

Optical emission and kinetic reactions of a four-atomic rare gas halide exciplex: Ar₃F

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A new broadband emission from electron beam excited high pressure Ar/F₂ and Ar/NF₃ mixtures at (435 ± 50) nm is reported. This gas phase spectrum as well as a previously unassigned broadband emission at (455 ± 55) nm observed in optically excited liquid Ar/F₂ mixtures is assigned to the four-atomic rare gas halide exciplex Ar₃F. Ar₃F is produced by three-body collisions from Ar₂F, but is easily destroyed by two-body collisions due to its small binding energy.

I. INTRODUCTION

After the discovery of diatomic rare gas halide excimers, extensive spectroscopic studies soon revealed the existence of the triatomic rare gas halides Rg₂X.^{1,2}

Ab initio and diatomics-in-molecule calculations showed that the exciplexes Rg₂X have a triangular shape and may be described as a bound state of a diatomic rare gas ion Rg₂⁺ and a halogen ion X⁻.³⁻⁶ Since the triatomic rare gas ions Rg₃⁺ are bound with respect to their diatomics by about 0.2–0.3 eV,⁷⁻⁹ one could expect that the four-atomic rare gas halides Rg₃X are stable at room temperature.

This work presents spectroscopic evidence for the existence of the four-atomic rare gas halide exciplex Ar₃F. The spectroscopic assignment is confirmed by a reinvestigation of the kinetic reactions of the trimer Ar₂F. The kinetic reactions of electron beam excited mixtures of argon and a fluorine donor were investigated in detail by Marowsky *et al.*¹⁰ and Böwering *et al.*¹¹ Both groups found abnormalities in the temporal pulse shapes of Ar₂F, in particular, at high electron densities that can now be explained by electron quenching.¹² Furthermore, in both investigations the Ar₂F intensity became constant for high argon pressures, suggesting that Ar₂F is not the exciplex with the lowest energy in these mixtures.

II. EXPERIMENTS

Gas mixtures consisting of high purity argon (99.9995%), F₂ and NF₃, were transversely pumped by a pulsed electron beam. The typical maximum electron current density on the optical axis of the gas cell was 200 A/cm² as measured by a Faraday cup probe and a calorimeter. The maximum electron energy was 1 MeV and the pulse width was 10 ns. An area of 10 × 2 cm was irradiated by the electron beam. The time-integrated fluorescence spectra were recorded by an optical multichannel analyzer (OMA III) using a 0.25 nm Jarrel–Ash spectrometer with 0.5 nm resolution. The spectral sensitivity of this detection system is almost wavelength independent between about 400–550 nm; however, its sensitivity decreases sharply between 400–350 nm, as well as beyond 650 nm. The time dependence of the fluorescence of the ArF and Ar₂F transitions at 193 and 285 nm, respectively, as well as a new blue continuum at 435 nm, was measured using either a fast vacuum photodiode (ITT

F4000) or a photomultiplier (RCA C3100A). Spectral selection was obtained with appropriate interference and color glass filters. The fluorescence pulses were recorded by a transient digitizer (Tektronix R7912). The rise time of the photodiode detection system was about 2 ns, and that of the photomultiplier was less than 3 ns. The data from the OMA and the transient digitizer was stored and processed by two minicomputers.

III. RESULTS

Spectra of electron beam excited Ar–F₂ mixtures in the wavelength range from 200 to 550 nm are shown in Fig. 1. The well-known Ar₂F emission appears as a broadband with a maximum at 285 nm [Figs. 1(a) and 1(b)]. On the long wavelength side of Ar₂F, a broad continuum appears with a maximum at (435 ± 3) nm, and a spectral width of at least

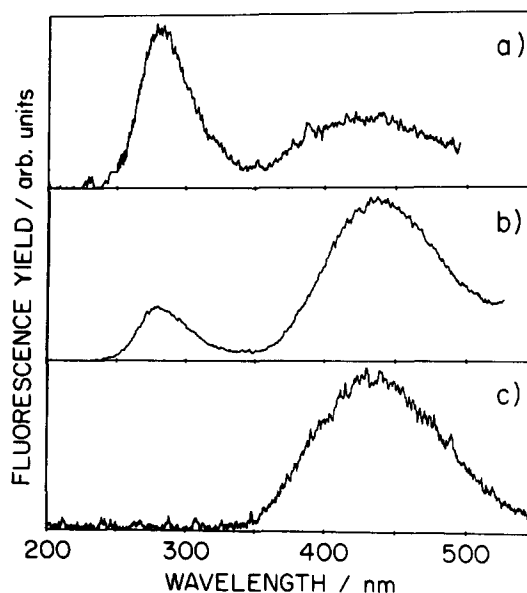


FIG. 1. Spectra from electron beam excited Ar/5 Torr F₂ mixtures between 200–550 nm. 1(a) and 1(b) show the Ar₂F emission centered at 285 nm as well as a new emission in the visible centered at 435 nm. The intensity of the new emission relative to the Ar₂F intensity increases considerably when the Ar pressure is increased from (a) 2 atm to (b) 8 atm. 1(c) shows the emission from a 3 atm Ar/5 Torr F₂ mixture observed through a color glass filter with a cutoff at about 350 nm. The Ar₂F spectrum disappears as well as the slight increase of the visible emission for wavelength larger than 480 nm, demonstrating that this is due to Ar₂F appearing in second order.

100 nm FWHM. The spectral shape of this emission is slightly narrowed on the short wavelength side due to the decreasing spectral sensitivity of the detection system. On the red side for wavelengths larger than 480 nm, the Ar₂F spectrum appears in second order.

It was shown in a number of experiments that the emission around 435 nm appears only when argon and a fluorine donor, either F₂ or NF₃, are together in the gas mixture. The emission is not due to gas impurities. In particular, it is not caused by Kr₂F which shows a broadbanded emission in the same spectral region. However, the Kr₂F emission spectrum has its maximum at shorter wavelength (~410 nm) and is much narrower. This emission is also not due to an emission around 220 nm appearing in second order, which was verified by observing it through a color glass filter with a wavelength cutoff at about 350 nm [Fig. 1(c)]. It is also apparent from Figs. 1(a) and 1(b) that the blue emission increases strongly in intensity relative to the Ar₂F emission when the argon pressure is raised from 2 atm (a) to 8 atm (b).

The temporal development of the dominating emissions from electron beam excited argon/fluorine mixtures is shown in Fig. 2. The ArF(B-X) fluorescence at 193 nm follows the pumping pulse with a width of about 10 ns, indicating the rapid depopulation of this state by radiation and quenching processes. At high argon pressures ArF is mainly quenched by three-body collisions to Ar₂F.^{10,11} Therefore, the Ar₂F fluorescence increases on a time scale given by the width of the ArF fluorescence. Subsequently, the Ar₂F fluorescence decreases exponentially with a decay time of about 100 ns. The new blue fluorescence continuum exhibits a temporal rise time on the order of the half-width of the Ar₂F fluorescence and decays on the same time scale or slower than the Ar₂F fluorescence. This is shown clearly in Fig. 3. For increasing fluorine pressure, the Ar₂F decay frequency increases linearly. For small fluorine pressures, the decay of the blue fluorescence follows the Ar₂F decay, whereas the blue emission decays more slowly than Ar₂F for high F₂ pressures. This temporal behavior of the blue fluorescence indicates that Ar₂F is the precursor of the new species emitting the blue continuum.

The quenching constant of Ar₂F by F₂ may be obtained from Fig. 3. The value of $1.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ is somewhat lower than the previously published values, ranging from $1.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ to $2.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.^{2,10,13} The quenching constant for the species causing the blue emission by F₂ may be estimated from the dashed line to be about $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

IV. ANALYSIS AND DISCUSSION

In summary, a broadband emission is observed on the long wavelength side of Ar₂F in electron beam excited Ar/F₂ mixtures, and Ar₂F is obviously the precursor of the species emitting the blue continuum. An exciplex consisting of more than two argon atoms and a fluorine atom is expected to have these properties. In the following kinetic analysis, it will be demonstrated that the experimental findings are consistent with an assignment of the blue continuum to the transition from the first electronically excited state in Ar₃F to its repulsive ground state.

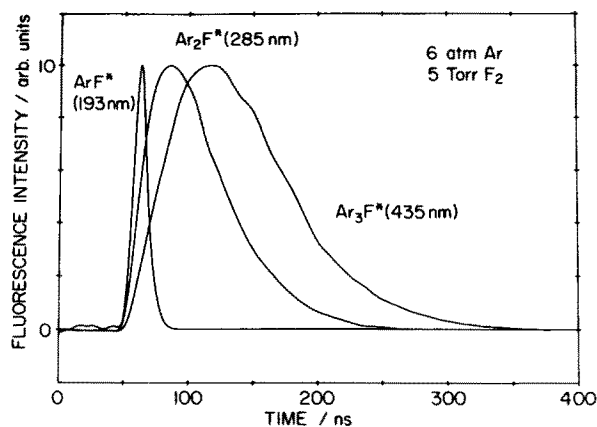


FIG. 2. Temporal dependence of normalized fluorescence signals from ArF, Ar₂F, and Ar₃F. Note the increase in the blue signal until the Ar₂F signal is well beyond its maximum.

An analysis of the geometry as well as the electronic structure of Ar₃F is difficult without further theoretical support. The center of the Ar₃F emission is shifted by about 1.5 eV relative to Ar₂F. The binding energy of Ar₃⁺ relative to Ar₂⁺ can only account for about 0.2 eV.⁷⁻⁹ Therefore, the large energy shift of the Ar₃F emission relative to the Ar₂F spectrum has to be attributed largely to a stronger repulsion of the Ar₃F lower potential than the Ar₂F lower state. This is qualitatively sustained by the relatively large bandwidth observed for the Ar₃F emission of at least 0.65 eV FWHM compared to the Ar₂F bandwidth of 0.31 eV FWHM (Fig. 1). There exists indirect experimental⁷ as well as theoretical⁹ evidence that the Rg₃⁺ ions should be linear. However, for symmetry reasons, one should expect a tetrahedral structure (C_{3v}) of the Rg₃F exciplexes.

The binding energy of the Rg₃F molecule relative to the Rg₂F molecule is expected to be of the same order or even smaller than the binding energy of the Rg₃⁺ relative to Rg₂⁺ ions. It appears therefore reasonable to assume that Ar₃F may be easily destroyed by two-body collisions. On the other hand, in order to observe radiation from these molecules, they have to form a bound state. This is possible through three-body collisions with Ar₂F. Therefore, the following reaction equilibrium is expected:

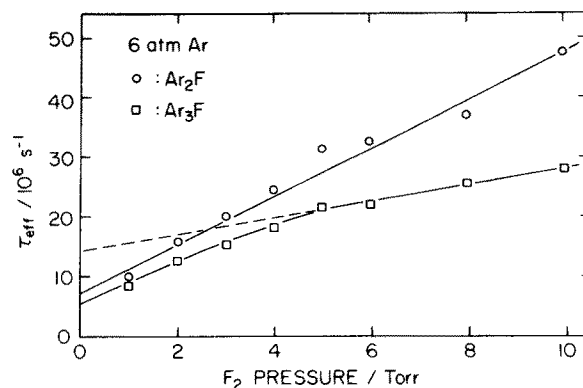
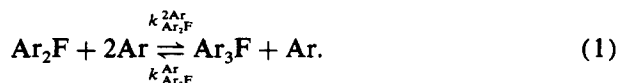


FIG. 3. Inverse decay time of Ar₂F (O) and Ar₃F (□) as functions of the F₂ pressure. Ar₃F always decays more slowly than Ar₂F. For small F₂ pressures, the Ar₃F decay is determined by its precursor Ar₂F.



This immediately explains earlier observations^{10,11} showing the Ar₂F population density becoming argon pressure independent for high argon pressures, a behavior that is not expected for the lowest bound excimer state in any system. For several atmospheres of argon, three-body quenching of ArF by argon occurs on a subnanosecond time scale,^{10,11,13} and ArF is almost completely converted to Ar₂F. Therefore, the Ar₂F density is proportional to the pumping density, which is in first order proportional to the argon pressure. For sufficiently high argon pressures, the depopulation processes of Ar₂F scale as the square of the argon pressure, whereas the back reaction from Ar₃F increases the Ar₂F density proportional to the argon pressure [Eq. (1)]. This yields a constant Ar₂F population in the limit of high argon pressures, which was, in fact, observed.

Since the binding energy of Ar_{*n*}⁺ clusters with *n* > 3 with respect to Ar₃⁺ is smaller than 0.05 eV,⁸ Ar_{*n*}F complexes with *n* > 3 are expected to be thermally unstable. Ar₃F is, therefore, the lowest bound state in the electron beam excited Ar/F₂ system. Its intensity should increase proportional to the argon pressure in the limit of high argon pressures because the energy input is approximately proportional to the argon pressure. A detailed kinetic analysis yields, for the time-integrated fluorescence signals *I*_{Ar₂F} and *I*_{Ar₃F}, as measured by the OMA:

$$\frac{I_{\text{Ar}_3\text{F}}}{I_{\text{Ar}_2\text{F}}} = \frac{\tau_{\text{Ar}_2\text{F}}}{\tau_{\text{Ar}_3\text{F}}} \cdot \frac{k_{\text{Ar}_2\text{F}}^{2\text{Ar}} [\text{Ar}]^2}{\tau_3^{-1} + k_{\text{Ar}_3\text{F}}^{\text{Ar}} [\text{Ar}]} \quad (2)$$

$\tau_{\text{Ar}_2\text{F}}$ and $\tau_{\text{Ar}_3\text{F}}$ are the radiative lifetimes of Ar₂F and Ar₃F, respectively; τ_3 is the effective lifetime of Ar₃F including quenching, i.e., by the fluorine donor. The rate constants are defined in Eq. (1), and [Ar] denotes the argon concentration. It follows that $I_{\text{Ar}_3\text{F}} \sim [\text{Ar}]$ for $k_{\text{Ar}_3\text{F}}^{\text{Ar}} [\text{Ar}] \gg \tau_3^{-1}$, in agreement with the previous discussion.

When $I_{\text{Ar}_3\text{F}} [\text{Ar}]^2 / I_{\text{Ar}_2\text{F}}$ is plotted vs the argon pressure, a straight line with a positive intersection on the vertical axis is predicted from Eq. (2). Experimental results extracted from spectra like those presented in Fig. 1 are shown in Fig. 4. The experiment agrees well with Eq. (2).

If the blue emission is due to Ar₃F and Ar₃F is the lowest bound state in electronically excited Ar/F₂ mixtures, the emission should also be present in liquids where collisional processes proceed even more rapidly than in gases at pressures of a few atmospheres.

The fluorescence spectra obtained for optically excited liquid Ar/F₂ mixtures by Jara *et al.*¹⁴ exhibit an unassigned fluorescence around 455 nm, with a bandwidth (FWHM) of 110 nm. Considering the red shift and broadening of the liquid phase emissions relative to the gas phase emissions observed for other rare gas halide species, the 455 nm band in liquid Ar/F₂ mixtures may be assigned to the Ar₃F emission. Jara *et al.*¹⁴ also observed a weak and somewhat narrower spectrum around 445 nm in liquid N₂/F₂ mixtures. In the gas phase experiments of this work, no notable emission from N₂/F₂ mixtures was obtained in this wavelength range.

If Ar₃F exists as a bound state, Kr₃F and Xe₃F should

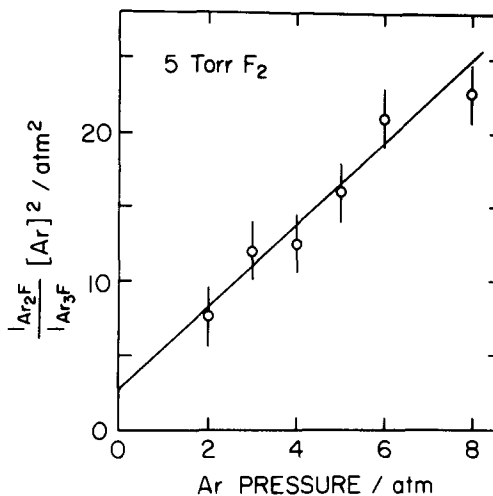


FIG. 4. $I_{\text{Ar}_3\text{F}} [\text{Ar}]^2 / I_{\text{Ar}_2\text{F}}$ as functions of the argon pressure [see Eq. (2)]. The experiment yields a straight line with positive intersection—an expected result for the equilibrium given in Eq. (1).

also be stable due to the higher binding energies of the krypton and xenon trimer ions relative to their dimer ions.^{8,9} If the energy shift from Kr₂F to Kr₃F is assumed to be about the same as the Ar₂F–Ar₃F shift of about 1.5 eV, the Kr₃F emission is expected in the 800 nm region. An emission from Xe₃F should appear even further in the infrared, assuming that these molecules do not predissociate due to a crossing of potential surfaces correlating to the ground state with the lowest excited state. An experimental search for Kr₃F in the wavelength region between 450–650 nm did not reveal any broadband emission from Kr/F₂ mixtures that could be assigned to Kr₃F.

V. SUMMARY AND CONCLUSIONS

A new broadband emission in the blue, observed from electron beam excited Ar/F₂ and Ar/NF₃ mixtures, has been assigned to Ar₃F. Although the structure and electronic states of this exciplex are not yet quite clear, the kinetic behavior of this species appears to allow for a unique assignment. This is confirmed by the observation of a similar emission from liquid Ar/F₂ mixtures.¹⁴

The existence of four atomic rare gas halide exciplexes could have a profound impact on the scaling behavior of rare gas halide lasers. The KrF laser still suffers from not yet completely understood nonsaturable absorptions, possibly due to Kr₂F, in particular, for high Kr concentration laser schemes.^{15,16} Recently, doubts have been raised whether these absorptions are mainly caused by Kr₂F because the absorption cross section of this molecule appears to be too small to account for the observed effects.¹⁷ Four atomic rare gas halide exciplexes such as Ar₃F or Kr₃F are likely to appear in high concentrations in high-pressure laser systems, in particular, Kr₃F in krypton-rich KrF lasers. In order to estimate their influence on the laser process, especially as absorbers of the laser radiation, theoretical efforts to understand their electronic structure, as well as experiments to determine their absorption behavior, appear necessary.

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