New excimer emission bands of noble-gas halides

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Excitation of the gas mixtures Ar/F_2, $Ar/Kr/F_2$, and $Kr/Xe/F_2$ by a beam of fast electrons has produced broad emission bands centered at 290, 420, and 480 nm. These bands are attributed to formation of molecules consisting of one halid atom and two inert atoms.

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1. Excitation of mixtures of inert gases with fluorine by an electron beam gives rise to the excimers ArF*, KrF*, and XeF*, the emission of which in the 190-, 250-, and 350-nm bands is extensively used at present to obtain intense light generation in the ultraviolet (see, e.g., [1–3]). In the present investigation of the emission spectra of the gas mixtures Ar/F_2, $Ar/Kr/F_2$, and $Kr/Xe/F_2$, in a wide wavelength interval from 270 to 520 nm, we have observed new bands located at 290, 420, and 480 nm. The character of the pressure dependence of the emission intensity of these bands points to the possibility of formation of complex compounds of inert gases with halogens.

2. The mixtures in questions were excited with an electron beam having the parameters $E=600$ keV, $j=100$ A/cm^2 and $\tau=20$ nsec. The electron beam

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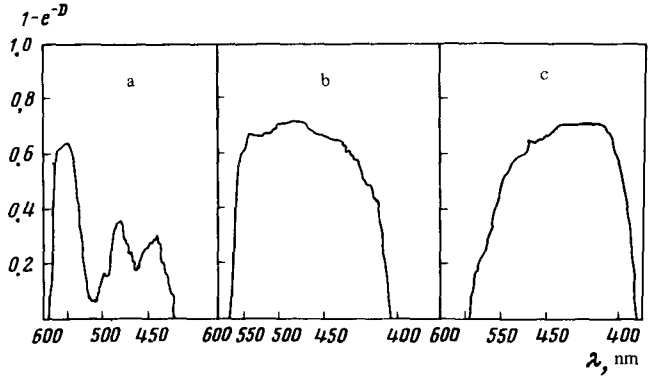

FIG. 1. Emission spectra of mixtures of inert gases with fluorine in the wavelength range from 270 to 520 nm at a particle concentration 2×10^{20} cm^{-3} and a temperature 293 K: a—Xe/F_2 (1000/1), b—$Kr/Xe/F_2$ (1000/10/1), c—$Ar/Kr/F_2$ (1000/10/1). The intensities of spectra b and c are weaker than that of spectrum a by a factor of 10. *D*—film photographic density.

entered the working chamber, which could be cooled with liquid nitrogen or heated with nichrome coils, through a tantalum foil 50 μm thick. We used in the experiments argon 99.99% pure, xenon 99.9% pure, and krypton 98.7% pure,

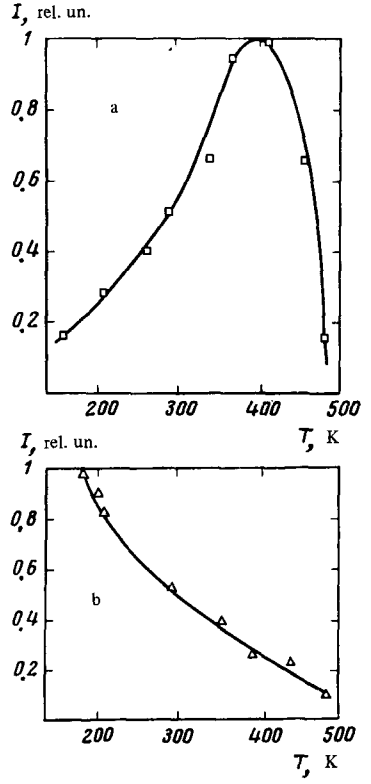

FIG. 2. Intensities of the 250-nm (a) and 420-nm (b) bands vs temperature in the gas mixture $Ar/Kr/F_2$ (1000/10/1) at a particle concentration 2×10^{20} cm^{-3}.

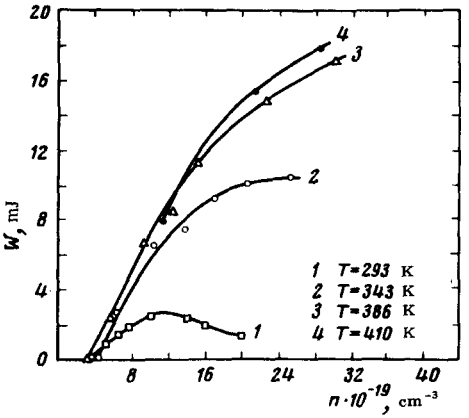

FIG. 3. Pressure dependence of the lasing energy at the wavelength 248.6 nm in the mixture $Ar/Kr/F_2$ (1000/10/1) at various temperatures.

with 1% xenon content. The emission in the 190—460 nm range was registered with a VM-1 monochromator having a resolution of 2 nm and with a photoreceiver ÉLU-FT, ahead of which a luminophor was placed. The emission spectra in the 360—1000 nm range were photographed with the aid of an ISP-51 spectrograph on an RF-3 film having a resolution 0.4—1 nm. In the investigation of the stimulated $Ar/Kr/F_2$ (1000/10/1) radiation the laser resonator was made of spherical mirrors ($r = 3$ m) placed inside the chamber, with reflection coefficients $R_1 = 97\%$ and $r_2 = 93\%$ ($T \sim 4\%$) at a wavelength 248.6 nm. The volume of the active region was 4 cm^3, the diameter of the employed mirrors was 1 cm, and the distance between mirrors was 10 cm.

3. Figures 1(a)—1(c) show the emission spectra of the mixtures of the inert gases with fluorine. Broad emission bands centered at 290, 420, and 480 nm, respectively, are observed in the mixtures Ar/F_2 (1000/1), $Ar/Kr/F_2$ (1000/10/1), and $Kr/Xe/F_2$ (1000/10/1). Superimposed on the 420 and 480 nm bands are weak emission bands observed in the Xe/F_2 mixture (see Fig. 1), and due to the presence of the xenon impurity in the krypton. The ratio of the intensities of the 420 and 480 nm bands to the emission intensity of the excimers KrF* (250 nm) and the ratio of the intensity of the 290 nm band to the emission intensity of ArF* (190 nm) have a practically linear pressure dependence in the range 1—8 atm. A strong temperature dependence of the intensities of the 420 and 250 nm bands is observed in the $Ar/Kr/F_2$ (1000/10/1) mixture (see Fig. 2). At temperatures from 150 to 400 K, the intensities of the spontaneous and induced emission of the KrF* molecules increase (see Fig. 3) and the intensity of the 420 nm band decreases correspondingly.

4. The observed new emission bands can be attributed to radiative decay of excimers consisting of the one halide atom and two inert atoms. The binding energy of such three-atom excimers, say Ar_2F^*, should exceed the energy of the two-atom excimers ArF* by an amount equal to the binding energy of the molecular ion Ar_2^+, while the repulsion potential in lower state to which the excimers go after emitting a light quantum is higher, owing to the presence of the third repelling particle. This leads to a long-wave shift and to a strong broadening of the corresponding emission bands. Consider, for example, the formation of three-atom excimers in the Ar/F_2 mixture. Under the influence of

the electron beam, excited atoms Ar* are produced in the gas and interact with the remaining mixture components in the following manner:

$$Ar^* + F_2 \xrightarrow{k_1} ArF^* + F,\quad Ar^* + 2Ar \xrightarrow{k_2} Ar_2^* + Ar,\quad Ar_2^* + F_2 \xrightarrow{k_3} Ar_2F^* + F,$$
$$Ar_2^* \xrightarrow{\tau_1} 2Ar + h\nu_1,\quad ArF^* \xrightarrow{\tau_2} Ar + F + h\nu_2,\quad Ar_2F^* \xrightarrow{\tau_3} 2Ar + F + h\nu_3, \qquad (1)$$

where τ_i are the spontaneous lifetimes and k_i are the rate constants of the excimer-production processes. In the quasi-stationary regime, it follows from (1) that the ratio of the spontaneous intensities of the excimers Ar_2F^* and ArF^* is

$$\frac{\tau_2}{\tau_3}\frac{[Ar_2F^*]}{[ArF^*]} = \frac{k_2k_3}{k_1}\frac{[Ar]^2}{k_3[F_2] + \tau_1^{-1}}, \qquad (2)$$

and at a fixed ratio $[F_2]/[Ar]$ of the fluorine and argon concentrations, the intensity ratio increases with increasing pressure first quadratically and then changes to the linear dependences noted above for the 290 and 190 nm bands. Consequently, the 290-nm emission band in the Ar/F_2 mixture can be due to radiative decay of the Ar_2F^* excimers. The 420-nm emission band in the $Ar/Kr/F_2$ (1000/10/1) mixture is apparently due to formation of ArKrF* excimers, since the concentration of the Kr_2F^* excimers produced in this mixture is low. The complexes ArKrF* are formed from the excimers ArKr*, which produce an intense 135-nm emission band at low temperatures.[4] The observed temperature dependences of the intensities of the spontaneous and induced emission of the 250 nm band (Figs. 2 and 3) can therefore be attributed to the competitions between the processes of formation of the excimers KrF* and ArKrF* and the strong temperature dependence of the rate constants of the excimer formation, e.g., $\sim\exp(T_0^2/T)$ for Xe^*_2.[5] The rapid decrease of the 250-nm band intensity at temperatures above 400 K is probably due to nonradiative deactivation of the KrF* excimers. In the $Kr/Xe/F_2$ mixture, the 480-nm emission band is due mainly to formation of KrXeF* excimers, since the concentration of the Kr_2F^* excimers, whose emission probably does make some contribution to this band, is small because of the rapid transfer of the excitation from the Kr_2^* to the Xe atoms, while the xenon concentrations is too small for the formation of Xe_2F^* excimers.

The observed broad emission bands of noble-gas halides can be used to develop tunable visible-light lasers, and also for the generation of ultrashort ($\sim 10^{-15}$ sec) light pulses.

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