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Nonresonant collision-induced absorption in Xe/Cl₂ mixtures

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Mixtures of Xe and Cl_2 have been irradiated at 193 nm with a pulsed ArF laser. The collision-assisted laserinduced absorption results in emission of XeCl (*B* and *C*) at 308 and 340 nm, respectively. The intensity of XeCl emission is found to vary linearly with ArF laser power, indicating the occurrence of a single photonassisted collision-induced process. The temporal characteristics of the emission vary substantially with the number density of each reagent showing fast formation and decay rates at high densities, but slower rates at lower densities. A kinetic mechanism is proposed in which a $(XeCl_2)^*$ transient complex is initially formed and that complex subsequently dissociates to yield XeCl^{*}.

We report here evidence for collision-induced, single-photon excitation of XeCl* in Xe/Cl₂ gas mixtures pumped at 193 nm, a wavelength at which neither individual reagent appreciably absorbs. Recently, there have been several computational^{1,2} and experi $mental^{3-5}$ studies of systems where a laser field which is not in resonance with stable states of "separated" collision partners, i.e., the isolated reagents, effects the outcome of a collisional event. An elegant illustration of this process has been published by Brooks and co-workers, 6 who, in a crossed beam single collision experiment, studied the production of HgBr(B) while irradiating the collision zone defined by the intersecting beams of K and HgBr₂ with laser radiation at 590 nm. HgBr(B) is energetically inaccessible in the absence of the laser field, and neither of the reagents absorbs the laser radiation. The present results for excitation of XeCl* in mixtures of Xe and Cl₂ pumped at 193 nm represent another example of a collision-induced laser-assisted chemical reaction.

In our experiments 193 nm radiation from a pulsed ArF laser (100 mJ/pulse, 12 nsec pulsewidth, 10 Hz) was passed through a fused silica cell (2.5 cm dia. \times 15 cm long) containing mixtures of Xe and Cl₂ at room temperature. Visible and UV side fluorescence from the cell was dispersed spectrally in a 1 m monochromator and monitored with an optical multichannel analyzer or fast photomultiplier. Measurements were made of (1) the spectrum of the fluorescence between 190 and 900 nm, (2) the dependence of the fluorescence at 308 nm on laser pump power, and (3) the temporal shape of the fluorescence on reagent (Xe and Cl_2) and buffer (He) gas densities. Experiments were carried out with both focused and unfocused pump beams $(10^7 - 10^9 \text{ W/cm}^2)$ for several mixtures of reagent gases (Cl₂-0.5 to 10 Torr; Xe-5 to 760 Torr; He-O to 800 Torr).

Figure 1 is an energy level⁷⁻¹² diagram of the $Xe-Cl_2$ system. Absorption by the $Xe-Cl_2$ collision pair may occur at internuclear separation(s) at which the 193 nm photon energy becomes resonant with the energy separation of the ground and excited state $Xe-Cl_2$ potential energy surfaces. We postulate that absorption at 193

nm produces an excited state of $XeCl_2$ which dissociates upon collision to form $XeCl^*(B, C)$. This process is endothermic by less than 500 cm⁻¹ and thus should proceed rapidly via collisions with background gas. Evidence for this formation mechanism is given below.

Examination of fluorescence spectra showed that the only discernible emission from any of the gas mixtures was from the *B* and *C* states of XeCl at 308 and 340 nm, respectively. Broadband emission at 470 nm from Xe_2Cl^{13} also appeared in gas mixtures containing high Xe concentrations. No other identifiable atomic or molecular emission was seen between 200 and 900 nm. The band fluorescence at 308 nm indicated emission from a vibrationally relaxed XeCl (*B*) state even for total gas pressures in the absorption cell as low as 5 Torr. The fluorescence intensity showed a linear de-



FIG. 1. Energy level diagram of Xe/Cl₂. Energy of Xe + Cl₂ defined as zero. Xe states from Ref. 11. Cl₂ states from Ref. 8. XeCl states, Ref. 9. XeCl₂ from Ref. 10. Separation of XeCl (*B*, *C*) discussed by Refs. 7, 8, and 14. E. A. of Cl₂ given by Ref. 12. R_x calculated by R_x (Å) = 14.35/ ΔE (eV).

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FIG. 2. XeCl (B) fluorescence signal vs pulse energy. Circles indicate ArF excitation. Triangles indicate KrF excitation. Solid points, focused laser. Open circles, unfocused laser. Solid lines, slope = 1 passing through experimental ArF data points. Note curvature of solid points at high pulse energy. Solid line, slope = 2 passing through KrF data.

pendence on both Xe and Cl₂ number densities.

The XeCl $(B \rightarrow X)$ fluorescence intensity at 308 nm was monitored as a function of incident pump power in order to help establish a mechanism for excitation of XeCl*. Typical laser power dependence data are plotted in Fig. 2. The fluorescence intensity obtained using both focused and unfocused pump laser beams is seen to increase linearly with pump laser power at 193 nm. This result rules out two photon pumping mechanisms such as those proposed in earlier studies of rare-gas halogen mixtures pumped at 193 nm.¹⁴⁻¹⁶ As a check on this finding the Xe/Cl_2 gas mixtures were also excited at 249 nm using a KrF laser. Radiation at 249 nm has insufficient photon energy to excite XeCl* from ground state Xe and Cl_2 in a single-step process. The data (see Fig. 2, solid triangles) showed a clear quadratic dependence of the XeCl* fluorescence intensity on pump laser power indicating that two 249 nm photons are necessary to form XeCl*.

Measurements were also made of the pulse shape of the emitted 308 nm light as a function of reagent and buffer gas concentrations. For these measurements the 308 nm fluorescence was monitored using a fast photomultiplier (3 nsec risetime) and oscilloscope (500 MHz bandwidth). The pulse shapes were found to have both slower rise and decay times at lower reagent densities $(e^{-1}$ times of 100 and 500 nsec, respectively for 5 Torr Xe and 0.5 Torr Cl₂) than at higher densities (5 nsec rise and 10 ns decay times for 750 Torr Xe and 10 Torr Cl₂). These results strongly suggest that production of XeCl* proceeds via absorption at 193 nm by the Xe-Cl₂ collision pair followed by collisional dissociation by the background gas. In order to check this hypothesis we examined the fluorescence pulse shapes for gas mixtures containing 0.5 Torr Cl₂, 5 Torr Xe and increasing pressures of helium from 50 to 800 Torr. The time integrated 308 nm fluorescence in these experiments was found to increase with

He pressure up to 200 Torr but to remain relatively constant thereafter. Both the rise and decay times of the fluorescence pulses were found to decrease as He was added. We believe that the increase in XeCl^{*} fluorescence results from collisional dissociation of an XeCl^{*}₂ intermediate state into XeCl^{*} (B, C) and Cl. At pressures above 200 Torr the conversion to XeCl^{*} is essentially complete. Thus, the sequence of reactions for the production of XeCl^{*} following irradiation of Xe/Cl₂ mixtures at 193 nm is believed to be

$$Xe + Cl_2 + h\nu - XeCl_2^*, \tag{1}$$

$$XeCl_{*}^{*} + M \rightarrow XeCl_{*}^{*} + Cl + M.$$
⁽²⁾

Both the linear dependence of the fluorescence on pump intensity and reagent densities, and the absence of fluorescence from other than vibrationally relaxed XeCl* indicate that pumping is by a single photon which accesses the XeCl* (B, C) states near the bottom of their potential wells.

There is the possibility of a concurrent process, namely, absorption by chlorine molecules at 193 nm. An excited state might be created which subsequently could react with Xe via a harpoon mechanism¹⁷ to form XeCl^{*}. However, no evidence of Cl_2^* was observed even at the highest Cl_2 densities.¹⁸ This alternative process would not explain the variation of XeCl B-Xfluorescence with He density either, since the rate of XeCl* formation from reaction of excited molecular chlorine with xenon would be independent of He density. Furthermore, absorption by Cl_2 at 193 nm is known to be quite weak $(\sigma \simeq 10^{-21} \text{ cm}^2)^{19}$ and is thought to result in dissociation into Cl atoms,²⁰ Even if translationally energetic Cl atoms were formed under these conditions, they would have insufficient energy to react with Xe to form XeCl^{*}. (The reaction of these translationally "hot" Cl atoms with Xe to form XeCl* is calculated to be ~ 2.5 eV endoergic, thus making this reaction mechanism unlikely.) The apparent saturation of the 308 nm fluorescence (Fig. 2, solid points) implies an absorption cross section of ~ 10^{-18} cm², i.e., $\sigma = h\nu/I_{sat}$, where $h\nu = 10^{-18}$ J and $I_{sat} \approx 1$ J/cm², which is significantly larger than that for Cl₂. Thus, any contribution to the XeCl* fluorescence signal due to initial absorption by Cl_2 is expected to be minimal.

The identity of the excited state of $XeCl_2$ pumped at 193 nm is at present unknown. The moderately large absorption cross section (10^{-18} cm^2) estimated above, together with the slow rate of formation of XeCl* measured at low gas densities indicates that the XeCl, reservoir state is relatively stable. The ground state of XeCl₂ is thought to lie about 1.8 eV above the Xe-Cl₂ asymptote, ¹⁰ which explains why XeCl₂ has not been observed at room temperature. No fluorescence ascribable to XeCl^{*}₂ emission was observed which could verify the energy of ground state XeCl₂. However, absorption by XeCl₂ might be amenable to study using matrix isolation techniques.²¹ Our results suggest the existence of a bound state lying approximately 4.6 eV above the ground state of XeCl₂. Ab initio calculation of the XeCl₂ states would be invaluable in providing a basis for better understanding of the phenomena described here.

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