Formation of XeI(B) in low pressure inductive radio frequency electric discharges sustained in mixtures of Xe and I$_2$

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Low pressure excimer discharges ($<$1–5 Torr) are of interest for use as ultraviolet sources for lighting applications. XeI(B) is an attractive candidate for excimer lamps due to the low corrosive properties of iodine. The excimer is thought to be formed by either harpoon or ion-ion recombination reactions, the latter of which requires a third body. The formation of the excimer at low pressures is therefore problematic. To address this issue, an investigation was conducted to determine the kinetic processes which produce XeI(B) in a low pressure (0.5–5 Torr) inductive radio frequency discharge sustained in Xe and I$_2$. The diagnostics applied in this study include laser-induced fluorescence, optical absorption spectroscopy, and optical emission spectroscopy. Our results indicate that for the experimental conditions, Xe+I$_2^{**}\rightarrow$XeI(B)+I is a major reaction producing the excimer. This result differs from studies performed at higher pressures which concluded that the harpoon reaction between Xe* and I$_2$ or ionic recombination between Xe$_2^+$ and I$^-$ are the major sources of XeI(B). © *1996 American Institute of Physics.* [S0021-8979(96)03222-7]

I. INTRODUCTION

Low pressure rare gas-halogen electric discharges producing excimer radiation are attractive candidates for ultraviolet (UV) lamps. Although there are many existing UV lamps which use mercury, deuterium, and xenon gas mixtures, rare gas-halogen excimers generate UV radiation in broad bands at wavelengths generally not provided by existing sources. In applications, where the wavelength is not critical, such a multiwavelength UV source may be of interest. Mercury lamps are the most common source of UV radiation due to their high efficiency. However, the use of mercury in these lamps poses disposal and environmental problems. An efficient UV source that is more environmentally benign such as rare-gas halogens, would be a significant advance in the field.

Most of the current research on UV excimer lamps has been at high pressures (several hundred Torr or more), and have used microwave discharges or dielectric barrier discharges as excitation sources.[1–9] Due to their high operating pressures, these discharges are typically either confined to small volumes or are filamentary. Lower pressure discharges which operate as a uniform glow may be more applicable as general lighting sources. In this regard, radio frequency (rf) low pressure inductive discharges operating at a few Torr could be a viable source for lighting.[10–14] The rf inductive discharges typically do not require large voltages to drive displacement currents as in capacitively driven discharges. From a plasma ignition standpoint, a low pressure discharge can be initiated at lower voltages thereby simplifying the electrical driving circuitry. This is particularly important for rare-gas halogen mixtures which are typically highly attaching.

In this article, we report on an investigation of low pressure (0.5–5 Torr) rf inductive discharges sustained in Xe/I$_2$ mixtures for production of UV radiation from XeI($B\rightarrow X$) at 253 nm. The XeI($B\rightarrow X$) excimer was chosen for this study due to the low reactivity of iodine with lamp materials compared to fluorine and chlorine mixtures as used in more conventional excimer lighting sources. We found that at the pressures and gas mixtures of interest, XeI(B) is likely formed by a reaction between ground state xenon and excited states of I$_2$, Xe+I$_2^{**}\rightarrow$XeI(B) + I. This conclusion differs from works performed at higher pressures where it was found that the harpoon reaction or ion-ion recombination are the dominant excimer forming reactions.[15,16]

A brief overview of the kinetics of Xe/I$_2$ discharges is given in Sec. II followed by a description of the experiment in Sec. III. A discussion of our experimental results for excited state emission and absorption in Xe/I$_2$ discharges appears in Sec. IV, followed by our concluding remarks in Sec. V.

II. KINETICS IN Xe/I$_2$ DISCHARGES

The majority of research on the kinetics of rare gas and halogen mixtures for the development of excimer lasers has been performed at high pressures (few hundred Torr to a few atmospheres).[15] It is generally accepted that at these pressures the rare-gas-halide excimers are primarily formed through either the ''harpoon'' reaction or ionic recombination.[15–18] In the harpoon reaction, excited states of the monomer or dimer rare gas collide with the molecular halogen, producing the excimer state. For example, in the Xe/I$_2$ system XeI(B) may be formed by
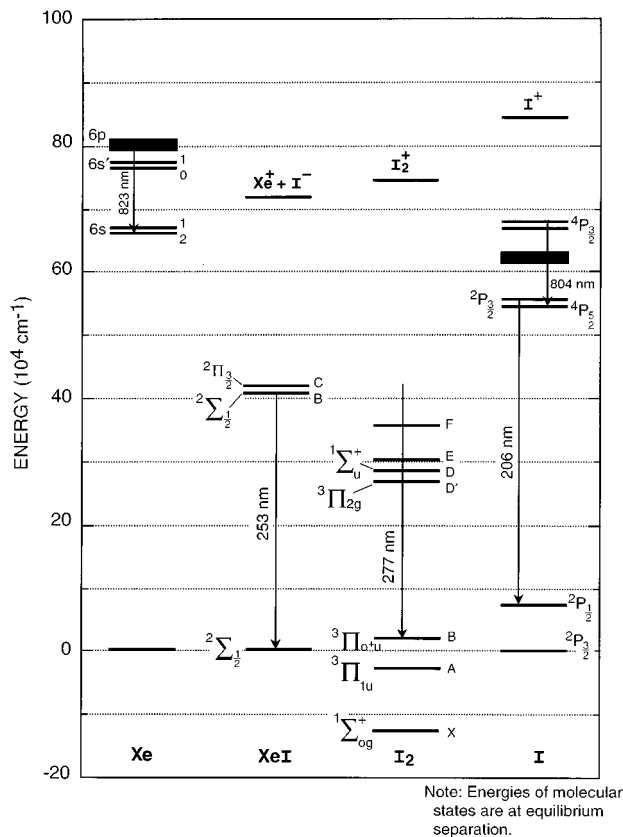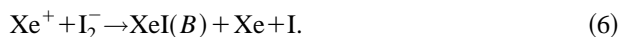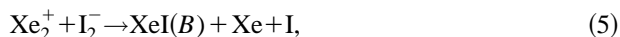
[a]Electronic mail: mjk@uiuc.edu

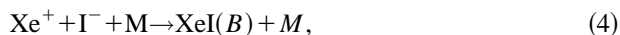FIG. 1. Energy level diagram of states of interest in the Xe/I_2 system.

FIG. 2. Schematic of the experimental apparatus. (a) Electrical circuit for inductively powering the discharge cell. (b) Layout for optical diagnostics.

$$Xe_2^* + I_2 \rightarrow XeI(B) + Xe + I, \tag{1}$$

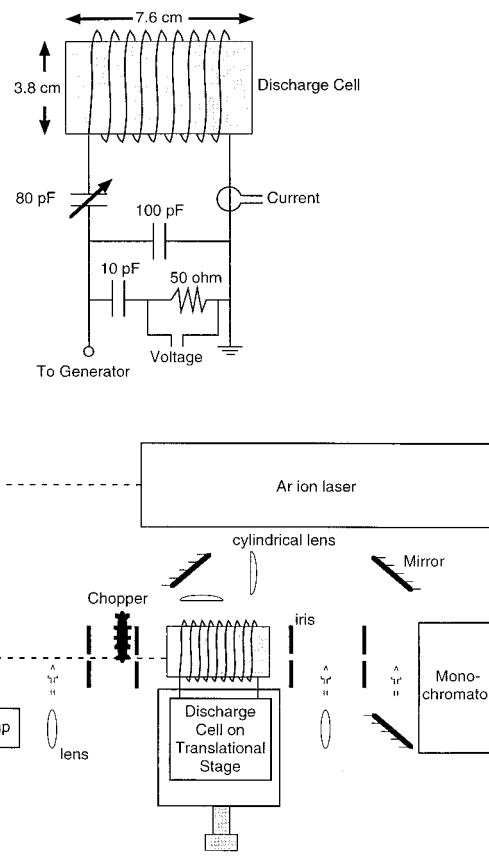$$Xe^* + I_2 \rightarrow XeI(B) + I. \tag{2}$$

(An energy level diagram of the states of interest is in Fig. 1.) The former process is not expected to be important at low pressures since the formation of Xe_2^* requires a third body. The ion recombination processes include

$$Xe_2^+ + I^- \rightarrow XeI(B) + Xe, \tag{3}$$

$$Xe^+ + I^- + M \rightarrow XeI(B) + M, \tag{4}$$

$$Xe_2^+ + I_2^- \rightarrow XeI(B) + Xe + I, \tag{5}$$

$$Xe^+ + I_2^- \rightarrow XeI(B) + Xe + I. \tag{6}$$

In all cases, the ion-ion recombination reaction either directly requires a third body (reaction 4) or a third body is required to generate a reactant (Xe_2^+ or I_2^-). Therefore, one should expect these reactions to diminish in importance at low pressures. Typically, the harpoon reaction is the major reaction for excimer formation at 10s Torr pressure and ion-ion recombination is the major reaction at 100s Torr pressure or more.

A 2-body reaction which can, based on energetics, result in formation of XeI(B) is reverse harpoon reaction.

$$Xe + I_2(^3P, {}^1D) \rightarrow XeI(B) + I. \tag{7}$$
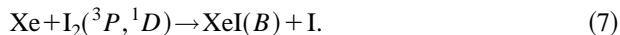
This reaction is attractive for formation of XeI(B) at low pressures, since a third body is not needed, and when operating at large mole fractions of I_2. Under these conditions, a large proportion of the discharge energy is channeled into the I_2 and the electron energy distribution may be cut off, thereby reducing the rate of formation of the rare gas excited states. O'Grady and Donovan,[19] and Bibinov et al.[20] cite evidence that XeI*(B) may be formed by the reverse harpoon reaction. In pulsed radiolysis experiments of Xe/I_2 mixtures, Cooper et al.[21] state that formation of XeI(B) cannot be explained by the direct harpoon reaction. They attributed formation of the exciplex by the reverse harpoon reaction or by ionic recombination. Their experiment addressed pulsed radiolysis of $\approx$0.3 Torr I_2 and 50–250 Torr Xe contained in quartz cells.

III. DESCRIPTION OF THE EXPERIMENTAL SETUP

The kinetic processes leading to excitation of XeI(B) in an rf excited low pressure discharge were investigated using a suite of diagnostics including plasma induced optical emission spectroscopy, laser induced fluorescence (LIF), and optical absorption spectroscopy. The experimental setup and diagnostics will be described in this section and are shown schematically in Fig. 2.

The discharge was sustained in cylindrical quartz tubes, 3.8 cm diam and 7.6 cm long, sealed with various mole fractions of xenon and iodine. Iodine crystals, 99.8% assay, were purified by several freeze, pump, thaw, and resublimation cycles in an iodine trap prior to filling the discharge cells. After a cell is filled to the desired partial pressures of

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xenon and iodine, the side arm of the cell is sealed off. The cell is then mounted in the center of the coil of the discharge system and held in place by two or three thin glass rods sandwiched between the cell and the inductive coils.

The rf coil for the system is made of 0.64-cm-diam copper tubing. The axial length of the coil is 6.5 cm and consisted of eight and three-quarters turns. The inside diameter of the coil is 4.43 cm. The current through the coil is measured using a Pearson Electronics, Inc. current transformer with a 100 mV/A output. The voltage measurement is accomplished with a capacitive voltage divider. The signals are detected by a Hewlett Packard 54510A digitizing oscilloscope. Variable rf power is supplied to the coil at 11.3 MHz from a WaveTek model 148 signal generator amplified by an ENI A-300 rf amplifier. Forward and reflected power was measured using a Bird Electronics Corporation model 43 power meter.

The coil and discharge tube were mounted on a translational stage to allow radially resolved optical measurements. Measurements were typically taken 0.06 cm apart. The discharge cell is allowed to warm up for several hours before any measurements are taken to allow the heating of the cell to reach a steady state. The warm up period was terminated when the rf power deposited in the discharge remained steady for half an hour.

Optical emission and LIF were detected using a monochromator and photomultiplier. The monochromator was a 35 cm McPherson Instrument model EU-700 equipped with a 1180 lines/mm diffraction grating blazed at 5000 Å and with the monochromator slit width set at 333 μm. The output from the PRI model photomultiplier (R955 tube) was fed into a Tektronix model 11402 digitizing oscilloscope. The laser beam and source light for absorption were modulated by a chopper with signal detection by a lock-in amplifier. A high pass filter, $\lambda \geq 5200$ Å, was used when observing spectra above 5000 Å to eliminate second order peaks in this region. Radially resolved measurements were made by defining an axial segment of the discharge at constant radius using a pair of irises having 1.95-mm-diam holes.

Laser-induced fluorescence was used to measure the radial variation of the density of molecular iodine. A Coherent Innova 70 argon-ion laser operating at 5145 Å coincides with $X(^1\Sigma_{0g}, \nu'=0) \to B(^3\Pi_{0u}, \nu''=43)$ absorption in I_2.[22–24] The subsequent I_2 fluorescence is detected at 5440 Å $[B(^3\Pi_{0u}, \nu''=43) \to X(^1\Sigma_{0g}, \nu'=5)]$ as a measure of the I_2 density. The LIF is observed at right angles from the laser beam.

Absorption spectroscopy was used to determine the radial variation of the density of $Xe(6s_{12})$ metastable. Radiation at $\lambda=8232$ Å from a xenon lamp was passed through the cell, and absorbed by the $Xe(6s_{12} \to 6p_{12})$ transition. For all conditions of interest, absorption is nearly linearly proportional to the $Xe(6s_{12})$ density.

IV. XeI(B) FORMATION

The previously described diagnostics were applied to low pressure discharges of 0.25, 0.5, 1.0, and 5.0 Torr Xe with 0.3 Torr I_2. Mixtures of 0.1 Torr I_2 with 0.5 and 1.0 Torr Xe were also investigated. Note that these mole frac-
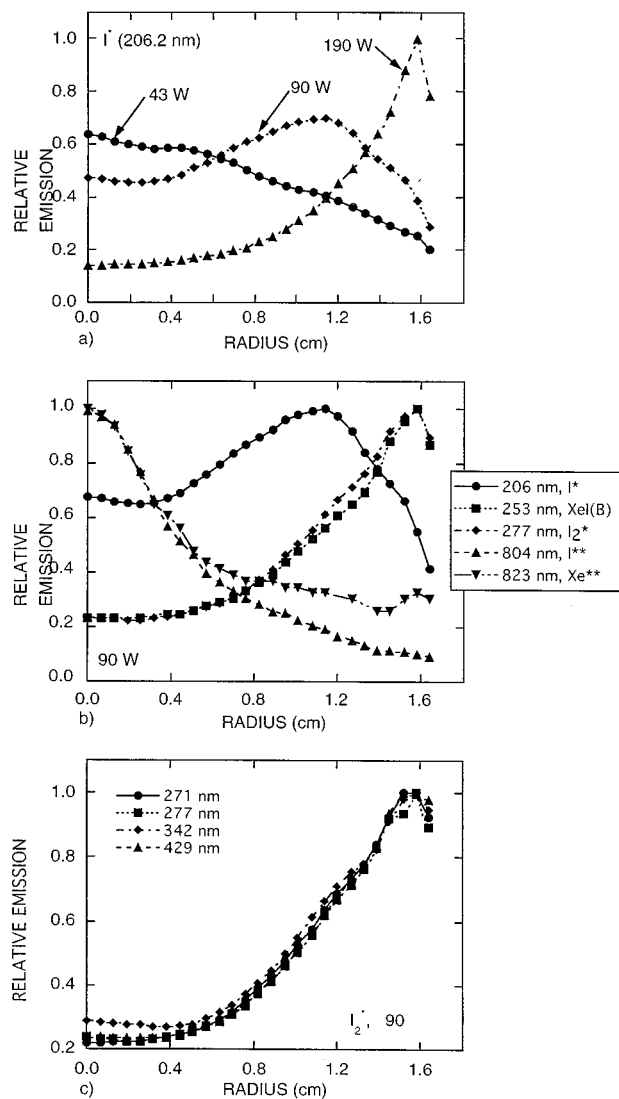

FIG. 3. Optical emission as a function of radius for a gas mixture of 1 Torr Xe/0.3 Torr I_2. (a) I* ($^2P_{3/2} \to ^2P_{1/2}$), $\lambda=2062$ Å for different power depositions. (b) I*, I**, I_2^*, Xe**, and XeI($B \to X$) at 90 W. (c) I_2^{**} at 90 W. Emission from excited states of I_2^{**} (D,E,F) have similar radial profiles, indicating a common population mechanism.

tions are rich in the halogen compared to those typically used for excimer lasers. The radial variation of the optical emission from atomic iodine at 206.2 nm ($^2P_{3/2} \to ^2P_{1/2}$) is shown in Fig. 3(a) for different power depositions. The radial variations of optical emission from selected states of I*, I_2^*, Xe*, and XeI($B \to X$) at a power deposition of 90 W are shown in Fig. 3(b). The discharge cell contained 1 Torr Xe and ≈ 0.3 Torr I_2.

The radial peaks of the optical emission from the D, E, and F states of I_2 are located near the outer edge of the discharge cell. These peaks are found near the wall in large part because the iodine concentration is highest at that location. Molecular iodine is largely dissociated in the plasma and is reformed by recombination of iodine atoms at the wall. However, at low discharge powers, the I_2 emission peaks at the center of the discharge cell where the plasma density is highest. The emission from the D, E, and F states

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of I_2 behave similarly as a function of radius which indicates that these states are populated in a similar fashion and are probably collisionally mixed within a vibrational manifold [see Fig. 3(c)]. In general, $I_2^*(B \rightarrow X)$ emission at 544 nm is frequently similar as a function of radius to the upper level emissions of I_2^{**}. This similarity may result from several of the upper level transitions terminating on the B state, for example $I_2^{**}(F \rightarrow B)$ 277 nm emission and $I_2^{**}(D,E \rightarrow B)$ 429 nm emission.

The emission from I^* also peaks near the wall at higher power deposition. Since the observed emission originates from states in excess of 6 eV from the ground state, excitation of these states is sensitive to the tail of the electron energy distribution. To some degree, the observed shift in emission to the wall at higher power deposition and hence electron density may be due to a reduced skin depth for the electromagnetic field. At higher powers, and smaller skin depths, the electron temperature is likely to be higher near the wall. In essence, the discharge is becoming largely inductively coupled. However the radial dependence of each species (I^*, I^{**}, Xe^{**}) is unique based on the electron energy distribution cross section for excitation and species density.

As previously discussed, $XeI(B)$ may be formed by the harpoon reaction ($Xe^* + I_2 \rightarrow XeI(B) + I$) and/or the reverse harpoon reaction ($Xe + I_2^{**}(^3P, ^1D) \rightarrow XeI(B) + I$). Since the lifetime of $XeI(B \rightarrow X)$ (15 ns) is short compared to any quenching or transport timescales, the radial dependence of its emission is a direct indication of the radial dependence of its source function. Therefore, if the harpoon reaction is the dominant source of $XeI(B)$, then the product $[Xe^*] \cdot [I_2]$ should have the same radial dependence as the emission of $XeI(B \rightarrow X)$. This assumes that the rate coefficient for the formation reaction only weakly depends on radius. Analogously, if the reverse harpoon reaction is the dominant source of $XeI(B)$, then the product $[Xe] \cdot [I_2^{**}]$ should have the same radial dependence as the emission of $XeI(B \rightarrow X)$. If both are major sources of $XeI(B)$, then the radial dependence will be a combination of the two.

The density of the I_2 ground state and of $Xe(6s_{12})$ are shown in Fig. 4(a) for a power deposition of 43 W and a gas mixture of $Xe/I_2 = 1.0$ Torr/0.3 Torr. The product of these densities and the $XeI(B \rightarrow X)$ emission are shown in Fig. 4(b). Over a wide range of operating conditions, the product of $[Xe^*] \cdot [I_2]$ and the $XeI(B \rightarrow X)$ emission have significantly different radial dependencies. For example, at the power deposition of 90 W, $XeI(B \rightarrow X)$ emission also significantly differs from $[Xe^*] \cdot [I_2]$, as shown in Fig. 4(c). These results suggest that the harpoon reaction is not a significant source of $XeI(B \rightarrow X)$ radiation for these conditions.

To determine if formation of $XeI(B)$ results from the reverse harpoon reaction, one may compare the radial dependence of I_2^{**} to that of $XeI(B \rightarrow X)$. If $XeI(B)$ is formed by the reverse harpoon reaction and assuming that the Xe ground state is a weak function of radius, then $XeI(B)$ and I_2^{**} emission should have the same radial form. For all conditions investigated, we did indeed observe that the radial dependence of $XeI(B \rightarrow X)$ emission paralleled that from I_2^{**}, an example of which is shown in Figs. 4(b) and 4(c).
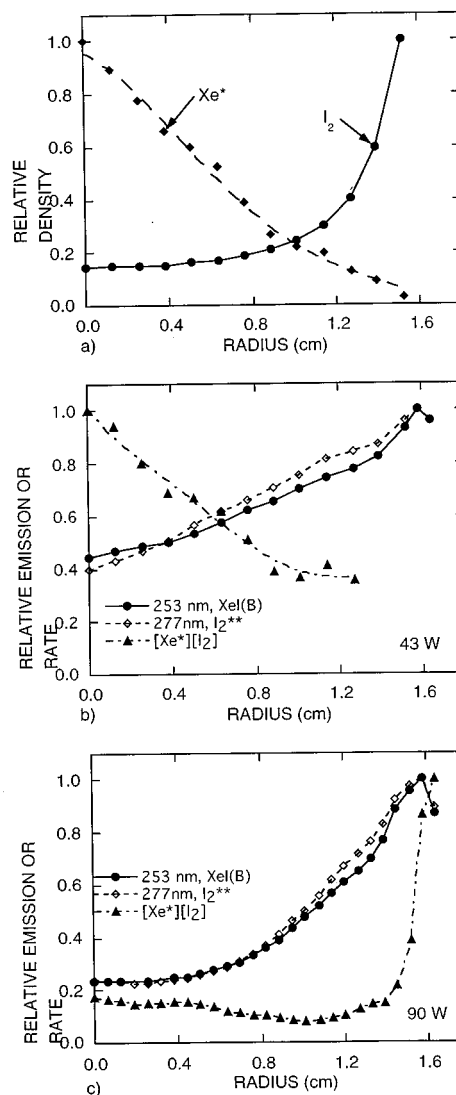

FIG. 4. Radial dependence of optical emission for $XeI(B \rightarrow X)$ and its precursors (1 Torr Xe/0.3 Torr I_2). (a) $Xe(6s_{12})$ density and I_2^{**} emission, precursors for the harpoon channel (46 W). (b) Excitation function for $XeI(B)$ through the harpoon channel, and emission from I_2^{**} and $XeI(B \rightarrow X)$ (46 W). (c) Excitation function for the harpoon channel and optical emission at 90 W. This disparity between the harpoon excitation functions, and similarity to I_2^{**} emission for XeI^* emission provides evidence for the reverse harpoon reaction.

We also found that the time dependent emission of $XeI(B \rightarrow X)$ during the afterglow of a modulated discharge was also similar to the I_2^{**} emission. The metastable $(6s_{12})$ state of Xe and Xe^{**} emission decayed significantly faster than the $XeI(B \rightarrow X)$ emission.

The 429 and 342 nm emission of I_2^{**} are from states that do not have sufficient energy to form the exciplex through the reverse harpoon reaction whereas the 277 and 271 nm emission of I_2^{**} are from states that do have sufficient energy. The radial dependence from these disparate states is nearly identical over a wide range of conditions, as shown in Fig. 3(c). Even though the precise states of I_2^{**} from which $XeI(B)$ can be formed through the reverse harpoon reaction are not known, all measured emissions of I_2^{**} (D,E,F) are similar in their radial dependence. Although not conclusive, these observations strongly suggest that the contributing state
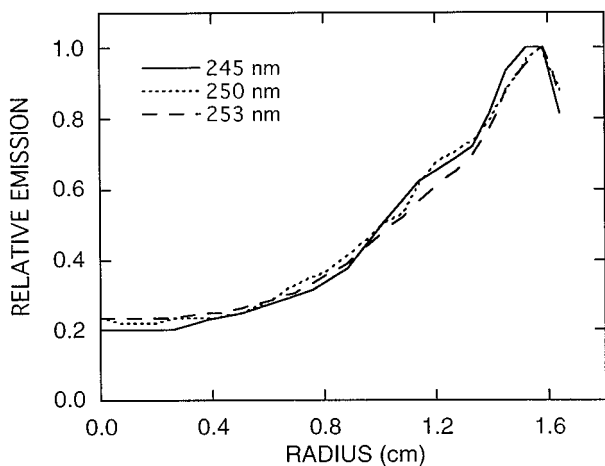
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FIG. 5. Emission from various vibrational levels of XeI(B) as a function of radius. Given the low rate of collisional mixing at low pressures, the vibrational levels of XeI(B) are likely excited by the same mechanism.

of I_2^{**} to the reverse harpoon reaction will also have this dependence.

The radial variation of the XeI($B \rightarrow X$) emission originating from different vibrational levels of the B state was also examined, and the results are shown in Fig. 5. No substantial differences were observed in the radial variation for the 245 nm ($^2\Sigma_{1/2}$, $v' \approx 12$), 250 nm ($^2\Sigma_{1/2}$, $v' \approx 5$), and 253 nm ($^2\Sigma_{1/2}$, $v' \approx 0$) emissions other than the 245 nm emission of XeI(B) is much weaker than the 250 and 253 nm emission. Since collisional mixing of the XeI(B) manifold is slow at the pressures of interest, these results may imply that the lower vibrational levels of XeI(B) are populated in the same manner.

V. CONCLUDING REMARKS

Observations of optical emission and measurements of optical absorption in Xe/I_2 inductively coupled discharges at low pressure (<1–5 Torr) have been performed. The relative emission of excited states of I, I_2, and Xe, and of XeI(B) have been measured as a function of radius. By formulating the excitation functions for XeI(B) from the precursor densities, and comparing their radial dependence to that for XeI($B \rightarrow X$) emission, one can assess the likelihood for a given excitation process. In doing so, we find that the harpoon reaction [Xe*+$I_2 \rightarrow$XeI(B)+I] is not a major contributor to formation of the exciplex for our conditions. Our observations do indicate that a reverse harpoon reaction [Xe + $I_2^{**} \rightarrow$XeI(B) + I] may be a major precursor channel. Although other researchers have proposed this mechanism, it is generally accepted that the harpoon or ion-ion recombination processes are the major sources of XeI(B) in conventional discharges. The conditions of our experiment differ from

previous works in that not only is the pressure lower, thereby diminishing the importance of 3-body reactions, but the iodine mole fraction is higher. These conditions contribute towards a larger proportion of the discharge power being directly expended in generating iodine excited states at the expense of decreasing the excitation fraction of xenon excited states. The low mole fraction of the halogen in rare-gas halogen lasers compared to the values used here is usually necessary due to laser absorption by the halogen. In rare-gas-halogen excimer lamps, where absorption is less of an issue, the option to operate with large mole fractions of the halogen is viable, thereby opening the reverse harpoon reaction channel for excitation of the exciplex.

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