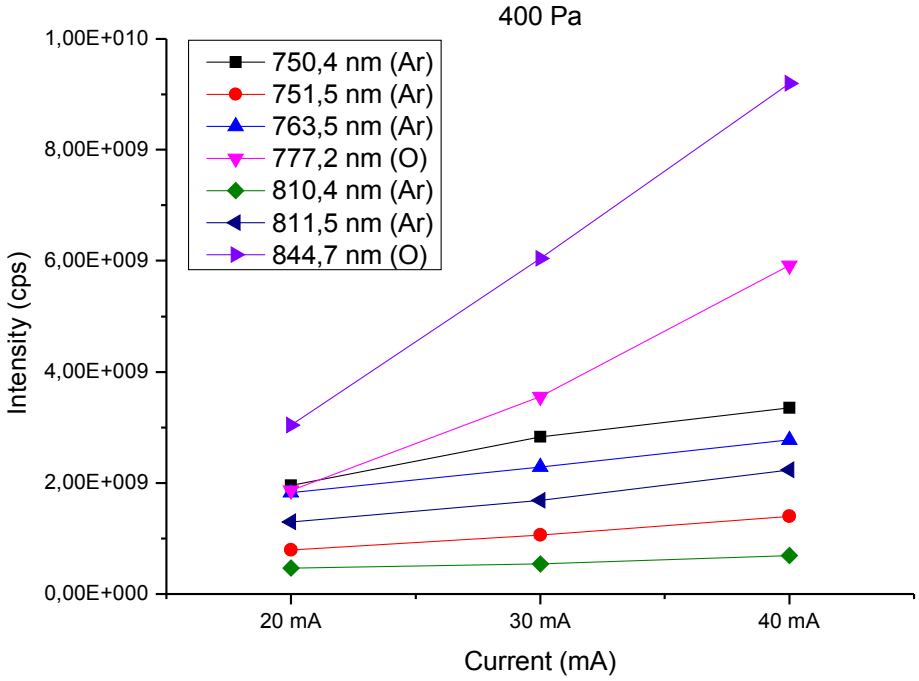


Figure 5.36 *Current dependence of particular spectral lines for Ar/O_2 = 1 % and pressures 200 and 400 Pa, respectively).*

Shorter main free path also leads to the decrease of O/O_2 ratio due to the decrease of the dissociation of oxygen molecule (as was experimentally found and described in previous chapter). This could, according to the equation E 5.3 support $O(^5P)$ excitation.

Figure 5.37 shows current dependence of the atomic oxygen line at 777,2 nm for various mixture compositions. It can be seen, that intensity of this line increases with increasing Ar/O_2 ratio in the mixture. The increase is more striking for higher discharge currents.

The variations of the intensities of the atomic oxygen lines and molecular A-band in dependence on the Ar/O_2 ratio were studied through the same normalization as for pure oxygen – we have concentrated on the mutual ratios of the both atomic oxygen lines at 777,4 nm and 844,7 nm with respect to the head of the atmospheric A-band of oxygen molecule. The results can be seen in following figures. Figures 5.38 and 5.39 show 777,2 nm/759,4 nm and 844,2 nm/759,4 nm intensity ratios, respectively, for various mixture compositions. Increase of the both ratios with increasing discharge current was observed.

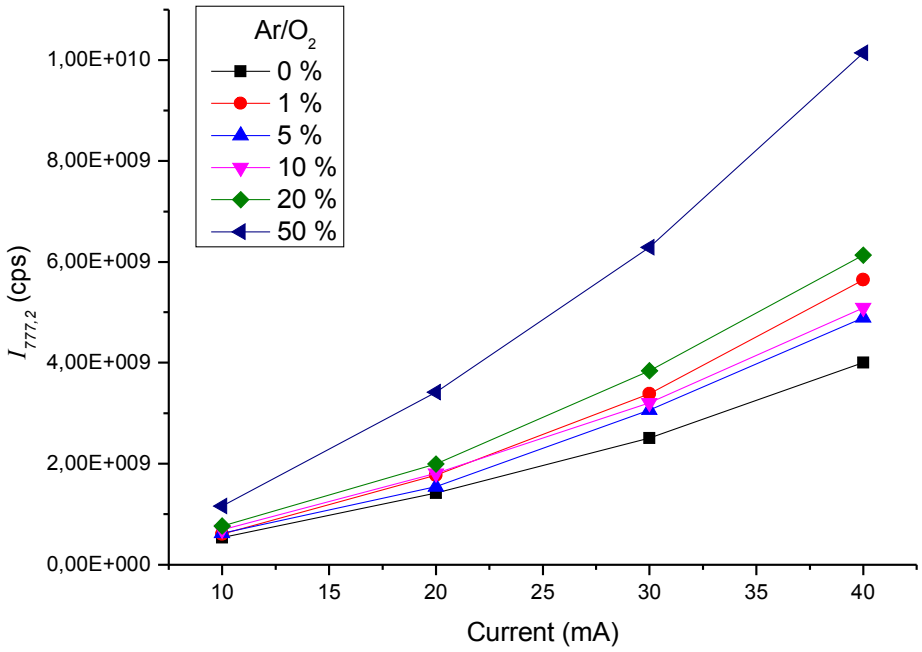


Figure 5.37 *Current dependence of intensity of 777,2 nm atomic oxygen line for various Ar/O_2 ratios (400 Pa).*

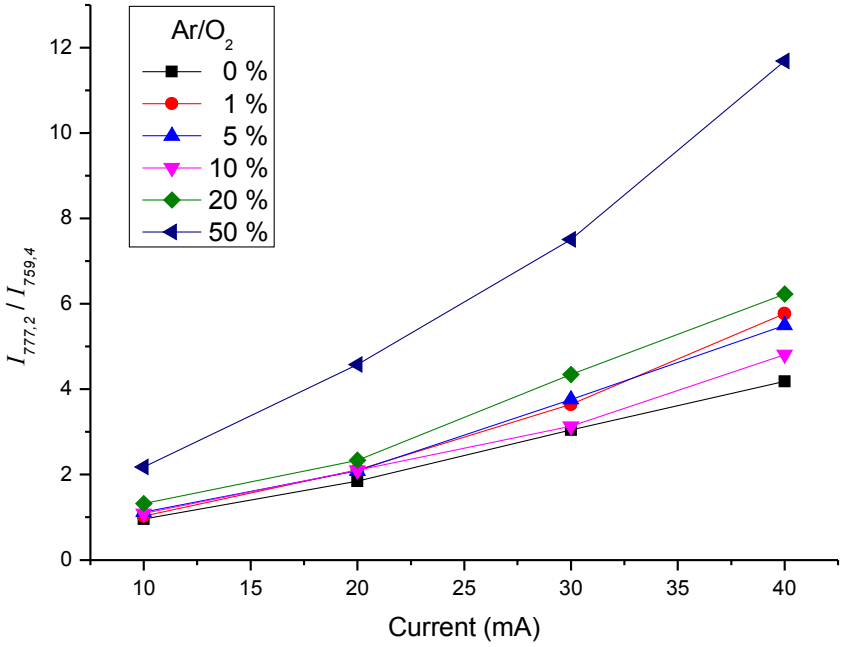


Figure 5. 38 *Current dependence of the 777,2 nm/759,4 nm intensity ratio for various Ar/O₂ ratios (400 Pa).*

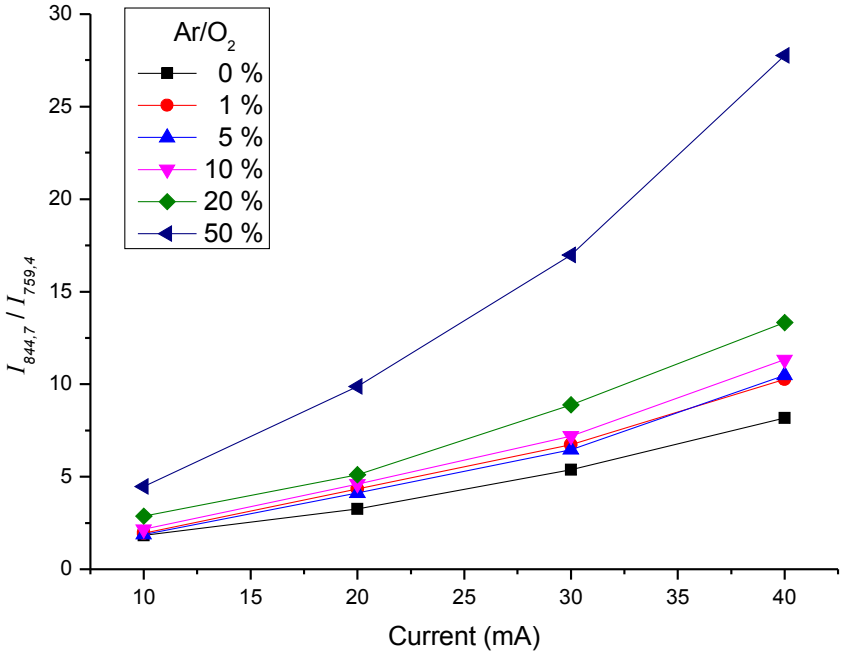


Figure 5. 39 *Comparison of the 844,7 nm/759,4 nm intensity ratio for various Ar/O₂ ratios (400 Pa).*

5.2.2.3 Rotational Temperature

We have focused on the influence of argon on the possibility of the T_{rot} determination. Considering oxygen-argon mixture, the atomic argon spectral line 763,5 nm was observed over oxygen atmospheric A-band, as can be seen in Figure 5.40. However, it did not affect those oxygen rotational lines, which are used for the rotational temperature determination, like it happens for example oxygen-nitrogen mixtures [74]. Nevertheless, the particular lines of ${}^{P}P$ and ${}^{P}Q$ branches for wavelengths above approximately 768 nm became unreadable with increasing Ar/O_2 ratio. The rotational temperature was therefore determined from rotational lines matching rotational numbers 12-20 only in these mixtures.

As can be seen in Figures 5.41 – 5.44 for particular pressures, the T_{rot} increases with the increasing discharge current in a linear way practically independently on the Ar/O_2 ratio, from which the increase with the supplied power could be concluded. This is in a good agreement with previous measurements performed for the pure oxygen case.

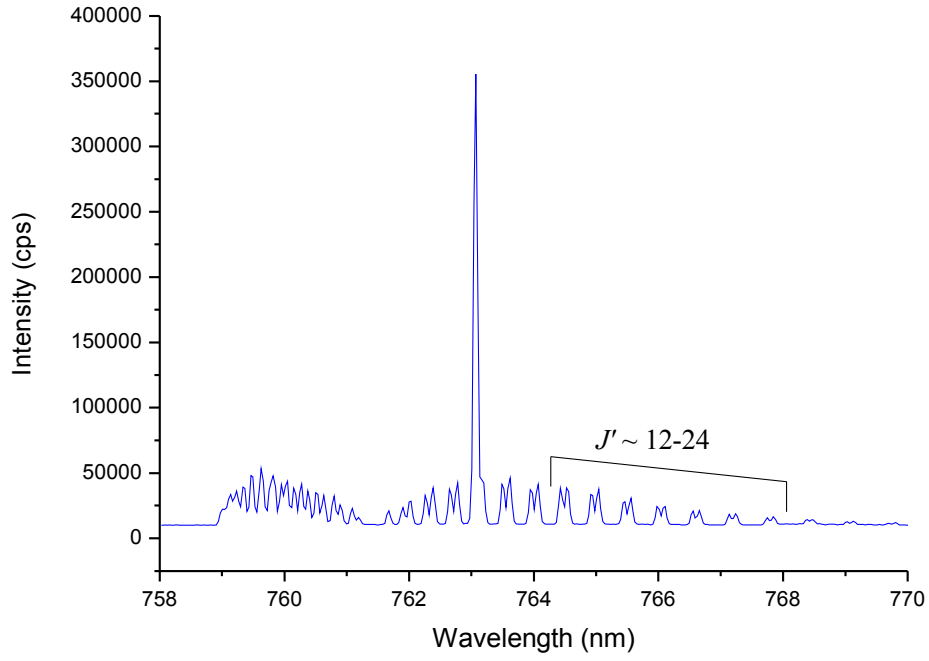


Figure 5.40: *The spectral lines of the A-band used for determination of the rotational temperature (300 Pa, 30 mA, Ar/O_2 = 20 %; J' denotes rotational number).*

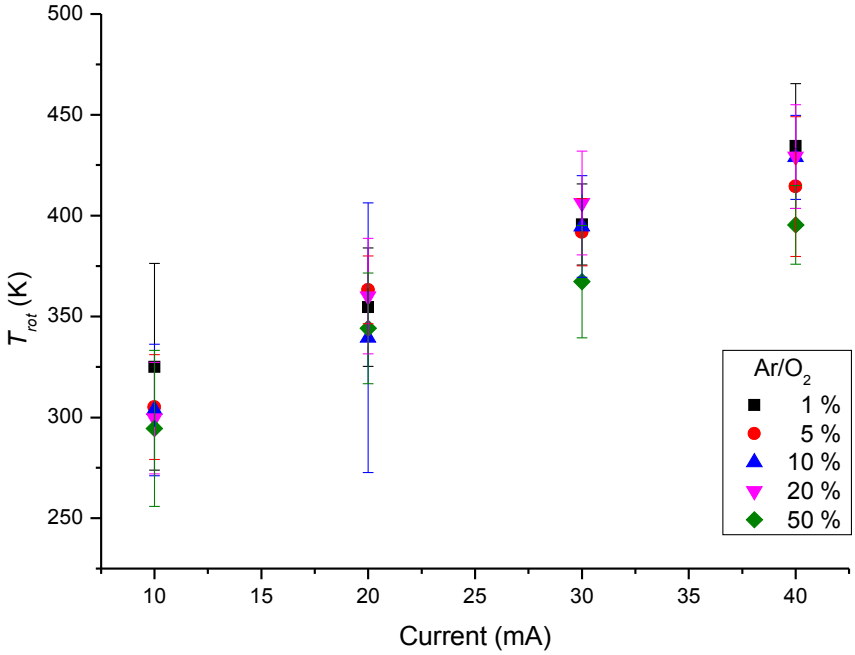


Figure 5.41: *Current dependence of the rotational temperature T_{rot} for various mixture compositions (200 Pa).*

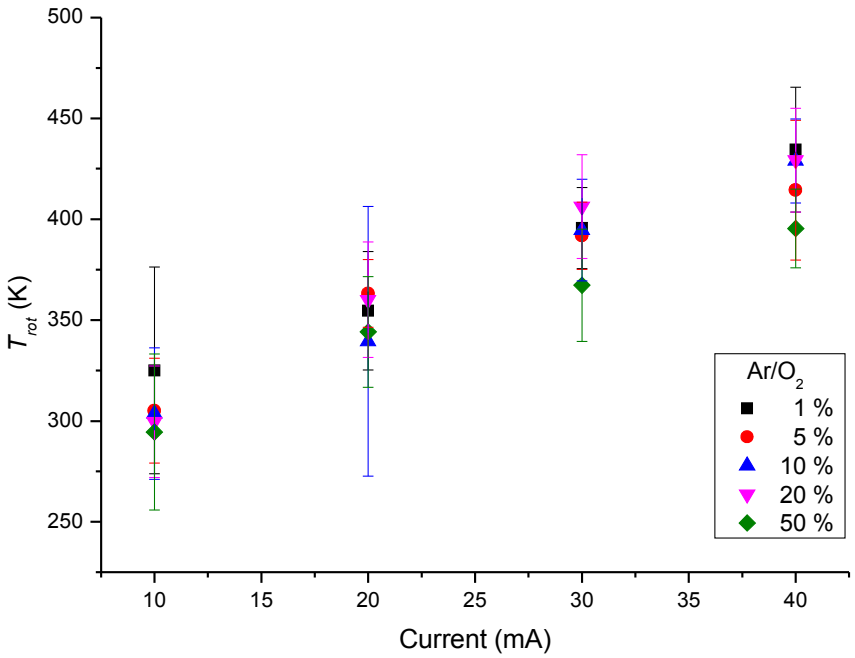


Figure 5.42: *Current dependence of the rotational temperature T_{rot} for various mixture compositions (300 Pa).*

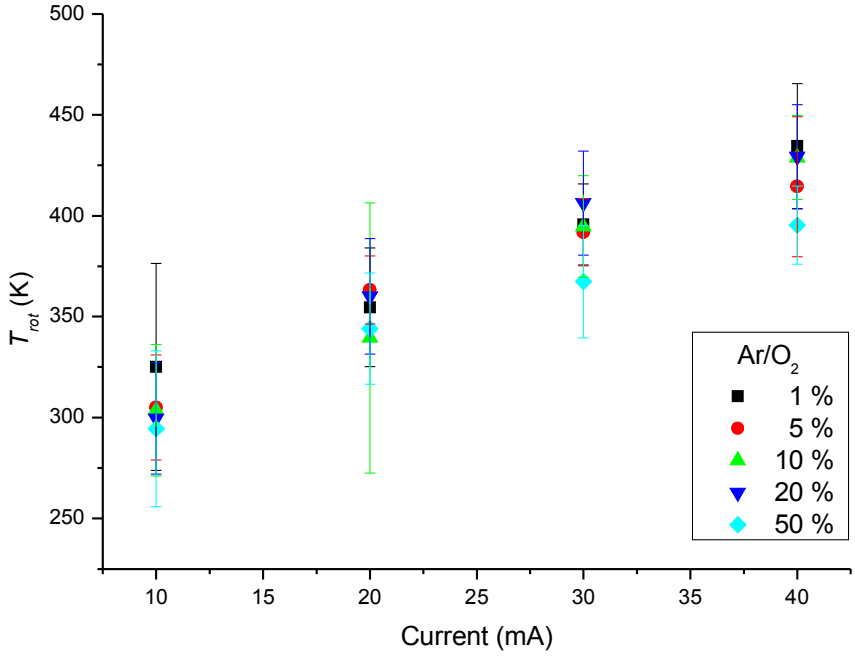


Figure 5.43: *Current dependence of the rotational temperature T_{rot} for various mixture compositions (400 Pa).*

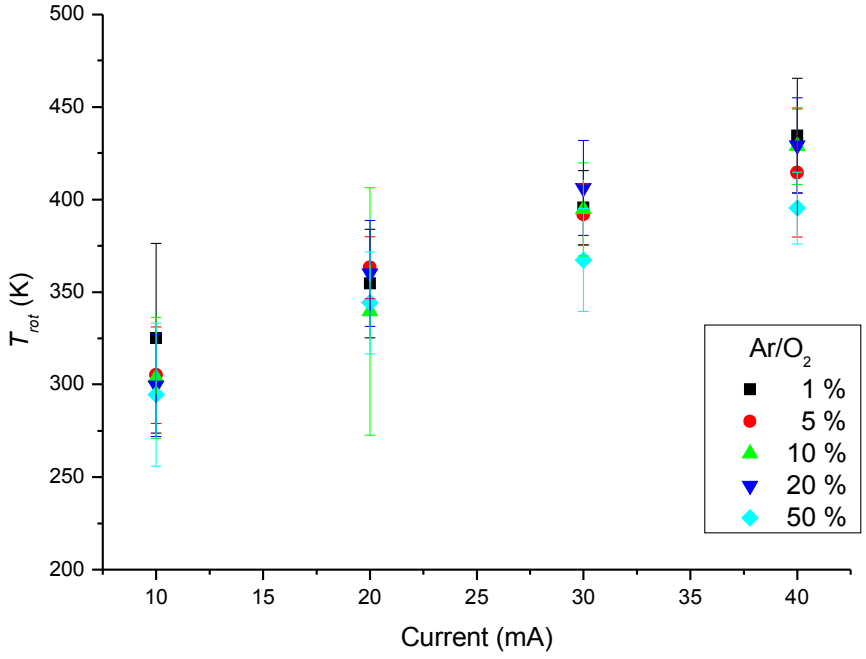


Figure 5.44: *Current dependence of the rotational temperature T_{rot} for various mixture compositions (500 Pa).*

Moreover, the rotational temperature is independent on the mixture composition within the experimental error, which was estimated as the standard deviation obtained over several measurements under the same physical conditions. Examples of such behaviour can be seen in Figures 5.45 – 5.46. This behaviour was observed for the whole range of parameters under which our measurements were taken. Addition of argon into oxygen discharge does not therefore affect rotational temperature of oxygen molecules for Ar/O_2 ratio up to 50 %. This is an important result, because T_{rot} obtained from emission spectra can now be used as a good estimation of the kinetic temperature of the oxygen particles not only in pure oxygen but even in studied oxygen mixtures with argon [73] (A.2).

Illustrative summarizing dependence of the rotational temperature T_{rot} on the on the deposited power, obtained from measurements under all studied conditions (rough data), can be seen in Figure 5.47.

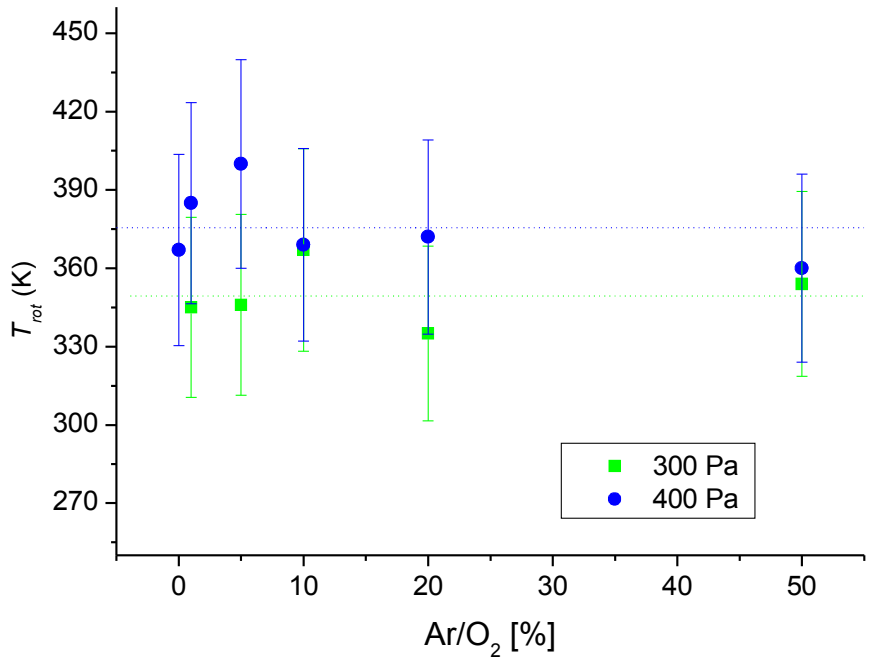


Figure 5.45: *Dependence of the rotational temperature T_{rot} on Ar/O_2 ratio (400 Pa, 20 mA)* [73] (A.2).

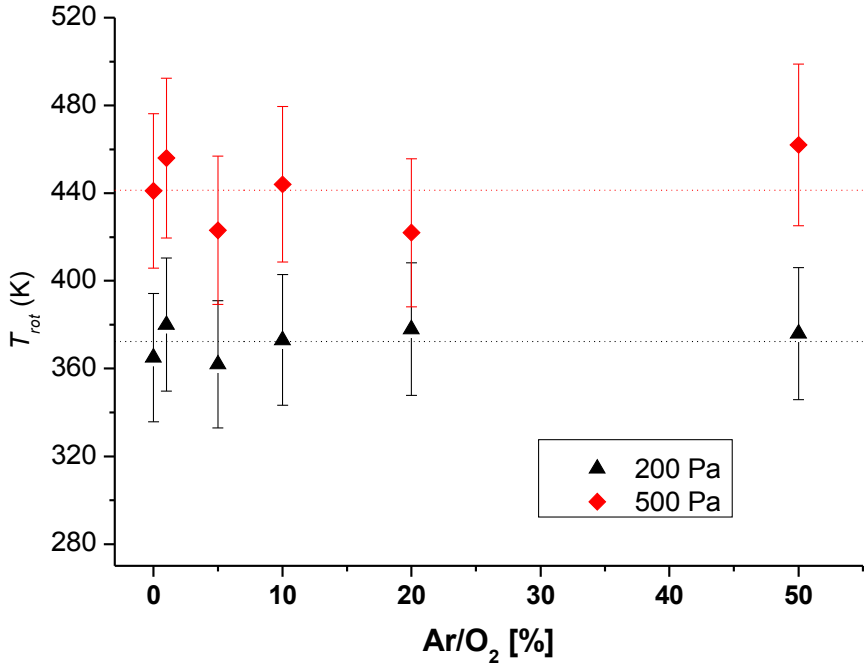


Figure 5.46: *Dependence of the rotational temperature T_{rot} on Ar/O_2 ratio (400 Pa, 40 mA)* [73] (A.2).

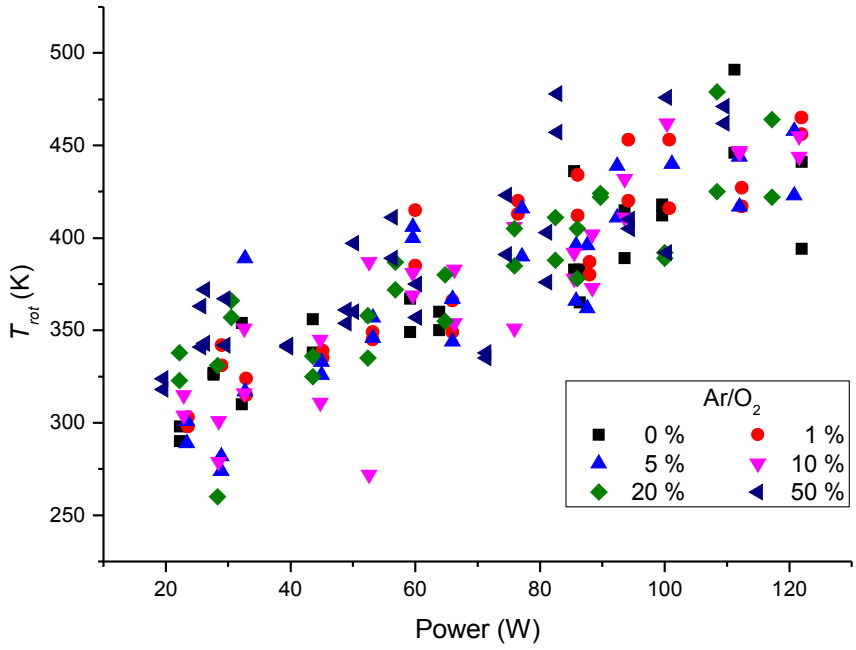


Figure 5.47: *Dependence of the rotational temperature T_{rot} on the deposited power* [73] (A.2).

5.2.2.4 Measurements in the Discharge Tube Made of Silica

Considering the oxygen-argon mixtures, the discharge sustained in the tube made of Silica was studied for the pressure 400 Pa under the same concentration ratios as in case of the Pyrex tube.

In Figure 5.48 is shown current dependence of intensity of 777,2 nm of atomic oxygen line for various Ar/O_2 mixtures. As can be seen, the atomic oxygen line increases with discharge steeply for higher Ar/O_2 ratios. This effect can be observed particularly for the discharge current 30 mA and 40 mA. Considering lower discharge currents, the observed difference for mixtures up to 10 % can be neglected. The similar behaviour was observed also for the 844,7 nm line. Also the shape of dependences of ratios of the both atomic oxygen lines and the head of the atmospheric A-band was similar, as can be seen in Figure 5.49. However, the increase of Ar/O_2 ratio has a smaller effect, especially for low discharge currents.

Comparison of experimental results obtained from measurements in the both particular discharge tubes is shown in Figures 5.50 and 5.51. Considering the dependence on the Ar/O_2 ratio, apparent increase in relative intensities of atomic lines and the head of A-band was observed with 1 % of Ar introduced into the discharge. Then it was followed with small decrease for Ar/O_2 ratio increased up to 10 % and than the relative intensities increased again. The differences in values of these intensity ratios could be observed particularly for Ar/O_2 ratios up to 10 % and they increase with increasing discharge current.

The relative intensity of both atomic lines was generally higher in the discharge tube made of Silica. This effect was for higher discharge currents.

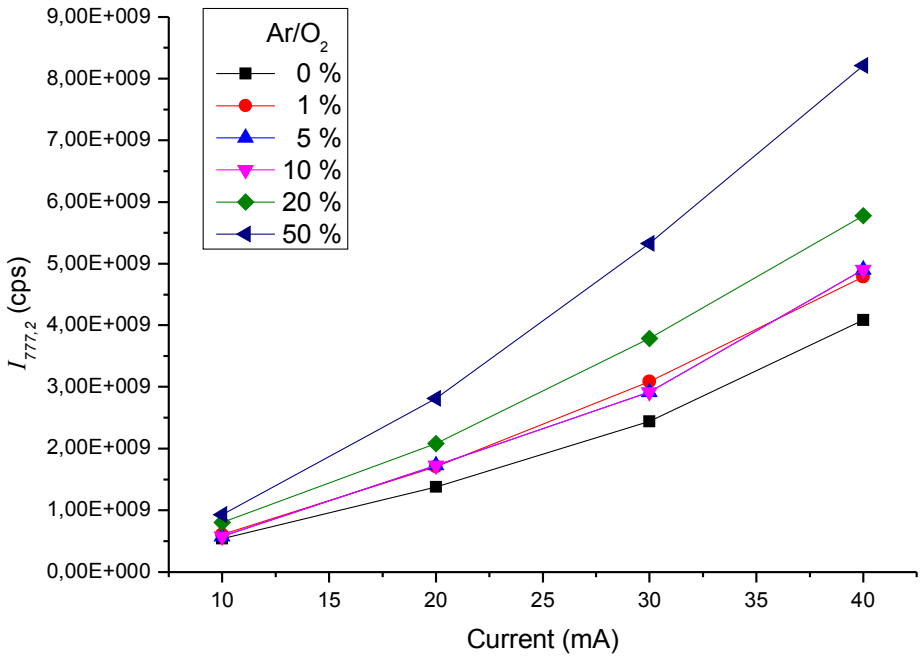


Figure 5.48 *Current dependence of intensity of 777,2 nm atomic oxygen line.*

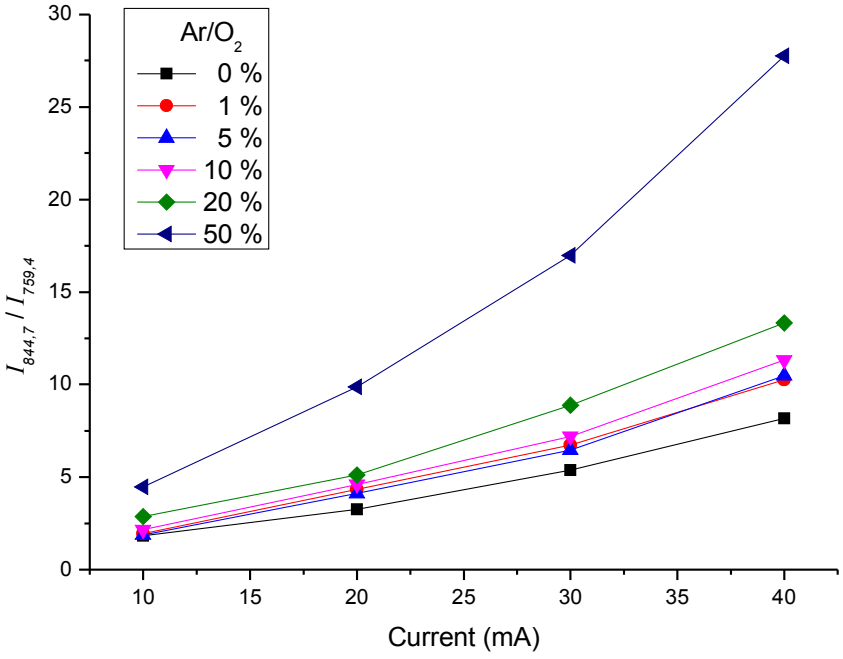


Figure 5.49 *Current dependence of the 844,7 nm/759,4 nm intensity ratio.*

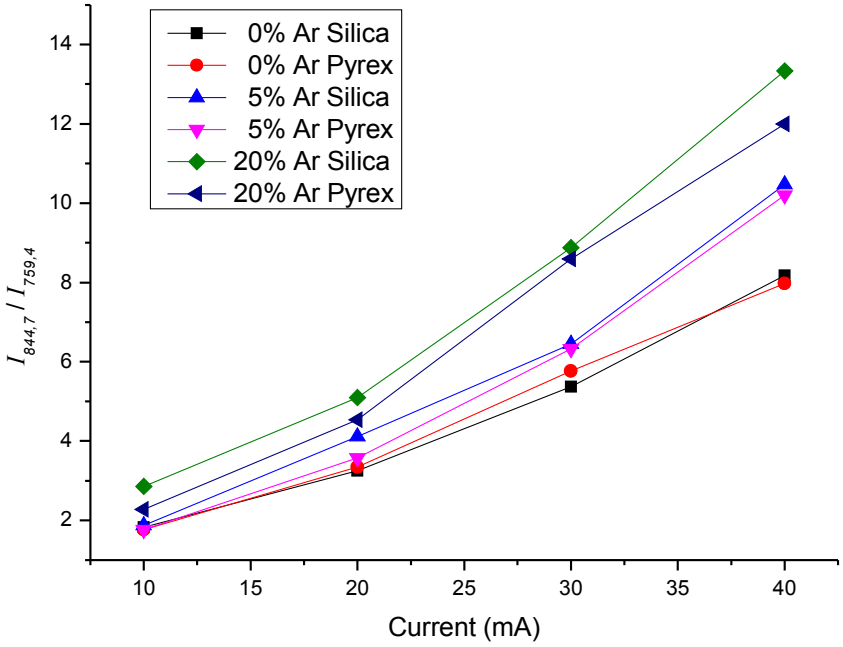


Figure 5.50 *Comparison of the of the 844,7 nm/759,4 nm intensity ratio in the both discharge tubes.*

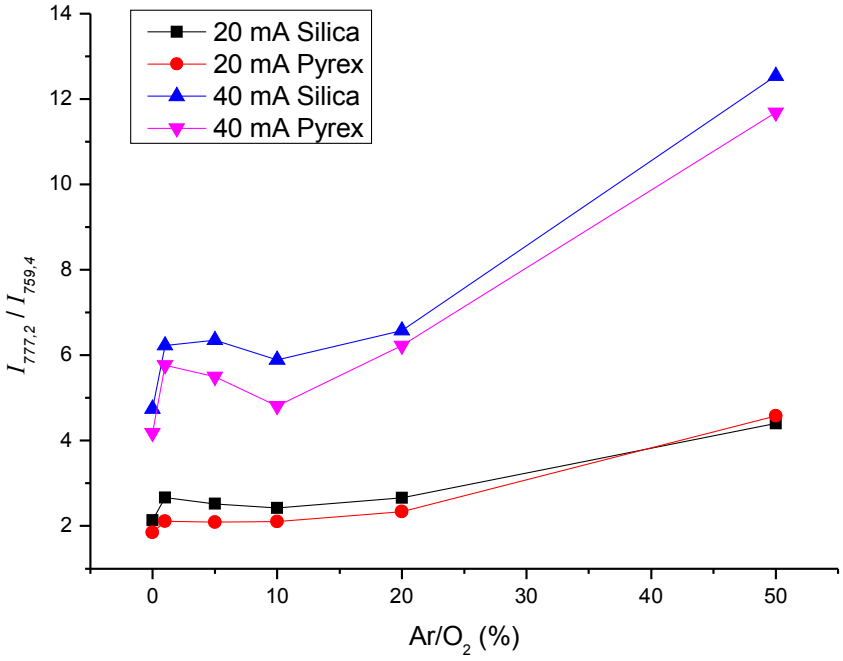


Figure 5.51 *Dependence of the 777,2 nm/759,4 nm intensity ratio on the Ar/O_2 ratio.*

6. Summary

The presented thesis brings the comprehensive and systematic study of DC glow discharge in oxygen for medium pressures up to 1750 Pa, which enables the comparison with the previous results obtained at the low pressures (up to about 300 Pa).

With respect to the objectives of the thesis, we concentrated on the study of properties of discharge plasma depending on the discharge parameters (i.e. on the pressure and discharge current) and on the material of the discharge tube (Silica or Pyrex glass).

We focused on the dissociative conditions regarding the atomic oxygen, which we studied through the relative intensities of spectral lines corresponding to the neutral atomic oxygen and band of neutral oxygen molecule, respectively. The increased dissociation was observed with decreasing pressure, increasing discharge current and by introducing argon into the oxygen.

The main focus of our work was devoted to the range of existence of the two forms of the positive column of the discharge, which are generally defined according to the values of axial electric field strength. The usage of probes for measurements of axial electric field strength itself strongly affected the range of existence of the both forms. However, we managed to obtain spectral data both for H and T forms, respectively, which can distinguish the particular form of the discharge. The ratio of studied atomic oxygen lines at 777,2 nm and 844,7 nm was found as the distinctive parameter [67] (A.4). Different behaviour of the rotational temperature in the both particular forms was also observed [73] (A.3).

For conditions, under which the positive column of the discharge was stable and consisted of the H form only, we also studied glow discharge sustained in oxygen mixtures with argon for various concentration ratios. The presence of argon systematically led to increase of relative intensities of the atomic oxygen lines.

Study of the discharge properties in two different discharge tubes showed, that the material of the wall significantly affects the value of the intensities of the spectral lines of atomic oxygen and therefore also relative intensities of atomic oxygen lines with respect to the head of molecular band. These relative intensities were generally

higher in the discharge tube made of Silica, practically independently on Ar/O_2 ratio for oxygen-argon mixtures. For the case of pure oxygen, the influence of the material was found more important for lower pressures.

Considering the existence of the H and T form of the discharge, similar spectral properties were observed in the both discharge tubes. However, the the T form started to appear at 500 Pa in the discharge tube made of Pyrex glass, while in Silica at about 650 Pa. Also the range of co-existence of the both forms was shifted to higher pressures in the Silica discharge tube.

Throughout all studied conditions, we also determined the rotational temperature T_{rot}, which approximately corresponds to the kinetic temperature of neutral particles in discharge. As it was found in the both discharge tubes, T_{rot} was increasing with increasing pressure and discharge current [66] (A.1). Moreover, T_{rot} performed the flat radial profile [67] (A.4).

Considering the Ar/O_2 mixtures, T_{rot} performed the flat profile also with respect to Ar/O_2 ratio under studied range of parameters [73] (A.2).

The obtained results were continuously presented in journals as well as in conference proceedings, the observed spectral properties of oxygen-argon mixtures are being prepared for journal presentation currently. The experimental data were also employed as the input data for the numerical study of the plasma–solid interaction in electronegative gas mixture [75] and also for kinetic model of the H-form of the positive column, which is just about to be sent for publishing.

During the final processing of the obtained experimental data, two new diagnostic methods where put in operation, which naturally bring upcoming quests regarding the studied topic – determination of the particle concentrations by the help of the absolute calibration of the spectroscopic system as well as estimation of the electron concentration by the help of toroidal resonator. These could bring new interesting insight into problem of the existence of the both forms of the positive column of the discharge.

References

[1] Coburn, J.W., Chen, M.: J. Appl. Phys. **51** (1980), 3134.

[2] DiMauro, L.F., Gottscho, R.A., Miller, T.A.: J. Appl. Phys. **56** (1984), 2007.

[3] Premachandran, V.: Appl. Phys. Lett. **58** (1991), 1600.

[4] Morimoto, T.: Jpn. J. Appl. Phys. **32** (1993), Part 1-3A, 1253.

[5] Wen-an Loong: J. Appl. Phys. **30** (1991), 7B, 1319.

[6] Musil, J., Matouš, J., Rajský, A.: Czech. J. Phys. **43** (1993), 533.

[7] Muralidhar, G.K., Mohan, R.G., Menon, A.G., Mohan, S.: Thin Solid Films **224** (1993), 137.

[8] Kylián, O., Colpo, P., Rossi, F.: Czech. J. Phys. **56** (2006), B 1250.

[9] Ceccone, G., Gilliand, D., Kylián, O., Rossi, F.: Czech. J. Phys. **56** (2006), B 672.

[10] Vasiljeva, A. N., Klopovskiy, K. S., Kovalev, A. S., Lopaev, D. V., Mankelevich, Y. A., Popov, N. A., Rakhimov, A. T., Rakhimova, T. V.: J. Phys. D: Appl. Phys. **37** (2004), 2455.

[11] Raizer, Y.P., Gas Discharge Physics (1991), Springer-Verlag Berlin Heidelberg, 122.

[12] Klotz, H.D., Drost, H., Timm, U., Schulz, W.: Ann. Phys. **472** (1966), 301.

[13] Arutunyan, G.G., Galechyan, G.A., Tavakalyan, L.B.: Beitr. Plasmaphys. **23** (1983), 271.

[14] Hrachová, V., Kylián, O., Kaňka, A.: Vacuum **76** (2004), 433.

[15] Zvoníček, V., Tálský, A.: WDS'95 Proceedings of Contributed Papers (1995) Prague, 231.

[16] Kylián, O., Hrachová, V., Kaňka, A.: Czech. J. Phys. **53** (2003), 219.

[17] Gousset, G., Touzeau, M., Vialle, M., Ferreira, C.M.: Plasma Chem. Plasma Proc. **9** (1989), 189.

[18] Gousset, G., Ferreira, C.M., Pinheiro, M., Sá, P.A., Touzeau, M., Vialle, M., Loureiro, J.: J. Phys. D: Appl. Phys. **24** (1991), 290.

[19] Sabadil, H.: Beitr. Plasmaphys. **13** (1973), 235.

[20] Amiryan, A.A., Arutunyan, G.G., Galechyan, G.G. a Tavakalyan, L.B.: Beitr. Plasmaphys. **25** (1985), 289.

[21] Ferreira, C.M., Gousset, G., Touzeau, M.: J. Phys. D: Appl. Phys. **21** (1988), 1403.

[22] Ferreira, C.M., Gousset, G.: J. Phys. D: Appl. Phys. **24** (1991), 775.

[23] Güntherschulze, A.: Zeitschrift der Physik **42** (1927), 763.

[24] Seeliger, R., Wichman, A.: Annalen der Physik **9** (1951), 235.

[25] Pearse, R.W.B., Gaydon, A.G.: *The Identification of Molecular Spectra,* Whitefriars Ltd., London, 1971.

[26] Seeliger, R.: Zeitschrift für Naturforschung **8a** (1953), 74.

[27] Pekárek, L., Šícha, M.: Czech. J. Phys. **B 10** (1960), 749.

[28] Sabadil, H.: Beitr. Plasmaphys. **6** (1966), 305.

[29] Sabadil, H.: Beitr. Plasmaphys. **8** (1968), 299.

[30] Řezáčová, V.: Czech. J. Phys. **B 20** (1970), 126.

[31] Drost, H., Timm, U., Pupke, H.: Ann. Phys. **467** (1963), 186.

[32] Keren, H., Avivi, P., Dothan, F.: Physics Letters **56A** (1976), 85.

[33] Kocian, P., Mayor, J.M.: Proceedings of 13rd ICPIG (1977), Berlin, Germany, 253.

[34] Vicharev, A.L., Ivanov, O.A., Kuzněcov, O.Ju., Stepanov, A.N.: Fizika plazmy **15** (1989), 838.

[35] Dettmer, J.W.: *Discharge Processes in the Oxygen Plasma*, PhD. Thesis, Air Force Flight Dynamics Lab., Wright-Patterson AFB, OH. School of Engineering 1978.

[36] Kaňka, A.: *Studium procesů v binární směsi s elektronegativním plynem*, PhD. Thesis, Charles university, Faculty of Mathematics and Physics, Prague, 1996 (in czech).

[37] Hrachová, V., Kaňka, A.: Vacuum **48** (1997), 689.

[38] Hrachová, V., Langr, A.: Proceedings of 18th ICPIG (1987), Swansea, Great Britain, 776.

[39] Hrachová, V.: Proceedings of 15th ICPIG (1981), Minsk, SSSR, 709.

[40] Hrachová, V.: Proceedings of 17th ICPIG (1985), Budapest, Hungary, 834.

[41] Hrachová, V., Kaňka, A., Tichý, M., Kudrna, P.: Le Vide suppl. B 291 (1999), 215.

[42] Schmiedt, L., Kaňka, A., Hrachová, V.: Czech. J. Phys. **56** (2006), B1040–B1044.

[43] Hrach, R., Hrachová, V., Vicher, M: Vacuum **76** (2004), 425.

[44] Hrach, R., Šimek, J., Hrachová, V.: Czech. J. Phys. **56** (2006), 1437.

[45] Pagnon, D., Amorin, J., Nahorny, J., Touzeau, M., Vialle, M.: J. Phys. D: Appl. Phys. **28** (1995), 1856.

[46] Cartry, G., Magne, L., Cernogora, G., Touzeau, M., Vialle, M.: Proceedings of 23rd ICPIG (1997), Toulouse, France, II-70.

[47] Klopovskiy, K.S., Lopaev, D.V., Rakhimov, A.T., Rakhimova, A.T., Smirnov, A.V.: Proceedings of 16th ESCAMPIG (2002), Grenoble, 171.

[48] Gousset, G., Touzeau, M., Vialle, M., Ferreira, C.M.: Plasma Chem. Plasma Proc. **5** (1985), 189.

[49] Gomez, S., Steen, P.G., Graham, W.G.: Appl. Phys. Lett. **81** (2002), 19.

[50] Gordiets, B., Ferreira, C.M., Nahorny, J., Pagnon, D., Touzeau, M., Vialle, M.: J. Phys. D: Appl. Phys. **29** (1996), 1021.

[51] Magne, L., Coitout, H., Cernogora, G., Gousset, G.: J. Physique III. **3** (1993), 1871.

[52] Veis, P., Cernogora, G.: Czech. J. Phys. **48** (1998), 75.

[53] Sabadil, H., Pfau, S.: Plasma Chem. Plasma Process. **5** (1985), 67.

[54] Linnett, J.W., Marsden, F.R.S., Marsden, D.G.H: Proc. R. Soc. **A234** (1956), 489.

[55] Wickramanayka, S., Hosokawa, N., Hatanka, Y.: Jpn. J. Appl. Phys. **30** (1991), 2897.

[56] Cartry, G., Magne, L., Cernogora, G.: J. Phys. D: Appl. Phys. **32** (1999), L53.

[57] Kim, Y.C., Boudart, M.: Langmuir **7** (1991), 2999.

[58] Johnson, E.O., Malter, L.: Phys. Rev. **80** (1950), 58.

[59] Touzeau, M., Vialle, M., Zellagui, A., Gousset, G., Lefebre, M., Pealat, M.: J. Phys. D: Appl. Phys. **24** (1991), 41.

[60] Kaňka, A., Hrachová, V.: Proceedings of 13th International Symposium on Plasma Chemistry– Vol. II, (Ed. C.K. Wu), 1997, Beijing, Peking University Press, pp. 517.

[61] Kaňka, A., Hrachová, V., Zicha, J., Čáp, J.: Czech J. Phys. **56** (2006), 619.

[62] Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2015). NIST Atomic Spectra Database (ver. 5.3), [Online].
Available: http://physics.nist.gov/asd [2016, May 4].
National Institute of Standards and Technology, Gaithersburg, MD.

[63] Krupenie, P.H.: J. Phys. Chem. Ref. Data **1** (1972), 423.

[64] Dreyfus, R.W., Jasinski, J.M., Walkup, R.E., Selwyn, G.S.: Pure Appl. Chem. **57** (1985), 1265.

[65] Arutunyan, G.G., Babalyants, L.P.: Contrib. Plasm. Phys. **30** (1990), 733.

[66] Schmiedt, L., Morávek, M.J., Kaňka, A., Hrachová, V.: Vacuum **84** (2009), 72–74. (A.1)

[67] Morávek, M.J., Schmiedt, L., Laca, M., Kaňka, A., Hrachová, V.: Phys. Scr. 2014 (T161): Art. No. 014056 (5 pages), 2014. (A.4)

[68] Schmiedt, L., Laca, M., Kaňka, A., Hrachová, V.: WDS'12 Proceedings of Contributed Papers (2012) Prague, Part II, 64–69.

[69] Schmiedt, L., Kylián, O., Hrachová, V., Kaňka, A.: Czech. J. Phys., **54** (2004), C816-C821.

[70] Schmiedt, L., Morávek, M.J., Kaňka, A., Hrachová, V.: Open Chem. 13 (2015), 399–403.(A.5)

[71] Schmiedt, L., Kaňka, A., Hrachová, V.: Vacuum 85 (2011), 1093–1095. (A.3)

[72] Schmiedt, L., Kaňka, A., Hrachová, V.: WDS'10 Proceedings of Contributed Papers (2010) Prague, Part II, 76.

[73] Schmiedt, L., Kaňka, A., Hrachová, V.: Vacuum **85** (2010), 489. (A.2)

[74] Schmiedt, L., Hrachová, V., Morávek M.J., Mičienka, S., Kaňka, A.: WDS'09 Proceedings of Contributed Papers (2009) Prague, Part II, 219.

[75] Hrach, R., Roučka, Š., Hrachová, V., Schmiedt, L.:Vacuum, **84** (2009), 94.

List of Abbreviations

n_e	electron density
n_-	density of O^- negative ion
n_+	density of O_2^+ positive molecular ion
J_0	Bessel function of the zero order
ρ	relative distance from the discharge tube axis
r	distance from the axis of the discharge tube
R	discharge tube radius
η	relative density of negative ions
E	electric field strength
l	mean free path of oxygen molecules
n_g	neutral O_2 molecule density
n_{e0}	electron density at the axis of the discharge tube
E/p	reduced electric field strength
p	pressure
Φ_+	flux of particles impacting the surface
Φ_-	flux of the particles reflected from the surface
γ	wall interactions probability
V_S	space potential
I_P	probe current
d	distance of the probes
I_{mn}	intensity of radiation related to the transition from the *n*-state to the *m*-state
A_{mn}	Einstein coefficient of spontaneous emission
ν_{mn}	frequency of radiation corresponding to the transition between *n* and *m* levels
$[X_n^*]$	concentration of particles X in quantum state *n*.
S_J	Hönl-London factor
E_J	energy of J quantum state
T_{rot}	rotational temperature
k	Boltzmann constant
f'	focal length
I_W	intensity of radiation corresponding to the wavelength W

Appendices

A.1 Schmiedt et al. (2009)

S**chmiedt, L.**, Morávek, M.J., Kaňka, A., Hrachová, V.: *Study of rotational temperature of oxygen DC glow discharge in Silica and Pyrex discharge tubes*, Vacuum **84** (2009), 72–74. doi: 10.1016/j.vacuum.2009.06.008.

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Study of rotational temperature of oxygen DC glow discharge in Silica and Pyrex discharge tubes

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Keywords:
Glow discharge
Oxygen
Emission spectra
Rotational temperature

A B S T R A C T

Active DC glow discharges in oxygen have been studied in Silica and Pyrex discharge tubes for medium pressures up to 550 Pa and for discharge currents up to 40 mA. Electric field strength measured by a double-probe technique was found to increase with the pressure and to decrease with the discharge current, which is typical for DC glow discharges. We have focused on the emitted radiation. The rotational temperature (T_{rot}) of molecular oxygen was determined from the ^{P}P and ^{P}Q branches of the well-resolved atmospheric A-band of molecular oxygen at 760 nm. Good agreement between values of T_{rot} obtained from particular branches was found. The increase of the rotational temperature with increasing pressure and discharge current has been observed in both discharge tubes, however, the values of rotational temperature were systematically higher in the tube made of Pyrex glass. This difference was explained by the particular thermal conductivity of the tube material.

1. Introduction

The DC glow discharge in oxygen and its mixtures in the pressure range of about hundreds of Pascals can be utilized in miscellaneous applications such as plasma etching [1] or plasma oxidation [2], thin layer deposition [3], formation of superconducting materials [4] and sterilization [5,6]. Therefore a study of properties of oxygen discharge in this pressure range is very important topic. The kinetic temperature of neutral particles is one of the important discharge parameters. This temperature governs rate constants of various processes such as diffusion or dissociation [7,8]. Direct measurement of this temperature using a thermocouple placed in the active plasma can affect the plasma or cause instability of the discharge. On the other hand, applying a thermocouple during the decay regime or measuring temperature on the wall of the working area can lead to distorted results. The possibility of using different indirect methods for kinetic temperature determination has been discussed over several years.

One of these methods is optical emission spectroscopy. This method is based on measurement of temperature determined from energy levels of rotationally excited states which are supposed to obey the Boltzmann energy distribution. This assumption can be affected by the lifetime of the excited levels used for temperature measurements which is much shorter than the collision time in low pressure discharges. Therefore, equilibrium between the rotational temperature of an excited state and the kinetic temperature must be checked first. This condition has already been discussed and verified by Touzeau et al for [9] an oxygen discharge. The rotational temperature T_{rot} is obtained from the measurable emission of the forbidden atmospheric A-band (transition $b^1\Sigma_g^+ - X^3\Sigma_g^-$), whose upper state is highly populated due to efficient creation by electron collisions and very low quenching by ground state molecules and atoms, respectively [10,11]. Detailed description of this method can be found in ref [9].

The rotational temperature T_{rot} has already been determined for a DC glow oxygen discharge for pressures up to 300 Pa [12] in our laboratory using the ^{P}P branch of the A-band. The main aim of presented contribution is to extend the pressure range to medium pressures to study the possibility of determination of rotational temperature from particular branches of the band. The possible influence of discharge tube material, i.e. Silica and Pyrex glass, on the rotational temperature will also be investigated. A study of these two materials under active DC glow discharge conditions has not been realized yet.

2. Experimental

The DC glow discharge sustained in pure oxygen has been studied by means of optical emission spectroscopy and a double-probe method. Two geometrically identical U-shaped discharge tubes (inner diameter 22 mm) made from different materials (Silica and Pyrex glass) were utilized for our measurements. The central

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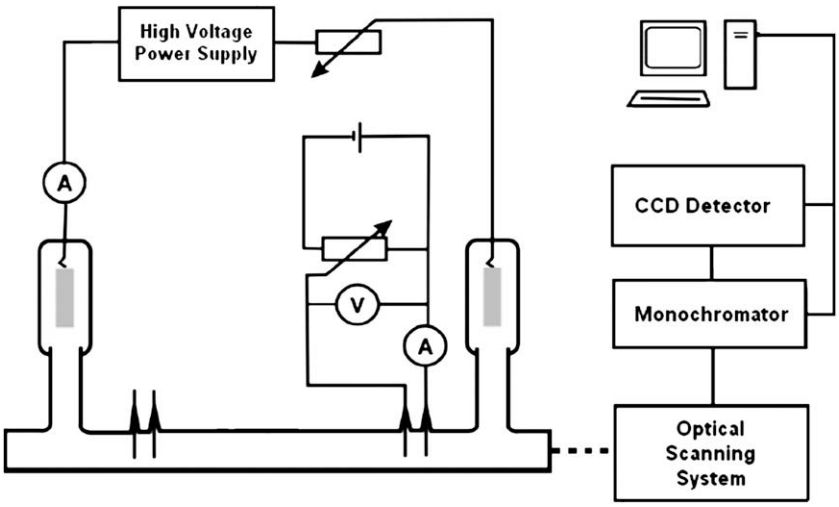

Fig. 1. Experimental set-up for optical emission spectroscopy and electric circuit for the double-probe diagnostics.

parts of the discharge tubes (length 340 mm) were equipped with head – on planar windows and two pairs of cylindrical platinum probes (length 5 mm, diameter 0.1 mm) used for measurements of electric field strength.

Spectra of emitted radiation were analysed using a monochromator (Jobin Yvon–Spex Triax 550 (focal length 550 mm)) with a plane grating (1200 grooves/mm) with spectral resolution 0.05 nm. The monochromator is equipped with an MTE CCD 1024×256-16 detector linked to the CCD 3000 controller which is connected to the PC. The CCD detector is thermo-electrically cooled by means of a Peltier couple to the typical operating temperature 245 K for reduction of electric noise. This arrangement allowed us to detect emission spectra in the range 200–1050 nm. For the Pyrex glass the limit of the spectral range was lower, i.e. 350 nm, due to its transmissive properties. The emission spectra have been recorded in the direction of the optical axis of the system as can be seen in Fig. 1.

Great attention has been devoted to the purity of the experimental system to avoid affecting plasma properties by the presence of impurities [12–15]. Discharge tubes were heated up to 420 °C before each measurement and they were pumped for several hours, using a turbomolecular pump pre-pumped by diaphragm pump. The pressure in the vacuum system, checked after this procedure by full range gauge, was better than 5×10^{-5} Pa.

Our measurements were realized in spectrally-pure oxygen from Linde (declared purity better than 10 ppm) for the pressure range 200–550 Pa and for discharge currents up to 40 mA.

3. Results

Axial electric field strength was determined by means of the double-probe method. Examples of measured values of E are shown in Fig. 2. It can be seen that the axial electric field E increases with the pressure and slightly decreases with the discharge current. This behaviour, which is typical for DC glow discharges, and also numerical values of axial electric field were found to be almost the same for both discharge tubes.

We have focused on the determination of rotational temperature T_{rot} of neutral O_2 particles from the atmospheric A-band. Good spectral resolution enabled us to distinguish particular lines around the band origin at 761.9 nm. These lines form so-called ^{P}P and ^{P}Q branches of the band [16]. Comparison of the values of T_{rot} obtained from particular bands for two different discharge currents can be seen in Fig. 3. Good agreement between values of rotational temperature obtained from both specified bands was found.

Variations of T_{rot} with changes of discharge parameters were studied too. Pressure dependence of rotational temperature

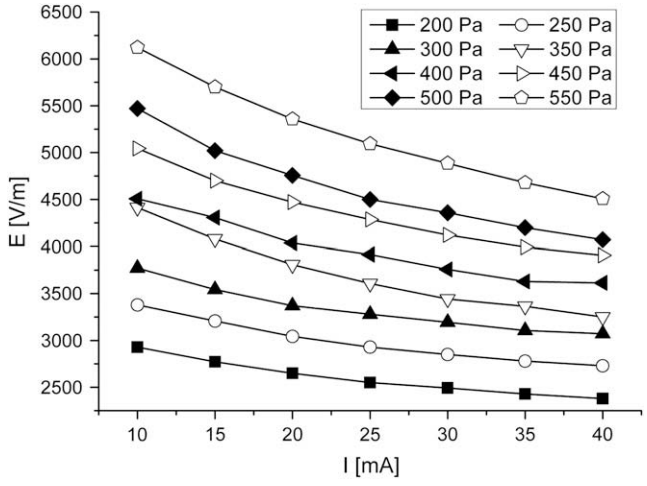

Fig. 2. Dependence of axial electric field strength E on the discharge current (Silica).

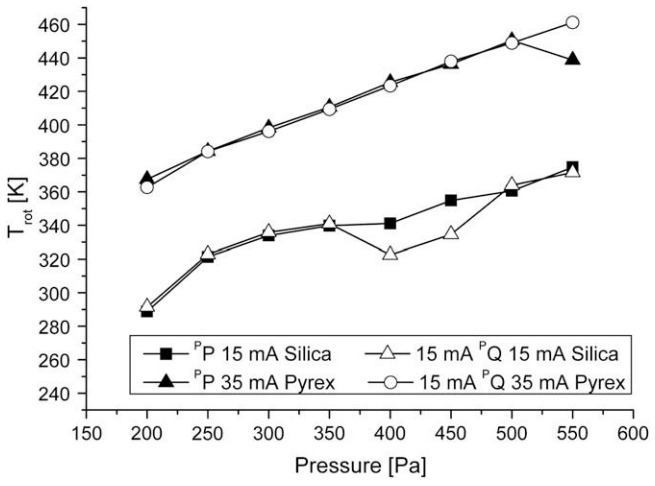

Fig. 3. Comparison of T_{rot} obtained form ^{P}P and ^{P}Q branch, respectively.

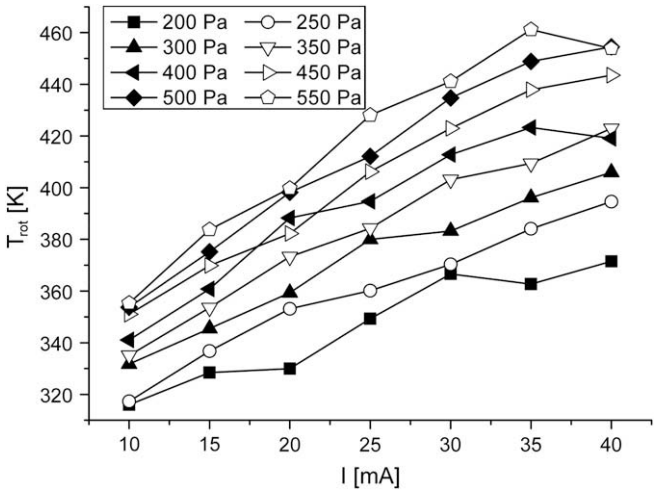

Fig. 4. Dependence of T_{rot} on the pressure and discharge current (Pyrex glass).

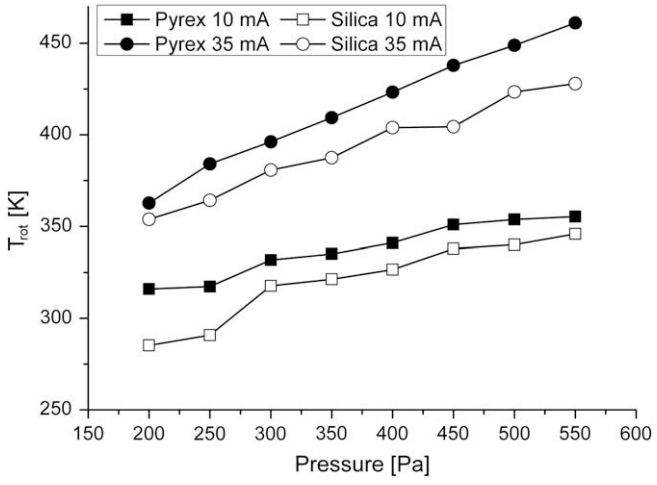

Fig. 5. Comparison of T_{rot} pressure dependence for both discharge tubes.

determined from the ^{P}Q branch of the Boltzmann plot ([9]) is shown in Fig. 4 for Pyrex glass. As can be seen, an increase in the rotational temperature T_{rot} with increasing pressure and discharge current has been observed. As similar dependence was observed in Silica. This behaviour can be explained by increasing the power fed to the discharge.

To investigate the possible effect of discharge tube material on the temperature, two different discharge tubes were used for our measurements. As can be seen in Fig. 5, the rotational temperature T_{rot} seems to be higher in the Pyrex discharge tube than for Silica. This effect was observed over the whole range of parameters for which our measurements were made. The difference could be probably explained by the different thermal conductivity of Pyrex glass (1.14 W/mK) and Silica (1.38 W/mK). For the medium pressure range studied results are similar to previous measurements for pressures 80–270 Pa [17].

4. Conclusion

An increase of the axial electric field strength E with the pressure and its slight decrease with discharge current was observed in both (Silica and Pyrex) discharge tubes. It was found that the rotational temperature T_{rot} of oxygen molecules can also be determined from the ^{P}Q branch of the well-resolved atmospheric A-band as well as from the previously used ^{P}P branch. Good agreement between values of T_{rot} obtained from these two particular branches was observed. The rotational temperature T_{rot} increased with increasing pressure and discharge current in both discharge tubes. However, the temperature seems to be higher in the Pyrex discharge tube than in the Silica. The difference is probably due to the different thermal conductivity of Pyrex and Silica.

Acknowledgments

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References

[1] Morimoto T. Jpn J Appl Phys 1993;Part 1–3A:1253.
[2] Wen-an Loong. Jpn J Appl Phys 1991;7B:1319.
[3] Musil J, Matouš J, Rajský A. Czech J Phys 1993;43:533.
[4] Muralidhar GK, Mohan RG, Menon AG, Mohan S. Thin Solid Films 1993;224:137.
[5] Kylián O, Colpo P, Rossi F. Czech J Phys 2006;56B:1250.
[6] Ceccone G, Gilliand D, Kylián O, Rossi F. Czech J Phys 2006;56B:672.
[7] Dagdigian PJ, Forch BE, Miziolek AW. Chem Phys Lett 1988;148:299.
[8] Gousset G, Ferreira CM, Pinheiro M, Sá PA, Touzeau M, Vialle M, et al. J Phys D Appl Phys 1991;24:290.
[9] Touzeau M, Vialle M, Zellagui A, Gousset G, Lefebvre M, Pealat M. J Phys D Appl Phys 1991;24:41.
[10] Lawton SA, Novick SE, Broida HP, Phelps AV. J Chem Phys 1977;66:1381.
[11] Slanger TG, Black G. J Chem Phys 1979;70:3434.
[12] Kylián O, Kaňka A, Hrachová V. Czech J Phys 2003;53:219.
[13] Zvoníček V, Tálský A. In: Proceedings of WDS'95. 1995. p. 231.
[14] Hrachová V, Kylián O, Kaňka A. Vacuum 2004;76:433.
[15] Schmiedt L. Thesis, Charles University in Prague; 2007.
[16] Herzberg G. Molecular spectra and molecular structure – I. Spectra of diatomic molecules. New York: Van Nostrand; 1957.
[17] Kylián O. Ph.D. thesis, Charles University in Prague; 2003.

A.2 Schmiedt et al. (2010)

Schmiedt, L., Kaňka, A., Hrachová, V.: *Rotational temperature of oxygen molecules in DC glow discharge in O_2–Ar mixtures sustained in discharge tube made from Pyrex glass,* Vacuum **85** (2010), 489–492. doi: 10.1016/j.vacuum.2010.01.018.

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Rotational temperature of oxygen molecules in DC glow discharge in O_2–Ar mixtures sustained in discharge tube made from Pyrex glass

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Keywords:
Glow discharge
Oxygen–argon mixtures
Emission spectra
Rotational temperature
Middle pressures

A B S T R A C T

The active DC glow discharge sustained in pure O_2 and O_2–Ar mixtures with Ar/O_2 concentration ratios up to 50% has been studied in a Pyrex discharge tube for pressures up to 500 Pa and for discharge currents up to 40 mA. The electric field strength and emission spectra parameters of the discharge were studied by means of the double-probe method and optical emission spectroscopy.

The electric field strength was found to increase with the pressure and decrease with the discharge current, which is typical for DC glow discharges. Considering O_2–Ar mixtures, the values of electric field strength decreased with Ar/O_2 ratio.

We have focused on the emitted radiation. The rotational temperature T_{rot} of molecular oxygen was determined from the well-resolved atmospheric A-band at 760 nm. The increase of the rotational temperature with increasing deposited power has been observed for all studied Ar/O_2 ratios. Moreover, it has been found that values of T_{rot} are independent of the mixture composition.

1. Introduction

The DC glow discharge in oxygen and its mixtures can be utilized in miscellaneous applications such as thin layer deposition [1], plasma etching [2] or sterilization [3]. The study of properties of such discharges is still a very important topic.

The kinetic temperature of the neutral particles is related to important discharge parameters. It governs rate constants of various processes such as dissociation or diffusion [4,5]. It is therefore a parameter required for computer modelling too. However, direct determination of this temperature is rather problematic. Therefore several indirect methods of kinetic temperature determination have been discussed over several years.

One of these methods is optical emission spectroscopy. This method is based on measurement of so-called rotational temperature determined from energy levels of rotationally excited states. The key assumption at this point is that these states obey the Boltzmann energy distribution. This method was developed and verified by Touzeau et al. [6] for the case of oxygen. The rotational temperature T_{rot} of oxygen molecules is obtained from the measurable emission of the forbidden atmospheric A-band corresponding to the transition $(b^1\Sigma_g^+, v = 0) - (X^3\Sigma_g^-, v = 0)$, which is observable as a result of the high population of its upper state due to electron collisions and very low quenching by ground state molecules and atoms, respectively [7,8]. We have discussed the possibility of the determination of T_{rot} with respect to particular branches of the A-band in our previous paper [9]. Results for two discharge tubes from different materials have been introduced.

The influence of the addition of another gas into oxygen on the rotational temperature T_{rot} of oxygen molecules is the object of our present study. Argon is one of the important technical gases which is often used in mixtures with oxygen. The main aim of this contribution is therefore to study any possible dependence of T_{rot} on the Ar/O_2 ratio in the oxygen–argon mixtures.

2. Experimental

The DC glow discharge was sustained in a U-shaped discharge tube made from Pyrex glass with inner diameter 22 mm. The central part of the discharge tube (length 340 mm) was equipped with head-on planar windows and two pairs of cylindrical platinum probes (length 5 mm, diameter 0.1 mm) used for measurements of electric field strength. The discharge was generated using a Glassman HV power supply of EQ series (0–10 kV, 0–120 mA) connected in current-controlled mode.

Spectra of emitted radiation were analysed by means of a Jobin Yvon–Spex Triax 550 (focal length 550 mm) monochromator using a plane grating (1200 grooves/mm) with maximum spectral resolution 0.024 nm for the wavelength of 546.07 nm. The monochromator is equipped with an MTE CCD 1024x256-16 detector

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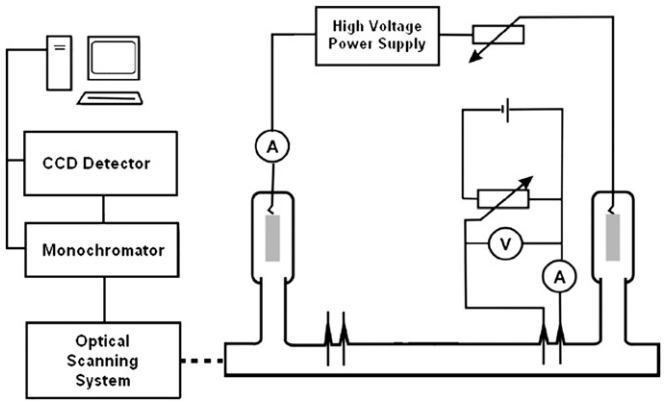

Fig. 1. Experimental set-up for optical emission spectroscopy and electric circuit for the double-probe diagnostics.

linked to the CCD 3000 controller which is connected to the PC. The CCD detector is thermo-electrically cooled by means of a Peltier couple to the typical operating temperature 245 K to reduce electrical noise. With respect to transmissive properties of Pyrex glass, this arrangement allows us to detect emission spectra in the range 350–1050 nm. The emission spectra were detected in the axial direction. The experimental set-up of our measurements is schematically shown in Fig. 1.

The rotational temperature T_{rot} of molecular oxygen was determined from a Boltzmann plot of intensities of spectral lines corresponding to the ^{P}P branch of the atmospheric A-band with rotational quantum numbers 12–24 (table of wavelengths of corresponding lines as well as molecular constants can be found in ref [6]). The lower values of the rotational numbers were not considered due to the presence of the argon line in the oxygen emission spectra. In addition, lines with higher values of rotational number could not be used due to overlapping of spectra of the A-band with emission spectra from the transition ($b^1\Sigma_g^+$, $v = 1$) – ($X^3\Sigma_g^-$, $v = 1$) [6]. The spectral sensitivity of our spectrometer was not considered because of its flat profile in the whole spectral range covering lines of the A-band (i.e. 764.5–767.8 nm).

The axial electric field strength E was determined using the double-probe method [10].

Great attention was devoted to the experimental system to avoid impurities affecting plasma properties [11–14]. The discharge tube was placed into the heating furnace (temperature in the furnace

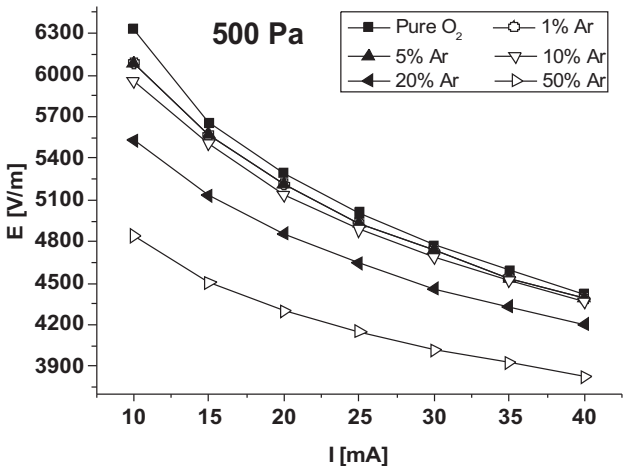

Fig. 2. Dependence of axial electric field strength E on the discharge current ($p = 500$ Pa).

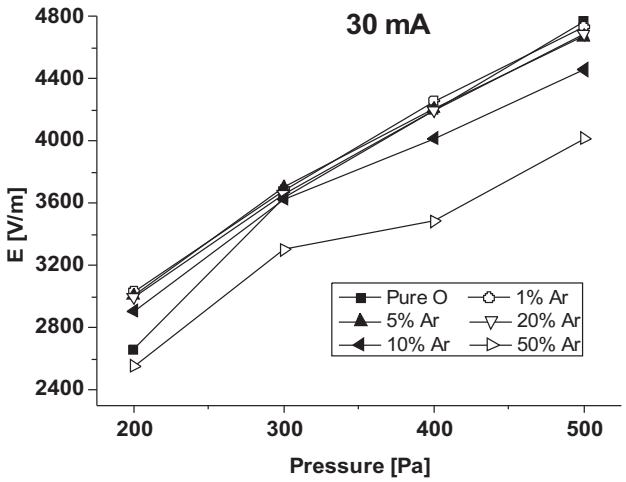

Fig. 3. Pressure dependence of axial electric field strength ($I = 30$ mA).

checked by a thermocouple was 420 °C) before each measurement and it was pumped for several hours, using a turbomolecular pump pre-pumped by diaphragm pump. The pressure in the vacuum system, checked after this procedure by a compact full range gauge PKR 261 (Pfeiffer Vacuum), was better than 5×10^{-5} Pa.

Our measurements were made in spectrally pure oxygen from Linde production (declared purity better than 10 ppm) and in oxygen–argon mixtures with Ar/O_2 ratio of 1, 5, 10, 20 and 50% in a total pressure range 200–500 Pa. The measurements were performed for discharge currents 10–40 mA.

3. Results and discussion

It has been found that the axial electric field strength decreases with increasing discharge current and increases with increasing pressure. The examples of this behaviour, which is typical for DC glow discharges, are shown in Figs. 2 and 3, respectively. As can be seen from both figures, the values of E decrease with increasing Ar/O_2 ratio. This can be explained by the replacement of the oxygen molecules by argon, which has generally lower values of E as an atomic gas.

We have focused on the determination of rotational temperature T_{rot} of neutral O_2 particles from atmospheric the A-band. The examples of the detected emission spectra with denotation of spectral range used for the estimation of T_{rot} can bee seen in Fig. 4a and b. It can be seen in Fig. 5 that T_{rot} increases with the supplied power for all studied Ar/O_2 ratios. This is in a good agreement with previous measurements obtained for the pure oxygen case. The curves for particular gas mixtures are not significantly different. The rotational temperature is therefore independent on the mixture composition within experimental error for the whole range of parameters for which our measurements were taken. This can be seen in Fig. 6a and b. Error bars in these figures correspond to standard deviation of approximately 10%. Addition of argon into the oxygen discharge does not therefore affect the rotational temperature of oxygen molecules for an Ar/O_2 ratio up to 50%. This is an important result, because T_{rot} obtained from emission spectra can now be used as a good estimation of the kinetic temperature of the oxygen particles not only in pure oxygen, but also in oxygen mixtures with argon.

The next task is to study rotational temperature in oxygen–argon mixtures with Ar/O_2 ratios over 50% and also at higher pressures,

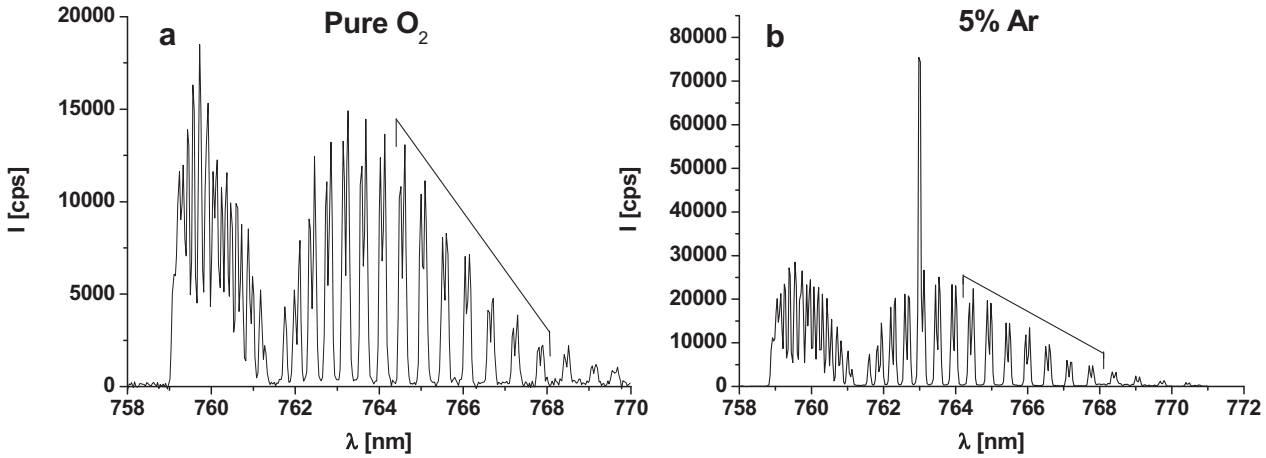

Fig. 4. (a) Atmospheric A-band ($I = 30$ mA, $p = 400$ Pa, pure oxygen). Spectral lines used for the estimation of T_{rot} (rotational quantum numbers 12–24) are denoted. (b) Atmospheric A-band ($I = 30$ mA, $p = 400$ Pa, $Ar/O_2 = 5\%$). Spectral lines used for the estimation of T_{rot} (rotational quantum numbers 12–24) are denoted.

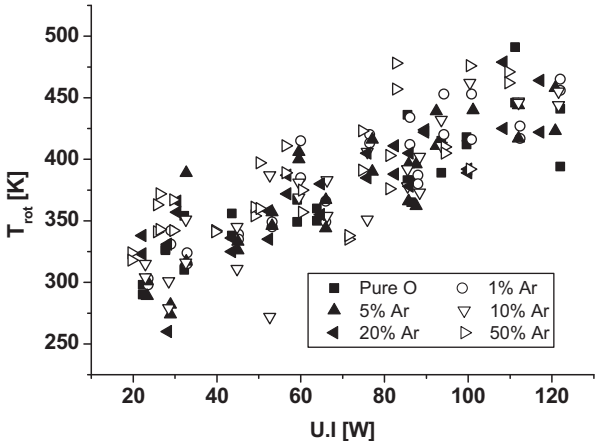

Fig. 5. Dependence of T_{rot} on the deposited power ($p = 200$–400 Pa, $I = 10$–40 mA).

where two different forms of oxygen discharge (so-called T-form and H-form) can exist (see for example ref [14,15]).

4. Conclusion

An increase of the axial electric field strength E with the pressure and its slight decrease with discharge current was observed. Values of E were found to decrease with increasing Ar/O_2 ratio as a result of replacement of oxygen molecules with the atomic gas.

It was found that the rotational temperature T_{rot} of oxygen molecules is independent of the Ar/O_2 ratio for the whole range of parameters for which our measurements were made. T_{rot} is therefore a good estimation of the kinetic temperature of oxygen particles even in oxygen–argon mixtures with Ar/O_2 ratios up to 50%. An increase of T_{rot} with the power was observed.

Acknowledgments

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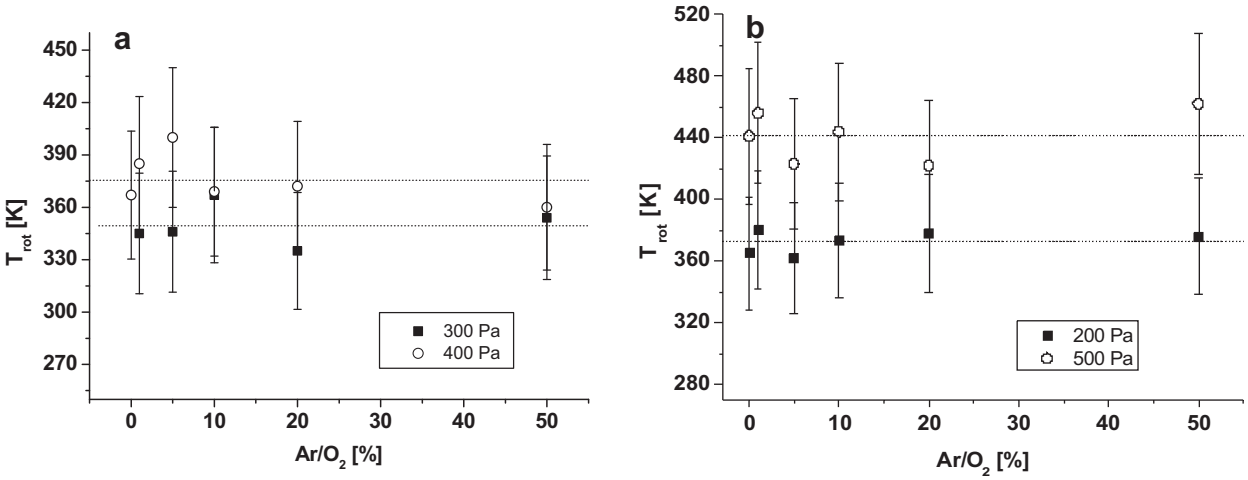

Fig. 6. (a) Dependence of T_{rot} on the Ar/O_2 ratio ($I = 20$ mA). (b) Dependence of T_{rot} on the Ar/O_2 ratio ($I = 40$ mA). Spectral lines corresponding to the ^{P}P branch of the atmospheric A-band were used.

thank for financial support of Vakuum Praha Company and to the Grant Agency of Charles University Prague, Project GAUK-18908/2008.

References

[1] Musil J, Matouš J, Rajský A. Czech J Phys 1993;43:533–40.
[2] Morimoto T. Jpn J Appl Phys 1993;(Part 1–3A):1253–8.
[3] Ceccone G, Gilliand D, Kylián O, Rossi F. Czech J Phys 2006;56B:672–7.
[4] Gousset G, Ferreira CM, Pinheiro M, Sá PA, Touzeau M, Vialle M, et al. J Phys D Appl Phys 1991;24:290–300.
[5] Dagdigian PJ, Forch BE, Miziolek AW. Chem Phys Lett 1988;148:299.
[6] Touzeau M, Vialle M, Zellagui A, Gousset G, Lefebvre M, Pealat M. J Phys D Appl Phys 1991;24:41–7.
[7] Lawton SA, Novick SE, Broida HP, Phelps AV. J Chem Phys 1977;66:1381–2.
[8] Slanger TG, Black G. J Chem Phys 1979;70:3434–8.
[9] Schmiedt L, Moravek MJ, Kaňka A, Hrachová V. Vacuum 2010;84:72–4.
[10] Raizer YP. Gas discharge physics. Berlin, Heidelberg: Springer-Verlag; 1991. pp. 122.
[11] Hrachová V, Kylián O, Kaňka A. Vacuum 2004;76:433–6.
[12] Kylián O, Kaňka A, Hrachová V. Czech J Phys 2003;53:219–27.
[13] Zvoníček V, Tálský A. In: Proceedings of Week of doctoral students '95. Charles University Prague; 1995. p. 231–6.
[14] Schmiedt L. Thesis, Charles University in Prague; 2007.
[15] Güntherschulze A. Z Physik 1927;42:763–72.

A.3 Schmiedt et al. (2011)

Schmiedt, L., Kaňka, A., Hrachová, V.: *Study of rotational temperature of oxygen molecules in H and T forms of DC glow discharge sustained in pure oxygen*, Vacuum **85** (2011), 1093–1095. doi: 10.1016/j.vacuum.2011.01.027.

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Study of rotational temperature of oxygen molecules in H and T forms of DC glow discharge sustained in pure oxygen

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ABSTRACT

The active DC glow discharge sustained in pure oxygen has been studied in a Silica discharge tube by means of optical emission spectroscopy and double-probe diagnostics for pressures 600, 750 and 1000 Pa and for discharge currents up to 40 mA. Two different forms of positive column of the discharge (high-gradient H form and low-gradient T form) were observed. Our investigation was focused on the variations of the rotational temperature T_{rot} determined from emission spectra of molecular oxygen (atmospheric A-band at 760 nm) in the dependence on the discharge current and on the pressure with respect to the existence of the two forms of the discharge. An increase of the rotational temperature with increasing discharge current has been observed. Moreover, higher values of T_{rot} were found in the H form compared with the T form.

1. Introduction

The DC glow discharge in oxygen and its mixtures is a medium of great importance. It can be utilized in many applications (e.g. plasma etching [1], sterilization [2] or thin layer deposition [3]) and therefore it is often subject of both experimental and computational studies. One of the important discharge parameters is the kinetic temperature of the neutral particles which often governs rate constants of various processes such as dissociation or diffusion [4,5]. Several indirect methods of determination of the kinetic temperature in the active discharge were discussed due to the possible problems with direct experimental determination. Considering the case of oxygen, the kinetic temperature can be simply obtained by its comparison with rotational temperature T_{rot} determined from emission spectra of the oxygen molecule [6]. We have discussed the possibility of the determination of T_{rot} with respect to particular branches of the A-band in our previous paper [7]. Recently we have also found that the rotational temperature T_{rot} of oxygen molecules remains independent of the Ar/O_2 ratio when argon is introduced into the discharge [8]. These measurements were performed for pressures up to 550 Pa.

In the present study we deal with rotational temperature determined for higher pressures up to 1000 Pa, where phenomena in two different forms of positive column of the DC glow oxygen discharge can be observed. According to the value of axial electric field strength we distinguish the high-gradient H form (axial electric field strength of about a few kVm^{-1}), which is typical for positive column in low-pressure molecular discharges, and the low-gradient T form (electric field strength of about hundreds of Vm^{-1}), which starts to appear at pressures of about a few hundreds of Pascals [9]. Both forms can also differ in other parameters [10–15] and can exist simultaneously but in different parts along the discharge tube depending on the pressure and discharge current. The main aim of our contribution is to study variations of the rotational temperature T_{rot} with respect to the existence of the two forms of the discharge.

2. Experimental

The experimental system is schematically shown in Fig. 1. The DC glow discharge was sustained in U-shaped Silica discharge tube with inner diameter 22 mm. The central part of the discharge tube (length 390 mm) was equipped with head-on planar windows and two pairs of cylindrical platinum probes (length 5 mm, diameter 0.1 mm) used for measurements of electric field strength. The discharge was generated by power supply Glassman HV of EQ series (0–10 kV, 0–120 mA) connected in current-controlled mode.

The axial electric field strength E was determined by means of a double-probe method [16]. The measurements were performed with two pairs of probes in order to compare properties of the discharge in two different parts of the discharge tube. The distance between two probes in the pair was approximately 15 mm and the distance between both pairs was approximately 21 cm.

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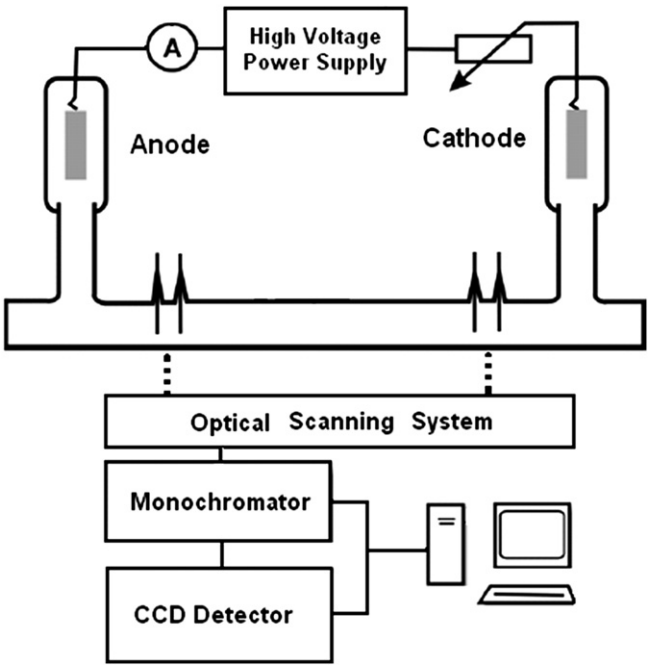

Fig. 1. Experimental set-up for optical emission spectroscopy.

The spectra of emitted radiation were analysed by a monochromator (Jobin Yvon–Spex Triax 550 (focal length 550 mm)) using a plane grating (1200 grooves/mm) with maximum spectral resolution 0.024 nm for the wavelength of 546.07 nm. The monochromator is equipped with an MTE CCD 1024 × 256-16 detector which is thermo-electrically cooled by means of a Peltier couple to the typical operating temperature of 245 K. This system allows us to detect emission spectra in the range 200–1050 nm. The emission spectra were detected in the direction perpendicular to the optical axis at two positions corresponding to the regions of the particular forms.

The experimental system was treated in the usual way to avoid affecting plasma properties by presence of impurities. The discharge tube was heated up to 420 °C and pumped for several hours before each measurement using a turbomolecular pump pre-pumped by a diaphragm pump. The ultimate pressure in our system after this procedure was better than 5×10^{-5} Pa.

Our measurements were made using spectrally pure oxygen produce by Linde (declared purity better than 10 ppm) using pressures 600, 750 and 1000 Pa and discharge currents of 10–40 mA.

3. Results and discussion

Two pairs of probes were employed to investigate the axial electric field strength E on both cathode and anode side of the discharge tube. Results are shown in Fig. 2a for cathode and Fig. 2b for the anode pair, respectively. It has been found that, for 600 Pa, only the H form was present in the discharge while, for both higher pressures, the T form was also detected. For the H form a decrease in electric field strength with increasing discharge current was found. Also values of E for a pressure of 750 Pa were higher compared with the values for 600 Pa. Both facts represent typical behaviour for a low-pressure discharge. As can be seen in Fig. 2b, the values of E in the T form does not show any obvious current dependence, which is in an agreement with our previous results [17].

The electric field strength for a pressure of 1000 Pa measured by probes on the cathode side showed interesting behaviour. The shape of the current dependence corresponds to that for the H form

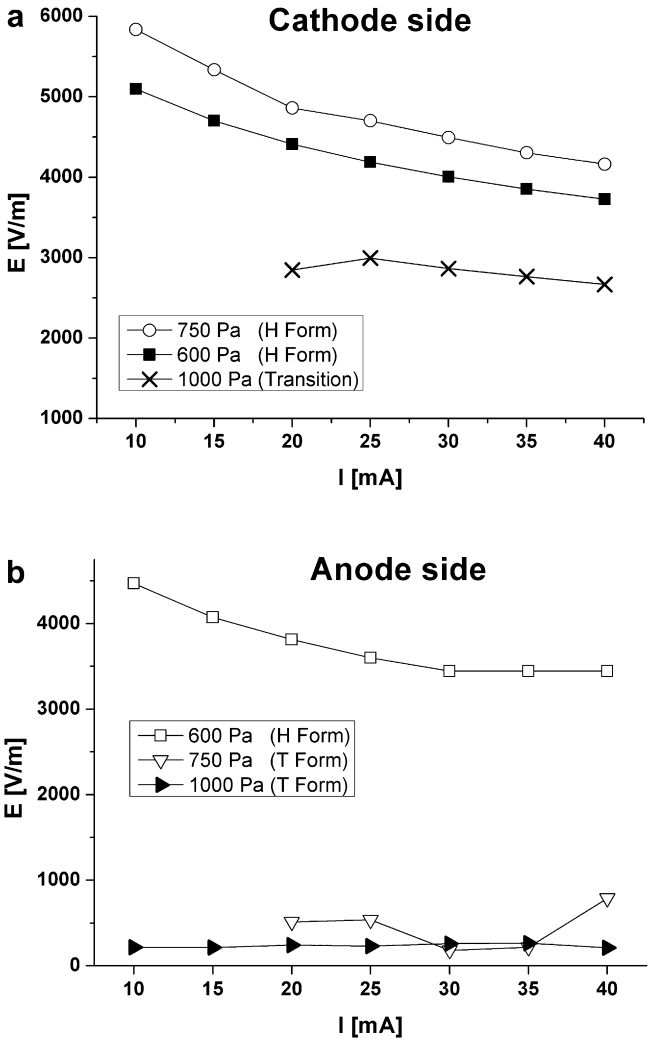

Fig. 2. a: Current dependence of axial electric field strength measured on the cathode side (H form is observed. Lower values for 1000 Pa correspond to a transition towards T form). b: Current dependence of axial electric field strength measured on the anode side (H form is observed for 600 Pa, while T form for 750 Pa and 1000 Pa).

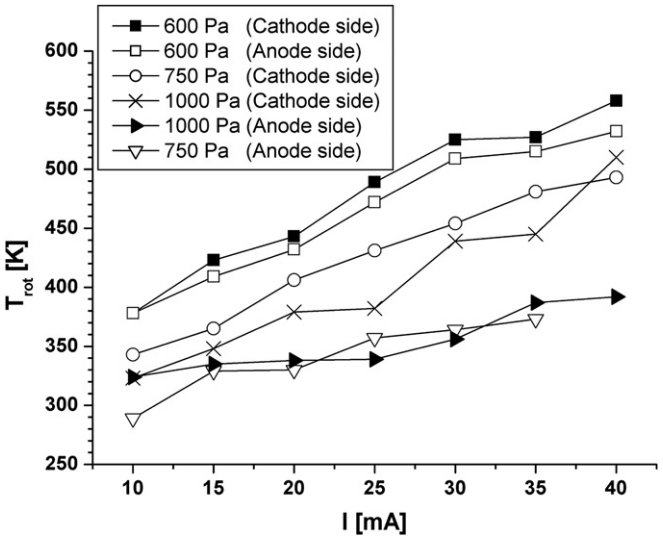

Fig. 3. Dependence of T_{rot} on the discharge current.

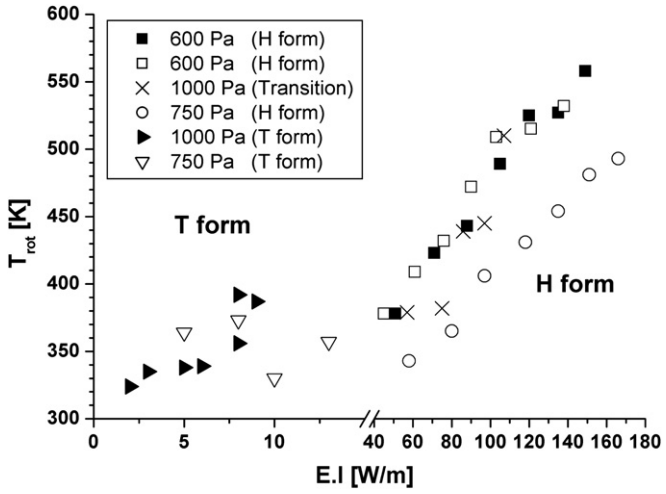

Fig. 4. Dependence of T_{rot} on the power.

as can be seen in Fig. 2b (values for 10 and 15 mA are not presented since for these discharge currents we were not able to perform E measurements due to the presence of striations around the measuring probes). On the other hand, the values of E are systematically lower compared to the case of 750 Pa and even 600 Pa. This can possibly be explained by the fact that the T form is developed in a greater volume of the discharge tube so that the pair of probes on the cathode side is measuring the electric field strength where there is a transition between both forms. More measurements will be needed to make any conclusion whether the junction between the H form and the T form is smooth or abrupt.

Our investigation was focused on the determination of rotational temperature T_{rot} of neutral O_2 particles. The temperature T_{rot} was determined from a Boltzmann plot of intensities of spectral lines corresponding to the ^{P}P branch of the atmospheric A-band with rotational quantum numbers 8–20 (a table of wavelengths of corresponding lines as well as molecular constants can be found in ref [6]).

Results are presented in Fig. 3. It can be seen that T_{rot} increases with the discharge current for all conditions under which our measurements were taken. This is in good agreement with our previous results for lower pressures. Moreover, values of the rotational temperature seem to be higher in the H form. This fact could correspond to the energy gain from the electric field strength as shown in Fig. 4, where the dependence of T_{rot} on the power supplied is presented. While a linear increase of T_{rot} with increasing $E.I$ in the H form was observed, no obvious dependence was found for the T form.

As regards the error of the estimation of the T_{rot}, on the other hand, one usually considers the standard deviation obtained from a large number of measurements, which is in our case approximately 8%. Therefore, detailed measurements will be needed for better understanding of energy dissipation in both discharge modes.

4. Conclusion

Two different forms of positive column of DC glow oxygen discharge were observed. While for pressure of 600 Pa only the usual H form was found in the whole discharge tube, for 750 and 1000 Pa T form also appeared in the anode side of the tube. Considering H form, standard decrease of the electric field strength with increasing discharge current was observed. The same dependence in T form needs to be investigated in greater details.

The increase of the rotational temperature T_{rot} of oxygen molecules with discharge current was observed for all conditions under which our experiments were performed. That is in good agreement with our previous results for lower pressures. It has also been found that T_{rot} is higher in the H form of the discharge compared to the T form. Moreover, linear increase of T_{rot} with the fed power was observed in H form.

Acknowledgements

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References

[1] Morimoto T. Jpn J Appl Phys; 1993. Part 1–3A: 1253-8.
[2] Ceccone G, Gilliand D, Kylián O, Rossi F. Czech J Phys 2006;56B:672–7.
[3] Musil J, Matouš J, Rajský A. Czech J Phys 1993;43:533–40.
[4] Gousset G, Ferreira CM, Pinheiro M, Sá PA, Touzeau M, Vialle M, et al. J Phys D Appl Phys 1991;24:290–300.
[5] Dagdigian PJ, Forch BE, Miziolek AW. Chem Phys Lett 1988;148:299.
[6] Touzeau M, Vialle M, Zellagui A, Gousset G, Lefebvre M, Pealat M. J Phys D Appl Phys 1991;24:41–7.
[7] Schmiedt L, Moravek MJ, Kaňka A, Hrachová V. Vacuum 2010;84:72–4.
[8] Schmiedt L, Kaňka A, Hrachová V. Vacuum 2010;85(4):489.
[9] Güntherschulze A. Zeitschrift der Physik 1927;42:763–72.
[10] Seeliger R. Z Naturforsch 1953;8a:74.
[11] Vicharev AL, Ivanov OA, Kuznĕcov OJ, Stepanov AN. Fizika plazmy 1989;15:838.
[12] Řezáčová V. Czech J Phys 1970;B 20:126.
[13] Keren H, Avivi P, Dothan F. Phys Lett 1976;56A:85.
[14] Kocian P, Mayor JM. Proceedings of 13rd ICPIG. Berlin, Germany; 1977, 253.
[15] Hrachová V, Langr A. Proceedings of 18th ICPIG. Swansea, Great Britain; 1987, 776.
[16] Raizer YP. Gas discharge physics. Berlin Heidelberg: Springer-Verlag; 1991. 122.
[17] Schmiedt L. Thesis, Charles University in Prague, Faculty of mathematics and physics; 2007.

A.4 Morávek et al. (2014)

Morávek, M.J., **Schmiedt, L.,** Laca, M., Kaňka, A., Hrachová, V.: *Radial profiles of the emission spectra of dc glow discharge sustained in molecular gases at medium pressures*, Phys. Scr. 2014 (T161): Art. No. 014056 (5 pages), 2014.
doi: 10.1088/0031-8949/2014/T161/014056.

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Phys. Scr. **T161** (2014) 014056 (5pp) doi:10.1088/0031-8949/2014/T161/014056

Radial profiles of the emission spectra of dc glow discharge sustained in molecular gases at medium pressures

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Abstract

The results of a study of the radial dependence of the emission spectra of the active dc glow discharge sustained in pure oxygen and in mixtures of CO_2, N_2 and He are presented. Optical emission spectroscopy has been employed to determine parameters such as rotational and vibrational temperature. Considering the CO_2–N_2–He mixtures, we were also able to determine the [CO]/[N_2] relative concentration using the method of optical emission actinometry. The dc glow discharge in pure oxygen has been studied for pressures of 200–400 Pa and for discharge currents 20 and 40 mA. The profile was found to be flat, independent of the discharge parameters and an increase in the rotational temperature with increasing pressure and discharge current was observed. The radial profile of the vibrational temperature of nitrogen in the CO_2–N_2–He mixture was flat for all studied pressures (400–1330 Pa) and all discharge currents (10–40 mA). The radial profile of the [CO] relative concentration exhibited a local maximum at approximately half the radius of the discharge tube for 400 Pa. It increased uniformly from the centre to the wall of the tube at a pressure of 1330 Pa.

Keywords: glow discharge plasma, oxygen plasma, emission spectroscopy, positive column forms

(Some figures may appear in colour only in the online journal)

1. Introduction

The dc glow discharge sustained in molecular gases and their mixtures can be utilized in many technological applications. The positive column of such discharges is a medium producing species that can play an important role as the active particles in many processes. Considering, for example, dc glow discharge in oxygen, the atomic oxygen generated in the positive column is used for plasma sterilization [1], thin layer deposition [2] or plasma etching [3]. Another important application of dc glow discharges in molecular gases is the pumping of upper energy levels in gas lasers such as a CO_2 laser, where the active medium is formed by carbon dioxide (the working gas), helium (the coolant) and nitrogen. These lasers are widely used for industrial cutting and welding as well as in medical applications, e.g. [4–6].

We have already studied the properties of dc glow discharge both in oxygen [7, 8] and CO_2 laser [9–11] mixtures. In our measurements, optical emission spectroscopy was employed to determine the plasma parameters such as rotational and vibrational temperature. The rotational temperature T_{rot} of the oxygen molecule can be determined from the atmospheric A-band of the emission spectra of the discharge. Moreover, the equilibrium of T_{rot} with the kinetic temperature of neutral particles in a dc oxygen discharge has been verified [12]. The vibrational temperature corresponds to the shape of the electron temperature dependences in the CO_2–N_2–He mixtures. Therefore, these temperatures are related to the energetic properties of the discharge. Considering the CO_2–N_2–He mixtures, we were also able to determine the [CO]/[N_2] relative concentration using the method of the optical emission actinometry with nitrogen as the actinometer [13].

All these parameters can vary radially in a positive column of dc glow discharge. The main aim of the presented contribution is to study the radial dependence of rotational and

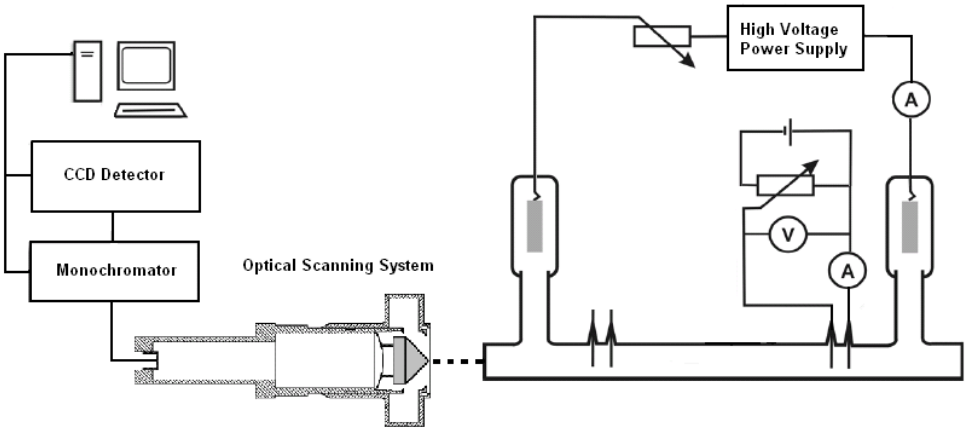

Figure 1. Experimental set-up for spectral measurements.

vibrational temperature of the discharge as well as the radial profiles of the [CO]/[N_2] relative concentration.

2. Experimental setup

The discharge space consisted of a *U*-shaped silica tube with inner diameter 22 mm. The central part of the discharge tube (length 390 mm) was equipped with two head-on planar windows and two pairs of cylindrical platinum probes (length 5 mm and diameter 0.1 mm). A schematic of the apparatus is shown in figure 1.

The emitted radiation was collected by a special radial optical system of our original construction, which focused the emitted radiation from the volume in the form of a hollow cylinder to optical fibre linked to a monochromator [14]. The monochromator (Jobin–Yvon Triax 550, focal length of 550 mm) with a plane grating (1200 grooves mm^{-1}) was equipped with an MTE CCD 1024 × 256-16 detector linked to a CCD 3000 controller connected to a PC. The CCD detector was thermo-electrically cooled by a Peltier couple to an operating temperature of 245 K. The spectral resolution was 0.024 nm at the wavelength of 546.07 nm. The spectra were collected in the range of 753–850 nm for pure oxygen and 365–594 nm for the CO_2–N_2–He mixtures.

The discharge tube was placed in an electric furnace and heated up to 420 °C (measured by a thermocouple) while being pumped before each set of measurements to avoid affecting the plasma by impurities or residual atmosphere. A turbo-molecular pump pre-pumped by a diaphragm pump was utilized. The pressure in the vacuum system checked after this procedure by a compact full-range gauge PKR 261 (Pfeiffer Vacuum) was better than 5×10^{-5} Pa. The axial electric field strength within the positive column of the discharge was measured by the double-probe compensation method [15] for all mixtures in the whole pressure and current range. Spectrally pure oxygen, carbon dioxide, nitrogen and helium produced by Linde (with a declared purity of 5.0) were used for the discharge gases. The measurements were performed for total pressures in the range of 200–400 Pa and currents of 20–40 mA for pure oxygen, and in the range of 400–1330 Pa for the CO_2–N_2–He mixtures and discharge currents of 10–40 mA.

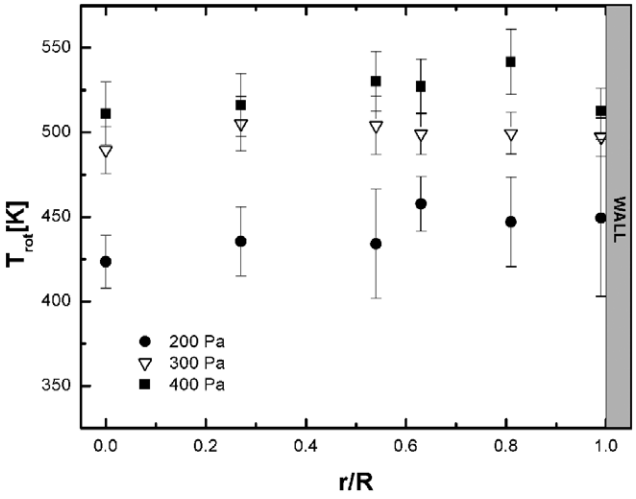

Figure 2. Normalized radial profile of the rotational temperature T_{rot} of a pure oxygen discharge.

3. Results and discussion

3.1. Pure oxygen

The rotational temperature T_{rot} of the oxygen molecules has been determined from the Boltzmann plot obtained from the ^PP branch of the well-resolved atmospheric A-band [16] for rotational quantum numbers 12–24. Details of this procedure can be found in, e.g. [12].

An example of the radial profile of the rotational temperature T_{rot} is seen in figure 2. The *x*-axis corresponds to the position of the radial scanner normalized to the radius of the discharge tube. Each position of the movable mirror is related to the radius of the circular ring, from which an optical signal is detected. Values on the *x*-axis therefore represent the ratio *r/R,* where *r* denotes the radial position and *R* the radius of the discharge tube, respectively. This normalization has already been used in our previous measurements.

As can be seen from the figure, the radial profile of T_{rot} is flat, independent of pressure. The same profile was found in the dependence on the discharge current. This confirms the previous results obtained experimentally in our laboratory. Moreover, an increase in T_{rot} with increasing pressure and

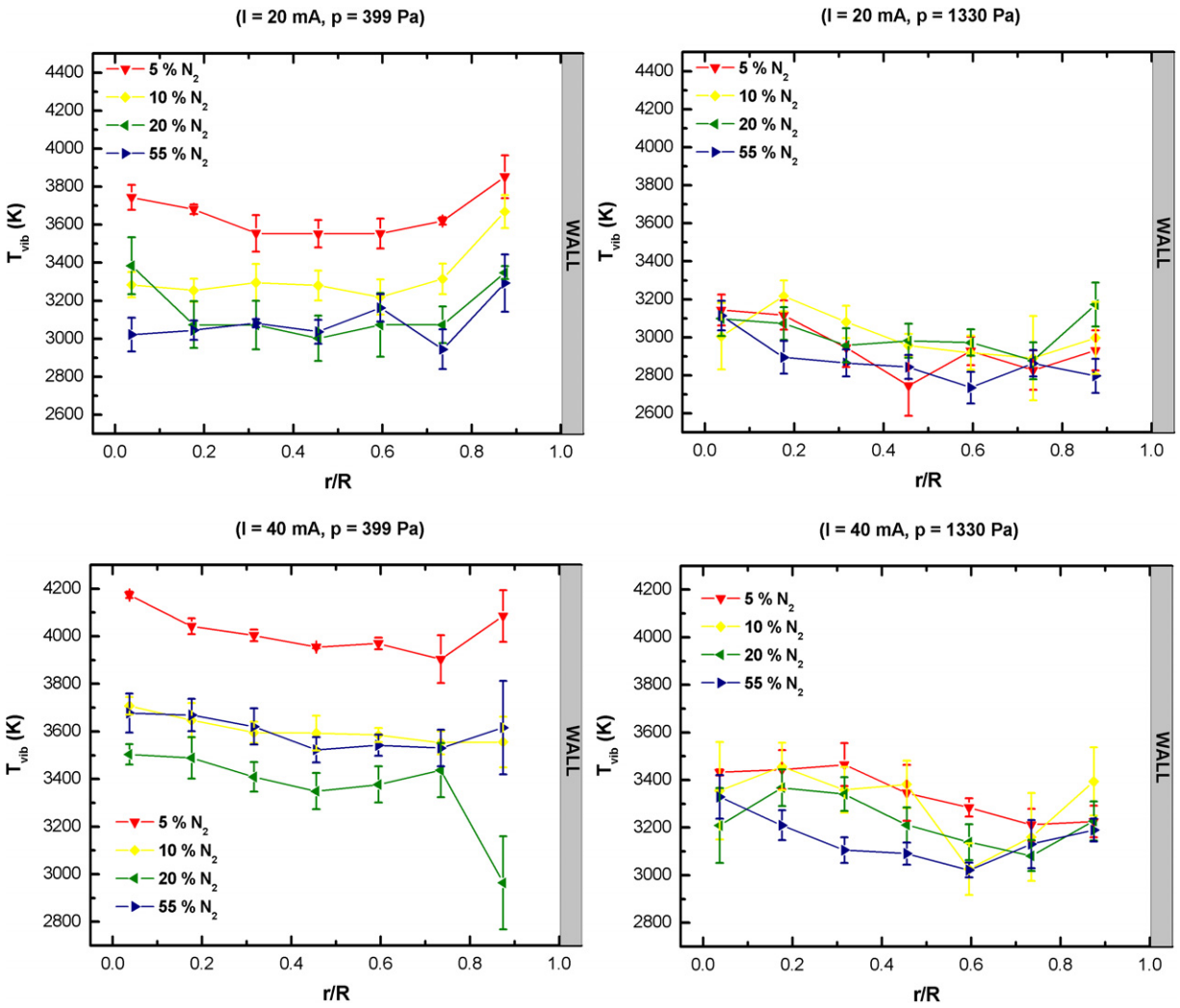

Figure 3. Normalized radial profile of the nitrogen vibrational temperature T_{vib} in CO_2–He–N_2 mixtures for various [N_2] concentrations and discharge parameters.

discharge current was observed. This behaviour can be explained by increasing the power fed to the discharge [7].

3.2. CO_2–N_2–*He mixture*

We have studied four different mixtures of carbon dioxide, nitrogen and helium. Mixtures with 6% CO_2, 20% N_2 and 74% He and 5% CO_2, 55% N_2 and 40% He, which are used in industry under the LASAL 63 and LASAL 83 trademarks, were chosen as the starting mixtures. To study the influence of the nitrogen ratio, two other mixtures, with 6% CO_2 and 10% N_2 and with 6% CO_2 and 5% N_2, were prepared and studied. The results are shown in figures 3 and 4.

The vibrational temperature of nitrogen was deduced from the spectra of the second positive band of nitrogen ($C^3\Pi_u \rightarrow B^3\Pi_0$, $\Delta v = 2$ and head at 380.5 nm). The almost flat profile of the vibrational temperature of the nitrogen molecules was observed in the whole pressure range and for all discharge currents studied. The temperature increase with an increasing discharge current and lowering pressure, which corresponds to the overall energy fed to the discharge. The difference between the mixtures was found at lower pressure, whereas it was almost not present for the high pressure. A higher vibrational temperature was observed for the mixtures with a low ratio of nitrogen. This behaviour can be explained as a consequence of the occurrence of the standing ionization waves, which appeared significant at low nitrogen ratios and low pressure. These striations caused an additional axial electric field strength in the discharge as high as a few tens of V cm^{-1} [15], which heats up the electrons. As the main source of the nitrogen vibrational energy in this type of discharge is collisions with electrons, this additional heating is transferred to the nitrogen molecules.

The profiles of concentration of carbon monoxide were derived from the intensity of the 483.5 nm line of the Ångström band of CO ($B^1\Sigma(v = 1) \rightarrow A^1\Pi(v = 1)$), compared to the 380.5 nm line of the second positive band of N_2. At low pressure, the concentration exhibited a local maximum at approximately half of the discharge tube radius, which was best seen for the mixture containing 10% N_2. However, the concentration was uniformly rising from the centre to the wall for all studied mixtures at high pressure. This can be explained as a race between two mechanisms of carbon dioxide reassociation:

$$CO + O + M \rightarrow CO_2 + M, \quad (1)$$

$$(CO)_W + (O)_W \rightarrow (CO_2)_W, \quad (2)$$

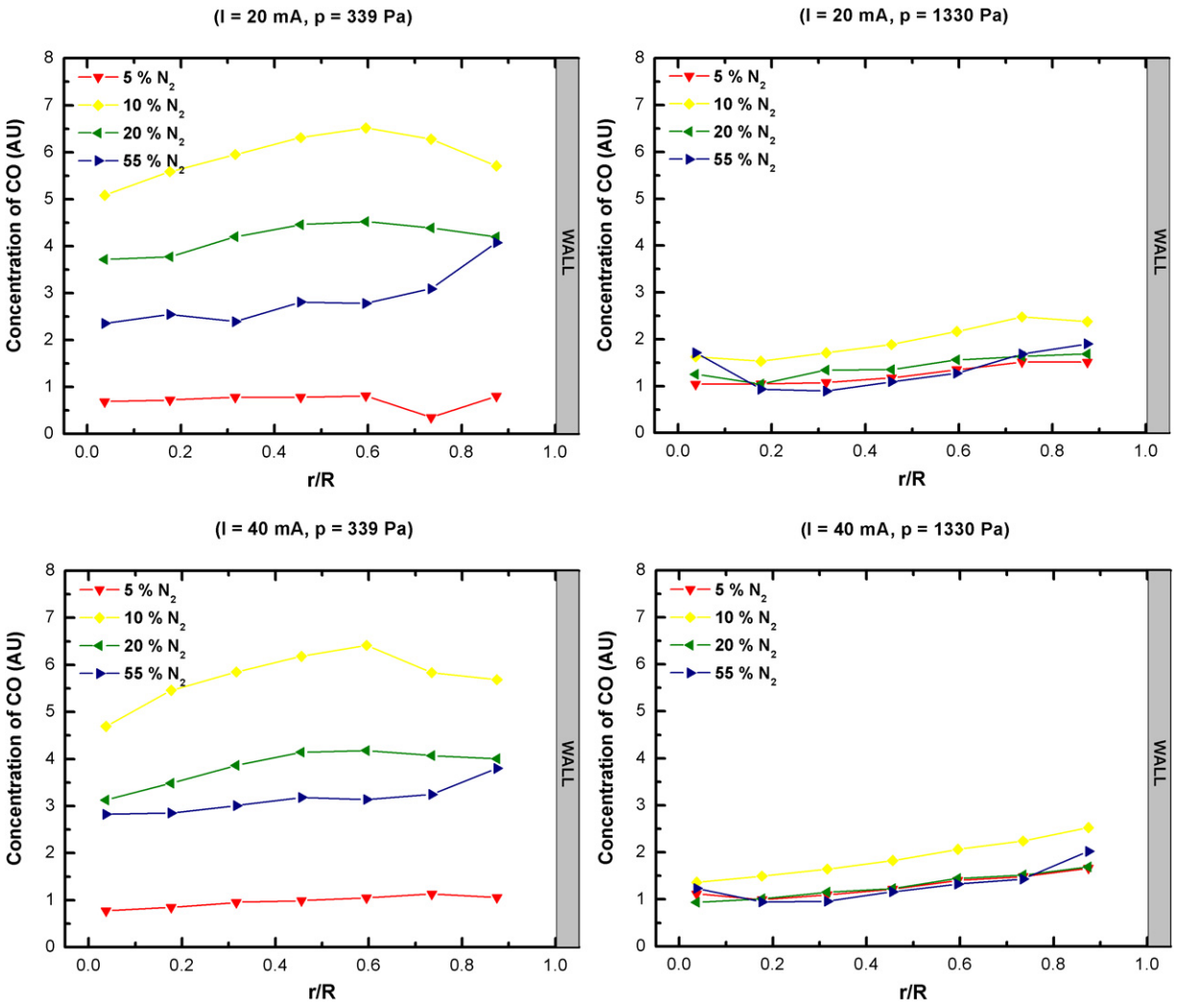

Figure 4. Normalized radial profile of the [CO] relative concentration in CO_2–He–N_2 mixtures for various [N_2] concentrations and discharge parameters.

where the 'M' is any neutral particle and '$()_W$' denotes a particle adsorbed on the wall. Process (1) occurs mainly in bulk discharge, which is why it is highly favoured at high pressures. However, our measurements show that the process (2) is still effective at pressures as high as 400 Pa.

This behaviour was best seen in the mixture with 10% N_2, because this mixture exhibited the highest rate of dissociation of the carbon dioxide molecule.

4. Conclusion

The radial profiles of the rotational temperature of oxygen molecules have been determined from the ^PP branch of the well-resolved atmospheric A-band. The profile was found to be flat, independent of the pressure and discharge current. Moreover, an increase in the rotational temperature with increasing pressure and discharge current has been observed.

The radial profile of the vibrational temperature of nitrogen was almost uniform for both studied pressures and all discharge currents. However, different values of the vibrational temperature for different nitrogen ratios in the mixture were observed. This result corresponds to the enhanced presence of striations in the positive column of the discharge.

The radial profile of the [CO] relative concentration exhibited a local maximum at approximately half of the radius of the discharge tube for 400 Pa. At the pressure of 1330 Pa, however, the [CO] relative concentration was uniformly rising from the centre to the wall of the tube for all studied mixtures. The observed behaviour can be explained by different regeneration processes of the CO_2 molecule.

Acknowledgment

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References

[1] Kylián O, Colpo P and Rossi F 2006 *Czech J. Phys.* **56** B1250
[2] Musil J, Matouš J and Rajský A 1993 *Czech J. Phys.* **43** 533
[3] Lu X Y *et al* 2003 *New Carbon Mater.* **18** 191
[4] Kostov K G *et al* 2009 *Braz. J. Phys.* **39** 322
[5] Bogaerts A *et al* 2002 *Spectrochim. Acta* B **57** 609
[6] Mathevet P *et al* 1994 *Gynecol. Oncol. Aug.* **54** 175
[7] Schmiedt L *et al* 2009 *Vacuum* **84** 72
[8] Schmiedt L, Kaňka A and Hrachová V 2010 *Vacuum* **85** 489
[9] Schmiedt L *et al* 2004 *Czech. J. Phys.* **54** C816

[10] Aftanas M, Hrachová V and Kaňka A 2006 *Czech. J. Phys.* **56** B596
[11] Moravek M J *et al* 2012 *Vacuum* **86** 780
[12] Touzeau M *et al* 1991 *J. Phys. D: Appl. Phys.* **24** 41
[13] Coburn J W and Chen M 1980 *J. Appl. Phys.* **51** 3134
[14] Kaňka A *et al* 2006 *Czech. J. Phys.* **56** 619
[15] Raizer J P 1991 *Gas Discharge Physics* (Berlin: Springer)
[16] Herzberg G 1957 *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules* (New York: Van Nostrand) p 166

A.5 Schmiedt et al. (2015)

Schmiedt, L., Morávek, M.J., Kaňka, A., Hrachová, V.: *T- and H- forms of dc oxygen discharge at medium pressures: spectroscopic study*, Open Chem. **13 (**2015**),** 399–403. doi:10.1515/chem-2015-0050.

Open Chem., 2015; 13: 399–403

Research Article **Open Access**

Lukáš Schmiedt*, Matěj Jan Morávek, Adolf Kaňka, Věra Hrachová

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 Trot 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_{rot}, determined from the emission spectra of oxygen molecules, with respect to both particular forms [12]. T_{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 $[O^{\cdot}]$

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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 5.10^{-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

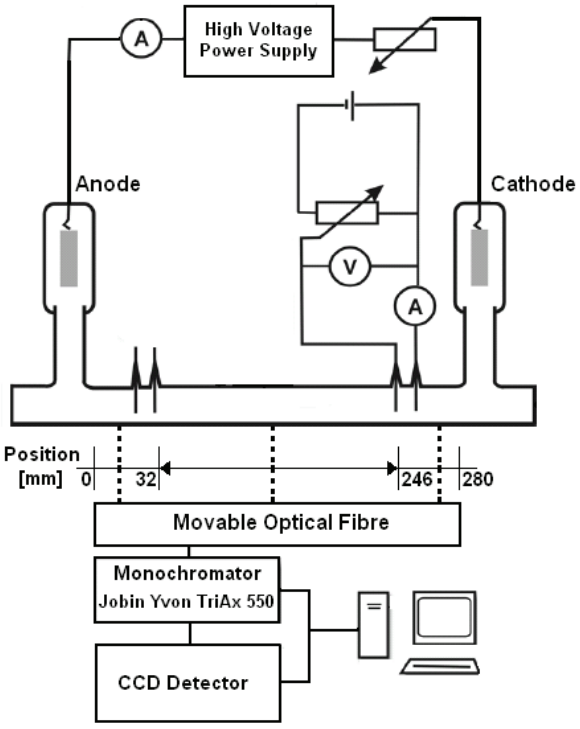

Figure 1: Experimental setup for both electric and spectroscopic measurements.

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 $3p^5P \rightarrow 3s^5S^0$) 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}/I_{845} 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

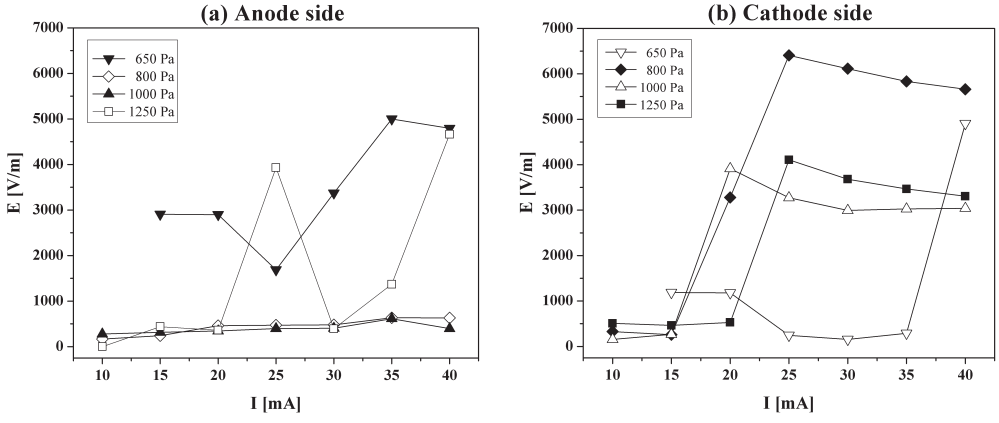

Figure 2: Axial electric field strength measured both on anode (a) and cathode (b) pairs of probes with respect to pressure and discharge current. Low-gradient T-form appeared for higher pressures and lower discharge currents. Values for p = 1250 Pa may be unreliable due to presence of striations.

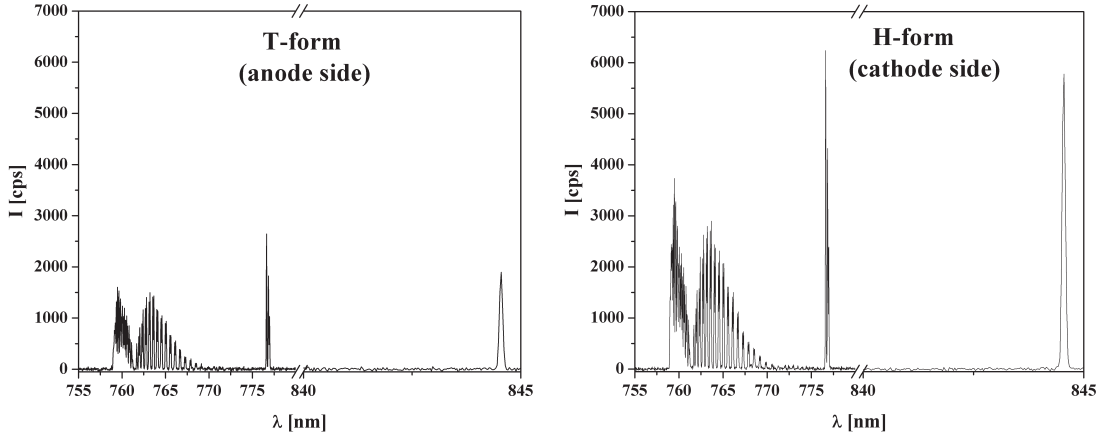

Figure 3: Examples of the emission spectra of both forms (p=650 Pa, I=20 mA).

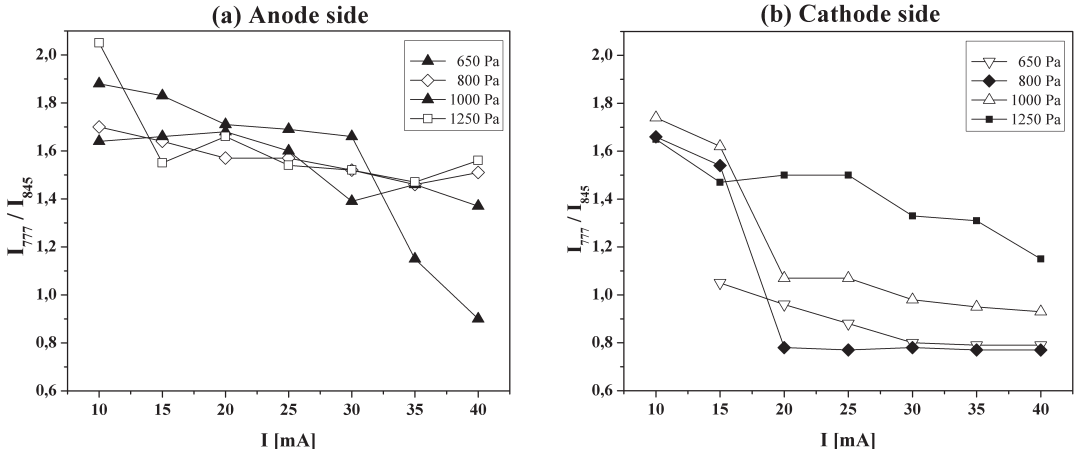

Figure 4: Relative intensity of the atomic oxygen lines I_{777}/I_{845} determined both on anode (a) and cathode (b) side of the tube with respect to the total pressure, which is closely connected to the occurrence of different forms of positive column of DC glow discharge.

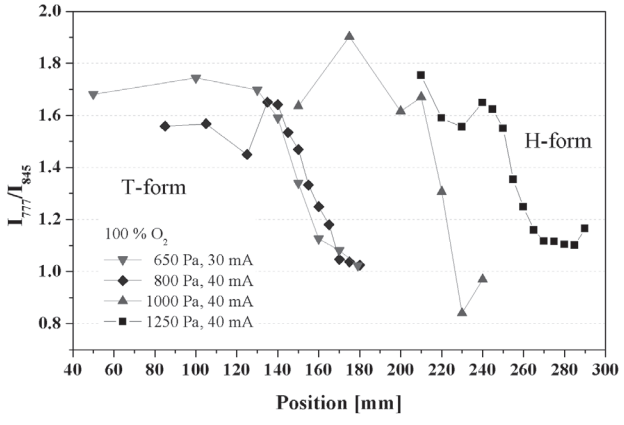

Figure 5: Longitudinal profile of the relative intensity of the atomic oxygen lines I_{777}/I_{845} for different pressures. The transition region between the T-form and H-form can be clearly seen and corresponds to the change in visible radiation.

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 (A-band) of molecular oxygen with head at 759.4 nm, with corresponding transitions $O_2(b^1\Pi_g^+, v = 0) \rightarrow O_2(X^3\Sigma_g^-, v = 0)$). 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].

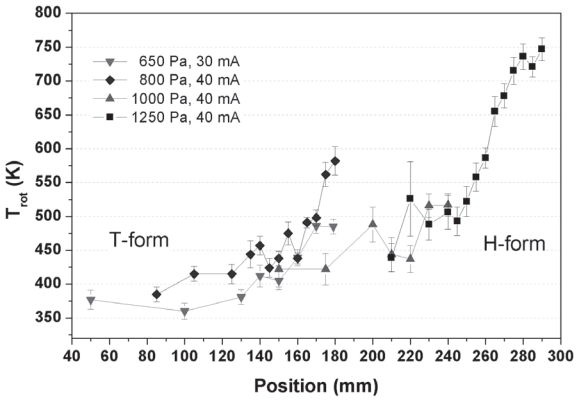

Figure 6: Longitudinal profile of the rotational temperature T_{rot} of oxygen molecules.

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 Trot was also observed

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References

[1] Clément F., Held B., Soulem N., Polystyrene thin films treatment under DC pulsed discharges conditions in nitrogen-argon and oxygen-argon mixtures, Eur. Phys. J. Appl. Phys., 2002, 17, 119-130.

[2] Komlev A.E., Shapovalov V.I., Shutova N.S., Magnetron discharge in an argon-oxygen mixture for deposition of a titanium oxide film, Tech. Phys., 2012, 57, 1030-1033.

[3] Bogdanov E.A., et al., Scaling laws for the spatial distributions of the plasma parameters in the positive column of a dc oxygen discharge, Tech. Phys. 2003, 48, 1151-1158.

[4] Shepelenko A.A., Estimates of maximal concentrations of singlet delta oxygen in a DC discharge, High Temperature, 2007, 45, 439-445.

[5] Richter A., et al., Dynamic behaviour of an oxygen dc discharge, J. Plasma Phys., 2009, 75, 71-84.

[6] Seeliger R., Untersuchungen aus dem Gebiet der Gasentladungsphysik, Zeitschrift für Naturforschung, 1953, 8a, 74-79, (in German).

[7] Řezáčová V., Electron density in the oxygen discharge plasma, Czech. J. Phys. 1970, B 20, 126-131.

[8] Vicharev A.L., et al., Characterization of the T-. and H-form of the glow discharge in oxygen, Fizika plazmy, 1989, 15, 838-843, (in Russian).

[9] Hrachová V., Kaňka A., Study of the admixture influence on the oxygen spectra properties, Vacuum, 1997, 48, 689-692.

[10] Hrachová V., Kaňka A., Tichý M., Kudrna P., Study of T and H forms in positive column of glow discharge in oxygen and ist mixtures with neon and argon, Le Vide, 1999, suppl. B 291, 215-217.

[11] Hrachová V., Kylián O., Kaňka A., Study of the vacuum purity influence on oxygen and nitrogen spectra properties in DC glow discharge, Vacuum, 2004, 76, 433-436.

[12] Schmiedt L., Kaňka A., Hrachová V., Study of rotational temperature of oxygen molecules in H and T forms of DC glow discharge sustained in pure oxygen, Vacuum, 2011, 85, 1093-1095.

[13] Kocian P., Mayor J. M., Atomic species in the low-pressure discharge plasma in oxygen, In: Proceedings of 13rd ICPIG, Berlin, Germany, 1977, 253-254.

[14] Schmiedt L., Morávek M.J., Kaňka A., Hrachová V., Study of rotational temperature of oxygen DC glow discharge in Silica and Pyrex discharge tubes, Vacuum, 2010, 84, 72-74.

[15] Raizer J. P., Gas discharge physics, Springer-Verlag, Berlin, Heidelberg, 1997.

[16] Gousset G., et al., Electron and heavy-particle kinetics in the low pressure oxygen positive column J. Phys. D: Appl. Phys., 1991, 24, 290-300.

[17] Ivanov V.V., et al., Experimental and theoretical investigation of oxygen glow discharge structure at low pressures, IEEE Trans. Plasma. Science, 1999, 27, 1279-1287.

[18] Touzeau M., et al., Spectroscopic temperature measurements in oxygen gases, J Phys D: Appl. Phys, 1991, 24, 41-47.