THE DISSOCIATION MECHANISM OF SOME INORGANIC FLUORIDES IN THE OPTICAL BREAKDOWN PLASMA

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ABSTRACT

The dissociation of SF_6, NF_3 and SiF_4 in the optical breakdown plasma of CO_2 laser radiation in the presence of some buffer gases have been investigated. The main dissociation mechanism of inorganic fluorides at the buffer gases pressure of $>$ 50 torr is thermal dissociation. SF_6 and NF_3 dissociate at lower pressure of buffer gases (5-30 torr) by dissociation attachment mechanism.

1. INTRODUCTION

The plasma generated in focusing the powerful pulse laser radiation into a gaseous medium possesses a number of specific properties (the electron temperature reaches hundreds of eV's, and the electron density exceeds $10^{19}cm^{-3}$ at a gas pressure of 1 atm (1). Under the optical breakdown (laser spark) conditions the chemical reactions proceed at high speeds and are of practical interest (2). The present work is devoted to studying the mechanism of SF_6, NF_3 and SiF_4 dissociation in the optical breakdown plasma generated in focusing the TEA CO_2 laser radiation (1.4J) in the medium of various buffer gases.

2. EXPERIMENTAL

In the experiments TEA CO_2 laser (CO_2:N_2:He =1:1:5 at 0.8 atm) and nonselective resonator (P18) was used. The pulse duration at the half-height was about 150ns with a total duration of about 1 μs. The pulse energy was kept constant (1.4J). The laser radiation was focused by a NaCl lens

(F=10 cm) inward in glass cell (3.4 cm in diameter and 7.5 cm in length). The presence of the optical breakdown was determined by glow from the lens focus area. The amount of non-decomposed fluorine in the cell was determined after ten optical breakdowns by the IR spectra using the ИКС-22 spectrophotometer.

3. DISCUSSION OF THE RESULTS.

Figs.1 and 2 show dependences the SF_6, SiF_4 and NF_3 fluorides fraction remaining undissociated after ten optical breakdowns in the cell versus the buffer gas pressure

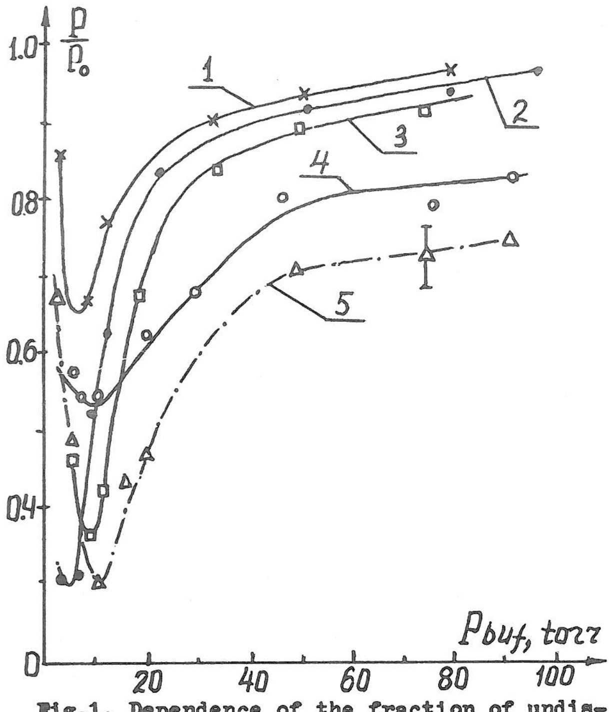

Fig.1. Dependence of the fraction of undissociated SF_6 (P/P_o) after ten optical breakdowns on the buffer gas pressure. 1-CO_2, 2 - Br_2, 3 - NO_2, 4 - NO, 5-Xe. P_o is the initial pressure of SF_6 in the cell (0.3 torr). P is the pressure of undissociated SF_6.

The most probable mechanism of SF_6 and NF_3 dissociation by electron impact is associated with the processes of dissociation attachment (3,4). For example, with SF_6 the process of electron attachment $e+SF_6 \xrightarrow{K_3} SF_6^-$, which does not result in dissociation is concurrent with the processes of dissociative attachment $SF_6 + e \xrightarrow{K_1} SF_5^- + F$ (1); $SF_6 + e \xrightarrow{K_2} SF_5 + F^-$ (2).

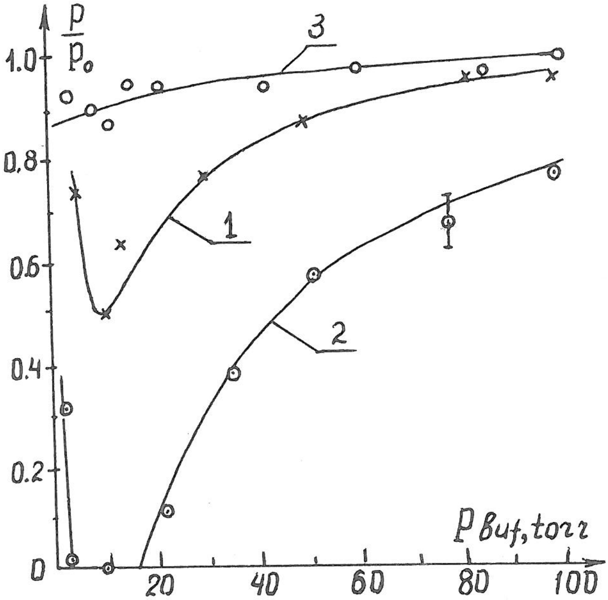

Fig.2. Dependence of the fraction of undissociated NF_3 (curve 1,2) and SiF_4 (curve 3) P/P_0 after ten optical breakdowns on the buffer gas pressure 1 -Xe, 2 -CO_2, 3 -Xe. Po is the initial pressure of NF_3 and SiF_4 in the cell are 1,0 and 0,5 torr, respectively.

The ratios K_1, K_2 and K_3 depend on the average electron energy $\mathcal{E}_0$. At low pressures (< 50torr) $\mathcal{E}_0 \sim \frac{e^2E^2}{m\omega^2}\,\frac{\nu_{elast}R_0^2}{D_a}$ (where Da is the ambipolar diffusion coefficient, R_0 - is the laser spark radius, m,M are the mass of the electron and molecules, respectively; ν_{elast}

is the frequency of elastic electron collisions; E, ω are the amplitude and frequency of the electromagnetic field, respectively) depends quadratically on the gas pressure (3) and is equal to about 10 eV. In this case the ratio K_2/K_3, which was about 10^{-3} at room temperature rises to unity (4). This is indicative of dominant proceeding of reaction (2) resulting in fluoride dissociation by the dissociation attachment mechanism. The pressure increase leads to a change in the electron energy balance so that the fraction of energy spent for heating and excitation of the buffer gas particles rises. When the characteristic time of electron cooling resulting from the impacts, $\tau_{cool} \sim \frac{M}{m} \cdot 1/N_{buf} \cdot K_{elast}$, (where K_{elast} is constant of the elastic electron-molecule collisions and N_{buf} is buffer gas density) is much less than the time of the ambipolar diffusion of particles from the spark region, $\tau_{diff} \sim R_0^2/6D_a$, the laser radiation is transformed almost completely into heat in the spark region. Thus, the main mechanism of fluoride dissociation at a pressure of > 50 torr is thermal dissociation. The level of the thermal dissociation of fluorides depends on the temperature of buffer gas heating, which is lower in the case of molecular gases (CO_2, NO_2 etc.) compared to that of atomic gases (Xe). SiF_4 interacts with electron by the dissociative attachment mechanism within a narrow energy range from 10.5 to 13 eV (5) and is likely to have a low value of the constant of dissociation attachment reaction rate. Therefore it is stable in the optical breakdown plasma.

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