

I*(²P_{1/2}) production from CH₃I photodissociation at 236 nm

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The quantum yield of I*(²P_{1/2}) production from CH₃I photolysis at 236 nm in the gas phase has been measured as 0.69 ± 0.03. The implication is that direct excitation to the ¹Q₁ excited state is significant at this wavelength. The dynamics of I* formation at other excitation energies covering the entire A-band of absorption of CH₃I has been discussed in the light of this measurement.

PHOTODISSOCIATION dynamics of methyl iodide in its A-band has been the subject of many investigations over the past four decades^{1–10}. Methyl iodide dissociation has been particularly interesting, since it acts as a prototype for understanding polyatomic fragmentation. The lowest energy absorption band of methyl iodide is broad. It starts at 360 nm and extends up to 210 nm. This band, which is also known as the A-band of methyl iodide, has been attributed to the excitation of n(nonbonding)-electrons of iodine to the σ* molecular orbital of the C–I bond. Three transitions, ¹Q₁ ← N (peaks around 239.8 nm), ³Q₀ ← N (peaks around 261 nm), and ³Q₁ ← N (peaks around 299.8 nm) underlie this band¹¹. A variety of techniques have been employed by various groups to investigate the dynamics of methyl iodide photodissociation. However, most studies have employed photolysis wavelengths close to the peak of the A-band absorption, that is, 261 nm. In our laboratory we have investigated the dissociation dynamics of a series of alkyl iodides, including CH₃I near the blue and red edge regions of the A-band^{9,12,13}. We have monitored the I* quantum yield as a function of wavelength covering the entire A-band. The quantum yield of I* production reveals the dynamics of the C–I bond breaking in alkyl iodides. Near the peak of the absorption maximum, the ³Q₀ ← N transition, which is polarized parallel to the C–I bond, carries about 80% of the transition strength, and leads to the formation of 75% of the iodine atoms in the spin-orbit excited state. The ³Q₀ state correlates asymptotically to I* product, and any I that is produced in the photodissociation of CH₃I at wavelengths close to the A-band maximum comes from a curve-crossing mechanism in the excited state. The molecules excited initially to the repulsive ³Q₀ state mix with the ¹Q₁ state by breaking the initial symmetry through coupling to a vibrational mode with A' symmetry. However, more recent studies on methyl iodide dissociation

have revealed direct participation of the ¹Q₁ ← N transition at shorter wavelengths and that of the ³Q₁ ← N transition at longer wavelengths respectively. In this communication, we report the I* quantum yield from methyl iodide photodissociation at 236 nm which is close to the peak of the ¹Q₁ ← N transition. At this wavelength, the tail of the next shorter wavelength absorption band of methyl iodide, i.e. B-band, which starts at 190 nm and extends up to 210 nm, becomes accessible. We discuss the dynamics of the C–I bond rupture in the light of our measurement as well as of the data taken from the literature covering the entire A-band of methyl iodide.

The experimental part has been described in detail elsewhere¹⁴. In brief, two ultraviolet laser beams (one pump and another probe) are crossed perpendicular inside a high vacuum chamber which is continuously pumped at a base pressure of ca 2 × 10^{–6} torr. Methyl iodide is leaked into the chamber through a needle valve and a pressure of 30–40 mtorr of the gas is maintained throughout the experiment. The nascent concentrations of product iodine atoms (I*(²P_{1/2}) and I(²P_{3/2})) are monitored after 400 ns of their production, by the technique of two-photon laser-induced fluorescence (TPLIF)³. The ratio of the concentrations of I* and, I plus I*, is defined as the quantum yield, φ* (φ* = [I*]/([I] + [I*]), where [] represents the concentration. The quantum yield was determined directly from the TPLIF signal. The ratio of the measured TPLIF signal intensities S(I) and S(I*) is proportional to the ratio of the [I] and [I*] respectively, and we can write

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

The relative absorption cross-sections, transition probabilities, experimental factors, etc. for the I and I* two-photon excitations are absorbed in the proportionality constant *k*. We have taken the value of *k* = 1, since our value of φ* (0.75) for CH₃I at 266 nm agrees well with the same (0.76) found by Riley and Wilson² from the time-of-flight photofragment spectroscopy. Thus, the quantum yield at 236 nm is obtained directly from the TPLIF spectra of I and I* as φ* = S(I*)/{S(I) + S(I*)}. The value of φ* at this wavelength is 0.69 ± 0.03. The uncertainty in the data is obtained by taking several measurements on different days. The I* quantum yield from methyl iodide dissociation measured by our group and others is plotted in Figure 1 as a function of dissociation wavelength.

The quantum yield peaks with the absorption spectrum¹¹ of CH₃I and goes down as we go to the wings of the spectrum. According to a simple one-dimensional classical Landau–Zener model⁴ which has been used in the past to explain the quantum yield data, the quantum yield should decrease with increasing wavelength. 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

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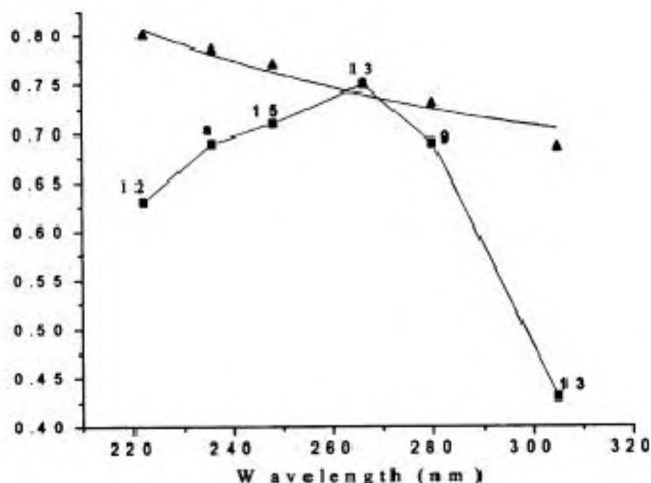


Figure 1. Plot of ϕ^* from methyl iodide (solid squares) and from Landau–Zener (L–Z) model (solid triangles) against various excitation wavelengths. Solid line connects the neighbouring experimental quantum yields. Dotted line is an exponential fit through the L–Z quantum yields. The number marked against the squares indicates the reference number in the text from where the values have been taken. Letter (a) in the plot represents the quantum yield value from the present work.

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

where V_{12} is the coupling term between the 3Q_0 and the 1Q_1 states, 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

$$\phi^* = \exp(-\zeta/v), \quad (3)$$

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 approximation² at the wavelength of excitation according to

$$E_{\text{trans}} = 1/2 \mu_{\text{R-I}} v^2 = (\mu_{\text{C-I}}/\mu_{\text{R-I}}) (E_{\text{avl}}), \quad (4)$$

where $\mu_{\text{C-I}}$ and $\mu_{\text{R-I}}$ are the reduced masses of C and I, and R (the alkyl radical) 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 (2.4 eV) and E_{so} , the spin-orbit excitation energy of the iodine atom (0.942 eV). If we take the measured quantum yield at 266 nm as 0.75 and calculate the value of the parameter ζ , we find $\zeta = 1173 \text{ ms}^{-1}$. With this value of ζ , we have calculated the quantum yield at other wavelengths using eqs (3) and (4); they are plotted in Figure 1 along with the measured quantum yields. In the blue wing of the absorption spectra, i.e. at wavelengths below 261 nm, it is apparent from Figure 1 that the observed trend is contrary to what is expected according to this popular model. In other words, the measured quantum yields at 248 (0.71)¹⁵, 236 (0.69) and 222 (0.63)¹² nm are lower than that at 266 nm. This observation leads to two direct infer-

ences: (1) a simplistic one-dimensional description of the dynamics of C–I bond breaking is not adequate; and (2) at wavelengths blue to the A-band maximum, the only mechanism for production of I cannot be through the direct excitation of the parallel $^3Q_0 \leftarrow N$ transition followed by crossing to the singlet 1Q_1 state. What is the possible reason for seeing less I^* than predicted at 236 nm by the one-dimensional curve-crossing model and a fairly extensive wave packet dynamics calculation by Hammerich *et al.*¹⁶? Simultaneous excitation to the 3Q_0 as well as 1Q_1 states is a distinct possibility at this wavelength. In fact, Penn *et al.*⁵ have studied the dissociation of methyl iodide at 229.4 nm by the time-of-flight technique and found that the anisotropy parameter $\beta = 1.60$. This implies that the transition is $\approx 80\%$ parallel. If we assume that the same is more or less true at 236 nm dissociation, then we would expect a quantum yield of 0.78. But a quantum yield of 0.69 implicates that about 10% of the methyl iodide molecules are excited direct to the 1Q_1 state from the ground state. The rest of the molecules are excited to the allowed 3Q_0 state. The predominantly perpendicular $^1Q_1 \leftarrow N$ transition becomes partially allowed due to vibronic coupling. This fact was not considered in the quantum yield calculations of Hammerich *et al.*¹⁶ and in all one-dimensional curve-crossing models.

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