

Formation and quenching mechanisms of the electron beam pumped (XeRb)⁺ ionic excimer in different buffer gases

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The ionic excimer molecule XeRb⁺ is formed in an electron beam excited gas mixture of Xe, Rb, and a buffer gas. The formation and quenching mechanisms of ionic excimers are investigated by measuring the XeRb⁺ fluorescence as a function of the gas composition and gas pressure. The formation of XeRb⁺ is achieved by a three-body association reaction between Xe⁺, Rb, and a buffer gas atom. For the buffer gases He, Ne, or Ar the values of the important formation rate constants are determined from the observed fluorescence signal decay.

In the search for new vacuum ultraviolet laser media rare gas alkali ions are promising candidates because of their excimerlike properties. Since the first theoretical proposals^{1,2} much experimental work has been done on these ionic excimers. The XeRb⁺ is a typical representative of an ionic excimer formed by a rare gas ion (Xe⁺) and an alkali atom (Rb). The XeRb⁺ molecule has been generated by ion beam,^{3,4} gas discharge,⁵ and by laser produced plasmas.⁶ Because of the very high pumping powers required to obtain laser action, electron beam pumping⁷⁻⁹ is also an obvious choice. This letter discusses the formation and quenching mechanisms of XeRb⁺, pumped by a coaxial electron beam, as a function of the gas composition.

A description of the modified coaxial electron beam, which is used for these measurements, has already been given in a previous letter.⁹ The heated anode tube which contains the gas mixture and the alkali metal is powered through a pulse forming line by a Marx generator (typically 300 A/cm², 175 keV, 10 ns FWHM). The power deposition in the gas is measured with the pressure jump technique. In He a power deposition of 0.35 MW/cm³/bar can be obtained. In Ne and Ar these values are, respectively, 0.8 and 1.4 MW/cm³/bar. The active length of the heated anode tube is 24 cm and has a flat temperature distribution. The light emitted by the ionic excimers is led through a vacuum monochromator on a scintillator plate. The scintillator fluorescence signal is then detected by a photomultiplier. In this way the fluorescence peak intensity and decay frequency are measured as a function of the gas composition. Measurements have been performed for gas mixtures containing Ar, Ne, or He as buffer gas. The total gas pressure has been varied between 1 and 8 bar. The Xe percentages in the gas mixtures were 2.5%, 5.0%, and 10.0%. By varying the temperature of the anode tube, the Rb vapor pressure has been varied between 2 and 20 mbar.

The transition wavelength of XeRb⁺ lies around 164.5 nm.^{3,4} Because the Xe₂^{*} transition at 172 nm has a large bandwidth, the fluorescence signals had to be corrected for a small background signal at pressures above 4 bar.

In Fig. 1 typical traces are shown of the fluorescence signal and of the excitation current pulse as measured inside the tube. The rise time of the fluorescence pulse coincides with the duration of the excitation pulse except for low pressures where the rise time is somewhat longer. The signal

exhibits a single exponential decay. The decay time is corrected for the scintillator decay if it was shorter than 15 ns. The reproducibility of the signals was within 10%.

Figure 2 shows the dependency of the fluorescence peak intensity and the decay frequency on the Rb density for the buffer gases Ar and Ne, at a constant Xe density of 4.4×10^{18} cm⁻³, and a constant buffer gas density of 8.8×10^{19} cm⁻³. The fluorescence peak intensity saturates at higher Rb densities due to photoabsorption of the Rb vapor. The decay frequency increases linearly with the Rb density for both Ar and Ne. Figures 3 and 4 show the fluorescence peak intensity and the decay frequency for a gas mixture containing 12 mbar Rb (380 °C) and 5% Xe as a function of total gas pressure for the buffer gases Ar, Ne, and He. By using a heavier buffer gas the peak intensity increases. At higher pressure the intensity seems to saturate for the Ar and Ne mixtures, while for He the peak intensity still increases linearly. With Ar or Ne as the buffer gas the saturation of the peak intensity at higher pressures seems to be accompanied by a saturation of the decay frequency (Fig. 4).

The dependency of the decay frequency on the Xe density is shown in Fig. 5 for the different buffer gases at a total gas pressure of 8 bar at 380 °C and a Rb vapor pressure of 12 mbar. The decay frequency increases slightly with increasing Xe density. The fluorescence peak intensity is also dependent on the Xe density. An optimum occurs at a Xe fraction of

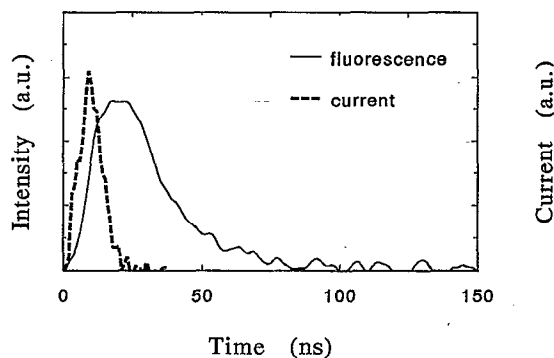


FIG. 1. Typical traces of the (XeRb)⁺ fluorescence signal and of the excitation current pulse as measured inside the tube [gas mixture: 94.7% Ar, 5% Xe, and 0.3% Rb (12 mbar) at a total gas pressure of 4 bar, and a gas temperature of 380 °C].

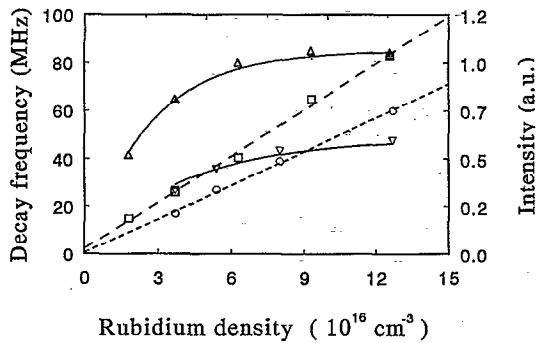
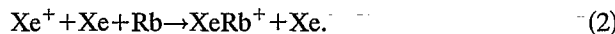


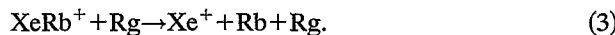
FIG. 2. Fluorescence peak intensity (solid lines) and decay frequency (dashed lines) as a function of the rubidium density with $[Xe]=4.4 \times 10^{18} \text{ cm}^{-3}$ and a rare gas density of $8.8 \times 10^{19} \text{ cm}^{-3}$ (Δ , \square Ar; ∇ , \circ Ne). The dashed lines are fittings to Eq. (4) with the rate constants of Table I.

about 5% for all the buffer gases used. Comparing the Ar, Ne, and He intensities it can be seen (Fig. 3) that for the same gas mixture the intensity (I) increases in the order $I_{\text{He}} < I_{\text{Ne}} < I_{\text{Ar}}$. The higher peak intensities combine with shorter decay times so the integrated energy is in the same order of magnitude.

Most of the energy deposited by the electron beam form buffer gas ions (Rg^+). These buffer gas ions form Xe^+ by charge transfer reactions. Finally Xe^+ produces XeRb^+ by one of the following three-body association reactions:



Mantel *et al.*¹⁰ proposed a dissociation reaction of XeRb^+ in the form



The effect of reaction (3) is to lower the rate of increase of the decay frequency of Xe^+ with pressure. The effective formation rate of XeRb^+ also decreases.

The effective lifetime (τ_{eff}) of ionic excimers is very short.^{11,12} Assuming the charge transfer reactions from buffer gas ions to Xe^+ to be very fast, the fluorescence signals reflect the time dependency of the precursor Xe^+ . Assuming

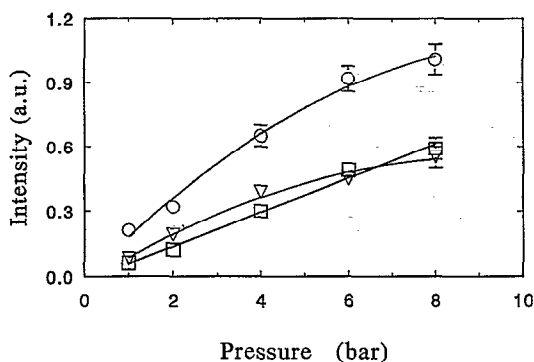


FIG. 3. Fluorescence peak intensity as a function of total gas pressure for several buffer gases with $[\text{Rb}]=12.7 \times 10^{16} \text{ cm}^{-3}$, $\text{Xe}=5\%$, (\circ Ar; ∇ Ne; \square He). The temperature was kept constant at 380 °C.

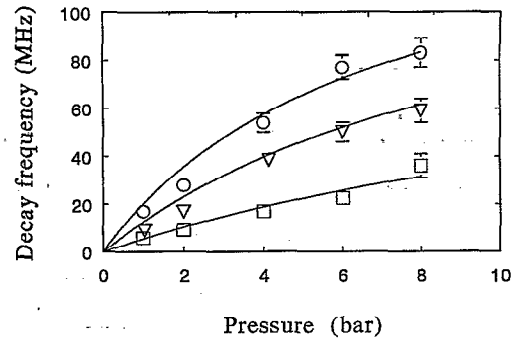


FIG. 4. Fluorescence decay frequency as a function of total gas pressure for several buffer gases with $[\text{Rb}]=12.7 \times 10^{16} \text{ cm}^{-3}$, $\text{Xe}=5\%$, (\circ Ar; ∇ Ne; \square He). The temperature was kept constant at 380 °C. The solid lines represent the decay frequency as calculated with Eq. (4), with the rate constants of Table I.

quasi-stationary equilibrium between Xe^+ and XeRb^+ , the theoretical measured decay frequency ($1/\tau$) of Xe^+ would be given by

$$1/\tau = \frac{(k_1 + \alpha k_2)[\text{Rb}][\text{Rg}]}{1 + \tau_{\text{eff}}[\text{Rg}]\{(k_1 + \alpha k_2)[\text{Rb}] + k_3\}} \quad (4)$$

Here k_1, k_2 , and k_3 are the rate constants of the reactions 1, 2, and 3. The constant α is given by the density ratio $[\text{Xe}]/[\text{Rg}]$. The effective lifetime τ_{eff} is assumed to be 1 ns. The measured decay frequencies from Figs. 2, 4, and 5 are fitted according to Eq. (4) resulting in the rate constants of Table I. A reasonable agreement between model and measurements is obtained in this way. From Fig. 5 the rate constant k_2 is obtained, also shown in Table I. Both the formation rate constant k_1 and the dissociation rate constant k_3 increase with heavier buffer gases. The values of k_1 are in the same range as the values of the analogous formation rate constants of KrK^+ in He and Ne mixtures reported by Mantel *et al.*¹⁰ The increase of the dissociation rate at higher pressure leads to a saturation effect of the decay frequency.

In analogy to Schumann *et al.*,¹¹ the Xe density should not be too high because of the high quenching rate of XeRb^+ by Xe, leading to the formation of Xe_2^+ . This quenching

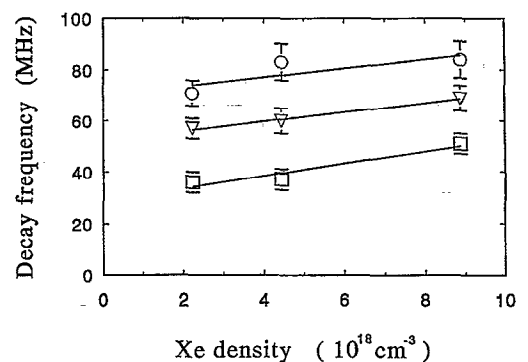


FIG. 5. Fluorescence decay frequency as a function of the xenon density for several buffer gases with $[\text{Rb}]=12.7 \times 10^{16} \text{ cm}^{-3}$ and a rare gas density of $8.0 \times 10^{19} \text{ cm}^{-3}$ (\circ Ar; ∇ Ne; \square He). The solid lines represent the decay frequency as calculated with Eq. (4), with the rate constants of Table I.

TABLE I. The rate constants k_1 , k_2 , and k_3 of reactions (1)–(3) for three different buffer gases. The rate constants are determined by fitting the measured decay frequencies of Figs. 2, 4, and 5 to Eq. (4).

Buffer gas	k_1 (10^{-30} cm ⁶ /s)	k_2 (10^{-29} cm ⁶ /s)	k_3 (10^{-11} cm ³ /s)
He	3.6	3.4	0.2
Ne	8.6	2.9	0.8
Ar	15	2.4	1.5

mechanism shows up in a maximum of the peak intensity at Xe fractions of about 5%. The peak intensity increases by using a heavier buffer gas, because of the higher formation rate ($1/\tau$), producing XeRb⁺, and the higher power deposition in the gas mixtures. With Ar or Ne as buffer gas the flattening of the decay frequency, which is proportional to the effective formation rate of XeRb⁺, causes a saturation effect of the peak intensity at higher pressures.

In conclusion we can say that the XeRb⁺ ionic molecule is formed in a three-body association reaction between Xe⁺, Rb, and a buffer gas atom. At higher pressures the XeRb⁺ molecule dissociates, which can be noticed in a flattening of the measured decay frequency as a function of pressure. The rate constants of the important formation and dissociation

reactions of XeRb⁺ have been determined by fitting the measured decay frequencies of the fluorescence signals to a simple model. Both the formation and the dissociation rate constant increase with the use of heavier buffer gases. The dissociation reaction limits the effective formation rate of the XeRb⁺ molecule at higher gas pressures.

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