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Reactive quenching of two-photon excited xenon atoms by Cl₂

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Total binary and tertiary quench rates have been measured for the reaction Xe $(5p^5np, np', n = 6,7) + Cl_2$ at thermal temperatures. Xenon atoms are excited by state-selective, twophoton absorption with an ultraviolet laser. The time-dependent fluorescence from the excited atom in the infrared, visible, and from XeCl* (B) product near 308 nm have been measured with subnanosecond time resolution. The decay rates are measured as a function of Cl_2 pressure to 20 Torr and Xe pressure to 400 Torr. The measured reaction rates $(k_2 \sim 10^{-9}$ cm³ s⁻¹) are consistent with a harpoon model described in a separate paper. We also measure large termolecular reaction rates for collisions with xenon atoms $(k_3 \sim 10^{-28} \text{ cm}^6 \text{ s}^{-1})$. Total product fluorescence has been examined using a gated optical multichannel analyzer. We measure unit branching fractions for high vibrational levels of XeCl* (B) with very little C state fluorescence observed.

I. INTRODUCTION

We present in this paper a study of state-to-state, electronic energy transfer from $Xe^{*5}p^{5}np$, np' following twophoton laser excitation. This study has direct application to understanding the energy pathways and reaction processes important in the chemistry of the XeCl excimer laser.

This work extends to reactive collisions^{1,2} previous experiments measuring the state-to-state intramultiplet quenching of Xe* $6p[1/2]_0$, $6p[3/2]_2$, and $6p[5/2]_2$. We also report measurements for higher Rydberg states $6p'[1/2]_0$, $6p'[3/2]_2$, $7p[1/2]_0$, $7p[3/2]_2$, and $7p[5/2]_2$ and of termolecular reaction processes for Xe* 6p observed at higher xenon pressures. These reactions of neutrals are important in modeling of excimer lasers.

A. Reactions of Xe (5p⁵np) with Cl₂

Current models of the XeCl excimer laser have assumed that the primary energy pathway involves the formation of the ions Xe^+ and Cl^- , followed by three-body ion-ion recombination to the lasing transition,

$$Xe^{+} + Cl^{-} + M \rightarrow XeCl^{*}(B,C) + M, \qquad (1)$$

where M is generally the buffer gas. These models include extensive sets of reactions involving processes such as B to Cstate mixing, radiative decay, quenching, and ion reactions. Reactions with neutrally excited atoms such as Xe* and Xe^{*} have also been included,³ but the reaction rates used in some models are those measured by Setser for Xe*(5 p^5 6s).⁴⁻⁶ These rates predict that the ion channels dominate over neutral channels for the production of XeCl*(B,C). The best models are not in agreement with the available laser data and several workers have suggested a greater importance for neutral channels.⁷

We had expected that the cross sections for reactive energy transfer to $XeCl^*(B,C)$ might be larger for the higher energy $Xe^*(np)$ states than those measured for $Xe^*(6s)$ by Setser.⁴⁻⁶ Reactive transfer is expected to proceed by the harpoon reaction

$$Xe^{*}(np) + RCI \rightarrow Xe^{+} + RCl^{-} \rightarrow XeCl^{*} + R,$$
 (2)

where RCl indicates a general chloride. In Fig. 1, we show various crossings of estimated covalent potential curves of Xe^{*} and Cl₂ with ion surfaces. If reactions occur primarily at the crossings, we expect transfer cross sections $Q \sim \pi R_c^{2.5}$ The crossing radii suggest that the cross sections for $Xe^{*}(6p)$ states are larger than for $Xe^{*}(6s)$, and even larger cross sections for the higher lying states of $Xe^{*}(7p)$. There are expected difficulties with this simple single crossing model. The charge transfer interaction between the reactant and the ionic channels varies exponentially with internuclear separation (crossing radius); hence, though crossings with $Xe^{*}(np)$ occur at larger separations than $Xe^{*}(6s)$, they might not be as effective. In addition, the electron affinity of some reactants such as Cl₂ is rapidly varying at the equilibrium internuclear separation, making the reaction cross section sensitive to bond stretching as the collision pair approaches the crossing.⁵ In the experiments described here we test these effects by exciting states of $Xe^*(np,np',n=6,7)$ which have decreasing ionization potentials and appropriately increasing crossing radii.

B. Alternate reactions

In general, alternate energy processes than those described by Eq. (2) can occur. Fine-structure changing and quenching reactions with energy disposal in translational energy (T),

$$Xe^{*}(np_{i}) + RCl \rightarrow Xe^{*}(np_{j}) + RCl \quad (E \rightarrow T)$$

 $Xe^{*}(np_i) + RCl \rightarrow Xe^{*}(ns,nd) + RCl \quad (E \rightarrow T)$ (3)

or electronic energy (E),

$$\operatorname{Xe}^{*}(np) + \operatorname{RCl} \rightarrow \operatorname{Xe}(5p^{6}) + \operatorname{RCl}^{*}(E \rightarrow E)$$
 (4)

can occur. Energy disposal in such nonreactive collisions can also be in vibrational (V) or rotational (R) excitation of RCl. We have examined the possibility for reactions of the



FIG. 1. Crossings between ionic and valence potential surfaces for xenon and chlorine mixtures. Only the valence states which can be two-photon pumped are indicated. The arrow indicates the effect of bond stretching during the reaction. The lower curve is at the Cl–Cl equilibrium separation for Cl₂ while the upper curve is the ionic potential for the Cl–Cl separation for ground Cl₂. Bond stretching due to varying excited states of Cl₂ or Xe^{*}-Cl₂ interaction will give values between these limits.

forms of Eqs. (3) and (4) by searching for fluorescence from these product channels. No search is reported here for vibrational or rotational excitation of the molecular product in the ground electronic state.

Subsequent to our beginning these experiments, Setser *et al.* have published measurements of quenching of two-photon excited states of $Xe^*(6p)$ by chlorides.⁸ We compare our measurements with those of Setser here. We also describe in this paper the effects of termolecular collisions which occur at higher buffer gas pressures.

C. Termolecular reactions

Traditional studies of excitation transfer have emphasized the microscopic behavior of energy transfer in twobody collisions at low pressures. At densities approaching that of liquids, reactions are limited by transport of the reactants; and microscopic interactions at short ranges are relatively unimportant. In high pressure gases, one might observe both the effects of transport and the alteration of microscopic reactions by three-body collisions (termolecular reactions).

Previously, Collins and co-workers observed that charge transfer rates are enhanced by collisions with a third body.⁹ We observed in our laboratory increased rates for dissociative recombination and charge transfer for Ar_2^+ .^{10,11} For charge transfer reactions, Collins has explained enhanced rates as resulting from glancing collisions which are converted to inwardly spiraling orbits by collisions with a third, nonreactive body.⁹

Recently, several theories of reactions at intermediate densities have been developed. Initially, these calculations

were applied to ion-ion recombination^{12,13} and ion-electron recombination.¹⁴ Calculations for neutral atomic recombination have followed.¹⁵ This theoretical effort has now encouraged experimental effort at higher densities.

In reactions of neutral systems, three-body collisions are known to be important for molecular association

$$\mathbf{A^*} + \mathbf{B} + \mathbf{X} \rightarrow \mathbf{AB^*} + \mathbf{X},$$

where the collision with a third body is required to relax the bonding pair into the well. In our recently published study of quenching of $Xe^{*}(6p)$ in pure xenon, we reported a termolecular quenching reaction which we described as resulting *not* from molecular association, but enhanced deactivation

$$Xe^{*}(6p[1/2]_{0}) + Xe + Xe \rightarrow Xe^{*}_{i} + Xe + Xe.$$

In recent conference proceedings, Collins and co-workers reported similar termolecular quenching reactions for helium metastables.¹⁶ The reaction rates reported here are to our knowledge the first rates for a termolecular *reactive* collision

$$Xe^{(6p[1/2]_0)} + Cl_2 + Xe \rightarrow XeCl^* + Cl + Xe$$

It now appears that termolecular reactions are universal to many forms of energy transfer reactions.

II. EXPERIMENT

Experiments reported here are done in a new apparatus constructed for studying energy transfer to chlorides. The apparatus is similar to one described earlier for studies of multiplet mixing in xenon.^{1,2} Chlorine and mixtures of raregases are premixed into a stainless steel cylinder and then admitted to a small stainless experimental chamber with sapphire and MgF₂ windows mounted onto ultrahigh-vacuum (UHV) flanges. The chamber and gas handling system were baked and evacuated to pressures below 10^{-9} Torr for several days before filling. Afterwards, the chamber and gas handling system were passivated for several weeks before beginning experiments.

The errors in the measurements of the Cl₂ pressure deserve additional discussion. Mixtures of xenon and chlorine were prepared in a separate bottle and added to the chamber. Xenon is first added to the chamber and the mixture bottle to a pressure measured with a MKS capacitance manometer. Then the gas is cryogenically condensed into the mixture bottle. A known pressure of chlorine was added to the chamber and again pumped cryogenically into the mixture bottle (volume ratios are accurately known). The bottle is then heated to room temperature (20 °C) and allowed to thermalize. This was important as we found the reaction rate to be sensitive to the temperature of the gas. All gas lines were insulated to prevent changes in temperature. After the gas is added to the chamber, variations in total pressure as a function of time were measured using a 10 Torr, differential capacitance manometer. In early experiments after passivation, the loss of Cl₂ gas was observed as a function of time. After a period of approximately one month we observed only small changes in pressures. Decay curves measured over sequential 15 min intervals had measured quench rates which correlated accurately with the measured pressures. The pressure was then measured before and after each decay curve to determine the error in the Cl_2 pressure.

The states $Xe^*6p[1/2]_0$, $6p[3/2]_2$, $6p[5/2]_2$, $6p'[1/2]_0$, $6p'[3/2]_2$, $7p[1/2]_0$, $7p[3/2]_2$, and $7p[5/2]_2$ are excited in two-photon transitions¹ using a frequency doubled dye laser pumped by a 1 kHz XeCl laser (Math Sciences XL410). The fluorescence is detected in the UV, visible, and infrared using a JY640 monochromator with either a cooled RCA 8852 PMT or a cooled and gated, intensified, optical multichannel analyzer (OMA, PAR 1420). Fluorescence in the vacuum ultraviolet is detected using a 1 m concave grating monochromator of our own design¹⁷ and detected with a Hamamatsu R972 or an EMI 9789Q. A third optical port allows detection of the total laser induced fluorescence in the VUV using a Hamamatsu solar blind PMT (R972).

We have also measured the time dependent fluorescence of the reactant state (state excited by the laser) and product states for pressures of 1-450 Torr. The time dependence of the fluorescent light intensity is determined by the delayedcoincidence, single-photon counting technique. The overall instrument response for the frequency doubled pump laser and the infrared detector is shown in Fig. 2. If a reactant state $|i\rangle$ is coupled only by excitation transfer to a product state $|j\rangle$ and each state decays to all product channels at a rate v_i and v_j , respectively, then we expect coupled differential equations with the solutions,

$$n_{i}(t) = n_{0}e^{(-v_{i}t)},$$

$$n_{j}(t) = \frac{k_{ij}[\text{Cl}_{2}]n_{0}}{v_{j} - v_{i}} \{e^{(-v_{i}t)} - e^{(-v_{j}t)}\},$$
(5)

where n_i and n_j are the state populations, n_0 is the initial population excited by the laser, and k_{ij} is the excitation transfer rate between the states. These expected time dependences must be convoluted with the measured instrument response to extract the correct exponential decay rates v_i and v_j . By measuring the exponential decays as a function of pressure, we can obtain a Stern-Volmer plot of the states' relaxation rate, $v = v_{rad} + k$ [Cl₂] as a function of the chlorine density. The slope of the data as a function of density yields the total quench rate. An example plot is shown in Fig. 3 for the case of Xe*(6p[1/2]_0).

III. RESULTS

In general we might expect quenching of $Xe^*(np)$ by both chlorine and xenon. For $Xe^*(6p)$ we have previously measured the decay rates for collisions with xenon^{1,2} and these rates have been recently confirmed by Setser and coworkers.¹⁸ Since reactive transfer to Cl_2 is expected to proceed through an ionic intermediary as described by Eq. (2), we might expect termolecular processes to be important as in



FIG. 2. Total laser and IR detector instrument response. The line is a least squares fit of a gaussian convoluted with an exponential. The FWHM of the gaussian is 0.66 ns while the exponential decay constant is 0.63 nsec.

FIG. 3. Sample data showing the time dependent laser induced fluorescence from directly excited Xe* $6p[1/2]_0$ in 2.4 Torr xenon and 0.101 Torr chlorine. The data was obtained by delayed coincidence timing. The line is a least-squares fit including the instrument response.

charge transfer reactions.^{9,10} In general then we expect the decay of $Xe^*(6p)$ to be described by

$$v_{q} = v_{0} + k_{\{\text{Xe}\}}^{(2)} [\text{Xe}] + k_{\{\text{Xe}\}}^{(3)} [\text{Xe}]^{2} + k_{\{\text{Cl}\}}^{(2)} [\text{Cl}_{2}] + k_{\{\text{Cl}\}}^{(3)} [\text{Cl}_{2}]^{2} + k_{\{\text{XeCl}\}}^{(3)} [\text{Xe}] [\text{Cl}_{2}],$$
(6)

where v_0 is the radiative decay rate and $k_i^{(2)}, k_i^{(3)}$ represent bimolecular or termolecular reaction rates for a specie. In Fig. 4 we show the decay rates for Xe*6p[1/2]₀ as a function of chlorine pressure in a Stern–Volmer plot. The error bars shown are one standard deviation for the decay rates determined from least-squares fitting of data as shown in Fig. 3, including deconvolution of the measured instrument response in Fig. 2.

The error bars in pressure are determined by the measured range of Cl_2 pressures as described in the experimental section. As seen in Fig. 4, the quench rates increase linearly with pressure indicating that a bimolecular reaction is dominant

$$Xe^{*}(6p[1/2]_{0}) + Cl_{2} \rightarrow XeCl^{*} + Cl;$$
(7)

hence, the chlorine dependence for the quench rate is described by

$$v_q = v_{\{Xe\}} + k_{\{Cl\}}^{(2)} [Cl_2],$$
 (8)

where

$$v_{\{Xe\}} = v_0 + k_{\{Xe\}}^{(2)} [Xe] + k_{\{Xe\}}^{(3)} [Xe]^2$$
(9)

is the quench rate due to the xenon component of the mixture as measured previously.^{1,2} Termolecular reactions involving two Cl₂ molecules were found to have a negligible reactivity. The only remaining unmeasured rate $k {}^{(3)}_{\text{(xeCl)}}$ can be determined by plotting the difference rate, $\Delta \nu$,

$$\Delta v = k {}_{\text{{XeCl}}}^{(3)} [\text{Xe}] [\text{Cl}_2]$$

= $v_q - v_{\text{rad}} - k {}_{\text{{Xe}}}^{(2)} [\text{Xe}] - k {}_{\text{{Xe}}}^{(3)} [\text{Xe}]^2 - k {}_{\text{{Cl}}}^{(2)} [\text{Cl}_2]$
(10)

TABLE I. Total bimolecular collisional quench rates $(k {\binom{2}{\{C\}}})$ for Xe* $5p^5np$ in chlorine.

Bimolecular rates $(10^{-10} \text{ cm}^3/\text{s})$							
State	IP (eV)	(This work)	(Setser)*	(calc. πR_c^2)			
6p[5/2]2	2.44	12.8 ± 0.3	13.3 ± 1.0	12.5			
6p[3/2]2	2.31	15.5 ± 0.2	14.5 <u>+</u> 1.0	15.0			
6p[1/2]0	2.19	17.9 ± 0.2	14.6 ± 1.0	17.8			
6p'[3/2]2	2.38	18.6 ± 0.5		13.5			
6p'[1/2]0	2.29	21.9 ± 1.0		15.2			
7p[5/2]2	1.17	30.7 ± 1.9		1,051			
7p[3/2]2	1.13	36.1 ± 1.2		1,938			
7p[1/2]0	1.11	29.5 ± 0.8		2,898			
5d[1/2]1	2.21	9.2 ± 0.5		17.7			

^a J. K. Ku and D. W. Setser, Appl. Phys. Lett. 48, 689 (1986).

as a function of xenon pressure at fixed chlorine pressure and where v_a is the experimentally measured decay rate. The difference rate is most easily measured by adding the correct amount of xenon to the evacuated chamber. The chamber had been thoroughly passivated as described previously. We then measured the decay rate for the excited atom in "pure" xenon. This rate accounts for all negative terms on the righthand side of Eq. (10) not involving the quenching by chlorine. In addition this rate may have additional quenching due the presence of a small amount of chlorine displaced from the walls by the xenon buffer gas. The difference of these two rates minus the bimolecular quenching by chlorine that we report in Table I yields the difference rate in Eq. (10) due to termolecular reactions. This experimental technique should eliminate possible systematic errors due to the displacement of an unknown amount of chlorine from the walls of the chamber. Because the quenching due to "pure" xenon and the displaced amount is measured at every xenon pressure, the pressure dependence of the displacement is properly accounted for in the measurements. Note that if the added



FIG. 4. Pressure dependent decay rates determined as a function of Cl_2 pressure at a fixed xenon pressure of 5.0 Torr. The error bars represent one standard deviation in the fitted decay rates and the full variation in chlorine pressure during the experiment. The decay rates are for (a) Xe* $6p[1/2]_0$, (b) Xe* $6p[3/2]_2$, and (c) Xe* $6p[5/2]_2$.

chlorine is lost to the walls, we would observe a measureable change in the total pressure as described above. We used a large Cl₂ pressure of 10 Torr in order to emphasize the effects of $k_{\text{XeCl}}^{(3)}$ [Xe] [Cl₂] over the quenching caused by xenon. The difference rates Δv are shown as a function of xenon pressure in Fig. 5. The errors include all the uncertainties in measuring all the quench rates in Eq. (8) and (9). We summarize the measured reaction rates in Table II. Termolecular rates were not observable for $Xe^{*}(6p')$ and $Xe^{*}(7p)$ because the bimolecular rates were so large. Even for the large termolecular rates reported in Table II, the termolecular contribution to the total quench rate is small over the experimental pressure ranges. The major errors shown for our termolecular rates result from errors in subtracting the bimolecular component. The termolecular reaction rates in xenon are even larger than those reported earlier for charge transfer processes^{9,10}; however, no termolecular rate was observed for argon buffer gases. Several models for the termolecular reactions are discussed in the companion paper.¹⁹

The results for the bimolecular rates in Table I show a systematic increase in quench rate with decreasing ionization limit up to the Xe*(7p) states where the reaction appears to "saturate." The reaction rates for Xe*(7p) are comparable to free electron dissociative attachment rates to Cl_2 at thermal energies.^{20,21} In general, it is known from studies of Rydberg states reacting with halogen molecules that the reaction rates are limited by the free electron attachment rate²² of the halogen acceptor molecule. This is sometimes referred to as the "free electron attachment model."²³

The Xe*(6p') rates are found to be considerably larger than the simple πR_c^2 model would suggest. This model works extremely well for the Xe*(6p) states (see Table I). In principle, Xe*(6p') should involve the Xe⁺ 5p⁵[²P_{1/2}] ionization limit (13.433 eV); therefore, they should have about the same crossing radii as the Xe*(6p) states. However, the magnitudes of the measured reaction rates for Xe*(6p') indicate significant charge transfer through the

TABLE II. Termolecular rates $(k_{CI-Xe}^{(3)})$ for Xe* 5p⁵ 6p with Cl₂.

Termolecular rates $(10^{-28} \text{ cm}^6/\text{s})$				
State	(This work, Xenon)	(This work, Argon)		
6p[1/2]0	3.5 ± 0.5	< 0.5		
6p[3/2]2	1.4 ± 0.5	< 0.1		
6p[5/2]2	1.8 ± 0.5	< 0.1		

lower Xe⁺ $5p^5 [^2P_{3/2}]$ ionization limit (12.127 eV). This is contrary to the observation by Sadeghi et al.24 of the propensity for ion-core conservation. Their conclusions were based on spectroscopic measurements from the metastable states Ar $4s({}^{3}P_{0})$ and Ar $4s({}^{3}P_{2})$. They observed *D*-X emission from reactions of halogens with $Ar({}^{3}P_{0})$ and not with Ar(${}^{3}P_{2}$) (the D state is correlated with ${}^{2}P_{1/2}$ core states while the B and C states are primarily correlated with ${}^{2}P_{3/2}$ core states⁴). For the $Xe^{*}(6p')$ states we have observed no D-X emission (expected at 235.8 nm⁴). If D-X is present, the transition is obscured by the B-X emission. Sadeghi et al. do not observe much difference in the reaction rates for the reactions of argon metastables with Cl₂; however, this is to be expected since the difference in the core splitting in argon is small (0.177 eV),²⁵ thus the crossings for both the $Ar^+({}^2P_{3/2})$ and $Ar^+({}^2P_{1/2})$ ionic limits will be about the same. In the case for xenon, the core splitting is much larger $(1.306 \text{ eV})^{26}$; hence, there will be a pronounced difference in the crossing radii due to the difference of the ionization limits, thereby enabling one to easily observe a disparity in the reaction rates. It is not understood at this time whether the observed mixing of core states in xenon is unique to reactions with excited p electrons (Sadeghi excited s electrons) or due to the higher Z in xenon which makes spin-orbit effects larger.

In Table I we compare our measured bimolecular rates with those measured recently by Setser.⁸ We obtain agree-



FIG. 5. The difference in quench rates described by Eq. (10) for (a) $6p[1/2]_0$, (b) $6p[3/2]_2$, and (c) $6p[5/2]_2$ are measured as a function of xenon pressure at fixed chlorine pressure of 10 Torr. The slope is the termolecular quench rate. The error bars represent the total errors in measuring the difference rate.

ment with his measurements within the reported error bars for $6p[3/2]_2$ and $6p[5/2]_2$, though our measurements have smaller errors. For $6p[1/2]_0$ we obtain a larger reaction rate. This larger rate is more consistent with the simple πR_c^2 theory. All the bimolecular rates for Xe* 6p which are reported in Table I are consistent with the harpoon model described earlier, and are significantly larger than rates measured earlier for Xe*(6s).⁴⁻⁶

IV. BRANCHING FRACTIONS

We have investigated the extent to which intramultiplet and intermultiplet relaxation, and electronic excitation transfer as described by Eqs. (3) and (4) contribute to the quenching of the xenon excited states. Of particular importance to the XeCl laser is the question whether the enhanced reaction rate in termolecular collisions leads to the XeCl*(B) lasing state or to other channels such as lower xenon excited states. We have made spectral scans from 150 nm to 900 nm to search for fluorescence from product channels other than XeCl*(B) for xenon pressures ranging from 10 Torr to 100 Torr.

We observe no fluorescence from Cl* or Cl₂^{*}. The only observed fluorescence results from highly vibrationally excited XeCl*(*B*) at low pressures as observed by Setser.⁸ As the pressure is increased the molecule vibrationally and rotationally relaxes before fluorescence, as is expected. At pressures of 100 Torr of xenon, we observe weak continua at 267 and 275 nm. These bands are obscured by fluorescence from high-vibrational bands of XeCl*(*B*) and have not been observed previously.^{4-6,8} The integrated intensity of XeCl*($C \rightarrow A$) is very weak as well (less than 2%) when exciting Xe*(6p). We have not searched for vibrationally excited ground state Cl₂; but this product is not expected.⁴⁻⁶ We find for reactive quenching of Xe*(6p) by Cl₂, 99% of all reactions produce XeCl*(*B*) for all xenon pressures to 250 Torr.

For very low pressures (less than 0.100 Torr) of Cl_2 and high pressures of xenon (over 100 Torr), we observe broad fluorescence over the range of 380 nm to 700 nm with a maximum around 490 nm when exciting the higher Rydberg states Xe*(6p¹,7p). This band is attributed to Xe₂Cl fluorescence.²⁷ There are several possible formation processes that can produce Xe₂Cl:

$$Xe^{*}(6p' \text{ or } 7p) + Xe \rightarrow Xe^{*}(6s) + 2Xe \rightarrow Xe_{2}^{*}(A^{1}\Sigma),$$
(11a)

$$\operatorname{Xe}_{2}^{*}(A^{1}\Sigma) + \operatorname{Cl}_{2} \to \operatorname{Xe}_{2}\operatorname{Cl}^{*} + \operatorname{Cl}, \qquad (11b)$$

$$Xe^{*}(6p' \text{ or } 7p) + 2 Xe \rightarrow Xe_{2}^{**},$$
 (12a)

 $Xe_2^{**} + Cl_2 \rightarrow Xe_2Cl^* + Cl, \qquad (12b)$

$$Xe^{*}(6p' \text{ or } 7p) + Cl_{2} \rightarrow XeCl^{*}(B,C) + 2 Xe$$
$$\rightarrow Xe_{2}Cl^{*} + Cl, \qquad (13)$$

where processes (11) and (12) involve forming Xe^{*}₂ complexes first, followed by reaction with Cl_2 to form Xe₂Cl^{*}. Process (12) forms Xe^{*}₂ directly from the initially excited state while process (11) involves intermultiplet quenching followed by Xe₂^{*} formation. Process (13) involves formation of Xe₂Cl^{*} from the XeCl^{*}(B,C) state, and this is the process currently favored in the literature.²⁸ In those studies however, Xe₂Cl^{*} was produced by either electron beam excitation or photoassociation. In our study, when the Cl₂ pressure was increased, the broad fluorescence from Xe₂Cl^{*} disappeared even though the XeCl^{*}(B) intensity increases. This result eliminates the possibility of process (13) in our experiments; namely, the formation of Xe₂Cl^{*} through production of XeCl^{*}(B). Further studies will be needed to determine whether process (11) or (12) is dominant.

We have examined the degree that collisional deactivation of $Xe^{*}(6p)$, as described by Eqs. (3) and (4), contributes to the quenching process. In Fig. 6 we plot the production of Xe* $6p[3/2]_1(2p_7)$ and $6p[3/2]_2(2p_6)$ with and without Cl₂, while selectively exciting $6p[1/2]_0(2p_5)$. No change in the intensity of the product channels is observed with the addition of chlorine, though we do observe an increased broadening of the transitions. The only contributions to reactions of the form of Eq. (3) are collisions with xenon as studied earlier.^{1,2} We conclude that all of the quenching of $Xe^{*}(6p)$ by Cl_2 over the buffer gas pressure range from 10 to 250 Torr results in the product XeCl*(B). Only for the higher energy $Xe^* 6p'$ and 7p manifolds do we find significant production of $XeCl^*(C)$. A XeCl(B,C)spectrum resulting from excitation of $Xe^{*}7p[5/2]_{2}$ is shown in Fig. 7. The ratios of integrated intensities for production of XeCl(B) and XeCl(C) are summarized in Table III. The wavelength region for the intensity I_{B-X} is defined to be 320 nm to 235 nm, and the intensity I_{C-A} is defined to be 460 nm to 320 nm. The xenon pressure was 10 Torr and the chlorine pressure 0.010 Torr.



FIG. 6. Fluorescence of $Xe \delta p[1/2]_0$ and the product channels $Xe \delta p[3/2]_2$ and $\delta p[3/2]_1$ while exciting $Xe \delta p[1/2]_0$ selectively. Curve (a) is without Cl₂ and the measured intensity has been multiplied by a factor of 10. Curve (b) is with 6 Torr Cl₂.

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FIG. 7. XeCl(B,C) florescence spectra from 270 nm to 380 nm while exciting Xe* $7p[5/2]_2$. The xenon pressure was 100 Torr while the chlorine pressure was 0.100 Torr. Similar data is obtained at 10 Torr xenon and 0.100 Torr chlorine.

V. CONCLUSIONS

We show in Table I a comparison of the measured reaction rates with the harpoon model. This model includes the effects of the attractive covalent potentials, though these corrections are small at the large distance of our crossings. The valence potential can be written

$$V(R) = E(Xe^*) - \frac{C_6}{R^6}$$
(11)

where C_6 is long-range interaction between Xe* and Cl₂. For Xe*(6p) we have estimated C_6 with chlorine using the measured C_6 with Xenon,²⁹ the known C_6 and polarizability for Cl₂ (1.62×10⁶ cm⁻¹ Å⁶ and 4.6 Å³),³⁰ the Slater Kirkwood formula³⁰ to relate α for Xe* to C_6 for Xe*–Xe*, and the combination approximation³¹

$$\frac{\alpha_a \alpha_b}{C_{ab}} = \frac{1}{2} \left(\frac{\alpha_a \alpha_a}{C_{aa}} + \frac{\alpha_b \alpha_b}{C_{bb}} \right).$$
(12)

We find C_6 for Xe^{*}(6p) - Cl₂ = 1.17×10^7 cm⁻¹ Å⁶. At the distance of the crossing the contribution to the potential is small, hence the valence potential is essentially flat. The crossing radius R_c can be determined by equating the ionic and valence potentials:

$$\frac{e^2}{R_c} + \frac{e^2\alpha}{2R_c^4} = IP(Xe^*) - EA(Cl_2) + \frac{C_6}{R_c^6},$$
 (13)

where IP is the ionization potential for the particular excited state, EA is the electron affinity of the halogen, and α is the sum of polarizability of the ions. At long range the contribution to the potential by the polarization can be neglected and one has a simple Coulomb potential. A simple harpoon model assumes that the reaction occurs whenever the reactants reach the crossing radius R_c as given by Eq. (13). The cross section for this model was given by Lijnse³² and reviewed by Gislason.³³ Gislason also reported the resultant reaction rate

FABLE III. Integrated ratio of intensities for
$$XeCl(B)$$
 and $XeCl(C)$.

	6p[1/2] ₀	6p'[3/2] ₂	7 <i>p</i> [1/2] ₀	7p[3/2] ₂	7p[5/2] ₂
$\frac{I_{B-X}}{I_{C-A}}$	~ 50	1.06	1.51	1.28	1.33

where he defined a reduced temperature

$$T_r = kTR_c^6/C_6.$$
 (15)

For all three states shown in Table I, $T_r > 20$, and we can use the approximation

$$f(T_r) = 1 + T_r^{-1} - (2/5)T_r^{-2} + \cdots.$$
 (16)

For this model we obtain the results shown in Table I. There is some controversy as to the proper value for the electron affinity.⁶ We have used the vertical electron affinity for Cl₂ of 1.02 eV for the calculation in Table I. In experiments with alkali halides,33 this value for the electron affinity leads to a cross section which is too small; however, in our case, the model is in excellent agreement with our experiment. Of particular interest is the increase in the measured reaction rates with increased excited state energy. The model predicts a similar increase because the crossing radius is larger for states with smaller ionization potentials. As stated earlier, one might expect the increase in radius to be offset by a decrease in the charge transfer probability at the crossing. Indeed, as shown in Table II, the higher Rydberg $Xe^{*}(7p)$ states are found to be considerably smaller than πR_c^2 , although they have substantially larger experimental cross sections ($\sim 900 \text{ Å}^2$). In an accompanying paper we describe a more detailed, multistate, Landau-Zener model for the harpoon reaction.¹⁹ This calculation is also in good agreement with the experiment and demonstrates that the smaller charge transfer probabilities observed at larger crossing radii are compensated by the large density of crossings that exist in the multistate calculation.

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 $k(T) = \pi R_c^2 < v(T) > f(T_r),$

(14)

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