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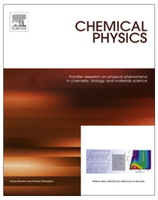

Study on the ultrafast dynamics of o-xylene cation by combined fs-photoelectron imaging-photofragmentation spectroscopy

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ABSTRACT

Ultrafast dynamics of o-xylene cation has been studied by time resolved fs-photofragmentation (PF) spectroscopy in combination with photoelectron imaging (PEI). In the experiment, multiphoton ionization is used to prepare the o-xylene cation characterized by PEI. The ultrafast dynamics of o-xylene ions are measured by monitoring the time dependent parent-ion depletion and the fragment-ion formation, simultaneously. An ultrafast relaxation time of the parent ion of 734 (±61) fs has been observed. The PEI-PF measurements support the interpretation of this relaxation channel to a combination of internal conversion between the two ionic states (D_0 and D_1) and intramolecular vibrational-energy redistribution process within the D_0 state.

1. Introduction

Understanding the nature of inter- and intra-molecular dynamics in detail and visualizing the flow of energy and charge in neutral or ionized molecular systems in real time, is a long standing challenge for physical chemists and chemical physicists [1,2]. Thus investigation on the timescale of molecular motions has attracted a great deal of attention over the last two decades [3–6] andreferencestherein. Besides a vast array of investigations that are focused on molecular neutrals, fs time-resolved studies on molecular cations are rarely reported [7–10]. Reasons for that are difficulties in the appropriate preparation and identification of the ion states. An adequate characterization of the produced ions can inherently be achieved by combining photoelectron imaging and photofragmentation method (PEI-PF) in a pump–probe experiment. For demonstration we investigate the ultrafast dynamics of the o-xylene $C_6H_4(CH_3)_2$ cations by time resolved (PEI-PF) spectroscopy.o-xylene plays an important role in combustion as they are a major component of aromatic compounds in gasolines [11]. PEI experiments for excited state dynamics of the neutral o-xylene have been reported previously [12,13], but to the best of our knowledge, ultrafast dynamics of cationic o-xylene have not been addressed so far. In PEI-PF, the ionization is achieved by fs-multiphoton absorption and the vibronic excitation of the generated cations is characterized by imaging the emitted photoelectrons. After the initial pump photon absorption, the ions are excited to an energetically higher electronic state by a time delayed probe photon interaction. Presuming fragmentation of the highly excited ions, ultrafast ion dynamics can be measured monitoring the parent-ion $C_6H_4(CH_3)_2^+$ depletion and the fragment-ion $C_6H_4CH_3^+$ formation as a function of the probe pulse delay.

2. Experiment

The experiments were performed with a home-built double-sided velocity map imaging setup [14]. Briefly, 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) [15] and lateral VMI (Velocity Map Image) [16] focus at the image plane. The molecular beam was produced by seeding o-xylene (Sigma Aldrich, 99.0% purity) in helium buffer gas (1.5 atm) through a miniature valve (Fa. Gyger) pulsed at a rate of 400 Hz.

The near infrared (at ∼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 passed an optical delay stage (PI, M-403.4PD), acting as a delay 'probe' beam. Pump and probe pulses were merged with a dichroic mirror and focused into the molecular beam chamber by an $f = 400$ mm lens. To find the optimal pump conditions, PEI images of o-xylene have been recorded, using multiphoton ionization at intensities, at which no fragmentation

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products have been simultaneously observed on the TOF-ion detection side. Fragmentation occurs by additionally applying the probe pulse at zero time delay. The probe intensity is such, that no o-xylene ionization is observed applying the probe only. The energetic resolution is limited by the bandwidth of the applied laser pulses to ~200 cm^{-1} (FWHM).

3. Results and discussion

The ionization energy of o-xylene has been measured to be 8.56 eV by Andrew and coworkers via mass analyzed ZEKE spectroscopy [17]. At least six photons at 800 nm (1.55 eV) are required to ionize o-xylene. The main ion-fragmentation product is $C_6H_4CH_3^+$ (due to CH_3 loss) and the corresponding appearance energy of 11.8 eV has been reported [18]. Thus, a six-photon or even seven-photon ionization process will not produce the fragments, directly.

Measurements with a 400 nm pump beam have shown that with 4 photons at 400 nm (energetically like 8-photon at 800 nm) the ionization produces efficiently the $C_6H_4CH_3^+$ fragments [18]. It is thus appropriate to choose a multiphoton processes at 800 nm, providing 7-photons that can populate the D_1 state without reaching the methyl fragmentation threshold. To optimize the ionization mechanism avoiding higher order photon processes, the laser intensity for the pump multiphoton ionization has been chosen to about 3×10^{12} W/cm^2 by minimizing the photo-fragmentation signal and optimizing the electron imaging (spectra) for minimal disentanglement.

The PEI image of o-xylene, at a pump pulse intensity that is not sufficient for observing ion fragmentation is shown in Fig. 1. The bands with different radii result from photoelectrons with different kinetic energies. The photoelectron kinetic energy (PKE) distribution derived from the PEI by lin-Basex algorithm [19] is shown in Fig. 2. The arrows indicate the maximum possible electron energies of 0.74 eV by six-photon and 2.29 eV by seven-photon absorption of pump pulse. The observed bands are named as 1–9 in Fig. 2 with increasing the kinetic energy. For orientation we will give a brief description of the observed energy map. All peak positions and selected differences are summarized in Table 1 and an energy ionization scheme is depicted in Fig. 3.

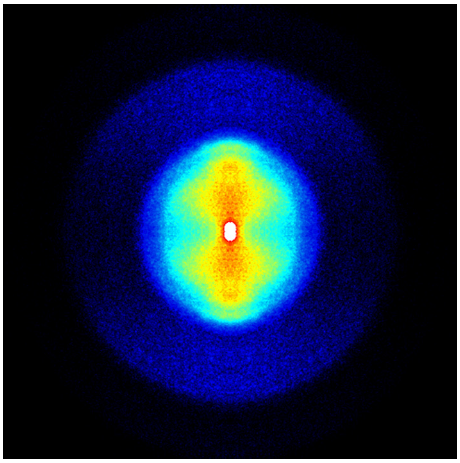

Fig. 1. Photoelectron image of the multiphoton ionization by pump pulse at 800 nm. The linear polarizations of the laser beam are aligned vertical in the plane of the figure.

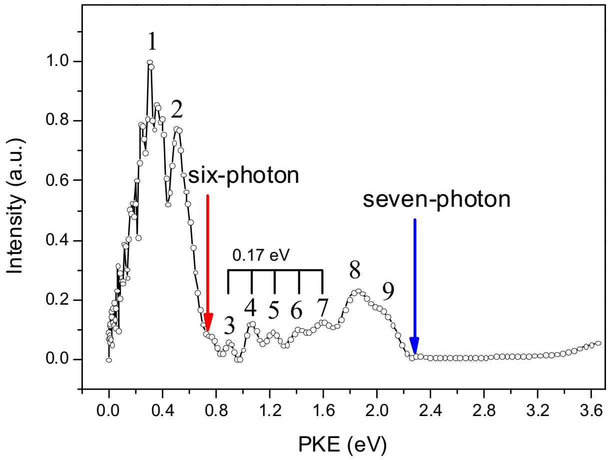

Fig. 2. Photoelectron kinetic energy distribution of the multiphoton ionization extracted from the photoelectron imaging by lin-Basex program [19].

The two main contributions peaks 1 and 2 correspond to six-photon, whereas the faint peaks 3–9 relate to seven-photon ionization. Table 1 shows that the difference of 0.2 eV between peak 1 and 2 is the same as between peak 8 and 9. Moreover, the difference between peaks 1 and 8 (and thus also of peaks 2 and 9) is 1.55 eV, which equals the one-photon energy of the pump pulse. Peak 1 and 2 can be assigned to two different regions of vibrational excitation in the D_0 ground ionic state, while peaks 8 and 9 correspond to the same states after seven-photon ionization. The energies of these two vibrational excitations can be inferred from calculating $E_v = 6\,h\nu - D_0 - E_{peak} = 0.44$ eV (~3549 cm^{-1}) and 0.24 eV (~1935 cm^{-1}) with a difference of ~1614 cm^{-1}.

To assign these two peaks, density functional theory (B3LYP/6-311++G(d,p)) calculations have been performed with GAUSSIAN 09 [20] to determine vibrational frequencies in the D_0 state. However, the two mentioned peaks do not match any specific vibrational progression. It is likely that the observed peaks correspond to combined excitations of several different modes that could not be resolved.

Methyl substituent lifts the degeneracy of benzene orbital upon the ionization, which leads to an electronic splitting of cationic states. The two resulting ionic states (D_0, D_1) have an energy difference of $\Delta E(D_0 - D_1) \sim 0.45$ eV (3630 cm^{-1}) [21]. Thus, considering a seven-photon ionization, both ionic states become accessible and peaks observed between 0.8 and 1.8 eV (peaks 3–7) can in principle result from vibrationally excited states in D_1 and D_0. However, the assignment of these peaks to D_0 would yield rather high excitations with vibrational energies between 5721 cm^{-1} (peak 7) and 11286 cm^{-1} (peak 3). At these high energies we do not expect such a clear and equidistant progression of peaks as observed in Fig. 2. The energy difference between each consecutive peak from 3 to 7 is ~0.17 eV (1370 cm^{-1}). Thus, it is more reasonable to interpret these peaks as a vibrational combination bands in D_1. This assumption is supported, regarding the onset of the vibrational levels in both ionic states after 7 photon ionization. The energy difference between peak 7 (onset D_1) and 9 (onset D_0) corresponds to the electronic splitting of the cationic states. The contribution that has been related to the lowest vibration energy (peak 7) in D_1 is observed at 1.58 eV PKE corresponding to 2092 cm^{-1} above D_1. Fig. 2 exhibits a diffuse featured peak at energies lower than peak 1, which probably corresponds to the replica of peak 7 with 6-photon process. However, the noise level in this energy domain impedes a reliable assignment to a 6-photon process equivalent to the 7-photon process of peak 7.

The nine contributions in the PKE distribution represent an energy map of the ion states populated in the probe pulse interaction. The relative populations in distinct ion states can be deduced from the ratio of electron intensities integrated over a certain velocity range. The two six-photon ionization peaks (1, 2) account