

Dynamics of I*($^2P_{1/2}$) production from fluorinated alkyl iodides at 266, 280, and \sim 305 nm

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In this paper, we present I*($^2P_{1/2}$) quantum yield, ϕ^* from the gas phase photodissociation of a series of perfluoroalkyl iodides at three different wavelengths 266, 280, and \sim 305 nm. The iodine atoms in the ground I($^2P_{3/2}$) and spin-orbit excited I*($^2P_{1/2}$) states were monitored directly by a two photon laser induced fluorescence scheme. The I* quantum yields for the fluorinated alkyl iodides are found to be much higher than their corresponding alkyl iodide analogs over the entire A band. However, ϕ^* remains more or less unchanged as a function of photolysis wavelength for the perfluoroalkyl iodides with the exception of CF₃I in which it drops monotonically as a function of wavelength. Unlike in normal alkyl iodides, branching at the α position does not affect the ϕ^* in perfluoroalkyl iodides. The prediction of I* yield using the one dimensional Landau-Zener soft-radical-impulse model is opposite to what is seen from our measurements. In all the fluorinated alkyl iodides, the CF₃ in-plane rocking mode which can take the initially excited 3Q_0 state to the 1Q_1 state through the crossing region appears to be weakly coupled to the C-I stretch resulting in low yield of I atom in the dissociation process.

INTRODUCTION

Photodissociation dynamics of alkyl iodides and fluorinated alkyl iodides has been the subject of many investigations because they serve as model systems for studying polyatomic fragmentation.¹⁻⁷ The first UV absorption band (A) of the alkyl iodides starts at ca. 230 nm and extends up to 330 nm. This is due to the promotion of a nonbonding electron from the iodine atom to the antibonding σ^* molecular orbital ($n \rightarrow \sigma^*$ transition) of the C-I bond. Photoexcitation of the A band results in the rupture of the C-I bond in ca. 10^{-13} s to produce alkyl radical and iodine atoms both in the ground ($^2P_{3/2}$) and spin-orbit excited ($^2P_{1/2}$) states in the following manner:



where X stands for H, D, or F atom. According to Mulliken⁸ the $n \rightarrow \sigma^*$ transition is composed of three overlapping transitions from the ground state (1A_1) to the repulsive 3Q_1 , 3Q_0 , and 1Q_1 states in the increasing order of energy. He predicted that the $^3Q_0 \leftarrow ^1A_1$ is polarized parallel to the C-I bond and produces I* as the dissociation product. The $^3Q_1 \leftarrow ^1A_1$ and $^1Q_1 \leftarrow ^1A_1$ transitions are polarized perpendicular to the C-I bond axis and produce I. Gedanken and co-workers using magnetic circular dichroism (MCD), resolved the contributions of the three transitions to the A band in various alkyl iodides^{9,10} including CF₃I.¹¹ They found that the parallel transition to the 3Q_0 state is dominant (about 84% of the total absorption in CF₃I) and the absorption maxima corresponding to the transitions to 3Q_1 , 3Q_0 , and 1Q_1 states occur around 301.8, 264.1, and 237.9 nm, respec-

tively. Although I* is the major product from alkyl iodide dissociation near the A band maximum, a significant amount of I is also formed due to a curve-crossing mechanism in the excited state. This has been confirmed by several techniques, which can measure the angular distribution and the spin-orbit state of the resulting iodine atoms. However, whether the initial excitation in the A band region resulting in both I and I* products is solely to the 3Q_0 state remains controversial.

Earlier¹²⁻¹⁴ we reported wavelength dependent I* yields in a series of long as well as branched alkyl iodides. While the dynamics of I* production in linear alkyl iodides was explained using the well-known 1D classical Landau-Zener model,¹⁵ the same model failed to explain the I*/I branching ratio in the α -branched iodides as a function of wavelength. The model also could not explain the observed I* yields in CH₃I and CD₃I where the potential energy surfaces are nearly the same.¹⁶ This brought out the importance of the multidimensional nature of the potential energy surfaces (PESs) involved in the dynamics. The intersection between the 3Q_0 and 1Q_1 surfaces has been pointed out¹⁷⁻²¹ as a conical intersection. The branching requires distortion of the initially excited C_{3v} geometry into a C_s geometry which can effectively couple the 3Q_0 and 1Q_1 states. Person *et al.*²² had pointed out that e -symmetry vibrations that distort the alkyl iodide out of the C_{3v} geometry are effective in coupling these states. They had shown that in CF₃I thermal excitation of low frequency bending modes, indeed, leads to enhanced coupling and subsequently more I atom is produced from the CF₃I dissociation. Therefore, higher perfluoroalkyl iodides having many low frequency vibrations should yield more I compared to CF₃I.

The early work on fluorinated alkyl iodides was by

Donohue and Wiesenfeld⁴ who reported the quantum yield of I* production using broadband flash photolysis. Since then the dynamics of perfluoroalkyl iodides have been studied by several groups using a variety of techniques to monitor I* products.^{15,23–34} Recently the dissociation dynamics of CF₃I and other fluorinated alkyl iodides has been studied by photofragment translational spectroscopy.^{22,35–42} Experimental I*/I branching ratios do not agree well with the relative contribution of the excited states as determined from MCD studies. The I* yield is still a subject of some uncertainty. Felder,⁴² Hwang *et al.*,³⁸ Furlan *et al.*,³⁹ and Kang *et al.*⁴⁰ have investigated the I* yield from CF₃I in the red wing of the A band. They could not explain the I* yield from the ratio of the absorption cross sections to the three different excited states alone. Kang *et al.*⁴⁰ explained their data assuming a simple one dimensional Landau–Zener-type curve crossing between the ³Q₀ and ¹Q₁ states at 277 and 304 nm. If this is true and the direct excitation to the ³Q₁ state at these wavelengths is not significant as suggested by Furlan *et al.*,³⁹ Felder,⁴² and earlier by Hwang and El-Sayed³⁸ then the other longer chain fluorinated alkyl iodides should show marked decrease in the I* yield upon dissociation in the red region of the A band. The dynamics will then be purely kinematic in origin and a simple one-dimensional curve crossing can describe the I* yields. In this paper, we probe some of these mechanisms of C–I bond rupture in fluorinated alkyl iodides at three different photolysis wavelengths by direct measurement of the I and I* yields with two photon laser induced VUV fluorescence³² (TPLIF). We also investigate the effect of radical size and shape (branching) on the dynamics of I* production.

EXPERIMENT

The apparatus used in our experiment has been described in detail elsewhere.^{14,43} The perfluoroalkyl iodides were bought from Aldrich Chemicals, USA, decolorized with sodium bisulfite and distilled prior to each experiment. The sample pressure was maintained at 40–50 mTorr in a stainless steel chamber which was evacuated continuously using a 4 inch diffusion pump backed by a mechanical pump. The pressure inside was monitored by a MKS baratron gauge. The pump and probe lasers were aligned perpendicular to each other at the center of the cell. The TPLIF signal in the vacuum ultraviolet was collected using a solar blind (Thorn EMI, 9433) photomultiplier tube (PMT) placed on the top of the chamber. The fourth harmonic of a Nd:YAG laser (DCR-3G, Spectra Physics) was used for dissociation at 266 nm (18 mJ/pulse). The second harmonic of the dye laser was used for the photolysis at 280 nm (~4 mJ/pulse). The tunable UV light for probing the fragments I (304.7 nm) and I* (306.7 nm) were obtained from the second harmonic of another dye laser. The TPLIF signal was recorded by scanning the probe laser across the two photon absorption lines of I and I*. The photodissociation at ~305 nm was carried out with the probe laser alone with tight focusing at the center of the cell. A power dependent study shows that three photons from the same pulse are absorbed, one photon breaks the C–I bond and the other two subsequent photons probe the iodine atoms. To collect the vacuum ultraviolet TPLIF signal effi-

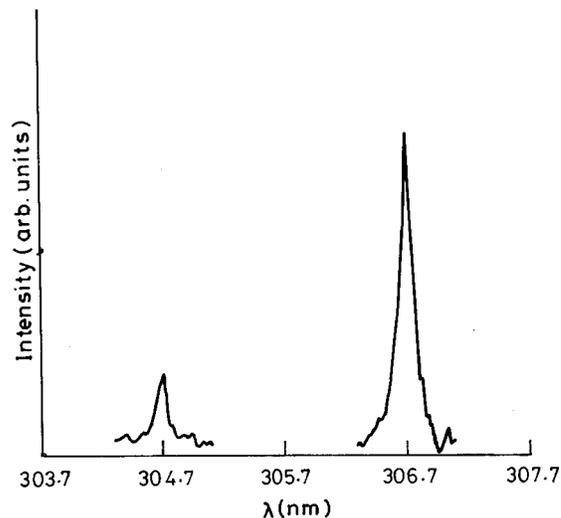


FIG. 1. Typical TPLIF spectra of I and I* from perfluorobutyl iodide dissociation at 280 nm.

ciently the gap between the PMT and the MgF₂ window was flushed continuously with dry nitrogen. The PMT output was amplified (X25), averaged in a gated boxcar averager (SRS 250) and displayed on a stripchart recorder.

RESULTS AND DISCUSSION

The TPLIF spectra were recorded by scanning the probe laser across the two photon absorption lines of I (304.7 nm) and I* (306.7 nm). The relative quantum yield of I* is given as, $\phi^* = [I^*]/([I] + [I^*])$, where [] represents the corresponding number density. ϕ^* was determined directly from the VUV emission spectra. The experimental signal intensities $S(I)$ and $S(I^*)$ are proportional to [I] and [I*], respectively, and we can write

$$S(I^*)/S(I) = k[I^*]/[I]. \quad (3)$$

The constant k contains relative absorption cross sections, transition probabilities for the I and I* two photon excitations, etc. Since our ϕ^* value (0.75) for CH₃I dissociation at 266 nm is in good agreement with the same (0.76) found by Riley and Wilson¹ from photofragment spectroscopy, we take $k = 1$ and thus, the ϕ^* values are derived directly from the TPLIF signal intensities of I and I*. Typical spectra from I and I* are shown in Fig. 1. The quantum yield for I* production at three different wavelengths for a series of fluorinated alkyl iodides are listed in Table I.

In the two-laser experiments, the signal was checked to vary linearly with the pump laser power. In the single laser experiment the very small difference in the absorption coefficients at 304.7 and 306.6 nm is ignored. A power dependence study at ~305 nm shows that three photons are involved, implying that one photon breaks the C–I bond and two subsequent photons probe the resulting iodine atoms.

A. I* quantum yield from CF₃I

A number of experimental^{22,33,35,38–41} and theoretical^{17–21,44,45} studies have been carried out to understand the effect of photon energy and that of curve crossing

TABLE I. Quantum yield of I* (ϕ^*) from perfluoroalkyl iodides at different excitation wavelengths and electron affinity of R* (R=perfluoroalkyl).

Molecule	ϕ^*	ϕ^*	ϕ^*	Electron affinity of R* (eV)
	266 nm	280 nm	~ 305 nm	
CF ₃ I	0.89 \pm 0.05	0.79 \pm 0.03	0.63 \pm 0.02	0.072
C ₂ F ₅ I	0.97 \pm 0.03	0.75 \pm 0.03	0.83 \pm 0.05	0.53
<i>n</i> -C ₃ F ₇ I	0.83 \pm 0.02	0.89 \pm 0.03	0.90 \pm 0.05	0.72
<i>n</i> -C ₄ F ₉ I	0.75 \pm 0.03	0.80 \pm 0.03	0.87 \pm 0.02	0.85
<i>n</i> -C ₆ F ₁₃ I	0.82 \pm 0.02	0.74 \pm 0.03	0.82 \pm 0.01	0.93
<i>i</i> -C ₃ F ₇ I	0.83 \pm 0.01	0.80 \pm 0.03	0.89 \pm 0.02	1.39

in the photodissociation dynamics of CF₃I in the A band. We find ϕ^* (0.89) is maximum for CF₃I at 266 nm and falls off to 0.63 at ~ 305 nm. At 266 nm, Ershov²³ reported ϕ^* as 0.91. However, more recent results of Felder,³⁵ Van Veen *et al.*,³³ and Person *et al.*²² from time-of-flight experiments at 248 nm are in good agreement with our value of 0.89 for CF₃I near the A band maximum. Van Veen *et al.* had predicted that 97% of the absorption near the peak is due to the ³Q₀ state. However, only 90% I* is produced because some of the excited molecules in the ³Q₀ state crossover to the ¹Q₁ state and produces ground state iodine atoms. Felder, on the contrary, concluded that near the peak of the A band direct excitation to the ¹Q₁ state plays a much more significant role. Person *et al.* measured a ϕ^* value of 0.87 at 100 °C which is close to our ϕ^* obtained at room temperature. From our measurement as well as from results obtained by Person *et al.* it appears that the ³Q₀ state contributes $\sim 90\%$ to the total absorption in the Franck–Condon region. Only 10% contribution to the absorption near the peak comes from the ¹Q₁ state. However, the actual value of I* measured in an experiment near the absorption maximum will depend largely on experimental conditions like the temperature of the molecules, the exact wavelength of the photolysis laser and its polarization characteristics, etc. The contribution of the ³Q₀ state to the overall absorption will be close to 84% which was predicted by Gedanken¹¹ from MCD studies.

At 280 nm we find ϕ^* as 0.79. Kim *et al.*⁴¹ have studied the dynamics of CF₃I dissociation at 277 nm and reported the anisotropy parameter β for the I* and I channels as 1.83 and 0.96, respectively. They have shown using the photofragment imaging technique that I* is produced purely from the parallel transition ³Q₀ \leftarrow N at this wavelength. However, I atoms are produced by two pathways: (i) direct dissociation from the ³Q₁ state and (ii) curve crossing dissociation from the initially excited ³Q₀ state to the ¹Q₁ state. They calculated the ϕ^* value as 0.87 at 277 nm. Furlan *et al.*³⁹ have probed the CF₃I dissociation at 275–303 nm by photofragment translational spectroscopy. They derived the I/I* branching ratio direct from the time-of-flight spectrum. At 279 nm they obtained $\phi^*=0.90$. They inferred that there is no significant contribution from the ³Q₁ state up to 296 nm and the I* quantum yield alters monotonically between 275 and 296 nm. They rationalized the I atom production as originating from the curve crossing mechanism. Our direct probing method of I and I* atoms yields a value of ϕ^* which is much lower than the results obtained by Kim *et al.*

as well as by Furlan *et al.* This may be explained by the fact that our measurements were made at a much higher temperature than their measurements. In fact, Felder⁴² had pointed out earlier that there is a strong temperature dependence of the absorption cross section and that the absorption to the ³Q₀ state (correlates with I* asymptotically) increases with increasing temperature at the red wing region of the A band.

At ~ 305 nm our value for the quantum yield of I* production in CF₃I is 0.63. This is in close agreement with the value of ϕ^* (0.69) at 304 nm reported by Kang *et al.*⁴⁰ They have used state selective ionization and pulsed-field time-of-flight mass spectrometry to probe CF₃I dissociation dynamics. They have used the recoil velocity of iodine atoms from the earlier work of Hwang and El-Sayed³⁸ on CF₃I to calculate the I* quantum yield. However, these results are in disagreement with ϕ^* reported by Furlan *et al.*³⁹ Furlan and co-workers have measured a ϕ^* value of 0.37 at 303 nm which is consistent with the findings of Felder⁴² at 308 nm. Felder pointed out that the relative excitation probability of the ³Q₀ and ³Q₁ states changes significantly with the translational temperature of the CF₃I molecular beam. In fact, according to Felder, a change of 8 K in the translational temperature can alter the I* yield drastically. However, another factor that will affect the quantum yield measurement in molecular beams is the amount of clusters present. Syage⁴⁶ reported that methyl iodide clusters dissociate more readily to produce I atoms than I* atoms at 304 nm. Although it is not very clear why our results and the results of Kang *et al.* are in disagreement with that of Furlan *et al.*, the amount of I atom production remains to be significant at this dissociation wavelength. However, I* is still the major product from CF₃I unlike in the case of CH₃I where I is the major product at this wavelength. In fact, at all the photolysis wavelengths used in this study CF₃I produces more I* than CH₃I. This is in contradiction to what is predicted by a one-dimensional Landau–Zener soft-radical-impulse model used successfully by Godwin *et al.*¹⁵ to explain the trends in quantum yield of I* production in normal alkyl iodides. In this model only the crossing between the ³Q₀ and the ¹Q₁ states is considered along the C–I distance and ϕ^* is given by

$$\phi^* = \exp \frac{-4\pi^2(V_{12})^2}{h|\Delta F|v}, \quad (4)$$

where V_{12} is the coupling term, ΔF is the difference in gradients at the crossing point, and v is the velocity of the molecule at the crossing point. V_{12} and ΔF are generally unknown quantities and can be absorbed in a parameter ζ as

$$\phi^* = \exp(-\zeta/v), \quad (5)$$

where $\zeta = 4\pi^2(V_{12})^2/h|\Delta F|$. The recoil velocity, v is calculated either from the translational energy (E_{trans}) or from the available energy (E_{avl}) invoking the soft-radical-impulse approximation at the wavelength of excitation according to

$$E_{\text{trans}} = 1/2 \mu_{\text{R-I}} v^2 = (\mu_{\text{C-I}}/\mu_{\text{R-I}})(E_{\text{avl}}), \quad (6)$$

where $\mu_{\text{C-I}}$ and $\mu_{\text{R-I}}$ are the reduced masses of C and I and R and I, respectively. E_{avl} is given by $h\nu - D_0 - E_{\text{so}}$ with ν being the excitation frequency, D_0 the dissociation energy of the C–I bond and E_{so} , the spin–orbit excitation energy of

TABLE II. Crossing velocity of the alkyl iodides calculated from the reported value of the translational energy corresponding to the I^* channel. The extra energy available to the I channel comes only after crossing and hence does not contribute to the crossing velocity.

Compound	248 nm		304 nm	
	E_t (kJ/mol)	v (m/s)	E_t (kJ/mol)	v (m/s)
CH ₃ I	148 (Ref. 51)	4697	66 (Ref. 40)	3136
CF ₃ I	123 (Ref. 36)	2346	83 (Ref. 38)	1927
C ₂ H ₅ I	118 (Ref. 51)	3162	54 (Ref. 40)	2139
C ₂ F ₅ I	87 (Ref. 52)	1683	57 (Ref. 37)	1363

the iodine atom (0.942 eV). Using the measured translational energy for fluorinated as well as normal alkyl iodides available in the literature, we have calculated the velocity at the crossing point using Eq. (6). The data at two photolysis wavelengths are shown in Table II. It appears from the table that at any particular excitation energy, the fluorinated iodides have lower velocity at the crossing point compared to their corresponding unsubstituted analogs. This would mean that CF₃I moves slowly on the excited state surface and has a better chance of making a nonadiabatic transition to the 1Q_1 state from the initially excited 3Q_0 state. Godwin *et al.*¹⁵ have shown that the values of ζ at any given wavelength calculated from the first member of each family predicts the quantum yield of I^* correctly for other molecules belonging to the family. They calculated ζ for CH₃I and CF₃I at 248 nm and found that the value of this parameter for CH₃I was ca. 100 times greater than that of CF₃I. If we take their ζ -value for fluorinated alkyl iodides (10 m/s) and use it for calculating ϕ^* at 266 nm, we find the value of ϕ^* close to 0.99 for all the members of the fluorinated iodide family. However, ϕ^* thus calculated is much higher than, as well as different from what we measure directly by the TPLIF technique. All these analysis imply that a better description of branching is necessary to explain the observed quantum yield in CF₃I vis-à-vis in CH₃I.

Person *et al.*²² had proposed that e -symmetry vibrations which take the molecule away from the original C_{3v} geometry to the C_s symmetry at the conical intersection of the 3Q_0 and 1Q_1 surfaces, will play an important role to determine the branching to the I channel. In fact, *ab initio* calculations at the HF/3-21G level using a GAUSSIAN-94⁴⁷ set of programs have been carried out for both CH₃I and CF₃I. The ν_6 (CH₃/CF₃ rock) mode which belongs to E -symmetry under the C_{3v} point group transforms to A' -symmetry under the C_s geometry which can couple the 1Q_1 and 3Q_0 states effectively at the crossing region. This mode which is at much higher frequency (885 cm⁻¹)⁴⁸ in CH₃I than in CF₃I (265 cm⁻¹)⁴⁹ is, perhaps, coupled more strongly to the C-I mode in the excited state of the former than the latter. Thus, the CF₃ in-plane rock in CF₃I although has a low frequency, is weakly coupled to the C-I stretch and cannot take it out of the C_{3v} geometry effectively. The molecule continues its journey on the initially excited 3Q_0 surface until it

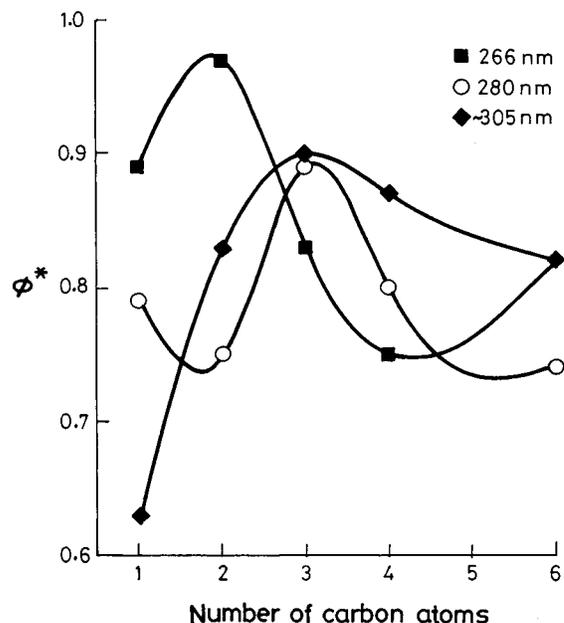


FIG. 2. I^* quantum yield from perfluoroalkyl iodides at 266, 280, and \sim 305 nm as a function of radical size.

asymptotically goes to the I^* product. This explains why CH₃I at all wavelengths has lower ϕ^* than CF₃I.

B. Higher fluorinated n -alkyl iodides

The quantum yield of I^* for other higher perfluoroalkyl iodides near the A -band maximum is usually found close to 1.0 and does not depend very much on the structure of the perfluoroalkyl radical in contrast to normal iodoalkanes as reported by earlier authors.²³⁻³¹ We also observe a similar effect from ϕ^* measurements on the above iodides. From Table I, it is clear that the quantum yields of these iodides are very high at all the wavelengths employed by us. Also no clear trend is observable as we examine the quantum yield as a function of photolysis wavelength or radical size. We find that ϕ^* is more for all the perfluoroalkyl iodides at \sim 305 nm than at 266 or 280 nm. Figure 2 displays the variation of ϕ^* as a function of radical size. This is in sharp contrast to what is observed for the corresponding alkyl iodides.¹² Although for CF₃I, ϕ^* decreases with increasing excitation wavelength as seen in the case of normal alkyl iodides, for the higher fluorinated iodides no such clear trend is found.

The quantum yield of I^* production from fluorine substituted and unsubstituted alkyl iodides was correlated to the ionization potential of the alkyl radical by Donohue and Wiesenfeld.⁴ They concluded that the alkyl groups which can easily donate an electron, that is, alkyl radicals with low ionization potential will cause a small spin-orbit splitting in the excited state resulting in low I^* yield. Also Ivanov *et al.*²⁴ had shown with MO-LCAO-SCF (molecular orbitals, linear combination of atomic orbitals, self-consistent field) calculations a strong correlation between the localization of σ^* electron on the iodine atom and a reduction in spin-orbit coupling and hence a decrease in quantum yield of I^* in alkyl iodides. Therefore, the quantity that should be a measure of the magnitude of spin-orbit splitting must be

the electron affinity of the alkyl group. The fully fluorinated alkyl groups are strong electron withdrawing groups and we have calculated their electron affinity at the HF/3-21 G level using a GAUSSIAN-94⁴⁷ set of programs. The electron affinity is taken as the difference in energy between CF_3^{\bullet} and CF_3^- , that is, $(E_{R^{\bullet}} - E_{R^-})$ is the electron affinity of the alkyl radical, in general. The calculated values are listed in Table I. It appears that the electron affinity increases as we go down in the table but the I^* yields do not follow the same trend. Thus, the extent of spin-orbit splitting although scales with the electron affinity and is important, does not play any significant role in the dynamics of dissociation. If we apply the one-dimensional Landau-Zener analysis discussed above to explain the dynamics, we expect a decrease in ϕ^* within a given family at any particular wavelength as the radical size increases. This is not found for the fluorinated alkyl iodide family from our results. This indirectly leads us to believe that a simplistic one-dimensional Landau-Zener model is not adequate to describe the dynamics of I^* production in fluorinated alkyl iodides. For a better rationalization of the data, at least a two-dimensional Landau-Zener-type description is needed where another vibrational mode coupled to the C-I stretch is taken into consideration.

For the higher perfluoroalkyl iodides we carried out *ab initio* calculations at the HF/3-21G level using a GAUSSIAN-94⁴⁷ set of programs and found that CF_3I has two vibrations and $n\text{-C}_3\text{F}_7\text{I}$ has 12 vibrations below 500 cm^{-1} which is consistent with experimental determination of their vibrational frequencies.^{49,50} In a multidimensional scenario if the number of low frequency modes strongly coupled to the C-I bond stretching, is solely responsible for the dynamics of I^* production, we would expect a smaller value of ϕ^* for $n\text{-C}_3\text{F}_7\text{I}$ than CF_3I . This expectation is borne out of the fact that effective coupling between the C-I stretch and low frequency modes will allow the molecule to cross over to the 1Q_1 state and produce more I product. However, the values of ϕ^* are high and comparable between these two molecules at all wavelengths studied by us. The implication is that the coupling between the 3Q_0 and 1Q_1 states does not depend on all the low frequency modes but on a particular mode of A' symmetry which can couple these two states effectively. After careful examination of the nature and symmetry of low frequency vibrations in $\text{C}_2\text{F}_5\text{I}$, $\text{C}_3\text{F}_7\text{I}$, $\text{C}_4\text{F}_9\text{I}$, and $\text{C}_6\text{F}_{13}\text{I}$ we find that all these molecules have a CF_3 in-plane-rock mode around 250 cm^{-1} with A' symmetry. This mode must be weakly coupled to the C-I stretch, thereby, not facilitating access to the I product channel during the dissociation. To the contrary, the same mode which is of higher frequency (approximately 1000 cm^{-1}) in the normal alkyl iodides must be strongly coupled to the C-I stretch leading to more I production in the dissociation.

C. Branched perfluoroalkyl iodides

It is clear from Table I that the effect of branching on ϕ^* in fluorinated alkyl iodides is not significant unlike in their branched alkyl iodide analogs. The quantum yield of I^* production from $n\text{-C}_3\text{F}_7\text{I}$ and $i\text{-C}_3\text{F}_7\text{I}$ have been studied and compared by various groups^{4,23,28,31} using different tech-

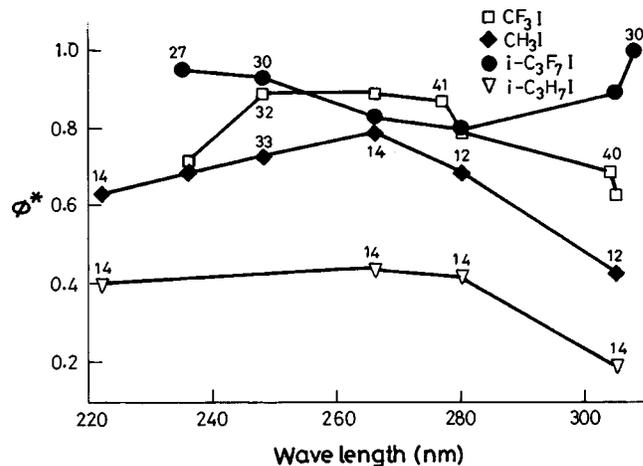


FIG. 3. The plot of ϕ^* against excitation wavelength in (\square) CF_3I , (\blacklozenge) CH_3I , (\bullet) $i\text{-C}_3\text{F}_7\text{I}$, and (∇) $i\text{-C}_3\text{H}_7\text{I}$. (The number marked against each point indicates the reference number in the text from which the value has been taken. The unmarked points are adapted from the present work.)

niques. Smedley *et al.*³¹ studied the quantum yield from 265–336 nm by monitoring the ir-emission from I^* . They concluded that ϕ^* 's are identical at 266 nm and drop off in both cases toward the red. The measured quantum yield at 266 nm was 1.0. The yield measured by us at this wavelength for both $n\text{-C}_3\text{F}_7\text{I}$ and $i\text{-C}_3\text{F}_7\text{I}$ is the same and it is 0.83. In fact, in no cases did we find that ϕ^* is 1.0. This is perhaps due to the advantage offered by the TPLIF technique for the detection in which both I and I^* are detected whereas in the infrared emission technique I is never detected. At longer dissociation wavelengths we find that the ϕ^* for both $n\text{-C}_3\text{F}_7\text{I}$ and $i\text{-C}_3\text{F}_7\text{I}$ remains more or less the same. There seems to have no significant effect due to branching of the alkyl chains at the α -carbon atom, on ϕ^* .

If we compare ϕ^* for $i\text{-C}_3\text{H}_7\text{I}$ and $i\text{-C}_3\text{F}_7\text{I}$ (Fig. 3) over the entire A band, we find that I^* yield from the α -branched fluorinated alkyl iodides are significantly higher than that from the α -branched alkyl iodides at all wavelengths. In fact, the same observation is made if we compare ϕ^* from CH_3I and CF_3I over the wavelength range we have used. Therefore, we can safely state that, in general, the fluorinated alkyl iodides will have a higher I^* yield than the corresponding alkyl iodides. But why does branching not alter the dynamics? This is because the CF_3 in-plane-rock in $i\text{-C}_3\text{F}_7\text{I}$ although is of low frequency (263 cm^{-1}), is not strongly coupled to the bond that breaks. It appears from our quantum yield measurements that the extent of coupling of this particular mode to the C-I stretch is about the same in $i\text{-C}_3\text{F}_7\text{I}$ as well as $n\text{-C}_3\text{F}_7\text{I}$ near the 3Q_0 and 1Q_1 intersection.

SUMMARY

The results discussed in this paper may be summarized as follows:

- (i) The quantum yields of I^* production from photodissociation of perfluoroalkyl iodides are much higher than their normal alkyl iodide analogs at any wavelength within the entire A band.

- (ii) Unlike in normal alkyl iodides, ϕ^* in perfluoroalkyl iodides remains unaltered by branching at the α -carbon site.
- (iii) No general trend in ϕ^* is observed among the different perfluoroalkyl iodides as a function of photolysis wavelength or radical size except in CF_3I where the ϕ^* drops monotonically as a function of wavelength starting from the peak of the absorption spectrum.

The above results could not be explained by invoking the popularly used one-dimensional Landau–Zener soft-radical-impulse model. We have identified the CX_3 in-plane rocking mode in alkyl iodides as the mode which couples the I and I^* product channels effectively. The extent of coupling of this mode to the C–I bond stretch near the crossing region is not easy to estimate, at present. However, this quantity holds the key to our understanding of the dynamics of I^* production in the photodissociation of fluorinated alkyl iodides. Since accurate *ab initio* excited state potential energy surfaces, for large molecules like the perfluoroalkyl iodides used in this study, will be difficult to obtain, a two-dimensional Landau–Zener model where the C–I stretch and the CX_3 in-plane rocking modes are included should be in order. The latter model may also help us understand the branching dynamics to I and I^* channels, albeit qualitatively, for this interesting class of molecules.

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