Ultrafast dynamics of ethylbenzene cations probed by photofragmentation and photoelectron spectrometry
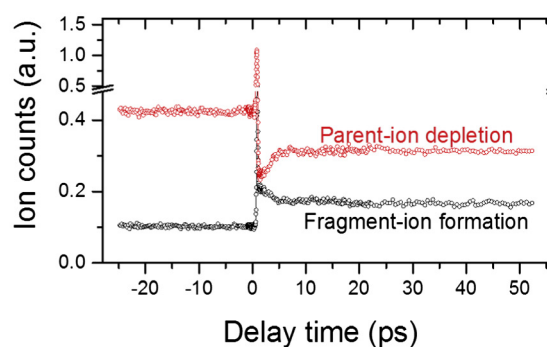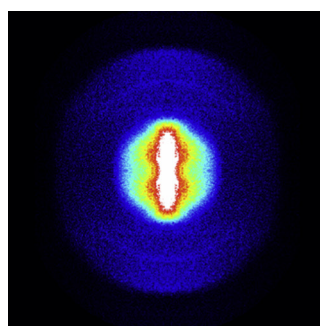
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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Ultrafast dynamics of ethylbenzene (EB) cation has been studied by time-resolved photofragmentation mass-spectrometry (PFMS) in combination with photoelectron spectrometry. EB cations were prepared by multiphoton ionization. The photoelectron spectrum was registered by photoelectron velocity map imaging (PEVMI) and the observed bands were assigned to different cation states. The ultrafast dynamics of these cation states are measured by monitoring the time dependent parent-ion depletion and the fragment-ion appearance, simultaneously. An ultrafast relaxation time of the parent ion of 2.50 (±0.13) ps has been inferred, which is attributed to a dissipative intramolecular vibrational redistribution (IVR) process within the D_0 cation state. The results were compared with o-xylene cations, an isomer of EB.

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Introduction

Ultrafast electronic relaxation processes [1] play a central role in photochemistry and photobiology. The two major nonradiative pathways are internal conversion (IC) due to electronic nonadiabaticity and intersystem crossing (ISC) induced by spin–orbit coupling. In polyatomic molecules that are excited to higher electronic states, IC and ISC to vibronic levels of lower electronic states are two dominant mechanisms. Electronic relaxation processes can be unveiled [2–8] by ultrafast laser spectroscopy. Besides a vast array of investigations that are focused on molecular neutrals, fs time-resolved studies on molecular cations are rarely reported [9–12]. Tracking the transient dynamics of ion states is challenging. In a previous paper, we demonstrated that an adequate characterization of the produced ions can be achieved by combining PEVMI with PFMS in a pump–probe experiment [13].

In this present study, we investigate the ultrafast dynamics of the EB cations. EB plays a great role in combustion chemistry.

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Compared with benzene, toluene and xylene, it has a higher reactivity and thus exhibits noticeably different combustion properties such as short ignition delay time [14] and a high flame speed [15]. Photoionization [16–18], photodissociation dynamics [19,20] and excited dynamics of the neutral EB [21] have drawn great attention. To the best of our knowledge, ultrafast dynamics of cationic EB has never been addressed so far. In our experiment, the ionization is achieved by fs-multiphoton absorption (pump) and the population of the generated cations is characterized by imaging the emitted photoelectrons. After ionization, the ions are excited to an energetically higher electronic state by a time delayed probe photon interaction [13] from where fragmentation may occur. Presuming fragmentation of the excited ions, ion dynamics can be measured monitoring the excited parent-ion $C_6H_5C_2H_5^+$ depletion and the fragment-ion $C_6H_5CH_2^+$ formation as a function of the probe pulse delay. The aim of the current study is to unveil redistribution processes taking place within the lowest electronic ion states by IC and IVR.

Experiment

The experiments were performed with a home-built double-sided velocity map imaging setup [21]. The system consists of two symmetrical, collinear 50 cm long time-of-flight (TOF) mass spectrometers sharing the same interaction region for detecting electrons and ions at opposite sides. Each spectrometer comprises a 7 element electrostatic optic providing a coincident longitudinal (Wiley–McLaren) [22] and lateral VMI (Velocity Map Image) [23] focus at the image plane. VMI's can be registered with a 2-stage MCP/phosphor detector (Proxivision GmbH) read out by a CCD camera (Hamamtsu Orca-03G).

The near infrared (∼800 nm) output of a fs laser system (Clark-MXR CPA-1000) was split into two beams with equal intensity. One part was used as 'pump' beam, while the other part was frequency doubled to ∼400 nm in a beta barium borate crystal (BBO type I) and acts as a delayed 'probe' beam after passing an optical delay stage (PI, M-403.4PD). The pump and probe pulses have a duration of less than 100 fs. The cross-correlation of the pump and probe is about 110 fs. Both beams were merged by a dichroic mirror to propagate on the same axis with parallel polarization adjusted by half wave plates and thin film polarizers.

The molecular beam (MB) was produced by expansion of ∼2% EB (Sigma Aldrich, 99.0% purity) diluted in helium buffer gas at a pressure of 1.5 bar through a miniature valve (Fa. Gyger) pulsed at a rate of 400 Hz. After skimming, the molecular beam enters a differentially pumped chamber where it reaches the common interaction region of the two independent TOF spectrometers 5 cm downstream of the skimmer. The TOF axis is orthogonal to the MB in a horizontal plane. The vertical laser beams are focused into the molecular beam by an $f = 400$ mm lens with their polarization pointing along the MB, i.e., parallel to the two detector planes.

The energy of the pump laser pulse was optimized to produce the highest possible multiphoton ionization yield, yet avoiding direct fragmentation due to higher order photon interactions. All photoelectron images of EB have been recorded with pump pulse energies at which only spurious fragmentation was observed applying the pump pulse only. With interaction of the probe pulse alone, almost no ionization signal was observed. To achieve such condition, the energies for the pump- and the probe pulses are chosen to ∼20 uJ and ∼1.5 uJ for the measurement, respectively.

Results and discussion

The prepared cation states

Gunzer and Grotemeyer measured an EB ionization energy of 8.77 eV via MATI spectroscopy [16]. The energy map of the lowest ion states of EB is depicted in Fig. 1 [16,24]. The photoelectron bands expected in our experiment after multiphoton ionization are indicated by black arrows. At least six photons at 800 nm (1.55 eV) are required to ionize EB. The main ion-fragmentation product is $C_6H_5CH_2^+$ (due to CH_3 loss) and the corresponding appearance energy of 10.81 eV has been reported [18]. The absorption of six photons will not produce fragments, directly. At the chosen pump pulse intensity of about 2×10^{12} W/cm^2, ionization with seven or more photons produced only negligibly few fragments [18,25]. Thus a minimal entanglement of photoelectron images can be expected.

At a wavelength of 800 nm, 7 photons suffice to ionize EB to the D_1 ionic state at 9.29 eV but not to the D_2 state at 11.25 eV [24]. The photoelectron image of EB by multiphoton ionization (@800 nm) as registered by the detector CCD camera is shown in Fig. 2(a). The radial distance of a hit indicates the transverse momentum of photoelectrons. At the chosen electro-static settings of the TOF race the detector range (maximum diameter) covers momenta of photoelectrons leaving the ionization process with a kinetic energy between 0 and 3.5 eV. The linear polarizations of the laser beams are aligned vertical in the plane of the figure. The photoelectron spectrum derived from this PEVMI by lin-Basex algorithm [26] is shown in Fig. 2(b). The arrows in Fig. 2(b) indicate the maximum possible kinetic energies of 0.53 eV after absorption of six photons and 2.08 eV of seven photons at a wavelength of 800 nm (pump) in respect to the ionic D_0 state. The observed bands are marked as band I, band II and band III in Fig. 2(b) corresponding to the notation in Fig. 1.

The strongest contribution, band I (see Fig. 2(b)), can safely be attributed to a six-photon excitation to D_0, whereas the faint bands II and III are interpreted as seven-photon ionization to states D_0 and D_1, respectively. The ethyl substituent lifts the degeneracy of benzene orbital, which leads to an electronic splitting of cationic states. The two lowest resulting ionic states (D_0, D_1) have an energy difference of ∼0.52 eV [20]. With six-photon ionization (9.3 eV), it is unlikely to reach the D_1 state at the threshold energy of 9.29 eV resulting in close to zero kinetic energy electrons. Actually, no peak at zero photoelectron energy is observed. Only band I in the regime of six-photon ionization is present and can therefore be attributed to ionization to the D_0 state by six photons.

With seven photons, both ionic states (D_0, D_1) become accessible, yielding band II and III in the photoelectron image shown in Fig. 2(b). The energy difference between band I and band III is less than one-photon energy (1.55 eV). Thus band III can be assumed to be due to ionization to vibrationally excited ionic D_0 states with
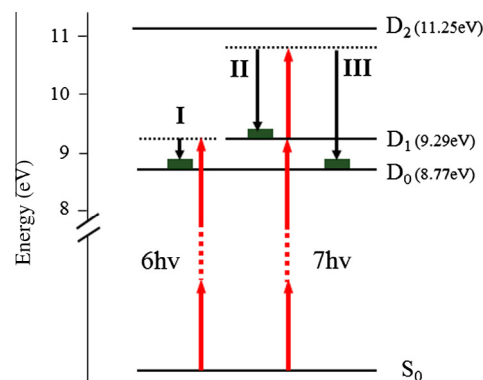
Fig. 1. Ionization scheme and corresponding assignments of the multiphoton ionization [16,24]. The expected photoelectron bands are arbitrarily numbered I to III. S_0 is the ground state. The D_0, D_1 and D_2 stand for the ionic ground state, and the first two lowest excited states, respectively. The thresholds of these states marked in brackets are taken from Refs. [16,24].