Kinetic Studies of Ar$_2$F* in Fast Transverse-Discharge-Excited He–Ar–F$_2$ Mixtures

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Abstract. Time-resolved and time-integrated spectra for various He–Ar–F$_2$ mixtures excited by a fast transverse discharge were recorded. The fluorescence of ArF* and Ar$_2$F* was investigated and the radiative lifetime and emission characteristics of Ar$_2$F* were determined. A mechanism for the formation of Ar$_2$F* is suggested.

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Rare-gas halide exciplex molecules which radiate from a strongly bound excited state to a repulsive ground state were first observed by Velazco and Setser [1, 2]. Detailed spectral and structural analysis studies as well as ab initio calculations were reported soon thereafter [3]. While these diatomic RgX* molecules were investigated, discovery of a new class of triatomic rare-gas halide exciplex molecules was made [4]. The broad-band continuum emissions of triatomic rare-gas halides were identified as transitions between ionically bound excited states (Rg$_2^+$ X$^-$) and repulsive covalent lower states, that dissociate to ground state atoms [5].

The triatomic exciplex Ar$_2$F* has a broad continuum emission centered around 290 nm [6, 7]. It therefore merits consideration as a potential candidate for a widely tunable uv laser. Previously, the formation and decay processes of Ar$_2$F* in Ar–F$_2$ and Ar–NF$_3$ mixtures were investigated by Nakano et al. [6], Lorentz et al. [4], Marowsky et al. [8] using electron beam excitation, and by Chen and Payne [11] and Chen et al. [12] using proton beams. Bôwering et al. [13] report on the kinetics of Ar$_2$F* from e-beam excited Ar–NF$_3$ and He–Ar–NF$_3$ mixtures. Corresponding data obtained under conditions of direct electric discharge have not been published so far.

Discharge excitation is very attractive under two aspects:

1) Low energy electrons feature large excitation cross-sections, which translates to a high pumping efficiency [10].
2) High pulse repetition rates, that is high average laser powers, are possible. Understanding the kinetics initiated by a fast discharge is a prerequisite to evaluate the chances of a directly pumped Ar$_2$F* laser and should thus be rewarding.

In this contribution we report on our investigation about the kinetics of He/Ar/F$_2$ mixtures excited by a TEA discharge. The partial pressures of the three gas components were varied, the ranges are given in Sect. 1. Since the electron temperature is lower in the discharge than under e-beam excitation conditions, a different reaction kinetics may be expected. Backed by experimental observations this paper suggests a scheme leading to the formation of Ar$_2$F*. It also reports the radiative lifetime of this trimer and the rate constant for quenching by F$_2$.

1. Experimental

The experimental setup is shown in Fig. 1. A detailed description of the fast TEA discharge can be found elsewhere [14]. A main capacitor (200 nF) charged to 36 kV resonantly charges 40 nF capacitors to produce a fast discharge. The pump power density is estimated to be about 30 MW/cm$^2$. Laser gases are premixed in a circulation system before being admitted to the discharge chamber. Partial and total pressures are measured by a capacitance gauge (MKS Baratron, Model 170 M-26 B).
Gas pressures were varied within the ranges 0.05–6 mbar for $F_2$, 50–3800 mbar for He, and 50–2500 mbar for Ar. Ratios $He:Ar$ varied between 60 : 1 and 1 : 2. Total pressure was $\leq 4000$ mbar. Time integrated spectra were recorded using a spectrograph in conjunction with a uv-sensitized OMA system (B+M Spektronik, Model OSA 500 equipped with scintillator). Time resolved measurements of $Ar_2F^*$ and $ArF^*$ emissions were made using fast photodiodes (Hamamatsu R 617 S-5) connected to a dual beam scope (TEK 7844). In this case, discrimination between $ArF^*$ (193 nm) and $Ar_2F^*$ (290 nm) was achieved by narrow band filters.

2. The Formation of $Ar_2F^*$

Before presenting our results it seems appropriate to establish a basis for their interpretation by briefly listing some of the processes that can possibly result in the formation of the laser active species from $He/Ar/F_2$ mixtures. Excited and ionized Ar which initiates the formation process may either be generated directly (electron impact) or via collisions involving $He^*$ and $He^+_e$:

$He^* + Ar \rightarrow Ar^* + He,$  
$He^+_e + Ar \rightarrow Ar^* + 2He,$  
$He^* + Ar \rightarrow He + Ar^* + e^-,$  
$He^+_e + Ar \rightarrow 2He + Ar^*.$  

Reaction (1) proceeds slowly $[10]$ compared to processes (2–4) $[10, 17, 18]$. Both excited and ionized Ar atoms are channelled into the excited dimer state via the following termolecular reactions:

$Ar^* + Ar + He \rightarrow Ar^+_2 + He,$  
$Ar^* + 2Ar \rightarrow Ar^+_2 + Ar,$  
$Ar^* + Ar + He \rightarrow Ar^+_2 + He,$  
$Ar^* + 2Ar \rightarrow Ar^+_2 + Ar.$  

$ArF^*$ formation is considered to occur via ion-ion recombination:

$Ar^+_2 + F^- \rightarrow ArF^* + Ar,$  
$Ar^* + F^- + (M) \rightarrow ArF^* + (M)$  

(11)

(where $M$ is an arbitrary collision partner) and/or by formation reactions like $[10]$:

$Ar^* + F_2 \rightarrow ArF^* + F.$  

Finally, these excited and ionized dimers participate in reactions resulting in the formation of the trimer $Ar_2F^*$:

$ArF^* + Ar + Ar \rightarrow k_{11} Ar_2F^* + Ar,$  
$ArF^* + Ar + He \rightarrow k_{12} Ar_2F^* + He,$  
$Ar^+_2 + F_2 \rightarrow k_{13} Ar_2F^* + F,$  
$Ar^+_2 + F^- + (M) \rightarrow k_{14} Ar_2F^* + (M).$  

Figure 2, in a simplified form, visualizes the formation mechanism for $ArF^*$ and $Ar_2F^*$, as it is suggested by (5–15).

The rate equation describing the mechanism of formation of $Ar_2F^*$ can thus be written

$$\frac{d}{dt} [Ar_2F^*] = k_1 [ArF^*][Ar]^2 + k_2 [ArF^*][Ar][He]$$

$$+ k_3 [Ar^+_2][F_2]$$

$$+ k_4 [F^-][Ar^+_2][M] - \frac{[Ar_2F^*]}{\tau}. \quad (16)$$

$\tau$ is the effective exponential decay constant of $Ar_2F^*$. It is given by

$$\tau^{-1} = \tau_{290}^{-1} + k_5[F_2] + k_6[Ar] + k_7[He] + k_8[Ar]^2$$

$$+ k_9[He]^2 + k_{10}[Ar][He]. \quad (17)$$