

Multiphoton ionization and dissociation of CH₃I at 266 and 355 nm

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The mechanisms of multiphoton ionization (MPI) and dissociation of CH₃I have been studied using time-of-flight (TOF) mass spectrometer at 266 and 355 nm. MPI mass spectrum at 266 nm consists mostly of fragment ions. This is consistent with a neutral-fragment photoionization mechanism in which rapid one-photon dissociation occurs from the repulsive potential energy surface followed by MPI of neutral photofragments. The observation of parent ions at 355-nm excitation is indicative of parent-ionic ladder mechanism in which the parent ions are produced directly by two-photon excitation resonantly excited to Rydberg *C* state and then ionized through additional one-photon absorption to produce CH₃I⁺. Fragment ions are produced by dissociation of CH₃I⁺.

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The photodissociation dynamics of methyl iodide (CH₃I) has been the subject of much recent work. CH₃I has become a prototypical system for photodissociation experiment and theory^[1–5]. Extensive studies of CH₃I photodissociation have led to important insights into the mechanisms of fragment internal energy disposal, curve crossing, and angular momentum correlation mechanisms^[4,6,7]. The diffuse absorption bands observed in ultraviolet (UV) spectrum of CH₃I are denoted as *A* band, which arises from the promotion of a nonbonding $5p\pi$ electron centered on the iodide atom to a C–I antibonding orbital. Dissociation of CH₃I through the *A* state has been studied in the range of 229–333 nm^[8,9]. In the VUV region, the transition to the Rydberg states consists of a sharp series of lines between 200 and 170 nm. The absorption spectra of these states have been recorded by several groups^[10]. Higher lying Rydberg states arising from $6p \leftarrow 5p\pi$ transitions have been investigated by Gedanken and Dobber *et al.*^[11,12] using resonance enhanced multiphoton ionization (REMPI) spectroscopy.

In this paper, we report the multiphoton ionization (MPI) of CH₃I at 266 and 355 nm to investigate the photoexcitation and dissociation channels of CH₃I. Of particular interest is a comparison of the dissociation dynamics of CH₃I at two different excitation processes. The results demonstrate that the photoreactions are initiated by exciting CH₃I into the directly dissociative *A* state (266 nm) and the Rydberg *C* state (via 355-nm two-photon resonance excitation).

The apparatus used in our studies has been described in detail in Ref. [13]. Briefly, the apparatus consists of a time-of-flight (TOF) mass spectrometer used in conjunction with a nanosecond laser system. The TOF mass spectrometer is composed of a molecular beam source and a main vacuum chamber. The main vacuum chamber includes electrode plates, a flight tube, and a detection system. Carrier gas (about 1 atm of Ar) is bubbled through a reservoir containing the liquid CH₃I (> 99.9%) at room temperature. The resulting vapor is supersonically expanded through a pulsed nozzle with a 0.8-mm-diameter orifice. A skimmer with a 1-mm diam-

eter is used to collimate the beam before it enters the vacuum chamber. Molecular beam passes through the skimmer and then is ionized by a focused laser beam. The ions are detected by a pair of microchannel plates which are positioned at the end of the drift tube (100 cm). The output signals are digitalized by a 500-MHz digital oscilloscope. All the time delays are provided by a pulse generator DG535.

Figure 1 shows a typical TOF mass spectrum observed for the beam of CH₃I at 266 nm. Major ions in the spectrum are I⁺ and CH₃⁺. In addition, there are some weak signals of H⁺, C⁺ and CH_{*n*}⁺ (*n* = 1, 2). It has been known that repulsive *A* state of CH₃I gives rise to five states: *A*₁, *A*₂, and three *E* states due to the strong spin-orbit

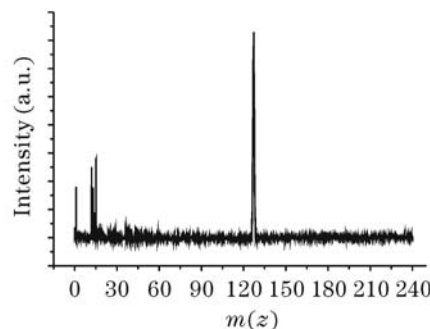


Fig. 1. MPI mass spectrum for CH₃I at 266 nm.

Table 1. Excitation Energy of *A* Band of CH₃I

State	Contracted SOCI ^a	Uncontracted SOCI
¹ A ₁ (1A ₁)	0.0	0.0
³ Q ₂ (1E)	4.455	4.457
³ Q ₁ (2E)	4.629	4.629
³ Q ₀₋ (1A ₂)	4.984	4.991
³ Q ₀₊ (2A ₁)	5.089	5.067
¹ Q ₁ (3E)	5.450	5.448

a: *ab initio* contracted spin-orbit configuration interaction (SOCi) calculations.

coupling induced by the I atom^[14]. One-photon electric-dipole transitions are allowed from $1A_1$ ground state to both E and A_1 excited states, whereas transitions to A_2 state require the absorption of two photons^[11]. Table 1 shows the excitation energy of A band of CH_3I ^[2]. The energy of 266-nm photon is 4.67 eV. From Table 1, CH_3I is excited into $2E$ state by one-photon absorption, which causes a fast C—I bond dissociation^[11]. Thus significant fragments are formed and extensive formation of fragment ions attributes to the multiphoton ionization of the neutral CH_3 and I photofragments. It is noted that the one-photon photolysis should produce an equal number of CH_3 and I fragments, but the signal of I^+ is much stronger than that of CH_3^+ in our experiments. The MPI cross section of CH_3 radical is smaller than that of I atom, which can induce the small ratio of CH_3^+ to I^+ . This is consistent with the results in Ref. [15].

The mass spectrum resulted from MPI of CH_3I at 355 nm is shown in Fig. 2. The formation of CH_3I^+ ions is indicative of direct ionization of CH_3I molecule via multiphoton process. Fragment ions such as CH_3^+ and I^+ are presumably produced from the photodissociation of CH_3I^+ ions by additional photo-absorption. One-photon wavelength of 355 nm does not access any of the excited electronic states, but CH_3I molecule can be excited to Rydberg C state via two-photon resonance excitation. Then the parent ions CH_3I^+ are expected to be produced through an additional one-photon absorption. These ions are formed predominantly in the ground electronic state (\tilde{X} state), which is split by spin-orbits interaction into the $\tilde{X}E_{3/2}$ and $\tilde{X}E_{1/2}$ levels at 9.538 and 10.165 eV respectively^[16]. According to Table 2, the energy of three 355-nm laser photons (10.5 eV) is under the appearance potential of CH_3^+ and I^+ , so CH_3I^+ gives rise to transition from both $\tilde{X}E_{3/2}$ and $\tilde{X}E_{1/2}$ levels to the excited \tilde{A} state through an additional one-photon absorption. At this energetic level, dissociation of CH_3I^+ leads to

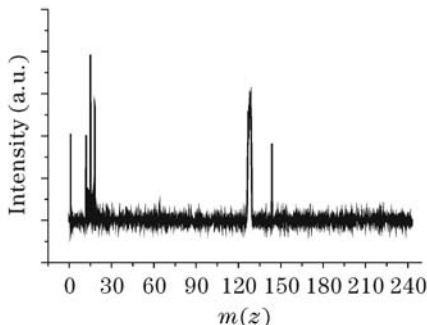


Fig. 2. MPI mass spectrum for CH_3I at 355 nm.

Table 2. Appearance Potential (AP) of CH_3I^+ and Its Dissociation Fragment Ions

Ion	AP (eV)
$\text{CH}_3\text{I}^+ (^2E_{3/2})$	9.538 ^[16,17]
$\text{CH}_3\text{I}^+ (^2E_{1/2})$	10.165 ^[16,17]
$\text{CH}_3\text{I}^+ (^2A_1)$	11.906 ^[17]
CH_3^+	12.24 ^[17]
I^+	12.87 ^[17]

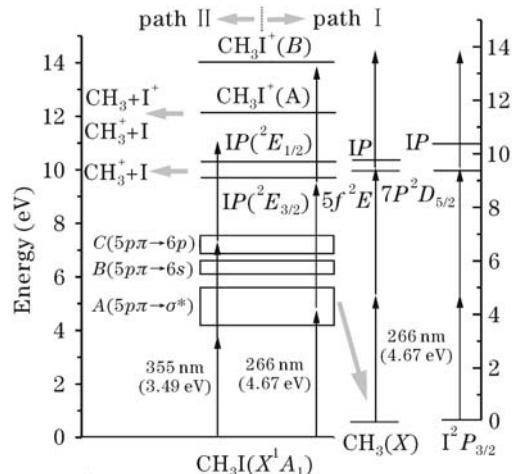
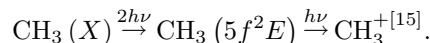
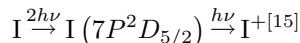
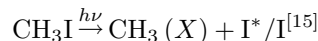


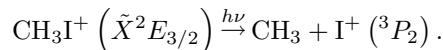
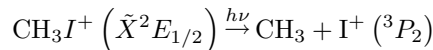
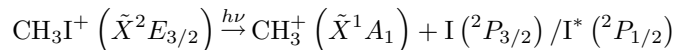
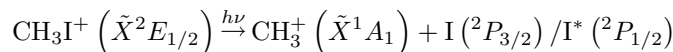
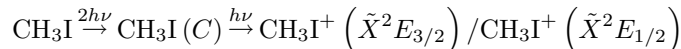
Fig. 3. Ionization pathways of CH_3I .

formation of I^+ and CH_3 radicals. Also, this state is able to predissociate into vibrational continuum of \tilde{X} state, producing CH_3^+ and I atom.

The energy diagram (see Fig. 3) represents the formation mechanism of neutral fragments and ionic products. Path I is the dissociation of excited neutral CH_3I and subsequent ionization of the dissociation products at 266 nm:



Path II is that the three-photon ionization of CH_3I forms CH_3I^+ and a consecutive photodissociation of CH_3I^+ forms the fragment ions of CH_3^+ and I^+ at 355 nm. The MPI mass spectrum demonstrates that the signal intensity of CH_3^+ is stronger than that of I^+ , which illustrates that the dissociation of CH_3I^+ into CH_3^+ and I is the dominant channels,



The multiphoton ionization and dissociation processes of CH_3I molecule have been studied by means of TOF mass spectroscopy at 266 and 355 nm. The results show that it is possible to clarify the ionization and fragmentation process of CH_3I . At 266 nm, CH_3I molecule is one-photon excited to A band, which induces prompt dissociation, leading to neutral I atoms and CH_3 radicals.

The dissociated I and CH₃ fragments in photolysis undergo two-photon resonance excitation, plus one-photon ionization to form CH₃⁺ and I⁺. For 355 nm, the photoreactions are initiated by exciting CH₃I into the Rydberg *C* state via two-photon resonance excitation. Parent ions CH₃I⁺ are produced from additional one-photon absorption. In succession, a part of parent ions dissociate to produce fragment ions.

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