The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments, and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 January 1985 for a fuller description of Letters to the Editor.

NOTES

The displacement reactions of the triatomic rare gas halide excimers

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In order to optimize the performance of diatomic and triatomic rare gas halide excimer lasers, appropriate gas mixtures have been developed in recent years. Especially when heavier rare gases such as argon or krypton are used as buffer gases their excited atoms may react rapidly with the halogen donor to form stable rare gas halide molecules. Subsequently, these molecules react with the heavier rare gases such as krypton or xenon in a so-called displacement reaction yielding a xenon or krypton halide molecule. In KrF* lasers for instance, the reaction $ArF^* + Kr \rightarrow KrF^* + Ar$ is one of the dominant formation channels for the upper laser state.[1] To the best of our knowledge measurements of the rate coefficient for displacement reactions for the diatomic rare gas halides have been published only by Rokni *et al.*[2] and Morgan and Szoke.[3] The latter authors also propose a displacement reaction for the triatomic species Ar_2F^* with krypton in order to form KrF* according to $Ar_2F^* + Kr \rightarrow KrF^* + 2Ar$. For the broadband excimer laser XeF(C→A) emitting in the blue green region the reaction $Ar_2F^* + Xe \rightarrow XeF^* + 2Ar$ is expected to contribute considerably to the production of the upper laser level due to the high buffer gas pressure in this laser.[4] In this letter we give the first measured rate coefficients for the quenching of Ar_2F^* by krypton and xenon and Kr_2F^* by xenon, and compare the results to a classical calculation for these rate coefficients.

The experimental setup used in these investigations has been described in detail elsewhere.[5] An intense electron beam (1 MeV, 200 A cm^{-2}, 10 ns FWHM) was used to excite a gas mixture at high pressures. The temporal evolution of the light emitted by the triatomic species Ar_2F^* around 290 nm and Kr_2F^* around 420 nm was measured using a fast photomultiplier. The spectral region of the observed emissions was defined by appropriate color glass filters and interference filters. The decay rate of Ar_2F^* was observed in gas mixtures containing 6 atm argon, 5 Torr NF_3, and varying amounts of krypton and xenon. Furthermore, the decay rate of the Kr_2F^* fluorescence as a function of the xenon pressure was investigated in Ar/Kr/Xe/NF_3 mixtures.

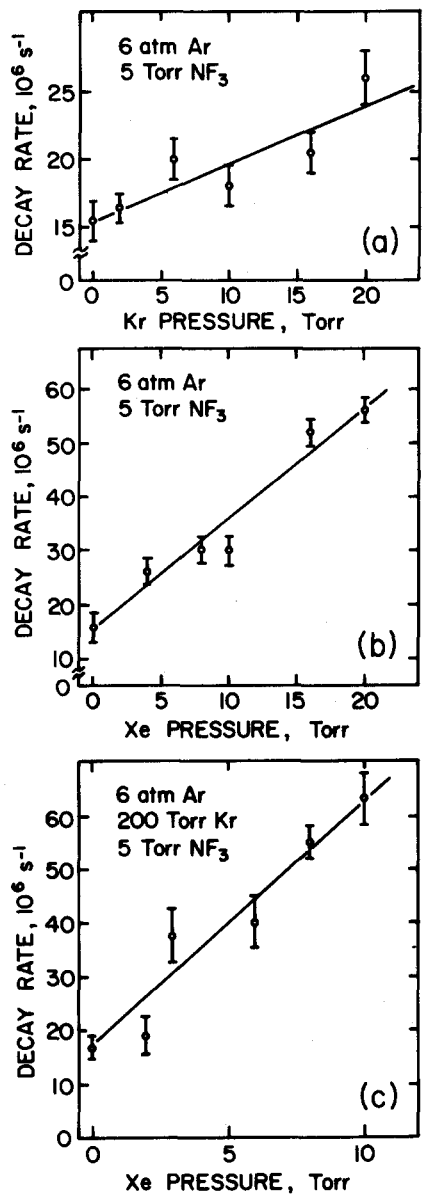

FIG. 1. Decay rates for the triatomic rare gas fluorides as a function of the quenching rare gas pressures (a) $Ar_2F^* + Kr$, (b) $Ar_2F^* + Xe$, and (c) $Kr_2F^* + Xe$.

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TABLE I. Calculated and measured reaction rates for rare gas fluoride diatomic and triatomic molecules.

Reaction	k_{calc} 10^{-10} cm^3 s^{-1}	k_{exp} 10^{-10} cm^3 s^{-1}	Reference
(1) ArF* + Kr → products	1.6	3.3	3
		15	2
(2) ArF* + Xe → products	1.7	43	2
(3) KrF* + Xe → products	1.5		
(4) Ar_2F^* + Kr → products	1.3	0.13 ± 0.05	This work
(5) Ar_2F^* + Xe → products	1.3	0.61 ± 0.11	This work
(6) Kr_2F^* + Xe → products	1.1	1.4 ± 0.3	This work
(7) ArKrF* + Kr → Kr_2F^* + Ar	1.3[a]	0.2	2

[a] Assuming a branching ratio of 1.0.

Exponential decays of the trimer fluorescence pulses were observed in each case. Figure 1 shows the resulting Stern–Volmer plots. Within the experimental uncertainties straight lines are obtained. This indicates the dominance of two body quenching processes compared to three body quenching for pressures up to 20 Torr of the quenching rare gas. It was demonstrated in previous investigations that the quenching rate constants of Ar_2F^* and Kr_2F^* by Ar and Kr_2F^* by Kr are of the order of only several 10^{-14} cm^3 s^{-1}.[6–8] Variation of the buffer gas pressure has, therefore, little influence on the decay rates of the trimers. Due to the relatively high argon and krypton pressures used in the present investigation the trimer formation rate is much faster than the decay rate,[6,8] which is determined by radiative decay and two body quenching (Fig. 1). The quenching rate coefficients may be determined according to

$$\tau^{-1}([M]) = \tau_0^{-1} + k^M_{Rg_2F}[M].$$

$\tau^{-1}([M])$ is the total decay rate observed as a function of the concentration of the quenching rare gas [M]. $k^M_{Rg_2F}$ is the appropriate rate coefficient and τ_0^{-1} the intersection for zero pressure. τ_0^{-1} has also been calculated in each case considering the radiative lifetimes and quenching coefficients of the trimers as summarized in Ref. 1 yielding good agreement with the measured values given in Fig. 1. The experimentally determined value for the rate constants $k^M_{Rg_2F}$ as well as calculated values are given in Table I.

The experimental results for the trimers show a strong dependence on the specific system and appear to increase with the atomic number of the rare gas in the trimer molecule as well as the quenching rare gas. For comparison experimental results for the quenching of ArF* by krypton and xenon and ArKrF* by Kr are quoted.

The calculated values are estimates based on a classical Langevin theory for the cross section of a dipole-induced dipole interaction between the polar rare gas halide molecule and the polarizable quenching rare gas atom.[9] Whereas the calculated values are nearly independent of the specific reaction, the measured values exhibit considerable scatter. Considering the approximations in the calculation and experimental errors, agreement may be stated for the value obtained in Ref. 3 for reaction (1) and reaction (6) measured in this work. However, when lighter rare gases are involved, the quenching rates for the trimers remain considerably below the classical limits [reactions (4), (5), and (7)]. Even when a branching ratio of unity is assumed for a formation of KrF* and XeF* via reactions (4) and (5), respectively, the corresponding formation rates are far below the previously estimated values.[3,4]

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