

# Photodissociation dynamics of small molecules: Dissociation of alkyl iodides in the near ultraviolet

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In this article we have briefly presented various techniques that are employed to study photodissociation dynamics of small molecules in the gas phase, insofar the energy partitioning among the product modes is concerned. Dynamics of dissociation of methyl iodide as well as other related iodides  $\sim 260$  nm have been treated in detail citing several experimental techniques utilized to obtain nascent energy distribution in the fragments. The influence of excited state potential energy surfaces on the quantum yield of excited iodine atom ( $^2P_{1/2}$ ) production, or in the release of most of the available energy into the vibrational modes of alkyl fragments have been discussed.

SINCE the discovery of lasers in 1958, photodissociation dynamics with special emphasis on final state distribution has grown tremendously in several directions<sup>1,2</sup>. Here we shall make a modest attempt to present some of the primary aspects in this field taking alkyl iodide photolysis in the near uv as examples. This includes some of our own work in the area as well.

Photodissociation dynamics is a study of the distribution and conservation of energy. A molecule with  $n$  atoms in its ground electronic state is excited to a higher electronic state by absorption of a photon. After the jump the molecule finds itself in an unstable or metastable configuration. It then moves to a more stable or lower energy configuration which may be achieved either by isomerization or dissociation. If one or more bonds are broken and the fragments fall apart, the process is called 'direct dissociation'. A more complex process in which the excited molecule executes a number of vibrations and/or rotations before the bonds are broken is known as 'predissociation'. In either case the initial photon energy is distributed into a) work done to produce the fragments, b) relative translational energy of the fragments, and c) internal energy of the products. For example, the energy conservation in the dissociation of a triatomic ABC ( $ABC \rightarrow A + BC$ ), may be written as

$$E_{ABC} + E(h\nu) = D^0(A-BC) + E_t + E_A + E_{BC} \quad (1)$$

where  $E_{ABC}$  is the internal energy of the triatomic,

$E(h\nu)$  the photon energy, and  $D^0(A-BC)$  the dissociation energy of the A-BC bond.  $E_t$  is the translation energy of the fragments.  $E_A$  and  $E_{BC}$  are internal energies of the A and BC fragments respectively. The available energy for partitioning into electronic, translational, vibrational, and rotational energy is then

$$E_{avail} = E_t + E_A + E_{BC} \quad (2)$$

Another conservation equally important for photo-fragmentation is the conservation of momentum. From the conservation of linear momentum we can write

$$\mathbf{P}_{ABC} = \mathbf{P}_A + \mathbf{P}_{BC} \quad (3)$$

and for the conservation of angular momentum

$$\mathbf{J}_{ABC} + \mathbf{j}_{h\nu} = \mathbf{j}_A + \mathbf{L}' + \mathbf{J}_{BC} \quad (4)$$

where  $\mathbf{J}$ s are the respective angular momenta. The photon adds or subtracts one unit of angular momentum and through expansion in a supersonic jet  $\mathbf{J}_{ABC} \approx 0$  is obtainable.  $\mathbf{j}_A$ , the electronic angular momentum of the fragment A can also be neglected in comparison with either the orbital angular momentum  $\mathbf{L}'$  or the rotational angular momentum  $\mathbf{J}_{BC}$  of the product BC. These result in a simple relation  $|\mathbf{L}'| = |\mathbf{J}_{BC}| = \mu v b$ , where  $\mu$  is the reduced mass of the fragment,  $v$  the relative velocity and  $b$  the exit channel impact parameter.

In general, the quantities measured in a photodissociation experiment are either scalar or vector. Energy of any kind (e.g. translational, vibrational, rotational, etc.) is a scalar quantity whereas, angular momentum of the resulting fragments, recoil velocity, electric vector of the dissociating light, etc. fall under the vector category. For the dissociation of ABC equation (2) summarizes the scalar-scalar correlation whereas there are mainly four vector-vector correlations among  $\mathbf{E}$ , the electric vector of the incident radiation,  $\boldsymbol{\mu}$ , the transition dipole of the parent molecule,  $\mathbf{v}$ , the recoil velocity of the fragments, and  $\mathbf{J}$ , the rotational angular momentum vector of a fragment. These are (1) the  $\mathbf{E}-\boldsymbol{\mu}-\mathbf{v}$  correlation, which implies that the alignment of  $\boldsymbol{\mu}$  in the

laboratory frame of reference by polarized photolysis light leads automatically to an alignment of  $\mathbf{v}$ ; (2) the  $E-\mu-J$  correlation, which results in an alignment of fragment rotational angular momentum in the laboratory frame; (3) the  $\mathbf{v}-J$  correlation, which, although independent of the laboratory frame, can provide information on the alignment of all three vectors  $\mu$ ,  $\mathbf{v}$ , and  $J$ ; and (4) the  $E-\mu-(\mathbf{v}-J)$  correlation, which combines all the above three correlations. Ideally one would like to know all the quantities in the right-hand side of equation (2) as well as all the different vector-vector correlations. These vector-vector correlations will not be discussed here. Interested readers are encouraged to consult the excellent articles by Houston<sup>3</sup> and Hall and Houston<sup>4</sup> on this subject. We will focus on the scalar-scalar correlation in a photodissociation.  $E_A$  can be determined directly by monitoring the emission of A or by probing the excited state(s) of A by spectroscopic means.  $E_t$  is measured by the time-of-flight technique<sup>5,6</sup> where one measures the translational energies of the fragments directly by measuring the time taken by them to fly a known distance. The identity of the fragments is generally determined mass spectrometrically from their charge to mass ( $e/m$ ) ratio. The translational energy distribution is also measured from Doppler profile of the resulting products<sup>7</sup>. Internal energy of BC ( $E_{BC}$ ) is normally probed by the techniques of laser-induced fluorescence (LIF)<sup>8</sup> or resonance enhanced multiphoton ionization (REMPI)<sup>9</sup>. Thus a complete picture of energy partitioning in the products is obtained.

From photodissociation results it is also possible to extract certain other (which are not discussed above) important quantities such as lifetime<sup>10</sup> or structure<sup>11</sup> of the excited state from which the molecule dissociates. The ultimate aim of photodissociation experiments is the extraction of the potential energy surface(s) (PES) from the experimental data. Once the potential function is known one can, in principle, solve the Schrodinger equation to map out the entire history (the past, present, and the future) of the molecule. More often than not, several potential energy surfaces are involved in the photodissociation process, and one would like to find out the different product channels associated with them and if they cross.

In what follows we discuss the various techniques applied to measure the energy partitioning in a photolysis experiment with special emphasis on the technique of LIF. Results on the measurement of  $I^*$  ( $^2P_{1/2}$ ) quantum yield in the alkyl iodide dissociation in the near uv by various techniques have been presented along with a possible explanation for such observations.

### Fragment fluorescence

One of the simplest photodissociation experiments which provides most of the detailed information

regarding energy partitioning among the different product modes involves monitoring fragment emission followed by a bond fission. The emitted light is normally dispersed through a monochromator and a ro-vibrational spectrum is obtained. From the analysis of the spectrum information on the electronic, vibrational and rotational energies of the emitting specie is obtained. CN fragment fluorescence has been observed in the near uv fragmentation from a variety of cyanides, isocyanides and their deuterated analogues<sup>12,13</sup>. For atomic fragments generated in a photolysis experiment monitoring the emission directly provides information regarding the electronic energy of the atom. Measurements have been made on the generation of Se ( $^1S$ ) from OCS<sub>e</sub> (ref. 14), S ( $^1D$ ) and S ( $^1S$ ) from OCS<sup>15</sup>, and  $I^*$  from CH<sub>3</sub>I (ref. 16). Fragment fluorescence from larger moieties (more than diatomic) has also been observed but the amount of information obtainable from these experiments depends largely on our understanding about the spectroscopy of the fragment.

### Time-of-flight photofragment spectroscopy

One of the most elegant ways to study photofragment dynamics is by crossing a laser with a molecular beam and measuring the angular distributions and the time-of-flight (t-o-f) of the fragments with a mass spectrometer. In the t-o-f technique the fragments after production traverse a fixed distance before being detected in the interior of a mass spectrometer in a time-resolved manner. One directly obtains the translational energy distribution from the data, and using equation (2) the internal energy content of the product(s) may also be deduced. By varying the polarization of the incident laser light it is possible to study the angular distribution of the products in the same t-o-f set-up. Retention of the polarization of the incident light beam in the fragment can be related to the lifetime of the excited state and to the orientation of the transition moment with respect to the molecular axis in some simple cases and will not be discussed here. The theory of the basic photoejection dynamics and angular anisotropy has been described in detail by Zare<sup>17</sup> and Yang and Bersohn<sup>18</sup>. A large number of diatomic and polyatomic dissociations have been studied by the t-o-f technique and in this context the reader may consult the review article by Leone<sup>19</sup> for an excellent account.

### Laser-induced fluorescence of photofragments

In another type of photodissociation experiment the internal state distribution of the fragments is probed directly by the technique of LIF. In this 'pump' and 'probe' experiment, one laser (the pump laser) disso-

ciates the molecule and a second (the probe laser) is tuned so that its frequency matches that of an absorption line of a fragment of interest. After absorption the specie goes to an electronically excited state which can radiate. The detected fluorescence is used as a measure of the absorption of particular quantum states and hence their population<sup>20</sup>. If the distribution over the combined rotational and vibrational states is known from the LIF spectra, then from conservation of energy, kinetic energy distribution can be furnished. Due to the high degree of sensitivity, the spatial and temporal resolution available, and the non-intrusive nature of the LIF technique, it is one of the most powerful tools to study spectroscopy and/or collision-induced processes. With narrow bandwidth lasers, the LIF technique can also be used to probe Doppler velocity widths which gives translational energy distribution and product alignment during dissociation<sup>21</sup>.

### Experimental set-up

The experimental apparatus, in principle, is very simple and Figure 1 shows a typical arrangement to study the internal energy distribution of photofragments in our laboratory. Several laboratories around the world have various designs but the main features remain the same. In our system, the photodissociation as well as the probe lasers are commercially available pulsed YAG laser pumped dye lasers (Spectra Physics) the fundamental of which can be doubled with the help of KDP\* crystals to generate tunable uv radiation. The two laser beams are crossed perpendicularly in a stainless steel chamber equipped with multiple ports and blackened inside to avoid stray light. The laser entrance and exit arms are fitted with Brewster angle quartz

windows as well as a few light baffles to avoid reflected light beams. The chamber is pumped with a 4-inch diffusion pump and the desired gas is introduced into the chamber through a leak valve. The typical sample gas pressure is 70–80 mTorr inside the chamber which is monitored by a Baratron pressure gauge (MKS-122A). Signal, depending on the nature of detection is collected at a mutually perpendicular direction at a suitable detector (a photomultiplier tube or an ion collector), amplified by a DC-300 MHz amplifier and fed into a signal averager. The output from the signal averager is displayed on a stripchart recorder. The delay between the pump and the probe lasers is adjusted with the help of an external time delay generator (Stanford Research System DG-535). Typically 1  $\mu$ s delay in time at 100 mTorr total pressure corresponds to one collision during the observation time. A delay of 500 ns at 70–80 mTorr total pressure is set in order to avoid any significant relaxation of the nascent populations. In our experiment, we have used a single laser to dissociate alkyl iodides as well as probe the nascent  $I^*$  quantum yield by the technique of two photon LIF. The second Harmonic of Rhodamine-640 dye is focused tightly with a 5-cm f.l. quartz lens in the middle of the chamber. The typical laser pulse energy is 1 mJ. The LIF signal is collected using a solar blind PMT (Thorn EMI), amplified ( $\times 25$ ), sent to a boxcar averager and recorded on a stripchart recorder. The commercially obtained or freshly prepared methyl, ethyl, propyl, isopropyl and *t*-butyl iodides were decolourized with 10% sodium bisulphite solution and dried with anhydrous  $MgSO_4$ . Finally, fractionally distilled alkyl iodides were used for the experiment.

### Quantum yield of $I^*$ production in the photolysis of alkyl iodides

Methyl iodide and its substituted analogues have received substantial attention as excellent model systems for investigating the photodissociation dynamics of small molecules. The reason is partly historical since the first observation of an inverted population of  $I^*$  by a photodissociation process was reported in this molecule<sup>16</sup>. In addition,  $CH_3I$  can be regarded as a quasi-triatomic molecule and hence is an ideal system to understand the dissociation dynamics. This molecule absorbs in the range 350–170 nm due to a  $n-\sigma^*$  transition. The photodissociation of this molecule in its first absorption band (*A*-band) is particularly interesting since the dynamics of the vibrational excitation during the simple C–I bond rupture is relatively well confined and is extremely fast. This has offered a unique opportunity for theoreticians<sup>22</sup> to model detailed photodissociation dynamics under the simplified assumption of 'collinear pseudotriatomic dissociation'.

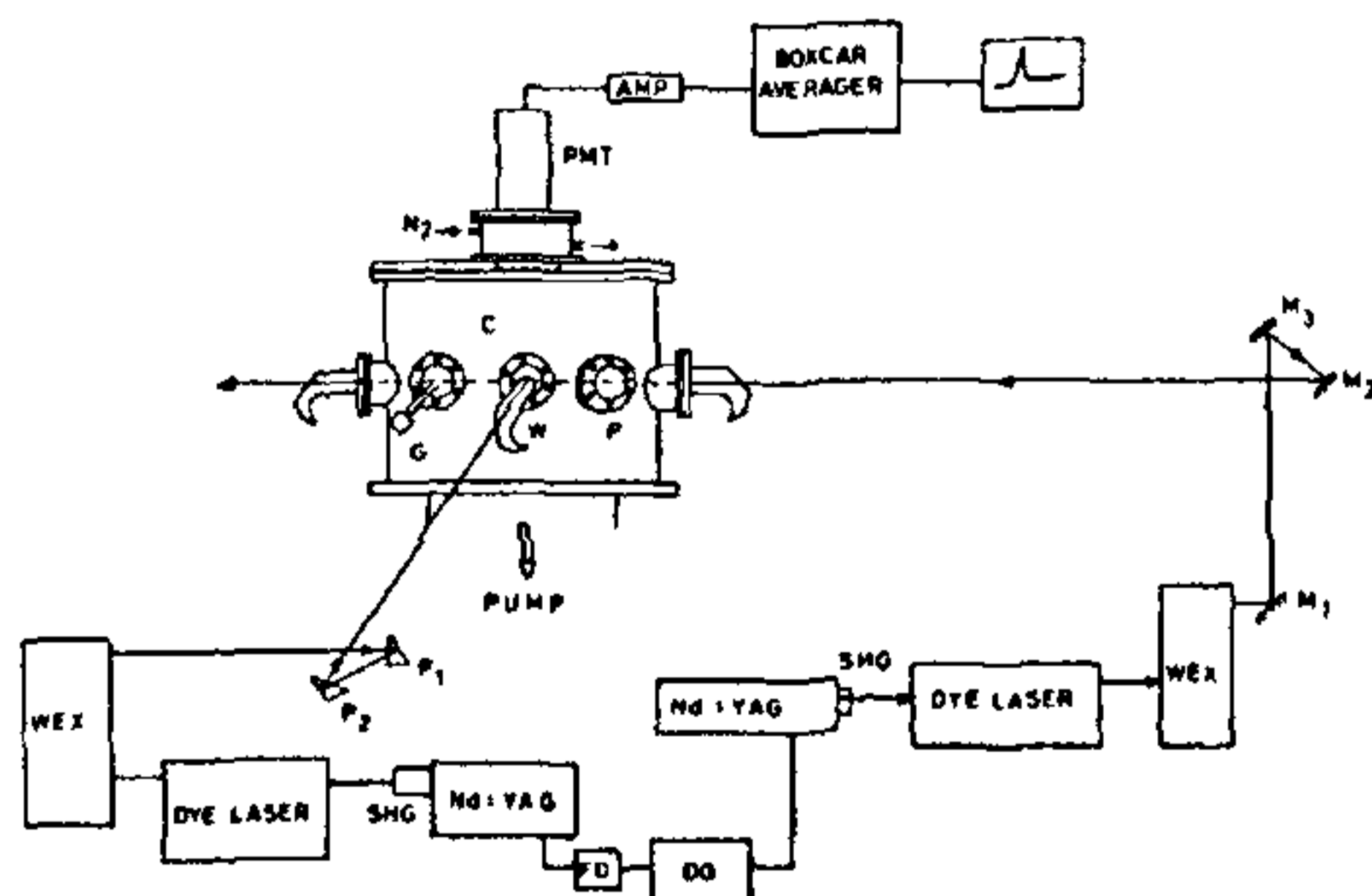


Figure 1. Schematic 'pump-probe' set-up M, Mirrors; P, prisms; AMP, amplifiers; PMT, photomultiplier tube, SHG, second harmonic generator, P, port; W, wood's horn; G, pressure gauge; C, stainless steel chamber, FD, frequency divider; DG, delay generator.

Gedanken and Rowe<sup>23</sup> using magnetic circular dichroism (MCD) resolved the *A*-band in the absorption spectrum of CH<sub>3</sub>I. The MCD spectrum has three components corresponding to <sup>1</sup>Q<sub>1</sub>←N (peaks at 239 nm), <sup>3</sup>Q<sub>0</sub>←N (peaks at 261 nm), and <sup>3</sup>Q<sub>1</sub>←N (peaks at 300 nm) transitions. The ground state for methyl iodide is <sup>1</sup>A<sub>1</sub>. Both the ground (<sup>1</sup>A<sub>1</sub>) and the first excited states (<sup>3</sup>Q<sub>0</sub>) have A<sub>1</sub> symmetry in the C<sub>3v</sub> point group and, therefore, the cylindrical symmetry must be preserved during dissociation. Another interesting feature is that the <sup>3</sup>Q<sub>0</sub> state which correlates with I\* crosses over to the <sup>1</sup>Q<sub>1</sub> state correlating (Figure 2) with the ground state iodine atom, I (<sup>2</sup>P<sub>3/2</sub>). This crossing is made symmetry allowed through E-type vibrations.

First photodissociation experiments on methyl iodide were carried out simultaneously by Riley and Wilson<sup>24</sup> and Dzvonik *et al.*<sup>25</sup> using the t-o-f technique. It was concluded that the transition in methyl iodide at 260 nm is <sup>3</sup>Q<sub>0</sub>←<sup>1</sup>A<sub>1</sub> and the major products are CH<sub>3</sub> radical and I\*. The main reason for production of a small amount of I is predissociation into the <sup>1</sup>Q<sub>1</sub> state. Following that Sparks *et al.*<sup>26</sup> carried out a sophisticated t-o-f experiment on CH<sub>3</sub>I at 266 nm. They extracted the vibrational distribution of CH<sub>3</sub> fragment from the t-o-f spectrum. From geometrical considerations the only vibrational excitation possible in CH<sub>3</sub> is the umbrella bend (ν<sub>2</sub>) for both I and I\* channels, and the distribution was found to peak at V=2. To confirm that Hermann and Leone<sup>27</sup> measured the IR emission from CH<sub>3</sub> radicals produced from CH<sub>3</sub>I at 266 nm and 248 nm. At 266 nm very good agreement with the measurements of Sparks *et al.*<sup>26</sup> was found. But at 248 nm the vibrational distribution peaked again at

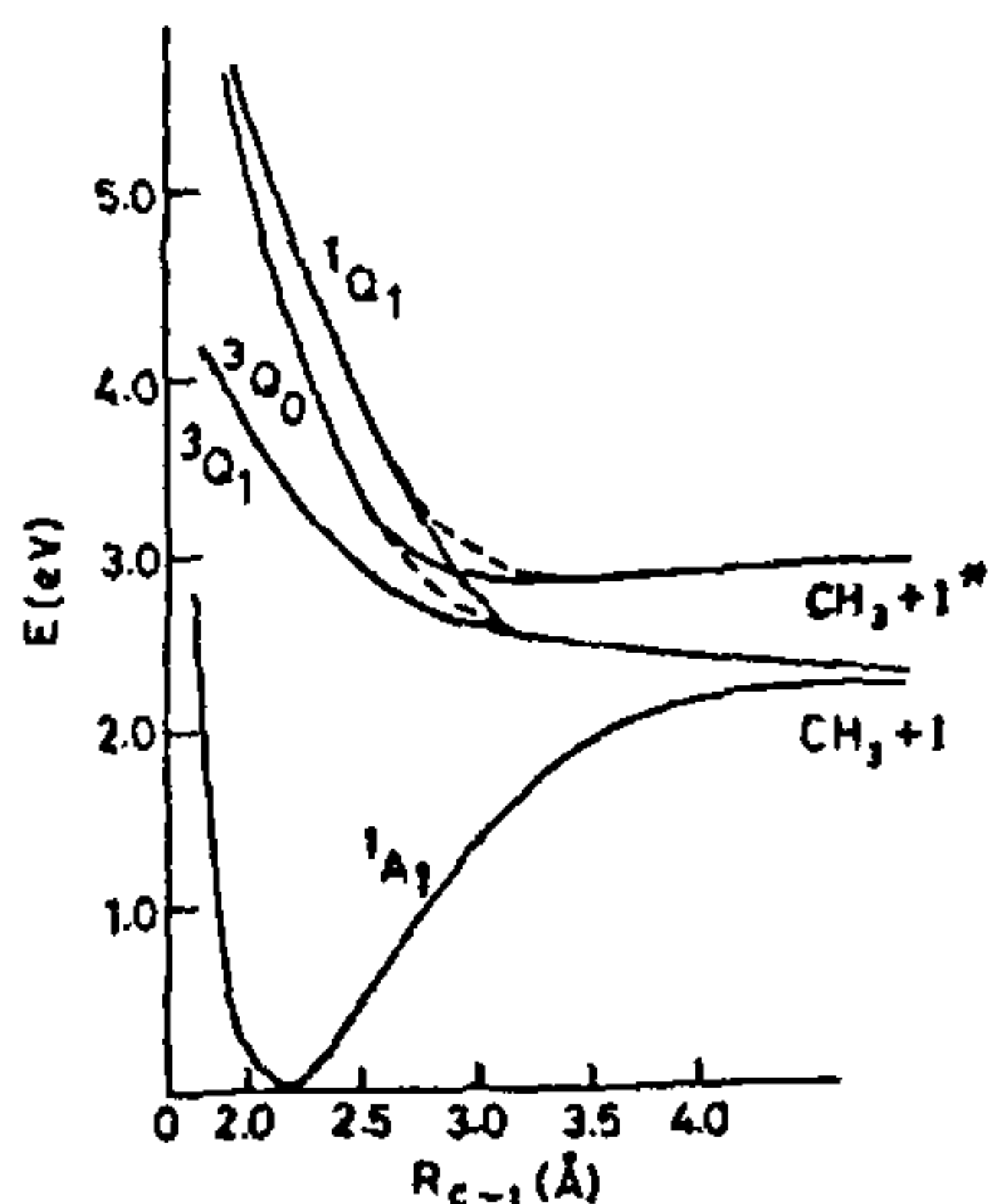


Figure 2. Relevant potential energy surfaces of methyl iodide (not in scale). Broken lines show the region of avoided crossing

V=2 which differed markedly from the theoretical prediction of Shapiro and Bersohn<sup>28</sup> who using a simplistic Frank-Condon theory with corrections for final state interactions estimated the distribution to peak at V=4. In 1984 van Veen *et al.*<sup>29</sup> undertook a new t-o-f study in CH<sub>3</sub>I at 248 nm. They found that there were two distinct channels of dissociation, one leading to I and the other to I\* products. The vibrational distribution was derived by fitting the experimental spectrum for two channels separately. The peak of the vibrational distribution was at V=2 at 248 nm. The excited state lifetime was estimated from the experimental data ~55 fs. This is in agreement with the direct dissociation mechanism suggested by Dzvonik *et al.*<sup>25</sup>. The relative quantum yield  $\Phi^*$  ( $[I^*]/([I] + [I^*])$ ) of excited iodine atom production was obtained indirectly and found to be  $0.71 \pm 0.02$ . The quantum yield of I\* production was also obtained by Brewer *et al.*<sup>30</sup> using a two-photon laser-induced fluorescence technique. In this technique, the transition involved in the two-photon absorption step for the I atom is <sup>2</sup>D<sub>5/2</sub>←<sup>2</sup>P<sub>3/2</sub> and for the I\* is <sup>2</sup>D<sub>3/2</sub>←<sup>2</sup>P<sub>1/2</sub>. The excited atoms decay to the ground state first by emission of an ir photon followed by emission of a vuv photon which is detected. A distinct advantage of this method is that both the ground and the excited states of iodine are detected (in many techniques only one is detected). The relative quantum yield for I\* production in 248 nm dissociation of CH<sub>3</sub>I was determined as  $0.76 \pm 0.02$ . The results obtained by the two independent techniques seem to have a good agreement.

Barry and Gorry<sup>31</sup> studied the fragmentation dynamics of CH<sub>3</sub>I at 248 nm by the t-o-f spectroscopy. They observed excitation of the ν<sub>2</sub>-umbrella mode and the distribution peaked at V=2 for the I\* channel but extended up to V=8 for the I channel. From angular measurements they identified the initial transition (<sup>3</sup>Q<sub>0</sub>←<sup>1</sup>A<sub>1</sub>) as parallel (I\* channel) and the ground state iodine atoms are formed by the curve crossing mechanism between the <sup>1</sup>Q<sub>1</sub> and <sup>3</sup>Q<sub>0</sub> states. Using the two-photon LIF technique Godwin *et al.*<sup>32</sup> measured the quantum yields for production of I and I\* for a series of alkyl iodides at 248 nm. They used a model which incorporates impulsive energy disposal for the dissociation followed by Landau-Zener description of the <sup>3</sup>Q<sub>0</sub>-<sup>1</sup>Q<sub>1</sub> curves crossing. In their model the I\* quantum yield was calculated using the expression

$$\Phi^* = \exp(-2\pi V_{12}/\hbar|\Delta F|v) = \exp(-\zeta/v) \quad (5)$$

where  $V_{12}$  is the coupling term,  $\Delta F$  the difference in gradients at the crossing point and  $v$  the velocity through the crossing point. The value  $\Phi^*$  thus obtained matches well with the experimental value. But the reason for population inversion in CH<sub>3</sub> umbrella vibration was not clear. Ogorzalek *et al.*<sup>33</sup> have studied

the vibrational distribution of the methyl fragment at 266 nm using a multiphoton ionization technique. They could not confirm the population inversion in the vibrational distribution of  $\text{CH}_3$ . This apparent contradiction about the internal energy distribution of the methyl fragment led to recent studies of photodissociation of  $\text{CF}_3\text{I}$  and related molecules by Felder<sup>34</sup> and Hwang *et al.*<sup>35,36</sup>. At 248 nm (ref. 34) the initial excitation in  $\text{CF}_3\text{I}$  involves two different potential energy surfaces  $^3Q_0$  (80%) and  $^1Q_1$  (20%) which yields both  $I$  and  $I^*$  directly as well as through the curve crossing mechanism. At 304 nm (refs. 35, 36) however, the excitation is to the  $^3Q_0$  and  $^3Q_1$  excited states.  $I^*$  atoms are formed predominantly from  $^3Q_0 \leftarrow ^1A_1$  transition while the ground state iodine atoms are formed from both the perpendicular  $^3Q_1 \leftarrow ^1A_1$  (70%) and the parallel  $^3Q_0 \leftarrow ^1A_1$  (30%) transitions followed by a curve crossing to the  $^1Q_1$  state. In agreement with the known theoretical and experimental results, the vibrational excitation in  $\text{CF}_3$  is mainly to the  $\nu_2$  mode (umbrella vibration) and originates from the  $^3Q_0$  potential energy surface as suggested by van Veen *et al.*<sup>37</sup>. However, in contradiction to van Veen *et al.*<sup>37</sup>, Hwang *et al.* also predicted that the dynamics of the curve crossing plays an important role in understanding the discrepancy between the theoretical predictions and experimental results.

In our laboratory we have probed the nascent quantum yield of  $I^*$  for  $\text{CH}_3\text{I}$  and related analogues at  $\sim 305$  nm using the technique of two-photon laser-induced vuv fluorescence. A typical LIF spectrum is displayed in Figure 3.  $\Phi^*$  has been obtained directly from the spectrum. They are listed in Table 1. In clear

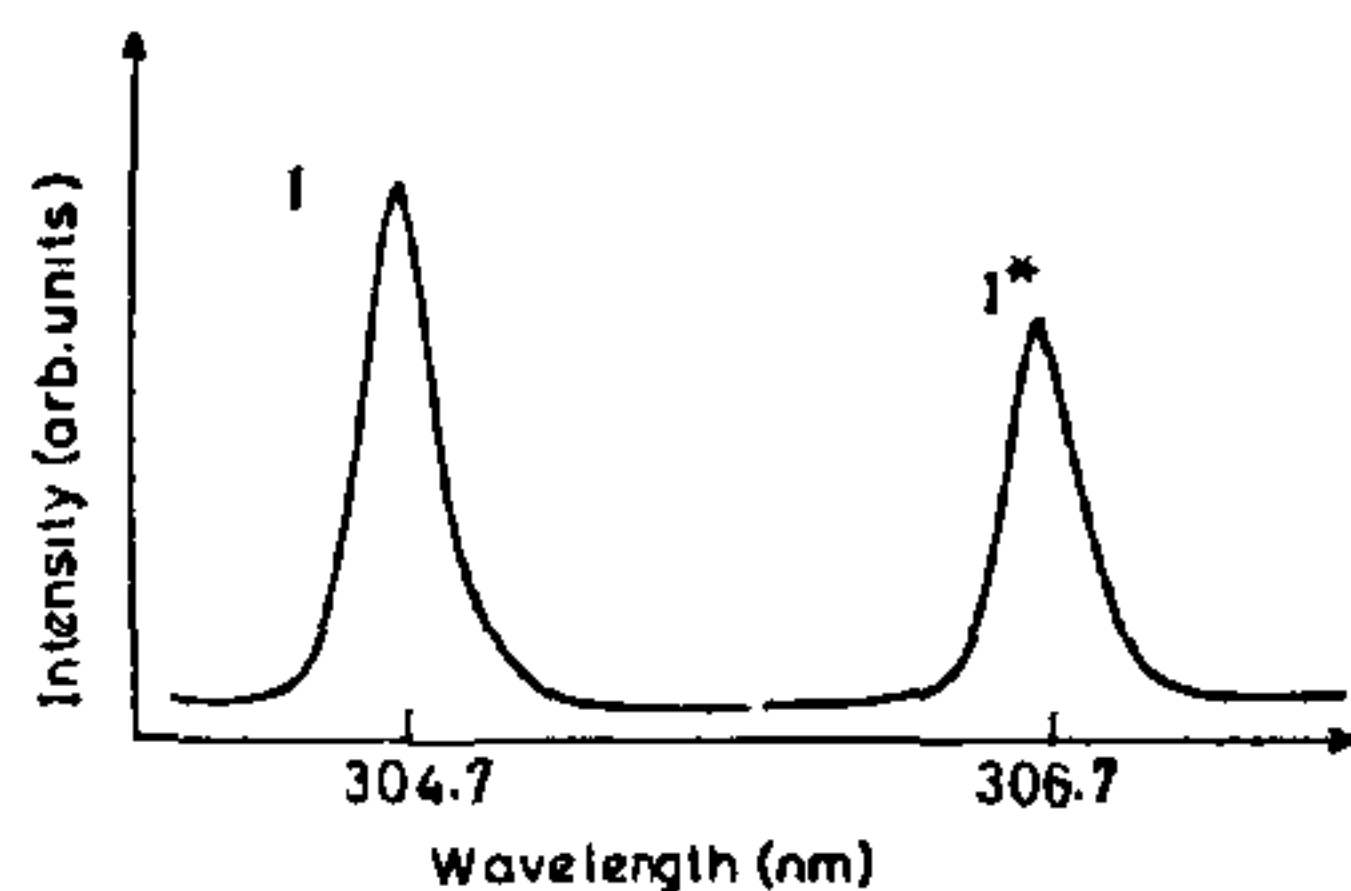


Figure 3.  $I$  and  $I^*$  LIF spectra from methyl iodide at 304.7 nm and 306.7 nm.

Table 1. Relative quantum yield ( $\phi^*$ ) of  $I^*$  production in alkyl iodide photodissociation

Compound	$\phi^*$ at	
	248 nm**	305 nm
Methyl iodide	0.73	0.43
Ethyl iodide	0.64	0.39
<i>n</i> -Propyl iodide	0.56	0.35
<i>i</i> -Propyl iodide	0.23	0.19
<i>t</i> -Butyl iodide	0.03	0.12

\*\*From ref. 32.

contrast with 248 nm or 266 nm results,  $I$  is the major product at this wavelength. This discrepancy may be due to the fact that at this wavelength the excitation is not confined mainly to the  $^3Q_0$  state and a substantial contribution comes from the lower energy  $^3Q_1$  state.  $I$  atoms are produced from the  $^3Q_1$  state as well as due to curve crossing between the  $^3Q_0$  and  $^1Q_1$  states. When we go down the alkyl iodide series the quantum yield for  $I$  atom production increases. Since the absorption band of these alkyl iodides are almost overlapping (with the exception of  $\text{C}_2\text{H}_5\text{I}$  (ref. 38)), one would expect the quantum yield to be similar at any dissociation wavelength. However, we see a difference which suggests that the kinematics at the curve crossing region as pointed out by Godwin *et al.*<sup>32</sup> is important and an impulsive model for energy disposal with realistic potential energy surfaces would provide a good description of the dynamics. We also predict, like in fluorinated alkyl iodides, that most of the available energy will be released into the internal excitation of the alkyl radicals. However, a detailed understanding of the internal excitation in the alkyl radicals will depend on the multidimensional nature of the curve crossing in the excited state.

### Concluding remarks

After two decades of research by various groups on alkyl iodides in general and methyl iodide in particular, we understand the following about their dissociation dynamics around 260 nm.

- 1) The excitation is confined to the C-I bond and the dissociation is direct ( $\sim 55$  fs).
- 2) Production of ground state iodine atom is due to a nonadiabatic process between the  $^3Q_0$  and  $^1Q_1$  states. Only a very small amount of the available energy is released into product translation and most of the energy goes into the umbrella vibration of the resulting alkyl radicals. Therefore, treating alkyl iodides as a pseudotriatomic molecule is a realistic approximation.
- 3) Direct excitation to the  $^3Q_1$  state is also possible by changing the wavelength of excitation but this will be accompanied with excitation to the  $^3Q_0$  state as well.

However, we do not still understand the different umbrella vibrations associated with different excited states and possible reasons for an inverted vibrational distribution. A multidimensional PES description with many vibrational modes, of the excited state dynamics is necessary to understand the vibrational outcome of these experiments better.

Finally, why is there such a great fascination in the photodissociation of small molecules? The real reasons are the appealing theoretical simplicity of the process and the availability of variety of lasers and various

other technological improvements which allow one to carry out conceptually simple experiments. Moreover, very often several potential energy surfaces are involved in the process and one wishes to know the efficiency of surface crossing and the region in configuration space where this occurs.

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## Probing interatomic potentials using low-energy ion beams

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An overview is provided of the utility of a new ion collision technique, translational energy spectrometry (TES), in probing molecular potential energy surfaces. TES is a gas-phase collisional technique in which the analysis of the changes in the kinetic energy of a projectile ion which has undergone collision with a

neutral atom/molecule furnishes information about the interaction potential between the projectile and the target. An advantage this technique offers over conventional spectroscopic and laser-based methods is relatively easy access to intrinsically unstable species such as singly charged radicals and multiply charged molecular ions.

QUANTITATIVE insight into interatomic potentials which govern the dynamics of chemical transformation processes continues to elude physicists and chemists

even though sophisticated quantum mechanical methodologies and powerful laser techniques have enabled increasingly detailed studies to be carried out of atomic