

Photodissociation of C_6H_5I , C_6F_5I , and related iodides in the ultraviolet

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

I. INTRODUCTION

The literature is rich with reports on alkyl iodide dissociation in the *A* band.^{1–10} The *A* band of alkyl iodide arises due to promotion of a nonbonding electron from the iodine atom to the antibonding σ^* molecular orbital ($\sigma^*\leftarrow n$ transition) localized on the C-I bond. Excitation in the *A* band results in a direct (fast) dissociation of the C-I bond leading to the formation of an alkyl radical and the iodine atoms in their ground $I(^2P_{3/2})$ and spin-orbit $I^*(^2P_{1/2})$ excited states. The $\sigma^*\leftarrow n$ transition in alkyl iodides is composed of three overlapping transitions from the ground state (*N*) to the repulsive 3Q_1 , 3Q_0 , and 1Q_1 states in increasing order of energy in accordance with Mulliken's¹¹ prediction. According to Mulliken, the excitation to the 3Q_0 state is polarized parallel to the C-I bond and produces I^* , whereas the transitions to the other two states (i.e., 3Q_1 and 1Q_1 states) are polarized perpendicular to the C-I bond axis and produces I . Later Gedanken and co-workers confirmed for various alkyl iodides^{12,13} including CF_3I (Ref. 14) using magnetic circular dichroism (MCD) that the *A* band, indeed, has three underlying transitions and about 80% of the transition strength near the absorption maximum is carried by the parallel ${}^3Q_0 \leftarrow N$ transition. The study of alkyl iodide dissociation dynamics in the near ultraviolet has mostly been confined to the *A* band.

The aryl iodides form another class of interesting molecules in which the $\pi^*\leftarrow\pi$ transition of the benzene ring overlaps with the $\sigma^*\leftarrow n$ transition of the C-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 $\pi^*\leftarrow\pi$ transitions in this region. The three singlet-singlet transitions occur at about 255, 200, and 178 nm and they have been assigned to ${}^1B_{2u}(S_1)\leftarrow{}^1A_{1g}$, ${}^1B_{1u}(S_2)\leftarrow{}^1A_{1g}$, and ${}^1E_{1u}(S_3)\leftarrow{}^1A_{1g}$ transitions, respectively, by Doering.¹⁷ Three other singlet-to-triplet transitions occur at about 320, 255, and 218 nm and the corresponding transitions are ${}^3B_{1u}(T_1)\leftarrow{}^1A_{1g}$, ${}^3E_{1u}(T_2)\leftarrow{}^1A_{1g}$, and ${}^3B_{2u}(T_3)\leftarrow{}^1A_{1g}$, 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 π electrons analogous to that in benzene and (ii) excitation of the *n* electrons similar to that in alkyl iodides. The fluorine-substituted benzenes are found¹⁸ to have three singlet-singlet transitions similar to those in benzene. The $T_2\leftarrow S_0$ transition was not observed in fluorinated benzene. Instead, a new singlet-singlet transition with a maximum at ~ 230 nm was observed which was called the *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 σ molecular orbitals by 2–3 eV (Refs.

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19 and 20) and the π molecular orbitals by ~ 1 eV. Frueholz *et al.*²¹ have suggested that the $T_2 \leftarrow S_0$ transition might be weak in fluorobenzene, since it is suppressed by the intense $S_1 \leftarrow S_0$ transition. From the observed absorption profiles of benzene and fluorobenzene, it is clear that fluorine substitution has a profound effect on the transitions in the region of 200–350 nm.

The pioneering work on the photodissociation of aryl iodides by Bersohn and co-workers,^{22–24} 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.*²⁵ studied the ultraviolet dissociation of C_6H_5I 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 S_1 state (belonging to the $\pi^* \leftarrow \pi$ 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 translation spectroscopy, El-Sayed and co-workers^{26–30} have measured the translational energy and angular distributions of iodine atoms from iodobenzene, pentfluoriodobenzene, and related iodides. In C_6H_5I , surprisingly, only the $I(^2P_{3/2})$ 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 C_6F_5I (Ref. 29) and C_6H_5I (Ref. 30) was relatively strong and was measured by them. In C_6H_5I , the fast I atoms were interpreted to have originated from a prompt dissociation process via direct excitation from the 3Q_0 repulsive state of the $\sigma^* \leftarrow n$ 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 $\pi^* \leftarrow \pi$ 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 $\pi^* \leftarrow \pi$ 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 $\sigma^* \leftarrow n$ states resulting in I-atom production. The two-channel pathway for dissociation in iodobenzene photodissociation was verified by Cheng *et al.*³¹ using a kinetic-energy-resolved time-of-flight mass spectrometer (KETOF) 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.*²⁹ studied the dissociation dynamics of pentafluoriodobenzene at 304 nm. They measured the I^* quantum yield as 0.07 from

the photolysis of C_6F_5I 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 $\pi^* \leftarrow n$ charge-transfer (CT) states to play an important role in the dissociation dynamics by interacting with both the $\sigma^* \leftarrow n$ and $\pi^* \leftarrow \pi$ 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.*³² 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 $\sigma^* \leftarrow n$ states does not lead to any I^* production as has been reported by El-Sayed and co-workers.^{27,28} The only iodide known until now that does not produce any I^* , is *t*-butyl iodide³³ for which a near zero I^* quantum yield has been reported at 248 nm. In pentafluoriodobenzene according to Griffiths *et al.*²⁹ 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 $\pi^* \leftarrow \pi$ transition of the latter.

II. EXPERIMENT

The experimental setup used in the present investigation is described in detail elsewhere.¹⁰ 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 (DCR-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 fluorescence³³ (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 ($\times 25$), averaged in a

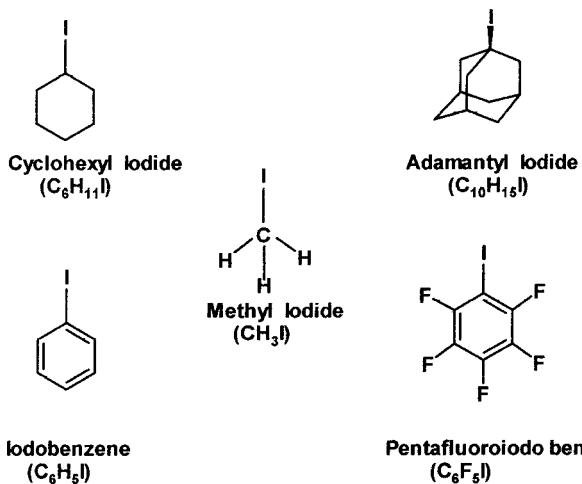


FIG. 1. Structures of C_6H_5I , C_6F_5I , $C_6H_{11}I$, $C_{10}H_{15}I$, and CH_3I .

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 pentafluorooiodobenzene 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 $[\dots]$ represents concentration. As the experimental signal intensities $S(I)$ and $S(I^*)$ are directly proportional to $[I]$ and $[I^*]$, respectively, we can write

$$S(I^*)/S(I) = k[I^*]/[I]. \quad (1)$$

The constant k contains relative two-photon absorption cross sections of I and I^* and the instrument factor for their detection.

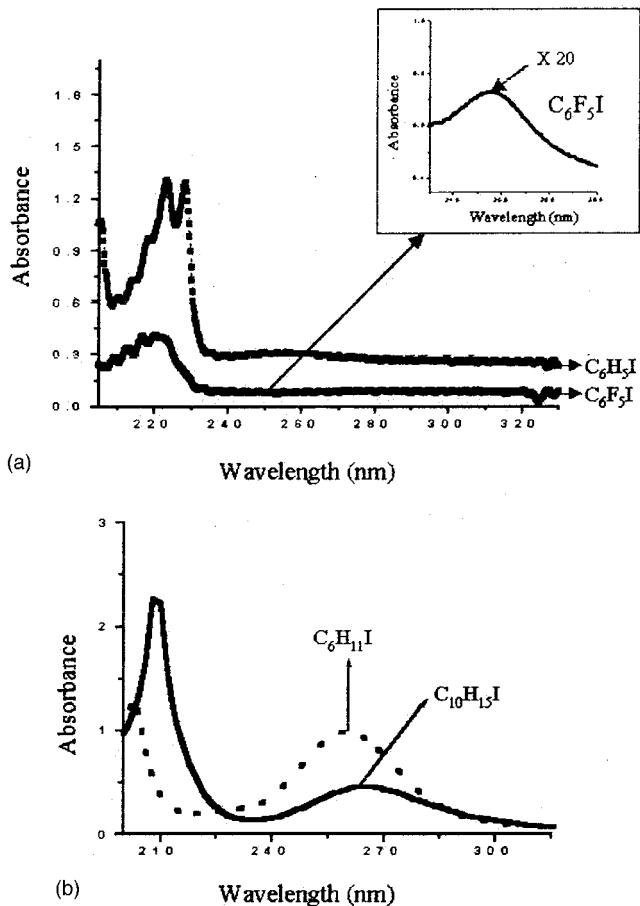


FIG. 2. (a) Gas-phase absorption spectra of iodobenzene and pentafluorooiodobenzene. (b) Absorption spectra of cyclohexyl and adamantly iodide.

tion. The ϕ^* value for CH_3I (taken as the reference compound) was measured before each experiment at all the excitation wavelengths to determine the value of k . For CH_3I , the measured ϕ^* 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 ϕ^* values of CH_3I 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 ϕ^* from CH_3I and compared that with the value listed in Table I. If the two values of ϕ^* matched, k was taken as 1. Otherwise, k was obtained by taking the ratio of the ϕ^* 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 C_6H_5I and C_6F_5I

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, pentafluorooiodobenzene, 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

TABLE I. Relative quantum yield of I^* formation from C_6H_5I , C_6F_5I , CH_3I , $C_6H_{11}I$, and $C_{10}H_{15}I$ at 222, 236, 266, 280, and ~ 305 nm dissociation.

Compounds	ϕ^* (222 nm)	ϕ^* (236 nm)	ϕ^* (266 nm)	ϕ^* (280 nm)	ϕ^* (~ 305 nm)
$C_6H_{11}I$	0.47 ± 0.005	0.58 ± 0.03	0.50 ± 0.02	0.55 ± 0.03	0.30 ± 0.01
$C_{10}H_{15}I$	0.62 ± 0.02	0.63 ± 0.01	0.45 ± 0.005	0.53 ± 0.02	0.27 ± 0.02
CH_3I	0.63 ± 0.02^a	0.69 ± 0.03^b	0.75 ± 0.03^c	0.69 ± 0.02^d	0.43 ± 0.01^a
C_6H_5I	0.62 ± 0.02	0.59 ± 0.01	0.51 ± 0.01	0.58 ± 0.01	0.24 ± 0.01
C_6F_5I	0.64 ± 0.03	0.63 ± 0.015	0.58 ± 0.03	0.59 ± 0.04	0.49 ± 0.03

^aFrom Ref. 8.

^bFrom Ref. 40.

^cFrom Ref. 44.

^dFrom Ref. 6.

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^{9,34–36} 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 that 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^{19–21} 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.*²⁸ 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^* . The indirect channel, which takes a longer time to yield final products, may produce more I through the 1Q_1 pathway. In the indirect channel, the coupling between the 1Q_1 and 3Q_0 states becomes more effective by the interaction of the out-of-plane ring vibrations with the C-I stretch. Now the question arises as to which of the ring type state excitations are involved in the indirect dissociation pathway and what are their contribution to the total transition strength. In the 200–300 nm region there are four transitions ($S_1 \leftarrow S_0, T_3 \leftarrow S_0, T_2 \leftarrow S_0, S_2 \leftarrow S_0$) of the $\pi^* \leftarrow \pi$ type in aryl iodides in addition to the three alkyl iodide type ($\sigma^* \leftarrow n$) transitions. Among the four π -type transitions, two are singlet-singlet type and the other two are singlet-triplet type. Based on the selection rules for a single-photon transition, the absorption cross section for the $S_1/S_2 \leftarrow S_0$ excitation will be more than that of the $T_2/T_3 \leftarrow S_0$ excitation. The excitation to the S_2 state peaks at ~ 200 nm, whereas the transition to the S_1 state peaks at ~ 260 nm in benzene. Careful examination of Table I reveals that there is a 15% and 5% increase in the I^* formation in aryl iodides in comparison to cyclohexyl iodide in the region of 220–240 and 260–300 nm, respectively. However, the I^* quantum yield from the aryl iodides is more in comparison to cyclohexyl iodide in the 220–260 nm region than in the region 260–300 nm. This implies that the contributions of the S_2 and S_1 states of the benzene ring are about 15% and 5% to the total I^* yield at 220–260 and 260–300 nm, respectively. That is, the contribution of a benzene-type transition is more pronounced in the region of 220–260 nm, whereas its con-

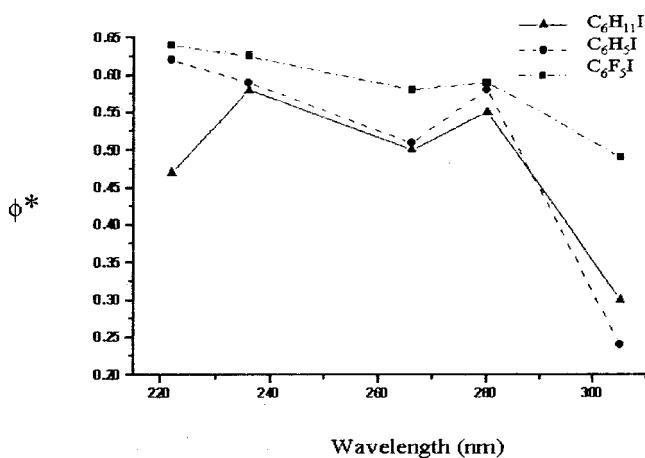


FIG. 3. Plot of ϕ^* vs wavelength from iodobenzene, pentafluoriodobenzene, and cyclohexyl iodide.

tribution is less in the 260–300 nm region. This is also manifested in the absorption spectra of aryl iodides: i.e., the molar extinction coefficient of the $\pi^* \leftarrow \pi$ transition is more than that of the $\sigma^* \leftarrow n$ transition in the 220–260 nm region. In the longer-wavelength region (260–300 nm) the molar extinction coefficient of the benzene-type transition is less in comparison to the alkyl-iodide-type transition. Earlier Dunn and Iredale¹⁶ had shown that the observed extinction coefficient for iodobenzene at 260 nm, $\epsilon = 665 \text{ l mol}^{-1} \text{ cm}^{-1}$, is equivalent to the added extinction coefficient of the C-I bond ($\epsilon = 400\text{--}500 \text{ l mol}^{-1} \text{ cm}^{-1}$) and of the benzene ring ($\epsilon = 220 \text{ l mol}^{-1} \text{ cm}^{-1}$) in the 260–300 nm region. We thus infer that the dissociation dynamics of aryl iodides is influenced by the participation of the S_2 state in the 220–260 nm region and by the S_1 state at longer wavelengths. The S_2 state influences the dynamics of I^* production more than the S_1 state.

The I^* quantum yield at ~ 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 pentafluorooiodobenzene 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 ~ 305 nm, which means that at the red edge the contribution of the $\pi^* \leftarrow \pi$ transition of benzene ring is only marginal to the overall I^* production. Moreover, the possible benzene-type transition at ≥ 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 ~ 300 nm.^{12,14} Fairbrother *et al.*³⁵ 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_2F_5I , n - C_3F_7I , and *i*- C_3F_7I 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 pentafluorooiodobenzene 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 $\pi^* \leftarrow \pi$ transitions. To explain the observed dynamics in pentafluorooiodobenzene at 304 nm Griffiths *et al.*²⁹ invoked the presence of a low-lying CT state which is lower in energy in pentafluorooiodobenzene than in iodobenzene. The CT state originates from the excitation of a $5p\pi$ nonbonding iodine electron to the π^* molecular orbital of the benzene ring. They suggested that this CT state mixes better with the $\sigma^* \leftarrow n$ transition in pentafluorooiodobenzene 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 pentafluorooiodobenzene 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 pentafluorooiodobenzene does not reflect the effect of fluorination on ϕ^* to the same extent at all the dissociation wavelengths. The effect of fluorination is prominent only at dissociation wavelengths ≥ 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 $\pi^* \leftarrow \pi$, $\sigma^* \leftarrow n$, and the two CT states (one singlet and another triplet arising due to the transition of $5p\pi$ nonbonding iodine electron to the π^* molecular orbital) are shown. The low-lying triplet CT state will be energetically closer to the lowest-energy state of the $\sigma^* \leftarrow n$ 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 pentafluorooiodobenzene 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 ~ 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

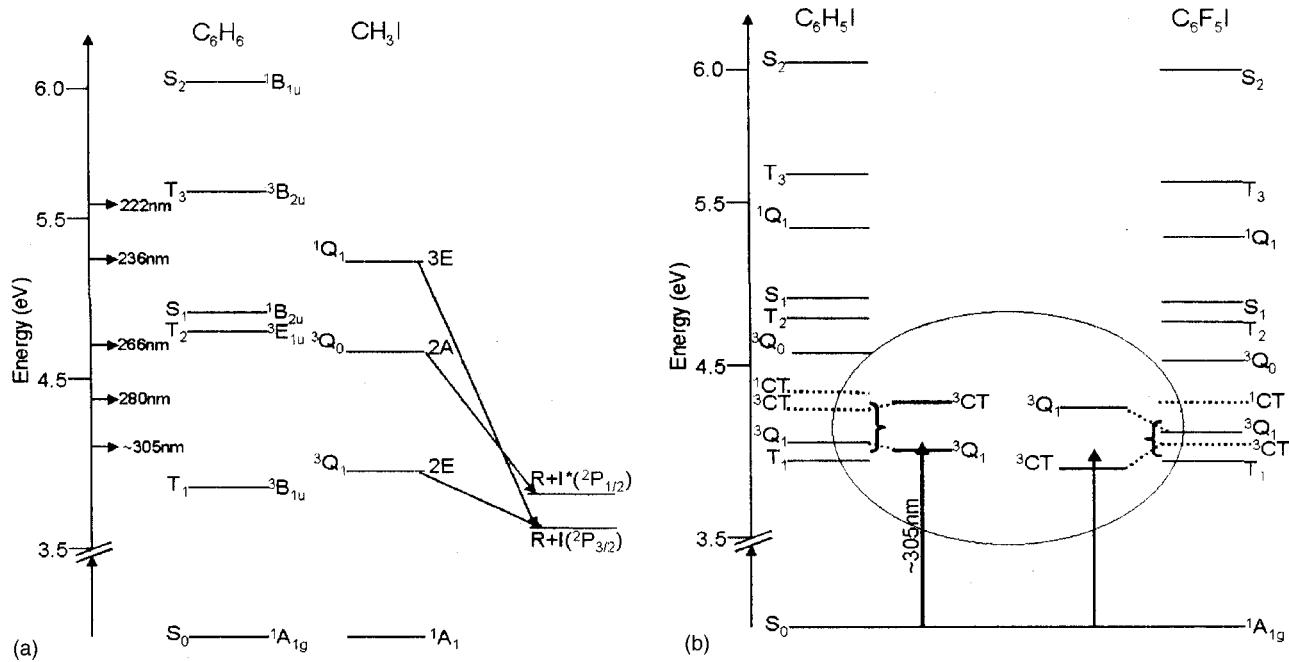


FIG. 4. (a) Energy correlation diagram presenting $\pi^* \leftarrow \pi$ and $\sigma^* \leftarrow n$ transitions in benzene and methyl iodide, respectively. (b) Model energy correlation diagram presenting $\pi^* \leftarrow \pi$, $\sigma^* \leftarrow n$, and $\pi^* \leftarrow n$ (CT state) in C_6H_5I and C_6F_5I . The states inside the ellipsis represent the relative positions of the 3Q_1 state and CT state.

other ring systems.³⁷ Adamantane is one of the few multicyclic systems which is thermodynamically stable. The heats of formation of cyclohexane (-123.1 ± 0.79 kJ/mol) (Ref. 38) and adamantane (-134.4 ± 2.3 kJ/mol) (Ref. 39) are comparable and hence make them right systems to choose to study the effect of ring strain on the dissociation dynamics. The I^* yield is found to be more or less the same for these iodides at dissociation wavelengths ≥ 240 nm, whereas at the blue wing excitation, the I^* formation is more from adamantyl iodide than from cyclohexyl iodide. The formation of equal amounts of I and I^* from these iodides at the dissociation wavelengths ≥ 240 nm suggests that at this wavelength region the dynamics is similar for both the iodides. The I^* formation is $\sim 50\%$ near the absorption maximum of their A band and falls off at the red edge. Production of more I^* near the absorption maximum is similar to what is seen in the case of normal alkyl iodides. The formation of more 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 I^* quantum yield is 0.27 for cyclohexyl iodide at 248 nm. Their measured value is found to be less than the I^* yield at 266 nm measured by us in the present investigation. To make sure that the formation of more 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 I and I^* , the slope was found to be 0.87 and 1.0, respectively (data not shown). This confirms that the formation of I and I^* at 266 nm is indeed due to a single-photon process. Also, at the red edge, the dynamics of 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 I^* production from these iodides is similar to that of normal alkyl iodides at dissociation wavelengths ≥ 240 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,^{41–43} is involved in the dissociation of the cyclic iodides at ≤ 240 nm. The formation of more 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 I^* upon photodissociation in the A band. The 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 $\pi^* \leftarrow \pi$ transition in the dynamics of I^* production from iodobenzene and pentafluoriodobenzene 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 $\sigma^* \leftarrow n$ transitions leading to more I* product.

(3) At photolysis wavelengths ≤ 300 nm, the formation of I has only two contributions, whereas at the red edge (≥ 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.

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