EXPERIMENTAL STUDY AND MODELLING OF FORMATION AND DECAY OF ACTIVE SPECIES IN AN OXYGEN MICROWAVE DISCHARGE

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1. Introduction. Cold oxygen plasma sources based on microwave or DC low pressure discharges are currently studied both from theoretical and experimental points of view due to their important role in various applications, for example: polymer treatment, oxidation of thin film, catalysis, plasma etching and biochemical depollution . To improve such applications, it is necessary to know better the processes of formation and decay of active species responsible for the chemistry in these systems and to estimate their concentration and fluxes, especially ground state $O(^3P)$, metastable states $O(^1D)$, $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ as well as the translational energy or gas temperature of the medium.

In this contribution we report a spectroscopic study of an oxygen microwave discharge from which we have obtained absolute concentrations of excited species, as well as the corresponding modelling which shows a fair agreement with experimental results and has given the dissociation ratio of molecular oxygen and the oxygen atom recombination coefficient on the wall. The aim of this paper is to give new results on the concentration of $O(^5P)$ and $O_2(b)$ in a microwave oxygen plasma and information on the chemical mechanism. These results can be interesting for the chemical plasma community working on the sterilization by discharges and on many other applications using oxygen plasmas.

2. Experimental set-up. The plasma was produced in a silica tube (12 mm outer diameter; 10 mm inner diameter) crossing a cylindrical resonant cavity connected to a Thomson-CSF microwave generator (2450 MHz, 15 - 1500 W). The oxygen pressure is measured by a MKS 122A baratron and the flow is controlled by means of an Alfagaz RDM280 mass flow-meter. The experimental conditions are the following: pressure, 3 mbar; absorbed microwave power, 150 W; flow-rate, 50 sccm (i.e. $mL.min^{-1}$ (300 K, 1 bar)).

Optical emission is analysed by means of a Jobin-Yvon HRS1 monochromator (focal length: 588 mm, grating: 1220 groves/mm) and a Hamamatsu R928 photomultiplier; light from the plasma is collected by an optical fibre perpendicular to the cylindrical reactor axis and guided to the entrance slit of the monochromator. The optical fibre Schott (type UV) have a length of 50 cm and for a radiation of 760 nm, the aperture angle (2α) is about 80° at 50% transmission (120° at 0% transmission). The following spectral features are studied along the reactor axis downstream of the microwave cavity as a function of the distance d (distance from the antenna of resonant cavity)

- Line 777.4 nm emitted by the excited neutral oxygen atom (transition $3p\ ^5P$ - $3s\ ^5S°$)

- Atmospheric system of excited oxygen molecule (transition $b^1\Sigma_g^+$, $v=0$ - $X^3\Sigma_g^-$, $v=0$) characterised by its head-line at 759.4 nm and its origin-line at 761.9 nm.

For obtaining the absolute intensities the optical system was calibrated using a procedure described in a previous work on a microwave nitrogen plasma [1].

It was supposed that the gas temperature T_g was equal the rotational temperature T_{rot}. To obtain T_{rot}, different emission bands were analysed and the results were compared: the (0, 0) band of the atmospheric system of O_2 ($b\ ^1\Sigma_g$ - $X\ ^3\Sigma_g$), and the partially resolved band (3, 0) of the first positive system of N_2 ($B\ ^3\Pi_g$ - $A\ ^3\Sigma_u^+$) (4% of nitrogen was added to oxygen). The two methods gave a rotational temperature of the same order of magnitude.

3. Kinetic model. A low-temperature plasma is a self-consistent system in which chemical composition and physical characteristics not only control but also depend on the rates of homogeneous and heterogeneous reactions. Analysis of such a system has to be based on the simultaneous solution of the total set of coupled equations describing the plasma properties. The model described here was based on self-consistent solution of the Boltzmann equation for plasma electrons, the equations of the $O_2(X)$ vibrational kinetics, and the rate balance equations for the most important species of the O_2 plasma. Some of the parameters necessary to obtain the solution were taken from the experiment or were used as fitting values. These parameters will be discussed below.

In order to calculate the rate coefficients corresponding to the electron-heavy particle reactions, it is necessary to determine the electron energy distribution function (EEDF). In this work the EEDF was obtained by means of the solution of the homogeneous Boltzmann equation using the two-term expansion in spherical harmonics. We assumed that the Boltzmann equation is stationary because under our experimental conditions: $\omega >> \tau^{-1}$ where ω is the frequency of the electric field and τ is the characteristic electron energy relaxation time. In this case, the effective DC field approximation can be used. We took into account the electron collisions with $O_2(X,v)$, $O_2(a\ ^1\Delta)$ and $O(^3P)$. Superelastic collisions are represented by the following transitions: $O_2(X,v=1-4) \rightarrow O_2(X,v=0)$, $O_2(a\ ^1\Delta) \rightarrow O_2(X)$, $O_2(b\ ^1\Sigma) \rightarrow O_2(X)$, $O_2(b\ ^1\Sigma) \rightarrow O_2(a\ ^1\Delta)$, $O(^1D) \rightarrow O(^3P)$ and $O(^1S) \rightarrow O(^3P)$. Since the electron concentration in microwave discharges is quite high, we took into account the electron-electron collisions as well.

For the description of vibrational kinetics the following processes determining the $O_2(X,v)$ population were taken into account
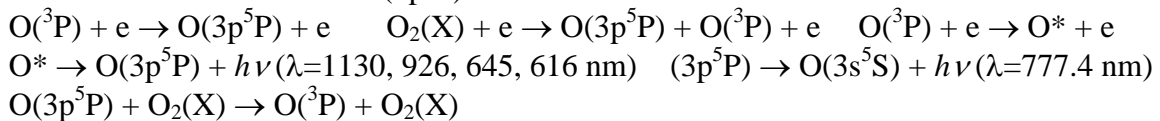1) e-V processes $O_2(X,v=0) + e \leftrightarrow O_2(X,v=1-4) + e$
2) V-V single quantum exchange $O_2(X,v) + O_2(X,m) \leftrightarrow O_2(X,v-1) + O_2(X,m+1)$
3) V-T single quantum exchange between molecules $O_2(X,v) + O_2(X) \leftrightarrow O_2(X,v-1) + O_2(X)$
4) V-T multi-quantum exchange with atoms $O_2(X,v) + O(^3P) \leftrightarrow O_2(X,m<v) + O(^3P)$
5) V-h single quantum heterogeneous relaxation on the reactor walls
$O_2(X,v) + wall \leftrightarrow O_2(X,v-1) + wall$

The rate constants for V-V and V-T exchanges were calculated using the experimental values of K_{01} and K_{01}^{10} constants, SSH theory for anharmonic oscillator and Ceck approximation as formula of linkage.

The kinetic scheme included 53 reactions describing formation and destruction of the main species of oxygen plasma such as $O_2(X)$, $O_2(a^1\Delta)$, $O_2(b^1\Sigma)$, $O_2(A^3\Sigma)$, O_3, $O(^3P)$, $O(^1D)$, O^- and $O(^1S)$. The rate constants were taken from literature and were calculated on the EEDF base.

The modelling needs to know the values of the effective reduced electric field E/N and the electron concentration n_e which were not measured. It was shown in [2] that the dependence of E/N on $N \times r$ (r is the discharge tube radius) was the same in DC, RF and microwave discharges. As the gas temperature along the discharge tube is known , N was calculated and the dependence $E/N = f(N \times r)$ was used to obtain E/N. The n_e value was used as a fitting parameter.

For fitting, the experimentally measured concentrations of $O_2(b^1\Sigma_g^+, v=0)$ and $O(^5P)$ were used. The $O_2(b^1\Sigma_g^+)$ and $O(^5P)$ concentrations were calculated using emission probabilities $A = 0.085$ s^{-1} and 3.4×10^7 s^{-1}, respectively. According to [3], we have assumed the following kinetics for creation and loss of the $O(3p^5P)$ state
$O(^3P) + e \rightarrow O(3p^5P) + e \qquad O_2(X) + e \rightarrow O(3p^5P) + O(^3P) + e \qquad O(^3P) + e \rightarrow O^* + e$
$O^* \rightarrow O(3p^5P) + h\nu\,(\lambda=1130, 926, 645, 616$ nm$) \qquad (3p^5P) \rightarrow O(3s^5S) + h\nu\,(\lambda=777.4$ nm$)$
$O(3p^5P) + O_2(X) \rightarrow O(^3P) + O_2(X)$

The rate constants of electron collisions were calculated on the EEDF base. The quenching rate constant for $O(3p^5P)$ by $O_2(X)$ is taken equal to 1.08×10^{-10} cm^3.s^{-1}. The probability γ_O of heterogeneous recombination for $O(^3P)$ atoms was used as the second fitting parameter According to literature data, the heterogeneous deactivation for $O_2(b^1\Sigma)$ can occur with a probability of about $(0.22 - 4.4) \times 10^{-2}$, so this deactivation coefficient was used as a fitting

parameter as well. However, contrary to n_e and γ_O, it was assumed that this parameter did not depend on the d coordinate.

    4. Results and discussion. The electron concentration obtained from the fitting procedure is reproduced in Fig. 1. To a certain extent, we can check the value of the electron concentration obtained and the value of the assumption about the local dependence $E/N = f(N{\times}r)$. From the heat conductivity equation, where to a first approximation longitudinal dependence is neglected, the average temperature has to be a linear local function of absorbed power density. The absorbed power density is directly proportional to the electron concentration. Fig. 2 shows the temperature measured as a function of the absorbed power density which was obtained on the base of EEDF calculations and electron concentrations. This Figure shows that the relation assumed above really exists.
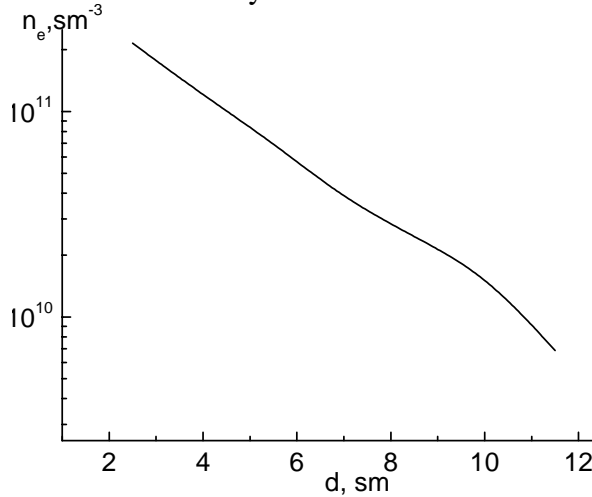


Fig. 1. Electron density as a function of d distance.
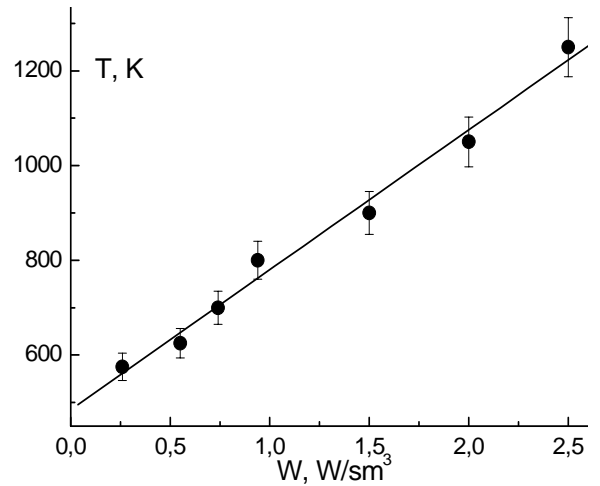
Fig. 2. Average gas temperature as a function of absorbed powder.

    The calculated concentrations of $O_2(b\ ^1\Sigma)$ molecules and $O(^5P)$ atoms together with the corresponding experimental data are shown in Fig.3,4. We consider that the predicted and calculated values are in fair agreement. The calculated data were obtained using the $O_2(b^1\Sigma)$ heterogeneous deactivation probability of $2.6{\times}10^{-2}$.
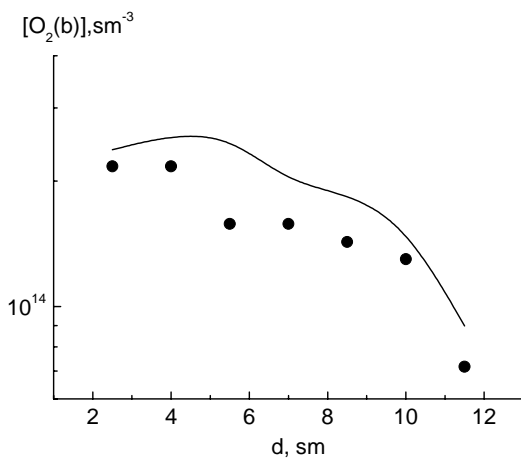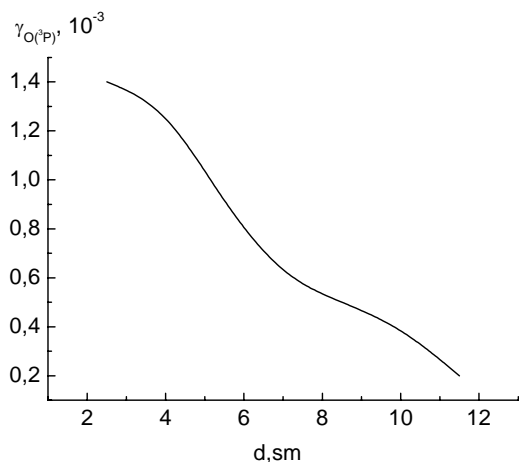

Fig. 3. The $O_2(b^1\Sigma)$ molecule densities as a function of d distance. Line is calculation, points are experiment.
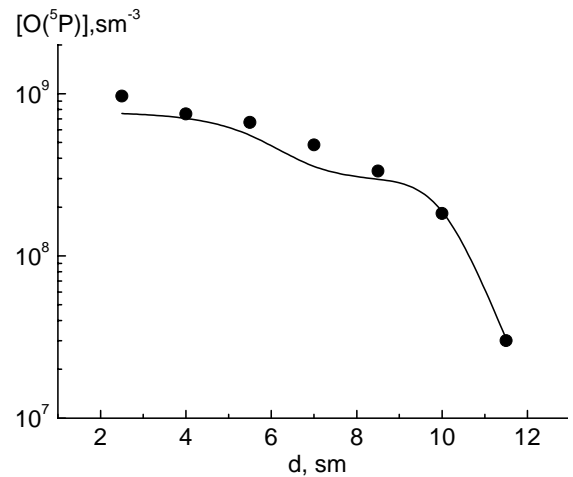
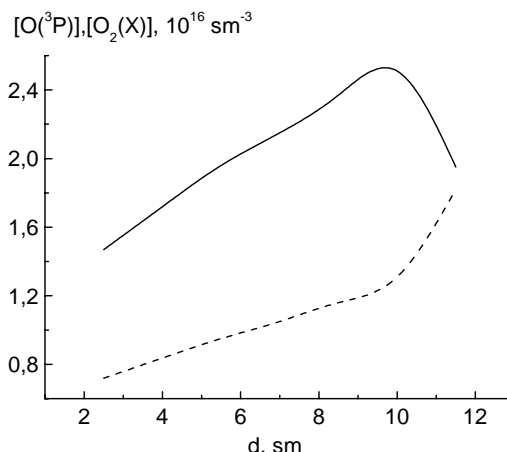**Fig. 4.** The $O(^5P)$ atom densities as a function of d distance. Line is calculation. points are experiment.

    The heterogeneous recombination coefficient for $O(^3P)$ atoms is shown in Fig.5. The form of this dependence is not surprising because the wall temperature decreases when the distance d increases. Values are two orders of magnitude less than those obtained for microwave discharge ($\sim$0.1) by Pinheiro *et al.* [2]. At the end of the discharge, γ is in fair agreement with the

value obtained usually in afterglow. The large discrepancies observed between different authors concerning the recombination probabilities depend strongly not only on the nature of the chemical material and its temperature but also on the real surface conditions determined by the "history" of the material.

Fig. 5. The $O(^3P)$ atom probabilities of heterogeneous recombination as a function of d distance.

Fig. 6. The $O(^3P)$ atom and $O_2(X)$ molecule densities as a function of d distance. Solid line is $O(^3P)$ atom densities, broken line is $O_2(X)$ molecule densities.

The main processes of atomic oxygen formation are O_2 dissociation by electron impact. The main process of atomic loss is heterogeneous recombination. In spite of the decrease in the dissociation rate when the distance d increases, the $O(^3P)$ concentration increases (Fig.6). This is due to a faster decay of the heterogeneous recombination probability than of the dissociation rate decay. The conversion to oxygen atoms ($[O] / 2[O_2]_{initial}$) reaches about 33 - 50%.

As the electron concentration in microwave discharge is higher than in DC, and heterogeneous recombination coefficients are approximately of the same order of magnitude, the $O(^3P)$ atom concentrations are higher than the $O_2(X)$ concentrations. As a result the vibrational distributions of $O_2(X)$ are in quasi-equilibrium. The combination of high atomic concentrations and high gas temperatures leads to a predominant role of V-T transfer during $O_2(X,v)-O(^3P)$ collisions, so the vibrational temperature is very close to the gas temperature. Hence, it is possible to ignore collisions between vibrationally excited molecules and heavy-particle as well as second kind collisions with vibrationally excited molecules for EEDF calculations.

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