

EFFECT OF CHLORINE DONORS ON THE FORMATION AND QUENCHING OF THE TRIATOMIC EXCIMER Xe_2Cl^*

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Received 5 February 1983; in final form 25 April 1983

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

1. Introduction

Since the first observation and characterization of the triatomic exciplexes [1–3], several studies have been carried out to improve their laser performance. Most efforts have centered on the trimer Xe_2Cl^* [4–6]. So far CCl_4 is the only donor which has revealed gain for Xe_2Cl^* and demonstrated laser action for electron-beam-pumped high-pressure rare-gas halide mixtures [3,7]. Mixtures containing Cl_2 and HCl , which are effective donors for the diatomic precursor XeCl^* , have not shown any gain for the trimer. This behavior is somewhat similar to the recently characterized excimer Xe_2Br^* [8] for which optimum results were also obtained with CBr_4 and CHBr_3 as halogen donors. It is the purpose of this paper to discuss the role of various chlorine donors on the formation and quenching behavior of the electron-beam-pumped triatomic excimer Xe_2Cl^* , and to report experimentally determined quenching rates and a more accurate value for the radiative lifetime for this trimer.

2. Experimental apparatus

Mixtures of high-purity argon (6 atm), xenon (300 Torr) and various chlorine donors (0.1 Torr up to 10 Torr) 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 ≈ 100 A/cm² at the optical axis of a stainless-steel reaction cell. Details of the apparatus and the experimental techniques have been described [3]. The optical emission from the excited species was monitored by two fast vacuum photodiodes (ITT F4000 S5). Interference and color glass filters were used to define the spectral region of interest (308 nm for XeCl^* and 500 nm for the trimer Xe_2Cl^*) for each diode. The photodiode signals were recorded with a Tektronix 7904 transient digitizer, and an optical multichannel analyzer (OMA I) was used to observe temporally integrated emission spectra. Both the transient digitizer and the OMA I were interfaced to a DEC 11/23 minicomputer. Computer software allowed integration of the OMA data over various spectral regions and temporal integration of the photodiode signals. An accurate determination of the Xe_2Cl^* decay time as a function of the partial pressures of argon, xenon and the chlorine donor was obtained by least-squares fitting to the decay of the photodiode signals.

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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 discharge-excited excimer lasers. However, the discussion of experimental results is limited to CCl_4 , HCl , and Cl_2 , since the measured Xe_2Cl^* intensities were substantially higher (i.e. by a factor of two) than for the other abovementioned chlorine donors, and the emission showed significantly less degradation upon successive excitation. In fact, the fluorescence spectrum obtained with CH_4 , CHCl_3 , CH_2Cl_2 or CH_3Cl was dominated by the 431.5 nm band of the CH radical indicating structural breakdown of the donor, which may give rise to severe quenching of the UV precursor by donor fragments.

The temporal behavior of the Xe_2Cl^* emission is shown in fig. 1 with the concentrations of the three chlorine donors adjusted in order to obtain an optimum trimer fluorescence yield. The fluorescence peaks of Xe_2Cl^* emission for Cl_2 and HCl were normalized against the pulse height of the Xe_2Cl^* emission using CCl_4 as donor. The pulse shapes of Xe_2Cl^* , with CCl_4 and HCl as the donor are quite similar, whereas with

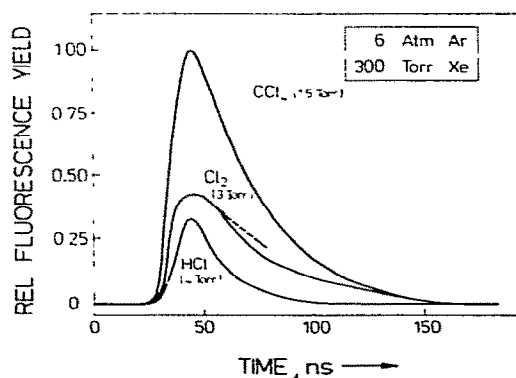


Fig. 1. Superposition of Xe_2Cl^* fluorescence pulses for various chlorine donors obtained at an optimum donor pressure as indicated.

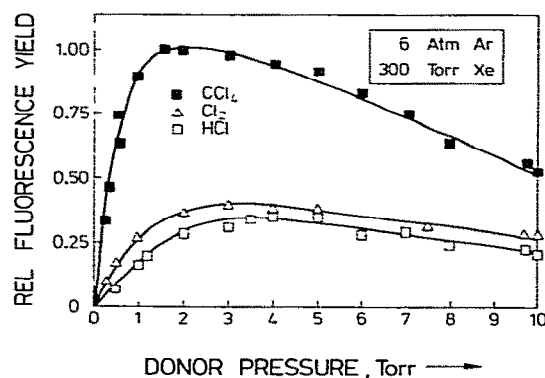


Fig. 2. Normalized Xe_2Cl fluorescence yields as a function of chlorine donor pressure.

Cl_2 no simple exponential decay behavior could be established.

The donor pressure dependence of the Xe_2Cl^* fluorescence intensity has also been studied as shown in fig. 2. The Xe_2Cl^* fluorescence is found to increase monotonically with increasing 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 , CHCl_3 , or Cl_2 for pressures up to 4.0 Torr are shown in fig. 3. Least-squares fits of the experimental data points resulted in the following Xe_2Cl quenching rates of chlorine donors, $k(\text{RCI})$:

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

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

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

Both the quenching rates for CCl_4 and Cl_2 are in close agreement with previously measured values, $6.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [4,9], and $2.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [10], respectively, while to the best of our knowledge trimer quenching by HCl has not yet been reported.

A decay frequency $\tau^{-1} = 7 \text{ MHz}$ for the trimer can be derived from the common intersection point in fig. 3. The radiative lifetime $\tau_{\text{Xe}_2\text{Cl}}$ of Xe_2Cl^* is related to $1/\tau$ by the relation

$$1/\tau = 1/\tau_{\text{Xe}_2\text{Cl}} + k(\text{Ar}) [\text{Ar}] + k(\text{Xe}) [\text{Xe}]. \quad (1)$$

Here $k(\text{Ar})$ and $k(\text{Xe})$ denote the respective quenching rates and the quantities in brackets the concentrations

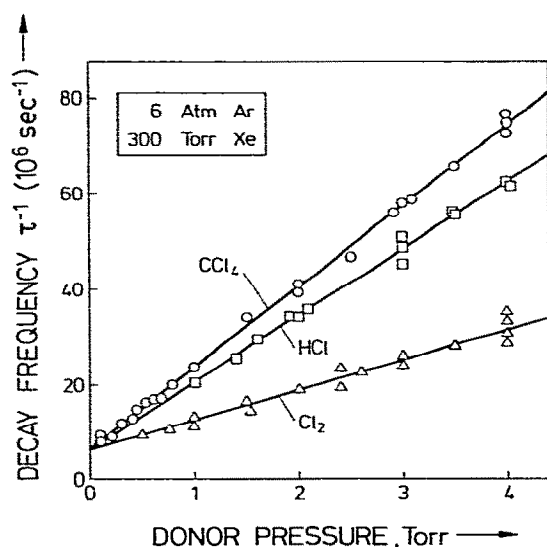


Fig. 3. Xe_2Cl decay frequency as a function of the halogen donor pressure.

of argon and xenon. With $k(\text{Xe}) \leq 6 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ [10], xenon quenching even at a Xe partial pressure of 300 Torr can be neglected. The value of $\tau_{\text{Xe}_2\text{Cl}}$ 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 $k(\text{Ar}) = (1.5 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. This gives a value for the radiative lifetime of Xe_2Cl^* of $\tau_{\text{Xe}_2\text{Cl}} = 210 \pm 25 \text{ ns}$. This value may be compared to other measurements in the literature that range from 185 ns [10] to 210 ns [11] and 250 ns [12].

4. Discussion

The essential kinetic pathways leading to the formation of triatomic exciplexes have been discussed in a number of papers (ref. [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:

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

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 RCl characterized by the quenching rates $k(\text{RCl})$:

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

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

$$I_{\text{UV}} = [1/\tau_{\text{Xe}_2\text{Cl}}(\text{XeCl})] \int_0^\infty [\text{XeCl}^*] dt, \quad (4a)$$

$$I_{\text{VIS}} = [1/\tau_{\text{Xe}_2\text{Cl}}(\text{Xe}_2\text{Cl})] \int_0^\infty [\text{Xe}_2\text{Cl}^*] dt. \quad (4b)$$

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

$$\frac{I_{\text{UV}}}{I_{\text{VIS}}} = \frac{\tau_{\text{Xe}_2\text{Cl}}(\text{Xe}_2\text{Cl})}{\tau_{\text{Xe}_2\text{Cl}}(\text{XeCl})} \frac{1/\tau + k(\text{RCl}) [\text{RCl}]}{k(\text{Ar}, \text{Xe}) [\text{Ar}] [\text{Xe}]}. \quad (5)$$

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 $k(\text{RCl}) [\text{RCl}]$. According to eq. (5), the ratio $I_{\text{UV}}/I_{\text{VIS}}$ 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.

The efficiency of CCl_4 in producing XeCl^* can be related to its higher dissociative attachment rate coef-

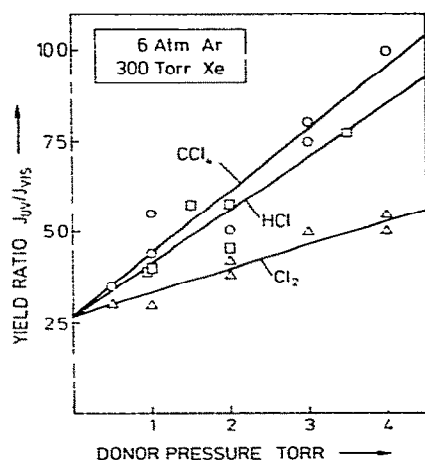


Fig. 4. Dependence of the ratio of the UV to visible fluorescence yields upon donor partial pressure. The yield ratios are obtained from time-integrated OMA data, using consecutive shots with appropriate UV and visible filtering.

ficient as compared to Cl_2 and HCl [13,14]. The dependence of the yield ratio $I_{\text{UV}}/I_{\text{VIS}}$ upon partial pressure of the selected chlorine donors is shown in fig. 4. As predicted by eq. (5), the ratios show approximately the same halogen donor pressure dependence as the decay rates of Xe_2Cl^* depicted in fig. 3. Although the scatter of the experimental data points is considerably higher than the scatter in the Stern–Volmer plots of fig. 3, least-squares fits resulted in a common intersection point at zero donor pressure. The donor pressure range has been limited to 4 Torr since higher pressures resulted in different quenching rates due to an increasing influence of slow precursor formation processes (for details see ref. [15]). The intercept at zero donor pressure may be used to determine independently the three-body quenching rate $k(\text{Ar}, \text{Xe})$ which has been derived from the buffer gas dependence in ref. [4] to be $1.5 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$. Such a determination based upon an evaluation of fig. 4 requires an accurate knowledge of the absolute UV and visible fluorescence yields.

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, compared to the other donors, chlorine has a low production efficiency for the XeCl^* precursor with the excitation conditions that exist in our experimental ap-

paratus. 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-lived 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 $\text{Cl}(4\text{P})$ states are possible candidates for these slow precursors 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^* .

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. 4 support 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.

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