

The multiphoton ionization spectrum of methyl iodide revisited: 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*

Received 5 January 2011; Accepted (in revised version) 14 January 2011
Published online 28 February 2011

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.

PACS: 82.50.Pt, 82.80.Ms, 82.80.Rt, 33.15.Ta

Key words: methyl iodide, multiphoton ionization, photofragmentation, photoionization, mass spectra

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 $6s$, $6p$, 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

*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 predominant 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.

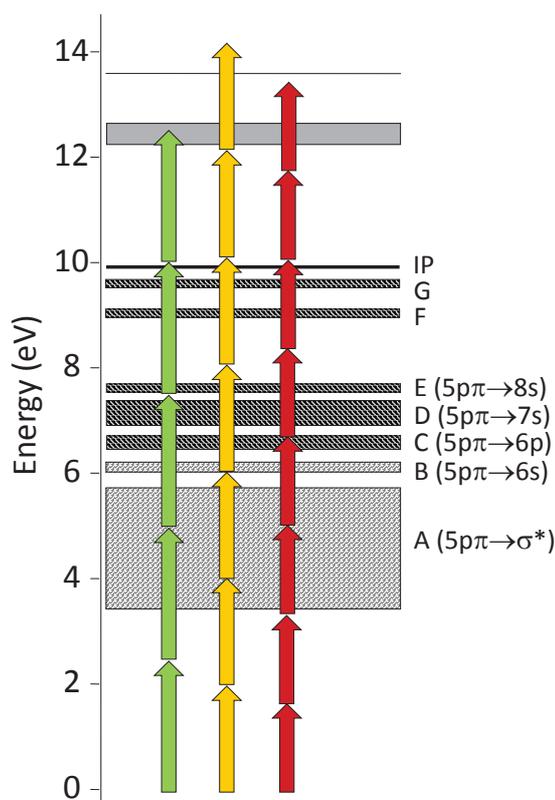


Figure 1: Schematic showing energy levels of methyl iodide. Arrows showing the photon energies (and corresponding visible colors) of the laser employed here are included.

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).