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EMISSION KINETICS OF A HgBr DISCHARGE EXCILAMP

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A kinetic model of the working medium of a discharge excilamp on the B–X transition of mercury bromide, HgBr, excimer molecules has been proposed. The model explains the non-monotonic dependence of the excilamp radiation intensity on the partial pressure of mercury dibromide molecules by the attachment of electrons to these molecules. HgBr(X) molecules were found to transit into the HgBr(B) excited state due to their collisions with high-energy electrons, thereby improving the excilamp characteristics.

Keywords: excilamp, gas discharge plasma, kinetics, excimer radiation, mercury halides.

1. Introduction

Excimer lamps (excilamps) are sources of radiation in the UV and visible spectral ranges. They have been intensively studied within the last three decades [1–13]. In order to create a working medium of excilamps, the gas discharges similar to discharges in excimer lasers are used [1]. However, unlike the latter, excilamps produce cheaper polychromatic radiation intended for the illumination of large areas and volumes. In comparison with ordinary lamps, excilamps have a higher spectral density of radiation power: more than 80% of the total power is emitted in a narrow band 2 to 5 nm in width. Owing to these advantages, excilamps are widely applied in modern photophysics, photochemistry, and photobiology [3–5].

Excilamps based on mercury monohalides are promising to be used in the visible spectral range. Their radiation emission occurs owing to electronic-vibrational transitions in $HgBr^*$ ($\lambda = 502$ nm) and/or $HgCl^*$($\lambda = 557$ nm) excimer molecules. The working mixture HgX_2-M, where X = Br or Cl, and M = Ne, He, or Xe, is excited with pulse-periodic discharges.

Typical kinetic models [6, 9, 10, 13], which involve the kinetics of a gas discharge plasma, dissociative excitation of HgX_2 molecules, and deactivation and radiation emission of HgX(B) molecules cannot explain the experimental dependence of the energy emitted by HgX(B) molecules on the partial pressure of HgX_2. In experiments, when the $HgBr_2$ vapor pressure, P_{HgX_2}, increased from a few tenths to 0.5–1 kPa, the emission intensity I grew by an order of magnitude. The further increase of P_{HgX_2} to 1.5 kPa made I approximately half as high [6, 8]. However, ordinary theoretical models predict that the increase of P_{HgX_2} should be accompanied by a monotonic growth of both the generation rate of HgX^* molecules and the excilamp efficiency.

Our work differs from the previous ones as follows: 1) we calculate the coefficient of electron losses that characterizes the excilamp efficiency reduction associated with the electron attachment to HgX_2 molecules, and 2) we consider the excitation of electron states in HgX(B) molecules as a result of the collisions between HgX(X) molecules and electrons of the gas discharge plasma. The calculations were carried out without adjustable parameters. The theoretical pre-

diction agrees well, both qualitatively and quantitatively, with the measured dependences of I on the partial pressure of HgX_2 molecules.

2. Kinetic Model of Excilamp Plasma

In the proposed kinetic model, we consider the gas discharge plasma in the $HgBr_2$–Ne mixture as a set of two subsystems. One of them contains free electrons, and the other heavy particles: molecules, atoms, and ions. Different characteristic times are required for the equilibrium to be established in these subsystems. Relaxation in the electron subsystem is the most rapid, and we assume that, within the time interval much shorter than the discharge one, the Maxwellian distribution of electrons over their velocities characterized by the temperature T_e is established. If T_e and the time dependence of the electron concentration, $n(t)$, are known, the equations of physico-chemical kinetics can be used to calculate the concentration of heavy particles and the radiation power emitted by HgX(B) molecules.

The electron concentration $n(t)$ can be determined on the basis of the data of experiments, in which the current density in the gas discharge, $j(t)$, is measured. However, it should be noted that, while measuring $j(t)$, we cannot register all electrons formed in the electric discharge. This circumstance is related to the fact that some of the created electrons attach to electronegative molecules; in our case, HgX_2:

$$e + HgX_2 + (M) \xrightarrow{k_a} HgX_2^- + (M). \quad (1)$$

Since reaction (1) withdraws electrons from the sequence of processes resulting in the formation of HgX(B) molecules, the efficiency of a light source diminishes. This reduction was studied by calculating the coefficient of electron losses introduced in this work for the first time.

Calculations in the framework of the proposed kinetic model were carried out in two stages. At the first stage, a formula for the total rate of conduction electron generation in the gas discharge, $R(t)$, was postulated. Using $R(t)$, the electron concentration $n(t)$ was calculated analytically within the operational method. The obtained dependence $n(t)$ enabled the assumption about the form of $R(t)$ to be verified, because now the current density $j(t) = = evn(t)$, where e is the electron charge, and v is the drift vector of electrons, is known: this is a quantity that can be measured experimentally. At the second stage, the determined $n(t)$ dependence was used to solve numerically a system of kinetic equations for the concentrations of heavy particles. As a result, we obtained the radiation emission intensity by HgX(B) molecules, $I(t)$. This dependence is also known from experiments. Hence, a comparison of the calculated and experimental dependences $j(t)$ and $I(t)$ allows one to verify the proposed kinetic model. In the framework of this approach, a number of specific features inherent to electric discharges in the mixtures of inert gases with HgX_2 can explained. In particular, a nonmonotonic dependence of the emitted energy $\int I(t)dt$ on the HgX_2 concentration is explained.

3. Coefficient of Electron Losses

Let the rate of electron generation $R(t)$ and the electron concentration $n(t)$ be related to each other by the kinetic equation

$$\frac{dn}{dt} = R(t) - r_a\, n. \quad (2)$$

Here, we denote the rate of electron attachment to electronegative HgX_2 molecules in reaction (1) by $r_a \equiv k_a\,[HgX_2]$, where k_a is the constant of electron attachment, and $[HgX_2]$ the concentration of HgX_2 molecules.

Let us introduce the quantity $n_0(t) = \int_0^t R(s)ds$ equal to the number of electrons generated in a unit volume and rewrite Eq. (2) in the form

$$n(t) + r_a \int\limits_0^t n(s)\, ds = n_0(t). \quad (3)$$

The solution of Eq. (3) can be found, by using the operational method. Let the direct Laplace transformation of $n_0(t)$ give $N_0(p)$. Then, from Eq. (3), we get the Laplace transform of $n(t)$:

$$N(p) = \frac{p}{p + r_a} N_0(p). \quad (4)$$

Formula (4) can be used to recover the original function $n(t)$ for any $n_0(t)$.

The calculated dependences $n(t)$ agree well with the experimental ones, if

$$n_0 = n_{\rm m} \begin{cases} 0, & t < 0, \\ 2\,\exp\left(-\dfrac{t-t_0}{\tau}\right) - \exp\left(-\,2\,\dfrac{t-t_0}{\tau}\right), & t > 0, \end{cases} \quad (5)$$

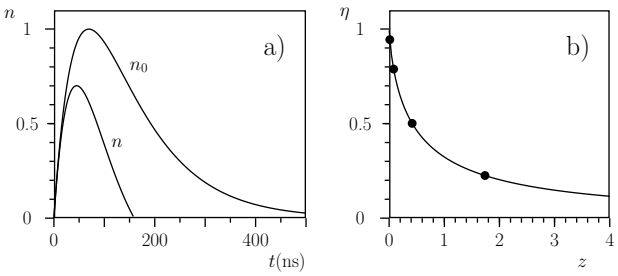

Fig. 1. Concentration of generated electrons and those survived in the discharge: curves n_0 and n were determined using Eqs. (5) and (6), respectively (*a*). $t_0 = 30$ ns and $z = 1$. Coefficient of electron losses η as a function of the parameter z. Points correspond to $\eta(z)$ values found at calculations, whose results are shown in Fig. 2 (*b*)

where $\tau \equiv t_0/\ln 2$. In this case, we obtain

$$n = 4\, n_{\rm m}\, \max\left[0;\right.$$
$$\left.\frac{\exp\left(-\frac{t}{\tau}\right)}{(1-z)} - \frac{2\exp\left(-2\frac{t}{\tau}\right)}{(2-z)} - \frac{z\exp\left(-z\frac{t}{\tau}\right)}{(1-z)(2-z)}\right], \qquad (6)$$

where $z \equiv r_a\, \tau$. The plots of functions (5) and (6) are shown in Fig. 1, *a*.

Equation (3) makes it possible to analyze the fraction of electrons that attach to molecules and, hence, leave the subsystem of light particles, reducing the excilamp efficiency. Let us introduce the coefficient of electron losses, which defines a decrease of the concentration of electrons as a result of their attachment to electronegative molecules,

$$\eta = \int\limits_{-\infty}^{\infty} n(t)\, dt \Big/ \int\limits_{-\infty}^{\infty} n_0(t)\, dt. \qquad (7)$$

If $\eta = 1$, process (1) does not reduce the light source efficiency. If $\eta = 0$, all free electrons attach to HgX_2 molecules, so that the transformation of the electric discharge energy into the energy of light becomes impossible.

The dependence of the coefficient η on the parameter z calculated for Eq. (5) is depicted in Fig. 1, *b*. According to the results of calculations, if $z = 1$, the excilamp efficiency becomes three times lower due to reaction (1). Under those conditions, the reduction of the maximum radiation power is not so large: the ratio between the maxima of $n(t)$ and $n_0(t)$ equals 0.7.

4. Kinetics of Heavy Particles

The kinetics of heavy particles in HgX_2–M plasma was simulated on the basis of the standard model describing a laser on the HgX(B–X) transitions [1]. The following processes were taken into account (see Table). Process 1a is the creation of HgX(B) molecules as a result of the dissociation of HgX_2 molecules at their collisions with electrons. The dissociation rate constant k_d was evaluated using the data of work [15]. The quantum yield of the formation of a molecule in the state B $^2\Sigma^+_{1/2}$ amounts to 0.2÷0.25 for the electron energy $\epsilon = 5 \div 10$ eV. Collisions between electrons and HgX_2 molecules are also accompanied by the formation of HgX molecules in the ground state (reaction 1b) and the ionization (process 2). Electronically excited HgX(B) molecules transit into the ground state either by emitting a photon (process 10) or not (process 11). HgX(X) molecules can either dissociate at their collisions with the atoms of a buffer gas M (process 6) or form a three-atomic HgX_2 molecule at their collisions with X_2 halogen molecules (process 8). Besides direct reactions 6 and 8, we took inverse reactions 7 and 9 into account. The rate constants of dissociation reactions 6 and 13 are [17]

$$K^{(d)}_{\rm AX} = K_{\rm AX}\left(\frac{T}{1000\, K}\right)^{1/2} \exp\left(-\frac{D_{\rm AX}}{k_{\rm B}T}\right) K^{(r)}_{\rm AX}, \qquad (8)$$

where A = Hg or X, $K_{\rm HgX} = 0.6\times10^{24}$ cm^{-3}, $D_{\rm HgX} = 0.48$ eV [18], $K_{\rm X_2} = 10^{24}$ cm^{-3}, $D_{\rm X_2} = 1.97$ eV [18], and T is the gas temperature measured in Kelvins.

Reactions 1, 10, and 11 dominate in the electric discharge plasma [1,6,7,9,10,13]. Making allowance only for them, the radiation intensity I for the transition HgX(B) $\rightarrow$ HgX(X) in the quasistationary approximation is described by the formula

$$I = \frac{h\nu\, k_{\rm d}\, n\, [{\rm HgX_2}]}{1 + \tau_{\rm r}\left(k_{\rm M}\, [{\rm M}] + k_{\rm HgX_2}\, [{\rm HgX_2}]\right)}, \qquad (9)$$

where $h\nu$ is the photon energy. According to Eq. (9), the intensity I increases with the concentration $[HgX_2]$ and approaches the constant value

$$I_{\rm s} = \frac{h\nu\, k_{\rm d}}{\tau_{\rm r}\, k_{\rm HgX_2}}\, n. \qquad (10)$$

Formula (10) makes it evident that, in order to explain the experimental data, the dependence of n on

Kinetics of heavy particles in HgX_2–M plasma [a)]

No.	Process	Rate constant	Formula or source
1.a, 1.b	$e + HgX_2 \begin{cases} \rightarrow HgX(B) + X + e \\ \rightarrow HgX(X) + X + e \end{cases}$	$k_d = 2 \times 10^{-9}$ cm^3/s	Estimation [b)]
		$\kappa\, k_d,\ \kappa = 4$	[1]
2	$e + HgX_2 \rightarrow HgX_2^+ + 2e$	$k_i = 1.8 \times 10^{-9}$ cm^3/s	[14, 15]
3	$e + HgX_2 \rightarrow HgX_2^- \rightarrow HgX(X) + X^-$	k_a	(12)
4	$e + HgX(X) \rightarrow HgX(B) + e$	k_e	(11)
5	$e + HgX(X) \leftarrow HgX(B) + e$	$k_e \exp\left(\frac{E_B - E_X}{T_e}\right)$	
6	$HgX(X) + M \rightarrow Hg + X + M$	$K^{(d)}_{HgX}$	(8)
7	$HgX(X) + M \leftarrow Hg + X + M$	$K^{(r)}_{HgX} = 10^{-32}$ cm^6/s	Estimation [c)]
8	$HgX(X) + X_2 \rightarrow HgX_2 + X$	$k_x = 8 \times 10^{-11}$ cm^3/s	
9	$HgX(X) + X_2 \leftarrow HgX_2 + X$	$500 \exp\left(-\frac{13100}{T}\right) k_x$	[6]
10	$HgX(B) \rightarrow HgX(X) + h\nu$	$\tau_r = 23 \times 10^{-9}$ s	[16]
11	$HgX(B) + Q \rightarrow HgX(X) + Q$	$k_Q = 2{,}3 \times 10^{-10}$ cm^3/s, Q = HgX_2	[16]
		$k_Q = 5 \times 10^{-13}$ cm^3/s, Q = Ne	[16]
12	$X + X + M \rightarrow X_2 + M$	$K^{(r)}_{X_2} = 3.5 \times 10^{-33}$ cm^6/s	
13	$X + X + M \leftarrow X_2 + M$	$K^{(d)}_{X_2}$	(8)

a) X stands for Br, J, or Cl, and M for Ne or He. Numerical values of rate constants are given for the mixture $HgBr_2$–Ne; b) According to data of works [1, 6] for $E/P = 2$ V/(cm Torr); c) According to data of work [1].

[HgX_2] has to be taken into account. In this work, this was done by calculating coefficient (7).

We extended the standard kinetic model of a HgX(B–X) lamp, by considering the excitation of the state HgX(B) in collisions of electrons with the HgX(X) molecules. A possibility for reaction 4 to be an additional channel for the creation of HgX(B) molecules was indicated in work [7]. A formula for the rate constant of electron-induced transitions in two-atom molecules was obtained in theoretical work [19] as

$$k_e = \frac{16\sqrt{\pi}\,|\mu_{BX}|^2}{3\,a\,p_0} \exp\left(\frac{E_X - E_B}{2\,k_B T_e}\right) \times \\ \times K_0\left(\frac{E_B - E_X}{2\,k_B T_e}\right), \qquad (11)$$

where $p_0 = (2\,k_B T_e m_e)^{1/2}$, k_B is the Boltzmann constant, and K_0 the modified Bessel function. For the transition between the states HgBr(B) and HgBr(X), we have $E_B - E_X = 23480$ cm^{-1} and $\mu_{BX} = 4$ D; from whence, we find the rate constant $k_e = 2.9 \times \times 10^{-7}$ cm^3/s if $T_e = 8$ eV. The rate constant for the inverse reaction is 1.4 times higher.

The rate constant of reaction (1) was determined by the formulas taken from work [20] and using the data of work [21]:

$$k_a = \sigma_f \frac{\varepsilon^\star\,\Delta\varepsilon}{k_B T_e} \sqrt{\frac{8}{\pi\, m_e\, k_B T_e}} \exp\left(-\frac{\varepsilon^\star}{k_B T_e}\right). \qquad (12)$$

Here, $\sigma_f = 0.6 \times 10^{-17}$ cm^2, $\varepsilon^\star = 3.7$ eV, $\Delta\varepsilon = = 0.5$ eV, and m_e is the electron mass.

5. Intensity of Radiation Emitted by HgX(B)

In this work, the rate $R(t)$ is assumed to weakly depend on the concentration of HgX_2 molecules in the gas mixture. At the first stage, we selected $R(t)$ and calculated $n(t)$. Then, using the function $n(t)$, we solved the system of equations determining the time dependences for the HgX_2, HgX(X), HgX(B), X, X_2, and Hg concentrations and calculated the radiation power emitted by HgX(B) molecules.

The calculations were carried out for the following parameters: the buffer gas pressure $P = 107$ kPa, the temperature T varied from 365 to 465 K, $T_e = 8$ eV, $v = 2.7{\times}10^6$ cm/s, and $n_m = 4.62{\times}10^{13}$ cm^{-3}. The pressure of saturated HgX_2 vapor was determined using the following formula interpolating tabular values [22]:

$$\lg P_{HgX_2} = -\frac{4470}{T} + 11.50 - 0.05\left(\lg T - \frac{T}{40}\right). \qquad (13)$$

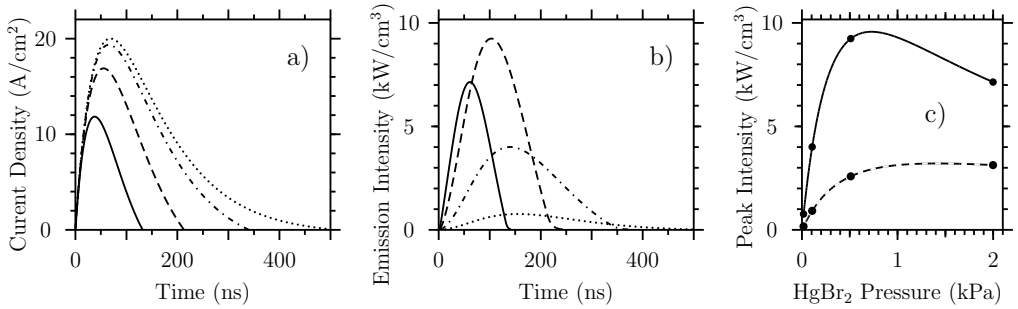

Fig. 2. Current (a) and emission intensity (b) pulses found for various $HgBr_2$ pressures, and (c) the emission intensity as a function of the $HgBr_2$ pressure. Points in Fig. 2, c mark the maximum values of intensities for curves in Fig. 2, b. The dashed curve demonstrates the results of calculations with $k_e = 0$

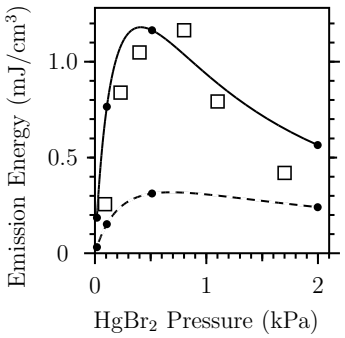

Fig. 3. Theoretical values of excilamp emission energy. Squares correspond to the experimental values of emission intensity (in arbitrary units) taken from Fig. 1.19 in work [6]. The dashed curve shows the results of calculations omitting reactions 4 and 5

Here, P_{HgX_2} is the HgX_2 pressure measured in Torr units (1 Torr = 133.3 Pa), and T the temperature in Kelvins.

The system of kinetic equations for the concentrations was solved numerically, by using the Gear method. The results of calculations are shown in Fig. 2, where the current density in a gas discharge, $j(t)$, and the specific power of radiation, $I(t)$, are compared. In addition, Fig. 2, c exhibits the peak intensity of radiation, and Fig. 3 the radiation energy. The found dependence of the radiation energy on the pressure of saturated HgX_2 vapor agrees well with experimental data [6].

The proposed kinetic model differs from the previous ones in that it involves the HgX(X–B) transitions arising owing to the collisions between HgX molecules and electrons. The rate constants for these transitions were determined theoretically, with no adjustable parameters. In order to elucidate the role of reactions 4 and 5, we calculated the intensity of radiation emitted by a lamp in the case $k_e = 0$. The results of these calculations are shown in Figs. 2, c and 3 by dashed curves. The figures testify that both the peak radiation power and the radiation energy of a lamp decrease by approximately a factor of four at $k_e = 0$. Of no less importance is the fact that, along with quantitative changes, qualitative ones are also observed. Namely, the dependence of the excilamp radiation power on the HgX_2 pressure ceases to be non-monotonic, which contradicts experimental data. Hence, the population of the HgX(B) state owing to collisions between plasma electrons and HgX(X) molecules substantially enhances the excilamp radiation intensity. Reactions 4 and 5 must be taken into account in the kinetic models of working medium of excimer light sources.

Reaction 4 allows one to predict some unexpected features of radiation emission by excilamps on the HgX(B—X) transitions. For example, in the recent experiment [13], two sequential current pulses with a time interval of an order of 100 ns were passed through a working medium of an excilamp on HgBr(B–X) transitions. The amplitudes of current pulses were approximately equal, but the peak power in the second radiation pulse exceeded that in the first pulse by more than twice. Qualitatively, this effect can be explained by the fact that, before the second current pulse, a significant amount of HgBr(X) molecules were stored in the working medium during the first emission pulse. As a result of their collisions with electrons, these molecules were transferred into the excited state, so that the intensity of excilamp radiation increased by more than 100%.

6. Conclusions

The main result of this research consists in the development of the kinetic model for the radiation emission of a mercury halide excimer lamp. An important element of the model is the coefficient of electron losses introduced for the first time. This coefficient takes into account the attachment of gas-discharge electrons to electronegative halide-containing molecules. It was shown that this process directly affects the efficiency of an excimer light source. A method to calculate the coefficient of electron losses analytically is proposed, which simplifies the evaluation of the excimer light source efficiency. The proposed kinetic model is used to explain the dependence of the radiation intensity of an excilamp based on the $HgBr(B \to X)$ transitions on the partial pressure of $HgBr_2$ molecules. An importance of collisions between electrons and excimer molecules giving rise to the electron transitions between the HgBr(X) and HgBr(B) states is elucidated for the first time. The results of calculations are quoted for the mixture of $HgBr_2$ with Ne. However, this model can also be used to calculate and optimize the parameters of an excimer light source, in which other buffer gases and other excimer molecules, in particular, HgCl and HgI, are used.

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КІНЕТИКА ВИПРОМІНЮВАННЯ
ГАЗОРОЗРЯДНОЇ HgBr ЕКСИЛАМПИ

Р е з ю м е

Запропоновано кінетичну модель робочого середовища газорозрядної ексилампи на переході B–X ексимерних молекул броміду ртуті HgBr. Модель пояснює немонотонну залежність інтенсивності випромінювання ексилампи від парціального тиску молекул дібромід ртуті прилипанням електронів до цих молекул. Встановлено, що в зіткненнях з високоенергетичними електронами молекули HgBr(X) переходять у збуджений стан HgBr(B), завдяки чому характеристики ексилампи покращуються.