The multiphoton ionization spectrum of methyl iodide revisted: 1.67–2.2 eV excitation

Debra Jo Scardino, Matthew D. McDowell, Jacob D. Graham, and Nathan I. Hammer*

Department of Chemistry and Biochemistry, University of Mississippi, University, MS 38677, USA

Abstract. The study of the multiphoton ionization of methyl iodide has a long and storied history. Here, we revisit this topic and present spectra of each of the photoionization and photodissociation fragments (C^+, CH^+, CH_2^+, CH_3^+, CH_3I^+, and I^+) using a custom time-of-flight mass spectrometer and a tunable dye laser over the excitation range of 550–740 nm (2.2–1.67 eV). The choice of this wavelength range allows for excitation through the *A* state and resonant ionization through higher energy levels using 4+1, 5+1, or 6+1 photons for excitation and ionization. Although the various fragments yield very similar spectra, fewer fragment ions are observed with increasing wavelength.

1 Introduction

The multiphoton dissociation and ionization (MPI) of methyl iodide (CH_3I) has been a subject of intense study for many years [1–40]. This interest is due to methyl iodide's nearly ideal role as a model system for investigating fragmentation pathways, both theoretically and experimentally. It has high symmetry (C_{3v} point group) and is easily ionized via the iodide chromophore yielding easily assignable spectra. A schematic energy level diagram for methyl iodide is shown in Fig. 1. Most evident is a low-lying broad dissociative region termed the *A*-band. This region represents the $5p \, \pi \rightarrow \sigma *$ transition and results in dissociation to form CH_3+I. Higher energy states (*B*, *C*, and Rydberg states) arise from excitation to the 6*s*, 6*p*, and higher energy states.

In 1982, Gedanken *et al.* [5] reported MPI spectra of methyl iodide over a wide energy range showing the appearance of multiple fragments, including CH_3^+, I^+, and CH_3I^+. Since

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*Corresponding author. *Email address:* nhammer@olemiss.edu (N. I. Hammer)

that time, there has been a lot of interest in the fragmentation pathways of the alkyl halides and especially in the mechanism by which the fragment ions are created [8, 9, 11, 17, 25–27, 29, 33, 34, 38, 39, 41]. The predominent conclusion drawn over the years is that ions are formed from photodissociation followed by ionization of the neutral CH_3 and I photofragments. However, Lehr *et al.* [34] in 2001 confirmed the simultaneous presence of neutral and cationic fragment channels. Also in 2001, Zhang *et al.* [42] recorded MPI spectra of multiple mass fragments with photon energies from 2.9 down to 2.5 eV and concluded that because of the similar vibrational structure, each fragment originated from photodissociation of multiphoton ionized molecular parent ions. Li *et al.* [39] also investigated this question more recently in 2007 using 266 and 355 nm (4.66 and 3.49 eV) photons. They argued that different processes occurred using the different excitation wavelengths.
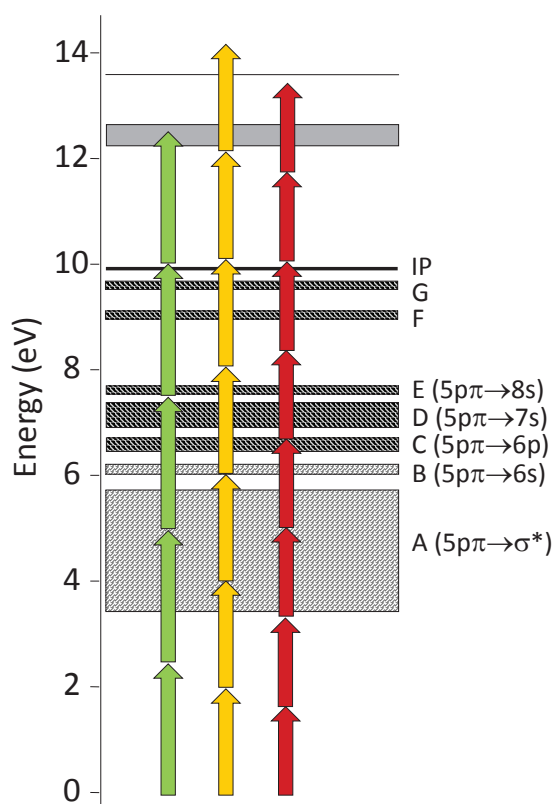

Figure 1: Schematic showing energy levels of methyl iodide. Arrows showing the photon energies (and corresponding visible colors) of the laser employed here are included.

Here, we revisit this topic and present spectra of each of the photoionization and photodissociation fragments (C^+, CH^+, CH_2^+, CH_3^+, CH_3I^+, and I^+) using a custom time-of-flight mass spectrometer and a tunable dye laser over the excitation range of 550–740 nm (2.2–1.67 eV).

The choice of this wavelength range allows for excitation through the *A* state and resonant ionization through higher energy levels using 4+1, 5+1, or 6+1 photons for excitation and ionization. In this approach, the available photon energy is gradually lowered and the effects on the production of the various ions can be observed.

2 Experimental

Methyl iodide was introduced into a custom-built time-of-flight mass spectrometer using a Parker Hannifin Series 9 General Valve and Iota One pulse valve driver. The base pressure in the source chamber was approximately 1×10^{-7} torr and a pressure of approximately 8×10^{-7} torr was maintained while multiphoton ionization spectra were being collected. Methyl iodide was ionized using the focused (10 cm lens) 560–740 nm output from a Continuum ND6000 tunable dye laser that was pumped with the 10 Hz doubled output from a Continuum Surelite I-10 Nd:YAG laser. A number of dyes and mixtures of dyes, including Rhodamine 590, 610 and 640, DCM, and LDS 698 and 722, were employed for the data reported here and power curves for these dyes and dye mixtures are shown in Fig. 2. The power of the laser output was carefully monitored and maintained at approximately 400 mW. After ionization, fragments were accelerated into the mass spectrometer and detected using a microchannelplate detector. The signal was visualized using a digital oscilloscope and a custom data acquisition program written in National Instruments *Labview*. Spectra from each of the fragment ions were collected simultaneously and approximately three individual scans for each region were summed to construct the final spectra.
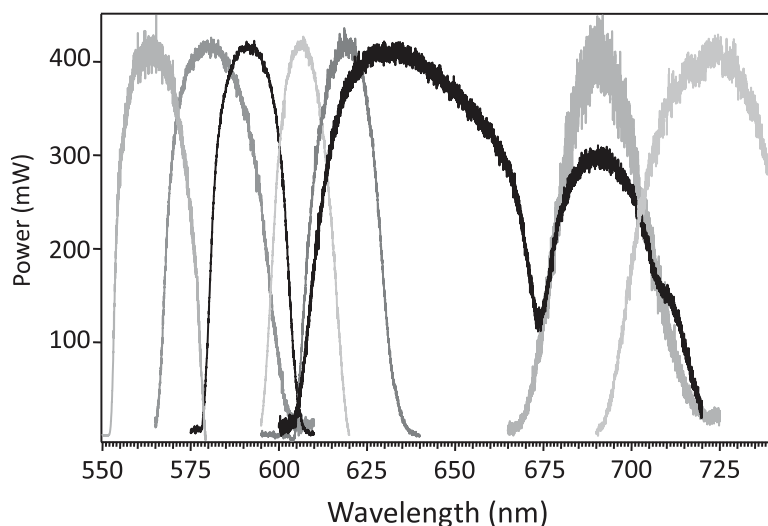

Figure 2: Power curves for the laser dyes employed here.

3   Results and discussion

Fig. 3 shows a representative mass spectrum including the parent ion CH_3I^+ and the various fragment ions C^+, CH^+, CH_2^+, CH_3^+, and I^+. Shown in Fig. 4 are the MPI spectra using the excitation wavelength range of 560–74 nm. In 1982, Gedanken *et al.* reported similar spectra over most of this range by acquiring the total ionization signal [5]. These authors assigned the features of the spectra to atomic resonances of iodine. Gedanken *et al.* also compared the mass-resolved ionization signal of CH_3^+ to the overlapped CH_3I^+/I^+ over a narrow range (584–606 nm, 2.05–2.12 eV) and saw little difference between the spectra as is also evident in Fig. 3. Later, Zhang *et al.* compared the mass-resolved MPI signal from methyl iodide, but over the higher energy region 430–490 nm (2.53–2.88 eV) [42]. These authors also observed little difference between the spectra of the different fragments and argued that the fragments must have originated from the photodissociation of multiphoton-ionized molecular parent ions. Here, we extend the spectral window of mass-resolved MPI signal out to 740 nm.
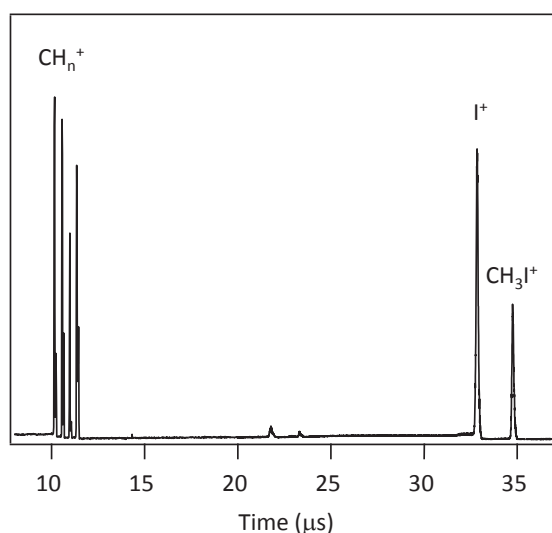

Figure 3: Mass spectrum showing the parent ion CH_3I^+ and the various fragment ions C^+, CH^+, CH_2^+, CH_3^+, and I^+.

From the spectra presented in Fig. 4, the apparent trend is that decreasing photon energy results in fewer observed fragments. This in manifested in different fragments exhibiting different MPI spectra, especially at higher wavelengths. In particular, there is an abrupt difference in the spectra when comparing C^+ and CH^+ at lower wavelengths (higher energy) and CH_2^+ and CH_3^+ at higher wavelength (lower energy). Past 580 nm (< 2.15 eV), little structure (and hardly any ion signal) is observed for C^+. The same is true for both CH^+ and CH_2^+, which for above approximately 625 nm (< 2.00 eV), little structure or ion signal is observed in the spectra.

There are likely two possible explanations for the observed MPI spectra. The results pre-
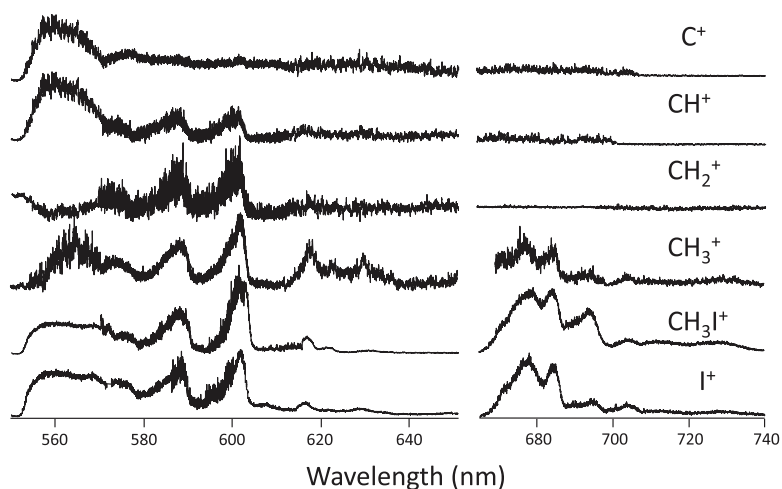
Figure 4: Multiphoton ionization spectra for the various fragments of methyl iodide.

sented here are consistent with a subsequent fragmentation of the highly excited molecular CH_3I^+ cation [39]. As less excess photon energy is available with increasing wavelength, fewer fragments are possible. This explanation agrees with the argument made in 2001 by Zhang, *et al.* [42] who saw similar spectra from the various fragments using higher energy photons. The other possibility popular in the literature is that MPI occurs on the dissociated fragments. Excitation through the dissociative *A* state first leads to the rapid formation of CH_3 and I fragments. MPI of the CH_3 fragment then leads to the observation of C^+, CH^+, CH_2^+, and CH_3^+ cations. Here, however, it appears that with much lower photon energy (< 2.0 versus > 2.5 eV) the smaller fragments cannot be formed. This would suggest that the first mechanism, dissociation of the CH_3I^+ cation, is likely the origin of the fragment ions.

4   Conclusions

In this contribution, we have extended the study of the multiphoton ionization of methyl iodide out to 740 nm, and have collected spectra of the CH_3I^+ parent ion and the C^+, CH^+, CH_2^+, CH_3^+, and I^+ fragment ions. Although the various fragments yield very similar spectra, fewer fragment ions are observed with increasing wavelength. In particular, C^+ is no longer observed at photon energies lower than 2.15 eV and CH^+ and CH_2^+ are no longer created with wavelengths above 625 nm (< 2.00 eV). These results suggest that the fragments observed here result from subsequent fragmentation of the molecular CH_3I^+ cation, rather than MPI of the dissociated fragments and that the absence of ion production is due to decreasing photon energy.

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