

Reactions in the afterglow of time modulated inductive discharges of Xe and I₂ mixtures

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An investigation was conducted using absorption and emission spectroscopy of the afterglow from rf inductive discharges in Xe/I₂ mixtures. RF power at 11.5 MHz was supplied to coils surrounding a cylindrical discharge cell. Total pressures were between 0.8 and 5.3 Torr. Measurements were made as a function of radius and time following the termination of the discharge. Results presented here indicate that in the afterglow the XeI* excimer is formed by highly excited I₂ and ground state Xe. Evidence is also presented that ion-ion neutralization is a major precursor reaction for the formation of other excited species in the afterglow. © 1998 American Institute of Physics. [S0021-8979(98)03120-X]

I. INTRODUCTION

Radio frequency (rf) inductively excited discharges of Xe and I₂ mixtures may be a means of providing multiwavelength UV lighting sources. The gas kinetics of rare gas/halogen mixtures have been previously studied for a variety of applications, especially in the development of excimer lasers. These mixtures have been studied mainly at high pressures from a few hundred Torr to a few atmospheres.¹ A few studies of the rare gas halides have been conducted at lower pressures, 20–80 Torr, primarily using pulsed radiolysis.^{2–4} Those studies which were not conducted using pulsed radiolysis, such as using UV excitation, generally addressed exciting specific states of the molecular halogen or the rare gas metastable.^{5–7}

At higher total pressures, a few hundred Torr or more, negative ion-positive ion reactions tend to be the dominant precursor process for formation of the rare gas halide exciplexes. At these pressures, the ion-ion recombination reactions involve three-body processes either directly in the reaction or indirectly through precursor reactions which provide the necessary reactants. When operating a discharge at low pressures, the rate at which three-body processes occur are greatly diminished. At tens of Torr total pressure, the harpoon reaction becomes the dominant precursor reaction in which the excited or metastable rare gas reacts with the ground state molecular halogen:



There is some question as to whether the harpoon reaction dominates at 10³ Torr total pressure specifically for Xe/I₂ mixtures as opposed to other rare gas halides.^{4,8,9}

Low pressure (0.8–5.3 Torr), inductively excited, rf discharges in Xe/I₂ mixtures have been investigated to determine the kinetics and radiative processes leading to UV emission from atomic and molecular species, including the

XeI* exciplex. In this article, evidence is presented that the exciplex XeI*(B) is also formed through the reverse harpoon reaction in the afterglow of the discharge as with the steady state discharge.¹⁰ Evidence is further presented which indicates that ion-ion neutralization is a major precursor reaction for the formation of other excited species in the afterglow in addition to I*(²P_{3/2}).¹¹ Although the results presented here are for specific gas mixtures, they are representative of the entire pressure range (0.8–5.3 Torr) investigated.

II. THE EXPERIMENTAL APPARATUS

The basic experimental apparatus has been previously discussed and will only be briefly described here.^{10,11} The discharge cell was filled with an iodine partial pressure of approximately 0.3 Torr, the vapor pressure of I₂ at room temperature. The partial pressure for Xe ranged from 0.5 to 5.0 Torr. The diagnostics used on the afterglow produced by rf inductively coupled discharges of Xe/I₂ mixtures included optical absorption spectroscopy and emission spectroscopy. RF power at 11.5 MHz was supplied to cylindrical coils surrounding the discharge cell.

Power to the discharge coils was modulated on and off to observe decay of emission from excited states. Observations were made as a function of radius in the discharge and of time following termination of the discharge. Decay of power to the coils occurred in a few microseconds for the capacitively coupled discharges and less than a microsecond for the inductively coupled discharges. As the power into the system is increased, the discharge abruptly switches from a capacitive mode to an inductive mode. The current and voltage waveforms for the coils shows a large phase shift between the voltage and current which decrease after the switch to the inductive mode. With capacitive coupling, optical emission decay is a few microseconds which is the same as the electric time constant of the discharge circuit. When the discharge is inductively coupled, the optical emission

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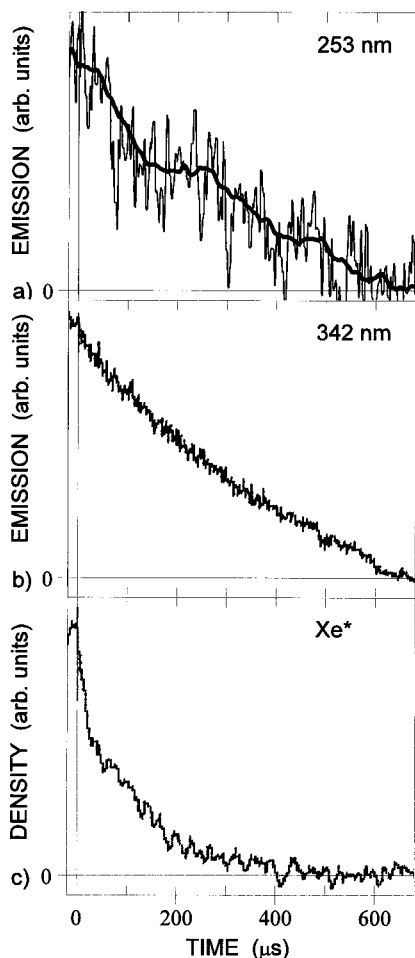


FIG. 1. Comparison of XeI^* and I_2^{**} emission decay and Xe^* metastable decay for 1.0 Torr $\text{Xe}/\approx 0.3$ Torr I_2 discharge cell following termination of the discharge. Although 342 nm emission is from an I_2^{**} state that does not participate in the reverse harpoon reaction it represents those states that do. Given is (a) $\text{XeI}^*(B \rightarrow X)$ 253 nm, (b) $\text{I}_2^{**}(D' \rightarrow A')$ 342 nm, (c) $\text{Xe}^*(6s_{12})$ metastable.

decays in 100's μs . This decay is not necessarily exponential.

III. $\text{XeI}(B)$ FORMATION

Previous work demonstrated that the reverse harpoon reaction given by



is the dominant precursor reaction for $\text{XeI}^*(B \rightarrow X)$ emission, as opposed to the harpoon reaction, in the steady state discharge. In the case of the reverse harpoon reaction, a highly excited halogen molecule reacts with the ground state rare gas atom instead of the metastable rare gas atom reacting with the ground state halogen molecule. Note that the partial pressures of Xe and I_2 quoted here are for the initial gas fill. The molecular iodine is more than 90% dissociated, as determined from laser-induced fluorescence (LIF) measurements. This makes the density of Xe two to four orders of magnitude larger than I_2 during the discharge.

There are several indications that the reverse harpoon reaction also occurs in the afterglow. First, there is no unex-

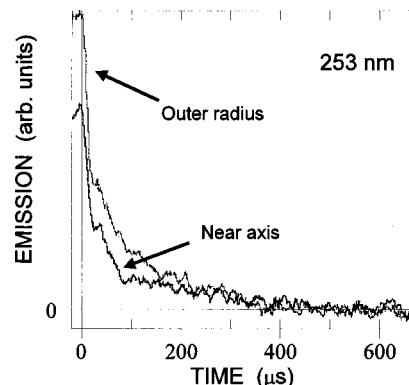


FIG. 2. For 0.5 Torr $\text{Xe}/\approx 0.3$ Torr I_2 , ≈ 40 W power, the XeI^* emission is greater at the radial edge than at the center as with I_2^{**} emission.

pected change in XeI^* emission when power is modulated off to indicate a different mechanism from the steady state discharge. Further, the time-dependant emission for $\text{XeI}^*(B \rightarrow X)$ 253 nm is consistently the same as for I_2^{**} under varying conditions as would be expected if the reverse harpoon reaction dominated. This correlation is shown in Fig. 1. Although the comparison is made with $\text{I}_2^{**}(D' \rightarrow A')$ 342 nm emission, a state that does not directly lead to the XeI^* exciplex, all I_2^{**} emission has a similar time history. I_2^{**} emission was principally recorded at 271 nm ($G \rightarrow X$), 277 nm ($F \rightarrow B$), 342 nm ($D' \rightarrow A'$), 429 nm ($E, D \rightarrow B$). All of the forgoing transitions for I_2^{**} begin from states with overlapping vibrational manifolds strongly suggesting that the I_2^{**} states which can react with ground state Xe to form XeI^* are populated in a similar fashion.¹²

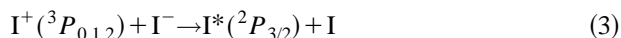
The $\text{XeI}^*(B \rightarrow X)$ emission has a different time dependence than the time dependence of the $\text{Xe}^*(6s_{12})$ metastable decay or Xe^{**} optical emission. Although the difference in form is inconclusive with respect to determining which mechanism is responsible for formation of the exciplex without knowledge of the change in I_2 density, the fact that the XeI^* emission has a significantly longer decay time than the Xe^* metastables is conclusive. If XeI^* is formed by the harpoon reaction, then XeI^* emission would cease with the depletion of the Xe^* metastables and this does not occur. The $\text{XeI}^*(B)$ state has a lifetime of about 15 ns and so its emission tracks its rate of formation. This leaves reaction (2) as the likely process for formation of the exciplex. It is doubtful that another yet undiscovered mechanism is responsible for XeI^* formation considering the volume of work completed in this area.

The previous arguments are strong indications that the reverse harpoon reaction is the dominant excitation process. If reaction (2) is responsible for populating XeI^* then certain trends for XeI^* and I_2^{**} emission should follow. XeI^* emission in the afterglow is greater at the outer radius of the discharge than along the axis. This is also true for I_2^{**} as shown in Fig. 2. This correlation is required since ground state Xe is roughly uniform in density across the radius of the discharge tube. This fact by itself does not preclude the harpoon reaction since even though the metastable Xe density is greater in the center of the discharge than the edge as

with Xe** emission, the I₂ density is larger at the edge. The difference in emission between the radial edge and center is essentially the same for both I₂** and XeI* as required for the reverse harpoon reaction to dominate. For other excited state emission, such as I*(²P_{3/2}→²P_{1/2}) 206 nm and I**(⁴P_{3/2}→⁴P_{5/2}) 804 nm, the time dependence of the decay varies from center to edge in a distinctly different manner.

IV. ION-ION NEUTRALIZATION

It was previously demonstrated that ion-ion neutralization given by

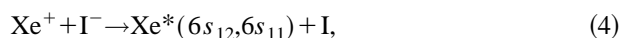


is the dominate precursor reaction for I*(²P_{3/2}→²P_{1/2}) emission in the afterglow. It is quite plausible that ion-ion neutralization paths are responsible for populating excited states of other species which result in UV emission in the discharge or its afterglow. Emission decay data provides evidence of that occurrence.

A mechanism other than ion-ion neutralization that might result in the excitation is collisions of Xe* metastables with other species causing the upper states of these species to be populated. This is not likely since Xe* metastables decay quickly with there being no change in the longer decay of I*, I**, and I₂** occurring after the loss of Xe*. This process would also not explain the nonexponential decay of I₂**, for example, unless some process was continuing to populate the xenon metastable state after termination of power to the discharge. Electron-ion recombination will not be likely at lower pressures since three-body processes are greatly diminished. One possible exception may be I₂⁺ + e → I₂** + I, but this process cannot account for Xe** and I₂** emission.

Long optical emission decay times after electron thermalization may be explained by radiation trapping or imprisonment.¹³⁻¹⁵ This process occurs when the photon emitted during electronic relaxation is reabsorbed by another particle of the same species in the lower state prior to exiting the discharge cell. This may happen a number of times resulting in the extended decay. In the case of radiation trapping the decay will still be exponential with the decay occurring on a longer time scale. However, the decays observed here are often not exponential, especially at higher powers, and this indicates another source for populating the excited states.

It has been previously determined that I⁻ densities, resulting from dissociative attachment, increase following electron thermalization and this increase may result in the nonexponential decays observed.¹¹ Suggested ion-ion neutralization paths for xenon and molecular iodine emission are



Preventing the complete thermalization of electrons by maintaining a low power deposition following discharge termination decreased the emission of I*, I**, and I₂** as would be expected for neutralization of a positive ion with I⁻. Although Xe* and Xe** are only slightly affected, these states decay much more rapidly. Electron thermalization occurs in

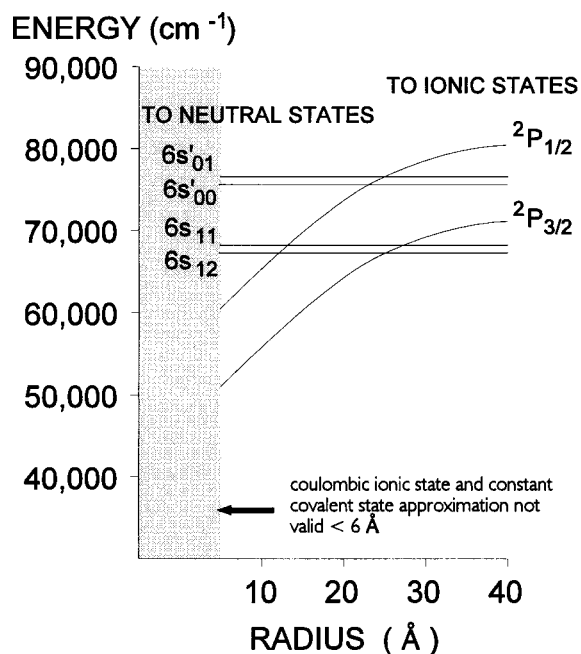
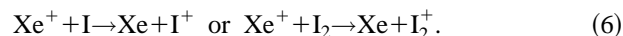


FIG. 3. Xe⁺ and I⁻ neutralization. The diagram indicates preferential population of the 6s₁₁ and the 6s₁₂ states of Xe.

10's μs which is slightly shorter than the decay times of Xe*. The more rapid decay of excited xenon occurs since the precursor ion Xe⁺ in reaction (4) can be additionally depleted via charge exchange reactions with iodine:



Landau-Zener theory provides an indication of which states may be populated by ion-ion neutralization.^{11,16-18} Possible ion-ion neutralization paths for reaction (4) are displayed in Fig. 3. Since the majority of Xe⁺ ions will be in the ground state, Xe*(6s₁₁) and Xe*(6s₁₂) are preferentially populated. At higher applied powers, the fraction of Xe⁺(²P_{1/2}) ions will increase resulting in more 6s' and lower 6p states of Xe** being populated. Since Xe**(6s₁₁, 6s₁₂) states are favored, Xe** emission may result from Xe* + χ → Xe** + χ, where χ may be hν, e, M*, etc. This is plausible since Xe**(6p₁₂, 6p₀₀, 6p'₁₂) and Xe*(6s₁₁) emission always decay in the same manner.¹¹

V. CONCLUDING REMARKS

In conclusion, the XeI* exciplex is formed in the afterglow by highly excited I₂ and ground state Xe as opposed to the harpoon reaction. Ion-ion neutralization is a major precursor reaction for the formation of other excited species present in the afterglow such as Xe*, Xe**, I₂^{*}, and I₂** and not just for I*(²P_{3/2}). Since the emission does not significantly drop when the power is modulated off, this indicates that ion-ion neutralization plays an important role as well in the steady state discharge for high power inductively coupled discharges of Xe/I₂. These conclusions may well apply to rare gas/halogen mixtures other than Xe/I₂.

ACKNOWLEDGMENTS

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¹*Excimer Lasers*, edited by Ch. K. Rhodes (Springer, Berlin, 1984).

²I. Nakamura, F. Kannari, and M. Obara, *Appl. Phys. Lett.* **57**, 2057 (1990).

³K. Tamagake, D. W. Setser, and J. H. Kolts, *J. Chem. Phys.* **74**, 4286 (1981).

⁴S. P. Mezyk, R. Cooper, and J. Sherwell, *J. Phys. Chem.* **97**, 9413 (1993).

⁵B. V. O'Grady and R. J. Donovan, *Chem. Phys. Lett.* **122**, 503 (1985).

⁶H. Hemmati and G. J. Collins, *J. Appl. Phys.* **51**, 2961 (1980).

⁷N. K. Bibinov, I. P. Vinogradov, and L. D. Mikheev, *Sov. J. Quantum Electron.* **13**, 516 (1983).

⁸R. Cooper, F. Grieser, and M. C. Sauer, *J. Phys. Chem.* **81**, 1889 (1977).

⁹R. Cooper, L. S. Denison, P. Zeglinski, C. Roy, and H. Gillis, *J. Appl. Phys.* **54**, 3053 (1983).

¹⁰P. N. Barnes and M. J. Kushner, *J. Appl. Phys.* **80**, 5593 (1996).

¹¹P. N. Barnes and M. J. Kushner, *J. Appl. Phys.* **82**, 2150 (1997).

¹²P. N. Barnes, Ph.D. thesis, University of Illinois at UC, 1996.

¹³T. Holstein, *Phys. Rev.* **72**, 1212 (1947).

¹⁴D. G. Hummer and P. B. Kunasz, *J. Quant. Spectrosc. Radiat. Transf.* **16**, 77 (1976).

¹⁵H. M. Anderson, S. D. Bergeson, D. A. Doughty, and J. E. Lawler, *Phys. Rev. A* **51**, 211 (1995).

¹⁶R. E. Olson, J. R. Peterson, and J. Moseley, *J. Chem. Phys.* **53**, 3391 (1970).

¹⁷R. E. Olson, F. T. Smith, and E. Bauer, *Appl. Opt.* **10**, 1848 (1971).

¹⁸M. J. Kushner, *J. Appl. Phys.* **54**, 39 (1983).