POPULATION DENSITY OF $B^2\Sigma^+_{1/2}$ - STATE OF MERCURY MONOBROMIDE AND MONOCHLORIDE IN EXCIMER RADIATION SOURCES

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The numerical calculation of the $B^2\Sigma^+_{1/2}$ - state population in $HgBr^*$ and $HgCl^*$ molecules for weakly ionised (degree of ionisation $\leq 10^{-6}$) gas-discharge plasma of a pulse-periodic discharge in binary mixtures of mercury dibromide and dichloride with helium and neon has been carried out versus the value of parameter E/p at the ratio $HgBr_2(HgCl_2)$:He(Ne)=0.5:99.5 and total pressure of the mixture equal to 115 kPa. The $B^2\Sigma^+_{1/2}$ -state populations in mercury monohalides were found out from a kinetic equation for the population of this state. The population of the $B^2\Sigma^+_{1/2}$ -state in HgBr* molecules is equal to $3.25\cdot10^{13}$ cm^{-3} and it is 5.2 times larger than for HgCl* molecules in mixtures with helium and 4.6 times in mixtures with neon at E/p=3 V cm^{-1}(mm Hg)$^{-1}$. The populations of HgBr* and HgCl* molecules in mixtures with helium are larger than those in mixtures with neon. Maxima populations of the $B^2\Sigma^+_{1/2}$ -state in mercury monohalogenides are obtained with E/p = 2-5 V cm^{-1}(mm Hg)$^{-1}$.

Data on populations of the upper operating level ($B^2\Sigma^+_{1/2}$ -state) of mercury monohalogenides are necessary for the optimisation of parameters and characteristics of the gas-discharge excimer radiation sources on mixtures of mercury dihalides with rare and other gases. The measurements of populations of mercury monobromides and monochlorides in gas-discharge plasma of working mixtures of excimer radiation sources were not carried out. In [1-4] the calculations of populations of mercury monohalogenides ($HgCl^*$, $HgBr^*$ and HgI^*) were made for working media based on mixtures of mercury with halogen-containing molecules and rare gases, mercury dibromide with helium, mercury dibromide with neon, mercury dibromide both with neon and admixtures of xenon and nitrogen.

We have calculated the populations of the $B^2\Sigma^+_{1/2}$-state in HgBr* and HgCl* molecules for weakly ionised (degree of ionisation $\leq 10^{-6}$) gas-discharge plasma of a pulse-periodic discharge in binary mixtures of mercury dibromide and dichloride with helium and neon vs the value of parameter E/p at the ratio $HgBr_2(HgCl_2)$:He(Ne)=0.5:99.5 and total pressure of the mixtures equal to 115 kPa. Such percent ratio was selected from optimal conditions of approaching to the most effective compositions of mixtures by energy characteristics of discharge radiation, which were obtained experimentally in a gas-discharge excimer lamp [5].

The populations of the $B^2\Sigma^+_{1/2}$-state in mercury monohalogenides were found from a kinetic equation for the population of this state [6]:

$$\frac{d[HgX^*]}{dt} = k_d[HgX_2][N_e] - ([HgX^*]/\tau_{HgX^*}) - k_q[HgX^*][HgX_2], \quad (1)$$

where $[HgX^*]$, $[HgX_2]$, $[N_e]$ are the concentrations of HgX^* (X=Br, Cl), HgX_2 and electrons, k_d is the rate constant of molecular dissociation of HgX_2 by electronic shock, τ_{HgX^*} is the radiative lifetime of HgX^*, k_q is the quenching rate constant of HgX^*.

The first term in equation (1) determines the population rate of the $B^2\Sigma^+_{1/2}$-state due to the dissociative excitation by electrons. The second term describes the decay of the $B^2\Sigma^+_{1/2}$-state due to spontaneous radiative transitions. The third term governs quenching due to collisions of HgX^* molecules in the $B^2\Sigma^+_{1/2}$-state with HgX_2 molecules.

For quasi-stationary case it is possible to obtain the expression for the population from equation (1):

$$[HgX^*]=(k_d\,[HgX_2]\,N_e)/(\tau^{-1}_{HgX^*}+k_q\,[HgX_2]). \quad (2)$$

Let us find out the conditions, under which it is possible to consider a mode of a pulse discharge steady. For this purpose it is necessary that the duration of an exciting pulse be bigger than characteristic times of processes which have an influence on the concentration of excited $HgBr^*$ and $HgCl^*$ molecules. For our case this time should be bigger than characteristic transient time of a quasi-stationary electron energy distribution function (EEDF), time of dissociation of $HgBr_2^*$ and $HgCl_2^*$, time of quenching and radiation lifetime of the $B^2\Sigma^+_{1/2}$-state in $HgBr^*$ and $HgCl^*$. The transient time of quasi-stationary distribution of electrons, i.e. the time of "tracking" EEDF for changes of an electric field strength and concentrations of plasma components is approximately equal to the relaxation time of mean energy of electrons [7]:

$$\tau=\frac{mv_e}{e^2E^2}\bar{\varepsilon}\ , \quad (3)$$

where m is the mass of an electron, e is the charge of an electron, E is the electric field strength, $\bar{\varepsilon}$ is the mean energy of electrons, $v_e=N\left(\frac{2}{m}\right)^{1/2}\int_0^\infty U^2Q(U)f(U)dU$ is the frequency of elastic collisions of electrons with atoms of helium or neon, N is the concentration of atoms He or Ne in the mixture, $Q(U)$ is the effective cross-section elastic scattering of electrons on helium or neon atoms, $f(U)$ is an isotropic part of an EEDF normalized by the condition: $\int_0^\infty U^{1/2}f(U)dU=1$.

To determine a quasi-stationary distribution function of electrons on energies in a gas-discharge excimer lamp the Boltzman equation for electrons was numerically resolved, on this basis the electronic kinetic factors were determined. The E/p value ranged 1-30 V cm^{-1}(mm Hg)$^{-1}$ in calculations. The concentrations of $HgBr_2$ and $HgCl_2$ varied from 0.2% up to 2%.

The executed estimations of the time of EEDF establishment according to the formula (3) in a mixture $He:HgBr_2$=99.5:0.5 demonstrate, that at E/p=20 V·cm^{-1}(mm Hg)$^{-1}$ for an operating pressure of 115 kPa was less than $\tau \le 8$ ns.

The time of dissociation (t_d) of $HgBr_2$ and $HgCl_2$ by electronic shock and time of quenching (t_q) of the $B^2\Sigma^+_{1/2}$-state of $HgBr^*$ and $HgCl^*$ by molecules of mercury dihalides were estimated from formulas:

$$\tau_d \sim \left(k_d[HgX_2]\right)^{-1}\ , \quad (4)$$

$$\tau_q \sim \left(k_q[HgX_2]\right)^{-1}\ , \quad (5)$$

where k_d for our case is equal to $7.8\cdot10^{-9}$ cm^3/s and $6\cdot10^{-10}$ cm^3/s for $HgBr_2$ and $HgCl_2$ at E/p=20 V·cm^{-1}(mm Hg)$^{-1}$, respectively [2], $[HgX_2]$ is the concentration of $HgBr_2$ and $HgCl_2$ under work conditions (~ 10^{17} cm^{-3}), k_q for $HgBr_2$ and $HgCl_2$ is equal to $2.7\cdot10^{-10}$ cm^3/s and $5.5\cdot10^{-11}$ cm^3/s, respectively [6].

The estimations of times of dissociation and quenching give the values < 20 ns and < 100 ns respectively for the whole E/p range. The radiation lifetimes of the $B^2\Sigma^+_{1/2}$-state $HgBr^*$ and $HgCl^*$ revealed to be 23.2 ns and 22.2 ns, respectively [8, 9]. Thus, the characteristic times of basic processes which have an influence on the concentrations of excited $HgBr^*$ and $HgCl^*$ molecules are much less than pulse duration of pumping (~150 ns), that allows one to use the solution (2) for the population of the $B^2\Sigma^+_{1/2}$-state in $HgBr^*$ and $HgCl^*$ molecules.

Table 1. Electron concentrations and populations of the $B^2\Sigma^+_{1/2}$ -state in HgBr and HgCl.

E/p, $V\cdot cm^{-1}(mm\ Hg)^{-1}$	1	2	3	4	5	6	8	10	20	30
$He:HgBr_2$										
N_e, $10^{12}cm^{-3}$	21.0	11.0	7.5	5.8	4.6	3.9	3.0	2.4	1.3	1.1
$[HgBr^*]$,$10^{12}cm^{-3}$	4.5	26.5	32.5	32.5	30.5	29.0	26.5	21.0	16.5	15.5
$Ne:HgBr_2$										
N_e,$10^{12}cm^{-3}$	16.0	8.8	6.2	4.9	4.0	3.5	2.7	2.9	1.4	1.1
$[HgBr^*]$,$10^{12}cm^{-3}$	23.0	28.5	27.5	26.0	24.5	23.5	22.5	20.5	16.0	15.0
$He:HgCl_2$										
N_e,$10^{12}cm^{-3}$	20.5	11.0	7.5	5.5	4.6	3.7	3.0	2.5	1.4	1.1
$[HgCl^*]$,$10^{12}cm^{-3}$	1.5	6.1	6.2	5.4	5.1	4.6	4.3	3.9	2.8	2.5
$Ne:HgCl_2$										
N_e,$10^{12}cm^{-3}$	17.0	9.1	6.3	4.9	4.0	3.5	2.8	2.3	1.4	1.1
$[HgCl^*]$,$10^{12}cm^{-3}$	7.1	6.0	5.1	4.5	4.0	3.9	3.5	3.2	2.6	2.3

The electron concentration N_e was calculated in accordance with the known formula

$$N_e=j/(ev_{dr}), \qquad (6)$$

where j is the current density in the discharge, e – charge of electron, v_{dr} - drift velocity of electrons.

The current density of a coaxial lamp (j=2.5 A/cm^2) was calculated on the current, which was measured in its inter-electrode space (147 A) and cross-sectional area of discharge (S_{int}=42.4 cm^2, S_{ext}=99 cm^2) [5]. The values for drift velocity of electrons were taken from the results of calculation of transport characteristics [2].

The results of numerical calculations of the population of the $B^2\Sigma^+_{1/2}$-state of mercury monohalogenides and electron concentration (for optimal concentrations of $HgBr_2$ and $HgCl_2$ molecules in discharge through quartz glass) in an interval E/p=1÷30 $V\cdot cm^{-1}(mm\ Hg)^{-1}$ are presented in the table. The population of the $B^2\Sigma^+_{1/2}$-state in HgBr* is higher than in HgCl*. In the mixture with helium the population of HgBr* and HgCl* molecules is bigger than those in the mixture with neon. Maxima of populations of the $B^2\Sigma^+_{1/2}$-state in mercury monohalogenides are obtained with E/p=2÷5 $V\cdot cm^{-1}(mm\ Hg)^{-1}$.

Let us compare the behavior of the population of the $B^2\Sigma^+_{1/2}$-state in HgCl*, HgBr* with dependences of radiation intensity of gas-discharge plasma in our experiments [10]. For this purpose we shall estimate the field strength E applied to the plasma. Since pulsed voltage is applied to a circuit "dielectric - gas mixture" the field strength E applied to the plasma will make a fraction of the total field strength that is determined finally by the voltage drop across the impedance of dielectric and plasma.

The capacitive resistance of an insulator is written as $X_c=1/(\omega C)$, where ω is the frequency of a leading edge of a pumping pulse and C is the capacity of the insulator. It is

known that for a glass insulator the capacity can be estimated as $C=C_0S$, where C_0=2 pF/cm^2 is the specific capacity of working dielectric with thickness of 2 mm. At the duration of a leading-edge pumping pulse of t_f =10 ns [10] the value of capacitive resistance X_c=50 Ω, the resistance of plasma in such systems is usually smaller by order [11]. Therefore the field strength on plasma is less by order than the field strength on dielectric - plasma interval. Let us determine the value of pressure p for E/p=2÷5 V·cm^{-1}(mm Hg)$^{-1}$:

$E/p=U/(dp)$=3000/(1.5p)=2÷5 V·cm^{-1}(mm Hg)$^{-1}$.

From here p=400-1000 mm Hg (p=53.3-133.3 kPa). This estimate for the pressure agrees well with the experimental values of the pressure corresponding to the maximum of emission intensity for mercury monohalogenides [10].

The obtained data on the population of the $B^2\Sigma^+_{1/2}$ - state of $HgBr^*$ and $HgCl^*$ molecules in a gas-discharge excimer lamp [1] are high and they are close to the detected data on the population in active media of lasers at the same values E/p [12]. This allows one to hope that powers of these excimer radiation sources will achieve the levels sufficient for practical purposes.

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ЗАСЕЛЕНОСТІ $B^2\Sigma^+_{1/2}$ - СТАНУ МОНОБРОМІДУ ТА МОНОХЛОРИДУ РТУТІ В ЕКСИМЕРНИХ ДЖЕРЕЛАХ ВИПРОМІНЮВАННЯ

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Зроблено чисельний розрахунок заселеності $B^2\Sigma^+_{1/2}$ - стану моногалогенідів ртуті ($HgBr^*$ та $HgCl^*$) для слабоіонізованої (ступінь іонізації ≤10^{-6}) газорозрядної плазми імпульсно-періодичного розряду в подвійних сумішах дибромідy та дихлориду ртуті з гелієм та неоном залежно від величини параметра E/p при співвідношенні $HgBr_2(HgCl_2)$:He(Ne) = 0.5:99.5 та загальному тиску сумішей 115 кПа. Концентрація моногалогенідів ртуті в $B^2\Sigma^+_{1/2}$ - стані знаходилась з кінетичного рівняння для заселеності цього стану. Її значення для молекул $HgBr^*$ ($3.3\cdot10^{13}$ см$^{-3}$) вище, ніж для молекул $HgCl^*$ в 5.2 раза в сумішах з гелієм і в 4.6 раза в сумішах з неоном при E/p = 3 В·см$^{-1}$·мм рт. ст$^{-1}$. Заселеності молекул $HgBr^*$ та $HgCl^*$ більші в сумішах з гелієм, ніж з неоном. Максимальні значення заселеності $B^2\Sigma^+_{1/2}$ - стану моногалогенідів ртуті знаходяться в області значень параметра E/p = 2÷5 В·см$^{-1}$·мм рт. ст$^{-1}$.