# PRODUCTION AND QUENCHING OF XeCl(B, C) AND Xe<sub>2</sub>Cl\* INITIATED BY TWO-PHOTON EXCITATION OF Xe AND Xe<sub>2</sub>

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The rare-gas halide excimer, XeCl(B, C), was produced in gas-phase mixtures of Xe and Cl<sub>2</sub> by reactions initiated by the twophoton excitation of atomic xenon and xenon dimers in the wavelength region 246.5 to 258 nm. The production mechanisms of XeCl(B, C) were identified and characterized. Excitation of xenon dimers resulted in photoionization, and the resulting xenon ions participated in the mechanism that produced XeCl(B, C). The rate constant for the quenching of Xe<sub>2</sub>Cl(4 <sup>2</sup> $\Gamma$ ) by Cl<sub>2</sub> was determined to be  $k = (3.9 \pm 0.4) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

#### 1. Introduction

The rare-gas halide excimers XeCl(B, C) and  $Xe_2Cl(4 \ ^2\Gamma)$  have been produced photochemically in gas-phase mixtures of xenon and molecular chlorine by optical excitation at a number of wavelengths in the UV. Several mechanisms have been identified that lead to the production of these rare-gas halide excimers with excitation between 157 and 314 nm: collision-induced absorption [1-5], free-bound absorption between Xe and photolytically (or discharge-) generated Cl atoms [6-8], direct excitation of either Xe atoms or chlorine molecules [9-12], and excitation of Xe-Cl<sub>2</sub> van der Waals complexes [13,14]. The numerous entrance channels to the XeCl(B, C) potential and the rich photochemistry of the relatively simple but highly reactive Xe/Cl<sub>2</sub> system makes this an attractive system to study and characterize.

In this work, the mechanisms responsible for XeCl(B, C) production in mixtures of xenon and molecular chlorine excited in the wavelength range 246.5 to 258 nm were determined. Two mechanisms, two-photon excitation of both Xe atoms and of Xe dimers, were identified as the initial steps in photochemical processes initiated at different wavelengths in this range. These reaction channels were differentiated spectroscopically, as well as by the distinctive temporal profiles of the XeCl(B) fluores-

cence, and the dependence of the XeCl(B) time-integrated emission on Xe pressure was observed for excitation of Xe and  $Xe_2$ .

At high Xe pressures, the three-body reaction between XeCl(B, C) and two Xe atoms producing  $Xe_2Cl(4 \ ^2\Gamma)$ , herein referred to as  $Xe_2Cl^*$ , becomes the dominant loss channel for XeCl(B, C):

$$XeCl(B, C) + Xe + Xe \rightarrow Xe_2Cl^* + Xe.$$
 (1)

The triatomic excimer,  $Xe_2Cl^*$ , has a broad emission band peaked near 480 nm (for the excimer in the gas phase) and has been made to lase [15,16]. Analyses of the XeCl(B, C) and Xe<sub>2</sub>Cl\* laser systems require reliable rate constants for the efficient quenching of the triatomic excimer by halogen-containing species. Thus, the rate constant for the quenching of Xe<sub>2</sub>Cl\* by Cl<sub>2</sub> was measured in this system and compared with results obtained using other techniques.

## 2. Experimental

The experiments were performed in a stainless steel reaction cell [5] having a Teflon-coated interior. The excitation source was a tunable, frequency-doubled dye laser (Lambda Physik 2002E) pumped by an XeCl excimer laser (Lambda Physik 201E). The dye laser was operated with coumarin 102 dye, had a nominal linewidth of  $0.2 \text{ cm}^{-1}$ , and yielded a fre-

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quency-doubled output of typically 0.2 mJ/pulse in a 12 ns fwhm pulse. The laser beam either passed through the cell unfocused, or was focused into the center of the reaction cell by a 25.4 cm focal length. fused silica lens. The fluence (power) of the unfocused and focused laser beams were typically 5 mJ/  $cm^2$  (0.4 MW/cm<sup>2</sup>) and 650 mJ/cm<sup>2</sup> (500 MW/  $cm^2$ ), respectively. The reaction cell was fitted with fused silica windows through which the laser beam was passed and fluorescence was viewed. Fluorescence was detected at right angles to the laser beam by photomultiplier tubes (PMTs) fitted with filters to pass either the 308 nm XeCl(B) emission or the Xe<sub>2</sub>Cl\* emission between 450 and 500 nm. Excitation spectra were obtained by scanning the dye laser frequency and recording the PMT signal with a boxcar integrator (SRS 265). Temporal profiles of the fluorescence signals were obtained by recording the PMT signals with a transient digitizer (Tektronix 7912AD). The energy of the frequency-doubled dye laser beam was measured with a pyroelectric joulemeter (Gentec ED-100A). The gases, chlorine (Matheson UHP) and xenon (Spectra Gases, 99.999%), were used without further purification.

#### 3. Results and discussion

## 3.1. Production of XeCl(B, C)

Irradiation of mixtures of Xe and  $Cl_2$  in the wavelength range 246.5 to 258 nm produced emission from XeCl(B) and Xe<sub>2</sub>Cl\*. Weak emission from XeCl(C), which is in equilibrium with XeCl(B) [17], was also observed at 350 nm. Excitation spectra were recorded using mixtures of from 0.04 to 0.3 kPa Cl<sub>2</sub> (0.3 to 2 Torr) with from 1.3 to 100 kPa Xe (10 to 800 Torr) and detecting either the XeCl(B) or Xe<sub>2</sub>Cl\* fluorescence. At high Xe pressures, similar excitation spectra were obtained by detecting either the XeCl(B) or the Xe<sub>2</sub>Cl\* emission.

At low Xe pressures, XeCl(B) emission was observed when the laser excited the narrow spectral lines of the dipole-allowed two-photon transition from ground-state Xe atoms to the  $6p[1/2]_0$ ,  $6p[3/2]_2$ , and  $6p[5/2]_2$  levels. As the Xe pressure increased, the two-photon atomic transitions in the excitation spectra broadened asymmetrically. At high Xe pressures, additional broad features grew in the spectrum due to dipole-allowed two-photon transitions of xenon dimers [18]. An excitation spectrum recorded in the region 246.7 to 250.5 nm is shown in fig. 1. The XeCl(B) emission intensity varied quadratically with laser power for excitation of both xenon atoms and dimers (fig. 2). Thus, excitation spectra were normalized by the square of the laser power. Wavelength calibration was performed using the transitions in atomic Xe as reference points.

The excitation spectrum in fig. 1 shows XeCl(B) production following two-photon absorption by xe-



Fig. 1. Fluorescence excitation spectrum produced by irradiation (800 mJ/cm<sup>2</sup>) of 134 kPa Xe and 0.3 kPa Cl<sub>2</sub>. The fluorescence signal was normalized by the square of the laser power.



Fig. 2. Dependence of 308 nm fluorescence signal on laser power for focused and unfocused excitation of the atomic transition to Xe  $6p[3/2]_2$  (circles), and the transition in Xe<sub>2</sub> at 248.7 nm (squares) in a mixture of 0.04 kPa Cl<sub>2</sub> and 134 kPa Xe. Lines are least-squares fits to the data. The slopes of these lines, *n*, have error limits  $\pm 0.1$ .

non dimers to excited gerade states of  $Xe_2$  which correlate to a ground-state Xe atom and a Xe atom in the 5d[7/2]<sup>3</sup> state. Emission produced following excitation of the two-photon, dipole-forbidden (dipole-quadrupole-allowed) atomic transition to 5d[7/2]<sup>3</sup> at 247.0 nm is evident and the intense dipole-allowed two-photon atomic transition to  $6p[1/2]_0$  is peaked at 249.6 nm. The emission of KrF excimer lasers lies in the 248 to 249 nm spectral region where excitation of Xe/Cl<sub>2</sub> gas mixtures is dominated by transitions of xenon dimers. Thus, XeCl(B) production by KrF excimer laser excitation of these gas mixtures is the result of excitation of Xe<sub>2</sub>.

The excitation spectra observed were similar to the spectra obtained from two-photon-excited pure Xe by Gornik et al. [19] who detected VUV and IR emission. The line positions of the vibrational transitions converging toward the  $5d[7/2]_3^{\circ}$  level of Xe observed here are in reasonable agreement with the work of Gornik et al., and the work of Dehmer, Pratt, and Dehmer [20] who produced cold Xe<sub>2</sub> by a supersonic nozzle expansion and used resonance-enhanced multiphoton ionization detection. Clearly, in this work, xenon atoms and dimers are the carriers of the spectra. The photo-produced excited xenon species react with Cl<sub>2</sub> to produce the rare-gas halide excimers.

The temporal profiles of the XeCl(B) emission obtained from a mixture of 0.04 kPa Cl<sub>2</sub> and 27 kPa Xe produced by unfocused laser excitation (2 mJ/ cm<sup>2</sup>) of atomic xenon, and by focused excitation of molecular xenon are shown in figs. 3a and 3b, respectively. The emission shown in fig. 3a is produced by the two-photon excitation of the  $5p^{5}6p[1/2]_{0}$  state of atomic Xe at 249.6 nm. Typically, atomic excitation produced XeCl(B) fluorescence that displayed a rapid rise, followed by a decay that was nonexponential for a short initial time, but then became exponential. The prompt rise reflects the rapid radiative loss ( $\tau = 11$  ns) [6,21], quenching, and reactive loss of XeCl(B) [1,5,6,11,12]. The rate of fluorescence decay is governed by the production of XeCl(B). The rate of the exponential fluorescence decay increased with Cl<sub>2</sub> concentration at constant Xe concentration, giving a rate constant of  $k = (7.0 \pm 0.5) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, where the error limit is  $(1\sigma)$  obtained from a weighted least-



Fig. 3. Temporal profiles of XeCl(B) emission following excitation of (a)  $Xe(6p[1/2]_0)$ , at 249.63 nm, 0.08 mJ/pulse, unfocused and (b)  $Xe_2$  at 247.16 nm, 0.20 mJ/pulse, focused. The spike at early time in (b) is from scattered laser light. Both traces are for 100 laser shots but note different time scales for (a) and (b).

squares fit to the data obtained by exciting  $Xe(6p[3/2]_2)$  at a Xe concentration of  $1.9 \times 10^{19}$  cm<sup>-3</sup>. At this Xe concentration, collisional deactivation of Xe(6p) [22,23] is more rapid than both reaction of Xe(6p) with Cl<sub>2</sub> [9] at the chlorine concentrations used, and three-body reactions with Xe forming excited xenon dimers [24], Xe<sup>\*</sup><sub>2</sub>, which rapidly undergo radiative decay [25,26]. Thus, reactions forming XeCl(B, C) occur predominantly with long-lived Xe(6s) atoms. The observed rate constant is in good agreement with that previously determined for the reaction of Cl<sub>2</sub> with Xe(<sup>3</sup>P<sub>2</sub>),  $k=7.2 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [27].

The time dependence of the XeCl(B) emission generated by excitation of the transition in Xe<sub>2</sub> at 249.16 nm is shown in fig. 3b. The maximum emission intensity from XeCl(B) occurred 200 ns after the laser pulse. The maximum fluorescence occurred earlier as the Xe concentration increased. No emission was observed when the gas mixture was irradiated with an unfocused laser at the wavelength of the transitions in  $Xe_2$ .

The delayed production of XeCl(B) under focused excitation of Xe<sub>2</sub> implies that the species reacting to produce XeCl(B) was not produced directly by the optical excitation. This delayed production is characteristic of the mechanism of XeCl(B) formation involving ionic processes, as seen in the two-photon ionization of Xe at 193 nm [5,28]. Xenon ions undergo a three-body reaction with Xe atoms to form dimer ions, which at low Cl<sub>2</sub> pressures [5], undergo dissociative attachment with an electron [28-30]:

 $Xe^+ + Xe + Xe \rightarrow Xe_2^+ + Xe, \qquad (2)$ 

$$Xe_2^+ + e^- \rightarrow Xe^{**} + Xe. \tag{3}$$

The above mechanism is consistent with the observations of Dehmer, Pratt, and Dehmer [31] who found that laser excitation of  $Xe_2$  in the wavelength range 242.5-260.0 nm can produce xenon ions by resonance enhanced, (2+1)-photon ionization via two mechanisms: (1) Excited states of  $Xe_2$  reached by two-photon absorption may predissociate to a ground-state atom and an excited-state Xe atom. The excited Xe atom then absorbs another photon and is ionized. (2) An excited state of  $Xe_2$  reached by twophoton absorption can itself absorb a photon and be ionized. The excited states of  $Xe_2^+$  that are accessed, however, are either weakly bound or dissociative [32,33] and the ground state of  $Xe_2^+$  is bound by only 1.02 eV [34]. Thus, with the excess energy available, direct ionization of Xe<sub>2</sub> will yield predominantly Xe<sup>+</sup>. The Xe<sup>+</sup> ions produced by either process can then react by reactions (2) and (3) to form dimer ions and finally excited Xe atoms. The excited Xe atoms cascade down through the 6p and 6s manifolds by collisional and radiative processes [22,23,35], and react with  $Cl_2$  to produce XeCl(B, C) [9,27]. The temporal profile of the XeCl(B) fluorescence decay shown in fig. 3b is consistent with the above mechanism.

Only a small increase in the rise time of the XeCl(B) fluorescence was observed when a nonpredissociative level of  $Xe_2$  was excited (251.1 nm) compared to excitation of a predissociative level (247.2 nm). Dramatic changes of the fluorescence profile would not be expected because direct ionization of  $Xe_2^*$  yields a large fraction of  $Xe^+$  and because reaction (3) is faster than reaction (2) at a Xe pressure of 200 kPa and the focal conditions used [29,30].

The quadratic dependence on laser power observed for the (2+1)-photon ionization of Xe<sub>2</sub> implies that the ionization step is saturated. This conclusion is consistent with the high power densities required to observe the two-photon process in Xe<sub>2</sub> and the ionization probability of an excited Xe atom [36]. When the atomic transition was excited at high power densities, the XeCl(B) fluorescence decay profile lengthened and became non-exponential, evidence that ionization of Xe\* was occurring in the focal region. Fluorescence from reactions initiated by non-ionizing transitions in xenon outside the focal region still dominated the fluorescence signal because of the broad collection angle of the detector.

The dependence of the XeCl(B) time-integrated emission on Xe pressure differed for excitation of atomic xenon and xenon dimers, as shown in fig. 4 for gas mixtures containing 0.04 kPa Cl<sub>2</sub>. For excitation of atomic xenon, the XeCl(B) integrated emission reached a maximum near a Xe pressure of 30 kPa and then decreased at higher Xe pressures. The excitation rate of atomic xenon is proportional to the Xe concentration. Above 30 kPa, quenching is dominated by the three-body reaction of XeCl(B)



Fig. 4. Dependence of 308 nm time-integrated emission on Xe pressure for focused excitation of xenon atoms ( $6p[3/2]_2$  at 249.6 nm) and xenon dimers (248.7 nm). Gas mixtures contained 0.04 kPa Cl<sub>2</sub>.

with Xe to form Xe<sub>2</sub>Cl<sup>\*</sup>. The quadratic dependence of the quenching rate on the Xe concentration results in the XeCl(B) integrated emission decreasing with Xe. The Xe<sub>2</sub>Cl<sup>\*</sup> emission intensity rose linearly with Xe pressure above Xe pressures of 30 kPa. The ratio of the Xe<sub>2</sub>Cl<sup>\*</sup> to the XeCl(B) integrated emissions increased linearly with the square of the xenon pressure, as in ref. [5], indicating that reaction (1) is the major route producing Xe<sub>2</sub>Cl<sup>\*</sup>.

The XeCl(B) integrated emission obtained by excitation of Xe<sub>2</sub> rose with Xe pressure below 50 kPa and then remained constant with further additions of Xe, in contrast to the behavior observed for excitation of atomic Xe. The xenon dimer concentration varied quadratically with Xe concentration and can be estimated [37] to be 0.7 kPa for a Xe pressure of 113 kPa at 300 K. Thus, the quadratic dependence of the excitation rate on Xe concentration canceled the quadratic dependence of the quenching rate, and the integrated emission was independent of the Xe concentration.

# 3.2. Quenching of Xe<sub>2</sub>Cl\*

The quenching of  $Xe_2Cl^*$  was studied by analyzing the  $Xe_2Cl^*$  fluorescence that was produced following unfocused laser excitation of  $Xe/Cl_2$  mixtures. The laser excited the two-photon transition in groundstate atomic xenon, producing  $Xe(6p[3/2]_2)$ . The excited Xe atoms reacted with  $Cl_2$  to produce XeCl(B, C), which then underwent three-body reaction with Xe to produce the triatomic excimer. The processes that resulted in the loss of  $Xe_2Cl^*$  in this system were

$$Xe_2Cl^* + Xe \xrightarrow{k_4} products,$$
 (4)

$$Xe_2Cl^* + Cl_2 \xrightarrow{\kappa_5} \text{products},$$
 (5)

$$Xe_2Cl^* \xrightarrow{\epsilon_{rad}} 2Xe + Cl + h\nu.$$
 (6)

The time dependence of the  $Xe_2Cl^*$  emission can be described [38] by

$$[\operatorname{Xe}_{2}\operatorname{Cl}^{*}](t) = C[\exp(-\lambda_{1}t) - \exp(-\lambda_{2}t)],$$

where, in this case, assuming Xe<sub>2</sub>Cl\* was produced by the three-body reaction of XeCl(B) with Xe,  $\lambda_1$ is the decay constant of the XeCl(B) emission and  $\lambda_2$  is the decay constant of the Xe<sub>2</sub>Cl\* emission. The data fit this form well, however; because the initial decay of the XeCl(B) emission is in some cases nonexponential,  $\lambda_2$  were taken from the single exponential decay of the Xe<sub>2</sub>Cl\* emission observed after the XeCl(B) emission had completely decayed and was no longer detectable. The Xe<sub>2</sub>Cl\* emission was analyzed for at least two lifetimes to obtain

 $\lambda_2 = \tau_{rad}^{-1} + k_4 [Xe] + k_5 [Cl_2].$ 

The values of  $\lambda_2$  were plotted as a function of Cl<sub>2</sub> concentration (fig. 5) to yield  $k_4 = (3.9 \pm 0.4)$  $\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This rate constant was obtained from a linear least-squares fit to the data and the error limit includes estimates of experimental uncertainties. Since quenching of Xe<sub>2</sub>Cl\* by Xe is slow [1,11,12,39] and can be neglected, the intercept in fig. 5 gives a radiative lifetime for Xe<sub>2</sub>Cl\* of  $\tau_{rad} = 300 \pm 50$  ns.

The value of  $k_5$  obtained in this work is in excellent agreement with the midrange of previously reported values [1,7,11,12,40] listed in table 1. The technique used in this work avoids direct excitation or photolysis of the quenching species, Cl<sub>2</sub>, and thus is complementary to some previous measurements [7,11,12]. Ionic species which complicate analysis in actual laser systems are not present in these mea-



Fig. 5. Decay rate of Xe<sub>2</sub>Cl<sup>\*</sup> fluorescence observed after XeCl(B) emission had decayed, plotted as a function of Cl<sub>2</sub> concentration at 297 K. Gas mixtures contained 80 kPa Xe (600 Torr). The statistical error limits of the individual decay rates are smaller than the data point symbols. A weighted least-squares fit to the data gave  $k_5 = (3.9 \pm 0.4) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and an intercept yielding  $\tau_{rad} = 300 \pm 50$  ns.

Table 1 Rate constant for quenching of Xe<sub>2</sub>Cl\* by Cl<sub>2</sub>

Rate constant <sup>a)</sup>	Ref.
$(2.2\pm0.2)\times10^{-10}$	[40]
$(2.6\pm0.3)\times10^{-10}$	[1]
$(3.9\pm0.4)\times10^{-10}$	this work
$(4.0\pm1.0)\times10^{-10}$	[7]
$(4.5\pm0.4)\times10^{-10}$	[11]
$(5.2\pm0.2)\times10^{-10}$	[12]

<sup>a)</sup> Units are  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>,

surements. The smaller values of  $k_5$  obtained in other studies could have resulted from incomplete deconvolution of reaction (1) from the exponential decay.

## 4. Conclusions

The rare-gas halide excimers, XeCl(B, C), were produced in gas-phase mixtures of xenon and molecular chlorine by reactions initiated by the excitation of xenon atoms and xenon dimers in the wavelength range 246.5 to 258 nm. Resonant twophoton excitation of the ground state of atomic xenon produced excited-state atoms which reacted with chlorine. At high xenon pressures, reactions initiated by two-photon absorption by xenon dimers took place. At the laser intensities required for the observation of two-photon transitions in Xe<sub>2</sub>, two-photon absorption was followed by absorption of a third photon that ionized either the excited Xe<sub>2</sub> or an excited Xe atom produced by the predissociation of excited  $Xe_2$ . The ions then participated in the reaction mechanism producing XeCl(B, C). At high xenon pressures, the major loss channel of XeCl(B, C) was the three-body reaction with Xe that produced Xe<sub>2</sub>Cl\*. This production of the triatomic excimer permitted study of the quenching of Xe<sub>2</sub>Cl\*.

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