

Luminescence characteristics of Xe₂Cl excimer molecules under pumping the dense Xe–CCl₄ gas mixtures with a pulsed electron beam

A.I. Mis'kevich, Guo Jinbo

Abstract. Temporal and spectral characteristics of the luminescence of dense Xe–CCl₄ gas mixtures of different composition, excited by a 5-ns pulsed electron beam, were measured. The energy of the electrons amounted to 150 keV and the electron beam current pulse amplitude was 5 A. The gas mixtures were used containing Xe (38–700 Torr) and CCl₄ (0.03–0.3 Torr). The studies were performed within the wavelength range 200–1200 nm using a MAYA-2000Pro diffraction grating spectrometer and a RIGOL DS 5022 ME fast digital oscilloscope. The luminescence lifetimes of the excimer molecules XeCl* (band with $\lambda_{\max} = 308$ nm) and Xe₂Cl* (band with $\lambda_{\max} = 486$ nm) were measured, as well as the constants of quenching by the components of the gas mixture for Xe₂Cl* molecules. A model of plasma-chemical processes for dense Xe–CCl₄ gas mixtures with a very low content of the CCl₄ donor is proposed. It is shown that in such ‘poor’ mixtures Xe₂Cl* molecules are mainly produced as a result of recombination of the Xe₂⁺ and Cl⁻ ions.

Keywords: active medium, excimer, luminescence, Xe₂Cl.

1. Introduction

Dense mixtures of inert gases with halogens (F₂, Cl₂, Br₂, I₂) or halogen-containing chemical compounds (NF₃, CCl₄, HCl, Freon, etc.) efficiently convert the energy of charged particles into light radiation, the conversion efficiency attaining 30% and greater [1, 2] at the expense of the formation of diatomic and triatomic excimer molecules. The use of diatomic excimer molecules of inert gases halogenides (XeF, XeCl, XeBr, KrCl, etc.) makes it possible to achieve high efficiency of generating UV radiation by pumping with an electron beam [1, 3, 4], electric discharge [5–7], and optical radiation [8–11]. The use of triatomic halogenide molecules (Xe₂Cl, Xe₂F, Kr₂Cl, etc.) is promising for efficient light generation in the visible range of wavelengths with the possibility of smooth wavelength tuning with the range as wide as 1000 Å and greater [12, 13].

The experimental data, presently available in the literature on the radiative characteristics of gas mixtures, in which triatomic excimer (triplex) molecules are produced, were obtained in the media with a high partial pressure of the halogen-containing admixture, commonly, not smaller than 1 Torr [14, 15]. In our opinion, such pressures are excessive for efficient for-

mation of triatomic excimer molecules and do not facilitate getting a maximal yield of radiation in the given gas mixture. For example, Fig. 1 presents the luminescence spectra of the Xe–CCl₄ gas mixtures with a high and a low content of CCl₄. It is seen that the radiation yield within the band ⁴2Γ–¹2Γ of the molecule Xe₂Cl ($\lambda = 420–650$ nm) strongly depends on the pressure of the halogen-containing admixture, and at the CCl₄ partial pressure 0.03 Torr is more than by ten times greater than the radiation yield of the mixture with high (~0.5 Torr and more) pressure of this admixture.

In the present paper we consider the radiative characteristics of dense xenon mixtures Xe–CCl₄ with a minimal content of a halogen-containing admixture CCl₄. The experimental studies of the spectral and temporal characteristics of

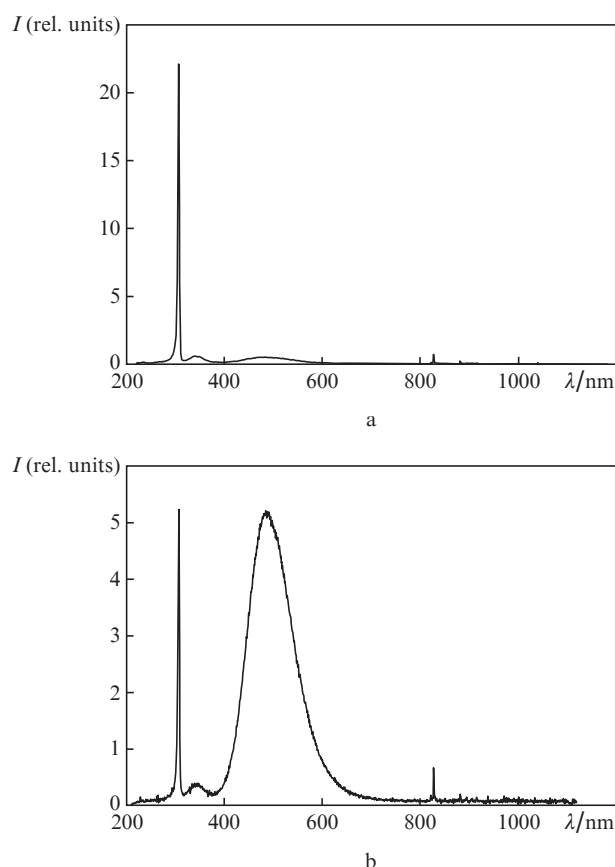


Figure 1. Luminescence spectra of the gas mixtures Xe–CCl₄ with $p_{\text{CCl}_4} =$ (a) 0.43 and (b) 0.03 Torr and $p_{\text{Xe}} = 500$ Torr, excited by a pulsed electron beam.

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the luminescence were performed for the mixtures, containing CCl_4 under the pressure $p_{\text{CCl}_4} = 0.03\text{--}0.3$ Torr and Xe under the pressure $p_{\text{Xe}} = 38\text{--}700$ Torr.

2. Experimental setup

The block diagram of the experimental setup for measuring the spectral and temporal characteristics of the luminescence of gas mixtures excited by a pulsed beam of fast electrons with the energy 150 keV and alpha-particles from ^{238}Pu with the energy 5 MeV is shown in Fig. 2. The duration and amplitude of the electron pump pulse are equal to 5 ns and 5 A, respectively. In contrast to the setup, described in [16], the design of the present one was completed with the chamber (14) with the isotope source of alpha-particles (15), having the activity amounting to 5 mCi ($\sim 2 \times 10^8$ decay s^{-1}), which allowed simultaneous measurements of the luminescence spectra under the pulsed excitation of the gas mixture by the electron beam and permanent monitoring of its composition purity using the excitation by alpha-particles. Both chambers were connected in sequence, and together with the mixture circulation pump represented a united gas volume. Careful cleaning of Xe (and the mixture Ar–Xe) from molecular impurities was carried out directly before the puffing of halogen-containing admixture CCl_4 by means of continuous pumping of the gas through the filter (11), containing a titanium sponge heated to 700 °C. This procedure is of extreme importance, because the presence of even a small amount of molecular gases in the mixture causes strong quenching of the excimer fluorescence. The efficiency of the gas cleaning system operation was checked by observing the luminescence of impurity nitrogen ($\lambda = 337.1$ nm) under the excitation of the cleaned gas mixture by alpha-particles from the isotope source ^{238}Pu . The entire cycle of gas cleaning took 8–10 min, after which the content of residual

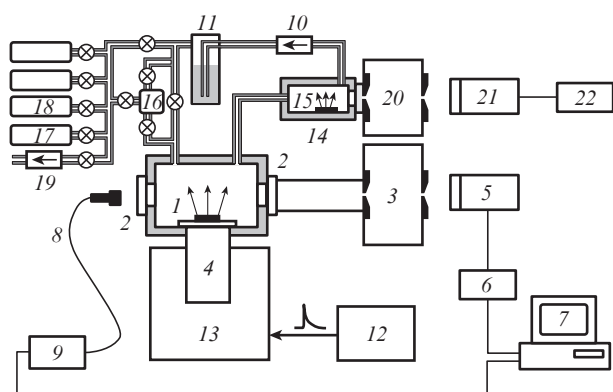


Figure 2. Block diagram of the experimental setup for measuring spectral and temporal characteristics of luminescence of Xe– CCl_4 gas mixtures under the excitation with a pulsed beam of fast electrons with the energy 150 keV and ^{238}Pu alpha-particles with the energy 5 MeV: (1) chamber; (2) quartz window; (3) MDR-23 monochromator; (4) ‘Arina-2’ electron accelerator; (5) photomultiplier; (6) Rigol DS 5022 digital oscilloscope; (7) personal computer; (8) optical fibre waveguide; (9) MAYA-2000Pro spectrometer; (10) circulatory pump; (11) titanium filter; (12) accelerator start-up and synchronisation unit; (13) high-voltage power supply of the accelerator; (14) additional chamber with two quartz windows; (15) ^{238}Pu source of alpha-particles; (16) measuring pipe; (17) vessel with gaseous Xe; (18) vessel with liquid CCl_4 ; (19) forevacuum pump with nitrogen trap; (20) MDR-23 diffraction spectrometer; (21) counter of single-electron pulses based on the FEU-100 photomultiplier; (22) Ch3-34A frequency meter.

molecular gases in the cleaned gas did not usually exceed $10^{-4}\%$.

To prepare the mixtures with a small content of CCl_4 , the method of measuring volume was applied, in which the pipe (16) was used. The ratio of the measuring pipe volume to that of all communications was equal to 0.01, which made it possible to provide the pressures of admixture gases in the mixture as small as ~ 0.05 Torr and smaller with high precision. Mixing the gases from the measuring volume and the main one was implemented using the circulatory pump (10) with the filter (11) switched off after completing the procedure of the main gas cleaning.

3. Results of the measurements

Under the excitation by high-energy particles the monohaloid compounds are efficiently produced in the mixtures of inert gases with halogens. These compounds are diatomic and triatomic excimer molecules. The potential curves of such molecules are shown in Fig. 3.

According to [1], the ground state of the diatomic molecule XeCl has a covalent bond and at infinitely large interatomic distance correlates with the ground state $^1\text{S}_0$ of the inert gas atom and the ground P-state of the halogen atom, consisting of two closely spaced sublevels, namely, the level $^2\text{P}_{3/2}$, pos-

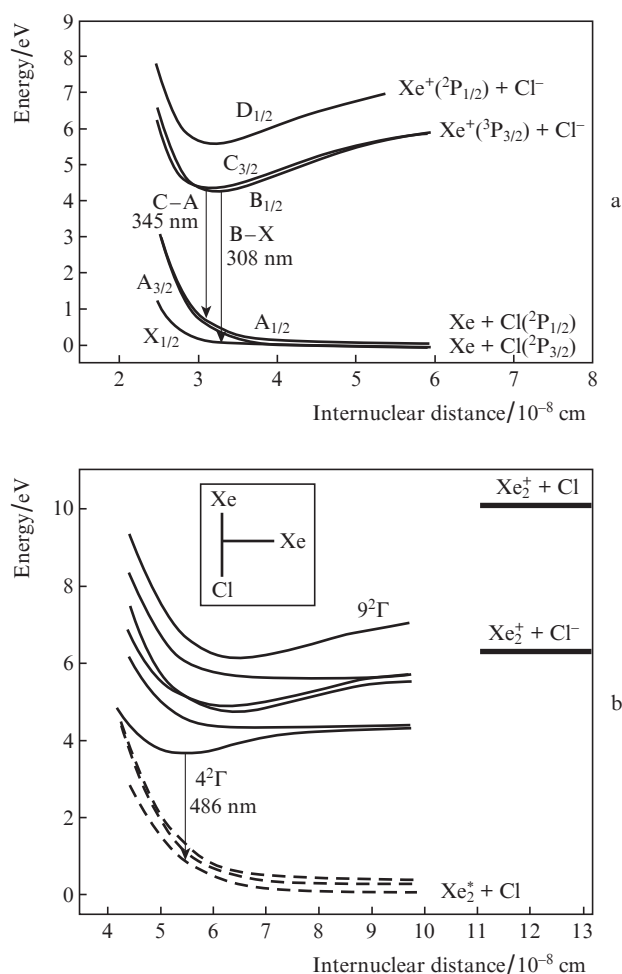


Figure 3. Potential curves of monohaloid excimer molecules (a) XeCl and (b) Xe_2Cl (according to the data of Refs [17–19]). Inset shows the structure of the Xe_2Cl molecule, used in the calculation.

sessing the lowest energy, and the level $^2P_{1/2}$, which is by 0.11 eV higher [20]. Due to this fact, the ground state of the XeCl molecule also consists of the weakly-bound X-state, formed by the atoms Xe (1S_0) and Cl ($^2P_{3/2}$), and the dissociative A-state, formed by the atoms Xe (1S_0) and Cl ($^2P_{1/2}$) (Fig. 3a).

The excited states of the XeCl* molecule are characterised by the ionic bond with charge transfer and at infinite inter-nuclear distance correlate with the states $^2P_{1/2,3/2}$ of the positive ion Xe⁺ of the inert gas and 1S_0 of the negative halogen ion Cl⁻ [1]. Figure 3a shows the usually observed transitions in the XeCl* molecule: the intense narrow band B–X with $\lambda_{\max} \sim 308$ nm and the broad weaker band C–A with $\lambda_{\max} \sim 345$ nm.

The triatomic molecule Xe₂Cl has a broad emission band in the wavelength range 420–650 nm with the maximum at $\lambda_{\max} = 500$ nm. According to [13], this emission is caused by the transitions between the strongly bound ion upper state of the molecule Xe₂Cl*, formed by the ions Xe₂⁺ and Cl⁻, and the lower dissociative state, formed by the excited molecule Xe₂^{*} and the atom Cl in the ground state (Fig. 3b). Table 1 summarises the energy characteristics of some components of the Xe–CCl₄ mixture plasma, involved in the formation of the excimer molecules XeCl* and Xe₂Cl*.

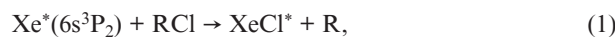
Table 1. Energy characteristics of the plasma components of the Xe–CCl₄ mixture, involved in the synthesis of the excimer molecules XeCl* and Xe₂Cl*.

Plasma component	Parameter	Energy/eV	References
Xe ⁺	Ionisation potential	12.129 ($^2P_{3/2}$)	[20]
		13.43 ($^2P_{1/2}$)	[20]
Xe ₂ ⁺	Depth of potential well	1.03	[18]
Xe* (5p ⁵ 6s)	Energy level	9.57 (1P_1)	[20]
		9.44 (3P_0)	[20]
		8.43 (3P_1)	[20]
		8.31 (3P_2)	[20]
CCl ₄ ⁺	Ionisation potential	11.1–1.47	[21]
		7.92	[21]
		13.1	[21]
		12.9	[21]
CCl ₄	Energy of bond break-up	2.9–2.916 (CCl ₃ + Cl)	[17, 21]
CCl		2.8 (C + Cl)	[21]
CCl ₃	Energy of electron affinity	> 2.10 ± 0.35 (CCl ₃ ⁻)	[21]
Cl		3.82 (Cl ⁻)	[21]

Figure 1b shows a typical luminescence spectrum of the Xe–CCl₄ gas mixture with a low content of CCl₄, excited by a beam of fast electrons with the energy 150 keV. The spectrum consists of the bands of the excimer molecule XeCl*: the intense band with the maximum at $\lambda_{\max} = 308$ nm (transition B–X), the weaker bands with $\lambda_{\max} = 345$ nm (transition C–A), and the broad high-intensity band in the wavelength range 400–650 nm, belonging to the triatomic excimer molecule Xe₂Cl* (transition $4^2\Gamma-1^2\Gamma$). In the long-wavelength region of the spectrum ($\lambda > 800$ nm) the weak lines of the 6p–6s transition of atomic xenon are observed, the intensity of which decreases with the growth of CCl₄ concentration.

The maximal intensity of the bands with $\lambda_{\max} = 308$ and 345 nm of the XeCl* molecule is achieved in the gas mixtures Xe–CCl₄ and Ar–Xe–CCl₄ at atmospheric pressure with the concentrations of CCl₄ ~ 0.01 %. For the band $4^2\Gamma-1^2\Gamma$ of the molecule Xe₂Cl* ($\lambda_{\max} = 486$ nm) the optimal concentration

of CCl₄ amounts to $\sim 5 \times 10^{-3}$ %. Exceeding this value leads to strong quenching of the luminescence (Fig. 1a). Of great importance is the fact that in the mixtures of optimal composition the total intensity of Xe₂Cl* molecule radiation in the range 400–650 nm (transition $4^2\Gamma-1^2\Gamma$) by more than five times exceeds the intensity of the XeCl* molecule radiation in the band with $\lambda_{\max} = 308$ nm (Fig. 1). Earlier [13, 18] it was noted that the formation of Xe₂Cl* molecules in xenon-containing media occurs as a two-stage process, involving the XeCl* molecules:



Here RCl and R denote the donor chlorine-containing molecule and the donor molecule radical, and M is the atom of buffer gas. The luminescence spectra in the bands B–X and $4^2\Gamma-1^2\Gamma$ of the molecules XeCl* and Xe₂Cl*, presented in Fig. 1, with the large difference of luminescence lifetimes taken into account (33 and 150 ns, respectively), evidence in favour of a different independent mechanism of populating the $4^2\Gamma$ -levels of the molecule Xe₂Cl*, not associated with the channel of the ‘intermediate’ XeCl* molecule formation. Therefore, the obtained experimental data on the luminescence spectra of dense gas mixtures Xe–CCl₄ and Ar–Xe–CCl₄ of the optimal composition, as well as the performed measurements of the luminescence lifetime for the molecular bands $4^2\Gamma-1^2\Gamma$ (Xe₂Cl*) and B–X (XeCl*), confirm the necessity to reconsider the existing conceptions of the mechanisms, responsible for the formation of Xe₂Cl* molecules in these media.

The measurements of temporal characteristics of luminescence were carried out in the mixtures, containing CCl₄ ($p_{\text{CCl}_4} = 0.03-0.3$ Torr) and Xe ($p_{\text{Xe}} = 38-600$ Torr) and were performed for the molecular bands of XeCl* and Xe₂Cl* at the wavelengths, corresponding to their maximal intensities: 308 nm (B–X), 345 nm (C–A), and 486 nm ($4^2\Gamma-1^2\Gamma$). As an example, in Figs 4a and b we present the time dependences of the radiation intensity within the B–X band of the XeCl* molecule ($\lambda_{\max} = 308$ nm) and the $4^2\Gamma-1^2\Gamma$ band of the Xe₂Cl* molecule ($\lambda_{\max} = 486$ nm) in the Xe–CCl₄ gas mixtures at high (500 Torr) and low (152 Torr) pressures of Xe, the pressure of CCl₄ being always low (0.036 Torr). For clarity, Fig. 4c shows the oscillogram of the pump electron beam current. At a high Xe pressure (Fig. 4b) the population of the B-state of the XeCl* molecule appears almost immediately after the pump pulse, whereas the population of the $4^2\Gamma$ state of the Xe₂Cl* molecule appears with a temporal delay of $\sim 50-70$ ns. In the mixtures with a low content of Xe (Fig. 4a) the increase in the temporal delay of the radiation pulses in the $4^2\Gamma-1^2\Gamma$ band of the Xe₂Cl* molecule up to 120–140 ns is observed. Such a delay time is determined by the time of formation of the molecular ion Xe₂⁺, as well as by the process of ion–ion recombination and ambipolar diffusion of ions in Xe. The contribution of the reactions (1) and (2) to the population of $4^2\Gamma$ -state of the Xe₂Cl* molecules is determined by the area under the peak at the leading edge of the luminescence pulse with $\lambda_{\max} = 486$ nm (Fig. 4a), which is an insignificant part of the total ‘area’ of this pulse.

The luminescence lifetimes for the B–X and $4^2\Gamma-1^2\Gamma$ bands of the XeCl* and Xe₂Cl* molecules depend on the CCl₄ content in the mixture (Fig. 5). The strongest dependence is

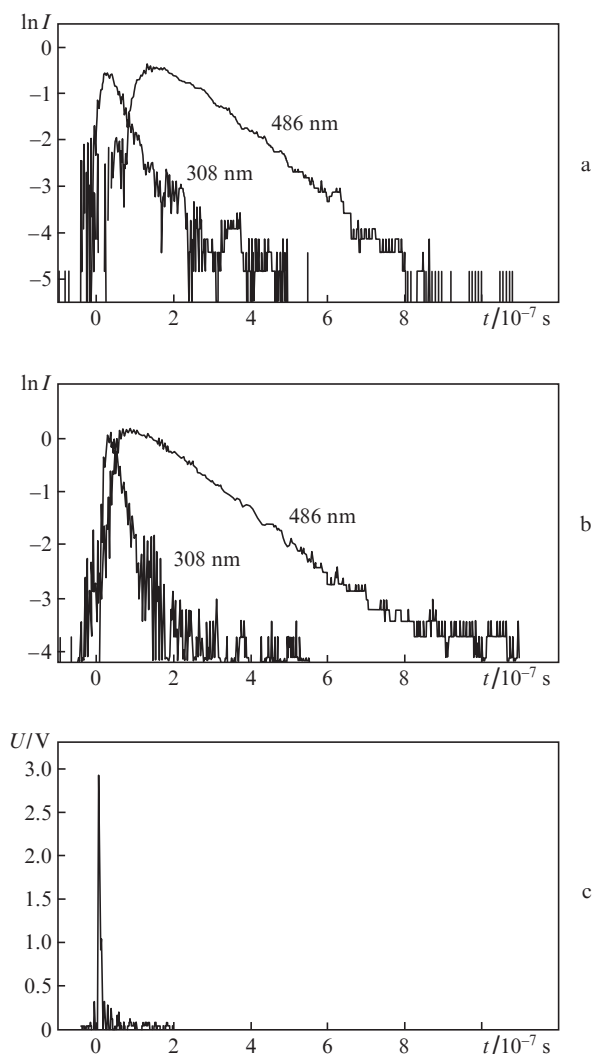


Figure 4. Intensity of luminescence (in relative units) in the B–X band of the XeCl^* molecule ($\lambda_{\text{max}} = 308$ nm) and the $4^2\Gamma-1^2\Gamma$ band of the Xe_2Cl^* molecule ($\lambda_{\text{max}} = 486$ nm) at (a) $p_{\text{Xe}} = 152$ Torr, $p_{\text{CCl}_4} = 0.036$ Torr and (b) $p_{\text{Xe}} = 500$ Torr, $p_{\text{CCl}_4} = 0.036$ Torr, as well as (c) the electric current pulse of pump electrons.

observed in the $4^2\Gamma-1^2\Gamma$ band of the Xe_2Cl^* molecule (Fig. 5b). The measurements of time dependences of the radiation intensity within the molecular bands for the mixtures of different composition allow determination of the quenching constants of the excited states B and $4^2\Gamma$ by the Xe atoms and CCl_4 molecules.

Figure 6 presents the results, obtained for the B–X band of the XeCl^* molecule ($\lambda_{\text{max}} = 308$ nm) and the $4^2\Gamma-1^2\Gamma$ band of the Xe_2Cl^* molecule ($\lambda_{\text{max}} = 486$ nm). The constants of quenching by the CCl_4 molecules and the luminescence lifetimes were determined from the dependences of $1/\tau$ on the partial pressure p_{CCl_4} (Fig. 6) and appeared to equal $1.98 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and 33 ns (at $p_{\text{Xe}} = 500$ Torr) for the B-state of the XeCl^* molecule ($\lambda_{\text{max}} = 308$ nm) and $2.29 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (at $p_{\text{Xe}} = 500$ Torr) for the $4^2\Gamma$ -state of the Xe_2Cl^* molecule ($\lambda_{\text{max}} = 486$ nm), respectively.

The Xe atoms can also cause quenching of the XeCl^* molecules, but their contribution manifests itself essentially weaker than that of CCl_4 molecules. According to our estimates, the constant of collisional quenching of the B-state of XeCl^* molecules by xenon atoms is less than $4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.

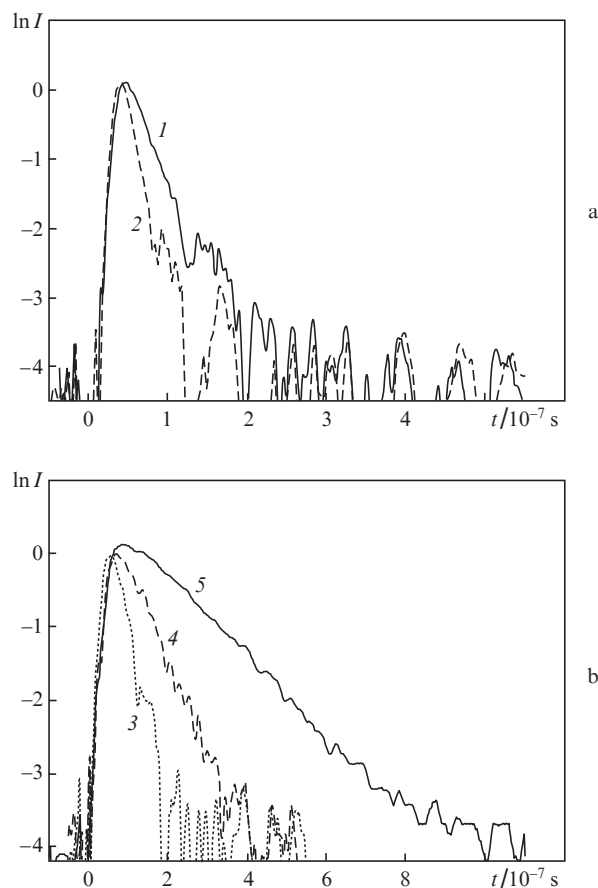


Figure 5. Luminescence intensity (in relative units) in (a) the B–X band of the XeCl^* molecule ($\lambda_{\text{max}} = 308$ nm) and (b) the $4^2\Gamma-1^2\Gamma$ band of the Xe_2Cl^* molecule ($\lambda = 486$ nm) in gas mixtures Xe– CCl_4 at $p_{\text{CCl}_4} = 0.036$ (1, 5), 0.324 (2, 3), and 0.072 Torr (4), $p_{\text{Xe}} = 500$ Torr.

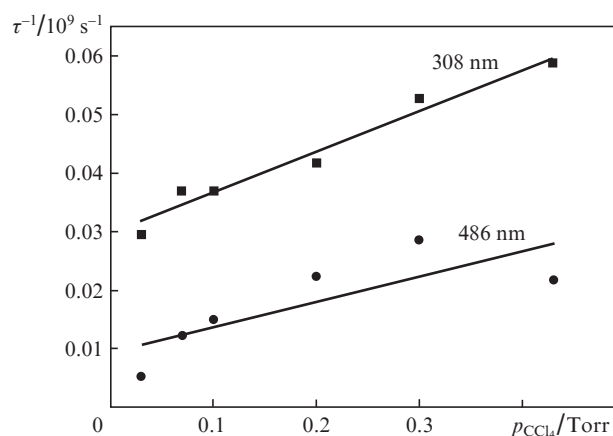


Figure 6. Inverse fluorescence time for the B–X and $4^2\Gamma-1^2\Gamma$ bands of the XeCl^* and Xe_2Cl^* molecules versus the partial pressure of CCl_4 in the gas mixture Xe– CCl_4 at $p_{\text{Xe}} = 500$ Torr. The excitation of the mixture was implemented using a pulse of electrons with the energy 150 keV and the duration 5 ns.

It is worth noting that the measured luminescence lifetime for the B–X band ($\lambda_{\text{max}} = 308$ nm) of the XeCl^* molecule is essentially greater than the radiative lifetime of the B state, which is equal to 11 ns according to the data of Ref. [11]. This can be explained only by the existence of less efficient (as compared to the radiative decay) channel of populating the

considered state. Indeed, for the population of the upper level $N(t)$ at the moment of time t in the general case one can write the equation

$$dN(t)/dt = R(t) - N(t)A, \quad (3)$$

where A is the Einstein coefficient for the considered transition; and $R(t)$ is the function, describing the process of the upper level population, including that at the expense of slower (as compared with the pumping) plasma-chemical processes. In this case, the term $R(t)$ accounts for all possible plasma-chemical processes of population and deactivation of the level, except the radiative decay. Obviously, the luminescence lifetime of the level will coincide with the radiative lifetime $\tau = 1/A$ only if $R(t) = 0$.

The form of the function $R(t)$ can be determined from the measured temporal dependences of the luminescence intensity in the B–X band of the XeCl* molecule. Since the intensity can be expressed as $I(t) = N(t)A$, taking Eqn (3) into account, we obtain

$$R(t) = (1/A)dI(t)/dt + I(t). \quad (4)$$

Figure 7 shows the functions $R(t)$, calculated using Eqn (3), and the obtained oscillograms. It is seen that the population of the B state of the XeCl* molecule occurs presumably quickly, while the population of the 4²Γ state of the Xe₂Cl* molecule is a much slower process. It should be noted, however, that at the initial stage of the excitation of the gas mixture, ~5%–10% Xe₂Cl* molecules appear at the expense of the reactions (1) and (2) (Figs 7b and d).

Obviously, these specific features of the excitation of B- and 4²Γ-states of the excimer molecules XeCl* and Xe₂Cl* in high-density Xe–CCl₄ gas mixtures reflect the character of the actual population mechanisms (see Table 2). A fast charged particle with a high energy (in our case an electron with the

energy 150 keV), passing through the Xe–CCl₄ gas medium with a low concentration of the halogen-containing admixture, produces the Xe⁺ ions, excited Xe* atoms, and secondary electrons of the ionisation cascade (reaction 1). At a high pressure of the buffer gas (~1 atm) due to the triple collisions the atomic Xe⁺ ions during a few nanoseconds turn into the molecular ions Xe₂⁺, and the excited atoms Xe* turn into the excited molecules Xe₂* (reactions 2 and 3). The electrons of the ionisation cascade are thermalised, losing their energy in elastic and inelastic collisions with Xe atoms. According to Ref. [22], the thermalisation time of an electron from the beam having the energy 150 keV and a fast δ-electron in xenon at atmospheric pressure is smaller than 1 ns.

Thermalised electrons actively participate in the dissociative recombination of the Xe₂⁺ molecular ions (reaction 4) and in the formation of negative ions (CCl₄⁻) by sticking to the electronegative admixture (reaction 5). The analysis of the luminescence curves for the B–X band of the XeCl* molecule ($\lambda_{\text{max}} = 308$) and the 4²Γ–1²Γ band of the Xe₂Cl* molecule ($\lambda_{\text{max}} = 486$ nm) (see Figs 4 and 5) shows that the major channels of formation of diatomic excimer molecules are the collisions of excited atoms and molecules of xenon with the CCl₄ molecules (reactions 8 and 9), while for triatomic excimer molecules this role is played by the reactions of ion-ion recombination of the positive Xe₂⁺ ions with the negative Cl⁻ ions (reaction 7). The excited Xe₂* molecules and monohaloid excimer molecules XeCl* and Xe₂Cl* decay via spontaneous radiation (reactions 11, 12, and 14). The molecules XeCl* and Xe₂Cl* experience additional quenching due to collisions with Xe atoms and CCl₄ molecules.

The luminescence yield in the mixture Xe–CCl₄ can be estimated by the area under the peaks of luminescence bands

$$S = \int_{\lambda_1}^{\lambda_2} I(\lambda) d\lambda,$$

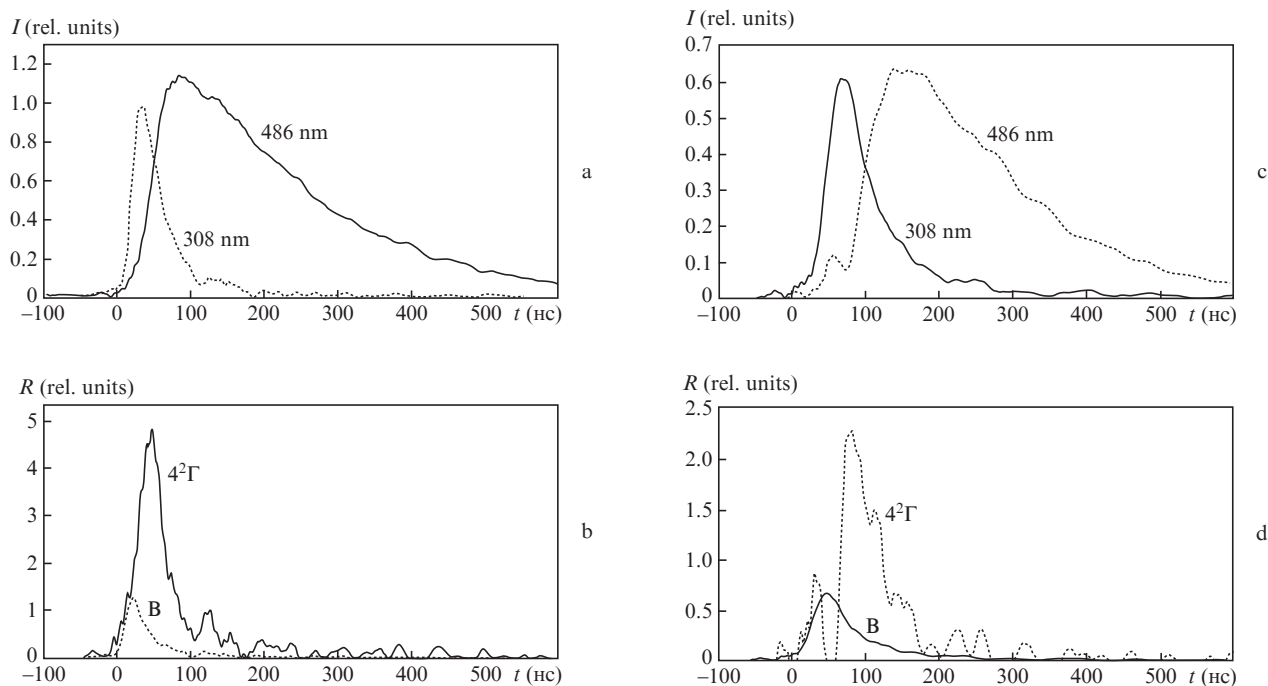


Figure 7. Time dependences of the luminescence intensity in (a, c) the B–X and 4²Γ–1²Γ bands and (b, d) the functions $R(t)$ for the states B and 4²Γ for the gas mixtures Xe–CCl₄ at (a, b) $p_{\text{Xe}} = 500$ Torr, $p_{\text{CCl}_4} = 0.035$ Torr and (c, d) $p_{\text{Xe}} = 152$ Torr, $p_{\text{CCl}_4} = 0.036$ Torr.

Table 2. Characteristics of the basic plasma-chemical processes, accompanying the excitation of the dense gas mixture Xe–CCl₄ with charged high-energy particles.

No.	Reactions	Reaction characteristics	References
1	Xe + β → Xe ⁺ + e _δ + β Xe + β → Xe* + β Xe + e _δ → Xe ⁺ + 2e	w = E/N(Xe ⁺) = 1.7I _i = 20.6 eV N(Xe*) = 0.4N(Xe ⁺) E ₁ = 0.31I _i = 3.76 eV	[22]
2	Xe ⁺ + 2Xe → Xe ₂ ⁺ + Xe	k ₂ = (1.8–3.5) × 10 ⁻³¹ cm ⁶ s ⁻¹	[22]
3	Xe* + 2Xe → Xe ₂ * + Xe	k ₃ = (2.5–8.5) × 10 ⁻³² cm ⁶ s ⁻¹	[22]
4	Xe ₂ ⁺ + e → Xe* + Xe	k ₄ = 8.1 × 10 ⁻⁵ (T _e /300 K) ^{-0.6} cm ³ s ⁻¹	[22]
5	CCl ₄ + e → CCl ₄ ⁻ → CCl ₃ + Cl ⁻ CCl ₄ + e → CCl ₃ + Cl ⁻	k ₅ = 7 × 10 ⁻⁸ cm ³ /c (for T _e = 0.25 eV)	[23] [26, 27]
6	Xe ⁺ + Cl ⁻ + Xe → XeCl* + Xe	k ₆ = 1.7 × 10 ⁻⁶ cm ³ s ⁻¹ at N _{Xe} = 2.7 × 10 ¹⁹ cm ⁻³	[25]
7	Xe ₂ ⁺ + Cl ⁻ + Xe → Xe ₂ Cl* + Xe	k ₇ = 1.6 × 10 ⁻⁶ cm ³ s ⁻¹ at N _{Xe} = 2.7 × 10 ¹⁹ cm ⁻³	[25]
8	Xe** + CCl ₄ → XeCl* (B, C) + CCl ₃		
9	Xe ^m + CCl ₄ → XeCl* (B) + CCl ₃		
10	Xe ₂ ⁺ + CCl ₄ → Xe ₂ Cl* + CCl ₃		
11	Xe ₂ ⁺ → 2Xe + hν (172 nm)	A = 2 × 10 ⁸ s ⁻¹ (λ = 172 nm, 0 _u ⁺) A = 10 ⁷ s ⁻¹ (λ = 147 nm, 1 _u)	[25]
12	XeCl* → Xe + Cl + hν (308 nm)	A ⁻¹ = 11 ns A ⁻¹ = 33 ns	[1] Present paper
13	XeCl* (B, C) + 2Xe → Xe ₂ Cl* + Xe	k ₁₃ = (0.8–1) × 10 ⁻³⁰ cm ⁶ s ⁻¹	[24]
14	Xe ₂ Cl* → 2Xe + Cl + hν (486 nm)	A ⁻¹ = 245 ns A ⁻¹ = 135 ns A ⁻¹ = 147 ns	[11] [14] Present paper
15	Xe ₂ Cl* + CCl ₄ → products	k ₁₅ = 2.29 × 10 ⁻⁹ cm ³ s ⁻¹ k ₁₅ = (5–7) × 10 ⁻¹⁰ cm ³ s ⁻¹	Present paper [14]
16	XeCl* + CCl ₄ → products	k ₁₆ = 1.98 × 10 ⁻⁹ cm ³ s ⁻¹	Present paper
17	XeCl* + Xe → products	k ₁₇ < 4 × 10 ⁻¹² cm ³ s ⁻¹	Present paper
18	Xe ₂ Cl* + Xe → products	No quenching observed	Present paper

Notes: β denotes the pump electron with the energy 150 keV; e_δ is the δ-electron with the energy E = 1–2 keV; e is the electron with the energy E ~ 1–2 eV; I_i is the ionisation potential of the Xe atom; w is the energy of the pair Xe⁺ + e; N(Xe⁺) and N(Xe*) is the number of Xe⁺ ions and the excited Xe* atoms, respectively; E₁ is the mean energy of secondary electrons, produced by the pumping electron with the energy E; and T_e is the temperature of thermalised electrons.

recorded using the MAYA-200Pro spectrometer [here I(λ) is the time-integrated intensity of luminescence at the wavelength λ]. Figure 8 shows the area S of the B–X band of the

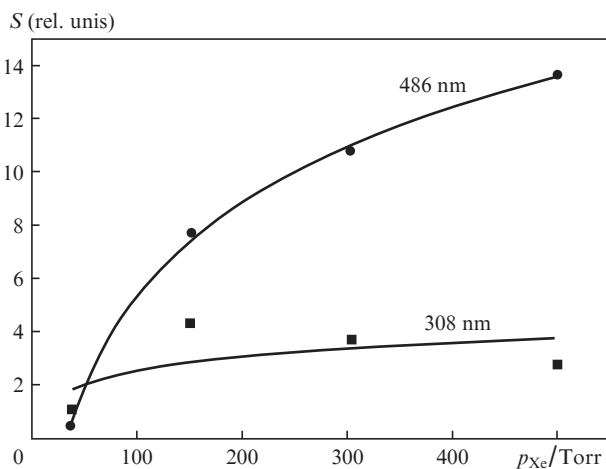


Figure 8. Area S of the excimer bands of the molecules XeCl* and Xe₂Cl* in the gas mixture Xe–CCl₄ versus the pressure of Xe at a constant partial pressure of CCl₄ (p_{CCl₄} = 0.036 Torr). The excitation of the mixture was implemented using a pulse of fast electrons with the energy 150 keV and the duration 5 ns.

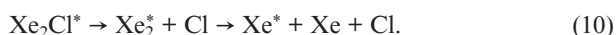
XeCl* molecules (λ_{max} = 308 nm, Δλ = 290–315 nm) and the 4²Γ–1²Γ band of the Xe₂Cl* molecules (λ_{max} = 486 nm, Δλ = 400–650 nm) for the mixture, containing CCl₄ at a pressure 0.03 Torr, as a function of the Xe pressure. It is seen that with increasing pressure a monotonic increase in energy, emitted within the band of the Xe₂Cl* molecule, is observed. At the donor pressure p_{CCl₄} = 0.036 Torr this dependence is described by the empirical formula S = a(1 + bp_{Xe}^c), where a = -2.17623 × 10⁷; b = -0.92349; c = 0.02256; p_{Xe} is expressed in Torr units. Under the xenon pressures exceeding 150 Torr, the luminescence yield in the band with λ_{max} = 486 nm can be estimated using the formula S = const · (1 + p_{Xe}^{1/2}), and in the band with λ_{max} = 308 nm – using the formula S = const · (1 - 8 × 10⁻⁴p_{Xe}).

At very small concentrations of a halogen-containing admixture CCl₄ the process of restoring the mixture composition after the burn-out of this component under the pump action at the expense of reactions 5, 8–10 (Table 2) is very important. The high efficiency of conversion of the pump energy into the radiation of the Xe₂Cl* molecule (band 430–650 nm), in our opinion, may be associated with the multiple use of both the molecule CCl₄ itself and all radicals, forming it, including the atomic Cl, in the process of pumping:





This is an idealised extended scheme of all possible plasma-chemical reactions. In reality only some of them can be implemented. Unfortunately, in the literature the available information about the mechanisms of formation, the properties of the negative ions of the CCl₄ molecule, and the radicals, forming it, is rather limited. However, the reaction (9) will be always present in the plasma-chemical model and play a particular role in increasing the efficiency of the formation of the Xe₂Cl* molecules, since the component, necessary for its implementation, i.e., the atomic chlorine, arises in the course of radiative decay of this molecule:



The produced atomic chlorine can repeatedly participate in the chain of plasma-chemical reactions (5)–(9).

The experimental results evidence in favour of the fact that the restoration of the mixture composition after the pumping pulse occurs fast enough and is not accompanied with its significant degradation.

4. Conclusions

The studies of luminescence of high-density Xe–CCl₄ gas mixtures with low content of halogen-containing donor CCl₄ (~5×10⁻³%) have demonstrated the anomalously high luminescence yield in the 4²Γ–1²Γ band of the Xe₂Cl molecule (λ = 430–650 nm), which is more than by five times higher than the luminescence yield for the mixture with a high content of CCl₄. It is established that the main channel of formation of the Xe₂Cl molecules in this case is provided by the reactions of ion–ion recombination of the positive molecular ions Xe₂⁺ with the negative CCl₄⁻ ions and negatively charged radicals, forming the CCl₄ molecules. The measurements of temporal characteristics of luminescence have shown that the molecular states 4²Γ (Xe₂Cl*) and B (XeCl*) experience strong collisional quenching by the molecules CCl₄ (the quenching rate constant ~2×10⁻⁹ cm³ s⁻¹). This is just the fact that explains the increased luminescence yield of the gas mixture Xe–CCl₄ at low concentrations of the halogen-containing donor.

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