

EXPERIMENTAL STUDY OF CHLORINE DONORS FOR THE TRIATOMIC EXCIPLEX Xe_2Cl

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ABSTRACT

The influence of various chlorine donors, specifically CCl_4 , Cl_2 and HCl , on the formation and decay of the trimer Xe_2Cl^* has been studied experimentally for electron beam-excited mixtures of argon, xenon and various halogen donors. Quenching rates of the trimer fluorescence for each donor have been determined. A radiative lifetime for Xe_2Cl^* of 210 ± 25 ns was measured.

INTRODUCTION

Since the first observation and characterization of the triatomic exciplexes or trimers [1-3], studies to improve their laser performance have been carried out. Experiments have been directed towards a better understanding of the production mechanism of the trimer Xe_2Cl^* [4-6]. So far CCl_4 is the only donor which has revealed gain for Xe_2Cl^* and showed laser action in the afterglow regime of electron beam-pumped high pressure rare gas halide mixtures [3,7], whereas Cl_2 and HCl , which are effective donors for the diatomic precursor XeCl^* , has not shown any gain. It is the purpose of this paper to discuss the role of various donors on the formation and quenching behavior of the triatomic excimer Xe_2Cl^* in electron beam-excited mixtures of Ar, Xe and a particular chlorine donor.

EXPERIMENTAL SET-UP

Mixtures of high purity argon (6 atm), xenon (300 Torr) and various chlorine donors (0.1 Torr up to 10 Torr) in a stainless steel reaction cell were transversely pumped by an electron beam generated by a Physics International Pulserad 110 accelerator (1 MeV, 15 kA, 10 ns). The electron beam current density was $\sim 100 \text{ A/cm}^2$ at the optical axis of the reaction cell. Details of the apparatus and the experimental techniques have been described elsewhere [3].

RESULTS

In this work the chlorine donors, CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3Cl , HCl , and Cl_2 were studied. The series CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3Cl was investigated in order to determine the influence of increasing donor complexity due to chlorine substitution by hydrogen. The donors, HCl and Cl_2 , were chosen because of their simple chemical structure and because of their widespread use as donors for production of XeCl^* in electrically excited excimer lasers. The detailed discussion of experimental results is limited to CCl_4 , HCl , and Cl_2 . Figure 1 shows for comparison the fluorescence spectra of electron beam-excited mixtures of argon, xenon and the various halogen donors.

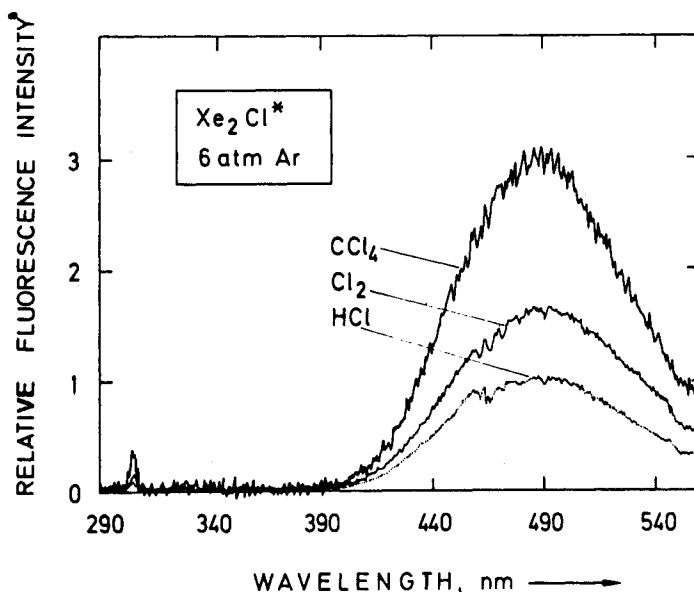


Fig. 1 Fluorescence spectra of narrowband Xe_2Cl^* emission at 308 nm and broadband trimer emission, centered at 500 nm (spectra not corrected for OMA I vidicon spectral response).

The Xe_2Cl^* fluorescence was found to increase monotonically with increasing donor pressure up to 1.5 ± 0.1 Torr for CCl_4 , 3.0 ± 1.0 Torr for Cl_2 and 4.0 ± 1.0 Torr for HCl , and subsequently slowly decreases with increasing chlorine donor pressure.

Stern-Volmer plots of the Xe_2Cl^* fluorescence decay using CCl_4 , HCl , or Cl_2 for donor pressures up to 4.0 Torr resulted in the following quenching rates of Xe_2Cl^* :

$$k(\text{CCl}_4) = (5.4 \pm 0.5) 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

$$k(\text{HCl}) = (4.3 \pm 0.4) 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

$$k(\text{Cl}_2) = (2.2 \pm 0.2) 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

The quenching rate for CCl_4 is in close agreement with the value $6.0 \cdot 10^{10} \text{ cm}^3 \text{ s}^{-1}$ reported in Refs. [4,8]. The Cl_2 quenching rate is in good agreement with the value $2.6 \cdot 10^{10} \text{ cm}^3 \text{ s}^{-1}$ reported in Ref. 9 while to our knowledge trimer-quenching by HCl has not yet been reported in the literature.

A decay frequency $\tau^{-1} = 7 \text{ MHz}$ can be derived from a common intersection point in the Stern-Volmer plots. The radiative lifetime τ_{rad} of Xe_2Cl^* is related to $1/\tau$ by the relation

$$1/\tau = 1/\tau_{\text{rad}} + k(\text{Ar}) \cdot [\text{Ar}] + k(\text{Xe}) \cdot [\text{Xe}] \quad (1)$$

Here $k(\text{Ar})$ and $k(\text{Xe})$ denote the respective quenching rates and the quantities in brackets the concentrations of argon and xenon. With $k(\text{Xe}) \leq 6 \cdot 10^{13} \text{ cm}^3 \text{ s}^{-1}$ according to Ref. [9], xenon-quenching even at a Xe partial pressure of 300 Torr can be neglected. The value of τ_{rad} strongly depends on the magnitude and precision of the Ar-quenching rate for Xe_2Cl^* . Re-evaluation of the data points of Ref. [9] with inclusion of recently obtained results yields a quenching rate $k(\text{Ar}) = (1.5 \pm 0.4) \cdot 10^{14} \text{ cm}^3 \text{ s}^{-1}$. This gives a value for the radiative lifetime of Xe_2Cl^* of $\tau_{\text{rad}} = (210 \pm 25) \text{ ns}$. This value may be compared to other measurements in the literature that range from 185 ns [9] to 210 ns [10] and 250 ns [11].

DISCUSSION

The essential kinetic pathways leading to the formation of triatomic exciplexes have been discussed in a number of papers [3] and references therein), in particular the formation of Xe_2Cl^* in Refs. [4,6,9-11]. Three-body collisional quenching of the diatomic precursor is the major kinetic pathway for the build-up of trimers, such as Xe_2Cl^* , Xe_2Br^* , Xe_2F^* , Kr_2F^* , and Ar_2F^* . However, distinct differences occur in the formation of the precursor excimer depending on the electron density and other experimental conditions such as the selected halogen donor and its electron attachment rate for producing Cl^- .

It has been shown in Ref. [4] that in high-pressure Ar-buffered rare gas halide systems three-body collisional quenching of XeCl^* by argon and xenon is the primary pathway which leads to Xe_2Cl^* . The production via collisions of XeCl^* with two Xe atoms can be neglected due to the large Ar/Xe pressure ratio. The time dependence of the Xe_2Cl^* concentration is given by the following differential equation:

$$\frac{d}{dt}[\text{Xe}_2\text{Cl}^*] = k(\text{Ar}, \text{Xe})[\text{Ar}][\text{Xe}][\text{XeCl}^*] - \frac{1}{\tau_{\text{eff}}} [\text{Xe}_2\text{Cl}^*] \quad (2)$$

Here $k(\text{Ar}, \text{Xe})$ denotes the production rate constant for the trimer Xe_2Cl^* , and the effective lifetime τ_{eff} is given by eq. (1) with additional quenching by the halogen donor RCI characterized by the quenching rates $k(\text{RCI})$:

$$1/\tau_{\text{eff}} = 1/\tau + k(\text{RCI}) [\text{RCI}] \quad (3)$$

The UV and visible fluorescence yields may be defined by the following integrals:

$$I_{uv} = \frac{1}{\tau_{rad}(XeCl)} \int_0^{\infty} [XeCl^*] dt, \quad (4a)$$

$$I_{vis} = \frac{1}{\tau_{rad}(Xe_2Cl)} \int_0^{\infty} [Xe_2Cl^*] dt \quad (4b)$$

Since the Xe_2Cl^* concentration vanishes for $t \rightarrow \infty$, integration of eq. (2) yields the ratio I_{uv}/I_{vis} :

$$\frac{I_{uv}}{I_{vis}} = \frac{\tau_{rad}(Xe_2Cl)}{\tau_{rad}(XeCl)} \cdot \frac{1/\tau + k(RCl)[RCl]}{k(Ar, Xe)[Ar][Xe]} \quad (5)$$

This ratio decreases with increasing argon and xenon partial pressure until a constant value is reached as determined by two-body quenching of the trimer by the rare gases. The important quantity for a donor comparison is the product $k(RCl)[RCl]$. According to eq. (5), the ratio I_{uv}/I_{vis} increases with increasing quenching rate of the halogen donor and with donor pressure. The usefulness of a halogen donor for optimization of the trimer fluorescence yield is therefore determined by two properties: (i) its efficiency in producing the diatomic precursor excimer, and (ii) its rate of quenching trimer fluorescence.

No detailed studies of the $XeCl^*$ precursor production have been carried out in this work. The efficiency of CCl_4 in producing $XeCl^*$ can be related to its higher dissociative attachment rate coefficient as compared to Cl_2 and HCl [12,13]. The dependence of the yield ratio I_{uv}/I_{vis} upon partial pressure of the selected chlorine donors is shown in Fig. 2. As predicted by eq. (5), the ratios show approximately the same halogen donor pressure dependence as the decay rates of Xe_2Cl^* . The donor pressure range has again been limited to 4 Torr since higher donor pressures resulted in different apparent quenching rates due to an increasing influence of slow precursor formation processes (details see Ref. [14]). In principle the intercept at zero donor pressure may be used to independently determine the three-body quenching rate $k(Ar, Xe)$ which has been derived from the buffer gas dependence in Ref. [4] to be $1.5 \cdot 10^{-31} \text{ cm}^3 \text{ s}^{-1}$. Such a determination based upon an evaluation of Fig. 2 requires an accurate knowledge of the absolute UV and visible fluorescence yields.

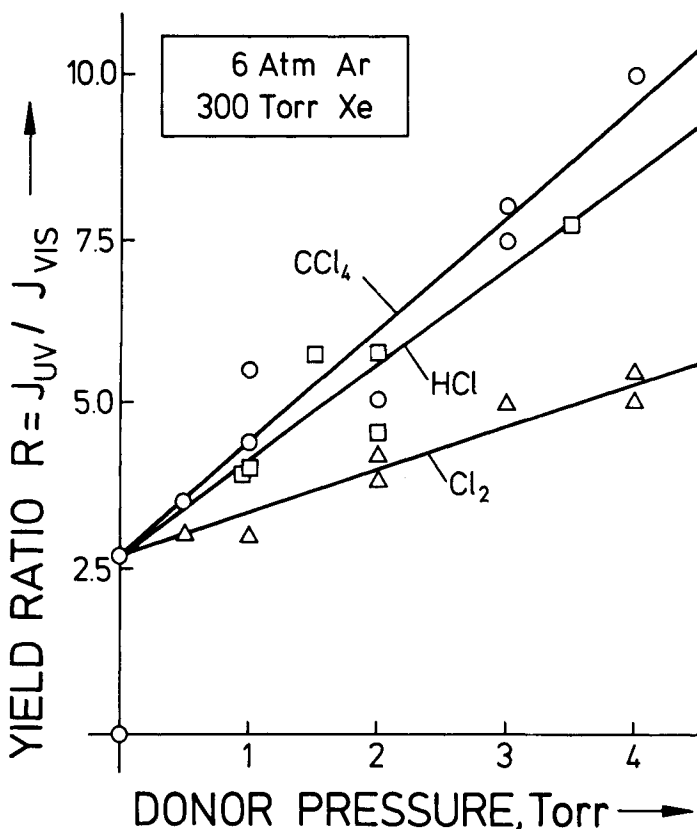


Fig. 2 Dependence of the ratio of the UV to visible fluorescence yields upon donor partial pressure. The yield ratios are obtained from time-integrated OMA data, using consecutive shots with appropriate UV and visible filtering.

Due to its small quenching rate for the Xe_2Cl^* fluorescence, Cl_2 would be expected to be the best donor for formation of this trimer. However, chlorine has only a low production efficiency for the XeCl^* precursor with the excitation conditions that exist in our experimental set-up as compared to the other donors. The XeCl fluorescence pulses always show decay times that are comparable to the decay time of the pumping pulse when HCl and CCl_4 are used as chlorine donors. This rapid production mechanism for XeCl is characteristic of ionic reactions. For low Cl_2 concentrations, however, the XeCl fluorescence pulses show decay times up to 120 ns in the limit of vanishing Cl_2 partial pressure. This observation indicates the existence of a long living species which lead to XeCl production because the radiative lifetime of XeCl is considerably shorter than this observed decay time [5]. Xe_2 and atomic $\text{Cl}(4P)$ states are possible candidates for these slow precursors of XeCl . The observation of the Xe_2 fluorescence at 172 nm through an appropriate interference filter gave no clear evidence that Xe_2 was another precursor of XeCl . By monitoring the decay times of XeCl , Xe_2Cl , and Xe_2 as a function of

the Cl_2 pressure, it was found that Xe_2^* is not a precursor of Xe_2Cl^* because at Cl_2^* pressures of more than 2 Torr Xe_2Cl^* decays more rapidly than Xe_2^* . This supports the simple model leading to eq. (2) which considers only XeCl^* as a precursor of Xe_2Cl^* .

Experiments using the more complex donors proved less successful with respect to the trimer fluorescence yield. As is known from diatomic excimer formation, the production efficiency decreases with increasing complexity of the donor structure [15]. This has been experimentally established by the experimental results obtained with the donor series $\text{CCl}_4 \dots \text{CH}_3\text{Cl}$.

In summary, it has been demonstrated that the usefulness of the chlorine donor, CCl_4 , for Xe_2Cl^* formation is primarily due to its high efficiency in producing the XeCl^* precursor under the described electron beam excitation conditions. The excellent agreement between theory and experiment as depicted in Fig. 2 supports the kinetic model that describes trimer build-up in terms of a three-body clustering reaction involving the rare gases Ar and Xe and the precursor XeCl^* . The high trimer quenching rate for CCl_4 limits the donor partial pressure to 1.5 Torr for optimum Xe_2Cl^* fluorescence.

ACKNOWLEDGEMENTS

This work was supported in part by the Office of Naval Research, the National Science Foundation and the Robert Welch Foundation.

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