Photodissociation of \( \text{C}_6\text{H}_5\text{I}, \text{C}_6\text{F}_5\text{I}, \) and related iodides in the ultraviolet

K. Kavita* and Puspendu K. Das
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

The quantum yields of \( \text{I}^*(2P_{3/2}) \) production from iodobenzene and pentafluoriodobenzene at five different dissociation wavelengths of 222, 236, 266, 280, and \( \lambda = 305 \) nm are presented and compared with those obtained from nonaromatic cyclic iodides (i.e., cyclohexyl iodide and adamantyl iodide). The \( \text{I}^*(2P_{3/2}) \) and \( \text{I}^*(2P_{1/2}) \) atoms generated in the photolysis of the above iodides were monitored using a two-photon laser-induced fluorescence technique. From the measured \( \text{I}^* \) quantum yields, two general observations are made for aryl iodides. They are that (i) the \( \text{I}^* \) yield is influenced by the \( \sigma^* \rightarrow n \) as well as \( \pi^* \rightarrow \pi \) transitions at all photolysis wavelengths within the \( \text{A} \) band and (ii) there is a clear indication of a fluorescein substitution effect on the dynamics of \( \text{I}^* \) production. The contribution from the benzene type \( \pi^* \rightarrow \pi \) transition varies with excitation wavelength. Fluorine substitution in aryl iodides is found to increase the \( \text{I}^* \) quantum yield similar to what is reported in alkyl iodides. The effect of fluorine substitution is more pronounced at the red edge of the \( \text{A} \) band excitation than at any other wavelengths. This is explained by invoking the presence of a charge-transfer state arising due to the transition of a \( 5p \pi \) nonbonding iodine electron to the \( \pi^* \) molecular orbital near the red edge of the \( \text{A} \) band. This charge-transfer state is coupled more strongly to the \( 3Q_1 \) state of the \( \sigma^* \rightarrow n \) transition in pentafluoriodobenzene than in iodobenzene. The dynamics of \( \text{I}^* \) formation is found to be unaltered by ring strain in cyclic iodides except at the blue wing excitation. At the blue wing, \( \text{B} \)-band transitions affect the dynamics of \( \text{I}^* \) production in cyclic iodides, leading to the formation of more \( \text{I}^* \) from adamantyl iodide.

I. INTRODUCTION

The literature is rich with reports on alkyl iodide dissociation in the \( \text{A} \) band.\(^1\)–\(^10\) The \( \text{A} \) band of alkyl iodide arises due to promotion of a nonbonding electron from the iodine atom to the antibonding \( \sigma^* \) molecular orbital \( \sigma^* \rightarrow n \) transition localized on the \( \text{C}-\text{I} \) bond. Excitation in the \( \text{A} \) band results in a direct (fast) dissociation of the \( \text{C}-\text{I} \) bond leading to the formation of an alkyl radical and the iodine atoms in their ground \( \text{I}^*(2P_{3/2}) \) and spin-orbit \( \text{I}^*(2P_{1/2}) \) excited states. The \( \sigma^* \rightarrow n \) transition in alkyl iodides is composed of three overlapping transitions from the ground state \( \text{N} \) to the repulsive \( 3Q_1, 3Q_0, \) and \( 1Q_1 \) states in increasing order of energy in accordance with Mulliken’s\(^11\) prediction. According to Mulliken, the excitation to the \( 3Q_0 \) state is polarized parallel to the \( \text{C}-\text{I} \) bond and produces \( \text{I}^* \), whereas the transitions to the other two states (i.e., \( 3Q_1 \) and \( 1Q_1 \) states) are polarized perpendicular to the \( \text{C}-\text{I} \) bond axis and produces \( \text{I} \). Later Gedanken and co-workers confirmed for various alkyl iodides\(^12,13\) including \( \text{CF}_3\text{I} \) (Ref. 14) using magnetic circular dichroism (MCD) that the \( \text{A} \) band, indeed, has three underlying transitions and about 80% of the transition strength near the absorption maximum is carried by the parallel \( 3Q_0 \rightarrow \text{N} \) transition. The study of alkyl iodide dissociation dynamics in the near ultraviolet has most been confined to the \( \text{A} \) band.

The aryliodides form another class of interesting molecules in which the \( \pi^* \rightarrow \pi \) transition of the benzene ring overlaps with the \( \sigma^* \rightarrow n \) transition of the \( \text{C}-\text{I} \) bond in the 200–320 nm region.\(^15,16\) The absorption spectrum of benzene in the 200–350 nm region has been well studied. There are three singlet (\( S \)) and three triplet (\( T \)) states corresponding to the \( \pi^* \rightarrow \pi \) transitions in this region. The three singlet-singlet transitions occur at about 255, 200, and 178 nm and they have been assigned to \( 1B_{2u}(S_1) \rightarrow 1A_{1g}, 1B_{1u}(S_2) \rightarrow 1A_{1g}, \) and \( 1E_{1u}(S_3) \rightarrow 1A_{1g} \) transitions, respectively, by Doering.\(^17\) Three other singlet-to-triplet transitions occur at about 320, 255, and 218 nm and the corresponding transitions are \( 3B_{1u}(T_1) \rightarrow 1A_{1g}, 3E_{1u}(T_2) \rightarrow 1A_{1g}, \) and \( 3B_{2u}(T_3) \rightarrow 1A_{1g} \), respectively. Doering has also observed that the transitions to the first singlet and the second triplet (\( S_1 \) and \( T_2 \)) overlap. The absorption spectrum of iodobenzene is complex in the region of 200–350 nm, as it involves two types of transitions: (i) excitation of ring \( \pi \) electrons analogous to that in benzene and (ii) excitation of the \( n \) electrons similar to that in alkyl iodides. The fluorine-substituted benzenes are found\(^18\) to have three singlet-singlet transitions similar to those in benzene. The \( T_2 \rightarrow S_0 \) transition was not observed in fluorinated benzene. Instead, a new singlet-singlet transition with a maximum at \( \lambda \approx 230 \) nm was observed which was called the \( \text{C} \) band and was not seen previously in benzene. In general, substitution of hydrogen atoms in planar aromatic and nonaromatic molecules by fluorine atoms is found to stabilize the \( \sigma \) molecular orbitals by 2–3 eV (Refs.

*Present address: Department of Chemistry, Columbia University, New York, NY 10027.
The pioneering work on the photodissociation of aryl iodides by Bersohn and co-workers, where the angular distribution of the ground-state iodine atoms was measured, suggests that there are two dissociation pathways and predissociation plays an important role in the C-I bond breaking dynamics in aryl iodides. Pence et al. studied the ultraviolet dissociation of C₆H₅I by monitoring the infrared fluorescence from I*. They found no measurable I* signal at 308 nm, but reported I* quantum yields of 0.25 and 0.08 at 248 and 193 nm, respectively. They explained that the initial excitation at 248 nm takes the molecule to the S₁ state (belonging to the π*→π transition) from where it crosses to the σ* state and then dissociates. They, however, did not put forward any rationale for not observing any I* at 308 nm. Later, using state-selective one-dimensional photofragment translational spectroscopy, El-Sayed and co-workers have measured the translational energy and angular distributions of iodine atoms from iodobenzene, pentfluoroiodobenzene, and related iodides. In C₆H₅I, surprisingly, only the (2P₃/₂) channel was detected and two velocity distributions were found at 218 and 266 nm. No I* signal was observed at 218 and 266 nm, although at another wavelength (304 nm) the time-of-flight signal from I* produced from C₆F₅I (Ref. 29) and C₆H₅I (Ref. 30) was relatively strong and was measured by them. In C₆H₅I, the fast I atoms were interpreted to have originated from a prompt dissociation process via direct excitation from the 3Q₀ repulsive state of the σ*→n transition. This is accompanied by a large fraction of the available energy being released into the internal modes of the phenyl ring. They also showed for the fast dissociation channel that the rate of internal energy redistribution increases as the amount of available energy increases. The slow I atoms are produced by another channel through a predissociation mechanism starting from an initially excited π*→π state and with a range of dissociation times on the molecular rotation time scale. For the slow channel, the rate of intramolecular energy redistribution from the π*→π state could not be correlated to the excess energy available in the dissociation. They invoked two mechanisms for the production of slow I atoms. In one, the initially excited state couples with some dark states and energy is dissipated through other means than dissociation. In another, some of these dark states couple with the repulsive σ*→n states resulting in I-atom production. The two-channel pathway for dissociation in iodobenzene photodissociation was verified by Cheng et al. using a kinetic-energy-resolved time-of-flight mass spectrometer (KETOFl) capable of resolving the kinetic energy in the femtosecond time scale. In their experiment the “direct-mode” dissociation in iodobenzene at 278 nm occurred in 400 fs and a “complex-mode” dissociation in 600 fs. Griffiths et al. studied the dissociation dynamics of pentafluoriodobenzene at 304 nm. They measured the I* quantum yield as 0.07 from the photolysis of C₆F₅I at 304 nm and observed that it is ca. 14 times greater than that from iodobenzene. They also suggested that fluorine substitutions bring in the π*→n charge-transfer (CT) states to play an important role in the dissociation dynamics by interacting with both the σ*→n and π*→π states near 304 nm excitation. However, they did not study the effect of excitation energy variation on the I* quantum yield. Recently, Unny et al. have studied the photodissociation of iodobenzene at 266 and 304 nm and shown that their results are in good agreement with El-Sayed and co-workers both in the mode of dissociation and in the energy distribution mechanism.

We have chosen iodobenzene in this study since it is rather unusual that C-I bond breakage through the repulsive σ*→n states does not lead to any I* production as has been reported by El-Sayed and co-workers. The only iodide known until now that does not produce any I*, is t-butyl iodide for which a near zero I* quantum yield has been reported at 248 nm. In pentafluoriodobenzene according to Griffiths et al. we expect that the I* quantum yield should decrease as a function of increasing excitation energy since energy redistribution rate will be faster in the prompt channel. In order to probe some of these issues, here we report the measurement of I* quantum yield from iodobenzene and pentafluoriodobenzene at five different wavelengths in the near ultraviolet at 222, 236, 266, 280, and ~305 nm spanning a range of ~80 nm. The photolysis of cyclohexyl and adamantyl iodides was also carried out since these molecules are similar to iodobenzene and pentafluoriodobenzene in the sense that they all are cyclic, but lack the π*→π transition of the latter.

II. EXPERIMENT

The experimental setup used in the present investigation is described in detail elsewhere. In brief, the experiments were carried out at a sample pressure of ca. 40–60 mTorr inside a stainless-steel chamber which was pumped continuously by a diffusion pump backed by a mechanical pump. Two laser beams (the pump and the probe) were crossed perpendicular to each other in the middle of the chamber. The dissociation wavelengths of 222 (~1 mJ/pulse) and 236 nm (~2 mJ/pulse) were obtained by mixing dye second harmonic (280 and 305 nm, respectively, for 222 and 236 nm) with the fundamental (1064 nm) of a Nd:YAG laser (DCL-3G, Spectra Physics) in a KDP crystal. The pump beam at 266 nm (~20 mJ/pulse) was generated from the fourth harmonic of the same Nd:YAG laser. Photolysis wavelength of 280 nm (~5 mJ/pulse) was produced by the second harmonic of the dye laser (PDL-2, Spectra Physics). Another Nd:YAG pumped dye laser (PDL-2, Spectra Physics) was frequency doubled to produce tunable UV radiation (304–307 nm, 0.05–0.1 mJ/pulse) for probing I and I* both using a two-photon laser-induced fluorescence (TPLIF) scheme. The TPLIF spectra were recorded using a solar blind (Thorn EMI, 9423 B) photomultiplier tube (PMT) mounted on the top of the chamber by scanning the probe laser across the two photon absorption lines of I (304.7 nm) and I* (306.7 nm). The PMT output was amplified (~25), averaged in a
gated boxcar averager (SRS 250), and displayed on a strip-chart recorder. The space between the magnesium fluoride window and the solar blind PMT was purged continuously with dry nitrogen. The pump laser polarization was not varied since in our experiments atomic species like iodine atoms are detected which are spherically symmetric and their recoil direction with the rotation of the pump laser polarization should not affect the TPLIF signal intensity. In the case of ~305 nm dissociation, the probe laser alone was used. One photon from the laser pulse dissociated the molecules and two subsequent photons from the same pulse probed the I and I* atoms. For the two-laser experiments, the probe laser power was kept very low so that the probe alone did not produce much signal. When the pump beam was turned on, the increase in the signal was taken as directly proportional to the concentration of the atoms monitored. All aryl and cyclic iodides were obtained commercially, decolorized with sodium bisulfite and fractionally distilled before use. While distilling, the first and last fractions were discarded and the boiling point of each compound was monitored and found to be close to its theoretical boiling point within experimental error.

III. RESULTS AND DISCUSSION

The structures of the aryl and cyclic iodides studied here are shown in Fig. 1. The gas phase absorption spectra of iodobenzene and pentafluoroiodobenzene were recorded in a Hitachi U-3000 spectrometer using a quartz cell and are shown in Fig. 2(a). Due to the low vapor pressure of cyclohexyl and adamantyl iodides, their absorption spectra were recorded in n-heptane and are shown in Fig. 2(b). The relative quantum yield of I* production is given as \( \phi^* = [I^*]/([I] + [I^*]) \), where \([ \cdot ]\) represents concentration. As the experimental signal intensities \( S(I) \) and \( S(I^*) \) are directly proportional to \([I] \) and \([I^*] \), respectively, we can write

\[
S(I^*)/S(I) = k[I^*]/[I].
\]

The constant \( k \) contains relative two-photon absorption cross sections of I and I* and the instrument factor for their detection. The \( \phi^* \) value for CH₃I (taken as the reference compound) was measured before each experiment at all the excitation wavelengths to determine the value of \( k \). For CH₃I, the measured \( \phi^* \) value (0.75) by us [using the right-hand side (RHS) in Eq. (1)] at 266 nm matched very well with the same (0.76) found by Riley and Wilson¹ from photofragment spectroscopy and we, therefore, take the value of \( k \) to be 1. In fact, the \( \phi^* \) values of CH₃I listed in Table I were taken as reference values for quantum yield measurement at all the excitation wavelengths. Before each experiment with an aryl iodide, we first determined the \( \phi^* \) from CH₃I and compared that with the value listed in Table I. If the two values of \( \phi^* \) matched, \( k \) was taken as 1. Otherwise, \( k \) was obtained by taking the ratio of the \( \phi^* \) values from methyl iodide. The measured I and I* signals from aryl iodides were scaled accordingly. The I* quantum yields from all the iodides at five different excitation wavelengths are listed in Table I.

A. Dissociation dynamics of C₆H₅I and C₆F₅I

From Table I it is clearly seen that more than 50% of the product iodine atoms are produced in the spin-orbit excited state from the photolysis of iodobenzene, pentafluoroiodobenzene, and cyclohexyl iodide at 222, 236, 266, and 280 nm. It also appears (Fig. 3) that the I* yield from cyclohexyl iodide is slightly less than that from the other two iodides at all excitation wavelengths spanning the absorption profile in

---

**FIG. 1.** Structures of C₆H₅I, C₆F₅I, C₆H₁₁I, C₁₀H₁₅I, and CH₃I.

**FIG. 2.** (a) Gas-phase absorption spectra of iodobenzene and pentafluoroiodobenzene. (b) Absorption spectra of cyclohexyl and adamantyl iodide.
the near ultraviolet. From previous studies of alkyl and perfluoroalkyl iodides it is known that the dissociation of alkyl and perfluoroalkyl iodides in the A band (200–310 nm) results in the formation of both I and I*. Excitation at 222, 236, 266, or 280 nm takes the alkyl iodides to one or more of the three repulsive excited $3Q_1$, $3Q_0$, and $1Q_1$ states. The major pathway for the formation of I is by crossing to the $1Q_1$ state from the initially excited $3Q_0$ state which carries most of the transition strength within the A band. However, involvement of the $1Q_1$ and $3Q_1$ states in the initial excitation process has also been suggested by some investigators for both alkyl and perfluoroalkyl iodides. The dissociation of iodobenzene, pentafluoriodobenzene, and cyclohexyl iodide produces both ground and spin-orbit excited iodine atoms, which indicates that the same repulsive states are involved in the exit channel. The formation of more I* from the aryl iodides in comparison to cyclohexyl iodide specifically at the blue wing excitations implicates another transition apart from the $\sigma^* \leftarrow n$ of the C-I bond is involved in the dissociation. Excitation to the ring states ($\pi^* \leftarrow \pi$ transition) has been suggested by earlier authors at these energies. The ring $\pi^* \leftarrow \pi$ transition is predissociative via the $3Q_0$ state of the $\sigma^* \leftarrow n$ transition in iodobenzene. Freitas et al. have studied iodobenzene dissociation at 218 and 266 nm. They probed only the ground-state iodine atom and reported that the formation of I results from two sources: (1) A prompt dissociation pathway from the direct excitation to the $3Q_0$ repulsive state followed by a 100% curve crossing to the $1Q_1$ state which correlates to I. (2) An indirect dissociation path where the initial excitation is to a ring state ($\pi^* \leftarrow \pi$ transition) followed by curve crossing to the repulsive $3Q_0$ state which then makes a perfect cross over to the $1Q_1$ state to produce I.

Although why Freitas et al. did not observe the I* channel remains unknown, it is possible that in their experiment the I* atoms which are produced with very little translational energy disappeared into the pump before being detected. In any case, the production of I* as observed by us is only possible if a significant fraction of the molecules dissociate from the final $3Q_0$ repulsive state irrespective of the mechanism of excitation. Perhaps both the direct and indirect pathways for dissociation are active as suggested by earlier investigators. However, in the prompt or direct dissociation channel, we believe, contrary to what has been reported by Freitas et al., that the initial excitation to the $3Q_0$ state produces a significant amount of I*.

![Image](image.png)

**FIG. 3.** Plot of $\phi^*$ vs wavelength from iodobenzene, pentafluoriodobenzene, and cyclohexyl iodide.

### Table I. Relative quantum yield of I* formation from C$_6$H$_5$I, C$_6$F$_5$I, CH$_3$I, C$_6$H$_{11}$I, and C$_{10}$H$_{15}$I at 222, 236, 266, 280, and $\sim$305 nm dissociation.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\phi^*$ (222 nm)</th>
<th>$\phi^*$ (236 nm)</th>
<th>$\phi^*$ (266 nm)</th>
<th>$\phi^*$ (280 nm)</th>
<th>$\phi^*$ ($\sim$305 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{6}$H$</em>{5}$I</td>
<td>0.47±0.005</td>
<td>0.58±0.03</td>
<td>0.50±0.02</td>
<td>0.55±0.03</td>
<td>0.30±0.01</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{15}$I</td>
<td>0.62±0.02</td>
<td>0.63±0.01</td>
<td>0.45±0.005</td>
<td>0.53±0.02</td>
<td>0.27±0.02</td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>0.63±0.02$^a$</td>
<td>0.69±0.03$^b$</td>
<td>0.75±0.03$^c$</td>
<td>0.69±0.02$^d$</td>
<td>0.43±0.01$^e$</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{11}$I</td>
<td>0.62±0.02</td>
<td>0.59±0.01</td>
<td>0.51±0.01</td>
<td>0.58±0.01</td>
<td>0.24±0.01</td>
</tr>
<tr>
<td>C$<em>{10}$F$</em>{15}$I</td>
<td>0.64±0.03</td>
<td>0.63±0.015</td>
<td>0.58±0.03</td>
<td>0.59±0.04</td>
<td>0.49±0.03</td>
</tr>
</tbody>
</table>

$^a$From Ref. 8.  
$^b$From Ref. 40.  
$^c$From Ref. 8.  
$^d$From Ref. 6.  
$^e$From Ref. 44.
that of the extent. Recently, Baklanov et al.\(^1\) is produced via only one route.

The \(I^*\) quantum yield at \(\sim 305\) nm is found to be less than 0.5 for all the iodides studied here. In other words, \(I\) is the major product unlike in all the other wavelengths. Earlier Pence et al.\(^{25}\) have reported the upper limit of \(I^*\) to be 0.004 from the photolysis of iodobenzene at 308 nm. But significant \(I^*\) quantum yield from both iodobenzene and perfluoroiodobenzene measured by us suggests that indeed a substantial amount of \(I^*\) is produced in the photolysis of these two iodides in the UV. The \(I^*\) quantum yield for iodobenzene differs by only 5% to that of cyclohexyl iodide at \(\sim 305\) nm, which means that at the red edge the contribution of the \(\pi^* \rightarrow \pi\) transition of benzene ring is only marginal to the overall \(I^*\) production. Moreover, the possible benzene-type transition at \(\geq 300\) nm is a singlet-triplet transition which is expected to have very little strength. The mechanism of more \(I\) formation at this wavelength could be due to direct excitation to the \(3Q_1\) state. It is known from the MCD study of alkyl and perfluoroalkyl iodides that within the A-band absorption, the \(3Q_1\) state peaks \(\sim 300\) nm.\(^{12,14}\) Fairbrother et al.\(^{33}\) have shown that excitation of methyl iodide at 333 nm involves both the \(3Q_0\) and \(3Q_1\) transitions to the same extent. Recently, Baklanov et al.\(^{36}\) have measured the \(I^*\) quantum yield of \(C_6F_5I, n-C_4F_7I,\) and \(i-C_4F_6I\) at 355 nm using a resonant two-photon ionization (R2PI) detection scheme for both \(I\) and \(I^*\) and reported that the formation of \(I\) is more for these iodides at this wavelength. They inferred that the formation of \(I\) at this wavelength has some contribution from the direct excitation to the \(3Q_1\) state. Therefore, at the red edge of the absorption band of \(C_6H_5I\) and \(C_6F_5I, I\) atoms are produced by three different mechanisms, whereas \(I^*\) is produced via only one route.

**B. Effect of fluorine substitution on the dissociation dynamics of iodobenzene**

At all the dissociation wavelengths employed in the present investigation, it is apparent that the fluorination of iodobenzene leads to increased \(I^*\) production (Fig. 3). The effect of fluorination is more pronounced at the red edge excitation than at other wavelengths. The formation of more \(I^*\) from pentafluoroiodobenzene than from iodobenzene is not surprising, since it is known from earlier studies\(^{5,10}\) on alkyl iodide dissociation that fluorination increases the \(I^*\) quantum yield. The formation of more \(I^*\) in alkyl iodides upon fluorination was attributed to the decrease in the coupling strength between the \(3Q_0\) and \(1Q_1\) states. However, in aryl iodides the situation is more complex due to the presence of the \(\pi^* \rightarrow \pi\) transitions. To explain the observed dynamics in pentafluoroiodobenzene at 304 nm Griffiths et al.\(^{29}\) invoked the presence of a low-lying CT state which is lower in energy in pentafluoroiodobenzene than in iodobenzene. The CT state originates from the excitation of a \(5\rho\pi\) nonbonding iodine electron to the \(\pi^*\) molecular orbital of the benzene ring. They suggested that this CT state mixes better with the \(\sigma^* \rightarrow \pi\) transition in pentafluoroiodobenzene and results in a reduction of the spin orbit coupling between the \(3Q_0\) and \(1Q_1\) states leading to the formation of more \(I^*\). If this state is responsible for the reduction in the coupling strength between the \(3Q_0\) and \(1Q_1\) states in pentafluoroiodobenzene as suggested by Griffiths et al., then its effect will be felt to the same extent at all the excitation wavelengths. However, this is not observed in the present investigation. In other words, the measured \(I^*\) yield from pentafluoroiodobenzene does not reflect the effect of fluorination on \(\rho^\pi\) to the same extent at all the dissociation wavelengths. The effect of fluorination is prominent only at dissociation wavelengths \(\geq 300\) nm. The clear implication is that the \(3Q_1\) state, which becomes important at longer wavelengths, is involved in the dynamics. In order to develop a better understanding of the observed result near the red edge excitation, we present a tentative correlation diagram [Figs. 4(a) and 4(b)] between the reactants and products. The correlation diagram has been developed based on the existing literature on the energy levels of methyl iodide,\(^{12}\) benzene,\(^{17}\) perfluorobenzene,\(^{18}\) and iodobenzene.\(^{32}\) In this diagram, the relative positions of \(\pi^* \rightarrow \pi, \sigma^* \rightarrow \pi,\) and the two CT states (one singlet and another triplet arising due to the transition of \(5\rho\pi\) nonbonding iodine electron to the \(\pi^*\) molecular orbital) are shown. The low-lying triplet CT state will be energetically closer to the lowest-energy state of the \(\sigma^* \rightarrow \pi\) transition, which is the \(3Q_1\) state, and they are expected to interact. As a result of this interaction, the \(3Q_1\) state is likely to shift from its original position. From our measured values of \(I^*\) quantum yield we believe that this shift is to the blue for pentafluoroiodobenzene as depicted in Fig. 4(b). At \(305\) nm this blueshift reduces the contribution of the \(3Q_1\) state to the total absorption strength and leads to the lowering of \(I\) atom production from \(C_6F_5I.\)

**C. Dissociation dynamics of nonaromatic cyclic iodides**

The \(I^*\) yield measured from cyclohexyl and adamantyl iodides at 222, 236, 266, 280, and \(\sim 305\) nm is listed in Table I. Both the molecules belong to six-membered ring systems. One of them (cyclohexyl) has a monocyclic ring, whereas the other (adamantyl iodide) belongs to a tetracyclic system. From the structure it appears that the monocyclic system should be more stable than the tetracyclic system due to the increase in strain at the bridged carbon atoms in the latter. The stability of the cyclic systems depends on the ring size, and it is known that six-member rings are more stable than...
Adamantane is one of the few multicyclic systems which is thermodynamically stable. The heats of formation of cyclohexane \(~ \Delta H_{f} \approx 2123.1 \text{ kJ/mol} \) \(^{38}\) and adamantane \(~ \Delta H_{f} \approx 2134.4 \text{ kJ/mol} \) \(^{39}\) are comparable and hence make them right systems to choose to study the effect of ring strain on the dissociation dynamics. The \( \text{I}^* \) yield is found to be more or less the same for these iodides at dissociation wavelengths \( \lambda > 240 \text{ nm} \), whereas at the blue wing excitation, the \( \text{I}^* \) formation is more from adamantyl iodide than from cyclohexyl iodide. The formation of equal amounts of \( \text{I} \) and \( \text{I}^* \) from these iodides at the dissociation wavelengths \( \lambda > 240 \text{ nm} \) suggests that at this wavelength region the dynamics is similar for both the iodides. The \( \text{I}^* \) formation is \(~ \approx 50\% \) near the absorption maximum of their \( A \) band and falls off at the red edge. Production of more \( \text{I}^* \) near the absorption maximum is similar to what is seen in the case of normal alkyl iodides. The formation of more \( \text{I} \) from the cyclic iodides near their absorption maximum compared to alkyl iodides suggests that the curve crossing probability between the initially excited \( ^3Q_0 \) to the \( ^1Q_1 \) state is more in the cyclic systems. Earlier Godwin et al.\(^2\) had reported that the \( \text{I}^* \) quantum yield is 0.27 for cyclohexyl iodide at 248 nm. Their measured value is found to be less than the \( \text{I}^* \) yield at 266 nm measured by us in the present investigation. To make sure that the formation of more \( \text{I}^* \) at 266 nm in the present investigation is only from the single-photon dissociation at this wavelength, the pump power dependence of the TPLIF signal was carried out. From a log-log plot of laser power versus the signal intensity for both \( \text{I} \) and \( \text{I}^* \), the slope was found to be 0.87 and 1.0, respectively (data not shown). This confirms that the formation of \( \text{I} \) and \( \text{I}^* \) at 266 nm is indeed due to a single-photon process. Also, at the red edge, the dynamics of \( \text{I}^* \) production from the cyclic systems appears to be the same as that of the normal alkyl iodides. It is, therefore, safe to infer that the dynamics of \( \text{I}^* \) production from these iodides is similar to that of normal alkyl iodides at dissociation wavelengths \( \lambda \approx 240 \text{ nm} \).

At the blue wing of the \( A \) band, the dynamics is very similar to that of the alkyl iodide dissociation. This can only be explained by invoking the contribution of the next higher excited state in the dissociation in this wavelength region as was done earlier in the case of perfluoroalkyl iodides.\(^{40}\) The next shorter-wavelength absorption band, that is, the \( B \) band,\(^{31 – 43}\) is involved in the dissociation of the cyclic iodides at \( \lambda \approx 240 \text{ nm} \). The formation of more \( \text{I}^* \) from adamantyl iodide suggests that the contribution of the predissociative (\( E,1 \)) \(^2\) state of the \( B \) band is more in this molecule than in cyclohexyl iodide. This is also evident from the absorption spectra [Fig. 1(b)] where the \( B \) band is shifted to the red by 6 nm in adamantyl iodide (peak at 210 nm) in comparison to that of cyclohexyl iodide (peak at 204 nm). Based on the above discussion, we conclude that the ring strain does not exert much influence on the dynamics of dissociation of cyclic iodides.

IV. SUMMARY

(1) Both iodobenzene and pentafluoriodobenzene produce large amounts of \( \text{I}^* \) upon photodissociation in the \( A \) band. The \( \text{I}^* \) quantum yield increases with fluorine substitution at all dissociation wavelengths, although the effect is more pronounced at the red edge of the \( A \)-band excitation.

(2) The contribution of the ring \( \pi \leftrightarrow \pi \) transition in the dynamics of \( \text{I}^* \) production from iodobenzene and pentafluoroiodobenzene varies with the photolysis wavelength.
Among the low-lying benzene $S_2$, $S_1$, and $T_1$ states, the $S_2$ state is more strongly coupled to the $\sigma^* \rightarrow n$ transitions leading to more $I^*$ product.

(3) At photolysis wavelengths $\leq 300$ nm, the formation of I has only two contributions, whereas at the red edge ($\geq 300$ nm) dissociation, I atoms are produced by three different mechanisms.

(4) In cyclic iodides the dynamics of dissociation is not affected by the ring strain.

ACKNOWLEDGMENT

We thank the Department of Atomic Energy, Government of India, for generous funding.