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Ultrafast photodissociation dynamics of *n*-butyl iodide in the *A*-band

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Abstract. Ultrafast photodissociation dynamics of *n*-butyl iodide in the *A*-band has been studied by femtosecond time-resolved mass spectroscopy coupled with ion imaging. The time constant of *n*-C_4H_9I in the *A*-band with one photon excitation at ∼267 nm is measured to be ∼(58±6) fs. The ion images of I ($^2P_{3/2}$) and I^* ($^2P_{1/2}$) at ∼267 nm and ∼274 nm are obtained and analyzed to yield corresponding speed and angular distributions. The dependences of dissociation mechanism on excitation wavelength and the size of the alkyl radical are discussed.

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Key words: *n*-butyl iodide, ultrafast dynamics, pump-probe, photodissociation, ion imaging

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1 Introduction

The photochemistry of alkyl halides in the *A*-band has attracted substantial attention in recent years. One important reason is that it has been realized that halogen atoms and halogen-containing radicals are efficient chemical species for the destruction of stratospheric ozone [1,2]. Alkyl halides may release halogen atoms or produce halogen-containing radicals following UV absorption. The decay of them in the atmosphere depends largely on their photodissociation rates and product channels in the ultraviolet region. Thus, it is important to determine their photodynamic behavior for assessing their environmental impact. Another reason is that the excited potential energy surfaces (PES) for alkyl halides are known to exhibit multiple surface crossings [3–5]. Together with the spin-orbit interactions, it has made the alkyl halides interesting systems for both theoretical and experimental studies.

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Alkyl iodides are particularly interesting since they offer a unique opportunity to understand the effect of size and structure of the alkyl radicals on the dynamics of dissociation [5]. So far, photodissociation studies in the ultraviolet region have mainly focused on short alkyl iodides [3–12]. As the simplest alkyl iodide, photodissociation of methyl iodide has been the active focus and serves as a paradigm for research into photodissociation processes that occur along a repulsive potential surface of the excited state [6–10]. Other short-chain alkyl iodides such as ethyl iodide (C_2H_5I) [4], *n*-propyl iodide (n-C_3H_7I) [11, 12] and *i*-propyl iodide (i-C_3H_7I) [11, 12] have also been investigated extensively and intensively in the UV region by ion velocity imaging technique. Compared to short-chain alkyl iodides, n-C_4H_9I was less focused as an homologue. Studies on it were rare and only limited to Photofragment Translation Spectroscopy (PTS) [13].

In our previous paper [14], we have reported the effect of branching of α-carbon atom on photodissociation mechanisms of alkyl iodides, which is based on comparison of photodissociation dynamics of n-C_4H_9I and sec-C_4H_9I at ∼267 nm. As the alkyl group becomes more branched, the mixing of the bending motions about the α-carbon atom with the C–I stretching in the photodissociation of alkyl iodides becomes more significant.

In this paper, we focus on the photodissociation dynamics of n-C_4H_9I in the *A*-band in detail, including time constant, the dependences of dissociation mechanism on excitation wavelength and the size of the alkyl radical. With the advent of femtosecond pump-probe technique, the time constant of n-C_4H_9I in the *A*-band is measured by time-resolved mass spectroscopy. Using ion imaging technique [15, 16] coupled with resonance enhanced multiphoton ionization (REMPI), the dissociation behavior of n-C_4H_9I at ∼267 nm and ∼274 nm is obtained. Each dissociation parameters are compared to get the dependent dissociation mechanism on excitation wavelength. Energy partitioning of n-C_4H_9I is compared with small alkyl iodides to get insights into the dependent dissociation mechanism on the size of the alkyl radical.

2 Experimental methods

The experimental setup of the two-dimensional photofragment velocity ion imaging has been described in detail elsewhere [17], which is similar to what Eppink and Parker have reported [15, 16]. Briefly, it consists of a homebuilt time-of-flight mass spectrometer and a two-dimensional position sensitive detector. A molecular beam is produced with a pulsed valve and intersects a linearly polarized tunable ultraviolet laser in the reaction region, which is located in the second stage of the vacuum chamber. The generated ions were extracted and accelerated by the electrostatic immersion lens and projected onto a two-dimensional (2D) detector consisting of two microchannel plates coupled with a P47 phosphor screen and a charge-coupled device camera.

The details of our femtosencond laser system have been described elsewhere [18]. Briefly, the seed beam was generated by a commercial Ti:sapphire oscillator pumped by a CW second harmonic of an Nd:YVO_4 laser, and then amplified by an Nd:YLF pumped regenerative ampli-