FORMATION AND DECOMPOSITION OF O_3 IN OXYGEN GLOW DISCHARGES AND IN THEIR AFTERGLOWS

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ABSTRACT

The O_3 concentration has been measured by Hg-light absorption by O_3 at $\lambda = 2537$ Å and compared with theoretical results of a kinetical model. Within the discharge the density of O_3 as a function of the current (or the electron density, respectively) reaches a remarkable maximum. In the afterglow the ozon density can be appreciably higher than within the discharge tube.

1. INTRODUCTION

The production of ozone in low-pressure oxygen glow discharges and the steady-state ozone concentration has been investigated in /2/. There it was shown that excited molecules, O_2^* ($a^1\Delta g$), and negative ions play an important role in the reaction kinetics of O_3.
Investigations of the O-atom concentration in the flowing afterglow in /1/ showed the total absence of O-atom decay in the early afterglow. This suggested the O production via the process $O_2^* + O_3 \rightarrow 2O_2 + O$ and stressed, on the other hand, the importance of O_3 in the kinetics of O atoms in the afterglow.
In the present paper the O_3 production in the afterglow is more thoroughly investigated. Theoretical calculations of the reaction rates give some insight into the main reaction path's of the plasma within the discharge and in the afterglow.

2. EXPERIMENTAL

The measurements were performed with the arrangement shown in Fig. 1. Oxygen was fed through a liquid nitrogen trap into the straight discharge tube and then into the straight afterglow tube. From the measured absorption of the 2537Å-Hg light by O_3 the density n_3 of O_3 was calculated using the relation $I = I_0 \exp(-n_3 \sigma l)$. l means the length of the glass tube. The absorption cross section σ was determined by the synthesis of a definite quantity of pure O_3 corresponding to the reaction $O + O_2 \cdot S \rightarrow O_3 \cdot S$ /1/, S means a surface cooled by liquid nitrogen. We found: $\sigma = (7.0 \pm 1.0) \cdot 10^{-18}$ cm^2.
During these experiments we stated that ozone is partially decomposed in vessels, the walls of which were in contact with discharged oxygen. This kind of the wall activity maintains for

times of order of one hour after the interruption of the discharge current.

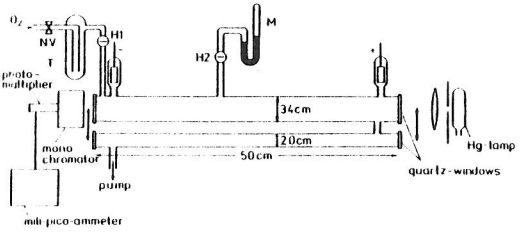

Fig. 1
Experimental arrangement

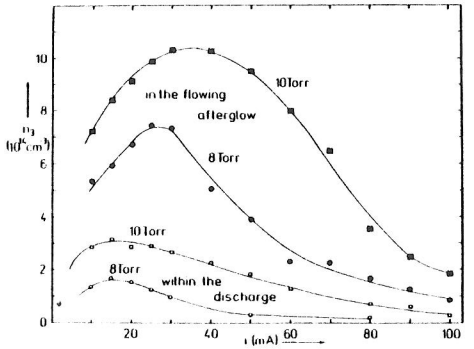

Fig. 2
Measured ozon concentration within the discharge and in the afterglow

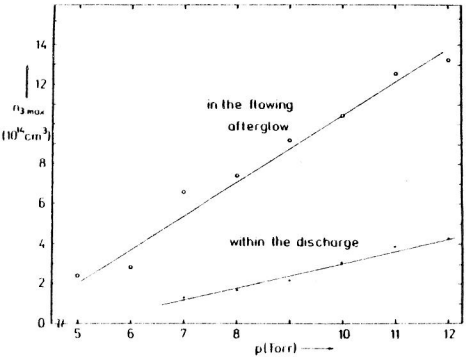

Fig. 3
Maximum ozon concentration in dependence on the pressure

3. THEORETICAL MODEL

The measured ozone concentration within the discharge and in the afterglow will be compared with the results of a kinetic model previously developed /2,3/. In this model the plasma is assumed to consist of the following 11 kinds of particles which interact according to about 70 elementary reaction processes:

O, O_2, O_3, $O_2^*(a^1\Delta_g)$, O^+, O_2^+, O_3^+, O^-, O_2^-, O_3^-, e.

The system is described by a complete set of time-dependent rate equations and the equation of state. There are no special boundary conditions considered. The reactive collision cross-sections and rate constants, respectively, are given in /2,3/.

The steady-state solutions of these equations as a function of the external parameters, i.e., pressure (p), gas, ion and electron temperature (T_G, T_I, T_e) have been discussed in detail in /2,3/. For example, the left-hand side of Fig. 4 shows the possible steady-state concentration of ozone for different electron concentrations (which is related to the electron temperature) and for p = 10 Torr, T_I = 2000 K, T_G = 300 K. Such states can only exist for electron temperatures above a certain lower limit. In the case of the mentioned parameters the threshold is approximately 10 000 K.
In order to describe the temporal development of the 11 partial partical concentrations in the decaying plasma of the afterglow we start from a certain steady state (see Fig. 4) and assume the electron temperature to be suddenly reduced below this threshold (in the present calculation we assumed T_e = 9000 K, but it can be shown that, in fact, the concentration of the neutrals is almost independent of the exact value of T_e).

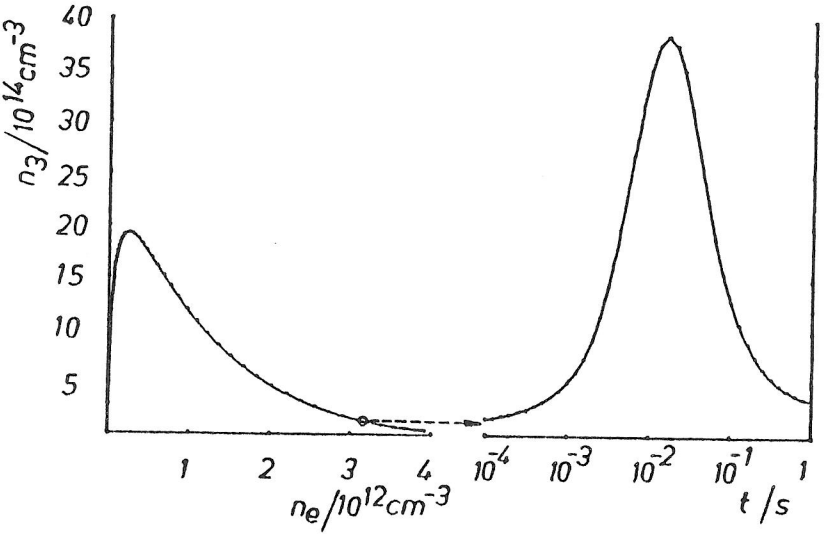

Fig. 4: Calculated ozone concentration for a steady-state oxygen plasma and for a decaying plasma

o = initial value of n_3 for the decay problem (corresponding to 15 000 K electron temperature within the discharge)

p = 10 Torr, T_G = 300 K and T_I = 2000 K are kept constant.

The resulting system of time-dependent rate equations has been numerically integrated using an integration technique suitable for stiff differential equations. Here we focus our attention only to the behaviour of the ozone concentration up to 1 second after switching off the discharge (Figs. 4,5). A more detailed discussion of the other plasma components, in particular of the charge carriers and the excited $O_2^{\uparrow}$ -molecule will be given in a forthcoming paper.

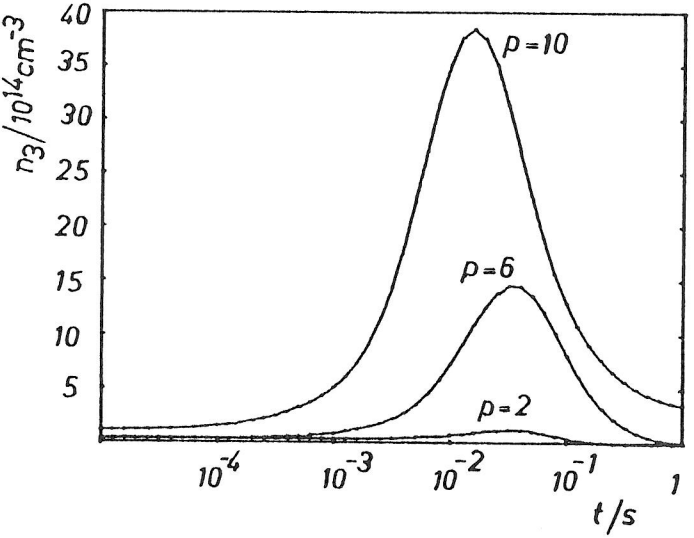

Fig. 5: Calculated time dependence of the ozone concentration in the afterglow for different pressures and T_G = 300 K, T_I = 2000 K. The electron temperature of the initial steady-state is T_e = 15 000 K.

4. RESULTS AND DISCUSSION

As may be seen from Figs. 2-4 the ozone concentration after leaving the discharge chamber can reach much higher values than in the initial steady state. Moreover, the maximum ozone concentration that appears after about 0.02 s is twice as large as the highest possible steady-state concentration at all (Fig.4). However, this high ozone concentration is observed only for very short a time ($\approx$ 0.05 s). In order to compare these results with the experimental data obtained along the glass tube of Fig. 1 we have to take the mean value of the curves of Fig. 4 and Fig. 5. respectively. Since the delay time of the gas stream within the afterglow tube is of the order of 1 s we obtain a mean value that is by about a factor 6 higher than the initial steady-state value (for p = 10 and 6 torr) and agrees well with the experimental observation (see Fig. 2). For very low pressure and low flow velocities this factor decreases and can become smaller than 1 as may be concluded from Fig. 5. (0,4 for p = 2 torr).

The maximum ozone density measured within and outside of the discharge tube is shown in Fig. 3. there is a linear increase with the pressure. It should be noted that the calculated values of the steady-stste ozone concentration are higher than the measured ones and the maximum appears at higher electron densities. Possible reasons for this discrepancy are discussed in /3/.

Considering the reaction rates for the different elementary reaction processes some insight can be gained into the chemical kinetics of the plasma. Thus, e.g., it is found that under steady-state conditions the main production and decomposition processes of ozone are

$$O+O_2+M \longrightarrow O_3+M, \quad O^-+O_2^* \longrightarrow O_3+e$$

(the latter in the region of the maximum O_3 concentration) and

$$O_3+e \longrightarrow O_2+O^-, \quad O_3+e \longrightarrow O+O_2^-, \quad O_3+O \longrightarrow 2O_2,$$

respectively. Outside of the discharge the electrons and ions recombine very quickly, so for times $\gtrsim$ 1 ms the plasma kinetics is dominated by long-lived chemically active species. In this region ozone is mainly decomposed by the process

$$O_2^* (a^1\Delta_g) + O_3 \longrightarrow 2O_2 + O.$$

Details will be given in a forthcoming paper.

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