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Photodissociation of Partially Fluorinated Alkyl Iodides in Their A-Band

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Photodissociation dynamics of partially substituted alkyl iodides with fluorine atoms at β and γ positions has been investigated. The iodine atoms in the ground I($^2P_{3/2}$) and spin−orbit excited I*($^2P_{1/2}$) states produced in the ultraviolet photolysis of CF_3CH_2I, $C_6F_{13}CH_2CH_2I$, and $C_8F_{17}CH_2CH_2I$ have been detected using a two photon laser induced fluorescence (TPLIF) scheme. The I* quantum yield of the above iodides at 222, 236, 266, 280, and ∼305 nm corresponding to the red and blue wings as well as the peak of their A-band absorption spectrum has been determined. The I* yield from β and γ-substituted iodides is found to remain more or less unchanged as a function of excitation wavelength below 262 nm, which is the peak of their A-band. The observed dynamics at 222, 236, and 266 nm can be adequately described by the known Landau−Zener curve crossing model between the $^3Q_0$ and $^1Q_1$ states. However, at wavelengths above 262 nm, the measured I* quantum yield of β and γ-substituted alkyl iodides reflects that the $^3Q_1$ state has a significant contribution to the overall dynamics. The electronic effect exerted by fluorine on the dynamics appears to wither as the substitution moves further away from the C−I bond.

Introduction

Excitation of alkyl iodides in their A-band breaks the C−I bond in less than ca. 100 fs to produce iodine atoms in their ground I ($^2P_{3/2}$) and the spin−orbit excited I*($^2P_{1/2}$) states, as well as alkyl fragments with varying degrees of internal excitation. The dissociation may be schematically represented as

$$R-I \rightarrow R\,(v, j) + I\,(^2P_{3/2}) \qquad (1)$$

$$\rightarrow R\,(v, j) + I^*(^2P_{1/2}) \qquad (2)$$

where R, represents the alkyl or fluorinated alkyl group. The A-band of these iodides arises due to the excitation of a nonbonding electron of the iodine atom to an antibonding molecular orbital localized primarily on the C−I bond ($n \rightarrow \sigma^*$ transition). The study of photodissociation of these iodides serves as a model in the investigation of dynamics of bond breaking in polyatomic molecules.[1−5] According to Mulliken[6] the $n \rightarrow \sigma^*$ excitation in methyl iodide is composed of three overlapping transitions from the ground state, N to the repulsive $^3Q_1(2E)$, $^3Q_0(2A_1)$, and $^1Q_1(3E)$ states in the increasing order of energy. He predicted that the $^3Q_0 \leftarrow N$ is polarized parallel to the C−I bond axis and correlates asymptotically to I* product, while the $^3Q_1 \leftarrow N$ and $^1Q_1 \leftarrow N$ transitions are polarized perpendicular to the C−I bond and produces I. Gedanken et al.,[7,8] using magnetic circular dichroism (MCD), resolved the contributions of these three transitions to the total absorption spectrum in various alkyl iodides including CF_3I. They reported that a parallel transition to the $^3Q_0$ state is dominant (about 84% of the total absorption) in CF_3I and the structure of the A band can be decomposed into three bands arising from transitions to the $^3Q_1$, $^3Q_0$, and $^1Q_1$ states and peaking around 301.8, 264.1, and 237.9 nm, respectively.

A large number of experimental[9−38] and theoretical[39−43] investigations has been carried out to elucidate the energy disposal, branching ratio (I*/I), and other aspects of the photodissociation dynamics of alkyl[9−22] and fluorinated[23−38] alkyl iodides. It has been shown that the energy disposal in the dissociation process is dependent on the structure and the nature of the substituent on the alkyl radical. Infrared emission,[24,26] VUV laser induced fluorescence,[9,12,14,15,18−20] and resonance enhanced multiphoton ionization (REMPI)[35,37] have been employed to obtain the product I*/I branching ratio from normal as well as fluorinated alkyl iodides in the past. The I* quantum yield at excitations near the absorption maximum is found to vary from 0.75 for methyl iodide[1] to 0.20 for *tert*-butyl iodide.[19] In alkyl iodide dissociation, the formation of I near the A-band maximum at 260 nm is generally understood in terms of the well-known classical one-dimensional Landau−Zener curve crossing model between the $^3Q_0$ and $^1Q_1$ states. In this model, the probability of curve crossing from the initially excited $^3Q_0$ state to the $^1Q_1$ state depends on two factors: the coupling of these two interacting potential energy curves at the conical intersection in a multidimensional potential energy surface (PES) scenario and the relative velocity of the dissociating fragments at the intersection. The nature of the PES does not vary significantly for molecules belonging to the same family such as the *n*-alkyl iodides. In such examples, the dynamics of I* production is purely kinematic in origin or, in other words, is guided by the laws of classical mechanics. But when the nature of the PES changes with substitution of an electronegative atom (or group) at the α-carbon atom, the dynamics is guided primarily by electronic factors, i.e., is dependent on the actual nature of the PES.[11] The electronic effect, which is prominent in fluorinated alkyl iodides, is also observed in the normal α-branched alkyl iodides. The extent of I* formation from the photodissociation of fluorinated alkyl iodides near the A-band maximum is found to be more than from the normal alkyl iodides[23−26] and does not depend very much on the radical size as well as branching at the α-carbon atom.[12,38]

In this paper, we investigate how is the dynamics of I*

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formation affected by substitution of fluorine atom(s) at the β or γ carbon positions, that is, away from the C−I bond, as a function of excitation energy. We have chosen partially fluorinated alkyl iodides, such as CF_3CH_2I, $C_6F_{13}CH_2CH_2I$, and $C_8F_{17}CH_2CH_2I$, and measured the I* yield at five different wavelengths covering the entire A-band. Kwok et al.[44] have recorded the resonance Raman spectra of CF_3CH_2I in cyclohexane and through quantitative resonance Raman intensity analysis using time dependent wave packet calculations concluded that the short time (∼15 fs) dynamics of CF_3CH_2I has a large amount of multidimensional character. They have shown that the C−I stretch motion is mixed with several different normal modes and there is no clear separation of the time scale of the C−I bond rupture and vibrational degrees of freedom of the rest of the molecule. On the contrary, the ethyl iodide photodissociation in the A-band has a very low degree of internal excitation.[45] Thus, one would expect electronic effects (that is, changes in the PES) to have a significant influence on the dynamics as the fluorine atoms stay farther away from the C−I bond in CF_3CH_2I. We address some of these issues in this work.

Experimental Section

The experimental setup used in our laboratory has been described in detail elsewhere.[18] All of the alkyl iodides were obtained commercially, decolorized with sodium bisulfite, and fractionally distilled prior to each experiment. The experiments were carried out at a sample pressure of ca. 50−70 mTorr in a stainless steel chamber. The chamber was pumped continuously with a diffusion pump backed by a rotary pump. The pump and the probe laser beams (both unpolarized) were aligned perpendicular to each other at the center of the chamber. The VUV fluorescence from the fragments I and I* was detected using a solar blind (Thorn EMI, 9433) photomultiplier tube (PMT) mounted on top of the chamber. The pump beam at 266 nm (∼20 mJ/pulse) for dissociation was obtained from the fourth harmonic of a Nd:YAG laser (DCR-3G, Spectra Physics). Dissociation wavelengths of 222 (∼1 mJ/pulse) and 236 nm (∼2 mJ/pulse) were obtained by mixing the dye second harmonic (280 and 304 nm, respectively, for 222 and 236 nm) with the fundamental (1064 nm) of the same Nd:YAG pump laser in a KDP crystal. Another Nd:YAG pumped dye laser (probe) was frequency doubled to produce tunable UV radiation (304−307 nm) for detecting the fragments I and I*, using a two photon laser induced fluorescence (TPLIF)[9] scheme. 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). In the case of ∼305 nm dissociation, the probe laser alone was focused tightly at the center of the chamber. The VUV fluorescence signal was collected through a magnesium fluoride window. The space between the window and the PMT was purged continuously with dry N_2. The PMT output was amplified (×25) and averaged in a gated boxcar signal averager (SRS250) and fed to a stripchart recorder.

Results

The absorption spectra of the linear partially fluorinated alkyl iodides reported in this paper were recorded using a Hitachi U-3000 spectrometer (Figure 1). The VUV emission spectra from I and I* were recorded by scanning the probe laser across their two photon absorption lines.

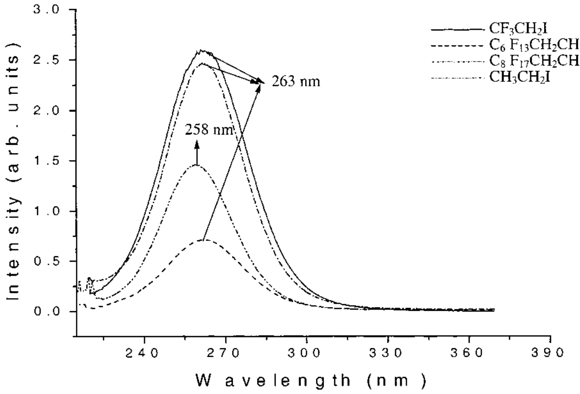

Figure 1. 1. Absorption spectra of CF_3CH_2I, $C_6F_{13}CH_2CH_2I$, and $C_8F_{17}CH_2CH_2I$ in cyclohexane. CH_3CH_2I spectrum is also shown for comparison.

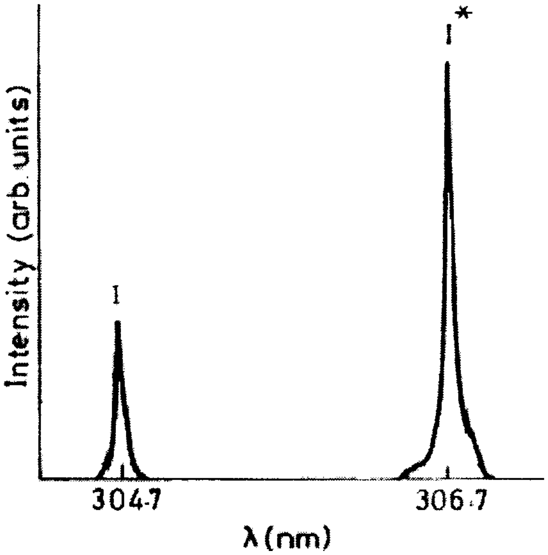

Figure 2. 2. Typical two photon laser induced fluorescence spectra of I and I* from 280 nm photolysis of CF_3CH_2I.

Typical TPLIF spectra of I and I* from CF_3CH_2I photolysis at 280 nm are shown in Figure 2. The relative quantum yield of I*, $\phi^* = [I^*]/([I] + [I^*])$, where [ ] represents concentration, was determined directly from the fluorescence signal. The ratio of the measured TPLIF signal intensities S (I) and S (I*) are proportional to the ratio of the [I] and [I*], respectively and we can write

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

The relative absorption cross sections, transition probabilities for the I and I* two photon excitations, and other experimental factors are absorbed in the proportionality constant k. We have taken the value of $k = 1$, since our value of ϕ^* (0.75) for CH_3I at 266 nm agrees very well with the same (0.76) found by Riley and Wilson[1] from photofragment spectroscopy. Thus, the ϕ^* values are obtained directly from the TPLIF spectra of I and I*. The quantum yield for I* production obtained at five different excitation wavelengths for the partially substituted alkyl iodides are listed in Table 1.

In the pump−probe experiments, the laser powers were kept at such level that the signal changed linearly with the pump laser power and the probe alone did not show any TPLIF signal. In the single laser experiments (at ∼305 nm), a power dependence study confirmed that three photons are involved in the process, implying that one photon is involved in the C−I bond rupture and two subsequent photons in probing the resulting iodine atoms.

TABLE 1: Relative Quantum Yield of I* Production from the Photolysis of Partially Fluorinated Alkyl Iodides[a]

compounds	ϕ^* at 222 nm	at 236 nm	at 266 nm	at 280 nm	at ~305 nm
CF_3CH_2I	0.80 ± 0.07	0.78 ± 0.03	0.81 ± 0.03	0.73 ± 0.02	0.52 ± 0.05
$C_6F_{13}CH_2CH_2I$	0.69 ± 0.06 (0.69)	0.65 ± 0.03 (0.66)	0.70 ± 0.02 (0.62)	0.74 ± 0.02	0.71± 0.03
$C_8F_{17}CH_2CH_2I$	0.61 ± 0.05 (0.67)	0.44 ± 0.02 (0.64)	0.59 ± 0.01 (0.59)	0.48 ± 0.04	0.42 ± 0.02
CH_3CH_2I	0.57 ± 0.02		0.72 ± 0.02	0.60 ± 0.02	0.39 ± 0.02
CF_3CF_2I	0.74 ± 0.07	0.78 ± 0.03	0.97 ± 0.03	0.75 ± 0.03	0.83 ± 0.05
$C_8F_{17}I$	0.67 ± 0.06	0.83 ± 0.03	0.76 ± 0.02	0.75 ± 0.02	0.73 ± 0.03

[a] The calculated values from 1-D Landau−Zener model are shown in parentheses.

Discussion

For CF_3CH_2I, $C_6F_{13}CH_2CH_2I$, and $C_8F_{17}CH_2CH_2I$, at all dissociation wavelengths employed in this work, I* is found to be the major product except for $C_8F_{17}CH_2CH_2I$ at 236 and ~305 nm, where the I* formation is less than 50% (Table 1). In linear alkyl iodides, the formation of I near the A-band maximum, that is, near 260 nm is generally explained by invoking the well-known one-dimensional curve crossing model between the $^3Q_0$ and $^1Q_1$ states. This model combines the soft radical model for energy disposal[11] with the one-dimensional Landau−Zener description of the curve crossing probability. The probability of crossing from the initially excited $^3Q_0$ state to the final $^1Q_1$ state is given by

$$P = 1 - \phi^* = \exp[-4\pi^2 (V_{12})^2/h|\Delta F|v] = \exp[-\zeta/v] \qquad (4)$$

where, V_{12} is the coupling term between the two adiabatic potentials, ΔF is the difference in potential gradients, and v is the velocity of the molecule at the crossing point. Because both V_{12} and ΔF depend on the characteristics of the $^3Q_0$ and $^1Q_1$ potential energy surfaces at the crossing point, they are grouped together in a parameter, $\zeta = \{4\pi^2(V_{12})^2/h|\Delta F|\}$. The recoil velocity, v, can be calculated from the available energy (E_{avl}) at the wavelength of excitation by invoking a "soft radical impulse"[12] using the following equation

$$E_{trans} = (1/2)\mu_{R-I}v^2 = (\mu_{C-I}/\mu_{R-I})(E_{avl}) \qquad (5)$$

where, E_{trans} is the amount of energy that goes to the translational motion, μ_{C-I} and μ_{R-I} are the reduced masses of C and I and R and I, respectively. E_{avl} is $h\nu - D_o - E_{so}$, with ν being the excitation frequency, D_o the dissociation energy of the C−I bond and E_{so}, the spin−orbit excitation energy of the iodine atom (0.942 eV). The probability of crossing to the $^1Q_1$ state depends on two factors: the nature of the radial part of the nonadiabatic coupling (V_{12}) of the two interacting states, $^3Q_0$ and $^1Q_1$, and the velocity of the molecule at the crossing point. It is difficult to say anything about V_{12} and ΔF without a knowledge about the exact excited state potential energy surfaces. But the velocity at the crossing point can be obtained rather accurately from the available energy using eq 5. The I* quantum yield is expected to decrease with a reduction in velocity at the crossing point because the molecule will then spend more time in that region and have a higher probability of jumping to the $^1Q_1$ surface. The velocity is contemplated to decrease as the radical size increases or the excitation energy is lowered. Because the dissociation energy of the C−I bond in CF_3CH_2I is known ($D_o = 2.39$ eV),[29] we can calculate the value of the parameter ζ in eq 4 from the measured quantum yield. We find that the value of the parameter is 311, 317, and 223 m/s at 222, 236, and 266 nm, respectively. Assuming that the average value of ζ (288.5 m/s) is valid for the other two partially fluorinated alkyl iodides studied here, we have calculated I* quantum yields and they are listed in Table 1. The calculated yields show the same trend as the observed yields, and in some cases they match rather well. However, in two instances ($C_6F_{13}CH_2CH_2I$ at 266 nm and $C_8F_{17}CH_2CH_2I$ at 236 nm) there is deviation from the predicted yields. The unexpectedly low I* yield from $C_8F_{17}CH_2CH_2I$ at 236 nm can only be explained by assuming a significant contribution from the direct excitation to the $^1Q_1$ state at this wavelength. This is likely because in CH_3I, it has been reported[22] that the transition at 229.4 nm has less parallel character than at 266 nm. The implication is that the contribution of the $^1Q_1$ state (perpendicular transition) to the total transition strength is higher at 229.4 nm. In absence of the component spectral profiles of the A-band of $C_8F_{17}CH_2CH_2I$, it is difficult to predict the exact position, extent of contribution, and width of the $^1Q_1$ transition. However, it appears that this component reaches a maximum near 236 nm and the spectral shape remains sufficiently narrow so that the contribution from direct excitation to the $^1Q_1$ state becomes insignificant at 222 nm. Thus, the observed dynamics of I* production in partially fluorinated alkyl iodides in the blue region of the A-band is reasonably well described by invoking only the $^3Q_0$ and $^1Q_1$ states. The initial excitation at these wavelengths takes the molecules primarily to the $^3Q_0$ state, and a certain fraction of them cross over to the $^1Q_1$ state to produce the ground-state I atom. However, a small fraction of $C_8F_{17}CH_2CH_2I$ molecules at 236 nm undergo direct excitation to the $^1Q_1$ state, which finally results in more I, atom product than expected.

The I* quantum yields at 280 nm are ~0.73 for both CF_3CH_2I and $C_6F_{13}CH_2CH_2I$ and 0.48 for $C_8F_{17}CH_2CH_2I$. At ~305 nm the quantum yields are 0.52, 0.71, and 0.42 for CF_3CH_2I, $C_6F_{13}CH_2CH_2I$, and $C_8F_{17}CH_2CH_2I$, respectively. At these wavelengths substantial amounts of I atoms are produced, which is not the case at wavelengths ≤262 nm. This implies that a mechanism other than the $^3Q_0$ to $^1Q_1$ curve crossing is contributing to the I atom formation at excitation wavelengths >262 nm. From Figure 1 it appears that in partially fluorinated alkyl iodides, the A-band absorption maximum is slightly red shifted with respect to that of ethyl iodide. In the absence of MCD spectra for the partially fluorinated alkyl iodides, it is difficult to know accurately the contribution of the three transitions (from the ground state to the $^3Q_1$, $^3Q_0$, and $^1Q_1$ states) to the total transition strength at any excitation wavelength. However, by careful inspection of the MCD spectra[7,8] of CH_3I, CF_3I, and CH_3CH_2I, we make a few generalized observations: (i) fluorination shifts the peak positions of the above three transitions marginally, but their relative contributions to the absorption spectrum vary significantly; (ii) increase in the alkyl chain length leads to a large shift in the peak positions corresponding to the three transitions as well as alters their relative contributions to the total absorption spectrum; and (iii) branching at the α-carbon position has more or less the same effect on the A-band (relative contributions as well as peak positions) as increasing alkyl chain length. On the basis of these observations, we expect the relative contributions of the $^3Q_0$ and $^3Q_1$ states to the total absorption spectrum of partially fluorinated alkyl iodides to fall between that of normal and fully fluorinated alkyl iodides (e.g., CF_3CH_2I should fall between CH_3CH_2I and CF_3CF_2I). In fully fluorinated iodides the trend in the I* yields at dissociation wavelengths >262 nm[38] could not be explained by the 1D Landau−Zener model. In partially fluorinated iodides ϕ^* is, in general, lower than that of the fully fluorinated alkyl iodides but comparable to that of the linear alkyl iodides. We have demonstrated earlier[14,15,19,20] that in linear alkyl iodides at photolysis wavelengths ≥300 nm, contribution from the low energy transition ($^3Q_1 \leftarrow N$) cannot be undermined. This mechanism has also been supported by experiments from other groups. Hwang et al.[34] reported that in CF_3I at 304 nm, 35% of the total absorption is carried by the $^3Q_1$ state. Kim et al.[37] investigated CF_3I at 277 nm using the photofragment imaging technique and showed that 68% of the total amount of I comes from the curve crossing dissociation mechanism ($^3Q_0$ to $^1Q_1$) and 32% from the direct excitation to the $^3Q_1$ state.

From all of these results, we infer that in partially fluorinated alkyl iodides, the $^3Q_0$ and $^3Q_1$ states, are excited simultaneously at 280 and ∼305 nm. Hence, at the red edge excitation I atoms are produced by the curve crossing mechanism between the $^3Q_0$ and $^1Q_1$ states as well as by direct dissociation from the $^3Q_1$ state.

Summary

Four primary conclusions can be drawn. (1) The substitution of fluorine atoms in the β-position in alkyl iodides increases the I* quantum yield. However, substitution at the γ-position has far less significant influence on the I* quantum yield. (2) I* is the major product from partially fluorinated alkyl iodides over the entire A-band with a few exceptions. The dissociation dynamics is satisfactorily describable through the well-known one-dimensional Landau−Zener curve crossing model between the $^3Q_0$ and $^1Q_1$ states at wavelengths ≤262 nm. (3) The perpendicular $^3Q_1$ state plays a significant role in the dynamics of β- and γ-fluorinated alkyl iodides at wavelengths >262 nm. (4) Electronic effects on dynamics will tend to be more pronounced in alkyl iodides when substitutions are made at the α-carbon atom (the C−I bond). Substitutions further away from the C−I bond will have a less significant impact on the observed dynamics.

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