J. Indian Inst Sci., Sept.–Oct. 1996, **76**, 555–564.

Photodissociation dynamics of alkyl iodides: I*($^2P_{1/2}$) production in the ultraviolet

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Received on January 31, 1995; Revised on August 7, 1995

Abstract

In this paper the dissociation of a series of α-, β-branched and *n*-alkyl iodides at different wavelengths in their A-band of absorption is discussed. Photofragments I and I* formed during dissociation are probed by the two-photon laser-induced fluorescence technique in our laboratory. Our results along with the data collected by others seem to throw light on the overall understanding of the dissociation dynamics of alkyl iodides in their A-band of absorption

Keywords: Photodissociation dynamics, quantum yield, alkyl iodides, laser-induced fluorescence.

1. Introduction

Over the last three decades, photodissociation dynamics has developed into an important field of research[1-3]. Detailed information regarding the dynamics of dissociation is emerging from the experimental results on the energy partitioning among the various modes of the photofragments.

Photodissociation dynamics of methyl iodide in the lowest lying A-absorption band (extending from 210–350 nm and peaking at 260 nm) which arises from $n_I \rightarrow \sigma^*_{C-I}$ ($X \rightarrow A$) transition has been the subject of intense research starting from the experiment by Kasper and Pimental[4]. Furthermore, methyl iodide can be considered a pseudo-triatomic[5] by treating the three hydrogens of the methyl group as equivalent to an atom of mass $3m_H$ and it has thus become a test molecule for the development of new theoretical models for dissociation of triatomics. A systematic study of the photodissociation of a series of alkyl iodides offers an opportunity to understand the effect of factors such as alkyl radical size, structure, substituents and wavelength on the dynamics.

The early photofragment experiments on methyl iodide were carried out by Riley and Wilson[6] and Dzvonik *et al*[7]. The results of Riley and Wilson's experiment at 266.2 nm showed that at this wavelength I($^2P_{1/2}$) (henceforth referred to as I*) is the main product. The anisotropy parameter, $\beta(1.81 \pm 0.33)$ obtained for methyl iodide by Dzvonik *et al.*, confirmed that near the peak of the A-band (260 nm) the transition dipole is mainly parallel to the C–I bond. Gedanken and Rowe[8] resolved the A-band of methyl iodide using magnetic circular dichroism (MCD). According to them, the A-band has three components that are designated in Mulliken's notation[9] as N → $^3Q_1$, N → $^3Q_0$ and N → $^1Q_1$ transitions. Then N → $^3Q_0$ is a parallel transition while the other two are perpendicular.

Subsequent to the MCD study on methyl iodide, several groups came up with a variety of techniques to investigate the photodissociation dynamics of alkyl iodides. The photofragment infrared emission studies on methyl iodide by Baughcum *et al.*[10] resulted in a quantum yield of 0.81 ± 0.03 for I* production at 248 nm. Sparks and coworkers[11,12] carried out another time-of-flight (TOF) experiment on methyl iodide at 266 nm. They extracted the ν_2 (umbrella mode of methyl iodide) vibrational distribution of methyl fragments from the spectrum and found that it peaked at v = 2. Hermann and Leone[13] subsequently measured the infrared emission from CH_3 radicals produced from methyl iodide at 248 and 266 nm. Their results again showed that at 248 nm, the vibrational distribution peaked at v = 2, which differed from the theoretical results of Shapiro and Bersohn[5] who had predicted a maximum at v = 5 at that wavelength. Brewer *et al.*[14] measured the quantum yield of I* production for a series of alkyl iodides at 248 nm using a two-photon laser-induced fluorescence (TPLIF) detection scheme for both I and I* atoms. In 1984, a new TOF experiment on methyl iodide at 248 nm was carried out by van Veen *et al.*[15] They found the CH_3 (v_2) vibrational distribution to peak at $v = 2$ for both the I and I* channels. For the I channel, the distribution was broader and contained vibrations up to $v = 7$. Using a diode laser to probe the dissociation dynamics of methyl iodide at 266 nm, Hess *et al.*[16] found the I* quantum yield as 0.73 ± 0.04. Godwin *et al.*[17] measured the quantum yield for the production of I* (ϕ*) for a series of alkyl iodides at 248 nm using the TPLIF technique and explained the ϕ* values by adopting a Landau–Zener curve-crossing model. They observed that the dynamics of I* production varies with the alkyl radical size, structure at the α- and β-carbon atoms and substitution. Penn *et al.*[18] for the first time probed methyl iodide dissociation at a wavelength away from the A-band maximum, *i.e.*, 229.4 nm and found that I* is the major product from methyl iodide. In 1989, Ogorzalek *et al.*[19] again looked at the vibrational distribution of CH_3 at 266 nm using multiphoton ionization technique for detecting CH_3 and CD_3 fragments and measured their vibrational population ratio. Polarized emission spectroscopy was adopted by Lao *et al.*[20] to investigate the dissociation dynamics of methyl iodide at 266 nm. Recently, from the photofragment spectroscopic study on methyl iodide, Hertz and Syage[21] have estimated the ratio of cross sections ($\sigma_{\parallel}/\sigma_{\perp}$) and the curve-crossing probability (P) between $^3Q_0$ and $^1Q_1$ states. Attempts have been made by Kang *et al.*[22] to understand the dynamics of dissociation of *n*-butyl iodide at 277 and 304 nm using TOF spectroscopy. Multiphoton ionization detection has been employed by Garrett *et al.*[23] to study the dynamics of CH_3I dissociation in the red edge of the A-band absorption, *i.e.*, in the 325–335 nm region.

In spite of the fact that methyl iodide is well studied, the literature on the higher branched homologs is scarce. This may be ascribed to the fact that these iodides pose problems in performing detailed *ab-initio* calculations due to their large size and structural complexity. The early TOF experiment of Riley and Wilson[6] demonstrated that *n*-propyl iodide produces I* as the major product at 266.2 nm, while isopropyl iodide generates more of I. Donohue and Wiesenfeld[24] studied the broad-band photolysis of a number of alkyl iodides and determined the branching ratios of I* and I using time-resolved atomic absorption spectroscopy. They found that the yields of I and I* depend on the structure of the alkyl group. The ϕ* values obtained by Brewer *et al.*[14] for a series of alkyl iodides show that I* is produced in larger quantities from the *n*-alkyl iodides, than from the secondary or tertiary alkyl iodides at 248 nm. Godwin *et al*[25] have investigated the photodissociation dynamics of *n*-propyl and isopropyl iodides at 248 nm and described the energy disposal by an impulsive model. Gedanken[26] studied the magnetic circular dichroism of the higher alkyl iodides in the A-band region and attributed the larger yield of I in *t*-butyl iodide to the greater interaction between the excited states in this iodide, compared to that in CH_3I and CF_3I. Photofragmentation of a series of alkyl iodides has also been studied by Zhu *et al*[27] They obtained the [I*]/[I] branching ratio by measuring the translational energy of the recoiling photofragments and found that the fraction of available energy going into the internal modes increases from 12.5% for methyl iodide (I* channel) to 64% for isopropyl iodide (both I and I* channels). In brief, most of the experiments described above were carried out near the A-band maximum.

In our laboratory[28-32], the relative quantum yield of I* (ϕ^*) has been determined in the red and blue edges of A-band absorption of α- and β-branched iodides. The results obtained at different wavelengths and their implications to the excited state surfaces of alkyl iodides will be reviewed in this paper

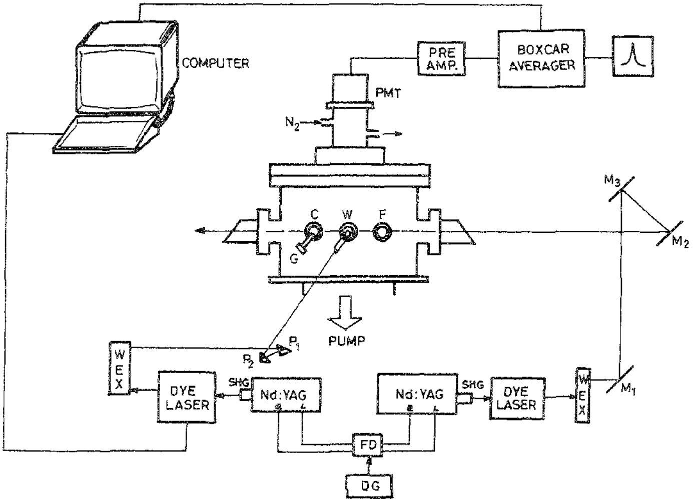

FIG 1. Schematic diagram of our experimental set-up C chamber, W.window, F:flange, G gauge, P_1, P_2:prisms, M_1, M_2, M_3:mirrors, DG delay generator, FD frequency divider, Q–Q:switch trigger, L:lamp trigger, WEX: wavelength extender, PMT.photomultiplier tube, SHG:second harmonic-generating crystal, and N_2:nitrogen gas

2. Experimental set-up

The apparatus used in our experiments is shown in Fig. 1. Briefly, a sample gas of pressure 50–70 mtorr is maintained in an eight-port-cylindrical stainless steel chamber and is continuously pumped by a diffusion pump backed by a rotary pump. The pressure inside the chamber is monitored by an MKS Baratron gauge (model 122 A). At the centre of the chamber the pump and the probe lasers are crossed perpendicular to each other and the signal is detected in the third perpendicular direction using a photomultiplier tube (PMT). Different wavelengths at which the experiments are performed are obtained as follows.

The second harmonic of an Nd:YAG laser is used to pump a dye laser. Rhodamine-6G dye in spectroscopic-grade methanol is used. It has an emission maximum around 560 nm, which is frequency doubled in a wavelength extender using a KD*P (potassium dideuterated phosphate) crystal to obtain 280 nm light. Further frequency up-conversion to get 222 nm is achieved by mixing the dye second harmonic (280 nm) with the Nd:YAG fundamental (1064 nm) in a KDP crystal. The fourth harmonic of the Nd: YAG fundamental, *i.e.*, 266 nm light, is generated by using two SHG crystals in the harmonic generator. The probe laser at ~305 nm is obtained by frequency doubling the fundamental of the dye laser. The dye used in this laser is sulforhodamine-640 in spectroscopic-grade methanol. The dye laser output (608–614 nm) is converted through a wavelength extender to tunable UV light (304–307 nm). A typical delay of 400 ns between the pump and the probe lasers is maintained to avoid collisional relaxation of the nascent photofragments. The resulting iodine fragments are detected by the TPLIF technique. In this technique, initially the iodine atom is excited to an upper state by absorption of two photons. It then relaxes to an intermediate state by emitting an IR photon followed by a VUV photon to come back to the initial state. In our experiments the VUV fluorescence is collected. At the ~305 nm dissociation, probe laser alone is used. The VUV fluorescence from the I and I* fragments is collected by a solar blind PMT through a magnesium fluoride window. The space between the window and the PMT is purged continuously with dry nitrogen to avoid any loss of VUV fluorescence by air absorption. The signal from the PMT is amplified (25 times), averaged (over 30 shots) in a boxcar averager and fed to a strip chart recorder.

The alkyl iodides are either prepared by standard procedures or obtained commercially. All the iodides are decolorized with 10% sodium bisulfite, dried over magnesium sulfate and fractionally distilled (over copper turnings) under reduced pressure prior to each experiment.

3. Results and discussion

The TPLIF spectra are obtained by scanning the probe laser across the two-photon absorption lines of I (304.7 nm) and I* (306.7 nm). Typical TPLIF spectra of I and I* are displayed in Fig. 2. From the spectral intensities, the relative quantum yield for I* is obtained using the expression

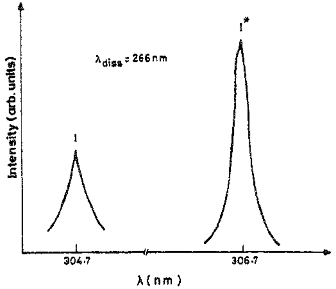

FIG. 2 Typical TPLIF spectra of I and I* produced from ethyl iodide at 266 nm.

$$\phi^{*}=\frac{[I^{*}]}{[I]+[I^{*}]}=\frac{S}{S+S^{*}}.$$

The notation [ ] represents the respective concentrations and S and S*, the I and I* spectral intensities. Here we consider [I] and [I*] to be directly proportional to their signal intensities. No calibration is done to our raw data, since our ϕ^* (0.79) for methyl iodide at 266 nm agrees well with that (0.76) found by Riley and Wilson[6] from photofragment spectroscopy. The quantum yields for I* production obtained for *n*-alkyl iodides are listed in Table I. From the ϕ^* values it is clear that at 222 and 266 nm, I* is the major product, whereas at ~305 nm I is the major product. This indicates that two different mechanisms for I* production are operating at these photolysis wavelengths. A detailed description can be found in our earlier work[28–32].

The I* quantum yields derived from the TPLIF spectra of the α-branched alkyl iodides, *viz.*, methyl, ethyl, isopropyl and *t*-butyl iodides are provided in Table II. The ϕ^* values indicate that for the higher α-branched alkyl iodides, *viz.*, isopropyl and *t*-butyl iodides, irrespective of the dissociation wavelength, the ground state iodine atom is produced predominantly. At 266 nm the excitation is centred at the $^1A_1 \rightarrow {}^3Q_0$ transition.

Table I
I* quantum yield (ϕ^*) for *n*-alkyl iodides at different dissociation wavelengths†

Iodide	ϕ^* *at*		
	222 *nm*	266 *nm*	~305 *nm*
Methyl	0.63 ± 0.02	0.79 ± 0.02	0.43 ± 0.01
Ethyl	0.57 ± 0.02	0.72 ± 0.02	0.39 ± 0.02
n-Propyl	0.54 ± 0.02	0.66 ± 0.02	0.35 ± 0.02
n-Butyl	0.51 ± 0.02	0.64 ± 0.03	0.30 ± 0.02

†Taken from Uma and Das[29,31]

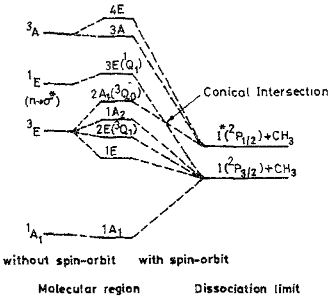

FIG 3 A schematic correlation diagram of the potential energy surfaces for CH_3I (adapted from Yabushita and Morokuma[33])

The correlation diagram obtained by Yabushita and Morokuma[33] (Fig. 3) shows that this transition correlates to the formation of CH_3 + I* at the dissociation limit and hence we expect I* as the major product. However, as we go from methyl to *t*-butyl iodide, more of I is produced which can be explained qualitatively on the basis that the number of high-frequency vibrational modes is increased in the *t*-butyl iodide, allowing nonradiative energy transfer of the excess energy after the C–I bond rupture. Also, the $^3Q_1$ component of *t*-butyl iodide absorption is shifted to 282 nm, and a significant contribution from this state which leads to I at 266 nm cannot be ruled out.

Production of substantial amounts of I* at ~305 nm indicates that a simultaneous excitation mechanism to both $^3Q_0$ and $^3Q_1$ states is operating at this wavelength. Alternatively, the initial excitation at this wavelength takes the molecule to the $^3Q_1$ state which has a barrier at the exit channel, resulting in only some of the molecules crossing the barrier to produce I. The other molecules crossover to the $^3Q_0$ state and dissociate forming I*. The existence of such a barrier will be revealed only when an exact multidimensional PES of the alkyl iodides becomes known.

It is noteworthy that the ϕ^* for *t*-butyl iodide peaks at 222 nm, unlike other iodides. If we plot the absorption spectrum of *t*-butyl iodide and the quantum yields at different

Table II
Quantum yield (ϕ^*) in α-branched alkyl iodides at different dissociation wavelengths†

Iodide	ϕ^* *at*		
	222 *nm*	266 *nm*	~305 *nm*
Methyl	0.63 ± 0.02	0.79 ± 0.02	0.43 ± 0.01
Ethyl	0.57 ± 0.02	0.72 ± 0.02	0.39 ± 0.02
i-Propyl	0.40 ± 0.02	0.44 ± 0.03	0.19 ± 0.02
t-Butyl	0.33 ± 0.03	0.20 ± 0.03	0.12 ± 0.03

†Adapted from Uma and Das[32].

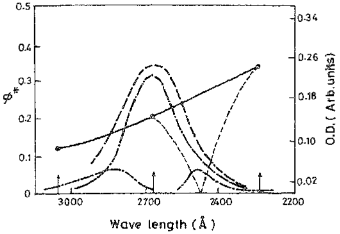

FIG. 4. Diagram representing the absorption spectrum (dashed line) of *t*-butyl iodide (taken from Gedanken[26]), the components (dot–dash line) derived by considering the reported peak values[26] and the experimentally observed ϕ^* (solid line) at different dissociation wavelengths. ϕ^* at 248 nm is taken from Brewer *et al*[14]

wavelengths (Fig. 4), we find that the I* yield goes down with decreasing energy, while the absorption goes through a maximum at ~267 nm. At 222 nm, the contribution from both $^3Q_0$ and $^1Q_1$ transitions is responsible for the observed ϕ^*. However, the zero quantum yield for I* production in *t*-butyl iodide at 248 nm, reported by Brewer *et al.*[14], points out that some other energy relaxation pathways are involved in the process. In fact, if we compare the I* quantum yields in *n*-butyl and *t*-butyl iodides at any wavelength, we find that *t*-butyl iodide produces less I*. It may be that *t*-butyl iodide has many more high-frequency modes compared to *n*-butyl iodide that couple to the C–I bond excitation and thereby act as an energy sink after the excitation. This results in mainly I as the product.

We have studied the photodissociation of isobutyl and neopentyl iodides to understand the effect of β-branching on the dynamics of dissociation. The ϕ^* values obtained for a series of β-branched alkyl iodides at different dissociation wavelengths are listed in Table III. We find that the I* yields of the β-branched iodides do not vary significantly at any given wavelength. This is in sharp contrast to what is observed in the α-branched alkyl iodides. But this is not very surprising since the $n \rightarrow \sigma^*$ transition is highly localised, and in the time scale of dissociation (~55 fs) of these iodides, the probability of energy randomization through the high-frequency vibrational modes a carbon atom away is small. In other words, an energy sink for ultraviolet excitation in alkyl iodides cannot be effectively introduced by chemical modifications at the β-carbon atom.

Table III
ϕ^* in the β-branched alkyl iodides at different dissociation wavelengths

Iodide	ϕ^* *at*		
	222 *nm*	266 *nm*	~305 *nm*
Ethyl	0.57 ± 0.02	0.72 ± 0.02	0.39 ± 0.02
n-Propyl	0.54 ± 0.02	0.66 ± 0.02	0.35 ± 0.02
i-Butyl	0.54 ± 0.02	0.71 ± 0.01	0.35 ± 0.02
Neopentyl	0.56 ± 0.02	0.67 ± 0.01	0.21 ± 0.03

4. Conclusions

The dynamics of I* production from a variety of alkyl iodides have been investigated in their A-band of absorption. For smaller alkyl iodides below 300 nm, I* is the major product from the dissociation, whereas above 300 nm, I is the dominant product. For the α-branched alkyl iodides, the change in ϕ^* in going from methyl to *t*-butyl iodide is large. The dynamics is altered drastically by substituents at the α-carbon atom. Moreover, high-frequency vibrational modes that couple to the C–I stretch (where the $n \rightarrow \sigma^*$ transition is localised) seem to act as a sink for accepting excess energy after the initial excitation. The β-branched iodides do not exhibit any marked change in ϕ^* from the corresponding *n*-alkyl iodides and hence we infer that the alkyl iodide dissociation is indeed direct and localised at the C–I bond excitation over the entire A-band in the ultraviolet.

Acknowledgement

We thank Mr P. V. Ramakrishnan for assistance in electronic circuit design and troubleshooting. Enlightening discussions with Drs J. Chandrasekhar, R. Sumathy and D. Sengupta are gratefully acknowledged. Generous support from the Director, Indian Institute of Science, the Departments of Science and Technology and Atomic Energy, Govt. of India, is thankfully acknowledged.

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