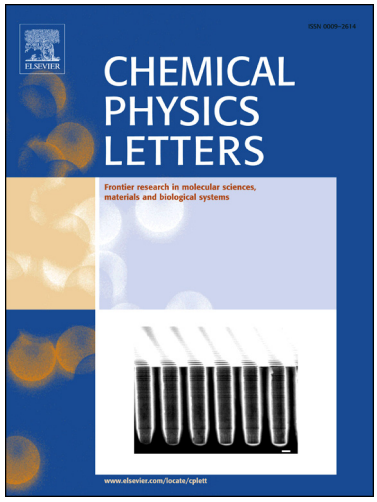

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Photodissociation Dynamics of Iodocyclohexane upon UV Excitation by Femtosecond Pump-probe Technique

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Abstract

The photodissociation dynamics of iodocyclohexane in the A-band and C-state have been investigated by femtosecond time-resolved time-of-flight mass spectroscopy. Iodocyclohexane was pumped by 266 nm pulse to its A-band. The following dissociation dynamics is prompt and direct. The time it takes for the progression of the wave packet from the dissociative state to the dissociating asymptotic region is around 180 fs. The C-state was excited by 200 nm pump pulse and it has predissociative character with predissociation time of about 600 fs, which may have contributions from multiple vibrational modes.

Keywords: Iodocyclohexane, pump-probe, femtosecond, lifetime, photodissociation, predissociation

1. Introduction

Femtosecond laser pump-probe technique is a powerful tool to unravel the details of fast dissociation processes, in particular when state-selective versus non-selective ionization schemes are employed. Resonance-enhanced multiphoton ionization (REMPI) with femtosecond time-resolved time-of-flight mass spectroscopy (TOF-MS) permits direct identification of reaction species.

Photodissociation of alkyl iodide has been a popular area of investigation, in view of the fundamental interest in photodissociation dynamics[1–9] and its potential effect on ozone depletion[10–14]. Photodissociation studies in the ultraviolet have mainly focused on noncyclic alkyl iodides. Methyl iodide (CH_3I)[1–5], the smallest alkyl iodide, has been investigated extensively and now becomes benchmark system in the field of photodissociation dynamics. Larger alkyl iodides like ethyl[6], *n*- and *i*-propyl[7], *n*-butyl iodide[8] have also been studied extensively. Through these studies, detailed information of photodissociation dynamics has been obtained. However, compared with noncyclic alkyl iodides, there have been fewer studies on the photolysis of cyclic alkyl iodides.

The UV absorption spectra of iodocyclohexane (*c*-$C_6H_{11}I$)[15–17] are similar to those of other alkyl iodides, which show a relatively weak and broad band at lower excitation energy centered around 260 nm, traditionally labeled as the A-band. Photoabsorption in this range involves excitation of an electron from a non-bonding p orbital of iodine to an anti-bonding σ^* molecular orbital localized on the C-I bond[18]. The transition of $\sigma^* \leftarrow n$ is dissociative along the C-I bond, producing iodine atoms in their ground I($^2P_{3/2}$) and spin-orbit excited I($^2P_{1/2}$) states (henceforth denoted as I and I*, respectively). At higher excitation energy (199-205 nm), the absorption spectra are composed mainly of four sharp peaks, which are labeled as the B- and C-state of axial and equatorial iodocyclohexane[16].

The photodissociation of iodocyclohexane has been studied by some groups[17, 19, 20]. Freitas *et al.*[19] investigated photolysis of iodocyclohexane at $\lambda \sim$304 nm by state-selected photofragment translational spectroscopy and identified two sub-groups within the I* atom velocity distribution which they attributed to dissociation of the axial and equatorial conformers. Zhang *et al.*[20] reported a velocity map imaging (VMI) study of iodocyclohexane photolysis at 266 and 277 nm, finding that the I and I* products both display near-limiting parallel recoil anisotropy. More recently, Zaouris *et al.*[17] studied the photodissociation of iodocyclohexane using VMI following excitation at many wavelengths within its A-band (230-305 nm). They concluded that the dissociation dynamics within A-band is prompt. They also performed electronic structure calculations and concluded that the bulk of the A-band absorption is associated with transition to the $4A'$ state. The majority of I atom products arise via non-adiabatic transition from the $4A'$ potential energy surface (PES) via conical intersection(s) with one or more PESs correlating with ground state products.

So far, photodissociation studies of iodocyclohexane are

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