

QUENCHING AND FORMATION PROCESSES OF XeF AND Xe₂F EXCIMERS

R. Sauerbrey, W. Walter

Physikalisches Institut, Am Hubland, D-8700 Würzburg, F.R. Germany

F.K. Tittel, W.L. Wilson, Jr.

Electrical Engineering Department, Rice University, Houston, TX 77251

ABSTRACT

Two- and three-body quenching and formation constants for electron beam-excited XeF(B,C) and Xe₂F have been measured. XeF(C) is identified as the precursor of the triatomic rare gas excimer Xe₂F² which radiates around 614 nm with a spectral bandwidth of 125 nm.

INTRODUCTION

The XeF-Xe₂F system has recently attracted special interest for several reasons. It is the only rare gas halide excimer system for which laser action has been obtained for the C→A transition at 480 nm¹⁻³. Kinetic studies of XeF^{4,5} showed that the B state lies about 650 cm⁻¹ above the C state, which leads to collisional mixing effects between both states. The existence of Xe₂F, the product of a three-body quenching process of XeF, was only recently demonstrated^{6,7}, although corresponding triatomic species have been known for some time for many other diatomic rare gas halides⁸.

This paper describes the quenching processes of XeF(B,C) with special emphasis on three-body quenching and the formation of Xe₂F. Experiments were carried out using short pulse electron beam excitation of xenon containing rare gas-NF₃ mixtures. Observations of the temporal behavior of the XeF(B,C) and Xe₂F intensities as well as the fluorescence yields allowed the determination of the various rate constants.

EXPERIMENTAL APPARATUS

Details of the experimental apparatus have been described elsewhere⁸. Gas mixtures consisting of high purity argon, xenon and NF₃ were transversely pumped by a pulsed electron beam (1 MeV, 15 ka, 10 ns). The typical maximum electron current density on the optical axis of the reaction cell was ~ 200 A/cm². An area of 10 x 2 cm was irradiated by the electron beam. The spectrally resolved fluorescence was recorded by an OMA I detection system. The temporal dependence of the fluorescence was measured by a fast vacuum photodiode or a photomultiplier and recorded by a transient digitizer. The data from the OMA and the digitizer were stored and processed by a PDP 11/23 minicomputer.

EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 1 shows the fluorescence spectrum of an electron beam-excited Ar/Xe/NF₃ mixture between 250 nm and 720 nm. The XeF(D → X) and B → X transitions occur at 265 nm and 352 nm, respectively. A broad structured continuum is observed that extends from 400 nm to

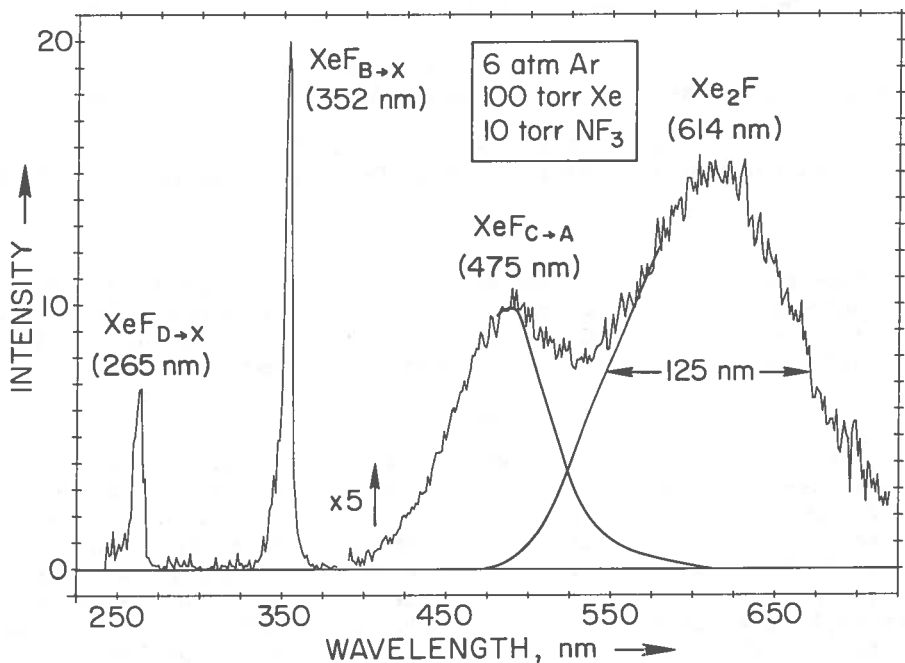


Fig. 1: Fluorescence spectrum of an e-beam excited Ar/Xe/NF₃ mixture. The solid lines indicate the spectral shape of the XeF(C→A) and Xe₂F emission.

XeF(C→A) emission whereas the long wavelength peak is due to Xe₂F⁶. Mixed triatomic excimers like Ar XeF* can be excluded because the red continuum was also observed in Xe/NF₃ mixtures. The Xe₂F* emission wavelength was calculated to lie between 615 nm and 808 nm. The lower bound of this calculation is in agreement with the measured value. The solid lines in Fig. 1 indicate the spectral shapes of the two transitions. The maximum of the Xe₂F emission was determined to lie at (614 ± 5) nm with a spectral bandwidth (FWHM) of (125 ± 5) nm. In high pressure (> 1 atm) Ar/Xe/NF₃ mixtures, rapid vibrational relaxation in the XeF(B→X) and XeF(C→A) transition was observed. This makes it possible to describe the XeF(B,C) system as two states that are coupled by collisional mixing. However, for Xe/NF₃ mixtures, no vibrational relaxation in the B → X and the C → A transition was observed up to pressures of 4 atm. A kinetic scheme depicting the main reactions for the gas mixture used in the present experiments is shown in Fig. 2.

The two- and three-body quenching of XeF(B,C) was studied in high pressure Ar/Xe/NF₃ mixtures. Fig. 3 shows the temporal behavior of XeF(B), XeF(C) and the Xe₂F fluorescence as well as the electron beam pulse as measured by a Faraday cup probe. The maximum of the XeF(B) emission occurs at the end of the electron beam pulse

XeF* - Xe₂F* Kinetics

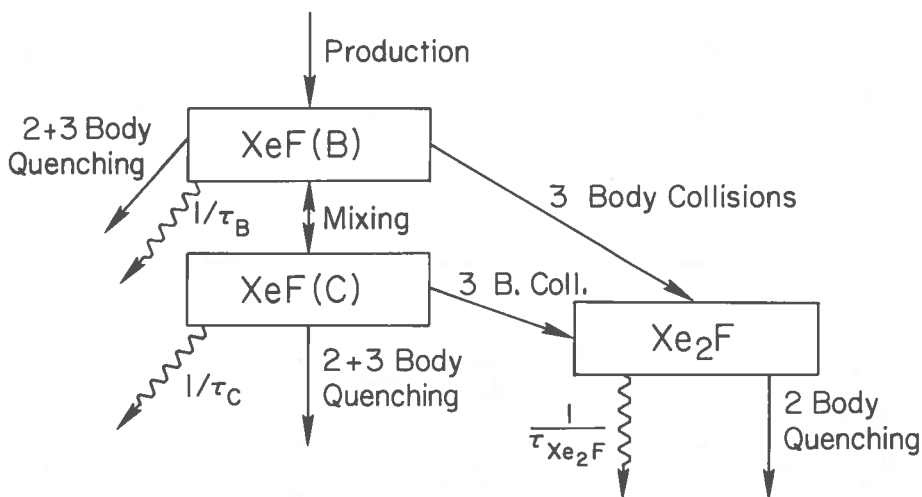


Fig. 2: Important kinetic pathways in the XeF-Xe₂F system for electron beam excitation.

indicating direct production of the B state primarily by fast neutral and ionic reactions. The C-state emission is somewhat delayed since its population results via collisions from the B-state.

By observing the spectral shape of the B→X and the C→A emission of XeF in Ar/Xe/NF₃ and the Xe/NF₃ mixtures, the population of higher vibrational levels of the B- and C-state was qualitatively studied for different gas pressures. A different behavior was observed for Xe/NF₃ and Ar/Xe/NF₃ mixtures. Gas mixtures containing a high xenon pressure (100 Torr to several atm) and low NF₃ partial pressure showed a large population in higher vibrational levels of the B- and the C-state for all pressures investigated in the present experiments up to 4 atm. No indication for vibrational relaxation was observed in Xe/NF₃ mixtures. In Ar/Xe/NF₃ mixtures, however, vibrational relaxation in the B- and C-state was observed for pressures higher than ~ 2 atm. This observation severely restricts the determination of rate coefficients from Xe/NF₃ mixtures, whereas for high argon buffer gas pressures the rate coefficients can be attributed to reactions affecting primarily the lowest vibrational levels of the XeF B- and C-states.

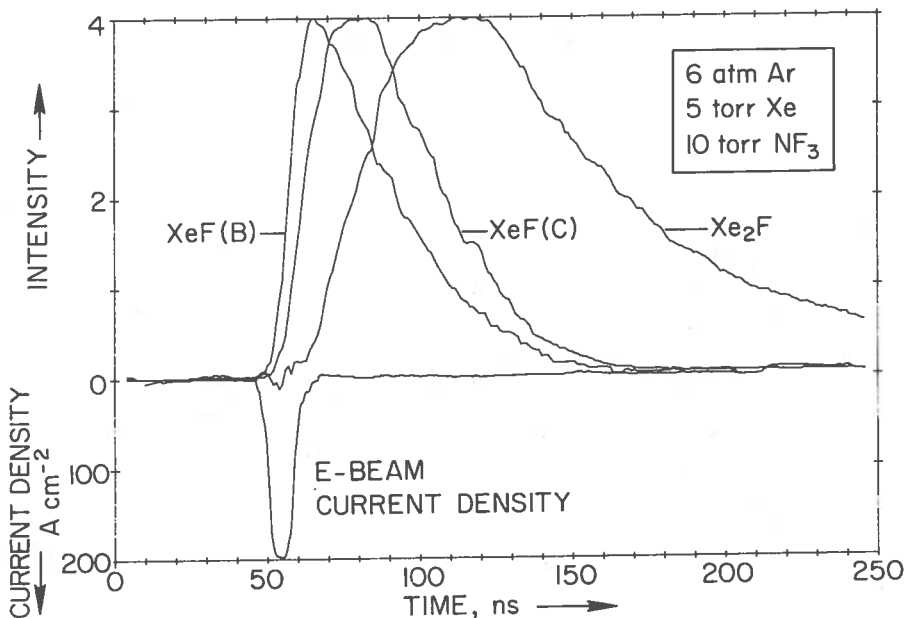


Fig. 3: Temporal dependence of the e-beam current and the normalized XeF(B), XeF(C) and Xe₂F emission.

The XeF(B) state is created via rapid production reactions following electron beam excitation. Collisions primarily with buffer gas atoms subsequently establish thermal equilibrium between the B- and the C-state population which is achieved in a short time scale compared to the time scale of typical decay processes under high pressure conditions. Due to the fact that the C-state lies approximately 700 cm^{-1} below the B-state, under normal conditions only about 4% of the total XeF population is in the B-state. Therefore when quenching reactions in the XeF system are studied under high pressure conditions, primarily quenching of the C-state is observed. Both states decay via radiation and two- and three-body quenching. The most important product of a three-body quenching process of XeF(C) is Xe₂F. It decays by radiation with a radiative lifetime of $(152 \pm 19) \text{ ns}$ and two-body quenching. In order to determine the two- and three-body quenching rate constants for the B and C state, the decay frequencies for both states were measured as a function of the partial pressures of Ar, Xe and NF₃. Due to collisional mixing effects a detailed rate equation analysis is required in order to extract quenching and formation rate constants for the XeF-Xe₂F system from the temporal behavior of the fluorescence pulses as well as the fluorescence yields.

In Table I the results of such an analysis are summarized and compared to those obtained in Refs. [4] and [5]. A relatively high two-body rate constant k_{C}^{Xe} is obtained for the quenching of XeF(C) by xenon in this work and Ref. [4]. This can be explained by

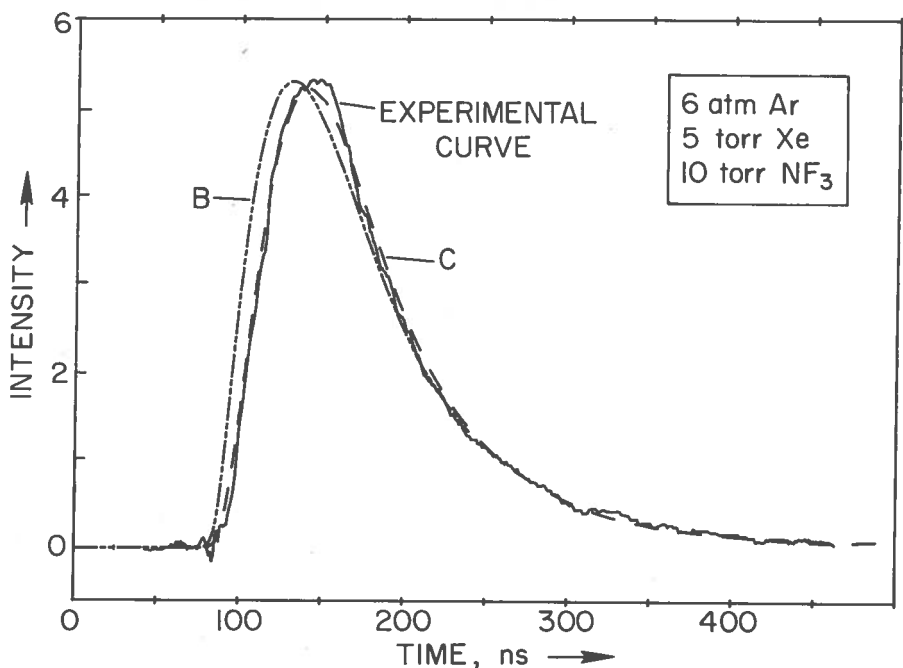


Fig. 4: Experimentally observed and calculated temporal Xe_2F fluorescence pulses. For the calculated curve denoted by B it was assumed that XeF(B) is the precursor of Xe_2F whereas the C curve was calculated for a Xe_2F formation from XeF(C) .

calculations of the potential surfaces of a XeF-Xe collision⁹, which show a potential crossing between an attractive Xe_2F state correlated to XeF(C) and a repulsive state at short internuclear distances. As these potentials interact, this can lead to a predissociation of a short-lived Xe_2F complex into XeF(A) and Xe as a result of a XeF(C)-Xe collision.. This high two-body quenching of XeF(C) by Xe together with collisional coupling between the B and the C state also explains the virtually nonexistent vibrational relaxation in Xe/NF_3 mixtures. XeF(C) decays primarily by quenching with xenon before vibrational relaxation can occur. Since the binding energy of Xe_2F is only ~ 0.5 eV relative to XeF(C) and Xe , highly vibrational excited XeF(C) molecules cannot form Xe_2F . This might explain the small three-body quenching constants k_C^{XeXe} in pure xenon atmospheres compared to three-body quenching k_C^{XeAr} in a high pressure argon atmosphere.

In order to study the formation of Xe_2F , the temporal Xe_2F fluorescence emission was calculated from the experimentally observed

Table 1: Kinetic Reactions for XeF and Xe₂F

Reaction		This work	Black et al Ref. [4]	Brasheers, Setser Ref. [5]
1) XeF(C) + NF ₃ → products	$k_{C}^{NF_3}$	$(1.5 \pm 0.3) \cdot 10^{-11} \frac{cm^3}{s}$		$(1.4 \pm 0.6) \cdot 10^{-11} \frac{cm^3}{s}$
2) XeF(C) + Ar → products	k_{C}^{Ar}	$< 1 \cdot 10^{-14} \frac{cm^3}{s}$	$(7 \pm 7) \cdot 10^{-15} \frac{cm^3}{s}$	$(5 \pm 2) \cdot 10^{-14} \frac{cm^3}{s}$
3) XeF(C) + Xe → products	k_{C}^{Xe}	$(1.2 \pm 0.3) \cdot 10^{-10} \frac{cm^3}{s}$	$1.9 \cdot 10^{-10} \frac{cm^3}{s}$	$(1.8 \pm 0.5) \cdot 10^{-11} \frac{cm^3}{s}$ (a)
4) XeF(B) + Ar → XeF(C) + Ar	k_{BC}^{Ar}	$(1.5 \pm 0.3) \cdot 10^{-11} \frac{cm^3}{s}$	$(1.4 \pm 0.2) \cdot 10^{-11} \frac{cm^3}{s}$	$(0.86 \pm 0.11) \cdot 10^{-11} \frac{cm^3}{s}$
5) XeF(B) + e ⁻ → XeF(C) + e ⁻	$k_{BC}^{e^-}$	negligible		(b)
6) XeF(C) → Xe + F + hν	τ_C	(97 ± 5) ns	(101 ± 2) ns	(c)
7) XeF(C) + Ar + Xe → products	k_{C}^{XeAr}	$(3.9 \pm 0.5) \cdot 10^{-31} \frac{cm^3}{s}$		(d, g)
8) XeF(B) + 2 Ar → products	k_{B}^{ArAr}	$< 3 \cdot 10^{-33} \frac{cm^6}{s}$		(e)
9) XeF(C) + 2 Ar → products	k_{C}^{ArAr}	$< 3 \cdot 10^{-33} \frac{cm^6}{s}$		
10) XeF(C) + 2 Xe → products	k_{C}^{XeXe}	$(4 \pm 1) \cdot 10^{-32} \frac{cm^6}{s}$		$< 3 \cdot 10^{-31} \frac{cm^6}{s}$ (f)
11) XeF(C) + 2 Xe → Xe ₂ F + Xe	k_{CP}^{XeXe}	$(2.7 \pm 0.6) \cdot 10^{-32} \frac{cm^6}{s}$		(f)
12) XeF(C) + Xe + Ar → Xe ₂ F + Ar	k_{CP}^{XeAr}	$(1.1 \pm 0.3) \cdot 10^{-31} \frac{cm^6}{s}$		
13) Xe ₂ F + NF ₃ → products	$k_X^{NF_3}$	$(7.8 \pm 1.2) \cdot 10^{-13} \frac{cm^3}{s}$		
14) Xe ₂ F + Xe → products	k_X^{Xe}	$(1.0 \pm 0.2) \cdot 10^{-13} \frac{cm^3}{s}$		
15) Xe ₂ F + Ar → products	k_X^{Ar}	$(2.8 \pm 0.9) \cdot 10^{-14} \frac{cm^3}{s}$		
16) Xe ₂ F → 2 Xe + F + hν	τ_X	(152^{+19}_{-10}) ns		

(a) value of [5] measured for a high but unknown vibrational temperature

(b) in the afterglow of short pulse e-beam excitation

(c) see also R.W. Wayant and J.G. Eden, *IEEE J. Quantum Electron.* **QE-15**, 61 (1975)

(d) $(3 \pm 1.5) \cdot 10^{-31} cm^6 s^{-1}$, M. Rokni, J.H. Jacob, J.A. Mangano and R. Brodus, *Appl. Phys. Lett.* **30**, 458 (1977).

(e) $(1.5 \pm 0.5) \cdot 10^{-32} cm^6 s^{-1}$, same Ref. as d)

(f) value of this work measured for a high, unknown vibrational temperature

(g) $3 \cdot 10^{-31} cm^6 s^{-1}$, V.H. Shui and C. Duzy, *Appl. Phys. Lett.* **36**, 135 (1980)

XeF(B) and XeF(C) fluorescence pulses. For the calculations, three-body quenching of XeF(B,C) leading to the formation of Xe₂F and two-body quenching of Xe₂F was assumed. The results are shown in Fig. 4. For the calculated curve denoted by B, a production of Xe₂F only from XeF(B) was assumed, whereas the C-curve was calculated for a Xe₂F production from the XeF(C) state. From the excellent agreement of the C-curve with the experimental curve and the deviation of both from the B-curve, it can be concluded that XeF(C) is the precursor of Xe₂F.

CONCLUSIONS

Kinetic processes of XeF and Xe₂F have been investigated experimentally in electron beam excited Ar/Xe/NF₃ mixtures. An investigation of the Xe₂F production process showed that XeF(C) is the precursor of Xe₂F.

No indications for a possible formation of Xe₂F via Xe₂* were observed. Furthermore, no three-body quenching of Xe₂F by NF₃, xenon or argon could be found which seems to be a general feature of all rare gas halide compounds.

Like the other triatomic rare gas halides Xe_2F is a possible candidate for a tunable excimer laser. Due to its short radiative lifetime and long emission wavelength compared to other trimers, its cross section for stimulated emission at the emission maximum is relatively high ($1.2 \cdot 10^{-17} \text{ cm}^2$). Also gain reduction by broadband and narrowband absorbers should be lower in the red part of the visible spectrum than for shorter wavelengths. However, because of the strong xenon quenching of $XeF(C)$, the production efficiency for Xe_2F is considerably lower than for other trimers, which will make it difficult to obtain laser action with Xe_2F .

ACKNOWLEDGEMENTS

This work was supported in part by the Office of Naval Research, the National Science Foundation and the Robert A. Welch Foundation. R. Sauerbrey would like to acknowledge support by the Deutsche Forschungsgemeinschaft.

REFERENCES

1. W.K. Bischel, N.N. Nakano, D.J. Eckstrom, R.M. Hill, D.L. Huestis and D.C. Lorents, *Appl. Phys. Lett.* **34**, 565 (1979).
2. W.E. Ernst and F.K. Tittel, *IEEE J. Quantum Electron.* **QE-16**, 945 (1980).
3. R. Burnham, *Appl. Phys. Lett.* **35**, 48 (1979).
4. G. Black, R.L. Sharpless, D.C. Lorents, D.L. Huestis, R.A. Gutcheck, T.D. Bonifield, D.A. Helms and G.K. Walters, *J. Chem. Phys.* **75**, 4840 (1981), also *Lasers '79*, Orlando, FL, December 14, 1979.
5. H.C. Brashears and D.W. Setser, *J. Chem. Phys.* **76**, 4932 (1982).
6. W. Walter, R. Sauerbrey, F.K. Tittel, and W.L. Wilson, Jr., *Appl. Phys. Lett.* **41**, 387 (1982).
7. R. Sauerbrey, W. Walter, F.K. Tittel and W.L. Wilson, Jr., *J. Chem. Phys.*, Jan. 15, 1983.
8. F.K. Tittel, G. Marowsky, W.L. Wilson, Jr. and M.C. Smayling, *IEEE J. Quantum Electron.* **QE-12**, 2268 (1981).
9. D.L. Huestis, *Topical Meeting on Excimer Lasers*, Charleston, SC (Sept. 1979).

Excimer-Laser Interface Chemistry
for Microelectronic Processing

R.M. Osgood, Jr.*

Department of Electrical Engineering
Columbia Radiation Laboratory
Columbia University
New York, New York 10027

Abstract

Because of their UV wavelengths and high average powers, excimer lasers can be used in a variety of processing applications for microelectronics fabrication. These new applications are based on using the laser light to control or initiate chemical reactions at a gas solid interface. This paper will review a series of such applications.

94-243X/83/100256-10 \$3.00 Copyright 1983 American Institute of Physics