

The influence of the Ne/Ar buffer gases on the XeI₂ excimer radiation intensity in a dielectric barrier discharge at moderate pressures

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The paper presents the comparative results concerning the excimer intensity radiation emitted by a xenon-iodine gas mixture with and without buffer-gases, namely Ar and Ne, in a dielectric barrier discharge (DBD) at moderate pressure. The excimer radiation reaches an optimum for a given value of the gas mixture total pressure due to the existence of two antagonist processes: the “harpoon” reaction and the quenching reaction. Changes appear in the presence of the buffer-gas. Thus, the addition of the Ar to the XeI- excimer gas mixture diminishes the excimer radiation intensity while the Ne addition produces an enhancement of the emitted radiation.

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1. Introduction

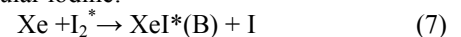
Excimers represent a class a molecules formed by the combination between a halogen and a rare gas. These molecules do not exist in the ground state which is unstable but only in an excited state. By a dissociating de-excitation process it can be generated UV excimer radiation which is a quasi-monochrome radiation. A molecular band is emitted at the transition from the upper excited molecular state to the lower level of the non-excited unstable molecule. The study was performed in a dielectric barrier discharge (DBD) having a plasmagen gas mixture formed by the rare gas-xenon (R_g), the halogen (X)-iodine and the *buffer gases* – neon /argon .

The formation of the excimer molecules starts with the excitation and ionization of the xenon atoms and molecular iodine by high energy electrons collisions produced in glow-DBD phase [1-7]:



At low pressure (0.5-5) Torr the major reaction for the excimer formation seems to be the *reverse Harpoon* –

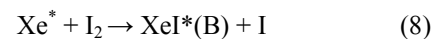
reaction between ground state xenon and excited states (³P, ¹D) of molecular iodine:



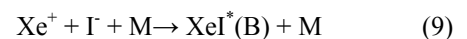
This reaction is a two-body reaction and for this reason is attractive for the formation of excimer molecules at low pressure.

At high pressure (10-760 Torr) the XeI* molecules excimer are generated either by the *Harpoon- reaction* or the three-body ionic recombination, depending on the range pressure of work.

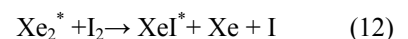
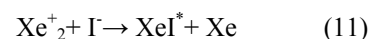
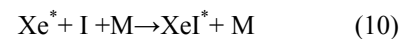
Thus, at 10s Torr pressure the major reaction for excimer formation is the *Harpoon reaction*. The excited states of the xenon atoms are transferring an electron to the iodine molecule (or compounds containing iodine) and form electronically excited states of the excimer molecules:



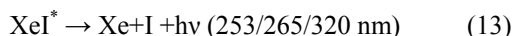
At 100s Torr pressure the major reaction for excimer formation is the ionic recombination:



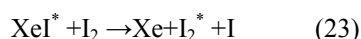
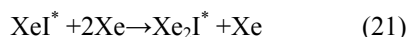
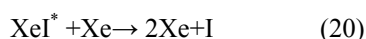
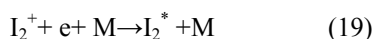
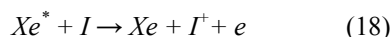
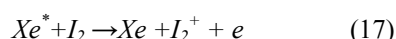
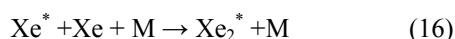
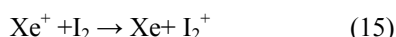
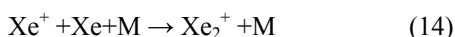
There are still other indirect reactions involved in the generation of the excimer molecules like the following:



The electronically excited excimer molecules XeI(B) decay radiatively to the molecular ground state in connection with the rapid excimer molecule dissociation attributed to bound-free transitions:



The mechanisms of excimer generation compete with the quenching mechanisms:



As it can be observed from the reactions (14) and (16) the direct precursors of the excimer, namely Xe⁺ and Xe*, are consumed but in exchange appear far- precursors of the excimer, namely Xe₂⁺ and Xe₂*.

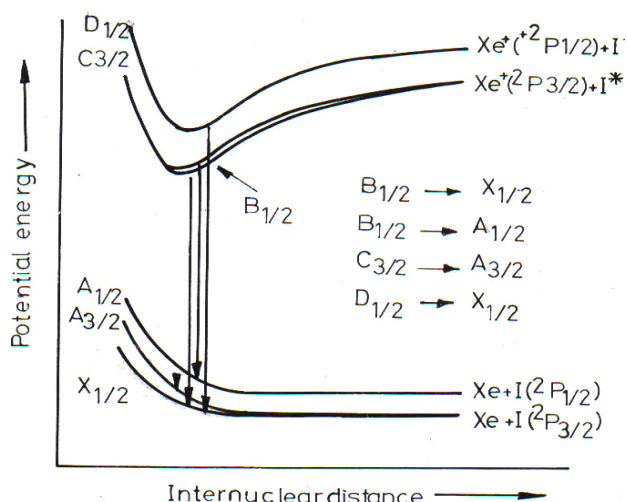


Fig. 1. Potential energy diagram of XeI* excimer molecule.

The ionizing Penning reactions (17) and (18), become very important at high partial pressure of iodine, consuming lots of Xe*, one of the most important precursor of XeI* excimer. In the same time, the molecular

iodine produces an increase of the iodine dimer radiation and quenches the excimer XeI* - reaction (23).

From the reactions (21) and (22) it can be observed the formation of the trimer Xe₂I* process which is increasing with the high pressures.

A diagram of the potential energy for the xenon-iodine excimer molecule is given in the Fig. 1. The ground-state X_{1/2} is formed from the ground-state ¹S of the noble gas atom and the ²P (s=1/2, l=1, m_l=0) energetic level of the halogen atom. The A ²P_{1/2,3/2} state derives from the ground-state ¹S of the noble gas atom and the ²P (s=1/2, l=1, m_l=±1) energetic level of the halogen atom. The three excited levels – B_{1/2}, C_{3/2} si D_{1/2} – derive from the ²P positive noble gas ion and ¹SX⁻ negative halogen ion.

The transitions D_{1/2}/ B_{1/2} → X_{1/2} and C_{1/2}/B_{1/2} → A_{1/2} inclusive the wavelengths values associated for the principal excimers are presented in the Table 1.

Table 1.

R _g	X	R _g X* D _{1/2} →X _{1/2} (nm)	R _g X* B _{1/2} → X _{1/2} (nm)	R _g X* C _{1/2} →A _{1/2} (nm)	R _g X* B _{1/2} → A _{1/2} (nm)	R _g 2X* (nm)
Ne	F	106	108	110	111	±145
Ar	F	185	193	203	204	290±25
Ar	Cl	-	175	-	195	245±15
Ar	Br	-	165	172	183	-
Kr	F	220	248	275	272	400±35
Kr	Cl	200	222	240	235	325±15
Kr	Br	-	207	222	228	~318
Kr	I	-	190	195	225	-
Xe	F	264	351	460	410	610±65
Xe	Cl	236	308	345	340	450±40
Xe	Br	221	22	300	325	440±30
Xe	I	203	253	265	320	~375

As the transitions are of molecular type, λ is corresponding to the peak-value of the spectral emission band. The intensity of the emitted radiation and the half-width of the spectral lines emitted in different transitions are very different. For instance, the D_{1/2} → X_{1/2} transition generates the shorter wavelength while his intensity is much weaker than for the B_{1/2} → X_{1/2} transition, fact which indicates that the population of the upper energetic level D_{1/2} is diminished by non-radiative processes. The B_{1/2} → X_{1/2} transition is the strongest of all because the electronic orbitals *sp* have the largest overlap from the valence orbitals.

Typical emission of XeI* excimer provides an intense narrow-band radiation at λ= 253 nm within dielectric barrier discharge. This spectral line proceeds from the transition B_{1/2}→X_{1/2}. In the diagram, X_{1/2} represents the ground state and the B_{1/2} the first vibrational excited state of the rare gas/halogen molecule excimer. Other spectral lines that could appear in the discharge are λ =206nm and λ=342nm from the atomic respectively molecular iodine and the excimeric spectral lines λ=265nm, 320nm and

375nm, suitable to the transitions between vibrational excited states $C \rightarrow A$, $B \rightarrow A$ and respectively the Xe_2I^* trimer spectral line (Table 1).

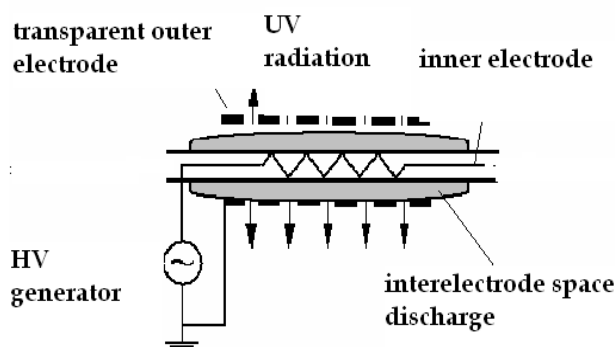


Fig. 2. Geometry of cylindrical excimer UV discharge

2. Experimental set-up

A classic cylindrical coaxial lamps configuration was used in our experiments. The UV radiation generated was radiating outward the discharge device.

The lamp is composed of two concentric quartz tubes, outer and inner metallic electrodes, both made by steel, an external RF high voltage generator (up to 20kV), and a heating system of the iodine pure crystals. The discharges were matching at a sinusoidal voltage value of about 4kV with the frequency range between 20–400 kHz. The high voltage was applied on the inner electrode, while the outer UV mesh transparent electrode was grounded. The experimental set-up was presented in detail in our previous paper [8]. In order to record the emission spectra an OMA (Optical Multichannel Analyzer), spectral range between 200-900 nm, and 1.5nm resolution, was used. The integration time was in the range of 0.5-1 ms.

3. Results and discussion

It was measured the dependence of the spectral excimer intensities on the percentages of *buffer gases*, in order to establish the influence of their addition at the emitted radiation intensity of the xenon – iodine primary mixture.

The spectral intensities that appear in the graphs are relative being given in arbitrary units. The total pressure of the gas mixtures varied in the range of 20-45 Torr. High purity (99.998%) rare gases–Xenon, Iodine, Argon and Neon were used in the experiments.

As it can be observed from the Fig. 3, the intensity of the excimer radiation with $\lambda = 253$ nm in the presence of argon as *buffer-gas* is lower than that which is obtained without using buffer gas, at the same value of the total gas pressure, which is 35 Torr. In the same time, the intensity of the trimer Xe_2I^* is higher in the presence of *buffer gas* than in his absence. This behavior can be explained taking

into account the possibility that the molecules of argon displace xenon in reactions (14) and (16) by quenching the precursors Xe^+ and Xe^* or in reaction (20) by quenching the excimer XeI^* , which leads to the decreasing of the excimer radiation. This behavior of argon could be produced by the fact that Ar spectrum of the excited energetic levels in Paschen notation is formed by 4 *s*- lines ($1s_2-1s_5$) and 10 *p*- lines ($2p_1-2p_{10}$), which increase the possibility of collisional couplings with the xenon atoms levels, followed by non-radiative deexcitation. From the reactions (21) and (22) results that the intensity of Xe_2I^* trimer spectral band centered at $\lambda = 375$ nm can increase for the same reason.

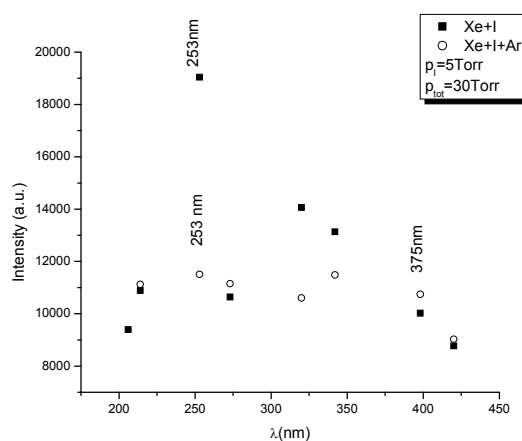


Fig. 3. Emission spectrum of XeI respectively $(Xe+I+Ar)$ gas mixtures in a DB discharge.

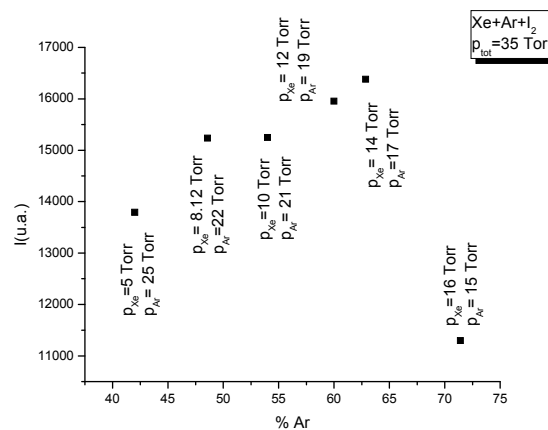


Fig. 4. The dependence excimer intensity for $\lambda = 253$ nm on the argon percentage for $(Xe+I+Ar)$ gas mixtures in a DB discharge.

From the Fig. 4 results that the intensity of the main excimer spectral line $\lambda = 253$ nm reaches an optimum at a percentage of 62.85% argon, respectively 11.42% iodine. As in the case of the $(Xe+I_2)$ gas mixture after a given value of the iodine partial pressure, the intensity of the 253nm spectral line diminishes due to the formation of the iodine I_2^* dimer based on the three-body reactions (19), (23).

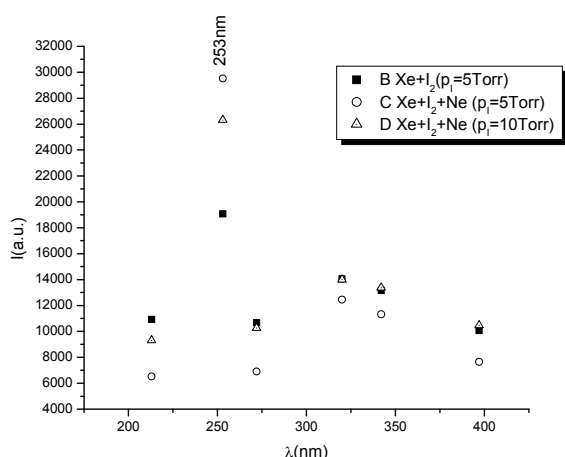


Fig. 5. Emission spectrum of XeI respectively (Xe+I+Ne) gas mixtures in a DB discharge

In the Fig. 5 is presented the emission spectrum of (Xe+I₂) gas mixture with the iodine pressure of 5 Torr, and the emission spectra of (Xe+I₂+Ne) gas mixture with the iodine pressure of 5 Torr, respectively 10 Torr. As it can be observed, the main excimer line intensity $\lambda=253\text{nm}$ is higher in the presence of Ne buffer gas (graph B) than in his absence (graph C). This behavior could be attributed to the fact that neon atoms could stand for the third body in the reactions (9) and (10).

The excimer radiation intensity emitted by a (Xe+I+Ne) gas mixture at a total pressure of 35 Torr and an iodine partial pressure of 10 torr is lower than the excimer intensity emitted in the same experimental conditions but with a partial iodine pressure of 5 Torr. According to the reported literature data [5], increasing the iodine partial pressure, the Penning reactions (17) and (18) and the reaction (23) are destroying many Xe* (B) excimer molecules, decreasing in this way the emitted excimer radiation (graph D).

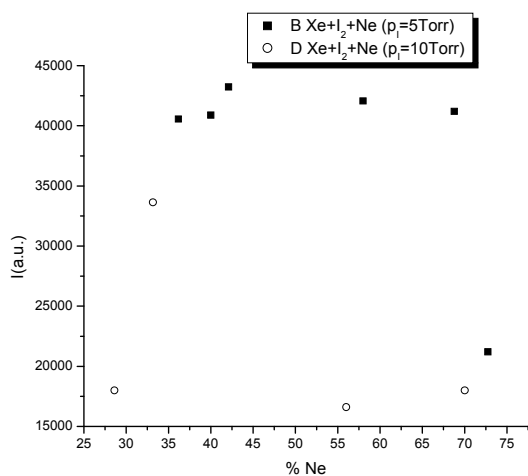


Fig. 6 The dependence excimer intensity for $\lambda=253\text{nm}$ on the neon percentage for (Xe+I+Ne) gas mixtures in a DB discharge.

The excimer intensity reaches an optimum for a neon percentage value of 42.85% (at a partial pressure iodine of 5 Torr) respectively 34.28% (at a partial pressure iodine of 10 Torr). It can be observed that the relative intensity of the 253 nm spectral line is lower at high concentration of iodine. The total gas mixture pressure was kept at 35 Torr value –Fig. 6.

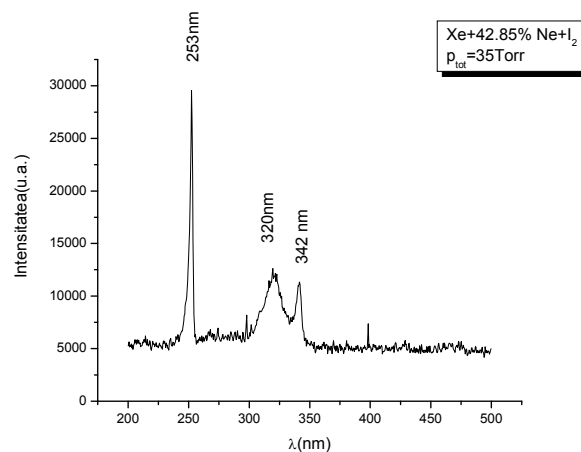


Fig. 7. Emission spectrum of (Xe+42.85%Ne+I) gas mixture in a DB discharge at $p_{\text{tot}}=35\text{ Torr}$

In Fig. 7 is presented the dependence of the excimer intensity for (Xe+42.85%Ne+I) gas mixture at a total pressure of 35 Torr. It can be observed that the excimer spectral line $\lambda=320\text{nm}$ and the molecular iodine spectral line $\lambda=342\text{ nm}$ are very intensive.

4. Conclusions

The addition of a buffer gas to the primary xenon-iodine mixture produces, according to the circumstances, an increasing of the 253 nm main excimer spectral line, like in the case of the neon addition or a decreasing, like in the case of argon addition. Other spectral lines emitted by the main excimer or iodine dimer are influenced too in the process of the buffer gases addition.

The mechanisms on which is based this emission of the excimer radiation emitted by the xenon-iodine gas mixture seem to be quiet different comparing with the case of other excimers like KrCl* or XeCl*, in the sense that the optimum excimer intensity is reached for much lower iodine percentages than for chlorine.

It was be necessary a future study of the XeI* mechanisms formation in order to optimize the device of the excimer lamps based on the xenon-iodine mixture.

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