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Spectral and energy parameters of multiband barrier-discharge KrBr excilamps

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Abstract. **The spectral and energy characteristics of multiband barrier-discharge coaxial KrBr excilamps are studied experimentally at pressures from a few tens of Torr to 0.4 atm. It is shown that an increase in the Br_2 concentration reduces the emission intensity of $KrBr^*$ molecules with respect to the emission intensity of Br_2^* molecules and reduces the total emission power of the excilamp. This can be explained by the nonradiative decay of exciplex $KrBr^*$ molecules caused by their quenching by molecular bromine. The emission power and efficiency in the $Kr : Br_2 = 400 : 1$ mixture at a pressure of ~ 230 Torr and a discharge gap of 8.5 mm were 4.8 W and 2.4 %, respectively.**

Keywords: *excilamp, ultraviolet emission, Br_2^*, $KrBr^*$.*

1. The sources of spontaneous ultraviolet (UV) and vacuum ultraviolet (VUV) radiation at bound-free transitions in excimer (R_2^*, X_2^*) or exciplex (RX^*) molecules, where R are inert gases (Ar, Kr, Xe) and X are halogens (F, Br, Cl, I) have become the object of many studies in the last two decades (see, for example, reviews [1 – 4] and references therein). The authors of [5] proposed to call such sources excilamps. The excilamp spectrum represents, as a rule, a comparatively narrow and intense emission band of half-width 2 – 15 nm for RX^* molecules and up to 30 nm for R_2^* molecules. Along with emission in the $B \rightarrow X$ band, the spectrum of the plasma of exciplex molecules RX^* can contain the $D \rightarrow X$, $C \rightarrow A$, and $D \rightarrow A$ transition bands of the same molecule. However, their contribution to the emission power at high gas pressures is very small, and excilamps are usually characterised by their emission in the $B \rightarrow X$ band.

One of the important directions in the investigation of excimer and exciplex optical media is the study of working mixtures with emission spectra containing the bands of different and the same molecules. For example, the luminescence spectra of a krypton mixture with molecular bromine at moderate pressures exhibit the emission bands of Br_2^* and $KrBr^*$ molecules, whose contributions to the total emission power can be varied by varying the concentration ratio of the gases in the mixture. Nevertheless, for brevity such an emitting system is called a KrBr excilamp. The studies of KrBr excilamps are comparatively few in number. The emission spectra of a low-pressure longitudinal glow discharge KrBr excilamp in the spectral range from 150 to 300 nm studied in [6] contained the lines of bromine atoms at 163.3 and 157.6 nm along with the bands of Br_2^* and $KrBr^*$ molecules. It was shown that the contribution of molecular bands to the emission increased with increasing the mixture pressure from 0.3 to 7.8 Torr. A further increase of pressure in the glow discharge leads to the discharge contraction and quenching. Probably for this reason no studies were performed at higher pressures. When a working mixture is excited by a barrier discharge, restrictions on pressure are removed. Thus, the emission spectrum of a planar KrBr excilamp with a window of area 4.7 cm^2 at a total pressure of 285 Torr exhibited the dominating band of $KrBr^*$ molecules, however, the average radiation power was low (3 mW) [7, 8].

The average radiation power was increased in a coaxial excilamp [9]. At a mixture pressure up to 190 Torr, emission spectra containing several bands were obtained. By varying the partial pressure of krypton and Br_2, it was possible to change the radiation power in the bands of Br_2^* and $KrBr^*$ molecules

In this paper, we present the results of the systematic studies of the spectral and energy characteristics of coaxial barrier-discharge $Kr - Br_2$ lamps, which were initiated in [9]. Because the emission spectrum of a KrBr excilamp is specific, it is necessary to study in detail the behaviour of individual emission bands because the relative contributions of the bands of $KrBr^*$ and Br_2^* molecules to the average radiation power will be different at different pressures and different discharge gaps. Such studies have not been performed so far. The aim of our work is to achieve the greatest average radiation powers and efficiencies in multiband KrBr excilamps.

2. Experiments were performed with two coaxial lamps (Fig. 1) made of fused quartz (Fused Quartz, Type 214, General Electric) with transmission ~ 75 % at 200 nm. The lamps had different diameters and lengths determining the discharge gap length d and the emitting surface area S (Table 1). The external electrode had the spiral shape and transmission more than 72%, while a massive electrode located inside the inner tube was made of an aluminium – magnesium foil. Gas in the space between tubes was excited by ~ 2-μs voltage pulses with amplitudes up to 4 kV applied to electrodes at a pulse repetition rate of a few tens of

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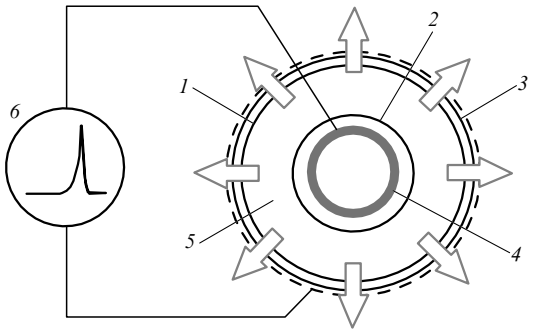

Figure 1. Cross section of the coaxial excilamp emitter: (*1*, *2*) external and internal quartz tubes; (*3*) external perforated electrode; (*4*) internal high-voltage electrode reflector; (*5*) gas-discharge gap; (*6*) pulsed power supply.

Table 1. Design and power supply parameters of KrBr excilamps.

Excilamp number	d/mm	S/cm^2	f/kHz
1	11	941	76.3
2	8.5	405	80.8

kilohertz. The power consumed by the excilamp depended on the voltage pulse amplitude and repetition rate.

The radiation power supplied to the discharge and emission spectra were measures by varying the pressure of bromide and inert Kr gas vapours. Krypton–bromine mixtures were prepared in the working volume of the excilamp. After optimisation, excilamp emitters were sealed off and tested in the autonomous regime. The stable operation of excilamps was provided by cooling the lamp tube with a fan located near the tube end.

The radiation power of lamps was measured with a H8025-222 photodetector (Hamamatsu Photonics K.K.) with the spectral sensitivity maximum at 222 nm. The emission spectrum of the discharge was recorded in the 200–300-nm region with a high-resolution HR4000 spectrometer (Ocean Optics B.V.) with a 1200 lines mm^{-1} grating. The input power was measured by the oscillograms of voltage and current pulses. The current and voltage oscillograms from a current shunt and a voltage divider were recorded with a TDS 224 oscilloscope (Tektronix Inc.).

3. The emission spectrum of the $Kr-Br_2$ mixture exhibits the $\sim$ 207-nm $B \rightarrow X$ band of $KrBr^*$ molecules, the weak 222-nm $C \rightarrow A$ and 228-nm $D \rightarrow A$ bands of these molecules and the 291-nm $D' \rightarrow A'$ band in Br_2^* molecules (Fig. 2). As the bromine fraction in $Kr:Br_2$ mixtures is decreased from 100 : 1 to 400 : 1, the relative intensity of the emission bands of $KrBr^*$ molecules increases and the intensity of Br_2^* bands also weakly increases (Fig. 2a). For a fixed $Kr-Br_2$ ratio in the mixture, the increase in the mixture pressure also leads to the increase in the intensity of $KrBr^*$ bands, the contribution of the $D' \rightarrow A'$ band of Br_2^* molecules being almost invariable (Fig. 2b).

Because we did not calculate the kinetics of reactions in this study, we interpreted qualitatively our results by analysing the results of calculations performed for the working mixtures of XeCl, KrCl [10], XeI [11], and KrI excilamps [12] and distinguished by analogy a number of reactions involved in the formation and destruction of Br_2^* and $KrBr^*$ molecules:

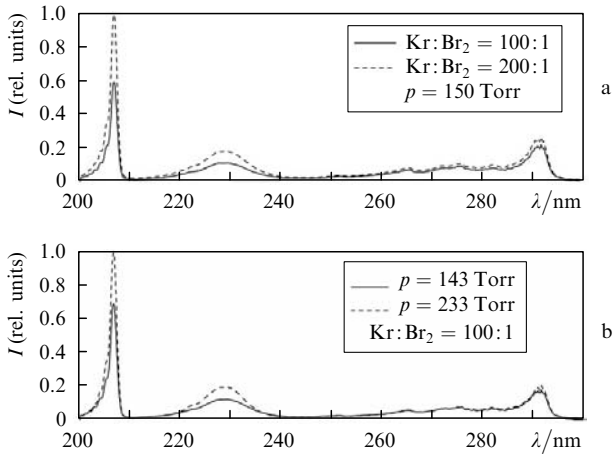

Figure 2. Emission spectra of KrBr excilamp 2 at the fixed mixture pressure of 150 Torr (a) and two different pressures at the fixed ratio $Kr:Br_2 = 400:1$ (b).

$$Kr + e \rightarrow Kr^* + e, \quad (1)$$

$$Kr + e \rightarrow Kr^+ + 2e, \quad (2)$$

$$Br_2 + e \rightarrow Br + Br^-, \quad (3)$$

$$Br_2(Br) + e \rightarrow Br_2^*(Br^*) + e, \quad (4)$$

$$Br(Br^*) + e \rightarrow Br^+ + 2e, \quad (5)$$

$$Kr^* + Kr + Kr \rightarrow Kr_2^* + Kr, \quad (6)$$

$$Kr^* + Br_2 \rightarrow KrBr^* + Br, \quad (7)$$

$$Kr_2^* + Br_2 \rightarrow KrBr^* + Kr + Br, \quad (8)$$

$$Br_2(Br_2^*) + e \rightarrow Br_2^{**} + e, \quad (9)$$

$$Kr + Br_2^{**} \rightarrow KrBr^* + Br, \quad (10)$$

$$Kr^+ + Br^- + Kr \rightarrow KrBr^* + Kr, \quad (11)$$

$$KrBr^* \rightarrow Kr + Br^*, \quad (12)$$

$$KrBr^* + Br_2 \rightarrow Kr + Br + Br_2, \quad (13)$$

$$Kr^*(Kr_2^*) + Br_2(Br) \rightarrow Kr(2Kr) + Br_2^*(Br^*), \quad (14)$$

$$Kr^*(Kr_2^*) + Br \rightarrow Kr(2Kr) + Br^*, \quad (15)$$

$$Br^* + Br_2 \rightarrow Br + Br_2^*, \quad (16)$$

$$Br^+ + Br^- \rightarrow Br_2^*, \quad (17)$$

$$Br_2^* + Br_2(Br) \rightarrow Br_2 + Br_2(Br), \quad (18)$$

$$Br^* + Br(Br_2) \rightarrow Br + Br(Br_2), \quad (19)$$

$$Br_2^*(Br^*) + Kr \rightarrow Br_2(Br) + K, \quad (20)$$

$$Kr^* + Kr + Br_2 \rightarrow KrBr^* + Br + Kr, \quad (21)$$

$$Br^+ + Br^- + Kr \rightarrow Br_2^* + Kr. \quad (22)$$

By analogy with the formation of KrI^* and I_2^* molecules in KrI excilamps [12, 13], we can conclude that $KrBr^*$ molecules at moderate pressures are produced successively due to the electron-impact formation of excited krypton atoms and ions (1), (2) and then in processes (7), (8), (10), (11), but mainly in the course of harpoon reactions (7), (8), (10). The contribution of three-particle reactions (11) is small at pressures up to 200 Torr. Exciplexes are destructed due to predissociation (12) [14] and quenching of $KrBr^*$ by molecular (13) and atomic bromine. The excitation energy transfer to bromine molecules and atoms in reactions (14) and (15) reduces the concentrations of Kr* and Kr_2^*, which restricts indirectly the formation of KrBr* molecules.

The Br_2^* molecules can be produced in reactions (4), (14), (16), (17), and (22), and Br^* and Br_2^* can be quenched in reactions (18)–(20). In addition, a weak emission of Br_2^* can be explained by the reabsorption of radiation by molecular bromine.

As the mixture pressure is increased, the total radiation power of the KrBr excilamp increases first due to reactions (7), (8), (4), (14), (16), and (17) and then due to reactions (11), (21), and (22), achieves its maximum and then decreases. The radiation power decreases at high pressures due to the increase in the nonradiative decay of excimers and exciplexes when the number of collisions between them and neutral particles increases. Such behaviour is typical for KrCl, XeCl, KrI, and KrBr excilamps (see, for example, [2, 8, 10]).

Figures 3 and 4 present the dependences of the luminosity of excilamps 1 and 2 in the emission bands of $KrBr^*$ and Br_2^* molecules on the total mixture pressure. One can see that in mixtures with a large content of bromine ($Kr:Br_2^* = 100:1$) the luminosity in the bands of KrBr* molecules is smaller than that in the bands of Br_2^* molecules or comparable to it (Figs 3a and 4a). This is explained by quenching of exciplexes by molecular bromine. A comparison of the intensities of the $KrBr^*$ and Br_2^* bands shows that a decrease in the concentration of bromine in the working mixture reduces the influence of quenching processes (13), (18), (19), (20), while harpoon reactions (7) and (16) of the formation of exciplex molecules and Br_2^* proceed more efficiently (Figs 3b–c and 4b–c). As a result, as the fraction of Kr in the mixture is increased, the luminosity of the $KrBr_2^*$ bands noticeably increases; the luminosity of Br_2^* molecules also increases, but weaker (Fig. 2a).

Figure 5 presents the luminosities of the $KrBr^*$ and Br_2^* bands obtained for optimal total mixture pressures as functions of the krypton fraction in the mixture. One can see that there exists the optimal ratio $[Kr]/[Br_2]$ and the reduction of the Br_2 fraction down to 0.2 % (Fig. 5) leads to a decrease in the luminosity of $KrBr^*$ and B_2^* bands.

Thus, the average radiation power of the excilamp increases with increasing pressure and the Kr fraction in the mixture due to the increase in the intensity of $KrBr^*$ emission bands. Figures 3 and 4 also show that the luminosity P_{sp} depends on the gas discharge gap d.

It was found earlier [8] in experiments with a KrBr excilamp with a 2-mm discharge gap and the $Kr:Br_2 = 30:1$ mixture that the radiation power at the $B \rightarrow X$ transition in $KrBr^*$ molecules weakly depended on the mixture pressure. This is consistent with our assumption about strong quenching of $KrBr^*$ by molecular bromine and explains why the luminosity of 0.6 mW cm^{-2} ($f = 20$ kHz) achieved in [8] is lower than that in our experiments.

It follows from our measurements that the maximum luminosity of the KrBr lamp is achieved when the discharge gap is $d_{opt} \sim 8.5$ mm (excilamp 2). In the case of smaller discharge gaps, the radiation power is lower, as follows from comparison with data reported in [8]. Excilamps 1 and 2 can be compared because they have close voltage pulse repetition rates f (see Table 1). Under optimal radiation power conditions, the luminosities of excilamps 1 and 2 with the

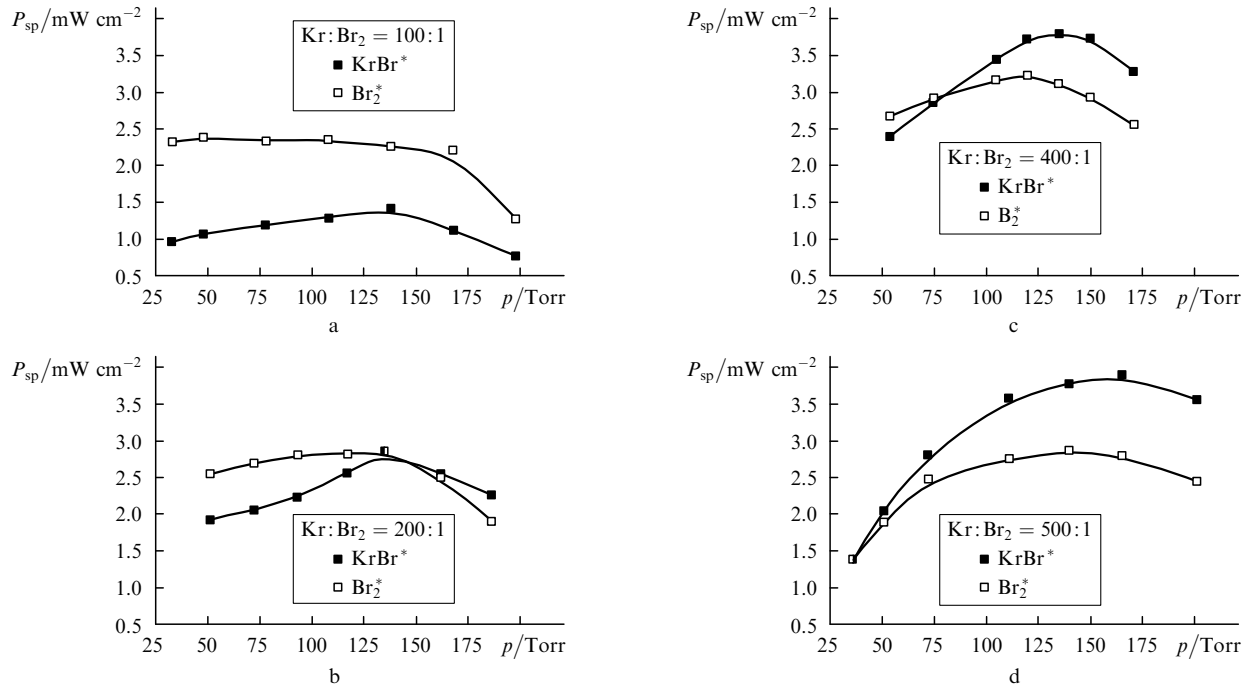

Figure 3. Dependences of the luminosity of excilamp 1 in the emission bands of $KrBr^*$ and Br_2^* molecules on the working mixture pressure for different $Kr:Br_2$ ratios.

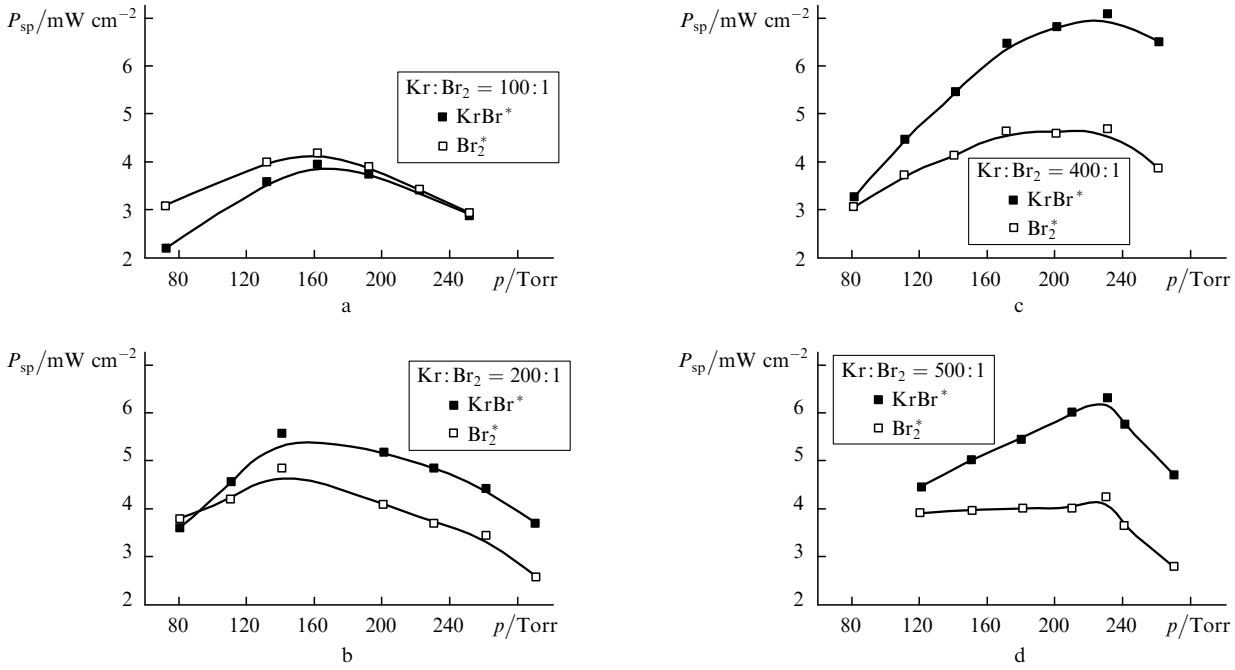

Figure 4. Dependences of the luminosity of excilamp 2 in the emission bands of $KrBr^*$ and Br_2^* molecules on the working mixture pressure for different $Kr:Br_2$ ratios.

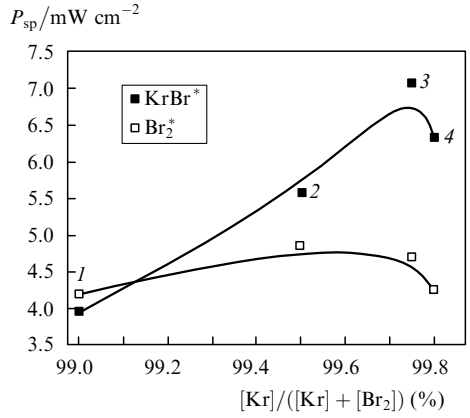

Figure 5. Dependences of the luminosity of excilamp 2 in the emission bands of $KrBr^*$ and Br_2^* molecules, obtained at optimal total mixture pressures, on the krypton fraction in the $Kr:Br_2$ mixtures 100:1 (*1*), 200:1 (*2*), 400:1 (*3*), and 500:1 (*4*).

$Kr:Br_2 = 400:1$ mixtures and pressures 120 and 231 Torr achieved 6.95 and 11.8 mW cm^{-2}, respectively. The optimal discharge gap $d_{opt} = 7.5$ mm close to the value obtained in our experiments was obtained in [15] where barrier-discharge XeBr lamps were studied for $d = 2.5$, 5.5, 7.5, and 10.5 mm.

We found earlier that excilamps operated most efficiently when microscopic discharges were formed in the discharge gap, which represented two cones with their bases lying on the surfaces of dielectrics (quartz tube walls) and their apexes connected [16]. In this regime, the high average radiation power was obtained and the lamp efficiency was close to its maximum value. If $d > d_{opt}$, a filament channel appears between apexes of the cones, the luminosity of this channel being lower than that of the cones whose height decreases. In fact the discharge is contracted in the filament channel and, hence, its radiation power is low. As a result, with increasing d up to 11 mm in our experiments with KrBr excilamps, the radiation power decreases because a conical microscopic discharge transforms to a filament discharge with flat 'bottoms'. For $d < d_{opt}$, the radiation power also decreases because microscopic discharges in the form of two cones cannot be formed.

The highest radiation powers achieved for excilamps are presented in Table 2. One can see that the radiation powers for excilamps 1 and 2 differ by a factor of 1.5 although the emitting surface area of excilamp 1 is greater than that of excilamp 2 by a factor of 2.3 (Table 1). This is explained by the fact that the ratio of the luminosities of excilamps is $P_{sp2}/P_{sp1} \sim 1.7$. Therefore, we can assume that, by scaling excilamp 2 so that its emitting area becomes corresponding to the radiation power of excilamp 1, it is possible to achieve the average power of ~ 11 W. Figure 6 presents the dependences of the average power of excilamp 2 and its efficiency on the total pressure of the gas mixture for $Kr:Br_2 = 400:1$.

Table 2. Maximum radiation powers of excilamps 1 and 2 and conditions for their obtaining.

Excilamp number	P/W	$Kr:Br_2$	p/Torr
1	6.5	400:1	120
2	4.8	400:1	231

4. We have studied the spectral and energy characteristics of barrier-discharge multiband KrBr excilamps at pressures from a few tens of Torr to 0.4 atm. Coaxial KrBr excilamps of different sizes have been used. It has been shown that the discharge gap of ~ 8.5 mm provides the maximum radiation energy. The conditions have been studied under which the energy is redistributed between the emission bands of Br_2 and $KrBr^*$ molecules. As the fraction of Kr in the mixture is increased, the luminosity in the $KrBr^*$ bands noticeably increases, while the luminosity

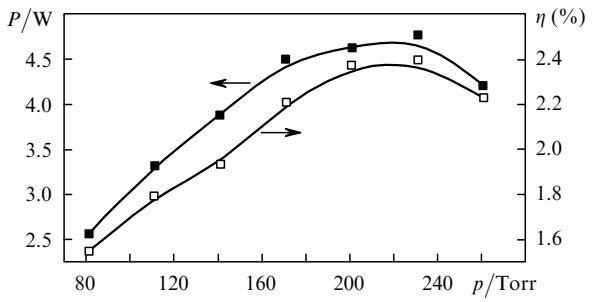

Figure 6. Average radiation power and efficiency of excilamp 2 for the $Kr:Br_2 = 400:1$ mixture.

in the Br_2^* bands increases only weakly. An increase in the concentration of Br_2 leads to the nonradiative decay of $KrBr^*$ exciplexes due to quenching by molecular bromine. As a result, the radiation intensity at transitions in $KrBr^*$ decreases compared to that in Br_2^* and the total radiation power of the excilamp decreases.

The maximum luminosity and radiation efficiency of the excilamp have been obtained for the $Kr:Br_2 = 400:1$ mixture at a total pressure of 231 Torr and the discharge gap 8 mm. They were 4.8 W and 2.4 %, respectively. The excilamps manufactured based on our studies can find applications in technologies for purification of water from microorganisms and organic pollutants.

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