

PACS numbers: 52.80. – s; 33.60.Cv
DOI: 10.1070/QE2007v037n01ABEH013312

Emission of I_2^* molecules in a barrier discharge

S.M. Avdeev, E.A. Sosnin, V.F. Tarasenko

***Abstract*. The energy and spectral emission characteristics of a barrier discharge are studied in mixtures of inert gases with iodine vapour. The emission spectrum exhibits a strong 342-nm $D' \rightarrow A'$ molecular band of the I_2^* molecule, the 206.2-nm resonance line of iodine, and a group of emission bands of iodine. Small admixtures of Ne (5 %) to the $Ar - I_2$ mixture increase the emission efficiency and power by a factor of 2 – 2.5. A sealed off I_2 excilamp with the emission maximum at 342 nm is fabricated.**

Keywords: *excilamp, UV radiation, homonuclear I_2^* halogen.*

1. Introduction

Spontaneous UV and VUV emission at the free-bound transitions in RX^* halides and R_2^* dimers of inert gases has attracted great attention in the last two decades [1]. Such systems emitting due to the decay of excimer or exciplex molecules were called excilamps in [2]. The working mixtures used in excilamps represent binary and multicomponent mixtures containing inert gases and halogens, which can emit both a single narrow intense band containing up to 80 % of the total emitted energy, and several bands of excimer R_2^* and exciplex RX^* molecules. Such sources are a promising alternative to traditional luminescence light sources.

At present the conditions for obtaining the efficient luminescence of dimers of inert gases (for example, Xe_2^*, Kr_2^*, et al.) and halides of inert gases (for example, $XeCl^*$, $KrCl^*$, $XeBr^*$, XeI^*, et al.) are well studied, but these conditions for homonuclear halogens I_2^*, Br_2^*, Cl_2^*, F_2^* were analysed only in few papers, although the mechanisms of their luminescence are known, as a rule.

The first investigations and first models of emission of homonuclear halogens Br_2^* and I_2^* showed that their luminescence is related to the $^3\Pi_{2g} \rightarrow {}^3\Pi_{2u}$ transitions [3, 4] (or the $D' \rightarrow A'$ transitions in a different notation [5]). It was pointed out in [5] that these transitions can contribute to luminescence of F_2^* and Cl_2^* molecules.

In this paper, we attempted to find the conditions for obtaining the most efficient emission of I_2^* molecules and studied the spectral and energy characteristics of this emission. A relatively weak emission of these molecules in excilamps is usually observed along with a more intense emission of KrI^* [6] and XeI^* exciplexes [7]. We tried to produce conditions under which the contribution of I_2^* molecules to the total emission would be maximal.

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Received 23 June 2006
Kvantovaya Elektronika **37** (1) 107 – 110 (2006)
Translated by M.N. Sapozhnikov

2. Experimental

Unlike the authors of [3, 7], we excited the working mixture by a barrier discharge. A barrier discharge is a discharge in which the flow of current is limited at least by one dielectric layer and the characteristic size of electrodes considerably exceeds the interelectrode gap.

Such a discharge has a great parametric flexibility. By varying the external parameters of a barrier discharge such as its voltage (from hundreds of volts to a few kilovolts), the working mixture pressure p (from fractions of torr to 10^3 Torr), the gas-discharge gap d (1 – 10 mm), the parameters of the discharge plasma can be controlled in a broad range: the average electron temperature – from 1 to 10 eV, the ionisation degree – from 10^{-4} to ~ 1, and the electron concentration – from 10^{11} to 10^{15} cm^{-3}. In addition, in lamps with two dielectric barriers, a contact between the electrode and working mixture is excluded, which increases their service life [8]. A barrier discharge represents (depending on pressure) either a homogeneous discharge or randomly located microdischarges (in particular, in the form of separate filaments) in which the duration of the current flow does not exceed a few tens nanoseconds [9]. It is interesting to use the barrier discharge for obtaining the emission of I_2^* molecules.

Figure 1 shows the design of a lamp. Bulb (*1*) is made of two coaxial KU-1 quartz tubes of diameters 2.2 and 4.6 cm.

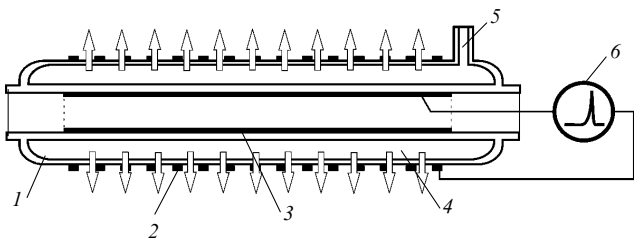

Figure 1. Lamp design: (*1*) bulb; (*2*) perforated electrode; (*3*) one-piece electrode; (*4*) discharge gap; (*5*) outlet for changing working mixtures; (*6*) high-voltage generator; the arrows show the direction of output emission.

The working region length of the lamp is 9 cm. External electrode (*2*) was spiral shaped and transmitted outside more than 95 % of emission from the discharge gap. One-piece electrode (*3*) was made of an aluminium – magnesium foil. The gas in gap (*4*) was excited by applying to the electrode the microsecond, ~5.5-kV voltage pulses in the form of a meander. The pulse repetition rate could be varied from18 to 120 kHz. The power supplied to the plasma depended on the voltage pulse amplitude and repetition rate and achieved 70 W for the maximal repetition rate.

We varied in experiments the pressures of iodine and added inert gas vapours and measured the emission power, the power supplied to the discharge, and emission spectra. Mixtures were prepared in the following way. First a small amount of crystalline iodine (0.05 – 0.10 g) was placed into the bulb, then the bulb was filled with an inert gas, a discharge was ignited in it, and iodine passed to the gas phase. Then, the mixture was repeatedly dissolved to find the conditions under which the emission intensity became maximal, the gas filling system was closed, and experiments were performed. To provide a stable emission during experiments, the bulb was cooled with a fan placed near its end.

The lamp emission power was measured with a FEK22-SPU photodetector with the known spectral sensitivity. The emission spectrum of the discharge and its time dependence were recorded with a system of three HR4000 spectrometers (Ocean Optics B.V.) with 1200 lines mm^{-1} diffraction gratings and a resolution of 0.25 – 0.31 nm operating in the spectral range from 200 to 410 nm. The power supplied to the discharge was measured from the oscillograms of voltage and current pulses by the method proposed in [10]. The current and voltage oscillograms from a current shunt and a voltage divider were recorded with a TDS 224 oscilloscope (Tektronix Inc.).

3. Results and discussion

A barrier discharge in pure iodine was studied under the following conditions: $p \leqslant 1$ Torr, the specific input power was $W_{sp}^{in} \leqslant 100$ mW cm^{-3}, and the ratio of the maximal field strength to pressure was $E_0/p \sim 6 \times 10^3$ V cm^{-1} $Torr^{-1}$. The lamp luminosity was rather low and did not exceed 0.11 mW cm^{-2}. Under these conditions, the 206.2-nm resonance line of atomic iodine, exceeding the intensity of the $D' \rightarrow A'$ emission band of the I_2^* molecule by a factor of 56, dominates in the emission spectrum.

Consider the mechanism of formation of the X_2^* molecule. If the pressure of a gas mixture is low, the dissociative attachment of low-energy electrons to X_2 halogen molecules can occur:

$$e + X_2 \rightarrow X^- + X. \qquad (1)$$

In this case, if conditions in the medium (field strength, pressure, the presence of easily ionised additions) allow also the production of halogen-containing positive ions) X^+ or RX^+), the $^3\Pi_{2g}$ states can appear at low pressured due to ion – ion recombination

$$X^- + X(RX^+) \rightarrow X_2^*(^3\Pi_{2g}) + (R). \qquad (2)$$

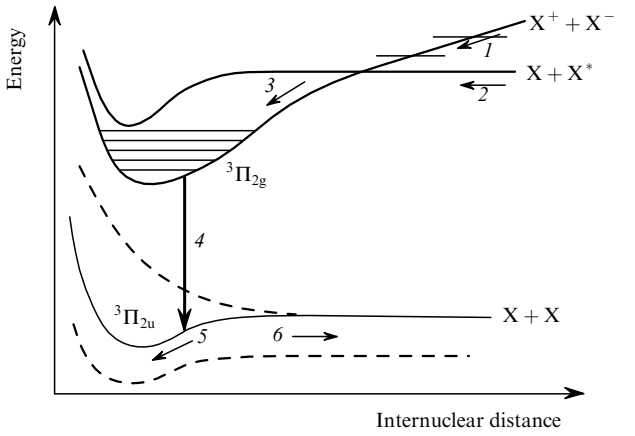

Figure 2. Simplified scheme of kinetic processes related to the luminescence of diatomic halogens [11]: (*1*) ion – ion recombination; (*2*) harpoon reaction; (*3*) relaxation of the $^3\Pi_{2g}$ state; (*4*) emission; (*5*) vibrational relaxation of lower levels; (*6*) dissociation of molecules from the $^3\Pi_{2u}$ state.

The excited states of homonuclear halogens can be also produced in harpoon reactions

$$X^* + X \rightarrow X_2^*(^3\Pi_{2g}). \qquad (3)$$

Figure 2 presents the simplified scheme of the formation and relaxation of some states of halogens [11].

The fast vibrational relaxation at high pressures [arrow (*3*) in Fig. 2] results in the population of the lowest molecular levels. Unlike dimers of inert gases, the $^3\Pi_{2u}$ levels to which the radiative transition occurs are not necessarily the lowest in energy in this case. Therefore, relaxation can continue after the radiative transition [arrow (*4*)]. Subsequent collisions in the gas favours the rapid vibrational relaxation of these levels [arrow (*5*)] or even result in the dissociation of molecules from the lower state [arrow (*6*)].

The low emission intensity of iodine vapour in a barrier discharge can be explained as follows. In a barrier discharge in pure iodine at high field strengths, along with electron attachment (1), many I^+ ions can be formed, and I_2^* molecules should be produced via the ion – ion channel (2). However, this channel is efficient only at high pressures, while the residual pressure of iodine in our case is low ($p \leqslant 1$ Torr). For this reason, the intensity of the $D' \rightarrow A'$ emission band of molecular iodine is comparable with those of weak emission lines of singly and doubly ionised iodine atoms. Therefore, as follows from general considerations, to increase the role of mechanism (2) in a barrier discharge, it is necessary to add inert gas to the mixture for reducing the ratio E_0/p. We verified this conclusion experimentally. After the addition of inert Xe gas into iodine vapour, the emission intensity noticeably increased and the 253-nm $B \rightarrow X$ band of XeI^* appeared in the wavelength range 200 – 410 nm. However, the intensity of the $D' \rightarrow A'$ band of the I_2^* molecule remained low. Similarly, the emission spectrum of the iodine – neon mixture contained the weak $D' \rightarrow A'$ band of the I_2^* molecule and many emission lines of atomic neon.

The maximum emission powers with the $D' \rightarrow A'$ band of I_2^* dominating in the spectrum were obtained only after addition of argon into iodine vapour. Therefore, all the

results will be presented below for the $Ar-I_2$ mixtures because we are interested in the conditions for obtaining the intense emission of the homonuclear I_2^* halogen.

Figure 3 presents the typical emission spectrum of the $Ar-I_2$ mixture at elevated pressures. The spectrum exhibits the intense 342-nm $D' \rightarrow A'$ molecular band and the intense 206.2-nm resonance line of atomic iodine. The emission of argon is suppressed. In addition, there exists a group of bands at 288, 283.2, 277.2, 271.6, 248, and 237.9 nm. These bands correspond to the well-known iodine markers. The spectrum in this region is similar, for example, to the spectrum of iodine in an arch discharge [12]. As the argon pressure was increased from 15 to 330 Torr, the half-width of ther $D' \rightarrow A'$ band of I_2^* decreases from 3.5 to 2.3 nm, which is caused by the enhancement of the vibrational relaxation of the $^3\Pi_{2g}$ state of the I_2^* molecule.

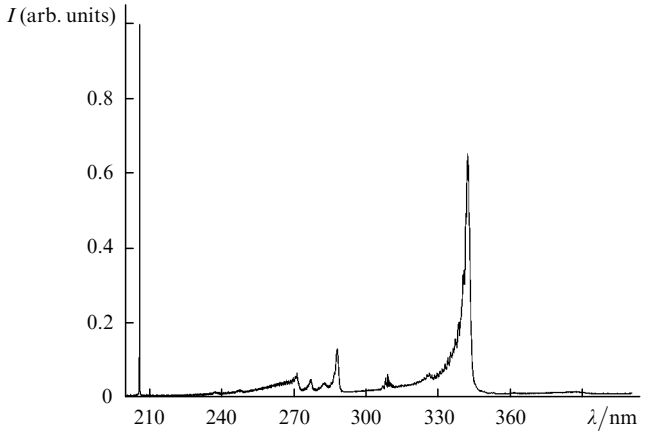

Figure 3. Emission spectrum of the barrier discharge in the argon–iodine vapour mixture ($p = 330$ Torr).

Figure 4 illustrates the dependence of the power and efficiency of barrier-discharge emission on the argon pressure. The energy consumption of a power supply during experiments was constant and equal to 26.4 W. For the Ar pressure about 200 Torr, the ratio E_0/p in the discharge decreases by more than two orders of magnitude (down to ~ 30 V cm^{-1} Torr^{-1}) compared to its value for the discharge in pure iodine, thereby favouring the production of I_2^* molecules via the ion–ion channel (2). The estimate of the contribution of the harpoon channel is complicated because it requires the knowledge of the balance of the formation and deexcitation of I^* atoms.

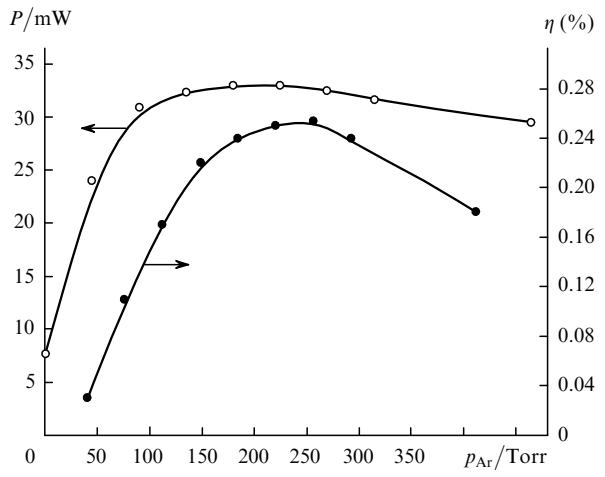

Figure 4. Dependences of the emission power P and efficiency η of the barrier discharge on the argon pressure p_{Ar}.

Figure 5 presents the dependences of the power and efficiency of barrier-discharge emission on the input power P^{in} for argon pressures close to optimal values (see Fig. 4). One can see that the emission efficiency achieves its maximum at the input power ~ 15 W (the specific input power is $W_{sp}^{in} = 170$ mW cm^{-3}) and then decreases, while the emission power continues to grow.

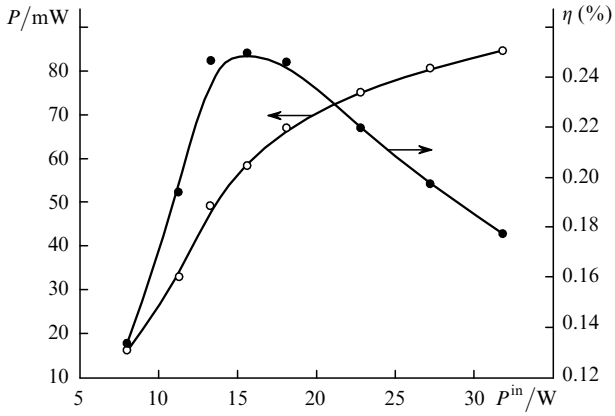

Figure 5. Dependences of the emission power P and efficiency η of the barrier discharge on the input power P^{in} ($p = 330$ Torr, voltage pulse repetition rate is $f = 53$ kHz).

An interesting feature of the barrier discharge in the system under study is a high transition threshold of the discharge from the volume burning phase to the microdischarge phase (Fig. 6), to which the values $P^{in} = 66$ W

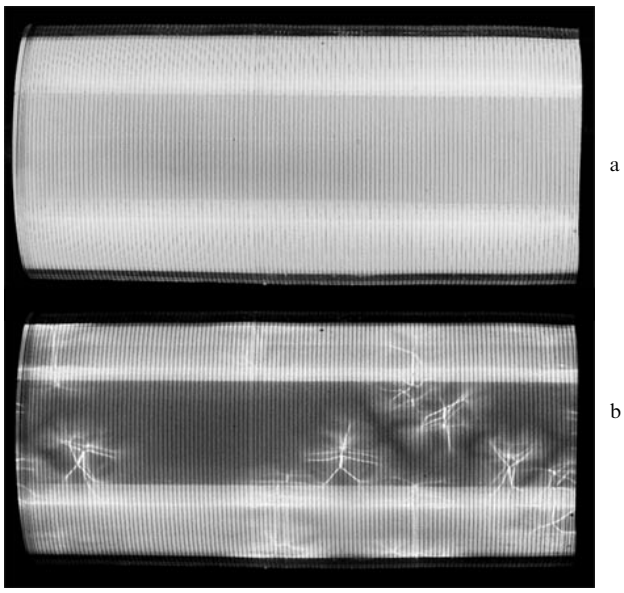

Figure 6. Photographs of the volume (a) and microdischarge (b) burning phases of the discharge for different energy inputs to the medium ($p = 330$ Torr).

and $W_{sp}^{in} = 700$ mW cm^{-3} corresponded. In exciplex Kr(Xe)–Cl_2 and Xe(Kr)–Br_2 systems, the threshold is achieved at energy inputs that are approximately 1–1.5 orders of magnitude lower than that in the Ar–I_2 mixture (see, for example, [13, 14]). It is interesting that the maximum emission efficiency for I_2^* molecules is achieved for $W_{sp}^{in} \sim 170$ mW cm^{-3}, when the discharge is completely inhomogeneous. At the same time, the maximum of the efficiency of the KrCl, XeCl, and XeBr excilamps is usually achieved on passing from the volume burning of the barrier discharge to microdischarges having the form of cones. In our case, such microdischarges are not observed, and when the specific input power achieves the value $W_{sp}^{in} \sim 800$ mW cm^{-3}, the passage occurs at once to filament microdischarges, in which the emission efficiency is low (which can be demonstrated by extrapolating the curve in Fig. 5).

We have shown in our previous studies that small additions of inert (buffer) Ne and He gases to binary mixtures resulted in the increase in the average emission power of exciplex lamps [15, 16]. Therefore, to increase the emission efficiency, we also studied triple mixtures (buffer gas–Ar–I_2) and found that small additions of Ne to the argon–iodine mixture can increase the emission efficiency and power of the barrier discharge by more than a factor of 2–2.5 (Fig. 7).

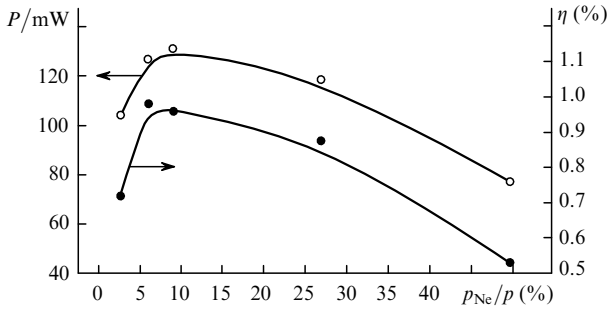

Figure 7. Dependences of the emission power P and efficiency η of the barrier discharge on the neon fraction in the Ne–Ar–I_2 mixture ($p = 330$ Torr).

4. Conclusions

We have obtained a barrier discharge in the argon–iodine mixture which emits predominantly the $D' \rightarrow A'$ band of the homonuclear I_2^* molecule. The maximum emission efficiency and power density were ~1 % and 1.8 mW cm^{-2}, respectively. The sealed off I_2 excilamp with the emitting area of 130 cm^2 and the average power of 150 mW is fabricated. This lamp can be used as a source of narrowband radiation at 342 nm for scientific studies, for example, in photobiology for investigation of photoreactivation of microorganisms. The lamp has a potentially long service life due to the use of an electrodeless discharge and is an ecologically safe radiation source because it does not contain mercury vapour.

Acknowledgements. The authors thank D.V. Schitz for his technical assistance. This work was supported by the ISTC (Project No. 2706).

References

1. Kogelschatz U. *Proc. SPIE Int. Soc. Opt. Eng.*, **5483**, 272 (2004).
2. Boichenko A.M., Skakun V.S., Tarasenko V.F., Fomin E.A., Yakovlenko S.I. *Laser Phys.*, **4** (3), 635 (1994).
3. Tellinghunsen J. *Chem. Phys. Lett.*, **49** (3), 485 (1977).
4. Mulliken R.S. *J. Chem. Phys.*, **55** (1), 288 (1971).
5. Diegelman M. *PLF-Report №33 (D-8046) Max-Plank-Inst., Proektgruppe Laserforschung* (München, 1980).
6. Zhang J.Y., Boyd I.W. *Appl. Phys. B*, **71**, 177 (2000).
7. Shuaibov A.K., Grabovaya I.A. *Zh. Prikl. Spektrosk.*, **72**, 840 (2005).
8. Sosnin E.A., Erofeev M.V., Lisenko A.A., Shitts D.V., Tarasenko V.F. *Opt. Zh.*, **69**, 77 (2002).
9. Eliasson B., Kogelschatz U. *IEEE Trans. Plasma Sci.*, **19** (2), 309 (1991).
10. Lomaev M.I. *Opt. Atmos. Okean.*, **14**, 1091 (2001).
11. McCusker M., in *Excimer Lasers*. Ed. by C.K. Rhodes. (New York: Springer-Verlag, 1979; Moscow: Mir, 1981).
12. Fruth H.F. *Phys. Rev.*, **31**, 614 (1928).
13. Lomaev M.I., Tarasenko V.F., Shitts D.V. *Pis'ma Zh. Tekh. Fiz.*, **28**, 74 (2002).
14. Sosnin E.A., Avdeev S.M., Kuznetsova E.A., Lavrent'eva L.V. *Prib. Tekh. Eksper.*, **5**, 111 (2005).
15. Lomaev M.I., Skakun V.S., Sosnin E.A., Tarasenko V.F., Patent no. RU 2154323 C1, Priority from 01.06.98.
16. Sosnin E.A., Tarasenko V.F., Schitz D.V. Patent no. RU 2200356 C2, Priority from 22.03.01.