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Emision of Cl_2^* molecules in a barrier discharge

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***Abstract*. The energy and spectral parameters of emission of a barrier discharge in chlorine and its mixtures with inert gases are studied experimentally. The barrier discharge in chlorine was homogeneous at pressures up to ~ 9 Torr and its spectrum contained the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$, $^3\Pi_{2g} \rightarrow {}^3\Sigma_{2u}^+$ and $^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ bands of Cl_2^* molecules. After the addition of an inert gas, the 257.8-nm $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$ band made the main contribution to the spectrum. The maximum efficiency and power of the Cl_2 excilamp were obtained for the chlorine – argon mixture and amounted to 0.7 % and 1.3 W, respectively.**

Keywords: *excilamp, UV radiation, excited Cl_2^* dimer.*

Spontaneous UV and VUV radiation at the bound – free transitions of the RX^* halides and R_2^* dimers of inert gases have attracted the attention of researchers [1, 2] and finds applications in scientific experiments [3]. The authors of paper [4] proposed to call systems emitting due to the decomposition of excimer or exciplex molecules excilamps. At present, the conditions providing the efficient luminescence of dimers of inert gases (for example, Xe_2^* and Kr_2^*) and halides of inert gases (for example, $XeCl^*$, $KrCl^*$, $XeBr^*$, and XeI^*, etc.) are well studied. However, the investigations of these conditions for dimers of X_2^* halogens in a barrier discharge are inadequate.

The spectra of these molecules were initially studied to identify the electronic states involved in the emission of excimer lasers. It has been found that the intense emission bands of Br_2^*, I_2^*, F_2^*, and Cl_2^* molecules correspond to the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$ transitions (which are also denoted by $D' \rightarrow A'$) [5, 6]. Emission in the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$ band of halogen dimers in excimer lasers at pressures above 1.5 atm is caused by the relaxation of I_2^*, Cl_2^*, and Br_2^* molecules from upper energy levels in collisions with buffer gas molecules. The efficiency of collision relaxation depends on the buffer gas pressure and type [7].

Later, the spontaneous emission of X_2^* halogen dimers was obtained under different conditions in glow [8] and transverse volume [9] discharges and upon excitation by synchrotron radiation [10]. The barrier discharge plasma was investigated only is several papers. Thus, it was found in [11] that the plasma emission was mainly determined by the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$ band of I_2^* molecules and the maximum efficiency and radiation power density were ~ 1 % and 1.8 mW cm^{-2}, respectively. In [12], the emission spectrum of Cl_2^* dimers was observed. However, the energy parameters and emission efficiency of the barrier discharge plasma in chlorine were not determined. The aim of our paper is to make up for these deficiencies.

Experiments were performed in bulbs of the design described in detail in [11]. The bulbs were made of two coaxially arranged quartz tubes with gaps between them varying from 2 to 11 mm. One electrode located on the external tube had the shape of a spiral and transmission above 93 %. A continuous electrode located in the internal tube was made of an aluminium – magnesium foil. Fused quarts tubes (type 214, General Electric) transmitting ~ 75 % at a wavelength of 200 nm were used. The useful length of the lamp was 31 cm. The gas in the space between tubes was excited by 1.8-μs, 5-kV pulses from a two-polar voltage generator. The pulse repetition rate f could be varied from 40 to 108 kHz. The electric power supplied to the plasma depended on the voltage pulse amplitude and repetition rate, as well as on the mixture pressure and composition and achieved 230 W at the maximum pulse repetition rate. Examples of current and voltage oscillograms for the excilamp are presented in Fig. 1.

We varied in experiments the pressure of halogen vapour and added inert gases (He, Ne, Ar), measured the emission power and power supplied to the discharge, and recorded emission spectra. To provide the stable operation of the excilamp, the lamp bulb was cooled by a radial fan placed near its end.

The emission power of the lamp was measured with a Hamamatsu H8025-222 photodetector with the spectral sensitivity maximum at 222 nm, and the emission spectrum of the discharge was recorded by using a setup consisting of two HR4000 spectrometers (Ocean Optics B.V.) with 2400-lines mm^{-1} gratings operating in the spectral range from 200 to 350 nm. The supplied power was measured from oscillograms of voltage and current pulses recorded with a TDS 224 Tektronix oscilloscope.

A barrier homogeneous discharge in chlorine burned at pressures up to ~ 9 Torr. The emission spectrum of the barrier discharge plasma under these conditions exhibited the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$, $^3\Pi_{2g} \rightarrow {}^3\Sigma_{2u}^+$, and $^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ bands of Cl_2^* molecules at 256.4, 307.4, and 200 nm, respectively (Fig. 2). The same bands were observed earlier in a glow discharge [6, 13] and a transverse volume discharge in

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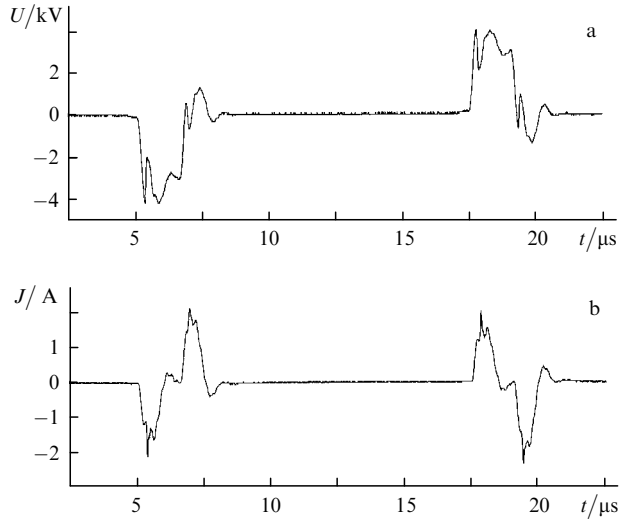

Figure 1. Oscillograms of voltage U (a) and current J (b) pulses in the Cl_2 excilamp for the $Ar : Cl_2 = 400 : 1$ mixture at a pressure of 300 Torr, $f = 80$ kHz, and $d = 8.5$ cm.

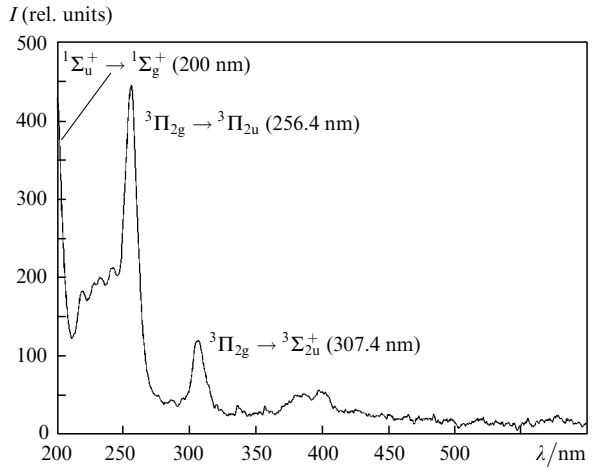

Figure 2. Emission spectrum of the barrier-discharge Cl_2 excilamp in pure chlorine at a pressure of 6 Torr.

chlorine [9]. The half-width of the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$band of the Cl_2^* molecule at a pressure of 1 Torr was 10 nm.

The addition of inert gases He, Ne or Ar to chlorine accelerates collision relaxation of Cl_2^* molecules from upper states to the $^3\Pi_{2g}$ state and then to the $^3\Pi_{2u}$ state due to radiative transitions [14]. As a result, the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$ emission band begins to dominate with increasing the inert gas pressure and its maximum shifts to 257.8 nm.

The maximum intensity of this band was achieved by adding Ar to chlorine, which provided uniform emission in the discharge gap at specific energy inputs to the medium up to 0.9 W cm^{-3}. As the energy input was further increased, microscopic discharges appeared against the volume emission background. In the mixture of chlorine with Kr at pressures above 500 Torr, the energy input to the medium decreases, resulting in the decrease in the average emission power and efficiency. In chlorine mixtures with Ar, this does not occur at pressures up to 1 atm.

As the argon pressure was increased from 3.5 to 609 Torr in the $Ar : Cl_2 = 400 : 1$ mixture, the half-width of the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$ band of Cl_2^* molecules decreased from

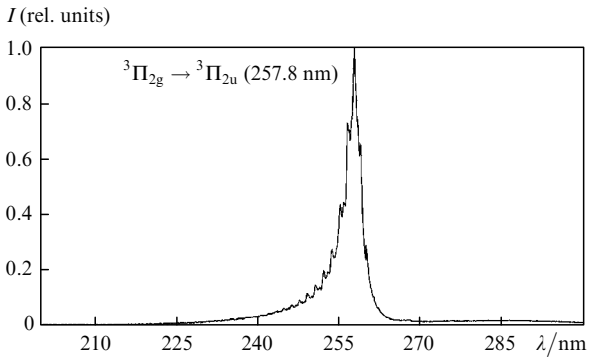

Figure 3. Emission spectrum of the barrier-discharge Cl_2 excilamp in the $Ar : Cl_2 = 200 : 1$ mixture at a pressure of 240 Torr. The half-width of the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$ band of the Cl_2^* molecule is 2.9 nm.

8.2 to 2.9 nm, which is caused by the acceleration of the vibrational relaxation of the $^3\Pi_{2g}$ state. The typical emission spectrum is presented in Fig. 3.

The main channel of formation of X_2^* dimers at moderate pressures is the reaction of energy transfer from X^* to X_2 [15], in our case, the reaction

$$Cl^* + Cl_2 \rightarrow Cl_2^* + Cl. \quad (1)$$

This reaction occurs after the reactions [14, 16]

$$Ar + e \rightarrow Ar^* + e, \quad (2)$$

$$Ar^* + Cl_2 \rightarrow ArCl^* + Cl, \quad (3)$$

$$Ar + Cl_2^* \rightarrow ArCl^* + Cl, \quad (4)$$

$$Ar^+ + Cl^- + Ar \rightarrow ArCl^* + Ar, \quad (5)$$

$$ArCl^* \rightarrow Ar + Cl^*. \quad (6)$$

The contribution of the radiative decay of $ArCl^*$ to the plasma luminescence is small [17] due to the predissociation of this molecule [18].

As the fraction of chlorine in the $Ar - Cl_2$ mixture was decreased, the intensity of the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$ emission band of Cl_2^* increased. The maximum power was achieved in the $Ar : Cl_2 = 400 : 1$ mixture. As the concentration of chlorine in the mixture was decreased from 0.01 % to 0.005 %, the maximum of the emission intensity shifted to the region of higher pressures.

Figure 4 presents the dependences of the emission power and efficiency of the Cl_2 excilamp on the mixture pressure for discharge gaps $d = 8.5$ and 10 mm. The maximum average emission power and efficiency were 1.3 W and 0.76 % at a pressure of ~ 300 Torr, $d = 8.5$ mm, and $f = 80$ kHz. As d was increased up to 10 mm, the emission power and efficiency decreased almost by half. For $d = 2$ mm, the average emission power of the Cl_2 excilamp decreased almost by an order of magnitude. The increase in the pulse repetition rate from 40 to 80 kHz was accompanied by the increase in the emission power and efficiency. As f was further increased, the emission power saturated and the emission efficiency decreased.

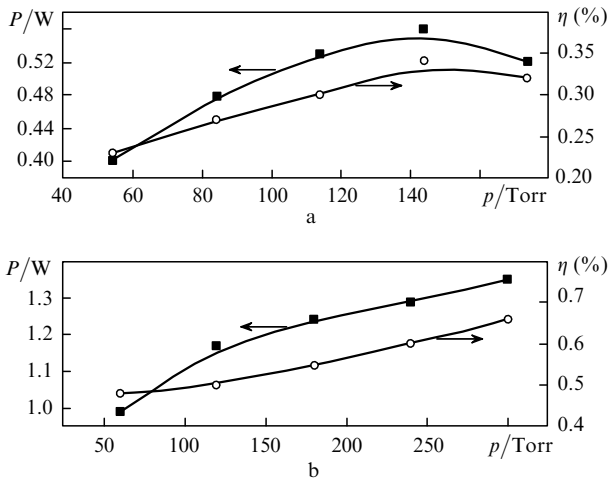

Figure 4. Dependence of the average emission power P and efficiency η of the Cl_2 excilamp on the pressure p of the $Ar : Cl_2 = 400 : 1$ mixture for $f = 80$ kHz, $d = 10$ (a) and 8.5 mm (b).

Thus, we have shown in this paper that the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$ emission band of the Cl_2^* molecule dominates in the emission spectrum of the $Ar : Cl_2 = 400 : 1$ mixture in the pressure range from tens torr to 1 atm, the emission power and efficiency being 1.3 W and 0.76 %, respectively. Under optimal power and efficiency conditions, the discharge with argon was homogeneous, unlike the discharge in barrier-discharge exciplex lamps. Because the partial pressure of chlorine under optimal power and efficiency conditions is close to the chlorine pressure in XeCl and KrCl excilamps, the life of working mixtures of the Cl_2 excilamp can be expected to be close to that of XeCl and KrCl excilamps (several thousands hours [19]).

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